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Tristimulus measurements (CIELAB 76) of port wine colour

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Tristimulus-Messungen (CIELAB 76) der Portweinfärbung

Zusammenfassung: An 87 frisch bereiteten und alternden sortenreinen Portweinen — 5 Lagen und bis zu 6 Jahrgänge — wurden gemäß der methodischen Richtlinie „CIELAB 76“ die Tristimulus-Farbwerte bestimmt und mit den Ergebnissen herkömmlicher Meßmethoden verglichen. Es bestanden enge Korrelationen zwischen a^* (Rotkomponenten) und $A_{520\text{nm}}$, zwischen Farbsättigung und Farbintensität und eine enge negative Korrelation zwischen L^* (Klarheit) und der Farbintensität. Eine lose Korrelation bestand zwischen b^* (Gelbkomponenten) und $A_{420\text{nm}}$; infolgedessen entsprach der Winkel der Farbnuance nicht der Farbtönung. Bei den Tristimulus-Parametern bestanden enge Korrelationen zwischen L^* oder der Farbsättigung und a^* . Bei einzelnen Portweinen variierte L^* linear, aber negativ, mit dem Farbnuance-Winkel; wegen zusätzlicher und wechselnder phenolischer Bräunung, die von der Sorte abhing, bestätigte sich diese Beziehung für die Gruppe der insgesamt untersuchten Weine nicht. In Anthocyan-Modellösungen verursachte zunehmendes L^* (durch abnehmende Pigmentkonzentration oder gesteigertes pH) eine lineare Verringerung des Farbnuance-Winkels, aber einen Anstieg der Farbtönung; das letztere wurde auf die Dissoziation assoziierter Anthocyanmoleküle zurückgeführt. Die Messung des Farbnuance-Winkels bei alternden Portweinen weist auf das Vorkommen zweier konkurrierender Alterungsmechanismen hin, bei denen Acetaldehyd beteiligt bzw. nicht beteiligt ist. Der Farbnuance-Winkel eignet sich besser zur Charakterisierung der Farbnuance von Rotweinen als die Farbtönung.

Key words: ~~port~~ ^{dessert} wine, variety of vine, pigment, phenols, aldehyde, analysis, statistics.

Introduction

The accepted colour analysis for red wines is by measurement at two wavelengths, 520 nm and 420 nm (RIBÉREAU-GAYON 1974 and 1982). Young wines have a large absorbance peak at 520 nm, and as wine ages, the absorbance at 520 nm decreases and there is an increase in absorbance in the yellow/brown region at 420 nm. SUDRAUD (1958) suggested that the calculations of colour density (defined as the sum of absorbance at 520 nm and 420 nm and expressing the intensity of colour) and tint or nuance (defined as the ratio of absorbance at 420 nm to that at 520 nm and expressing the shade of colour) provide a useful way of describing the colour of wine. Recently, the colours of young port wines made from many individual grape cultivars during several years have been measured using these parameters (BAKKER *et al.* 1986).

The rapid method recommended by the Office International de la Vigne et du Vin (1978), and described also by TANNER and BRUNNER (1979) is similar. Colour density is defined in the same way as proposed by SUDRAUD (1958), but the colour nuance is expressed in terms of hue angle (in degrees).

The reference method for wine colour (O. I. V. 1978) involves measuring at four wavelengths, 625, 550, 495, and 445 nm, followed by calculation of tristimulus values according to the Commission Internationale de l'Eclairage (C. I. E.), first published in 1931; but this additional sophistication appears to have been little used, probably because of the time consuming calculations.

Although the colour measurements at two or four wavelengths can be determined quickly, the information gained is limited in comparison with the colour the eye perceives over a much wider spectrum (380—770 nm). Therefore it is anticipated that tristimulus measurements, in which colour is integrated over the whole of the visible spectrum, will give more accurate information about the colours of port wines.

