Effect of Resin Extraction on Toasted Wood Flavours in Wine

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Confidentiality

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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.

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Abstract

Woods other than the traditional oak wood have been studied for their applicability to winemaking, aiming to produce wider ranges of wine flavours with a distinctiveness associated with New Zealand.

Prior studies with woods other than oak have shown that unpleasant flavours from infusion of some woods could be linked to the presence of resin. The main thrust of this research was to test the hypothesis that any wood free of resin would be suitable for flavouring wine since all trees are composed of the same major constituents.

The study involved various organic solvent extractions to remove resins from manuka, macrocarpa, totara, kahikatea, radiata pine, gorse, and American oak, prior to toasting and wine infusion. The woods were cut to a defined chip dimension, and Soxhlet-extracted with dichloromethane before toasting to 200 and 210°C for two and three hours, respectively. These were the light and heavy toasts. In discriminative triangle trials comparing unextracted with resin-extracted infusion treatments in unwooded chardonnay at the two toasting levels, the 50 panellists could distinguish a difference in only three of the 14 trials. The exceptions were manuka heavy toast ($P < 0.01$), and both macrocarpa toasts ($P < 0.05$). The remaining 11 trials did not elicit significant levels of correct judgements from the panellists. The mass of resin recovered ranged from 1% (gorse) to 11 % (manuka), but there was no relationship between the quantity of resin and the discrimination results.

Other parameters relating to the wood chips were measured in parallel to the discrimination trials. Colour changes in untoasted woods due to resin extraction were usually statistically significant but minor. Colour changes were unrelated to weight losses due to extraction. Light and heavy toasting resulted in significant and often major changes in colour parameters due to resin extraction. However there was no clear pattern of change and thus had no meaningful outcomes.

In the discrimination trials, subtleties of the responses to macrocarpa and manuka, suggested that not all resin was extracted by the single extraction with dichloromethane. A further extraction of toasted chips not used for infusion showed that resinous matter was still present in all woods, although pyrolytic generation of dichloromethane-soluble matter could not be excluded. These collective results prompted an exhaustive extraction of wood chips prior to a hedonic trial with manuka, macrocarpa, and American oak. The solvents in

sequence were dichloromethane, hexane and diethyl ether. Each extracted some resinous matter, clearly showing that the single dichloromethane extraction prior to the discrimination trials left some resin in the chips, potentially affecting wine flavour.

The triple-extracted woods were light toasted and infused in wine destined for a hedonic trial in six retail wine shops, for which the overall statistical significance was $P < 0.001$. The 121 consumers found that the unwooded chardonnay (control) was most favoured whereas the wine infused with macrocarpa was very significantly the least favoured. Its dislike was clearly caused by presence of its resin in the wine and/or because of a very low flavour threshold for that resin. The manuka treatment was numerically the most favoured ahead of American oak, but not significantly so.

The resins extracted at various points of this study were also evaluated by panellists focusing on descriptive qualities. These descriptions and the results of the discrimination and hedonic trials led to the conclusion that variation in wine flavour when infused with toasted wood was in most cases not related to the occurrence of resin in woods.

Finally, future research possibilities have been described, with an emphasis of the most potentially useful wood, manuka.

Chapter 1

Introduction

1.1 The New Zealand wine industry

Grapes are produced in greater amount than any other fruit in the world because of their vital role in wine production. Countries such as France, Italy, Spain, USA, Argentina, and Australia are the top wine-producing countries of which France and Italy alone produce about one third of the total world wine production.

New Zealand is a very small player in the world wine market. While 28,000 millions of litres (ML) of wines were produced world-wide, New Zealand produced only 133 ML in 2006 (Table 1).

Table 1 New Zealand statistics for wineries and wine production

Year	Number of wineries in New Zealand	Wine Production (ML)
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
2006	530	133.2

Statistical overview of New Zealand wine (Anonymous, 2007)

However rather than producing large-scale production of wines, the New Zealand wine industry has been focusing on the production and promotion of premium wines to compete overseas because the large-scale production output of overseas wineries such as the Californian or Australian would be more cost effective at the lower end of the wine market.

The shift towards producing up-market premium wines unique to New Zealand has created the edge to succeed in the highly-competitive international market. For example, the reputations of sauvignon blancs, especially from the Marlborough region, and certain chardonnays are well established for their uniqueness and intense fruit tastes. Sauvignon Blanc and Chardonnay have become the New Zealand's most widely planted white varieties. In the case of red wines, Pinot noir has also been well suited to New Zealand climate and its production volumes are increasing due to its growing popularity (Domine, 2004).

However New Zealand is limited in producing great varieties of wines. For instance, New Zealand climate is not well suited to harvest the traditional red varieties and also wines from other New Zealand grape varieties are not so distinguished from overseas grape varieties. Therefore the New Zealand wine industry would lose the competitiveness in the world market if it relies on one or few wine varieties. There is a strong need to research other varieties of wine which can compete on distinctiveness and overall quality rather than on price. This is the main driving force for this research, aiming to develop a unique flavour dimension beyond grape, climate, soil, and other known factors affecting wine flavours.

1.2 Containers for wine production and storage

Historically amphorae, long earthenware vessels fitted with stoppers, were used for transport and storage of goods but later used as wine containers in Roman times. From 1800 BC, wooden barrels were most commonly used for liquid storage since they are much lighter and harder (Sanderson, 2007).

Oak has been used for over 2000 years for vinification, transportation, ageing, and storage of wine. Many types of wood have been used during this period, but only oak has been used for wine cooperage because of its characteristics suitable for barrel construction. Oak can be bent into barrel shape when heated and has a fine grain structure that minimizes leakages. Oak is also directly involved in chemical interactions with wine that can have positive effects on its flavour and therefore has been the choice of wood for the wine barrel construction (Johnson, 1992).

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

Figure 1 Different wine storage methods over time. (a) Roman amphora (Council, 2007) (b) oak barrel (c) stainless wine tank (Steel, 2007)

The current wine industry uses modern winemaking containers made of stainless steel for fermentation and bulk storage of wines because stainless steel is durable, maintains excellent sanitation conditions in the course of wine production, and also can be used indefinitely (Figure 1). Stainless steel is an inert material to any reaction therefore does not impart any flavours to wine. It is impermeable to air and leak-proof. Many stainless steel tanks are double-jacketed and have coolant or hot medium, circulating between the inner and outer walls therefore enable winemakers accurately adjust tank's temperatures for fermentation process and storage period (Mueller, 2007). White wines in New Zealand have greatly benefited from stainless steel technology, inherited from the dairy industry. Cool fermentation in temperature-controlled stainless steel is the normal method for Sauvignon Blanc and Chardonnay.

New Zealand wine industry has been introducing innovative approaches to wine making such as the stainless steel techniques however it appears that many New Zealand wineries show extensive use of oak barrels for wine maturation because barrels represent tradition, quality and 'first-class' image in the eyes of the wine tasting public.

1.3 Oak barrels

Oak has traditionally been used in wine fermentation and/or maturation, because it has physical properties such as high tensile strength, pliability, and relative impermeability, which make it the wood of choice for barrel construction. The oak barrel has a significant role in the maturation of wine. Besides a physical storage container, the barrel provides extractable material to the wine and allows for chemical modifications to take place. These processes are considered to be associated with high quality wines.

To be used for barrel construction, the wood must be straight-grained, possessing vessels and fibres running parallel to the length of the trunk and also should exhibit both strength and resilience. The wood also must be free of pronounced or undesirable odours that could taint the wine (Jackson, 2000). In all these aspects, oak is the only wood that meets the criteria.

The process of barrel making consists of cutting, seasoning, and toasting. Wood logs are firstly cut into staves with desired thickness, approximately 2.7cm. Once cut, they are dried outdoors and exposed to the weather for preferably about three years since one year per centimetre is desired (Jackson, 2000). This process, also called seasoning, is the controlled process of reducing the moisture content of the timber so that it is properly suited to the ageing of wine. Intense dehydration takes place during the first 10 months so that the wood matures to improve its physical, aromatic and organoleptic qualities (Ribereau-Gayon, 2006) . Seasoning takes place in the open air, in large, level spaces. Factors necessary for the natural seasoning of oak are rain, wind, various temperatures, and the micro-organisms, principally a limited fungal microflora which cause enzymatic reactions. These factors ensure a refinement of the wood characterised by a diminution of the phenolic compound content and elimination or transformation of the astringent and bitter substances. Seasoning of oak wood achieves a balance between its own level of humidity and the surrounding hygrometric conditions in order to avoid distortion and shrinkage of oak wood therefore the barrel remains watertight (Vivas, 2007). Moreover it is generally considered that naturally dried oak gives a more pleasant woody, vanilla-like character.

Once seasoning process is completed, the inner and outer surfaces are periodically dampened with water to soften the wood. The wood can also be steamed prior to firing for wood softening purpose. Not only does moistening limit the rate of heating, but it also produces the steam that promotes the hydrolytic breakdown of hemicelluloses, lignins, and tannins. These wood components will be discussed in detail in the following section. After sufficient softening of the wood, the staves are slowly pulled together and temporarily positioned by hoops to be assembled into a barrel which is then placed above an open fire for approximately twenty minutes in order to result in breakdown of complex compounds into simpler structures, also called pyrolysis. It produces positive sensory changes in the characteristics of the wood (Jackson, 2000).

During the maturation of wines in the oak barrels, oxygen is very slowly introduced into wines through the small pores of the oak barrel staves, involving reactions between air oxygen and various substances in wine such as phenolics, aldehydes, sugars, and others (Margalit, 2004). This oxidation process causes the changes in wine colours (light yellow to deeper white wines, and violet red shifting to tawny red in red wines), its transparency, bouquet and taste. The changes in flavour that occur in wine are usually regarded as beneficial when there is a slow and periodic consumption of small amounts of oxygen over a period in the maturation of red wine, but usually detrimental to white wine (Clarke, 2004).

Along with the seasoning of the staves and the toasting of the barrel, the species and geographical origin of the oak wood also affect the pool of oak extractives, resulting in different concentrations of flavour-active compounds. (Cerdan, 2002). French oak and American oak are most commonly used for the barrel constructions to mature generally premium table wines. French oak barrels are perceived to be the higher quality barrels than American barrels. However it does not necessarily mean American oak is inferior to French oak because types and concentrations of the extractible compounds are different. The French oak barrels cost between $US 700 and $US 900 compared to American oak barrels at $US 250 to $US 350 (Winebusiness, 2004).

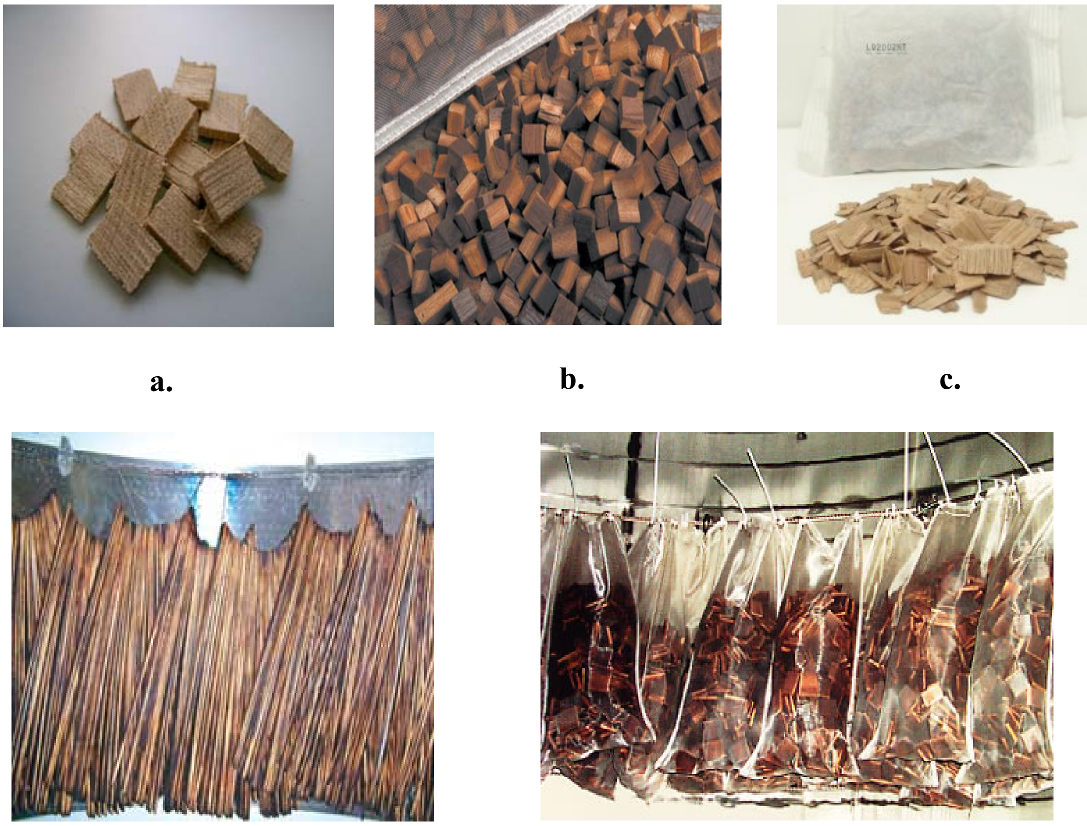
Aromatic compounds extracted from oak become progressively exhausted with barrel reuse. Due to the high costs of oak barrels, a range of new techniques to lengthen the lifespan of barrels have been developed such as shaving off the innermost layers to permit renewed access to oak flavourants (Jackson, 2000). Latest developments include inserting long oak staves inside old barrels as shown in figure 2, and putting oak chips or blocks in the barrels (Warner, 2002).

Figure 2 Insertion of oak staves inside an old oak barrel (Warner, 2002)

1.4 Alternatives to oak barrels

Non-barrel oaking methods based on 'wood in wine instead of wine in wood' have been used in the current world wine industry due to their economic efficiencies. As discussed in the earlier section, the price of quality French oak barrel, which is normally 225 litres producing about 300 bottles, costs approximately $US 800 therefore it would add $2 to 3 per bottle whereas using oak alternatives can impart the oaky taste and complexity at a fraction of the cost per bottle(Gawel, 2002). In addition, the maintenance cost of the barrels adds further cost to the wine production.

The alternative methods include the uses of oak chips, oak cubes, oak staves, and oak planks combined with the advanced techniques of stainless tanks for the maturation process. The size of the chips put in wines is normally irregular but 3-5mm in thickness is appropriate for extraction of the flavour compounds (Martinez, 2001). Small and thin oak chips are also used in teabags for instant diffusion of oak flavour in wines. The oak cubes are cut in larger dimensions than the chips, about 6mm on each side therefore the extraction process tends to take longer but it is considered to provide fuller flavour extraction and ease of using them in larger ageing containers (Alexander, 2004).



a. b. c.

d. e.

Figure 3 Alternatives to oak barrels **(a)** untreated oak chips **(b)** toasted oak cubes in stainless tank (Brewer, 2007) **(c)** oak chip in teabag (Annapolis, 2007) **(d)** oak staves hung inside tank **(e)** oak segments in bags hung inside tank (Stavin, 2007).

Oak staves are often cut in the form of fans, as shown in Figure 3d. A stave fan contains several staves that are 6cm wide and 90cm long bundled together. They are normally seasoned for three years and considered to be high quality. Oak segments weighing approximately 9kg are put in a plastic bag with very small pores to induce slow and controlled diffusion of oak compounds during the maturation period (Stavin, 2007). Once the maturation process is completed these alternative medium can be easily removed and the staves even can be reused and also the stainless tanks are hygienically kept after indefinite uses.

As discussed in the previous section, oxygen is slowly introduced into wine over the ageing period in the traditional oak barrels, enhancing colour and aromas of wines. This slow oxidization process can be simulated by micro-oxygenation technique which controls the slow oxidation of barrel-ageing in wines that are kept in stainless steel tanks. Oak tannins in the wine are the main compounds oxidised to soften their astringency. Micro-oxygenation not only enhances wine flavours but also reduces the cost of the ageing process.

1.5 Composition of wood and its role in wine flavouring

The major constituents of all trees as in oak are – cellulose, hemicellulose, and lignin which are insoluble polymers with complex structures. Smaller compounds are also present in woods such as tannins, small amounts of lipids (oils, fats and waxes), and lactones. Wood cell walls primarily consist of about 50% of cellulose, 20% of hemicelluloses, and 30% of lignins (Jackson, 2000).

1.5.1 Cellulose

Cellulose is produced as long fibres of polymerized glucose. Cellulose is the most abundant natural polymer consisting of linear chain of glucose units joined by β-1, 4 glycosidic linkages. One cellulose chain contains about 10,000 glucose units. Three hydroxyl groups in each glucose unit form hydrogen bonds which gives woods much of its strength and resilience. Because of the high resistance of cellulose to both enzymatic and nonenzymatic degradation as in heating, cellulose is not likely involved in the development of oak flavour in wines (Jackson, 2000).

