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EXTRACTION OF COLOUR DURING FERMENTATION

OF PINOT NOIR WINES AND ITS STABILITY ON AGEING

A dissertation submitted

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of

Horticultural Science

G.F. Steans

Department of Horticulture and Landscape

Lincoln College

CANTERBURY, NZ

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ABSTRACT

The characteristics of the major pigments in red wines are discussed and the results of an experiment to stabilise the peak of colour extraction which occurs during fermentation are presented.

It was found that the peak which occurs early during the fermentation is due to the formation of anthocyanin aggregates and that this could be stabilised by the addition of a solution of commercial grape tannin.

This resulted in aged wines which were pressed at 43 hours after innoculation having similar colour densities to those wines fermented to dryness in the presence of the grape skins.

Treated wines showed increases in the amount of polymerised anthocyanin present at fifteen months despite an increase in the amount of polymerised colouring material deposited during this time.

KEY WORDS : Colour; Pinot noir ; Malvidin-3-glucoside ; Anthocyanins ; Tannin ; Polymers ; Wine.

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1.0 INTRODUCTION

It is generally understood that the main pigments in red wines are the anthocyanins and tannins (Ribereau-gayon 1974). Of these, the anthocyanins are responsible for the bright red colours in young red wines and the group of complex compounds referred to collectively as 'tannins,' for the yellow tints. They also confer colour stability as wines age.

Powers <u>et al.</u> (1980) identified the five major anthocyanin pigments in Pinot noir grown in Washington State, and found that malvidin-3-glucoside (M-3-G) made up the greatest proportion of these, as is shown in Table 1.

Table 1

Major Pigments of Pinot Noir

Anthocyanin	% of Total
Delphinidin-3-glucoside	5.35
Cyanidin-3-glucoside	3.22
Petunidin-3-glucoside	5.99
Peonidin-3-glucoside	21.1
Malvidin-3-glucoside	64.3

In discussing the colour reactions and properties of anthocyanins therefore it is reasonable to consider those of Malvidin-3-glucoside as representative of the group.

1.1 Effect of pH

Ribereau-Gayon (1974) has examined the properties of anthocyanins in some depth and has shown that in weakly acid solutions the red oxonium form (A) is in reversible equilibrium with a colourless pseudo base form (B). This is shown in figure 1.1 .



Figure 1.1 : Effect of pH on Anthocyanin

Figure 1.2 : Reactions of Malvidin-3-Glucoside





He demonstrated in a synthetic medium that the colour density of Cyanidin-3,5-diglucoside (measured as absorbance at 510 nm) was six times greater at pH 2.9 than at pH 3.9 although the absorbance at 278 nm was not changed significantly.

As the absorbance at 510 nm is involved with the structure of the bonds around the 'central heterocycle' (Ribereau-gayon 1974) and not the aromatic component it may be assumed that the same conditions apply also to the monoglucoside.

He reports that Berg in 1963 determined that the dissociation constant for Malvidin-3-glucoside has a value close to 3. This means that at a pH of 3.0 a red wine will have about half of its anthocyanins present as the red form and the other half in the colourless form.

Malvidin-3-glucoside has been shown (Timberlake 1982) to form a blue coloured quinoidal base with the further increase in alkalinity of the solution. It has been stated in the same paper that the presence of the blue form has been detected at pH values as low as 2.0 and that a nearly colourless chalcone form also exists in equilibrium although at low concentrations relative to the red flavylium form.

The reactions of M-3-G. can be summarised as shown in figure 1.2.

1.2 Bisulphite Condensation

In 1964 Jurd showed that bisulphite ions may form addition products with anthocyanins by reaction with the carbon atom at position 2 in a similar manner to the reaction of hydroxyl ions at this position. The effect is the same - the anthocyanin is declourised.

The reaction tends to be transitory in wine however since as the bisulphite ions are removed from solution by irreversably binding to such compounds as aldehydes, the equilibrium shifts in favour of the oxonium form of the anthocyanin.