The CIELAB convention introduced in 1976 overcomes several of the shortcomings of the previous conventions, such as a non-linear colour space (MCLAREN 1980). The L^* a^* b^* values describe a three dimensional colour space. The vertical axis L^* is a measure of lightness, from completely opaque (0) to completely transparent (100), while on the hue-circle a^* is a measure of redness (or $-a^*$ of greenness), and b^* of yellowness (or $-b^*$ of blueness).

Although there are several publications on wine colour and anthocyanins using different tristimulus conventions (ROBINSON *et al.* 1966; JOSLYN and LITTLE 1967; VAN BUREN *et al.* 1974; LITTLE 1977 a and b), there are few data on the analyses of wines using the CIELAB 76 convention. TIMBERLAKE (1981) and TIMBERLAKE and BRIDLE (1980 and 1983) reported data on a young red table wine and BAKKER and TIMBERLAKE (1985) used this convention to distinguish tawny from ruby ports. Since micro-computers now enable the quick and easy calculation of tristimulus values, it was feasible to investigate the colours of young port wines using CIELAB 76 tristimulus colorimetry. In this paper the tristimulus parameters obtained by CIELAB 76 for many freshly-made single cultivar port wines are presented and are compared with the conventional two wavelength colour measurements described elsewhere (BAKKER *et al.* 1986). Changes in colours of typical ports on ageing are also described, including the effects of varying aldehyde content.

Materials and methods

Port wines

Port wines were made on a pilot scale at Long Ashton from Portuguese grapes and fortifying spirit as described previously (BAKKER and TIMBERLAKE 1985).

Colour measurements

Colour absorbance measurements were made with a Pye Unicam SP 8—100 spectrophotometer using glass cells of 1 mm path length and scanned over the range 770—380 nm. Simultaneously a desk calculator (Hewlett-Packard 9815A) collected transmission data every 10 nm and calculated the L^* , a^* , b^* values for illuminant D65 and a 10° observer, according to the most recent CIELAB 76 convention (MCLAREN 1980). Hue angle (h) was calculated from $h = \arctan b^*/a^*$ and saturation (or chroma) was calculated as $[(a^*)^2 + (b^*)^2]^{0.5}$. In this convention, redness is denoted by a hue angle of 0° and yellowness is represented by 90° . An increase in hue angle between these values signifies that the colour is becoming more yellow whereas a decrease in hue angle signifies increasing redness. On the hue-circle, 360° is identical to 0° , hence redness is also denoted by 360° . Blueness is denoted by a hue angle of 270° ; values decreasing from 360° to 270° thus represent increasing blueness. Very young port wines often have a hue angle of 350° , indicating a violet hue. In order to calculate the mean of hue angles, values below 360° were taken as negative values (e. g. 350° was taken as -10°). Tint and colour density were calculated from absorbance (A) values in the usual way (BAKKER *et al.* 1986).

Total pigments

Total pigments were measured as described previously (BAKKER *et al.* 1985).

Ports with varying aldehyde contents

Fermented grapes were pressed and the must was divided into three parts. One part was fortified with brandy as a control with a normal content of aldehyde (port CA). The second part was fortified with brandy and 200 mg l⁻¹ of acetaldehyde was added (port HA). The third part was used to make a port as low as possible in aldehydes (port LA) as follows. Ethanol (BP, aldehyde free) was used for fortification instead of brandy and small amounts of SO₂, calculated to bind all free aldehydes, were added at the beginning and at intervals during the first 6 months of storage.

Table 1
Tristimulus means and standard deviations (SD) for each cultivar
Tristimulus-Mittelwerte und Standardabweichungen (SD) der einzelnen Rebsorten

