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**Characterization of Regional Examples
of New Zealand Pinot Noir
by Means of Sensory and Chemical Analysis**

A thesis
submitted in partial fulfilment
of the requirements for the Degree of
Doctor of Philosophy

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Elizabeth Tomasino

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Declaration

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There are four main Pinot noir wine regions in New Zealand: Central Otago, Marlborough, Martinborough and Waipara. These regions specialize in this variety as the soil, climate and other conditions are well suited to this grape. Beside being grown in these regions the wines are also marketed as regional products. Place of origin labelling implies that wines from one region will have different aroma and flavour characteristics from wines from other regions. This project determined the characteristics that best differentiate the regional styles of New Zealand Pinot noir. Marlborough Pinot noir was characterized by greater raspberry, red cherry, red fruit and red berry aromas, longer finish length and more harmonious balance. Martinborough Pinot noir was characterized by greater black cherry, chocolate, oak and spice aromas and oak tannin. Waipara Pinot noir was characterized by greater barnyard, herbal and violet aromas and in-mouth fruit density/concentration. Central Otago Pinot noir was characterized by fuller body. As regional wines were found to be stylistically different, the ability of tasters to discriminate regional wines was tested using paired comparison and sorting analysis. Tasters were not successful at discriminating regional wine examples using these techniques. This may be due to conceptual models that are not representative of the regional wines.

In order to determine the possible causes of these regional differences the chemical composition of the wines was also investigated. Three HS-SPME-GC-MS methods were

developed specifically for Pinot noir wine to measure 34 different volatile organic compounds. One method measured compounds found at higher concentrations, namely esters and alcohols, the second method measured volatile fatty acids and the third measured trace compounds present at very low concentrations.

With the two sets of information, sensory and chemical, it was possible to find relationships using canonical correlation analysis. Results indicated four aroma compounds of particular importance: ethyl octanoate, ethyl decanoate, 2-phenyl ethanol and benzaldehyde. Addition/omission tests were used to determine the influence of each compound on Pinot noir aroma. The compounds were added in combination and at varying concentrations to a wine matrix, which consisted of a commercial Pinot noir that contained low levels of the compounds of interest. In 8 of 10 triangle tests panellists were able to successfully identify samples with different concentrations of the components.

Panellists also used descriptive analysis to determine the influence of these compounds. From the descriptive analysis results it was found the 2-phenyl ethanol influenced the perception of violet aroma, ethyl octanoate influenced red cherry aroma and the combination of ethyl octanoate and ethyl decanoate influenced black cherry aroma. The measurement of the effect of these aroma compounds is a first step to understanding some factors of regional style since red cherry, black cherry and violets were descriptors that characterize the regional styles of New Zealand Pinot noir.

Keywords: addition test, benzaldehyde, canonical correlation analysis, ethyl decanoate, ethyl octanoate, HS-SPME-GCMS, New Zealand, 2-phenyl ethanol, Pinot noir, place of origin, regionality, volatile fatty acids

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Chapter 1

Introduction

Is it reasonable to say that food products from different regions can be distinguished from one another? Many producers believe that this is so as certain products are marketed as originating from a specific region. Some examples of product of origin foods include Vermont cheddar cheese, California raisins, Parma ham and Florida oranges and grapefruit (Centner et al. 1989; Kotler et al. 1993; Papadopoulos 1993). Products, such as wine, that have extensive histories or traditions may create a competitive advantage by using place of origin, as part of the name or on the label. This suggests that geographic origin produces quality attributes that cannot be duplicated in other locations.

In many cases food producers provide more regional information than is required by law if they believe that consumers will prefer their product over those from other locations (Golan et al. 2000). This regional aspect to marketing communicates to the consumer that the product has specific qualities that are based on the environment in the region of origin. The addition of country of origin (COO) or region of origin information is used to take advantage of regional loyalty and also to signify product quality (Patterson et al. 1999). Of all agricultural products that use COO and region-based labels none are more frequently associated with “place” than wine (Thode & Maskulka 1998). This association is so strong that many countries have put in place regulatory systems to protect these place names. The most well known is probably the Appellation Contrôlée (AC) system in France in which the wine region and winery are listed on the label but not the grape variety (Berard & Marchenay). Other countries have created similar systems, such as the American Vineyard Appellations (AVA) system in the United States, Denominazione di Origine e Controlata (DOC) in Italy, Wine of Origin certificate in South Africa and Geographical Indications in New Zealand (Cholette et al. 2005; Barker 2006).

The marketing success of place of origin labelling is dependent upon the product (Ahmed et al. 2004) but has been quite successful for wine. This type of marketing offers a competitive advantage both in foreign and domestic markets (Ittersum et al. 2003). For example, Pinot noir wine labelled as produced in New Zealand would be recognized as different from that produced in another country; similarly Pinot noir labelled as Central Otago would be recognized as different from Pinot noir produced in other locations within New Zealand

(Ittersum et al. 2003). Felzensztein et al. (2004) provide an excellent overview of how country and place of origin labelling are utilized by the wine industry. Place of origin is used to differentiate wines in foreign markets, acts as a marker of quality and effects perception for all consumers except those brand new to wine.

Sensory Characteristics in Regards to Place of Origin

In order for place of origin or regional branding to be successful, the definition of a typical style for the regional wine is required (Easingwood 2007; Grainger 2009). Specifically, this regional definition refers to the sensory characteristics of the wine. In the French Appellation Contrôlée system all wines from the same area must have shared sensory qualities that can be perceived by wine consumers, and wine experts (INAO-DIR-2008-02 rev 1). However the elaboration of which sensory characteristics are key to regional differentiation is not straightforward. Wines that come from the same region may share many related sensory attributes, but they do not need to possess all of the same key attributes (Rosch & Mervis 1975).

Currently there are two ways in which sensory analysis is used to investigate region of origin. Regionality studies investigate which sensory characteristics are important to each region, defining a specific regional style. Typicality studies investigate how the sensory characteristics of the wines best fit the regional style in the case where regionality or a regional concept has already been established. Unfortunately there is no consensus on how to measure regionality and typicality. Most studies take a large number of products from a number of regions and attempt to discover similarities in the sensory characteristics of products from each region (Tonietto et al. 2005; Fisher 2006; Maltman 2008; Cadot et al. 2010; Maitre et al. 2010).

Characterization of common sensory attributes that correspond to place of origin have been successful for several varieties of white wine (Moio et al. 1993; Moio et al. 1994; Ballester et al. 2005; Ballester et al. 2008; Esti et al. 2010). In New Zealand the characterization of Marlborough Sauvignon blanc has been particularly successful. Sauvignon blanc wine from Marlborough was found to be clearly different from those produced in France and other countries (Lund et al. 2009). Additionally to be considered a typical Marlborough Sauvignon blanc the wine must exhibit passion fruit, tropical, citrus, stone fruit, herbaceous, green capsicum, boxwood and grassy notes (Parr et al. 2007). Further investigation found that

Sauvignon blanc wines from France also had clear regional differences within the country, while Marlborough wines did not exhibit further sub-regional differences beyond the Marlborough region of origin (Parr et al. 2010).

Very few studies have investigated regionality and typicality of red wines in comparison to work done on white wines. Much of the sensory research has focused instead on characterizing red wine varieties (Heymann & Noble 1987b; Falque et al. 2004; Varela & Gambaro 2006; Preston et al. 2008; Mansfield & Vickers 2009). To date red wines from Rioja and the Loire Valley have been investigated (Cadot et al. 2010; Etaio et al. 2010; Perrin & Pages 2010). Several studies have attempted to characterize regional styles of Pinot noir, although these studies did not attempt to link the sensory characteristics to typicality. Pinot noir regions investigated include Oregon (Haeger 2004), British Columbia (Cliff & Dever 1996), cooler regions of Australia (Easingwood 2007) and Burgundy (Aubry et al. 1999a).

The Conceptual Model

Conceptual models play an important role in the identification of regional products. A conceptual model can be described as a prototype or internalized standard of a product that has been formed in the mind of an individual (Gallarza et al. 2002; Casabianca et al. 2005a; Jaffre et al. 2009). In the case of wine, an individual's prototype will contain specific sensory characteristics that relate to the wine of interest (Richard 2005). Conceptual models of varietal wines, e.g. Chardonnay, have been found to be based on perceptions of similarity between wines; not all wine sensory aspects are included because individuals weight which characteristics are most important (Ballester et al. 2005). A taster will recall important sensory characteristics and compare these with aroma and taste of the wine. Conceptual models have been applied to regional wine styles. Wines that contain sensory characteristics that are the same or similar to the regional conceptual model are then categorized as being produced from the same geographic location (Parr et al. 2007).

Experience with a wine style affects the development of the conceptual model and evaluation of products. The more regional wines consumed by an individual the greater the chances that the resulting conceptual model contains aspects that are shared with other experienced individuals (Ballester et al. 2008). Specifically when investigating descriptive terms used for typical wine assessments, studies have shown that experts use conceptual models or prototypes when describing wines (Urdapilleta et al. 2011). Experts use words or series of

words that they have previously categorized into a prototype for that wine style (Brochet & Dubourdieu 2001).

Chemical Characteristics in Regard to Place of Origin

As with the sensory characteristics of wine, research has attempted to characterize regional wines based on chemical characteristics. These chemical characteristics include both volatile and non-volatile compounds. Volatile compounds refer to organic compounds that may produce an aroma. Non-volatile compounds are those that are not aromatic, may directly influence texture and mouth-feel characteristics, and may also indirectly affect the aroma perception of volatile compounds (Rapp & Versini 1995; Dufour & Bayonove 1999; Lund et al. 2008). Besides having an effect on sensory perception the chemical composition of wine has also been used to determine wine authenticity, e.g. to verify that wines labelled as French were grown and made in France (Baxter et al. 1997; Arvanitoyannis et al. 1999; Bevin et al. 2006).

Several studies have quantified elemental composition of wine and linked this to region of origin (Suhaj & Korenovska 2005). The concentration of 13 different elements were found to be linked to the white, rosé and red wine regions of origin in the Canary Islands (Perez-Trujillo et al. 2011); 10 different elements were found to differentiate wines from the Niagara Peninsula and the Okanagan valley in Canada (Taylor et al. 2003); metallic ions were important in the differentiation of wines from three sub-regions of Rioja (Gonzales-Larrana et al. 1987); rubidium and lithium could correctly classify wines from north-western Spain (Latorre et al. 1994); and, a suite of elements were found to classify a range of red wines from New Zealand into seven of the main wine growing areas (Angus et al. 2006).

Other research has focused on isotopic ratios. In Slovenia, isotope ratios differentiated wines from coastal and continental regions (Ogrinc et al. 2001); in Bordeaux isotope ratios could differentiate between the different sub-regions (Martin et al. 1999); isotope and elemental composition was found to successfully classify wines from Alsace, Burgundy, Beaujolais and the Loire Valley in France (Day et al. 1995); and the isotope ratio of strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) showed clear regional differences in wine grown on granite, basaltic and mixed soils (Barbaste et al. 2002), and could be used to differentiate both French and Italian wines (Horn et al. 1993) and Portuguese wines (Almeida & Vasconcelos 2001).

The use of fluorescence spectroscopy to create a spectroscopic “fingerprint”, has also been successful at characterizing different wine varieties, country of origin and typicality for French and German wines (Dufour et al. 2006) and Rioja wines (Airado-Rodriguez et al. 2011). The main wavelength bands that were used in the analysis were those that related specifically to wine phenols. The concentration of a range of phenolics, including tannins and anthocyanins, were found to differentiate Spanish red wines (Jose et al. 1990; Gil et al. 1995), Greek wines (Kallithraka et al. 2001; Makris et al. 2006) and wines from around the world (McDonald et al. 1998).

Besides classification of region of origin through non-volatile composition, the volatile composition is of great interest. Most research has focused on determining the volatile composition of specific wine varieties (Bonino et al. 2003; Ferreira & de Pinho 2003; Cabredo-Pinillos et al. 2004; Yu et al. 2006; Noguerol-Pato et al. 2009) but some work has investigated the effect of region on volatile composition. It is presumed that since wines from a similar region do have similar sensory properties then the volatile composition should be similar. Riesling wines from Northern Italy, Germany and South Africa were successfully differentiated based on their concentrations of free and bound C₁₃-norisoprenoids and monoterpenes (Marais et al. 1992). Region of origin for Cabernet Sauvignon and Pinotage wines from South Africa were differentiated based on the concentrations of amyl acetate and hexanol (Marais et al. 1981). A range of volatiles were responsible for differentiating Rias Baixas wines from other varietal wines in Spain (Garcia-Jares et al. 1995). Sauvignon blanc from New Zealand was found to be different from Sauvignon blanc produced in other countries based on the concentration of several methoxypyrazines (Lund et al. 2009).

Relationships Between Sensory and Chemical Characteristics

Determination of the chemical composition underlying regional sensory differences can be very advantageous. This information might be used to help educate the consumer, create new brands, determine what steps in the wine-making process are necessary to produce important compounds and more. However determining relationships between wine chemical composition and sensory perception of red wine is particularly difficult. There are many aroma compounds present in wine but not all of these contribute to the actual perceived aroma of that wine. Aroma active compounds are those that can typically break through the aroma buffer, described by Escudero et al (2004) as consisting of aromatic fermentation products present in all wines. In some cases a single compound may be effective while in other

instances several compounds from the same family may have a similar effect. The ability to break through the so called aroma buffer and to play a role in wine aroma is generally dependent on the concentration and perception threshold. Typically activity can vary as aroma compounds may function as an impact compound, be a major contributor to the perceived aroma, be a net contributor to aroma in combination with other compounds or provide a subtle aroma to the wine and enhance or depress other aromas (Ferreira 2010).

Several techniques that have been used to investigate the impact of aroma compounds include Gas Chromatography-Olfactometry (GC-O), Aroma Extraction Dilution Assay (AEDA) and olfactory aroma values (OAV) (Acree & Barnard 1994; Grosch 1994; Guth 1997b). However in many instances these techniques are not representative of the true aroma of wine as they investigate the aroma perception of single compounds. Research has found that aroma perception changes when compounds are present in a complex mixture, such as wine, and therefore aroma characterization by GC-O and other methods is not representative of the wine aroma itself (Ribereau-Gayon et al. 1975a). Ferreira et al (2010) provides an excellent overview of aroma chemistry in wine and the different roles of aroma compounds in wine. Aroma compounds may influence aroma as single impact compounds, influence aroma when part of a family of similar compounds or influence aroma when part of several groups of families of compounds. Understanding the influence of these compounds on wine aroma is the key to establishing the relationship between chemical and sensory data.

Pinot noir, as with most red wines, does not contain any genuine impact compounds. However it has been found that groups of similar compounds can be net contributors to specific aromas (Jarauta et al. 2006; Escudero et al. 2007). There are many studies that have quantified a range of aroma compounds in this wine (Table 1.1) (Schreier et al. 1980; Allen et al. 1994; Aubry et al. 1997; Fang & Qian 2005a; Fang & Qian 2006; Louw et al. 2006; Pineau et al. 2007). There are also many studies that have attempted to characterize the aroma of Pinot noir wines using descriptive analysis (Guinard & Cliff 1987; Cliff & Dever 1996; Aubry et al. 1999a). But there are few studies that have investigated the influence of the aroma compounds on the sensory perception of Pinot noir.

Project Aims

New Zealand has an excellent climate for growing Pinot noir as this varietal prefers cooler average growing season temperatures that range from 14 to 16°C (Jones 2006). Improved

understanding of factors best suited for different varieties has led to the development of specific Pinot noir regions within New Zealand, namely: Central Otago, Marlborough, Martinborough (Wairarapa) and Waipara. As stated above, place of origin as a marketing instrument is only successful when there are genuine differences between products. The four main Pinot noir wine regions are quite different as they span several degrees of latitude from Martinborough at 40°S to Central Otago at 45°S. Between them, the four regions contain many different soils and individual mesoclimates (Cooper 2008). It is suggested that the variation in the soil and climate may be enough to produce stylistically different wines (Anderson 2009), although other factors including, viticultural practices, winemaking, marketing, place identity and legal aspects are also important (Moran 2006; White et al. 2009). However, based on the differences between the four Pinot noir wine growing regions of New Zealand, different wine styles might be expected. Many tasters have commented on the uniqueness of Pinot noir from each of these regions (Pinot Noir New Zealand 2010) but no definitive sensory analysis has been conducted to date on commercial wines produced from these regions. This current PhD project aims to determine and characterise existing sensory differences in regional New Zealand Pinot noir as well finding possible relationships with aroma composition.

The research investigates the characteristics of New Zealand Pinot noir wines from each of the four main regions. It also investigates pre-existing conceptual models or ideas about regional Pinot noir amongst untrained, but experienced wine tasters.

It was anticipated that differences in sensory characteristics would be reflected in the aroma chemistry. However not all volatile compounds will have a sensory impact. In order to identify those compounds that were important for the sensory attributes that characterize New Zealand Pinot noir, methods were developed to quantify a number of volatile compounds and relationships with sensory characteristics were investigated.

The major aim of this project was to identify compounds that were important to New Zealand Pinot noir aroma and specifically those aroma attributes that were important for regional differentiation.

Thesis Structure

Including this introduction, this thesis contains eight chapters. Chapter 2 outlines the main research objectives and methodology used throughout the project. Chapters 3, 4, 5, 6, and 7

are results prepared as journal papers. For these chapters only a brief objective is indicated as the introduction material is found in Chapters 1 and 2. However, the references for each of the results chapters are included in the recognized format of the target journals. Chapter 8 provides the overall conclusions from the project and is followed by a complete list of references. Figure 1.1 details how results chapters are related as methods and data contribute to more than one chapter. The arrow colours in Figure 1.1 show the analysis path for each results chapter.

Table 1.1

Ranges of concentration found for aroma compounds previously in Pinot noir

Aroma Compound	Units	Perception threshold	Olfactory Description	Allen et al. 1994	Aubry et al. 1997	Fang & Qian 2005b	Fang & Qian 2006	Louw et al. 2006	Pineau et al. 2007	Schreier 1980
<i>Acetates</i>										
Ethyl acetate	mg/L	123 ^a	Sweet fruity							1.80-2.60
Ethyl phenylacetate	µg/L	n/a	n/a				1.25-6.10			0.00-20
2-Methylbutyl acetate	µg/L	n/a	n/a				53-130			
3-Methylbutyl acetate	µg/L	0.03 ^a	Fruity, banana				240-547			130-390
2-Methylpropyl acetate	mg/L	1.6 ^a	Sweet, floral							0.02-0.05
Phenethyl acetate	µg/L	250 ^a	Fruity, floral, honey				7.81-25	60-90		20-70
<i>Acids</i>										
Butyric acid	mg/L	10 ^b	Cheese					0.22-0.30		
Isobutyric acid	mg/L	0.05 ^a	Rancid					0.58-2.75		
Isovaleric acid	mg/L	33.4 ^c	Parmesan, sweat					0.54-0.61		
Octanoic acid	mg/L	0.5 ^a	Fatty, rancid					0.30-0.59		
Propionic acid	mg/L	8.1 ^a	Pungent					8.74-22.99		
<i>Alcohols</i>										
Benzyl alcohol	mg/L	200 ^a	Dried fruit				1.11-2.01			0.36-0.85
1-Butanol	mg/L	150 ^a	Fruity							0.76-3.00
2-Butanol	mg/L	n/a	n.a							0.00-0.04
3-Methyl-1-butanol	mg/L	30 ^a	Smoky, spicey, nail polish							142.5-204.2
Euegnol	µg/L	5 ^d	Clove, balsamic				2.83-4.13			
Guaiacol	µg/L	9.5 ^c	smoky				73-177			
Hexanol	mg/L	8 ^c	Toasted, green					1.24-1.89		
2-ethyl-1-hexanol	mg/L	0.86 ^e	Moldy, musty							0.01-0.15
cis-3-Hexen-1-ol	mg/L	0.606 ^c	cut grass, leafy							0.16-0.32
trans-3-Hexen-1-ol	mg/L	8 ^d	vegetable							0.00-0.04
1-Heptanol	mg/L	2.5 ^f	Herbal, leafy, green							0.03-0.07
4-Methyl-1-pentanol	mg/L	n/a	n/a							0.02-0.09
1-Octanol	mg/L	n/a	n/a							0.04-0.07
1-Pentanol	mg/L	n/a	n/a							0.11-0.30
3-Methyl-1-pentanol	mg/L	n/a	n/a							0.03-0.11
4-Methyl-1-pentanol	mg/L	n/a	n/a							0.02-0.09

Table 1.1 Continued

Aroma Compound	Units	Perception threshold	Olfactory Description	Allen et al. 1994	Aubry et al. 1997	Fang & Qian 2005b	Fang & Qian 2006	Louw et al. 2006	Pineau et al. 2007	Schreier 1980
<i>Alcohols continued</i>										
2-Pentanol	mg/L	n/a	n.a							0.03-0.06
2-Phenyl ethanol	mg/L	14 ^a	Floral, roses				23.70-37.40	11.46-14.65		9.9-20.8
2-Methyl-1-propanol	mg/L	40 ^a	Nail polish, fruit vert							51.9-96.1
<i>Esters</i>										
Ethyl anthranilate	µg/L	n/a	n/a		50-500		0.16-0.80			
Methyl anthranilate	µg/L	300,000 ^g	Fruity, grape		50-500					
Ethyl butanoate	µg/L	20 ^c	Fruity, strawberry				114-215			130-670
Ethyl 2-methyl butanoate	µg/L	0.018 ^a	Honey sweet							0.03-0.09
Ethyl 3-methyl butanoate	µg/L	0.003 ^a	Fruity, sweet apple				9.0-79.4			20-110
Ethyl cinnamate	µg/L	1.1 ^a	Fruity, cherry, plum		50-1500		1.92-6.36			
Ethyl dihydrocinnamate	µg/L	1.6 ^a	Fruity, balsamic		800-3250		0.35-1.21			
Ethyl decanoate	µg/L	200 ^h	Fruity, waxy				79-142			20-80
Ethyl 2-furoate	mg/L	16 ^a	n/a							0.00-0.03
Ethyl hexanoate	µg/L	5 ^b	Fruity, strawberry				179-296			200-470
Ethyl octanoate	µg/L	2 ^d	Sweet, fruity				182-283			170-410
Ethyl 2-methylpropanoate	µg/L	18 ^c	Fruity, apple				132-769			120-400
Ethyl 3-phenylpropanoate	µg/L	21 ⁱ	Fruity, honey				0.38-1.51			
Methyl vanillate	µg/L	3,000 ^h	Vanilla, spicy				26.80-43.20			
<i>Ethyl phenols</i>										
4-Ethylguaiaicol	µg/L	33 ^d	Cloves				nd-5.62			40-400
4-Ethylphenol	mg/L	0.44 ^a	Stables, horse sweat							0.49-1.80

Table 1.1 Continued

Aroma Compound	Units	Perception threshold	Olfactory Description	Allen et al. 1994	Aubry et al. 1997	Fang & Qian 2005b	Fang & Qian 2006	Louw et al. 2006	Pineau et al. 2007	Schreier 1980
<i>Methoxypyrazine</i>										
3-Isobutyl-2-methoxypyrazine	ng/L	2 ^a	Green pepper	<0.70						
3-Isopropyl-2-methoxypyrazine	ng/L	2 ^a	Green pepper	<0.30						
<i>Norisoprenoids</i>										
β-damascenone	μg/L	0.85-2.1 ^j	Rose				4.49-9.42		0.24-0.47	
β-ionone	μg/L	90 ^k	Berry, violets				0.23-0.63			
<i>Sulfur Compounds</i>										
Dimethyl disulfide	ng/L	2,500 ^a	Asparagus, rubbery			nd—36				
Dimethyl sulfide	μg/L	10-160 ^a	Onion, garlic, truffle			11.90-26.41				
Dimethyl trisulfide	ng/L	n/a	n/a			nd-21				
Hydrogen sulphide	μg/L	0.8 ^e	Rotten eggs			2.11-9.26				
Methanethiol	μg/L	0.3 ^a	Stagnant water			1.19-2.92				
Methionol	mg/L	1 ^a	Cooked cabbage, dirty socks			1.13-1.97				
Ethyl thioacetate	μg/L	n/a	n/a			0.35-13				
Methyl thioacetate	μg/L	50 ^e	Mushrooms			1.50-9.21				
<i>Terpenes</i>										
Citronellol	μg/L	100 ^a	Citronella				3.70-9.41			
Geraniol	μg/L	30 ^c	Floral, fruity, citrus				5.60-24.20			
Linalool	μg/L	25.2 ^c	Citrus, orange, floral				8.60-14.40			
Nerol	μg/L	400 ^e	Floral, spicy				2.38-11.23			
<i>Miscellaneous</i>										
3-ethoxy-2-butanone	mg/L	n/a	n/a							0.04-0.16
γ-nonolactone	μg/L	135-238 ^d	Coconut, wood				10.30-18.00			

^a Escudero et al. 2007; ^b Guth 1997b; ^c Ferreira et al. 2000; ^d Dunlevy et al. 2009; ^e Ribereau-gayon 2000; ^f Zea et al. 2001; ^g Nelson et al. 1977; ^h Ibanez et al. 1999;

ⁱ Pino & Fajardo 2011; ^j Pineau et al. 2007; ^k Genovese et al. 2007

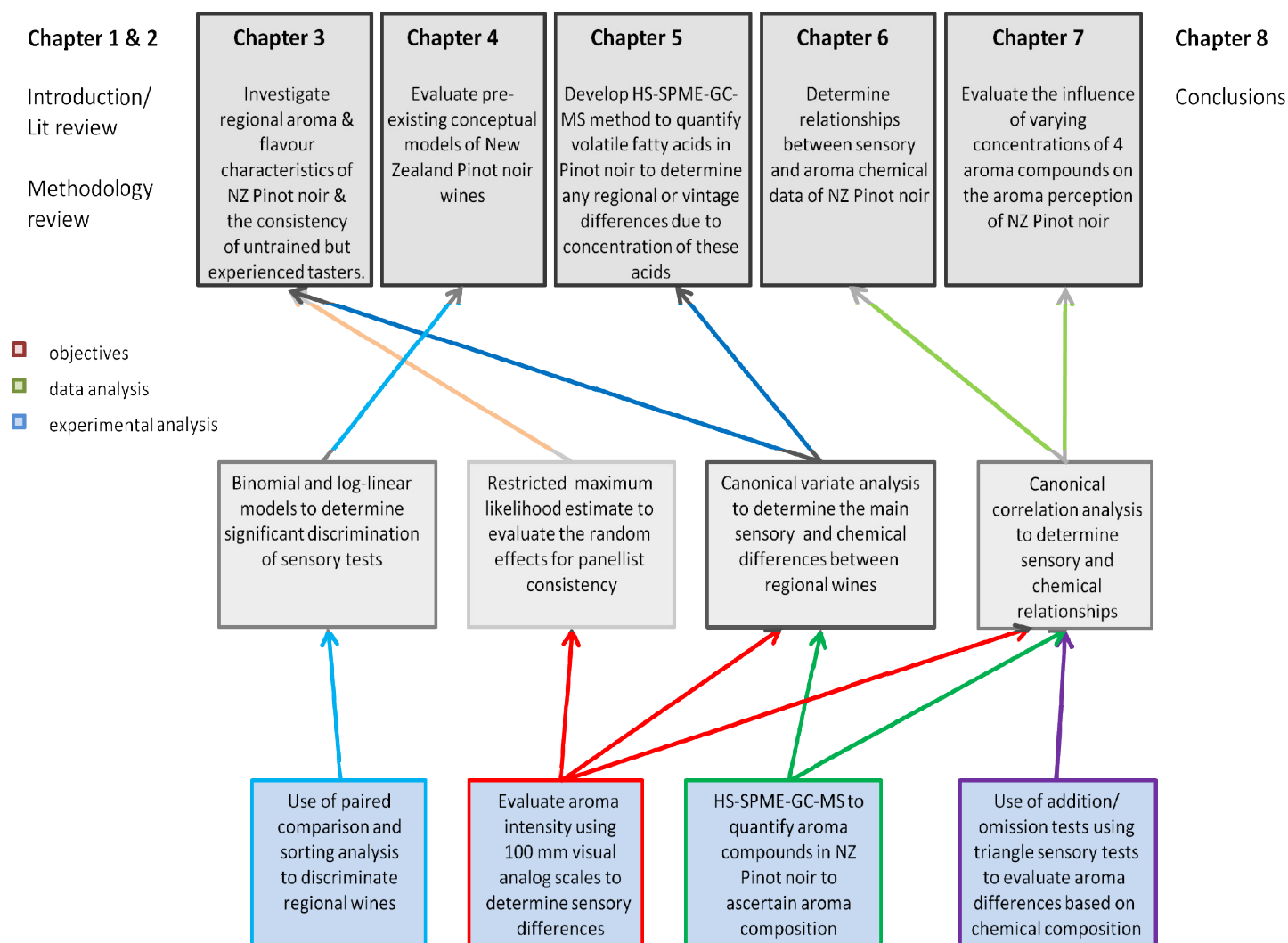


Figure 1.1

Format and structure of chapters and research experiments of the thesis

Chapter 2

Methodology

Sensory Methods

Discrimination tests are frequently used as a first step to identify regional differences (Aubry et al. 1999b). In particular, paired comparisons evaluate a single sensory parameter, such as sweetness, to investigate similarity or dissimilarity between products (Larson-Powers & Pangborn 1978). The object of the discrimination test is to determine if a change in a treatment or method of production alters the sensory perception of the item. In some instances a difference is desired as in creating a new product, while in others it is not, such as using a new ingredient to reduce production costs.

Paired Comparison

In this study the tasters were not asked to evaluate the products based on a specific sensory attribute. Instead they were required to determine if the wines presented originated from the same region or not. The use of paired comparison in this manner was novel as it focused on cognitive decisions and previous experience, in the form of conceptual models. Several cognitive decisions are used when evaluating regional styles; the process relies on tasters' aroma perception, recognition of the different aromas present in wines and if these differences are great enough for wines to be classified into different categories, based on region of origin (Parr 2007). Additional complexity arises as these cognitive decisions can be unique for each individual. Regional classification criteria will vary between tasters as each taster will have their own set of criteria for how different the aroma profile of the wine might be before the wines can be considered from different regions (Ennis & Ashby 1993; Rousseau et al. 1998; Rousseau & O'Mahony 2001).

