Chemical Analysis of Extracts of New Zealand Woods in Wine

Mona Kaushal

Thesis submitted to the Auckland University of Technology
in partial fulfillment of the degree of

Master of Applied Science
(Food Science)

Auckland University of Technology

June 2007

Table of Contents

List of Tables

List of Figures

Appendices

Attestation of Authorship

I declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material formerly published or written by another person, which to a considerable level has been accepted for the qualification of any degree or diploma of a university or any other institute of higher learning. All the reference material used in this thesis has been fully referenced.

Signed …….

Date…….

Acknowledgement

I would like to thank my supervisor Dr. Roger Whiting and co-supervisor, Dr. John Robertson. A big thanks and a lot of appreciation goes to Dr. Owen Young. The degree of enthusiasm, effort, commitment and his brilliant ideas provided during the period of this research were astonishing. They all provided great support, outstanding guidance, energy and enthusiasm throughout my research. Without their guidance and advice, my research would not have been such an amazing experience for me.

I would like to thank Simon Nunns at Coopers Creek Vineyard Limited for the supply of the 2004 vintage, unoaked, Gisborne *chardonnay*, and Mr Andrew Vincent, South Pacific Timber, Eden Terrace, for the supply of the woods used in this project.

Last, but not least, I thank my family: my parents, Dharam Paul Kaushal and Raj K., for giving me life in the first place, for educating me and also for unconditional support and encouragement to pursue my interests.

Confidentiality

This thesis is to be examined under confidentiality, and an embargo is to be placed on library access until such time as the Research Office of the Auckland University of Technology has had the opportunity to protect any intellectual property.

Abstract

Background

Reliance on a restricted range of grape varieties and flavour profiles is potentially a risky situation for sustainability of the New Zealand wine industry. Competitors in other countries may offer very similar products at lower cost. Whereas geographical exclusivity may help to minimize this risk, New Zealand wines with few exceptions tend to follow copyable European models. There is a need to broaden the production base into other wine styles that could compete on distinctiveness and overall quality rather than on price. Oak, usually in the form of barrels, is the traditional way of flavouring wines with distinctive caramel, smoke- like and vanillin notes. Use of woods other than oak to flavour wine may be the way to introduce new wine styles.

Aim

This project examines the chemistry of the application of New Zealand woods instead of oak to flavour wine.

Methods

A range of woods was selected based on existing use and botanical similarity (oak, and cherry and silver beech), or on their association with the New Zealand ethos and botanical similarity (matai, feijoa, macrocarpa, pohutukawa, radiata pine, totara, kahikatea, rimu, and manuka). Wood chips cut to 2 x 1 x 0.25 cm – instead of barrels – were toasted at two levels, 200°C for two hours, deemed light toast, and at 210°C for three hours, deemed a dark toast. The parameters investigated were moisture content after drying to 110°C, wood weight losses resulting from the different toasting levels, colour measurements in Hunter colour space, ultraviolet spectrophotometric analysis of extractables, and their gas chromatographic analysis.

Results

Of the woods measured, oak had the lowest moisture content. The weight loss of oak chips at 200°C was much greater than that of other woods, but the colour change did not indicate losses due to severe charring. Other woods that showed severe weight loss on dark toasting (rimu, macrocarpa) did char severely. Colour measurements showed that toasting did not greatly affect the hue angle (the basic colour) of the chips, but the colour

intensity (saturation) was strongly reduced, as was the overall reflectance of light (L* value). Light toasting yielded higher concentrations of extractables as determined by spectrophotometry between 200 and 400 nm.

Model and real wines treated with six of the woods at both toasting levels were analysed by gas chromatography. At both toasting levels, American oak yielded the greatest number of extractables. American oak, manuka, and matai added similar number of compounds in the model and real wine light toast treatments, whereas pohutukawa, silver beech and totara yielded more compounds in the real wine than in the model wine.

2-(Methoxymethyl)-5-methoxyphenol was unique to both toasting levels of American oak in real wine. Similarly, 3,4-dimethyl phenol, 5-methyl-2-furaldehyde and 5-butyldihydro-4-methyl-2(3H)-furanone, were detected only in real wine treated with American oak toasted at both levels. In all wood treatments, 4-hydroxy-3-methoxy cinnamaldehyde and 3,5-dimethoxy-4-hydroxy cinnamaldehyde were present in model wine but not in real wine. This was attributed to the presence of SO_2 in real wine. The greatest expression of 4-hydroxy-3-methoxy cinnamaldehyde was in the manuka dark toast treatment, where its relative concentration was approximately 10 fold higher than in other wood treatments. 4-(2-Hydroxyethyl)phenol was detected only in manuka dark toast in model wine, whereas it appeared in all wood and toast treatments in real wine. Its greatest expression was in matai light toast and silver beech dark. 4-(Ethoxymethyl)-2-methoxy phenol was detected only in the matai and totara dark toast treatments in both the model and real wine.

Furfural and vanillin were present in both real and model wines for all wood treatments. American oak, manuka, and totara showed the greatest expression.

Conclusion

As determined by ultraviolet absorption and gas chromatography, there were patterns of extraction common to all woods and both toast levels, as well as several unique and near unique patterns. This research was limited to physical and chemical changes, but preliminary sensory trials – unreported here – suggest that manuka may be a good commercial flavour prospect. It certainly had an extractable profile resembling that of American oak.

Chapter 1

Introduction

1.1 Worldwide wine production

Wine can be prepared from any fruit, but its production from the fruit of *Vitis* dominates production. From its Mediterranean origins, wine is now produced in many warm temperate climates around the world. Data from the Organisation Internationale de la Vigne et du Vin (OIV) reveals that world wine production was 26,090 ML in 2002 (Organisation Internationale de la Vigne et du Vin (OIV), 2002). France, Italy, Spain, USA, Argentina and Australia are the leading wine producing countries of which France is the largest. Together, France and Italy produce about 40% the world's wine (Jackson, 2000).

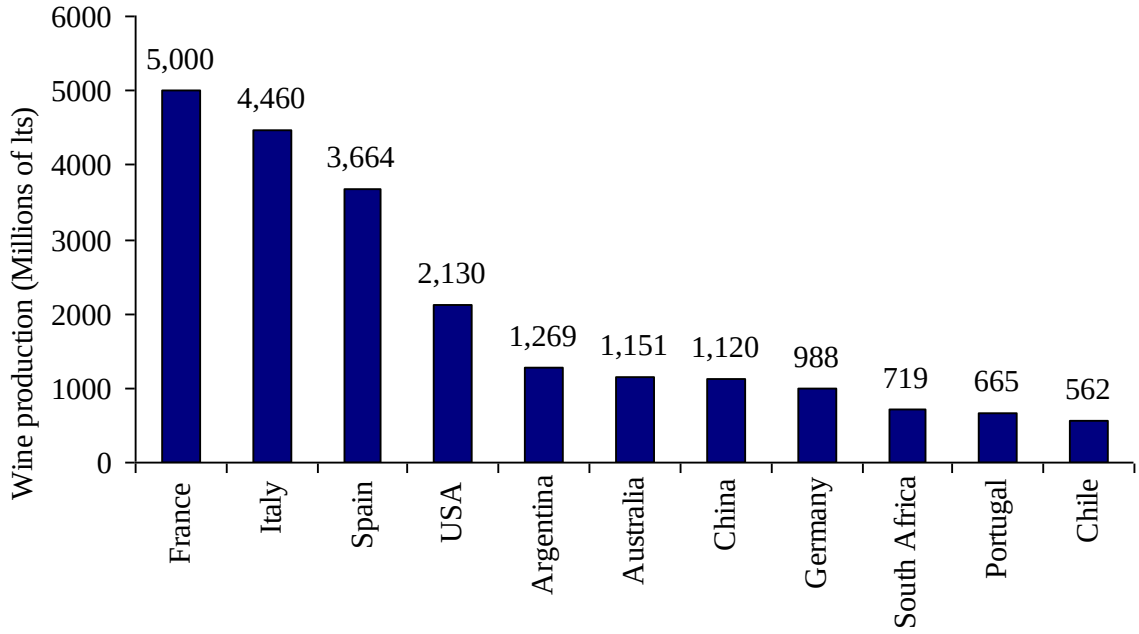


Figure 1 Top wine producing countries, redrawn from Organisation Internationale de la Vigne et du Vin (2002)

New Zealand is only a tiny player in the world wine market. Of a total global wine production of about 27,000 ML, New Zealand produced only 119 ML in 2004. The country is forecast to produce over 130 ML by 2007 (New Zealand Vineyard & Wine Industry Review, 2005). The number of wineries and total production of wine in New Zealand is summarized in Table 1.

Table 1 New Zealand statistics for wineries and wine production (Statistical Review, 2005)

Year	Number of wineries in New Zealand	Total production (ML)
1994	190	41.1
1995	204	56.4
1996	238	57.3
1997	262	45.8
1998	293	60.6
1999	334	60.2
2000	358	60.2
2001	382	53.3
2002	398	89.0
2003	421	55.0
2004	463	119.2
2005	516	102.0

New Zealand wines can be and often are distinctive and for this reason and their generally high quality, they have made an impact in the highly-competitive international market. New Zealand is mostly known for its intensely fruity and dry whites, especially *sauvignon blanc*s and certain *chardonnay*s. *Sauvignon blanc* wine, especially from the Marlborough area, is the flagship variety of New Zealand wine industry. No other international producers of wine from this grape variety can match the distinctive style of these wines (New Zealand Vineyard & Wine Industry Review, 2005). However, wines from other grape varieties are not so distinguished and therefore command no special place in world market. In this respect, *pinot noir* has been identified as a wine variety well suited to New Zealand climate and its production volumes are increasing.

Reliance on one or a few wine varieties is potentially a dangerous situation for the New Zealand wine industry. There is a need to broaden the marketing base into other varieties of wine that compete on distinctiveness and overall quality rather than on price. Indirectly, that need is the driving force for the present research, which aims to develop a flavour dimension beyond, grape, climate and soil and other factors known to affect wine flavour.

1.2 Containers for wine production and bulk storage

Being a liquid, wine has to be fermented and stored in watertight containers. Historically two major classes have been used, amphoras (earthen jars) and oak barrels. Amphoras were used to store and transport a wide range of goods, but the most common use in Roman times

was for wine (Sanderson, 2006). From about 1800 BP, wine was increasing stored wooden barrels, which were lighter and less brittle. A very wide range of liquid and solid goods were stored and transported in barrels (Sanderson, 2006).

Oak has been used for making barrels for millennia. It was widely available in Europe, was able to be bent into curved shapes when heated, and had a fine grain structure that minimized leakage and air transmission. The heating of oak planks for barrel construction causes a limited pyrolysis of the wood. When pyrolysed wood comes in contact with wine, the pyrolysis products leach into the wine. These products added a flavour dimension to wine that was generally favourable (Margalit, 2004).

a. **b.** **c.**

Figure 2 Different storage methods for wine with the change of time. **a.** Roman amphoras (Museu National Arqueologic de Tarragonna, n.d.) **b.** Wooden barrels (Okanagan Barrel Works Ltd., 2001) **c.** Stainless steel tanks (Mueller, 2007)

Much contemporary fermentation, and bulk storage of wines is done in stainless steel tanks. Compared with oak barrels, stainless steel tanks are more durable, sterilized, easy to clean and can be reused indefinitely. Stainless steel tanks are thus efficient and cost-effective. Many of them are double-jacketed, circulating coolant between the inner and outer walls. This allows winemakers to adjust the tank's temperature so that they can manage the fermentation speed (Mueller, 2007). Stainless steel is a relatively neutral material that does not impart flavours to wine. The use of stainless steel was pioneered in

New Zealand, where the dairy industry used wide range of containers for milk and milk products. When adapted to winemaking, the resulting wine was 'cleaner[1]' than European equivalents, leading to the flavour styles current in New Zealand.

Although the New Zealand wine industry had an iconoclastic approach to wine making through good hygiene and stainless steel techniques, an inspection of typical New Zealand winery shows extensive use of oak barrels for wine maturation. Whereas this gives winemaking a romantic aura, it also shows that the iconoclastic approach applied in New Zealand has its limits.

1.3 Oak barrels

Historically barrels have been made from many woods (Harder, 2007), including acacia, alder, ash, eucalyptus, poplar, beech, pine, chestnut, and oak. Oak was singled out as the best type of wood to store wine, both for its lack of porosity, and for the organoleptic properties contributed to the final product. Other woods might not have the ability to be used in barrel construction due to the leakage of liquid, or that they might impart characteristics to the wine which were not desirable (Harder, 2007).

Though unsupported by objective research, it is widely held that French oak (*Quercus robur* and *Q. petraea*) is better than American oak (*Q. alba*) which is again better than Italian or Slavonian oaks (Morales et al., 2004). Whatever the source of oak, winemakers usually declare the source of their barrels, which implies some importance to the choice of wood. It may be that barrel price governs choice, but it seems clear that once a particular wine has established a market position, the winemaker will aim for flavour consistency. This will require the continued use of single type of barrel and a defined level of oak pyrolysis.

The wine industry name for pyrolysis is toasting, which is discussed in more detail later. In outline, the breakdown of the lignin component of oak is responsible for generation of different flavour compounds in wine (Margalit, 1997). Fermentation and especially maturation of wine in oak barrels yield wines with distinctive flavour compounds. Over 200 compounds identified in wine are directly attributable to oak. Most of these components are only detectable with gas chromatographic detectors, but there are over 10 that can be readily sensed through taste and aroma, such as vanillin (Margalit, 1997).

[1] Cleaner is an ill-defined term often used by wine connoisseurs that refer to fruity styles.

The other feature of wines matured in oak barrels is the very slow introduction of oxygen through the pores of the oak barrel staves. Oxygen ages wine, often to advantage, in ways that are beyond the scope of this thesis. However, if a wine bottle is left at room temperature for a day or more, its taste deteriorates rapidly. This is because the wine has overaged through the introduction of too much oxygen.

Barrels made of French oak cost almost US $600 whereas barrels made of American oak cost about $300 (Taylor, 2006). However, American oak is not necessarily inferior to French oak, just different. It costs less because when cutting it into staves, there is less waste (Manuel, 2002) and French oak barrels presumably require importation to the USA. A barrel of wine holds approximately 300 bottles of wine, so the additional cost of oak barrels is $1 to $2 per bottle of wine assuming a single use. The maintenance of oak barrels is about $50-$60 a year per barrel (Manuel, 2002).

New barrels impart more flavours to the wine than previously used barrels. By the time a barrel is about five years old, it is practically neutral as far as its influence on the taste of the wine is concerned (Jackson, 2000). A range of techniques has been developed to lengthen the use of barrels. These include shaving or honing the inside of used barrels, or inserting new thin inner toasted staves (Miller, 2004). Honed barrels are usually inferior to new oak barrels because barrel strength has been lost and staves may crack, usually the bottom ones (Margalit, 2004). In New Zealand, once barrels have passed their useful life the barrels are often halved latitudinally and sold as garden planters. However, the wood can also be recycled as oak planks and chips in for use in winemaking.

1.4 Alternatives to oak barrels

Fermenting or ageing wine in wooden barrels amounts to putting wine into the wood but in an alternative technique, wood can be added to wine. Since wood is being put into wine and not wine into wood, the entire surface area is usable and not just 40% as in barrels (Arapitsas et al., 2004). Moreover, stainless steel or other non-wood tanks can be used attaining an oaked character. Toasted oak planks, staves, chips, oak cubes, oak powder and shavings are all used commercially, with the smaller sizes often held in a porous, flavour-neutral bag that can be conveniently withdrawn when required (Manuel, 2002). The use of oak powder is less common than chips because it tends to produce flavour that is too strong (Manuel, 2002), although arguably this may simply be a matter of total surface area expose to wine and time of exposure.

Most methods specify using toasted wood chips at a ratio of 3 to 5 g L^{-1} of wine for a period of 2 to 14 days (Ryan, 2004). The cost of ageing wine is about US $1 per bottle in French oak barrels, 50 cents in American oak barrels, and approximately one cent for wood chips (Manuel, 2002). Another technique uses oak cubes, cut to larger dimensions than chips. A stave fan contains staves that are typically 5 cm wide and 7 cm deep by 1 m long. A hole is drilled in one end of each stave that connects all the staves in a fan shape with stainless steel wire (Gawel, 2002; Stavin, 2005).

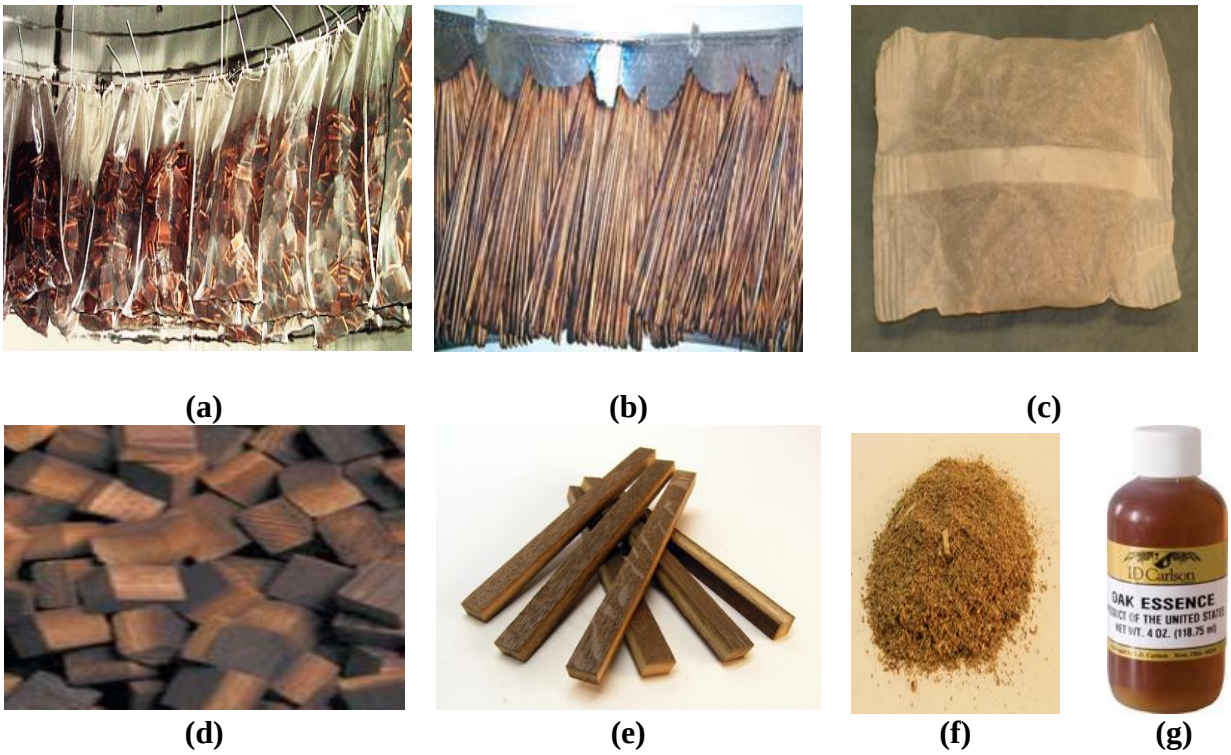


Figure 3 Alternatives to oak barrels **(a)** bags of chips tied to stainless wire cable inside a tank (Gawel, 2002) **(b)** staves fan held with stainless wire (Stavin, 2005) **(c)** oak chips in a tea bag **(d)** oak cubes **(e)** oak planks **(f)** oak powder **(g)** oak essence (Okanagan Barrel Works Ltd., 2001)

Oak planks can also be used. These are used either as longer planks held vertically or shorter staves stacked in a log cabin fashion at the bottom of the tank. As with chips, cubes and staves, these systems are more cost effective than barrels. The method is also practical as once sufficient oak character has been imparted, the planks can be lifted out, dried and later reused. Stainless steel tanks can also be lined with oak staves (Jackson, 2000; Manuel, 2002).

Figure 4 A stainless steel tank lined inside with toasted oak staves (Stavin, 2005)

The flavours generated from ageing wine with these alternatives can differ from the wine aged in the barrels. There are many reasons for this. For example, with chips and staves suspended inside a tank, the wine surrounds the oak while in a barrel the wine is in contact with only one side of the stave. This differential between the interior (wet, low oxygen levels) and exterior (dry, high oxygen level) seems to be important as far transferring compounds from the toasted staves into the wine (Jackson, 2000). Oxygen cannot diffuse across stainless steel. However, a difference in flavour profile is one thing and the final wine quality is something else, and it is entirely possible that cooperage companies are simply trying to protect their business. Nonetheless, exposure of wine of low level oxygen diffusion is possible only in barrels unless other methods are applied, as discussed in the next section.

The French Institut National des Appellations d'Origine (INAO) has banned the use of oak chips in most French wines (Kakaviatos, 2006). Oak chips have already been in use for some years in *vin de pays* – the basic cheap supermarket wine – but not at higher quality levels (Kakaviatos, 2006). The INAO claims that the use of oak chips is not 'appropriate' for these wines because its use is likely to mask the 'terroir' (the sense of soil origins), the

principle on which the appellation controlled system is built (Wine Communications Group Inc., 2006). INAO remains concerned that using oak chips may damage the quality of wine in higher quality appellations. Although oak chips-practice was recently approved by the European Commission – and France is a member of the European Union (EU) – the INAO remains concerned that using oak chips may damage the quality of wine in higher quality appellations (Wine Communications Group Inc., 2006). The European Commission's decision was designed to help modernise and relaunch EU wines on the world market after meeting with strong competition from New World winemakers (Kakaviatos, 2006).

Where the INAO permits the use of wood chips and similar shapes, they can be used only under certain conditions. The chips must be oak; they can be toasted but not charred; toasting must leave the surface intact, not powdery; apart from toasting, no other chemical, enzymatic or physical treatments may be used; and there can be no indication on the label that the wine has been fermented or aged in a barrel, even if oak chips have been used in conjunction with oak barrels (Kakaviatos, 2006).

1.5 Micro-oxygenation

As noted earlier, small quantities of oxygen slowly enter oak barrels from the air during maturation and this has a positive effect on quality. This can not occur when wine is matured in a stainless steel tank in the presence of chips. Micro-oxygenation is patented method of controlled introduction of oxygen into wine, to mirror the slow oxidation that occurs with barrel ageing. The tannins in the wine are the main oxidisable compounds present. Oak tannins are glycosides of ellagic or gallic acid polymers, and these are rather astringent product (Jackson, 2000). The oxidation of these tannins softens this astringency.

1.6 Nature of wood and lignin

Wood is comprised mainly of cellulose, hemicellulose and lignin which are three insoluble polymers with complex structures. There are other compounds with smaller molecular weight such as lactones, phenols and tannins which can be extracted in wine or solvents (Arapitsas et al., 2004).

Table 2 Composition of European and American oaks (Anon., 1995)

Species	Percent composition by weight				
	Cellulose	Hemicellulose	Lignin	Extractives	Ash
European					
Quercus petraea	38	29	25	4.4	0.3
Q. robur[a]	39-42	19-26	25-34	3.8-6.1	0.3
Q. petraea[b]	22-50	17-30	17-30	2-10	–
American oak					
Q. alba[c]	44	24	24	5.4	1.0
Q. alba[d]	42	28	25	5.3	0.2
Q. prinus[e]	41	30	22	6.6	0.4
Q. stellata[f]	38	30	26	5.8	0.5

a. *Q. robur* is English oak or Limousin oak, widespread throughout Europe
b - *Q. petraea* is the French oak
c - American white oak from swampy land in Georgia
d - American white oak from dry uplands in Tennessee
e - *Q. prinus* is chestnut oak
f - *Q. stellata* is post oak

Cellulose is the most abundant natural polymer on dry land and possibly on earth, and consists of linear chains of glucose units. Cellulose is a long chained polysaccharide consisting of glucose units joined via β-1,4 glycosidic bonds. It is a water insoluble molecule, non digestible by humans and makes up approximately 40 to 45% of wood dry weight. The cellulose gives rise to the timbers strength because of not only its crystalline structure but also the relationship and interaction between cellulose molecules (Margalit, 2004). The role of cellulose in wine maturation, if any, is unknown (Anon., 1995).

Hemicellulose is a smaller and thermally less stable molecule than cellulose. It is two-dimensional and made up of mainly five and six carbon sugars including glucose, xylose, mannose, rhammnose, arabinose and galactose. Hemicellulose contributes to 25 to 35% of dry wood weight (Margalit, 2004).

The third main compound in wood is lignin. Lignin is large, complex, three-dimensionally branched phenylpropanoid polymers (Jackson, 2000). Only a little is known about lignin except that it is extremely hard to break down and requires a lot of mechanical and enzymatic energy to fully degrade. The structure of lignin is different in different woods. In hardwoods, for example oak, lignin largely comprises polymers of guaiacyl and syringyl.

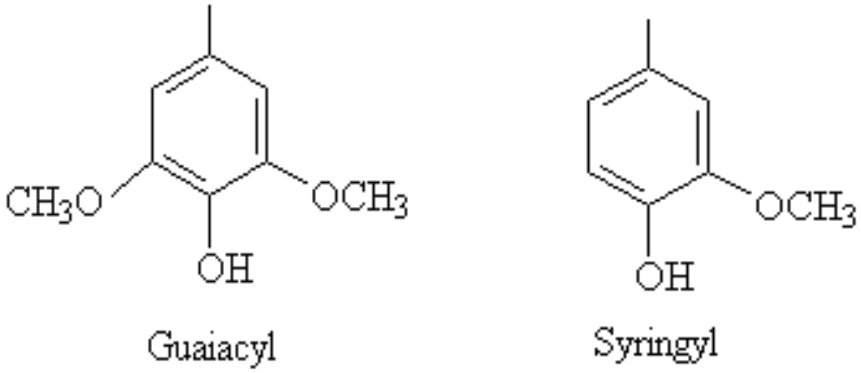


Figure 5 The guaiacyl and syringyl building blocks of oak wood lignin, redrawn from Anon. (1995)

Tannins are polymeric phenols. Although these are only a small fraction of the wood composition, they play a big part in the impact on wine flavouring during maturation and oxidation (Doussot et al., 2002).

1.7 Chemical nature of flavour compounds from toasted oak

Oak is chemically a pure wood, unlike many tree species such as pine and rubber trees that contain resin canals which result in strong flavour- extractives(Anon., 1995). The major constituents of oak are the three building blocks of all woody plants - cellulose, hemicellulose and lignin - plus tannins and small amounts of lipids (oils, fats and waxes). An exception, which applies mainly to American white oak, is the oak lactones. The breakdown of these constituents adds specific flavours into wine (Waterhouse & Ebeler, 1998).

1.7.1 Cellulose

Cellulose's role in wine maturation and ageing has not been proven. Cellulose can play a role in bacterial action in wine maturation, pairs of glucose units can break away and the resulting compound, cellobiose, can act as a nutrient in Brettanomyces yeast activity in wines (Margalit, 2004).

1.7.2 Hemicellulose

Breakdown of hemicellulose yields furfural, hydroxymethyl furfural, maltol, cyclotene and sugar condensation products which give brown colour of caramel. Acetic acid and very small amounts of methyl alcohol are also formed. Thus the breakdown of hemicellulose yields wood sugars which add toasty flavours, body and colour to the matured product. With

the exception of furfural these compounds have sweet-associated burnt sugar or caramelized aromas and flavours. In addition there are numerous other compounds released during toasting which have similar characteristics.

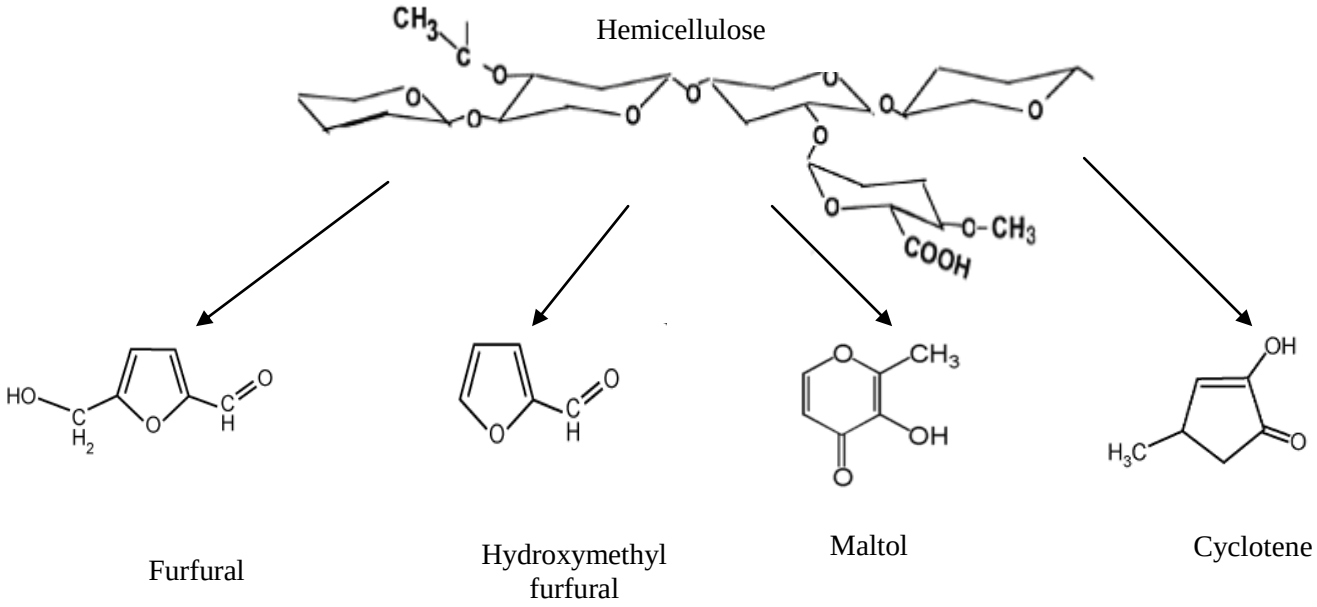


Figure 6 Production of known toasty flavours by breakdown of oak hemicellulose, redrawn from Jackson (2000)

1.7.3 Lignin

Oak lignin is a hardwood lignin which consists of two building blocks, the guaiacyl and syringyl structures. In matured drinks, these two building blocks give rise to two groups of compounds- coniferaldehyde, vanillin and vanillic acid in one group from the guaiacyl structure, and sinapaldehyde, syringaldehyde and syringic acid from the syringyl structure. These compounds collectively known as phenolic aldehydes with vanillin being the most significant compound (Vichi et al., 2007). Application of gentle heat or mild acid attack releases these compounds. On extra heat treatment, lignin complex can break down into much simpler structures - the steam volatile phenols which are responsible for the smoky aroma and flavours often found after barrel maturation when the inside of the barrel is charred (Manuel, 2002; Margalit, 2004).