Cultivar	Site ¹⁾	No. of years	L*		Hue angle (°)		Saturation	
			Mean	SD	Mean	SD	Mean	SD
Souzão	Tua	2	40.6	6.8	10.6	6.7	65.5	3.7
Tinta da Barca	Tua	2	59.5	5.6	359.0	3.9	43.5	7.6
Touriga Nacional	Tua	6	65.4	4.8	358.0	2.9	39.7	8.1
Touriga Nacional	V	3	65.6	0.9	357.9	1.9	36.2	3.4
Touriga Francesa	SB	5	67.1	4.4	354.9	2.6	35.6	3.7
Malvesia Preta	SB	4	67.4	10.2	355.2	3.0	38.3	11.9
Viera da Natividade	V	1	68.9	—	0.3	—	42.1	—
Tinta Santarem	Tua	5	72.4	4.6	359.0	0.4	35.7	7.0
Touriga Francesa	BC	4	73.0	8.2	353.6	3.8	32.6	7.7
Tinta Barroca	Tua	6	75.9	3.6	356.1	5.3	26.9	4.5
Tinta Amarela	Tua	4	77.0	5.8	356.5	5.6	28.9	7.0
Tinta Roriz	Tua	6	78.1	5.3	357.2	3.0	23.0	6.7
Tinta Amarela	BC	4	78.3	3.3	355.3	4.0	28.0	2.4
Touriga Nacional	P	2	78.4	4.2	359.3	1.7	23.7	6.2
Cornifesto	P	2	79.4	2.0	359.8	4.9	25.7	1.2
Tinta Francisca	SB	3	79.8	2.5	1.7	5.4	19.6	2.8
Donzelinho	Tua	2	81.3	0.4	358.4	8.2	24.2	2.2
Tinta Francisca	Tua	5	81.8	4.1	359.4	5.9	20.6	5.3
Rufete	Tua	5	83.1	2.6	3.2	10.7	18.7	3.0
Tinto Cão	Tua	6	83.5	3.1	350.0	3.1	22.1	6.1
Tinta Barroca	BC	5	83.8	2.8	350.2	2.0	20.4	3.8
Tinta Francisca	BC	1	83.8	—	353.4	—	21.1	—
Tinto Cão	BC	1	86.2	—	349.0	—	18.5	—
Mourisco	Tua	5	86.4	3.1	13.7	9.7	14.4	4.2

¹⁾ Abbreviations: SB = Santa Barbara, V = Vilarça, BC = Baixo Corgo, P = Pinhão.

Results

Tristimulus values of young single cultivar ports

The mean and standard deviation (SD) of L^* , hue angle and saturation values were obtained for 89 freshly-made ports made from 16 cultivars from 5 different sites over a varying number of years (1–6) (Table 1). Because not all ports were analysed for the same number of years, the means cannot be compared because they contain a seasonal influence. However, the effect of cultivar has been shown to be much larger (3.7–9 times) than the effect of season on these results (BAKKER *et al.* 1986). Comment is limited to ports indicative of the colour range; Touriga Nacional (Tua and Vilarica) consistently gave dark ports, with bluish hue angles and high saturations, while Mourisco gave light ports with brownish hue angles and low saturations.

Comparison of tristimulus and conventional measurements

Ports made from Souzão grapes were omitted from all statistical analysis (which are accordingly given for 87 ports) because its excessive colour gave tristimulus values far removed from the general bulk of ports (Table 1).

There were many high correlations (r) between the tristimulus parameters and the traditional analysis at two wavelengths determined on these young ports, e. g. between a^* (redness) and A_{520nm} ($r = 0.975$), L^* and colour density ($r = -0.987$), L^* and total pigment ($r = -0.906$). Colour saturation, which has heavy weighting of the dominant colour redness in these young ports, also correlated well with colour density ($r = 0.946$).

There was zero correlation between b^* and A_{420nm} ($r = 0.002$) and as a result the correlation between tint, the traditional measure of brownness, and hue angle was relatively weak ($r = 0.711$). Unlike redness which has a clearly defined λ_{max} , brownness is more difficult to measure in young port wines since it has no clear spectral peak; the wavelength chosen for measurement (420 nm) is arbitrary. Hence CIELAB 76 gives the more meaningful measure of brownness in wines.

