The influence of base wine composition and wood maturation on the quality of South African brandy

by

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DECLARATION

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Mrs Caroline L. C. Snyman

SUMMARY

Brandy production is a multi-step process that involves grape harvesting, base wine fermentation, distillation, wood maturation and blending. Within each of these production process steps there are a number of factors that can influence the composition and resultant quality of the base wine, unaged and wood matured distillates. These factors include geographic and climatic features of the origin of grapes used, viticultural practices, grape maturity, grape variety, vintage variation, vinification techniques, storage of the base wine prior to distillation, distillation technique, age and origin of oak wood used for maturation and barrel toasting levels.

The composition of flavour is extremely complex in wine and distilled beverages such as brandy. A multitude of compounds can take part in the formation of flavour, and it is rare that a particular compound, that is solely responsible for nuances of a specific flavour, is identified. Thus, taking brandy production factors and the nature of aroma and flavour into account, it is clear that thorough understanding of the complexities affecting the perception of quality in brandy is difficult.

In commercial brandy production, standard operating procedures do not allow for the separate distillation of brandy base wines from different producers and mixing of base wines from different regions and producers thus occurs. This makes it difficult to determine whether the quality determination of the base wine is in fact an indication of the quality of the resultant distillate after the required period of wood maturation. Therefore, the aim of this study is to determine whether there is any merit in storing and distilling brandy base wines from different producers and regions separately. This was done by firstly determining the demographic and production factors that influence brandy base wine composition. Secondly, the influence of brandy base wine composition on the quality of the respective unaged potstill distillates as well as the ultimate style and quality of the three-year old wood matured potstill distillates was determined.

For this purpose, four potstills with a capacity of 2000 L each were isolated and used for commercial scale distillations of 33 and 25 brandy base wines in 1999 and 2000, respectively, at the Distell distillery in Worcester. The experimental outlay used in the study closely emulated Distell's standard operating procedures for commercial brandy production.

Chenin blanc and Colombar are the two most popular grape varietals used in the making of brandy base wine in South Africa. Due to the complexity of the brandy production process, the first part of the study only focussed on South African young Chenin blanc wines, with a predominantly fermentation derived aroma. The concentration of iso-amyl acetate, hexyl acetate, ethyl caprylate, ethyl caprate, 2-phenethyl acetate and octanoic acid was significantly higher in wines awarded gold and silver medals and decreased significantly with subsequent decreases in quality categories. Ethyl lactate exhibited the opposite pattern. A quality predictor model based on the behaviour of 21

volatile compounds quantified in these wines had a resonable prediction accuracy when having to predict the quality of wines made in the same vintages as it had been trained on. It was significantly poorer when tested on a completely different vintage of wines to the ones it had been trained on. The number of vintages, number of wines per vintage and the number of compounds quantified for the model influence its prediction accuracy.

Twenty-seven volatile compounds were quantified in 33 and 25 brandy base wines, their unaged and three year old distillates from 1999 and 2000, respectively. ANOVA and CART analysis showed that vintage, region, harvest time, choice of cultivar and yeast strain can have a significant influence on the volatile compound composition of brandy base wines, their unaged and three year old distillates. These factors as well as the volatile compound composition were also found to influence the sensory quality of these products. Base wines, unaged and three year old distillates originating from the De Doorns region, which predominantly cultivates table grapes, were of significantly lower quality than those from the remaining regions. Products made from grapes harvested early in the season were of significantly higher quality. The volatile aroma compound composition was found to differ significantly between the 1999 and 2000 base wines and distillates, irrespective of the exclusion of those samples that had undergone partial or complete malolactic fermentation. Consequently, quality indicating compounds may vary from vintage to vintage. The relationship between the quality of brandy base wines and the concentration of n-butanol, iso-amyl acetate, ethyl lactate, ethyl caprylate, octanoic- and decanoic acid was the same as that reported in young Chenin blanc wines in this study. In unaged distillates, increased levels of ethyl lactate also exert a negative influence on distillate quality. Iso-amyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, n-butanol, octanoic acid, ethyl caprate and decanoic acid showed some positive correlation, whilst iso-butanol, ethyl lactate, acetic acid, acetaldehyde and ethyl acetate showed a significant negative correlation to three-year old distillate quality.

Sensory descriptive analysis on selected good, average and poor quality distillates using the South African brandy aroma wheel showed that there are small differences in profile between the good and average distillates, there were however significant differences between the good and poor quality distillate profiles throughout maturation. After three years of wood maturation, the aroma profile of poor quality distillates can be characterised by prominent herbaceous and woody aromas, which are more intense than the fruity aromas. Good quality distillates contained characteristically intense fruity aromas.

Volatile compound concentration differences were noted during the course of and after three years of wood maturation and in barrels of varying ages. Distillates matured in new block barrels exhibited significant differences in volatile and wood compound composition after three years when compared to remaining barrels used. The style classification of the three-year old potstill distillate was influenced by demographic and production factors and volatile compound composition, but not by the sensory quality of the distillates.

In summary, vintage, region, cultivar, harvest time and choice of yeast strain have a significant influence on the volatile composition of brandy base wines, their unaged and

three year old potstill distillates, which in turn affects the sensory quality of these products. These effects cannot be viewed in isolation as they jointly exert an influence on the composition and quality of these products. From a commercial perspective, this study has provided a valuable indication as to which production and demographic factors can influence the quality and style of potstill brandy. Thus, future brandy base wine intake should, as far as possible, take place in such a manner to allow base wines originating from the same cultivar or region or harvest time or combination thereof (and to a lesser extent yeast strain) to be received simultaneously at the distillery for distillation.