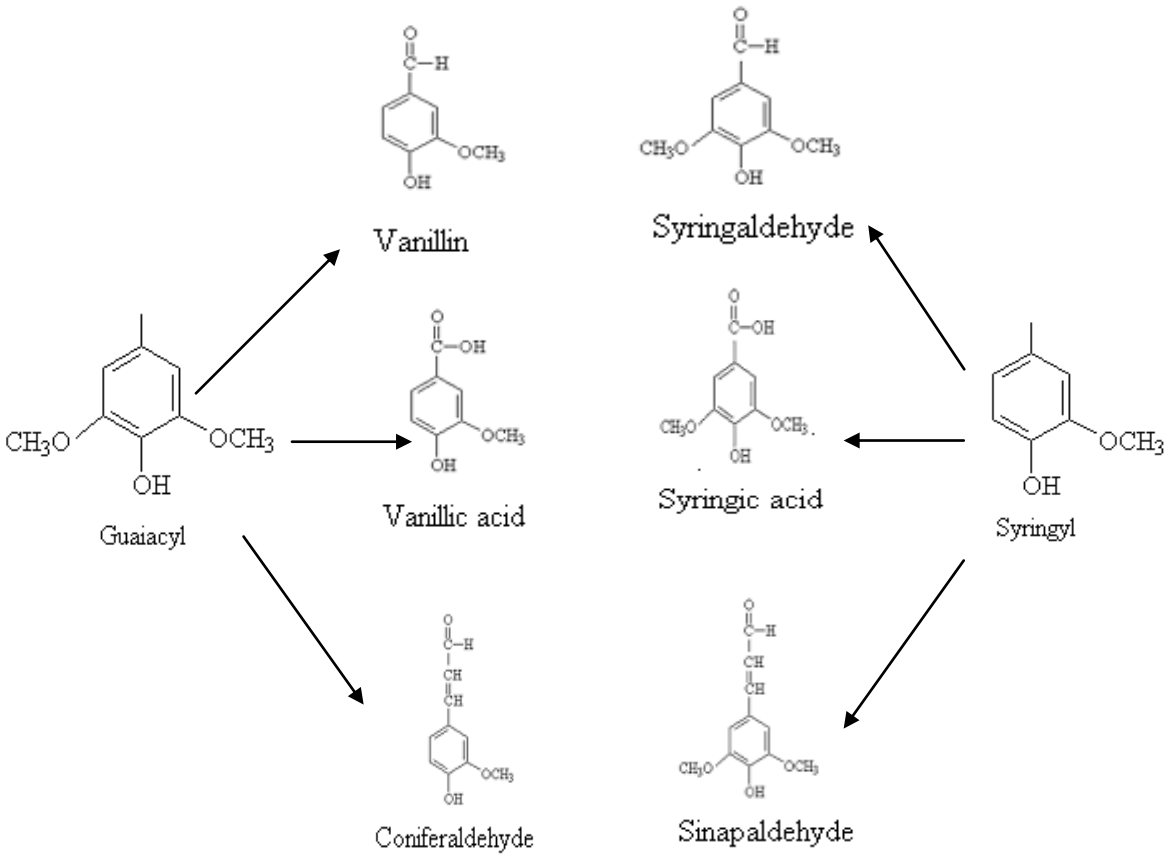


Figure 7 Phenolic aldehydes released from oak wood on maturation, redrawn from Margalit (2004)

1.7.4 Tannins

Oak tannins are described as hydrolysable because they can be broken down into simpler parts in the presence of water and acidity, unlike grape tannins which are condensed and are less destructible. Oak tannins are formed in the growing tree for the purpose of food storage. In oak these compounds are termed ellagitannins. Ellagitannins are formed when glucose combines with ellagic and sometimes gallic acid. The resulting compounds are both astringent and bitter and are very unpleasant. It is a major part of the process of seasoning and toasting (or charring) to break down the tannins and render them more acceptable. Tannins also play an essential role in maturation by enabling oxidation and the formation of a slight fragrance in wines (Anon., 1995).

The wood tannin reacts with oxygen in the presence of a transition metal - e.g., iron, copper or manganese - to release activated oxygen which oxidize alcohol to acetaldehyde. More alcohol combines with the acetaldehyde and creates a new compound in the drink, diethyl acetal, often just called acetal. This compound has a strongly ethereal influence on

the product giving it delicacy and top-note. Tannins are relatively easily broken down during seasoning and toasting which enhances the flavours (Jackson, 2000).

1.7.5 Lactones

The oak lactones possess a strong woody character and contribute to the unique aroma and flavour of bourbon. Although they occur in all oak woods used for cooperage, the cis-isomer occurs in much higher levels in American white oak compared to other species. The cis- isomer has a stronger character than the trans- isomer (Carrillo et al., 2006).

Both these compounds come from small amounts of lipids - oils, fats and waxes - in the oak and increase significantly during seasoning and toasting. They can also decrease during toasting.

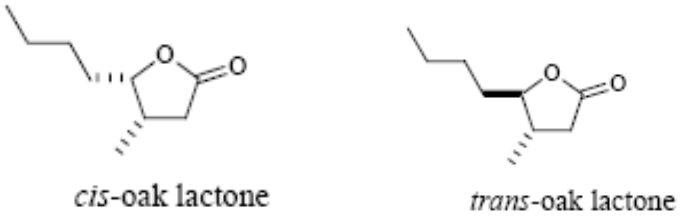


Figure 8 The oak lactones (Anon., 2004)

The full names for these compounds are cis-β□-methyl-γ-octalactone and trans-β-methyl-γ-octalactone. Both isomers are described as woody and coconut-like with the cis version much stronger. The cis-isomer has been reported as rose-like and trans-isomer as being celery-like (Pollnitz et al., 1999).

1.8 Aim of the study

The aim of this research was to find woods and treatments that could mimic traditional oak or create unique flavours in wines that might have market opportunities for New Zealand producers. The methods used involved the use of wood chips rather than barrels. The results were investigated by weight loss results on different toasting levels of the woods, their toasted colour, and spectrophotometeric and gas chromatographic analyses of toasted wood extractables in wine.

At the outset, it was decided to source single samples of woods from many species, rather than many samples of a lesser number of species. The reason for this was that because the work is completely new, a wide ranging survey would be better at this point in time.

Chapter 2

Materials and Methods

2.1 Woods

2.1.1 The plan and choice of woods

The selection of the woods was made on a number of criteria. These were association with New Zealand – either by nativity or by long-standing exotic origins, availability in untreated forms, broad representation from different plant families, historical use as a food-smoking wood, and botanical links to oak. Oak is an angiosperm and is a member of the Order Fagales as are cherry Beech and silver beech, whereas some other woods are gymnosperms and hence more distantly related. Table 3 lists the wood chosen and their source.

Table 3 Woods used for the project, the source and supplier

Common name	Botanical name	Source	Supplier
Matai	*Prumnopitys taxifolia*	Unknown	South Pacific Timber (Eden Terrace)
Feijoa	*Feijoa sellowia*	Hamilton	Dr O.A. Young
Macrocarpa	*Cupressus macrocarpa*	Unknown	South Pacific Timber (Eden Terrace)
Pohutukawa	*Metrosideros excelsa*	Maraetai	Mr B. Cook
Radiata pine	*Pinus radiata*	Unknown	South Pacific Timber (Eden Terrace)
Totara	*Podocarpus totara*	Unknown	South Pacific Timber (Eden Terrace)
Kahikatea	*Dacrycarpus dacrydioides*	Unknown	South Pacific Timber (Eden Terrace)
Rimu	*Dacrydium cupressinum*	Unknown	South Pacific Timber (Eden Terrace)
Cherry beech	*Nothofagus solandri*	Unknown	Rosenfeld Kidman (Penrose)
Silver beech	*Nothofagus menziesii*	Unknown	Rosenfeld Kidman (Penrose)
Manuka	*Leptospermum scoparium*	Waikato farmland	Dr O.A. Young
American oak	*Quercus alba*	Unknown	Rosenfeld Kidman (Penrose)

Matai, a member of the Podocarpaceae is found throughout New Zealand and is particularly abundant in the central North Island. In earlier decades it was used a s a general construction timber, particularly as flooring (Aalders, 2004).

Feijoa is a native of south-eastern Brazil and Uruguay where it grows naturally in subtropical to warm climates. As a member of the Myrtaceae, it is a relative of pohutukawa, as is obvious from the leaf and flower structures (Wellington Botanical Society, 2006). Feijoa was first introduced into New Zealand in 1908 (Anon., 2005) and occurs in the

warmer northern regions of New Zealand. Feijoa fruit has a sweet, aromatic flavour. The wood of this tree has no commercial value.

Macrocarpa's natural habitat is Point Lobos, near Monterey, in Northern California, and is also the native home of *Pinus radiata* (Aalders, 2004). Macrocarpa was introduced to New Zealand in the 1860. It is commonly used as tall windbreaks farm hedges throughout New Zealand (MacDirect Ltd., 2007).

The coastal species of pohutukawa is one of the most recognised New Zealand native trees. It is protected but its iconic status was the reason for its selection in this work. Its wood would be totally unsuitable as a timber except for minor decorative use if it could be sourced in legal and commercial quantities.

Radiata pine is a native of California but this is well adapted to the soils and climatic conditions of New Zealand and was chosen because it was readily available, and has been associated with New Zealand for approximately 80 years (Poole, 2006).

Totara and kahikatea are both New Zealand podocarps. Totara is a very straight grained, reddish timber originally used for construction and carpentry. Totara has been used in barrel construction (Coutts, 2005), but the staves were not bent, resulting in a cylindrical barrel. The abundance of natural oil minimizes microbial attack, it was previously commonly used as farm fencing posts (Aalders, 2004).

The podocarp kahikatea, also known as white pine, is one of New Zealand's tallest native trees up to 60 metres. As the name might suggest, the wood is pale in colour. It was previously known to make butter and cheese boxes for transport packaging. It is amazing that the butter or cheese were not reported to be tainted by the flavour of this wood (Aalders, 2004).

Rimu is another iconic podocarp previously used as a construction timber and still used as a decorative timber. Sushi plates, small wooden spoons and scoops are made from this wood (Aalders, 2004).

Forests dominated by beech (*Nothofagus*) species cover about 2.9 million hectare in New Zealand, and account for almost half of the total area of indigenous forest in New Zealand (Nick & Murray, 2004). Therefore, the two dominant silver beech and cherry beech were used for this project.

Manuka is a hardy native shrub that occurs throughout New Zealand. Its dense wood is slightly pink, but has no commercial value beyond firewood, for which it is highly prized, and as a smoking wood for fish and other food.

American oak, the final wood for this project is a traditional wood used for containment of wine at all stages of the wine making. Its flavour effects are frequently sought after in fermentation and maturation.

2.1.2 Preparation of the timber

The sourced wood was cut and chips of these woods were obtained. The woods were being cut with the band saw into the 1cm. thick strips and those strips were chipped with the use of Ryobi CMS 812 compound mitre saw and craft knife (whenever required) to get the desired 2 x 1 x 0.25 cm wood- chips.

2.1.3 Drying and toasting

The wood chips obtained were then toasted. Two levels of toasting were selected in terms of light (200°C for 2 hours) and heavy or dark toast (210°C for 3 hours). Two hundred grams of wood chips were taken for each toasting treatment. A convection oven, model MOV- 112F (Sanyo electric Biomedical Co., Ltd. Japan) was used for toasting wood chips. The oven was calibrated. Aluminum baking trays were used for toasting the wood chips and were wrapped into aluminum foil to avoid air exposure.

2.2 Wine

2.2.1 Source

A 100L sample of Gisborne unoaked *chardonnay* 2004 was donated by Simon Nunns of Coopers Creek Vineyard Limited. Its pH was 3.44, total acidity 6.8 g L^{-1}, residual sugars 4 g L^{-1}, with an alcohol content of 13% (v/v).

2.2.2 Model wine preparation

Model wine (Carrillo et al., 2006) was prepared in the AUT laboratory that contained 6 g L^{-1} of tartaric acid powder, 99% (BDH, England.), 13% ethanol (Scharlau ethanol absolute analytical grade, ACS, 99.8% in the deionised water). Finally, the pH was adjusted to 3.5 with sodium hydroxide. A total of 10L model wine was prepared.

2.2.3 Marination

The toasted chips were placed in dry, blue-capped 250 mL, Schott bottles. The ratio of timber chips to wine used was 5 g L^{-1}. First 30mL wine was added to the chips. A vacuum (pump) was then applied to extract the bulk of oxygen present in the wood chips. This vacuum was removed once the flow of bubbles ceased. The 250 mL, Schott bottles were then filled to overflowing, screw capped and stored in a dark place at room temperature in the laboratory for a period of two weeks. Both model wine and real wine were used for the marination.

2.2.4 Filtration

After the storage period the wines were individually filtered through glass-wool. Two 100mL bottles were filled to overflowing and were saved to perform the gas chromatographic analysis. The remaining wine from the 250 mL, Schott bottles were used to perform the spectrophotometry.

Figure 9 Wooded model wine stored in Schott bottles for further analyses

Figure 10 Wooded real wine stored in Schott bottles for further analyses

2.3 Instrumental analysis

2.3.1 Dry weight measures

Water content in the wood chipsfor the untoasted woods (excluding macrocarpa and feijoa) was measured. AOCS official method Aa 3-38 was modified to test moisture content. To measure the moisture content of the wood samples, Schott Duran glass dish was used. Twenty five grams of untoasted wood sample was placed in the Wilton utility oven (Manufacturing Laboratory Supplies Ltd., New Zealand) at 110ºC for 5 hours. After 5 hours, the samples were taken out of the oven and placed in a desiccator for 10 minutes to cool. They were then reweighed. The moisture content percent was calculated as follows:

$$\text{Moisture content (\%)} = \frac{\text{Loss in mass (g)}}{\text{Original sample mass (g)}} \times 100$$

2.3.2 Size of the wood chips

The size of the wood chips used for the maturation of wine may influence the extraction of the compounds from the wood into wine, and potentially from the wine into wood. Twenty wood chips for the untoasted woods were randomly picked for each wood type, and the thickness of the narrowest dimension was measured in millimetres with Vernier calipers.

2.3.3 Hunter colour measurements

A Hunter colorimeter (ColorFlex, Hunter Associates, Virginia, USA) was used to measure the colour of wood- chips (Figure 11).

The principle of the Hunter colour system is based on the concept of a colour space with the colour defined by three coordinates, L*, a*, and b* values (Coultate, 2002). The vertical coordinate L* is lightness from 0 (total light absorbance and therefore completely black) through grey (50) to 100 (complete light reflectance); the horizontal coordinate a* is greenness/redness, from – 60 (green) through grey to + 60 (red); an orthogonal horizontal coordinate b* is yellowness from – 60 (blue) to + 60 (yellow). It is shown in Figure 12.

Hue angle refers to the gradation of colour within the visible spectrum of light. Hue angle is arctangent (b*/a*) determined by rotation about the a* and b* axes.

Chroma or saturation is the intensity of a specific hue: a highly saturated hue has a bright, intense colour, while a less saturated hue appears gentler. Chroma of a colour is determined by a combination of colour intensity and how much it is distributed across the spectrum of different wavelengths (Young & West, 2001). Chroma is calculated as $\sqrt{(a^{*2} + b^{*2})}$. Thus L* (lightness), hue angle and chroma are independent values that theoretically describe all perceived light.

To measure wood chips colour, a Duran cylindrical glass dish (Schott, Germany) measuring 2.5 cm. was placed in the illuminant path of the instrument and was covered with a black cover. Daylight D65/10° illuminant/observer combination was selected to measure daylight colour that measures the colour in terms of L*, a* and b* values.

Figure 11 A Hunter colorimeter (ColorFlex, Hunter Associates, Virginia, USA)

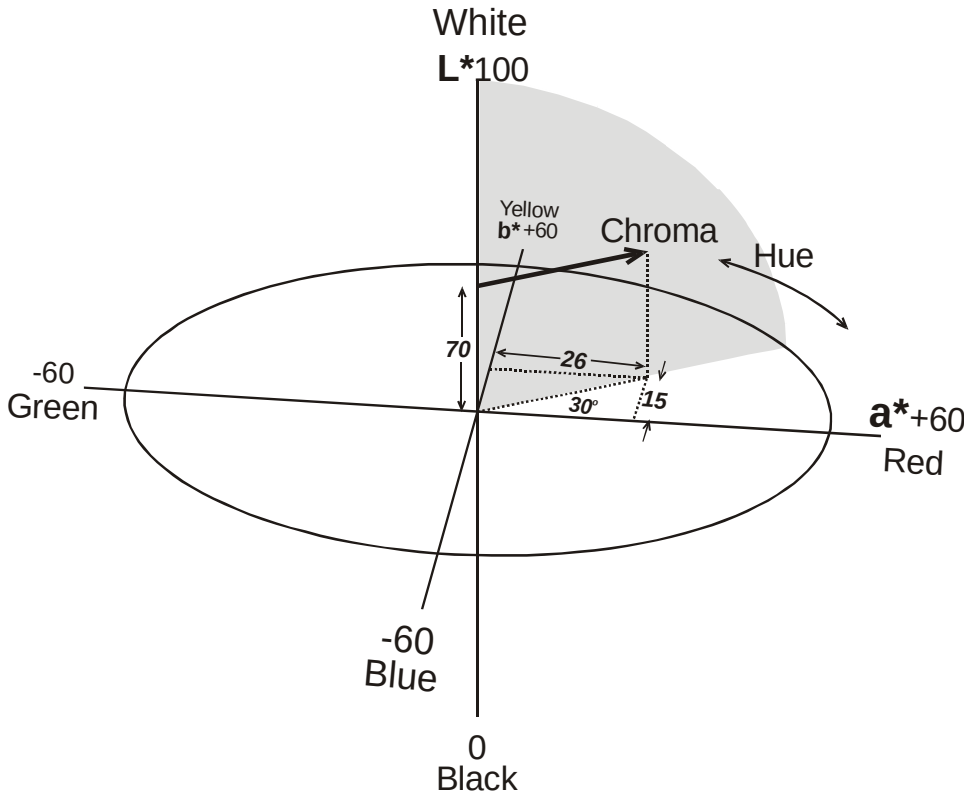


Figure 12 In L* a* b* colour space, the tip of the thick arrow is defined by its lightness (70 on a scale of 0 to 100), its redness (+26 on a scale of –60 to +60) and yellowness (+15). The hue is arctangent 15/26 (= 30°) and the chroma, or intensity, is the length of the thick line, $\sqrt{(15^2 + 26^2)}$ (= 30), redrawn from Young & West (2001)

2.3.4 UV absorbance

A Ultrospec 2100 pro UV/visible spectrophotometer and a quartz cuvette with a path length of 10mm were used. The program Biochrom data collection version 2.0 was used to collect all data. The same cuvette was used for every treatment.

Each wine sample was subjected to a wavescan analysis run between 200 and 400nm on slow scan. This was performed with the model wine prepared and woods in the model wine. A blank of model wine was used to zero the equipment followed by the samples diluted at a ratio of 1:3 of model wine volumes. The similar practice was done with Gisborne unoaked *chardonnay* 2004, where Gisborne unoaked *chardonnay* 2004 diluted at a ratio of 1:20 of distilled water (control) was used to zero the equipment followed by the woods in wine with same dilution.

2.3.5 Gas chromatography mass spectroscopy (GC-MS)

Extraction of the possible flavour compounds was done for American oak, pohutukawa, and silver beech, totara, manuka and matai for both toasting levels. Twenty grams of NaCl was added to 100 ml of the wooded wine sample (both model and real wine samples) and 1mL of 2-octanol solution, BDH reagent (70 mg/100 mL) was added as an internal standard (Arapitsas et al., 2004).

This mixture was extracted twice using 200 mL of an n-pentane and diethyl ether (1:1, v/v) mixture each time. The extraction of phenolic compounds from the wood was targeted by this method and other volatile compounds present in the wine such as esters and higher alcohols are not included. The obtained organic phase was washed three times with 30 ml of saturated sodium bicarbonate solution ($NaHCO_3$ analytical reagent, 99.5%) and once with 30 ml of distilled water. The organic layer was dried over sodium sulphate (Na_2SO_4) anhydrous powder, extra pure 99% (Scharlau Chemie S.A.). It was then placed in a pear-shaped flask equipped with a Vigreux column of 25 cm length and it was slowly concentrated to approximately 0.5 mL by heating in a water bath at 50ºC.

Figure 13 Extraction procedure for the flavour compounds

Each wine sample's extract was subjected to GC analysis, using a Trace GC Ultra gas chromatography (DSQ Thermoelectron Corporation), equipped with Factor Four $^{TM:}$ Capillary Column VF- 5 ms, (30 m length, 0.25 mm i.d., and 0.25 µm film thicknesses). Samples (1µL) were injected using split mode with a split ratio of 10. The helium carrier gas flow rate was set at constant flow of 1.5 mL min^{-1}. The injector temperature was 200°C. The interface temperature between column and detector was 250°C. A temperature program was developed where the column temperature programme was held at 80°C for 1 min, to 280°C at a rate of 10°C min^{-1}. Detection was carried out by mass detector. The detector gain was 2.00 V.

Figure 14 Trace GC Ultra GC-MS used for the gas chromatographic analyses

2.4 Data analysis

Microsoft Excel was used for recording data and analysis. The data was used to compare untoasted and toasted woods, colour measurements, moisture variation, spectrophotometric variations and other flavour compounds. Simple statistical methods in Excel were used to calculate means, standard deviations, linear regression lines and correlation coefficients. Graphs were prepared using SigmaPlot 8.0 (SPSS Inc., Chicago).

Chapter 3

Results and discussion of wood chip preparation and analysis

3.1 Thickness of the wood chips

The nominal dimensions were 2 x 10 x 20 mm, where the longest dimension was along the grain. Because reactions involving the wood would be determined by the thinnest dimension, measurements were made of that dimension (Table 4). Cherry beech and rimu chips were the thickest, and matai chips the thinnest by a considerable margin.

Table 4 Mean thickness of the narrowest dimension of untoasted wood chips ± standard deviations

Wood	Thickness of wood chips (mm)
Matai	2.22 ± 0.41
Feijoa	2.73 ± 0.72
Macrocarpa	2.46 ± 0.58
Pohutukawa	2.57 ± 0.84
Radiata pine	2.45 ± 0.51
Totara	2.67 ± 0.73
Kahikatea	2.49 ± 0.36
Rimu	3.10 ± 0.60
Cherry beech	3.17 ± 0.82
Silver beech	2.64 ± 0.52
Manuka	2.40 ± 0.65
American oak	2.70 ± 0.49

It is quite likely that the variations in thickness will have little effect on extraction of compounds, because the toasting will almost certainly open up the wood structure, and the two week exposure period should be long enough to equilibrate the compounds between wood and wine. However an effect of thickness cannot be excluded.

3.2 Weight loss on drying and toasting

Samples of the wood chips were dried at 110°C for 5 hours to determine the dry weight of the woods. This was not done for feijoa and macrocarpa because there was insufficient wood. Subsequently, fresh samples of wood chips were heated to 200°C for 2 hours – light toasting – or 210°C for three hours – heavy toasting. The results are expressed as weight loss percent of the original chips (Figure 15).

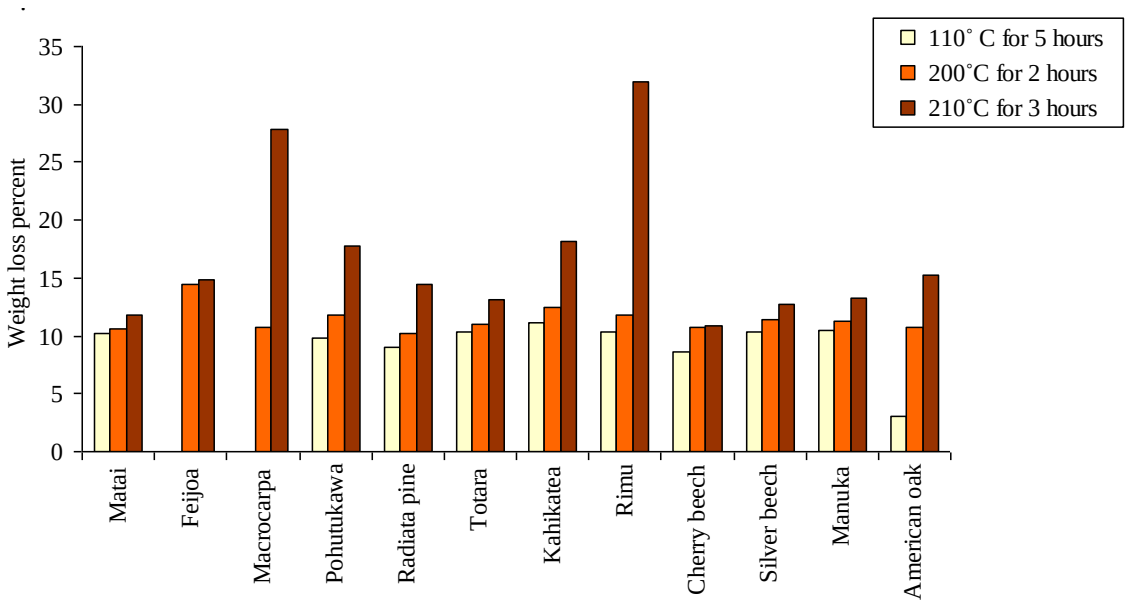


Figure 15 Weight loss percent in woods on drying and toasting

The data for moisture content (Figure 15) shows that, excluding American oak at 3.03%, the moisture contents of all other woods measured were similar, ranging between 8.68% (cherry beech) and to 11.07% (kahikatea), with a mean 10.02%.

When the woods were toasted at 200°C for 2 hours (light toast), all the woods lost weight due to pyrolysis and/or further loss of moisture. The mean loss was 11.4% ranging between 10.3 (radiata pine) and 14.4% (feijoa). However, close inspection of the data shows that the losses were greatest for oak. There was a seven percentage point between drying and light toasting, whereas the equivalent differences for other woods were much lower, no more that two percentage points. Equivalent data for feijoa and macrocarpa were not available. Thus on a weight basis, the greatest changes on light toasting occurred in oak.

On heavy toasting the differences in weight loss percent between woods were large. The mean loss was 16.8% ranging between 10.9 (cherry beech) and 31.9% (rimu). Thus, matai, feijoa, and the two beech species little changed, while macrocrapa and rimu suffered severe weight loss. These two woods generated copious quantities of smoke during heavy toasting with signs of burning (rimu particularly), thus accounting for the loss. Kahikatea also generated much smoke, but its weight loss on heavy toasting was not particularly severe.

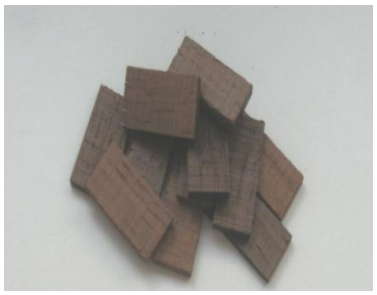
Plots of mean wood chip thickness against percent weight loss on drying, light toasting, and heavy toasting showed a random distribution of data for each plot (data not shown).

3.3 Appearance and colorimetry

Representative photographs of dried but untoasted woods (110°C for five hours), and the two toasting levels are shown in Figure 16. The basic colours (hues) were shades of red-brown, with a strong tendency to darker shades on toasting.

American oak (untoasted)

American oak (light toast)



American oak (dark toast)

Cherry beech (untoasted)

Cherry beech (light toast)

Cherry beech (dark toast)

Rimu (untoasted)

Rimu (light toast)

Rimu (dark toast)

Kahikatea (untoasted)

Kahikatea (light toast)

Kahikatea (dark toast)

Silver beech (untoasted)

Silver beech (light toast)

Silver beech (dark toast)

Matai (untoasted)

Matai (light toast)

Matai (dark toast)

Radiata pine (untoasted)

Radiata pine (light toast)

Radiata pine (dark toast)

Manuka (untoasted)

Manuka (light toast)

Manuka (dark toast)

Figure 16 Appearance of different woods on different toasting levels

The colour of the untoasted and toasted wood chips was measured in Hunter colour space. The daylight colour parameters L*, a* and b* were measured, and a* and b* values were used for the calculation of hue angle and saturation. The mean values are summarized in Table 5.