Interrelations between tristimulus parameters — comparisons with tint

There were several high correlations between the tristimulus parameters themselves in the freshly-made ports e. g. between L^* and a^* ($r = -0.944$), and between L^* and saturation ($r = -0.942$). These correlations indicate that redness is the most important colour in young ports and agree with the previous observation that increasing pigment content gives darker wines with higher saturation values (TIMBERLAKE and BRIDLE 1980 and 1983). There was little correlation between saturation and hue angle ($r = -0.203$); young ports vary widely in saturation but to a lesser extent in hue angle.

There was almost zero correlation ($r = 0.070$) between L^* and hue angle in the group of 87 ports examined. However, the relationship between these parameters is complicated, since in individual wines $-L^*$ and hue angle vary linearly. Thus TIMBERLAKE and BRIDLE (1980 and 1983) found that as the pigment content of a young red wine was decreased by dilution (with 10 % ethanol at constant pH), the wine became lighter, but also less brown. Within range L^* 50–94 the hue angle decreased linearly with increasing L^* ; in contrast tint values increased linearly. Their result was confirmed using a) solutions of increasing contents of pure malvidin 3-glucoside (the major anthocyanin of *Vitis vinifera*) and b) a white port coloured with increasing amounts of red grape skin extract (Touriga Nacional) to give colours within the range found for freshly-made red ports. Our results, confined to experiment b, are illustrated in Fig. 1:

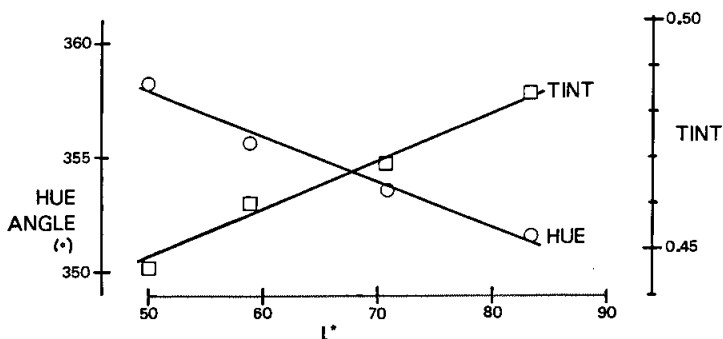


Fig. 1: Relation between L^* , hue angle (○) and tint (□) of a white port coloured with increasing total pigments by adding grape skin extract.

Beziehungen zwischen L^* , Winkel der Farbnuance (○) und Farbtönung (□) eines weißen Portweins, der mit steigenden Dosen von Beerenhautextrakt angefärbt wurde.

With increasing L^* , hue angle decreased linearly, whereas tint values increased linearly. The lack of correlation between L^* and hue angle in the group of freshly-made ports can be attributed to additional variation in brownness, independent of L^* , caused by enzymic browning of phenols present and dependent on many factors.

Influence of pH on tristimulus and tint values

The correlations between pH and any of the tristimulus parameters were low within the groups of freshly-made ports. However, when the pH values of individual ports were varied, it was found that L^* increased and saturation decreased in a linear fashion with increasing pH. Changes in hue angle were variable. Depending on cultivar, hue angle was found to decrease (as might be expected from the accompanying increase in L^* values), but also to remain relatively constant or even increase with increasing pH.

These changes and those of tint values also were studied using a) a pure malvidin 3-glucoside solution in a tartrate buffer, b) a red grape skin extract (Touriga Nacional) in tartrate buffer, and c) a red grape skin extract added to a pale white port as before. The pH values were varied between 3.3 and 4.2. The results of tests a and b showed that with increasing pH the hue angle decreased, but the tint increased, whereas with increasing pH test c displayed a constant hue angle and an increasing tint value.

Touriga Nacional port in particular behaved similarly to tests a and b: with increasing pH the hue angle decreased but the tint increased (Fig. 2). However, Mourisco port, a fairly light port made of grapes known to have a high content of polyphenol oxidising enzymes (BAKKER, unpublished results), showed an increase in both tint and hue angle with increasing pH values. Since phenolic brownness would be expected to increase with increasing pH values, the results suggest that Mourisco port had undergone enzymic browning to an appreciable extent. In contrast, Touriga Nacional must be relatively free of phenolic brownness since its hue angle falls with increasing pH. However, when Touriga Nacional port was diluted (in a tartrate buffer containing 20 % ethanol) to a L^* value comparable with Mourisco port, the hue angle increased slightly with increasing pH values. Presumably, this result can be attributed to the dissociation of the anthocyanin complexes (see 'Discussion'). Nevertheless, the slope of the increase in hue angles as well as the actual values of the hue angles for Mourisco port remained much higher than for Touriga Nacional port.