OPSOMMING

Brandewyn produksie is 'n veelvoudige proses wat die volgende insluit: pars van druiwe, basiswyn fermentasie, verstoking, houtveroudering en versnyding. Binne hierdie stappe is verskeie faktore wat 'n invloed op die samestelling en resultate van die basiswyn, onverouderde en verouderde distillaat kan hê. Hierdie faktore sluit die volgende in: geografiese ligging, klimaat toestande van die streek van herkoms, wingerdboupraktyke, graad van rypheid, druifvarieteit, wynoes variasie, wynbou tegnieke, opberging van basiswyn voor distillasie, distillasie tegnieke, ouderdom en oorsprong van akkerhout vir die veroudering, asook tot watter mate die vat gerooster is.

Die samestelling van geur in wyn en gedistilleerde produkte soos brandewyn is uiters kompleks. 'n Menigte samestellings kan deel vorm van die inhoud van die geur, en dit is raar dat 'n bepaalde verbinding alleenlik verantwoordelik is vir 'n kenmerkende geur. Weens die verskeidenheid van produksie faktore, aroma en smaak is volledige kennis van brandewyn ingewikkeld en kompliseerd om te verstaan.

In kommersiële brandewynproduksie, maak standaard werksprosedures nie voorsiening vir aparte distillasie van basiswyn van verskillende produsente nie, en die vermenging van basiswyn van verskillende streke en produsente kom voor. Dit maak dit moeilik om te bepaal of die kwaliteit van die basiswyn of die distillaat na die neergelegde periode van houtveroudering, in werklikheid 'n beslissende indikasie op die kwaliteit van die verouderde produk is. Daarom is een van die doele van hierdie studie om te bepaal of daar meriete in is om brandewyn basiswyn van die verskillende produsente en streke apart te berg en te verstook. Dit is gedoen deur eerstens, die effek van demografiese en produksie faktore op die samestelling van brandewyn basiswyn te bepaal. Daarna, om die invloed van brandewyn basiswynsamestelling op die kwaliteit van onderskeidelik die onverouderde distillate sowel as die uiteindelike styl en kwaliteit van die 3 jaar oue houtverouderde potketel distillate, te bepaal.

Vir hierdie doel, is vier potketels met 'n kapasiteit van 2000 liters elk geïsoleer en vir kommersiële skaal distillasies van 33 en 25 brandewyn basiswyne in 1999 en 2000, ondeskeidelik, by Distell Distillerdery, Worcester verstook. Die eksperimentele uitleg wat in hierdie studie gebruik is, ewenaar Distell se standaard verstokingsprosedures vir kommersiële brandewynproduksie.

Chenin blanc en Colombar is die twee mees populêre druifvarieteite vir die maak van brandewyn basiswyn in Suid-Afrika. As gevolg van die kompleksiteit van die brandewyn produksieproses, is die eerste gedeelte van die studie gefokus op die Suid-Afrikaanse jong Chenin blanc wyne, met 'n oorheersende fermentasie geur. Die konsentrasie van iso-amyl asetaat, heksiel asetaat, etiel kaprilaat, etiel kapraat, 2-phenetiel asetaat en oktanoë suur was aansienlik hoër in wyne wat met goud en silwer medaljes bekroon is en neem aansienlik af met afname in kwaliteit kategorieë. Etiel laktaat vertoon die teenoorgestelde patroon. 'n Kwaliteit voorspellersmodel, gebaseer op die gedrag van 21 vlugtige

komponente was opgestel. Die model het redelike akkuraatheid getoon op wyne van dieselfde oesjaar as waarop oorspronklik opgelei. Die model se voorspellingsakkuraatheid was aansienlik swakker toe dit vergelyk getoets is met wyne van 'n nuwe oesjaar. Die hoeveelheid oesjare, hoeveelheid wyne per oesjaar en die hoeveelheid verbindings gebruik in hierdie model sal die voorspellingsakkuraatheid beïnvloed.

Sewe-en-twintig vlugtige komponente was gekwantifiseer in 33 en 25 brandewyn basiswyne, die onverouderde en 3 jaar oue distillate vanaf 1999 en 2000, onderskeidelik. Variasie ontledings (ANOVA) en klassifikasie en regressie ontledings (CART) ontledings wys dat oesjaar, streek, parstyd, keuse van kultivar en gisrasse 'n aansienlike invloed op die vlugtige samestelling van brandewyn basiswyne asook hul onverouderde en 3 jaar distillate het. Hierdie faktore, sowel as die vlugtige verbinding samestellings, beinvloed ook bevind die sensoriese kwaliteit van hierdie produkte. Basiswyne, onverouderde en 3 jaar oue distillate wat vanuit die De Doorns streek, wat hoofsaaklik tafeldruif kultivars is, is van 'n swakker kwaliteit as die ander streke. Produkte wat gemaak is van druiwe wat vroeg in die seisoen gepars is, was van beter kwaliteit. Die vlugtige geurkomponentsamestellings het tussen die basiswyne en distillate van die 1999 en 2000 oesjare verskil, ongeag of party van die monsters gedeeltelike of volledige appelmelksuurgisting ondergaan het. Gevolglik, die konsentrasie van kwaliteitaanwysende komponente mag van seisoen tot seisoen verskil. Die verhouding tussen die kwaliteit van die brandewyn basiswyne en die konsentrasie van n-butanol, iso-amiel asetaat, etiel laktaat, etiel kaprilaat, oktanoë- en dekanoë suur was dieselfde soos gerapporteer oor die jong Chenin blanc wyne. In onverouderde distillate, het verhoogde vlakke van etiel laktaat 'n negatiewe invloed op distillaat kwaliteit veroorsaak. Iso-amiel asetaat, heksiel asetaat, etiel kaproaat, etiel kaprilaat, n-butanol, oktanoë suur, etiel kapraat en dekanoë suur 'n positiewe korrelasie, terwyl iso-butanol, etiel laktaat, asynsuur, asetaldehied en etiel asetaat betekenisvolle negatiewe korrelasie met 3jaar oue distillaat kwaliteit bewys.