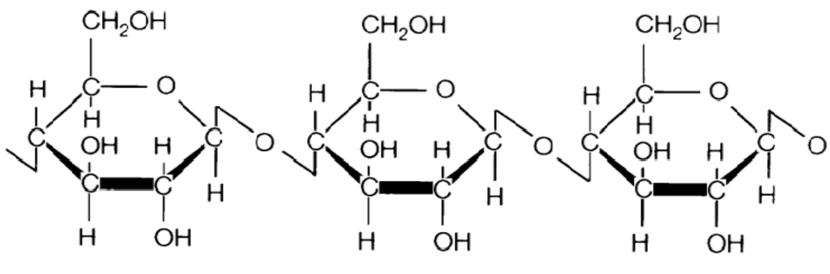
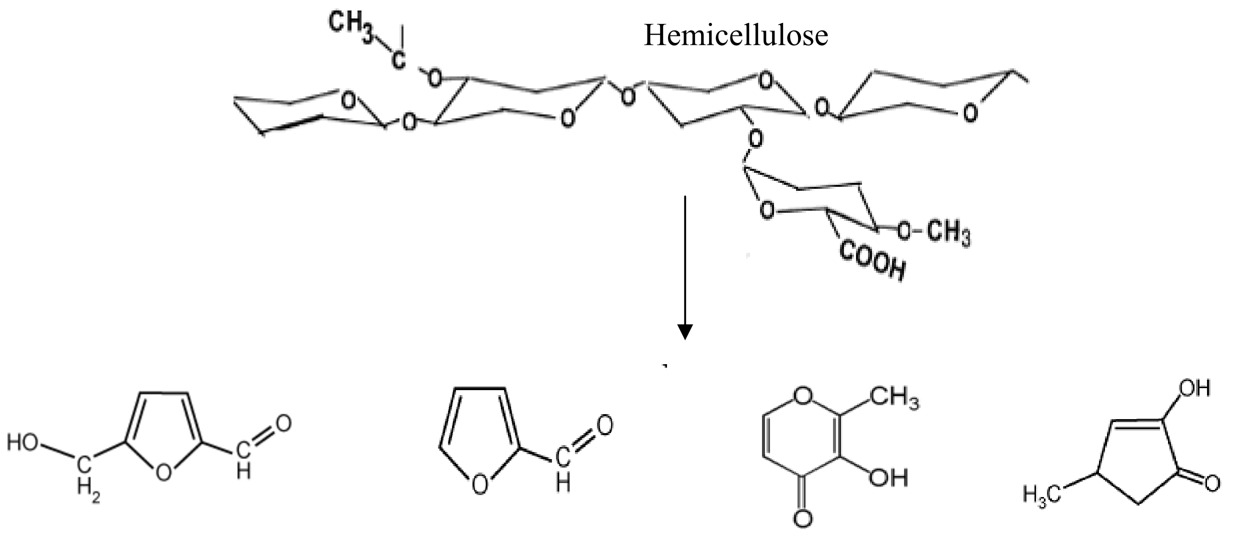


Figure 4 Cellulose consisting of linear chain of glucose units joined by β-1,4 glycosidic linkages (Colebrook, 2007)

1.5.2 Hemicellulose

Hemicellulose acts as binder linking the cellulose and lignins. Hemicellulose forms hydrogen bonds with cellulose, and it functions as structural material in wood in combination with cellulose. Hemicellulose is a two-dimensional polymer which consists of several simple sugars. While cellulose consists of purely glucose units, hemicellulose can be broken down into several simple sugars. These include five carbon sugars such as xylose and arabinose with a limited amount of the six carbon sugars such as glucose, galactose, mannose and rhamnose (Margalit, 2004).

When hemicellulose is heated as in firing of the staves during barrel manufacture, it breaks down into constituent sugars and these rapidly break down further into caramelization products. Products of hemicellulose brought about by heat treatment include furfural, maltol, cyclotene, and thoxylactone. This aspect of toasting of wood is very important in the development of toasty flavours (Ribereau-Gayon, 2006). Hemicelluloses slowly hydrolyze on exposure to the acidic conditions of wine, releasing both sugars and acetyl groups. The acetyl groups may be converted to acetic acid, which gives vinegar-like sour taste, during maturation.



Furfural Hydroxymethy Maltol Cyclotene

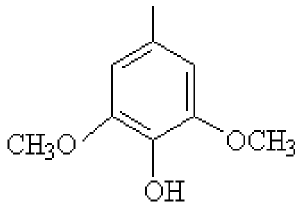
Figure 5 Production of known toasty flavours by breakdown of hemicellulose.

1.5.3 Lignin

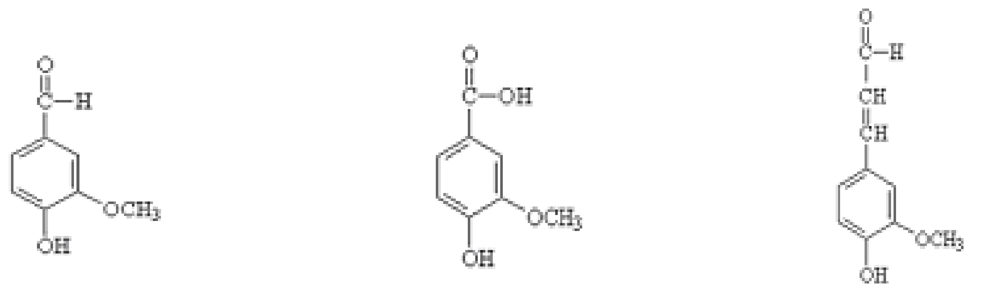
Lignin is a large, complex three-dimensionally structured phenylpropanoid polymer consisting of hydroxycinnamyl alcohols such as *p*-coumaryl, coniferly, and sinapyl alcohols

(Margalit, 2004). Lignin is relatively hydrophobic and aromatic in nature. It is located mostly in the cell walls but also spread throughout the wood. It limits water permeability and provides much of the structural strength of the wood.

Hardwood lignin such as oak lignin consists of two building blocks, the guaiacyl and syringyl structures. These two building blocks give rise to two groups of compounds in matured wines. Lignin degradation involves the action of both alcohol and oxygen. It is believed that ethanol reacts with certain lignins, forming ethanol-lignins. As the complexes break down, the lignin monomers (coniferyl and sinapyl alcohols) are released along with the ethanol. The phenolic alcohols slowly oxidize under the acidic conditions of wine to form sinapaldehyde and syringaldehyde and coniferaldehyde and vanillin. These are coniferaldehyde, vanillin and vanillic acid in one group from the guaiacyl structure, and sinapaldehyde, syringaldehyde and syringic acid from the syringyl structure (Jackson, 2000).

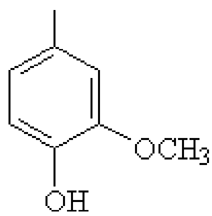


Guaiacyl



Vanillin   Vanillic acid   Coniferaldehyde

Figure 6 Guaiacyl building blocks of oak lignin



Syringyl

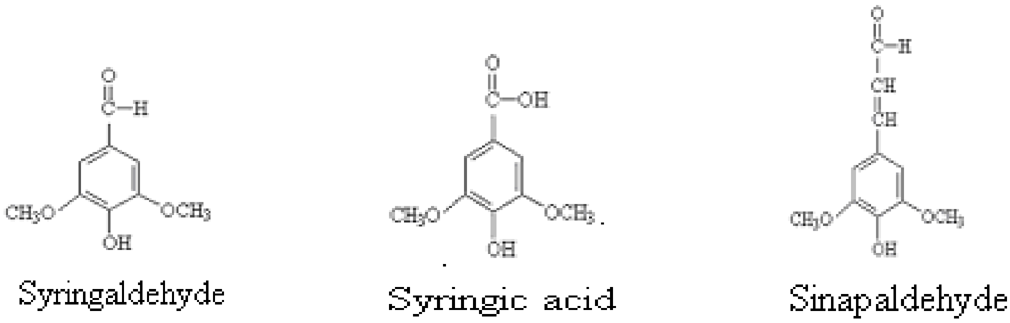
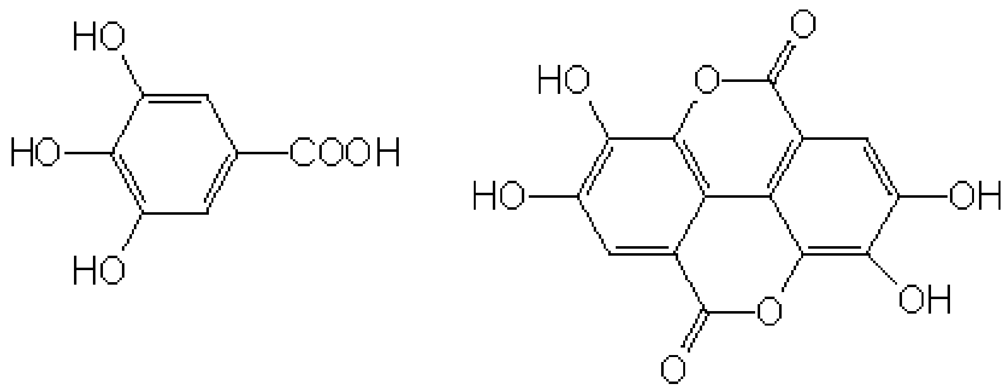


Figure 7 Syringyl building blocks of oak lignin

Toasting of the barrel, especially at 200°C, markedly augments the development of an oak bouquet such as woody, vanilla-like odours because when the extra heat is applied to the lignin, the lignin complex can be broken down into much simpler structures which are the steam volatile phenols. These are responsible for the smoky woody aroma and flavours often found after maturation.

1.5.4 Tannins

When the sapwood matures into heartwood, phenolic compounds may be deposited in the lumen. Phenolic compounds are important for the development of the characteristics and qualities of red wines and also of white wines but at much lower concentrations. Of these phenolic compounds, tannins are the most common in oak heartwood. Oak tannins are soluble polyphenols and they are the most abundant of the constituents of oak wood that are potentially extracted into the wine during ageing (Puech, 1999).



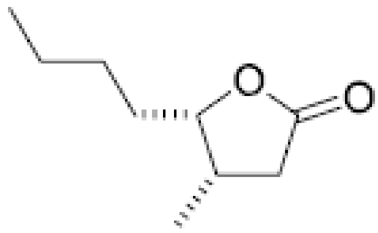
a **b**

Figure 8 Tannins **a**. gallic acid **b**. ellagic acid (Dharmananda, 2003)

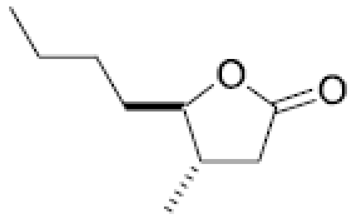
They are copolymers of gallic and ellagic acids with glucose. These tannins are also called gallotannins and ellagitannins respectively (Jackson, 2000). Oak tannins are hydrolysed into simpler structure in acidic conditions while grape tannins are condensed tannins which are not easily hydrolysed due to C-C bonds. Oak tannins are involved in the sense of astringency and bitterness, which defends against insect and fungal attacks. However the process of seasoning and toasting to break down the tannins render them more acceptable. The total hydrolysable tannins contained in oak wood is about 5 to 10% of its dry weight. Out of this content, only up to 300mg L^{-1} of phenolic compounds can be extracted into wine from a 225L barrel in one year of aging (Margalit, 2004).

1.5.5 Lactones

Lactones have a strong woody character and contribute to the unique aroma and flavour of whisky, brandy and wines aged in oak barrels. The woody, nutty, coconut and oaky aroma of the lactones is attributed mainly to *cis* lactones.



cis-**1**



trans-**1**

Figure 9 The oak lactones (Wilkinson, 2004)

Although they occur in all oak woods used for cooperage, the *cis* isomer occurs in much higher levels in American oak compared to other species. The *cis* isomer has a more intense character than the *trans* and influences all beverages which are matured in new or used American oak barrels. These two compounds come from small amounts of lipids (oils, fats and waxes) in the oak and their amounts increase dramatically during both seasoning and toasting. Although present in oak, and formed on toasting, oak lactones are extracted slowly by wine (Jackson, 2000).

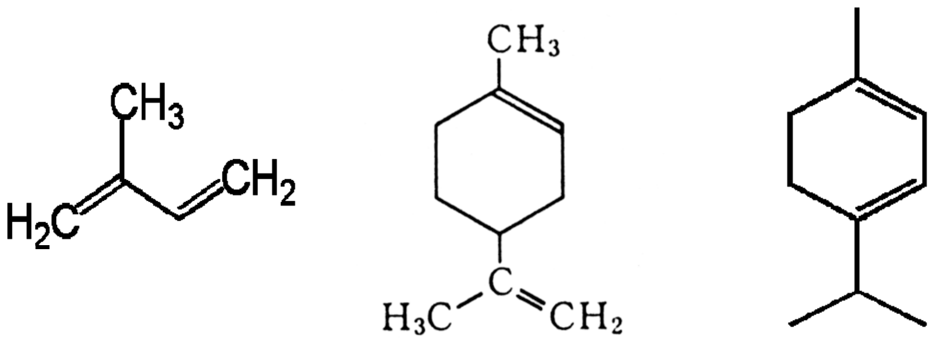
1.5.6 Resin

All trees consist of the same structural wood components but the amounts and compositions of resins vary with wood types. Wood resins consist of many different compounds from the low molecular mass waxes and fatty acids to the high molecular mass waxes, sterol esters and triglycerides. However the chemical components of wood resins cannot be defined precisely for a given tree species because chemical composition varies with tree part and also type of wood.

Wood extractives, commonly called resins, constitute 4 to 10% of the dry weight of normal wood of species but may be as much as 20% of the wood of tropical species. Resins generally consist of complex mixtures of many different compounds such as resin acids, free fatty acids, terpenes, waxes, steryl esters, sterols and triglycerides. The wood resin is viscous liquid, typically composed of mainly of volatile fluid terpenes, with components of dissolved non-volatile solids which make resin thick and sticky.

Terpenes are a large group of aromatic compounds widely distributed in nature, and one of the most diverse classes of metabolites. Terpenes consist of a wide range of substances which derive from a basic structure of a linear chain of five carbon atoms, as in isoprene (2-methyl-1, 3-butadiene). There are many terpenes, which all have the basic formula of C_5H_8 with two double bonds. Their structure can be open-chain or cyclic (Margalit, 2004).

Terpenes are generally composed of two, three, four, or six isoprene units which are called monoterpenes, sesquiterpenes, diterpenes, and triterpenes, respectively (Clarke, 2004). Monoterpenes are simple hydrocarbons and are likely odouriferous. They also exist as alcohols, aldehydes, ketones and esters. A number of monoterpene and sesquiterpene hydrocarbons with resin-like odours have been identified, including limonene, α-terpinene, *p*-cimene and myrcene, as well as sesquiterpene alcohols such as farnesol (Ribereau-Gayon, 2006). Monoterpenes are synthesized and stored in specialised structures whose cells express all the genes necessary for monoterpene biosynthesis. For example, specialised epithelial cells in conifers form resin ducts with large central storage cavities to serve as a defence by virtue of their toxicity to invading organisms (Crozier, 2006).



a **b** **c**

Figure 10 Examples of terpenes **a**. isoprene **b**. limonene **c**. α-terpinene

1.6 Attributes of resins to wines

Resin in each wood species have very unique chemical and physical characteristics, and that may lead to the generation of a wide range of different flavour profiles for woods if used in beverage applications as in wines. Historically resins have been applied to the wine making. The Greek wine, *retsina*, is Greece's best-known white wine which is flavoured with pine resin. One of the theories that *retsina* came about is that the ancient Greeks kept wines in ceramic amphorae sealed with pine gums to prevent spoilage by oxygen. The pine resin then would leach into the wine from the lip of the vessel and flavour the wine during ageing, resulting in creation of a very unique wine and an acquired taste. *Retsina* is still one of the most common wines in Greece today (Lichine, 1974).

However due to the presence of different amount of resins and their unique characteristics, some resinous woods may not be used in wine flavouring medium due to its negative affect on wine flavours. However if resins with supposedly negative organoleptic attributes to wines are removed from resinous woods, those woods may be applied to the wine ageing process.

Previous studies at the Auckland University of Technology, AUT, have established that other woods in the form of flat square chips can also work as flavourants, but with flavours distinct from those of oak. In 2006 a number of sensory trials took place in AUT and liquor stores in Auckland to assess flavours of New Zealand chardonnay infused with twelve different woods including woods indigenous to New Zealand such as Manuka and Totara. In some cases panellists preferred the flavours from these woods however in other cases the flavours created by woods such as macrocarpa were judged to be very unpleasant. The inspection of these results from 2006 has suggested that the unpleasantness might be related to the organoleptic characteristics and varying amount of resins in woods.

As mentioned earlier, the favourable flavours from wood extracts in wine derive from the pyrolytic breakdown of major wood components such as lignin. If resin is responsible for unpleasant flavours and pyrolytic products from wood components are responsible for pleasant flavours, it follows that any wood free of resin would be suitable for flavouring wine since all trees are composed of the same major constituents. The hypothesis is untested and is the main thrust of this research.

1.7 Resin removal

The amount and composition of the resin is dependent on wood species, wood age and location of wood within the tree. The various classes of wood resins have different chemical and physical behaviours therefore it is very difficult to completely remove them during processing of wood. The major extractives are generally resin acids and fatty acids, fatty acid esters such as steryl esters, waxes, and triglycerides, and neutral compounds as exemplified by fatty alcohols and sterols (Adrian, 1997).

The currently used conventional approach to reduce the deposition of wood resins is solvent-extraction with various solvents as in pulp industry. Seasoning of logs is also used to reduce certain substances of resins in the pulping industry however it is insufficient to reduce the pitch deposits in pulps. In addition, Vivas (2007) reported that natural wood seasoning is insufficient to reduce the level of resins in oak however it leaches mostly hydrolysable substances such as ellagitannins that causes bitterness in wine.

Farrell et al. (1993) reported that a biological treatment of wood chips using specific isolants of *Ophiostoma piliferum*, wood-inhabiting fungi, which resulted in a reduced resin of wood chips. Their study showed that not only did overall resin content decreased with treatment of wood chips with the strains of *O. piliferum* but also many free resin acids and fatty acids were significantly reduced. However the biotechnological approach appeared effective only on certain wood types such as pine and under specific pulping conditions. Efforts for larger and more selective fungal screening and optimization of the biotechnological approaches are being performed (Gutierrez, 1998).

The solubility of wood in various solvents is a measure of the extraneous components content. No single solvent is able to remove all the extraneous materials. Some solvents formerly used for extraction of woods and pulps, such as benzene and chlorinated hydrocarbons, are no longer widely used because of their toxicity or environmental effects. Therefore several solvents are being tested for their efficacy for extraction of woods. Solvents such as dichloromethane, hexane, acetone, methanol, etc. are generally being used individually and also in various mixed forms. Various combinations of solvents in a Soxhlet extractor were used to extract resins from wheat straw for analysis of resin contents by Sun et al. (2003) and found that the yields of the resin extractives were generally consistent with the order of polarity of the solvent; dichloromethane, hexane, and petroleum ether. Similar results were also found by Wallis et al. (1997) that the resin extractions from pine woods decreased with reduced polarity of the solvent. However both studies showed that no single solvent was able to extract all the resins individually and different combinations of solvents removed different resin components. Moreover the genre of wood species would add more complexity to the resin extractions to be efficient.