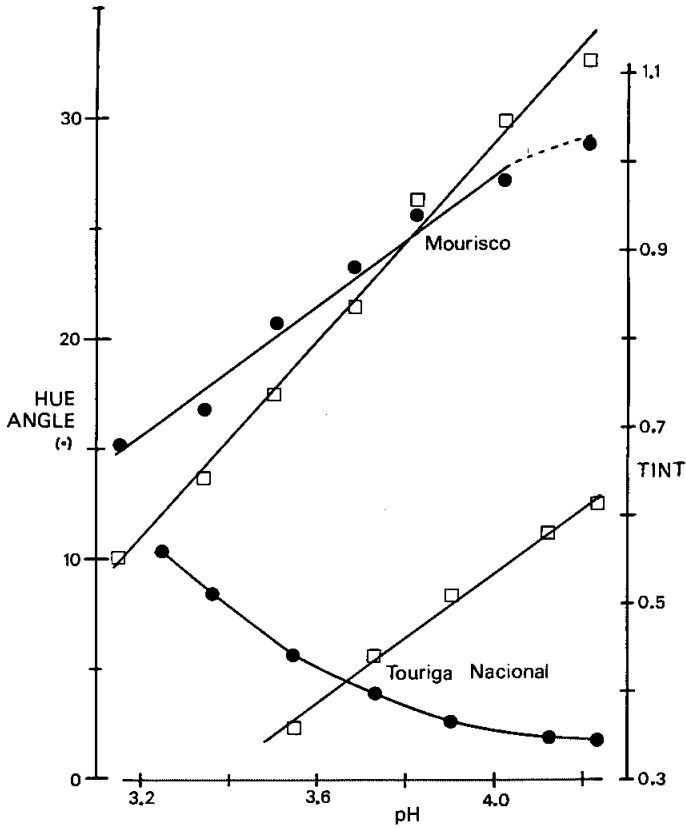


Fig. 2: Relation between L^* , hue angle (●) and tint (□) of freshly-made Mourisco and Touriga Nacional ports.

Beziehungen zwischen L^* , Winkel der Farbnuance (●) und Farbtönung (□) frisch bereiteter Portweine der Sorten Mourisco and Touriga Nacional.

Colour changes on port ageing

On ageing all ports became darker (lower L^* and higher saturation values) for several months before becoming lighter. Changes in L^* and hue angle in a typical port wine, Tinta Barroca, made in 5 successive years (1978–82) were analysed over a period of 28 months (Fig 3). Changes in saturation showed a similar pattern to $-L^*$ and are not shown. The hue angles of ports generally increased with time but some showed an initial decrease in hue angle. Possible explanations for these changes will be suggested below.

The correlations between the tristimulus and conventional measurements and between the tristimulus parameters themselves observed in freshly-made ports were maintained during ageing. Thus for the 1980 ports measured 4, 16 and 28 months after fortification, correlation coefficients were as shown in Table 2. As in the freshly-made ports, correlation coefficients for b^* versus A_{420nm} and hue angle versus tint were much lower (0.192, 0.360, 0.619 and 0.754, 0.581 and 0.893 respectively after 4, 16 and 28 months).