Table 5 Mean lightness, hue angle and saturation values for woods at different toasting levels

Wood	Lightness L*			Hue angle (arctan b*/a*)			Saturation ($\sqrt{(a^2 + b^2)}$)		
	Untoast	Light toast	Heavy toast	Untoast	Light toast	Heavy toast	Untoast	Light toast	Heavy toast
Matai	59.53	50.93	29.96	1.20	1.16	1.06	31.12	27.78	18.11
Feijoa	59.05	33.43	31.80	1.29	1.06	1.07	20.68	17.40	19.10
Macrocarpa	64.82	55.70	16.33	1.16	1.23	0.76	28.21	26.50	3.00
Pohutukawa	56.55	30.03	15.82	1.07	0.82	0.82	21.01	13.60	3.00
Radiata pine	64.55	64.55	26.43	1.29	1.35	1.01	20.68	23.64	13.72
Totara	47.81	37.70	27.59	1.02	0.99	1.00	24.82	20.37	14.28
Kahikatea	68.48	59.28	39.23	1.32	1.29	1.15	28.11	28.60	23.10
Rimu	48.90	41.57	22.70	1.12	1.12	0.99	26.49	22.03	6.63
Cherry beech	54.49	45.53	29.07	0.95	0.99	0.99	21.71	18.50	14.70
Silver beech	60.17	50.16	34.66	1.09	1.07	1.08	20.74	16.84	16.68
Manuka	59.61	50.27	19.51	1.13	1.08	0.85	21.33	20.00	7.70
American oak	46.46	43.39	23.14	1.20	1.24	0.95	19.67	19.12	7.37

The data were then normalized, where the untoasted wood chips were adjusted to 100, and toasted results were scaled accordingly.

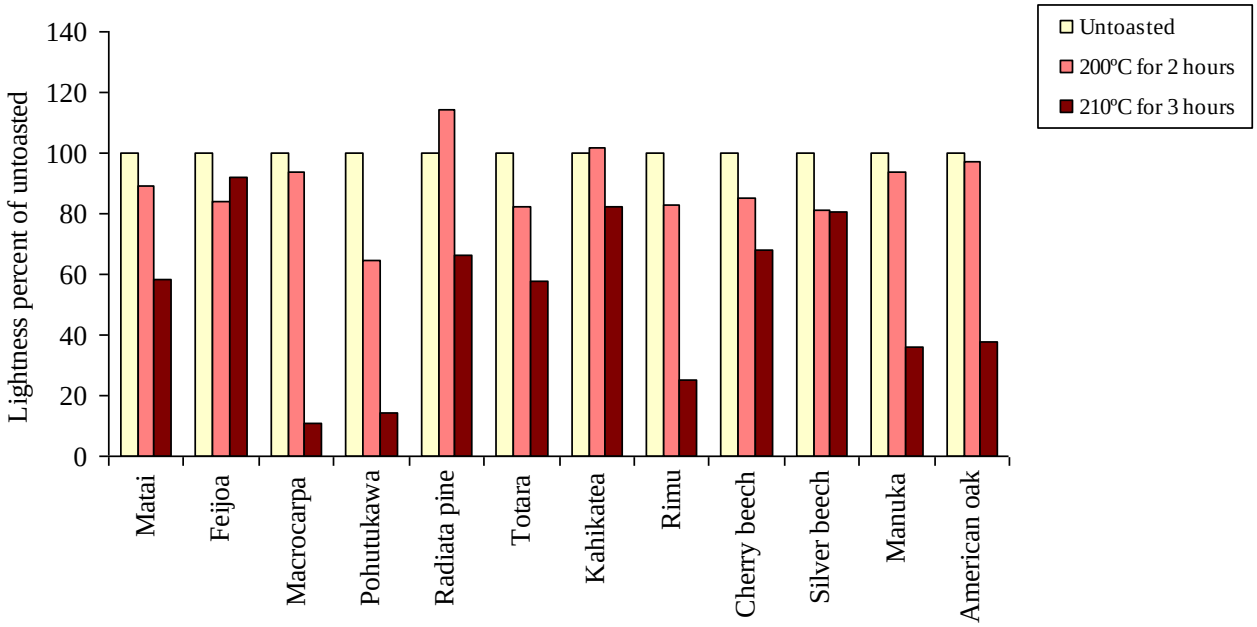


Figure 17 Difference in the lightness data of woods at different toasting levels

For all woods except radiata pine, lightness – which is a measure of percent light reflected – decreased with light toasting (Figure 17). For this treatment, the outstanding woods for high loss of reflectance were feijoa and pohutukawa. Radiata pine and oak were

at the other extreme. On heavy toasting all woods lost reflectance, particularly macrocarpa, pohutukawa and manuka. Whereas radiata pine was virtually unaffected by the light toast and was strongly affected by the heavy treatment.

When lightness percent of untoasted was plotted as a function of weight loss percent on toasting, there was an inverse linear relationship for light toasting (Figure 18). For dark toasting there was a much weaker relationship (Figure 19). Thus reflectance is an indicator of weight loss and therefore pyrolysis.

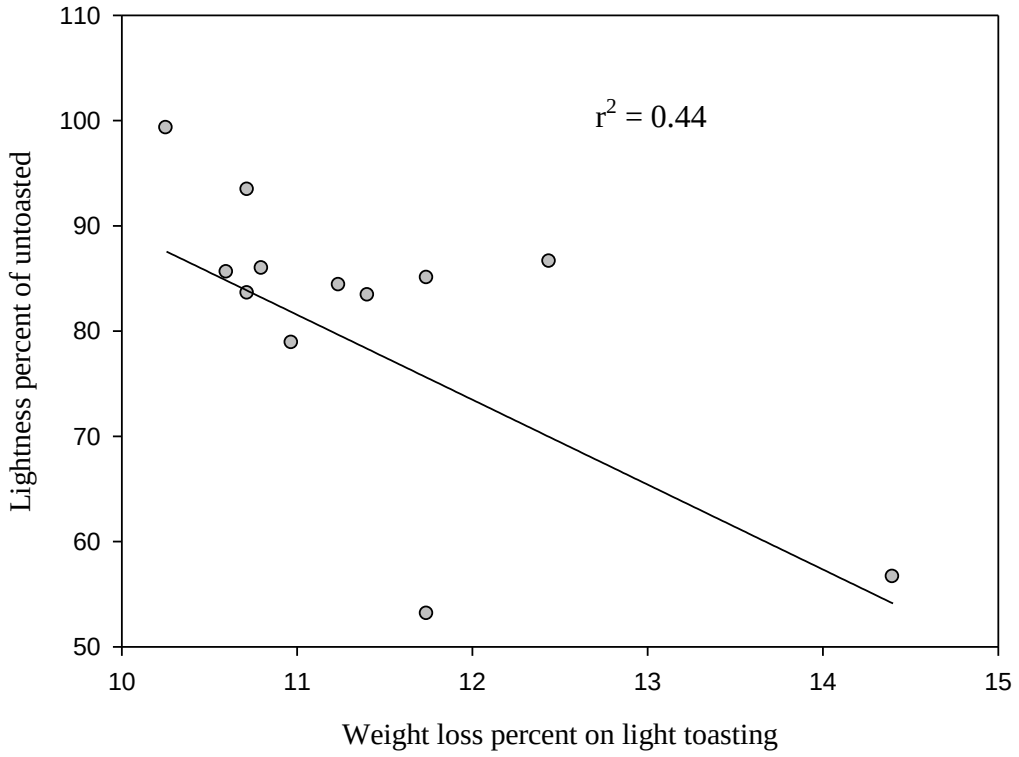


Figure 18 Plot of lightness percent of untoasted as a function of weight loss percent of wood chips on light toasting

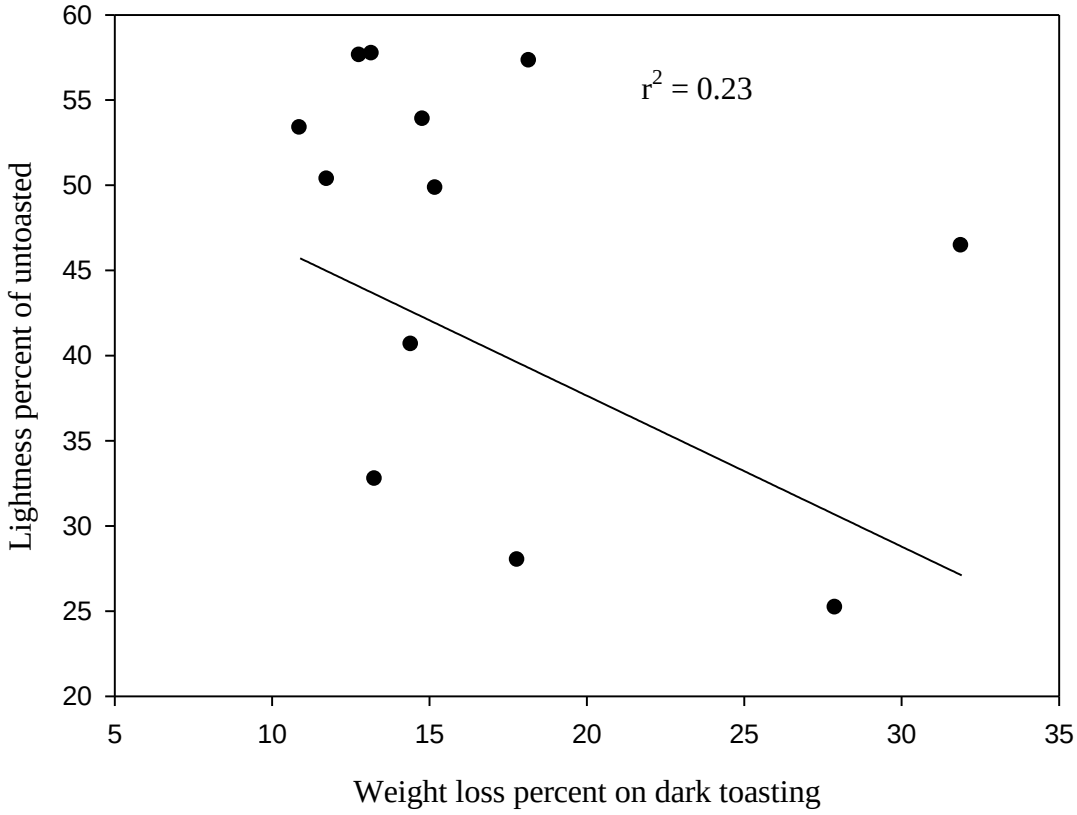


Figure 19 Plot of lightness percent of untoasted as a function of weight loss percent of wood chips on dark toasting

The fundamental colour of an object is its hue, expressed here as hue angle (Table 5). With the exception of feijoa and pohutukawa, there was little change in percent hue angle of the woods due to light toasting. Feijoa and pohutukawa were the same two woods that suffered high loss of reflectance on light toasting. On heavy toasting, totara and the two beeches retained the original hue of the untoasted wood. All other woods suffered a decrease in hue angle (Figure 20).

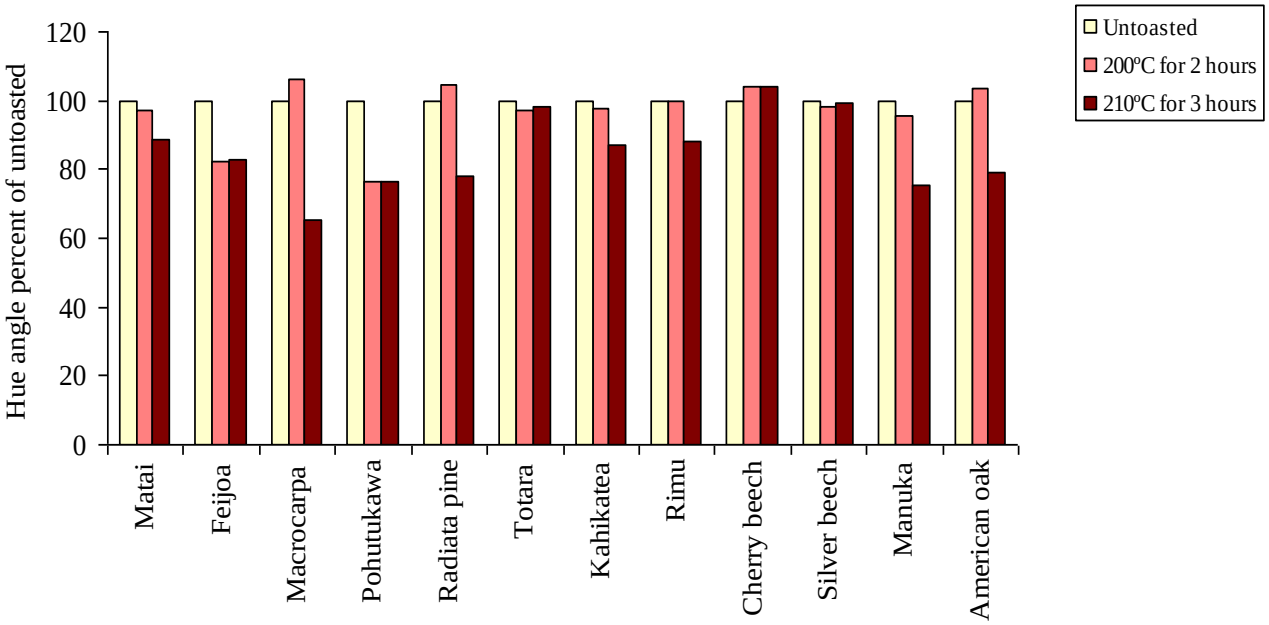


Figure 20 Difference in the hue angle data of woods at different toasting levels

When hue angle percent of untoasted was similarly plotted as a function of weight loss percent on toasting, there was again a clear inverse linear relationship for light toasting (Figure 21). For heavy toasting there was a much weaker relationship that was probably curvilinear (curvilinear line not fitted) (Figure 22). Thus percent loss in hue angle and percent weight loss are generally inversely related.

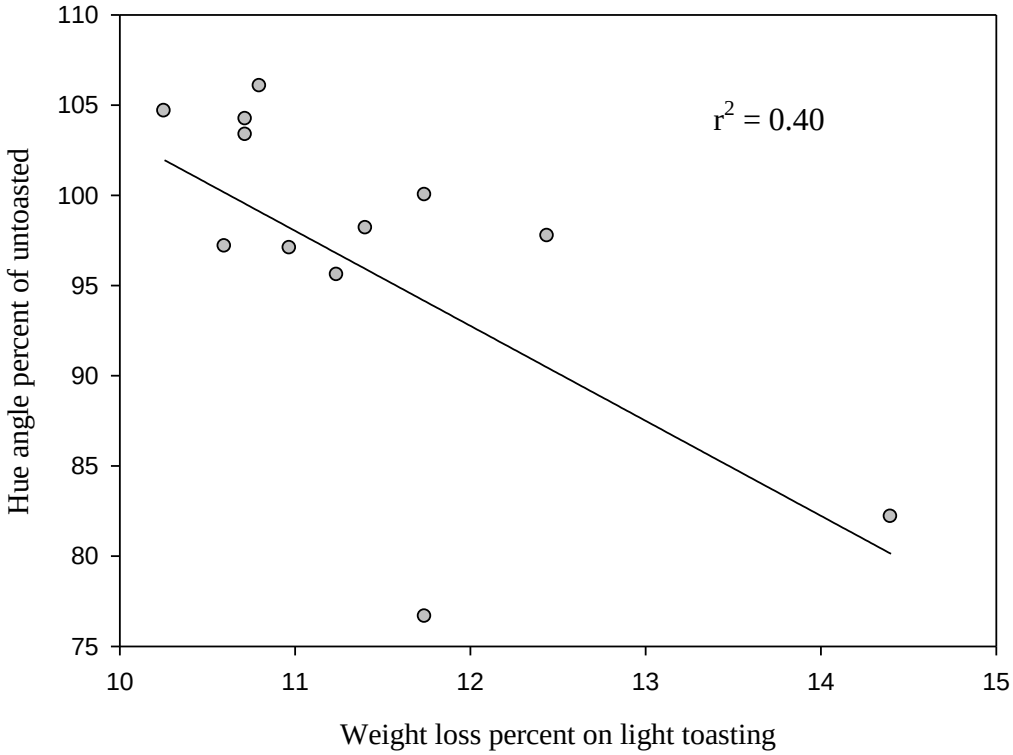


Figure 21 Plot of hue angle percent of untoasted as a function of weight loss percent of wood chips on light toasting

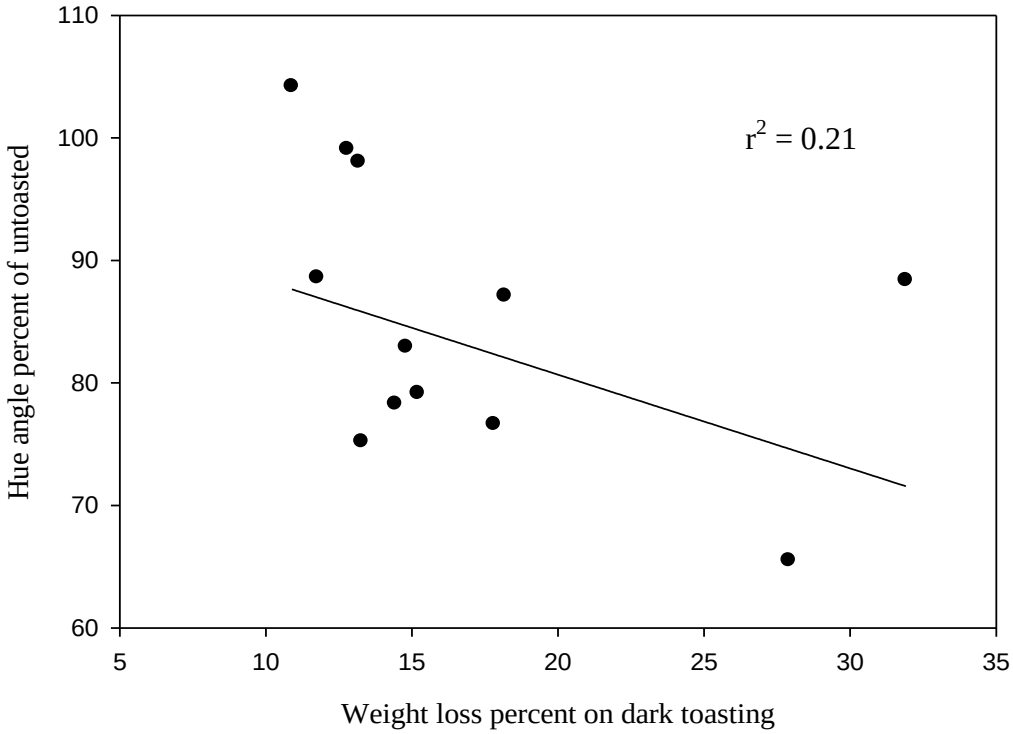


Figure 22 Plot of hue angle percent of untoasted as a function of weight loss percent of wood chips on dark toasting

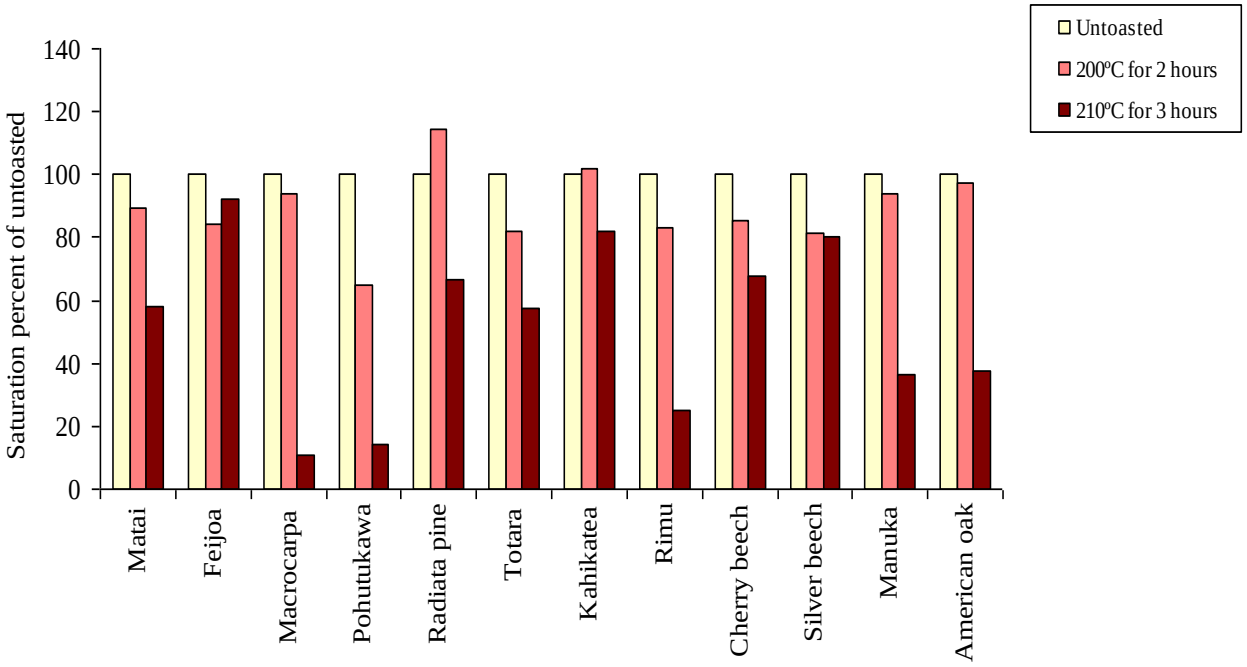


Figure 23 Effect of different toasting levels on the saturation of woods.

In all woods, saturation – or intensity of the hue – decreased on light toasting except for radiata pine, which showed a small increase, and kahikatea and American oak, which were unchanged (Figure 23). On light toasting, the largest decrease was for pohutukawa.

On heavy toasting, macrocarpa and pohutukawa showed severe loss of colour, closely followed by rimu. Of these three, macrocarpa and rimu were noted smoke generators on heavy toasting. Manuka and American oak also suffered a severe loss in colour saturation on heavy toasting. Feijoa suffered little.

When viewed as photographs, the intensity of colour appears to increase on toasting, but the data in Figure 23 shows that this appearance is more related to loss of light reflectance. In other words, true colour is usually being lost on toasting, not gained.

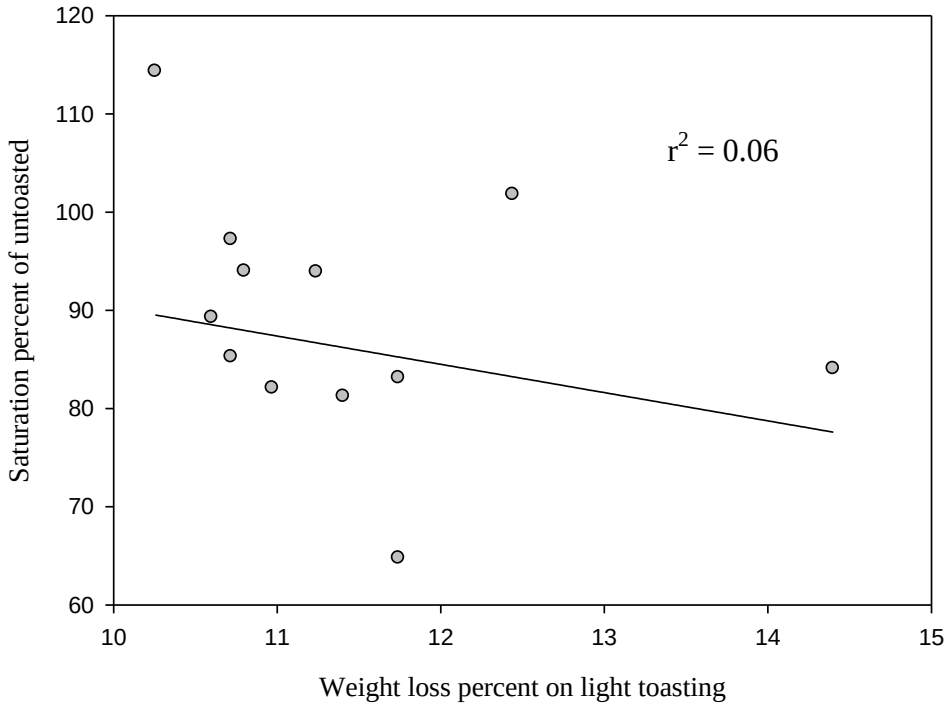


Figure 24 Plot of saturation percent of untoasted as a function of weight loss percent of wood chips on light toasting

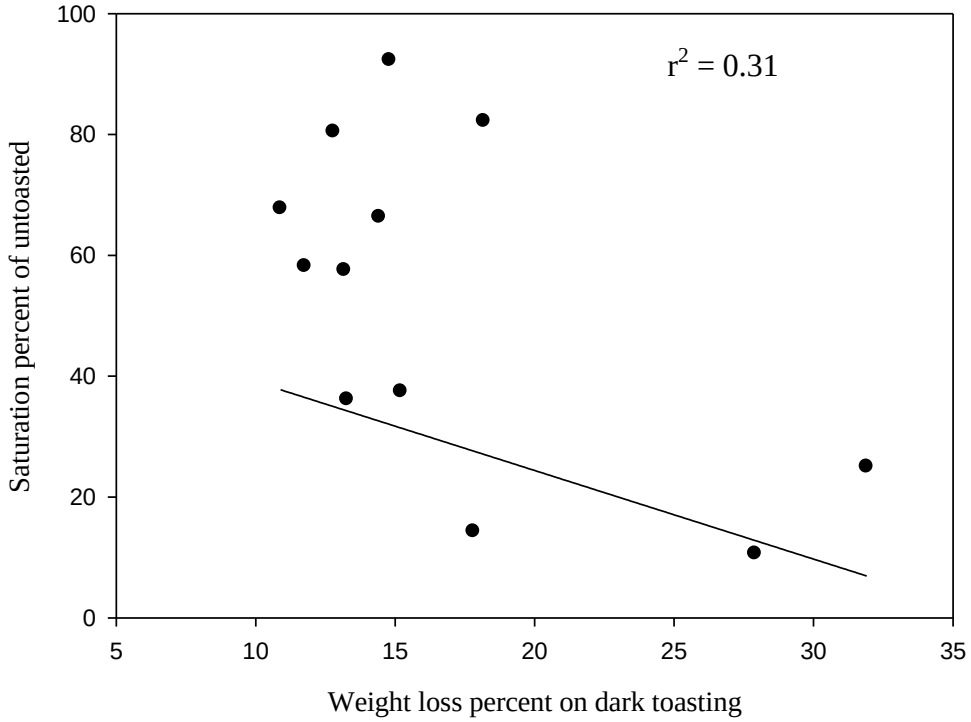


Figure 25 Plot of saturation percent of untoasted as a function of weight loss percent of wood chips on dark toasting

The plot of saturation percent of untoasted against weight loss percent on toasting showed an inverse relationship on heavy toasting. The equivalent plot for light toasting while inverse, was insignificant ($r^2 = 0.06$) (Figure 24, Figure 25). As with the lightness and hue angle, the losses in these variables were generally linked to percent weight loss due to pyrolysis.

Overall, each wood tended to behave in a different way in response to light and heavy toasting. However, there was a general theme of loss of lightness (reflectance), hue angle and saturation as the degree of pyrolysis increased, the latter manifest as weight loss percent. How these changes translate to extraction of toasted wood in a model wine is explored in the next chapter.

Chapter 4

Results for Model Wine

4.1 Introduction

The extraction of toasted woods in a model wine is described in this chapter. The extraction has been studied by ultraviolet spectrophotometry on the basis that there were no visible colour changes in wine due to exposure to toasted woods, but that lignin compounds are based on aromatic ring structures that absorb strongly in the ultraviolet range. For example, vanillin – a recognized flavour compound in oaked wines – is a phenol that absorbs in the ultraviolet region with peaks at 278 and 308 nm (Anon., 1996). Subsequently, gas chromatography has been performed on a selection of wooded model wines to describe the sorts of compounds that were generated on toasting and were extracted into the model wine.

4.2 Ultraviolet spectrophotometry

4.2.1 Model wine marinated with light toast wood chips (200°C for 2 hours)

Absorbances between 200 to 400 nm were obtained for all treatments. To achieve absorbances between 0 and 2 required an initial dilution of one part wooded model wine to two parts model wine. The absorbances were recorded against a reference of model wine. The initial dilution required that the data be multiplied by three to obtain true absorbances. The graphs presented here are plotted with a vertical axis ranging between –0.2 and 8.0 (Figure 26 and Figure 29), the latter value more than covering the data range. This was done so that the graphs for model wine could be directly compared with the equivalent graphs for real wine described in Chapter 5.

In Figure 26, there is clear evidence of electronic noise in the ultraviolet spectra especially in the range of 200 to 225 nm. The cause of this is likely to be high absolute absorbance due to solutes in this wavelength range. This results from the photometer measuring extremely low light levels where noise to signal ratios are high.