Because the resins of woods of interest in this study are not identified, three different solvents were used to ensure extraction of resins from wood chips as much as possible. Dichloromethane was the first choice of the solvent because dichloromethane is widely used as a solvent for dissolving a wide range of organic compounds especially fats, flavourings, and caffeine in the food industry. For further resin extractions, hexane and diethyl ether were selected. Hexane is commonly used as an inert solvent in organic reactions because it is very non-polar. It is commonly used to extract oils for cooking. Diethyl ether is also a common solvent to extract fats in laboratories.

Supercritical CO_2 extraction was not considered in this experiment because of its high cost and also the availability of the equipment was limited

1.8 Woods of interest

Because of the traditional relationship of oak species with wines as well as oak's unique and physical characteristics for barrel construction, not many other woods have been applied to wine making. However since the oak barrel alternatives have been introduced into wine industry and sustained ever-increasing popularity of their applications in wines, it has led to new studies on woods other than oak to create wines with unique flavours.

New Zealand is geographically isolated from the rest of the world. This geographical isolation provides New Zealand with exclusivity to certain botanical species with potential in applying to wine making. The previous wine studies at AUT involved the use of various woods other than oak to flavour New Zealand chardonnay. The woods used in the previous studies were matai (*Prumnopitys taxifolia*), feijoa (*Feijoa sellowia*), macrocarpa (*Cupressus macrocarpa*), pohutukawa (*Metrosideros excelsa*), radiata pine (*Pinus radiate*), totara (*Podocarpus totara*), kahikatea (*Dacrycarpus dacrydioides*), rimu (*Dacrydium cuppressinum*), cherry beech (*Nothofagus solandri*), silver beech (*Nothofagus menziessi*), manuka (*Leptospermum scoparium*), and American oak (*Quercus alba*). This range of woods was selected based on existing use in various applications, association with the New Zealand culture and botanical similarity.

White wines infused with these woods were evaluated by panellists and the general public. Their results showed that wines infused with certain woods such as macrocarpa and radiata pine resulted in extremely unpleasant and negative effects on wine flavours, presumably due to their unique and strong scent from woods. Most preferred woods were manuka and totara, with hedonic scores slightly higher than American oak. Given that American oak is being widely used in winemaking, manuka and totara showed that they were capable of adding pleasant flavours to wines. The woods that had scored the lowest hedonic scores presumably have high volume of resins and also their unique physical and chemical characteristics of the resins that might have resulted in the unpleasantness in wines. Among all 12 woods, the results from Gas Chromatography showed that American oak produced the most number of extractable compounds transferred to wine. They were 3,4-dimethyl phenol, 5-methyl-2-furaldehyde and 5-butyldihydro-4-methyl-2(3H)-furanone. However their role in wine flavour was not identified (Kaushal, 2007).

With the geographical exclusivity in mind, seven wood species including American oak have been selected in this study to explore their potentials as flavourants in wines. As shown in the previous studies, manuka and totara were selected again for their high potential in wine-flavouring application. The woods that had scored the lowest hedonic scores such as macrocarpa and radiata pine were also selected due to the possibility of their application in winemaking if the attribution of their resins to wine flavour can be completely removed. The following seven woods are selected for this ‘wood in wine’ study.

Manuka is an evergreen tea tree native to New Zealand. It grows to 2 to 5 m with dense branching with small leaves (Poole, 2007). The wood is often used as fire wood because of its long-lasting burning. Most importantly it is also commonly used as smoking timber to smoke meats and fish because it imparts a delicious flavour to foods. In the current New Zealand seafood industry, fresh salmon or snapper fillets are also smoked by manuka to impart its unique aroma to the fish. Its leaves had also been used as tea leaves in the 18th century because of its lightly bitter taste with sweet aroma. Due to its wide application in food and beverage it presumably has great potential in wine flavouring.

Cupressus macrocarpa is a species of cypress native to the central coast of California. It is an evergreen tree growing to 10-20 metre tall with its trunk diameter reaching approximately 1.0m. It is naturalised in New Zealand and with the common name macrocarpa and commonly used as fence posts, small manufactures and also decorative woods because of its fine colours. Macrocarpa has very strong and unique woody smell which would be considered not suitable for any applications in food and beverages. However it was selected to observe the effectiveness of resin extraction prior to the wine application.

Totara is a genus of *Podocarpacae* native to New Zealand. It grows to 20 to 25 metre tall and the trunk diameter attaining to 2 to 3 metres. It grows throughout New Zealand in lowland, montane and lower subalpine forest. It is solid therefore widely used in fence posts, furniture manufactures and also Maori carvings. It does not have distinctive or obvious odour but it is considered high in resin.

Kahikatea is a coniferous tree native to New Zealand. It grows to a height of approximately 55 metres with a trunk 1 m diameter. It is dominant in lowland forest and wetlands throughout New Zealand. Kahikatea does not impart any odour and it is light in weight therefore it was once used as boxes for food storage in the 19th century.

Radiata pine (*Pinus radiata*) is a genus of the Pinaceae family native to the Monterey peninsula of northern California. It grows to 15 to 30 m in the wild and reaches maturity in around 30 years in the New Zealand. It was first introduced into New Zealand in the 1850s. Over 90% of New Zealand's plantation forests are of radiata pine (Poole, 2007). It is widely used in construction materials, pulp, and paper.

Gorse is evergreen shrub in the subfamily Faboideae. The most widely known species is the Common Gorse native to Western Europe. It grows 2-3 metres in height in sunny sites, usually on dry soils. The leaves are highly flammable and the species regenerate rapidly after fire from fire-scattered and burned seeds. Gorse was introduced into New Zealand as an ornamental plant however now it has become naturalised and it is considered as invasive weed due to its aggressive seed dispersal. Gorse was selected in this study in spite of its negative public image because if it is capable of adding unique flavours to wine, its application in winemaking could not only be economic but also generate uniqueness to New Zealand wine.

Oak is a hardwood tree commonly used in the production of barrels because of its unique physical and chemical properties. In this study, American oak was used as the reference wood because American oak is being widely used in the wine industry. The other six woods were compared with American oak in terms of degree of attributing wood flavours to wines.

1.9 Aims of the study

New Zealand is well known for producing up-market premium table wines unique to New Zealand and its success has been continuing for many years in the competitive international wine market. However, New Zealand wine industry could be limited to producing variety of wines so there is a strong need to develop high quality wines with distinctiveness. Because of the latest developments of oak barrel alternatives in the winemaking it has led to research on woods other than oak for wine ageing. Previous research with the woods has shown that the undesired flavours in wine may be related to the presence of resins in woods.

The aim of this research was to investigate the effectiveness of resin extractions from the seven woods prior to wine infusion to create favourable flavours in wines as seen in traditional oak wood usage. The consumers' responses to the wines were evaluated to determine which wood species other than oak is most suitable for wine infusion process. Lastly, the extracted resins of each wood species were characterised and their organoleptic attributes to wines were also explored.

The main objectives of this study were to:

- Process the woods to chips with appropriate sizes for wine infusion and study their physical characteristics
- Examine the efficiency of the resin extractions from the woods by three different solvents
- Study the colour variations of the wood chips before and after the resin extractions and heat treatments
- Determine the effect of the resin extractions in response to wine flavours
- Determine the woods with the most potential in wine infusion application
- Study the organoleptic and physical characteristics of extracted resins

The research consisted of seven procedures: processing wood timbers and logs to small chips involving saws; resin extractions with various solvents in a Soxhlet extractor; heat treatment in an electric oven at set temperatures; colour variation of raw, resin-extracted, and toasted wood chips in Hunter colour space using the L*, a*,and b*; wine infusion in glass bottles; and sensory analyses of final wine products and extracted resins of the seven woods.

All experiments took place in the university laboratory environment under supervision for safety. The various sensory trials took place in the university food laboratory and liquor stores to examine the responses from the general public. The ethical issues involved in the sensory trials were approved by the AUT Ethics Committee.

Chapter 2

Materials and Methods

2.1 The selection and sourcing of woods

The woods were collected from various locations however the original source of the timbers collected from a company called ‘South Pacific Timber Limited, Eden Terrace, Auckland’ was unknown. The collected woods were used for all experiments throughout this study. The woods used in this research were selected with a view to geographical exclusivity in wine at retail therefore numbers of New Zealand native woods were selected.

Five woods including macrocarpa, totara, kahikatea, American oak and radiata pine were sourced from South Pacific Timber Ltd. They were collected in the form of flat, square flooring timbers which had never been chemically treated. Wild gorse stem, judged to be about 20 years old by the growth rings, was collected from Waikato farmland by Dr Owen Young. Manuka was collected in the form of round stems cut to firewood length from the Bark ‘N’ Firewood Bin Ltd., Albany.

Table 2 Selected wood species for the research

Common name	Botanical name	Source	Supplier
Manuka	*Leptospermum scoparium*	Kaitaia	Bark ‘N’ Firewood Bin[1]
Macrocarpa	*Cupressus macrocarpa*	Unknown	South Pacific Timber[2]
Totara	*Podocarpus totara*	Unknown	South Pacific Timber
Kahikatea	*Dacrycarpus dacrydioides*	Unknown	South Pacific Timber
Radiata pine	*Pinaceae*	Unknown	South Pacific Timber
Gorse	*Ulex*	Waikato	Dr Owen Young
American Oak	*Quercus alba*	Unknown	South Pacific Timber

[1]Bark ‘N’ Firewood Bin, Bush road, Albany, Auckland
[2]South Pacific Timber Ltd, Ruru St, Eden Terrace, Auckland

Except for gorse, because the source of each wood species was not known, each wood species selected for this study does not represent characteristics of the whole family of its species present in New Zealand. Furthermore the parts of each wood species that had been supplied by the timber companies were not identified therefore the data gathered from the study cannot represent each wood species. Thus the woods used in this study are only a ‘snapshot’. This is an acknowledged limitation of the study.

2.2 Wood cutting

The woods sourced in the beginning of the research were used for both discrimination and hedonic trials. For all tests in this study, woods were cut to only chip dimensions. The other wood forms such as cubes and staves were not considered in this study because the wood chip form would be better suited for resin extraction by the solvents and also be well-fitted inside the Soxhlet extractor. Wood shavings could have provided good resin extraction due to its high surface area however it was not used in this experiment because of its lack of size consistency. Powder form of woods were not used either because a grinder strong enough to grind the timbers to powder was not available during the cutting period.

2.2.1 Wood cutting for discriminative trials

The timbers and the wild stems were cut along the grains into long flat square strips by an electric circular blade in order to obtain an even cut with equivalent widths among the woods. The long square wood strips were then cut to approximately 20×10×3mm square chips against the grains by a clean handsaw.

2.2.2 Wood cutting for hedonic trials

The woods for hedonic trials were selected based on the results of the discrimination sensory trials. Therefore woods that resulted in statistically significance in the discrimination trials were selected for hedonic trials. The timbers and the wild stems were cut exactly in the same way as wood cutting for the discrimination trials. First they were cut by the electric circular blade along the grains to the long square strips and then cut to approximately 20×10×3mm square chips against the grains by, this time, an electric band saw. The electric band saw was available at the time of wood cutting for hedonic trials. However the cutting methods and the chip dimensions remained unchanged.

2.2.3 Thickness measurements

The dimensions of the wood chips used in wine aging may influence the transfer of flavour-active compounds from the wood to wine. Twenty raw, untreated wood chips of each species were randomly selected and the thickness of the narrowest dimension was measured by the Vernier callipers in millimetres.

2.3 Resin extraction

2.3.1 Resin extraction of woods for discrimination sensory trial

Wood resins were extracted using the Soxhlet system (Figure 10). Soxhlet extractors consist of three main parts: a distillation arm, Soxhlet chamber, and a round bottom flask. The accurately weighed wood chips were placed inside the thimble (25×80mm, Whatman, England), which is placed in the Soxhlet chamber. The round flask connected to the bottom of the chamber contained 120ml of solvent, dichloromethane. The distillation arm where cold water was kept running throughout the entire extraction process was connected to the top of the chamber. The temperature of the heating device was set above 70°C to ensure that dichloromethane whose boiling point is 40°C can be evaporated. The evaporated dichloromethane is condensed by the distillation arm, and then allowed to percolate through the wood chips contained in the thimble. The resin dissolved in the solvent is collected in the bottom flask. The time period of extraction was set for four hours.

After the completion of resin extraction, the wood chips were allowed to dry on glass plates at room temperature for over twenty four hours to allow complete evaporation of dichloromethane. The drying was carried out until the odour of dichloromethane was no longer detected by close nostril examinations and also the weight of the wood chips were measured for two consecutive days to observe any change in weight over the period of time. The extracted resin of each wood species dissolved in the solvent was transferred to a glass vial left to dry the solvent for few days, resulting in having only the resin inside the vial. Once the solvent was dried out, the collected resin was kept in the lid-closed vial for resin sensory evaluations.

Figure 11 Soxhlet apparatus, consisting of a vertical (reflux) condenser, and a cellulose thimble in the extraction chamber. The chamber has a siphon sidearm to return the resin-enriched solvent to the bottom boiling flask

After toasting all seven different wood chips, resin was further solvent-extracted from the previously extracted wood chips in order to observe whether any resin was present in the previously resin-extracted wood chips. The methods of the second resin extraction and the drying were identical to the procedures of the first extraction and drying.

The weight of the extracted resin was measured by the percent change in weight of the wood chips after the solvent-extraction and drying.

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

2.3.2 Resin extraction of woods for hedonic sensory trial

The resins of the chosen three wood species were extracted by the Soxhlet extractor with three different solvents; dichloromethane, hexane, and diethyl ether. This exhaustive extraction process was used in the preparation for the hedonic sensory trials in order to make sure all possible resinous contents could be extracted to get rid of any resin flavours in wines. The thimble was not used in this extraction process because the exhaustive resin extraction was solely focused on separating the resins from woody materials instead of collecting the resinous contents. As a result the resins were collected as well as woody dusts. Dichloromethane was used in the first extraction and then the wood chips were dried for over 24 hours. As in the drying procedure done for the discriminative trials, the wood chips were weighed twice for the consecutive two days to observe any change in weight of the chips. These dried wood chips were then resin-extracted again with hexane. The wood chips were dried over 24 hours and then lastly resin-extracted with diethyl ether.

After each extraction, the weight loss of wood chips was recorded to see how much resin was being extracted therefore the efficacy of resin extraction of each solvent was tested. The extracted resin was also collected in the glass vial after each solvent for resin sensory trials.

This exhaustive resin-extraction procedure was employed to ensure the complete resin-extraction. The temperature of the extraction was set above 70°C and the time period of extraction was four hours for each solvent therefore twelve hours for each wood species. The amount of each solvent used was 120ml in each extraction setup.

As in the previous extractions for the discriminative sensory tests, the resins of the three wood chips were further extracted with dichloromethane alone after toasting of the wood chips at 200°C for two hours to observe any presence of resinous contents in the toasted wood chips. The extraction after toasting was run for 4 hours at temperature set above 70°C.

2.4 Toasting of wood chips

The wood chips were toasted in an electric oven, ‘LabServe’, which maintains the temperature accurately throughout the entire toasting process. The heat treatment was carried out in an open area of AUT car park of WS building due to the generation of smoke from the toasting of the wood chips. Each wood chip species was placed on the oven proof ‘Pyrex’ glass plates covered with aluminium foils to prevent burning of the chips.

For the wood chips used in the discrimination trials, the resin-extracted and the unextracted wood chips underwent two different toasting levels; 200°C for two hours and 210°C for three hours called light and heavy toasting, respectively.

For the wood chips used in the hedonic trials, the resin-extracted wood chips received one level of toasting, the light toasting at 200°C for two hours.

2.5 Colour measurements

Colour is an important element in the development of food and beverage because colour can often affect the image of the food flavour therefore affect consumers' judgement decisions. Because the various treatments of the wood chips are significant factors in the development of wine flavours, the colour of each wood species was measured before and after the resin-extraction and heat treatments.

The colour was measured in Hunter colour system which 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 running from 0 which is complete light absorbance and therefore black, through grey (50) to 100 which is complete light reflectance. The horizontal coordinate, a*, is greenness/redness running from -60 (green) through grey to +60 (red). The orthogonal horizontal coordinate, b*, is blueness/yellowness from -60 (blue) to +60(yellow).

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 also called saturation is the intensity of a specific hue. For example, a highly saturated hue has a vivid, intense colour while a less saturated hue appears in the vertical range of black, grey, and white. Saturation is calculated as $\sqrt{(a^{*2} + b^{*2})}$. Therefore lightness, hue angles and chroma are values that describe all perceived light.

