PRE-FERMENTATION MACERATION OF PINOT NOIR WINE

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Two pre-fermentation treatments were investigated in Pinot noir (*Vitis vinifera* L.) wines. The effects of cold maceration and carbonic maceration on the wines' composition, colour parameters and sensory properties were examined. Cold maceration is a winemaking technique used to increase non-alcoholic extraction in Pinot noir winemaking prior to fermentation. It involves holding crushed grapes with approximately 100-150 mg l^{-1} SO_2 at low temperatures and is thought to increase the colour, aroma and flavour of the resulting wines. Carbonic maceration uses whole bunches that have undergone anaerobic metabolism to produce characteristically fruity and spicy wines. Pre-fermentation cold maceration produces wines that are higher in titratable acidity and monomeric anthocyanin content, but lower in colour density, hue and polymeric pigments. Reducing the maceration temperature below 10°C has little effect. Carbonic maceration produces wines that are lower in titratable acidity, monomeric anthocyanin content, and colour density but are higher in colour hue and amount of polymeric pigments.

Quantitative descriptive analysis was used to define the effects of these pre-fermentation maceration treatments on the sensory characteristics of the resulting wine. Trained panel members found that there were no discernable sensory differences in the compositional parameters despite measurable chemical differences. Investigation into the aroma and flavour characteristics of the wines found that carbonic maceration produces wines that were lower in berry aroma and higher in acetate or ester-type aromas than the control wines. These wines were considered to have specific raspberry, floral, sugar, cherry and chemical aromas. This chemical note was also observed in the flavour of the carbonic maceration wines. The temperature of the cold maceration process has no major effect on the aroma and flavour of the resulting wines. However, the 10°C maceration was higher in woody/tobacco aroma than the 4°C maceration, and the 10°C treatment was also higher in bitter flavour than all the other treatments. Cold maceration wines were found to have specific mixed berry, dried fruit and sweet-oxidised aroma characters, together with a blackberry flavour note.

KEYWORDS: Pinot noir wine; carbonic maceration; cold maceration; acidity; anthocyanins; colour; sensory; quantitative descriptive analysis; aroma; flavour.

Choose your own wine after this sort;

it must be fragrant and redolent,

having good odour and flavour in the nose;

it must sprinkle in the cup when it is drawn

or put out of the pot into the cup;

it must be cold and pleasant in the mouth;

and it must be strong and subtle of substance.

Andrew Boorde - Dyetry of Health, 1562.

It's a naïve domestic Burgundy without any breeding,

but I think you'll be amused by its presumption.

James Thurber.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER ONE

INTRODUCTION

Pinot noir is often considered to be a "difficult" grape variety from which to make consistently good wine (Pompilio, 1992; Smart, 1992). Factors such as region, climate, clone and vineyard management have large influences on the resulting wine quality, more so than with other varieties (Smart, 1992). Drouhin (1991) lists nine quality factors desirable in Pinot noir grapes in order to produce good wine. These include grape health, balanced sugar, acid and polyphenols, and fruitiness of aroma and flavour (Drouhin, 1991). Obviously, these attributes are intrinsically linked to good viticulture.

In terms of winemaking, Pinot noir is regarded as "demanding" and so must be vinified completely differently from other varieties (Smart, 1992). Winemaking methods used can include techniques ranging from handpicking the grapes to use of small fermenter vessels to fermentation of whole bunches, or totally destemmed grapes. The ripe or lignified bunch stems may be included in the must to "strengthen the structure of the wine" (Halliday and Johnson, 1992). Fermentation temperatures are allowed to rise as high as 35°C, and cap management may be by plunging and/or pumping-over (Drouhin, 1991). The wine may be placed into new oak barrels after or even before the end of fermentation.

Winemakers have tried many techniques to increase the colour, body and flavour complexity, with differing degrees of success. **"The whole thing with Pinot noir is the struggle to extract from the skins and seeds - to give the wine intensity".** (Gary Farrell quoted in Pompilio, 1992). The grapes of the *Vitis vinifera* cultivar Pinot noir are known to contain only non-acylated anthocyanin derivatives (Powers, Shively and Nagel, 1980), which is thought to cause the characteristic lower colour of the wine. It is important to maximise skin-contact time and hence the phenolic extraction in order to extract the anthocyanins present. Pre-fermentation maceration of the must is one method used to lengthen the period of skin contact. This may occur unintentionally, when wild yeasts take some days to start fermentation. Alternatively, it may be a deliberate technique which involves adding high levels of SO_2, and chilling the must to prevent the onset of fermentation (Halliday and Johnson, 1992; Norman, 1992). Forms of this "cold maceration" have been traditional in the production of Pinot noir (Norman, 1992), but have not been scientifically investigated. There is a distinct lack of literature on the subject, and most descriptions of the resulting wines are subjective. Cold maceration was one of the techniques that was investigated in this thesis.

The flavour of red wine is a complex field, and the winemaker must remember that the consumer is looking for ripe, concentrated aromas and flavours in Pinot noir (Comerford, 1988). It is also desirable to have complexity in the sensory characteristics, so that the wine has many dimensions and depth of flavour.

One way of increasing the complexity of a Pinot noir wine is to make a number of different portions by various winemaking methods. These portions can then be blended together in the final wine. This is where carbonic maceration can play a part. Wine made by this method has characteristic fruity/spicy aroma and flavour, and so can increase the fruitiness of the blended wine. Carbonic maceration has been well investigated (Amerine and Ough, 1968; 1969; Beelman and McArdle, 1974; Fuleki, 1974; Ducruet, 1984; Versini *et al.*, 1984; Edinger *et al.*, 1988; Miller and Howell, 1989; Tesniere *et al.*, 1989; 1991; Etievant *et al.*, 1991; Ramos *et al.*, 1993) but never in New Zealand, and full quantitative description of the wines has not been conducted. This study aimed to redress this lack of knowledge about carbonic maceration.

The main objectives of this thesis were therefore to determine the possible effect of two pre-fermentation treatments, cold maceration and carbonic maceration on the chemical composition, colour, aroma and flavour of Pinot noir wine.

The main body of this thesis has been written as two papers to be submitted for publication in the following two refereed journals; the *American Journal of Enology and Viticulture*, and the *Australian and New Zealand Wine Industry Journal*. Chapter Three is an investigation into the chemical composition and colour of macerated wines, and Chapter Four covers the sensory evaluation of these wines.

The review of literature (Chapter Two) covers literature relevant to the entire topic of the research. Each of the two papers (Chapters Three and Four) contains a shorter review of literature specific to that paper. Conclusions of the research are presented in each of the two papers and are brought together in the conclusions chapter (Chapter Five).

CHAPTER 2

REVIEW OF LITERATURE

2.1 CARBONIC MACERATION

2.1.1 INTRODUCTION

Carbonic maceration is a winemaking process that involves holding whole grape bunches in an anaerobic atmosphere before fermentation (Beelman and Gallander, 1979). The fruit undergoes an internal metabolism during this period which continues until lethal cell disruption of the berries occurs at around 2% ethanol. Organic acids (particularly malate), glucose and fructose are catabolized to ethanol and CO_2, and this is accompanied by changes to the aromatic characters of the grapes. The wine made from these grapes is light in colour, low in acid and tannin and has a characteristic fruity aroma and flavour (Johnston, 1982; Sneyd, 1989).

Traditional winemaking techniques of the Beaujolais region of France use a similar process to carbonic maceration called *vinification beaujolais*. Whole bunches are placed in tanks and the weight of the fruit crushes the bottom third of the grapes (Blackburn, 1984). This juice begins to ferment, thus filling the tank with CO_2 so that the remaining whole fruit undergoes an anaerobic fermentation. The *beaujolais* method is also influenced by the alcohol produced by fermentation of the free juice present. This has a leaching effect on the phenolic constituents of the grape bunches (Sneyd, 1989).

2.1.2 HISTORICAL BACKGROUND

The initial investigation of anaerobic metabolism of fruit was conducted by LeChartier and Bellamy in 1821. They observed that ripe fruit placed in a limited atmosphere absorbs all the available oxygen and releases an equivalent volume of carbonic acid. This was seen to occur despite the lack of micro-organisms and since alcohol is formed, is a type of fermentation (Johnston, 1982).

Pasteur stated that "all cells become fermentative ... in the absence of air... [and] if we destroy the fruit or crush it... it no longer produces alcohol or fermentation of any kind". His experiments on anaerobic treatment of grapes demonstrated the development of the same flavour and aroma as found in whole grape bunches present in fermenting must (Pasteur, 1969).

More thorough investigations began in 1934 when Michel Flanzy tried to develop conservation methods for whole grapes. Bunches stored under CO_2 became alcoholic and fizzy but were of palatable flavour. When these were vinifed they produced a light, surprisingly fruity wine (Blackburn, 1984; Sneyd, 1989). Researchers at the Institut National de la Recherche Agronomique in France have continued to investigate carbonic maceration and the associated anaerobic metabolism of grapes (McCorkle, 1974) They are currently examining the effects at the cellular level (Robin, Romieu, and Sauvage, 1989; Tesniere, Baumes, Bayonak and Flanzy, 1989; Tesniere, Nicol, Romieu and Flanzy 1991).

Amerine and Ough carried out extensive experimentation on various grape varieties under Californian conditions. They experienced considerable problems with excessive acetic acid production in the resulting wines. This is presumably due to bacterial spoilage of the

grapes as lactic acid bacteria will displace yeast to produce 'lactic spoilage' if anaerobiosis is not maintained (Blackburn, 1984). In general Amerine and Ough concluded that carbonic maceration was not beneficial to winemaking in California since it produces wines that are of inferior colour, excessive volatile acidity and low acidity (Amerine and Ough, 1968; 1969; Amerine and Fong, 1974).

2.1.3 BIOCHEMICAL PROCESS

Biochemically, carbonic maceration is a form of anaerobic metabolism or intracellular fermentation. When whole bunches are placed in a CO_2 filled container the berries absorb some of the CO_2 while simultaneously producing CO_2 by respiration. As the available oxygen is depleted to 5% or less the fruit begins intracellular fermentation (Sneyd, 1989). This is a series of enzyme-catalysed reactions within the grape berry cells (Beelman and Gallander, 1979) the most significant of which is the degradation of malate. There will also be a certain amount of grape sugar degraded through glycolysis.

2.1.3.1 MALATE DEGRADATION

Malate is catabolized in two steps by malic enzyme (EC 1.1.1.40):

$$\text{MALATE} + \text{NADP}^+ \xrightarrow[\text{enzyme}]{\text{malic}} \text{OXALOACETATE} \xrightarrow[\text{enzyme}]{\text{malic}} \text{PYRUVATE} + \text{CO}_2 + \text{NADPH}$$

(Franke and Adams, 1992). This is one of the usual routes of malate degradation, and is not specific to anaerobic metabolism. It is part of the anaerobic metabolism of organic acids (figure 2.1) and hence the end products of this catabolism are ethanol and CO_2. During carbonic maceration the alcohol content of the grapes reaches up to 2.2% (v/v) (Riberéau-Gayon, 1976; cited in Sneyd, 1989). It is thought that such levels are eventually

toxic to the berries' cellular enzymes and/or to membrane permeability (Robin *et al.*, 1989).

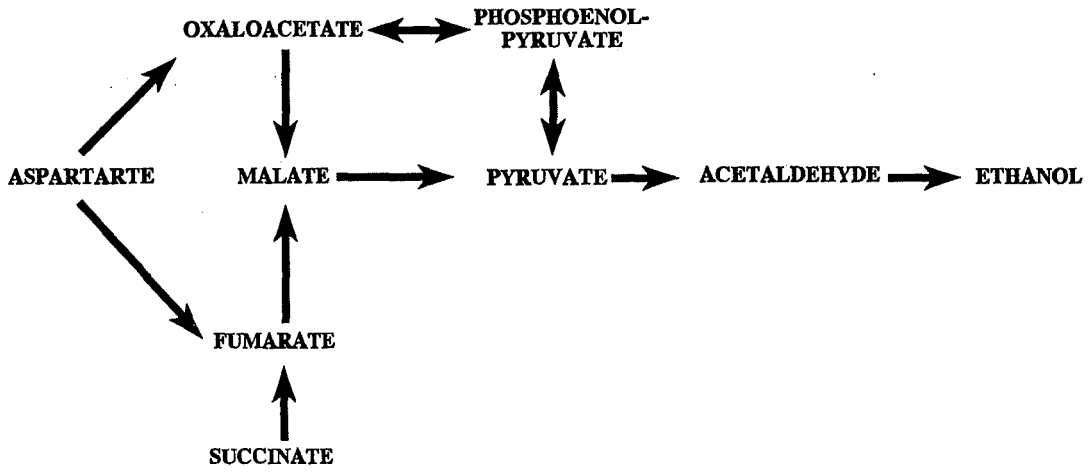

Figure 2.1 Possible routes for the anaerobic metabolism of organic acids (after Robin *et al.*, 1989).

Malate degradation is strongly affected by temperature, with a maximum rate achieved at 35°C (Sneyd, 1989). Ethanol content of the grapes' environment as is produced by the fermentation of juice in carbonic maceration has no effect on the rate of malate catabolism (Tesniere *et al.*, 1991). The overall effects of this decrease in malate are a decline in titratable acidity (TA) and concurrent pH rise (Beelman and Gallander, 1979). Reductions of up to 60% of the malate (Beelman and Gallander, 1979) and 3.5 g l^{-1} titratable acidity reduction with a pH increase of 0.6 pH units (Edinger, Holman, Gadd, Jackson and Bussman, 1988) have been recorded.

2.1.3.2 SUGARS

Although carbonic maceration does not involve yeast or bacterial metabolism about 10% of the total sugars is lost. This is due to catabolism of glucose and fructose during the intracellular metabolism (Tesniere *et al.*, 1991). Through glycolysis these sugars are converted to ethanol. This could possibly produce more of the ethanol than the malate degradation, although this is not clear in the literature.

2.1.3.3 OTHER ORGANIC ACIDS

Carbonic maceration causes changes in acids other than malate although tartrate and citrate levels remain constant. Succinate, fumarate and shikimic acid all increase with time while ascorbic and dehydroascorbic acids decrease by up to 50% (Sneyd, 1989).

2.1.3.4 NITROGENOUS COMPOUNDS

The level of soluble nitrogenous compounds increases during carbonic maceration, mostly due to an increase in the amount of amino acids present, particularly α-alanine, serine and γ-aminobutyrate (Sneyd, 1989). Recently Tesniere and colleagues experimentally confirmed this general increase in amino acids but noted decreased levels of glutamate, aspartate, alanine and serine. They proposed the first three of these are degraded in the TCA cycle to γ-aminobutyrate (figure 2.2). In the presence of exogenous ethanol the TCA pathway is repressed but the significance of this is not yet known (Tesniere *et al.*, 1991).

2.1.3.5 ETHANOL PRODUCTION

Ethanol is formed during carbonic maceration both as a result of the intracellular anaerobic metabolism, and fermentation of any juice present in the vessel. The intracellular formation is linear with time until the level becomes toxic. Accumulation of ethanol is

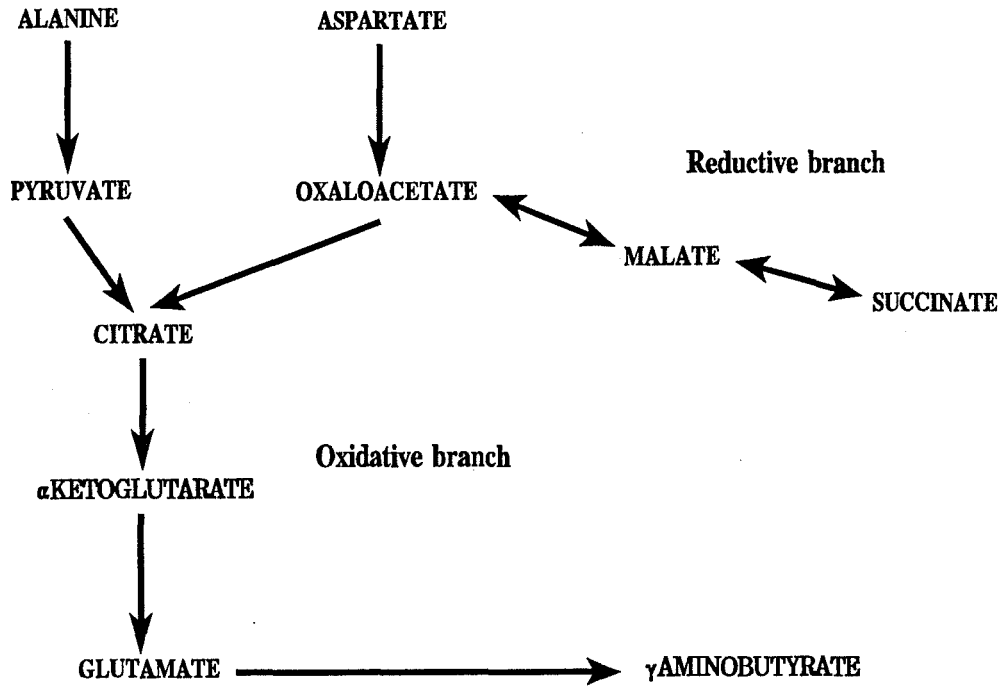

Figure 2.2 The tricarboxylic acid cycle as it relates to anaerobic amino acid metabolism in grapes (after Tesniere *et al.*, 1991).

exponential with increasing temperature (Saltveit and Ballinger, 1983) but has not been documented as exceeding 2.5% (Miller and Howell, 1989).

2.1.3.6 MINOR BY-PRODUCTS

Glycerol is formed during carbonic maceration and this formation is dependent both on temperature and ripeness of the fruit. Levels of one to five g l^{-1} have been reported (Johnston, 1982) as well as 15 to 20 mg l^{-1} methanol (Sneyd, 1989).

2.1.4 COLOUR ASPECTS

Polyphenolic compounds move from the skin to the pulp during carbonic maceration

(McCorkle, 1974). Anthocyanins are extracted into the flesh of the berries in a linear time relationship (Ramos and Macheix, 1990). Most of this extraction occurs in the first five days of carbonic maceration. During this time, tannin-anthocyanin complexes are probably forming within the berries (Ramos, Fleuriet, Rascalou and Macheix, 1993). Temperature also affects this phenolic movement, with the extraction rate four to five times greater at 35°C than at 15°C (Johnston, 1982). Tannin is predominantly found in the grape seeds and there is little opportunity to extract these phenolics during carbonic maceration. The final wine is low in colour due to the combined effects of high pH, and low anthocyanin and tannin content (Johnston, 1982).

2.1.5 AROMATIC COMPONENTS

Anaerobic metabolism of grapes significantly changes their aroma. This is due to secondary metabolism reactions which are influenced by the presence of ethanol in the berries (Tesniere *et al.*, 1991). Ethanol is accumulated due to both the intracellular malate degradation and fermentation of juice from crushed grapes in the container. The ethanol esterifies with the various grape components to give a noticeable increase in esters such as ethyl cinnamate, ethyl vanillate and ethyl lactate which are not present in the fresh grapes (Tesniere *et al.*, 1989).

Ramos *et al.*, (1993) suggested that the breakdown of hydroxycinnamoyl tartaric esters in the grape berry produces some of the characteristic aromas of carbonic maceration wines. The release of *p*-coumaric acid, in particular, from such esters would allow it to be metabolised into other aromatic compounds along with other compounds formed in the anaerobic metabolism (Ramos *et al.*, 1993).

Shikimate shows a general decrease over the period of carbonic maceration, although analysis demonstrates an initial increase in the first four days. This overall decrease is due to the conversion of shikimate to cinnamate (figure 2.3) which is then esterified to ethyl cinnamate. It is possible that this reaction decreases product inhibition on the system and allows more shikimate to be converted (Tesniere *et al.*, 1991).