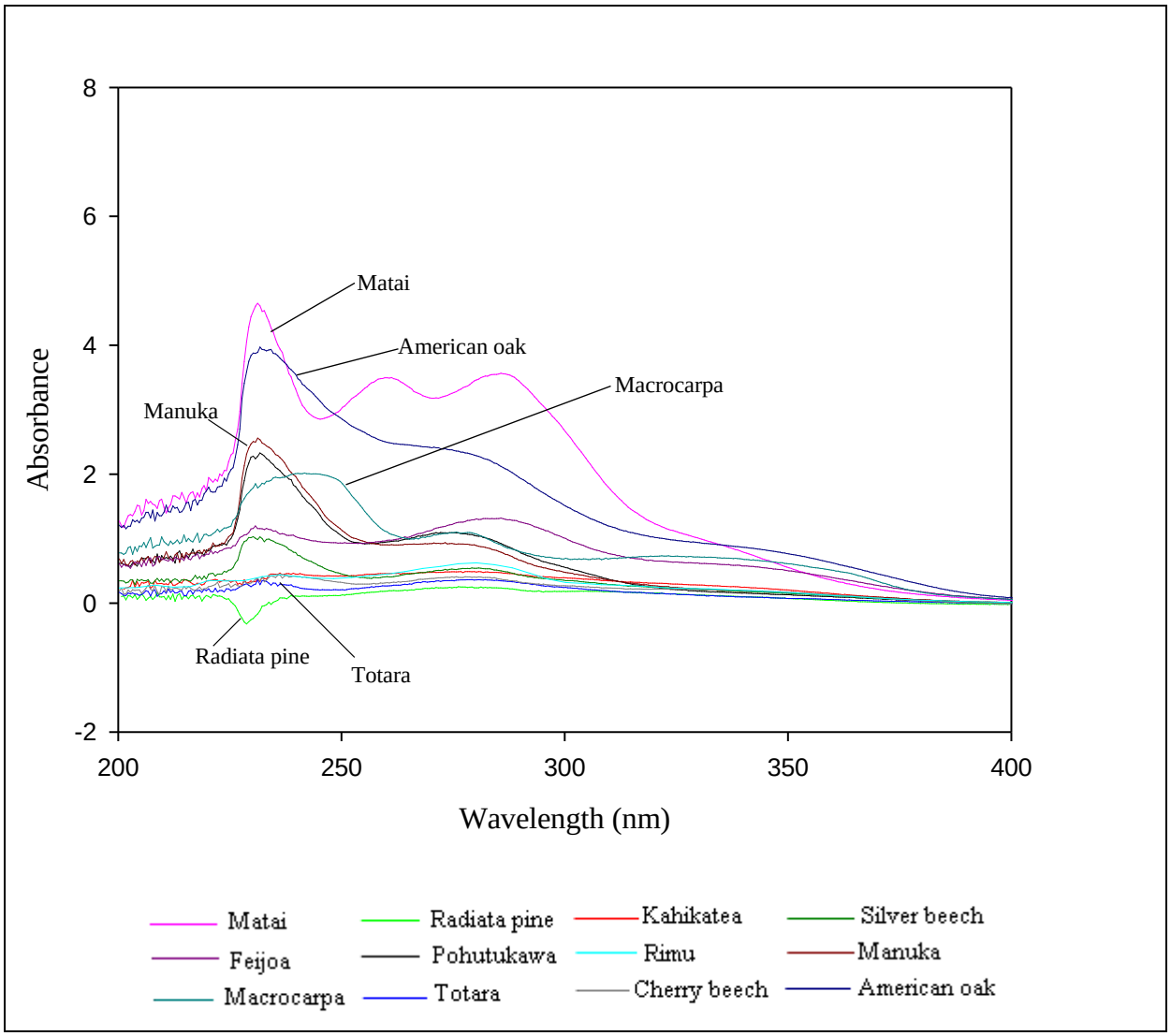


Figure 26 Absorbance of different wood treatments with light toast wood chips in model wine.

Matai showed the maximum peak absorbance followed by American oak, manuka, pohutukawa and macrocarpa (Figure 26). However, the maximum peak absorbance overlooks the fact that some woods absorbed over a wide range of wavelengths, but without obvious peaks. Therefore, the relative areas under the curve were calculated by summing the 401 individual readings (each representing 0.5 nm) for each scan between 200 and 400 nm. The left side of Table 6 shows data for light toast relative to the wood that absorbed the most, in this case matai. Its area was 741 arbitrary absorbance units, but was normalized to 100. Matai, American oak and macrocarpa had the highest values for relative areas, while radiata pine and totara absorbed the least.

Table 6 Relative area under the absorbance curve in the range 200 to 400 nm, normalized to the wood that absorbed the most, for light and dark toast treatments in model wine

Light toast		Dark toast	
Wood in descending order of relative area	Relative area normalised to matai	Wood in descending order of relative area	Relative area normalised to silver beech
Matai	100	Silver beech	100
American oak	83	Feijoa	66
Macrocarpa	47	Cherry beech	66
Feijoa	40	Kahikatea	65
Manuka	34	Pohutukawa	56
Pohutukawa	34	Matai	55
Silver beech	19	Manuka	54
Rimu	18	American oak	50
Kahikatea	17	Radiata pine	44
Cherry beech	13	Totara	28
Totara	10	Rimu	26
Radiata pine	6	Macrocarpa	21

Radiata pine showed negative absorbances around 226 to 234 nm. For model wine this phenomenon was puzzling, because to reduce absorbance would require the wood to extract some ultraviolet-absorbing matter from the model wine. Model wine is composed of water, ethanol and tartaric acid titrated to pH 3.5 with NaOH. A scan of model wine (one part plus two parts of water) was made, again subsequently remultiplying by three (Figure 27).

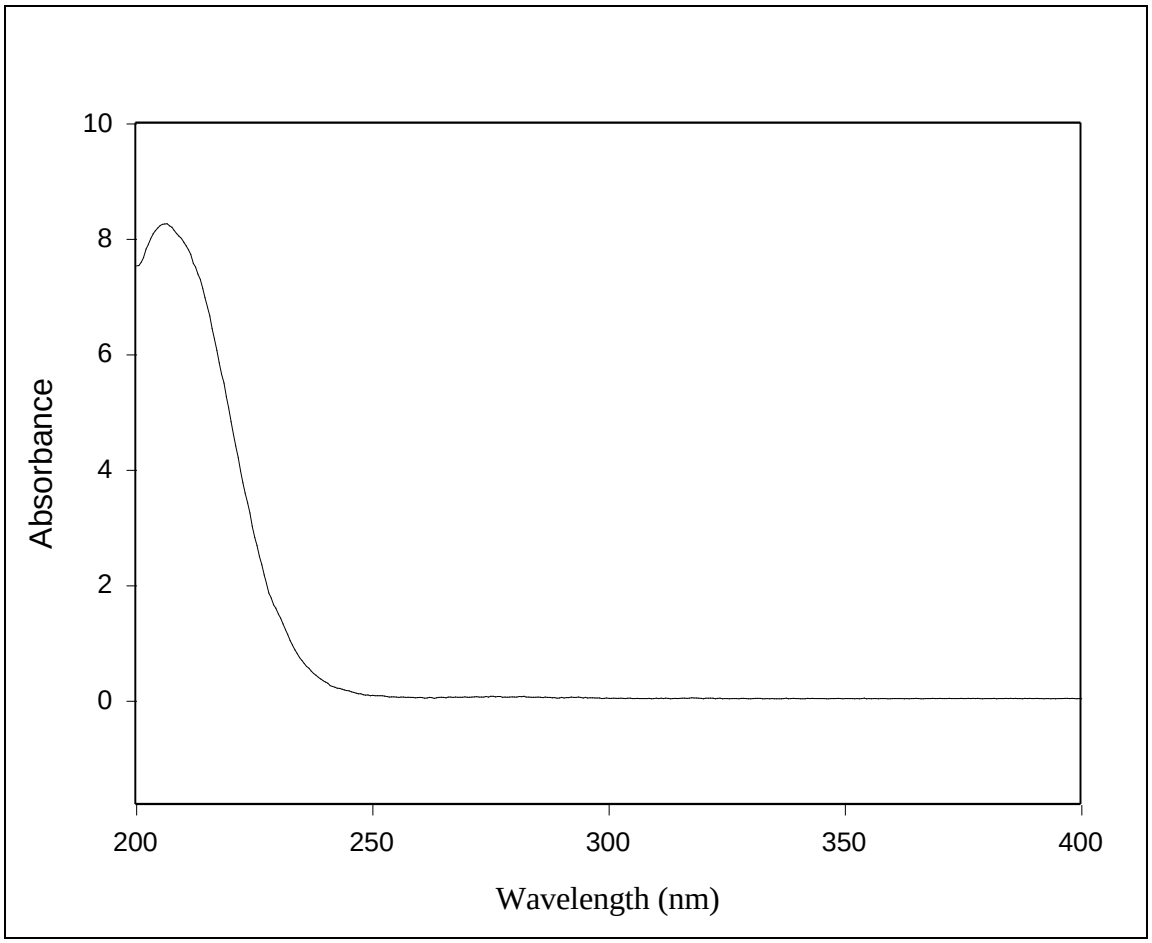


Figure 27 Ultraviolet absorbance of the model wine

The model wine absorbed light below 250 nm, but there was no peak around 226 to 234 nm, which if lost, would account for the negative absorbance (Figure 27).

In searching for the cause of this phenomenon, attention is drawn to the fact that of all the woods, radiata pine showed the least colour and weight loss on light toasting. But no model has been developed to explain the phenomenon in model wine.

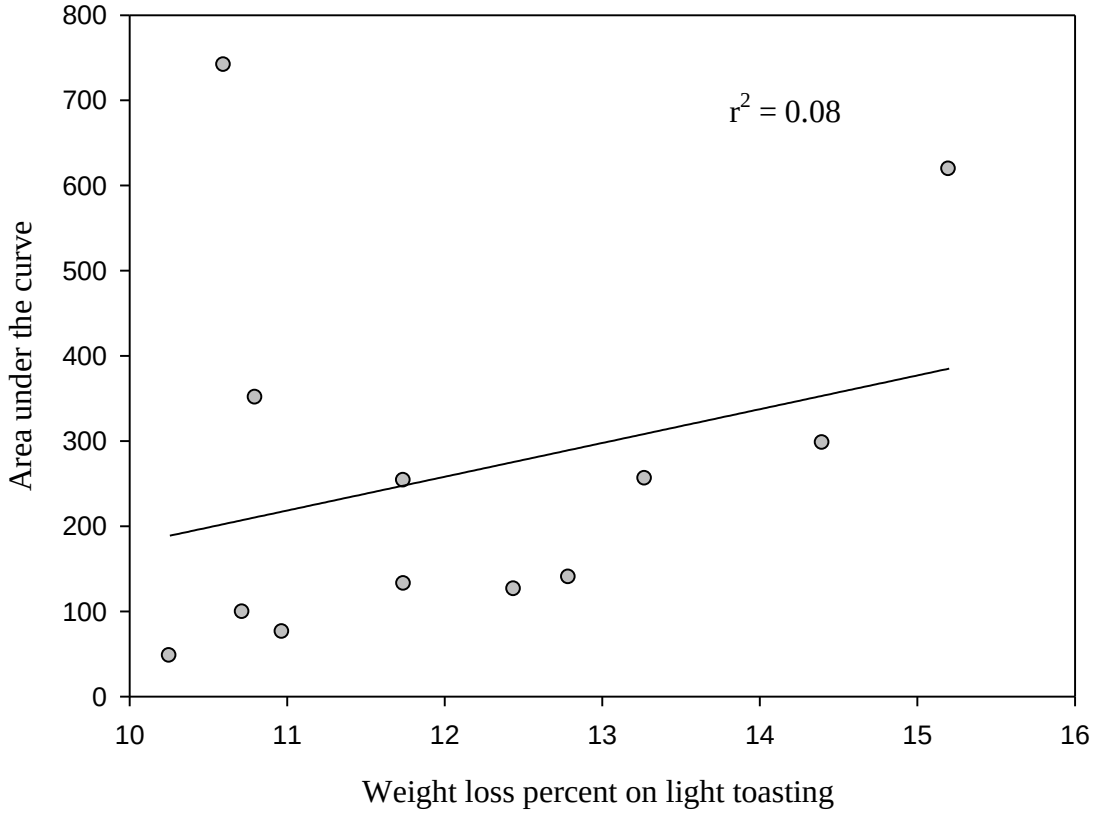


Figure 28 Plot of weight loss percent on light toasting as a function of total area under the ultraviolet absorbance curve between 200 and 400 nm. A least squares straight line has been fitted to the data

It was also hypothesised that the relative area under the absorbance curve between 200 and 400 nm for each toasting treatment (Table 6) might be related to the loss of weight on toasting, the argument being that low weight loss – but nonetheless some degradation of lignin – would result in substantial extraction of ultraviolet-absorbing matter from the wood chips. Figure 28 shows there was no relationship between total area and weight loss percent for light toasting.

4.2.2 Model wine marinated with dark toast wood chips (210°C for 3 hours)

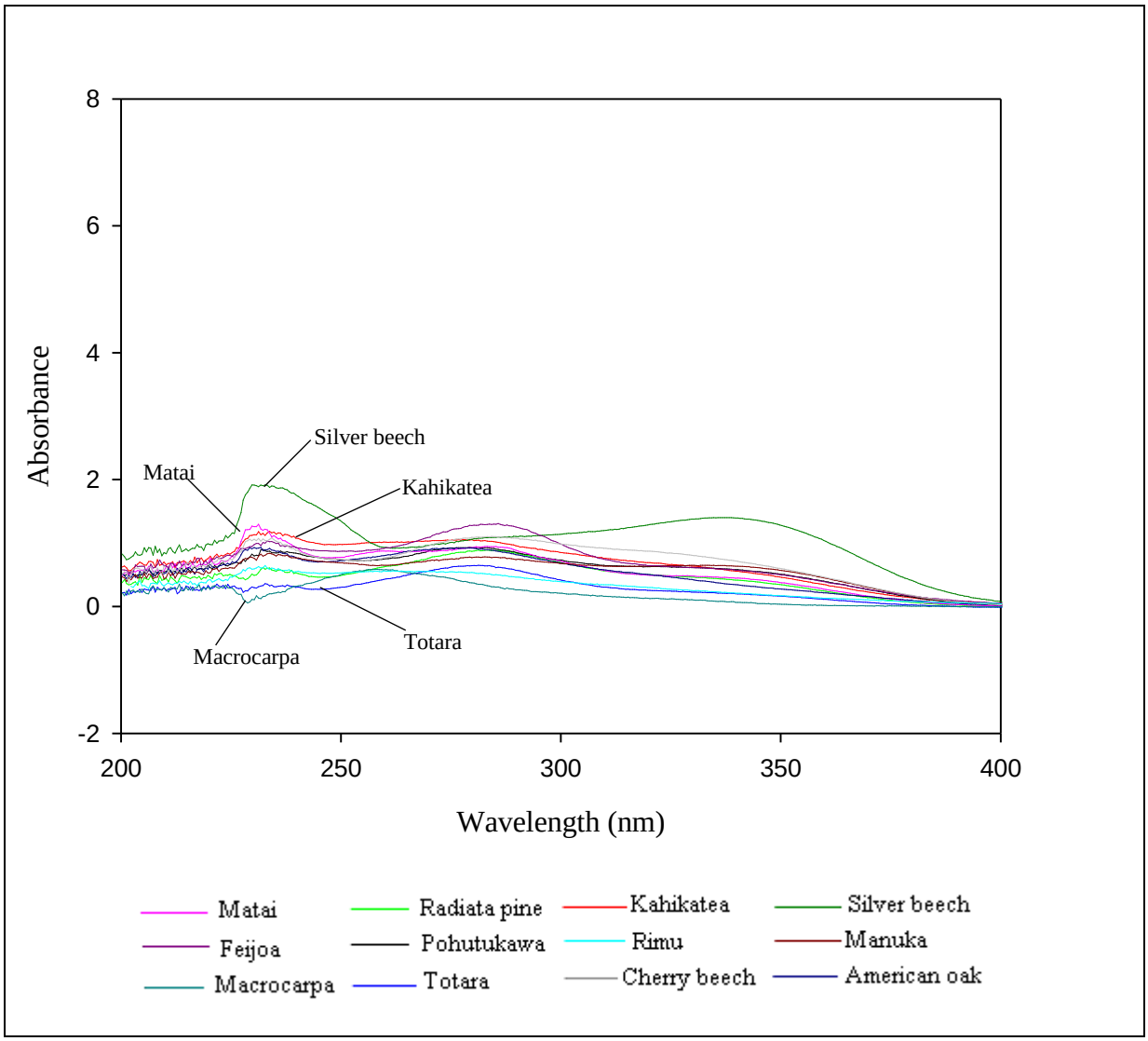


Figure 29 Absorbance of different wood treatments with dark toast wood chips in model wine.

As with the light toast, an initial dilution was made in order to bring the scans on scale. Again there was clear evidence of electronic noise in the spectra especially in the range of 200 to 225 nm, and probably due to high absolute absorbance.

Silver beech showed singificant absorbance peaks followed by matai, kahikatea, cherry beech, and feijoa. Manuka, pohutukawa, rimu, radiata pine and totara differed little from each other (Figure 29).

For the model wine dark toast (210ºC for 3 hours), the highest arbitrary value of summed absorbances between 200 and 400 nm was 432 for silver beech. This was normalised to 100 in Table 6, right side columns. This wood stood out from the others, with feijoa, cherry beech and kahikatea the next closest around 66. Rimu and macrocarpa added the least absorbing matter to the model wine. Both rimu and macrocarpa suffered severe weight loss on dark toasting, manifest as excess smoke production. This appears to be consistent with the low extraction into the model wine, the argument being that potentially absorbing matter was lost as smoke. A plot of total area under the curve from the absorbance data for each wood against the weight loss percent on dark toasting showed a weak inverse relationship (Figure 30) but the relationship was strongly determined by the rimu and macrocarpa data points, on the bottom right in that figure.

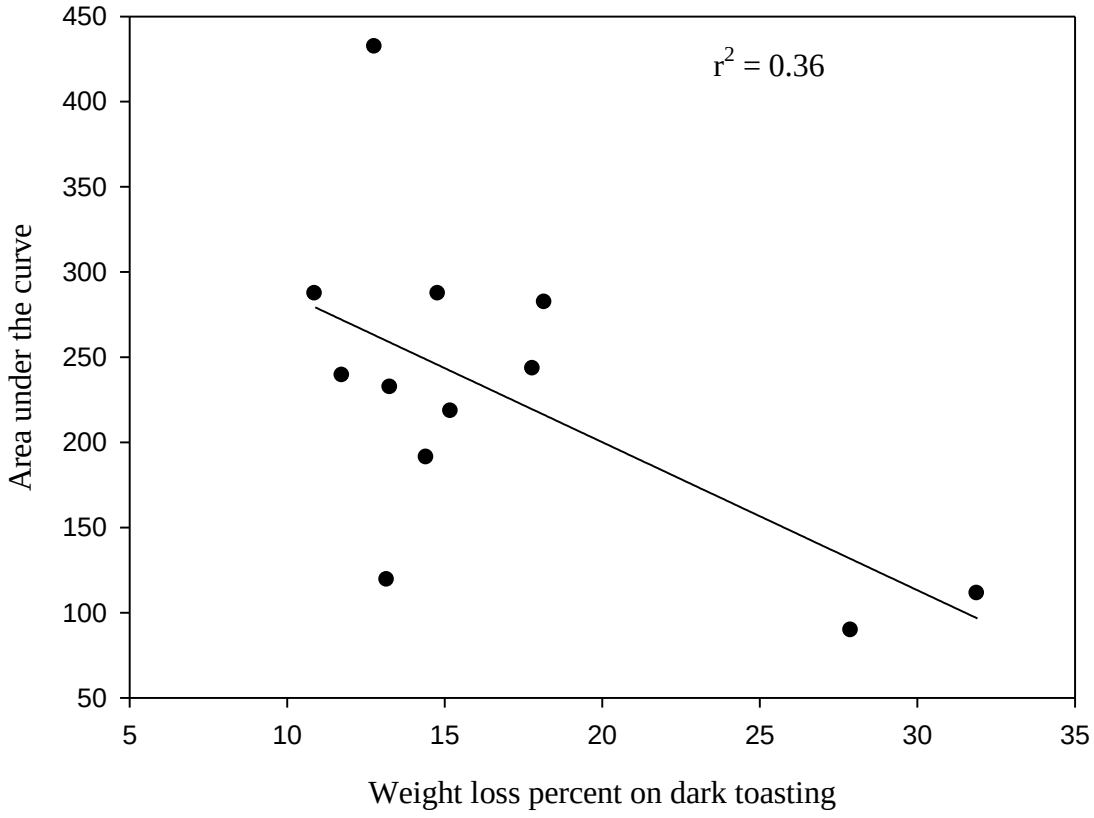


Figure 30 Plot of weight loss percent on dark toasting as a function of total area under the ultraviolet absorbance curve between 200 and 400 nm. A least squares straight line has been fitted to the data

4.2.3 Relationship between absorbances due to light and dark toasts

Figure 31 plots the relative normalised areas in Table 6 matched for each wood to see if there was any relationship between extraction patterns in model wine from light and dark toasts. There was clearly no relationship.

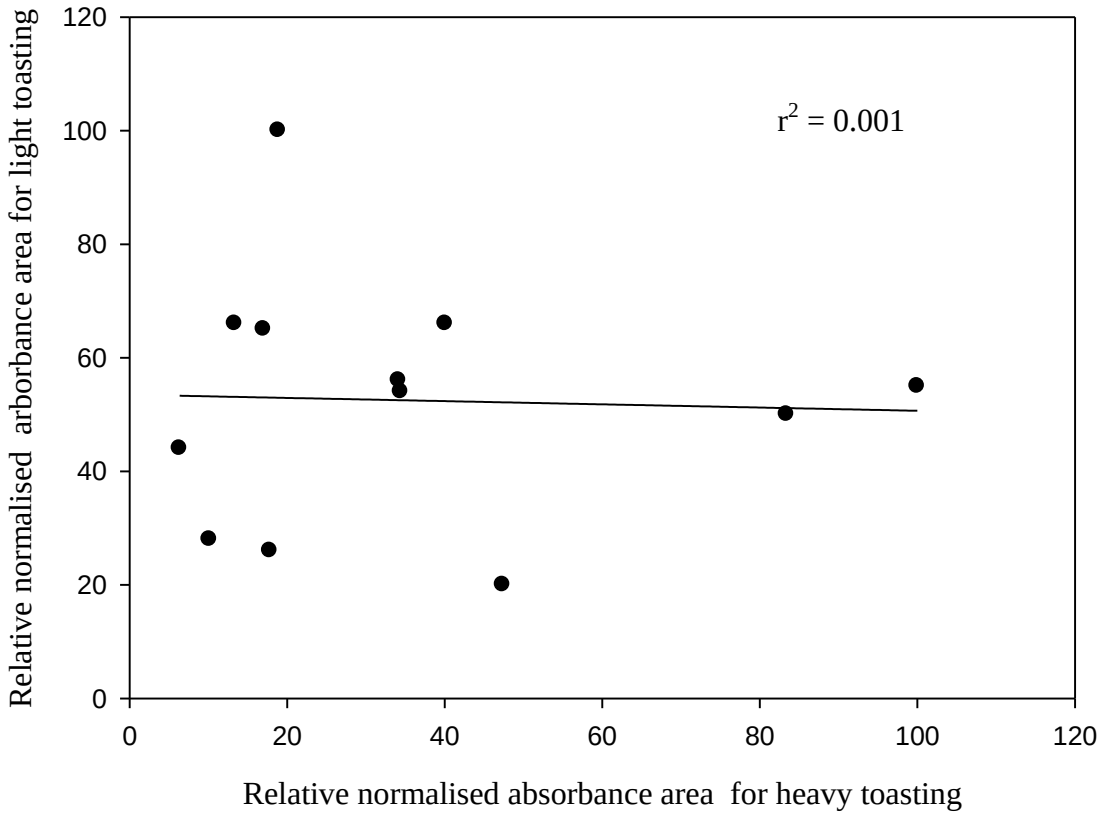


Figure 31 Plot of relative areas, normalised to 100, between 200 and 400 nm for light and heavy toasts in model wine. A least squares straight line has been fitted to the data

4.3 Gas chromatography

The analysis of the volatile compounds and other flavour compounds extracted from wood chips heated at 200°C for 2 hours and 210°C for 3 hours into the model wine was performed with good separation. Because of the effort involved, only six of the 12 woods were analysed. These were, American oak, manuka, matai, pohutukawa, silver beech and totara. American oak was an obvious choice; the others were chosen to roughly represent botanical families. Totara was included because preliminary sensory trials showed that flavouring with this wood was well favoured by consumers (Burns, 2004). Typical representative chromatographs, of manuka treatment at both toasting levels, are presented in

Figure 32 and Figure 33. All chromatographs for other woods and wine treatments are presented in the Appendices section. Identification was based on external standards (Table 7), where these were readily available, plus spectral library confirmation or on library reports alone. For the latter the pattern probability match had to be high, and the compound could plausibly be derived from wood. Table 8 lists compounds tentatively identified in model and real wines.

Table 7 Standards and their retention times

Volatile compound	Retention time (minutes)
2-Octanol	2.82
o-Cresol	3.32
p-Cresol	3.56
m-Cresol	3.66
2-Ethylphenol	4.42
3,4-Dimethylphenol	5.06
2-Isopropylphenol	5.20
2,4,6 Trimethylphenol	5.22
4-Isopropylphenol	5.47
3-Isopropylphenol	5.59
Thymol	6.35
Carvacrol	6.58
Vanillin	7.98

Table 8 Compounds tentatively identified in wooded (model and real) wine along with their retention times.

Volatile compound	Retention time (minutes)
Furfural	1.60
3-Phenyl-2-butanol*	1.83
5-Methyl-2-furaldehyde	2.44
o-Cresol	3.32
p-Cresol	3.52
2-Methoxyphenol	3.77
3,4-Dimethylphenol	5.04
Carvacrol	6.47
5-Butyldihydro-4-methyl-2(3H)-furanone	6.78
Vanillin	7.78
4-(2-hydroxyethyl)phenol	8.14
2-(Methoxymethyl)-5-methoxyphenol*	9.39
3,5-Dimethoxy-4-hydroxy cinnamic acid	10.33
4-(Ethoxymethyl)-2-methoxyphenol	10.80
Gallaldehyde	10.93
4-Hydroxy-3-methoxy cinnamaldehyde	11.81
3,5-Dimethoxy-4-hydroxy cinnamaldehyde	14.36

* These two were present only in real wine

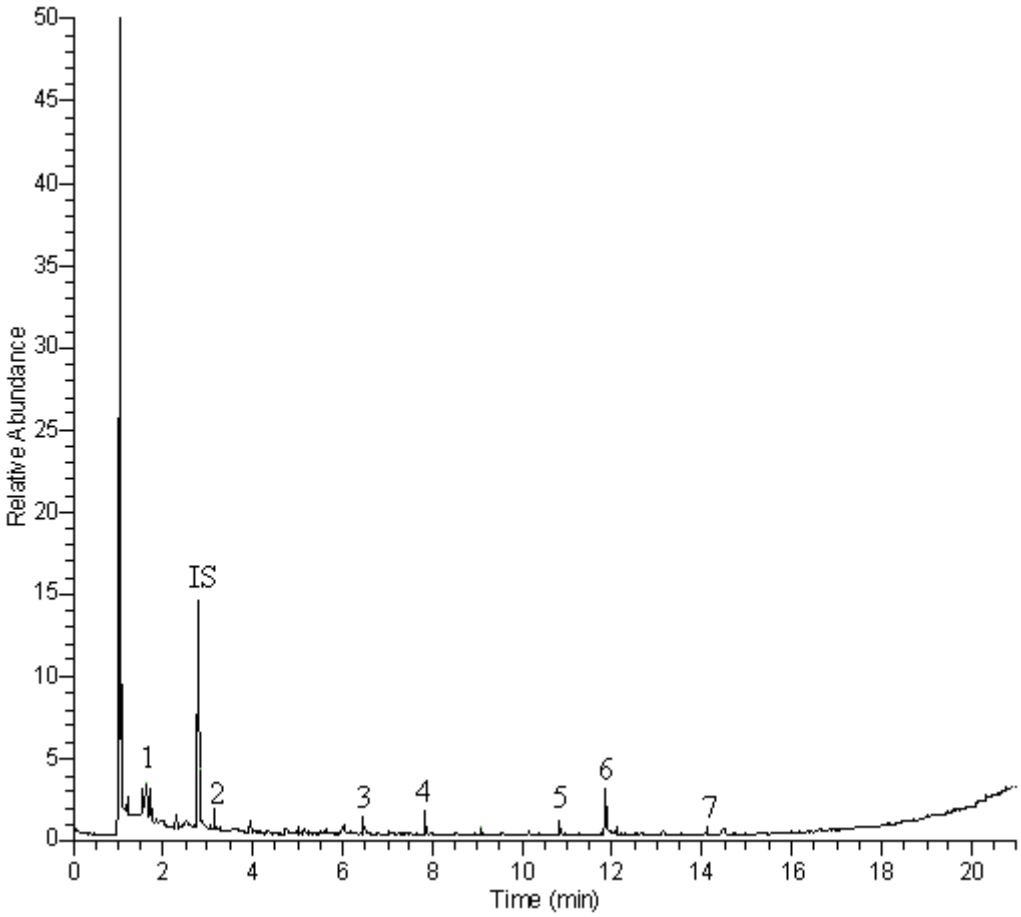


Figure 32 A typical gas chromatograph showing manuka light toast treatment with model wine. 1. Furfural 2. p-Cresol 3. Carvacrol 4. Vanillin 5. Gallaldehyde 6. 4-Hydroxy-3-methoxy cinnamaldehyde 7. 3,5-Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)

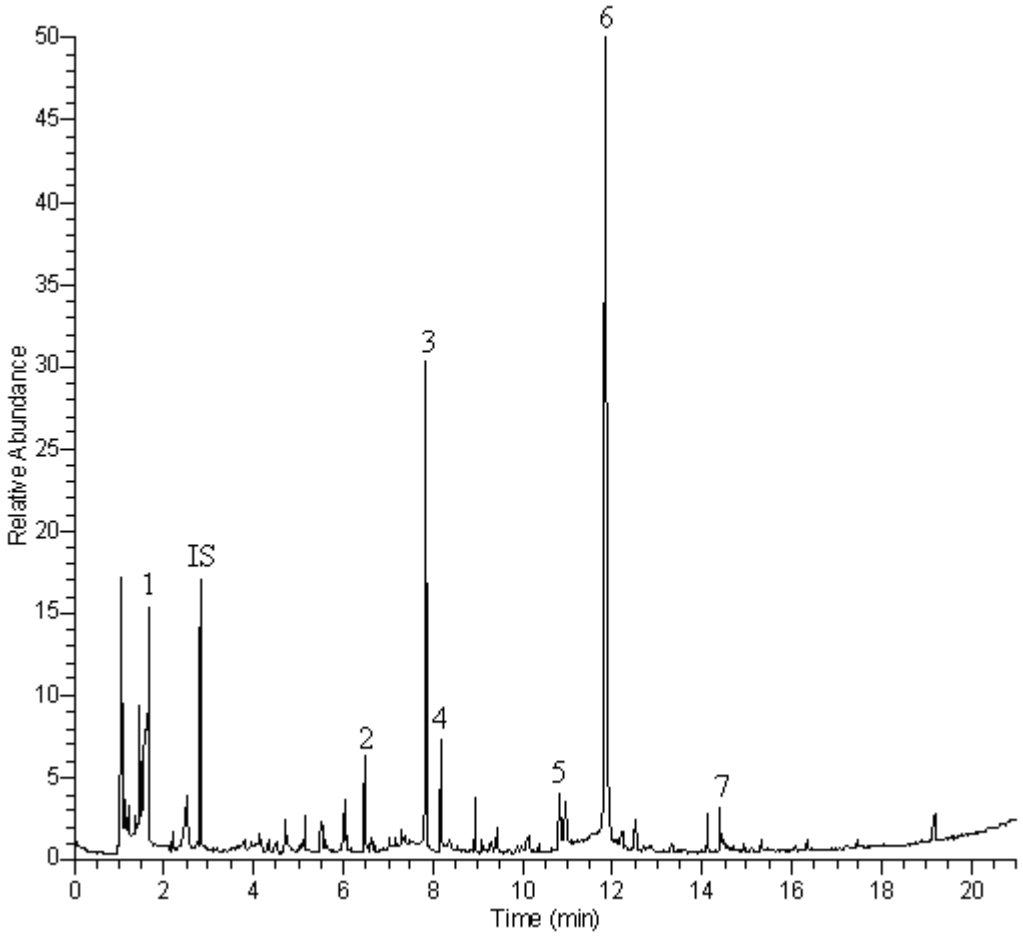


Figure 33 A typical gas chromatograph showing manuka dark toast treatment with model wine. 1. Furfural 2. Carvacrol 3. Vanillin 4. 4-(2- Hydroxyethyl) phenol 5. Gallaldehyde 6. 4- Hydroxy-3-methoxy cinnamaldehyde 7. 3,5-Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)

An internal standard (2-octanol) was used to quantify relative peak areas, and also to provide a reference point to compensate for variations in retention times caused by high ethanol content in the samples. (An example of this is seen with vanillin, which behaves differently when, as a standard, is injected as a methanolic solution (Table 7, 7.98 minutes), than when injected as part of a complex mixture in the extracting solvents diethyl ether and n-pentane (Table 8, 7.78 minutes.) The external standards were not used to quantify the amount of the compounds present in the different treatments. The peak areas were instead measured for each peak of interest in relation to the internal standard.