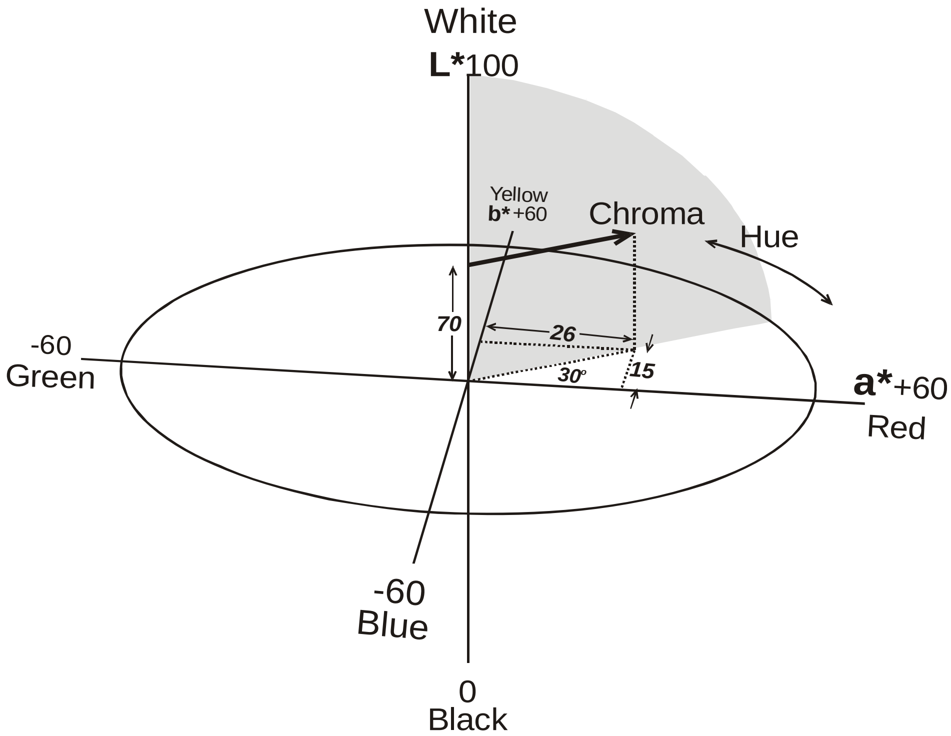


Figure 12 Hunter colour space. In L* a* b* colour space, the tip of the thick arrow is defined by it lightness (70 on a scale of 0 to 100), its redness (+26 on a scale of -60 to +60) and yellowness (+15). The hue is arctangent 15/26 (=30°) and the chroma, or intensity, is the length of the thick line, √(225 + 676) (=30) (Young, 2001)

The colour was measured by a Hunter colorimeter, ColorFlex (Hunter Associates Laboratory Inc., Virginia, U.S.). The wood chips were placed, evenly spread, in a cylindrical plastic dish measuring 2.5 inches. This was then placed in the illuminant path (sample port), covered with an opaque metallic black shroud. Daylight D65/10° illuminant/observer combination was selected to measure daylight colour expressed as L*, a*, and b*.

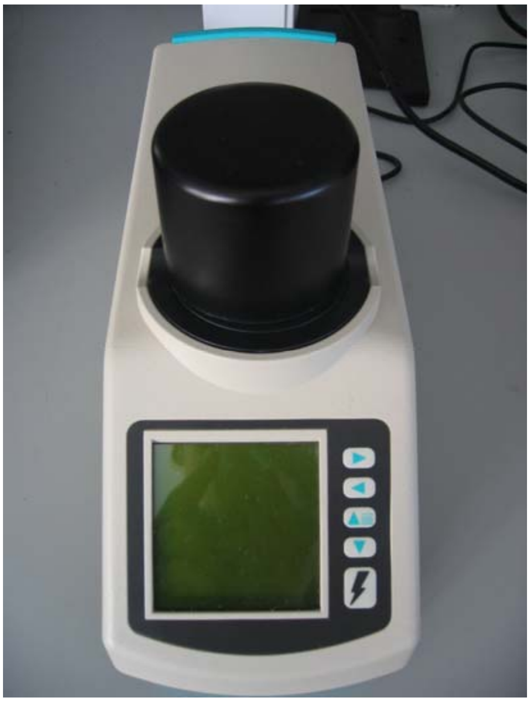


Figure 13 Hunter colorimeter, ColorFlex (Hunter Associates Laboratory Inc., Virginia, U.S.)

For the wood chips used in the discrimination trials, the colours were measured on the resin-extracted wood chips: untreated (raw); resin-extracted (untoasted); lightly toasted (resin-extracted); and heavily toasted wood chips (resin-extracted). The colours of unextracted wood chips were also measured after the two heat treatments: untreated (raw); lightly toasted; heavily toasted. The colour of each wood species was measured 10 times. Between each measure, the plastic dish filled with wood chips was lightly shaken to measure the surfaces of the wood chips evenly.

For the wood chips used in the hedonic trials, the colours were measured after each solvent extraction and lastly after light toasting. The colour of each wood species was measured 10 times and the plastic dish was shaken lightly as well.

2.6 Wine Source

Sixty litres of unoaked Gisborne Chardonnay 2005 was provided by Simon Nunns of Coopers Creek Ltd., Kumeu, Auckland. Cooled wine was transported to AUT in three of 20L plastic containers and immediately transferred to dry, clean 2.5L Winchester bottles. Wine was poured to the very top of each Winchester bottle to exclude air. Each Winchester bottle was covered with a Parafilm and then tightly closed with its matching screw cap. They were stored in a refrigerator with a set temperature at 4°C.

2.6.1 Infusion of wood chips in wine

Wine infusion method for both discrimination and hedonic trials was identical.

After the single or multiple resin extractions and toasting, 6 g of wood chips of each wood species was put into 150 mL of the unoaked New Zealand chardonnay in glass beakers for air removal. The 6 g of treated wood chips of each species were recovered and transferred to 1 L Schott bottles that were completely filled with fresh wine, close to 1.2 L. Thus the infusion rate was 5 g L^{-1}. The lids were tightly closed. After 14 days of infusion at ambient temperature in very subdued light, the wines were transferred, by filtration through glass wool to remove wood chips, to standard 750 mL wine bottles with screw caps. Handling was gentle to minimise aeration of wines. Each wine bottle was completely filled exclude air. Bottles were then stored at 4°C for up to two months, the period required for completion of trials. The possible loss of desirable flavour from wine during deaeration was disregarded because of its small volume (150mL) in 1.2 L of wine

Figure 14 The vacuum chamber used to deaerate wine

2.7 Sensory Trials

2.7.1 Discriminative sensory trial

The wine sensory trial was based on the principle of a triangle test, a form of discrimination test, in which panellists were asked to pick an odd wine sample out among three wine samples where two wine samples are identical. Each wine sample cup had a unique three digit code. Before each sensory trial, the wines were taken out from the refrigerator one day before each trial to bring the temperature of the wines to the room temperature.

The sensory trials took place in a well-ventilated and odour free food science laboratory at AUT. Staff members of AUT and students took parts in the trials. Participants who looked under the age of 20 had to provide formal photo identifications such as driver licenses or passports to take a part. If the formal identifications could not be provided, they were kindly asked to leave the tasting room. Before taking parts the panellists were told that noise was to be kept to minimum during tasting. The participating panellists were informed of that they were allowed to spit out if they did not want to swallow the wine samples.

One wine sensory trial was carried out for each wood species per day per week. The set-up and participating conditions of each wine trial remained unchanged. In each trial, there were two tasting stations set up. Wines infused with lightly toasted woods were presented in the first station and wines infused with heavily toasted woods in the second station. In each station, two samples were identical: two wines infused with resin-extracted woods against one wine infused with unextracted woods or vice versa.

Each tasting station set-up	
2 wine samples infused with resin-extracted woods versus 1 wine sample infused with unextracted woods	1 wine sample infused with resin-extracted woods versus 2 wine samples infused with unextracted woods

The order of presentation of the sampling cups with unique three digit codes followed a certain pattern supplied by Dr Owen Young. It was designed to ensure that each wine had the same frequency of exposure in each trial.

In the first tasting station, three plastic sampling cups (35ml) containing wines infused with lightly toasted wood chips were presented. The panellists were asked to taste the wines in a set order, from left to right, and then to pick the odd one out. For example, two identical resin-extracted samples with different code numbers were presented with a lightly toasted unextracted sample and vice versa.

Figure 15 Three wine samples with different three digit codes (two identical, one different)

When the first station was completed, the panellists were asked to eat a piece of crackers and drink a cup of water to clear their palates from the wine samples in the first tasting station.

In the second station, three cups of wine infused with heavily toasted wood chips were presented. As in the first tasting station, two identical resin-extracted samples with different code numbers were presented with an unextracted sample and vice versa. The tasting procedure was identical to the first station. When panellists finished their judgements complimentary chocolates were provided for appreciation. The panellists were not asked to write down any comments on the wines because the main goal was to observe the discrimination between the wines infused with unextracted and resin-extracted woods. However, the assessor carefully listened to any comments from the panellists during tasting.

In both tasting stations, 10ml of wine was provided in each 35ml plastic portion cup. Forty or more sensory panellists were recruited to establish significant results in each trial. The panellists were not informed of any information on the wine samples except they were New Zealand white wine.

Woods that had resulted in statistically significant differences between wines infused with unextracted and resin-extracted wood chips in the discriminative sensory trials were selected to be examined in the hedonic sensory trials to evaluate the consumers' responses to the wines.

2.7.2 Hedonic sensory trials

Hedonic trial, a form of acceptance test, is used to evaluate product acceptability or liking or to determine which products is the most acceptable or the most preferred. The hedonic sensory trials that employed the conventional nine-point hedonic scale, nine being 'extremely like' and 1 being 'extremely dislike', took place at five different liquor stores in Auckland. The participated panellists were considered as regular alcohol consumers as they had walked in to purchase liquors. The tasting stations were set up near the entrance of each store to approach the customers without difficulty. They were firstly asked if they wanted to take a part in the wine tasting. If they were willing to take a part, they were informed of the wine tasting procedures and given the ballots where customers were asked to express their liking and also leave some comments after tasting each wine sample. Each wine bottle had no labels but was allocated with a three-digit code on a white name sticker to blind the participating customers. The wine samples were served by the assessor in the set order according to each ballot. The order of presentation of the wine samples with unique three digit codes followed a certain pattern supplied by Dr Owen Young. It was designed to ensure that each wine had the same frequency of exposure in each hedonic trial. Each panellist was given a standard 225ml wine tasting glass and approximately 20ml of each wine sample was poured. After each glass of wine sample was taken by a customer the wine glass was wiped with clean, dry kitchen cloth to ensure the wines do not get mixed in the wine glass. The customers were asked to express their degree of liking on the ballots after tasting each wine sample. In the ballots the extent of liking for the wines was recorded by selecting a category on a hedonic (liking) scale that runs from 'extreme dislike' to 'extreme like'.

Each trial started at 4.30pm until the closing trading hours, normally 9pm, to recruit as many customers as possible. There was no limit of number of customers per trial therefore each trial has different number of population.

2.7.3 Qualitative analysis of extracted resins

The characteristics of the extracted resin of each wood were studied because the resin in each wood affects the wine flavour development during the aging period. The olfactory sensations and nasal feelings of the extracted resins of each wood were explored by descriptive sensory trials involving a group of 11 panellists. AUT staff members of the Applied Science department were recruited as the panellists. Because the panellists were not professionally trained, as in the case with general public consumers, common non-technical terms were used.

There were two different sets of extracted resins. In the first set, panellists were presented with single solvent-extracted liquid resins from untreated woods, resins from lightly toasted woods, and resins from heavily toasted woods. The resin samples were presented to the panellists in a set order: resins from untreated woods, resins from light toasts, and resins from heavy toasts. When the assessment of the first set was completed, the second set of resins in which resins extracted by each solvent; dichloromethane, hexane, and diethyl ether, were presented. The order of presenting the resins was resins extracted by dichloromethane, hexane, and lastly diethyl ether.

Each panellist was given a ballot where they were asked to write their comments after sniffing each resin. They were asked to express their comments freely and also given a list of words on the ballot to help them to describe their feelings. One panellist was assessed at a time with the assessor and given as much time as they needed to assess the resins. The trials took place in the well ventilated food science laboratory and the noise was kept to minimum during each trial. The identification of each wood resin and how the resins were gathered were not disclosed to the panellists. Short rest up to 5 minutes was allowed if requested.

2.8 Data analysis

Microsoft Excel was used for all data handling and preliminary statistical analyses. For colour measurements, the data are presented as bar graphs where means of 10 measurements are presented for each wood species. The colour measurements were scaled accordingly to the values of untreated wood values to calculate the percent change in colour values. For sensory evaluations, general linear model was used on the data of sensory hedonic scores, using Minitab Release 14 (Minitab Inc., Pennsylvania), and applying Tukey's test ($P < 0.05$) to test for differences between individual means of woods. The statistical interactions were also tested to evaluate the statistical significance by each factor such as wood treatment, gender, age group, and liquor stores.

Chapter 3

Dichloromethane Extractions and Toasting

3.1 Wood chip dimensions for all trials

The dimensions of the wood chips were nominally 20 x 10 x 3 mm. However there was considerable variation in dimensions, because of the precision of the handsaw was limited.

Table 3 Mean thickness of the untoasted wood chips

Wood	Thickness (mm)	Coefficient of variation (%)
Manuka	3.50 ± 0.77	22
Macrocarpa	3.18 ± 0.41	13
Totara	2.89 ± 0.65	22
Kahikatea	2.93 ± 0.47	16
Radiata pine	2.77 ± 0.45	16
Gorse	3.16 ± 0.86	27
A. Oak	2.81 ± 0.34	12

Data are means ± standard deviations of 20 chips, and percent coefficient of variation

As shown in Table 3, manuka wood chips were thicker than the others probably because of the irregular grain and stiffness of the wood made cutting difficult. Macrocarpa was collected in the form of flat tongue-in-groove flooring timber, which might have been easy to cut. However due to its brittle nature the mean thickness had to exceed 3 mm but with relatively less variation than the others. Gorse was very tough, and the variation of its thickness is the greatest among all the woods. The least variation of thickness and the thinnest cut was obtained with American oak because it was very uniform in its structure. Mechanised saw equipment would have resulted in more uniform chip sizes but such equipment could not be accessed at this stage.

On the face of it these differences may not seem to be important, but what was not known (and was not resolved in this thesis) was the effect of the thinnest dimension on solvent extraction, toasting and infusion in wine. Thus it would have been much better to use precision wood cutting tools. (These were accessed in some later experiments.)

3.2 Extraction of untoasted wood chips

3.2.1 Weight loss of wood chips

The proportion of resin and other matter soluble in organic solvent in each wood was determined by the weight loss after extraction with dichloromethane. For each species, the wood chips under study were divided into five replicate groups for extractions. The mass in each replicate was governed by how many chips could be fitted into the extraction thimbles, typically about 7 g, but as low as 6.0 g (totara) and as high as 7.5 g (manuka). After extraction the chips were quantitatively recovered from the thimbles and dried at room temperature over 48 hours. No significant weight change was observed between 24 and 48 hours indicating that the solvent had completely evaporated and the chips had equilibrated to ambient humidity.

Table 4 Mean percent weight loss of wood chips after extraction with dichloromethane

Wood	Weight loss (%)
Manuka	11.01 ± 0.21
Macrocarpa	4.39 ± 0.08
Totara	7.97 ± 0.17
Kahikatea	3.06 ± 0.12
Gorse	0.98 ± 0.08
Radiata pine	2.51 ± 0.08
American oak	4.47 ± 0.17

Data are means of five extractions ± standard deviations

Table 4 shows mean percent weight loss of each species after extraction. Manuka lost the greatest percent weight among all seven woods while gorse lost the least. Totara lost the second greatest percent weight, while macrocarpa, kahikatea, radiata pine, and American oak lost between 2 and 5 %. The weights lost were clearly dominated by resin (see below), other organic solvent-soluble matter, and there was probably a contribution, but unknown, due to moisture.

At the time it was presumed that all the resin had been extracted from each species because the masses loss were clearly significant (Table 4), and the wood had been cut in such a way as to facilitate extraction. This is because the grain direction was parallel to the shortest (3 mm) dimension. However, later work (Section 3.6) showed that not all the resin has been extracted by one exposure to dichloromethane.

After extraction and before toasting the colour of the chips was measured as reported in the Section 3.4.

The grand total weight of wood needed for wine infusion used in the discriminative trials was 24 g, and this experiment yielded enough wood to do that. Although the primary goal was to produce wood chips stripped of resins, the extracted resins (and any other matter) were also of interest. Thus, resins dissolved in dichloromethane in the round-bottom flasks after extraction were transferred to glass vials and left to evaporate at room temperature over three days. The vials were then sealed and held at room temperature for later study (Chapter 6).

3.3 Colour of untoasted wood chips after dichloromethane extraction

For this section, the daylight colour parameters, L*, a*, and b*, were measured in ten replicates for unextracted, and dichloromethane-extracted untoasted wood chips. CIE a* and b* values were used to calculate the hue angles and saturations. The means and standard deviations were summarised in Tables 5, 6, and 7. The primary comparisons made are between unextracted and solvent-extracted treatments.

3.3.1 Lightness after extraction of untoasted woods

In five of the seven woods, there was a decrease in reflectance after solvent extraction (Table 5, Figure 16), which was very marked in the case of manuka. Inspection of Table 5 shows that manuka suffered the greatest weight loss due to solvent extraction. This suggested that as resins were extracted, cavities that would or might appear in the wood chips would trap light, so lowering reflectance as measured by L* values. Appealing as this model was, there was only a very weak negative relationship between percent change in L* (Table 5) and weight loss of all woods (Figure 16). The cavity model is clearly too simplistic particularly as totara and kahikatea showed an increase in reflectance after extraction.