There are two main experimental concerns associated with the use of paired comparison tests: the order in which the samples are presented and panellist fatigue (Day 1969). Possible position and order effects do not occur when all possible combinations of samples are presented for evaluation (O'Mahony & Godman 1986; Masuoka et al. 1995). In many studies

there are too many samples for each individual to evaluate all possible orders. However, the influence of the order can be overcome using optimal experimental designs, such as the partially balanced incomplete block design (Ball 1997b; Graßhoff et al. 2004). Fatigue can reduce panellist sensitivity, as they have more difficulty discriminating following prolonged exposure to the wine (O'Mahony 1986). Fatigue also affects the individual's ability to concentrate when participating in sensory tests (Dijksterhuis & Piggott 2000). Normally to counteract fatigue, breaks and specific tasting protocols are employed (Carpenter et al. 2000; Cliff et al. 2007). In this study it was unknown how fatigue would affect the results; although a lack of concentration is most likely to contribute an error to the results. The number of wine pairs presented was consistent with previous sensory studies where the number of wines was low enough that fatigue was not an issue (Kontkanen et al. 2005; McCloskey et al. 2007; Etaio et al. 2008; Esti et al. 2010).

In statistical testing, the probability of a false positive is given by the α -level. To minimize this error α is normally set to 0.05 or lower and a greater number of correct answers are required for the results to be statistically significant. However, a concern with paired comparison tests is the high probability of a false negative or type II error, denoted by the symbol β . Sensitivity (also known as the statistical power) is directly related to the proportion of Type II errors. In general, the smaller the α -level the less sensitive ($1-\beta$) the test as Type II errors increase when the Type I errors decrease. Low sensitivity or power can be minimized by ensuring the sample size is large (Lawless & Heymann 1998) and previous research has shown that despite the loss of sensitivity, a two sample test can be more discriminating than a three sample test as less time elapses between tasting in a two sample test (Rousseau et al. 1998; Rousseau et al. 1999; O'Mahony & Rousseau 2002; Rousseau et al. 2002; Lau et al. 2004). When compared to other difference tests it is the lack of question specificity that results in a high false negative rate or Type II error (Ennis 1990). Thus, despite the high probability Type I errors, paired comparison can be an effective discrimination test and produce comparable results to triangle and duo-trio tests with a much lower probability of false negatives (Rousseau et al. 1998).

Sorting Analysis

Sorting analysis, another type of discrimination test, was also used to investigate pre-existing conceptual models or ideas about regional Pinot noir. Participants were required to sort wines into two groups based on similarity. This type of test has been successful in previous research to investigate concepts of typicality in New Zealand Sauvignon blanc (Parr et al. 2010), Chardonnay and Melon de Bourgogne wines (Ballester et al. 2008). Several different approaches to sorting can occur; those that offer a lot of freedom in the assessment and others that are very specific. Wines can be sorted based on their similarity, typicality to a regional style, or specific sensory attributes (Ballester et al. 2008; Parr et al. 2010; Perrin & Pages 2010). Sorting has been found to be successful when matching style to geographical origin, although this relies heavily on the participants' previous knowledge on the wine and region of origin, as well as on the wines included in the study (Maitre et al. 2010).

Descriptive Methods

For region of origin products, descriptive analysis methods are used to determine what sensory attributes characterize wines from different regions. Descriptive analysis, in which the intensity of attributes is evaluated using scaling, is normally performed with trained panellists (Hootman 1992b). Free-choice profiling, quantitative descriptive analysis (QDA) and the just about right profile (JAR) have been used previously to evaluate wine typicality and regional wine profiles (Perrin et al. 2008b; Cadot et al. 2010; Parr et al. 2010).

Descriptive analysis has been used in the past to distinguish important attributes of wine styles (Guinard & Cliff 1987; Heymann & Noble 1987a; De La Presa-Owens & Noble 1995; Cano-Lopez et al. 2008; Blackman & Saliba 2009; Mansfield & Vickers 2009) and regional or typical styles (Douglas et al. 2001; Kontkanen et al. 2005; McCloskey et al. 2007; Parr et al. 2007; Lund et al. 2009).

Descriptive analysis is preferred over sorting analysis to separate products when large numbers of attributes are used (Cartier et al. 2006). This method is also preferred as an analytical technique when investigating wine specificities (Maitre et al. 2010; Parr et al. 2010). However, one problem with descriptive analysis is panellist fatigue. This may be due

to palate fatigue in which the taster can no longer distinguish between aromas and flavours because the compound receptors in the olfactory bulb or on the tongue have been completely bound (Scott & Sherril 2008; Chaudhury et al. 2010). A second type of fatigue occurs when the olfactory and taste buds are functioning but the taster cannot concentrate. Therefore the taster can taste and smell differences but the brain is too tired to recognize these differences (Deppe et al. 2001). To minimize fatigue, the number of products evaluated are limited, the number of attributes limited and tastings are held at multiple sessions. Therefore to reduce the chance of fatigue there is the possibility that sensory attributes that may be important for regional differentiation are not included in the analysis. Maitre et al (2010) suggest that by combining a study with a limited list with descriptive analysis in which participants have a large list of attributes to choose from may reduce the chance that an important attribute has been missed.

Appropriate statistical analysis is required to analyze the results of descriptive analysis. Canonical variates analysis (CVA) was deemed as most appropriate as it included a grouping factor within the analysis and results display differences between the chosen groups rather than the individual products (Heymann & Noble 1989). The chosen grouping factor was the wine's region of origin. CVA, also known as discriminant analysis, is described by William Klecka (1980) as "a statistical technique which allows the researcher to study the differences between two or more groups of objects with respect to several variables simultaneously." These differences are reported as linear combinations that include all the variables, known as canonical variates. The greater the weighting of the variable within each variate, the more important that variable is to differentiation in the calculated dimension. Statistically significant dimensions were determined using a chi-square approximation.

Choice of Participants and Training

The participation of experienced tasters, trained or untrained tasters and consumers in wine analysis has been well studied (Gawel 1997; Hughson & Boakes 2002; Parr et al. 2002; Lawless 2006). The choice of taster depends on many factors including the time frame of study, objectives and sensory test. In this current project the experienced taster was chosen; this was important for two reasons. The first was that panellist training is a long-term commitment (Hootman 1992a) and is difficult when the pool from which panellists are drawn

is small. In this project the wine tasters, drawn from the local wine industry, were not available for long term training. Additionally, experienced tasters are able to recognize differences between wines and tend to share a standard vocabulary (Ballester et al. 2008). Panellist training is normally conducted to create a standard vocabulary across all tasters and research has shown that experienced wine tasters produce consistent results that are comparable to those obtained from trained sensory panels (Perrin et al. 2008a; Parr et al. 2010).

Another reason that experienced tasters were desired was these panellists are more likely to be familiar with sophisticated conceptual models of the wines which the wine consumers lack. Experienced tasters know the typical features and aromas that define specific wine styles. This knowledge allows experienced tasters to remember and match wines to a conceptual model (Solomon 1997; Hughson & Boakes 2002; Ballester et al. 2008).

Wine Aroma Analysis

Increasingly, the technique of choice for wine volatile compound analysis is Headspace-Solid Phase Micro-Extraction-Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS). This is a fast and effective way to obtain qualitative information on the volatile organic compounds (VOCs) present in wine. It becomes even more powerful when combined with stable isotope dilution (SID) analysis when quantitative data is required (Siebert et al. 2005). Many methods have been developed to investigate the wide range of VOCs found in wine (Lopez et al. 2002a; Marti et al. 2003; Perestrelo et al. 2008). Some methods have focussed on a specific class or small number of compounds (Rauhut et al. 1998; Ferriera et al. 2003; Fang & Qian 2005b; Wang et al. 2005; Carrillo et al. 2006; Campo et al. 2007; Rodriguez-Bencomo et al. 2009), some have focussed on compounds that evoke specific aromas, such as wine spoilage odours (Boutou & Chatonnet 2007), while other methods were developed for specific wine varieties (Bonino et al. 2003; Ferreira & de Pinho 2003; Cabredo-Pinillos et al. 2004; Yu et al. 2006; Noguerol-Pato et al. 2009).

Central to all HS-SPME-GC-MS procedures is the adsorption of VOCs from within the headspace of a sealed sample onto a specific SPME fibre which resides within a hypodermic needle. Following exposure to the headspace VOCs, the needle and fibre are withdrawn from

the sample headspace and the adsorbed VOCs are rapidly desorbed within the heated injection port of a gas chromatograph-mass spectrometer (GC-MS). Thereafter the VOCs undergo chromatographic separation within the GC's capillary column before entering the MS for qualitative and/or quantitative analysis.

Measurement of VOCs by HS-SPME is preferred over other methods, such as liquid-liquid extraction, as the results obtained are more precise, accurate and time efficient (Vairavamurthy & Mopper 1990; Pan et al. 1995; Kataoka et al. 2000; Vas & Vekey 2004). Additionally HS-SPME is more cost efficient because the fibre which adsorbs the VOCs from the sample headspace does not come into contact with the sample itself, thereby extending fibre life (Calle Garcia et al. 1998).

Methods to Link Sensory and Chemistry Data

Multivariate Statistical Analysis

A number of different multivariate statistical techniques have been used to determine which volatile organic compounds influence specific perceived aromas. These include principal component analysis (PCA), factor analysis (FA), partial least square regression (PLS) and discriminant analysis (Francis & Newton 2005). PCA analysis has been used to find relationships between sensory and chemistry data in Spanish white wine (Lozano et al. 2005), New Zealand Sauvignon blanc (Parr et al. 2007) and Missouri Sevyal blanc wine (Andrews et al. 1990). Factor analysis has been used to investigate Maccebo and Airen wines (Peinado et al. 2004) and the influence of esters on the aroma of young Spanish wine (Ferreira et al. 1995). PLS has been used to investigate the cause of fruity, floral and oak aromas in California Chardonnay (Lee & Noble 2003), differences in regional white and red wine from Spain (Lozano et al. 2007), the green, floral, tropical and developed aromas found in Australian Riesling (Cozzolino et al. 2006; Cozzolino et al. 2008), the relationship between vegetal aromas and methoxypyrazines in Cabernet Sauvignon (Noble et al. 1995; Preston et al. 2008) and with several different sensory and chemical characteristics for Greek red wine (Koussissi et al. 2008).

However, in this study the multivariate statistical analysis of choice was canonical correlation analysis (CCA). This multivariate technique has been employed to determine relationships

between sensory and chemical data (Rapp 1995; Arvanitoyannis et al. 1999; Barker & Rayens 2003; Berrueta et al. 2007; Takane & Hwang 2008). CCA attempts to quantify relationships that exist between two data sets by calculating pairs of linear combination. It is preferred as it limits the probability of the occurrence of Type I error, assesses multiple relationships within two sets of data and is considered to better reflect the complex reality of research (Hair et al. 2009). This technique has also been used to determine relationships between chemical composition and foam characteristics in Cava (Pueyo et al. 1995), phenolic compounds and oak usage (Simon et al. 2003), and the elemental profile of wine and region of origin (Fabani et al. 2010). In this current project CCA was used to investigate relationships between the aroma descriptive analysis and composition of volatiles in New Zealand Pinot noir.

Addition, Omission and Reconstitution Tests

Another important method to determine the effect of different aroma compounds in wine is through addition, omission and reconstitution tests (Escudero et al. 2004; Grosch 2004; Escudero et al. 2007; Loscos et al. 2007). For addition tests the specific aroma compounds or groups of compounds are added to a “base wine”. In omission tests the selected compound is left out of any addition. The choice of the base wine for the addition/omission tests is very important as the presence of the other aroma compounds present on wine have a great influence on aroma. However tests between de-aromatized and neutral wines give very different results, which are not necessarily representative of the actual wine (Escudero et al. 2007). Commonly a base wine is comprised of a synthetic wine (ethanol and water solution) or de-aromatized wine (Ferreira et al. 2002). One study used a “neutral” wine as the base wine for the addition test, not chosen based on the chemical concentrations but strictly on the lack of aroma characteristics (Cullere et al. 2007). To date there has only been one study that has based addition tests strictly on total concentration found in wine, investigating the aroma composition of Dornfelder (Frank et al. 2011).

The use of addition/omission tests have shown that isoamyl acetate influences the banana aroma in Maccabeo wines (Escudero et al. 2004), the importance of methoxypyrazines to the vegetal aroma in Sauvignon blanc and Spanish red wine (Escudero et al. 2007; King et al. 2011), the influence of guaiacol on toasty aromas and the importance of esters and norisoprenoids to the fruity aroma of wine (Escudero et al. 2007), the importance of

aldehydes to aged aromas (Cullere et al. 2007), the effect of 2-phenyl acetate on sweet and floral aromas and the relationship between linalool and 3-mercaptohexyl acetate to floral, Muscat aromas in Spanish white wines (Campo et al. 2005) and fresh and dry fruit characters in Spanish red wines (San-Juan et al. 2011). Much of the research has used addition tests, but omission tests have also provided information on the impact of the compounds to wine aroma. For instance, omission tests have shown that 3-mercapto-1-hexanol is the most important odorant to Grenache rose wine (Ferreira et al. 2002).

Reconstitution tests are similar to addition tests but in this case a synthetic or model wine is used. Aroma compounds are added to the synthetic wine to determine which compounds are having the most effect. The reconstituted mixture is compared to the real wine and if the aromas do not match then additional compounds are incorporated (Polaskova et al. 2008). Aznar et al (2001) used reconstitution tests to determine the impact of different wine extracts to the aroma of Rioja wines. Other reconstitution tests have been used to attempt to create a good base wine that can be used for further addition/omission tests (Escudero et al. 2004). The main concern with reconstitution tests is the lack of compounds when compared to the actual wine. Wine contains many aroma compounds that do not necessarily produce a strong aroma but are important to the wine aroma in an indirect manner. The lack of these compounds, many of which are unknown or cannot be measured maybe important to wine aroma (Ferreira et al. 2007; Ferreira 2010). Therefore many reconstitution tests are not overly effective as they do not truly represent wine. It is thought that to truly understand the influence and impact of a compound to wine a series of these tests are necessary.

Chapter 3

(a preparation for submission to the American Journal of Enology & Viticulture)

Regional Differentiation of New Zealand Pinot noir Wine by Expert Panellists using Canonical Variate Analysis

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Abstract

Pinot noir is the most widely planted red grape variety in New Zealand. Pinot noir wine is considered a premium product based on its price per volume. Within the country there are four main regions that produce Pinot noir: Central Otago, Marlborough, Martinborough and Waipara. To date no studies have attempted to classify the different styles of wine based on the region of origin within New Zealand. This current study aims to determine if regional Pinot noir styles do exist within New Zealand. The intensity of aroma, flavour and mouth-feel attributes of commercial regional wines from two vintages were investigated using descriptive analysis and canonical variate analysis. These four wine regions were found to produce stylistically different Pinot noir wines with the main differentiating attributes being: barnyard, black cherry, chocolate, herbal, raspberry, red cherry, oak, spice and violet aromas; and fruit density/concentration and red fruit flavours; and balance, body and finish length mouth feel characteristics. Additionally, the performance of untrained but experienced wine tasters was evaluated. A significant 3-way interaction (panellist x tasting session x wine) was only observed for two aroma attributes (chocolate and strawberry) in one of the two vintages (2007). Based on the results these experienced but untrained panellists could consistently distinguish between regional Pinot noir wines.

Keywords: canonical variates analysis, descriptive analysis, regional differentiation, New Zealand Pinot noir

Objective

This research investigates the characteristics of New Zealand Pinot noir wines from each of the four main regions and the consistency of untrained, but experienced wine tasters in Pinot noir sensory analysis.

Materials & Methods

Panellists. The tasting panel comprised of 21 experienced panellists (11 male, 10 female) from the Marlborough wine industry. The age range of the tasters was 28 to 53 with an average age of 35. Of the tasters, 16 were winemakers, two were viticulturists and three were engaged in wine and grape research. Panellists were not trained. Wine tasting experience ranged from six to 36 years with an average of 17 years. All tasters considered themselves experienced wine tasters, six considered themselves expert tasters and five had experience as wine judges. Fourteen of the tasters had participated in a wine sensory panel prior to this experiment and seven of the tasters had prior sensory training, although only one person had training specifically for Pinot noir.

Wines & Glasses. Four wines from each of the main Pinot noir producing regions (Central Otago, Marlborough, Martinborough and Waipara) and two vintages (2007 and 2008) were selected (32 wines in total) (Table 3.1). These wines were considered to be representative of each region based on professional opinion and marketing scheme. All grapes used in each wine were from the specified region. Most wines (30) were sealed using screw cap and two wines were under cork. All wines were stored at room temperature (20°C). For sensory evaluation, 50 mL samples were poured into black, ISO standard tasting glasses (International Organization for Standardization 1977). All glasses were coded with a random three digit number and covered with watch glasses.

Preliminary Tasting. A subset of panellists (six) participated in a preliminary tasting session to choose sensory attributes to be included in the full study. Panellists listed wine aroma and palate descriptors for each of the wines. After tasting, the main differences found between the wines were discussed. A final list was compiled from these attribute lists and previous sensory work on Pinot noir (Aubry et al. 1999, Guinard and Cliff 1987). Twenty five

attributes (15 aromas, four in-mouth flavour and six mouth-feel) were selected from the preliminary tasting session by consensus.

Tastings. The tastings took place during two separate periods. The 2007 wines were tasted in May/June of 2009 and the 2008 wines were tasted in May/June of 2010. The time period of the tastings was chosen to ensure that all wines were the same age when evaluated. All wines of the specified vintage were served at each of three tasting sessions. Wines were presented in a different random order at each tasting session to minimize any possible order effects. A balanced-incomplete block (BIB) design was used to create the random order for each tasting session and panellist (Ball 1997, Masuoka et al. 1995, O'Mahony and Godman 1986). A new bottle was opened every two days during the tastings and at the end of each day the open bottles were sparged with argon before sealing to prevent oxidation. Each year panellists participated in three tasting sessions in both years. At each session all wines for the chosen vintage were presented, therefore each wine was evaluated in triplicate by each panellist.

Panellists evaluated wines in a wine tasting room illuminated with a mix of artificial and natural light and the temperature was controlled to a constant 20°C. Tastings took place over five weeks with each panellist assigned individual sessions. On average each tasting lasted approximately one hour, although panellists were allowed as little or as much time as required to complete the task. The intensity of a set list of attributes was marked on a 100 mm horizontal visual analogue scale (VAS). Each attribute had a minimum and maximum word anchor. The word anchors for all aroma and in-mouth flavour attributes were “none” and “extreme” and were indented on the VAS. The word anchors for the mouth-feel attributes are listed in Table 3.2. Panellists first evaluated the aroma attributes followed by in-mouth flavour and mouth-feel attributes. They were instructed not to taste the wine until after evaluating the aroma attributes. Spit buckets and water were provided though panellists were not required to use them.

Data Analysis. Intensity ratings were quantified using a number between zero and 100 that corresponded to the distance from the left end of the VAS to the scribed mark. Restricted maximum likelihood (REML) estimation was used to determine the variance of the different random effects for each attribute as a measurement of consistency within and between the

panellists. The random effects were panellist (P), tasting session (T) and wine (W). Fixed effects were region and vintage. Canonical variate analysis (CVA) was carried out on all data with region as the classification variable. The objective of CVA is to produce a dimensional representation that highlights as accurately as possible the differences that exist between the subsets of data (Darlington et al. 1973). Results of CVA consist of linear combinations of all attributes that account for the greatest proportions of the variance between the regions. The attributes that had the largest contribution to each linear combination were used to explain the main differences between the regional wines. Between-region distances were calculated from the average positions of the regions along the canonical variates. All statistical analyses were carried out using Genstat 12.2 (VSN International Ltd.).

Results & Discussion

Panellist Performance: REML estimation for both 2007 and 2008 wines (Table 3.3) showed that the effect of panellist was significant ($P < 0.05$) for all attributes (i.e. averaged over wines and tasting sessions, attribute scores differed between panellists); in contrast, tasting session was not significant for most attributes (i.e. averaged over wines and panellists, scores for each tasting session were not different). The interactions between panellist, tasting session and wine were used to evaluate panellist performance for each sensory attribute.

The $P \times T \times W$ interaction demonstrated if panellists were using the VAS in the same way in each tasting session and for each wine. A significant $P \times T \times W$ interaction was found only for chocolate and strawberries for 2007 wines (Figure 3.1). For these attributes assessed on the 2007 wines, therefore, it seems that there was some inconsistency in the scores allocated by different panellists in the three tasting sessions for the different wines.

The three-way ($P \times T \times W$) interactions suggested that of all attributes, the results for strawberries and chocolate may be the least robust. It is unknown if this could have been corrected with training. A positive correlation between panel performance and training has not yet been established for complex products, such as wine (Wolters 1994). Problems with panellist consistency may not be able to be improved further because of panellist sensitivity to specific odours and the presence of specific anosmias (Lawless 1999). However, training may

not have been beneficial as the $P \times T \times W$ interactions only occurred for 2007 wines and not 2008 wines.

Significant $P \times T$ interactions were found for jam, oak, smoky and dark fruit attributes for the 2007 wines, and for raspberries, jam, oak, red fruit and graininess for the 2008 wines. A significant $P \times T$ interaction indicated that for these attributes panellists' average scores (across wines) did not vary consistently between tasting sessions. For example, the average intensity of jam for panellist 6 was less in tasting session 1 compared to tasting session 3 whereas the opposite was the case for panellist 11 (Figure 3.2). This was not unexpected as research has shown that the time of tasting and other environmental factors do cause variation between tasting sessions (Craig et al. 1981, Pages and Husson 2001) although the experimental design minimizes this effect.

Significant $P \times W$ interactions were found for savoury and graininess for 2008 wines. A significant $P \times W$ interaction indicated that for these attributes panellists' average scores (across tasting sessions) did not vary consistently between wines. As with $P \times T$ interactions, some $P \times W$ interactions were expected. Research has shown that the order in which samples are tasted effects the panellists perception (Jamieson and Petrusic 1975, Muir and Hunter 1992, Stone and Sidel 1985). In order to eliminate all $P \times W$ wines each panellist must taste the wines in every possible order. This is unrealistic with large numbers of samples. Experimental design, such as BIB, attempts to minimize any such effects, though sometimes all effects cannot be eliminated.

Regional Separation: Clear regional separation was found using CVA. All three of the variates were statistically significant at $P < 0.05$ and explained 44%, 37% and 19% of the total variance. Marlborough, Martinborough and Waipara wines were differentiated by CV1 and CV2. Central Otago was differentiated from the other three regions by CV3 (Figure 3.3). Correlation of the attribute vectors with canonical variates are shown in Table 3.4. Highly correlated attributes with CV1 include barnyard and herbal aromas and balance, for CV2 smoky aroma, graininess and oak tannins; for CV3 smoky and violet aroma and body.

The between-region distance indicated how similar or dissimilar each region was from the other regions. Central Otago and Martinborough were perceived as the most similar with the

smallest average between-region distance; Marlborough and Martinborough were perceived as the most dissimilar (Table 3.5).

The placement of the attribute vectors displayed which attributes characterized each region (Figure 3.4). Marlborough Pinot noir was characterized by greater raspberry, red cherry, red fruit and red berry aromas, longer finish length and more harmonious balance. Martinborough Pinot noir was characterized by greater black cherry, chocolate, oak and spice aromas and oak tannin. Waipara Pinot noir was characterized by greater barnyard, herbal and violet aromas and in-mouth fruit density/concentration. Central Otago Pinot noir was characterized by fuller body.

It should be noted that no aroma and flavour standards were used when choosing and evaluating these sensory attributes. Therefore there is a possibility that the meaning ascribed to particular terms may vary between panellists or between the groups of tasters, although all the panellists were experienced with wine evaluation. However similar attributes seemed to be grouped in terms of the correlations in the canonical variates. Red fruit aromas (raspberry, red cherry, strawberry and red fruit) were all positively correlated with CV1, dark fruit and savoury aroma and flavours (black cherry, chocolate, dark fruit, oak, savoury, smoky, spice) were negatively correlated with CV2 (Table 3.4). Additionally similar descriptors have been observed at informal wine tastings (Pinot Noir New Zealand 2010) and by winemakers, although prior to this study no formal evaluation of commercial wine had been undertaken. Marlborough wines have previously been characterized by red fruit, Martinborough wine by smoky, dark berry fruit and savoury notes and Waipara wines by herbal (Cooper 2008). This suggests that wine tasters have noticed and described the regional differences in Pinot noir from New Zealand and these results confirm those regional differences.

Of all the attributes important for regional differentiation, only three: chocolate, oak and red fruit were found to be involved in significant panellist interactions. Of these three only chocolate had a significant $P \times T \times W$ interaction. The chocolate attribute was important for Martinborough wines but this interaction was only found for 2007 wines and not for 2008 wines. Therefore despite the fact that oak and red fruit had $P \times T$ interactions, panellists consistently evaluated each wine in the same manner across each tasting session (i.e. for all wines panellist 17 rated the intensity of jam higher when compared to panellist 8 for tasting session 1).

Conclusion

These results suggest that a panel consisting of experienced wine tasters from New Zealand could consistently evaluate a number of sensory attributes of New Zealand Pinot noir wines. In two vintages, 19 of the 25 attributes had no significant interactions. All but two of the interactions were expected according to panellist performance found in other sensory work. It is possible that a small amount of training may be helpful for all P x T and P x W interactions but it is unknown if extensive training would produce more consistent results. Of the attributes with significant interactions, only chocolate was found to be important for the regional separation.

Pinot noir wines from the four main producing regions of New Zealand were able to be differentiated by using descriptive analysis and CVA, showing that specific sensory attributes were characteristic to specific wine regions. The important differentiating attributes concur with those that wine professionals have used to describe Pinot noir wine from these regions in the non-scientific literature. In selecting wines for this study the only consideration was that the grapes be sourced strictly from the specified region and that the wine was produced as a regional product. Thus, despite probable variations in grape growing and differences in production within a region, it appeared wines were broadly similar within a region and distinct from those of other regions.

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Tables and Figures

Table 3.1

Regional commercial wines used in the sensory study

Wine Product	Vintages	Region
Mt Difficulty	2007, 2008	Central Otago
Montana “Terroir Series” Gabriel’s Gully	2007	Central Otago
Gibbston Valley	2007, 2008	Central Otago
Amisfield	2007, 2008	Central Otago
Craggy Range “Zebra Vineyard”	2008	Central Otago
Stoneleigh Rapaura Series	2007, 2008	Marlborough
Montana “Terroir Series” Forgotten Valley	2007	Marlborough
Brancott Estate Reserve	2007, 2008	Marlborough
Brancott Estate Terraces “T”	2007, 2008	Marlborough
Villa Maria Southern Clays	2008	Marlborough
Martinborough Vineyard	2007, 2008	Martinborough
Palliser Estate	2007, 2008	Martinborough
Escarpment	2007, 2008	Martinborough
Ata Rangi	2007, 2008	Martinborough
Camshorn	2007, 2008	Waipara
Muddy Water “Hare’s Breath”	2007, 2008	Waipara
Greystone	2007, 2008	Waipara
Pegasus Bay	2007, 2008	Waipara

Table 3.2

Word anchors for mouth-feel attributes.

Mouth-feel Attribute	Minimum (left side)	Maximum (right side)
Graininess	Large particles	Fine particles
Oak tannins	None	Extreme
Bitterness	None	Extreme
Balance	Unbalanced	Harmonious
Body	Light	Full
Finish Length	Short	Extremely long

Table 3.3

Test statistic probability for interactions between random effects^a on all attributes for 2009 and 2010 tastings^b.

Attribute	2009				2010 ^c	
	P x T	P x W	T x W	P x T x W	P x T	P x W
<i>Aroma</i>						
Barnyard	-	-	-	-	-	-
Blackberry	-	-	-	-	-	-
Black cherry	-	-	-	-	-	-
Chocolate	***	**	-	*	-	-
Herbal	-	-	-	-	-	-
Plum	-	-	-	-	-	-
Red Cherry	-	-	-	-	-	-
Raspberries	-	-	-	-	*	-
Strawberries	***	***	***	***	-	-
Jam	**	-	-	-	*	-
Oak	*	-	-	-	*	-
Smoky	*	-	-	-	-	-
Spice	-	-	-	-	-	-
Savoury	-	-	-	-	-	*
Violets	-	-	-	-	-	-
<i>In-mouth flavour</i>						
Dark fruit	*	-	-	-	-	-
Fruit density/ concentration	-	-	-	-	-	-
Red fruit	-	-	-	-	*	-
Spice	-	-	-	-	-	-
<i>Mouth-feel</i>						
Balance	-	-	-	-	-	-
Bitterness	-	-	-	-	-	-
Body	-	-	-	-	-	-
Finish length	-	-	-	-	-	-
Graininess	-	-	-	-	**	*
Oak tannins	-	-	-	-	-	-

^a Panellists x tasting session (P x T), Panellists x Wine (P x W),

Tasting session x Wine (T x W),

Panellist x Tasting session x Wine (P x T x W)

^b (-) no significance, (*) significance, $p < 0.05$, (**) significance, $p < 0.01$,

(***) significance, $p < 0.001$

^c T x W and P x T x W are not shown as no significance was found for any attribute

Table 3.4

Correlations between attribute vectors and canonical variates.