This reaction is also affected by the pH of the solution since at values lower than about pH 3 decreasing amounts of the SO_2 are present as the bisulphite ion and more in the free SO_2 form (Eschenbruch 1983).

1.3 Reduction of Anthocyanins

Anthocyanins can also be reversibly decolourised by reduction (Ribereau-Gayon 1974) and is thought that this may account for the light colour of freshly fermented red wines

which gradually deepens as the effect of the strongly reducing enviormment (fermentation) declines. The mechanism of this reaction is thought to involve addition of a hydrogen atom to to the carbon atom at position 4 .

All these reactions which cause reversible decolourisation of anthocyanins involve the double bond between the oxygen at position 1 and the carbon at position 2 and the associated charge distribution.

If the double bond is present between these two atoms it appears that the solution is red and if it is not present at this position the anthocyanin solution is colourless.

The anthocyanin molecule therefore, can exsist in solution in two coloured forms (red and blue) and a colourless form, the relative amounts of each depending on pH, oxygen status and sulphur dioxide concentration.

This is why red wines exhibit variations in colour which range from light red to purple.

1.4 Effect of Ethanol on Colour

The phenomenon of colour loss during fermentation has been shown by Somers (1982) to occur in two overlapping phases.

He and Evans showed (1979) that as anthocyanins diffuse into the fermenting solution from the skin cells they rapidly aggregate to form colour stable structures due to hydrogen bonding and charge stabilisation as shown in figure 1.3.

As can be seen both red and blue forms may aggregate and in doing so they effectively shield the reactive site which is involved in the decolourisation reactions.

As the fermentation proceeds however, the increasing concentration of ethanol progressively breaks up these aggregates, due to the proton scavenging action on the hydrogen bonds, so that they are once again susceptible to decolourisation (Somers and Evans 1979).

At a similar time however it is thought that the extraction of phenolics into the solution is responsible for the progressive polymerisation of the anthocyanins. This condensation of the anthocyanins with phenols is thought to begin early in the fermentation process. Somers (1982) estimates that these polymeric pigments could account for "at least 25% of the wine colour density." by the end of fermentation.

It is this continuous modification of the anthocyanin aggregates and formation of stable polymerised pigments which constitutes the second phase of colour evolution.

This results in the progressive loss of free anthocyanins from the solution with a consequent increase in the concentration of polymerised forms and continues long after the fermentation is completed.

1.5 <u>General</u>

In earlier studies of colour changes during fermentation (Berg and Akiyoshi 1956, Bissell 1981), it was found that a peak of colour extraction occurred after about three days fermentation on the skins but that the colour density of mature (6 months) wines was proportional to the duration of skin contact time during fermentation.

Somers and Evans (1979) had also reported this and explained that the apparent loss of colour which occurred after this peak was due to the action of the alcohol on the hydrogen bonding as previously described. Bissell (1981) also verified the findings of Berg and Akioyshi that the amount of tannins in a red wine was proportional to the length of time it was fermented on the skins.

Since Berg(1963) maintained that polymerisation of anthocyanins with tannin accounted for the stability of colour in mature wine, Bissell suggested that it may be possible to stabilise the colour peak in young red wines by the addition of tannin. If this was so it would be possible to produce wines of good colour while having lower tannin levels by pressing off the skins at the peak. Conservation of the colour by the careful addition of tannin may then result in wines with a softer palate finish and therefore wider commercial acceptance.

This project was set up to deternmine whether it was possible to stabilise the colour peak in this way and to study the effects of tannin levels on colour stability in ageing Pinor noir wines.

MATERIALS AND METHODS

2.1 EXPERIMENTAL OUTLINE

Samples of free run must were taken from a two thousand litre tank of fermenting Pinot noir located at Larcomb Vineyards, Canterbury during the 1986 vintage.

The grapes were hand harvested and added to the tank after passing through a crusher/destemmer under an atmosphere of carbon dioxide. The must was innoculated with 1% by volume of a solution of reactivated dried yeast (Lalvin Montrachet strain M1107) obtained from The National Dairy Association Ltd., Christchurch.