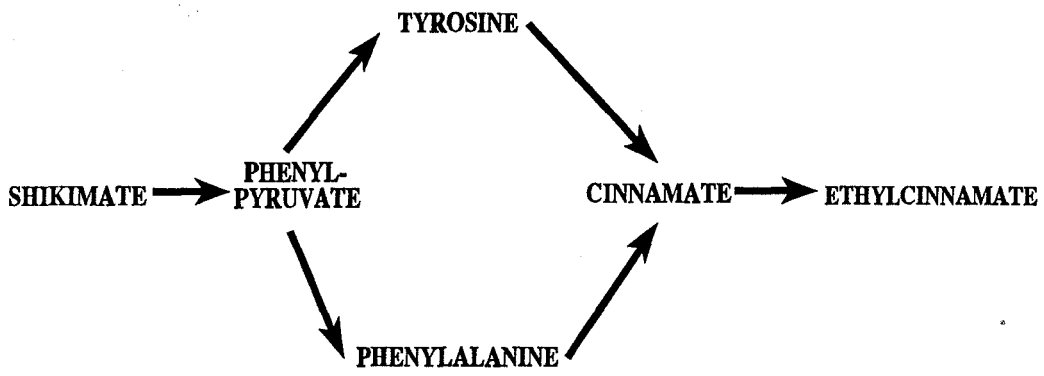

Figure 2.3 Biosynthesis of aromatic compounds from shikimate (after Tesniere *et al.*, 1991).

Gas chromatography (GC) using a "sniff detector", i.e. the human nose, of carbonic maceration wines has determined that the "strawberry/raspberry" aroma is due to ethyl cinnamate (Versini, Dalla Serra and Pellegrini 1984). Thorough investigation of carbonic maceration wines by gas chromatography-mass spectrometry (GC-MS) headspace analysis identified 22 compounds unique to these wines. Vinylbenzene and benzaldehyde were found in significant amounts and it is possible that these are formed from the degradation of shikimate. Benzaldehyde is possibly a contributor to the distinctive "cherry or kirsch-like" aroma of carbonic maceration wines (Ducruet, 1984). This observation is supported by Tesniere and colleagues who note the presence of benzaldehyde and its contribution to

the "cherry-like" note (Tesniere *et al.*, 1989).

The volatile phenols 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol and 4-vinylguaiacol are also important in the aroma of carbonic maceration treated grapes and wines. On the whole the ethyl derivatives are more significant. 4-ethylphenol can be perceived as either pleasant or unpleasant in wine depending on the concentration present, with an optimum at 2.2 ppm (Etievant, Issanchou, Marie, Ducruet and Flanzy, 1989).

2.1.6 DEACIDIFICATION

A significant effect of carbonic maceration is the reduction in acidity concomitant with the degradation of malate, in terms of both pH and titratable acidity. Malate degradation can be from 15 to 60% of the total malate initially present in the grapes (Beelman and Gallander, 1979). Several studies have demonstrated this phenomenon which typically shows as an increased pH and decreased TA in the finished wines (Beelman and McArdle, 1974; Fuleki, 1974; Edinger *et al.*, 1988; Miller and Howell, 1989). Beelman and McArdle applied carbonic maceration to French hybrid 'Chelois' grapes and found decreases of 15% of the TA, 15% of malate and 33% of the tartrate (Beelman and McArdle, 1974). Tartrate is generally not degraded in carbonic maceration and it is possible that the losses found here is due to other vinification practices (Beelman and Gallander, 1979). The most marked pH increase occurs in the first two days of maceration and then the rate stabilises. TA follows this pattern but shows more clearly a linear decrease with maceration time (Miller and Howell, 1989).

2.1.7 MALOLACTIC FERMENTATION

Wines that have been made by carbonic maceration are notably more susceptible to

malolactic fermentation. The combination of lowered acidity to a pH that is closer to ideal for malolactic bacterial growth, and increased nitrogenous compounds makes malolactic fermentation easier to achieve (Sneyd, 1989). In some cases this is more a case of spoilage since in hot climate wines this leads to an unacceptably low acid level (Johnston, 1982).

2.1.8 CESSATION OF CARBONIC MACERATION

Carbonic maceration ends with the death of the berries, which occurs when they contain up to 2.5% ethanol by volume (Miller and Howell, 1989). Possibly this concentration has deleterious effects on cellular enzymes and membrane permeability (Robin *et al.*, 1989). Certainly at around 1.5% ethanol (v/v) mitochondrial membrane permeability is affected. This can lead to loss of the neutral pH within the cell that is necessary for plant survival under anaerobic conditions (Romieu *et al.*, 1992).

That the ethanol content does not exceed 2.5% is possibly due to a number of factors. A feedback inhibition of glycolysis may occur that produces end-products other than ethanol. It has been suggested that there is an "inversion" of the Kreb's cycle that results in the ethanol substrates being converted to succinate (Flanzy 1974; cited in Miller and Howell, 1989). This is unlikely when the energetics of this reaction are considered. Alternatively, ethanol may have an end-product inhibition effect on alcohol dehydrogenase (ADH), which normally converts acetaldehyde to ethanol. This was disproved by Molina *et al.* who showed that ADH is still active at ethanol concentrations of 7.5%, and retains 25% effectiveness at 2.5% ethanol (Molina, Nicholas and Crouzet, 1989). Similarly Sauvage and colleagues found that grape aminotransferases, although inhibited by ethanol, still retain 90% activity at the ethanol concentration found in carbonic maceration (Sauvage, Romieu, Flanzy and Robin, 1991).

2.2 COLD MACERATION

This winemaking technique has recently begun to be applied to the vinification of Pinot noir in Burgundy, Oregon and New Zealand. It is also known as "cold soaking" in Oregon (Heald and Heald, 1993). It involves holding partially destemmed, crushed and highly-sulphured grapes at low temperature for periods of 5 to 10 days (Matthews, 1990b; Norman, 1992). There is a lack of information on this technique in the scientific literature, and most descriptions of the resulting wines are, at best, subjective.

Wines made by this method are said to have deep, opaque colour, concentrated fruit flavours of "plum and kirsch" and "full, soft tannins" (Matthews, 1990a). There is considerable debate in Burgundy if such wine styles are desirable. It is felt that this hides the influence of *terroir*, and that the wines made by pre-fermentative methods have more structure but less elegance and finesse (Drouhin, 1992).

The main proponent of cold maceration is Guy Accad, an oenological consultant in Burgundy. He believes that winemakers can achieve better extraction of anthocyanins and tannins from the fruit before fermentation (Norman, 1992), and that this is an aqueous extraction that has a quite different effect to the post-fermentation maceration commonly used for Pinot noir (Larry McKenna, personal communication, 1992). The crushed must is cooled to the desired temperature (8 to 15°C), sulphur dioxide added at a rate of 100 to 150 mg l^{-1}, and then held for 5 to 10 days (Norman, 1992). Fermentation begins as the must warms and through an added inoculum, if desired. The fermentation temperature is maintained at less than 30°C to conserve the ethanol and aromas, and chaptalisation is manipulated to achieve a slow fermentation. Post-fermentative maceration is avoided in

cold maceration, since Accad believes that the ethanol non-selectively extracts undesirable compounds from the must (Norman, 1992).

The high level of SO_2 used, up to three times the usual rate, acts as a solvent of the grape phenolics, and also prevents the spontaneous onset of fermentation. Critics say that this leads to excessive sulphites in the finished wines, but this is unlikely since the total SO_2 addition is no higher than that found in conventional vinification (Norman, 1992).

Winemakers of various Burgundian companies are adopting this method and Accad's philosophy on the viticulture and oenology of Pinot noir (Matthews, 1990a; Norman, 1992). Some of these ideas have been brought to New Zealand by winemakers who have worked a vintage in Burgundy and have been impressed by the effects of cold maceration. There is a need to investigate the parameters and effects of this technique so that the New Zealand wine industry can use it to advantage.

2.3 SENSORY EVALUATION

2.3.1 USE OF HUMAN SENSES TO ASSESS SENSORY PROPERTIES

The consumers' perception of any food or beverage is extremely important and this can only be assessed using the human senses. These senses have the ability to distinguish a huge number of distinct impressions (Cartwright *et al.*, 1952) and it is this ability that is capitalised on in sensory evaluation. Individuals vary widely in their response to any one sensory stimulus and in sensory evaluation groups of people are used as evaluating panels. This allows individual errors to be compensated for by the correct responses of the rest of the panel (Cartwright, Snell and Kelley, 1952).

Training and experience are vital in achieving true and accurate results. The assessors gain a sharpened perception of the sensory stimuli so they distinguish aroma and flavour notes of which untrained people would not be conscious (Clapperton and Piggott, 1979). Humans are the only means to measure sensory attributes that can subsequently be correlated with physical and chemical measurements (Civille and Lawless, 1986).

2.3.2 QUANTITATIVE DESCRIPTIVE ANALYSIS

Although in the past "experts" were solely responsible for the quality assessment of food products, a trained panel is now considered necessary to objectively quantify sensory properties. Quantitative descriptive analysis (QDA) was developed by Stone and colleagues in 1974 (Stone, Sidel, Oliver, Woolsey and Singleton, 1974) and has become the method of choice for sensory evaluation.

Panellists are trained to identify, quantify and describe the sensory properties of interest in the product (Stone *et al.*, 1974). Specific training for one product type, for example a varietal wine, involves familiarising the panellists with the style and then the specific wine of interest (McDaniel, Henderson, Watson and Heatherbell, 1988). Research has shown that experience with a particular product is more important than long-standing experience of general flavour assessment (Lawless, 1985).

The Wine Aroma Wheel, as designed by the American Society for Enology and Viticulture, is used to develop a shared vocabulary of descriptive terms for wine (Noble, Arnold, Buechsenstein, Leach, Schmidt and Stern, 1987). Panellists use a two-step process to assess the wine:

i discrimination of the aroma, taste and/or texture and detection of differences and amounts;

ii description and quantitation of the sensory characteristics present.

(McDaniel *et al.*, 1988).

2.3.3 IMPORTANCE OF LANGUAGE

Descriptive analysis provides a comprehensive verbal description of a product in terms of its sensory properties and the effectiveness of the evaluation relies on the language used (Stone and Sidel, 1985). The correct naming of a stimulus is one of the most difficult aspects of sensory evaluation. The use of a list of words to help panellists memories improves identification (Civille and Lawless, 1986). Panellists develop a common vocabulary - a "mental library" of expected attributes through training and round-table discussion (Civille and Lawless, 1986; McDaniel *et al.*, 1988).

2.3.4 SELECTION AND TRAINING OF PANELS

Panellists are selected for their acuity, motivation and availability (McDaniel *et al.*, 1988). The initial screening process is also the first stage of training, where individuals are required to correctly identify the four basic tastes. This may be followed by an interview where the panellist's interest, availability and personality are assessed (Martin, 1973).

Training for QDA may take up to six months but for most wine assessments a short, intense period specific to that wine type may be sufficient (McDaniel *et al.*, 1988). Noble (1988) suggests one to six weeks of training without specifying the number of hours spent each day (Noble, 1988). The original specifications of Stone and co-workers requires at least 20 hours of training (Stone *et al.*, 1974), later modified to six to ten hours (Stone and Sidel, 1985). Zook and Wessman recommend ten hours at a rate of one hour per day (Zook and Wessman, 1977).

The initial sessions involve familiarising the panellists with the general wine style, which can be done with commercially available wines as well as the wines under investigation (McDaniel *et al.*, 1988). Round-table discussion of these wines, guided by the panel leader, leads to generation of the descriptive terms. These terms are then characterised by use of aroma reference standards from the Wine Aroma Wheel. The panel members create the descriptors themselves and must both understand and feel comfortable with them in order to use them effectively (Zook and Wessman, 1977). It is not essential that each member of the panel agrees on the usefulness of the descriptors (McDaniel *et al.*, 1988) more that panellists are uniform in their use (Stone *et al.*, 1974). Once familiar with the descriptors the panel are guided through their first profile by the investigator, explaining the method as necessary (Martin, 1973).

Training assures both sensory acuity and uniform understanding of the method, sensory properties of interest and descriptive terms by the entire panel (Cartwright *et al.*, 1952).

2.3.5 USE OF QUANTITATIVE DESCRIPTIVE ANALYSIS

The panel are presented with wine samples under standardised conditions of temperature, lighting, humidity and presentation. Reference standards are present for panellists to define each of the attributes, and to compare that of the wine to the standard (Noble, 1988). "Quality" judgements are not made, as these are subjective assessments best made by the winemaker or consumers (McDaniel *et al.*, 1988). A scoresheet is used that lists the descriptors generated by the panel, each of which has an unstructured line scale next to it. The panellist marks on the scale a point which represents their perception of the attribute's intensity. Numerical scales are assigned later in data analysis (Zook and Pearce, 1988) to avoid any possible bias that may occur if numbers are used.

2.3.5.1 QUANTITATIVE DESCRIPTIVE ANALYSIS OF PINOT NOIR

QDA of Pinot noir wines from various viticultural regions of California demonstrated the uniqueness of the Carneros wines. These are significantly higher in the desirable berry, fruity and spicy characters and have less vegetal, leather and smoke/tar aroma than comparable wines (Guinard and Cliff, 1987).

Walter (1990) found differences between Canterbury, New Zealand, Pinot noirs from two different vineyards. In sensory terms eight of the descriptors were significant and the Larcomb vineyard produced wines that were higher than the St. Helena wines in all attributes but "berry" (Walter, 1990).

A comparative investigation of the effects of "Oregon" and two conventional maceration techniques during production of Pinot noir wines found that there is a considerable difference in the wines produced (Ewart and Gawel, 1993). The "Oregon" maceration involves adding a yeast inoculum to the top layer of crushed grapes in a small fermenter (1 x 3m), and allowing this to macerate for two days. The yeast starts to ferment the top layer, and so protects the remainder of the must from spoilage during this pre-fermentation maceration. After 48 hours, the must is hand-plunged twice daily until the end of fermentation. QDA of the finished wines established that the "Oregon" maceration had greater intensity of strawberry and cherry aromas, and less of the plum aroma.

Investigation of Pinot noir wines inoculated with various strains of malolactic bacteria showed clear sensory differences (McDaniel, Henderson, Watson and Heatherbell, 1987). The various strains used differently affected the overall aroma intensity and specific aroma notes of the wines, but no overall preference or quality rating was made as this is a subjective decision beyond the scope of the panel's assessment.

2.3.5.2 QUANTITATIVE DESCRIPTIVE ANALYSIS OF PROCESSING TRIALS

The effect of different processing methods on wine can be assessed by QDA. Methods as diverse as ultrafiltration, oak ageing and enzyme release of grape volatiles have been investigated. Ultrafiltration has been shown to have no effect on the sensory characteristics of Gewurztraminer and White Riesling wine (Flores, Heatherbell, Henderson and McDaniel, 1991). Oak ageing is known for its effect on the sensory properties of wine. Even the origin of the wood and the seasoning method before coopering have differing effects on the final wine (Francis, Sefton and Williams, 1992). Volatile compounds can be released from grapes by enzymatic or acid hydrolysis, and investigation

using QDA has shown a correlation between quality and certain sensory properties. In Shiraz, high quality is associated with non-berry sensory attributes such as stalky, earthy, cigar/tobacco and licorice which are derived from enzyme-freed precursor compounds (Abbott, Coombe and Williams, 1991). The effect of carbonic maceration on the sensory properties of wine has not been thoroughly investigated. Only one study was found and that focused on the influence of the phenolic constituents. The different grape varieties used in this study were differently affected by carbonic maceration. In general, significant differences in phenol characteristics of carbonic maceration wines occur over the first 12 months of ageing (Etievant *et al.*, 1989).

2.3.6 CORRELATION OF SENSORY AND ANALYTICAL DATA

Recently, research has begun to focus on correlating sensory and instrumental data. The frequency with which certain descriptive terms are used indicates their importance and isolating specific compounds by GC or GC-MS may identify the actual chemical compounds involved (Williams, Baines and Arnold, 1980). Investigation of Pinot noir wines by parallel descriptive analysis and GC demonstrated that wine aroma is a hugely complex phenomenon involving many inter-related compounds (McDaniel, Miranda-Lopez, Watson, Micheals and Libbey, 1990). Some of the aroma compounds have been identified but as yet their importance and role is undefined (Miranda-Lopez, Libbey, Watson and McDaniel, 1992).

2.4 COLOUR OF RED WINE

2.4.1 PHENOLIC CONSTITUENTS OF GRAPES

The phenolic constituents of grapes are important in red wine as they are intrinsic to the colour and sensory characteristics (Riberéau-Gayon, 1974). Their chemical and physico-chemical properties and inter-relationships are responsible for the dynamic changes observed as wine matures and ages (Somers, 1987).

Anthocyanins and procyanidins are of most significance in red wine; these are the pigments and tannins respectively and interact to form the colour and flavour (Riberéau-Gayon and Glories, 1987). These phenolics (figure 2.4) are mainly found in the skin, seeds and vascular tissue (Somers, 1987) and in order to extract these into the wine, vinification involves fermentation of the entire berry, crushed to release the pulp.

2.4.1.1 ANTHOCYANINS

These are the red and blue pigments found in many plant genera (Riberéau-Gayon, 1974) and their absence differentiates white grape varieties from the black (Somers, 1987). Five anthocyanidins are found in grapes: malvidin; petunidin; peonidin; cyanidin and delphinidin (Riberéau-Gayon, 1974). Of these, malvidin predominates in *Vitis vinifera* grapes (Riberéau-Gayon, 1982; Somers and Verétte, 1988). Anthocyanidins are present in *V. vinifera* as monoglucosides and acylated heterosides (Riberéau-Gayon, 1974) although Pinot noir lacks these acylated derivatives (Powers *et al.*, 1980; Riberéau-Gayon, 1982).

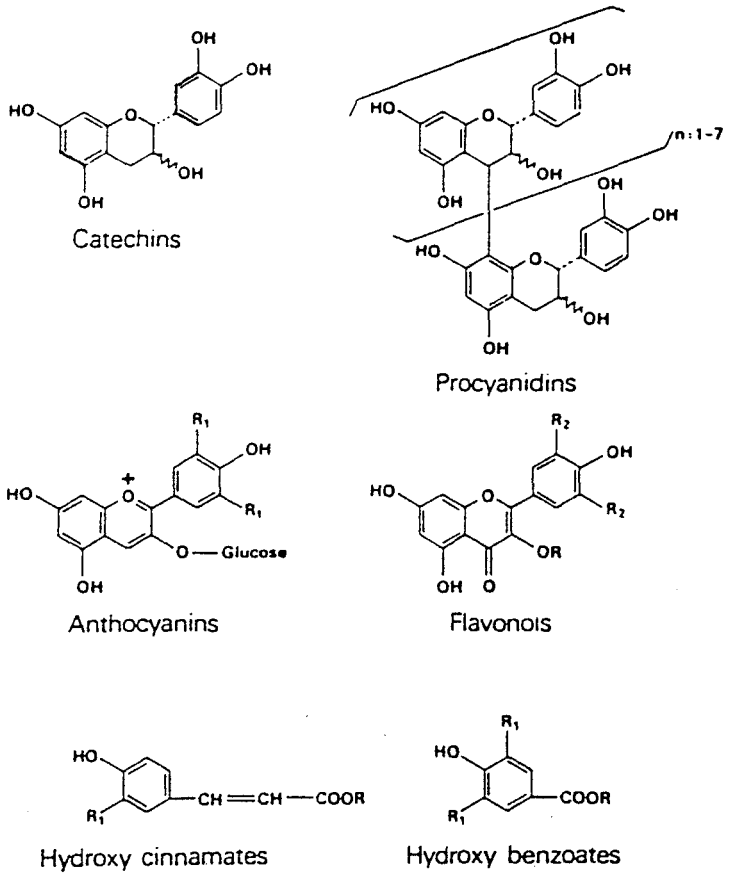

Figure 2.4 The phenolic components of *Vitis vinifera* (from Somers, 1987).

2.4.1.2 TANNINS

By definition, tannins are naturally occurring phenolics that are physically and chemically similar to substances that can convert fresh hides to leather. They are water and ethanol soluble, have molecular weights of 500 to 3000 and have the ability to precipitate alkaloids and proteins (Riberéau-Gayon, 1974). The tannins found in grapes are the condensed type collectively known as procyanidins, formed by polymerisation of catechins and leucoanthocyanidins (Somers, 1987). In addition, wine may contain hydrolysable tannin extracted from oak barrels during ageing, but these will not be considered in this review.

Procyanidins are reactive over long periods of time, and their reactions lead to the

formation of tannins of degrees of condensation, colour and astringency. Other interactions with peptides and polysaccharides or anthocyanins are vital to the development and maturation of red wine (Riberéau-Gayon and Glories, 1987).

2.4.2 PHENOLIC EXTRACTION

It is possible to extract from 15% (Somers and Pocock, 1986) to 30% of the total grape phenolics into wine (Riberéau-Gayon, 1974). The major factor influencing the amount of extraction is the length of time the grapes are left in the ferment (Riberéau-Gayon and Glories, 1987). The period of skin contact directly affects the tannin content and the colour of the wine so that after ageing the colour is directly proportional to the contact time (Berg and Akiyoshi, 1956).