Table 5 Mean lightness of untoasted woods after a dichloromethane extraction

Wood	Lightness (L*) Unextracted	Lightness (L*) Resin-extracted	[2]Statistical significance	Change from unextracted (%)
Manuka	[1]55.75 ± 1.14	52.20 ± 1.02	***	–6.37
Macrocarpa	59.05 ± 0.77	58.08 ± 0.39	**	–1.64
Totara	48.76 ± 0.32	49.52 ± 0.79	*	1.56
Kahikatea	56.06 ± 1.26	59.11 ± 0.84	***	5.44
Gorse	69.70 ± 1.19	68.17 ± 2.26	NS	–2.20
Radiata pine	61.93 ± 0.47	60.27 ± 0.92	***	–2.68
A. oak	53.88 ± 0.82	51.28 ± 0.55	***	–4.83
[3]Overall mean ± SD	57.88 ± 6.64	56.95 ± 6.49		

[1] Data are means of 10 readings ± standard deviations.
[2] NS, not significant; *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

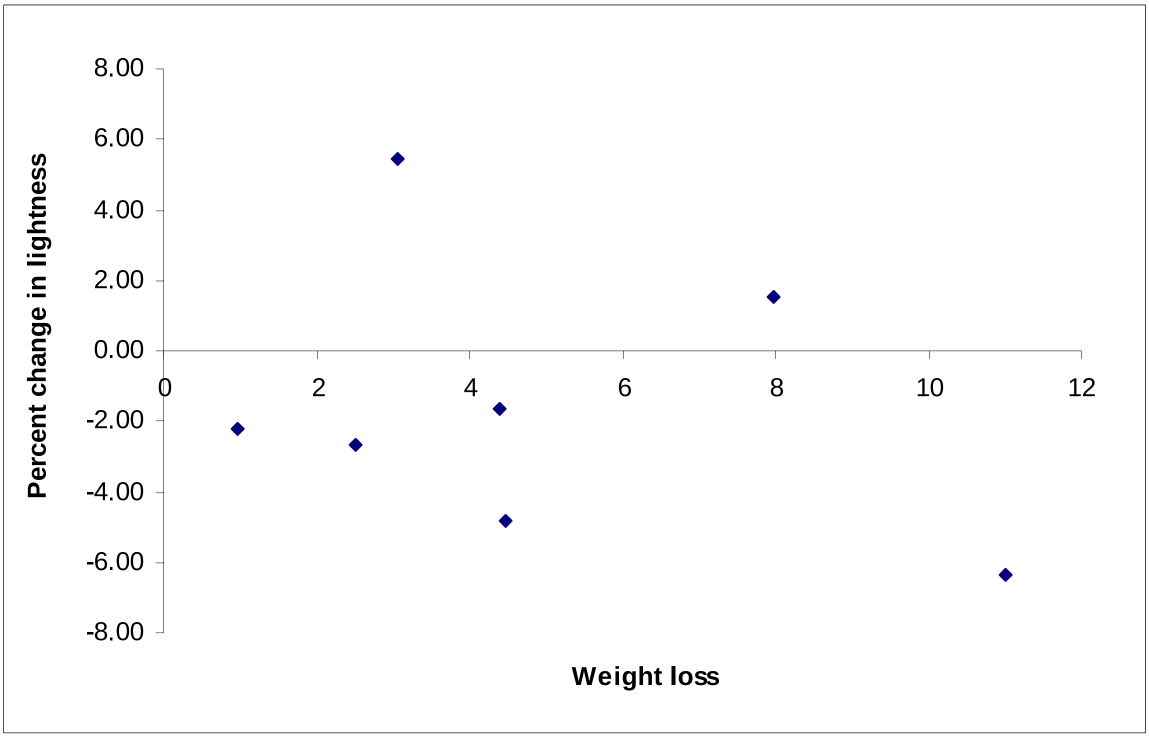


Figure 16 Relationship between percentage change in lightness and weight loss

3.3.2 Hue angles after extraction of untoasted woods

Independent of solvent extraction, the basic hue or colour of the woods lay between red and yellow. Higher angles mean a yellower hue. After solvent extractions, all seven woods resulted in significant changes in hue angles at either $P < 0.001$ or $P < 0.05$. As in the case of lightness after solvent extraction, greatest change in hue angles was observed in manuka, which also had lost the greatest weight loss. However, there was a very weak negative relationship between change in hue angles and the percent change as shown in Figure 17. Thus as weight was lost, the hue became slightly redder.

Table 6 Mean hue angles of untoasted woods after dichloromethane extraction

Wood	Hue angle (arctan b*/a*) Unextracted	Hue angle (arctan b*/a*) Resin-extracted	[2]Statistical significance	Change from unextracted (%)
Manuka	[1]1.19 ± 0.01	1.15 ± 0.01	***	–3.36
Macrocarpa	1.20 ± 0.01	1.19 ± 0.00	***	–0.83
Totara	0.96 ± 0.03	0.99 ± 0.01	**	3.13
Kahikatea	1.31 ± 0.00	1.33 ± 0.00	***	1.53
Gorse	1.46 ± 0.01	1.43 ± 0.01	***	–2.05
Radiata pine	1.23 ± 0.01	1.19 ± 0.00	***	–3.25
A. oak	1.20 ± 0.00	1.17 ± 0.13	***	–2.50
[3]Overall mean ± SD	1.22 ± 0.15	1.20 ± 0.14		

[1] Data are means of 10 readings ± standard deviations.
[2] NS, not significant; **, $P < 0.01$; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

Differences, although statistically significant, are small and unimportant. Extraction of resin did not cause change in hue, the basic colour of the wood. No relationship between hue and weight loss was observed as shown in Figure 17.

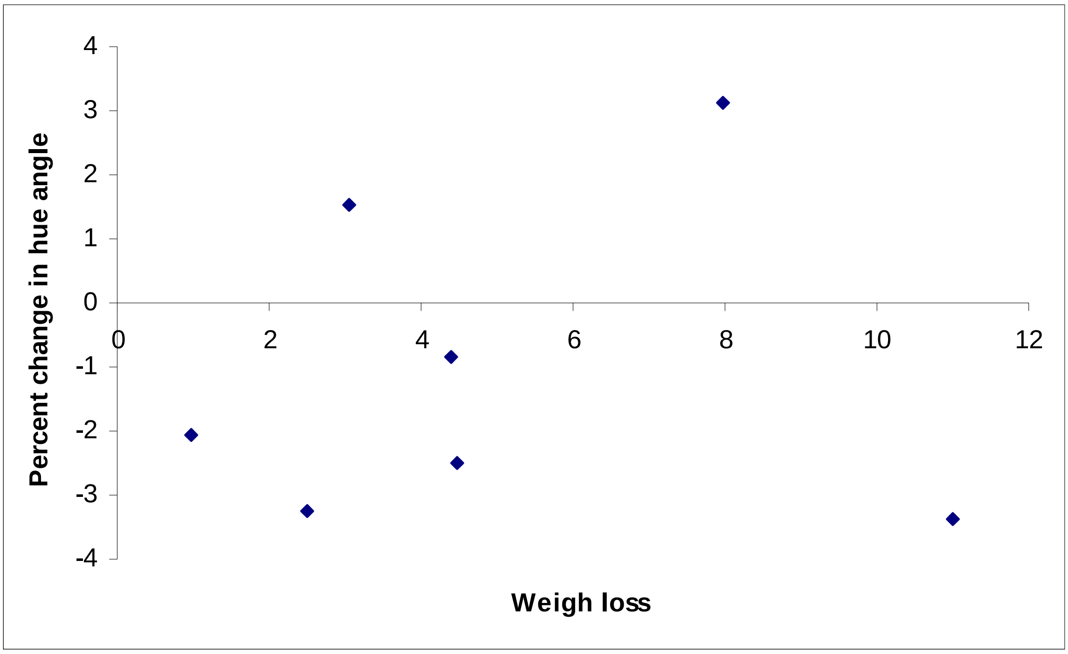


Figure 17 Relationship between percentage change in hue and weight loss

3.3.3 Saturation after extraction of untoasted woods

After the solvent extraction, manuka and gorse showed the greatest (negative) percent change in saturation ($P < 0.001$) while macrocarpa and American oak did not show any significant changes. This indicates that the resin extraction had the effect of washing out the intensity of colour from manuka and gorse. The remaining five woods showed positive percent change in saturation, indicating that they gained in intensity of wood colour after resin extraction. There is no obvious reason for the different outcomes regarding loss and gain of intensity of colour after resin extraction.

Table 7 Mean saturation of untoasted woods after dichloromethane extraction

Wood	Saturation ($\sqrt{(a^{*2} + b^{*2})}$) Unextracted	Resin-extracted	[2]Statistical significance	Percent change
Manuka	[1]22.32 ± 0.28	20.1 ± 0.39	***	–9.94
Macrocarpa	26.09 ± 0.36	26.1 ± 0.17	NS	0.04
Totara	26.17 ± 0.67	26.7 ± 0.64	*	2.03
Kahikatea	30.74 ± 0.45	32.4 ± 0.54	***	5.40
Gorse	24.27 ± 0.34	21.2 ± 0.44	***	–12.65
Radiata pine	20.94 ± 0.12	21.3 ± 0.41	**	1.72
A. oak	20.24 ± 0.44	19.8 ± 2.90	NS	2.17
[3]Overall mean ± SD	24.40 ± 3.65	23.9 ± 4.7		

[1] Data are means of 10 readings ± standard deviations.
[2] NS, not significant; *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

As shown in Figure 18, there was no relationship between weight loss and the percent change in saturation for all seven woods. No clear explanation could be found for the greatest change in saturation shown by gorse after losing the least amount of resin.

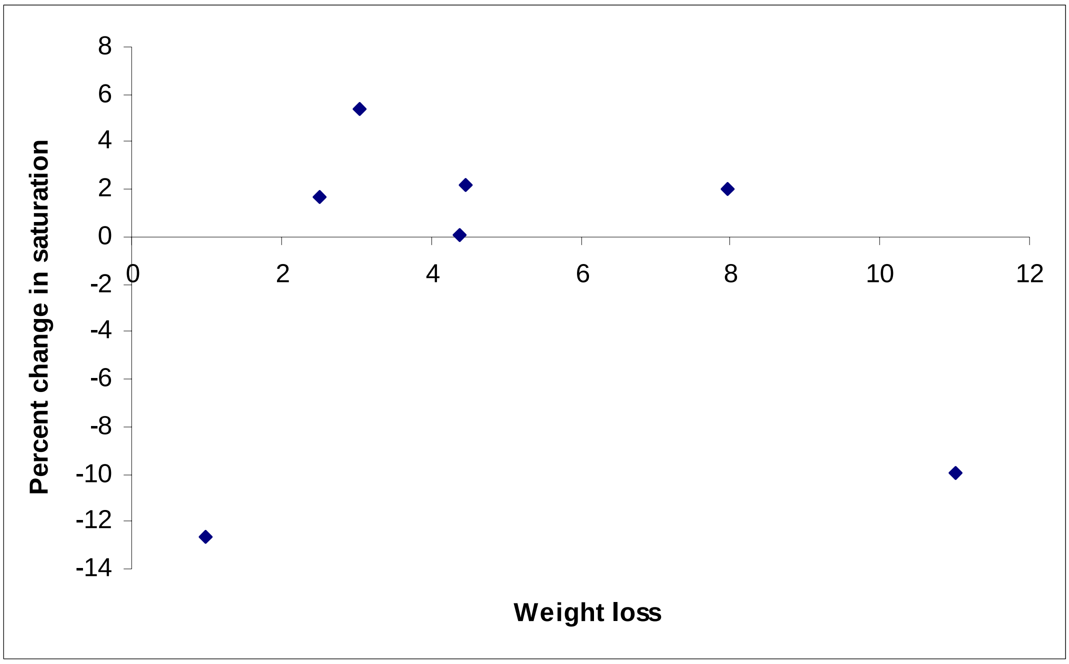


Figure 18 Relationship between percent change in saturation and weight loss

3.4 Toasting of unextracted and dicholoromethane-extracted wood chips

As detailed in Chapter 2, unextracted and resin-extracted wood chips were lightly and heavily toasted for 2 hours at 200°C and 3 hours at 210°C, respectively (Table 8).

Table 8 Heat treatment of the wood chips after dichloromethane extraction

	Unextracted		Resin-extracted	
Seven woods	Light toast	Heavy toast	Light toast	Heavy toast

Each wood species turned brown by the light toasting and dark brown by the heavy toasting, as previously described (Kaushal, 2007; Mahajan, 2008). In those studies, there was a tendency for kahikatea wood chips to catch fire, as witnessed by the generation of copious volumes of smoke escaping through the oven vents, and visible flames when the oven door was opened allowing ingress of air. In the present study this phenomenon occurred only with unextracted kahikatea wood chips subjected to a heavy toast. After toasting the colour of the chips was measured to compare with the unextracted colours.

3.5 Colour of toasted wood chips after dichloromethane extraction

For this section, the daylight colour parameters, L*, a*, and b*, were measured in ten replicates for unextracted, and dichloromethane-extracted toasted wood chips at the two toasting levels. CIE a* and b* values were used to calculate the hue angles and saturations. The means and standard deviations were summarised in Tables 9, 10, and 11. The primary comparisons made are between unextracted and solvent-extracted treatments.

3.5.1 Lightness after toasting of unextracted and resin-extracted woods

Within each group (light toast and heavy toast), the lightness of resin-extracted woods were compared with those of unextracted woods, to expose any effects caused by solvent-extraction. As shown in Table 9, the changes to the seven woods in both toasting groups showed either a very significant difference ($P < 0.001$) on none. Manuka, radiata pine, and American oak did not show significant change in lightness after light toasting. However, when they were heavily toasted, they lost reflectance greatly, manifest as large percent changes in lightness. Macrocarpa, totara, and gorse showed significant changes in lightness due to extraction after both light and heavy toasting at $P < 0.001$. In six of the seven woods resin extraction caused a loss in reflectance after heavy toasting. The reason for this is not clear, but it may have some physical basis (trapping of light) alluded to in the previous section.

Table 9 Lightness (L*) after toasting of unextracted and resin-extracted woods

	Light toast				Heavy toast			
Wood	Unextracted	Resin-extracted	[2]Significance	Change from unextracted (%)	Unextracted	Resin-extracted	Significance	Change from unextracted (%)
Manuka	[1]33.28 ± 0.63	34.03 ± 1.47	NS	2.25	26.62 ± 0.13	23.89 ± 0.91	***	–10.26
Macrocarpa	36.74 ± 0.20	34.63 ± 0.96	***	–5.74	29.07 ± 0.90	25.48 ± 0.47	***	–12.35
Totara	23.46 ± 0.61	28.60 ± 0.35	***	21.91	22.49 ± 0.30	23.49 ± 0.23	***	4.45
Kahikatea	36.38 ± 1.01	35.53 ± 1.01	NS	–2.34	23.96 ± 0.76	23.88 ± 0.23	NS	–0.33
Gorse	34.36 ± 0.55	31.94 ± 0.27	***	–7.04	26.86 ± 1.06	24.08 ± 0.24	***	–10.35
Radiata pine	41.86 ± 0.83	41.94 ± 0.53	NS	0.19	36.89 ± 0.40	30.10 ± 0.33	***	–18.41
A. oak	30.98 ± 0.31	30.82 ± 0.42	NS	–0.52	27.34 ± 0.26	21.81 ± 0.49	***	–20.23
[3]Overall mean ± SD	33.87 ± 5.71	33.93 ± 4.27			27.60 ± 4.64	24.68 ± 2.62		

[1] Data are lightness means of 10 readings ± standard deviations.
[2] NS, not significant; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

3.5.2 Hue after toasting of unextracted and resin-extracted woods

Within each group (light and heavy toast), the hue angles of resin-extracted woods were compared with those of unextracted woods, to expose any effects caused by the solvent-extraction. As shown in Table 10, all woods except radiata pine in the light toast group showed significant difference ($P < 0.001$) on none. Macrocarpa showed the greatest percentage change in hue angles in the light toast group. In the heavy toasting group, all seven woods showed significant differences either at $P < 0.01$ or $P < 0.05$. Although no significant change in hue was observed in the light toast for radiata pine, it showed the second greatest percentage change in hue angles in the heavy toast.

In lightly toasted woods, six of seven woods showed positive percentage change, indicating that resin extraction had the effect of making the chips yellower. In contrast, all woods in the heavy toast showed negative percent changes, indicating that they became redder after the solvent extraction. No obvious explanation for this clear difference between light and heavy toasting treatment could be found other than the difference in the temperature setting.

Table 10 Hue angles after toasting of unextracted and resin-extracted woods

	Light toast				Heavy toast			
Wood	Unextracted	Resin-extracted	[2]Significance	Percent change	Unextracted	Resin-extracted	Significance	Percent change
Manuka	[1]1.07 ± 0.01	1.11 ± 0.01	***	3.74	0.98 ± 0.01	0.96 ± 0.02	***	–2.04
Macrocarpa	0.97 ± 0.02	1.08 ± 0.00	***	11.34	1.05 ± 0.01	0.97 ± 0.01	***	–7.62
Totara	0.94 ± 0.01	1.02 ± 0.03	***	8.51	0.93 ± 0.01	0.91 ± 0.01	*	–2.15
Kahikatea	1.09 ± 0.03	1.14 ± 0.00	***	4.59	0.97 ± 0.02	0.96 ± 0.01	*	–1.03
Gorse	1.07 ± 0.00	1.08 ± 0.00	***	0.93	1.00 ± 0.01	0.92 ± 0.01	***	–8.00
Radiata pine	1.15 ± 0.01	1.15 ± 0.01	NS	0.00	1.11 ± 0.00	1.01 ± 0.01	***	–9.01
A.oak	1.05 ± 0.00	1.10 ± 0.01	***	4.76	0.99 ± 0.00	0.88 ± 0.02	***	–11.11
[3]Overall mean ± SD	33.87 ± 5.71	33.93 ± 4.27			27.60 ± 4.64	24.68 ± 2.62		

[1] Data are means of 10 readings ± standard deviations.
[2] NS, not significant; *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

3.5.3 Saturation after toasting of unextracted and resin-extracted woods

Within each toasting group (light and heavy), the saturations of resin-extracted woods were compared with those of equivalent unextracted woods. As shown in Table 11, woods in the light toast group variously showed positive and negative changes due to extraction. These changes were significant at either $P < 0.001$ or $P < 0.01$, or not significant in the case of manuka. Totara showed the greatest positive percent change while gorse showed the greatest negative percent change in saturation in the light toast group.

In the heavy toasting group by contrast, all seven woods showed a decrease in saturation due to extraction. All differences were highly significant ($P < 0.001$) except in the case of kahikatea. When the percent changes of the light and heavy toasts were plotted aginst each other there was no obvious pattern (data not shown). In short, each wood behaved differently in response to extraction and toasting.