Attribute	CV1	CV2	C3
<i>Aroma</i>			
Barnyard	-0.41	0.20	0.18
Black Cherry	-0.04	-0.17	0.16
Blackberry	-0.17	0.03	-0.03
Chocolate	-0.05	-0.27	0.19
Herbal	-0.57	0.17	0.17
Jam	-0.38	0.08	0.15
Oak	-0.05	-0.27	0.33
Plum	-0.18	-0.01	0.19
Raspberries	0.31	0.29	0.00
Red Cherry	0.11	0.17	-0.01
Savoury	-0.35	-0.27	0.30
Smoky	-0.22	-0.46	0.53
Spice	-0.10	-0.14	0.17
Strawberries	0.13	0.25	0.05
Violets	-0.11	0.28	-0.24
<i>Flavour</i>			
Dark Fruit	-0.18	-0.05	0.12
Red Fruit	0.31	0.15	0.02
Spice	-0.10	-0.10	0.25
<i>Mouth-feel</i>			
Balance	0.44	0.27	0.24
Bitterness	-0.33	-0.09	-0.13
Body	0.05	-0.20	-0.23
Finish Length	0.22	0.03	0.05
Fruit Density/ Concentration	-0.10	0.16	0.12
Graininess	0.31	0.46	0.37
Oak Tannins	-0.21	-0.54	-0.05

Table 3.5

Between region distances to display which regions are most alike and which are most different.

	Central Otago	Marlborough	Martinborough
Marlborough	0.516		
Martinborough	0.512	0.653	
Waipara	0.536	0.621	0.642

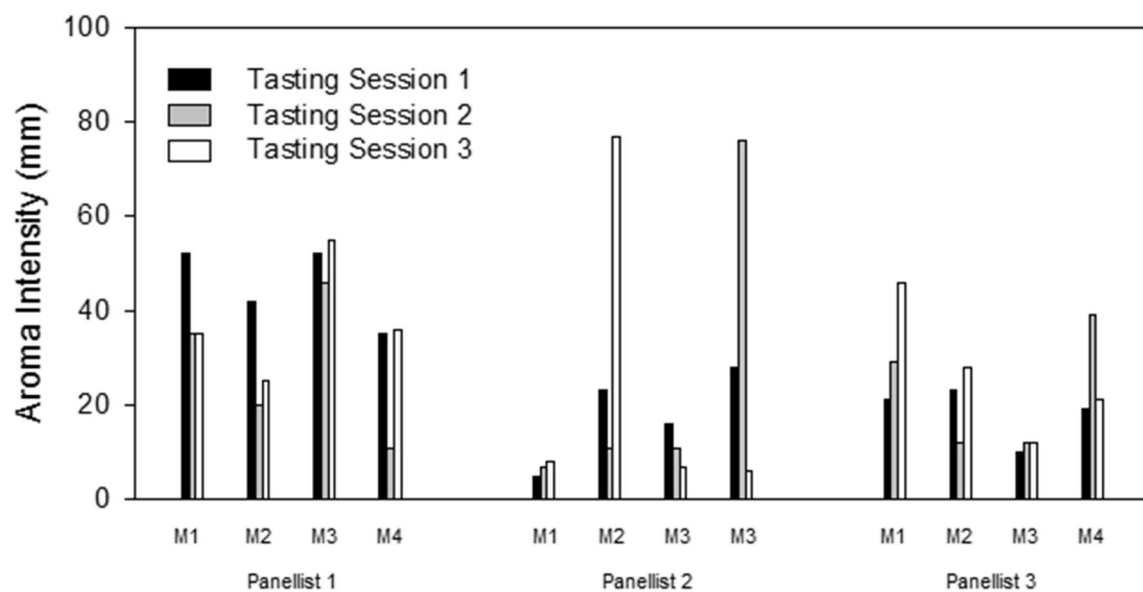


Figure 3.1

Illustration of the significant ($p < 0.05$) $P \times T \times W$ interaction for chocolate attribute for 2007 wines using a subset of the data (3 panellists and 4 wines: M1, M2, M3 and M4)

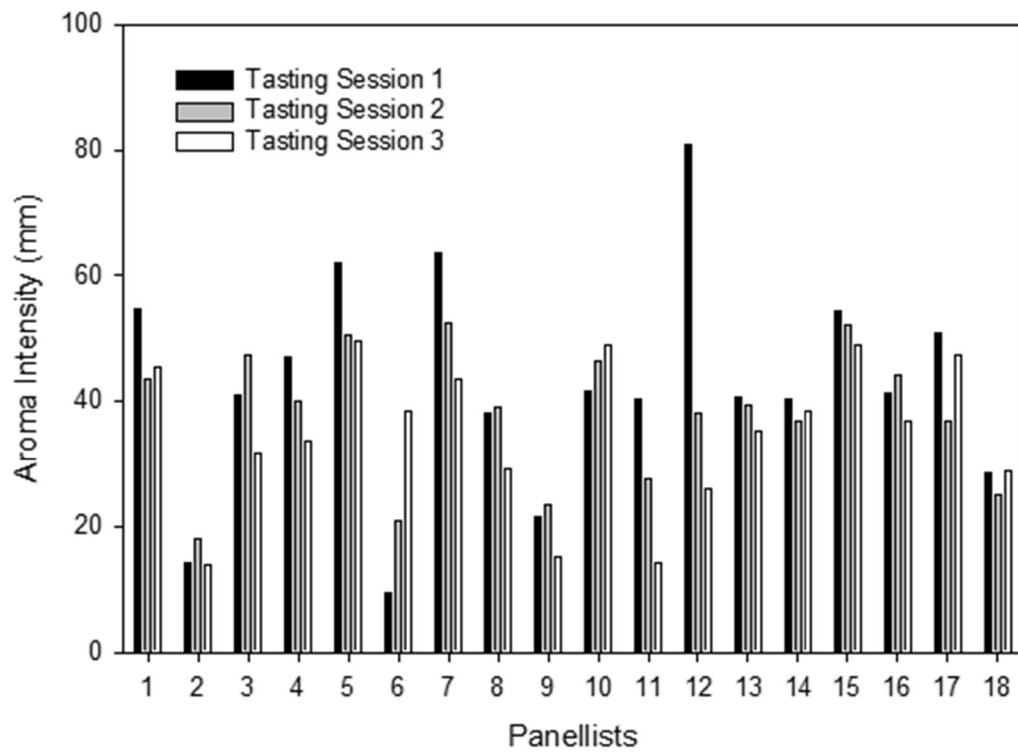


Figure 3.2

Illustration of significant ($p < 0.05$) P x T interaction for jam attribute from the 2007 wines

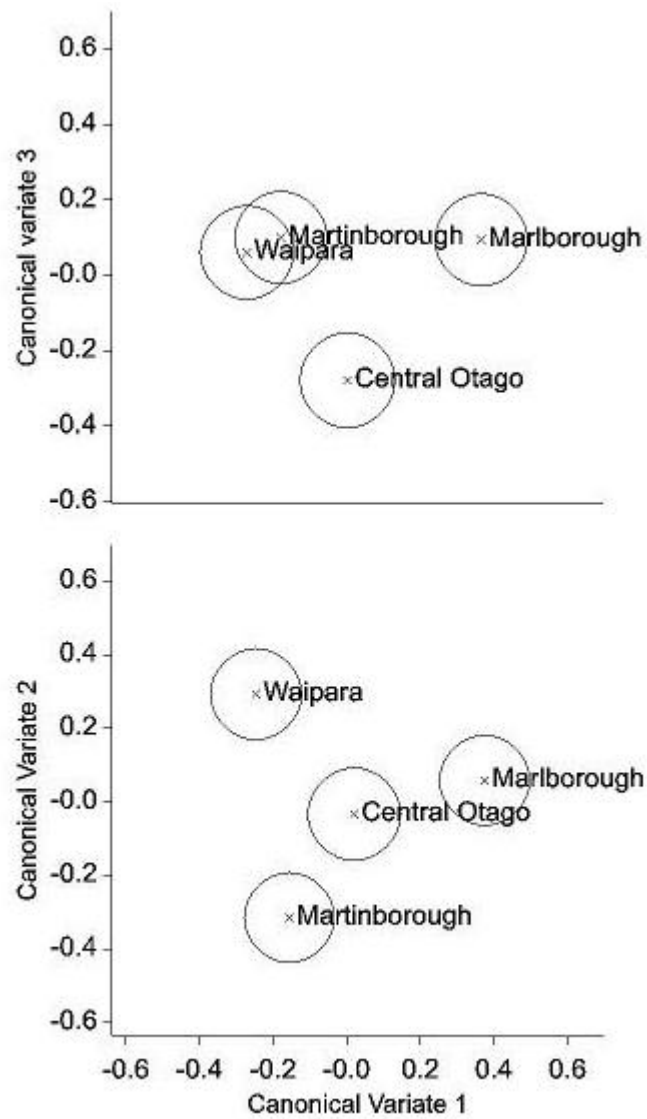


Figure 3.3

Separation of Pinot noir wines by region using canonical variate analysis. Circles represent 95% confidence intervals surrounding the region means for each regional grouping.

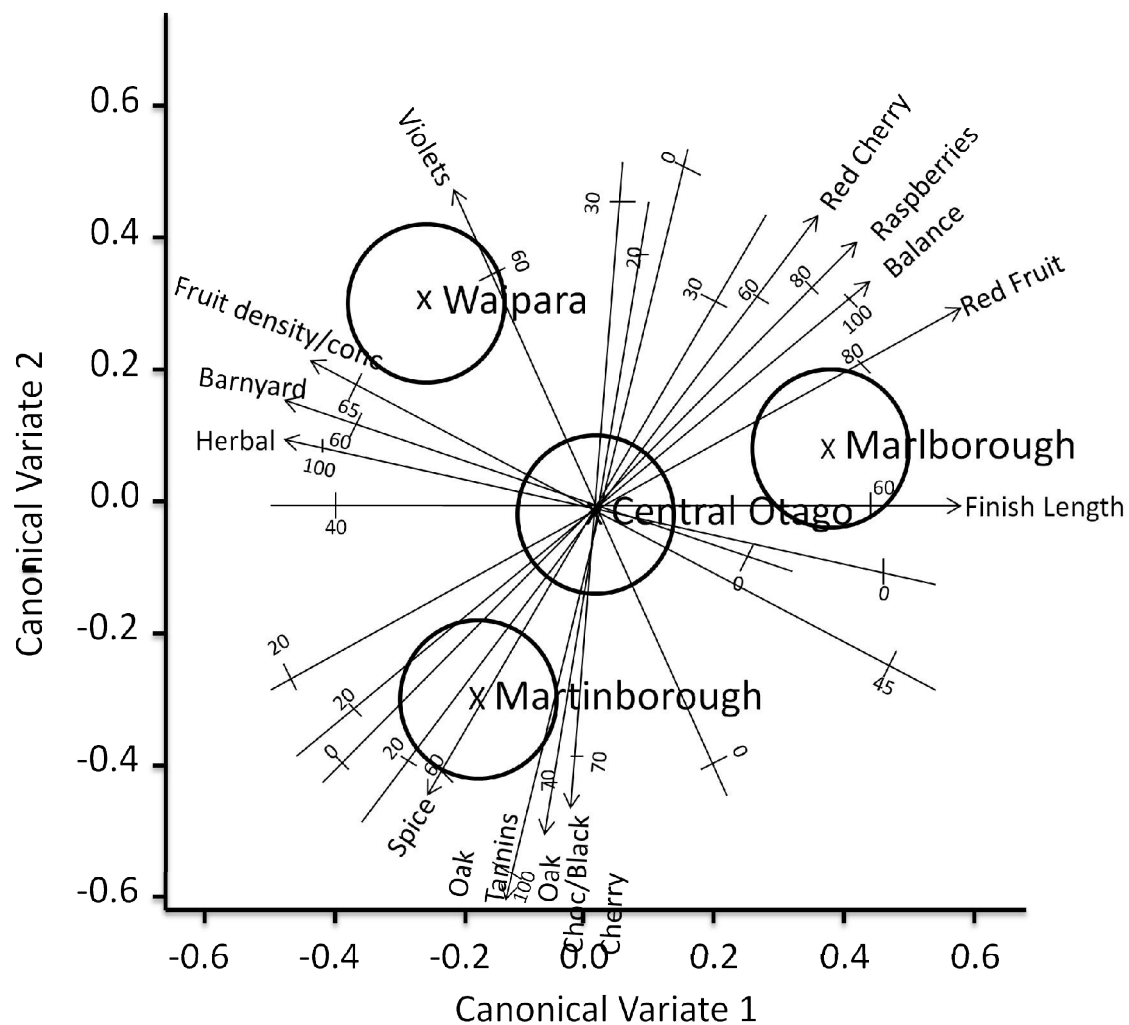


Figure 3.4

Pinot noir regional means and 95% confidence intervals with attribute vector loadings and intensity scales for CV1 and CV2. Only attributes that are important for regional differentiation are displayed.

Chapter 4

(a preparation for submission to Food Quality & Preference)

Paired Comparison and Sorting Analysis to Investigate Existing Regional Conceptual Models of New Zealand Pinot noir

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Abstract

The perceptual representations of experienced wine tasters of the aroma characteristics of New Zealand Pinot noir from different regions and their relationship to existing commercial wines was investigated. Paired comparison was used to determine if participants could determine if given wines were from the same region or different regions. Panellists were only successful at discriminating wines from Marlborough, a finding which appears to be linked to the panellists' experience with Pinot noir from this region. Sorting analysis was used to determine if participants could successfully separate the wines into two groups, (1) a specified region and (2) other regions. The panellists were also asked to indicate their confidence in the sorting decision by choosing from one of three levels (not sure, maybe sure and very sure) for each wine. A Poisson distribution was used to describe the probability of sorting the wines correctly based on the number of sorting tasks performed for each region. Three factors, region, confidence and grouping (i.e. whether panellists included the wine in the specified region or not) were tested for significance ($p < 0.05$). Confidence was not found to be significant and was removed from the analysis. For each region, the results showed that panellists were unsuccessful at sorting wines into the correct groups. Previous work determined that these wines were stylistically different, suggesting that panellists do not have perceptual representations that match the regional wines or that the degree of the differences between the wines were smaller than thought.

Keywords: conceptual model, paired comparison, pinot noir, sorting analysis

Objective

A conceptual model of a wine is best described as an internal standard in which certain aroma and flavour characteristics have been associated to a specific style, country or region based on previous experience. Such models are referenced by experts to describe and identify wines. This study investigates conceptual models or ideas about New Zealand regional Pinot noir and determines if these can be utilized to sort or categorize commercial wines.

Materials & Methods

Participants

Participants consisted of 19 experienced wine tasters (7 female, 12 male) from the Marlborough wine industry. Fifteen of the participants were winemakers, two participants were viticulturists and two were oenologists. All participants considered themselves experienced tasters and four participants considered themselves as expert tasters. Three of the participants had experience with formal wine judging. The mean age of the participants was 36.38 years (range = 29-52). The mean number of years in the wine industry was 14.38 years (range = 4-30). The mean number of years experience with New Zealand Pinot noir wine was 10.50 years (range = 6-19). Eight participants had taken part in sensory panels prior to this study but only six of these participants had any sensory training and no participants had sensory training specific to Pinot noir wines.

Wines

Wines in the study comprised 32 commercial Pinot noir wines from two vintages and four wines from each region: Central Otago, Marlborough, Martinborough and Waipara. Wines used in the paired comparison were from the 2007 vintage and wines used in the sorting analysis were from the 2008 vintage. Thirty of the wines were sealed with screw cap and two were sealed with cork. All wines selected were considered to be good examples of regional products with all grapes coming from the specified region. Grapes for two of the wines were grown and transported from Central Otago and vinified in Martinborough and Marlborough.

Fresh bottles were opened every two days over the course of the study. At the end of each day bottles were sparged with argon to prevent oxidation and were stored at room temperature (20°C).

Experimental Design & Sensory Procedure

The paired comparison and sorting analysis took place one year apart which ensured that both 2007 and 2008 wines were evaluated at the same bottle age. Both sensory tasks evaluated only the wine aroma using ortho-nasal olfaction. In each year participants attended three, one-hour tasting sessions. The participants were not limited in the amount of time available to complete the tastings, but most finished in less than 30 minutes. Tasting sessions were held in a tasting room with a mixture of natural and artificial light and a constant temperature of 20°C. For sensory evaluation 50 mL samples of wine were presented in standard, coded black ISO (International Organization for Standardization, 1977) wine tasting glasses.

For paired comparison, four wines from each of the four regions resulted in 24 same-region and 180 different-region wine pairs. Each pair could be presented in two orders. Therefore in total there were 408 possible wine pairs. Pairs that included the same wine were excluded to avoid confusion with traditional paired comparison. 12 pairs were evaluated in each session. Each wine pair can be presented in 12 different possible positions, with more than 10,000 possible positional combinations. With such a large number of possible pairs it is impossible for each participant to evaluate all pairs in all possible positions and orders. A partially balanced incomplete block (PBIB) design was used for the order and presentation of wine pairs to minimize any possible order effects (Ball, 1997; Malhotra, Jain, & Pinson, 1988). Because of the large number of different-region wine pairs to same-region wine pairs, the PBIB was designed so that each tasting session contained three same-region wine pairs. The PBIB was generated using Genstat 12.2 (VSN International Ltd). Participants were presented with 12 pairs of wines and asked if the wines in each pair were from the same region or different regions.

Of the 16 possible different wines available only eight were presented for each sorting task. Of these, four were from the specified region and four from other regions. PBIB was also used in sorting analysis to present wines in a unique order at each tasting session. The PBIB

was generated using Genstat 12.2 (VSN International Ltd). Participants were asked to sort the wine into two groups: (1) the specified region and (2) not-specified region. Participants were not provided with any commonly described characteristics of wine from the specified region and they were not asked to provide any description. For each wine, participants were also asked to rate their confidence in placing the wine in the chosen group. Three ratings were provided: “not sure”, “maybe sure” and “very sure”.

Data Analysis

A binomial distribution was used to analyse the paired comparison results. The given pairs was the causal variable and the participant response was the response variable. Order effects were calculated using accumulated analysis of deviance. Genstat 12.2(VSNI International Ltd) was used for all statistical analysis.

Data from the sorting experiment were first separated into four different groups based on specified region: Central Otago, Marlborough, Martinborough and Waipara. Each group was fitted to a log-linear model of the form:

$$\text{Ln(predicted counts)} = \text{constant} + \lambda_{\text{RO}} + \lambda_{\text{PR}} + \lambda_{\text{PC}} + \lambda_{\text{RO} \times \text{PR}} + \lambda_{\text{RO} \times \text{PC}} + \lambda_{\text{PR} \times \text{PC}} + \lambda_{\text{RO} \times \text{PR} \times \text{PC}}$$

where RO is the region of origin (Central Otago, Marlborough, Martinborough, Waipara), PR is the participant response (specified region, other region) and PC is the participant confidence (not sure, sure, very sure).

The constant is the overall mean for the natural log of the expected frequencies in the contingency table. The different effects (λ) include the effect factors for region of origin (RO), participant response (PR) and participant confidence (PC). The interaction effect factors include region of origin x participant response (RO x PR), participant response x participant confidence (PR x PC), region of origin x participant confidence (RO x PC) and region of origin x participant response x participant confidence (RO x PR x PC). This model was used to test the different effects to find relationships between the categorical data. Each effect is a ratio of the frequencies for each factor, i.e. λ_{RO} refers to the ratio of totals for specified region groups to total of non-specified region group. For an effect not to contribute

to the model it must equal zero i.e. the totals of not sure, maybe sure and very sure decisions are all equal. Effects that influence the model must not be equivalent to zero. Effects for interactions, also known as second order interactions, determine if the two factors in the effect are independent. A generalized linear mixed model was used to calculate any possible order effects. All statistics were calculated with Genstat 12.2 (VSN International Ltd).

Results

Paired Comparison

The influence of position and within-pair order was investigated. The random effects include wine pair, position and within-pair order. There was found to be no significant effect for any of those three random effects ($p > 0.05$). Additionally no significance was found for any of the possible effect interactions, wine pair x position, wine pair x order, position x order and wine-pair x position x order ($p > 0.05$).

Panellists were able to distinguish pairs of wine from the same region versus those from different regions ($p < 0.05$). For each type of wine pair, participants produced more correct than incorrect responses (Table 4.1). It was possible to investigate further the paired comparison data by region (Table 4.2). Only paired comparisons including wines from Marlborough gave a significant result ($p < 0.05$).

Because participants were better able to discriminate Marlborough wines from those of other regions and all participants were working in the Marlborough industry at the time of the tasting sessions, the experience of the participants in the Marlborough wine region was investigated. The paired comparison data were split into two groups: these from participants with 10 or more years in Marlborough (eight participants) and with fewer than five years (11 participants). There were no participants that had 5 to 10 years of experience. There was no significance in either group when pairs were analysed without regional classification. Significance occurred with added regional classification, but only for Marlborough pairs and participants who had 10 or more years experience in Marlborough ($p = 0.011$) (Table 4.3).

Sorting Analysis

The results of the sorting analysis experiment are given in Table 4.4. The order of the wines was not found to effect the sorting evaluation ($p=0.924$). Significance ($p<0.05$) was found for all four of the specified region models ($p=0.008$ for Marlborough and $p<0.001$ for Central Otago, Martinborough and Waipara), referring to the fit of the statistical model. The confidence parameter was removed from the log-linear models as it was not found to contribute any significance, as the majority of the time, maybe sure, was chosen as the confidence level.

The RO x PR interaction of the log-linear model indicated if participants could correctly group wines based on the specified region. None of the RO x PR interactions within each of the four different log-linear models was statistically significant, suggesting that no matter what the specified region, participants could not sort the wines based on their own personal conceptual models. Since participants were not able to successfully sort wines from the Marlborough wine region, the effect of experience was not investigated.

Discussion

In these discrimination tests the wine being tasted was compared to a regional example that was present in the participant's mind, the regional conceptual model (Casabianca et al., 2005). Many wine professionals have noted the differences between New Zealand Pinot noir regional styles (Pinot Noir New Zealand, 2010) and recently research has determined important aroma and flavour attributes that describe those regional styles (Chapter 3). Differentiation for regional wines was based on two different tasks: evaluation of wine pairs that were from the same or different region and sorting wines into two groups based on region. The information provided was limited to determine if participants had developed associations between aroma perception and the region of origin, resulting in robust regional conceptual models (Easingwood, 2006). Regional discrimination was based on the participants previous wine knowledge for the specified region (Maitre, Symoneaux, Jourjon, & Mehinagic, 2010).

The non-standard implementation of the paired comparison procedure relies on the participant's aroma perception, and their assessment of how different a wine must be in order

to be classified as from another region. Each participant will have their own set of criteria of how different the aroma profiles of the wines must be before they can be considered from different regions (Ennis & Ashby, 1993; Rousseau, Meyer, & O'Mahony, 1998; Rousseau & O'Mahony, 2001). For example, Marlborough wines have been classified as containing more intense red fruit aromas, but the question arises as to exactly how large of a difference in red fruit intensity must be present for Marlborough wines to be considered as not coming from Central Otago, Martinborough or Waipara? If the Marlborough wine is perceived as having only slightly more intense red fruit aroma then it may not be differentiated from wines from the other regions.

For the paired comparison procedure non-significant results occurred for both same-region and different-region pairs, except for Marlborough same-region pairs. This suggests two possibilities in the way that participants were discriminating wines. The first relates to the same-region wine pairs, in that participants did not correctly evaluate these pairs suggesting that the differences in perceived aromas were large enough that participants thought the wines were from different regions. The second possibility refers to the different-region pairs which were also unsuccessfully evaluated for all regions. This unsuccessful evaluation suggests that participants are using conceptual models that do not relate to the actual wine styles produced from the different regions. The wines from each region are different with specific sensory characteristics (Chapter 3), so the possibility that these wines are not different cannot be used to explain the non significant result.

The success at evaluating Marlborough same-region pairs is quite interesting, mainly because all the participants work in the Marlborough wine industry. More than 70% of same Marlborough pairs were evaluated correctly, suggesting that the aroma differences between the Marlborough wines were small enough that participants classified these wines as coming from the same region. It was initially presumed that the participants' experience and exposure to Marlborough Pinot noir might have been the driving factor to this success, as perhaps they were simply more familiar with Marlborough Pinot noir (Chambers & Smith, 1993; Li, Luxenberg, Parrish, & Gottfried, 2006; McClelland & Chappell, 1998).

With experience factored into the results it was found that those participants with 10 or more years in the Marlborough industry do differentiate Marlborough Pinot noir wines, while those with fewer than 5 years in Marlborough could not. However a similar pattern emerges when

the results are split based on experience as when the results were totalled, namely that participants were successful in evaluating Marlborough same-region pairs and unsuccessful in evaluating Marlborough different-region pairs. If experience was one of the main factors of regional discrimination then participants should have been able to differentiate Marlborough wines from other region wines.

In the sorting experiment, it was not the differences between the wines that was evaluated but the differences between the wines and a specified conceptual model. Participants could not correctly sort wines into the two given groups, specified region or other region, resulting in a non-significant result.

The results of both the paired comparison and sorting experiments suggest that wine professionals from Marlborough cannot differentiate regional wines apart when presented blind due to a lack of representative conceptual models. However this lack of differentiation may also be due to the choice of sensory tasks chosen for the experiments. The paired comparison was used in a non-standard method and may not be appropriate for regional differentiation. Sorting was chosen for the second experiment as this is used widely for regional differentiation (Ballester, Patris, Symoneaux, & Valentin, 2008; Parr, Valentin, Green, & Dacremont, 2010; Perrin et al., 2008). However Maitre et al. (2010) in their review of sensory methods used for such studies indicated the best methodology is not clear cut. They suggest that a combination of discrimination testing with descriptive analysis may provide more robust information. Additionally there are other sensory tasks such as forced choice tests that may be more appropriate as this type of test also provides information on the degree of differences being evaluated (Bende & Nordin, 1997; Solomon, 1990).

Conclusions

This study suggests that at the time these experiments were undertaken, wine experts in the New Zealand Marlborough wine industry have yet to develop robust conceptual models for regional Pinot noir wine. However this does not suggest that these specific styles do not exist, as previous work has shown that regional wines are different. The current conceptual models may not be representative of the regional wines or the perceptual differences that participants are using to classify wines are not as great as the differences currently used in the conceptual

models. In order for individuals to recognize these styles, education on the differences and degree of differences between the regional styles would be necessary.

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Tables and Figures

Table 4.1

Paired comparison results with counts for participant responses corresponding with the given wine pairs

<u>Wine Pair</u>	<u>Panellist Response</u>		<u>Total</u>	<u>Percent correct (%)</u>
	<u>Same</u>	<u>Different</u>		
Same	96	76	172	56
Different	254	304	558	54

Table 4.2

Paired comparison results with counts for participant responses corresponding with the given wine pairs including the regional classification

<u>Wine Pair</u>		<u>Participant Response</u>		<u>Total</u>	<u>Percent correct (%)</u>
		<u>Same</u>	<u>Different</u>		
Central Otago	Same Region	20	27	47	43
	Other Region ^a	127	157	284	55
Marlborough	Same Region	31	13	44	70
	Other Region ^a	128	157	285	55
Martinborough	Same Region	24	19	43	56
	Other Region ^a	138	138	276	50
Waipara	Same Region	21	20	41	51
	Other Region ^a	115	156	271	58

^a There are much more other region pairs as each pair can be assigned to two different regional classifications, e.g. Central Otago x Waipara pair can be counted as other region pair in both Central Otago and Waipara.

Table 4.3

P-values for binomial distribution based on participant experience for wine pairs as a whole and wine pairs with regional classification

<u>Participant Experience in Marlborough (years)</u>	<u>≤ 5</u>	<u>≥ 10</u>
Same vs. Different	0.068	0.228
Central Otago same vs. different	0.64	0.304
Marlborough same vs. different	0.055	0.011*
Martinborough same vs. different	0.937	0.655
<u>Waipara same vs. different</u>	<u>0.486</u>	<u>0.494</u>

*Significance (p<0.05)

Table 4.4

Contingency table that contains the counts when sorting wines into two groups: specified region or other regions.

Specified Region	Region of Origin	Panellist Response		
		Specified Region	Other Region	Total
Central Otago	Central Otago	30	31	64
	Marlborough	12	8	20
	Martinborough	9	16	25
	Waipara	6	13	19
	Total	57	71	128
Marlborough	Central Otago	5	8	13
	Marlborough	12	21	33
	Martinborough	7	5	12
	Waipara	6	8	14
	Total	30	42	72
Martinborough	Central Otago	10	10	20
	Marlborough	12	11	23
	Martinborough	44	22	66
	Waipara	15	12	27
	Total	81	55	136
Waipara	Central Otago	6	10	16
	Marlborough	8	8	16
	Martinborough	4	9	13
	Waipara	19	24	43
	Total	37	51	88

Chapter 5

(in preparation for submission to Australian Journal of Wine and Grape Research)

Development and Optimisation of a Headspace Solid-Phase Microextraction Method for the Analysis of Volatile Fatty Acids in New Zealand Pinot Noir to Elucidate Vintage and Regional Differences

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Abstract

Background and Aims: A new method that optimized parameters for HS-SPME-GC-MS was developed to quantify volatile fatty acids (VFAs). These compounds are very important to wine aroma. At high concentrations they are considered to contribute perceptions of wine spoilage. However at the lower concentrations in red wine they may contribute more positively to wine aroma.

Methods and Results: This method had individual VFA Limits of Detection (LOD) ranging from 0.001 µg/L for 3-methyl butanoic acid to 252 µg/L for ethanoic acid, Limits of Quantification (LOQ) of 0.002 µg/L for 3-methyl butanoic acid to 840 µg/L for ethanoic acid and recovery percentages ranged from 83 to 94%. VFAs in New Zealand Pinot noir were measured. Wines from the 2008 vintage contained significantly higher ($p < 0.05$) concentrations of butanoic acid and 3-methyl butanoic acid compared to the 2007 wine concentrations.

Conclusions: The method was both reliable and time efficient and has potential to provide a link to Pinot noir wine quality. VFAs were shown to be inappropriate as markers of regionality for New Zealand Pinot noir, but may be a marker for vintage.

Significance of Study: To date no information on VFA concentrations in New Zealand Pinot noir has been reported. As the concentrations of these VFAs differ, the aroma of the different vintages may also differ.