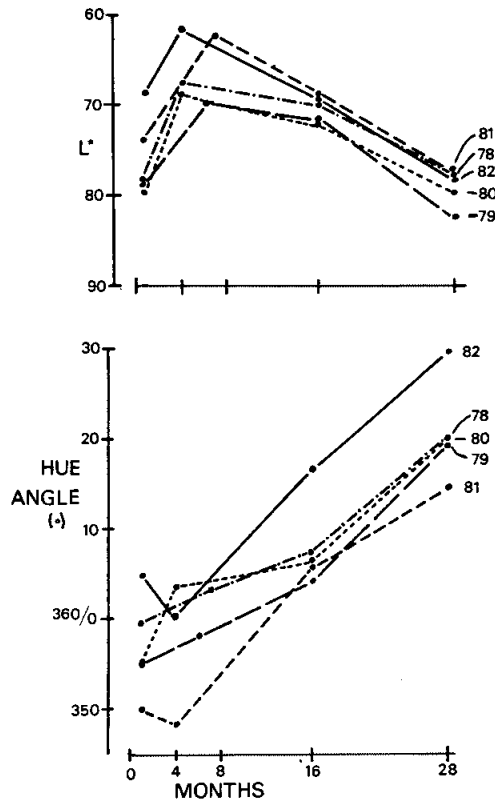


Fig. 3: Top: Changes in L^* values of Tinta Barroca ports made in 5 successive years (1978—82) analysed over a period of 28 months. — Bottom: Changes in hue angles of Tinta Barroca ports made in 5 successive years (1978—82) analysed over a period of 28 months.

Oben: Veränderung der L^* -Werte von Tinta-Barroca-Portweinen aus 5 aufeinander folgenden Jahren (1978—82) während eines Zeitraumes von 28 Monaten. — Unten: Veränderung der Farbnuance-Winkel von Tinta-Barroca-Portweinen aus 5 aufeinander folgenden Jahren (1978—82) während eines Zeitraumes von 28 Monaten.

Table 2

Correlations between tristimulus colour measurements and between tristimulus measurements and the traditional colour measurements for the 1980 ports after 4, 16 and 28 months

Korrelationen zwischen den Tristimulus-Farbmessungen sowie zwischen den Tristimulus-Messungen und den herkömmlichen Farbmessungen für die Portweine des Jahrgangs 1980 nach 4, 16 und 28 Monaten

Description	Correlation coefficients		
	4 months	16 months	24 months
a^* vs $A_{520\text{ nm}}$	0.971	0.983	0.999
L^* vs colour density	-0.975	-0.982	-0.992
L^* vs total pigments	-0.946	-0.979	-0.978
Saturation vs colour density	0.976	0.980	0.984
L^* vs a^*	-0.975	-0.986	-0.971
L^* vs saturation	-0.975	-0.970	-0.968

