THE COLOUR OF RED WINE

MARIA JOSEPHINE BIRSE

THE UNIVERSITY OF ADELAIDE

School of Agriculture, Food & Wine

Faculty of Sciences

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Abstract

The behaviour of pigments in red wine, namely anthocyanins and anthocyanin-derived pigments, was investigated at natural wine pH, at low pH and after addition of SO_2, namely SO_2 bleaching. An examination of current literature demonstrated absences in wine pigment research. Firstly, few researchers have published the colour properties of a particular wine pigment at different pH values and post-SO_2 bleaching. This was demonstrated using the CIELab colours of two individual anthocyanin-derived wine pigments (4-vinylcatechol and 4-vinylsyringol adducts to malvidin 3-glucoside), and an anthocyanin, malvidin 3-glucoside. The colours of the anthocyanin-derived pigments and their resistance to pH change and SO_2 bleaching were compared to malvidin 3-glucoside which was affected by media.

Generally, in the literature, wine pigments are characterized as individual components. But many pigments contribute to wine colour. So, two novel methods were created and demonstrated using red wines: Shiraz wines from four regions in Australia, and Cabernet Sauvignon wines made using two different strains, Saccharomyces cerevisiae (SC) or Saccharomyces bayanus (SB). The first method can be used to determine the CIELab colour of chromatographically separated wine pigments and allows their colours to be re-created, regardless of their identity. Thus objective measurement of pigment colour at its natural concentration in wine is now possible.

An additional method, the “post-column adjustment method” to pH-adjust and SO_2 bleach HPLC-separated wine pigments was created. The concentration and colour of HPLC-separated wine pigments at low pH, at wine pH and post-SO_2 bleaching can be measured. The method has highlighted the importance of the pH value when quantifying a wine pigment. For example, from low pH to wine pH, the apparent anthocyanin and pigmented polymer concentration was reduced, but the Vitisin A concentration was unchanged. SO_2 bleaching resulted in negligible anthocyanin concentration and a further reduction in pigmented polymer concentration, with Vitisin A unaffected. Relative quantities of wine pigments in both SC and SB Cabernet Sauvignon wines were not affected by pH change or SO_2 bleaching.

Also, using the Shiraz wines and Cabernet Sauvignon red wines, existing and improved colour measurement techniques were discussed. For the Australian Shiraz wines, grape origin was found to influence red wine colour, CIELab values provided enhanced colour measurements, and high wine colour (at natural wine pH) cannot be

attributed to individual monomeric anthocyanins (measured by HPLC analysis at low pH). Vitisin A was not responsible for differences in wine colour. SO_2-stable wine colour was related to regional differences. The percentage of SO_2 non-bleachable pigments was independent of wine region. Chemical index (ii) values indicated that the colour at 520 nm was attributable to pH-dependent wine pigments. Vitisin A and pigmented polymer concentrations correlated well with SO_2-stable wine colour. Pigmented polymer concentration may be the driving force behind wine colour density. Copigmentation was of no importance in the young red wine samples studied.

With the Cabernet Sauvignon red wines, the yeast strains used for fermentation affected wine colour and SO_2-stable wine colour. The change in wine colour density was not related to change in total red pigment colour or anthocyanin concentration. Pigmented polymer concentration, SO_2-stable wine colour and the percentage of SO_2 non-bleachable pigments were consistently higher in the SB wines.

The pH value was important when determining the colour of a wine or pigment. At low pH, the SC wines were more coloured than the SB wines. However, at real wine pH, the converse was true. For both wines, at low pH, the anthocyanin concentration was greater than the pigmented polymer concentration, indicating the importance of anthocyanins to wine colour only at low pH. But, at wine pH, the apparent anthocyanin concentration was much lower in both wines (for example, malvidin 3-glucoside provided more colour at low pH than at wine pH) than the apparent pigmented polymer concentration. Therefore, at wine pH, anthocyanins were less important to wine colour than pigmented polymers.

The concentrations of Vitisin A were similar in all three media, but colour losses were observed at wine pH and post-SO_2 bleaching. SB Vitisin A was more coloured. At low pH and at wine pH, Vitisin A was more coloured than malvidin 3-glucoside in both wines, even though the apparent Vitisin A concentration was lower. Differences in the colours of the SC and SB pigmented polymers peaks were observed at low pH, at wine pH and following SO_2 bleaching. The SB pigmented polymers were darker and more colourful, exhibited more colour absorbance and a slight bathochromic shift of λ_{max} value. From low pH to wine pH and following SO_2 bleaching, pigmented polymers become lighter, whilst retaining orange-red hues.