Beskrywende sensoriewe analises op geselekteerde, middelmatige en swak kwaliteit distillate (gedoen deur gebruik making van die Suid-Afrikaanse Brandewyn Aromawiel) wys dat daar klein verskille tussen die profiele van goeie en middelmatige distillate is. Daar is egter aansienlike verskille tussen goeie en swak kwaliteit distillataat profiele regdeur die drie jaar verouderingsperiode. Na 3 jaar van houtveroudering kan die geur profiel van swak kwaliteit distillate uitgeken word aan kruid- en houtagtige geure, wat meer intens as die vrugagtige geure is. Goeie kwaliteit distillate het intense vrugagtige-aroma eienskappe.

Vlugtige verbinding konsentrasie verskille is waargeneem gedurende en na die 3jaar houtverouderingsperiode in vate wat van ouderdomme verskil. Distillate wat in nuwe blokkies vate verouder is, vertoon aansienlike verskille in vlugtige en houtkomponent samestellings na 3 jaar wanneer dit met die, wat in die oorblywende ouer vate verouder is, vergelyk word. Die styl klassifikasie van die 3 jaar oue potketeldistillaat was deur demografiese en produksie faktore sowel as vlugtige verbinding samestellings beïnvloed, maar nie met die sensoriese kwaliteit van die distillate nie.

In opsomming, oesjaar, streek, kultivar, parstyd en keuse van gisrasse het 'n aansienlike invloed op die vlugtige komponent samestelling van die brandewyn basiswyne, onverouderde en 3 jaar oue potketel distillate, wat weer op hul beurt die sensoriese kwaliteit van die onderskeidelike produkte beïnvloed. Die effek van hierdie faktore kan nie in isolasie gemeet word nie, aangesien dit gesamentlik die kwaliteit van die produkte beïnvloed. Van 'n kommersiële perspektief het hierdie studie 'n waardevolle indikasie gelewer van hoe produksie en demografiese faktore die kwaliteit en styl van potketelbrandewyn kan beïnvloed. Daarom word voorgestel dat toekomstige brandewyn basiswyn innames, sover as moontlik, voorsiening moet maak om wyne van dieselfde kultivar, uit dieselfde streek, parsseisoen inaggeneem, of kombinasie daarvan, met 'n mindermate die gisrasse in aanmerking geneem, gelyktydig vir verstoking by die distilleerderye ontvang word sodat hierdie wyne apart van wyne met ander bogenoemde variasies verstook en verouder kan word.

This thesis is dedicated to my husband and family for their continuous love and support.

Hierdie tesis is opgedra aan my man en my familie vir hulle volgehoue liefde en ondersteuning.

BIOGRAPHICAL SKETCH

Caroline Snyman was born in Johannesburg, South Africa on 1 February 1975. She matriculated at Northcliff High School, Johannesburg in 1992 and enrolled at Stellenbosch University in 1993. She obtained a B.Eng degree in chemical engineering in 1996 and an MSc degree in Wine Biotechnology in March 1999. She has been employed as technical manager: spirits at Distell since January 2000.

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PREFACE

This thesis is presented as a compilation of eight chapters. Each chapter is introduced separately.

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Chapter 3 **RESEARCH RESULTS**
Yeast derived flavour compounds and their relationship to quality in young South African Chenin blanc wines

Chapter 4 **RESEARCH RESULTS**
The influence of vintage, region, cultivar, harvest time and yeast strain on the volatile composition of brandy base wines and unaged potstill distillates

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Chapter 6 **RESEARCH RESULTS**
The influence of wood maturation on the composition of potstill brandy distillates

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CHAPTER 1

INTRODUCTION AND PROJECT AIMS

1. GENERAL INTRODUCTION AND PROJECT AIMS

1.1 AN INTRODUCTION TO BRANDY PRODUCTION IN SOUTH AFRICA - A DISTELL PERSPECTIVE

The Oxford English Dictionary devotes three and a half of its three-column pages to the substantive "spirit". The twenty-first of its twenty-four major definitions is, "... a liquid of the nature of an essence or extract from some substance, especially one obtained by distillation..." – brandy is such a spirit. Other definitions of the same dictionary call upon such evocative words and phrases as, "the animating or vital principle", "life blood" and "soul". Brandy is such a spirit too – the soul or vital principle of the wine it is distilled from.

The earliest records of the distillation of wine in South Africa date back to 1672, but the quality of Cape Smoke produced over three hundred years ago could hardly be compared to the quality of South African brandies on the market today (Weitz, 1997). South Africans are fond of their brandy, whether enjoyed over ice and with their favourite mixer or savoured slowly on its own and currently brandy sales within South Africa total over 40 million litres per annum. Within the South African brandy category Distell, South Africa's largest producer of wines and spirits, has a market share of over 70%, which includes ownership of such brands as Klipdrift, Viceroy, Richelieu, Oude Meester, Mellowwood and Flight of the Fish Eagle.