The level of colour, phenolics and anthocyanins increases in the ferment over the first five or six days. After this the level of both colour and anthocyanin content decrease sharply (figure 2.5). The loss of colour is not well understood and several theories have been proposed to explain this phenomenon.

The anthocyanins self-associate when in high concentrations, as are found in wine. Since they are hydrophobic, they stack vertically to protect the anthocyanidins from hydration and so the colour increases (Hoshino, 1992). Such anthocyanin stacks persist only until the ethanol content of the new wine reaches a level that interferes with the hydrogen bonding of the water (Mazza and Brouillard, 1990). When the chromophores are dissociated, the colour is reduced. The extent of the colour loss is dependent on the particular juice or wine pH, anthocyanin content and alcohol level (Somers, 1980).

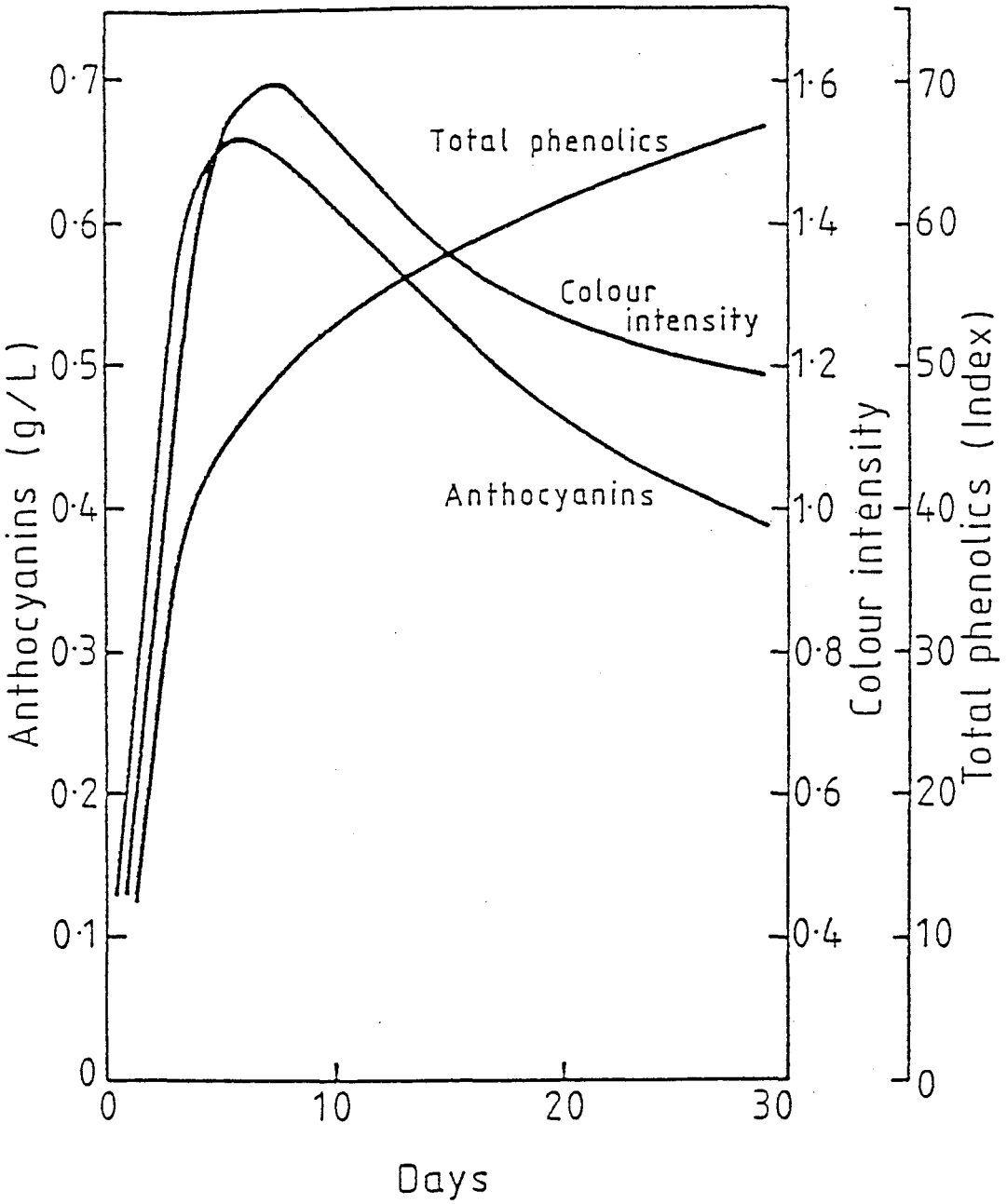

Figure 2.5 Effect of maceration on the evolution of anthocyanins, colour intensity and total phenolics during vinification (from Riberéau-Gayon and Glories, 1987).

Alternative theories suggest that the strongly reducing environment of fermentation may cause the reduction of the anthocyanins to colourless flavenes (Riberéau-Gayon, 1974). It may be possible that the anthocyanins are fixed onto yeast and grape cells and that these are lost at racking and pressing of the young wine. Certainly a great deal of pigment is found in the lees of finished wine (Riberéau-Gayon, 1976; cited in Bissell, Steans and Ewart, 1989) but the amount of colour loss is much greater than can be explained by this means (Somers and Evans, 1979). HPLC studies have shown that anthocyanins and tannins begin to interact during fermentation. Such reactions could result in the formation of small non-coloured polymers that may later be re-oxidised to the coloured form (Bakker, Preston and Timberlake, 1986). More likely, the loss of colour is due to co-pigmentation. This is a two-step interaction of anthocyanins and polyphenols, and effectively increases the colour after a transient reduction (Brouillard, Wigand and Cheminat, 1990).

Temperature affects the rate of phenolic extraction, so for example, anthocyanin content increases linearly with increased fermentation temperature (Lee *et al.*, 1977; cited in Bissell *et al.*, 1989). This is utilised in winemaking so that light, fruity wines are fermented at lower temperatures (20 to 25°C) and long-lived, tannic wines are produced by allowing the temperature to reach 30°C (Riberéau-Gayon and Glories, 1987). Excessively high temperatures and extended maceration time may result in a decrease of anthocyanins (Riberéau-Gayon, 1974). This is due to dissociation of the anthocyanin chromophores, and then hydration of the quinoidal bases, leading to a loss of the red colour (Hoshino, 1992).

2.4.3 INFLUENCES ON ANTHOCYANIN COLOURATION

2.4.3.1 pH

Anthocyanins exist in a pH-dependent equilibrium state of four major species (figure 2.6).

The pK_a of malvidin is close to pH 3 so that at wine pH approximately half of the anthocyanins are in the red flavylium form (Riberéau-Gayon, 1974). As the pH rises colour density decreases since increased pH leads to the formation of the colourless carbinol pseudo-base (Timberlake, 1980). The blue quinoidal base is important above pH 2 and has a small contribution to the violet hue of anthocyanin solutions (Somers and Verétte, 1988).

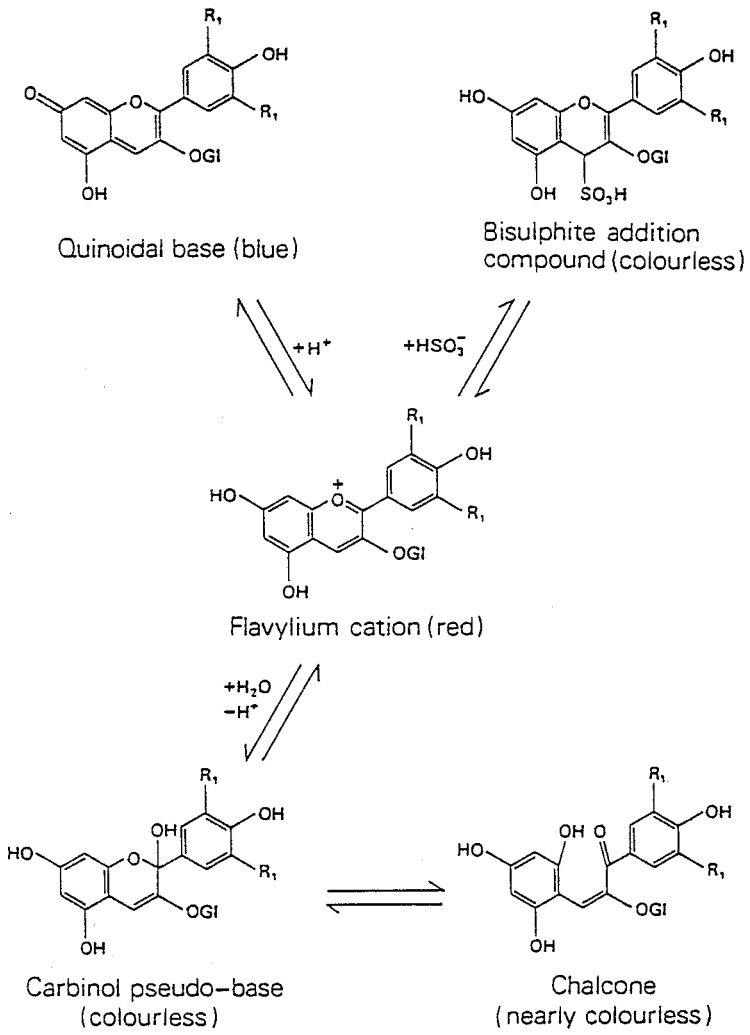

Figure 2.6 Anthocyanin equilibria at wine pH in the normal presence of SO_2 (from Somers and Verétte, 1988).

2.4.3.2 SULPHUR DIOXIDE

The addition of SO_2 to anthocyanins causes the formation of a colourless bisulphite addition compound with the flavylium cation (figure 2.6). In real terms the level of free SO_2 is the major influence on the pigmentation of red wine. This reaction is reversible as the bisulphite ions can be bound by other compounds such as acetaldehyde, pyruvic acid and sugars (Somers and Verétte, 1988; Riberéau-Gayon, 1974).

2.4.4 ANTHOCYANIN INTERACTIONS

Anthocyanins are not stable in dilute aqueous solutions such as wine (Goto and Kondo, 1991). At concentrations less than 50 μM (5×10^{-5} moles l^{-1}) anthocyanins will exist in monomeric form (Hoshino, 1992), but since in wine their concentration is up to 2mM (2×10^{-3} moles l^{-1}) (Somers and Verétte, 1988) it is likely that they will polymerise. They interact in two main ways to stabilise themselves: self-association and co-pigmentation.

2.4.4.1 SELF-ASSOCIATION

The colour of an anthocyanin solution increases more than would be expected due to the concentration (Timberlake, 1980). This is a deviation from the Beer-Lambert Law (Hoshino, 1992) and is why colour density must be measured on undiluted samples (Somers and Verétte, 1988). The increase in colour observed is due to the self-association of the anthocyanins. The anthocyanin cations, i.e. the red flavylium forms, will stack vertically due to hydrophobic interactions despite their mutual electrostatic repulsion (figure 2.7). This stacking forms a vertical helical structure with the anthocyanins as a hydrophobic core surrounded by hydrophillic glucose moieties (Hoshino, 1992) This structure protects the anthocyanidins at the core from hydration, which causes ionisation to the blue quinoidal base and thus loss of colour. The glucose moieties cause the entire

aggregate to be water-soluble (Hoshino, 1992).

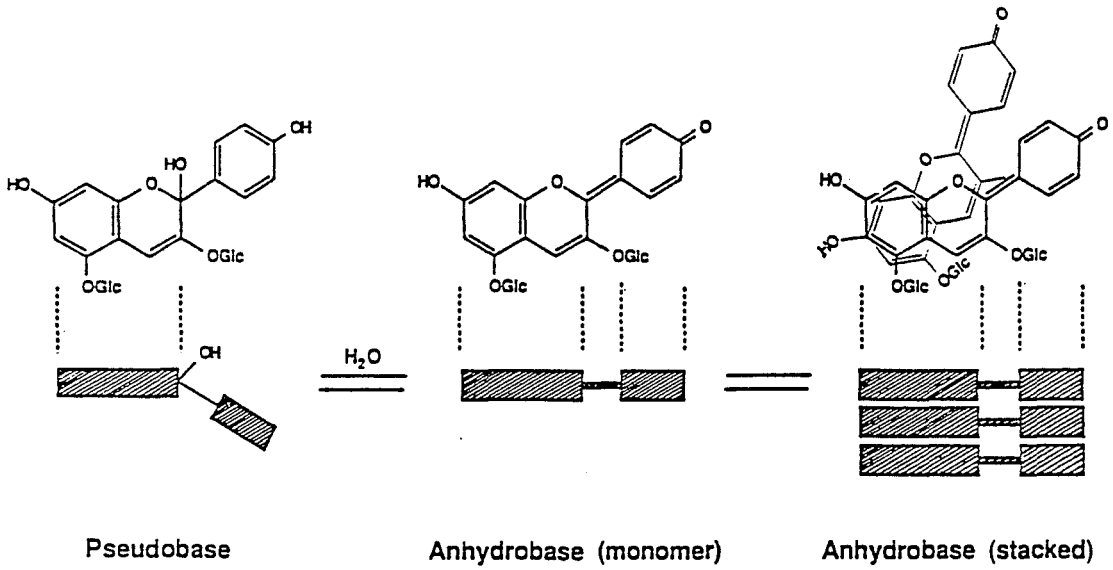

Figure 2.7 Stacking of anthocyanin molecules to prevent hydration and formation of the colourless pseudobase (from Goto and Kondo, 1991).

Increased temperature dissociates the anthocyanins, which causes destacking of the chromophores, and hence reduced colour (Goto and Kondo, 1991; Hoshino, 1992). Self-association is a major factor at low pH, since here the flavylium form predominates (Somers and Verétte, 1988).

2.4.4.2 CO-PIGMENTATION

A similar form of vertical helical stacking occurs in co-pigmentation (figure 2.7) (Goto and Kondo, 1991). Colourless molecules such as polyphenols and flavonoids act as co-pigments with anthocyanins to form the stacks (Brouillard *et al.*, 1990). The interaction of the co-pigments causes an increase in colour intensity and stability, as the anthocyanidin

quinoidal bases are protected from hydration (Timberlake, 1980; Goto and Kondo, 1991; Dangles and Brouillard, 1992). Experimentation *in vitro* has found that co-pigmentation is a two-step process that involves an initial transient loss of colour before a more than complete recovery, and slight change in colour (Brouillard *et al.*, 1990).

Co-pigment complexes of anthocyanins and co-pigments are formed by hydrophobic interactions (Mazza and Brouillard, 1990). Co-pigmentation only occurs in aqueous solutions, since it is driven by the hydrophobic interactions of the anthocyanins (Brouillard *et al.*, 1990; Goto and Kondo, 1991). In the absence of water, co-pigmentation does not occur (Brouillard *et al.*, 1990) and the presence of ethanol decreases the colour intensification (Mazza and Brouillard, 1990).

Catechin is a co-pigment of malvin that forms a highly stable co-pigment complex and the resulting colour is maximal at pH 3.5 (Dangles and Brouillard, 1992). It would therefore be an important co-pigment in red wine.

2.4.5 EVOLUTION OF COLOUR

The colour of young red wine is primarily due to the anthocyanin monomers (Iland, Ewart, Bruer and Hartnell, 1988). At the end of fermentation only 25% of the colour is due to polymeric pigments (Somers, 1980) but this increases rapidly as most of the colour change occurs in the first year after fermentation (Somers, 1971). Over this maturation period a gradual transition occurs from monomeric anthocyanins to polymeric pigments which are more resistant to decolourisation by pH and SO_2. This is accompanied by a colour change from purple-red to crimson-red and a mellowing in flavour (Somers and Verétte, 1988). A small amount of pigment may precipitate during cold stabilisation of the wine (Somers

and Evans, 1986) but this is not enough to be of great significance.

2.4.6 TANNIN INTERACTIONS

Tannins in wine are formed by the oxidative polymerisation of procyanidins and have characteristic astringency. Procyanidins may also combine non-oxidatively to produce non-hydrolysable tannins which are yellow-red in colour and less astringent than other forms of tannin. Highly polymerised tannin is formed by further polymerisation and these molecules continue to increase in size until they precipitate. Polysaccharides and peptides from the grapes can inter-react in these reactions to form condensation products that are thought to contribute to the "suppleness" of the wine (Riberéau-Gayon and Glories, 1987).

2.4.7 TANNIN-ANTHOCYANIN INTERACTIONS

Anthocyanin monomers react with phenolic compounds, principally tannin, to form reddish-brown polymers. This slow reaction is the major mechanism of phenolic condensation and eventually produces yellow xanthylium salts (Timberlake and Bridle, 1976). These combined anthocyanin-tannin complexes are less sensitive than the monomers to decolourisation by pH, SO_2 and reduction. At the same pH, a greater proportion of the anthocyanin-tannin complexes are in the coloured state than the free anthocyanins (Riberéau-Gayon and Glories, 1987).

The reactions between tannin and anthocyanin occur both oxidatively and non-oxidatively. In the absence of oxygen a direct condensation reaction produces colourless flavene intermediates. These are subsequently oxidised to the coloured flavylium form. The amount of oxygen required is so minimal that this process is considered to be basically anaerobic (Somers and Evans, 1986).

Oxidative combination of phenolics relies on the presence of acetaldehyde. This is produced both by microbial growth and the coupled oxidation of ethanol and phenols (Timberlake and Bridle, 1976). The acetaldehyde provides CH_3CH bridges between the phenols and this condensation continues until the complexes are so large that they precipitate. Larger amounts of tannin lead to the reaction being faster and more complete (Timberlake and Bridle, 1977). Another influential factor is the degree of polymerisation of the tannins. If these are only slightly polymerised the condensation results in the stabilisation of the wine colour. However, if the tannins are highly polymerised the complexes formed tend to precipitate, leading to a colour loss (Riberéau-Gayon and Glories, 1987).

There is some suggestion that in real conditions such acetaldehyde interaction is a secondary reaction of little importance. With normal handling and cellar conditions the amount of acetaldehyde needed to stabilise the colour could not be formed and so the anaerobic reactions are much more significant (Somers and Wescombe, 1987).

The interaction of anthocyanins and tannins also increases the amount of polymeric tannin retained in the wine. The polymers formed are more soluble, less precipitable and less absorbable and are hence more likely to remain in the wine. Anthocyanins affect the polymers in terms of the astringency, colour and quality of the finished wine, possibly due to this increased tannin retention. Certainly white wines vinified as if they were red will not contain polymeric phenols as the lack of anthocyanins precludes the retention of polymeric tannins in solution. Although anthocyanins have not been shown to have an appreciable flavour, they are important in the overall flavour of red wine due to this interaction with the all-important tannins (Singleton and Trousdale, 1992).

The interaction of phenolics is vitally important in stabilising and retaining colour in red wine. Pinot noir characteristically has low colour and this is due in part to the naturally low phenolic levels of the grapes. Winemakers are attempting to find methods of maximising phenolic extraction and retention in the wine (Bissell *et al.*, 1989). Adding oeno-tannin to wines after fermentation increases the colour density and stability over time (Steans, 1987). Other methods include the inclusion of stalks in the ferment, fermentation at high temperatures (Drouhin, 1991) and finishing fermentation in new barrels (Bissell *et al.*, 1989).

2.4.8 COLOUR MEASUREMENT

Measurement of red wine colour can be achieved by several methods. Spectral methods rely on the premise that up to 95% of the absorbance is due to the phenolic components (Somers and Verétte, 1988). Optical absorbances at 420nm and 520nm provide measures of colour hue and density (Somers and Evans, 1977) and are also indicative of the brown and red pigments respectively (Iland *et al.*, 1988).

Somers and Evans developed a spectral method based on a principle that allows for the colour modifying effects of SO_2, acetaldehyde and pH. Use of this technique also permits calculation of the amount of anthocyanins and phenolics present, including the anthocyanin equilibria, degree of colouration and "chemical age". This last is a numerical estimate of the ageing characteristics and the poymeric pigments of the particular wine (Somers and Evans, 1977).

When measuring colour by spectrophotometry, it is not possible to dilute the wine, as the concentration of the pigments does not follow Beer's Law (Somers and Verétte, 1988).

Spectral methods can be considered to overestimate the amount of anthocyanins as compared to HPLC analysis (Bakker *et al.*, 1986). It is possible that this apparent error is due to the ability of the spectral methods to measure parts of the polymeric pigment still sensitive to decolourisation (Rivas-Gonzalo, Gutierrez, Hebrero and Santos-Buelga, 1992).