Table 11 Saturation after toasting of unextracted and resin-extracted woods

Wood	Light toast				Heavy toast			
	Unextracted	Resin-extracted	[2]Significance	Percent change	Unextracted	Resin-extracted	Significance	Percent change
Manuka	[1]15.97 ± 0.61	16.39 ± 2.26	NS	2.63	13.69 ± 0.13	12.32 ± 0.69	***	–10.00
Macrocarpa	18.26 ± 0.42	20.23 ± 0.45	***	10.79	17.33 ± 0.63	14.54 ± 0.37	***	–16.10
Totara	12.39 ± 0.32	14.10 ± 0.79	***	13.80	12.27 ± 0.23	11.68 ± 0.14	***	–4.81
Kahikatea	23.70 ± 0.61	22.07 ± 0.61	***	–6.88	11.56 ± 0.62	11.47 ± 0.12	NS	–0.78
Gorse	18.97 ± 0.25	16.50 ± 0.21	***	–13.02	13.89 ± 0.39	8.63 ± 0.23	***	–37.87
Radiata pine	23.75 ± 0.38	22.69 ± 0.86	**	–4.46	21.09 ± 0.19	16.63 ± 0.24	***	–21.15
A. oak	14.53 ± 0.10	13.44 ± 0.13	***	–7.50	11.80 ± 0.09	6.74 ± 0.30	***	–42.88
[3]Overall mean ± SD	18.22 ± 4.36	17.92 ± 3.74			14.52 ± 3.50	11.72 ± 3.34		

[1] Data are means of 10 readings ± standard deviations.
[2] NS, not significant; **, $P < 0.01$; ***, $P < 0.001$
[3] Means were calculated from the means in the columns above

3.5.4 Summary of toasted colour changes due to solvent extraction

The greatest loss in lightness shown by manuka suggests that the wood cavities where resins had been extracted might have trapped light. However, the relationship between the weight loss due to the solvent-extraction and percent change in lightness was very weak. As in the lightness, greatest negative change in hue angle was observed in manuka. However a positive relationship between the weight loss and hue angle percent change was not evident.

After the solvent extraction, gorse lost the most saturation thus turning darker. As in the case of lightness and hue angle, manuka also showed significant percent change in saturation (second to gorse). However the relationship between saturation and weight loss was also found to be negative, especially after gorse which had lost the least amount of weight among the seven woods showed the greatest change in saturation.

Six of the seven heavily toasted woods lost reflectance after the solvent-extraction and all seven woods showed negative percent changes in hue angles thus became redder. The intensities of colour of all seven woods after the solvent-extraction were lost. However no obvious reason for the clear differences between the light and heavy toasts could be found.

3.6 Further extraction of dichloromethane-extracted, toasted wood chips

The toasted wood chips described so far in this chapter were destined for the main discrimination trials reported in Chapter 4. This work did not use all the toasted chips. These remaining chips were further extracted with dichloromethane. There were two reasons for this. First it was postulated that toasting might volatilise resins, so making extraction by solvent completely redundant. Second, it was possible that the act of toasting might liberate solvent-extractable compounds that could be of flavour interest.

All remaining seven lightly and heavily toasted woods that had already been resin-extracted and toasted at the two heating levels were further extracted using the same solvent, dichloromethane. In this extraction process, cellulose thimbles were not used in the Soxhlet extractor because the experiments were only designed to detect weight loss in toasted woods rather than quantitative recovery of dichloromethane-soluble matter. The capacity of the Soxhlet extractor was much greater when thimbles were not used. It was reasoned that an anticipated zero or small weight loss would be easier to detect in a larger mass of chips. Thus for each of the 14 wood chips types, a single extraction was performed and a statistical analysis was not possible. The results of the 14 extractions are shown in the Table 12.

Table 12 Weight loss of dichloromethane-extracted and toasted wood chips subjected to a further extraction with dichloromethane

Wood	Toasting level	Weight loss (%)
Manuka	Light	1.04
	Heavy	3.18
Macrocarpa	Light	0.62
	Heavy	1.63
Totara	Light	1.87
	Heavy	2.92
Kahikatea	Light	3.97
	Heavy	2.72
Gorse	Light	0.27
	Heavy	1.60
Radiata pine	Light	2.69
	Heavy	2.61
A. oak	Light	3.08
	Heavy	3.45

The extracted matters from the toasted wood chips were collected in the glass vials in the same way as for the earlier dichloromethane extractions. As shown in Table 12, further weight losses of toasted wood chips occurred. All 14 wood treatments lost weights between 0.2 and nearly 4% after the extractions. It was clear by inspection and smelling that the matter recovered was dominantly resinous, although traces of wood powder were evident that would have contributed to the losses in Table 12. Among the 14 wood samples, kahikatea light toast lost the most weight after the extraction, 3.97 %, while gorse light toast lost the least, 0.27 %. Except for kahikatea and radiata pine, each heavy toast of the five woods lost more weight than its respective light toast, indicating that toasting at higher temperature might have opened the wood chip cavities relatively more to lose the resinous contents and/or generated new solvent-soluble compounds of unknown identity.

This clearly shows that some resinous matter is still present inside the previous-extracted, toasted wood chips of all seven species.

The colour of the extracted resin from the heavy toasts was a lot darker brown than from the light toasts, possibly due to charred wood powder inside the resin. In Chapter 6, these extracted resins were assessed by the same panellists who also assessed the single extraction.

As stated above, this repeated extraction of toasted wood chips was a curiosity-driven experiment, not related to the main purpose of finding out what the effect of resin extraction would be on wine flavour. That is reported in the next chapter.

Chapter 4

Discriminative Evaluations of Wine

4.1 Introduction

The previous chapter reported the preparation and properties of unextracted and resin-extracted woods that were toasted in preparation for infusion in wine. This chapter mainly reports the discrimination trials – triangle tests – to show the effect, if any, of resin extraction. Although this chapter is short it nonetheless reports a lot of work, seven sensory trials with a minimum of 46 panellists over seven weeks.

4.2 Wine preparation

After evacuation of the 6 g of wood chips in a sample of wine (see Chapter 2) for 30 minutes, there were no air bubbles around the submerged wood chips and the wine. When pressure was returned to atmospheric, the floating wood chips sank indicating the effective removal of air from wood chips. Thus it was confidently expected that subsequent discrimination trials would not be confounded by wine oxidation.

Five completely filled wine bottles each containing about 800 mL were prepared for each wood species.

4.3 Triangle tests

Each wine trial was carried out once a week for each wood species. A sample of potential panellists at AUT recommended that the trials be held weekly, and this fitted well with room availability. Each sensory trial was held for approximately five hours until at least 45 panellists, mainly from the Schools of Applied Sciences and Engineering, had taken part. It took between 5 and 10 minutes for each panellist to assess all wine samples in the two tasting stations. If requested, panellists were allowed to take a short break between the two stations. Some did this. Between the two stations, every panellist was asked to eat some plain crackers with water.

Table 13 Triangle tests of unextracted and resin-extracted woods

Wood	Toasting level	Number of panellists correctly discriminating unextracted and resin-extracted treatments	Statistical significance[1]
Manuka	Light	19 of 50	NS
	Heavy	28 of 50	**
Macrocarpa	Light	26 of 50	*
	Heavy	24 of 50	*
Totara	Light	13 of 46	NS
	Heavy	19 of 46	NS
Kahikatea	Light	17 of 46	NS
	Heavy	17 of 46	NS
Gorse	Light	19 of 50	NS
	Heavy	19 of 50	NS
Radiata pine	Light	15 of 47	NS
	Heavy	13 of 47	NS
A. oak	Light	15 of 50	NS
	Heavy	15 of 50	NS

[1]NS, not significant; *, $P < 0.05$; **, $P < 0.01$

For trials with 50 panellists (manuka, macrocarpa, gorse, American oak), the minimum numbers of correct judgements required to establish significance are 23 and 26 out of the 50 response at the 0.05 and 0.01 levels respectively. The minimum number of correct judgements required to establish significance when the population is either 46 or 47 is 22 (Stone, 2004).

Among the trials, the trial where wine was infused with heavy toast manuka had the greatest number of people detecting a difference, 28 out 50. This showed that there was a significantly clear difference between the wines infused with the unextracted and the resin-extracted manuka wood chips ($P < 0.01$). Manuka had the highest resin content of the seven wood (table 4), approximately 11% by weight. On the face of it, the simple explanation for this would be that that extracting the resin from manuka would have caused the major flavour difference observed by panellists.

However, in wine infused with lightly toasted manuka, the effect of extraction could not be detected (NS, Table 13). Thus, the simple model did not extend to light toast infusion, placing the model in severe doubt.

Interestingly, all comments[1] from the panellists on the wine flavour treated with manuka were very positive regardless of resin extraction and also toasting level.

Both toasting levels of macrocarpa received the number of correct judgements to establish significance at $P < 0.05$. This indicates that there was a difference between the wine samples infused with the unextracted and the resin-extracted macrocarpa chips. However every comment on the wines infused with macrocarpa from the panellists was exceedingly negative. This shows that the wine infused with the resin-extracted macrocarpa still contained some matter with a negative effect on wine flavour.

As shown in Table 15, all other woods, totara, kahikatea, radiata pine, gorse, and American oak had the number of panellists able to discriminate lower than the threshold to establish significance. Even when the responses to these five woods x two toasting levels were summed (13 + 19 + 17 etc. = 162) and compared with the total number of panellists (46 + 46 + 46 etc.= 478), the frequency of correct discrimination was only 0.34, almost exactly as expected by chance alone.

It was concluded that there was no flavour difference between the wines infused with unextracted and resin-extracted toasted wood chips. Almost every panellist who tasted the wine samples infused with these five woods expressed that they could not tell any difference between them, and some expressed doubt about whether the wine samples were actually different. The time taken by panellists to assess the wines to detect any difference was much longer for these five than for manuka and macrocarpa, confirming vague or non-existent flavour differences. Among all the woods American oak scored the lowest number of panellists able to discriminate, 15 out 50, for both light and heavy toasts.

Extracting resins from the above five woods prior to toasting did not affect wine flavour as shown by the triangle tests. Except for manuka and macrocarpa, the resins of the other five unextracted woods might have been lost on toasting through evaporation, possibly accounting for the failure to detect a difference. This idea is supported by the obvious accumulation of resinous-like matter on the oven interior surfaces after toasting, and the weight losses recorded by Kaushal (2007). Weight losses were not recorded after toasting unextracted and resin-extracted chips (Chapter 3), data which in hindsight might have been

[1] As noted in Chapter 2, comments were not solicited, but were proffered in some cases

revealing. By this model unextracted wood chips would be predicted to lose more weight than resin-extracted chips. However, the further dichloromethane extraction of toasted, previously dichloromethane-extracted chips reported in Section 3.6 clearly shows that some resin-like matter remained after toasting at the two temperatures in all seven woods. This indicates that the resins would not totally have vaporised on toasting. It can be tentatively concluded that the resins of those five woods after toasting did not affect on wine flavour. There are two explanations for this. Either the residual resins were relatively flavourless in the face of other dominant wine and wood flavours, and/or the resinous matter did not diffuse into the wine. This latter explanation – if true – might be caused by insolubility of resin in water: ethanol mixtures of 87:13 (wine composition), compared with high solubility in pure organic solvents like dichlorometane, hexane and diethyl ether.

At this point of research the original hypothesis was refined: any wood completely free of resin could, after toasting, yield desirable flavour in wine after the manner of oak. To test this hypothesis two woods, manuka a native and macrocarpa an exotic, were chosen for further sensory trials since they were the only woods that showed significant differences in the triangle tests. Macrocarpa was of particular interest because of its marked deleterious effects irrespective of a single dichloromethane extraction.

In Chapter 3 it was shown that a single extraction with dichloromethane was inadequate for complete removal of resin and/or other dichloromethane-soluble matter. Therefore manuka, macrocarpa and American oak were exhaustively extracted by the three solvents prior to toasting and used to flavour wine subsequently assessed in hedonic trials. This is described in the next chapter.

Chapter 5

Wine Hedonic Trials

5.1 Introduction

The previous chapter showed that resin extraction of some wood species before chip toasting could affect the flavour of wine. On the basis of that result and the knowledge that a single dichloromethane extraction of wood chips did not extract all available resin and other apolar matter, the original hypothesis was refined to propose that any wood completely free of resin could, after toasting, yield desirable flavour in wine after the manner of oak. This hypothesis is tested in this chapter, by exhaustively extracting three woods, manuka, macrocarpa and American oak with three apolar solvents prior to light toasting and infusion in wine.

5.1.2 Wood chip dimensions

The nominal dimension of the wood chips of the three species was the same as for earlier work except that the actual dimensions were more precise because the chips were cut with a very sharp electric band saw and circular drop saw. Dimensions were not recorded.

5.1.3 Resin extractions by the three solvents

The resins of each wood species were consecutively extracted in Soxhlet extractors using the three different solvents in the order, dichloromethane, hexane, and diethyl ether. The extractions for each wood species were done in triplicate. This was because the capacity of the Sohxlet thimbles was limited to about 15 g and tens of grams were required for toasting and infusion. Thus the data shown are the totals of the triplicates (Table 14). Between the extractions by each solvent, the wood chips dried over 24 hours at room temperatures to ensure complete evaporation of the solvents. This was confirmed by no change in weight and no solvent smell by close nostril examination.

Table 14 Total weight loss of wood chips by resin extractions

Wood	Solvent	Before extraction (g)	After extraction (g)	Weight loss (%)	Total loss (%)
Manuka	Dichloromethane	44.89	39.16	12.76	
	Hexane	39.16	38.48	1.74	
	Diethyl ether	38.48	37.88	1.56	
					15.62
Macrocarpa	Dichloromethane	34.53	33.77	2.20	
	Hexane	33.77	33.35	1.24	
	Diethyl ether	33.35	33.04	0.93	
					4.32
A. oak	Dichloromethane	45.06	44.25	1.80	
	Hexane	44.25	43.93	0.72	
	Diethyl ether	43.93	43.35	1.32	
					3.79

The highest percentage of weight loss after exhaustive resin extraction was for manuka, 15.62%. For manuka only, dichloromethane was the most effective solvent among the three solvents, extracting seven times as much as the next most effective solvent, hexane. However, because dichloromethane was used before the other two solvents, it had the greatest opportunity to extract resin. But for macrocarpa and American oak, the three solvents were more closely matched in their effectiveness. These results and other subtleties of weight loss percent suggest significant chemical differences in the nature of the resins as might be expected for these diverse species (as is sensorially assessed in Chapter 6).

5.1.5 Colour measurements

The colour variables L*, a* and b* were measured after each extraction and finally after toasting. a* and b* data were converted to the derived values hue and saturation (Table 15).

Table 15 Colour measurements after each resin-extraction and the subsequent light toasting

Wood	Colour	Untreated	Dichloro-methane	Hexane	Diethyl ether	Light toast
Manuka	L*	52.40 ± 3.34	53.24 ± 0.41	51.96 ± 1.10	52.06 ± 0.21	29.70 ± 0.71
	[1]Hue	1.07 ± 0.00	1.09 ± 0.00	1.09 ± 0.01	1.11 ± 0.00	0.90 ± 0.02
	Saturation	18.78 ± 0.24	18.30 ± 0.09	18.26 ± 0.25	18.58 ± 0.10	9.28 ± 0.37
Macrocarpa	L*	63.13 ± 0.66	61.81 ± 0.32	61.44 ± 0.36	61.25 ± 0.10	40.33 ± 0.46
	Hue	1.26 ± 0.01	1.23 ± 0.00	1.23 ± 0.00	1.23 ± 0.00	1.12 ± 0.00
	Saturation	23.67 ± 0.17	23.72 ± 0.07	24.24 ± 0.12	23.91 ± 0.25	20.33 ± 0.15
A. Oak	L*	50.77 ± 0.65	53.57 ± 0.64	53.78 ± 0.62	52.97 ± 0.46	37.16 ± 0.25
	Hue	1.17 ± 0.00	1.17 ± 0.10	1.21 ± 0.00	1.20 ± 0.00	1.13 ± 0.00
	Saturation	20.30 ± 0.30	20.40 ± 0.40	19.39 ± 0.20	19.88 ± 0.10	14.91 ± 0.08

[1]Hue angles are in radians
All data are means of 10 replicates ± standard deviations

These data were not subjected to a formal statistical analysis because the differences due to solvent extraction were subtle to the point of being difficult to interpret from a chemical perspective. The colour changes on light toasting were large, and were dominated by decreases in light reflectance (L*) and saturation, the intensity of the colour. The differences were clearly highly significant. Hue, the basic colour of the wood was largely unaffected, confirming colour results obtained in Chapter 3

5.1.6 Wine infusion

The three triple-extracted wood chips were used to infuse wines. The maturation process was identical to the one used in the discrimination sensory trials. The wines were matured with the wood chips for 14 days, kept in the dark storage room. They were then transferred to the 750 mL wine bottles (completely filled), and held at 4°C until required for the hedonic sensory trials. This temperature was chosen to minimise any effect of wine aging in the five weeks required for this work.

5.2 Hedonic trials

As described in detail in Chapter 2, four different wine samples were presented to the incoming customers in each of five liquor stores. The wine treatments were chardonnay infused with lightly toasted manuka, lightly toasted macrocarpa, lightly toasted American oak, with unoaked chardonnay as the control. Most of the customers approached said they did not have time to participate and also did not show much interest in 'not commercially available' wines. Nonetheless each trial accessed 20 to 27 customers between 1630 and 2100 hours.

The results of hedonic scores of each wine are presented in Table 16. The statistical significance was evaluated for each of the factors wood species, gender, age group, liquor store, and customer.

Table 16 Means and standard deviations, and their statistical significances in the hedonic trials

Treatment (4)					Overall statistical significance
Manuka	Macrocarpa	American oak	Control		
6.84 ± 1.38^{ac}	3.25 ± 2.12^{b}	6.38 ± 1.69^{a}	7.03 ± 1.27^{c}		$P < 0.001$
Gender (2)					
Male		Female			
5.87 ± 2.19		5.89 ± 2.37			$P = 0.92$
Age group (4)					
18–29	30–39	40–49	50–70		
5.74 ± 2.37	5.69 ± 2.23	5.86 ± 2.27	6.21 ± 2.14		$P = 0.30$
Liquor store (5)					
Village Winery	Balmoral	Whangapararoa	Parklands	Meadowbank	
5.74 ± 2.73^{a}	5.53 ± 2.26^{a}	6.10 ± 1.89^{ab}	6.64 ± 1.86^{b}	5.36 ± 2.28^{a}	$P < 0.05$
Consumer (121)					
5.88 ± 2.25					$P < 0.001$

a, b,c : Means in a row bearing different superscripts are significantly different at $P < 0.05$
Numbers in parentheses indicate the numbers of each category

Among the three woods, manuka scored the highest hedonic scales, 6.84 corresponding to 'like moderately' on the hedonic scales. However manuka was not significantly different from American oak and the control. This indicates that the wine infused with resin-extracted manuka is equivalently pleasant as American oak and the control. Macrocarpa scored significantly lowest scales, 3.25 corresponding to 'dislike moderately' at $P < 0.05$ level, possibly due to the unique organoleptic characteristics of its resins which may still have remained inside the chips. This proves that the complete removal of macrocarpa resins by the three solvents to prevent any transfer of macrocarpa resins during infusion was not achieved.