Keywords: GCMS, New Zealand, Pinot noir, SPME, volatile fatty acids

Objective

The objective of this study was to develop an optimized Head Space Solid Phase Micro-Extraction Gas Chromatograph Mass Spectrometric (HS-SPME-GC-MS) method for quantifying VFAs in Pinot noir wine, using a SPME fibre and GC column setup that could also quantify a wide range of other VOCs in addition to VFAs. Generally, volatile fatty acids (VFAs) have been found to be important to wine aroma. A method that can accurately and reliably measure VFAs in Pinot noir is needed to investigate the importance of these compounds to aroma. This method was used to quantify VFAs in 32 Pinot noir wines selected from the four main Pinot noir growing areas in New Zealand to identify possible regional differences.

Materials & Methods

Samples and reagents A method that can accurately and reliably measure VFAs in Pinot noir is needed to investigate the importance of these compounds to aroma. A method that can accurately and reliably measure VFAs in Pinot noir is needed to investigate the importance of these compounds to aroma. HPLC Grade (ACS ISO UV-VIS) absolute ethanol was purchased from Scharlau Chemie, (SA, Australia). Deionised water was obtained from a Barnstead Nanopure II system. The purity of all reference and isotopically-labelled (deuterated) compounds was checked prior to use by GC-MS at a concentration of 5 mg/L. Pure reference compounds: butanoic acid, 3-methylbutanoic acid (common name, isovaleric acid), hexanoic acid (common name, caprylic acid) and octanoic acid (common name, caproic acid) were purchased from Sigma-Aldrich (NSW, Australia). Ethanoic acid (common name, acetic acid) was obtained from Merck (Auckland, New Zealand). Pure isotopically-labelled compounds, d₄-ethanoic acid and d₁₁-hexanoic acid were purchased from Sigma-Aldrich (Australia) and d₂-octanoic acid was obtained from CDN isotopes (NSW, Australia). Analysis parameters and purity information are found in Table 5.1.

The 32 Pinot Noir wines used in this study were commercial New Zealand wines from the 2007 and 2008 vintages (Table 5.2). Wines were taken from each of the four major Pinot noir growing regions in New Zealand, namely Marlborough, Martinborough, Waipara and Central Otago. A 30 mL sample of each wine was taken directly after opening each bottle. Samples were placed in 40 mL screw cap amber vials, with PTFE/Silicone septa (Supelco Bellefonte,

PA, USA, through Sigma- Aldrich, Australia), and frozen at -20°C until analysed. All wine bottles were opened two years after their vintage date.

Stock standard solutions of ethanoic acid, butanoic acid, 3-methybutanoic acid, hexanoic acid, d₁₁-hexanoic acid and d₂-ethanoic acid were prepared in 10% ethanol-water solutions. Because of their lower aqueous solubility, stock standard solutions of octanoic acid and d₂-octanoic acid were prepared in 100% ethanol (Scharlau Chemie). A composite standard was created using the stock solutions. This composite contained all the non-deuterated reference acids. A separate internal standard was prepared from the stock solutions containing the isotopically labelled (deuterated) compounds. Sub-samples of the composite standard solution were then placed in 9 mL amber vials and stored at -20°C until use. Each subsample was only used once, any excess was discarded. To prepare working standards for each analysis run, one of these composite standard sub-samples was thawed to room temperature and the required volumes needed to prepare each working standard (0 to 0.90 mL) plus the required volume (0.90 to 0 mL) of “wine matrix” (14% aqueous ethanol at pH 3.5) were pipetted, along with 8.06 mL of acidified deionised water (pH 3.5), into 20 mL amber glass, screw cap vials, 22.5 x 75.5 mm, followed by 40 µL of the composite isotopically-labelled internal standard solution (Table 5.1).

Optimization Parameters

Four important variables involved in all HS-SPME analyses of wine are: agitation time, salt (NaCl) amendment, incubation temperature and fibre extraction time. Previous work in our lab investigating other VOCs in wine identified the optimal headspace volume, sample dilution and sample volume (data not presented). Using published information and our own experience, we selected three agitation times (0, 5 and 10 mins), five different amounts of NaCl (0.0, 1.5, 3.0, 4.5 and 6.0 g per 9 mL sample), five incubation temperatures (30, 40, 50, 60 and 70°C) and six extraction times (10, 20, 30, 40, 50 and 60 mins). We used a stepwise approach to study and optimise each of these variables separately (Table 5.3). The effect of altering one variable was studied and optimized; that variable was then held constant while a second variable was optimised and so on until all four variables were optimized (Figure 5.1).

Chemical Stability

The stability of the prepared standards was tested over a period of 49 hours. For this, only the highest standard in the calibration curve was used with the composite internal standard added. Standards were held at room temperature (20°C) or chilled (8°C) in a temperature controlled

sample tray (CTC Analytics AG, Switzerland) to determine if temperature affected the stability of the compounds while the vials were waiting to be analysed. All standards were prepared at the same time and then analysed at 3 hour intervals, alternating between the 20°C and chilled standards.

Sample Preparation

All wine samples were diluted immediately prior to analysis. This sample dilution involved pipetting 0.90 mL of wine and 8.06 mL of acidified deionised water (pH 3.5) into 20 mL amber glass, screw cap vials, 22.5 x 75.5 mm, followed by 40 µL of the composite isotopically-labelled internal standard solution (Table 5.1). The volumes used were equivalent to a 10-fold dilution of the wine sample. Following sample dilution and internal standard addition, our initial procedure was as follows: NaCl (3 g) was added to the SPME vial and vials were tightly capped. Samples were then incubated initially for 10 minutes at 60°C during which time the vial was agitated at 500 rpm. After 10 minutes the SPME fibre was exposed to the headspace of the vial for a period of 30 minutes at 60°C, during which time the headspace volatiles were adsorbed onto the fibre. No agitation was used during the 30 minute extraction period due to the chance of breaking the fibre.

SPME fibre and conditioning

A 2 cm long Stableflex DVB/CAR/PDMS combination SPME fibre (p/n 57348-U, 50/30 µm thickness, 24 gauge) was selected for this work (Supelco Bellefonte, PA, USA, through Sigma- Aldrich, Australia). This type of fibre has been shown previously to be suitable for most VOC analyses in wine, including VFAs (Carrillo et al. 2006, Ferreira and de Pinho 2003). More importantly the DVB/CAR/PDMS coating is the only coating that has been found to work effectively with ethanoic acid (Abalos et al. 2000, Marco et al. 2004). Prior to use the SPME fibre was conditioned at 270°C in the injection port for 1 hour. Immediately prior to each sample analysis the SPME fibre was further conditioned in He for 10 minutes at 270°C in a fibre conditioning station attached to the Combi-Pal auto-sampler used with the Shimadzu GC-MS instrument.

Volatile Acid Analysis

Automated GC-MS analysis was carried out on a Shimadzu GC-MS-QP2010 gas chromatograph–mass spectrometer equipped with a CTC Combi-Pal autosampler (CTC-Analytics AG, Switzerland) using Version 2.50 of Shimadzu’s GC-MSsolution data

acquisition software. The NIST05 (National Institute of Standards and Technology) mass spectra library was used to confirm the identities of all standards. The chromatography was performed using two GC columns in series: a Rtx-Wax 30.0m x 0.25mm ID x 0.5µm film thickness (Polyethylene Glycol - Restek, Bellefonte, PA, USA) and a Rxi-1MS 15 m x 0.25 mm ID x 0.5µm (100% dimethyl polysiloxane - Restek, Bellefonte, PA, USA). A short guard column (Siltek deactivated guard column 5m x 0.25mm ID, Restek, Bellefonte, PA, USA) was added to the beginning of the columns as a way to extend column life and prevent damage from the high temperatures used at the injection port. This non-polar and polar combination of columns has been employed with good effect previously (Parr et al. 2007) and elsewhere (Fedrizzi et al. 2007, Rebiere et al. 2010, Yang and Choong 2001) because of its established ability to separate a wide range of VOCs present in wine, although it has not been used strictly for VFA analysis. Splitless injection was used for the first 3 minutes of the runtime, after which split mode was used at a 20:1 ratio. The helium (He) carrier gas was set to a constant linear velocity of 46.8 cm s⁻¹. The column oven was held at 50°C for 3 minutes, increased to 240°C at 10°C min⁻¹, then further increased to 250°C at 30°C min⁻¹ and held at this temperature for 5 minutes. The total run time was 27.3 minutes. The interface and MS source temperatures were set at 250°C and 200°C respectively and the MS was operated in electron impact mode (EI) at an ionization energy of 70 eV. Full scan mode was used for all standards. Retention times, target ions and qualifier ions for each compound are found in Table 5.1. All samples were analysed using a random sampling order.

Validation, Limit of Detection, Limit of Quantitation and Statistical Analysis

All HS-SPME optimization tests and wine sample measurements were performed in triplicate to ensure precision. Quantification was carried out using stable isotope dilution analysis procedures similar to those described in Siebert et al. (2005). Reference standard concentrations were plotted against the ratios of the reference compounds to their respective labelled internal standards (Table 5.1). Composite standards used for the calibration curves were analysed in duplicate with each curve having a high regression coefficient, $R^2 > 0.999$ (Table 5.1).

During each analytical run, every 20th vial was a reference sample, included to account for any possible instrument drift. Accuracy was assessed using spiked wine samples and calculating the recovery percentage (Table 5.4). Spiked samples also helped to determine any possible matrix effect on each analyte. Limit of detection (LOD) and limit of quantification

(LOQ) were calculated using the methods described in Callejon, Gonzalez, Troncosco & Morales (2008) and Miller & Miller (2005) (Table 5.4).

Canonical variates analysis (CVA) was calculated using Genstat 12.2 (VSN International Ltd.). The grouping variable for CVA was the wine region of origin.

Results & Discussion

Normally when optimizing a method for specific compounds, the parameters that produce the best GC peak shape or the greatest peak areas are desired (Arthur et al. 1992). These parameters include the four investigated in this current work, as well as fibre coatings, sample matrix, headspace volume, dilution and column composition (Kalua and Boss 2008, Rodriguez-Bencomo et al. 2009, Siebert et al. 2005). Many of the parameters have already been optimized for VFA analysis. For instance the concentration of ethanol in wine samples has been found to strongly influence the efficiency of HS-SPME sampling for other headspace VOCs (Fischer et al. 1997). Optimal efficiency to overcome that particular matrix effect was achieved by dilution of the wine sample with water (de la Calle Garcia et al. 1997, Parr et al. 2007, Robinson et al. 2009). Other parameters that were taken from previous work include the fibre choice, matrix composition (Abalos et al. 2000, Olivero and Trujillo 2011), column composition and headspace volume (Kemp 2010, Parr et al. 2007).

The pH of the solution in the vial is also important especially when quantifying VOCs which ionise in water. Volatile fatty acids have pKa values around 4.8 so at the pH of wine (c. 3.5) they are almost all present in their non-ionised, and therefore volatile forms (Pan et al. 1995). All standards and samples were diluted with water whose pH was adjusted to pH 3.5 to ensure that all acids were in the non-ionised forms.

Of most concern in this current work was quantification of ethanoic acid. It is the most soluble of the VFAs so the proportion of this compound existing within the vial headspace would have been less than for the longer chain, less soluble VFAs. In addition, it is known that the Stableflex DVB/CAR/PDMS combination SPME fibre favours compounds that have a high molecular mass (Ezquerro et al. 2003). These effects together may explain the much larger MS peak areas observed for octanoic acid compared to those observed for ethanoic acid, despite the ethanoic acid being present in much higher concentrations (Table 5.4). Much

of the method optimization of this current work therefore focussed on producing the best MS response, within the chosen constraints, for ethanoic acid.

Agitation

Agitation during incubation is very important for the quantification of VFAs. It accelerates the transfer of the acids to the fibre, which decreases the necessary extraction time (Kataoka et al. 2000). Peak areas greatly increased when agitation was undertaken versus no agitation. However extending the agitation time from five to 10 minutes produced no significant further increase in the peak area of the acids (Figure 5.1). Agitation was only used for the pre-incubation period as agitation during the extraction step tended to break the SPME fibres, particularly at high agitation speeds (Wang et al. 2005). For this current method, the optimal agitation time was therefore 5 minutes.

Salt Concentration

HS-SPME utilizes salt to decrease the solubility of the VOCs. This in turn increases the concentration of the VOCs in the headspace which accelerates their transfer onto the SPME fibre (Pawliszyn 2009). As expected, the VFA peak areas were found to increase as the total salt concentration increased (Figure 5.1). However the addition of more than 3 g of salt (NaCl) produced no further significant increases in the peak area. For this current method, the optimal quantity of NaCl was therefore 3 g.

Incubation Temperature

The incubation temperatures tested for method development ranged from 30 to 70°C (Figure 5.1). For HS-SPME analysis an incubation temperature is a compromise between a temperature high enough to promote the volatilisation of the VOCs from the wine matrix into the headspace, while being low enough to prevent significant subsequent desorption of those VOCs from the SPME fibre. A further complication is that different fibres selectively adsorb different compounds. All the VFAs quantified in this current study displayed increasing peak area as the temperature increased until 50°C. Thereafter, the peak areas of ethanoic acid, butanoic acid and 3-methyl butanoic acid began to decrease. Hexanoic acid, octanoic acid, d₁₁-hexanoic acid and d₂-octanoic acid all reached maximum peak areas at an incubation temperature of 60°C (Figure 5.1). For this current method, the optimal incubation temperature was chosen to be 50°C.

Extraction Time

The extraction time, or the length of time the fibre was exposed in the headspace of the vial, was tested at 10 minute intervals starting at 10 minutes and ending at 60 minutes. Ethanoic acid, had clearly achieved equilibrium on the SPME fibre after 30 minutes (Figure 5.1), while butanoic and 3-methyl butanoic acids did not appear to achieve equilibrium on the fibre until at least 40 minutes. Furthermore, the peak areas of the higher molecular weight acids, hexanoic, d₁₁-hexanoic, octanoic and d₂-octanoic acid, were all still increasing at 60 minutes extraction time. Based on the practicality of selecting an extraction time which did not exceed, or impact markedly on, the GC-MS run time, a 30 minute extraction time was deemed adequate for this method.

Stability

A time study was carried out to determine if any of the VFAs, both isotopically labelled and unlabelled, decomposed or degraded while waiting to be analysed. For our analytical system, when a batch of wine samples was analysed in triplicate, the last vial would have been sitting at room temperature for up to 48 hours before being sampled. If any of those compounds had changed their composition during that time this would have been apparent when scrutinising the peak area results. The peak areas obtained for all of these labelled and unlabelled VFAs in replicate samples held in chilled vials at 8°C and at room temperature over a 48 hour period did not vary, and produced essentially constant peak areas over that time frame (data not shown). Sample stability was therefore verified.

Validation, LOD & LOQ

Quantitative recovery of the various VFAs added as “spikes” to wine samples were all within the range 83 – 94% (Table 5.4). Best results are achieved when quantification is carried out using a deuterated internal standard whose chemical structure most closely matches the structure of the analyte (Siebert et al. 2005). This was confirmed during initial spike recovery tests for ethanoic acid when d₁₁-hexanoic was used as the internal standard and calculated recovery exceeded 120% (Table 5.4). However, when d₂-ethanoic acid was used instead, a more acceptable spiked recovery of 94% was observed.

The LOD and LOQ for each volatile acid are shown in Table 5.4. The LOD and LOQ values determined in this current work for octanoic acid and hexanoic acid were lower than values reported in other recent studies (Callejon et al. 2008, Rebiere et al. 2010).

In this current study, wines were analysed at the same age following bottling; two years. Therefore all 2008 wines were analysed on the GC-MS one year later than the 2007 wines. In order to identify and determine any possible instrumentation artefacts, two wine samples, stored frozen from 2007 were analysed along with the 2008 wines. No significant differences were found for the VFA content of those 2007 samples when analysed a year later thereby confirming the absence of any instrumentation artefacts (Table 5.4).

Volatile Fatty Acid concentrations in Pinot noir

The concentrations of the VFAs found in the 32 New Zealand Pinot noir wines (Table 5.4) span quite large ranges: from a factor of nearly 2 ($1,104$ to $1,941 \mu\text{g L}^{-1}$) in the case of hexanoic acid to a factor of nearly 4 (160 to $591 \mu\text{g L}^{-1}$) in the case of 3-methyl butanoic acid. The range of concentrations found for ethanoic acid (349 to 874 mg L^{-1}), butanoic acid (209 to $716 \mu\text{g L}^{-1}$) and octanoic acid (674 to $2,002 \mu\text{g L}^{-1}$) are intermediate between those extremes (Table 5.5). The concentration of ethanoic acid, butanoic acid, hexanoic acid and octanoic acid are within the range of concentrations found in Pinot noir wines of other origin and vintage (Feuillat et al. 1997, Girard et al. 1997, Louw et al. 2006, Massoutier et al. 1998, Miranda-Lopez et al. 1992).

In contrast to these acids, the range of concentrations of 3-methyl butanoic acid (160 to $591 \mu\text{g L}^{-1}$) was, on the whole, lower than that found in Pinot noir from South Africa (500 to $600 \mu\text{g/L}$) (Louw et al. 2006) and significantly lower than Pinot noir from France (900 to $1700 \mu\text{g/L}$) (Feuillat et al. 1997). These differences may possibly be attributable to differences in production methods. The Pinot noir wines in our study were all commercial products while the wines in the other two studies were research wines, investigating the effect of different yeasts. VFA production is highly dependent on yeast metabolism and juice nitrogen content (Bell and Henschke 2005) and the difference between the commercial yeasts used for our 32 NZ wines and those being investigated in research may have caused the differences in 3-methyl butanoic acid levels, although this was not the case for the other VFAs.

Further statistical analysis, using CVA, displayed the differences in VFA concentration based on region and vintage. CV analysis, also known as discriminant analysis, is described by William Klecka (1980) as “a statistical technique which allows the researcher to study the differences between two or more groups of objects with respect to several variables

simultaneously.” These differences are reported as linear combinations that include all the variables, known as canonical variates. The greater the weighting of the variable within each variate, the more important that variable is to differentiation in the calculated dimension. Statistically significant dimensions were determined using a chi-square approximation. The first and second canonical variates (CV1 and CV2, respectively) were found to be statistically significant ($p < 0.05$), when wines were separated using region and vintage classifications (Figure 5.1). No significance was found when wines were separated only by region. The greatest variance, 71%, is due to CV1 and 19% of the variance is due to CV2.

Each of the variates separates the wines in different ways; here CV1 separates the wines largely by vintage and CV2 appears to separate the wines largely by region and vintage. Therefore the main difference found between the wines was a vintage difference, as CV1 contains 71% of the variance. Based on the variable weights for CV1 and CV2 it was possible to determine which variables were most important for separating the wines by vintage and region (data not shown). The weightings indicate that the concentrations of butanoic and 3-methyl butanoic acid were the most important for differentiation along CV1, explaining the main vintage differences (Figure 5.1). Thus, Pinot noir wines from 2008 contain higher concentrations of both butanoic and 3-methyl butanoic acids than wines from 2007. Weightings show that ethanoic acid, hexanoic and octanoic acid concentration separate the wines along CV2, displaying some regional and vintage differentiation, although of the four regions, Central Otago did not display any vintage differences across CV2.

Differences in VFA concentration are typically attributed to yeast strain and nitrogen content, as these acids are formed during fermentation. It is plausible that the mineral nitrogen content of the must could be causing this vintage difference. Research has shown that it is not only the amount of nitrogen that effects VFA production but also the chemical form of that nitrogen. It is common practice to add diammonium phosphate (DAP) to low nitrogen ferments, to prevent stuck fermentation and the development of sulfur off odours (Bisson 1991). DAP supplemented fermentations have been found to produce higher levels of octanoic and decanoic acids and lower levels of the shorter chain and branched acids, including butanoic and 3-methyl butanoic acid (Ugliano et al. 2008, Vilanova et al. 2007). Nitrogen concentrations of musts were not determined as part of the study.

Waipara displayed the greatest separation in the 2D space defined by CV1 and CV2, between the 2007 and 2008 vintages (Figure 5.1). Besides an increase in butanoic and 3-methyl

butanoic acid concentration from 2007 and 2008, the 2008 vintage Waipara wines also had significantly higher concentrations of hexanoic and octanoic acids and lower concentrations of ethanoic acid compared to wines from the 2007 vintage. In addition to the region and vintage differences found between 2007 and 2008 wines, there were some smaller variations between the other regions, although these are not nearly as great as those found in Waipara.

CV analysis was performed using only regions as a grouping factor to discern if the regional separation noted was significant. Wines could not be differentiated by region when the vintage variable was removed from the calculation (data not shown). Therefore VFAs are not appropriate as markers of regionality for New Zealand Pinot noir, but may be markers for vintage and quality, as has been shown previously for wines in Bordeaux (Seeber et al. 1991).

Conclusions

A GC-MS method using HS-SPME was optimised to produce a suite of parameters that facilitated the quantification of VFAs in Pinot noir wines that was both reliable and time efficient. The optimization steps largely focussed on achieving acceptable results for ethanoic acid. The method was applied to 32 Pinot noir wines selected from two vintages which spanned the four main Pinot noir growing regions in NZ. It was found that the main differences in VFAs occurred between vintages which may be linked to mineral nitrogen content and the addition of DAP at ferment. The fast method time and the potential it offers to link to perceived “quality” makes this HS-SPME-GC-MS procedure a powerful tool for use by the New Zealand wine industry.

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Tables and Figures

Table 5.1

Quantification parameters for the 8 analytes.

Analyte	ISTD ^a	Retention Time (min)	Target Ion m/z	Confirming Ions m/z (% to Target Ion)	Calibration Range (1/10 dilution) (µg/l)	Standard Curve (R ²) ^c	Purity (%)	CAS No.
d ₄ -ethanoic acid	(1)	12.40	46	63 (72.33)			99.5	141-78-6
d ₁₁ -hexanoic acid	(2)	17.56	63	77 (42.89), 93 (12.39)			99	97-62-1
d ₂ -octanoic acid	(3)	19.89	62	74(32.93), 102 (11.97)			99	105-54-4
ethanoic acid	2,1 ^b	12.65	43	60 (82.11), 45 (84.41)	0 – 136,592	0.9994	98	66-25-1
butanoic acid	2	15.00	60	73 (26.55)	0 – 1463	0.9999	98	539-82-2
3-methyl butanoic acid	2	15.56	60	87 (17.95)	0 – 195	0.9996	98	123-66-0
hexanoic acid	2	17.62	60	73 (41.19), 87 (11.70)	0 – 780.5	0.9999	99	111-27-3
octanoic acid	3	19.93	60	73 (56.01), 101 (20.41)	0 – 976	0.9999	98	928-97-2

^a ISTD = internal standard

^b Internal standard 2 was used for analysis of wines in 2007 and internal standard 1 used for analysis of wines in 2008.

^c A quadratic function was fitted to each aroma compound standard curve. Seven standards were used to generate each curve.

Table 5.2

New Zealand Pinot noir wines analysed for VFAs

Wine Product	Vintages	Code	Region
Mt Difficulty	2007, 2008	C1, C5	Central Otago
Montana “Terroir Series” Gabriel’s Gully	2007	C2	Central Otago
Gibbston Valley	2007, 2008	C3, C6	Central Otago
Amisfield	2007, 2008	C4, C8	Central Otago
Craggy Range “Zebra Vineyard”	2008	C7	Central Otago
Stoneleigh Rapaura Series	2007, 2008	M1, M5	Marlborough
Montana “Terroir Series” Forgotten Valley	2007	M2	Marlborough
Brancott Estate Reserve	2007, 2008	M3, M6	Marlborough
Brancott Estate Terraces “T”	2007, 2008	M4, M8	Marlborough
Villa Maria Southern Clays	2008	M7	Marlborough
Martinborough Vineyard	2007, 2008	N1, N5	Martinborough
Palliser Estate	2007, 2008	N2, N6	Martinborough
Escarpment	2007, 2008	N3, N7	Martinborough
Ata Rangi	2007, 2008	N4, N8	Martinborough
Camshorn	2007, 2008	W1, W5	Waipara
Muddy Water “Hare’s Breath”	2007, 2008	W2, W6	Waipara
Greystone	2007, 2008	W3, W7	Waipara
Pegasus Bay	2007, 2008	W4, W8	Waipara

Table 5.3

Schematic for acid SPME optimization showing testing parameters for each step and the final method.

Optimization Step	Agitation (min)	NaCl (g)	Incubation Temperature (°C)	Extraction Time (min)
1	0, 5, 10	3	60	30
2	5	0, 1.5, 3, 4.5, 6	60	30
3	5	3	30, 40, 50, 60, 70	30
4	5	3	50	10, 20, 30, 40, 50, 60
Final Method	5	3	50	30

Table 5.4

Limit of detection, limit of quantitation and percent recovery for standard compounds.

Analyte	LOD (µg/L)	LOQ (µg/L)	Recovery (%)	Perception threshold (µg/L)
ethanoic acid	252	840	123*, 94**	200,000 ^a
butanoic acid	0.001	0.004	83	10,000 ^a
3-methyl butanoic acid	0.001	0.002	86	33.4 ^b
hexanoic acid	1.776	5.926	90	3,000 ^a
octanoic acid	2.678	8.926	89	500 ^b

*calculated using d₁₁-hexanoic acid, **calculated using d₂-ethanoic acid

^a Determined in 10% EtOH solution (Guth 1997)

^b Determined in synthetic wine, 14% EtOH, 7 g/L glycerine, 5g/L tartaric acid, pH 3.4 (Ferreira et al. 2000)

Table 5.5

Average Concentration of 5 Volatile Fatty Acids in New Zealand Pinot noir Wines with Standard Error

Wine	Vintage	Acetic acid (mg/L)	Butanoic acid (µg/L)	3-Methylbutanoic acid (µg/L)	Hexanoic acid (µg/L)	Octanoic acid (µg/L)
C1	2007	607 ± 6	209 ± 6	343 ± 3	1292 ± 15	1025 ± 40
C1**	2007	606 ± 6	215 ± 14	362 ± 10	1264 ± 8	951 ± 10
C2	2007	644 ± 3	330 ± 5	347 ± 2	1389 ± 9	1024 ± 8
C3	2007	671 ± 17	480 ± 33	391 ± 18	1542 ± 29	953 ± 20
C4	2007	553 ± 3	372 ± 11	294 ± 6	1497 ± 1	1081 ± 5
C5	2008	671 ± 1	433 ± 0	548 ± 1	1104 ± 2	939 ± 2
C6	2008	643 ± 1	579 ± 2	508 ± 2	1597 ± 1	1143 ± 2
C7	2008	690 ± 1	755 ± 3	493 ± 1	1744 ± 2	1157 ± 3
C8	2008	415 ± 13	466 ± 14	278 ± 8	1336 ± 41	760 ± 40
M1	2007	581 ± 5	316 ± 6	310 ± 2	1412 ± 12	1092 ± 22
M2	2007	553 ± 3	371 ± 35	294 ± 4	1497 ± 23	1081 ± 59
M3	2007	633 ± 35	314 ± 8	389 ± 6	1454 ± 14	1132 ± 7
M4	2007	592 ± 5	330 ± 4	389 ± 2	1356 ± 16	990 ± 17
M5	2008	559 ± 3	495 ± 0	398 ± 1	1142 ± 5	854 ± 3
M6	2008	662 ± 0	562 ± 1	352 ± 1	1169 ± 1	845 ± 1
M7	2008	874 ± 0	450 ± 1	591 ± 10	1210 ± 0	997 ± 0
M8	2008	760 ± 1	476 ± 1	541 ± 1	1147 ± 1	724 ± 2
N1	2007	586 ± 6	374 ± 4	267 ± 3	1272 ± 8	903 ± 10
N2	2007	590 ± 15	435 ± 8	240 ± 3	1320 ± 5	830 ± 19
N3	2007	516 ± 6	325 ± 10	322 ± 4	1533 ± 24	916 ± 18
N4	2007	549 ± 10	517 ± 16	278 ± 3	1679 ± 12	1061 ± 13
N4**	2007	541 ± 5	511 ± 21	279 ± 5	1700 ± 7	1054 ± 9
N5	2008	662 ± 3	562 ± 4	352 ± 2	1169 ± 6	845 ± 5
N6	2008	707 ± 1	534 ± 2	475 ± 0	1389 ± 3	1067 ± 1
N7	2008	524 ± 0	495 ± 0	371 ± 1	1202 ± 1	726 ± 2
N8	2008	606 ± 0	715 ± 1	335 ± 0	1579 ± 2	1062 ± 1
W1	2007	657 ± 40	339 ± 14	354 ± 8	1204 ± 5	841 ± 11
W2	2007	634 ± 4	394 ± 5	160 ± 0	1141 ± 4	674 ± 11
W3	2007	624 ± 10	425 ± 19	293 ± 7	1801 ± 24	665 ± 16
W4	2007	602 ± 14	290 ± 4	337 ± 2	1432 ± 17	1231 ± 24
W5	2008	538 ± 0	542 ± 1	710 ± 1	1453 ± 1	1033 ± 2
W6	2008	639 ± 1	373 ± 1	488 ± 1	1318 ± 3	1198 ± 3
W7	2008	349 ± 1	387 ± 0	258 ± 0	1165 ± 0	756 ± 1
W8	2008	702 ± 6	716 ± 7	539 ± 0	1941 ± 3	2002 ± 6

*Denotes wine region of origin: C- Central Otago, M – Marlborough, N – Martinborough, W - Waipara