The timetable of sampling was set up so that the majority of samples would be taken around the time of the peak of colour extraction. In this way it was hoped to closely follow the extraction of anthocyanins during the period of maximium movement into the solution.

Unfortunately as described later this object was not completely realised.

At each sampling, approximately 4 litres was taken, transferred to a sterile glass jar and brought back to the College winery.

An aliquot of each sample was analysed for reducing sugars and ethanol. The remainder was allowed to ferment to dryness in 4 litre glass jars under fermentation locks.

The data are included in the appendix.

Fermentation times for the samples varied, but all had fermented to dryness within 120 hours of inocculation while the tank fermentation was complete in 104 hours. The major cause of this variation was the difference in temperature of

the must related to the surface area-to-volume ratio of the different batches. As shown in the appendix the bulk tank fermented at a significantly higher temperature than ambient resulting in a faster reaction rate.

At dryness each wine was racked off gross lees under an atmosphere of food grade carbon dioxide, with the addition of 50 mg.l⁻¹sulphur dioxide, and placed in the cold room at 2°C for seven days to settle and cold stabilise.

Following a second racking the wines were analysed for total phenols as described later and the treatments applied as follows:

- A 10 % w/v solution of grape tannin ("Tanin VR" from Tonnelerie Demptos) was made up in 12%v/v "Analar" Ethanol. Tannin was obtained from Brewers and Winemakers supplies, Auckland.
- Each wine was sulphured to 50 mg.l⁻¹ and divided into two lots of two litres each.
- 3. Sufficient tannin solution was added to one of each lot to produce a total tannin concentration of 2.30 g.l⁻¹ as shown in table 1.

Sample Number	Time on Skins	Measured Tannin	Added Tannin	Total Tannin
	(hours)	g.1-1	ml 10% soln.	g.1-1
		·····		
1	0.00	0.544	34.92	2.01
2	19.00	0.966	26.48	2.27
3	43.25	1.750	10.80	2.30
4	49.00	1.927	7.23	2.27
5	54.25	1.938	7.04	2.35
6	67.00	2.045	4.90	2.33
7	93.50	2.271	0.38	2.40
8	104.00	2.290	0.00	2.30

Table 1 : Tannin Additions To Treated Wines

The samples were also analysed for 'free' SO_2 at this time and the level adjusted to 50 mg.l⁻¹ to ensure that malolactic fermentation did not take place.

The wines were allowed to stand at room temperature in full glass containers for a further three weeks to allow them to stabilise, after which they were decanted, passed through an eight micron "Sartorious" membrane filter using nitrogen gas pressure and then bottled in 375 ml dark green wine bottles. At this time a full analysis for sulphur dioxide (free and total), residual sugar, alcohol, colour, polymerised anthocyanins, total phenols and total acidity was performed.

The untreated wines were treated in the same way, with the exception of tannin solution additions.

The bottles were labelled (the prefix S denoting treated wines) and stored at cellar temperature for subsequent ageing and analysis.

2.2 SAMPLING DURING FERMENTATION

During the fermentation the must was thoroughly mixed with the skins approximately every three hours . Mixing was performed by pumping must from the bottom of the tank over the cap of skins until the skins were completely submerged again.

Once mixing was complete the sample of free run must was taken from the bottom tap of the tank.

Because the fermentation appeared to proceed at a faster rate than expected the temperature of the must was recorded after mixing at each sampling after the first. As these measurements showed a dramatic increase after about twenty

hours the cap temperature before mixing was also recorded from this time on.

The data are shown in the appendix.

2.3 ANALYSES

2.3.1 pH and Total Acidity

Total acid and pH were measured as described by Van Dam (1979) using a "Radiometer" model 28 pH meter standardised to pH 3.55 with saturated Potassium hydrogen phthalate solution.