There was no significant difference in means between males and females. The gender difference did not show any certain preferences to wines infused with the three woods.

Among the four age groups, there were no significant differences in means of liking the wines however there was a certain trend shown in the means that the liking of the wines increased as the age increased. It might be explained by the relatively more extensive experiences in drinking wines by the older age groups than the youngest age groups, 18-29. However it is concluded that there are no statistically significant differences between all age groups.

Significantly different means of liking only between the two stores were observed at $P < 0.05$ level. The Parklands store scored the highest hedonic scales but not significantly different from the Whangaparaoa store that scored the second highest hedonic scales. The means of likings in the four stores including the Whangaparaoa store were not significantly different. This indicates that the geographical location of the stores, except the Parkland store, did not significantly affect the differences in means. There was no reason could be found for the Parkland liquor store scoring the highest hedonic scores.

Among all 121 participants in the five trials, there was statistically clear difference in wine preferences at $P < 0.05$ level. The mean of all 121 participants, 5.88, corresponded close to 'like slightly'.

In Table 17, statistical interactions between the wood treatment and the other factors such as gender, age group, and outlet were explored.

Table 17 Statistical interactions between wood treatments and the other factors

Interaction	Statistical significance
Treatment x Gender	$P = 0.078$
Treatment x Age group	$P = 0.083$
Treatment x Outlet	$P < 0.05$

As shown in Table 17, there were no significant interactions between wood treatment and gender and age group because $P > 0.05$. This indicates that liking of the wines infused with the three different woods were not affected by either gender or age group. On the other hand, liking of the wines was affected by the outlet factor at $P < 0.05$ level, such that a certain liquor store or stores variously preferred the treatments. This interaction was not further pursued, because it only indicates a suburban difference in liking. (Significant gender and age interactions would have been much more interesting.)

5.3 Comments in each hedonic trial

In the following tables, the actual comments from all participants were recorded. However, not every participant wrote comments due to personal reasons, mostly time constraints. It must be emphasised that the consumers saw only three-digit number for each treatments

Table 18 Comments recorded at Mt Eden Village Winery

Wood	Comment
Manuka	Nice sweet taste, good chardonnay, nice, best-balanced, sweet, nice-sweet, balanced-sweet,
Macrocarpa	petrol-like weird taste, eucalyptus, bad different, hot, peppery, strong pine oil flavour, does not taste like a finished product, minty drink, gum-boots, petrol, terrible, not good, rubber-like, can't finish, petrol, not good, bad, can't drink
American oak	Different sour taste, drinkable but not good, yuk, ok, nice, sweet,
Control wine	Very nice, drinkable, nice, sweet, typical chardonnay,

Table 19 Comments recorded at Balmoral Wines and Spirits

Wood	Comment
Manuka	Lovely, nice
Macrocarpa	Smokey wood, can't drink, cumin-like, yuk, not good, sawdust, can't even try, hate extremely
American oak	Strong flavour but good, nice, not nice, typical chardonnay
Control wine	Best among 4, nice

Table 20 Comments recorded at Coast Liquor Whangaparaoa

Wood	Comment
Manuka	Not much flavour, nice, not bad but slightly off the palate, very nice, quite refreshing, nice but not as clean as A. oak, too sweet, sherry-like, fruity-mint
Macrocarpa	Horrible, has a real ethanol taste, taste very woody but nice, timber-like, not good, no unless you are pissed, a little bit bitter, nice-woody, oak-flavoured, awful, was it a joke?, not good, awful, methanol
American oak	Similar as control, nice, needs more work, bitter, very fresh but little after taste, smooth-nice, very nice, very good, sweet, beautiful
Control wine	Similar to A. oak[2], nice, likeable-dry, tastes ok but a little sour, nice but not clean as A. oak, cheese next time please, very cool taste

Table 21 Comments recorded at Parkland liquor

Wood	Comment
Manuka	Sulphur taste with a firm hold taste that hold warmly, the best among 4, very nice, sweet, good strong flavour, good, smooth taste, nice and full flavour
Macrocarpa	Strong with a bitey-taste in a good way with woody taste, bitter, very nice, smells like martini, woody, not good, terrible, petrol, weird woody, smokey woody in good way, not good, rubber-like
American oak	Smooth and mild fruity taste, ok, good
Control wine	Very nice, medium smooth taste, fruity taste, tropical, fruity, sweet,

[2] By this the consumer meant the treatment identified by its three-digit number.

like the most, too sweet

Table 22 Comments recorded at Meadowbank liquor

Wood	Comment
Manuka	strong, sweet, full-flavour, very nice, good chardonnay
Macrocarpa	very woody, not good, strong woody taste, plastic-rubber, not good flavour, strong in bad way, weird, doesn’t smell good, don’t want to drink, terrible
American oak	good, very nice, sweet, very nice, ok
Control wine	very sweet, sweet chardonnay, would have been better if kept cold, fruity

Manuka, American oak, and the control (unoaked wine) shared similar comments such as ‘nice’, ‘sweet’, ‘fruity’ and ‘full flavour’, and thus mostly pleasant comments, as shown in Table 18 to 22. However comments on macrocarpa were very different from the rest of the wood treatments. They were persistently negative comments such as ‘petrol-like’, ‘rubber-like’, ‘terrible’, ‘not good’, ‘very woody’, and ‘awful’. A small number of consumers appeared to like the macrocarpa-infused wine to some degree. However the comments in general were very negative as were their facial behavioural responses to the macrocarpa-infused wine.

Further discussion of the hedonic results is in the Conclusion, Chapter 7.

Chapter 6

Qualitative Assessments of Extracted Resins

6.1 Introduction

These assessments were made on two distinct groups of resins. The first was the resins recovered by a single dichloromethane extraction of wood chips from seven species. These seven resins were augmented by seven subsequent extractions of the light toast treatments and seven of the dark toasts. This makes 21 extracts in this first group.

The second group comprised the resins of the three woods, manuka, macrocarpa, and American oak that were extracted by the three consecutive solvents as described in Chapter 5, making nine extracts in the second group.

All these resins in vials were presented in an unvarying order to 11 untrained sensory panellists for descriptions of their odour characteristics. Also, their physical characteristics were examined and described by the author.

6.2 Physical characteristics of the extracted resins from seven wood species

After the single-solvent extractions by dichloromethane alone, the resins of the seven woods were collected in the glass vials. The appearances of the resins such as fluidity, colour, and texture in each wood species were very often different.

The resins of untoasted manuka, American oak, and gorse appeared to be dry and powdery. However when probed with a wooden toothpick, they were adhesive enough to stick to the inside of the vials. As shown in Figure 18, these were all dark yellow and were associated with dark brown powders that might have passed through the cellulose fibres of the thimbles.

The resins of untoasted macrocarpa, kahikatea, and totara were dark brown. Their resins were fluid except for totara resin which was solid. The resin of radiata pine was yellow and the most fluid of all.

The vials in the middle and on the right in Figure 18 show resins extracted after light and heavy toasting, respectively. There was no clear correlation of colour with intensity of toasting. As shown in Figure 19, kahikatea light and heavy toasts appear to have yielded the most resin among the seven woods and this corresponds to the results in Table 12 where kahikatea light and heavy toasts lost the most weight after extractions, 3.97 and 2.72 %, respectively.

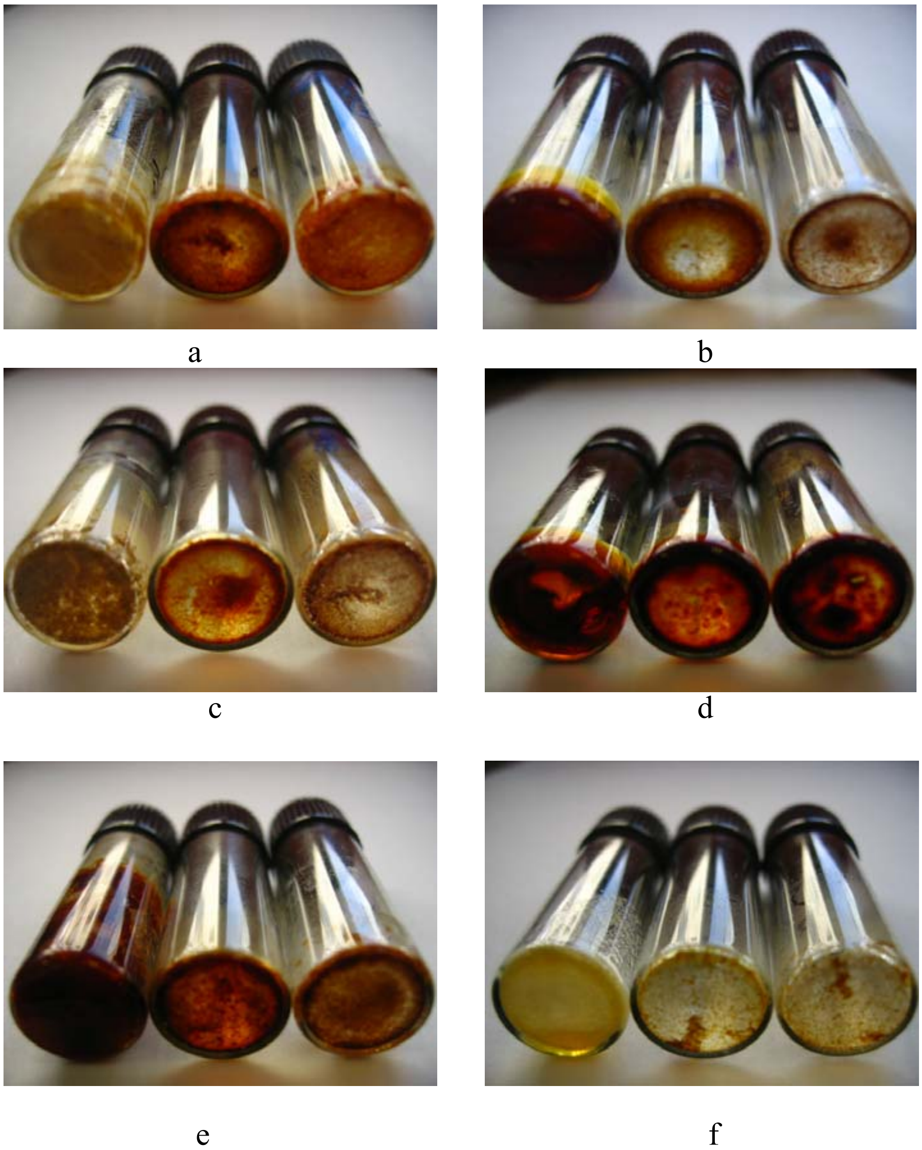


Figure 19 Resins of seven woods extracted by dichloromethane. The first vial on the left in each picture represents extracted resins before toasting. The middle vials are the extracted resins after light toasting, and vials on the right are the extracted resins after heavy toasting. (a) Manuka (b) macrocarpa (c) American oak (d) kahikatea (e) totara (f) radiata pine. Gorse is missing

6.3 Qualitative analysis of extracted resins from seven wood species

The assessment of the organoleptic characteristics of the extracted resins took place in the well-ventilated and odour free food science laboratory at AUT. The group of 11 volunteer panellists – AUT staff members and students – were asked to freely describe their olfactory sensations and nasal feelings for the extracted resins of each wood, 21 in all. The woods were not identified nor was the resin-extraction process. One panellist at a time assessed the extracts in a set order of presentation as shown descending in the 'Extraction' column in Table 23. All panellists were given as much time as they needed. The average time taken per panellist was approximately 15 to 20 minutes. Because the panellists were not professionally trained, and because there was a large number of vials to be assessed, the panellists found the process laborious and they had difficulty finding their words to describe some resins. Short breaks were requested from eight panellists to breathe in fresh air near windows and also to have short tea breaks.

In Table 23 some words are marked with 'x' to show the number of repeats of the same comments within each treatment. Most of the panellists used their own words but also referred to the list of words provided on the ballots (Appendix VI).

For resin from untoasted manuka, food-related words such as 'malty' and 'caramel-like' were mixed with non-food words such as 'antiseptic', 'mouldy', 'damp wood', and 'polish'. Words such as 'polish' and 'perfume' were not recorded for light and heavy toasts, but 'caramel', 'vanilla', and 'burnt woody' were most common. Interestingly these are terms often associated with favourable wine flavours.

The resin of untoasted macrocarpa scored the greatest number of words related to non-food. The predominant words were 'antiseptic', 'petrol', 'furniture polish', and 'kerosene'. Most of the panellists expressed discomfort when they smelt this resin. One panellist even immediately identified it as macrocarpa. Lightly and heavily toasted macrocarpa resins received some words such as 'vanilla', 'smokey', 'caramel', and 'burnt woody'. However descriptions such as 'polish remover' and 'petrol' were still given. This indicates that the toasted macrocarpa still carries a typical 'macrocarpa' odour.

Table 23 Comments on the extracted resins from seven woods, untoasted, light toasted and heavy toasted

Wood	Extraction	Comments
Manuka	Resin	Biscuit, dry tobacco, caramel x2, rubber, malty, antiseptic, perfume, cough syrup, mouldy, dry cleaners, woody, furniture polish, damp wood, pencil, furniture polish
	RLT[1]	Caramel x5, smokey tobacco x2, vanilla, chocolate, burnt wood x2, cough syrup, cough syrup
	RHT[2]	Malty, burnt x2, woody, tobacco, caramel x2, resinous wood fire x3, antiseptic, brown sugar, caramel
Macrocarpa	Resin	Antiseptic x3, pungent, petrol x2, pencil, furniture polish x4, macrocarpa, disinfectant, kerosene x2, rubber
	RLT	Woody, burnt caramel x2, tobacco x2, cooking oil, petrol x2, smokey x4, disinfectant, old furniture, pencil
	RHT	Vanilla, woody, woody vanilla x2, burnt, caramel, smokey x2, sweet burnt wood x2, biscuit, nail polish remover, coffee bean, nail polish remover
Totara	Resin	Furniture polish, none x9, gone off, vanilla
	RLT	Pencils, light smokey wood x3, dry plum, coffee beans x2, caramel, woody, damp, vinegar x2, cough syrup, burnt vinegar,
	RHT	Vanilla, rubber, malty, chocolate, smokey x2, nothing, old furniture x2, fresh cut wood
Kahikatea	Resin	Woody, none x7, gone off, antiseptic x2, grains
	RLT	Burnt wood x2, light smokey wood x2, dry plum, biscuit, coco beans, woody, cough syrup, gone off, cooking oil x2, cut wet wood
	RHT	Rubber, smokey tobacco, malty, burnt wood x4, cough syrup, nothing, antiseptic, smokey x2
Gorse	Resin	Pungent, malty, old cooking oil x5, mouldy wood, furniture polish, antiseptic, off resin, rubber, mouldy x2, old furniture
	RLT	Whisky, smokey x2, spicy cinnamon, light caramel x2, maple syrup, chemical, cough syrup, woody x2, old furniture, cooking oil, old cooking oil
	RHT	Pencil, smokey spice, dry plum, sticky sweet, malty, tobacco, smokey x2, burnt wood x3, cooking oil, old cooking oil
Radiata pine	Resin	Caramel biscuit, gone offx7, rubber x2, nail polish, pickled beans, rancid fat, sandust, vinegar,
	RLT	Pencil, cinnamon, vanilla, soil after raining, petrol, alcohol, smokey x2, sandust, burnt, burnt potato x2, furniture polish, oil
	RHT	Potato, fruity apple x2, woody, dry plum, furniture polish, moist wood, resinous smoke, vinegar, burnt caramel, olive oil, perfume, olive oil
American Oak	Resin	Rumx3, rubber, mouldy, rubber, sticky smell, perfume x2, attractive resin, cinnamon, vinegar x2, biscuit
	RLT	Rubber, smokey herbs, dry wood, burnt x2, caramel x2, musky, fresh cut wood, malty, vanilla, vinegar, mint oil
	RHT	Rum, none, woody x2, antiseptic, tobacco, smokey x2, vinegar x2, sweet smoke, burnt smell

[1]: Resin extracted from chips after Light Toasting
[2]: Resin extracted from chips after Heavy Toasting
x: Number of repeats of the same comments

For totara and kahikatea, ‘none’ was the most common word since panellists could not detect any odour for those two extracts. Light and heavy toast extracts of both totara and kahikatea received the most number of comments positively affecting the wine flavours such as ‘smokey wood’, ‘coffee beans’, ‘burnt wood’, and ‘caramel’. This suggests that totara and kahikatea may be used for wine infusion since they do not have negatively affecting odours. This result also supports the reason why kahikatea was used as transporting boxes for food items such as butter in the past.

The panellists mostly expressed the typical pine resin odour as ‘gone-off’ and ‘rubber’ possibly due to its ‘sour-odour’ character. After toasting at the two levels, the comments on extracts included some food-related words such as ‘burnt potato’, ‘fruity apple’, and ‘vanilla’. However words such as ‘polish’, ‘petrol’, and ‘perfume’ were still predominant.

The common words used to describe the gorse resins were ‘old cooking oil’ and ‘mouldy’ and the description of ‘old cooking oil’ remained in both of the light and heavy toast extracts. As seen in other heavy toasts, gorse heavy toast extract also received words such as ‘smokey’ and ‘caramel’.

The comments on the American oak resin were an interesting mix of words such as ‘rum’, ‘perfume’, ‘vinegar’, ‘attractive resin’, and ‘perfume’. After light and heavy toasts, the extracts engendered responses recorded were ‘burnt’, ‘caramel’, and ‘smokey’.