** Denotes 2007 wines that were run with 2008 wines to determine any machine effects

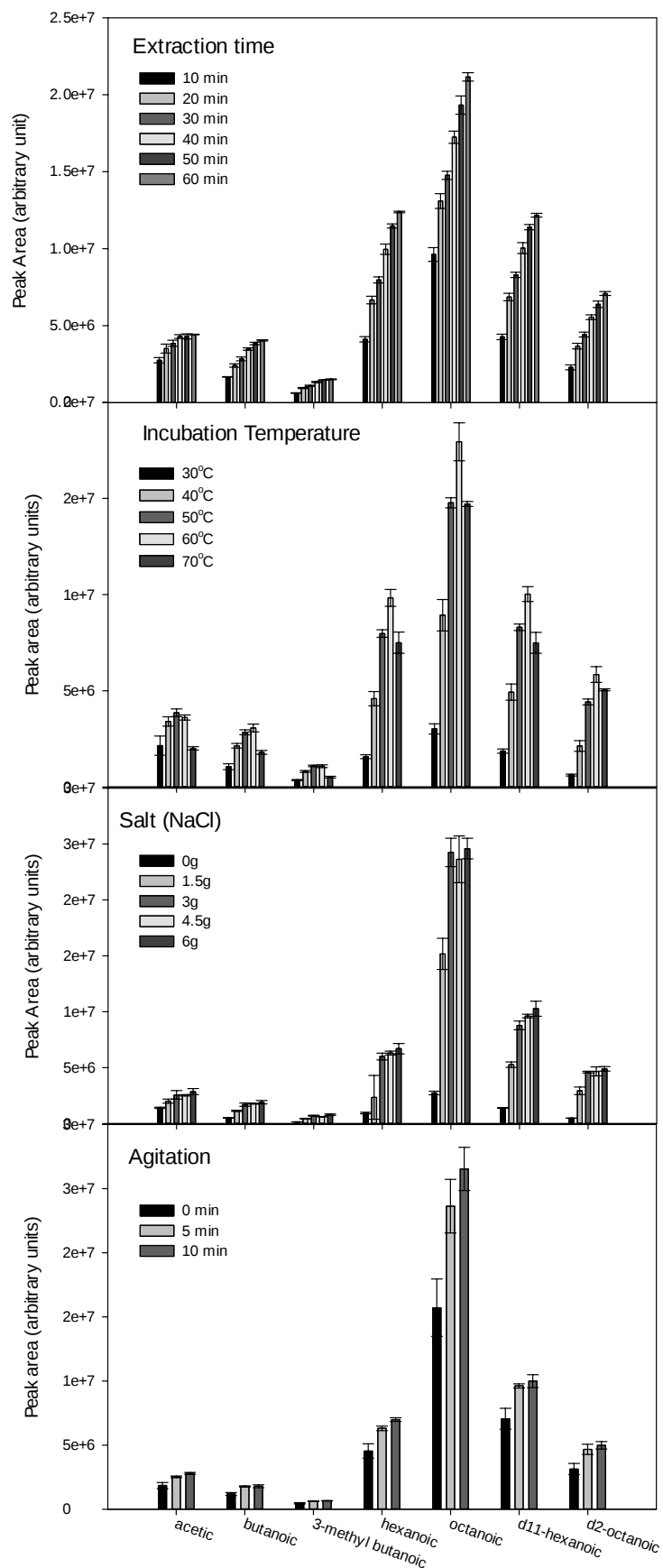


Figure 5.1
Peak area for each optimization step

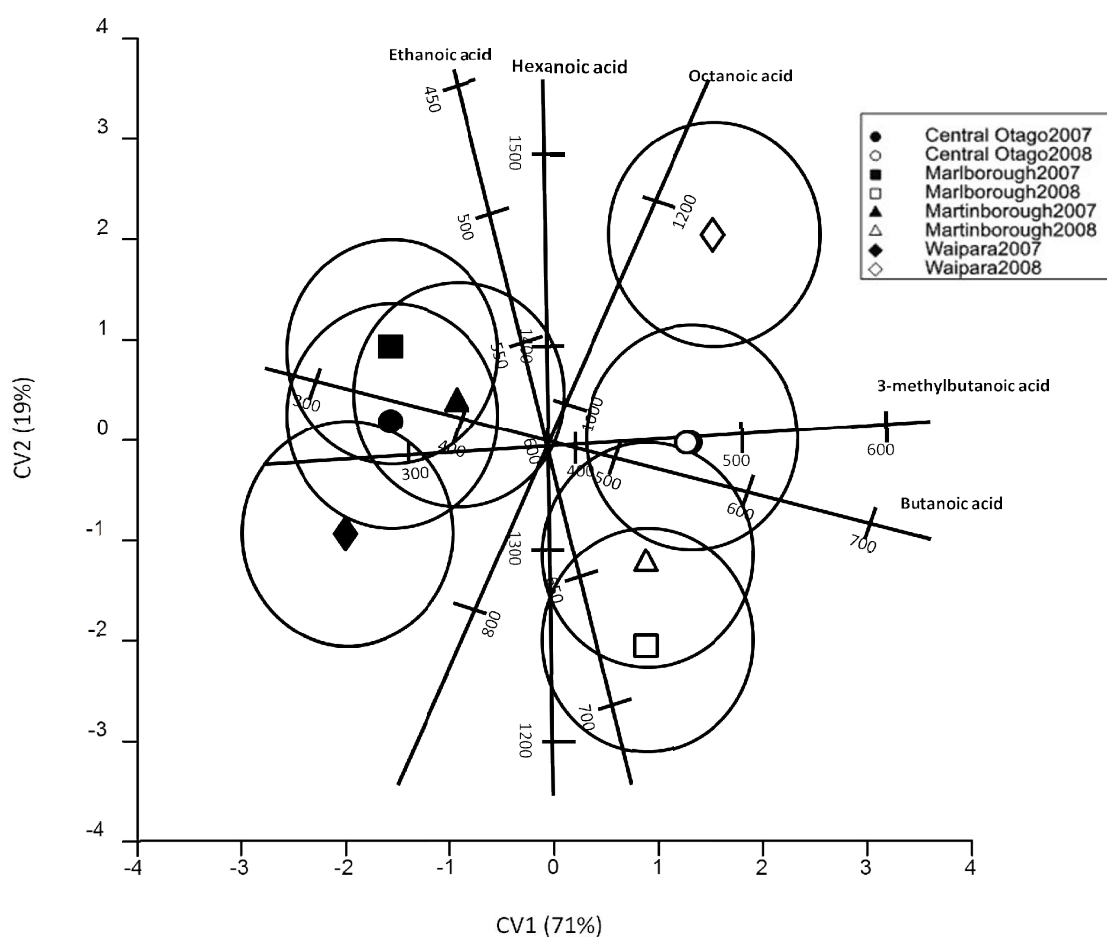


Figure 5.2

Regional and vintage separation of New Zealand Pinot noir wine using CVA, showing the region/vintage means with 95% confidence circles and acid concentrations scales in $\mu\text{g/L}$ (ethanoic acid - mg/L).

Chapter 6

(in preparation for submission to Food Research International)

Aroma Composition of New Zealand Pinot noir and its Relationship to Sensory

Characteristics Using Canonical Correlation Analysis

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Abstract

Canonical correlation analysis was used to investigate relationships between sensory and chemical data obtained from 32 New Zealand Pinot noir wines. Sensory information was collected by ranking the intensity of 19 different aroma attributes on a line scale.

Concentrations of 34 aroma chemicals were quantified using three SPME-GC-MS methods developed specifically for New Zealand Pinot noir wines. All data were standardized prior to statistical analysis. The largest correlation coefficient (0.386) was a sensory vector where 'black cherry', 'blackberry' and 'plum' had the largest coefficients and a chemical vector where ethyl octanoate, ethyl decanoate and 2-phenethyl ethanol had the largest coefficients. The second largest correlation coefficient (0.247) essentially resulted from a correlation where 'jam' and 'spice' had the largest sensory coefficients and benzaldehyde had the largest chemical coefficient. Thus, lower concentrations of ethyl octanoate, ethyl decanoate and 2-phenethyl ethanol were associated with higher intensities of the 'dark fruit' aromas and an increased concentration of benzaldehyde was associated with a higher intensity of 'spice' aroma and a decrease in the intensity of 'jam' aroma. These correlations provided a starting point for investigating which chemicals influence the aroma of New Zealand Pinot noir.

Objective

In this study two new HS-SPME-GC-MS methods were developed to measure volatile components in Pinot noir wine. The data, together with results from VFA analysis (Chapter 5) and sensory analysis (Chapter 3) were investigated using canonical correlation analysis. The objective of the study was to observe relationships between the aroma profile and composition of volatiles in New Zealand Pinot noir wine.

Materials and Methods

Wines

Thirty two commercial Pinot noir wines from the 2007 and 2008 vintages, eight from each of the four main Pinot noir sub-regions in New Zealand (Central Otago, Marlborough, Martinborough and Waipara) were used in both the sensory and chemical analysis (Table 6.1). All wines were considered typical regional products by their winemakers and 100% of the grapes used came from the specified region. Prior to chemical analysis all wine samples were stored as described in Chapter 5.

Sensory Analysis

Sensory analysis on the wines was conducted as described in Chapter 3 using 100mm visual analog scales to evaluate the intensity of a list of 18 aroma attributes (Table 6.2).

HS-SPME-GC-MS analysis of wines

It was not possible to employ a single GC-MS procedure to quantify the 34 different aroma compounds measured in this study. Three different HS-SPME-GC-MS methods were required to achieve the desired separation and sensitivity needed for accurate quantitation. The procedure for sample and reagent preparation was the same as used in Chapter 5, in which composite standards were created from stock solutions, except that acidified water was not used for sample preparation in Method 1 or 2 below. Wine samples were frozen and stored at -3°C until analysis. All wines were analysed in triplicate (one sample from three of the same bottles). For analysis, wines were brought to room temperature, diluted 10-fold with deionised water, spiked with a composite internal standard mix and salted out with 4.5 g

sodium chloride. Each sample was incubated for 10 min at 60°C with agitation at 500 rpm. The volatile organic compounds were adsorbed onto the SPME fibre in the sample head space for 60 minutes and then liberated from the fibre following injection into the GC port (method 1 & 2).

Method 1

Analysis of nine esters, one C5 alcohol, three C6 alcohols, one aromatic aldehyde and one aromatic alcohol were quantified using procedures described in Kemp (2010). In brief, samples were run on a Shimadzu GC-MS-QP2010 gas chromatograph–mass spectrometer (Shimadzu Scientific Instruments PTY Ltd, Oceania, NSW Australia) equipped with a CTC Combi-Pal autosampler (CTC-Analytics AG, Switzerland). The chromatography configuration contained a short guard column (5m x 0.25mm ID, Restek, Bellefonte, PA, USA) connected to dual columns in series: a Rtx-wax column (30m x 0.25mm ID x 0.5µm film thickness, polyethylene glycol, Restek) and a Rxi-1MS column (15m x 0.25mm ID x 0.5µm film thickness, 100% dimethyl polysiloxane, Restek). This combined column set up has been found to be suitable for measuring a wide range of aroma chemicals (Green, Parr, Breitmeyer, Valentin, & Sherlock, 2011; Kemp, 2010). Prepared diluted samples (10-fold) were incubated and agitated for 10 minutes at 60°C and exposed to a 2 cm 24 gauge Stableflex 50/30 µm DVB/CAR/PDMS SPME fibre (p/n 57348-U, Supelco, Bellefonte, PA, USA, through Sigma- Aldrich, Australia) at 60°C for 60 minutes. The SPME fibre was then desorbed in the GC injection port at 270°C for 10 minutes.

The GC used helium as the carrier gas set at a linear velocity of 33.5 cm s⁻¹. The GC oven temperature was held at 35°C for 3 minutes then ramped to 250°C at 4°C min⁻¹ and then held at this temperature for 10 minutes. The interface and MS source temperatures were set at 250°C and 200°C respectively, with the MS source operated in electron impact (EI) mode at an ionization energy of 70 eV. The MS acquisition mode was set to full scan for all 16 compounds. The NIST05 (National Institute of Standards and Technology) mass spectral library was used to confirm the identities for all standards used. Quantification parameters for all compounds and labelled standards were as shown in Table 6.3.

Method 2

Analyses of 14 low concentration compounds (listed in Table 6.4) were performed using a similar procedure to method 1 except that the acquisition mode was set to selected ion monitoring (SIM) for all 14 aroma compounds. This required improved separation in order to ensure the required sensitivity to detect these compounds in Pinot noir by reducing the presence of co-eluting compounds. To achieve this, the GC oven temperature ramp was also altered.

The carrier gas flow of the GC was set at a constant linear velocity of 33.5 cm sec^{-1} . The GC oven temperature was held at 35°C for 3 minutes, increased to 105°C at $3^{\circ}\text{C min}^{-1}$ and held for 10 minutes, then increased to 140°C at $2^{\circ}\text{C min}^{-1}$ and held for 10 minutes, then further increased to 250°C at $4^{\circ}\text{C min}^{-1}$ and held for 10 minutes. The total GC-MS runtime was 101.33 minutes. Quantitative parameters for all compounds and labelled standards are shown in Table 6.4.

Method 3

A separate method was used for the analysis of 5 volatile fatty acids (VFAs), due to the specific SPME fibre extraction conditions needed to measure VFA's with low vapour pressures such as acetic acid. The VFA procedure uses the same column configuration as Method 1 but differs in the HS-SPME extraction conditions, carrier gas flow (linear velocity) and the GC oven temperature ramp which was increased to ensure faster analysis of VFA acids, as they typically elute at higher temperatures on wax (polyethylene glycol) based columns. The increased carrier gas flow and temperature ramp meant the VFA's eluted in a shorter runtime of 27.33 minutes. Method parameters and concentrations for the five VFA's can be found in Chapter 5. All wines were analysed in triplicate, as for Method 1 and 2.

Non-Volatile Chemical Analysis

Ethanol content, pH, tartaric acid, residual sugar, and CO_2 were measured using a WinescanTM (Foss). Free and total sulphur were measured using FIAstarTM system (FOSS).

Statistical Analysis

Analysis of variance and canonical correlation analysis (CCA) were calculated with Genstat 12.2 (VSN International Ltd). All data was standardized prior to CCA by subtracting the average of each attribute or chemical for the individual wine measurement and then dividing by standard deviation of each attribute or chemical.

Results

Sensory Analysis

Significant differences ($p < 0.05$) were found for 12 of the 19 aroma attributes (Table 6.2). Of the attributes that were perceived as significantly different ‘blackberry’, ‘jam’, ‘oak’, ‘plum’, ‘raspberry’, ‘smoky’ and ‘spice’ have been found to be significant to differentiate Pinot noir wines from Burgundy, British Columbia and California (Aubry, Etievant, Sauvageot, & Issanchou, 1999; Campo, Ballester, Langlois, Dacremont, & Valentin, 2010; Cliff & Dever, 1996; Girard, Yuksel, Cliff, Delaquis, & Reynolds, 2001; Guinard & Cliff, 1987). Regional differences are discussed in detail in Chapter 3.

HS-SPME-GC-MS

The concentration of all measured volatile aroma chemicals were found to vary significantly between wines ($p < 0.05$) (Table 6.5). When compared to their published perception thresholds (Table 6.5), the aroma compounds fell into three categories: those which were present in all wines at concentrations below their perception thresholds, those present in concentrations in wines both below and above their perception thresholds and those present in wines at concentrations that were always above their perception thresholds (Cooke et al., 2009; V. Ferreira, Lopez, & Cacho, 2000; Guth, 1997b; Lopez, Ferreria, Hernandez, & Cacho, 1999; Zea, Moyano, Moreno, Cortes, & Medina, 2001). β -damascenone, β -ionone, γ -nonalactone, benzaldehyde, butanoic acid, cis-3-hexen-1-ol, ethyl decanoate, 4-ethyl guaiacol, ethyl heptanoate, furfural, geraniol, 1-heptanol, hexanoic acid, hexanol, hexyl acetate, isobuteraldehyde and trans-3-hexen-1-ol were all present at concentrations below perception thresholds (thresholds determined in water or ethanol solution). In contrast, ethanoic acid, ethyl butanoate, ethyl hexanoate, ethyl isobutyrate, ethyl isovalerate, ethyl octanoate,

eugenol, isoamyl acetate, linalool, 3-methylbutanoic acid, 3-methyl-1-butanol, octanoic acid and 2-phenylethanol were always present at concentrations above their perception thresholds. Ethyl cinnamate and ethyl pentanoate were found in wines at concentrations both below and above their perception thresholds. The perception threshold for ethyl anthranilate and phenol is currently unknown.

It should be pointed out that the perception threshold of most aroma chemicals found in wine were determined in water, ethanol or synthetic wine solutions. These solutions have found to nor be representative of wine and the actual perception threshold of these chemicals in complex solutions, such as wine, is unknown. Additionally some compounds, such as β -damascenone have very different perception threshold depending on the solution composition; 2-9 ng/L in water (Buttery, Teranishi, Ling, & Turnbaugh, 1990), 50ng/L in a 10-12% ethanol solution (Aznar, Lopez, Cacho, & Ferreira, 2003; Ferreira, Ortin, Escudero, Lopez, & Cacho, 2002; Kotseridis, Baumes, Bertrand, & Skouroumounis, 1999), 4.5 μ g/L in sweet white wine (Etievant & Bayonove, 1983), and 4-7 μ g/L in wine (Kosteridis & Baumes, 2000; Kotseridis et al., 1999; Sabon, Revel, Kotseridis, & Bertrand, 2002). Therefore because of the variation and unknown importance of the currently known chemical perception thresholds, the odour activity values (OAV) have not been calculated or used in this study. OAV's provide information on which compounds are present at below and above their perception thresholds and since the actual perception thresholds are unknown for these compounds in wine, the importance of this value is unknown.

A significant difference between the regions was found for 21 of the 31 compounds ($p < 0.05$). The other ten compounds: β -damascenone, ethyl-2-methyl butanoate, ethyl hexanoate, ethyl pentanoate, ethyl decanoate, furfural, geraniol, hexanol, hexyl acetate and 1-heptanol showed no significant regional differences. The chemical concentrations also differed depending on the vintage, with all compounds except hexanol, hexyl acetate, 4-ethyl guaiacol and trans-3-hexen-1-ol found to be significantly different between the vintages when using ANOVA ($p < 0.05$ to < 0.001). Regional differences of the volatile fatty acids are discussed in Chapter 5.

Regional and vintage separation for aroma chemicals was not significant using CVA. This provides further evidence that the aroma composition of Pinot noir is very complex with more than one compound most likely responsible for a single sensory characteristic. While they were not significant, several trends can be seen in the data between the two vintages:

2007 wines had on average higher concentrations of geraniol, while 2008 wines had higher concentrations of 1-heptanol, ethyl decanoate, furfural and 2-phenyl ethanol. Further analysis investigating different groups of chemicals showed significant vintage differences, namely with the volatile fatty acids. Those results are discussed in detail in Chapter 5.

Few studies have measured the concentrations of volatile organic components in Pinot noir, specifically commercial New Zealand wines. However it was found that the concentrations of cis-3-hexen-1-ol, ethyl 2-methylpropanoate, ethyl 3-methylbutanoate, ethyl cinnamate, hexanol, and linalool are consistent with reported levels found in Oregon Pinot noir (Fang & Qian, 2006) and New Zealand Pinot noir research wine (Kemp, 2010). The concentration of ethyl butanoate, ethyl hexanoate, ethyl pentanoate, ethyl octanoate, ethyl decanoate, eugenol, γ -nonalactone and hexanol were all higher than those reported by Fang (2006) and Kemp (2010). The concentration of ethyl anthranilate, β -damascenone, geraniol, hexanol and trans-3-hexen-1-ol are lower than those reported by Fang (2006), Kemp (2010) and Aubry (1997). This current study is the first instance that the concentrations of ethyl heptanoate, 1-heptanol, isoamyl acetate, hexyl acetate, benzaldehyde, furfural and 2-methyl propanal of New Zealand Pinot noir have been reported. The differences in chemical composition of the studied wines and those reported by Fang (2006) and Aubry (1997) can be reasonably attributed to regional differences, as the Pinot noir wines studied by those researchers were commercial wines from Oregon and France.

The differences in chemical composition when compared to those reported by Kemp (2010) are more likely due to wine-making differences as Kemp's wines were research wines and the ones in this study were commercial wines. Additional differences were also found when comparing the results in this study to research wines made from grapes from the same regions in New Zealand. The concentrations of cis-3-hexenol-1-ol, β -damascenone, hexanol, hexyl acetate, isoamyl acetate and 2-phenyl ethanol were found to be the same as these experimental wines. The concentrations of ethyl 2-methylpropanoate, ethyl butanoate, ethyl 3-methylbutanoate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, 3-methyl-1-butanol, hexanol, trans-3-hexen-1-ol and linalool were found to be greater than those found in research wines. The concentration of ethyl 3-methylbutanoate was found to be lower than those in research wines. (Maharaj 2008; Rutan 2009) It is unknown if these differences are due to production techniques or the difference in winemaking-scale between research wines and commercial production.

Non-volatile Chemical Analysis

General chemical analysis that include pH, tartaric acid, ethanol, residual sugar, free and total sulphur and CO₂ (data not shown). All parameters were found to be non-significant ($p < 0.05$) when comparing regions and wines and excluded from the correlation analysis.

Correlations

CCA was used to determine linear combinations of sensory data and linear combinations of chemical data with the greatest correlations. The first five canonical correlations, shown in Table 6.6, explain 45% of the total variance. Of the sensory data only 'spice' aroma did not have a standardized weighting greater than 80% in any of the 19 correlations. Of the 34 aroma chemicals, 3-methyl-1-butanol, 4-ethyl guaiacol, β -ionone, ethyl isobutyrate, hexanol, ethyl anthranilate, furfural, γ -nonalactone, hexanoic acid, hexyl acetate, isoamyl acetate, phenol and trans-3-hexen-1-ol did not have standardized weightings greater than 80%.

Results from correlation 1 suggest that concentrations of ethyl octanoate, ethyl decanoate and 2-phenylethanol are related to the perceived intensity of 'black cherry', 'blackberry' and 'plum' aromas. Correlation 2 shows a relationship between the benzaldehyde and the aromas of 'jam' and 'oak' and the flavour of 'spice'. Other relationships include: ethyl butanoate, ethyl decanoate and 2-phenylethanol influencing fruit density/concentration (correlation 3); ethyl butanoate, ethyl decanoate, 2-phenylethanol, butyric acid and linalool effecting 'oak' aroma (correlation 4); and β -damascenone, 1-heptanol, geraniol, linalool and eugenol influencing 'dark fruit' and 'blackberry' aromas (correlation 5).

Discussion

Canonical correlation analysis was successful at calculating sensory and chemical relationships in Pinot noir. In particular the first two canonical correlations display the strongest relationships between the data. The percent variance of these canonical correlations (14.44% and 9.25%) may be considered low when compared to other studies (Pueyo, Martin-Alvarez, & Polo, 1995). However this is due to the large range of attributes and chemicals

within the calculation. Some studies have attempted to increase the percent variance of the canonical correlations by reducing the number of terms or combining several attributes and chemicals into one group (Aznar et al., 2003). Since there is very little information known on the sensory and chemical relationships in Pinot noir we did not want to reduce any terms as it is possible that this would mask an important result.

The results of the first two canonical correlations appear very promising for Pinot noir aroma due to information already known about the aroma chemicals that are important in these correlations. It has been found that in combination with other esters, ethyl octanoate is responsible for the 'red berry' aroma of Merlot and Cabernet Sauvignon (B. Pineau, Barbe, Leeuwen, & Dubourdieu, 2009). In this study for the first correlation (Table 6.6) ethyl octanoate, ethyl decanoate and 2-phenethyl alcohol display a negative correlation with 'black fruit' aromas and positive correlation with 'red fruit' aromas. This suggests that the presence of ethyl octanoate may be acting in the same way as in those other red wines and is influencing the perception of 'red berry' aromas in Pinot noir.

The second canonical correlation suggests that benzaldehyde was related to 'oak' and 'jam' aromas and 'spice' flavour. By comparing the sensory intensity of these three attributes with wines that contained high and low concentrations of benzaldehyde, it was apparent that wines with higher concentrations of benzaldehyde were perceived as having greater intensities of 'oak' and 'spice' aromas and less intense 'jam' aroma. In wine, benzaldehyde is a fermentation product (Brander, Kepner, & Webb, 1980) and also influenced by oak. The concentration of benzaldehyde varies based on usage of oak and the origin of the oak wood (Cadahia, Simon, & Jalocha, 2003). Additionally benzaldehyde is formed in the grape and has been found to influence fruity aromas in wine (Ducret, 1984; Notte, M, & Liuzzi, 1992). It is likely that the second correlation describes a genuine influence of benzaldehyde on the aroma of Pinot noir.

Perception of aroma in Pinot noir is not clearly understood. Generally speaking, the aroma of a wine may be described in several ways. Aroma may be dominated by a single impact compound such as cis-rose oxide in Gerwurtraminer and linalool in Muscat (Guth, 1997a; P. Ribereau-Gayon, J. H. Boidron, & A. Terrier, 1975). Other wines are characterised by the presence of a family of compounds, such as methoxypyrazines and thiols in Sauvignon blanc (Tominaga, Furrer, Henry, & Dubourdieu, 1998). Normally the aroma of white wine can be

described by impact compounds or a family compounds, but the same is not true for red wines, with the exception of rotundone found in Shiraz wines (Wood et al., 2008). Red wines, including Pinot noir, typically do not have a specific aroma but instead are composed of many subtle aromas, as they are lacking in impact compounds (V. Ferreira, 2010; V. Ferreira, Escudero, Campo, & Cacho, 2007). Unlike the wines mentioned above, Pinot noir aroma cannot be described by the aroma of only one volatile compound or family of aroma compounds but is composed of many subtle nuances that are most likely due to a range of volatile compounds.

Another reason that Pinot noir aroma is complex is how aroma perception changes when chemicals are present in mixtures, as wine can contain hundreds of different aroma chemicals (V. Ferreira et al., 2007). For instance, research has shown that the perception threshold of several terpenes in a mixture is lower than the individual perception thresholds of these compounds. Ribereau-Gayon et al. (1975) determined that the perception threshold of linalool and geraniol together ($<90 \mu\text{g/L}$) was lower than the individual perception thresholds of linalool ($100 \mu\text{g/L}$) and geraniol ($132 \mu\text{g/L}$). Additionally chemicals may alter the perception threshold of compounds from a different class. For example, β -damascenone, a norisoprenoid, was found to lower the observed threshold of ethyl hexanoate and ethyl cinnamate (two esters), thereby increasing the fruity aroma of wine (Ferreira et al., 2002; B Pineau, Barbe, van Leeuwen, & Dubourdieu, 2007). Therefore just because the concentrations of many of the aroma compounds are present at much lower concentrations than their perception thresholds, does not mean that these compounds do not influence perceived aroma. Therefore it is not possible to discount the importance of chemicals that are present at very low concentrations and only focus on those found at concentrations above the determined perception threshold.

The role of some aroma compounds is undefined in Pinot noir, while their roles are well defined in other wines. For example, ethyl esters are considered to be very important to the perception of fruity aroma in red wine and for Cabernet sauvignon, Cabernet franc, Merlot and Grenache are typically found in concentrations much higher than their reported perception thresholds (Kosteridis & Baumes, 2000; Lopez, Ferreira, Hernandez, & Cacho, 1999; Sabon et al., 2002; Tao, Li, Wang, & Zhang, 2008; Zhang, Xu, Duan, Qu, & Wu, 2007). However the concentrations of these esters are typically much lower in Pinot noir and therefore are not considered to be important factors contributing to its aroma (V. Ferreira,

2010). This same conundrum occurs with the majority of the other aroma compounds found in Pinot noir. Nevertheless the canonical correlations presented in this research do provide important clues to the perception of aromas in Pinot noir and to how this wine differs from other red wines.

Conclusions

Canonical correlation analysis results suggested that the aroma nuances of Pinot noir are complicated with many different combinations of aroma chemicals responsible for specific aromas. The compounds and aromas involved in the first correlation displayed some similarities of Pinot noir with other wines, in that with ethyl octanoate, ethyl decanoate and 2-phenyl ethanol were associated with fruity aromas. Combined with what is known about the aroma of compounds in other wines, and how such compounds behave when in mixtures, the canonical correlation results suggest relationships for which aroma compounds are important for specific aroma attributes. In order to determine the validity of these canonical correlation results, sensory tests would need to be performed that investigate the influence of varying concentrations of the individual compounds or combinations of these compounds, with the chosen compound as the only difference in the tested wine or solution. This may prove to be challenging as reconstitution tests have proven to not be representative of actual wines (Escudero et al., 2004). Nevertheless, such a re-construction investigation was attempted and is the subject of the following chapter.

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Tables and Figures

Table 6.1

New Zealand Pinot noir wines analysed.

Wine Product	Vintages	Code	Region
Mt Difficulty	2007, 2008	C1, C5	Central Otago
Montana “Terroir Series” Gabriel’s Gully	2007	C2	Central Otago
Gibbston Valley	2007, 2008	C3, C6	Central Otago
Amisfield	2007, 2008	C4, C8	Central Otago
Craggy Range “Zebra Vineyard”	2008	C7	Central Otago
Stoneleigh Rapaura Series	2007, 2008	M1, M5	Marlborough
Montana “Terroir Series” Forgotten Valley	2007	M2	Marlborough
Brancott Estate Reserve	2007, 2008	M3, M6	Marlborough
Brancott Estate Terraces “T”	2007, 2008	M4, M8	Marlborough
Villa Maria Southern Clays	2008	M7	Marlborough
Martinborough Vineyard	2007, 2008	N1, N5	Martinborough
Palliser Estate	2007, 2008	N2, N6	Martinborough
Escarpment	2007, 2008	N3, N7	Martinborough
Ata Rangi	2007, 2008	N4, N8	Martinborough
Camshorn	2007, 2008	W1, W5	Waipara
Muddy Water “Hare’s Breath”	2007, 2008	W2, W6	Waipara
Greystone	2007, 2008	W3, W7	Waipara
Pegasus Bay	2007, 2008	W4, W8	Waipara

Table 6.2

Multiple Comparison (Tukey) of the average intensity from a 100mm Visual Analog Scale of 19 aroma and flavour attributes for New Zealand Pinot noir.