Commercial South African brandy production starts with the sourcing of brandy base wines from commercial wine producers. The grapes for these base wines originate predominantly from the Breede River valley (including Robertson, Rawsonville and Worcester), the Klein Karoo, De Doorns and Olifants river regions. The majority of these wines are made from either Chenin blanc and Colombar grapes, with lesser amounts of other varieties such as Ugni blanc, Palomino, Emerald Riesling as well as table grape varieties such as Sultana finding their way into brandy base wine. Chenin blanc and Colombar lend themselves to brandy base wine production due to their relative ease of management in the vineyard, their potential to produce high yields without significantly compromising grape quality and their ability to produce a clean, fruity brandy base wine. Wine producers present their base wines to the brandy producer, in this case Distell, for approval prior to the purchase. At this time the base wine is analysed to determine whether it meets the following criteria: alcohol content between 10 – 12 %v/v, residual sugar less than 4 g/L, volatile acidity less than 0.7 mg/L (measured as acetic acid) and total SO_2 content less than 20 mg/L. The wines are also evaluated organoleptically by two experienced tasters that form part of the spirits production team within Distell. Once base wines have met organoleptic and analytical approval, they are purchased and delivered to the distillery for distillation.

Batch-wise double distillation takes place in copper potstills. The first distillation involves distilling the wine to a so-called low wine or first distillate at between 28 to 30%

v/v. Low wine is then re-distilled and the second distillate product is separated into three fractions. The first fraction is called the heads fraction. It comprises approximately 1% of the entire volume to be distilled and is recovered during the first 15 minutes of distillation. The heads fraction contains highly volatile compounds, such as acetaldehyde, methanol and traces of sulphur containing compounds that are undesirable in the flavour of brandy. The second fraction, which is recovered in the next 6 to 8 hours, is called the heart. The heart, at between 68 to 70% v/v, is the desired distilled product that will be wood matured and will eventually form part of brandy as the consumer knows it. The third fraction is referred to as the tails. The tails contains compounds with a high molecular weight and comprises predominantly longer chain fatty acids, which impart a soapy, buttery, at times rancid character and are therefore highly undesirable in brandy. The total duration for the second distillation is between 10 to 12 hours. The heads and tails fractions are added to the succeeding batches of low wine in order to recover the ethanol that will have partly distilled over in these fractions.

The heart fraction is placed into oak casks of no larger than 340 litres for a minimum maturation period of three years (South African Liquor Products Act No. 60 of 1989). Within Distell, the majority of brandy casks are made from French oak from a number of forests. Due to their previous use as wine maturation barrels prior to being cleaned, shaven and re-toasted for use in brandy, the exact origin in terms of forest is not recorded. Brandies are matured for three, five, eight, ten, twelve, fifteen, twenty and twenty one years within Distell. However, the majority of brandies are only matured for three years as these form the basis of many of the high volume brandy brands in South Africa. Brandies are matured as lots with a certain number of barrels comprising a lot. The number of barrels within a lot is not a critical production factor, however, the average age of the barrels within a lot is critical as this determines the amount of wood character that will be imparted to the brandy distillate over the maturation period. After the prescribed period of wood maturation, the barrels within the lot are emptied and the matured distillate from these barrels is stored in tanks. At this time the brandy distillate is organoleptically evaluated in terms of quality as well as being classified as a particular brandy distillate style. This style classification will determine its end use within one of several brandy brands. Each of these brands is unique and distinctive in terms of its flavour profile and its measure of smoothness or hardness on the palate. Therefore, each of these brandy distillates must be tasted by a trained panel of tasters using style reference samples in order to gauge their mouthfeel and accordingly their style classification.

The final step in the production process is blending, which takes place within three legally prescribed brandy types in South Africa (South African Liquor Products Act 60 of 1989). The first type, called blended brandy, is bottled to an alcohol strength of 43% v/v. The alcohol content of blended brandies must contain a minimum of 30% of potstill distillate (at least three-years old) and a maximum of 70% neutral, unmatured wine spirit. The second type, called potstill brandy, is bottled at 38% v/v. The alcohol component of potstill brandy must comprise at least 90% of potstill distillate (at least three-years old) and

a maximum of 10% neutral wine spirit. Vintage brandy, also bottled at 38% v/v, is the third brandy type. The alcohol content of vintage brandy must contain a minimum of 30% potstill distillate (at least 8 years old), up to 60% of wine spirit (matured in oak for the same length of time as the potstill component) and up to 10% of neutral, unmatured wine spirit. Blended brandies are more commonly enjoyed with mixers whilst the fuller flavoured potstill and vintage brandies are more frequently enjoyed neat or over ice.

The number of steps involved in the brandy production process as well as the large number of compounds that can contribute to the flavour and aroma of a brandy, make thorough understanding of all of these effects on the product extremely complex and difficult. Ideally one would like to understand the joint effect of all of these factors on the product and yet also understand the individual contribution that each of these factors makes to brandy.

1.2 PROJECT AIMS

In commercial brandy production, standard operating procedures do not allow for the separate distillation of different brandy base wines. Instead, once the brandy base wines are approved and purchased, they are delivered to the distillery and stored in so-called charger tanks. These tanks vary in capacity, from 40 000 to 1 million litres. Due to the size of the charger tanks and the number of wine producers that can be delivering approved brandy base wines to the distillery at any day, it is not possible to store base wines from each producer separately. Thus mixing of the base wines occurs. However, a considerable amount of time goes into the analysis and approval of brandy base wines prior to purchasing. Thus, the ultimate aim of this study is to determine whether there is any merit in storing and distilling brandy base wines from different producers and regions separately, by determining the influence of brandy base wine composition on the quality of the respective unaged potstill distillates as well as the ultimate style and quality of the three-year old wood matured potstill distillates.