2.4.9 CORRELATION OF COLOUR AND WINE QUALITY

Red wine colour is a relatively simple parameter to assess, and "good colour" is thought to be inherent in a well-made wine. Wine quality is difficult to quantify, and so finding a correlation between perceived quality and a measurable attribute, such as colour, would be of benefit to winemakers (Somers, Evans and Cellier, 1983).

A comparative ranking of overall quality for Cabernet sauvignon and Shiraz found a clear linear relationship between colour density and quality scores (Somers and Evans, 1974). With Beaujolais wines, correlations between colour and flavour/aroma scores were significant. The judges' visual assessment of colour was also significantly correlated with instrumental measurements. This led the authors to conclude the colour measurements could be some indication of red wine flavour for wines of comparable winemaking methods, vintage and variety (Jackson, Timberlake, Bridle and Vallis, 1978). Further investigation of Australian Shiraz and Cabernet sauvignon showed a correlation between overall wine quality and α (the degree of anthocyanin ionisation) (Somers *et al.*, 1983). This is in contrast to the findings of Jackson and colleagues (1978) but this is thought to be due to the greater variation in free SO_2 levels in the Australian wines. Free SO_2 has a great influence on anthocyanin equilibria and hence on α. In general, pigment content and colour density are influential on wine quality but total anthocyanin content is most important.

CHAPTER THREE

THE EFFECTS OF COLD MACERATION AND CARBONIC MACERATION ON THE CHEMICAL COMPOSITION AND COLOUR PARAMETERS OF PINOT NOIR WINE.

3.1 ABSTRACT

Cold maceration is a winemaking technique used to increase pre-fermentative, non-alcoholic extraction in Pinot noir winemaking. It involves holding crushed grapes with approximately 100-150 mg l^{-1} SO_2 at low temperatures prior to fermentation, and is thought to increase the colour, aroma and flavour of the resulting wines. This method was investigated by small-scale winemaking trials and compared to conventional and carbonic maceration vinification methods in terms of the compositional and colour analyses of the finished wines. Pre-fermentation cold maceration was found to cause higher titratable acidity, total phenol and monomeric anthocyanin content, and lower colour density, hue and polymeric pigments in the wines. Reducing the maceration temperature below 10°C has little effect. Carbonic maceration produces wines that are lower in titratable acidity, monomeric anthocyanin content, and colour density but are higher in colour hue and amount of polymeric pigments.

KEYWORDS Pinot noir; cold maceration; carbonic maceration; acidity; anthocyanins; colour.

3.2 INTRODUCTION

Cold maceration (COM) is a winemaking technique that has been applied to Pinot noir in an effort to increase extraction and increase complexity for this "light-style variety". It has been used in Burgundy and introduced from there to New Zealand winemaking. It is a pre-fermentation treatment that involves holding crushed, destemmed grapes at temperatures around 10°C with up to 150 mg l^{-1} SO_2 to prevent wild yeast growth (Norman, 1992). This unusually high amount of SO_2 is thought to act as a solvent for the anthocyanins, although this has not been investigated. Wines vinified after this treatment are said to be deeper in colour, to have full soft tannins, and concentrated fruit flavours and aromas (Matthews, 1990).

Little is known about the mechanism of COM, and any descriptions of the effects are largely subjective. Literature on COM is lacking, and this investigation is thought to be the first quantitatively undertaken. This study attempts to quantitate the effect of COM, and specifically of temperature, on the chemical composition and colour parameters of Pinot noir wine.

Carbonic maceration (CM) is a pre-fermentation treatment that produces characteristically light and fruity red wines. Whole bunches of red grapes held under an anaerobic atmosphere undergo an internal metabolism of malic acid and sugar to produce ethanol, carbon dioxide and aromatic compounds (Johnston, 1982; Romieu *et al.*, 1992; Sneyd, 1989). The grapes are then crushed and vinified to produce wine that can be either a light rosé style or a blending component of a more complex, full bodied wine.

Investigation into CM dates back as far as 1879 when Pasteur investigated the anaerobiosis of grapes. He noted that whole grapes held anaerobically developed the same aroma and flavour as the whole bunches present in a fermenting must (Pasteur, 1969). More recent and detailed research has been conducted on various aspects of CM as a winemaking technique. These range from the effect of CM on the wines of various grape varieties (Amerine and Ough, 1968; 1969; Amerine and Fong, 1974; Beelman and McArdle, 1974; Edinger *et al.*, 1988; Fuleki, 1974; Miller and Howell, 1989). It is interesting to note that Amerine and Ough had difficulty in successfully establishing CM for Pinot noir grapes. They found that such thin-skinned grapes were susceptible to spoilage by "acetification" (Amerine and Ough, 1968; 1969). Other authors have noted this, and also found that CM wines are particularly susceptible to spontaneous malolactic fermentation (Edinger *et al.*, 1988; Fuleki, 1974). Other investigations have looked at the specifics of the aromatic changes (Ducruet, 1984; Etievant *et al.*, 1989; Tesniere *et al.*, 1991; Versini *et al.*, 1984) colour and anthocyanin changes (Ramos and Machiex, 1990; Ramos *et al.*, 1993), and the effects at the cellular level of the grape (Robin *et al.*, 1989; Romieu *et al.*, 1992; Tesniere *et al.*, 1989).

The effects of CM on the resulting wine have not been studied under New Zealand conditions. This paper attempts to quantitate the changes in chemical composition and colour parameters of Pinot noir wine due to CM and to compare these with COM and conventional vinification. The effects of these processes on the aroma and flavour of the wines are presented elsewhere (Goldsworthy *et al.*, 1994).

3.3 MATERIALS AND METHODS

3.3.1 Selection of grapes

Pinot noir grapes (*Vitis vinifera* L., clone 10/5) grown at Waipara, North Canterbury, New Zealand, were hand-harvested on 25 April 1992. Bunches were selected on the basis of high health, i.e. lack of fungal disease, bird damage or berry shrivelling, and carefully placed into 20L plastic buckets. The fruit was weighed, transported to Lincoln University and placed in storage at 4°C for 42 hours.

3.3.2 Microvinification

The winemaking procedures for each of the three treatments (control, 4°C and 10°C cold maceration, and carbonic maceration) are diagrammed in appendices 3.1, 3.2, and 3.3.

3.3.2.1 Control and cold maceration treatments

Grapes for the control (conventional fermentation) and COM treatments were destemmed and crushed by a Zambelli crusher/destemmer directly into 20L plastic buckets. Sulphur dioxide (SO_2) was added (as a 5% aqueous solution) to give 50 mg kg^{-1} crushed fruit and was thoroughly mixed through each container. Three replicates were set up for each treatment. Juice samples were taken from each replicate for sugar, pH, titratable acidity (TA), malic acid and total phenol analyses (table 3.1). Six randomly selected buckets were used as replicates for the COM treatment. Each of these had a further 50 mg kg^{-1} SO_2 mixed in and was placed in temperature controlled rooms at either 4°C or 10°C, according to treatment. The remaining must was allocated as control and these were placed at 20°C, inoculated with *Saccharomyces bayanus*, strain EC 1118 "Prise de mousse" (Lalvin), and left to ferment.

The COM treatments were held at their respective temperatures for six days. This had been shown in a preliminary trial (results not published) to be the optimal period for phenolic extraction into the juice. Juice samples were taken from each replicate for sugar, acidity and phenol analyses at the end of the maceration period (table 3.2). After this time, the buckets were placed at 20°C to warm for 12 hours before yeast inoculation, as for the control wines.

3.3.2.2 Carbonic maceration

Whole bunches of "high health" were selected to form the replicate treatments. These were dipped in an acidified 50 mg l^{-1} SO_2 solution, allowed to drain and placed in 20L plastic buckets. Randomly-selected berries were collected to provide a juice sample for initial pH, TA, °Brix, malic acid and phenol analysis (table 3.1). Carbon dioxide was used to flush the air from the buckets and establish an anaerobic atmosphere. The buckets were sealed with tightly-fitting lids and placed at 20°C for the 16 day maceration period.

Each of the replicates was checked daily for signs of wild fermentation or bacterial spoilage. The condition and aroma of the berries was noted and the bucket flushed from the bottom with CO_2 and resealed. After 16 days the treatments were destemmed and crushed, inoculated with *Saccharomyces bayanus*, strain EC 1118 "Prise de mousse" (Lalvin), and placed at 20°C to ferment.

Juice samples were taken from each replicate for pH, TA, sugar, malic acid, ethanol, and phenol analyses as at the end of the maceration period (table 3.2).

3.3.2.3 Wine handling

Fermentation rate was monitored by measuring the cap temperature and observing its height. The cap of skins in each bucket was punched down two or three times daily. As the wine temperature decreased, sugar content was measured by Clinitest™ tablets (Ames Division of Miles Laboratories, U.S.A.) and when this was around 0.25% the wines were considered to have finished fermentation. A hand-operated basket press was used to press the wine. Samples for full chemical analysis at the end of fermentation (table 3.3) were taken before the addition of 50 mg l^{-1} SO_2 to prevent malolactic fermentation.

The new wines were placed at 4°C to allow cold stabilisation. During the cold stabilisation period the wines were constantly maintained under CO_2 cover and racked once off the potassium bitartrate lees. To prevent oxidation, 30 mg l^{-1} SO_2 was added to each flask of wine at racking.

After approximately three months of cold stabilisation, the wines were racked again, with the addition of 20 mg l^{-1} SO_2. An additional 20 mg l^{-1} SO_2 was added before sterile filtration and bottling.

Bottling was done under nitrogen pressure with a Sartorius pressurised bottling system, into 0.5% SO_2-rinsed 375 ml bottles. The wine passed through two Whatman glass-fibre filters and a Sartorius 0.45 μm membrane filter before corking. The first bottle of each replicate was reserved for chemical analysis as at bottling (table 3.4) with the exception of colour analyses which had been conducted on unfiltered wine. The remaining bottles were placed in storage in a 12°C cellar for four months. After this time, the wines were subjected to

full chemical and colour analysis (table 3.5).

3.3.3 CHEMICAL ANALYSIS

Juice and wine analysis were conducted in duplicate by standard methods where possible. Soluble sugars were determined as °Brix by a hand-held ERMA (Japan) refractometer. Titratable acidity and pH were calculated by the method of Iland (1988) using a Bantex 300A digital pH meter. Malic acid, and D-lactic and L-lactic acid content were measured using Boehringer (Mannheim, West Germany) enzyme assay kits in conjunction with a Philips PU 8625 UV/VIS spectrophotometer.

The finished wines were also analyzed for residual sugar and alcohol content by the Combitest (Van Dam, 1979), total and free SO_2 by the Rankine aspiration method (Iland, 1988) and specific gravity by specific gravity bottle at 20°C, and sugar-free extract as in Amerine and Ough (1988).

Spectrophotometric methods were used to calculate both total phenols (Leonard, 1983) and colour parameters, including anthocyanin content, amount of polymeric pigments and colour hue and density (Somers and Evans, 1977).

3.3.4 STATISTICAL ANALYSIS

Data analysis of results was conducted using the statistical package "Minitab", release 7.2, (Minitab Inc.: Pennsylvania, U.S.A.). Two-way analyses of variance (ANOVA) were calculated. Statistical analyses for the determination of significant differences between treatment means were conducted using Fisher's Least Significant Difference (LSD) test.

3.4 RESULTS AND DISCUSSION

The compositional analyses of initial juice samples, and results following cold or carbonic maceration are reported in tables 3.1 and 3.2. The effects of carbonic maceration (CM) and cold maceration (COM) on the composition and colour of the wines at the completion of fermentation, at bottling and after four months storage are shown in tables 3.3, 3.4 and 3.5.

3.4.1 JUICE ANALYSIS

3.4.1.1 Initial samples prior to treatment

Replicate juice samples of the control, CM and COM treatments showed no significant difference in any of the parameters measured (table 3.1). This was to be expected.

3.3.1.2 End of maceration

Analysis of juice samples obtained at the end of the different maceration periods (table 3.2) showed results similar to those seen for the juice samples. pH of the control was significantly different ($p \leq 0.01$) from the other treatments. This may possibly be due to extraction of potassium from the skins of the COM and CM treatments during the maceration period, since there was no statistical difference in TA at this point. Total phenols were significantly lower ($p \leq 0.01$) in the control and CM wines. The COM treatments also contained visibly greater colour at this time, and this indicates considerable phenolic extraction during the cold maceration process. CM wines were notably different from the other wines at this point in that they contained around 2% alcohol and had significantly lower ($p \leq 0.01$) °Brix readings. This was to be expected at this stage of

production of carbonic maceration wines due to the effects of malate metabolism and glycolysis (Johnston, 1982; Sneyd, 1989). None of the other treatments contained any alcohol at this point, and their sugar content was similar to that at the beginning of the maceration period.

Sulphur dioxide content of the juices was low at the end of maceration (table 3.6). This was unexpected considering that up to 100 mg l^{-1} SO_2 were initially added to the COM treatments. The COM treatments contained less than 20 mg l^{-1} free SO_2 and between 35 and 52 mg l^{-1} total SO_2. The CM juices contained only a trace amount of free SO_2 and 43 mg l^{-1} total SO_2. These small amounts of SO_2 had no deleterious effects on the fermentation of the wines, as all rapidly fermented to dryness.

3.4.2 WINE ANALYSIS

3.4.2.1 End of fermentation

At the end of fermentation (table 3.3) there were differences in pH between the treatments. The pH of CM was significantly higher ($p \leq 0.05$) than the control and 10°C COM. The 4°C COM treatment was not significantly different from any of the other treatments. Despite the pH difference between the CM and 10°C COM, there was no significant difference in TA between the treatments at the end of fermentation. There were measurable differences in TA at this point, but variation within replicate treatments caused the lack of significant difference.

The CM treatment was significantly lower ($p \leq 0.01$) in malic acid than the other

treatments here, and at other times. This was due to the degradation of malic acid during the anaerobic maceration of the grapes in the first part of the CM procedure (Beelman and Gallander, 1979). In this experiment, malic acid was up to 25% lower in the CM wines than in the control and COM treatments. This result was comparable to malic acid reduction found in other experiments (Beelman and McArdle, 1974; Edinger *et al.*, 1988).

There was also a decrease in the amount of malic acid present in the juice (table 3.1) as compared to the control and COM wines at the end of fermentation (table 3.3). In this experiment, the various treatments show differing reductions in malic acid from 20% in the control to 30% in the 10°C COM (appendix 3.4). This decrease in the amount of malic acid was due to normal yeast fermentative metabolism. *Saccharomyces* species have been well documented as utilising malic acid under anaerobic, i.e. fermentative, conditions. The reductions previously observed range from 3 to 45% of the total malic acid present in the initial juice (Rankine, 1966; Whiting, 1976; Fowles, 1992). The level of malic acid decomposition is dependent more on the yeast strain than the initial acid content (Wagner *et al.*, 1986). Malic acid is converted to ethanol and CO_2 with concurrent formation of succinate and fumarate (Radler, 1986).

At the end of fermentation thin layer chromatography detected lactic acid in all of the wines. This may have been due to the metabolism of either yeast or malolactic bacteria. Since malolactic fermentation was to be avoided in this experiment, this was of some concern.

There was significantly more D-lactic acid ($p \leq 0.05$) in the COM wines when compared

to the other treatments at end of fermentation. The reason for this was unclear but it could be due to the COM process. As these were such small quantities of the lactic acid isomers, this difference was probably insignificant. No difference in L-lactic acid was found at completion of fermentation between any of the treatments. At the end of fermentation more of the D-isomer than the L-isomer was identified in the wines, with a range from 7 to 18% of the total being L-lactic acid. This can be attributed to normal yeast metabolism which can produce 1 g l^{-1} lactic acid during fermentation (Fowles, 1992). Yeasts usually produce D-lactic acid under anaerobic conditions, but *Saccharomyces* species can also produce up to 10% L-lactic acid. In contrast, bacterial action such as malolactic fermentation produces predominantly the L-isomer (Peynaud *et al.*, 1965; 1966). Therefore the small amount of lactic acid present in these wines was due to normal yeast metabolism and malolactic fermentation had not occurred.

The wine treatments were not different in alcohol content at the end of fermentation. Data analysis showed small significant differences ($p \leq 0.05$) in residual sugar at end of fermentation but these differences were small and were probably due more to methodological errors than real variation. At later analyses, there was no difference in alcohol content between treatments, and only small differences in residual sugar.

At the end of fermentation the control and CM treatments were significantly lower ($p \leq 0.01$) in total phenols than the COM treatments. This indicates that the phenolics extracted during COM are retained during fermentation.

There was no free SO_2 in any of the wines at the end of fermentation, and low quantities

of total SO_2. Such levels would not be expected to interfere with subsequent malolactic fermentation of the wines, although this was not investigated in this study.

In this study, CM wines had significantly lower ($p \leq 0.05$) anthocyanin content than the control and COM wines at the end of fermentation. Colour density was also lower here ($p \leq 0.01$) for the CM wines, whereas the control and COM treatments did not differ in density. The hue of CM wines was significantly higher ($p \leq 0.01$) than the other treatments at the end of fermentation and at subsequent analyses. The control wine had a higher hue ($p \leq 0.01$) than the COM treatments at the completion of fermentation.

Ionised anthocyanins are those in the coloured flavylium form and so are of importance when considering the potential colour of wine. α is a measure of the percentage of coloured forms of the anthocyanins (Somers, 1975). There was no difference in α between the control and 10°C COM treatments at the end of fermentation (appendix 3.5). The 4°C COM treatment was significantly lower ($p \leq 0.05$) in α than the control but was not different from either the 10°C COM or the CM wines. CM wines were also significantly lower ($p \leq 0.05$) in α than the control and the 10°C COM.

α supposedly correlates with both colour density and wine quality (Somers and Evans, 1977). The former is not a direct relationship, and this was shown here by the CM treatment being lowest in density at the end of fermentation, but not conclusively different in α. However, α does not take into account the SO_2 content of the wines. This may give a false indication of the wine colour indices and so it may be of more interest to consider α', the natural degree of anthocyanin ionisation (appendix 3.6). α' is the proportion of

ionised anthocyanins when an allowance is made for the bleaching effect of SO_2 (Somers and Evans, 1977). At the end of fermentation the cold and CM treatments were not different from the control in terms of α'. This indicates that CM produces wines with lower anthocyanin content, but the same proportion of coloured pigments as conventionally vinified wines. Conversely, COM wines had more anthocyanins but the same proportion of coloured pigments.

Chemical age is an index based on spectral data which estimates the amount of polymeric pigments present in the wine (Somers and Evans, 1977). At the end of fermentation, the CM treatment was significantly higher ($p \leq 0.05$) in polymeric pigments, as estimated by chemical age, than the other treatments. Both the COM wines had lower levels of polymeric pigments ($p \leq 0.05$) than the control wine (appendix 3.7).

3.4.2.2 Bottling

At bottling (table 3.4) the CM wine was significantly higher ($p \leq 0.01$) in pH than the other treatments. Titratable acidity of the 4°C COM treatment was the same as the control but was significantly different ($p \leq 0.05$) from the 10°C COM treatment. Of the treatments, CM treatment had the lowest TA at bottling. The decrease in TA observed between the end of fermentation and bottling was due to loss of potassium bitartrate during cold stabilisation of the wines. The control TA values were significantly different ($p \leq 0.01$) from the lower CM and higher COM TA values. There was no difference between the TA of the 4°C and 10°C COM treatments. The differences in TA between the control and COM treatments were not related to the malic acid content since this did not significantly differ between these treatments at any time. It can be assumed that these

differences are due to variation in the tartaric acid content of the wines.

Sugar-free extract was not measured at end of fermentation since new wines contain tartaric acid that will be lost during cold stabilisation. This contributes to a false measurement of extract (Eschenbruch *et al.*, 1981) and so in this experiment, measurements were made at bottling and after four month's storage. Measurements of sugar-free extract at bottling did show small differences but these were not statistically significant.

At bottling, the CM treatment had significantly ($p \leq 0.05$) lower amounts of total phenols than the two COM treatments. The control was not statistically different from either the COM or CM treatments, although there were measurable differences. This was unexpected since until this point the COM treatments had significantly more phenols than the other wines. The amount of total phenols of all treatments varied over the course of the experiment. The slight increase seen between measurements made at end of fermentation and those found at bottling may be due to continuing polymerisation of colour pigments and tannins.