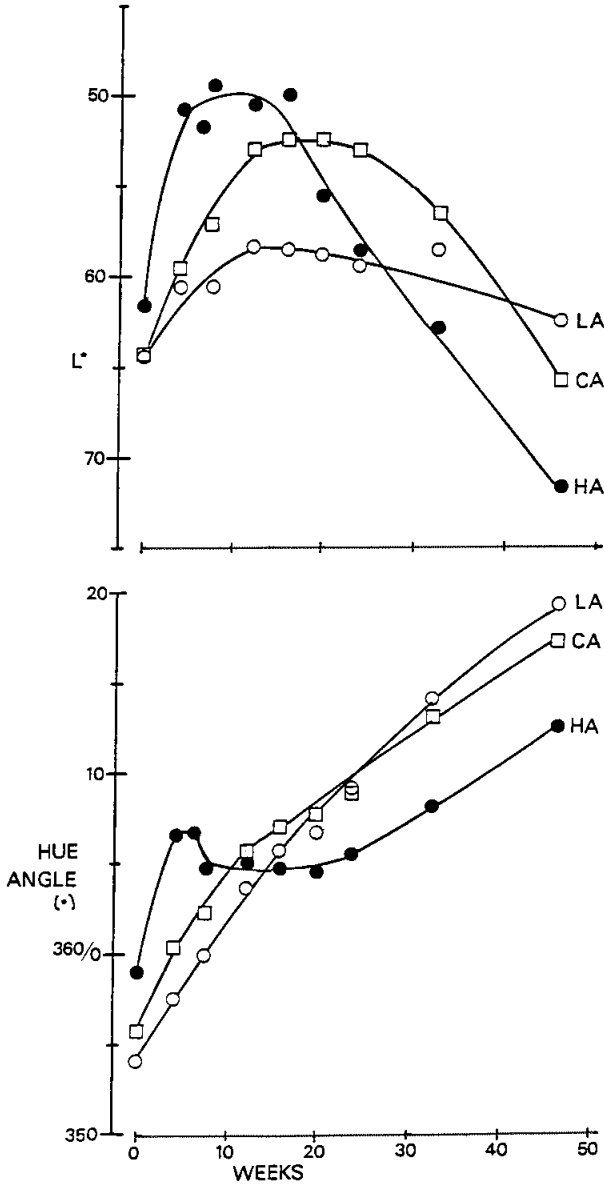


Fig. 4: Top: Changes in L^* values in a control port (CA, □), a port low in aldehydes (LA, ○) and a port high in aldehydes (HA, ●) during a 46 week period. — Bottom: Changes in hue angles in ports CA, LA and HA during a 46 week period.

Oben: Veränderung der L^* -Werte bei einem Kontrollportwein (CA, □), einem Portwein mit niedrigem Aldehyd Gehalt (LA, ○) und einem Portwein mit hohem Aldehyd Gehalt (HA, ●) im Verlauf von 46 Wochen. — Unten: Veränderung der Farbnuance-Winkel bei den Portweinvarianten CA, LA und HA im Verlauf von 46 Wochen.

The effect of varying port aldehyde content on brownness

Port wines contain 'free' aldehyde (mainly acetaldehyde derived from the added brandy), in excess of aldehyde bound to sulphur dioxide. The amounts can vary considerably during port ageing, depending upon the rates at which aldehyde reacts with anthocyanins and other phenolics, its rate of liberation from the aldehyde bisulphite complex due to oxidation of SO_2 , and its rate of formation from ethanol by oxidation (WILDENRADT and SINGLETON 1974). To ascertain the effect of the aldehyde content on port colour during ageing, three ports were prepared as described in the experimental section, viz. a control port (CA), a port low (LA) and a port high (HA) in aldehydes, and they were examined for up to 121 weeks.

During 24 weeks of storage the free aldehyde contents of the ports (as acetaldehyde) were within the ranges following as follows: port LA 0–22 mg l^{-1} , port CA 26–66 mg l^{-1} and port HA 187–228 mg l^{-1} . Changes in L^* and hue angle of these three ports during maturation are shown in Fig. 4. After 46 weeks the order of darkness ($-L^*$) of these ports was the same as the order of brownness; port HA was the lightest with the lowest hue angle and port LA was the darkest with the highest hue angle. But it has been established above that hue angle is affected by L^* : the darker a port (decreasing L^*), the browner it appears (increasing hue angle) and *vice-versa*. The magnitudes of the hue angles in these ports could be merely a result of their varying L^* values. To ascertain any additional effect on brownness it was thus necessary to eliminate the variable effect of L^* by examining these ports at the same L^* value (rather than at the same point in time). When this was done (BAKKER 1985) for $L^* = 75$, the values of hue angles and time taken to reach $L^* = 75$ were as follows: port LA had a hue angle of 32° after 121 weeks, port CA of 26° after 91 weeks and port HA of 16° after 65 weeks. Thus to achieve the same L^* value, which might be considered the same degree of ageing, the port low in aldehydes (LA) took longer than the control (CA) and was browner, whereas the port high in aldehydes took a shorter time but was less brown.

Discussion

Freshly-made wines

There is no doubt that CIELAB 76 adequately corresponds to what the eye actually sees and that there is a real effect of L^* on hue angle. L^* can be varied in two ways; the first is by changing the optical path length of the measuring cell at constant pigment concentration. Thus TIMBERLAKE (1981) reported that decreasing cell path length of young wine from 40 mm to 1 mm produced a fall in hue angle of 40° (causing increase in L^* of 44), and agrees with the common observation that young red wine in a thin film, say at the meniscus or periphery of a glass, appears bluer than when viewed through a much larger depth at the centre of a glass. In contrast, L^* was without effect on tint values since they were constant under these conditions (constant pigment concentration and pH) and independent of L^* .