2.3.2 Sulphur Dioxide

Free and 'total' sulphur dioxide were measured using the aspiration technique described by Van Dam.

2.3.3 <u>Residual sugars and Alcohol</u>

These were determined by the 'Combi-test' procedure described by Van Dam with one modification.

The 50 g of citric acid in the copper reagent was replaced by 32.7 g of di-sodium Ethylenediaminetetra-acetic

acid (M.Geisen pers.com.). This ensured that the sodium carbonate in the reagent stayed in solution. This gave identical results to that using the Van Dam reagent.

2.3.4 <u>Tannin</u>

Total tannins were determined by the Folin-Ciocoulteau method as described by Amerine and Ough(1980).

2.3.5 <u>Total Phenols</u>

These were determined as absorbance at 280 nm as described by Leonard (1983).

2.3.6 Colour

Colour density and hue were determined as described by Amerine and Ough(1980) on a Shimadzu model UV140-02 double beam spectrophometer.

A 1mm path length cell was used as red wines do not adhere to Beers law on dilution (Ribereau-Gayon1974).

2.3.7 Polymerised Anthocyanins

These were determined on the spectrophometer previously mentioned, according to the method of Somers as outlined by

Amerine and Ough(1980).

2.3.8 Absorbance Spectra

The absorbance spectrum of each wine was determined after twelve months in bottle using a Shimadzu UV-260 recording spectrophometer with a 1mm path length and a slit width of 5 nm.

2.3.9 Further Analyses

After fifteen months the wines were analysed for colour,total phenols, polymerised anthocyanins and absorbance spectra. The amount of deposit in each bottle was also determined at this time by filtering the contents of each bottle through a preweighed filter (Whatman No.541). After drying over silica gel at room temperature for seven days the weight of residue was determined to an accuracy of one milligram.

RESULTS AND DISCUSSION

3.1 ANALYSIS AT BOTTLING

The standard wine analyses routinely performed prior to bottling are shown in table 3.1.

Table 3.1 Wine Analysis at Bottling

Sample	Residual	Alcohol	pН	Total acid	Free	Total
Number	sugar g.l-1	% vol.		g.1-1	SOz	SOz
1	1.47	13.9	3.24	8.03	4.8	44.8
2	1.47	13.7	3.35	8.03	12.8	80.0
3	1.98	13.2	3.45	7.73	6.4	51.2
4	1.72	12.9	3.50	7.65	8.0	62.4
5	1.72	12.9	3.50	8.03	14.4	68.8
6	2.64	12.9	3.50	8.03	11.2	60.8
7	2.24	12.8	3.50	7.65	9.6	51.2
8	2.24	12.9	3.50	7.73	11.2	44.4

These analyses were performed at the time the samples were divided into two lots for treatment. Analysis of the treated wines following addition of the tannin solutions showed that these additions had no effect on the value of these parameters so that only the values determined prior to treatment are presented.

The apparent trend in the quantity of residual sugar to increase with skin contact is probably not significant since the method af analysis determines substances reducing alkaline copper sulphate not specifically sugars. In practical terms the differences reported are likely to be due to non fermentable sugars and other substances containing a keto - group.

The trend for alcohol to decrease with increasing skin contact reflects the fermentation conditions of the samples before and after collection. Those with the longer skin contact times have been subjected to higher fermentation temperatures before collection with the consequent loss of some portion of the volatile components which analyse as 'alcohol'.

The sampling times and temperature at various times during fermentation are shown in the appendix.

The temperature at which the samples fermented after collection was of the order of 12 °C (room temperature) and heat transfer from the small volumes involved would be such that the heating effect of fermentation was negligible.

The slight increase in total acidity is probably due to increased extraction of the acids into the must in the early stages of fermentation.

The differences in the amounts of free SO_2 present in the samples despite all recieving the same dose after racking is due to differing amounts of aldehydes and anthocyanins which loosely bind SO_2 in solution.

It has been widely reported that measurement of 'free' SO_2 by the aspiration method gives variable results because of this property of anthocyanins (eg Eschenbruch 1983).