After three months of cold stabilisation prior to bottling, the anthocyanin content of all wines had decreased. Although the COM wines contained measurably higher amounts of anthocyanins, these amounts were not significantly different from the control. The CM treatment was significantly ($p \leq 0.05$) lower in monomeric anthocyanins than the other treatments. This situation changed after sterile filtration at bottling where some of the anthocyanins were removed by the membrane filter (appendix 3.8).

There appears to have been some change to the wines at the time of bottling. Several of the colour measurements taken at this time show unexpected results - for example, α, total anthocyanins and colour density (appendices 3.5, 3.8, 3.9). It may be possible that the samples taken prior to filtration were slightly oxidised before the colour analyses were conducted.

At the time of bottling, the 10°C COM treatment was significantly higher ($p \leq 0.01$) in α′ than the other treatments. This indicates that the 10°C COM produces wine that had more potential colour in terms of α′ than standard vinification procedures or the 4°C COM. CM wines were significantly lower ($p \leq 0.01$) in α′ than the two COM treatments, but no different from the control.

The CM treatment did not differ statistically from the control in terms of polymeric pigments at bottling. This was despite the CM wines being measurably higher in this parameter calculated as chemical age. CM wines were significantly higher ($p \leq 0.01$) in polymeric pigments than the COM treatments at bottling. For the COM wines, the 10°C treatment was statistically lower ($p \leq 0.05$) in polymeric pigments than the control, whereas the 4°C treatment was not different.

3.4.2.3 After storage

Analysis after four months storage (table 3.5) showed no differences between pH values of the four treatments. There was little real difference in pH across the treatments at the various analysis stages. Variation in pH was less than 0.1 pH units and so was unlikely

to be significant in winemaking terms. Titratable acidity of all treatments showed an increase over the ageing period. The CM treatment was significantly lower ($p \leq 0.01$) in TA than the other treatments. Both COM wine treatments were higher in TA than the control ($p \leq 0.01$), which was the same trend as seen at bottling.

In subsequent sensory evaluation of these wines it was found that panellists could not distinguish the differing acidity of the wines (Goldsworthy, *et al.*, 1994).

Malic acid contents of the COM and control wines were significantly higher ($p \leq 0.01$) than the CM wine. COM does not appear to affect the malic acid content of the resulting wines. The reduction in malic acid seen in the CM wine was due to anaerobic metabolism during CM and was a similar reduction to that found by other researchers (Beelman and McArdle, 1974; Edinger *et al.*, 1988).

After four months storage, the CM wine had significantly more ($p \leq 0.01$) L-lactate than the control, which in turn was higher than both COM treatments. Since all treatments had decreased amounts of L-lactic acid at this point, these differences could have been due to uneven loss of lactic acid during cold stabilisation. In all wines L-lactic acid decreased during the period of the experiment which indicates that no further lactic acid metabolism occurred. The COM wines contained significantly higher ($p \leq 0.01$) amounts of D-lactic acid than the other treatments after storage. It was possible that the COM procedure affected these levels, but such small amounts are of negligible importance.

The CM treatment was significantly lower ($p \leq 0.05$) in sugar-free extract at analysis after four months storage than the COM wines, but was not different from the control. Extract levels in these wines were comparable to those found in Pinot noir by Eschenbruch and colleagues over a number of vintages (Eschenbruch *et al.*, 1981). Pinot noir is characteristically a light-bodied red wine containing lower levels of extract than other red varieties. These results indicate that the treatments investigated here do not significantly affect extract of the final wines.

Total phenols were highest in the COM wines ($p \leq 0.05$) at the end of this experiment, after storage. This indicates that COM was more effective in extracting and retaining phenols in wine than conventional fermentation. Further investigation is needed to identify these phenolic compounds, and to determine their origin and effect on wine.

After storage, the CM wine was found to be significantly lower ($p \leq 0.01$) in colour density and significantly higher ($p \leq 0.01$) in colour hue than the other treatments. Neither the control nor the COM treatments differed from each other in either of these two colour parameters.

Sterile filtration prior to bottling removed some of the anthocyanins in the wines. This may have resulted in there being no difference in anthocyanin content between the control and CM treatments after storage. After four months of ageing, the COM wines contain significantly more ($p \leq 0.01$) monomeric anthocyanins than the CM wines. Overall, the COM wines had more monomeric anthocyanins than the control wine. COM produced wines that had greater anthocyanin content than standard winemaking techniques.

After storage the control was significantly higher ($p \leq 0.01$) in α than the other treatments. The 4°C COM was significantly higher ($p \leq 0.01$) in α than the CM but was no different to the 10°C COM. It would appear from this that CM produces wines significantly lower in degree of anthocyanin ionisation than conventional vinification. But it is important to remember the effect of SO_2 on anthocyanins, that the SO_2 content of these wines is variable (table 3.6) and so to consider α'. In this experiment, after storage α' was not significantly different between the wine treatments. It appears then, that after some bottle storage the true proportion of anthocyanin colouration in COM and CM wines stabilises.

After storage, all of the wine treatments were significantly different ($p \leq 0.05$) in polymeric pigments. This was due to continued interaction of the polyphenolic compounds of the wines, which was to be expected during the cellaring of red wine. Over the course of the experiment, the chemical age indices of all treatments increase. Chemical age indices are reported to tend towards a value of 1 as the wines become older, and these results agree with the general pattern (Somers and Evans, 1977).

The SO_2 content of each wine was not monitored throughout the experiment but representative samples were checked at each analysis stage. All replicates were analysed after four month's of storage (table 3.6). There was no difference between the treatments in SO_2 content at this time. Since the control wine had 50 mg l^{-1} less SO_2 initially added than the COM treatments, it was not surprising that the former contained less total SO_2. There was considerable variation in SO_2 content between replicates, which leads to no overall statistical difference.

Presumably these low levels of free, i.e. effective, SO_2 would not be detrimental to malolactic fermentation subsequent to the use of these maceration techniques. The high final level of total SO_2 in these wines was due to continued addition of SO_2 during cold stabilisation to prevent malolactic fermentation occurring during storage of the wines. In a commercial winemaking situation, these levels would be considerably lower.

3.5 CONCLUSIONS

3.5.1 Carbonic maceration

Carbonic maceration wines were generally higher in pH than control wines and also had measurably lower TA, confirming earlier studies. These wines were also notably lower in malic acid than the other wines throughout the experiment. Previous research has found similar reductions in acidity of CM wines (Beelman and McArdle, 1974; Fuleki, 1974; Beelman and Gallander, 1979; Edinger *et al.*, 1988; Miller and Howell, 1989).

CM wines were found to be significantly lower in anthocyanin content and colour density than the control and COM wines. In general, CM wines are noted for their low colour due to the combined effects of high pH, low anthocyanin and tannin content (Johnston, 1982).

The CM wines were higher in colour hue than the other treatments, the hue increasing with vinification and ageing. This is characteristic of CM wines, which tend to quickly develop a brown colour, and generally age faster than conventionally-made wines (Beelman and McArdle, 1974).

Control and CM wines do not differ in total phenols despite the difference in on-skin

contact time during fermentation. This was attributed to phenolic extraction being most effective in the first few days of fermentation (Riberéau-Gayon and Glories, 1987). The CM treatment was higher in polymeric pigments than the control, which reflected the increased "age" of these wines. Anthocyanin ionisation (α) appeared to be lower in the CM wines, but if SO_2 is allowed for (α'), there is little real difference.

3.5.2 Cold maceration

COM wines tended to have slightly higher levels of titratable acidity than control wines, but showed no difference in pH or malic acid. This apparent difference in tartaric acid may be due to the COM procedure.

COM extracted more anthocyanins than the conventional vinification method, and also the CM treatment. There were no differences between the total anthocyanins extracted by COM at 4°C and 10°C. This indicates that the small temperature differences used here are having little effect on the anthocyanin extraction occurring during COM.

COM wines contained higher levels of total phenols than the control wine. This can be attributed directly to the COM procedure, as the COM wines contained more phenols in macerated juice and retained this higher level throughout vinification and storage. There were measurable but not statistically significant differences in total phenols between COM treatments at 4°C and 10°C. This suggests that such small temperature differences were not very influential in increasing phenolic extraction of must.

The α values for the wines in this experiment range from 7 to 27%, which was comparable

to that found in young Australian Shiraz and Cabernet Sauvignon wines and lower than Burgundy Pinot noirs (Somers, 1975). Such differences may be due to the SO_2 content of the wines, which relates more to the winemaking techniques used rather than compositional parameters. Natural anthocyanin ionisation (α') did not show large differences between the control and COM wines, which indicates that no true colour differences were achieved. This correlates with the observed lack of difference in colour density.

COM wines had potentially much greater colour in terms of anthocyanin content at the end of fermentation. In a commercial winemaking situation the anthocyanin content would be stabilised by interactions with tannins extracted during oak ageing. The loss of colour in the COM wines seen in this investigation was an artifact of the experimental procedure that did not allow oak ageing, or other conservational strategies.

All treatments show an increase in α' over the time of the experiment. This was to be expected as the wine colour will stabilise as polymeric pigments predominate over the free anthocyanins.

Polymeric pigments of COM wines were generally lower than in the control wines. This may be due to the higher SO_2 content of the COM wines slowing the rate of phenolic polymerisation.

TABLE 3.1

Compositional analyses of Pinot noir juice samples prior to pre-fermentation maceration.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
° Brix	20.67	19.60	21.47	20.47	0.130	NS
pH	3.21	3.17	3.21	3.19	0.726	NS
Titratable Acidity (g l^{-1})	10.90	10.73	10.98	11.05	0.422	NS
Malic acid (g l^{-1})	5.28	5.54	5.91	5.70	0.051	NS
Total Phenols (O.D. @ 280nm)	13.72	11.82	13.43	15.42	0.136	NS

Mean values within the same row designated by a different letter differ significantly ($p \leq 0.05$).

1 Least significant difference.

NS Not significantly different.

TABLE 3.2

Compositional analyses of Pinot noir juice samples at the completion of pre-fermentation maceration.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
° Brix	20.67a	12.83b	20.13a	20.43a	0.00	1.51
pH	3.21a	3.53b	3.46b	3.45b	0.00	0.097
Titratable Acidity (g l^{-1})	10.90	8.94	9.82	9.39	0.109	NS
Malic acid (g l^{-1})	5.28b	3.63a	4.83b	4.75b	0.004	0.771
Total Phenols (O.D. @ 280nm)	13.72a	12.58a	30.60b	37.12c	0.00	4.87

Mean values within the same row designated by a different letter differ significantly ($p \leq 0.05$).

[1] Least significant difference.

NS Not significantly different.

TABLE 3.3

Compositional and spectral analyses of Pinot noir wines made by pre-fermentation treatments at completion of fermentation.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
pH	3.36a	3.48b	3.43ab	3.38a	0.028	0.074
Titratable Acidity (g l^{-1})	10.27	9.33	9.70	10.03	0.053	NS
Malic Acid (g l^{-1})	4.53b	3.43a	4.64b	4.51b	0.000	0.609
D-Lactic Acid (g l^{-1})	0.229a	0.222a	0.260b	0.273b	0.002	0.021
L-Lactic Acid (g l^{-1})	0.043	0.039	0.042	0.026	0.137	NS
Residual Sugar (g l^{-1})	1.253b	1.253b	0.253a	0.503a	0.018	0.650
Alcohol (%)	11.03	11.00	11.26	11.08	0.803	NS
Total Phenols	22.52a	20.60a	25.23b	25.96b	0.009	2.872
Colour Density	5.55b	3.93a	5.24b	5.65b	0.000	0.528
Colour Hue	0.46b	0.68c	0.39a	0.38a	0.00	0.047
Total Monomeric Anthocyanins (mg l^{-1})	240.50b	172.92a	300.94c	303.34c	0.00	32.71
α	27.38c	20.91a	22.99ab	25.16bc	0.013	3.451
α′	27.03	20.85	19.99	25.58	0.071	NS
Polymeric pigments (Chemical age)	0.155b	0.265c	0.105a	0.085a	0.000	0.041

Mean values within the same row designated by a different letter differ significantly ($p \leq 0.05$).

[1] Least significant difference.

NS Not significantly different.

TABLE 3.4

Compositional and spectral analyses of Pinot noir wines made by pre-fermentation treatments at bottling.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
pH	3.22ab	3.37c	3.28b	3.18a	0.010	0.088
Titratable Acidity (g l^{-1})	8.45b	7.16a	9.48c	9.39c	0.000	0.509
Malic acid (g l^{-1})	4.63b	3.25a	4.14b	4.10b	0.008	0.553
Residual Sugar (g l^{-1})	1.253b	1.253b	0.253a	0.503a	0.018	0.650
Alcohol (%)	11.10	10.40	11.16	10.73	0.296	NS
Total Phenols	23.92ab	22.19a	26.51b	26.63b	0.030	3.129
Sugar-Free Extract (g l^{-1})	21.95	22.81	23.81	22.70	0.223	NS
Colour Density	5.964ab	5.550a	6.561b	5.781a	0.024	0.60
Colour Hue	0.515a	0.739b	0.539a	0.526a	0.007	0.119
Total Monomeric Anthocyanins (mg l^{-1})	216.70b	176.30a	243.60b	221.20b	0.012	34.10
α	12.79	11.95	14.24	11.35	0.768	NS
α'	24.06ab	19.91a	26.11b	31.22c	0.002	4.193
Polymeric pigments (Chemical age)	0.183bc	0.213c	0.157ab	0.138a	0.009	0.039

Mean values within the same row designated by a different letter differ significantly ($p \leq 0.05$).

[1] Least significant difference.

NS Not significantly different.

TABLE 3.5

Compositional and spectral analyses of Pinot noir wines made by pre-fermentation treatments after four months of storage at 12°C.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
pH	3.27	3.33	3.18	3.24	0.054	NS
Titratable Acidity (g l^{-1})	9.93b	8.38a	10.33c	10.33c	0.000	0.316
Malic Acid (g l^{-1})	4.16b	3.35a	4.40b	4.09b	0.005	2.391
D-Lactic Acid (g l^{-1})	0.221a	0.214a	0.267b	0.269b	0.001	0.025
L-Lactic Acid (g l^{-1})	0.022b	0.027c	0.019a	0.019a	0.000	0.002
Residual Sugar (g l^{-1})	2.38	1.75	1.94	1.69	0.621	NS
Alcohol (%)	10.88	10.48	11.30	10.80	0.087	NS
Total Phenols	17.12a	17.81a	20.74b	21.41b	0.020	2.836
Sugar-Free Extract (g l^{-1})	20.39ab	18.85a	22.13b	22.38b	0.030	2.391
Colour Density	2.68b	1.73a	2.48b	2.34b	0.003	0.394
Colour Hue	0.55a	0.83b	0.57a	0.56a	0.000	0.060
Total Monomeric Anthocyanins (mg l^{-1})	152.50a	142.50a	195.00b	195.90b	0.002	26.15
α	15.65c	6.49a	10.83b	9.91ab	0.002	3.449
α′	27.26	24.86	31.17	33.03	0.093	NS
Polymeric pigments (Chemical age)	0.227c	0.272d	0.180b	0.162a	0.008	0.008

Mean values within the same row designated by a different letter differ significantly ($p \leq 0.05$).

[1] Least significant difference.

NS Not significantly different.

TABLE 3.6

Sulphur dioxide content of Pinot noir juices and wines made by pre-fermentation treatments.

Time of Analysis	**Sulphur Dioxide (mg l^{-1})**	**Wine treatment**			
		Control	Carbonic maceration	4°C cold maceration	10°C cold maceration
End of maceration	Free SO_2	0	1.6	14.4	19.2
	Total SO_2	0	43.1	35.2	52.8
End of Fermentation	Free SO_2	0	0	0	0
	Total SO_2	9.6	16.0	24.5	26.1
Bottling	Free SO_2	3.2	6.4	3.2	8.0
	Total SO_2	12.8	36.8	24.0	38.4
Four months ageing	Free SO_2	14.4	21.87	26.13	27.73
	Total SO_2	84.27	88.00	106.67	120.87

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CHAPTER FOUR

THE EFFECTS OF COLD MACERATION AND CARBONIC MACERATION ON THE SENSORY PROPERTIES OF PINOT NOIR WINE.

4.1 ABSTRACT

Pre-fermentation maceration of Pinot noir grapes was investigated by small-scale winemaking trials. Quantitative descriptive analysis was used to define the effects of cold and carbonic maceration treatments on the sensory characteristics of the resulting wine. Trained panel members found that there were no discernable sensory differences in the compositional parameters despite measurable chemical differences. Investigation into the aroma and flavour characteristics of the wines found that carbonic maceration produces wines that are lower in berry aroma and higher in acetate or ester-type aromas than the control wines. These wines were considered to have specific raspberry, floral, sugar, cherry and chemical aromas. This chemical note was also observed in the flavour of the carbonic maceration wines. The temperature of the cold maceration process has no major effect on the aroma and flavour of the resulting wines. However, the 10°C maceration was higher in woody/tobacco aroma than the 4°C maceration. This 10°C COM treatment was also higher in bitter flavour than all of the other treatments. Cold maceration wines were found to have specific mixed berry, dried fruit and sweet-oxidised aroma characters, together with a blackberry flavour note.

KEYWORDS Pinot noir wine; cold maceration; carbonic maceration; sensory; quantitative descriptive analysis; aroma; flavour.

4.2 INTRODUCTION

In a recent paper (Goldworthy and Heatherbell, 1994) we reported on the effects of cold maceration (COM) and carbonic maceration (CM) on the composition and colour parameters of Pinot noir wines. The present paper further characterises the effect of these pre-fermentation maceration treatments in terms of the aroma and flavour.

COM and CM are two winemaking methods that have been used in the vinification of Pinot noir wine. Both are pre-fermentation treatments that are believed to have distinct effects on the aroma and flavour of the resulting wines.

Interest has recently developed in the use of cold maceration or "cold soak" for Pinot noir winemaking in both Burgundy and New World regions. Advocates of this technique assert that the non-alcoholic extraction gives the wine quite different grape flavours than are found in conventionally-made wines (Heald and Heald, 1993). COM is utilised to increase "plum and kirsch" flavours, as well as the tannin and colour of Pinot noir wine (Matthews, 1990). It has been encouraged in some Burgundy wineries by the oenological consultant Guy Accad as part of his overall philosophy on vinifying Pinot noir (Norman, 1992). The grapes are destemmed and crushed, a large amount of sulphur dioxide (100 to 150 mg l^{-1}) is added and the must is held at around 10 to 15°C. Extraction and maceration of the grapes continues for five to ten days (Norman, 1992) or until the fermentation begins due to inoculation or natural yeast flora (Matthews, 1990). The wine is then processed as usual. There is a distinct lack of technical literature investigating this technique and there is considerable interest in the wine industry to quantitate the effects on the resulting wine quality.

CM involves holding whole grape bunches under an inert atmosphere before the onset of fermentation. The grapes undergo an anaerobic metabolism, during which they utilise sugars and malic acid to produce energy (Beelman and Gallander, 1979). This combination of glycolysis and malic acid metabolism produces carbon dioxide and ethanol. It is the ethanol that halts the anaerobic process as it is toxic to the berry cells (Miller and Howell, 1989). During anaerobic metabolism, the flavour of the grapes changes due to secondary metabolic reactions influenced by the presence of ethanol in the cells. Esterification occurs to produce various fruity esters not found in the fresh grapes (Tesniere *et al.*, 1991). Such compounds produce the characteristic "strawberry/raspberry" (Versini *et al.*, 1984), "cherry" (Ducruet, 1984) and "cinnamon" (Beelman and McArdle, 1974) aromas and flavours found in the finished wines.

To date, little formal sensory evaluation involving trained panels has been conducted on CM wines. This investigation, using New Zealand wines, is thought to be the first using quantitative descriptive analysis on CM of Pinot noir wines. Fuleki (1974) used rank difference testing to compare Concord wines that had been made by standard and CM winemaking methods. The panel of expert wine tasters ranked flavour intensity relative to a control wine. CM wines were found to have less of the Concord flavour and aroma and were also perceived as less acidic and tannic than the control wine (Fuleki, 1974).

In one study, descriptive analysis was performed on Syrah, Mourvedre and Carignan wines that had undergone CM. Flavour and mouthfeel attributes were assessed after six and twelve months of ageing. Since this study was investigating the changes in volatile phenols of the

wines the results do not present a full description of the sensory attributes of the wines. It was noted that although the Syrah wines did not have any change in phenolic character, the Mouvredre and Carignan wines showed significant increases in their phenolic flavour after ageing (Etievant *et al.*, 1989).

This investigation utilises quantitative descriptive analysis to define the effect of CM and COM winemaking techniques on the aroma and flavour of Pinot noir wine.