Barnyard (p<0.001)			Black cherry (p<0.001)			Blackberry (p<0.001)		
Wine	Intensity	Conf. Int ^a .	Wine	Intensity	Conf. Int ^a .	Wine	Intensity	Conf. Int ^a .
N8	8.5	A	M6	31.1	A	M7	30.1	A
N6	10.6	A	M7	33.2	AB	N7	32.6	AB
N5	10.8	AB	W6	38.5	ABC	W6	34.7	AB
M6	11.3	AB	C7	39.8	ABCD	M6	36.9	AB
M7	11.3	ABC	C5	40.5	ABCD	W7	37.1	AB
M8	11.7	ABC	M5	42.3	ABCDE	M8	37.7	AB
M5	13.5	ABC	N5	43.2	ABCDE	N5	38.2	AB
C3	13.5	ABC	N7	43.7	ABCDE	N6	39.8	AB
M1	13.8	ABC	W5	43.7	ABCDE	W5	40.5	AB
C7	14.2	ABC	N8	44.8	ABCDE	C6	40.8	AB
W1	15.9	ABC	N6	45.6	ABCDE	C5	41.5	AB
W7	16.2	ABC	W7	46.1	ABCDE	M5	42.3	AB
M2	16.4	ABC	C6	46.3	ABCDE	C7	44.1	AB
N4	16.9	ABC	C1	47.2	ABCDE	C1	45.3	AB
N7	17.1	ABC	M8	47.6	ABCDE	C2	45.8	AB
C8	17.5	ABC	C8	47.8	ABCDE	M2	46.2	AB
W6	18.0	ABC	W4	48.8	ABCDE	C8	47.2	AB
C5	18.0	ABC	W2	49.4	ABCDE	M3	47.5	AB
C2	18.1	ABC	W8	50.0	ABCDE	C4	47.7	AB
C6	18.3	ABC	W1	50.2	BCDE	W8	48.2	AB
M4	18.7	ABC	C2	51.2	BCDE	W4	48.6	B
C1	19.9	ABC	M2	51.8	CDE	W1	49.1	B
W2	20.5	ABC	C4	51.9	CDE	M1	49.1	B
W5	21.4	ABC	M1	52.6	CDE	N3	49.2	B
C4	21.4	ABC	N2	52.9	CDE	C3	49.2	B
M3	22.5	ABC	C3	53.7	CDE	N8	49.2	AB
N2	22.9	ABC	W3	54.2	CDE	W3	49.9	B
N3	23.0	ABC	M3	55.5	CDE	N4	50.3	B
N1	23.1	ABC	N3	55.9	CDE	M4	50.4	B
W4	25.7	BC	N4	56.3	CDE	W2	50.5	B
W3	26.9	C	N1	58.0	DE	N2	50.5	B
W8	28.7	C	M4	60.4	E	N1	50.7	B

Chocolate (p=0.120)			Dark Fruit (p<0.001)			Fruit Density/Concentration (p<0.001)		
Wine	Intensity	Conf. Int ^a ..	Wine	Intensity	Conf. Int ^a ..	Wine	Intensity	Conf. Int ^a ..
M6	20.4	A	N7	36.7	A	N7	43.3	A
C6	22.8	A	M7	37.7	A	C5	45.8	A
M7	23.4	A	M6	40.5	AB	C2	47.4	A
W6	25.7	A	C5	43.4	ABC	M7	48.5	A
W2	26.2	A	C2	46.2	ABC	W5	48.8	A
C3	27.0	A	W6	46.4	ABC	M1	49.9	A
W3	27.0	A	W8	46.7	ABC	M2	50.3	A
W4	28.4	A	W5	46.8	ABC	W8	51.1	A
C1	28.4	A	M8	46.9	ABC	W1	51.3	A
C2	28.7	A	C6	47.6	ABC	N2	51.5	A
N5	29.3	A	W7	48.2	ABC	C4	51.7	A
N3	29.7	A	N5	48.8	ABC	N3	51.6	A
M2	30.4	A	N6	48.9	ABC	W3	51.7	A
M8	30.4	A	M1	49.2	ABC	W6	51.9	A
M3	30.7	A	W1	49.6	ABC	C8	52.7	A
C8	30.8	A	M2	49.8	ABC	C1	52.7	A
M5	30.9	A	W3	49.9	ABC	N6	52.8	A
W1	30.9	A	C8	50.7	ABC	C4	53.2	A
W7	31.8	A	C4	50.7	ABC	N8	53.7	A
C4	32.3	A	M5	51.3	ABC	M5	53.8	A
M1	32.4	A	C7	51.3	ABC	M8	53.9	A
N6	32.5	A	C3	51.3	ABC	C7	55.4	A
N7	32.6	A	C1	51.8	ABC	C3	55.8	A
N1	33.3	A	N3	51.8	ABC	W2	56.3	A
N4	33.5	A	N8	52.4	ABC	M3	56.6	A
C5	33.7	A	M3	53.2	ABC	N5	56.6	A
W5	34.4	A	N2	53.7	ABC	N4	57.0	A
W8	34.7	A	W2	54.6	BC	W4	57.8	A
N8	35.8	A	M4	55.6	BC	M4	57.8	A
M4	35.9	A	W4	56.6	BC	N1	59.4	AB
N2	35.9	A	N4	57.2	BC	M6	59.7	AB
C7	36.8	A	N1	57.6	C	W7	79.6	B

^a – for each attribute, values described by the same letters do not differ significantly (p<0.05)

Table 6.2 Continued

Herbal (p<0.001)

Wine	Intensity	Conf. Int ^a ..
M5	21.7	A
M5	22.4	A
W7	22.6	A
W5	22.9	A
M7	24.3	A
N8	24.8	A
C7	25.3	AB
M6	27.7	AB
W6	28.3	AB
M2	28.3	AB
C5	28.7	AB
C2	29.7	AB
M1	29.8	AB
N6	29.9	AB
M8	30.0	AB
N7	30.0	AB
C6	30.1	AB
M4	32.1	AB
C3	32.6	AB
M3	33.4	AB
C4	33.8	AB
C1	34.4	AB
W4	36.3	ABC
W8	36.3	ABC
N1	36.3	ABC
N4	36.4	ABC
W3	38.0	ABC
N3	38.8	ABC
N2	39.1	ABC
C8	41.3	ABC
W1	43.4	BC
W2	51.8	C

Jam (p<0.001)

Wine	Intensity	Conf. Int ^a ..
M7	23.2	A
N6	24.7	A
M8	25.7	A
C7	26.0	A
M5	26.3	A
N5	28.6	A
C6	29.0	A
C5	29.5	AB
N8	30.9	AB
W8	31.3	AB
W4	33.3	AB
M6	33.8	AB
M4	35.0	AB
W2	35.1	AB
M1	35.4	AB
C4	36.0	AB
C1	36.5	AB
W6	36.6	AB
W7	37.2	AB
W5	37.5	AB
W3	37.5	AB
C8	37.6	AB
C2	37.9	AB
C3	38.3	AB
N3	38.6	AB
M3	38.7	AB
N2	38.9	AB
N4	40.0	AB
M2	40.2	AB
N1	40.9	AB
N7	41.1	AB
W1	50.6	B

Oak (p<0.001)

Wine	Intensity	Conf. Int ^a ..
M6	34.7	A
C8	37.5	AB
W6	37.9	ABC
C7	38.5	ABC
N7	39.1	ABC
W7	39.1	ABC
W1	40.8	ABC
N5	41.8	ABCD
M7	44.4	ABCD
C1	44.4	ABCD
C6	43.9	ABCD
N8	44.1	ABCD
W4	44.5	ABCD
C3	44.6	ABCD
N6	44.7	ABCD
W2	45.0	ABCD
W5	45.5	ABCD
M2	45.6	ABCD
N3	45.9	ABCD
C2	46.0	ABCD
M1	46.3	ABCD
C5	47.0	ABCD
M4	47.2	ABCD
C4	47.4	ABCD
M3	47.5	ABCD
M8	47.6	ABCD
W3	48.8	ABCD
N4	51.6	BCD
W8	53.0	BCD
N2	53.7	CD
N2	53.7	BCD
M5	53.9	D

Plum (p<0.001)

Wine	Intensity	Conf. Int ^a ..
C7	33.7	A
M7	34.8	A
W6	35.7	A
C6	36.3	A
N6	37.4	AB
N5	39.8	AB
N8	40.0	AB
M6	40.5	AB
W7	40.7	AB
M5	40.8	AB
M8	40.8	AB
C5	43.0	AB
W8	43.6	AB
C8	44.0	AB
W5	44.9	AB
C1	46.3	AB
W2	46.4	AB
N3	46.6	AB
W4	46.7	AB
N7	47.1	AB
N2	47.3	AB
M4	47.3	AB
C4	47.6	AB
M3	47.7	AB
M1	48.2	AB
C3	48.3	AB
W3	48.9	AB
M2	49.0	AB
W1	50.6	AB
C2	50.7	AB
N4	53.9	B
N1	54.1	B

Raspberries (p<0.001)

Wine	Intensity	Conf. Int ^a ..
C8	26.1	A
N2	26.6	A
W2	28.0	A
N1	29.0	A
N4	31.6	AB
C1	32.2	AB
W8	33.1	AB
W5	33.2	AB
C6	33.4	AB
W6	33.8	AB
N6	33.9	AB
M5	34.7	AB
W3	35.6	AB
M4	35.6	AB
N3	36.0	AB
M8	36.3	AB
C4	36.3	AB
N7	36.5	AB
W4	36.6	AB
M2	37.1	AB
N8	38.2	AB
C2	38.3	AB
W7	38.5	AB
C7	38.5	AB
C5	38.9	AB
M1	39.0	AB
C3	39.3	AB
M3	41.2	AB
N5	41.9	AB
W1	42.6	AB
M7	42.8	AB
M6	51.4	B

Red Cherry (p=0.010)

Wine	Intensity	Conf. Int ^a ...
N6	29.1	A
N2	29.6	AB
C6	30.8	ABC
N1	31.9	ABC
W6	32.1	ABC
W2	35.3	ABC
N3	35.6	ABC
M8	35.9	ABC
N8	36.1	ABC
C1	36.2	ABC
C2	36.3	ABC
C8	36.9	ABC
W5	37.4	ABC
M7	37.8	ABC
M2	38.0	ABC
C4	38.3	ABC
W3	38.6	ABC
C5	38.9	ABC
M3	39.0	ABC
M4	39.0	ABC
C3	39.7	ABC
W1	40.4	ABC
W7	40.5	ABC
W4	40.9	ABC
N4	40.9	ABC
M5	41.7	ABC
M1	41.7	ABC
W8	42.5	ABC
C7	44.8	ABC
N5	46.1	ABC
N7	46.7	ABC
M6	49.8	A C

Table 6.2 Continued

Red Fruit (p=0.119)

Wine	Intensity	Conf. Int ^a ..
C8	41.4	A
C6	43.1	A
W8	43.5	A
N6	43.9	A
N2	44.0	A
N1	44.1	A
W2	44.7	A
W4	45.1	A
C1	45.4	A
M8	45.9	A
N3	46.6	A
N4	47.3	A
C4	47.3	A
W5	48.1	A
C2	48.7	A
M2	49.1	A
M1	49.1	A
W6	49.2	A
M5	49.2	A
C7	49.3	A
N5	49.3	A
W3	49.7	A
C3	49.8	A
N8	49.8	A
M7	49.9	A
M3	50.5	A
C5	51.3	A
W1	51.5	A
N7	52.1	A
M4	53.3	A
W7	56.0	A
M6	60.8	A

Savoury (p<0.001)

Wine	Intensity	Conf. Int ^a ..
N7	35.2	A
C7	35.5	A
N8	36.2	A
M8	37.6	A
W5	37.6	A
M2	38.1	A
M5	38.9	A
W6	39.6	AB
N5	40.5	AB
M1	40.5	AB
C2	41.2	AB
W7	42.0	AB
M6	42.3	AB
C3	42.3	AB
M4	42.6	AB
C6	43.0	AB
W4	43.2	AB
C4	43.3	AB
M7	43.4	AB
C5	43.7	AB
C8	44.0	AB
C1	44.9	AB
W8	45.1	AB
M3	45.3	AB
W1	45.5	AB
W2	45.6	AB
N6	45.8	AB
W3	47.5	AB
N3	49.1	AB
N4	50.0	B
N2	54.0	B
N1	54.4	B

Smoky (p<0.001)

Wine	Intensity	Conf. Int ^a ..
M6	24.8	A
C7	29.0	AB
W1	29.8	AB
N5	30.8	AB
M7	31.8	AB
W6	31.8	AB
C3	31.8	AB
C2	32.1	AB
C1	32.4	AB
W5	32.5	AB
M2	32.9	AB
W7	33.0	AB
C6	33.2	AB
C8	33.2	AB
W4	33.5	AB
C4	34.0	AB
M4	34.6	AB
M8	35.1	AB
N8	35.4	AB
C5	36.8	AB
M3	36.8	AB
M1	37.1	AB
W2	37.4	AB
N6	37.4	AB
N7	38.1	AB
W8	39.0	AB
W3	39.3	AB
M5	39.7	AB
N4	40.6	AB
N3	40.8	AB
N1	45.5	AB
N2	52.4	B

Spice (p=0.007)

Wine	Intensity	Conf. Int ^a ...
M6	35.6	A
W5	37.0	A
C7	37.3	A
W6	37.9	A
N5	39.0	A
N7	39.2	A
M7	39.8	A
W7	40.1	A
C5	40.1	A
M5	41.1	A
N8	41.7	A
C6	42.0	A
M2	43.0	A
C1	43.3	A
C2	43.6	A
M8	43.6	A
C8	44.3	A
W8	44.9	A
M3	45.3	A
C3	45.9	A
W3	46.0	A
W1	46.3	A
M1	46.6	A
W2	46.8	A
C4	47.2	A
N4	47.7	A
N6	48.0	A
W4	48.1	A
N2	49.1	A
N1	50.0	A
M4	50.1	A
N3	50.1	A

Spice (p=0.023)

Wine	Intensity	Conf. Int ^a ..
C8	39.0	A
W7	39.6	A
N7	40.2	A
C2	42.2	A
C5	42.6	A
M6	43.0	A
W5	43.1	A
M2	43.6	A
M7	43.6	A
C7	44.6	A
W6	44.8	A
M8	45.1	A
C1	46.6	A
M1	46.7	A
N3	47.5	A
W3	47.6	A
N5	47.7	A
N4	47.7	A
W1	48.4	A
N8	48.5	A
C3	48.5	A
W4	48.7	A
N6	49.2	A
C4	49.5	A
C6	50.1	A
W8	50.2	A
M4	50.5	A
W2	50.8	A
M5	51.5	A
M3	51.8	A
N1	51.9	A
N2	52.2	A

Strawberries (p<0.001)

Wine	Intensity	Conf. Int ^a ..
C6	21.6	A
N6	21.6	A
N1	21.8	A
N2	22.9	AB
W2	23.1	AB
W8	24.1	AB
N4	24.5	AB
C8	24.6	AB
W5	24.6	AB
M7	25.3	AB
C1	25.7	AB
N3	25.9	AB
C2	26.1	AB
W4	26.6	AB
C5	26.7	AB
M8	26.8	AB
C4	26.8	AB
M3	27.1	AB
W3	27.2	AB
W6	27.4	AB
M4	27.5	AB
M2	27.8	AB
M5	27.9	AB
M1	29.0	AB
N5	29.4	AB
C7	31.4	AB
W7	31.5	AB
N8	32.2	AB
C3	32.3	AB
N7	35.2	AB
W1	37.3	AB
M6	43.8	B

Table 6.3

Quantification parameters for the compounds in Method 1

Analyte	ISTD ^a	Ret. Time (min)	Target Ion m/z	Confirming Ions m/z (% to Target Ion)	Calibration Range ^b (µg/L)	Standard Curve (R ²) ^c	Purity	CAS No.	Rec. (%)	LOD (µg/L)	LOQ (µg/L)	Source
d5-ethyl butanoate	(1)	7.53	71	88 (33.41), 116 (31.65)			100					Lincoln
d3-isoamyl acetate	(2)	11.899	46	90 (18.19), 76 (9.82)			100					Lincoln
d5-ethyl hexanoate	(3)	16.109	93	120 (8.90), 34 (17.56)			100					Lincoln
d13-hexan-1-ol	(4)	18.675	64	50 (35.49), 78 (31.13)			98	16416-34-5				Sigma-Aldrich
d5-ethyl octanoate	(5)	22.985	93	106 (36.32), 74 (29.03)			100					Lincoln
d6-benzaldehyde	(6)	24.02	110	54 (36.98), 82 (88.45)			98	17901-93-8				Sigma-Aldrich
d5-ethyl decanoate	(7)	29.273	93	106 (43.61), 148 (4.84)			97					Lincoln
1-phenyl-d5-ethanol	(8)	29.3	93	84 (85.99), 127 (26.95)			98	90162-45-1				Isotech
Ethyl 2-methyl propanoate	1	7.53	71	88 (33.41), 116 (31.65)	0-93.9	0.9984	99	97-62-1	104	0.038	0.128	Sigma-Aldrich
Ethyl butanoate	1	9.359	88	101 (16.9), 60 (32.16)	0 – 45.12	0.9993	99	105-54-4	99	0.018	0.172	Sigma-Alrich
Ethyl 2-methyl butanoate	1	10.429	88	85(73.60), 57 (51.36)	0 – 9.76	0.9994	98	108-64-5	106	0.037	0.123	Sigma-Aldrich
Isoamyl acetate	2	11.997	43	87 (18.65), 73 (11.56)	0-365.85	0.9942	99	123-92-2	100	0.769	2.563	Sigma-Aldrich
Ethyl pentanoate	1	12.455	88	85 (94.39), 101 (30.90)	0 – 1.22	0.9979	98	539-82-2	99	0.006	0.019	Sigma-Aldrich
3-methyl-1-butanol	4	14.757	55	42 (), 70()	0 – 24390.2	0.997	99	123-51-3	97	11.807	39.357	Sigma-Aldrich
Ethyl hexanoate	3	16.239	88	115 (10.04), 60 (31.02)	0 – 73.17	0.9998	99	123-66-0	103	0.058	0.193	Sigma-Aldrich
Hexanol	4	19.00	56	55 (52.03), 84 (6.50)	0 – 609.76	0.9998	99	111-27-3	100	0.085	0.283	Sigma-Aldrich
Trans-3-hexen-1-ol	4	19.20	67	82 (64.50)	0 – 36.59	0.9992	98	928-97-2	99	0.011	0.037	Sigma-Aldrich
Ethyl heptanoate	3	19.702	88	113 (36.28)	0 – 1.22	0.9990	98	106-30-9	102	0.027	0.091	Sigma-Aldrich
Cis-3-hexen-1-ol	4	19.90	67	82 (48.46), 107 (15.82)	0 – 36.359	0.9996	98	928-96-1	98	0.011	0.038	Sigma-Aldrich
Ethyl octanoate	5	23.116	88	101 (38.67), 129 (11.52)	0 – 61.0	0.9992	99	106-32-1	96	0.039	0.234	Sigma-Aldrich
Benzaldehyde	6	24.0	106	21 (33.56), 77 (90.85)	0 – 2.44	0.9998	98	100-52-7	97	0.163	0.545	Sigma-Aldrich
Ethyl decanoate	7	29.396	88	101 (43.47), 143 (5.48)	0 – 48.8	0.9872	99	110-38-3	105	0.088	0.293	Sigma-Aldrich
2-Phenylethanol	8	29.4	88	92 (57.09), 122 (31.51)	0 – 4878	0.9958	99	60-12-8	99	1.188	3.959	Sigma-Aldrich

^a ISTD = internal standard , ^b 1/10 dilution

Table 6.4

Quantification parameters for the compounds in Method 2

Analyte	ISTD ^a	Ret. Time	Target	Confirming Ions m/z	Calibration Range ^b	Standard	Purity	CAS No.	Rec.	LOD	LOQ	Source
		(min)	Ion m/z	(% to Target Ion)	(µg/L)	Curve (R ²)			(%)	(µg/L)	(µg/L)	
d13-hexan-1-ol	(1)	24.79	64	50 (35.49), 78 (31.13)			98	16416-34-5				Sigma-Aldrich
1-phenyl-d5-ethanol	(2)	54.37	112	84 (85.99), 127 (26.95)			98	90162-45-1				Isotech
d12-hexanal	(3)	13.307	48	64 (61.16), 80 (24.38)			98	66-25-1				CDN isotopes
d3-hexyl acetate	(4)	22.517	46	64 (27.93), 84 (22.46)			99					Lincoln
d4-furfural	(5)	29.503	100	98 (89.95), 42 (85.70)			98	98-01-1				Lincoln
d3-linalool	(6)	37.583	121	136 (30.11)			99	78-70-6				CDN isotopes
d2-β-ionone	(7)	67.3	180	46 (80.49)			100					Lincoln
delta-Nonalactone	(8)	73.157	99	71 (59.93), 42 (58.16)			98	3301-94-82				SAFC®
2-methylpropanol	3	4.937	72	27 (279.50), 41 (219.82)	0 – 9.757	0.9999	99	78-84-2	93	0.046	0.157	Sigma-Aldrich
Hexyl Acetate	4	22.517	43	56 (62.82), 67 (1.89)	0 – 2.439	0.9994	99	142-92-7	100	0.019	0.064	Sigma-Aldrich
Furfural	5	29.25	96	95 (92.04), 39 (68.48)	0 – 146.3	0.9999		98-01-1	95	0.044	0.146	Sigma-Aldrich
1-heptanol	1	30.43	57	39 (84.40), 83 (34.16)	0 – 48.8	0.9994	99	111-70-6	108	0.142	0.473	Sigma-Aldrich
Linalool	6	37.583	121	136 (30.11)	0 – 7.805	0.9989		78-70-6	98	0.030	0.101	Sigma-Aldrich
β-damascenone	7	57.58	190	91 (60.73), 105 (42.66)	0 – 1.951	0.9995		23696-85-7	105	0.009	0.028	SAFC®
Geraniol	1	58.623	69	41 (91.88), 93 (14.96)	0 – 0.781	0.9988		203-377-1	97	0.009	0.029	Sigma-Aldrich
β-ionone	7	67.46	177	43 (99.80)	0 – 1.463	0.9989	96	14901-07-6	103	0.009	0.029	Sigma-Aldrich
Phenol	2	68.267	94	66 (39.01)	0 – 1.951	0.9970	99	108-95-2	101	0.024	0.080	Sigma-Aldrich
4-ethyl guaiacol	8	70.51	137	152 (34.08), 122 (14.96)	0 – 1.463	0.9996	98	2785-89-9	105	0.005	0.018	Sigma-Aldrich
γ-nonolactone	8	70.693	100	114 (54.15), 128 (46.39)	0 – 9.8	0.9986		104-61-0	116	0.039	0.131	Sigma-Aldrich
Ethyl cinnamate	8	75.463	131	103 (82.39), 77 (50.82)	0 – 1.95	0.9986	99	103-36-6	91	0.004	0.014	Sigma-Aldrich
Eugenol	2	76.383	164	149 (45.76)	0 – 4.878	0.9989	98	97-53-0	92	0.011	0.036	Sigma-Aldrich
Ethyl anthranilate	8	79.606	92	165 (31.82)	0 – 0.976	0.9959		87-25-2	55 ^d	0.002	0.008	Sigma-Aldrich

^a ISTD = internal standard^b 1/10 dilution^c Ms factor details the change in the total gain needed for each compound. The original program used a total gain of 1.5kV.^d Underestimated recovery result shows deltanonalactone was not suitable as the internal standard, however a labelled phenolic ester was not available during analysis, a recovery factor was used in the final calculation of the results to take account the low recovery

Table 6.5

Multiple Comparison (Tukey) of the average concentration ($\mu\text{g/L}$) found in Pinot noir for the 34 Measured compounds.

Ethyl 2-methylpropanoate ($p<0.001$)*Perception threshold – 18^a*

Wines	conc	Conf. Int ^a ..
N5	103.6	A
W2	113.8	AB
N1	114.2	AB
N4	132.2	ABC
N2	132.6	ABC
W3	139.9	ABCD
W1	153.3	ABCDE
C2	171.6	ABCDEF
M2	176.5	ABCDEFG
N3	185.2	BCDEFGH
M3	189.9	CDEFGH
M7	193.9	CDEFGHI
W7	197.3	CDEFGHI
N8	204.2	CDEFGHI
M1	211.2	DEFGHI
W4	221.0	EFGHIJ
C3	222.1	EFGHIJ
M4	228.6	FGHIJ
N7	230.8	FGHIJ
C7	242.7	FGHIJK
M8	247.6	GHIJK
C1	249.2	GHIJK
C4	253.8	HJKLM
W5	264.8	IJKLM
C8	290.2	JKLMN
W6	308.2	JKLMN
M5	322.8	LMNO
C6	332.9	MNO
C5	366.2	NO
M6	380.7	NO
N6	384.5	O
W8	558.8	P

Ethyl butanoate ($p<0.001$)*Perception threshold – 20^a*

Wines	conc	Conf. Int ^a ..
C2	116.4	A
W6	134.9	AB
C1	143.8	ABC
W3	155.3	ABCD
W1	161.9	BCDE
M3	164.8	BCDE
C3	165.6	BCDE
N3	165.8	BCDE
M1	167.0	BCDE
M2	167.2	BCDE
M4	169.7	BCDE
W4	177.3	CDEF
W2	178.1	CDEF
M7	178.3	CDEF
N1	179.7	CDEF
C4	185.7	DEFG
N2	197.6	EFGH
N7	198.6	EFGH
W5	209.3	FGH
M6	213.3	FGH
M8	214.2	FGHI
C5	216.0	FGHI
C6	219.6	GHI
N4	234.1	IJK
W7	253.5	JK
W8	271.0	JK
N5	272.4	JK
N6	272.8	JK
C8	276.1	K
M5	286.2	K
C7	289.4	K
N8	339.9	L

Ethyl 3-methylbutanoate($p<0.001$)*Perception threshold – 3^a*

Wines	conc	Conf. Int ^a ..
W2	11.6	A
N2	20.9	AB
W3	22.0	ABC
W1	24.4	ABCD
N4	24.8	ABCD
C1	24.9	ABCD
N5	25.2	ABCD
C2	25.2	ABCD
N1	25.5	BCD
W6	26.7	BCD
M1	29.0	BCDE
M7	29.7	BCDE
C3	30.7	BCDEF
W7	31.1	BCDEF
M2	31.2	BCDEF
M6	31.7	BCDEFG
N3	31.8	BCDEFG
M3	33.3	BCDEFGH
C4	34.6	CDEFGH
N7	34.9	CDEFGH
N8	35.7	DEFGHI
W4	37.0	DEFGHI
M4	41.3	EFGHIJ
C7	41.6	EFGHIJ
C8	43.7	FGHIJ
M5	44.8	GHIJ
W5	45.4	IJK
C6	45.5	IJK
M8	49.1	IJK
W8	51.0	J
C5	51.6	J
N6	51.8	J

Ethyl pentanoate ($p<0.001$)*Perception Threshold – 1.5^b*

Wines	conc	Conf. Int ^a ..
M1	0.9	A
C2	1.1	AB
M2	1.3	ABC
N3	1.4	ABCD
M3	1.5	ABCD
N1	1.5	ABCD
W6	1.6	ABCD
N4	1.6	ABCD
W1	1.7	ABCD
N7	1.7	ABCD
M7	1.7	ABCD
W5	1.8	ABCD
N5	1.9	ABCD
M6	1.9	ABCD
W4	1.9	ABCD
C5	1.9	ABCD
C4	2.0	ABCD
W7	2.1	ABCD
C3	2.1	ABCD
M4	2.1	ABCD
C1	2.2	ABCD
W8	2.2	ABCDE
C6	2.4	ABCDE
N2	2.4	ABCDE
M8	2.7	ABCDE
C7	2.8	ABCDE
W2	2.8	ABCDE
M5	3.1	BCDE
W3	3.1	BCDE
N6	3.3	CDE
N8	3.4	DE
C8	4.3	E

Ethyl hexanoate ($p<0.001$)*Perception threshold – 5^c*

Wines	conc	Conf. Int ^a ..
W1	299.3	A
C1	320.7	A
W6	328.3	A
W2	331.3	A
C2	334.7	A
M1	334.9	A
N2	339.2	A
N1	339.2	A
N7	346.2	A
M7	350.3	A
M4	358.3	A
M3	361.4	A
C4	364.5	A
M2	370.8	AB
C3	376.2	AB
C5	378.9	AB
M8	387.0	ABC
W4	396.9	ABC
M6	404.2	ABCD
C6	408.2	ABCD
M5	409.9	ABCD
N4	425.4	ABCD
N5	437.8	ABCD
W3	446.8	ABCDE
N6	452.6	ABCDE
W5	453.5	ABCDE
W8	525.6	BCDE
N8	535.7	CDE
C7	539.0	CDE
C8	557.4	DE
W7	559.4	DE
N3	593.8	E

Ethyl heptanoate ($p<0.001$)*Perception threshold – 220^d*

Wines	conc	Conf. Int ^a ..
M6	2.6	A
M1	2.9	AB
M2	3.0	AB
W6	3.1	AB
N3	3.2	AB
N7	3.5	ABC
M7	3.5	ABC
C2	3.6	ABCD
N5	3.6	ABCD
M3	3.8	ABCD
M5	3.9	ABCDE
M4	4.0	ABCDE
M8	4.0	ABCDE
W8	4.1	ABCDE
W5	4.1	ABCDE
C7	4.1	ABCDE
C5	4.2	ABCDEF
W4	4.3	ABCDEF
N8	4.3	ABCDEFG
C6	4.4	ABCDEFG
W7	4.4	ABCDEFG
N1	4.7	ABCDEFG
C4	4.8	ABCDEFG
N2	4.9	ABCDEFG
N6	5.1	BCDEFG
N4	5.9	CDEFGH
C1	5.9	DEFGH
W2	6.3	EFGH
W1	6.5	FGH
C3	6.7	GH
C8	8.1	HI
W3	9.2	I