3.2 COLOUR MEASUREMENTS

3.2.1 Colour Density

As shown in figures 3.1 and 3.2 the colour density at bottling and calculated as the sum of the absorbances at 420 and 520 nm shows a peak at about forty hours skin contact.

 $2\overline{2}$



Colour Density - Control Wines (A520 + A420)

Figure 3.1

Colour Density - Treated Wines (A420 + A520)



Figure 3.2

Unfortunately the fermentation in the bulk tank proceeded faster than anticipated so no samples were taken between 19 and 43 hours. Nevertheless the indications of a peak are supported by the work of Somers and Evans (1979).

After ageing in bottles for fifteen months the density of the control wines shows distinctly that the peak has disappeared. At skin contact times up to about 60 hours the colour density of aged control wines is less than that at bottling whereas those wines with longer contact times have increased in colour density to a small extent.

After fifteen months the treated wines on the other hand, show a marked increase in colour density from about 40 hours (the peak of extraction) indicating that the addition of tannin has stabilised this peak. At times less than 40 hours the treated wines show a smaller increase in colour density over the young wine but there is still an increase.

The treated wine at 104 hours skin contact shows an increase in colour density of about 150% of that of the control wine at the same time on skins.



Figure 3.3

Hue - Treated Wines (A420/A520)



Figure 3.4

3.2.2 Hue of The Colour

The hue or tint of the control wine (figure 3.3) exhibits a steady decline in the young wine with increasing skin contact while a fifteen months the hue is almost independent of the time on skins. As hue is a measurement of the yellowness of the colour it appears that there is either an increase in red, or a decrease in yellow pigments with time.

Examination of the recorded data (presented in the appendix) indicates that both occur but that the increase in absorbance at 520 nm has a slightly greater effect.

The treated wines (figure 3.4) show a steady decrease in yellow tint at fifteen months with increase in skin contact until about 50 hours after which the hue stabilises at about 30% of the zero time value while the young treated wines exhibit a much slower decline. At time zero the young wine shows a lower hue value than the corresponding aged wine while from forty hours the young treated wines have a higher hue than at fifteen months.

3.3 TOTAL PHENOLS

As shown in figures 3.5 and 3.5a, the total phenols in control wines at bottling describe a sigmoid rate of increase with time of skin contact. The movement of phenols into the solution starts slowly since most of the skin cells are intact. The base level of phenols at time zero represents those phenolics released into solution from the cells ruptured during the crushing /destemming process prior to innocculation.

The subsequent increasingly rapid movement into solution of phenolics is the result of cell breakdown as the enzymes in the fermentation build up. The rapidly increasing concentration of ethanol during this stage will also assist the dissolution of these compounds.

As the level of anthocyanins in the skins declines the level of phenolics in solution tends towards a plateau at about 70 hours.

After this time the phenolics entering the solution are likely to be wholly derived from the seeds and the much slower rate of increase in phenolics after 70 hours therefore is due to the relative difficulty with which they diffuse into the solution through the hard seed coat.

The decline in total phenolic content after ageing is



Total Phenols - Control Wines E280 units

Figure 3.5





Figure 3.5a

due both to polymerisation of these compounds with anthocyanins and to the copolymerisation of tannin molecules to the extent that the resultant compounds no longer remain in solution and are deposited.

An examination of the deposit formed in the bottles after fifteen months (figure 3.6) showed that the control wines had a relatively constant amount of deposit while the treated wines showed an increase in deposit from the 40 hour sampling.

Prior to this contact time the treated wines had similar qugantities of deposit to the control wines.

The treated wines, with the exception of an overall slight decrease with age, exhibit little variation in total phenolics at either bottling or after ageing, as was expected.

The increase in deposit in the treated wines after 40 hours skin contact is probably due to the constituent compounds present in the added tannin. It is likely that the level of polymerisation of compounds in this solution is already greater than that present in the control wines.