The pipelines feeding to four potstills of 2000 litre capacity each within a large commercial distillery belonging to Distell in Worcester, were adapted to be filled with brandy base wine from six 40 000 litre charger tanks. In this manner it was possible to separately receive, store and distill approximately 35 000 litres of each brandy base wine selected from different regions, producers and cultivars during the course of the two harvesting seasons. It is critical to bear in mind that due to the scale of this experiment and the ultimate aim of the study, the experimental outlay reflects commercial practice. Thus aspects such as the percentage of lees content distilled with each wine were not possible to control exactly, but was maintained at approximately 3%. Not all regions or producers cultivate all of the cultivars used in this study. Distillation took place over a period of almost three months and ran concurrently with the season's commercial distillations at the distillery. Distillery charger tanks are not fitted with cooling facilities and brandy base wines may not contain more than 20 mg/L of total SO_2. This necessitates a minimum storage

period between the completion of fermentation and distillation. The distribution of wines distilled per region and producer also closely reflects that of commercial practice during the course of the potstill distillation season. Another aspect affected by the experimental outlay is the sensory evaluation of the base wines, unaged and three-year old distillates. This is discussed in detail in section 5.2.3. The last aspect to be affected by the outlay of the study is the process of wood maturation. It is well known that oak wood composition can vary significantly from barrel to barrel (Singleton, 1995). The controllable factors in the wood maturation section of this study were the age of the barrels used and the storage conditions used. All distillates were wood matured in the same store and were thus subjected to the same temperature and humidity.

Bearing the above-mentioned factors in mind, the specific aims of this study were to determine:

1. The relationship between yeast derived flavour compounds and the quality of young South African Chenin blanc wines.
2. The possibility of establishing a flavour compound model that could be used to predict young Chenin blanc wine quality.
3. The influence of demographic (vintage and region) and production factors (cultivar, harvest time and choice of yeast strain) on the volatile composition of brandy base wines and their unaged potstill distillates.
4. The effect of the above-mentioned demographic and production factors as well as the volatile compound composition on the sensory quality of brandy base wines and their unaged distillates.
5. Aroma profiles for poor, average and good quality unaged potstill distillates using sensory descriptive analysis and the South African brandy aroma wheel (Jolly and Hattingh, 2001) and to monitor the changes taking place in each of these aroma profiles during the three-year wood maturation period.
6. The changes in volatile compound composition of potstill distillates during the three-year wood maturation period.
7. The differences in three-year old potstill distillate volatile compound composition as a result of oak maturation in barrels of differing ages.
8. Whether the above-mentioned demographic and production factors are still related to the volatile compound composition of three-year old potstill distillates and to determine to what extent this relationship, if any, differs from that observed in the unaged potstill distillates.
9. Whether three years of wood maturation significantly alters the sensory quality of potstill distillates when compared to the original base wine and unaged distillate sensory quality.
10. The effect of demographic and production factors and volatile compound composition on the sensory quality and style classification of three-year old potstill distillates.

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CHAPTER 2

LITERATURE REVIEW

Factors influencing the flavour and aroma of wines, distillates and oak matured spirits

2. LITERATURE REVIEW

FACTORS INFLUENCING THE FLAVOUR AND AROMA OF WINES, DISTILLATES AND OAK MATURED SPIRITS

2.1 INTRODUCTION

2.1.1 BRANDY

The word brandy originates from the Dutch word *brandewijn* meaning, literally "burnt" or distilled wine. This word is derived from the German *gebrantwein*. The Dutch, the dominant western European commercial force in the late 16th century, sought a cheap source of material to provide their soldiers with potable liquids. They imported huge quantities of wine, and later spirit, from various parts of western France, including the Muscadet, Cognac and Armagnac region. So important did this trade become that *brandewijn* became the international term for spirit produced from distilling wine, evolving eventually into the word brandy.

In *The Oxford Companion to Wine* (Robinson; 1994), the following headings are discussed at length: American brandy, Cyprus brandy, Eastern European brandy, French brandy, German brandy, Israeli brandy, Italian brandy, Latin American brandy, Portuguese brandy, South African brandy and Spanish brandy. This is proof enough that brandy is enjoyed internationally and continues to play an important agricultural and economic role in all of these countries and regions.

2.1.2 FLAVOUR AND AROMA OF WINES, DISTILLATES AND OAK MATURED SPIRITS

There has been much research into the flavour and aroma of alcoholic beverages over the past five decades. A major stimulus has been the recognition that aroma in itself invariably has a profound and complicated effect on the quality of an alcoholic beverage. A second reason for the active research has clearly been the rapid improvement in methods of analysis and aroma compound quantification. Intensive flavour and aroma research over the past few decades has led to the identification of more than 500 volatile compounds, additionally, taking non-volatile compounds into account, the number of identified compounds would be close to triple (Nykänen and Suomalainen, 1983). Accordingly, the composition of flavour is very complex in beer, wine and distilled alcoholic beverages. Because a multitude of compounds can take part in the formation of flavour it is rare that a special component is identified which is solely responsible for nuances of a specific flavour. Although different beverages can readily be distinguished from one another organoleptically, current analytical methods reveal surprisingly few differences in their chemical composition. The most

important differences appear in the quantitative, rather than qualitative composition of flavour and aroma compounds in beverages (Nykänen and Suomalainen, 1983; Postel and Adam, 1990a, b, c, d).