Table 6.5 Continued

Ethyl octanoate (p<0.001)Perception threshold – 2^c

Wines	conc	Conf. Int ^a ..
N7	410.2	A
C4	415.6	AB
M8	437.8	ABC
W3	442.6	ABCD
M1	463.8	ABCDE
N3	474.7	ABCDEF
C3	498.6	ABCDEFGF
M5	501.9	ABCDEFGH
C1	507.6	ABCDEFGH
W1	510.5	ABCDEFGHI
M6	512.1	ABCDEFGHI
N2	512.2	ABCDEFGHI
M2	528.6	BCDEFGHIJ
C5	537.0	CDEFGHIJ
W6	538.4	CDEFGHIJ
W2	544.2	CDEFGHIJ
M4	545.8	CDEFGHIJ
N4	548.8	CDEFGHIJ
C2	549.8	CDEFGHIJ
M7	552.1	CDEFGHIJ
C8	553.9	DEFGHIJ
C6	561.9	EFGHIJK
W5	587.7	FGHIJK
M3	598.0	GHIJK
N1	605.7	GHIJK
N5	613.2	HIJK
N6	623.8	IJK
N8	642.5	JK
W4	674.7	KL
C7	763.6	LM
W7	766.2	LM
W8	874.3	M

Ethyl decanoate (p<0.001)Perception threshold – 1100^f

Wines	conc	Conf. Int ^a ..
N2	154.2	A
W3	171.9	AB
C3	190.3	ABC
W2	207.8	ABC
N7	208.6	ABC
C2	210.4	ABC
N3	214.6	ABCD
W1	219.1	ABCD
C4	226.1	ABCD
C1	231.9	ABCD
W4	237.6	ABCD
N4	244.1	ABCDE
N1	247.0	ABCDE
M3	259.0	ABCDEF
M4	259.3	ABCDEF
M2	262.7	ABCDEF
M1	294.5	ABCDEF
C8	337.8	BCDEFGHI
M5	360.4	CDEFGHIJ
N6	387.8	DEFGHIJ
C5	417.8	EFGHIJ
M7	432.7	FGHIJK
C6	437.4	GHIJK
M8	449.6	HIJK
W6	499.5	IJKL
M6	518.5	JKL
N8	596.2	KLM
N5	629.5	LM
W8	702.0	MN
W7	848.6	NO
W5	940.3	O
C7	971.3	O

Ethyl cinnamate (p<0.001)Perception threshold – 1.1^e

Wines	conc	Conf. Int ^a ..
M6	0.8	A
W3	0.8	A
N1	1.2	AB
M8	1.3	ABC
M7	1.3	ABC
M5	1.4	ABCD
N4	1.5	ABCDE
W5	1.8	ABCDEF
N6	1.8	ABCDEF
W8	1.8	ABCDEF
C5	1.8	ABCDEF
N8	1.9	ABCDEF
M2	1.9	ABCDEF
C7	2.2	BCDEFGH
W6	2.2	BCDEFGH
C8	2.2	BCDEFGH
C4	2.3	BCDEFGH
M3	2.3	BCDEFGH
W1	2.3	BCDEFGH
C6	2.4	BCDEFGH
N7	2.4	CDEFGH
M1	2.5	DEFGH
N2	2.6	EFGH
W7	2.6	EFGH
M4	2.8	FGH
C3	2.8	FGH
C1	2.9	FGHI
W4	2.9	FGHI
W2	3.0	GHI
C2	3.1	HI
N5	4.0	I
N3	7.2	J

Ethyl anthranilate (p<0.001)

Perception threshold – n/a

Wines	conc	Conf. Int ^a ..
W3	1.5	A
C8	2.8	A
N1	3.0	A
N3	4.0	A
M6	4.0	A
M5	4.3	A
N2	4.4	A
M2	4.6	A
N7	4.8	A
M8	5.6	A
W2	5.7	A
C2	5.8	A
N5	6.8	A
C3	7.0	A
N4	7.1	A
M4	7.1	A
W7	7.1	A
M3	7.5	A
M1	7.5	A
W1	7.7	A
M7	8.7	A
N8	9.1	A
C4	10.6	A
W5	11.2	A
C6	12.5	A
C7	12.7	A
N6	14.5	A
C1	31.6	B
W4	32.4	B
C5	32.9	B
W6	38.5	BC
W8	51.4	C

3-Methyl-1-butanol (p<0.001)Perception threshold – 30,000^g

Wines	conc(mg/L)	Conf. Int ^a ..
M4	135.8	A
W2	143.2	AB
M2	146.0	AB
W6	146.5	AB
M1	151.7	AB
C1	152.4	AB
N2	153.5	AB
M3	161.0	ABC
C4	171.2	ABC
W1	171.9	ABC
C2	175.4	ABC
W4	176.2	ABCD
W3	182.2	ABCDE
M6	190.0	ABCDEF
M8	194.4	ABCDEF
M7	196.9	ABCDEF
N1	199.7	ABCDEF
N4	201.7	ABCDEF
C3	205.1	BCDEFG
N7	206.2	BCDEFG
N5	221.7	CDEFGH
N6	222.0	CDEFGH
M5	223.9	CDEFGHI
W5	226.6	CDEFGHI
W7	226.8	CDEFGHI
N3	242.3	DEFGHI
N8	244.0	EFGHI
C7	253.2	FGHIJ
C8	268.1	GHIJ
C5	281.9	HIJ
W8	289.0	IJ
C6	312.5	J

Hexanol (p<0.001)Perception threshold – 25.2^a

Wines	conc(mg/L)	Conf. Int ^a ..
N7	1.9	A
W8	2.0	AB
W6	2.1	AB
N5	2.2	ABC
M4	2.3	ABCD
C4	2.4	ABCDE
C1	2.4	ABCDE
W4	2.4	ABCDE
N3	2.4	ABCDEF
C7	2.4	ABCDEF
M3	2.6	ABCDEF
M2	2.6	ABCDEF
M8	2.7	BCDEFGH
M1	2.7	BCDEFGH
M7	2.8	CDEFGH
C5	2.8	CDEFGH
N1	2.9	DEFGHI
W1	2.9	DEFGHI
C6	2.9	DEFGHI
N8	2.9	DEFGHI
C2	3.0	DEFGHI
M5	3.0	DEFGHI
N2	3.1	EFGHIJ
N6	3.1	FGHIJ
W2	3.2	GHIJ
M6	3.3	GHIJ
C3	3.3	HIJ
W5	3.5	IJ
N4	3.5	IJ
C8	3.7	JK
W3	4.2	KL
W7	4.7	L

Table 6.5 continued

Trans-3-hexen-1-ol (p<0.001)Perception threshold – 8,000^e

Wines	conc	Conf. Int ^a ..
W6	56.9	A
N7	60.5	AB
W8	61.8	AB
N5	62.7	AB
C1	66.1	ABC
N6	67.5	ABC
M8	72.0	ABCD
M4	72.6	ABCD
N8	75.4	ABCD
W4	78.0	ABCD
M7	80.8	ABCD
C7	80.8	ABCD
N4	81.5	ABCD
M1	82.5	ABCD
M3	83.8	ABCD
N3	84.2	ABCD
N2	84.2	ABCD
C4	84.7	ABCD
C2	86.2	ABCDE
W5	87.3	ABCDE
N1	92.6	ABCDE
C6	93.4	ABCDE
W2	95.2	ABCDE
W1	95.8	BCDE
C5	98.4	BCDE
W7	103.7	CDE
M2	107.7	DE
W3	107.9	DE
M5	108.9	DE
M6	123.6	EF
C8	125.5	FG
C3	126.5	G

Cis-3-hexen-1-ol (p<0.001)Perception threshold – 606^a

Wines	conc	Conf. Int ^a ..
C5	24.2	A
C1	28.2	AB
M8	30.0	ABC
N8	33.6	ABCD
N7	34.6	ABCD
C6	34.8	ABCD
M5	35.3	ABCD
N5	36.1	ABCD
M1	36.9	ABCD
M2	37.5	ABCDE
W4	39.2	ABCDEF
W8	39.6	ABCDEF
M4	40.2	ABCDEF
C2	41.9	ABCDEF
W6	42.2	ABCDEF
C7	42.9	ABCDEF
C4	44.0	ABCDEF
M7	44.8	ABCDEF
M3	47.6	ABCDEF
N6	50.5	BCDE
C8	55.2	CDE
N2	57.5	DE
N1	57.9	DE
N3	58.1	DE
W5	63.2	EF
M6	64.6	FG
N4	65.4	FG
W7	65.7	GH
W3	76.5	HI
C3	82.4	I
W2	91.4	JK
W1	115.8	K

2-Phenyl ethanol (p<0.001)Perception threshold – 14,000^a

Wines	conc(mg/L)	Conf. Int ^a ..
N2	17.3	A
W3	18.0	A
M2	18.0	A
M4	18.8	A
N1	19.2	A
M1	19.8	A
N7	20.4	A
C2	20.7	A
C4	21.3	A
N3	21.3	A
N4	21.6	A
W2	21.8	A
C3	22.5	A
M3	23.0	A
W1	25.6	AB
C1	32.6	BC
C8	34.3	BCD
N6	35.4	CDE
M5	36.0	CDE
W4	41.3	CDEF
C5	41.8	CDEF
C6	42.5	DE
M8	44.5	EF
M7	47.2	FG
M6	50.7	GH
W6	52.2	H
N8	61.7	I
N5	64.4	I
W8	65.3	I
W7	97.7	J
C7	100.5	J
W5	100.7	J

1-Heptanol (p<0.001)Perception threshold – 2,500^d

Wines	conc	Conf. Int ^a ..
N1	12.2	A
W3	19.3	AB
C1	25.0	AB
W2	25.8	AB
M1	30.0	AB
W4	31.3	AB
W1	33.7	AB
C3	35.0	AB
M3	35.3	AB
M2	42.7	AB
N4	42.8	AB
C4	43.3	AB
N2	47.1	AB
M4	56.4	BC
N3	92.2	CD
M7	94.7	CD
C2	105.9	DE
M8	107.7	DE
M5	115.8	DEF
M6	115.9	DEF
C7	122.9	DEF
W5	124.3	DEFG
C5	125.6	DEFG
W8	129.9	DEFG
N8	135.3	EF
N5	138.0	EF
W7	154.6	FG
N7	162.8	GH
C6	170.2	H
N6	171.0	H
C8	246.8	I
W6	270.3	I

Isomyl acetate (p<0.001)Perception threshold – 30^d

Wines	conc	Conf. Int ^a ..
W1	148.5	A
N1	151.3	AB
N4	154.9	AB
N3	156.9	AB
C1	160.0	ABC
W2	160.8	ABC
N2	167.7	ABC
C2	175.7	ABC
W4	177.3	ABC
W3	186.2	ABCD
C4	189.8	ABCD
C3	206.0	ABCD
W6	210.5	ABCD
C8	211.1	ABCD
N7	211.9	ABCD
W7	214.4	ABCD
M6	216.7	ABCD
M4	221.3	ABCD
W5	222.4	ABCD
N8	225.0	ABCD
N6	230.7	ABCD
M1	232.5	ABCD
C5	234.2	BCDE
W8	244.4	CDE
M2	268.8	DE
M3	269.8	DE
M5	273.7	EF
M8	293.0	FG
N5	297.9	GH
C6	310.0	HI
M7	370.2	I
C7	377.5	I

Hexyl acetate (p<0.001)Perception threshold – 700^e

Wines	conc	Conf. Int ^a ..
N1	1.8	A
N3	2.5	AB
C4	3.0	ABC
W3	3.1	ABC
N4	3.2	ABC
C1	3.3	ABCD
W5	3.5	ABCDE
N7	4.0	ABCDEF
C6	4.1	ABCDEF
C3	4.2	ABCDEF
C7	4.5	ABCDEF
W8	4.6	ABCDEF
C8	4.9	ABCDEF
W6	5.4	BCDE
N2	5.4	BCDE
M8	5.6	CDE
N6	5.7	CDE
C5	5.8	CDE
W2	6.2	CDE
W7	6.6	DE
M7	6.6	EF
W1	6.7	EF
N8	6.9	EF
W4	7.3	FG
N5	8.0	GH
C2	8.3	HI
M5	8.3	HI
M1	8.6	HI
M6	11.5	IJ
M3	14.0	JK
M4	15.2	K
M2	15.7	K

Table 6.5 Continued

Benzaldehyde (p<0.001)*Perception threshold – 5,000^d*

Wines	conc	Conf. Int ^a ..
C7	5.1	A
C8	5.9	A
C4	7.2	AB
M4	7.7	AB
C5	8.5	ABC
C6	8.7	ABC
M2	9.3	ABC
M1	9.3	ABC
C3	9.4	ABC
M5	9.7	ABC
C2	10.0	ABCD
N1	10.2	ABCDE
N2	10.3	ABCDE
W8	10.8	ABCDE
N6	10.9	ABCDE
C1	11.0	ABCDE
N3	11.5	ABCDE
N4	11.9	ABCDE
W7	12.4	ABCDE
W4	12.9	ABCDE
W2	13.4	ABCDE
W1	13.6	ABCDEF
M8	14.7	BCDEF
N8	14.9	BCDEF
M3	16.8	CDEF
W5	18.6	DEF
W3	18.7	EF
N5	22.1	F
M6	31.0	G
N7	32.5	G
M7	39.3	G
W6	66.0	H

Furfural (p<0.001)*Perception threshold – 20-65^e*

Wines	conc	Conf. Int ^a ..
W3	91.9	A
M6	102.0	AB
N4	104.0	AB
C6	136.5	ABC
C1	159.1	BCD
C4	169.0	CDE
N1	189.2	CDEF
N2	195.6	CDEF
C3	213.3	DEFG
N3	218.5	DEFG
W1	222.9	EF
C7	228.0	EFGH
W2	231.0	EFGH
N8	234.7	FGH
M2	246.8	FGH
N6	268.9	GHI
W4	272.6	GHI
M1	289.7	HI
N7	313.0	IJ
C5	368.7	JK
M3	369.2	JK
M8	379.9	KL
W5	426.2	KLM
C2	429.6	KLMN
M4	440.9	LMN
W7	459.4	MN
M7	463.8	MNO
M5	491.1	NO
C8	524.7	O
N5	689.8	P
W6	702.0	P
W8	838.3	Q

2-Methyl propanal (p<0.001)*Perception threshold – 40,000^f*

Wines	conc	Conf. Int ^a ..
N1	11.7	A
W3	15.9	AB
N3	23.6	ABC
N2	25.2	ABCD
W1	29.3	BCDE
M2	32.6	BCDEF
C3	33.0	BCDEF
W2	35.2	CEDFG
C2	35.7	CDEFG
N4	35.8	CDEFG
N5	37.9	CDEFGH
C6	39.7	CDEFGH
C8	42.3	DEFGHI
M3	42.6	EFGHIJ
C4	42.7	EFGHIJ
C1	43.3	EFGHIJK
C7	44.4	EFGHIJK
N8	45.6	EFGHIJK
M6	46.6	FGHIJK
C5	47.6	FGHIJK
M1	47.8	FGHIJK
M4	49.6	FGHIJKL
W6	49.8	FGHIJKL
W4	50.6	GHIJKL
N7	53.8	HIJKL
N6	57.7	IJKL
W5	59.5	JKL
W7	60.0	KL
M7	66.4	LM
M8	66.6	LM
M5	79.4	MN
W8	85.7	N

Linalool (p<0.001)*Perception threshold – 25.2^d*

Wines	conc	Conf. Int ^a ..
C5	41.4	A
C7	50.0	AB
C6	51.2	AB
N5	62.5	ABC
N8	68.0	ABCD
N1	69.5	ABCD
W6	77.1	BCDE
M7	84.5	CDEF
N7	85.1	CDEF
W3	85.8	CDEF
W5	86.8	CDEF
C1	92.9	CDEFG
M5	97.8	DEFGH
M8	98.1	DEFGH
C2	100.7	DEFGH
N6	102.2	EFGH
W7	102.4	EFGH
W8	107.5	EFGHI
N3	108.8	EFGHI
M6	111.3	FGHIJ
M1	113.8	FGHIJ
M2	121.3	GHIJK
C8	122.0	GHIJK
W4	127.1	HIJK
N2	130.0	HIJK
C3	136.9	IJKL
M3	138.1	IJKLM
N4	142.8	JKLM
C4	146.6	KLM
W1	165.9	LM
M4	167.2	LM
W2	170.1	M

Geraniol (p<0.001)*Perception threshold – 30^c*

Wines	conc	Conf. Int ^a ..
C5	0.0	A
M8	0.0	A
N6	0.0	A
N7	0.0	A
N8	0.0	A
W7	0.0	A
W8	0.2	AB
C7	0.2	AB
W5	0.3	ABC
W6	0.3	ABCD
N5	0.4	ABCD
M5	0.4	ABCD
N1	0.5	ABCD
C8	0.5	ABCD
C6	0.5	ABCD
M1	0.6	BCDE
W3	0.7	BCDEF
M6	0.8	CDEF
C4	0.8	CDEFG
M7	0.8	DEFG
M4	1.2	EFGH
W4	1.2	FGH
M2	1.3	FGHI
C1	1.3	GHI
N2	1.6	HIJ
N4	1.8	IJ
N3	2.1	JK
M3	2.4	K
C2	2.6	KL
W2	3.0	LM
C3	3.3	M
W1	4.8	N

β-damascenone (p<0.001)*Perception threshold – 1,600^f*

Wines	conc	Conf. Int ^a ..
N1	0.6	A
W3	0.7	A
C1	1.0	AB
N2	1.2	AB
W2	1.3	ABC
C4	1.6	ABCD
W4	1.6	ABCD
M1	1.6	ABCD
C2	1.7	ABCD
W1	2.0	BCDE
C6	2.0	BCDE
N3	2.1	BCDEF
M7	2.1	BCDEFG
M4	2.2	BCDEFGH
M3	2.2	BCDEFGH
C7	2.2	BCDEFGH
N5	2.5	CDEFGHI
W6	2.6	DEFGHI
W7	2.7	DEFGHI
W5	2.7	DEFGHI
C5	2.7	DEFGHI
C3	3.0	EFGHI
M2	3.0	EFGHI
W8	3.3	FGHIJ
M6	3.3	GHIJ
M8	3.3	HIJ
M5	3.4	HIJ
N6	3.5	IJ
N4	3.6	IJ
N8	3.7	IJ
N7	3.7	IJ
C8	4.4	J

Table 6.5 continued

B-ionone (p<0.001)

Perception threshold – 90^h

Wines	conc	Conf. Int ^a ..
W3	0.1	A
N1	0.1	AB
W7	0.2	ABC
W2	0.3	ABCD
N2	0.3	ABCDE
M7	0.3	ABCDE
N3	0.3	ABCDEF
N7	0.3	BCDEF
W6	0.3	CDEFG
M3	0.3	CDEFGH
C1	0.3	CDEFGH
W1	0.3	CDEFGHI
N5	0.3	CDEFGHI
M1	0.4	CDEFGHIJ
C4	0.4	CDEFGHIJ
M5	0.4	CDEFGHIJ
C8	0.4	CDEFGHIJ
M2	0.4	DEFGHIJ
W4	0.4	DEFGHIJ
M4	0.4	DEFGHIJ
C2	0.4	EFGHIJ
N4	0.4	EFGHIJ
W5	0.4	FGHIJK
C7	0.5	GHIJKL
C3	0.5	HIJKL
N6	0.5	IJKL
C6	0.5	JKL
M8	0.5	JKL
W8	0.5	JKL
C5	0.6	KLM
N8	0.6	LM
M6	0.7	M

Phenol (p<0.001)

Perception threshold – n/a

Wines	conc	Conf. Int ^a ..
C6	0.0	A
C7	0.5	A
N5	0.8	A
M6	2.4	A
M7	4.1	AB
W5	4.7	AB
C5	5.5	ABC
W7	5.8	ABC
C2	7.1	ABC
N7	7.6	ABC
M5	7.7	ABC
N6	7.9	ABC
N8	8.1	ABC
W6	8.9	ABC
C4	10.3	ABC
W1	11.1	ABC
M4	11.3	ABC
C8	11.6	ABC
N3	11.9	ABC
W3	12.1	ABC
N1	12.1	ABC
W8	12.6	ABC
N4	12.7	ABC
C1	12.8	ABC
C3	12.8	ABC
W4	13.4	ABC
M2	13.9	ABC
M1	14.4	ABC
M8	15.4	ABC
W2	15.5	ABC
N2	19.0	BC
M3	21.2	C

4-Ethyl guaiacol (p<0.001)

Perception threshold – 33^e

Wines	conc	Conf. Int ^a ..
M6	0.8	A
W3	1.3	AB
N1	1.4	AB
C8	1.5	AB
C6	1.5	AB
C1	2.0	AB
N4	2.5	ABC
N8	2.5	ABC
C7	2.5	ABC
W7	2.6	ABC
C3	2.9	ABC
C2	3.1	ABC
M4	3.3	ABC
W2	3.3	ABC
M7	3.3	ABC
N5	3.4	ABC
M5	3.4	ABC
C5	3.5	ABC
C4	3.7	ABC
N2	3.8	ABC
W5	4.1	ABC
W1	4.1	ABC
M2	4.6	ABC
M3	5.1	ABC
M8	5.6	ABC
M1	5.9	ABC
N6	6.5	ABC
N3	10.5	BCD
N7	11.9	CD
W4	16.2	D
W6	39.2	E
W8	46.7	E

Eugenol (p<0.001)

Perception threshold – 5^e

Wines	conc	Conf. Int ^a ..
M6	19.0	A
C6	19.6	A
N7	22.4	AB
M7	24.5	ABC
W7	24.8	ABCD
N2	27.4	ABCDE
C7	28.6	ABCDEF
C8	30.6	ABCDEF
C4	34.2	ABCDEF
M8	34.7	ABCDEF
C2	38.3	ABCDEF
M5	38.7	ABCDEF
N3	42.7	BCDEFGHIJ
N6	45.2	CDEFGHIJK
W6	45.5	CDEFGHIJK
N5	45.9	DEFGHIJK
C5	46.8	EFGHIJK
M2	47.4	EFGHIJK
M4	47.8	EFGHIJK
W3	47.8	EFGHIJK
N8	49.5	FGHIJK
C3	51.4	GHIJKL
C1	53.3	HIJKL
N4	53.8	HIJKL
M1	53.9	HIJKL
W5	56.2	IJKLM
W1	62.5	JKLMN
M3	65.8	KLMN
N1	66.3	KLMN
W4	72.0	LMN
W2	75.9	MN
W8	80.1	N

Gamma-nonolactone (p<0.001)

Perception threshold – 135-238^h

Wines	conc	Conf. Int ^a ..
M6	16.6	A
W8	16.7	A
N1	17.0	A
M5	18.0	AB
M1	18.2	AB
C6	19.1	ABC
M7	19.2	ABC
W5	19.5	ABC
W3	21.0	ABC
W6	22.0	ABC
M2	22.2	ABC
N5	22.4	ABCD
M8	22.8	ABCDE
W7	22.9	ABCDE
W4	23.0	ABCDE
M3	24.9	BCDEF
C5	24.9	BCDEF
C7	25.2	BCDEF
M4	25.9	CDEF
N6	29.7	DEF
N7	29.9	EF
N8	30.7	FG
W2	31.6	FG
C1	37.3	GH
C4	37.3	GH
W1	40.9	H
C2	43.7	HI
N3	44.3	HI
N2	50.8	IJ
N4	53.7	J
C3	56.8	J
C8	56.9	J

^aV. Ferreira et al., 2000

^b Genovese, Lisanti, Gambuti, Piombino, & Moio, 2007

^c Guth, 1997b

^d Zea et al., 2001

^e Dunlevy, Kalua, Keyzers, & Boss, 2009

^f Rocha, Rodrigues, Coutinho, Delgadillo, & Coimbra, 2004

^g Prida & Chatonnet, 2010

^h Cooke et al., 2009

Table 6.6

Weightings for selected attributes and aroma compounds present in the first 5 canonical correlations.

	Canonical Correlations				
	1	2	3	4	5
% variance	14.44	9.25	7.72	7.05	6.78
<i>Attribute^a</i>					
Black Cherry	100	52	-3	31	-5
Blackberry	85	78	23	22	98
Dark fruit	64	62	22	12	100
Fruit density/conc	22	47	100	40	7
Jam	73	-100	4	23	24
Oak	29	88	-47	100	3
Plum	87	-33	-24	73	-7
Spice (F) ^b	35	94	-13	14	-18
<i>Aroma Compound^a</i>					
Ethyl butanoate	-61	16	-100	98	74
Ethyl octanoate	-100	8	-67	89	-1
Ethyl decanoate	-98	38	-88	100	59
2-Phenylethanol	-100	24	-86	97	43
1-Heptanol	-48	43	-78	74	94
Benzaldehyde	-32	100	-12	12	52
Linalool	62	-16	76	-89	-91
Geraniol	34	-13	66	-69	-92
β -damascenone	-16	41	-56	51	100
Eugenol	27	-21	63	-69	-90
Butyric acid	-62	43	-95	93	71

^a Attributes and aroma compounds in table are those that have greater than 80% standardized weighting in one or more of the correlations.

^b F – flavour attribute

Chapter 7

(in preparation for submission to Food Chemistry)

Influence of Benzaldehyde, Ethyl Decanoate, Ethyl Octanoate and 2-Phenyl Ethanol on the Aroma of New Zealand Pinot Noir

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Abstract

The influence of ethyl octanoate, ethyl decanoate, 2-phenyl ethanol and benzaldehyde on Pinot noir aroma was studied through addition tests. The choice of these aroma compounds was based on previous analysis investigating the sensory and chemical properties of New Zealand Pinot noir. These four compounds were added to a Pinot noir wine matrix consisting of a commercial Pinot noir wine diluted by 10%, using a de-aromatized form of the same wine. Ten different compound combination and concentrations were tested using triangle tests and descriptive analysis. Ethyl octanoate was found to influence the aroma perception of red cherry. Combination of ethyl octanoate and ethyl decanoate influenced the aroma perception of black cherry. 2-Phenyl ethanol influenced the aroma perception of violet and benzaldehyde influenced the aroma perception of oak and jam. This research is a first step to understanding some of aroma nuances that relate to New Zealand Pinot noir.

Objective

This study is the final experiment in a series of experiments investigating regional New Zealand Pinot noir. It has been found that Pinot noir wine from the regions of Central Otago, Marlborough, Martinborough and Waipara were stylistically different. A series of experiments were conducted to determine the sensory and aroma chemical differences and relationships. In chapter 6, several aroma compounds were identified to have relationships with sensory perception. Addition and omission tests of these identified compounds were conducted. The aim of these tests was to validate the canonical correlation results and provide more specific information about the aroma impact of the chosen compounds.

Materials and Method

Samples and Materials

Pure reference compounds ethyl 2-methylpropanoate, ethyl butanoate, ethyl 3-methylbutanoate, ethyl pentanoate, ethyl heptanoate, ethyl octanoate, benzaldehyde, 2-phenyl ethanol, 2-methylpropanal, linalool, geraniol, γ -nonalactone and eugenol were purchased from Sigma-Aldrich (Australia). LiChrolut® EN resin was purchased from Merck (New Zealand). Pinot noir wine was obtained from Pernod Ricard NZ Ltd.

Wine Matrix

The base wine used in this study was selected to contain low levels of the four key compounds of interest, namely benzaldehyde, ethyl octanoate, ethyl decanoate and 2-phenyl ethanol. This was necessary so that tests of these four compounds could be added to this base wine to cover the range of concentrations found in New Zealand Pinot noir (Chapter 6). A commercial 2010 Pinot noir wine from Pernod Ricard NZ Ltd. was selected as the base wine.

To achieve the required concentration of the listed four key compounds some dilution of this base wine was necessary. This was achieved through the use of a technique known as wine dearomatization where volatile organic compounds (VOC's) are absorbed onto an added solid media and removed by filtration, leaving a wine devoid of aroma. Lichrolut EN (Merck, New Zealand) was used as the dearomatization agent in this study, with 4 g/L added to the

wine which was left stirring for 18 hours under nitrogen. The final dearomatized wine was found to contain only two aroma compounds, 3-methyl-1-butanol and 2-phenyl ethanol. However the concentration of these two compounds was greatly reduced compared with that of the base wine. As a result of this reduction in concentration 3-methyl-1-butanol and 2-phenethyl alcohol were found to be within their expected concentration ranges within the wine matrix after the dearomatized wine was mixed with the base wine.

The resulting dearomatized wine was used to dilute the base wine to make a “wine matrix” in the ratio 90% base wine (commercial Pinot noir) and 10% dearomatized wine. This wine matrix was stored in 375 mL wine bottles, sparged with nitrogen and sealed with screw caps. It was made up one week before sensory analysis and was stored at 4°C until used.

Aroma Tests

A “control wine” was made from the wine matrix solution by the addition of nine background compounds (Table 7.1); this was to ensure the control wine contained these VOC’s at levels that are typically found in New Zealand Pinot noir wines (Chapter 6). The aim was to achieve a control wine that had all 34 measured aroma compounds within levels that had been found typical in New Zealand Pinot noir. The control wine was then used in all the sensory experiments, with various tests of the four key compounds benzaldehyde, ethyl octanoate, ethyl decanoate and 2-phenyl ethanol added to give high and low levels based on quantitative information determined in previous studies (Chapter 6).

Ten test combinations were used in total (Table 7.2) with two investigating the effect of benzaldehyde concentration, and eight tests investigating the effect of different concentrations of ethyl octanoate, ethyl decanoate and 2-phenyl ethanol on Pinot noir. Concentrations were based on the median, 1st and 3rd quartiles from the concentrations measured previously in 32 New Zealand Pinot noir wines (Chapter 6). The control wine and test wines were made at the beginning of each day during the tasting session time period. All tested wines were used only for that day and were then discarded.