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List of abbreviations

A	Absorbance value
a* value	CIELab colour value. On the hue-circle in the horizontal plane, a* is a measure of redness and –a* of greenness.
A^+	Ionized anthocyanin
a.u.	Absorbance units
b* value	CIELab colour value. On the hue-circle in the horizontal plane, b* is a measure of yellowness and – b* of blueness.
AWRI	The Australian Wine Research Institute
c	Concentration
CAV	Colour activity value
C* value	Chroma derived from a* and b* values. Equivalent to $(a^{*2} + b^{*2})^{½}$
CIELab	Combination of CIE and L*, a*, b* values
CIE	Commission Internationale d'Eclairage
DAD	Diode array detector
DAP	Diammonium phosphate
ΔE* value	ΔE* is the Euclidean distance between the two points in three-dimensional space and is used to compare two colours (represented by the subscripts 0 and 1) : $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{½}$ where $\Delta L^* = L_0 - L_1$; $\Delta a^* = a_0 - a_1$; $\Delta b^* = b_0 - b_1$.
ESI-MS	Electrospray ionization mass spectrometry
F	Flavanol
H* value	Hue value derived from a* and b* values. Equivalent to $\tan^{-1}$ (a*/b*)
l	Length
L* value	CIELab colour value. L* is a measure of lightness from completely dark (0) to completely white (100).
MLF	Malolactic fermentation
NWGIC	National Wine and Grape Industry Centre
PCC	Percentage colour contribution
RP	Reversed phase
s value	Saturation derived from a* and b* values. Equivalent to (C*/L*)
SB	*Saccharomyces bayanus* yeast strain
SC	*Saccharomyces cerevisiae* yeast strain
SO_2	Sulfur dioxide
SO_2-stable	"Stable" or not bleachable in the presence of the sulfite ion
${}^{s}_{w}pH$ value	Apparent pH values where *s* and *w* are the organic solvent system and calibration of the pH electrode using aqueous standards respectively.
WCD	Wine colour density
WCH	Wine colour hue

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Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis being made available in the University of Adelaide Library.

Maria Josephine Birse Date

Publications

Refereed journals:

1. "Structures and colour properties of new red wine pigments": Hakansson, A.E., Pardon, K., Hayasaka, Y., de Sa, M., and Herderich, M. (2003) Tetrahedron Lett. 44: 4887-4891. (Written under maiden name).

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3. "Are the colour properties and pigment profiles of wines affected by the use of the different yeast strains; *Saccharomyces cerevisiae and Saccharomyces bayanus*?" Hayasaka, Y., Birse, M., Eglinton, J., and Herderich, M. *prep.*

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Other publications:

1. "Anthocyanins, anthocyanin-derived pigments and the colour of red wine" Birse, M., Pollnitz, A., Kwiatkowski, M., Gockowiak, H., Parker, M., Eglinton, J., and Herderich, M. (2005). Proceedings of the Twelfth Australian Wine Industry Technical Conference held at Melbourne Convention Centre, Melbourne, Victoria on 24-29 July 2004, 303 – 304.

2. “CIELab colour values: enhanced wine colour measurement for use by the wine industry and in research applications” Birse, M., Pollnitz, A., and Herderich, M. (2005). Proceedings of the Twelfth Australian Wine Industry Technical Conference held at Melbourne Convention Centre, Melbourne, Victoria on 24-29 July 2004, 312 – 313.
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5. Article entitled Quality advances for grape and wine industry, Aust. N.Z. Wine Ind. J. (March/April 2006, Volume 21, Issue 3, 107 - 108) detailing my research outcomes.

Workshops:

“An introduction to colour analysis of red wine, 2006” – A half day workshop written by Maria Birse, edited by Ashley Ratcliffe and desktop published by River Murray Training Pty Ltd, Adelaide. Presentations written on behalf of the Cooperative Research Centre for Viticulture. Workshop includes four one hour seminars introducing and discussing colour, pigments in red wine, HPLC analysis and post column treatment of HPLC-separated data.

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