4.3 MATERIALS AND METHODS

4.3.1 Microvinification and chemical analysis of wines

The wines were made as previously described (Goldsworthy and Heatherbell, 1994). Small replicate lots (20 kg) of grapes containing 100 mg l^{-1} SO_2 were subjected to COM at 4°C and 10°C for six days prior to alcoholic fermentation. CM was conducted on whole bunches held under CO_2 at 20°C for 16 days. The wines had been sterile filtered, bottled and stored at 12°C for three months before sensory evaluation. Compositional analyses for acidity, residual sugar, extract, ethanol and sulphur dioxide were conducted on the wines at the time of sensory evaluation (table 4.2).

4.3.2 SENSORY EVALUATION

Sensory evaluation was conducted at the sensory science laboratories of the Horticultural and Food Research Institute of New Zealand Ltd. (HortResearch), Auckland, New Zealand. The

wines were transported from Lincoln University by air freight two weeks prior to evaluation and kept at ambient temperature. Three replicates of each of the COM and CM treatments were evaluated against three replicates of conventionally processed (control) wine.

Twelve panellists participated in the evaluation over a 10 day period. All members of the panel were part of a wine evaluation team previously selected for their sensory acuity for wine. All had had previous experience of quantitative descriptive analysis of experimental wines. Panellists were introduced to the objectives of the evaluation procedure, but this information was kept to a minimum to avoid biasing the results.

4.3.2.1 Panel training

Five consecutive training sessions were conducted, during which time the panel were introduced to all four of the wine treatments. The first session was a round-table evaluation and discussion of the wines' aroma and flavour characteristics. Wines were presented monadically to avoid colour comparisons between treatments, and the panellists were asked to assess the aroma, flavour and aftertastes of the wine. After the panellists had evaluated each wine sample, the panel's assessments were discussed. The frequency of use of the descriptors generated was calculated, and those with 20% or greater frequency were made as reference standard solutions for the next session. Standards were made from food or other products in control wine (table 4.1).

During the following session, the panellists were presented with the aroma standards, which were discussed and modified as necessary to achieve the desired character and intensity. Three

wine samples were presented monadically and assessed relative to the reference standards on a written scoresheet. All results were collated and discussed with the panel and inappropriate standards and descriptors were discarded. The remaining descriptors were assembled onto an evaluation sheet, which was presented along with the modified standards in the next training session. The rating scale was introduced at this point, an eight point intensity scale from 0 (absent) to 7 (intense) which was used in training and evaluation from this time. After evaluation, the panel were encouraged to comment on the descriptors for evaluation, and to suggest any additional ones they felt were lacking on the scoresheet.

In the fourth session the panellists were introduced to the testing booths and computer scoring facilities, under testing conditions of standardised temperature and humidity. The computer scoresheet system used was Computerised Sensory Analysis (CSA) (Compusense Inc., 170 Woolwich Street, Guelph, Ontario, Canada NIH 3V4). Red lighting was used since the colour differed between wine treatments. Before entering the booths, the panel were again presented with the aroma reference standards in conjunction with samples of control wine. The panellists were asked after the testing session to comment on the computer scoresheet. The scoresheet was modified to place descriptors in a chronological order of recognition. It was found that the panel lacked consensus and reliability in its scoring, and a further training session was held.

During the fifth session, particular emphasis was placed on the intensity scoring of the blackcurrant, berry and acetate descriptors, by referring the panel to aroma standards. Round-table discussion was used to reinforce the characteristics of these descriptors, and the

blackcurrant and berry descriptor standards were provided again. The assessment of two samples was then conducted under standard testing conditions, using the newly modified scoresheet. These results were discussed with the panel, emphasising the importance of clearly scoring any differences present, and avoiding mid-range scores. After a suggestion from the panel, the descriptors sulphur and chemical were deleted from the scoresheet since these were infrequently used during the evaluations. The final evaluation sheet consisted of eight aroma attributes: acetate, alcohol, blackcurrant, berry, honey, blackpepper, woody and sweet. The seven flavour attributes were alcohol, acid, blackcurrant, fruity, sweet, blackpepper and bitter. The panellists were encouraged when possible to further define the berry and sweet aroma attributes, the fruity flavour and to note any other characters observed.

4.3.2.2 Testing procedure

A randomised, balanced incomplete block design was used for the testing sessions. Panellists rated the perceived aroma and flavour attributes on an eight point intensity scale on a computer-generated questionnaire. Responses were entered by use of light pens directly placed onto the individual computer terminal screen. Data were collated at the end of each day of testing, particularly the comments on the specific fruity, berry, sweet and other aroma and flavour characteristics.

Fifty ml wine samples were poured 60 minutes prior to the evaluation session, covered with watchglasses and left at ambient temperature. Clear, 215 ml, tulip-shaped winetasting glasses were used, coded with three-digit random numbers. Distilled water and dry, unsalted crackers were provided for the panel to cleanse their palates between samples. Three samples were

evaluated by every panel member in each session, and these were presented in random order monadically to prevent colour comparisons. Three formal evaluation sessions were held over three consecutive days to assess the wines in triplicate over the entire panel.

4.3.3 DATA ANALYSIS

Statistical analysis of the sensory results was conducted using the statistical package REML on GENSTAT 5 (Committee of the Statistics Department, Rothamsted Experimental Station, Harperden, Hertfordshire). Individual analyses of variance (ANOVA) were run for each of the attributes. If significant, Fisher's Least Significant Difference test (LSD) was conducted ($p \leq 0.05$).

The chemical analyses were statistically analysed as explained in our previous paper (Goldsworthy and Heatherbell, 1994).

4.4 RESULTS AND DISCUSSION

4.4.1 Chemical composition

The wines did not differ in chemical composition to any great extent, with the exception of titratable acidity (table 4.2). The TA of the CM treatment was significantly lower than all other treatments, and the control was lower in TA than the COM wines. Since TA accounts for only part of the perception of acidity in wine (Rankine, 1989), it is possibly of more interest that the pH of the wines was not significantly different between treatments. The CM was significantly lower in sugar-free extract than the COM treatments, but no different to the control. However, such small variations were unlikely to be perceived by the panellists.

The relatively high level of SO_2 in these wines is to prevent spontaneous malolactic fermentation. If this had occurred, any sensory differences found might not have been due solely to the variation in winemaking procedure. It is not known if these SO_2 levels had any effect on the sensory parameters of the wines.

4.4.2 Sensory evaluation

The quantitative descriptive analysis results are presented in table 4.3, and illustrated in figures 4.1, 4.2, and 4.3. The panel did not identify large differences between the wine treatments. This was unexpected, since CM is recognised as causing changes to the aroma and flavour of wines, and COM is used specifically to alter sensory characteristics of Pinot noir wines. There are several possible explanations for these results. Firstly, the panel may have been insufficiently trained to describe possibly subtle differences. It might be that the small-scale winemaking procedures used, such as high levels of SO_2 additions, cold stabilisation and lack of oak ageing have reduced the effect of the pre-fermentation treatments. Or alternatively, the result of this experiment is that there are few obvious differences in Pinot noir wine made by these maceration treatments.

It was observed that the CM wines had altered considerably in their sensory characteristics from the end of the fermentation to the time of sensory evaluation. The strawberry/cherry/cinnamon characteristics initially perceived in the new wines were not detected by the panel, although optional descriptors did include some berry and cherry aromas.

4.4.2.1 Aroma attributes

Three of the eight aroma attributes were significantly different (table 4.3). For acetate, here considered to be an ester-type of smell, the aroma was higher in the CM treatment than in the control. The COM treatments were not significantly different in acetate aroma from either the control or the CM treatments.

The control wine was significantly higher in berry aroma than the CM treatment. There was no difference between the two COM treatments and both of these were not different from either the control or the CM wines.

In the optional question where panellists could further define the berry aroma (table 4.4), the carbonic treatment was identified by five of the twelve panellists as having a raspberry character. In general, the panel perceived that this treatment had more specific berry-type aroma notes than the COM or control wines. The 4°C COM treatment produced a wine which was identified as having a mixed berry (7 from 12 panellists) aroma. In contrast, the 10°C COM was described as having raspberry (5 from 12), blackberry (6 from 12) and mixed berry (4 from 12) notes.

The 10°C maceration treatment was significantly higher in woody/tobacco aroma than the 4°C treatment. Neither the control nor the CM were different in woody/tobacco aroma from the COM treatments.

Although sweet aroma was not statistically significant, optional use of further descriptors for

attribute definition is worth comment. Six of the twelve panellists used the term tropical for the sweet aroma of the control wine. In comparison to the control, the CM was described as having floral (7 from 12) and sugar (3 from 12) sweet aroma notes. Both COM treatments were considered to have dried fruit and oxidised type sweetness. The 10°C COM wine was rated higher in floral sweetness (7 from 12). Otherwise similar to the 10°C, the 4°C maceration was described as having sugar sweetness (5 from 12).

Four panel members considered that the CM had a "chemical" aroma which was not present in the control wine. They were unable to further define this term. It may be possible that this is an aroma of aged CM wines or a complex cinnamon/acetate/ester aroma. Chemical was also used to describe part of the aroma of the 10°C maceration wine (7 from 12), along with sulphur (4 from 12) and earthy (2 from 12).

4.4.2.2 Flavour attributes

Of the eight flavour attributes tested, only three were not significantly different (table 4.3). This may indicate that carbonic and COM pre-fermentation treatments have a greater influence on the flavour of wines than on their aroma.

The CM treatment was significantly lower in acid flavour than the 10°C COM but not lower than the control or 4°C maceration treatments. This does not correlate with the chemical acidity measurements made at the time of sensory evaluation (table 4.2). These physical results showed a clear difference in titratable acidity (TA) between the treatments. The CM wines were significantly lower in TA than the other treatments, and both the COM treatments

had higher TA than the control. It may be more important for sensory analysis that there was no difference in pH between the treatments, and so no flavour difference was identified.

CM treatments were perceived as being more sweet in flavour than the 10°C wines. The control and 4°C treatments did not differ from either the carbonic or 10°C maceration treatments. Again this does not bear any relation to the chemical measurements of residual sugar. This may be due to the levels present being well below the perceptible threshold for most people. This is usually around 5 g l^{-1}, although some individuals can perceive sugar as low as 0.4 g l^{-1} (Rankine, 1990).

The 10°C maceration wines were higher in blackpepper flavour than the carbonic wines. The control and the 4°C maceration were not different from either of the other two treatments in blackpepper flavour.

The 10°C COM treatment had more bitter flavour than all of the other treatments.

Description of the fruity flavours of CM wine led to the use of the term cherry by six of the panellists (table 4.5). The control was also considered to have some cherry flavour (4 of 12 panellists) but apart from this, the term was not applied to the flavour of either of the COM wines.

The control was described as having mixed berry (4 from 12) and raspberry (4 from 12) flavours, and these terms were not used as frequently for any of the treatments. Blackberry

flavour was commonly used to describe the fruity flavour of the 4°C and 10°C COM (5 from 12 and 4 from 12 respectively).

The CM wine was considered to have a chemical flavour by 4 panellists. This may be related to the chemical aroma previously discussed, but again no better definition could be obtained.

4.5 CONCLUSIONS

The panel were unable to perceive differences in chemical composition of the different wines. It was possible that the small differences in titratable acidity, residual sugar and sugar-free extract were below the threshold levels of the panel members.

The use of different temperatures for COM had no major effect on the aroma and flavour of the resulting wines, there being few statistically significant differences between these two treatments. One difference was that the 10°C maceration was higher in woody/tobacco aroma than the 4°C maceration treatment. This 10°C maceration treatment was also higher in bitter flavour than all of the other treatments. Specific aroma characters for the berry attribute of the 10°C maceration treatment included raspberry and blackberry. Both the COM treatments were considered to have mixed berry aromas as well as sweet dried fruit and oxidised characters. Blackberry flavour was commonly used to describe the fruity flavour of the 4°C and 10°C COM wines.

CM wines were found to be lower in berry aroma than the control wines. The panel did indicate that there was more raspberry character to the berry aroma of the CM wines. Other

specific aroma characteristics noted in the CM wines were chemical, floral, sugar, and cherry. The CM treatment was higher in acetate or ester-type aromas than the control, which was to be expected. Further definition by the panel of the fruit flavours of CM wines included the descriptor cherry. A chemical flavour was also identified that may be related to the chemical aroma previously discussed.

TABLE 4.1

Aroma descriptors and standards developed for panel training and sensory evaluation of Pinot noir wines.

Descriptor Term	Reference Composition[1]
alcohol*	-5 ml 96% (v/v) ethanol
oxidised*	-5 ml Corbans™ Select Medium Dry Sherry
blackcurrant	-10 fresh blackcurrants -5 ml Ribena™ blackcurrant juice -5 ml Barkers™ unsweetened blackcurrant juice
strawberry	-2 fresh, sliced strawberries[2]
sulphur*	-10 ml Watties™ whole canned peas -1 chopped, hard boiled egg
earthy*	-10g fresh earth
woody/tobacco	-10g tobacco and 5 strands oak wood
fruity	-15g Goldpac™ mixed dried fruit
vinegar*	-5 ml DYC™ malt vinegar
berry	-3 frozen blackberries and 3 frozen raspberries
green*	-1g alfalfa bean sprouts
blackpepper	-10 cracked peppercorns
acetate	-5 drops of ethyl acetate (BDH, England: reagent grade)
honey*	-5 ml clover honey
almond*	-2.5 ml Greggs™ almond essence

[1] All standards made up in 50 ml control wine the previous day (except strawberry[2]), and left to stand overnight. The standards were served in 150 ml glasses covered by watchglasses.

[2] Made one hour before evaluation.

* Used for panel training only.

TABLE 4.2

Chemical composition of Pinot noir wines made by conventional fermentation (control), carbonic maceration, and cold maceration at 4°C and 10°C.

Measurement	Wine Treatment				*p*	LSD[1]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration		
pH	3.27	3.33	3.18	3.24	0.054	NS
Titratable Acidity (g l^{-1})	9.93b	8.38a	10.33c	10.33c	0.000	0.316
Residual Sugar (g l^{-1})	2.38	1.75	1.94	1.69	0.621	NS
Alcohol (%)	10.88	10.48	11.30	10.80	0.087	NS
Sugar-free Extract	20.39ab	18.85a	22.13b	22.38b	0.030	2.391
Free SO_2 (mg l^{-1})	14.40	21.87	26.13	27.73	0.051	NS
Total SO_2 (mg l^{-1})	84.27	88.00	106.67	120.87	0.089	NS

Mean values within the same row not designated by the same letter differ significantly ($p \leq 0.05$).

[1] Least significant difference.

TABLE 4.3

Mean scores[1] of the aroma and flavour descriptors used for Pinot noir wines made by pre-fermentation treatments.

Attribute	Wine Treatment				LSD[2]
	Control	Carbonic maceration	4°C cold maceration	10°C cold maceration	
Aroma Attributes					
Acetate	2.10a	3.02b	2.34ab	2.32ab	0.76
Alcohol	2.50	2.52	2.45	2.44	NS
Blackcurrant	3.25	3.55	3.17	2.85	NS
Berry	3.29b	2.34a	2.79ab	2.83ab	0.71
Honey	1.41	1.51	1.44	1.01	NS
Blackpepper	1.26	1.06	1.16	1.11	NS
Woody	0.28ab	0.47ab	0.16a	0.54b	0.35
Sweet	2.21	2.31	2.71	2.14	NS
Flavour Attributes					
Alcohol	3.48	3.17	3.19	3.41	NS
Acid	3.19ab	2.71a	3.07ab	3.29b	0.54
Blackcurrant	3.06	2.98	2.90	2.99	NS
Fruity	2.75	2.89	2.73	2.66	NS
Sweet	2.26ab	2.30b	2.19ab	1.77a	0.57
Blackpepper	1.86ab	1.58a	1.83ab	2.14b	0.50
Bitter	1.45a	1.25a	1.60a	2.15b	0.53

[1] Scored on an eight-point intensity scale (0 = none, to 7 = intense). Means within the same row not designated by the same letter differ significantly ($p \leq 0.05$).

[2] Least significant difference.

TABLE 4.4

Optional descriptors used for further definition of specific aroma terms of Pinot noir wines.

Wine Treatment	Berry Aroma		Sweet Aroma		Other Aromas	
	Descriptor	Usage[1]	Descriptor	Usage	Descriptor	Usage
Control	Blackberry	6	Dried Fruit	4		
	Mixed berry	6	Floral	4		
			Oxidised	3		
			Tropical	6		
Carbonic Maceration	Mixed berry	3	Dried fruit	4	Chemical	4
	Raspberry	5	Floral	7		
			Oxidised	4		
			Sugar	3		
4°C Cold Maceration	Mixed berry	7	Dried fruit	5		
			Floral	3		
			Oxidised	4		
			Sugar	5		
10°C Cold Maceration	Blackberry	6	Floral	7	Chemical	7
	Mixed berry	4	Fresh fruit	3	Sulphur	4
	Raspberry	5	Fresh fruit	3		
			Oxidised	3		

[1] Indicates the number of panellists, where n = 12, that used this term to further characterise the aroma descriptor.

TABLE 4.5

Optional descriptors used for further definition of specific flavour terms of Pinot noir wines.

Wine Treatment	**Fruity Flavour**		**Other Flavours**	
	Descriptor	Usage[1]	Descriptor	Usage
Control	Cherry	4		
	Mixed berry	4		
	Raspberry	4		
Carbonic Maceration	Cherry	6	Chemical	4
4°C Cold Maceration	Blackberry	5		
10°C Cold Maceration	Blackberry	4		

[1] Indicates the number of panellists, where n = 12, that used this term to further characterise the aroma descriptor.

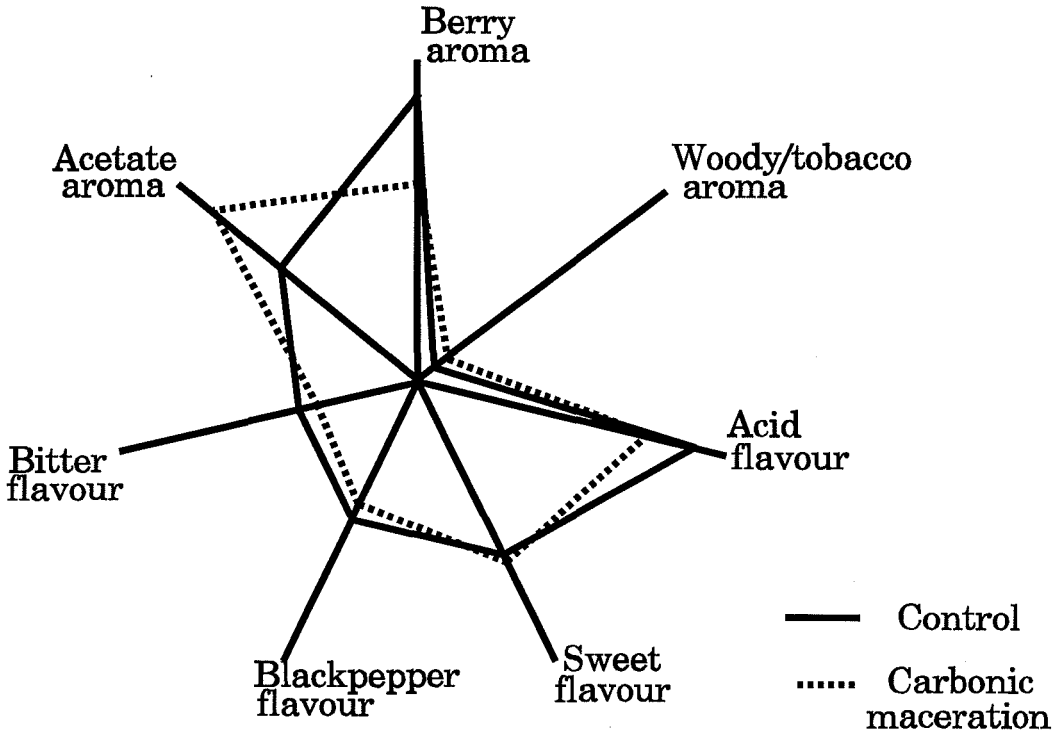

Figure 4.1 Comparison of descriptive profiles of control and carbonic maceration Pinot noir wines.