The volatiles compounds identified by the GC-MS analysis are summarised in Table 9 for the model wine treatments. This table also includes compounds that appeared only in real wine. Values for these two compounds, 3-phenyl-2-butanol and 2-(methoxymethyl)-5-

methoxy phenol, are therefore presented as dashes (–) in Table 9. Duplicate injections were made, and the mean values relative to the internal standard are reported along with their standard deviations.

There was a wide variation in the occurrence of compounds within and between woods and toasting levels, with range of 1 to about 600 detector response units relative to the internal standard. The flavour impact of these compounds (and of others below the detection limit) is not known, each could be as important as another. Thus, differences in trace compounds are potentially as important as differences in dominant compounds.

American oak added the most compounds to the model wine (Table 9) compounds when marinated with light toasted chips, and eight from the dark toasted chips. Thus for American oak, the light toast treatment was found to be more effective in imparting more potentially flavour-active compounds (although the importance of compounds below the limit of detection is unknown). Except for vanillin, the concentrations of the compounds common to both toasting treatments were not very different from each other.

Manuka added seven compounds on light and six compounds on dark toast treatment with the model wine. This wood was remarkable in showing high concentrations of furfural and vanilla compared with other wood treatments. For example, the furfural concentration in the manuka treatments was about 11 times greater than in the American oak

The dark toast treatment of manuka was particularly effective in the generation of vanillin and 4-hydroxy-3-methoxy cinnamaldehyde, the latter being the most dominant peak (590) in the entire model wine trial. Other woods and toast treatments showed only relatively low concentrations of this compound.

Matai added six compounds on light and five compounds on dark toast treatment. The dark toast produced about eight times as much 4-hydroxy-3-methoxy cinnamaldehyde and twice the concentration of vanillin as the light toast treatment.

Pohutukawa added only three compounds in the light toast treatment and five in the dark toast treatment, with a tendency for higher concentrations of compounds common to both toasts in the dark toast.

Silver beech added five compounds on light and four on dark toast treatment, again with a tendency for higher concentrations of common compounds in the dark toast. Totara added four compounds on light and five on dark toast treatment. Overall, the relative concentrations of these few compounds from totara were the lowest among all the woods.

Moreover, the concentration of compounds from the dark toast treatment differed little from the light.

Turning now to individual compounds, fufural, vanillin, 4-hydroxy-3-methoxy cinnamaldehyde, and 3,5-dimethoxy-4-hydroxy cinnamaldehyde were the compounds that were extracted from all six woods (Table 9). Furfural appeared in both toasting treatments, with its greatest expression in manuka. Furfural originates from the degradation of monosaccharides produced by partial hydrolysis of hemicellulose. It contributes to the character of dried, fruits and particularly that of burned almonds (Arapitsas et al., 2004).

3-Phenyl-2-butanol was not extracted in the model wine from any wood and toasting treatment.

Vanillin was also extracted from all six woods and both toasting treatments. Dark-toasted American oak and manuka treatments showed the highest concentrations. According to Arapitsas et al (2004), vanillin occurs as a result of lignin degradation. The vanillin concentration in the model wine was higher in the dark toast treatments than the light for all woods, which is consistent with that model. Totara showed the lowest concentration of vanillin.

4-Hydroxy-3-methoxy cinnamaldehyde was detected in the model wine treated with all the woods and toasting treatments. As for furfural and vanillin, its concentration was greatest for manuka, and usually higher in dark toast treatments. Totara showed the lowest concentration.

Apart from the above compounds that were extracted into all wood and toasting treatments, there were some compounds that were uniquely extracted from particular wood and toasting treatments. 5-Methyl-2-furaldehyde was detected only in American oak light toast for the model wine. This is formed as a result of thermodegradation of oak polysaccharides during toasting (Caldeira et al., 2006). 5-Butyldihydro-4-methyl-2(3H)-furanone is a so-called whiskey lactone that is important in spirits and wine flavour. The oak lactones possess a strong woody character and contribute to the unique aroma and flavours of bourbon and coconut (Belitz & Grosch, 1999). This lactone derives from oak lipids (Arapitsas et al., 2004), and was unique to the two oak treatments, but in higher concentration in the light toast. This is consistent with the results of Singleton (1995). He found that untoasted oak chips released more oak lactones to wines than did toasted, probably due to the thermodegradation of these heat-sensitive compounds or their loss by volatilisation when the

oak wood is subjected to very high temperatures. None of the other woods or toasting treatments produced this compound.

3,5-Dimethoxy-4-hydroxy cinnamic acid was similarly unique to oak, with low concentrations in both toasts.

3,5-Dimethoxy-4-hydroxy cinnamaldehyde was present in all wood treatments but not all toasting levels and was generally present in higher concentrations in wine treated with the dark toasted chips. The standout concentration of this compound was shown by model wine treated with silver beech dark toast followed by manuka, pohutukawa and American oak. Totara again showed the lowest concentration. The compound was not detected in the model wine treated with light toasted pohutukawa and totara, and the dark toasted matai treatment (Table 9).

Gallaldehyde was detected in the wine treated with dark toasted American oak, and in both toasting treatments of manuka. It also occurred in silver beech light toast.

Table 9 Relative detector responses of compounds extracted into model wine from several woods toasted to light and dark levels

Name of compound[¶]	American oak		Manuka		Matai		Pohutukawa		Silver beech		Totara	
	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast
[¶]Furfural	[†]24 ± 1	18 ± 1	260 ± 42	200 ± 28	3 ± 2	2 ± 1	2 ± 1	6 ± 1	3 ± 1	8 ± 1	4 ± 2	11 ± 1
3-Phenyl-2-butanol	–	–	–	–	–	–	–	–	–	–	–	–
5-Methyl-2-furaldehyde	12 ± 2											
o-Cresol*	6 ± 5				4 ± 2	11 ± 3		5 ± 2			8 ± 2	
p-Cresol*			7 ± 3									
3,4-Dimethylphenol*	3 ± 0	4 ± 3										
Carvacrol*	5 ± 2		4 ± 2		3 ± 1							
5-Butyldihydro-4-methyl-2(3H)-furanone	15 ± 4	6 ± 4										
Vanillin*	3 ± 0	26 ± 7	3 ±1	149 ± 21	6 ± 1	12 ± 1	1 ± 0	6 ± 4	3 ± 1	5 ± 4	1 ± 0	2 ± 2
4-(2-Hydroxyethyl)phenol				74 ± 31								
2-(Methoxymethyl)-5-methoxyphenol	–	–	–	–	–	–	–	–	–	–	–	–
3,5-Dimethoxy-4-hydroxy cinnamic acid	1 ± 0	1 ± 0										
4-(Ethoxymethyl)-2-methoxyphenol						2 ± 1						3 ± 2
Gallaldehyde		35 ± 21	57 ± 4	12 ± 1					8 ± 2			
4-Hydroxy-3-methoxy cinnamaldehyde	18 ± 4	15 ± 6	14 ± 4	590 ± 198	10 ± 3	80 ± 14	20 ± 7	24 ± 4	1 ± 0	56 ± 14	1 ± 1	1 ± 1
3,5-Dimethoxy-4-hydroxy cinnamaldehyde	14 ± 4	20 ± 14	21 ± 3	39 ± 11	4 ± 2			32 ± 5	8 ± 1	162 ± 51		2 ± 1

[¶] Compounds are in ascending order of elution time

[†] Data are 100 x peak area/peak area of internal standard ± standard deviations from duplicate injections. Blanks mean that the compound was not detected in that wood treatment but was present in other model winr treatments. – means not present in any model wine but present in real wine. None of the compounds was detected in the control model wine

* Compound identification by the Trace GC library, and confirmed with the external standards

Application of relatively gentle heat or mild acid attack releases complex phenolic aldehydes from wood. These complex phenolic aldehydes in turn break down to simpler structures, the steam volatile phenols, when extra heat is applied as occurs in toasting. These compounds are responsible for the smoky aroma and flavours often found after barrel maturation of wine (Anon., 1995).

The phenol carvacrol was present only in the model wine treated with light toast of American oak, manuka and matai, and then in low concentrations.

o-Cresol and p-cresol were present in low concentrations scattered throughout the 12 treatments. Cresols, like many other phenols, are responsible for medicinal flavours (Clarke & Bakker, 2004) and smoky flavours (Belitz & Grosch, 1999).

Another medicinal-like phenol, 3,4-dimethyl phenol was detected only in the wine treated with American oak toasted at both levels. Its uniqueness to oak puts it in the same category as 5-methyl-2-furaldehyde and 5-butyldihydro-4-methyl-2(3H)-furanone.

In contrast, 4-(2-hydroxyethyl) phenol was unique to the dark toasted manuka treatment (Figure 33), and 4-(ethoxymethyl)-2-methoxy phenol was detected in the model wine treated with dark toasted matai and totara.

The extraction of the compounds from the different woods at different toasting levels might be different for model wine and real wine. To compare the behavior of the model wine with the real wine, unoaked real wine was selected and similar ultraviolet and gas chromatography analyses were performed on this real wine. The results are presented in the next chapter.

Chapter 5

Results for Real Wine

5.1 Introduction

The extraction of toasted woods in a real wine is described in this chapter. The wine, and unoaked real wine from grapes grown in Gisborne, New Zealand, was treated with the wood chips of six different types of woods toasted to two levels, light and dark as described in Chapter 2. The methods of wine analysis were closely similar to those described for model wine reported in the previous chapter.

5.2 Ultraviolet spectrophotometry

5.2.1 Real wine marinated with light toasted chips (200°C for 2 hours)

As with model wine, it was necessary to dilute the wooded wines to achieve absorbances between 0 and 2 for the wavelength range 200 to 400 nm. Following the pattern with model wine required that the wooded real wine be diluted in the unwooded real wine, and that the absorbances be compared with the unwooded real wine as a spectrophotometric reference. A series of experiments with progressive dilutions to one part in 20 failed to reveal significant peaks in the wavelength range. This result was interpreted as follows. The unwooded real wine absorbed so strongly in the ultraviolet range, that any additional absorbance due to matter extracted from wood was difficult to measure against high background readings. Therefore, a different dilution method was required.

The wooded wines were diluted one part in 20 with water, as was the reference with unwoooded real wine. The initial dilution required that the absorbance data be multiplied by 20 to obtain true absorbances (Figure 34, Figure 36). Even at this high dilution, there was significant electronic noise in the ultraviolet scans, and greater at one part in 20 (real wine) than in model wine (one part in three). Moreover, the noise in real wine was obvious over a wider wavelength range, 200 to say 300 nm. There was also a shift of the absorbance peaks towards lower wavelengths in comparison to the model wine.

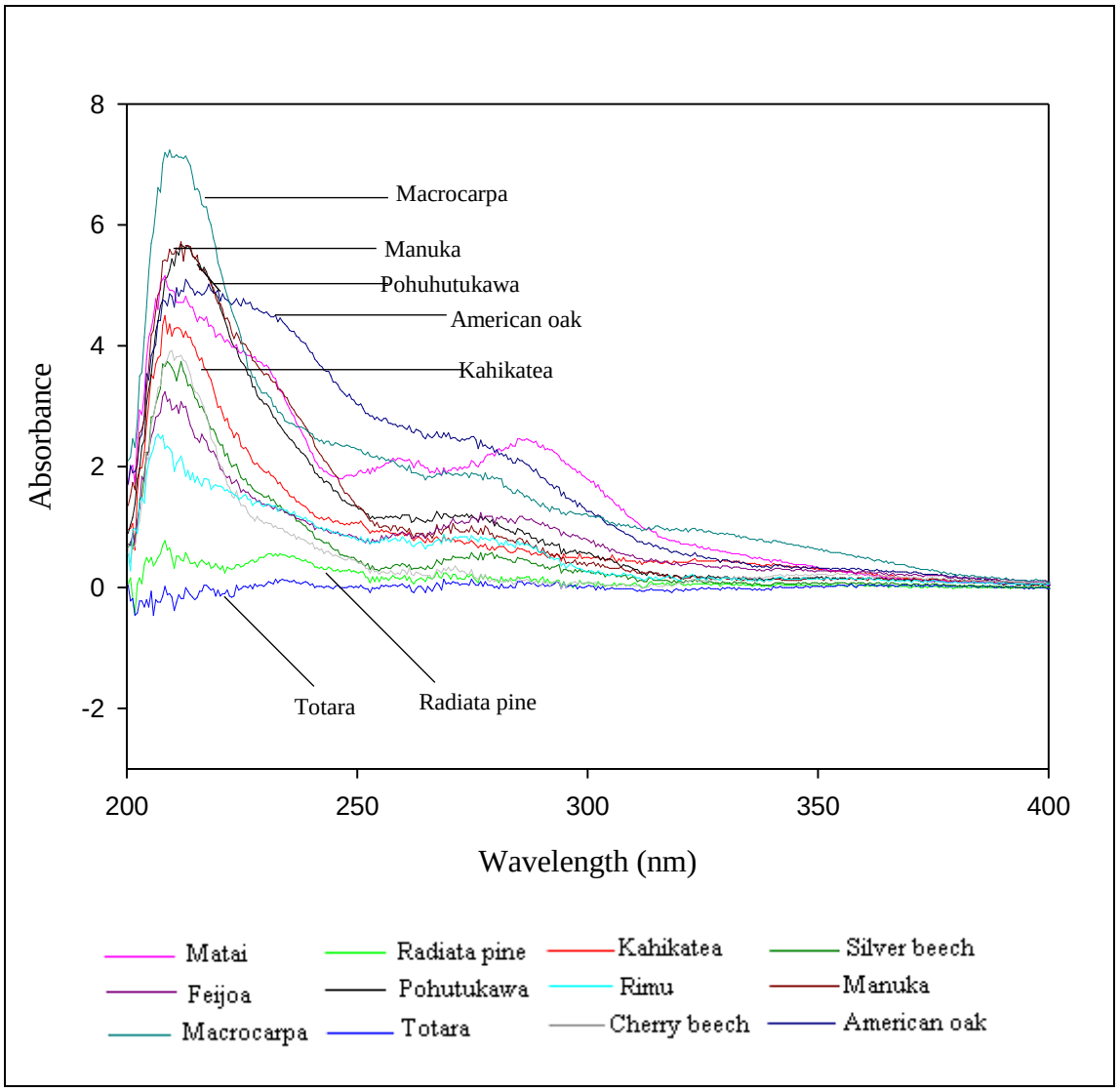


Figure 34 Absorbance of different wood treatments with light toast wood chips in real wine

In Figure 34, the peak absorbance was highest for macrocarpa. The absorbance pattern for American oak was distinctive in that it was relatively broad. This might indicate that American oak added a variety of compounds in the real wine on marination. As a group, manuka, pohutukawa, matai, kahikatea, silver beech, feijoa, rimu were rather similar in their absorbance patterns. Radiata pine and totara absorbed the least light and showed small negative values for absorbance around 200 to 290 nm, although this might be due to electronic noise.

Table 10 Relative area under the absorbance curve in the range 200 to 400 nm, normalised to the wood that absorbed the most, for light and dark toast treatments in real wine

Light toast		Dark toast	
Wood in descending order of relative area	Relative area normalized to American oak	Wood in descending order of relative area	Relative area normalized to cherry beech
American oak	100	Cherry beech	100
Macrocarpa	99	Matai	99
Matai	89	Silver beech	93
Manuka	66	Manuka	82
Pohutukawa	65	Kahikatea	78
Kahikatea	51	Radiata pine	64
Feijoa	46	Feijoa	64
Rimu	34	Totara	57
Silver beech	34	American oak	55
Cherry beech	30	Macrocarpa	18
Radiata pine	9	Pohutukawa	17
Totara	1	Rimu	-16

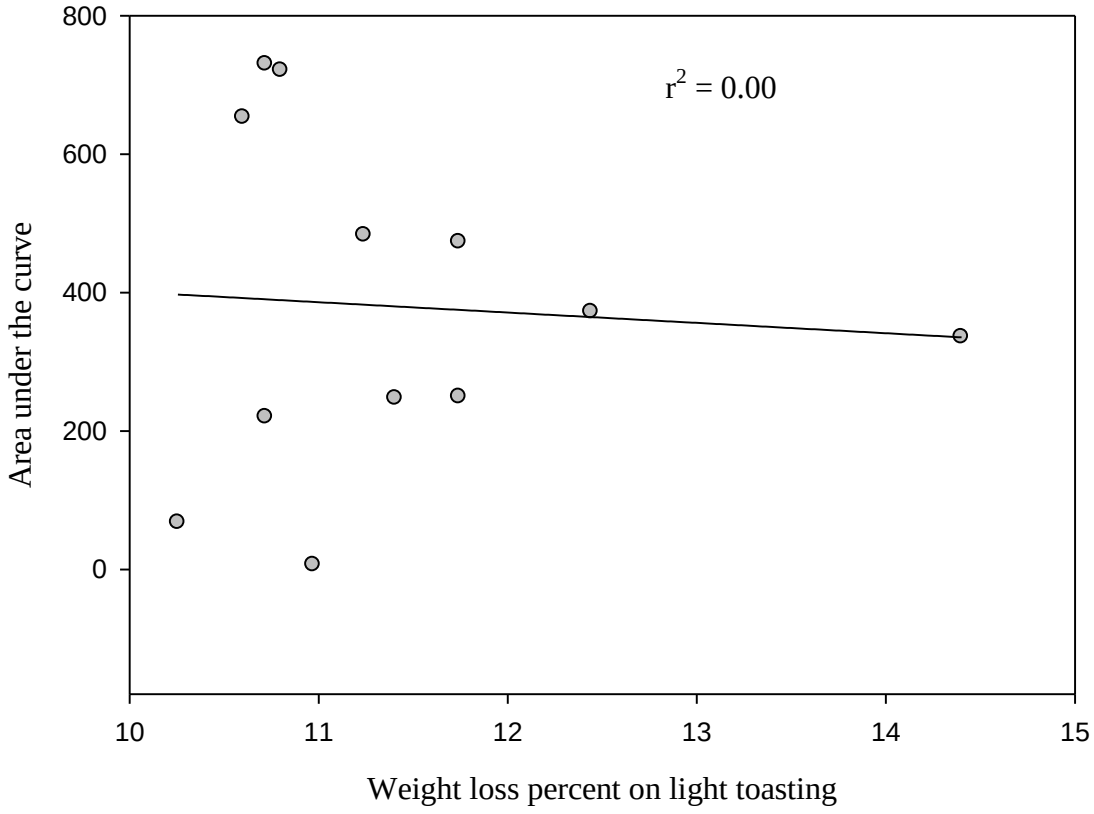


Figure 35 Plot of weight loss percent on light toasting as a function of total area under the ultraviolet absorbance curve between 200 and 400 nm. A least squares straight line has been fitted to the data

For the model wine it was hypothesised in Chapter 4, that the total area under the absorbance curve between 200 and 400 nm for each toasting treatment might be related to the loss of weight on toasting. The exercise was repeated with real wine data. Again, the total area under the curve was calculated by summing the 401 individual readings (each representing 0.5 nm) for each scan between 200 and 400 nm.

The left side of Table 10 shows data for light toast normalised to the wood that absorbed the most, in this case American oak. American oak's area was 730 arbitrary absorbance units, but normalized to 100. Macrocarpa was not significantly different (99). Matai was third. Radiata pine and totara absorbed the least.

When the total area under the curve from the absorbance data for each light toasted wood was plotted as a function of weight loss percent on light toasting, there was no relationship (Figure 35).

5.2.2 Real wine marinated with dark toasted chips (210°C for 3 hours)

As with the light toast, an initial dilution of one part in 20 was made to bring the scans on scale. There was clear evidence of electronic noise, the possible reason for which has been discussed in 5.2.1. In the real wine dark toast (210ºC for 3 hours), silver beech showed the maximum absorbance followed by matai (Figure 36).

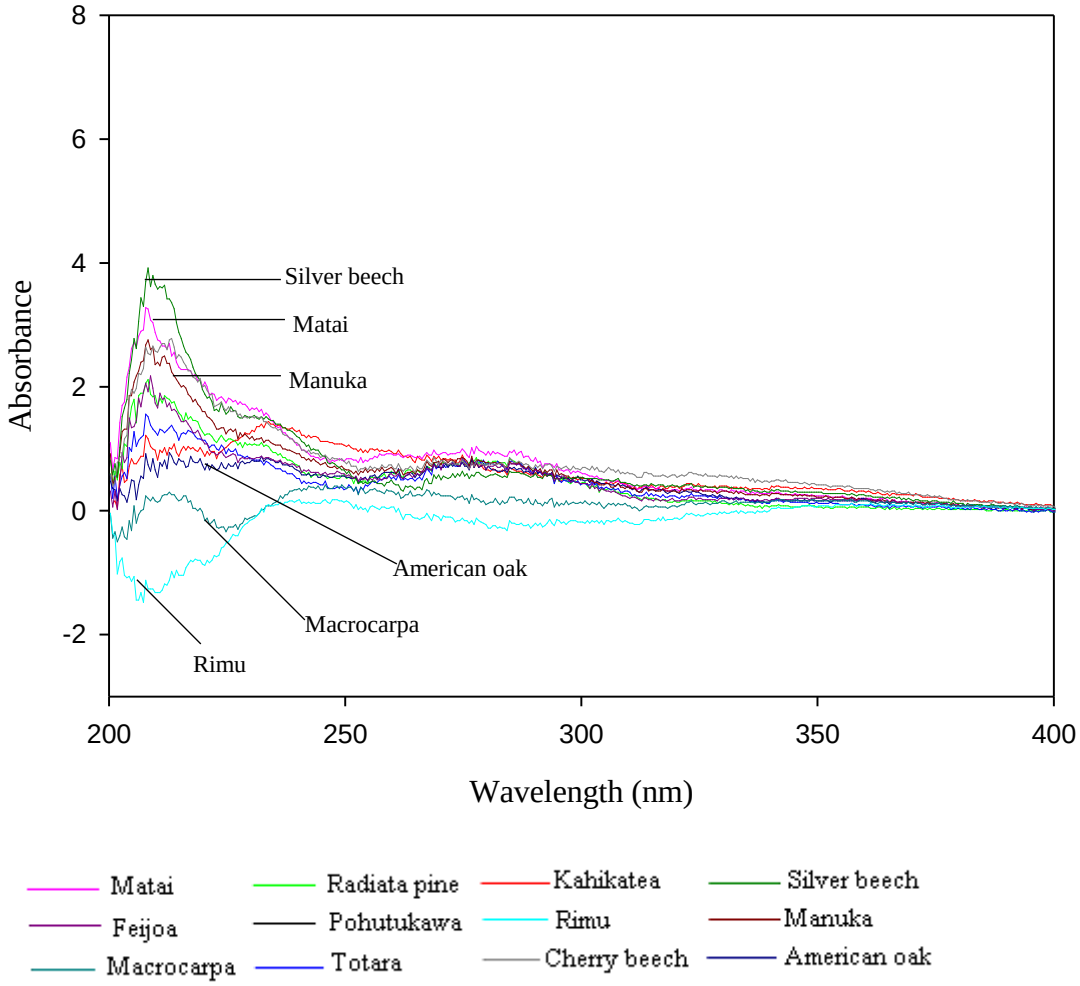


Figure 36 Absorbance of different wood treatments with the real wine dark toast

For the summed absorbances between 200 to 400 nm, the highest arbitrary absorbance value was 321 for cherry beech. This was normalised to 100 in Table 10, right side columns. Matai and silver beech were both in the 90s. Totara moved up the scale from 1 in light toast to 57 in dark toast. Rimu returned a negative value, –16. Rimu and macrocarpa (17) were the woods that produced a lot of smoke during dark toasting. The negative absorbance due to rimu might be an indication of the conversion of wood into charcoal, which may absorb ultraviolet light-absorbing compounds (phenols, proteins etc.) from the wine. This will be further discussed in Chapter 6.

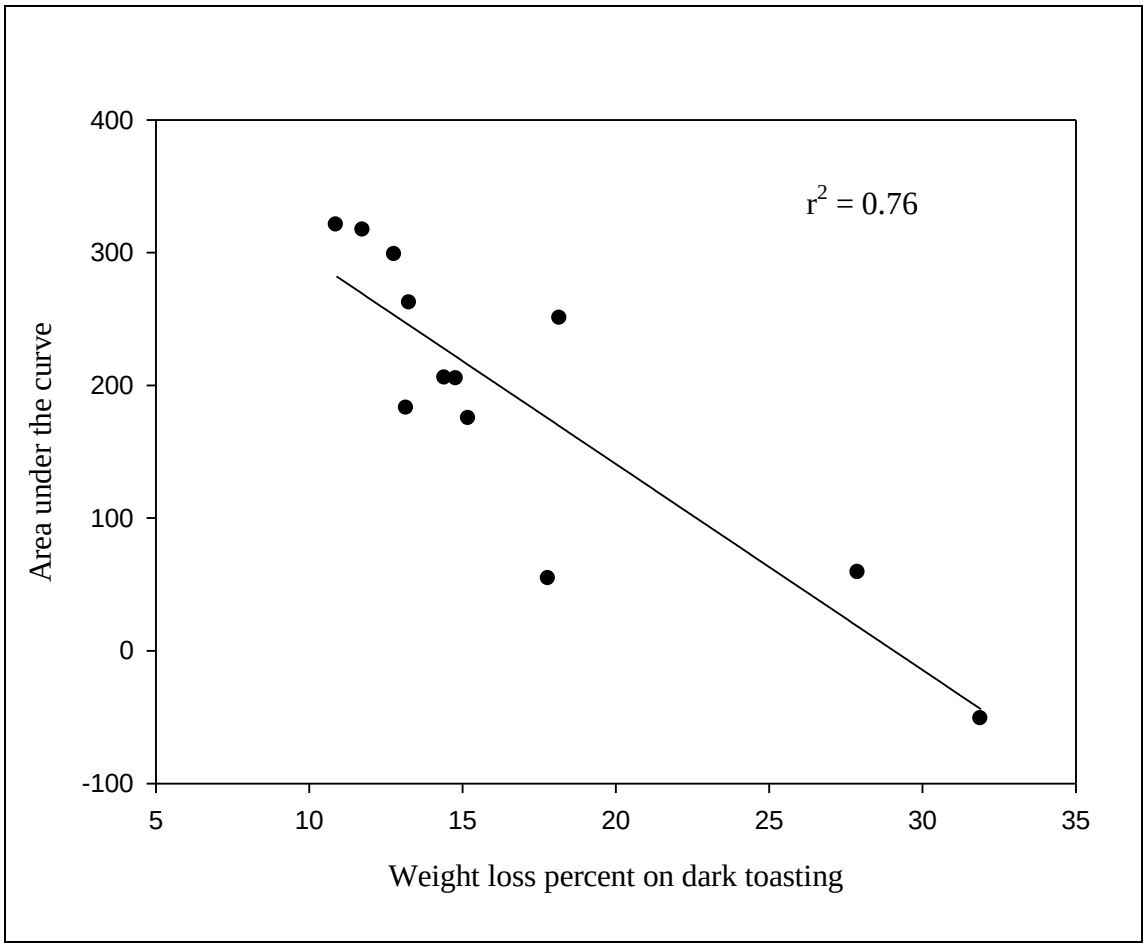


Figure 37 Plot of weight loss percent on dark toasting as a function of total area under the ultraviolet absorbance curve between 200 and 400 nm. A least squares straight line has been fitted to the data

When the summed absorbances between 200 and 400 nm for dark toasting were plotted against the weight loss percent on dark toasting there was a clear inverse relationship (Figure 37). High weight loss resulted in low extraction of ultraviolet-absorbing matter.