The words such as ‘burnt’, ‘smokey’, ‘vanilla’, and ‘caramel’ were common in all seven light and heavy toasted wood extracts. These words are considered to be positively affecting the development of wine flavours during infusion. However some woods retained unfavourable organoleptic characteristics in their resins even after the heat treatments. Macrocarpa was the best example. Among the seven woods, extracts of light and heavy toasts of macrocarpa appeared to still engender comments such as ‘disinfectant’, ‘petrol’, and ‘polish’ along with a few positive comments.

Resin does not seem to be a problem except for macrocarpa and radiata pine. Resins of the five woods showed that those five woods could be applied to wine infusion regardless of the resin extraction because their resins have either no odour or lost undesired odours after toasting.

All seven woods created the similar comments after the heat treatments however the heat treatments also created a wide range of words describing the organoleptic conditions of the resins due to the extensive differences in resins between the woods. This indicates that without the complete removal of resins in woods, the woods with undesirable organoleptic characteristics such as macrocarpa and radiata pine would still negatively affect the wine flavours.

6.4 Physical characteristics of multiply-extracted resins from three wood species

The resins of three untoasted woods – manuka, macrocarpa, and American oak – that were destined for the hedonic trial were recovered by three solvents as described in Chapter 5. Because extraction thimbles were not used during these extractions, the collected resins contained some wood powder as was obvious by inspection. For all three woods, the resin first extracted (by dichloromethane) was most fluid. The resins subsequently extracted by hexane and diethyl ether had more wood powders than resins and therefore appeared very powdery. However these latter extracts were still slightly adhesive when probed with a toothpick.

6.5 Qualitative analysis of multiply-extracted resins from three wood species

The extracted resins of the three woods were assessed by the same 11 panellists directly after the seven-wood, 21-resin assessment. The resins were assessed in the descending order shown in the 'Solvent' column in Table 24. As in the previous assessment, the panellists were not informed of the wood identity or the extraction process.

Table 24 Comments on the extracted resins by 3 different solvents

Wood	Solvents	Comments
Manuka	1	Cooking oil, rubber, furniture polish, dry shell, rubber, spicy, unpleasant, musky, old furniture, woody, seaweed x2, citrus
	2	Dry cleaners, herbs, dried fruit, cough syrup, lightly spicy, resin, damp, burnt, woody, light vinegar, cheese, light seaweed
	3	Grains, grass, old rubber, vinegar, pickled vegetables, fatty, rancid oil x2, cinnamon, light vinegar, biscuit, light seaweed
Macrocarpa	1	Cough syrup, pickled lemon, petrol x3, furniture polish x2, asphalt, diesel, macrocarpa, disinfectant, vinegar, antiseptic, dry cleaner x2, fresh rubber
	2	None x8, rubber, pencil, light furniture polish, woody x2,
	3	Vanilla, burnt wood x4, petrol x2, dry cleaners x2, antiseptic, resinous, none, rubber x2, woody
American Oak	1	Gone off, woody x7, burnt caramel, spicy, perfume x3, pencil,
	2	Biscuit, lightly smoked grass, dried fruit, none, lightly spicy, woody, wood resin, biscuit, perfume x2, vinegar, cookies, light woody
	3	Pencil, grass, furniture, none x3, woody, wood resin, perfume x3, vinegar, damp wood, light woody

1: dichloromethane
2: hexane
3: diethyl ether

Various comments were recorded on resins extracted by the consecutive solvent extractions from untoasted wood chips. Macrocarpa again received most number of words such as ‘furniture polish’, ‘petrol’, and ‘antiseptic’. Even though the change in weight of macrocarpa chips after resin extraction by hexane was 1.24%, ‘none’ was recorded eight times. This may indicate that hexane extracted resins much less than the other two solvents. This change in weight might have been caused by the presence of the macrocarpa powders.

American oak was perceived mostly as ‘woody’ among the three woods while extensively diverse words were used for manuka resin. This wide range of words to describe manuka resin resulted possibly due to lack of experiences with wood resins by the panellists and also vague organoleptic features of manuka resin compared to macrocarpa.

Further discussion of the resin results related to the discrimination (7 woods) and hedonic (3 woods) trials is in the Conclusion, Chapter 7.

Chapter 7

Conclusion

7.1 Introduction

The main thrust of this research was to test the hypothesis that any wood free of resin would be suitable for flavouring wine since all trees are composed of the same major constituents. In progressing to answer this question, the study addressed the weight loss of each wood species through resin extraction, colour changes of the wood chips, sensory evaluations of the wine flavours infused with seven different woods, and evaluations of the extracted resins. The results for the wood preparation were described in Chapter 3 and the results for the triangle sensory trials, the hedonic sensory trials, and the resin evaluations were described in Chapters 4, 5, and 6, respectively.

The main outcome of this work was that variation in wine flavour when infused with toasted wood was in most cases not related to the occurrence of resin in woods. In this chapter, the results leading to this outcome are discussed and a future study is recommended.

7.2 Resin extraction

Whereas 24 hour extractions with a single solvent, dichloromethane, were considered in the extraction design, it was rejected due to safety and logistical reasons. What was not known was if the single solvent applied for four hours to wood chips of the dimensions chosen would remove all the resins and like compounds. In the event it was found that further extraction of toasted wood chips that were not used for infusion yielded more resinous matter. It is possible that the pyrolytic events of toasting opened up fresh resin reservoirs that could be solvent-accessed and/or that toasting generated new classes of compounds that were soluble in dichloromethane. However it is unclear at this stage which is more responsible.

The discovery that further resinous matter could be extracted from the toasted woods prompted an exhaustive extraction of resin from (untoasted) woods destined for the hedonic trial, using three organic solvents that might be expected to cover all chemical solubility possibilities. When the three solvents were consecutively used on three 'hedonic' woods, manuka, macrocarpa, and American oak, each extracted some resin. Dichloromethane was the first of the consecutive solvents used and the weight losses due to it were different from those reported in Chapter 3 where seven wood species were singly extracted with dichloromethane in preparation for the discrimination trial. This difference could be explained by biological variability.

However, the fact that the second and third solvent extractions did remove more resin from three of the woods they were applied to means that all woods taking part in the discrimination trial probably contained some resin. This was obviously not intended nor desirable. The implications of residual resin will be discussed in the discrimination section later in this chapter.

If resin extraction from wood chips were to be a useful technology for the wine industry, a study would be needed to identify which solvent was most effective in extracting resins from each wood. Even though different weight losses of wood chips after resin extractions – single and triple – were observed in this study (between approximately 1 and 16 %), it is still not known how much resin in each wood species remained and affected discrimination and liking. The literature is scant on this point. In a wine and wood study (Sun, 2003), a 24-hour dichloromethane extraction was applied to oak wood to extract phenols. However, because it was not aimed at removal of resins, resin mass was not measured. In addition, the extraction time would need to optimised, and this would obviously depend on chip/sawdust size. The choice of equipment would depend on cost effectiveness and in this respect super critical fluid extraction with carbon dioxide might be viable. Supercritical fluids are substances with both gas- and liquid-like properties at temperature and pressures above their critical points (Dean, 1993). As examples, carbon dioxide and water, which are polar solvents below their critical points, behave as non-polar organic solvents when supercritical.

The above discussion of resin extraction concerns only organic solvents. Oak staves destined for wine barrel production are left exposed to air and rain for years before the barrels are constructed and toasted (Domine, 2004). This so-called 'seasoning' leaches hydrolysable substances such as ellagitannins so as to reduce bitterness in the resulting wine (Vivas, 2007). The solvent involved here is the classic polar solvent, water. Water extraction of flavour compounds could also be applied to wood chips, with the added possibility of heating and pH control. Heating to boiling point would also extract some resinous matter.

These research concepts are currently unexplored.

7.3 Extracted resin evaluations

A wide vocabulary was used to describe the extracted resins under various conditions; single-, triple-solvent extractions, and heat treatments. As shown in Chapter 5, even though the descriptions were not completely consistent there was a clear relationship between the words and the treatments. After toasting had been applied to the wood chips, the extracted wood resins were described mostly by ‘caramel’, ‘burnt’, and ‘smokey’, and less by ‘resin’ descriptors. This indicates that the toasting removes the organoleptic features of resins to some extent, probably through volatilisation. The fact that the resin of macrocarpa was not completely removed by solvents is positively related to the presence of words such as ‘petrol’ and ‘polish remover’ for the both lightly and heavily toasted macrocarpa wood chips that had been previously resin extracted.

7.4 Colour changes

Colour changes in untoasted woods due to resin extraction were usually statistically significant but minor. Each wood, however, was a story to itself, and colour changes were unrelated to weight losses due to extraction. Light and heavy toasting resulted in significant and often major changes in colour parameters due to resin extraction. However there was no clear pattern of change. Again, each wood was a story to itself. Overall, colour analysis had no fruitful outcomes. There was no colour difference detected by eyes between untreated and treated wine however further analyses on wine colours could have yielded some results.

7.5 Discrimination evaluations

The purpose of the discrimination trials were to determine if resin extraction prior to toasting resulted in a different wine flavour as judged by untrained panellists. Statistically significant differences were observed in wines infused with manuka heavy toast and both the macrocarpa light and heavy toasts.

In the case of macrocarpa, every panellist reported an ‘unpleasant’ flavour somewhere among the three glasses presented. But the data showed that only 26 and 24 panellists respectively of 50 correctly picked the odd sample out in the triange test. The fact that correct discrimination frequency was only about 50 % in spite of a universal dislike suggests one of two or both possibilities. One possibility is that the macrocarpa flavour lingers in the mouth resulting in a carryover effect (Meilgaard, 1991), which affects the next sampling after the first therefore confusing the panellists' ability to tell difference between the samples. The second possibility is that because the extracted wood chips still contained resin both the unextracted and resin-extracted treatments contained the unpleasant flavour, thus complicating discrimination. This effect would be compounded if the flavour detection threshold of the macrocarpa resin were low. As will be seen in the hedonic section this possibility is very likely.

Wine infused with manuka heavy toast received the most number of panellists with correct judgements and on the face of it could be explained by the fact that the weight proportion of resin in manuka was the highest among the seven woods (11%). However, totara at 8 % resin was not far behind and its two triangle tests were not significant. A simple explanation for this is that its resin did not have any odour and thus would not make any difference in wine flavour.

Based on the results of the discriminative trials, manuka and macrocarpa along with American oak were selected for hedonic trials to test their public acceptance. Manuka was an obvious choice based on the unsolicited but positive comments from the panellists. Macrocarpa was an important choice because of the clear discrimination trial results and because of the persistence of its resin odour. Oak-infused and unwooded wine were the controls. The rest of the test woods were not selected because they did not make any significant differences in wine flavours regardless of their resin extractions. This does not mean that they could not be applied to winemaking, but they would need to be further studied as to how they could be used to develop new flavours in wines.

As noted in the previous paragraph, panellists often proffered unsolicited opinions about the treatments. In hindsight, data collection should have extended to asking panellists the basis of their discrimination. This data could be used to help interpret hedonic results.

The results of the discrimination trials and resins assessments showed that negative flavours in wine due to wood were due to the nature of a resin rather than the mass of resin in the wood. Even though manuka, totara, and kahikatea had high resin contents, the resin present in the discrimination trials did not affect wine flavour, for whatever reason. This is also supported by the odour profiles of the resins from those three woods, which, in short, were difficult to smell. This has shown that certain woods could be used in wine infusion regardless of their resin content.

7.6 Hedonic evaluations

Exhaustive solvent extraction by the three solvents did not completely remove of macrocarpa resin, as clearly shown by the low mean hedonic score for this wood and the overwhelmingly negative comments. Equally, the solvents applied to the other woods may not have removed all their resin. But because any residual resinous matter was likely to be innocuous from a flavour perspective – as shown in resin assessment and the discrimination trials – it would not affect the hedonic outcomes. The unpleasant odour of macrocarpa might also be attributed to a possible very low odour detection threshold (Meilgaard, 1991). Thus, even if very small amounts of resin remained in the triply-extracted chips, consumers would still detect a bad flavour.

For all five liquor store trials, the control wine was the most liked possibly due to its sweet taste noted by many customers. But importantly, manuka-infused wine received the second highest mean hedonic scores, again in all five stores, exceeding the mean for American oak (but was not statistically different from the latter). On the face of it manuka could substitute for oak as a wine flavourant. However, the total hedonic trial recruited only 121 consumers and thus must be seen as a preliminary result.

7.7 Concluding remarks

Variation in wine flavour when infused with toasted wood was in most cases not related to the occurrence of resin in woods. Either the resins in toasted wood were lost in the toasting process, did not affect flavour, or as proposed in Chapter 4 were not extracted into the wine.

One wood, macrocarpa and possibly others of the Cupressaceae, was very difficult to remove its resin and therefore it affected wine flavours. Moreover, possibly because of its low odour threshold, its unique odour was persistent in all wines infused with the wood. Macrocarpa is clearly out of contention as a wine flavourant.

The standout wood in this study was manuka. Wines infused with manuka were more liked than wines infused with American oak in most of the hedonic trials. Because a resin-extracted light toasted manuka treatment could not be differentiated from the unextracted equivalent, the resin does not need to be extracted from manuka prior to wine infusion. Manuka is an unprotected native species and is freely commercially available, and therefore this wood should be further explored for wine applications.

In the hedonic trial, liking of wine infused with manuka was not significantly different from the liking of the American oak treatment. A logical future experiment would be discrimination trials between manuka and American oak treatments. In these trials, both woods should be water-extracted (and not) to simulate the lengthy seasoning period of staves destined for barrel production. Water extraction should remove the bitter ellagitannins prior to toasting and wine infusion. Further flavour outcomes can be expected. In addition, these water-extracted woods (both lightly toasted), can be infused in white and red wine to test their capability in both.

This research and future research with woods other than oak could be exploited by the wine industry to create new flavour dimensions for an ever-evolving New Zealand wine industry.

Appendices

Appendix I

Seven wood chips cut into the chip dimensions

a

b

c

d

e

f

g

Cut wood chips

a. Manuka b. Macrocarpa

c. Totara d. Kahikatea

e. Gorse f. Radiata pine

g. American oak

Appendix II

Sensory ballot used in the triangle tests. The combinations of the three digit codes varied in each ballot

Oaky Flavours in White Wine

I invite you to take part in a sensory trial as a part of my Master of Applied Science thesis project.
I want to know if possible differences in oaky flavours can be detected by consumers. To do this I have arranged a series of wine comparisons to be judged by triangle tests, where consumers are asked to pick the different sample among three. Forty or more responses are needed for clear answers.
You have to be 18 years or older to take part.
Your participation in this trial is entirely voluntary and you may withdraw at any time. You will first be asked if you want to take part. If you do, you will be presented with three wine samples that you have to taste in the set order. You may swallow or spit out after tasting.
As a reward for tasting you will be offered a piece of chocolate.
Every participant is in a draw to win $30 cash and the winner will be contacted by a mobile phone text. This is the only reason I will contact you.

At the completion of the work in September you are invited to discuss the results with Joseph Kang or Owen Young.

Wine comparison A

Panelist number 1 ____

Gender	M	☐	F	☐
Age group	18- 29	☐	30-39	☐
	40-49	☐	50-70	☐

Two of these three wine samples are identical.

Taste the samples from left to right and
pick one different sample. Circle it.

You must choose one, even if you have to guess.

924	108	761
________	________	________

Appendix III

The order of presentation of the sampling cups with unique three digit codes. It follows a certain pattern which ensures each wine has the same frequency of exposure in each trial. Three digit codes were varied in each trial.

[redacted]

Appendix IV

Table of number of correct judgements required to establish significance in sensory triangle tests

[redacted]

Appendix V

Sensory ballot used in each hedonic trial

Assessment of Oak Flavour in Chardonnay

Hi, my name is Joseph Kang. I am a Master of Applied Science student at AUT.
I would like to invite you to take a part in a sensory trial as a part of my thesis project.
You will be presented with four wine samples that you need to taste in the set order.
I would like your opinion of oakiness – if any – in these four wines.
Use any words to describe what you taste.

Gender M ☐ F ☐ **Panel Number:** 1

Age 18-29 ☐ 30- ☐

40-49 ☐ 50- ☐

How much do you like each of these wines?

Taste from left to right

For each wine tick the box that best describes your liking

	349	152	862	707
Like extremely	☐	☐	☐	☐
Like a	☐	☐	☐	☐
Like moderately	☐	☐	☐	☐
Like	☐	☐	☐	☐
Neither like nor dislike	☐	☐	☐	☐
Dislike slightly	☐	☐	☐	☐
Dislike moderately	☐	☐	☐	☐
Dislike a	☐	☐	☐	☐
Dislike extremely	☐	☐	☐	☐

Wine number	Comments
349	
152	
862	
707	

Appendix VI

Sensory ballot used in each wood resin assessment

Assessment of wood resins

I invite you to take a part in a sensory trial as a part of my thesis project.

In this trial, aromatic characteristics of a series of wood resins will be explored. You are asked to smell each glass vial containing wood resin of each wood type and then freely describe the olfactory sensations and nasal feelings (coolness, pungency, etc). Examine them in the set order**, resin → light → heavy**.

You may use any of the following words to describe the aroma of resins;

Alcohol, antiseptic, biscuit, brandy, burnt, caramel, cinnamon, citrus, coffee beans, cooking oil, cough syrup, damp, dry cleaners, furniture polish, gin, gone off, grains, malty, nail polish removers, pencils, perfume, petrol, potato, pungent, rough, rubber, rum, tobacco, vanilla, vinegar, whisky, woody, etc or choose your own expressions.

Gender: **M** ☐ **F** ☐

Age range: **18-29** ☐ **30- 39** ☐

40-49 ☐ **50-70** ☐

Wood		Comment
413	Resin	
	Light	
	Heavy	
297	Resin	
	Light	
	Heavy	
504	Resin	
	Light	
	Heavy	
126	Resin	

	Light	
	Heavy	
725	Resin	
	Light	
	Heavy	
228	Resin	
	Light	
	Heavy	
817	Resin	
	Light	
	Heavy	

Woods after various treatments

Wood	Extraction	Comment
913	1	
	2	
	3	
551	1	
	2	
	3	
115	1	
	2	
	3	

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