Wine flavour is classified according to the source of different compounds contributing to it. This includes varietal flavour (compounds present in the grapes), pre-fermentative flavour (compounds formed during operations of extraction and conditioning of must), fermentative flavour (produced by yeast and bacteria during alcoholic and malolactic fermentation) and post-fermentative flavour (compounds that appear during the ageing process through enzymatic or physico-chemical reactions both in wood or in the bottle) (Boulton *et al.*, 1995).

Fermentative flavour, is not only brought about by the conversion of directly fermentable substances, but also by the long-chain fatty acids, organic nitrogen-containing compounds, sulphur-containing compounds and many other compounds which are able to penetrate from the grape juice medium through the yeast cell wall membrane, where they participate in biochemical reactions producing numerous volatile substances as by-products. These may be secreted into the wine solution. Naturally, differing fermentation conditions also markedly influence the amounts of the aroma compound by-products formed (Baldwin *et al.,* 1967; Carnacini *et al.,* 1989; Delfini and Costa, 1993; Falque and Fernandez, 1996).

One must at all times bear in mind the importance of flavour and aroma in the brandy base wine as this forms the foundation for flavour and aroma characteristics to be found in the finished brandy product. Section 2.2 focuses on flavour and aroma research done only on South African Chenin blanc and Colombar wines, which are the most common cultivars used in the production of brandy base wine in South Africa.

Brandy is a distillate of wine and it thus follows that its initial chemical composition depends on the compounds present in wine that are sufficiently volatile to be distilled over into the resultant brandy spirit. The ratios of the compounds occurring in cognacs and brandies depend to a great extent on the way in which distillation is performed (Klaushofer and Bandion, 1968). Distillation methods and some of the theory behind distillation is therefore covered in section 2.3.

Although ethanol and water are the two major components of any distilled spirit, aroma and flavour character, as previously mentioned, depend on a multitude of minor compounds, commonly referred to as brandy congeners. The most abundant congeners of brandy are the quantitatively minor by-products of fermentation by yeast during brandy base-wine production (Guymon, 1974; Nykänen and Suomalainen, 1983; Riponi *et al.*, 1996). Higher (fusel) alcohols are the most abundant group of congeners and the ethyl esters of C_8 and C_{12} fatty acids are the next most abundant, provided that the wine is distilled along with a large fraction of its yeast lees (Guymon, 1974). Section 2.4 thus focuses on the currently known flavour and aroma compounds found in wine distillates and their origins, relationships and effects. The further effects of some of these compounds are discussed in section

2.5, whilst section 2.6 discusses the factors affecting the composition and therefore resulting quality of wine distillates.

During ageing in oak, many substances are extracted from the wood, some of which react with the compounds initially present in the spirit, especially ethanol. Thus, the wood ageing process produces a further diversity of minor constituents, which generally improves the complexity and again enhances the aroma and flavour of the brandy (Singleton, 1995).

Section 2.7 focuses on the wood congeners involved in the maturation of brandies and their effect on aroma and flavour. The factors influencing the presence and concentration of these wood congeners are also discussed.

Relatively little research has been published on the aroma compound composition of commercial brandies world-wide. Section 2.8 summarises the research to date on commercial brandies. The section covers the composition of some commercial European brandies as well as studies done on the chemical and statistical classification of brandies, the role of higher alcohols in brandy and the effect of complex media composition on the detection of sulphur compounds is also discussed.

It is however apparent that detailed knowledge of the effects and interactions between flavour and aroma compounds present in alcoholic beverages (whether they be synergistic or antagonistic) is still required.

2.2 THE FLAVOUR OF SOUTH AFRICAN CHENIN BLANC AND COLOMBAR

2.2.1 CHENIN BLANC AND COLOMBAR IN SOUTH AFRICA

Chenin blanc is one of the world's oldest noble cultivars and was already planted along the left bank of the Loire river near Anjou in 845. It was probably selected from indigenous, wild vines in the west-central part of France and was classified by the Russian botanist Negrul as *Proles occidentalis.* The cultivar was well-known as Chenere by the 13th century but was probably named after Mont Chenin in the Touraine area, where significant amounts were planted in the 15th century. Early Dutch East Indian trading records show that "Steendruiven" formed part of the earliest vine shipments to the Cape colony, which would indicate that the variety was already cultivated in Jan van Riebeck's time, although proof of plantings only exist from the Van der Stel era (De Villiers, 1987). For many years South African viticulturists and ampelographers believed that the South African Chenin blanc was a local mutation unique to South Africa, or that the variety had been cultivated from seeds, as there was no proof as to the exact origin of the local variety. However, in 1965, it was finally proven that the South African Chenin blanc really is the French Chenin blanc so famously planted in south-western France (De Villiers, 1987). Chenin blanc plantings comprise 32.3% of the total white vine-plantings in South Africa and 30.2% of the total hectares under vine in South Africa as at 30 November

2002 (SAWIS statistics). It is the Cape's stable white grape, being a well adapted, highly versatile variety that is related to the Loire Valley's famous Chenin blanc (Platter, 2002). Long considered to be the Cape's so-called orphan varietal, two distinct characteristics of Chenin blanc have forced winelands growers and cellarmasters to give the varietal a serious chance:

- Chenin blanc has the ability to make wines of many styles, through the entire range of sweetness, dryness, fruitiness, still or sparkling.
- It is trouble-free in the vineyard and is a moderately heavy bearer by nature (Platter, 2002).