5.2.3 Relationship between absorbances due to light and dark toasts

Figure 38 plots the relative normalised areas in Table 10 matched for each wood to see if there was any relationship between extraction patterns in real wine from light and dark toasts. There was clearly a strong positive relationship (Figure 38).

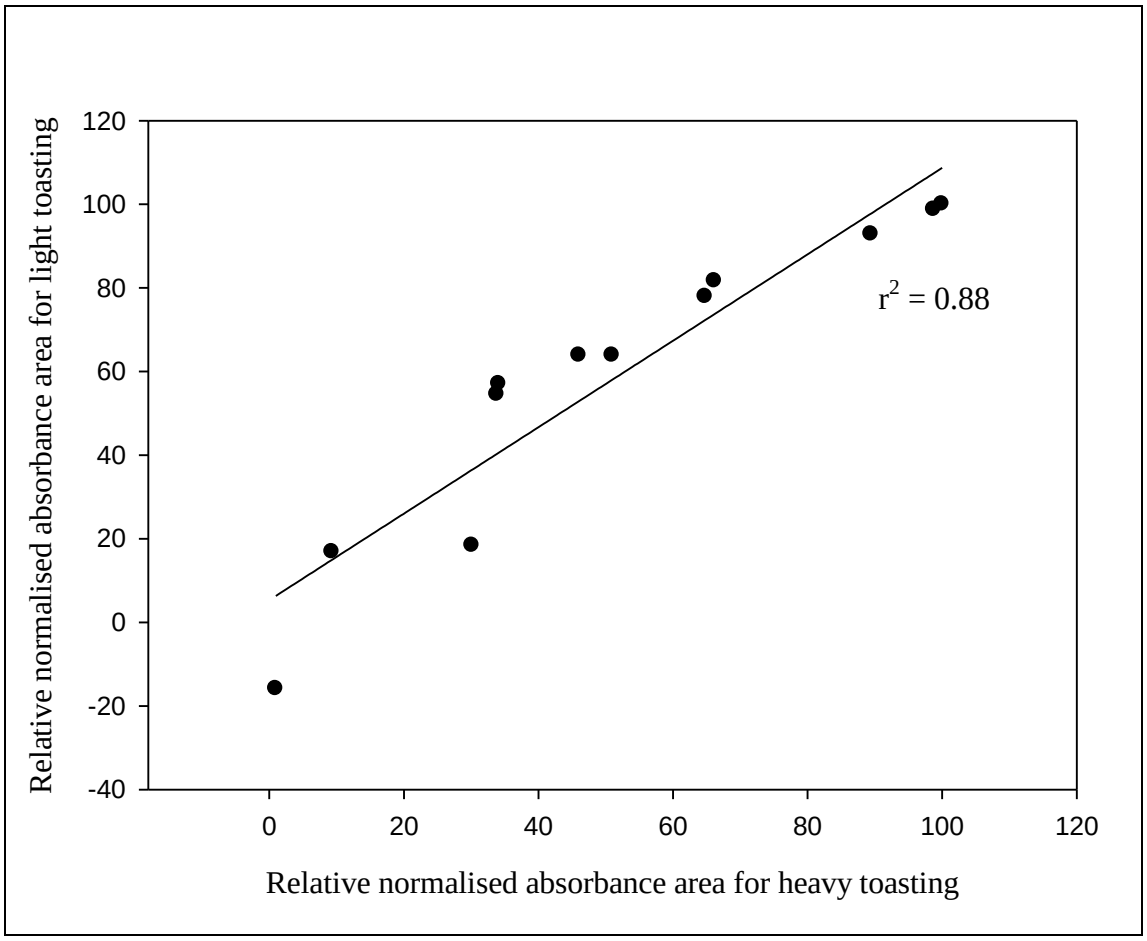


Figure 38 Plot of relative normalised areas between 200 and 400 nm for light and heavy toasts in real wine. A least squares straight line has been fitted to the data

5.3 Gas chromatography

Real wine treated with toasted wood chips was analysed for its contents of extracted compounds. Typical chromatograms– for manuka at both toasting levels –is presented in Figure 39 and Figure 40. All chromatographs for other woods and wine treatments are presented in the Appendices section.

Some compounds that were detected in the model wine treatments did not appear at all in the real wine treatments with different woods and toasting levels (Table 11). These were 3,5-dimethoxy-4-hydroxy cinnamic acid, 4-hydroxy-3-methoxy cinnamaldehyde and 3,5-dimethoxy-4-hydroxy cinnamaldehyde. These compounds are listed in Table 11 but there absence is indicated with dashes (–).

In contrast, two compounds not extracted into the model wine appeared in the real wine treatments. These two were 3-phenyl-2-butanol and 2-(methoxymethyl)-5-methoxyphenol.

In real wine, American oak added the greatest number of compounds as detected by the gas chromatography. Both light and dark toast treatments of American oak added 10 compounds (nine common to both toasts), but the concentrations of these common compounds waried. However, there was no consistent pattern (oak columns in Table 11).

Manuka added seven compounds on light and five compounds on dark toast treatment with the real wine. The light toast treatment of manuka was particularly more effective in the generation/extraction of o-cresol and 4-(2-hydroxyethyl) phenol when compared to its dark toasting treatment.

Matai added six compounds on light and dark toast treatments. The light toast yielded high concentrations of 3-phenyl-2-butanol o-cresol, and 4-(2-hydroxyethyl) phenol, the last being found in all the treatments analysed.

Pohutukawa also added six compounds in the light and dark toast treatment, with a tendency for higher concentrations of common compounds in the dark toast.

Silver beech also added six compounds in the light and dark toast treatment, again with a tendency for higher concentrations in the dark toast. The dark toast treatment of silver beech was particularly effective in the generation/extraction of 3-phenyl-2-butanol and 4-(2-hydroxyethyl) phenol.

Totara added five compounds on light and dark toast treatment. The concentrations of vanillin in the real wine treated with dark toasted wood chips was the highest among all the treatments analysed. It was present at five times the concentration in dark toast totara compared with light. In contrast, the concentration of other compounds from totara were higher in the light toast treatment.

Turning now to individual compounds, fufural, 3-phenyl-2-butanol, vanillin, o-cresol and 4-(2-hydroxyethyl)phenol were compounds that were extracted from all six woods but not necessarily in all toasting levels (Table 11). Furfural appeared in both toasting treatments, with its greatest expression in American oak in the real wine treatments. 3-Phenyl-2-butanol was a feature of silver beech for both toasting treatments followed by matai and manuka treatments. Vanillin was also extracted from all six woods and both toasting treatments, with dark-toasted totara showing the greatest expression. o-Cresol, was rather similarly represented in all the treatments except manuka dark and totara, and absent in the latter. 4-(2-Hydroxyethyl) phenol was reported in all wood and toasting treatments, and showed its greatest expression in matai light toast and silver beech dark.

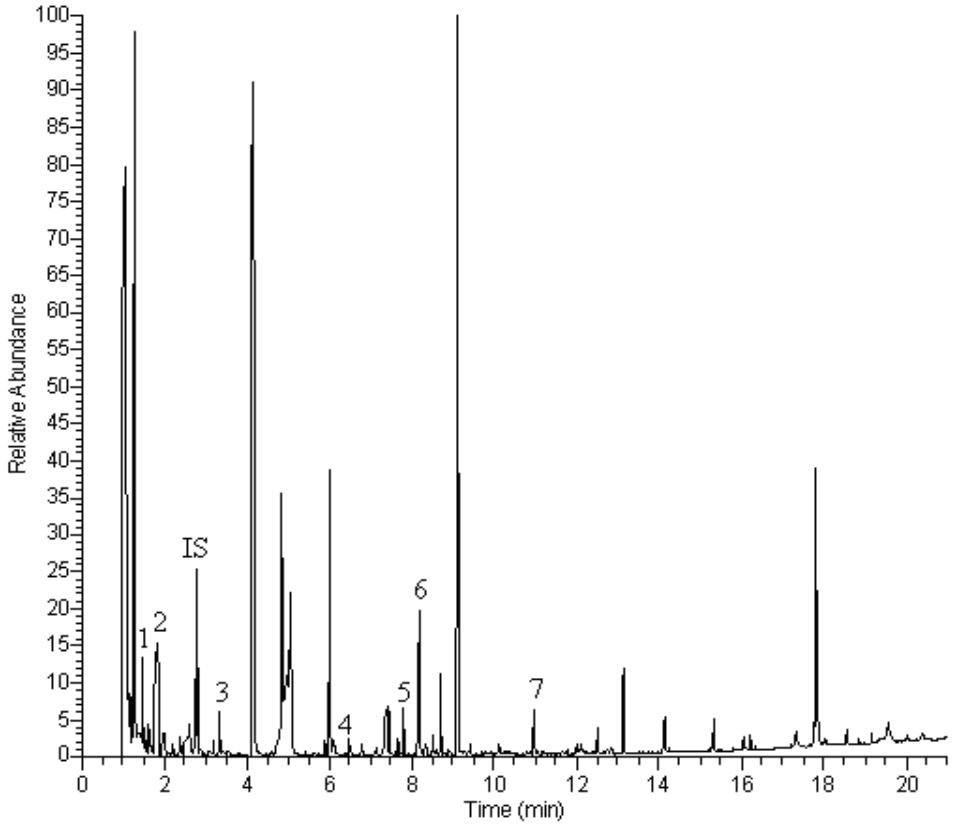


Figure 39 A gas chromatograph showing manuka light toast treatment with real wine. 1. Furfural 2. 3- Phenyl 2-butanol 3. o-Cresol 4. Carvacrol 5. Vanillin 6. 4-(2-Hydroxyethyl) phenol 7. Gallaldehyde IS = Internal standard (2-octanol)

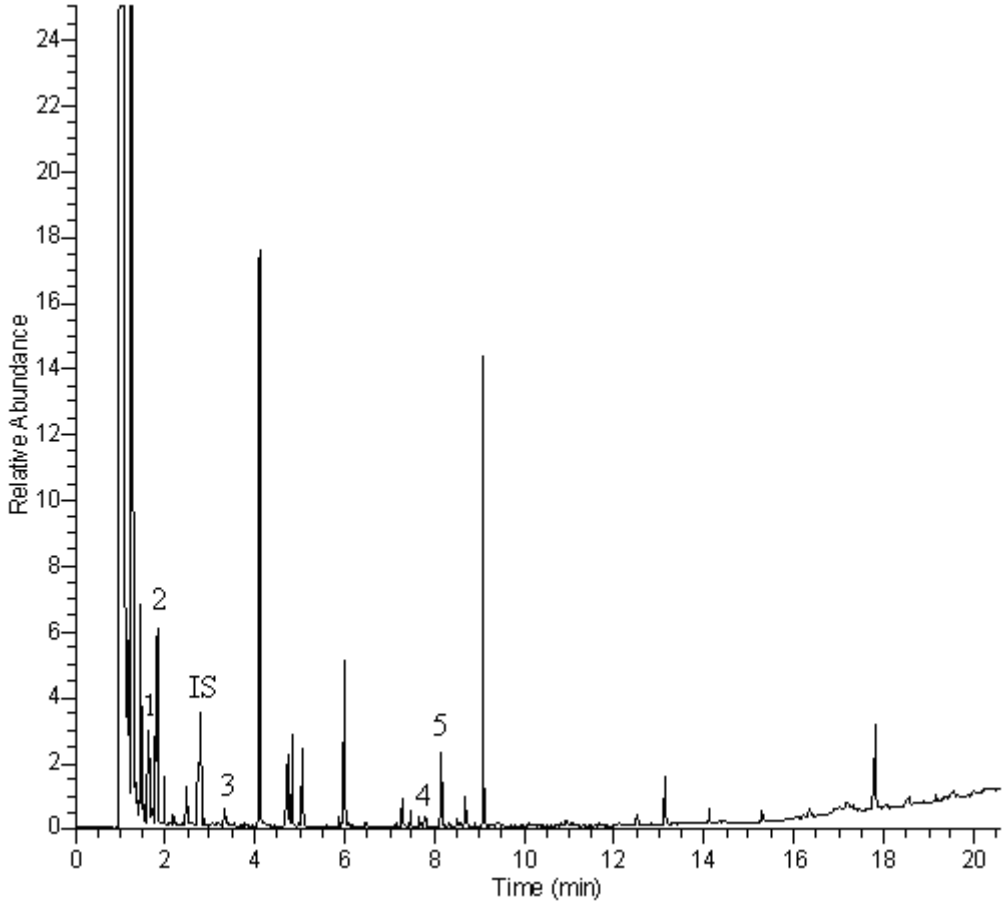


Figure 40 A typical gas chromatograph showing manuka dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3. o-Cresol 4. Vanillin 5. 4-(2-hydroxyethyl) phenol. IS = Internal standard (2-octanol)

Some compounds were unique to particular wood and toasting levels. 5-Methyl-2-furaldehyde and it was detected only in American oak for both toasting treatments with its greatest expression in the light toast. 3,4-Dimethylphenol was also unique to American oak in both light and dark toast treatments, likewise 5-butyldihydro-4-methyl-2(3H)-furanone was also unique to American oak. Finally, 2-(methoxymethyl)-5-methoxy phenol was also unique to American oak.

Table 11 Relative detector responses of compounds extracted into real wine from several woods toasted to light and dark levels

Name of compound[¶]	American oak		Manuka		Matai		Pohutukawa		Silver beech		Totara	
	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast	Light toast	Dark toast
[¶]Furfural	[†]127 ± 18	119 ± 8	5 ± 5	11 ± 4	5 ± 4	4 ± 1	4 ± 4	6 ± 4	11 ± 2	17 ± 3	7 ± 2	5 ± 3
3-Phenyl-2-butanol	19 ± 3	14 ± 3	55 ± 6	66 ± 1	116 ± 4	80 ± 6	8 ± 4	34 ± 17	222 ± 10	235 ± 23	36 ± 4	17 ± 3
5-Methyl-2-furaldehyde	15 ± 5	7 ± 3										
o-Cresol*	19 ± 3	16 ± 5	25 ± 3	1 ± 1	31 ± 9	24 ± 3	20 ± 4	32 ± 4	32 ± 8	27 ± 1	15 ± 6	
p-Cresol*						6 ±1		6 ± 0				
3,4-Dimethylphenol*	50 ± 8	74 ± 17										
Carvacrol*	7 ± 2		3 ± 3		5 ± 4	14 ± 2	5 ± 0					
5-Butyldihydro-4-methyl-2(3H)-furanone	15 ±6	6 ± 5										
Vanillin*	3 ± 2	5 ± 1	7 ± 3	2 ± 1	2 ± 1	9 ± 2	8 ± 3	7 ± 1	5 ± 3	8 ± 1	6 ± 3	30 ± 8
4-(2-Hydroxyethyl)phenol	70 ± 6	16 ± 4	50 ± 13	18 ± 6	123 ± 54	88 ± 6	32 ± 13	43 ± 21	57 ± 16	110 ± 18	89 ± 9	73 ± 25
2-(Methoxymethyl)-5-methoxyphenol	6 ± 1	1 ± 1										
3,5-Dimethoxy-4-hydroxy cinnamic acid	–	–	–	–	–	–	–	–	–	–	–	–
4-(Ethoxymethyl)-2-methoxyphenol						9 ± 1						7 ± 3
Gallaldehyde		6 ± 1	12 ± 1						23 ± 7	21 ± 4		
4-Hydroxy-3-methoxy cinnamaldehyde	–	–	–	–	–	–	–	–	–	–	–	–
3,5-Dimethoxy-4-hydroxy cinnamaldehyde	–	–	–	–	–	–	–	–	–	–	–	–

[¶] Compounds are in ascending order of elution time

[†] Data are 100 x peak area/peak area of internal standard ± standard deviations from duplicate injections. Blanks mean that the compound was not detected in that wood treatment but was present in other model winr treatments. – means not present in any real wine but present in model wine. None of the compounds was detected in the control realwine.s

* Compound identification by the Trace GC library, and confirmed with the external standards

Whereas o-cresol was expressed in nearly all treatments, its geometric isomer p-cresol was unique to dark toasted matai and pohutukawa treatments, and in similar concentrations. Carvacrol was present in only wine treated with light toasted American oak, pohutukawa, manuka, and both toast treatments of matai. 4-(Ethoxymethyl)-2-methoxy phenol was detected only in the matai and totara dark toast treatments. Gallaldehyde was detected in the wine treated with dark toasted American oak, and for the light toast treatment of manuka and both toast treatment of silver beech.

Thus, there were patterns of extraction common to all woods and both toast levels, as well as several unique and near unique patterns.

To compare the results for model and real wine, the behaviour of both as measured by ultraviolet spectrophotometry and gas chromatography were compared. The differences and the similarities are explored in the Chapter 6.

Chapter 6

Discussion for Model and Real Wines

6.1 Introduction

The results in Chapters 4 and 5 clearly showed that different types of woods and toasting treatments had a major influence on the extraction of various compounds into real and model wine. In this chapter the spectrophotometric results for model and real wines are compared and contrasted, as are the compounds extracted.

6.2 Ultraviolet spectrophotometry

In comparing the wavelength scans for both toasting treatments for model and real wine, there was a general shift of the main absorbance peaks towards the lower wavelengths in the real wine by about 20 nm. The pH of the model wine was 3.5 whereas that for real wine was 3.44. In hindsight it would have been better to have the pH values exactly equal, but this small difference in pH would not seem to make a big difference. Coloured phenolic compounds, like anthocyanins, can change colour with pH (Sanza & Dominguez, 2006) and it is quite likely that these changes will extend into the ultraviolet range.

In both real and model wines, light toasting often resulted in higher extractions (Table 12) as might be expected from inspection of Figure 26, Figure 29, Figure 34 and Figure 36.

Averaged over all woods, the area ratio (light/dark) was 1.35 and 2.44 for model and real wine, respectively. This sort of result is consistent with the results of Chatonnet, Cutzach, Pons, & Dubourdieu (1999) who found that extractables are higher during light to medium toasting and lower in heavy (dark) toasts. However, radiata pine, totara and the beechs consistently showed higher absorbances in dark toasts, where the ratios were less than unity. The cause of this is the probably the differing thermal stabilities of the woods (Chatonnet et al., 1997). Radiata pine was a good example of this. Light toasting left the wood virtually unchanged, as judged by colour and weight loss, but dark toasting caused massive changes in these properties. Overall each wood (or more accurately genus) had its own pattern of thermal destruction. This is also well illustrated in Table 6 and Table 10, where the rank orders of relative areas under the absorbance curves were very different between light and dark toasts.

Looking again at Table 12, it was instructive to plot the light/dark ratios for model wine against real wine (Figure 41). The correlation was weak ($r^2 = 0.34$) but positive, showing that patterns of extraction in model wine were partly reflected in real wine.

Table 12 Area under the curve (light/dark ratios) for model and real wine treatments

Wood	Model wine	Real wine
Matai	3.10	2.06
Feijoa	1.03	1.64
Macrocarpa	3.92	12.25
Pohutukawa	1.04	8.74
Radiata pine	0.25	0.33
Totara	0.63	0.04
Kahikatea	0.45	1.49
Rimu	1.19	-4.85
Cherry beech	0.34	0.69
Silver beech	0.32	0.83
Manuka	1.10	1.84
American oak	2.83	4.18
Mean ± SD	1.35 ± 1.23	2.44 ± 4.37

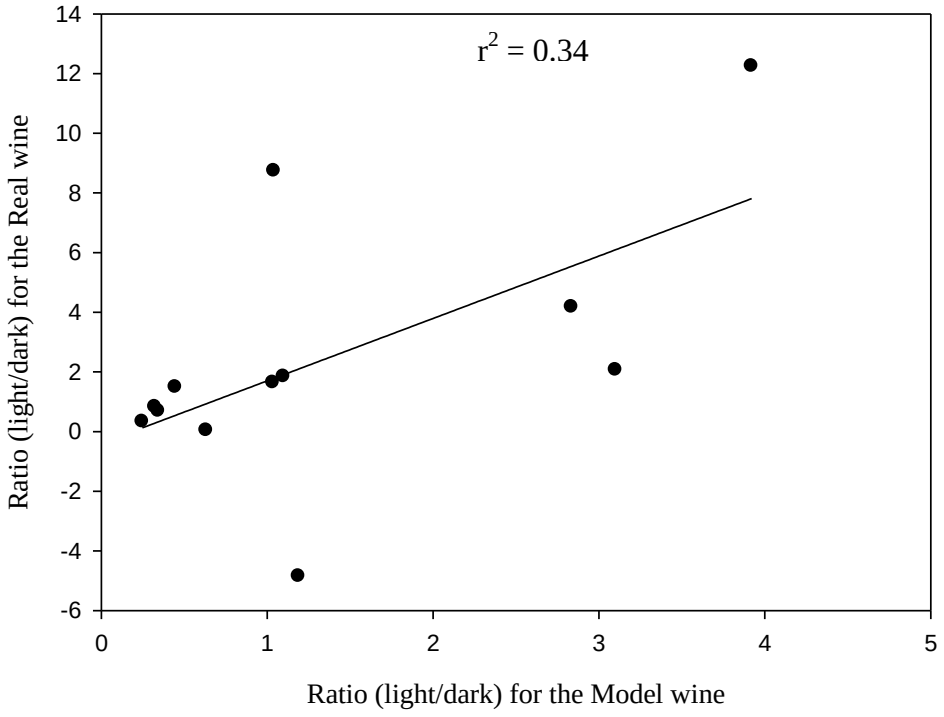


Figure 41 Plot of relative ratios (light/dark) of area under the curve between 200 and 400 nm between model and real wine. A least squares straight line has been fitted to the data

The scientific and cooperage trade literature is short on details of toasting temperatures, possibly due to commercial secrecy. Each cooperage has its own toasting methods (Swan et al., 1999). Moreover, the results of toasting in the present study show how different responses to temperature can be. Thus, what might be called a light toasting temperature for one wood can equate to dark toasting temperature for another species. Morales et al. (2004) used 180°C for 3 hours for toasting while Arapitsas et al. (2004) mentioned 200°C for 2 hours in their studies. In respect of oak staves, Chatonnet et al. (1999) state that at the heat exposed surface, 115-125°C is generally considered to be as light, 200-215°C as medium and 220-230°C as heavy (dark) toasting levels. According to these authors, changes produced by heating oak increase the concentrations of some compounds upto certain level of toasting. If toasting continues beyond that point, concentrations tend to decrease. Although around 120°C was not trialled in the present study, it seem likely from the responses obtained at 200 and 210°C with chips over several hours, that 120°C would have done little to the woods trialled here. However this has not been tested and the possibility remains that one of more of the woods would behave like oak reportedly does (Chatonnet et al., 1999). In the present study, what is considered a light toast would probably be considered a medium toast according to Chatonnet et al. (1999) and Swan et al. (1999) that is responsible for inducing larger changes in the extraction profile.

6.3 Gas chromatography

The spectrophotmetric data discussed in the previous section were all measured in the ultraviolet range, where phenolic compounds absorb strongly. The chromatographic results stemmed from (selective) extraction into diethyl ether/pentane (Chapter 2) and subsequent detection by a mass spectral detector, the response of which (peak area) is roughly proportional to the molecular mass (William & Charles, 2004). Thus it would appear unlikely that the two data sets for the six wood treatments analysed by gas chromatography should correlate. When relative detector responses (Table 9, Table 11) were summed across all compounds measured and compared with the relative summed absorbances in Table 6 and Table 10, there was no relationship (data not shown).

When relative detector responses were summed across all compounds in model and real wine, the sum was about 20% higher in real wine. However, this simple analysis ignores the individual variation between real and model wine treatments for each wood.

The most obvious differences were for 3-phenyl-2-butanol, 2-(methoxymethyl)-5-methoxyphenol, 4-hydroxy-3-methoxy cinnamaldehyde and 3,5-dimethoxy-4-hydroxy

cinnamaldehyde. For the first two, neither appeared in model wine, and for the second two neither appeared in real wine. Consider the first two. 3-Phenyl-2-butanol was present in all woods and toasting treatments in real wine, and 2-(methoxymethyl)-5-methoxyphenol was unique to both toasting levels of American oak in real wine. 4-Hydroxy-3-methoxy cinnamaldehyde appeared only in model wine in all woods and treatments. Its greatest expression was in manuka dark toast where its relative concentration was very roughly 10 fold higher than on woods on average.

4-(2-Hydroxyethyl)phenol was detected only in manuka dark toast in the model wine, whereas it appeared in all wood and toast treatments in the real wine, showing its greatest expression in matai light toast and silver beech dark.

3,4-Dimethyl phenol was detected only in the wine treated with American oak toasted at both levels. Its uniqueness to oak puts it in the same category as 5-methyl-2-furaldehyde and 5-butyldihydro-4-methyl-2(3H)-furanone. The cause of generation of these compounds in the heated oak wood is Maillard reaction (Caldeira et al., 2006), but why this should not extend to other woods is not known.

Looking now at the extraction profile for the variety of compounds extracted in both model and real wine treatments (Table 9, Table 11), American oak, manuka, and matai added similar number of compounds in the model and real wine light toast treatments, whereas pohutukawa, silver beech and totara yielded more compounds in the real wine than in the model wine. Further looking into detail, gallaldehyde was extracted from only American oak, manuka and silver beech for both model and real wines. Carvacrol was also extracted in only the light toast treatments of American oak, manuka and matai in model and real wines but in real wine both toast levels of matai added this compound to real wine including the light toast of pohutukawa. o-Cresol was expressed in light toast treatments of American oak and totara, dark toast treatment of pohutukawa and both toasting levels of matai. Whereas nearly all treatments in real wine expressed this compound except dark toast of totara. The geometric isomer p-cresol was unique to dark toasted matai and pohutukawa treatments in model wine whereas in real wine, it was extracted only in the real wine treated with light toast manuka. 4-(Ethoxymethyl)-2-methoxy phenol was detected only in the matai and totara dark toast treatments in both the model and real wine.

Now consider furfural and vanillin, compounds present in both real and model wines for all wood treatments. Compared with other woods (about 10 or less relative detector units), American oak and manuka had much higher concentrations of this compound in the model

wine (around 20 and 230 relative detector units, respectively), while in real wine the concentrations in oak and manuka were roughly reversed (120 and 10, respectively). The reason for this inversion is not known. Compared with furfural, the relative concentration range of vanillin was more restricted. In model wine the correlation between vanillin values for light and dark toasts was insignificant r = –0.28, but positive in real wine, r = 0.58. Inspection of Table 9 and Table 11 shows that in nearly all cases for real and model wine that the concentration of vanillin was higher for the dark toasts. Vichi et al. (2007) and Caldeira et al (2006) found the same result for oak.

Chatonnet et al. (1999) found the concentration of volatile compounds increase from light to medium toasting and then it decreases as heavy (dark) toasting is applied. In the present research, we have found more compounds in the light toast (200°C) to which they call a medium toast. Thus these results are consistent with the results of Chatonnet et al. (1999) and Doussot et al., (2002), who said that medium toasting drastically enhanced the loss of ellagitannins and the gain in volatile compounds.

Phenols originate from thermodegradation of lignins, in a second phase of degradation heating after the release of phenolic aldehydes (Jackson, 2000). Consequently, these compounds are found in higher concentrations when the toasting is more intense (Jackson, 2000). This was certainly true for model wine treatments but not so for real wine treatments. The reason for this difference is not known.

Oak lactone, also known as whiskey lactone, is 5-butyldihydro-4-methyl-2(3H)-furanone (Chatonnet et al., 1997). Several research groups, for example, Guchu, Diaz-Maroto, Perez-Coello, Gonzalez-Vinas, & Ibanez (2006) and Singleton (1995) reported that non-toasted oak chips released more oak lactone to wines than did the toasted, possibly due to thermodegradation of these heat-sensitive compounds or their loss by volatilisation when the oak wood was subjected to very high temperatures. In the present study, 5-butyldihydro-4-methyl-2(3H)-furanone concentrations were higher in the light toast of both model and real wine. This finding is consistent with the other research reports. It is restated that this compound was unique to oak.

6.4 Possible causes of differences in extraction profiles

In Chapter 2, it was noted that the pH of the model wines was 3.5, whereas that for the real wine was 3.44. A comment was made in Chapter 5 that the difference in pH could lead to differences in extraction. It was observed that the pH of the wine had less influence on the extraction process than the alcohol level because the accumulation of oak compounds

was higher in the wine with higher alcoholic content than in the wine with lower pH (Garde-Cerdan & Ancin-Azpilicueta, 2006). In the present study the effects of pH and ethanol concentration in the two wines are slightly different and are confounded by the other dissolved compounds, including SO_2, making up the real wine. Ancin, Garde, Torrea, & Jimenez (2004) found that SO_2 combined with 5-hydroxymethylfurfural, vanillin, syringaldehyde and coniferaldehyde delaying their free occurrence in the wine. The two cinnamaldehydes in the model wine in Table 9 did not appear in the real wine, Table 11, possibly because they were bound to SO_2. However, other aldeydes were present in both wines, perhaps consistent with the finding by Ancin et al., (2004) that furfural and 5-methylfurfural did not bind to SO_2, probably because their carbonyl group is not reactive enough (Ancin et al., 2004).