While not sufficient to cause precipitation in the



Deposit in Bottle after 15 Months

Figure 3.6

ethanolic solution as added to the wines, the resulting mixture contained sufficient additional compounds to cause this deposition.

In other words the wines fermented on the skins for 49 hours or longer contained sufficient additional phenolics to cause precipitation of polymers from the added tannin solution.

Timberlake and Bridle (1976) have shown that the polymerisation of anthocyanins with phenolics and the copolymerisation of phenolics is catalysed by the presence of acetaldehyde. They also showed that copolymerisation of M-3-G takes place with acetaldehyde acting as a three carbon bridge between the C8 or C6 positions of adjacent molecules.

It may be that the unusually large deposit in the control wine at 54 hours is the result of a higher concentration of acetaldehyde in this wine, however as the wines were not examined for acetaldehyde this can only be speculation.

3.4 DEGREE OF POLYMERISATION

Figures 3.7 and 3.8 show the degree of polymerisation



% Polymerised Anthocyanins Control Wines

Figure 3.7





Figure 3.8

of anthocyanins in control and treated wines respectively at the two analysis times.

The control wine at 19 hours contact shows a higher degeree of polymerisation than any of the other contact times at bottling. Close examination of the graph suggests that in fact the degree of polymerisation in these wines at this time rises to a peak around 20 hours and then declines to a stable low level from 50 hours to the end of fermentation.

This is compatible with the findings of Somers and Evans (1979) regarding the aggregation of anthocyanins and their reported insensitivity to bisulphite.

The degree of polymerisation present in the control wines after fifteen months varies between about 15% and 38% but in all cases is at least an order of magnitude greater than that at bottling.

The degree of polymerisation at fifteen months shows no clear pattern except that there may be less in the first two samples than in the later ones.

The variation between samples is more likely to be due to the relative amounts of anthocyanins involved in copolymerisation, polymerisation with phenolics, and in the

relative sizes of these polymers.

Bakker <u>et al.</u> (1986) have shown that the spectral method of determining polymeric colour is inaccurate since it as been found that bisulphate ions can react with complex polymeric pigments to some degree.

This would explain the variation in apparent degree of polymerisation existing in all these samples

The treated wines show an opposite trend to that in the control wines but in all cases at a higher level.

In this case the degree of polymerisation at fifteen months varies from around 60% at 19 hours skin contact with a steady decline to stable level at around 70 hours of about 50% polymerisation.

This decrease in the apparent degree of polymerisation with increasing skin contact is most likely due to the size of the polymers formed.

As more phenolics are extracted from the seeds into the wines with time the anthocyanins present are able to form larger polymers with them and the addition of more tannin has resulted in progressively greater amounts of these polymers depositing in the bottle. Again the method of determination

of the degree of polymerisation will confuse the picture to some extent.

3.5 ABSORBANCE SPECTRA

The scans of absorbance of the aged wines are shown in the appendix. In all cases the control wine is the lower line on the scan.

In all cases the treated wines exhibited greater absorbance than the control wines at all wavelengths. It is notable that the absorbance peak at 520 nm is not present in wines with skin contact times less than 43 hours and prior to this the absorbance at 420 nm is the major contributor to the total wine colour.

This indicates that the red chromophore of the anthocyanins from the early stages of colour extraction does not predominate in aged wines.

The increase in absorbance at 520 nm in treated wines over control demonstrates the enhancement of colour by tannins reported by several workers.

The increase in absorbance at 420 nm in treated

compared to control wines is most likley the result of the added tannin.

A scan of a similar solution to that used for tannin additions confirms this in that it absorbs strongly in the region 380 - 480 nm and has no peak at 520 nm.

4 CONCLUSION

Anthocyanins in fermenting must and ageing wine undergo a number of complex reactions.

As they move into the must from the skin cells they may aggregate to form structures of various sizes due to hydrogen bonding and charge redistribution. They may copolymerise by the formation of aldehyde bridges in the presence of acetaldehyde and as the concentration of phenolics increases they form polymers.