Chenin blanc can yield between 20 to 23 tons/ ha (with supplementary irrigation) and has moderate to strongly vigorous growth characteristics. In the Western Cape, budding takes place at the end of August to early September (5 to 7 days later than Colombar). Flowering takes place in the first part of November (2 to 3 days later than Colombar). However, Chenin blanc usually ripens in the second half of February (25 to 40 days earlier than Colombar) (De Villiers, 1987). The flavour and bouquet of Chenin blanc differs from region to region and may vary from a fine, estery character to intense honey and even a strong guava aroma (De Villiers, 1987).

Colombar has been cultivated in France since the 16th century, although predominantly for the purpose of producing a distilling wine for Cognac. It has been cultivated in South Africa since the 1920's, although it only expanded its application to table wine in the 1960's (De Villiers, 1987). Colombar plantings comprise 17.2% of the total white vine-plantings in South Africa and 16.7% of the total hectares under vine in South Africa as at 30 November 2002 (SAWIS statistics). From a viticultural point of view, Colombar is well adapted to the relatively warm South African climatic conditions. Generally, the grapes and wines are characterized by relatively high total acidities, which contribute to the production of well-balanced wines. It must be noted that the characteristic flavour of young wines from this cultivar is not directly derived from the grape, but is the result of compounds that are formed during fermentation. Ethyl esters of straight chain, saturated fatty acids and acetate esters of higher alcohols are produced by the reactions of ethanol and acyl co-enzyme A derivatives (Nordstrom, 1964 as quoted by Marais, 1986). These compounds have a prominent effect on wine aroma and are mainly responsible for the desirable fruity, young wine bouquet of white cultivar wines such as Chenin blanc and Colombar (Marais, 1986).

2.2.2 CHENIN BLANC AROMA

Augustyn and Rapp (1982) reported no measurable amounts of terpenoid components to be present in South African Chenin blanc grapes sourced from various origins. They quoted Wildenradt *et al.* (1974) in mentioning that terpenoid components have indeed been identified in local Chenin blanc leaves. Augustyn and Rapp (1982) speculated that local climatic conditions result in a poor terpenoid presence in the Chenin blanc grape leaf. Consequently, the concentration of the

terpenoid components translocated to the berries was below the detection limits used in their study. On the other hand, the lack of measurable amounts of terpenoid components may well be the result of some form of physiological block that inhibits the translocation of terpenoid contents from the leaf to the berry. They found the presence of 2,4-decadienal isomers to be characteristic of South African Chenin blanc grape juice and that the origin and degree of maturity had little effect on the concentration of aroma components studied. Thus the aroma of wines made from Chenin blanc grapes is predominantly fermentation derived, and is not complicated by grape derived components as is the case for Riesling and Sauvignon blanc, whose aroma is largely influenced by monoterpene and methoxypyrazine concentrations, respectively.

It has, however, been known for many years that South African white table wines produced from Chenin blanc grapes frequently exhibit a fruity flavour reminiscent of fresh guavas. This flavour, which occasionally also develops in wines made from Colombar grapes is generally regarded as highly desirable in white table wines, since it adds to their complexity. In fact, it is a general phenomenon that wines displaying the guava-like flavour are usually rated higher by sensory panels than wines lacking it. Du Plessis and Augustyn (1981) showed that sulphur compounds, particularly mercaptans contribute positively to wine aroma when present in low concentrations. They found that 4-methyl-4-mercapto-pentan-2-one, when added to neutral wine produces an aroma profile very similar to that found in South African Chenin blanc and Colombar. Young Chenin blanc and Colombar wines in South Africa often have an aroma which is likened to that of the guava fruit. Cosser *et al.* (1980) also identified 4-methyl-4-mercapto-pentan-2-one to be associated with a guava or “ribes” off-flavour in beer. Since this flavour cannot be detected in the grape itself, Van Rooyen *et al.* (1982) set out to study the factors affecting the occurrence and intensity of this flavour. Sensory evaluations of individual fractions of headspace extracts, recovered from guava-like flavoured wines, revealed no analogy between these fractions and the guava-like flavour. However, several of these odorous compounds and their ratios showed a definite relationship with either a classification of a guava-like intensity, or on the other hand, correlated significantly with the organoleptic intensity of this flavour. These variables were: ethyl butyrate, ethyl hexanoate, ethyl octanoate, hexanoic acid, hexyl acetate, 2-phenyl ethanol, total esters and the ratios ethyl butyrate: ethyl decanoate and ethyl butyrate: ethyl octanoate. However, throughout their study, the absolute concentration of ethyl butyrate and its concentration relative to that of ethyl decanoate or ethyl octanoate, were by far the most significant variables to serve as a basis for hypotheses in this regard. Van Rooyen *et al.* (1982) stressed that this particular flavour could be far more complex, possibly involving other compounds, and could not conceivably be fully explained by such simple combinations. Du Plessis (1975), for instance, found that absolute concentration increases of ethyl octanoate and ethyl decanoate in existing wines did not influence quality. Van Rooyen *et al.* (1982) thus concluded that

the important variable in this case could be ethyl butyrate, while high levels of the other two esters would probably indicate unfavourable conditions for the formation of a guava–like flavour.