Another possible way that differences might be generated between real and model wine concerns microbial activity. The literature has examples where reduction of acids and aldehydes, and decarboxylation occur in wine due to microbial action of for example the yeasts *Brettanomyces* and *Dekkera*. Garde-Cerdan et al. (2006) showed that microbiological transformation due to *Brettanomyces* occurs during the contact of wood with the wine. Furanaldehydes and phenolic aldehydes can be reduced biologically during ageing period to form their corresponding alcohols. (Dugelay et al., 1993) demonstrated that 4-hydroxycinnamic acid (coumaric acid) and 3-methoxy-4-hydroxycinnamic acid (ferulic acid) could be changed into the corresponding vinylphenols (i.e. 4-vinylphenol and 4-vinylguaiacol) by *Saccharomyces cerevisiae* decarboxylase activity.

In the present study the absence of the two cinnamaldehydes in real wine might be explained by microbially generated losses to, 3-phenyl-2-butanol which was present in all real wine treatments but no model wine treatments. In this respect, 2-(methoxymethyl)-5-methoxyphenol was absent in all model wines but present in one real wine treatment, American oak. But models of microbially-generated changes obviously depend on the presence of active yeasts or other microbes (Sefton et al., 1997), and there is no information about the microbial status of the *chardonnay* used.

According to Sefton et al. (1997), the concentration of vanillin in white wine was only one-third of that in model wines stored for the same period. These authors implicated biological transformation of vanillin by yeast. In the present study there was evidence for this effect in the dark toast treatments of American oak and manuka, but equally the reverse was true for some other treatments. Thus no conclusions can be drawn.

In summary, there are obvious differences in the extraction profiles of model and real wines, but there is no clear pattern and nor evidence as to cause, just possibilities. Thus, the present research opens a door to the future research studies on this theme.

The final conclusion in the next Chapter 7 will discuss the possibilities and recommendations for the future studies and the limitations of the present study.

Chapter 7

Conclusions and Future Research

This thesis has examined the chemistry of using New Zealand timbers to age, mature and flavour wine with woods other than the traditional French and American oak. The ultimate aim of this research is to find woods and treatments that could either mimic the utility of oak treatment and/or create unique flavours that could be exploited by the New Zealand wine industry. Reliance on imitation of European models could be potentially dangerous for the New Zealand wine industry, as equivalent wines can be produced in many countries leading to competition on price alone. The advantage of regional distinctiveness is well illustrated by the success of Marlborough *sauvignon blanc* wine internationally. Indirectly, distinctiveness is the driving force for the present research, which aims to develop a flavour dimension beyond, grape, climate and soil and other factors known to affect wine flavour.

The work involved the use of wood chips rather than barrels, because for reasons discussed earlier in this thesis the future of many oaked wines will lie in chips.

The parameters investigated were wood weight losses resulting from different toasting levels, colour measurements, spectrophotometric analyses of extractables, and gas chromatographic analysis of extractables.

A range of woods was selected based on existing use and botanical similarity (oak, and cherry and silver beech), or on their association with the New Zealand ethos and botanical similarity (matai, feijoa, macrocarpa, pohutukawa, radiata pine, totara, kahikatea, rimu, and manuka). Woods chips were toasted at two levels, 200°C for two hours, deemed light toast, and at 210°C for three hours, deemed a dark toast. These terms were somewhat arbitrary because each wood behaved differently to toasting, and indeed comparison with the results of Chatonnet et al. (1999) who worked with oak suggests that so-called light toasting in the present study is equivalent to medium toasting for oak.

The weight loss of oak chips at 200°C was much greater than that of other woods, but the colour change did not indicate losses due to severe charring. Interestingly, the moisture content of oak (determined by drying to a relatively cool 110°C) was the lowest of all the woods, and it might be argued that oak had ‘head start’ in pyrolysis. However, it is reasoned that exposure to 200°C would rapidly drive off all free water within tens of minutes. Other woods that showed severe weight loss on dark toasting (rimu, macrocarpa) did char severely.

Overall each wood behaved in a distinctive way to these toasting treatments, but with some botanical similarity between cherry and silver beech.

Colour measurements in Hunter colour space showed that toasting did not greatly affect the hue angle (the basic colour) of the chips, but the colour intensity (saturation) was strongly reduced, as was the overall reflectance of light (L* value). Beyond these generalities, each wood was a story to itself. The value of colour measurements is academic in this thesis but will have utility in commercial applications, because degree of toasting is probably a good indicator of extractables into wine. For example, when light toasted hue angle as a percent of untoasted hue angle was plotted as a function of weight loss percent on toasting, there was clear inverse linear relationship. The relationship was much weaker for dark toasting. Light toasting yielded higher concentrations of extractables as determined by spectrophotometry and gas chromatography. Thus, Hunter saturation and reflectance could be used to predict extractables into wine. Hunter colour space meters, although not cheap, are quick and reliable in their application.

Turning now to the identification and relative quantitation of extractables into model and real wine, it is clear that of the six woods added to wines, oak added the greatest number of compounds, and several of these were unique to oak. These compounds were 3,4-dimethyl phenol, 5-methyl-2-furaldehyde and 5-butyldihydro-4-methyl-2(3H)-furanone. However their contribution to flavour is unknown.

The presence of 4-hydroxy-3-methoxy cinnamaldehyde and 3,5-dimethoxy-4-hydroxy cinnamaldehyde in the model wine but their absence in real wine was attributed to the presence of SO_2 in real wine. It was proposed that the two cinnamaldehydes in the model wine did not appear in the real wine possibly because they were bound to SO_2 and would not be extracted into the diethyl ether/n-pentane phase. The reason for the presence of 3-phenyl-2-butanol in real wine only is not known. Generally, the array of compounds present in real wine but not model wine will be ultimately responsible for the differences in extraction. In this respect real wine may also have residual microbial activity.

Future research directions could include the following. The present gas chromatographic study was limited to six woods. The issue of a single sample of each species not being the representative of variation in wood properties due to climate, age of wood, location and soil should be addressed. At some point this should be extended to other woods, and the number of unequivocal identifications should be increased by the use of authentic external standards. Using selected woods, the range of temperature/time treatments should be extended in the

hope that temperature-dependent patterns of extractables might be observed; for example, vanillin concentration might increase with temperature to a point then decline. Another limitation of the present study was lack of data on the level of SO_2 in the real wine since no measurements were made. SO_2 is known to bind aldehydes. Scanning light and electron microscopy could be used in parallel to the chemistry to describe the pyrolytic events in physical terms.

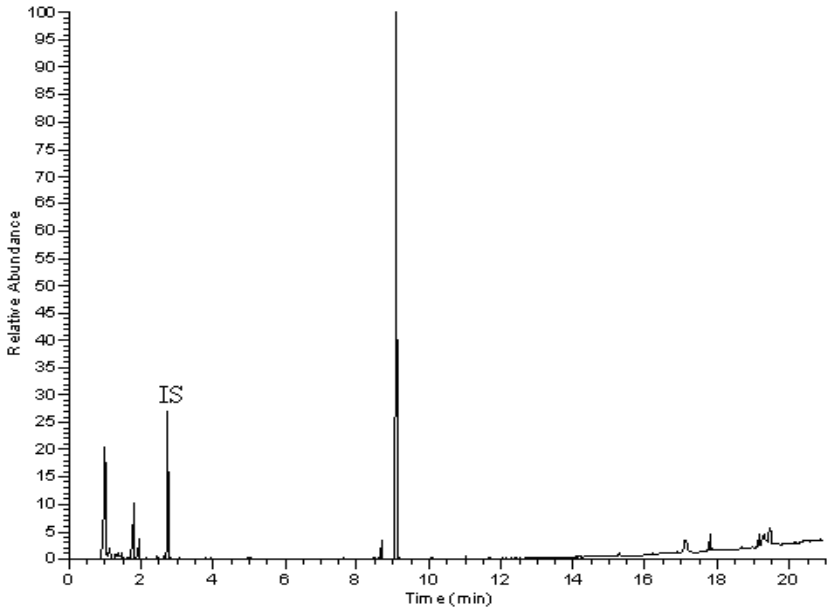
Finally, it must be noted that this research was limited to physical and chemical changes. At some point sensory trials using analytical panels (intensities of attributes) and consumer panels (hedonic; how much you like this wine?) must be conducted to identify commercially useful woods. From the available data and from preliminary sensory trials, manuka may be a good commercial prospect.

Whichever wood(s) is chosen for commercialisation, it must be continually available without significant legal and cultural obstacles, and this may prove to be the greatest challenge in 21st century New Zealand.

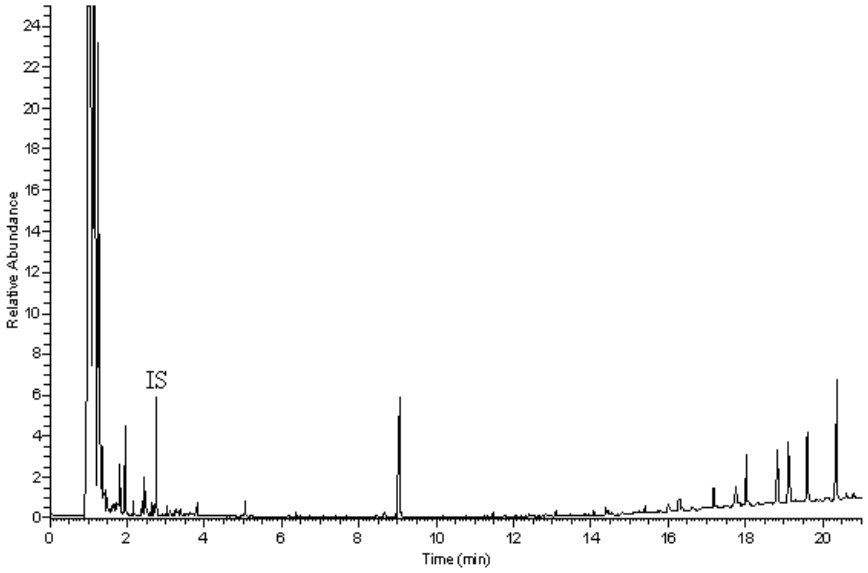
Appendices

Appendix – All Control

Control

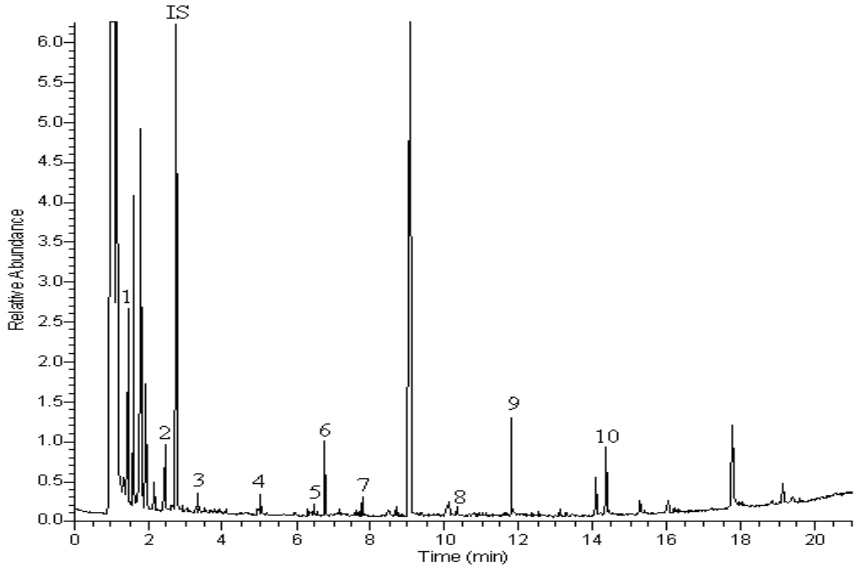


Appendix I A gas chromatograph showing water as a control. IS = internal standard (2-octanol)

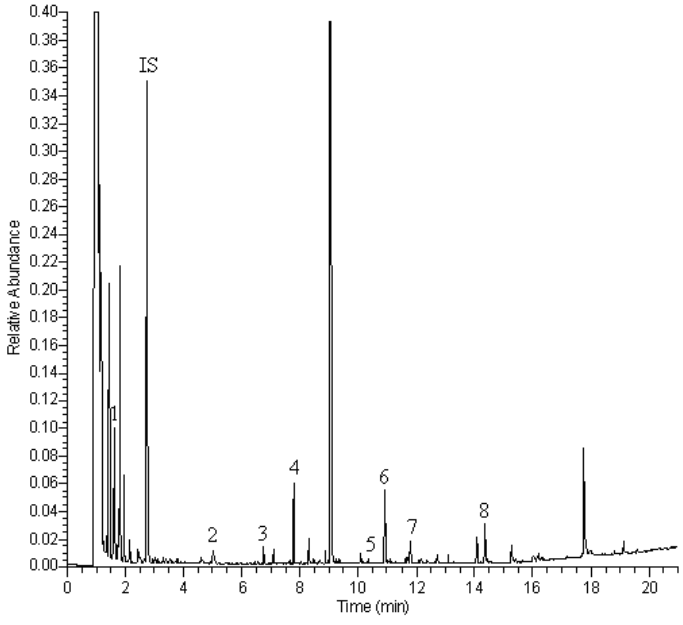


Appendix II A gas chromatograph showing model wine as a control. IS = internal standard (2-octanol)

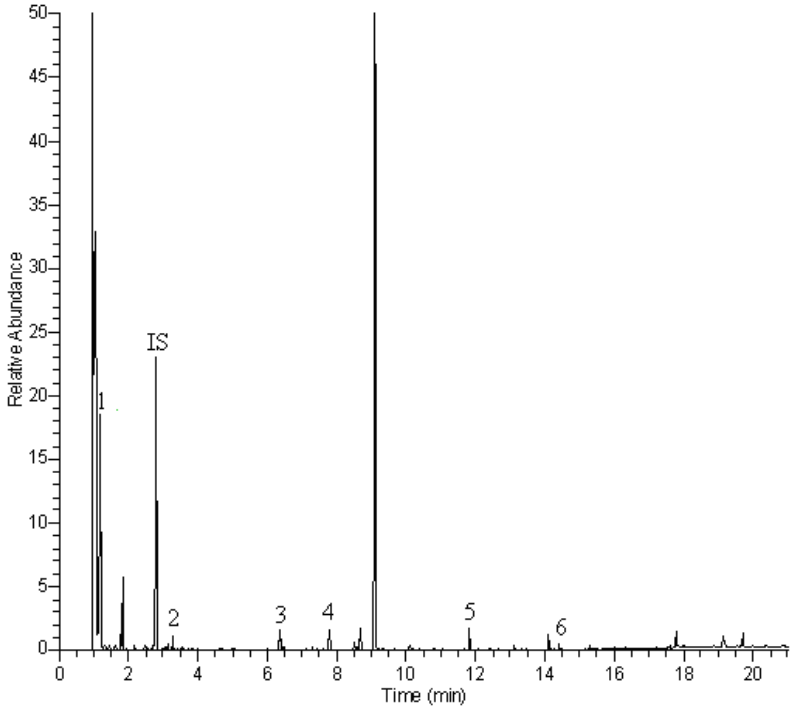
Appendix – Model wine treatments



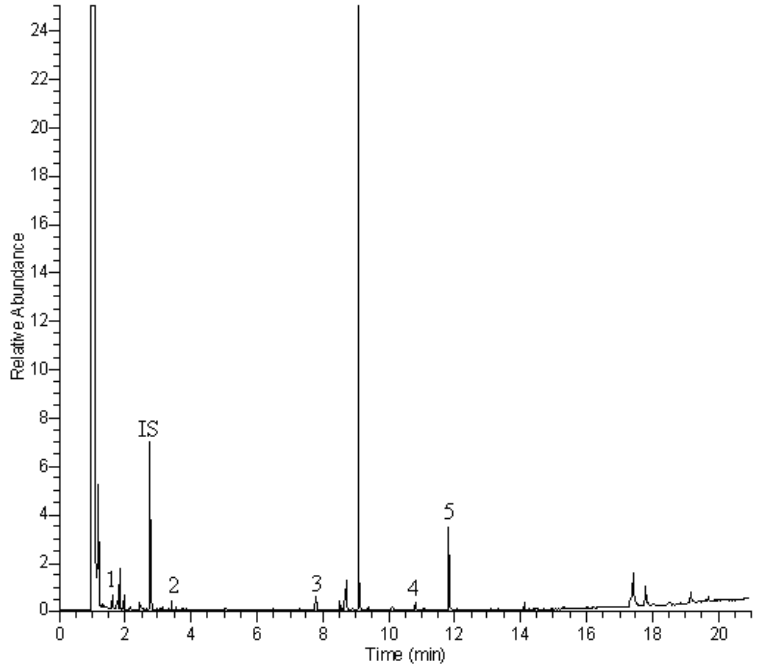
Appendix III A gas chromatograph showing American oak light toast treatment with model wine. 1. Furfural 2. 5-Methyl-2-furaldehyde 3. o-Cresol 4. 3,4-Dimethylphenol 5. Carvacrol 6. 5-Butyldihydro-4-methyl-2(3H)-furanone 7. Vanillin 8. 3,5-Dimethoxy-4-hydroxy cinnamic acid 9. 4- Hydroxy-3-methoxy cinnamaldehyde 10. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)



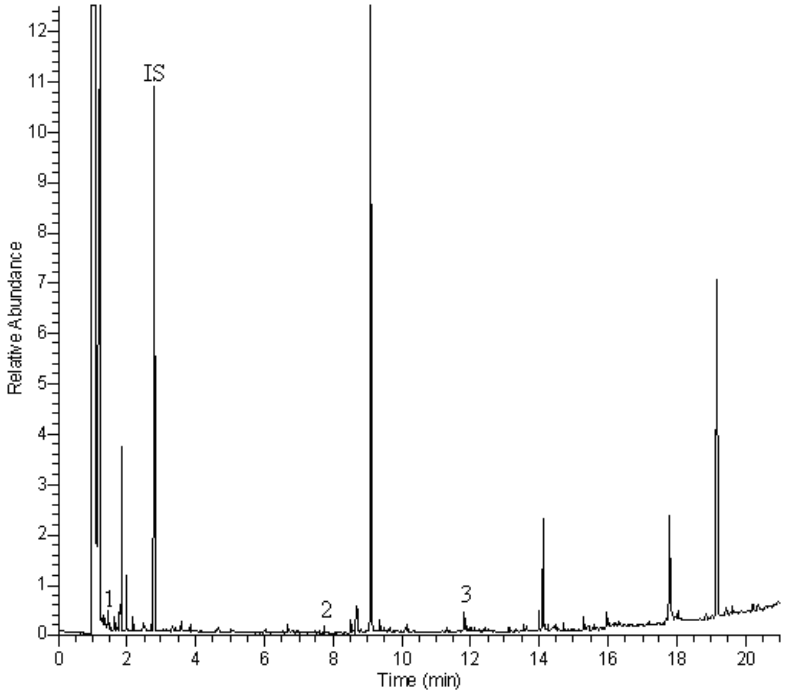
Appendix IV A gas chromatograph showing American oak dark toast treatment with model wine. 1. Furfural 2. 3,4-Dimethylphenol 3. 5-Butyldihydro-4-methyl-2(3H)-furanone 4. Vanillin 5. 3,5-Dimethoxy-4-hydroxy cinnamic acid 6. Gallaldehyde 7. 4- Hydroxy-3-methoxy cinnamaldehyde 8. 3,5-Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)



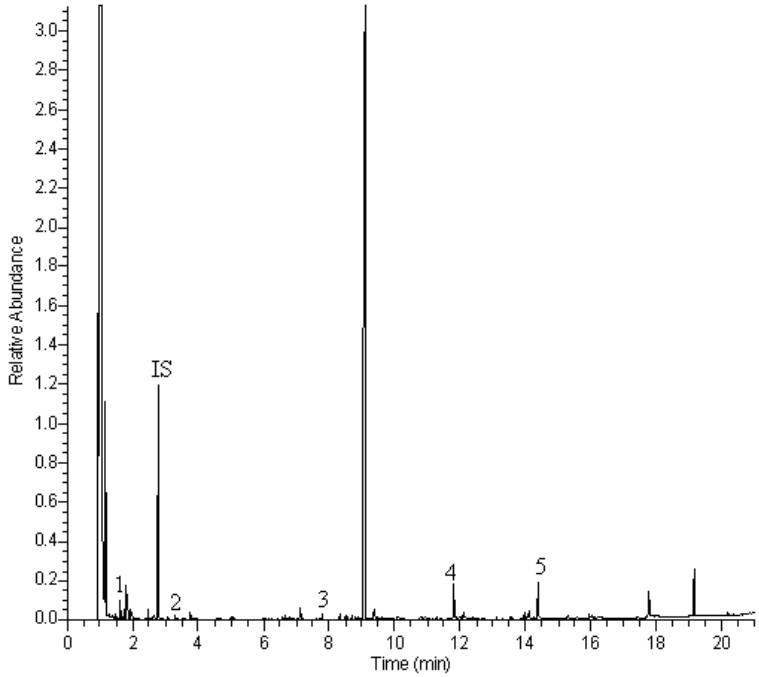
Appendix V A gas chromatograph showing matai light toast treatment with model wine. 1. Furfural 2. o-Cresol 3. Carvacrol 4. Vanillin 5. 4- Hydroxy-3-methoxy cinnamaldehyde 6. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)



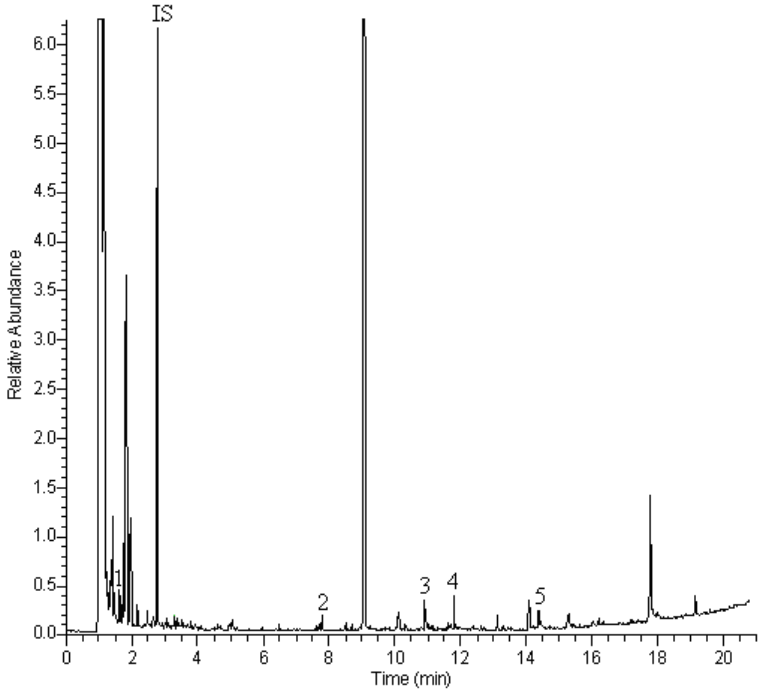
Appendix VI A gas chromatograph showing matai dark toast treatment with model wine. 1. Furfural 2. o-Cresol 3. Vanillin 4. 4-(Ethoxymethyl)-2-methoxyphenol 5. 4- Hydroxy-3-methoxy cinnamaldehyde IS = internal standard (2-octanol)



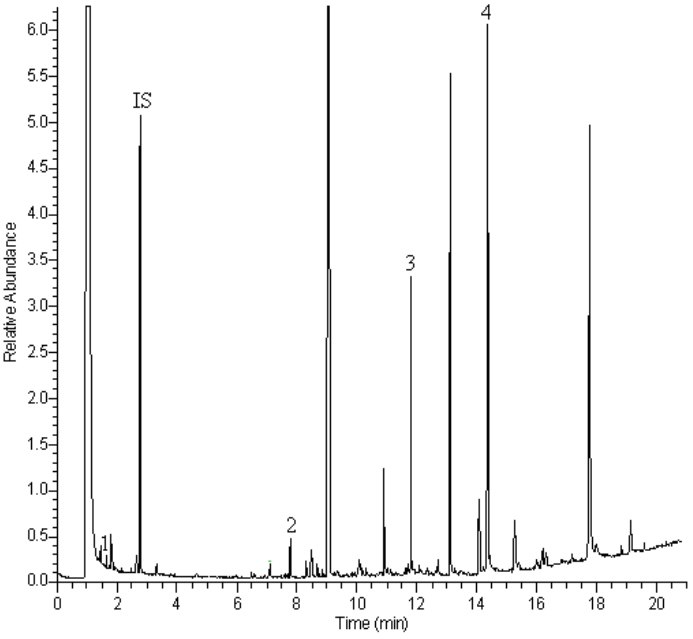
Appendix VII A gas chromatograph showing pohutukawa light toast treatment with model wine. 1. Furfural 2. Vanillin 3. 4- Hydroxy-3-methoxy cinnamaldehyde IS = internal standard (2-octanol)



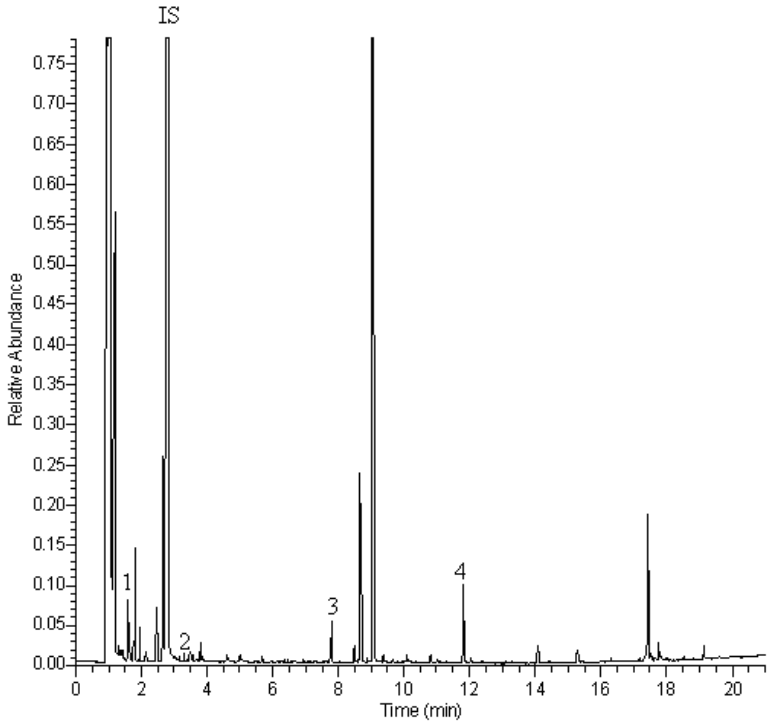
Appendix VIII A gas chromatograph showing pohutukawa dark toast treatment with model wine. 1. Furfural 2. o-Cresol 3. Vanillin 4. 4- Hydroxy-3-methoxy cinnamaldehyde 5. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)



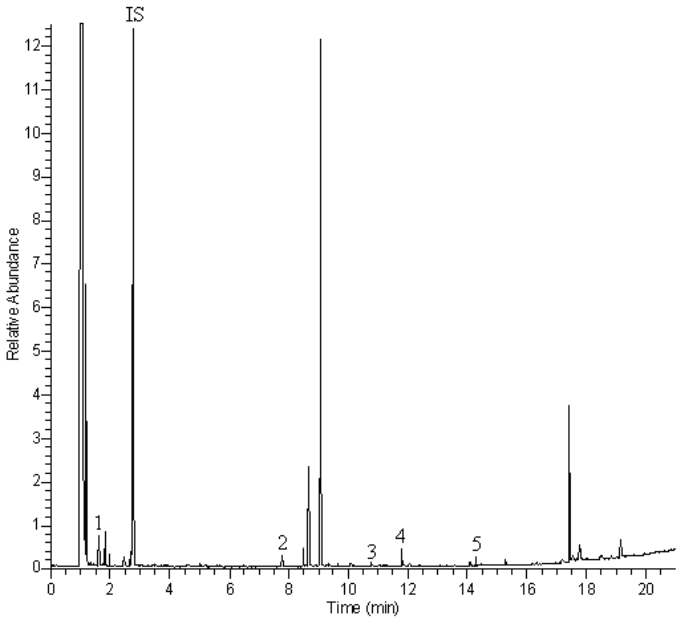
Appendix IX A gas chromatograph showing silver beech light toast treatment with model wine. 1. Furfural 2. Vanillin 3. Gallaldehyde 4. 4- Hydroxy-3-methoxy cinnamaldehyde 5. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)



Appendix X A gas chromatograph showing silver beech dark toast treatment with model wine. 1. Furfural 2. Vanillin 3. 4- Hydroxy-3-methoxy cinnamaldehyde 4. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)