The uncombined anthocyanins are susceptible to reversible decolourisation by reduction, decreasing pH and bisulphite addition. The aggregated anthocyanins and phenolic-anthocyanin polymers were originally thought to be insensitive to this decolourisation (Somers and Evans 1979). This has been questioned by Baranowski and Nagel (1986) who have shown by HPLC that the spectral method of determination of anthoyanins in their various combinations yields overestimates.

Although this present study was founded on the assumptions of Somers (1982) and Somers and Evans (1979) the recent findings of Baranowski and Nagel do not negate the results in general.

As the wines age the anthocyanins form polymers of everincreasing magnitude with the tannins present.

This results in stabilisation of the predominate red colour due to the condensation of the flavylium form of the anthocyanin with tannins (Baranowski and Nagel).

As the size of the polymers increases they may reach a magnitude at which they can no longer remain in solution and then precipitate. This is the cause of the formation of the deposit commomly found in aged red wines.

Although there was some reduction in the density of the colour due to deposition of some of the stabilised polymer at fifteen months, it was possible to stabilise the

peak of colour density found at 43 hours skin contact by the addition of tannin so that this colour was present after ageing.

Although the consumer acceptance of these treated wines was not tested it is technically feasible to produce well coloured wines by pressing at the peak of colour extraction and adding tannin to stabilise this colour.

Further work needs to be done to determine the minimium amount of tannin required to fix the colour peak and on the consumer acceptance of such wines.

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APPENDIX

Fermentation Conditions

Date	Time Mixed	Total Hours	Tempera Must	ture °C Cap	Sample Number
20/4	1500	0.00			1
	2200	7.00			
21/4	0300	12.00			
	0630	15.50			
	1000	19.00	22		2
	1300	22.00	22		
	1800	26.00	26	30	
	2100	29.00	25	30	
	2230	31.50	26	31	
	2330	32.50	26	32	
22/4	0400	37.00	26	31	
	0700	40.00	26	32	
	1015	43.25	24	28	3
	1300	46.00	24	28	
	1600	49.00	24	25	4
	2115	54.25	26	28	5
23/4	0630	63.50	24	25	
	1000	67.00	26	25	6
	1230	69.50	24	26	
	1600	73.00	26	26	
	2200	79.00	26	25	
24/4	0630	88.50	24	24	
	1130	93.50	25	26	7
	1900	104.00	25	26	8

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Analysis of Wines at Sampling

Time (h)	Alcohol %vol	Sugar g.l ⁻¹
0.00	0.00	236.0
19.00	1.10	
43.25	1.60	
49.00	8.40	97.1
54.25	9.70	35.2
67.00	9.90	22.9
93.50	10.90	
104.00	12.97	1.47

NOTE: Accurate measurements of reducing sugars were not taken as alcohol determinations gave sufficient indication of the status of the fermentation.

COLOUR MEASUREMENTS ON WINES

Absorbances at 420 and 520 nm (corrected for 10mm cell)

Sample	At	Bottling	At	15 Months
Number	A420	A520	A420	A520
Control	Wines			
1	0.980	0.740	0.430	0.290
2	1.30	0.930	0.575	0.465
3	2.550	2.150	1.540	1.825
4	1.480	1.900	1.680	2.275
5	1.780	1.980	1.480	1.730
6	1.600	2.100	1.745	2.500
7	1.580	2.120	1.820	2.695
8	1.550	2.100	1.802	2.570
Treated	Wines			
S1	0.980	0.740	1.245	0.760
S2	1.300	0.930	1.430	1.030
S3	2.550	2.150	1.965	2.740
S4	1.480	1.900	1.895	2.750
S5	1.780	1.980	1.885	2.855
S6	1.600	2.100	1.945	3.470
S7	1.580	2.120	1.915	3.380
S8	1.550	2.100	1.965	3.610



Spectra: Samples 1 and 2





Spectra: Samples 5 and 6



Spectra: Tannin solution