Wine Test Validation – HS-SPME GC-MS

The concentration of 34 aroma compounds in the dearomatized wine, wine matrix, control wine and ten tested wines were determined with the three HS-SPME-GC-MS methods as detailed in Chapter 5 and 6 (Table 7.3). Subsamples of the control and tested wines were taken over the three week period of the sensory analysis. These along with samples of the dearomatized wine and wine matrix were immediately frozen and kept at -4°C until they were analysed.

A time study was also undertaken to determine the stability of the wine matrix and tested wines. Subsamples were taken at 12-hour intervals for a period of 48 hours. The wine matrix was also tested once a week for a period of a month (the period of the sensory study) to ensure that the concentrations of aroma compounds remained consistent. No changes were noted over the course of the two different time periods. Additionally ethanol content for the wine matrix, control and addition tests was found to be consistent when checked using WinescanTM (FOSS).

Sensory Analysis

Panellists

Panellists consisted of 10 wine professionals (4 females, 6 males) from Marlborough area. Wine industry experience ranged from six to 30 years. Of the panellists, seven were winemakers, two were viticulturists and one was employed in wine research. All panellists had experience in wine sensory panels and one panellist had formal sensory training.

Tastings

Tastings occurred over the last three weeks in February 2011. Each panellist participated in three, one hour tasting sessions. Each session lasted approximately one hour. The tastings were held in a wine sensory room that had a mix of natural and ambient light and a constant temperature 20°C. Each tasting session consisted of 10 triangle tests and 5 wines for descriptive analysis. The aroma of the wine was evaluated with orthonasal olfaction.

Triangle Test

Ten different combinations were tested using triangle tests. 20 mL of each wine were presented in clear, ISO glasses. Each combination was compared to the control wine and presented once per session using a partially balanced incomplete block design (PBIB) to eliminate any possible order or position effects. They were also presented with a list of 15 aroma attributes used previously to describe the aroma of New Zealand Pinot noir (Chapter 3) and were asked to choose one or two attributes that they felt best described the difference between the wines in the triangle test.

Descriptive Analysis

Five of the 10 combinations were evaluated in each tasting session. Panellists were asked to rank the intensity of the 15 aroma attributes presented in the triangle tests. The order and position of each wine was determined using PBIB. 20mL of each wine were presented in black, ISO tasting glasses. The intensity of each attribute was marked on a 100 mm visual analog scale, VAS, with word anchors of “none and “extreme”.

Statistical Analysis

Statistical significance for the triangle tests was determined when the number of correct responses for a wine test was greater than the specified number of correct responses needed based on the chosen probability level and the number of tests (International Organization for Standardization, 2004). Frequency counts for the triangle test descriptive differences were calculated by tallying how many times the attribute was chosen and dividing this by the total number of descriptors chosen. Relationships between the concentration of the added aroma chemical and aroma perception were determined using canonical correlation analysis (CCA). CCA calculations were carried out using Genstat 12.2 (VSN International Ltd). All data was standardized prior to CCA.

Results and Discussion

Triangle Tests

The different triangle tests investigated if panellists were able to tell wines apart that contained different concentrations of benzaldehyde, ethyl octanoate, ethyl decanoate and 2-

phenethyl alcohol. In total each wine test was evaluated 30 times. Of the 10 tests, eight were statistically significant (Table 7.2). Panellists were not able to differentiate combinations in tests 5 and 10 from the wine control.

The differences in the concentrations when compared to the wine control are smaller than those used previously (Escudero, Gogorza, Melus, Ortin, Cacho, & Ferreira, 2004; Ferreira, Ortin, Escudero, Lopez, & Cacho, 2002; Grosch, 2004; Guth, 1997), as concentrations were based on those found in New Zealand Pinot noir. When compared to the wine control the amount of benzaldehyde differed by 7.1 - 8.9 µg/L (test 2) and 38 - 42 µg/L (test 1); ethyl octanoate differed by 196 - 390 µg/L (tests 4, 6, 8 and 9) and 324 - 384 µg/L (tests 3, 5, 7 and 10); ethyl decanoate differed by 163 - 188 µg/L (tests 3, 4, 6 and 10) and 326 - 478 µg/L (tests 5, 7, 8 and 9); and 2-phenyl ethanol differed by approximately 7 - 10 mg/L (tests 3, 4, 8 and 10) and 19 - 26 mg/L (tests 2, 6, 7 and 9). The results of 8 of the 10 triangle tests were statistically significant ($p < 0.05$). This suggests that even small changes in the concentration of these aroma compounds are enough to alter aroma perception.

Tests 1 and 2 evaluated the effect of high and low levels of benzaldehyde respectively. Both of these tests were found to be statistically significant (Table 7.2). In test 2, the benzaldehyde concentration of the test combination was 7.1 – 8.9 µg/L less than that of the wine control. This is the second time that a study has reported a change in sensory perception caused by such a small change in aroma compound concentration in red wine. Pineau et al. (2009) found that an increase the concentration of ethyl 2-methylpropanoate in Merlot and Cabernet Sauvignon by 23 µg/L was enough to evoke a change in sensory perception. Benzaldehyde is typically present in wine at concentrations below its threshold, as it was in test 1 and test 2. However the change in concentration obviously had an effect on aroma perception. This is the first study that looks at the influence of benzaldehyde in this manner and shows that it does influence the aroma perception of Pinot noir and appears to act as an aroma enhancer compound. It is also the first study that shows a change of as little as 7.1 µg/L can influence aroma perception.

Test 3 evaluates the effect of high levels of 2-phenyl ethanol in Pinot noir. Test 6 and 7 investigate high levels of 2-phenyl ethanol in combination with high levels of ethyl octanoate and ethyl decanoate. Test 9 evaluates high levels of 2-phenyl ethanol in combination with both of these esters. All of these tests gave statistically significant results ($p < 0.01$). 2-Phenyl

ethanol is a compound found at much higher concentrations than the other three aroma compounds investigated. This compound is found in all wines and considered to have a major impact on wine aroma (Ferreira & de Pinho, 2003; Guth, 1997; Kosteridis & Baumes, 2000; Kotseridis, Razungles, Bertrand, & Baumes, 2000; Li, Tao, Wang, & Zhang, 2008; Selli, Canbas, Cabaroglu, Erten, & Gunata, 2006). However previous research has shown increasing the concentration of 2-phenyl ethanol, even to levels found to be much higher than those found in Pinot noir, did not have any sensory effect (Escudero, Gogorza, Melus, Ortin, Cacho, & Ferreira, 2004). This research has found a different result as roughly doubling the concentration of 2-phenyl ethanol from approximately 33 mg/L to 59 mg/L, resulted in a significant change in perceived aroma. The difference in results may be due to the matrix in which the compound was added, as Escudero et al. (2004) added 2-phenyl ethanol to white wine and this study used a Pinot noir wine matrix. This would suggest that the other components of red wine are important for the perception of 2-phenyl ethanol. Test 10 evaluated low levels of 2-phenethanol. This result was non-significant. This suggests that the lack of 2-phenyl ethanol does not have an effect when reduced from the control level to a lower level. This agrees with results from Ferreira et al. (2002) and Escudero et al. (2004), in which no appreciable difference was found when 2-phenyl ethanol was omitted from a wine model.

Test 4 evaluated high levels of ethyl octanoate. Tests 6 and 8 evaluated high levels of ethyl octanoate in combination with high levels of one other compound, 2-phenyl ethanol and ethyl decanoate, respectively. Test 9 evaluated high levels of ethyl octanoate in combination with high levels of both 2-phenyl ethanol and ethyl decanoate discussed above. All of these triangle tests gave statistically significant results which indicate that the addition of ethyl octanoate to Pinot noir affects aroma perception. These results agree with previous work that has shown that an addition of 342 µg/L of ethyl octanoate to Merlot and Cabernet Sauvignon could be detected as significantly different from an “average” concentration (Pineau, Barbe, Leeuwen, & Dubourdieu, 2009).

Test 5 evaluated high levels of ethyl decanoate and this gave a non-significant result. However in tests 7, 8 and 9 when high levels of ethyl decanoate were present with high levels of ethyl octanoate and/or 2-phenyl ethanol a difference was found. Unfortunately the attributes used to describe the effect of 2-phenyl ethanol (plum, spice, violet) or ethyl octanoate (black/red cherry, savoury) alone, and those where ethyl decanoate was also at an elevated

concentration do not clarify the effect of increased ethyl decanoate. Esters in combination do have an additive effect, though this effect is dependent on the concentration of the esters (Lopez, Ferreira, Hernandez, & Cacho, 1999; Merwe & Wyk, 1981; Pineau, Barbe, Leeuwen, & Dubourdieu, 2009). However at the concentrations found in New Zealand Pinot noir as a single compound it appears to have a negligible sensory effect.

Descriptive Analysis

Relationships between the concentrations of benzaldehyde, ethyl decanoate, ethyl octanoate and 2-phenyl ethanol and the collected sensory data for the tested wines were determined by CCA show (Table 7.4). These results suggest that the concentration of both ethyl octanoate and ethyl decanoate are related to the perception of black cherry and chocolate aromas; the concentration of ethyl octanoate is related to the perception of raspberry and red cherry aromas; the concentration of benzaldehyde and ethyl decanoate is related to the perception of oak aroma and the concentration of 2-phenyl ethanol is related to the perception of violet aroma.

As expected there were no clear trends found between the aroma compound concentration and sensory attribute intensity, as it is known that Pinot noir does not contain any major impact compounds. The results suggest that these compounds are active in combination with other compounds present in wine and that the wine aroma cannot be clearly explained by one or two aroma compounds; instead, small changes in a number of aroma compounds are likely to result in varying stylistic differences. Other research supports the correlations produced in this study. A correlation between ethyl octanoate, ethyl decanoate and black cherry and a correlation between benzaldehyde and oak aroma were found when evaluating New Zealand Pinot noir (Chapter 6). 2-Phenyl ethanol has long been associated with the floral component of red wine and ethyl octanoate has been found to influence the perception of red fruit aromas, particularly raspberry and strawberry (Pineau, Barbe, Leeuwen, & Dubourdieu, 2009).

Of particular interest are the correlations that include ethyl decanoate as previously this compound has not been investigated since it was not found to impart its own aroma at concentrations found in wine. However these results suggest that the presence of higher concentrations of ethyl decanoate in conjunction with high concentrations of ethyl octanoate

subtly modifies aroma perception from red cherry aroma to a black cherry aroma. However the relationship between these two esters and a chocolate aroma is not so clear. Possibly these compounds may enhance those aromas that cause chocolate aroma. Many of the compounds responsible for chocolate include 2-methylpropanal, 2-phenyl ethanol and acetaldehyde, are present in Pinot noir, as both chocolate and wine are produced through yeast fermentation (Bailey, Mitchell, Bazinet, & Weurman, 1962).

The importance of ethyl octanoate to red-berry aromas has previously been noted in Cabernet Sauvignon and Merlot. Higher levels than average of ethyl octanoate in combination with ethyl butanoate, ethyl hexanoate and ethyl 3-hydroxybutanoate result in red-berry aromas, specifically strawberry and raspberry aromas (Pineau, Barbe, Leeuwen, & Dubourdieu, 2009). This current research confirms that ethyl octanoate does influence raspberry aroma but also correlates ethyl octanoate to red cherry aroma in Pinot noir.

The correlation between benzaldehyde, ethyl decanoate and oak aroma may be influential due to interactions found between woody and fruity aromas (Atanasova, Thomas-Danguin, Langlois, Nicklaus, & Etievant, 2004; Atanasova, Thomas-Danquin, Langlois, Nicklaus, Chabanet, & Etievant, 2005). Benzaldehyde is an aroma compound that originates in the grape but is also extracted from oak, although it does not have an oak-like aroma, but is described as cherry or jammy in red wine (Ducruet, 1984). In combination with the fruity aroma attributed to ethyl decanoate, there is the possibility that in conjunction with other aroma compounds these “fruity” aromas can change the perception of oak, either enhancing or masking oak perception.

The final correlation shows a relationship between the concentration of 2-phenyl ethanol and the intensity of violet aroma; as the concentration of 2-phenyl ethanol increases so does the intensity of violets (Figure 7.4). However when the concentration of 2-phenyl ethanol was higher than 52 mg/L this relationship changed as additional 2-phenyl ethanol did not cause an increase in violet intensity (data not shown). Other research has shown that at high concentrations any addition of 2-phenyl ethanol will not affect aroma (Cullere, Escudero, Cacho, & Ferreira, 2004). This current study has shown a maximum level where further differences in aroma perception occur in Pinot noir, whereas this is not known for other varieties. It is noteworthy that this compound was found to influence a floral aroma, as it has been described as producing a rose aroma in other wines (Baek, Cadwallader, Marroquin, &

Silva, 1997; Fang & Qian, 2005) and is an important aroma component found in roses (Oka, Ohishi, Hatano, Hornberger, Sakata, & Watanabe, 1999).

Choices of aroma attributes that best described the differences found in the triangle tests also agree with some of the correlations described above. Test 3 with high levels of 2-phenyl ethanol had violets as most frequent descriptor chosen. Test 6 with high levels of 2-phenyl ethanol and ethyl octanoate had violets and red cherry as the most frequent descriptor chosen. Test 4 with high levels of ethyl octanoate had red cherry as the most frequent descriptor chosen and Test 9 with high levels of 2-phenyl ethanol, ethyl octanoate and ethyl decanoate had black cherry and violet as the most frequent descriptor chosen. These descriptors match with the results obtained from the CCA. Additionally these results also support the correlations calculated previously relating chemical data to sensory data of New Zealand Pinot noir wine, in which the choice of aroma chemicals for this study was based (Chapter 6).

Conclusions

The different concentrations of these four aroma compounds, benzaldehyde, ethyl octanoate, ethyl decanoate and 2-phenyl ethanol do influence the aroma of Pinot noir wines. Only a small change in concentration, as little as 6 µg/L for benzaldehyde, was enough to result in a change in sensory perception. This supports one previous study that shows that small aroma compound concentration changes do effect aroma perception of red wine. This is the first time that ethyl decanoate has been found to be important to wine aroma, though it was only found to influence sensory perception when combined with other compounds. The influence of ethyl octanoate and 2-phenyl ethanol behaves in a similar manner as other red wines. However, as expected there is no clear trend that can be shown when comparing the compound concentration to sensory perception. The aroma of Pinot noir cannot be explained by one compound or a group of aroma compounds, instead it is the combination of a range of aroma compounds that are responsible for the aroma nuances present between different wine styles. Results suggest that certain compounds affected sensory perception in a similar manner as in other red wines. Four compounds were found to have an influence on aromas used to describe regional New Zealand Pinot noir. This can be considered a first step to determining what factors are important to the production of regional styles of New Zealand Pinot noir.

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Tables and Figures

Table 7.1

Compounds used in the background test and the concentration added to the wine matrix

<u>Aroma Chemical</u>	<u>Concentration added (ug/L)</u>
<i>Aldehydes</i>	
2-methylpropanal	25
<i>Esters</i>	
Ethyl 2-methylpropanoate	150
Ethyl 3-methylbutanoate	25
Ethyl heptanoate	5
Ethyl pentanoate	2
<i>Terpenes</i>	
Linalool	90
Geraniol	2
<i>Miscellaneous</i>	
γ -nonalactone	20
<u>Eugenol</u>	<u>45</u>

Table 7.2

List of addition tests and results from the triangle tests including the chosen aroma attributes with the highest frequency.

Test No.	Aroma Compound	High (+) /Low (-)	Average Conc. (µg/L)	Significance (p-value)	Aroma Difference
Control	Benzaldehyde		26 ±4.0		
	2-Phenyl ethanol ^a		33 ±2.7		
	Ethyl octanoate		702 ±37.2		
	Ethyl decanoate		377 ±54.8		
1	Benzaldehyde	+	66 ±2.0	<0.001	red cherry, raspberry
2	Benzaldehyde	-	18 ±0.9	<0.01	savoury
3	2-Phenyl ethanol ^a	+	55 ±2.0	<0.01	plum, spice, violets
	Ethyl octanoate	-	378 ±14.8		
	Ethyl decanoate	-	201 ±23.3		
4	2-Phenyl ethanol ^a	-	723 ±0.3	<0.05	black/red cherry, savoury
	Ethyl octanoate	+	1092 ±45.0		
	Ethyl decanoate	-	214 ±25.1		
5	2-Phenyl ethanol ^a	-	24 ±0.8	ns	
	Ethyl octanoate	-	371 ±19.9		
	Ethyl decanoate	+	855 ±8.4		
6	2-Phenyl ethanol ^a	+	59 ±0.4	<0.01	red cherry, violets
	Ethyl octanoate	+	991 ±41.3		
	Ethyl decanoate	-	203 ±24.0		
7	2-Phenyl ethanol ^a	+	52 ±0.8	<0.01	jam, smoky, barnyard
	Ethyl octanoate	-	378 ±14.8		
	Ethyl decanoate	+	703 ±10.5		
8	2-Phenyl ethanol ^a	-	23 ±0.1	<0.05	savoury
	Ethyl octanoate	+	929 ±39.0		
	Ethyl decanoate	+	737 ±31.8		
9	2-Phenyl ethanol ^a	+	58 ±3.9	<0.01	black cherry, violets
	Ethyl octanoate	+	898 ±23.8		
	Ethyl decanoate	+	814 ±31.0		
10	2-Phenyl ethanol ^a	-	26 ±5.2	ns	raspberries
	Ethyl octanoate	-	318 ±25.8		
	Ethyl decanoate	-	189 ±20.3		

^a mg/L

Table 7.3

Concentrations ($\mu\text{g/L}$) for the Wine Matrix and Wine Control to ensure that the 34 measured compounds were within the range of concentrations found in Pinot noir

Aroma chemical	Wine matrix	Wine Control	Range in Pinot noir*
<i>Esters</i>			
Ethyl 2-methpropanoate	121 $\pm$ 6.6	299 $\pm$ 7.7	104 - 559
Ethyl butanoate	245 $\pm$ 39.4	276 $\pm$ 20.1	116 - 340
Ethyl 3-methylbutanoate	14 $\pm$ 1.9	42 $\pm$ 2.2	12 - 52
Ethyl pentanoate	1 $\pm$ 0.3	3 $\pm$ 0.2	1 - 4
Ethyl hexanoate	453 $\pm$ 21.4	404 $\pm$ 15.7	300 - 593
Ethyl heptanoate	nd	4 $\pm$ 2.1	3 - 9
Ethyl octanoate	371 $\pm$ 41.5	702 $\pm$ 37.2	410 - 874
Ethyl decanoate	196 $\pm$ 2.4	377 $\pm$ 54.8	172 - 971
Ethyl cinnamate	3 $\pm$ 0.4	3 $\pm$ 0.3	1 - 7
Ethyl anthranilate	2.0 $\pm$ 0	3 $\pm$ 0	2 - 52
<i>Acetates</i>			
Hexyl acetate	12 $\pm$ 2.2	16 $\pm$ 11.0	2 - 16
Isoamyl acetate (mg/L)	417 $\pm$ 10.4	348 $\pm$ 20.5	149 - 378
<i>Alcohols</i>			
3-methyl-1-butanol (mg/L)	134 $\pm$ 43.0	186 $\pm$ 18.5	136 - 312
Hexanol (mg/L)	4 $\pm$ 0.2	4 $\pm$ 0.3	2 - 5
1-heptanol	68 $\pm$ 11.1	80 $\pm$ 22.0	12 - 270
cis-3-hexen-1-ol	85 $\pm$ 4.3	94 $\pm$ 4.5	24 - 116
trans-3-hexen-1-ol	134 $\pm$ 7.0	142 $\pm$ 15.3	62 - 127
2-phenylethanol (mg/L)	20 $\pm$ 0.7	33 $\pm$ 2.7	17 - 101
<i>Aldehydes</i>			
2-methylpropanol	nd	23 $\pm$ 3.8	12 - 86
Benzaldehyde	11 $\pm$ 2.8	26 $\pm$ 4.0	5 - 66
Furfural	151 $\pm$ 12.0	192 $\pm$ 11.5	92-838
<i>Norisoprenoids</i>			
β -damascenone	2 $\pm$ 0.4	2 $\pm$ 0.1	1 - 5
β -ionone	nd	1 $\pm$ 0.4	nd - 1
<i>Terpenes</i>			
Linalool	5 $\pm$ 0.6	91 $\pm$ 0.4	41 - 170
Geraniol	4 $\pm$ 2.1	8 $\pm$ 0.2	nd - 5
<i>Misc</i>			
Phenol	8 $\pm$ 0.2	10 $\pm$ 2.7	nd - 21
Eugenol	29 $\pm$ 3.5	86 $\pm$ 11.2	15 - 80
4-ethyl guaiacol	2 $\pm$ 0.3	2 $\pm$ 0.4	1 - 46
Gammanonalactone	16 $\pm$ 3.5	41 $\pm$ 0.1	17 - 57
<i>Acids</i>			
Acetic acid (mg/L)	701 $\pm$ 61.1	640 $\pm$ 33.6	415 - 874
Butanoic acid	650 $\pm$ 21.1	641 $\pm$ 33.2	209 - 716
3-methyl butanoic acid	517 $\pm$ 16.6	518 $\pm$ 16.1	160 - 591
Hexanoic acid	1401 $\pm$ 1.3	1403 $\pm$ 32.8	1104 - 1941
Octanoic acid	1425 $\pm$ 33.3	1355 $\pm$ 22.3	665 - 2002

*Range in Pinot noir determined from wine analysed in Chapter 6

Table 7.4

Weightings for each attribute and aroma compound present in the canonical correlations.

	Corr 1	Corr 2	Corr 3	Corr 4
%Variance	32	26	23	19
<i>Aroma compounds</i>				
Benzaldehyde	-88	25	100	59
Ethyl decanoate	100	-27	94	-56
Ethyl octanoate	98	100	-8	42
2-phenyl ethanol	55	-81	-11	100
<i>Aroma attributes</i>				
Barnyard	87	48	45	14
Black cherry	94	49	-13	21
Chocolate	100	-62	57	15
Oak	44	64	100	-30
Raspberries	36	97	34	-15
Red cherry	8	100	-36	-17
Savoury	86	37	13	-24
Violets	11	82	50	100

Chapter 8

Conclusions and Future Work

Pinot noir wines from Central Otago, Marlborough, Martinborough and Waipara are stylistically different. The main attributes that characterize these regional wines agree with those characteristics that have been noted in informal tastings conducted by wine professionals in the past. However this is the first time that scientific research has shown that these wines marketed as regional products are in fact different. Marlborough Pinot noir was characterized by greater raspberry, red cherry, red fruit and red berry aromas, longer finish length and more harmonious balance. Martinborough Pinot noir was characterized by greater black cherry, chocolate, oak and spice aromas and oak tannin. Waipara Pinot noir was characterized by greater barnyard, herbal and violet aromas and in-mouth fruit density/concentration. Central Otago Pinot noir was characterized by fuller body (Chapter 3).

The use of untrained but experienced tasters was successful for the sensory description of the wines (Chapter 3). Of the 25 sensory attributes studied, 19 had no significant interactions. A small amount of training may be beneficial in future studies but this is much less extensive than traditional training that can take several months (Plemmons & Resurreccion 2007). Additionally even with the lack of aroma standards the placement of the attribute vectors showed that panellists were grouping similar descriptors. This shows that in the future the wine industry can accomplish sensory analysis using staff that are experienced tasting wine, providing more opportunities for research within the winery or industry.

It is important to note that this regional differentiation was found with commercial wines, as the majority of research into New Zealand terroir has used research wine (Maharaj 2008; Rutan 2009; Kemp 2010), which is not representative of the products available to the consumer. As detailed in Chapter 6 the aroma composition of research wines and the commercial wines studied did show variation. Specifically some differences were found between research and commercial wines when focusing on the three of the four compounds of specific interest in this research (Chapter 7); ethyl decanoate, ethyl octanoate and 2-phenyl alcohol. All commercial wines in this study contained higher concentrations than the research wines measured in the above studies. Kemp 2010 research wines contained lower

concentrations of ethyl octanoate than those in this study, but the wines investigated in Maharaj (2008) and Rutan (2009) contained similar concentrations. The concentrations of 2-phenyl ethanol were found to be similar for commercial and research wines. This suggests that winemaking may be having an effect on some of the chemical composition variation. However at this time it is unknown if the winemaking-scale is the main cause of this variation or if variation is due to different vinification techniques used when compared to commercial production.

It should be noted that while experienced wine tasters could differentiate regional wines when focusing on specific attributes they were not successful when comparing the wines, with little or no information using paired comparison or sorting (Chapter 4). This suggests that wine education is needed for not only the consumer but the wine professionals, as they do not have a clear picture of what the main differentiating characteristics are for each region. The difficulty discriminating regional wines in paired comparison or sorting may be due to the fact that most wineries tend to focus on making wines strictly from that region and do not make Pinot noir from all four of the wine regions. Additionally a simple calibration correction may be necessary as the wine tasters conceptual models had larger differences than were actually apparent.

Further descriptive sensory analysis would be beneficial to further develop the attributes important for regional differentiation. This should include wines from other vintages and expanding the range of wines used. Additional work on sub-regional differences may also be beneficial as certain sub regional differences may be larger than regional differences, although this has not been found to be the case at present for Sauvignon blanc wines (Parr et al. 2010). Further studies would not only benefit from additional wines but also refining the list of attributes, excluding those that were not found to be important for differentiation and investigating new attributes.

Three HS-SPME-GSMS methods were successfully developed (Chapter 5 & 6). It was found that different conditions were needed for GCMS analysis depending on the compound of interest. Volatile fatty acid analysis required a different matrix that was at a pH similar to wine (Chapter 5). Trace analysis required the usage of single ion mode over SCAN mode in order to identify peaks (Chapter 6). The methods were more sensitive than those currently

available and were designed specifically for Pinot noir, whereas most methods are designed for a range of products or wine (Demyttenaere et al. 2003; Marti et al. 2003; Siebert et al. 2005; Perestrelo et al. 2008). This allows for more accurate quantification of aroma compounds in Pinot noir.

Aroma compound analyses provided results that both agree with previous research as well as report new information. Comparison with previous research is difficult as this is the first time that commercial New Zealand Pinot noir has been analyzed. Previous work investigated research wines or those from other locations around the world (Aubry et al. 1997; Fang & Qian 2006; Kemp 2010). Several compounds could not be analyzed with the developed methods and further research is required to quantify aldehydes and other compounds found at trace levels (Ebeler & Spaulding 1998; Lopez et al. 2002b). The use of multidimensional GC (MDGC) is necessary for those compounds that co-elute and cannot be clearly separated in traditional GC-MS (Chaintreau et al. 2006).

Relationships found between chemical and sensory data support what is known about Pinot noir aroma (Chapter 6). It cannot be characterized by a single compound or family of compounds but instead is a combination of nuances produced from a range of aroma compounds. The results from canonical correlation analysis show that it is a combination of compounds that most likely influences only one or two aromas. In many instances several compounds, such as 2-phenyl ethanol, are found to be important in several of the correlations.

The use of addition/omission tests (Chapter 7) paired with triangle tests and descriptive analysis provide some idea of how the four compounds of interest from canonical correlation analysis (Chapter 6), ethyl octanoate, ethyl decanoate, 2-phenyl ethanol and benzaldehyde influence the aroma of Pinot noir. The presence and increase in concentration of ethyl octanoate and 2-phenyl ethanol in Pinot noir behave in a similar way to other red wine, particularly Merlot and Cabernet Sauvignon. Ethyl octanoate influences red cherry aroma and 2-phenyl ethanol violet aroma. The impact of ethyl decanoate on Pinot noir aroma was found to alter the red cherry aroma to black cherry when in combination with ethyl octanoate. This is the first time that the impact of ethyl decanoate on red wine has been noted, as previous work has shown the compound to have no sensory effect. The influence of benzaldehyde on Pinot noir aroma is less clear. There appears to be some relationship with oak and jam

aromas, which does correspond with previous knowledge of this compound. It is found in the wine grapes and can also be extracted from oak barrels, having an influence on almond and red cherry aroma depending on the concentration. It is most likely that benzaldehyde does not impact one specific aroma on its own but works in conjunction with other aroma chemicals.

The results of the addition/omission tests are supported by previous work. Esters have been found to have an additive effect when in a mixture. 2-Phenyl ethanol is known to contribute a floral component to both white and red wine (Guth 1997b). Ethyl octanoate is one component of the red berry aroma of Merlot and Cabernet Sauvignon (Pineau et al. 2009). Benzaldehyde has long been associated with jam aromas and is present within the cell structure in plant, including oak wood (Ducruet 1984). The aroma behaviour of these chemicals in Pinot noir shows that small changes in concentration can have an effect on sensory perception and provide a greater understanding to the impact of aroma compounds on Pinot noir aroma and how this wine is both similar and dissimilar to other red wines. Additionally these tests also show that the choice of matrix or base wine for the addition/omission tests are very important as much research has used solutions that are not truly representative of wine. The other aroma compounds present in wine are important for the aroma perception of the chosen compounds.

These tests only investigate four aroma compounds found in New Zealand Pinot noir. Further research of interest could investigate the importance of other compounds as well as combinations. Comparing the concentrations of the four compounds in the commercial Pinot noir wines and the related aroma intensities show that these compounds interact with other compounds as there is no direct one to one relationship. Therefore further investigation into important aroma compounds is of interest. Additionally investigation into the formation of these aroma compounds and what production techniques influence their formation would also be of interest.

With this range of sensory and chemical tests a clearer picture of New Zealand regional Pinot noir has been found. The four compounds tested did influence the perception of specific aroma characteristics that are important for regional styles. Ethyl octanoate influenced red cherry aroma and this was a descriptor for Marlborough wines. A combination of ethyl octanoate and ethyl decanoate influenced black cherry aroma, a descriptor for Martinborough wines. 2-Phenyl ethanol influenced violet aroma, a descriptor for Waipara wines. Therefore

this research displays a first connection to regionality, as a link has been established between the aroma of the wines and the causes of these aromas. Further research as mentioned above is necessary to provide an even clearer on regional styles of New Zealand Pinot noir and the important production steps that create them.

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