The second way of varying L^* is by changing the pigment concentration at constant pH or by changing the concentration of coloured cationic forms of the anthocyanins (AH^+) by varying the pH. (L^* is due largely to AH^+ ions). As described in this paper, with increasing L^* , tint values increase. Such changes in tint values show that superimposed upon the general influence of L^* on hue angle described above is an

effect characteristic of the anthocyanins, which affects L^* , tint and hue angle. Anthocyanins are known to self-associate in red wine (TIMBERLAKE and BRIDLE 1980). At the pH of wines they deviate positively from Beers law, i. e. colour increases more than proportionally with increasing concentrations of AH^+ (decreasing L^*). Conversely, as L^* is increased, the concentration of AH^+ decreases and associated pigments dissociate to some extent. The increase in tint values with increasing L^* may thus be due to A_{520nm} being reduced relatively more than A_{420nm} . Dissociation of the pigment complexes at lower concentration also affects the hue angle. This effect is difficult to quantify for anthocyanins in isolation (since when L^* is varied, the hue angle is influenced), but if self-association is considered as a form of co-pigmentation, the general effect would be blueing. Thus increasing L^* values would cause less co-pigmentation resulting in less blueing, and *vice-versa*.

Colour changes in ageing ports

The findings can be explained as follows. In the control port (CA) two ageing processes are competing with each other: one polymerisation mechanism which does not involve acetaldehyde and which will be referred to as the non-aldehyde ageing (NAA), and another polymerisation mechanism involving acetaldehyde and which will be referred to as the aldehyde ageing (AA) (BAKKER and TIMBERLAKE, in print). Red wines (largely NAA) are known to increase in brownness on ageing, whereas it has been shown by TIMBERLAKE and BRIDLE (1976) that AA in model solutions results in an increased violet colour; thus the browning in a port will be modified by the extent to which the AA has occurred. The hue angle in the control port will be the net result of both processes. In the port with excess acetaldehyde the AA competed more successfully with the NAA, resulting in a port which was more violet, i. e. much less brown than the control. In the port low in aldehydes (LA), NAA was the dominant ageing mechanism (during the first 6 months at least) and resulted in the brownest port. It can be concluded that tristimulus analysis provides a useful technique to monitor colour changes in ruby ports, giving also an estimate of the relative extents of two different competing ageing mechanisms, AA and NAA, as reflected in the differences in brownness, when ports are compared at the same lightness value.

CIELAB 76 has proved useful also for distinguishing colour characteristics of white wines and apple juices, which have no clear λ_{max} . The merits of CIELAB 76 in sensory assessment and the way it correlates with visual colour assessment will be the subject of a further communication.

Summary

Tristimulus colour values were measured using the CIELAB 76 convention and compared with conventional measurements on 87 freshly-made and ageing single cultivar port wines from 5 sites for up to 6 years. There were high correlations between a^* (redness) and A_{520nm} , and saturation and colour density, and a high negative correlation between L^* (lightness) and colour density. There was little correlation between b^* (yellowness) and A_{420nm} ; consequently hue angle did not correspond to tint. Amongst the tristimulus parameters, there were high correlations between L^* or saturation and a^* . In individual ports L^* varied linearly but negatively with hue angle, but in the group of ports examined there was no significant relationship between L^* and hue angle because of additional variable phenolic browning depending upon cultivar. In model

anthocyanin solutions increasing L^* (by decreasing pigment concentration or increasing pH) caused a linear reduction in hue angle but an increase in tint; the latter was attributed to dissociation of associated anthocyanin molecules. Measurement of hue angle in ageing ports gives an indication of the relative occurrence of two competing ageing mechanisms, involving or not involving acetaldehyde. Hue angle is a more discriminating parameter for expressing the colour nuance of red wines than tint.

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