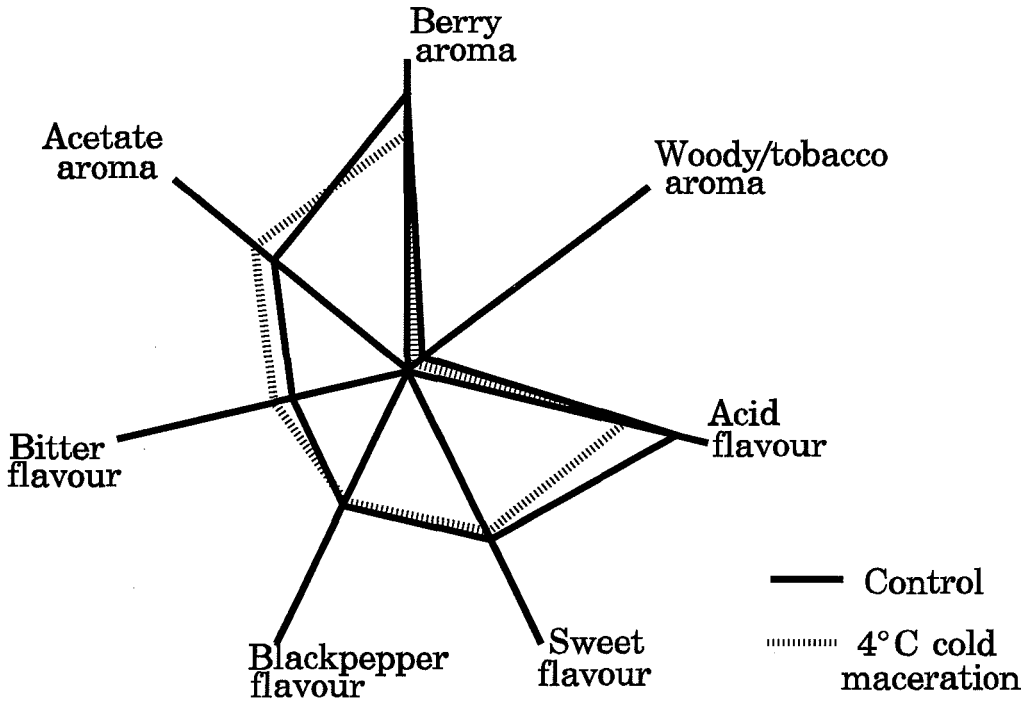

Figure 4.2 Comparison of descriptive profiles for control and 4°C cold maceration Pinot noir wines.

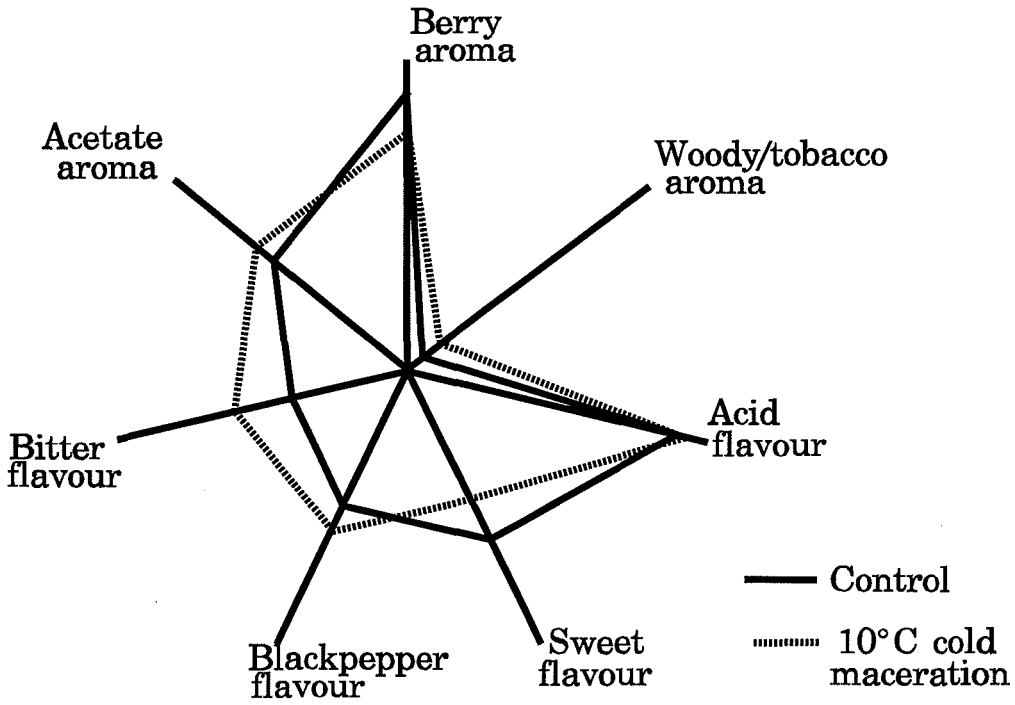

Figure 4.3 Comparison of descriptive profiles for control and 10°C cold maceration Pinot noir wines.

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CHAPTER FIVE

CONCLUSIONS

5.1 CHEMICAL COMPOSITION AND COLOUR PARAMETERS

Carbonic maceration of Pinot noir wines can be achieved if the grapes are maintained under an inert atmosphere. This was contrary to the findings of Amerine and Ough (1969) who found that this thin-skinned grape cultivar was extremely susceptible to acetic spoilage (Amerine and Ough, 1969).

The wines produced by carbonic maceration were lower in titratable acidity, malic acid, colour density, total monomeric anthocyanins and higher in colour hue, degree of anthocyanin ionisation and polymeric pigments. In general, these findings corroborate those in the literature.

Cold maceration was investigated for the first time. Application of this technique on Pinot noir wines showed that there was no appreciable difference between wines macerated at 4°C and 10°C. These cold maceration wines were considerably different from conventionally processed wines.

Cold maceration produces wines that were higher in titratable acidity, total phenolics and monomeric anthocyanin content, but lower in colour hue and polymeric pigment content than control wines. In this investigation, little difference was found in visible wine colour between cold maceration and control wines. This is thought to have been due to lack of

opportunity for anthocyanin interaction with tannins, and subsequent colour stabilisation. In a real winery situation, the wines would be aged in oak barrels, which would potentially lead to increased colour in cold maceration wines.

Cold maceration requires the addition of large amounts of SO_2, up to 150 mg l^{-1} (Norman, 1992). This may potentially slow or prevent malolactic fermentation in the wines, and so is of concern to winemakers. Results of this investigation have shown that little of this initial SO_2 addition persists after the alcoholic fermentation, and so should not be problematic.

5.2 SENSORY EVALUATION

The panel were unable to perceive differences in chemical composition of the different wines. It was possible that the small differences in titratable acidity, residual sugar and sugar-free extract were below threshold levels of the panel members.

The use of different temperatures for cold maceration had no major effect on the aroma and flavour of the resulting wines, there being few statistically significant differences between these two treatments. One difference was that the 10°C maceration was higher in woody/tobacco aroma than the 4°C maceration treatment. This 10°C maceration treatment was also higher in bitter flavour than all of the other treatments. Specific aroma characters for the berry attribute of the 10°C maceration treatment included raspberry and blackberry. Both the cold maceration treatments were considered to have mixed berry aromas as well as sweet dried fruit and oxidised characters. Blackberry flavour was commonly used to describe the fruity flavour of the 4°C and 10°C cold maceration wines.

Carbonic maceration wines were found to be lower in berry aroma than the control wines. The panel also indicated that there was more raspberry character to the berry aroma of the carbonic maceration wines. Other specific aroma characteristics noted in the carbonic maceration wines were chemical, floral, sugar, and cherry. The carbonic maceration treatment was higher in acetate or ester-type aromas than the control. Further definition of the fruit flavours of carbonic maceration wines by the panel included the descriptor cherry. A chemical flavour was also identified that may be related to the chemical aroma that was described.

5.3 FURTHER RESEARCH

5.3.1 COLD MACERATION

Research into the cold maceration of Pinot noir wines could focus on a number of different areas. The pre-fermentation maceration is affected by many factors other than the temperature differences that were studied here.

It is not known how the high levels of SO_2 that are used in the pre-fermentation stage affects the process of cold maceration. There may only be an anti-microbial effect of preventing the natural yeast flora from initiating fermentation. Alternatively, SO_2 may act as a solvent for the extraction of grape phenolics. The third option is that both of these phenomena occur simultaneously. Studies may also be able to ascertain optimal levels of SO_2 for use in cold maceration.

Pectolytic enzymes are currently used in winemaking to maximise juice extraction, and colour of red musts (Ough, Noble and Temple, 1975). There is potential for the application of such enzymes in cold maceration, due to time constraints or if the use of SO_2 was considered undesirable. The use of pectolytic enzymes may increase the extraction of cellular constituents and increase the benefits of cold maceration.

This study has only briefly investigated the phenolic content of the cold macerated juice and wines. High pressure liquid chromatography (HPLC) analysis could characterise the various phenol types and quantities present. It may be possible to differentiate the phenols that originate from skins and seeds, or the effects of aqueous extraction as compared to the

more usual alcoholic extraction.

In Burgundy, the length of the pre-fermentation maceration period is variable, depending on the winemaker. In this study, a period of six days was used based on maximal phenolic extraction, but it is not known if this is the optimal length of time. Further investigations could establish how long the maceration needs to be in order to maximise the effects of this process. This would possibly integrate with studies into the use of pectolytic enzymes and SO_2.

The newly-fermented wines contain much higher levels of monomeric anthocyanins than conventionally vinified wines, and so it would be of interest to determine the effects of barrel ageing of these wines. Presumably the cold maceration wines would have higher potential colour, as the monomeric anthocyanins would polymerise and stabilise by interaction with the oak tannins. An alternative process might be the addition of grape tannin, which has been shown to stabilise Pinot noir colour (Steans, 1987).

In discussion with winemakers, it has become apparent that there is some concern about achieving malolactic fermentation subsequent to cold maceration. Although this was not specifically investigated in this trial, it was found that free and total levels of SO_2 in the wine after fermentation were low enough not to cause any problem. Further experimentation could examine the growth of malolactic bacteria in cold macerated wines.

Once these basic parameters had been established, it would be advantageous to then run winery-scale trials. Although microvinification is considered to be an accurate indicator

of any winemaking process (Ewart and Sitters, 1991), it is of interest to the industry to see what happens in "real life". In conjunction with this, long-term investigation of the development of the wines in terms of the acidity, flavour, colour and phenolic components could yield valuable information.

5.3.2 CARBONIC MACERATION

Carbonic maceration has been thoroughly investigated, and this study mostly confirms the current knowledge. One aspect that is of considerable interest is the sensory evaluation of the aroma and flavour parameters. Quantitative descriptive analysis did not find the expected statistical significance of cherry/strawberry/cinnamon characters. This is possibly due to the evaluation being conducted on wines that were 8 months old, and they may have shown aromas and flavours that were more aged than typical of carbonic maceration wine. Certainly, *beaujolais nouveau* wines that have a carbonic maceration component are generally considered to be at their best immediately after fermentation. Conducting quantitative descriptive analysis on newly made carbonic wines may give a better indication of the true sensory nature of such wines.

Further to quantitative descriptive analysis, the carbonic maceration wines could be subjected to analysis by gas chromatography-mass spectrometry (GC-MS). This has been conducted on Merlot wines made by carbonic maceration and yielded valuable information on the aromatic volatiles (Ducruet, 1984). It would be interesting to investigate the characteristic aroma compounds of the carbonic maceration wines, and see how these differ from conventionally vinified wines.

There is also a need to determine the relationship between the chemical and sensory data collected by various methods. Some research has been conducted into this area, using Pinot noir wines and the technique *Osme* (Miranda-Lopez *et al.*, 1992). Once the aromatic compounds of carbonic maceration wines had been isolated by GC-MS, their sensory properties could then be defined.

Winemakers may add a proportion of whole berries to their ferments, particularly with Pinot noir. This is thought to reduce the available sugar in the must, and hence extend the fermentation time. Such berries may undergo a form of anaerobic metabolism similar to that seen in carbonic maceration. Investigation of this technique may provide useful information in terms of the changes to the composition and flavour of the resulting wine.

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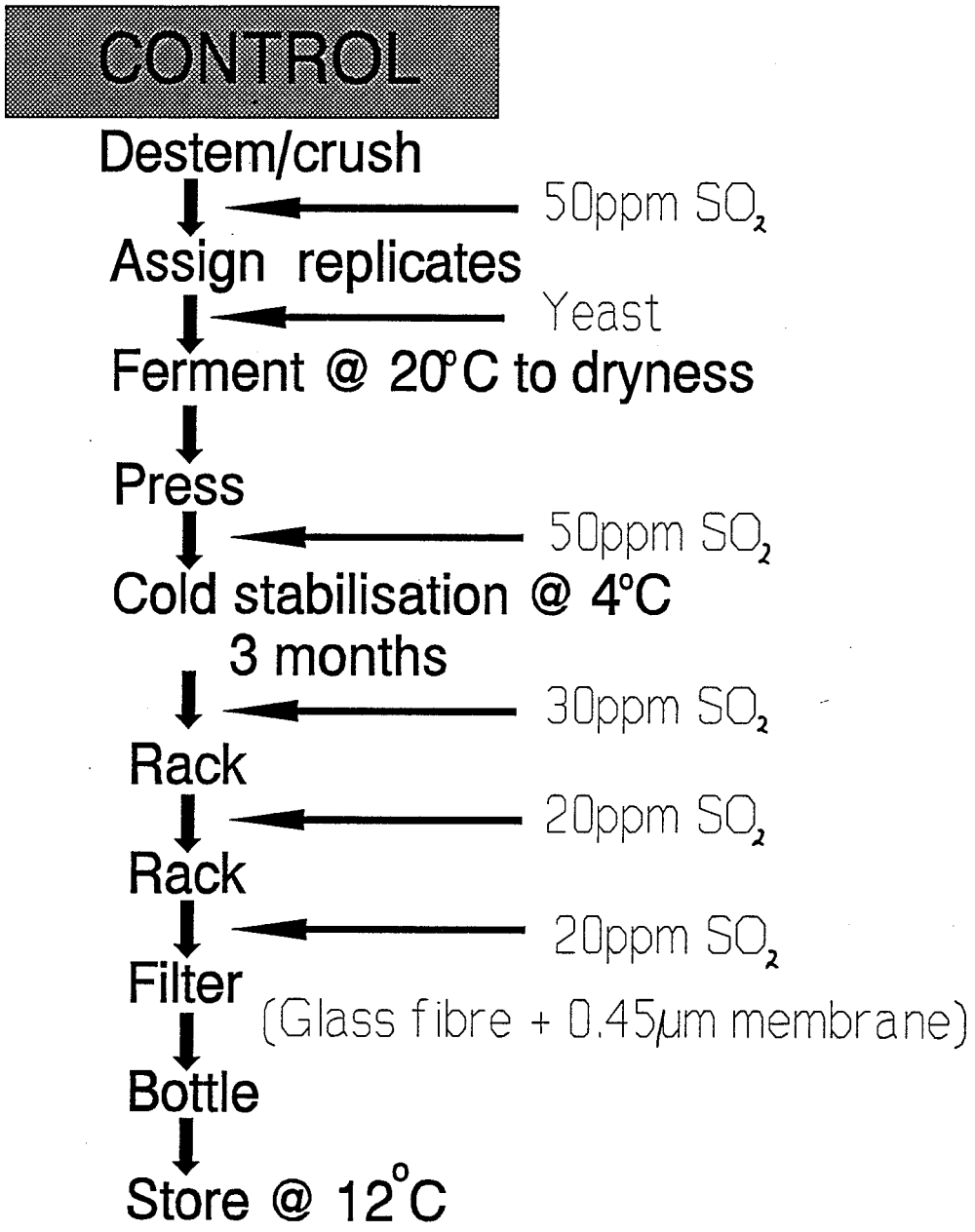
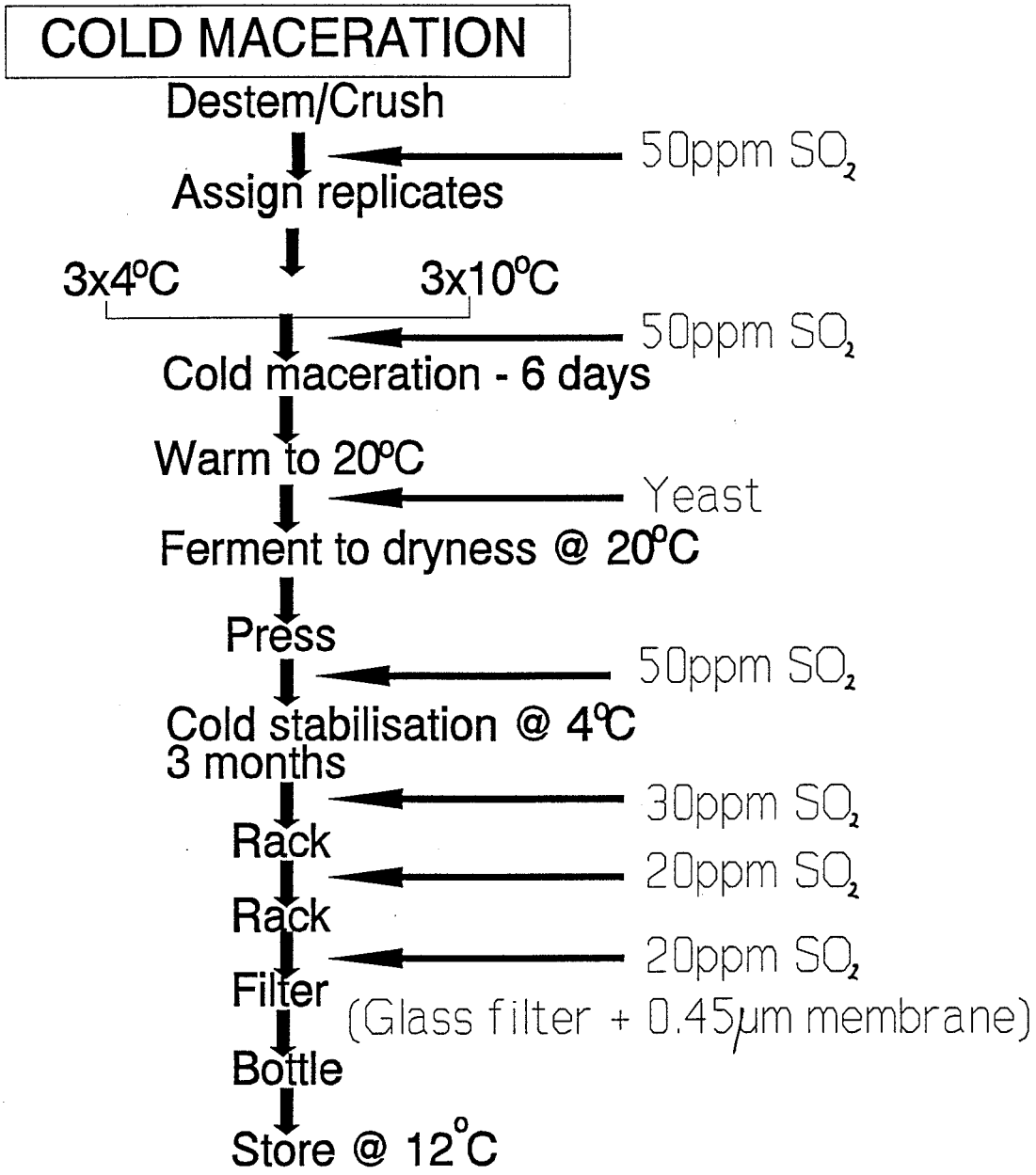
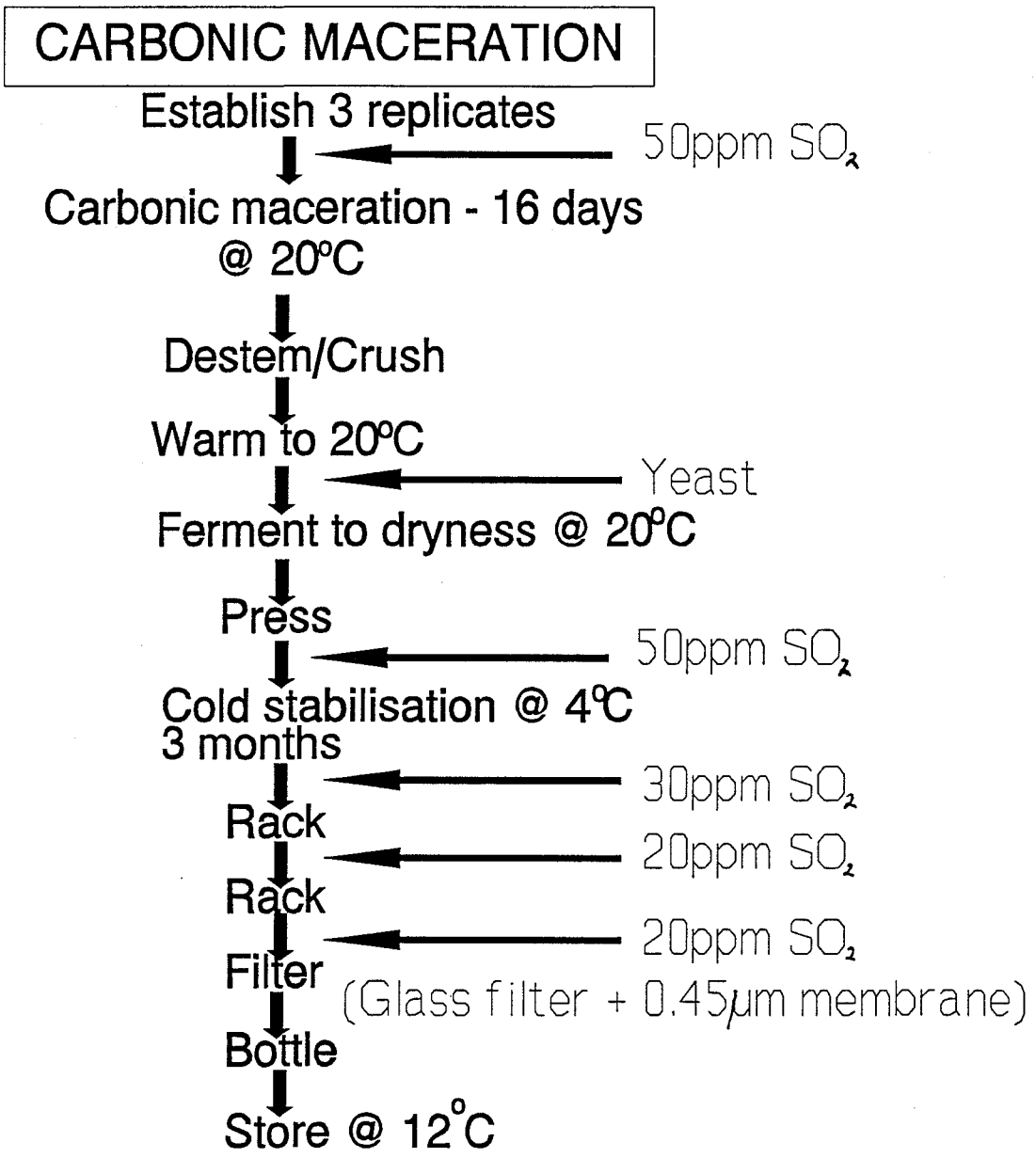