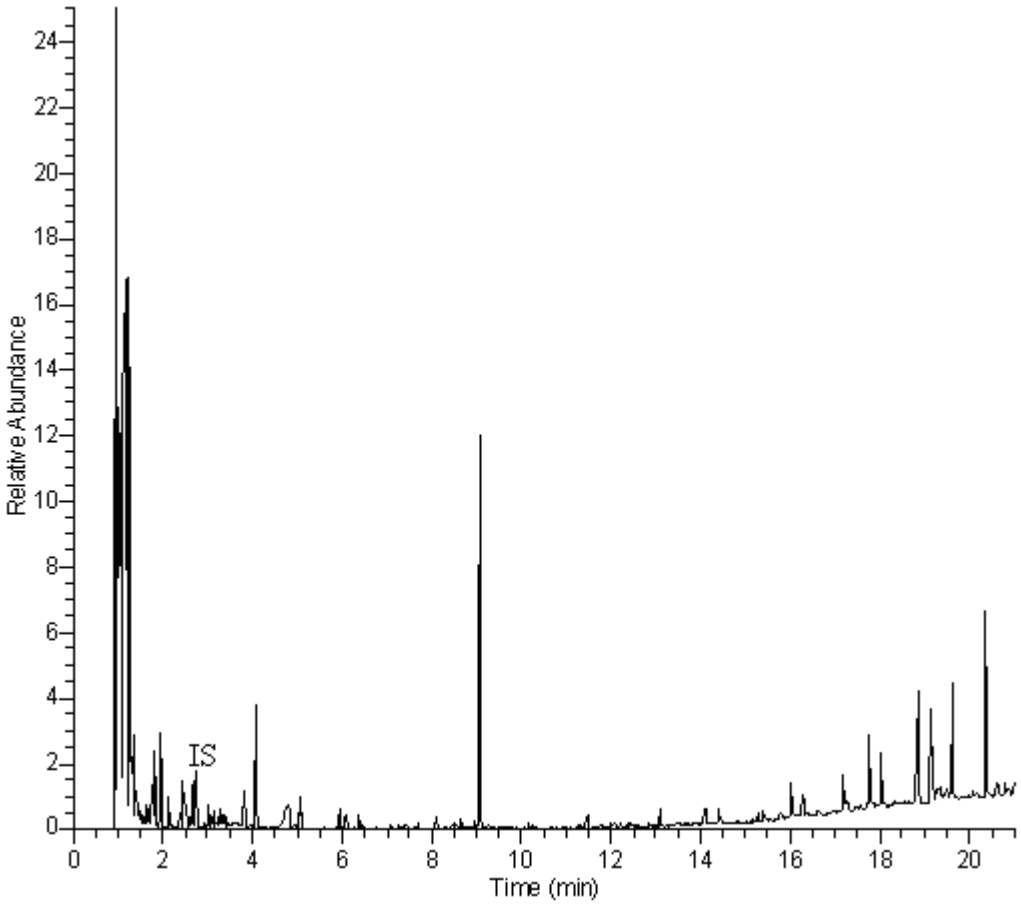


Appendix XI A gas chromatograph showing totara light toast treatment with model wine. 1. Furfural 2. o-Cresol 3. Vanillin 4. 4- Hydroxy-3-methoxy cinnamaldehyde IS = internal standard (2-octanol)



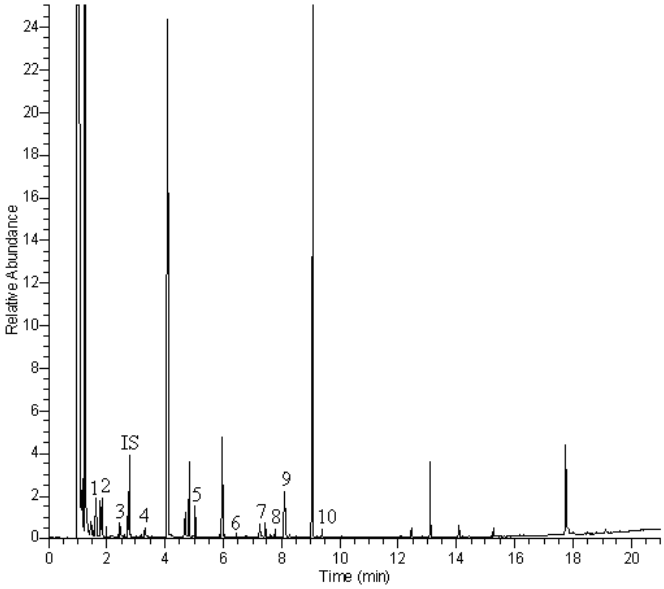
Appendix XII A gas chromatograph showing totara dark toast treatment with model wine. 1. Furfural 2. Vanillin 3. 4-(Ethoxymethyl)-2-methoxyphenol 4. 4-Hydroxy-3-methoxy cinnamaldehyde 5. 3,5- Dimethoxy-4-hydroxy cinnamaldehyde. IS = internal standard (2-octanol)

Appendix - Real wine control

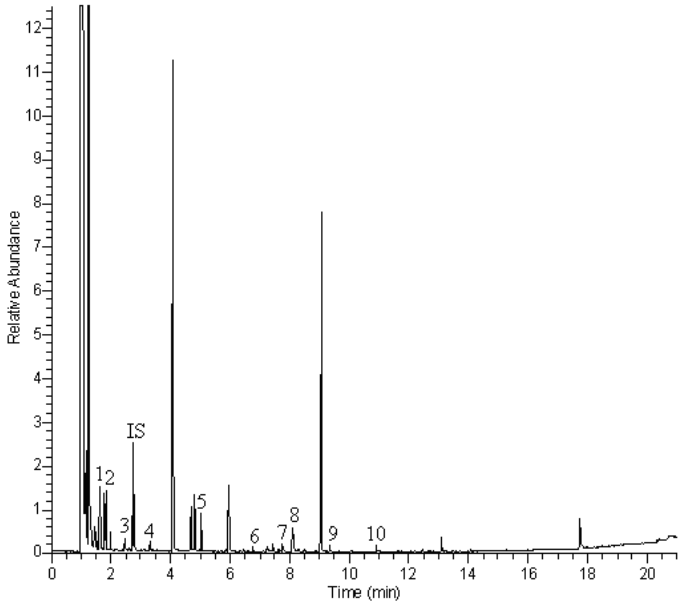


Appendix XIII A gas chromatograph showing control of real wine. IS = internal standard (2-octanol)

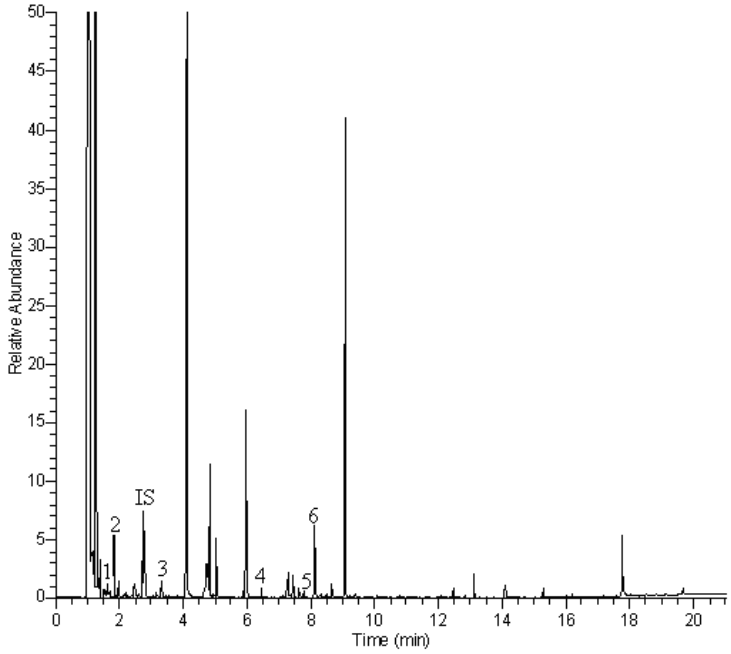
Appendix - Real wine treatments



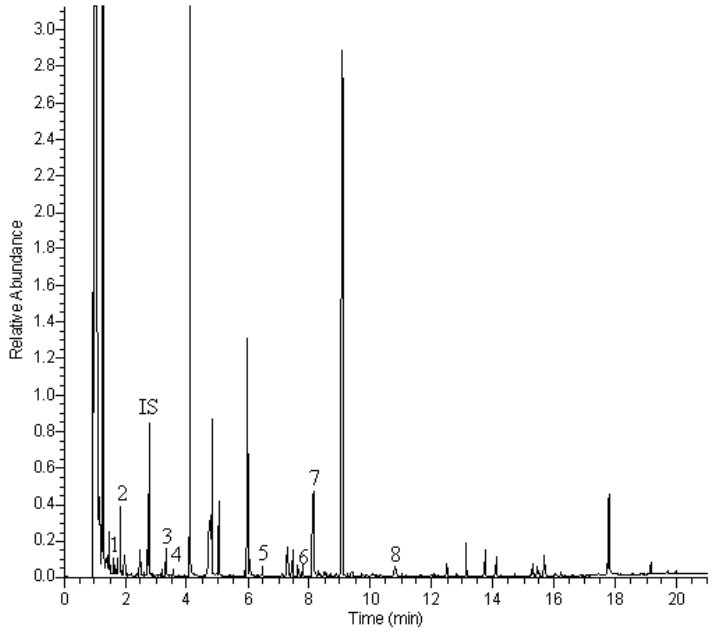
Appendix XIV A gas chromatograph showing American oak light toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3. 5-Methyl-2-furaldehyde. 4. o-Cresol 5. 3,4-Dimethylphenol 6. Carvacrol 7. 5-Butyldihydro-4-methyl-2(3H)-furanone 8. Vanillin 9. 4-(2-Hydroxyethyl)phenol 10. 2-(Methoxymethyl)-5-methoxyphenol IS = internal standard (2-octanol)



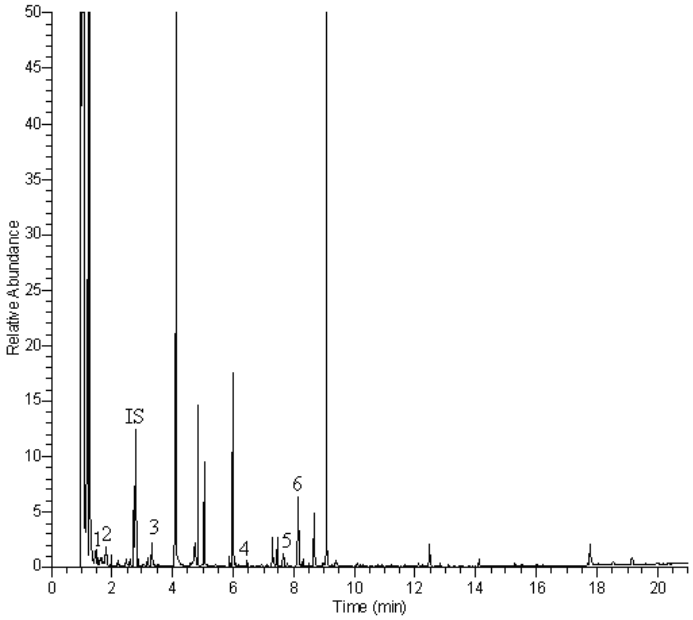
Appendix XV A gas chromatograph showing American oak dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3. 5-Methyl-2-furaldehyde. 4. o-Cresol 5. 3,4-Dimethylphenol 6. 5-Butyldihydro-4-methyl-2(3H)-furanone 7. Vanillin 8. 4-(2-Hydroxyethyl)phenol 9. 2-(Methoxymethyl)-5-methoxyphenol 10. Gallaldehyde IS = internal standard (2-octanol)



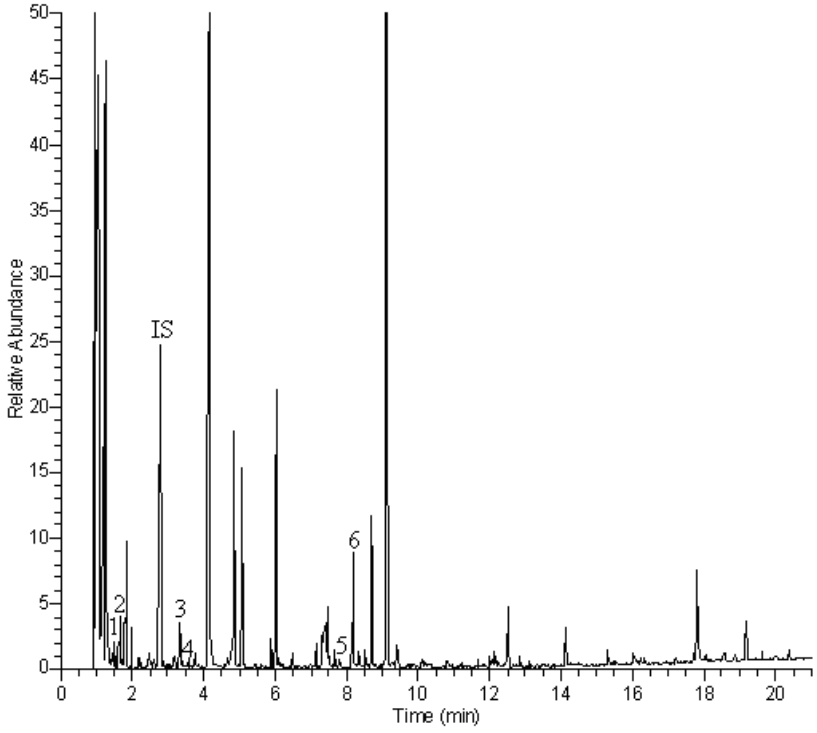
Appendix XVI A gas chromatograph showing matai light toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. Carvacrol 5. Vanillin 6. 8. 4-(2-Hydroxyethyl)phenol IS = internal standard (2-octanol)



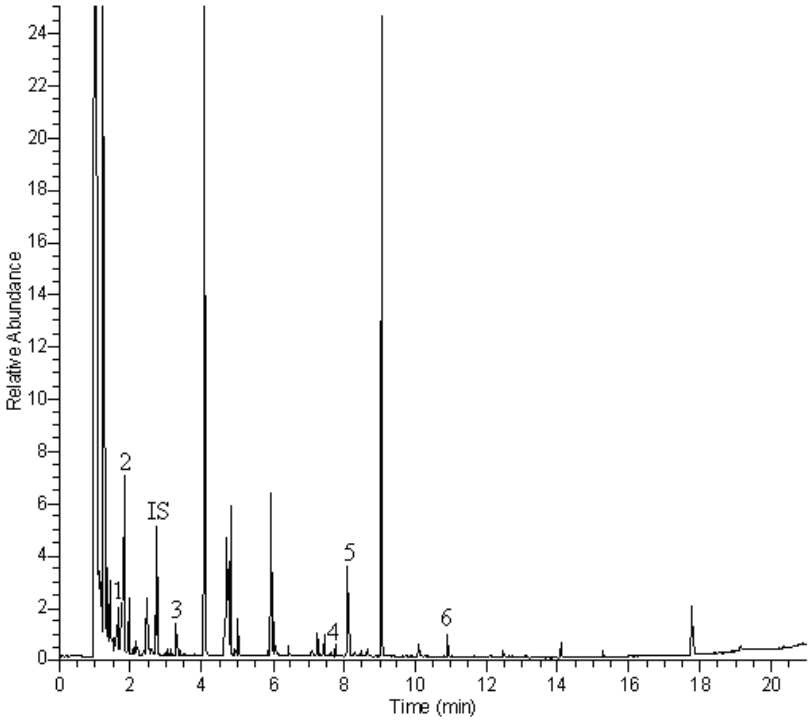
Appendix XVII A gas chromatograph showing matai dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. p- Cresol 5. Carvacrol 6. Vanillin 6. 7. 4-(2-Hydroxyethyl)phenol 8. 4-(Ethoxyethyl)-2-methoxyphenol IS = internal standard (2-octanol)



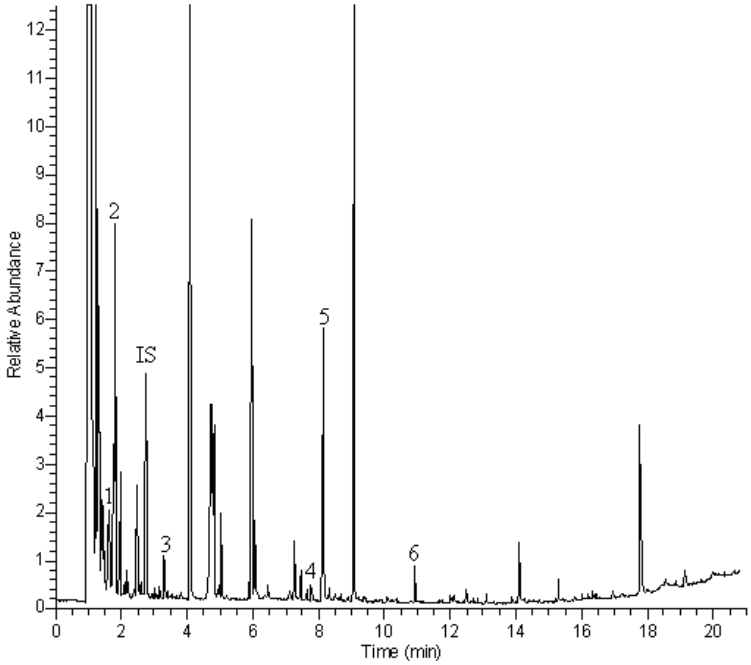
Appendix XVIII A gas chromatograph showing pohutukawa light toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. Carvacrol 5. Vanillin 6. 4-(2-Hydroxyethyl)phenol IS = internal standard (2-octanol)



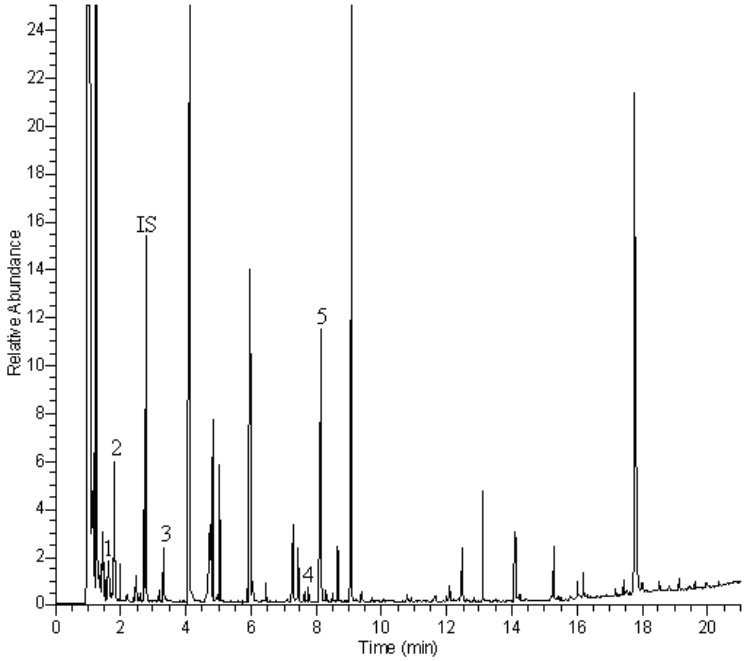
Appendix XIX A gas chromatograph showing pohutukawa dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. p-Cresol 5. Vanillin 6. 4-(2-Hydroxyethyl)phenol IS = internal standard (2-octanol)



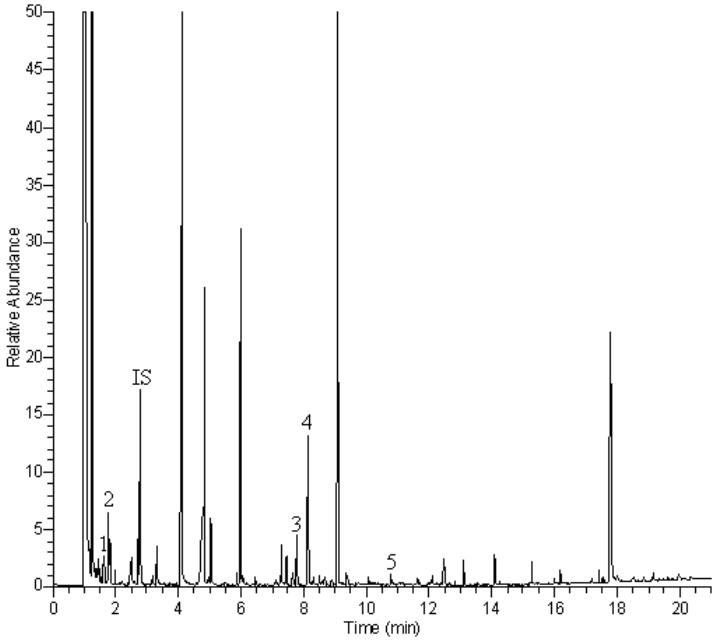
Appendix XX A gas chromatograph showing silver beech light toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. Vanillin 5. 4-(2-Hydroxyethyl)phenol 6. Gallaldehyde IS = internal standard (2-octanol)



Appendix XXI A gas chromatograph showing silver beech dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. Vanillin 5. 4-(2-Hydroxyethyl)phenol 6. Gallaldehyde IS = internal standard (2-octanol)



Appendix XXII A gas chromatograph showing totara light toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3 o-Cresol 4. Vanillin 5. 4-(2-Hydroxyethyl)phenol IS = internal standard (2-octanol)



Appendix XXIII A gas chromatograph showing totara dark toast treatment with real wine. 1. Furfural 2. 3-Phenyl-2-butanol 3. Vanillin 4. 4-(2-Hydroxyethyl)phenol 5. 4-(Ethoxyethyl)-2-methoxyphenol IS = internal standard (2-octanol)

References

Aalders, P. (2004). New Zealand Native Timbers used for craft [Electronic Version]. Retrieved 18 April, 2007, from http://www.woodcraft.co.nz

Aalders, P. (2004). New Zealand Native Timbers used for craft. Retrieved 18 April, 2007, from http://www.woodcraft.co.nz

Ancin, C., Garde, T., Torrea, D., & Jimenez, N. (2004). Extraction of volatile compounds in model wine from different oak woods: effect of SO2. *Food Research International, 37*(4), 375-383.

Anon. (1995). The Composition of Oak and an Overview of its Influence on Maturation. Retrieved 25 March, 2006, from http://www.google.co.nz

Anon. (1996). Chemical Summary For Vanillin. Retrieved 6 March, 2007, from http://cira.ornl.gov/documents/vanillin.pdf

Anon. (2004). Oak Lactones. Retrieved 12 November, 2006, from http://images.google.co.nz/imgres?imgurl=http://www.flavornet.org/gif/55013-32

Anon. (2005). The Feijoa – A brief history. Retrieved 13 September, 2006, from http://nchun.wordpress.com/feijoa

Arapitsas, P., Antonopoulos, A., Stefanou, E., & Dourtoglou, V. G. (2004). Artificial aging of wines using oak chips. *Food Chemistry, 86*(4), 563-570.

Belitz, H.-D., & Grosch, W. (1999). *Food chemistry* (2nd / ed.). Berlin ; New York: Springer.

Burns, H. (2004). *The Use of New Zealand Woods into Wine.* Auckland University of Technology.

Caldeira, I., Climaco, M. C., de Sousa, R. B., & Belchior, A. P. (2006). Volatile composition of oak and chestnut woods used in brandy ageing: Modification induced by heat treatment. *Journal of Food Engineering, 76*(2), 202-211.

Carrillo, J. D., Lo´pez, A. l. G., & Teresa Tena, M. (2006). Determination of volatile oak compounds in wine by headspace solid-phase microextraction and gas chromatography–mass spectrometry. *Journal of Chromatography, 1102*, 25-36.

Chatonnet, P., Henry, R., Denis, D., & Cutzach, I. (1997). Identification of Volatile Compounds with a "Toasty" Aroma in Heated Oak Used in Barrelmaking. *Journal of Agriculture, 45*, 2217-2224.

Clarke, R. J., & Bakker, J. (2004). *Wine flavour chemistry*. Oxford, UK ; Ames, Iowa: Blackwell Pub.

Coultate, T. P. (2002). *Food : the chemistry of its components* (4th ed.). Cambridge: Royal Society of Chemistry.

Coutts, P. (2005). Totara Vineyards. Retrieved 28 May, 2007, from http://www.cuisine.co.nz/index.cfm?pageID=7419&r=0

Doussot, F., De Jéso, B., Quideau, S., & Pardon, P. (2002). Extractives Content in Cooperage Oak Wood during Natural Seasoning and Toasting; Influence of Tree Species, Geographic Location, and Single-Tree Effects. *Journal of Agriculture and Food Chemistry, 50* (21), 5955 -5961.

Dugelay, I., Gunata, Z., Sapis, J. C., Baumes, R., & Bayonove, C. (1993). Role of Cinnamoyl Esterase Activities from Enzyme Preparations on the Formation of Volatile Phenols during Winemaking. *Journal of Agriculture and Food Chemistry, 41*, 2092-2096.

Garde-Cerdan, T., & Ancin-Azpilicueta, C. (2006). Review of quality factors on wine ageing in oak barrels. *Trends in Food Science & Technology, 17*(8), 438-447.

Gawel, R. (2002). Oak Barrel Alternatives in Winemaking,. Retrieved 14 September, 2006, from http://www.aromadictionary.com/articles/oakalternatives_article.html

Harder, A. (2007). The characteristics of different types of wood. Retrieved 25 May, 2007, from http://www.meyersmad.dk/meyers.asp?PageID=13461

Jackson, R. S. (2000). *Wine science : principles, practice, perception* (2nd ed.). San Diego: Academic Press.

Kakaviatos, P. (2006). Oak chips to be allowed in French wine. Retrieved 14 December, 2006, from http://www.decanter.com/news/82419.html

MacDirect Ltd. (2007). What is Macrocarpa and Lawson Cypress? Retrieved 13 May, 2007, from http://www.macdirect.co.nz/macrocarpa.asp

Manuel, D. (2002). Oak. Retrieved 18 September, 2006, from http://www.supermarketguru.com/page.cfm/206

Margalit, Y. (1997). *Concepts in wine chemistry*. San Francisco: Wine Appreciation Guild.

Margalit, Y. (2004). *Concepts in wine chemistry* (2nd ed.). San Francisco: Wine Appreciation Guild.

Miller, D. (2004). Wine Barrels. Retrieved 11 December, 2006, from http://www.cellarnotes.net/wine_barrels.htm

Morales, M. L., Benitez, B., & Troncoso, A. M. (2004). Accelerated aging of wine vinegars with oak chips: evaluation of wood flavour compounds. *Food Chemistry, 88*(2), 305-315.

Mueller, P. (2007). Wine Storage Tanks. Retrieved 7 September, 2006, from http://www.muel.com/ProductDivisions/ProcessingSystems_Equipment/Beverage/Wine/WineStorageTanks.cfm

Museu National Arqueologic de Tarragonna. (n.d.). Amphoras and Commerce. Retrieved 6 September, 2006, from http://www.mnat.es/eng/mnat/marq/marq22.html

New Zealand Vineyard & Wine Industry Review. (2005). Retrieved 1 September, 2006, from http://www.researchandmarkets.com/reports/295030/295030.htm

Nick, L., & Murray, D. (2004). Restoration of mountain beech (Nothofagus solandri var. cliffortioides) forest after fire. Retrieved 14 September, 2006, from http://www.nzes.org.nz/nzje/new_issues/NZJEcol28_1_125.pdf#search=%22Nothofagus%20solandri%20%20%22

Okanagan Barrel Works Ltd. (2001). Why Oak Barrels? Retrieved 6 September, 2006, from http://www.winebarrels.com/barrelsnew.html

Organisation Internationale de la Vigne et du Vin (OIV). (2002). World Comparisons. Retrieved 1 September, 2006, from http://www.winebiz.com.au/statistics/world.asp

Pollnitz, A. P., Jones, G. P., & Sefton, M. A. (1999). Determination of oak lactones in barrel-aged wines and in oak extracts by stable isotope dilution analysis. *Journal of Chromatography A, 857*(1-2), 239-246.

Poole, A. L. (2006). PINE RADIATA. Retrieved 26 April, 2007, from http://www.teara.govt.nz/1966/P/PineRadiata/PineRadiata/en

Sanderson, L. A. (2006). The Ancient History of Wine Retrieved 1 September, 2006, from http://www.lifeinitaly.com/wines/history.asp

Sanza, D. A., & Dominguez, N. I. (2006). Wine aging in bottle from artificial systems (staves and chips) and oak woods: Anthocyanin composition. *Analytica Chimica Acta, 563*(1-2), 255-263.

Sefton, M. A., Spillman, P. J., Pollnitz, A. P., Liacopoulos, D., & Skouroumounis, G. K. (1997). Accumulation of Vanillin during Barrel-Aging of White, Red, and Model Wines. . *Journal of Agriculture and Food Chemistry, 45 (7), 2584 -2589* (7), 2584 - 2589.

Statistical Review. (2005). Retrieved 1Sep, 2006, from http://www.nzwine.com/statistics

Stavin. (2005). Microoxygenation. Retrieved 18 December, 2006, from http://www.micro-ox.com/micro_tytib.htm

Swan, J. S., Hale, M. D., Mccafferty, K., Larmie, E., & Newton, J. (1999). The Influence of Oak Seasoning and Toasting Parameters on the Composition and Quality of Wine. *American Journal of Enology and Viticulture, 50:4*, 495-502.

Taylor, B. (2006). Encouraging industry to assess and implement cleaner production measures. *Journal of Cleaner Production, 14*(6-7), 601-609.

Vichi, S., Santini, C., Natali, N., Riponi, C., Lopez-Tamames, E., & Buxaderas, S. (2007). Volatile and semi-volatile components of oak wood chips analysed by Accelerated Solvent Extraction (ASE) coupled to gas chromatography-mass spectrometry (GC-MS). *Food Chemistry, 102*(4), 1260-1269.

Waterhouse, A. L., & Ebeler, S. E. (1998). *Chemistry of wine flavor* (Vol. 714). Washington, DC.

Wellington Botanical Society. (2006). TRIP REPORT Retrieved 17 June, 2007, from http://wellingtonbotsoc.wellington.net.nz/tripreports/2006/Hutt_Rata_walk.html

William, W., & Charles, G. (2004). Recent Advances in Quantitative Synthetic-Polymer Mass Spectrometry. Retrieved 15 March, 2007

Wine Communications Group Inc. (2006). French Propose Bans on Oak Chips as U.S. Wineries Embrace Oak Alternatives. Retrieved 14 December, 2006, from http://www.winebusiness.com/ReferenceLibrary/webarticle.cfm?dataId=45173

Young, O. A., & West, J. (2001). *Meat science and applications*. New York: Marcel Dekker.