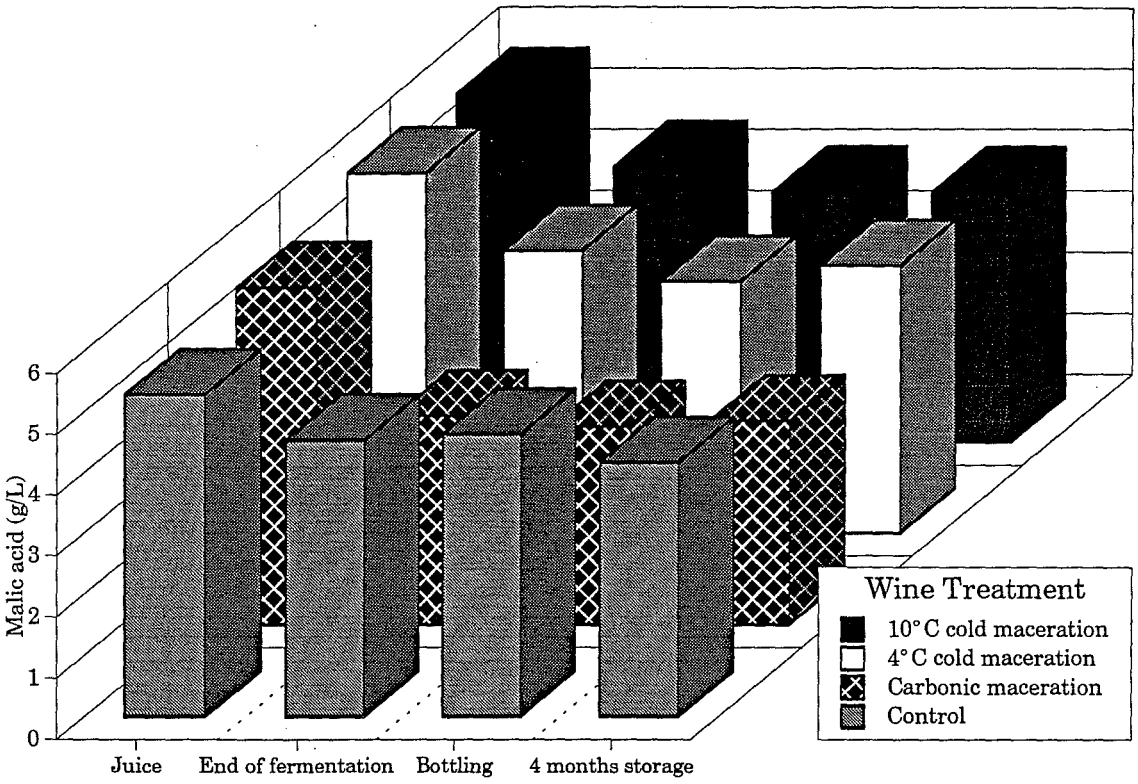
Appendix 3.1 Flowchart of winemaking procedure for control Pinot noir wines.



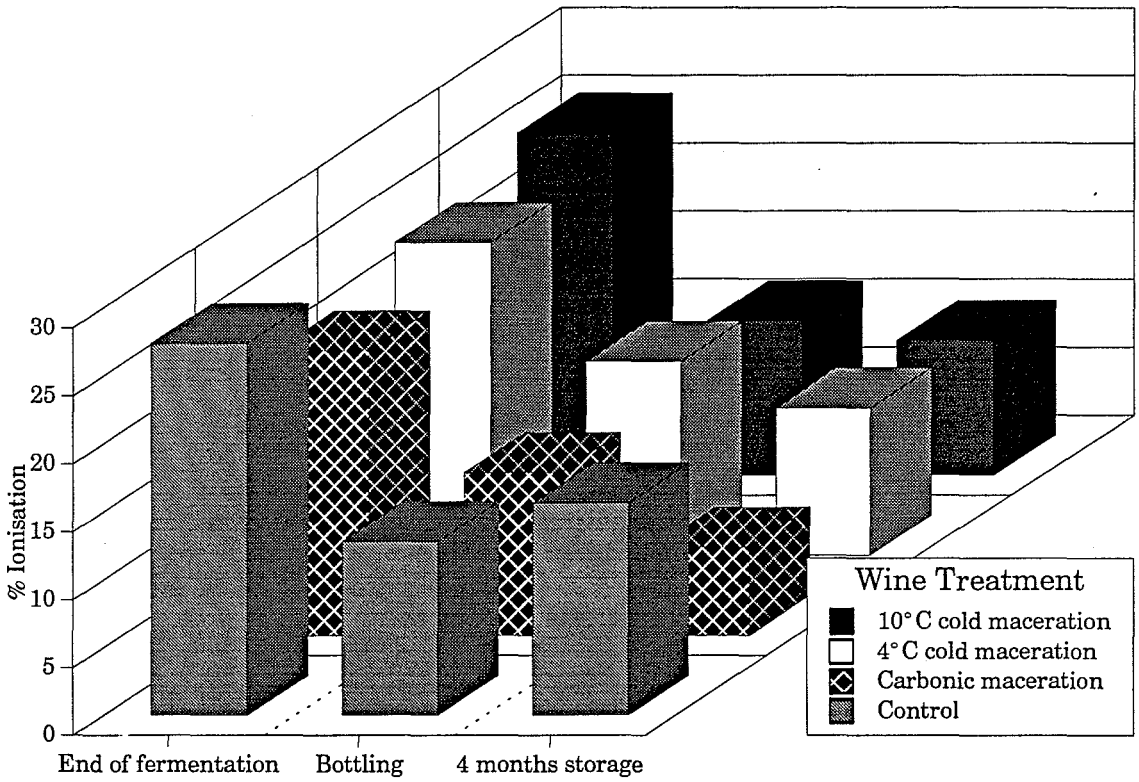
Appendix 3.2 Flowchart of winemaking procedure for cold maceration Pinot noir wines.



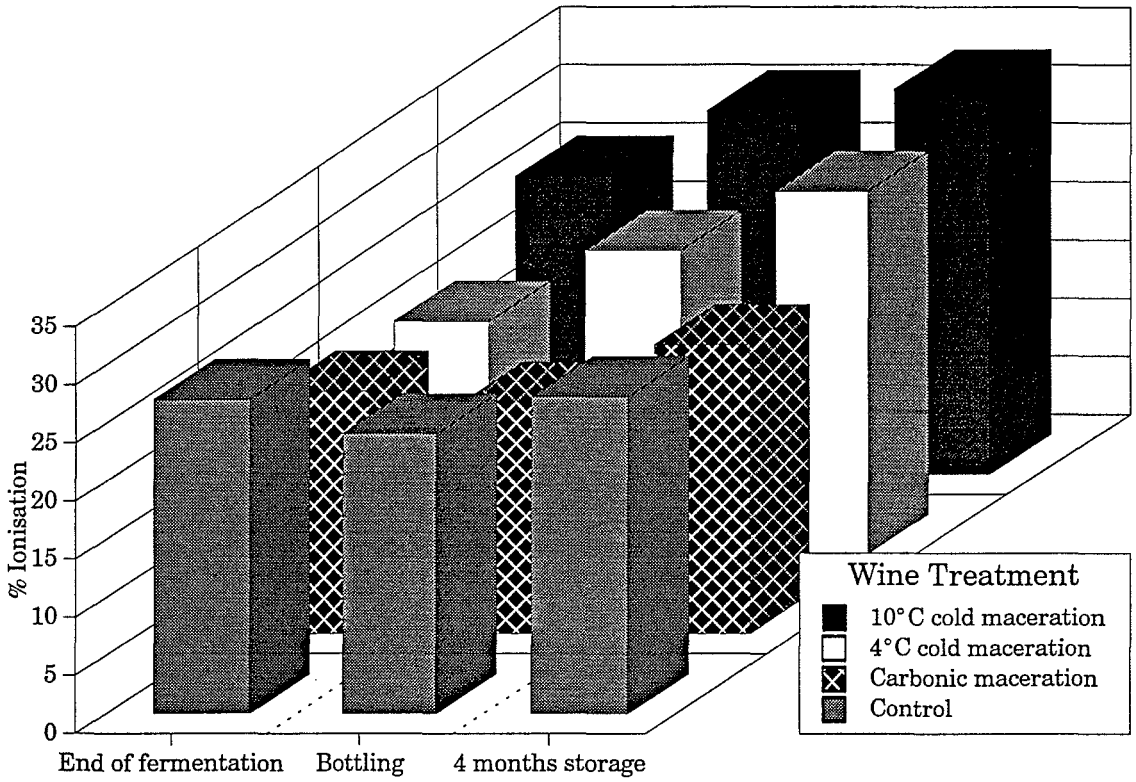
Appendix 3.3 Flowchart of winemaking procedure for carbonic maceration Pinot noir wines.



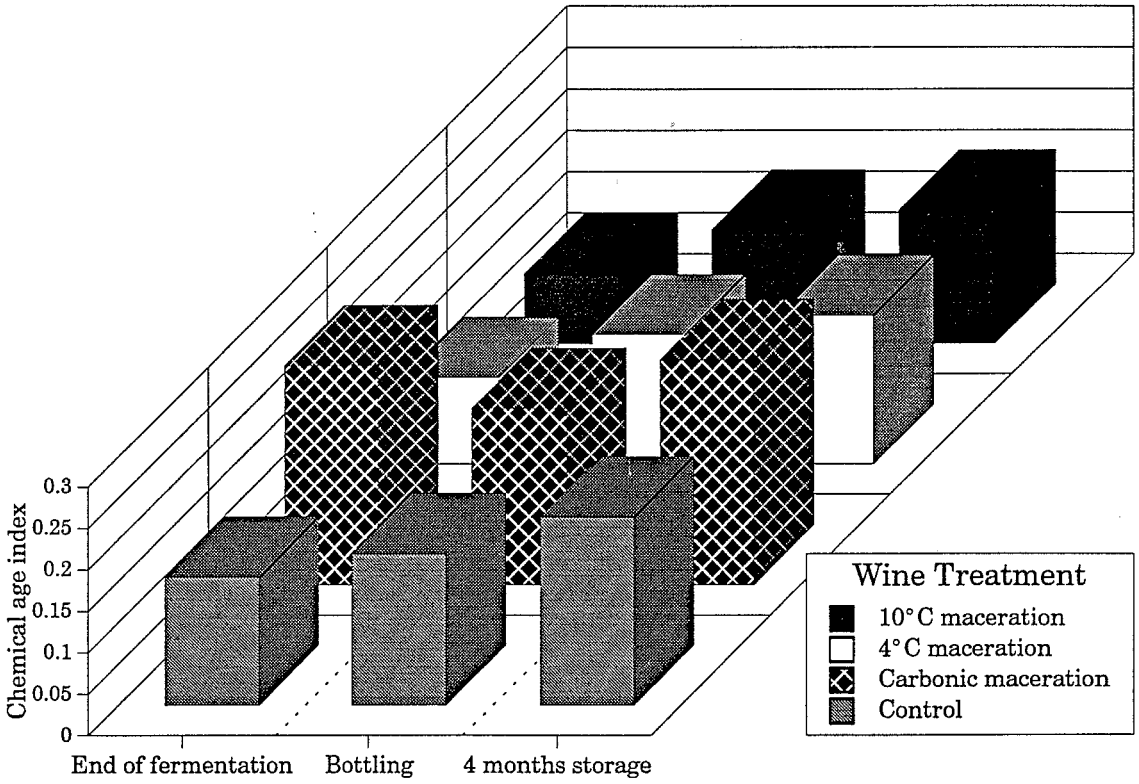
Appendix 3.4 Malic acid content of Pinot noir juice and wines subjected to pre-fermentation maceration.



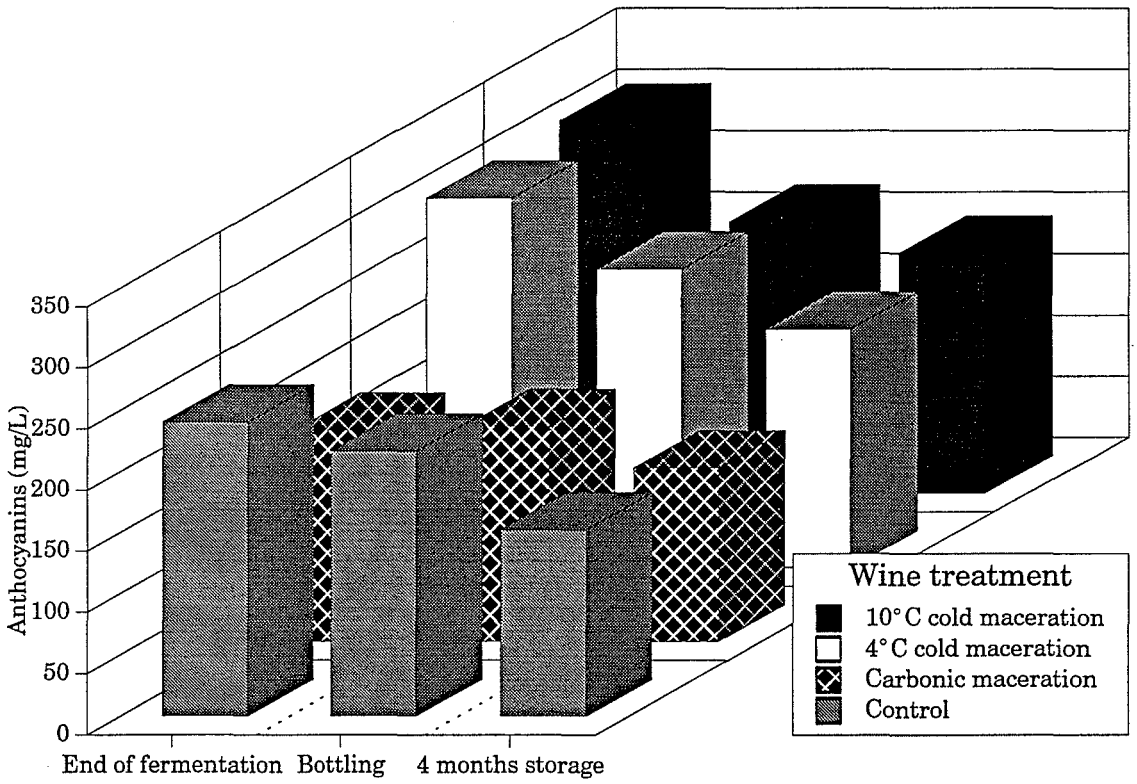
Appendix 3.5 Anthocyanin ionisation (α) for Pinot noir wines made by pre-fermentation maceration.



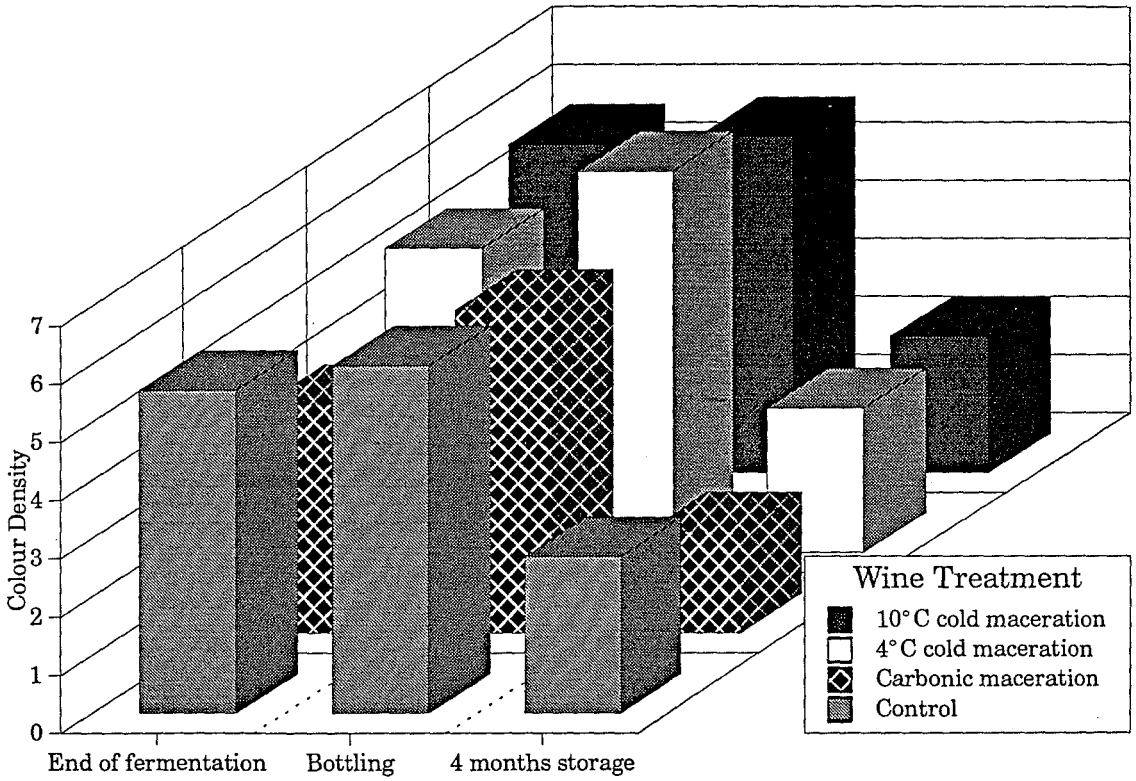
Appendix 3.6 Natural degree of anthocyanin ionisation (α') of Pinot noir wines made by pre-fermentation maceration.



Appendix 3.7 Polymeric pigments of Pinot noir wines made by pre-fermentation maceration treatments.



Appendix 3.8 Total monomeric anthocyanin content of Pinot noir wines made by pre-fermentation maceration.



Appendix 3.9 Colour density of Pinot noir wines made by pre-fermentation maceration treatments.