2.2.3 MULTIVARIATE ANALYSIS OF FERMENTATION FLAVOUR PROFILES OF SELECTED SOUTH AFRICAN WHITE WINES FOR QUALITY AND ORIGIN CLASSIFICATION

Wine quality is attributed to an integrated response of many individual constituents, some originating in the grapes, and others produced during fermentation. Grape juice composition and fermentation conditions are considered to be most important in this respect (Soles *et al.,* 1982 as quoted by Van Rooyen *et al.* 1984). Gas chromatographic analysis allows for the quantification of large numbers of volatiles and thus visual interpretation of such data becomes very difficult and in many cases almost impossible. Thus research into the relationship between chemical flavour profiles and sensory evaluation scores has progressed from simple correlation and regression studies to highly sophisticated pattern recognition techniques and the reduction of normally large numbers of variables to facilitate meaningful interpretation has become a major task for oenologists. Van Rooyen *et al.* (1984) used several multivariate statistical techniques to study the factors affecting the fermentation aroma and bouquet in South African white wines. By employing a variable selection procedure using the "SELECT" program on 16 esters, higher alcohols and short chain fatty acids with correlation to quality weighting as basis for selection, they found that an increase in the concentration of hexanoic acid coincides with an increase in sensory quality for Chenin blanc and Colombar.

Marais *et al.* (1981) applied stepwise discriminant analysis to gas chromatographic data of volatile compounds in order to determine the origin of selected South African Colombar and Chenin blanc wines. The Colombar wines originated from two regions, namely Stellenbosch and Robertson, while the Chenin blanc wines originated from Stellenbosch, Robertson and Lutzville. These regions are known to exhibit differences in climate and soil composition. They found that the components with the highest discriminant value for origin of Colombar were isoamylacetate (which was by far the most powerful discriminant for Colombar between the two regions) followed by hexyl acetate and iso-butanol. Hexanol had the highest discriminant values for Chenin blanc. All of the acetate esters and their corresponding higher alcohols, with the exception of hexyl acetate, are produced during the amino acid metabolism via the Ehrlich mechanism, as well as during amino acid synthesis by enzymatic reactions during the course of fermentation. The alcohol moiety of isoamylacetate derives from the de-amination of leucine, which, depending upon its availability, could lead to differences in the concentration of this ester in wines. However, they also suggested that the above-mentioned explanation may not fully account for ester concentration differences between wines and that

other factors during fermentation (temperature and yeast strain) may also account for differences.

Brander *et al.* (1980) speculated that hexanol concentrations in wine derive from linoleic and linolenic acids, which are likely constituents of the waxy bloom covering the skin of the berry. Brander *et al.* (1980) thus concluded that the process of skin contact as well as differences in the concentration of these acids amongst cultivars, or within a specific cultivar from different localities, could produce differences in hexanol concentration in wines. Aldave de las Heras *et al.* (1992) further studied the effect of skin contact on the composition of Vermentino and Semillon wines. They found that, at the end of alcoholic fermentation, the difference between control and maceration products, although small, involved mainly the C_{10} to C_{12} fatty acids. With a pre-fermentation process (skin maceration, pressing, settling) wines and musts showed an increase in C_6 compounds, although this difference was not organoleptically detectable on the wines. Drawert and Rapp (1966) reported that hexenal is formed during the grape processing stage when enzymatic oxidation is known to occur, and thus lands up in the press juice. The levels of hexenal may vary according to the degree of grape ripeness and methods of grape juice handling prior to fermentation. Hexenal is then reduced by yeast during fermentation to form the corresponding alcohol, hexanol. The study by Marais *et al.* (1981) found that hexanol was reasonably successful in discriminating amongst the Chenin blanc wines from the three different regions, whilst hexyl acetate was an origin discriminator for the Colombar wines. It follows that the presence of hexyl acetate is also dependant upon the C_6 precursors present in grape must (Marais *et al.*, 1981).

2-Phenyl ethanol is produced via the Ehrlich mechanism from the amino acid phenylalanine. Although this compound was found to be a discriminating indicator for Chenin blanc wines from Lutzville and Stellenbosch/ Robertson, it had no utility as a discriminant between the Chenin blancs from Stellenbosch and Robertson (Marais *et al.*, 1981). Äyräpää (1965) showed that 2-phenyl ethanol formation is reduced by nitrogen content above 100 ppm in the medium and increased by phenylalanine above 75 ppm. The findings of Rankine and Pocock (1969) agreed with Äyräpää (1965) in this regard. However, they assumed that the yeast had adequate nitrogen for protein synthesis and deamination of phenylalanine was therefore not necessary to provide further nitrogen. Yet when tested, the conversion was only 30 to 40% of that theoretically obtainable (Rankine and Pocock, 1969). In the same study, the addition of small amounts of 2-phenyl ethanol, in the order of 50 ppm, appeared to improve the quality of the wine. They also found that more 2-phenyl ethanol was formed by fermentation at 15° C and 25° C than at 35° C, and more was formed at pH 3.5 and 4.0 than at pH 3.0. They studied wines made from Clare Riesling, Pedro, Ugni blanc, Madeira, Semillon and Tokay and found that there appeared to be a relationship between the stage of ripeness of the grapes and the amounts of both n-hexanol and 2-phenyl ethanol present in the wines. In general, the more mature the grapes from the same variety had higher concentrations of 2-phenyl ethanol and

lower concentrations of hexanol. The correlation was not exact and when the data from all varieties was pooled it was not significant, however, for some of the individual varieties this trend was apparent.

It must, however, at all times be borne in mind that storage time and temperature has a marked effect on the shelf-life of white wines. Marais (1986) investigated the effects of storage time and temperature on the composition and quality of bottled Colombar wines. Marked decreases in the concentrations of ethyl esters, acetate esters and the intensity of young wine bouquet, as well as marked increases in the concentrations of diethyl succinate, dimethyl sulphide and the intensity of maturation bouquet were obtained with increases in storage time and temperature. Close relationships were found between the concentration of esters and young wine bouquet, as well as between dimethyl sulphide and maturation bouquet. It was clear from these results that, by storing wine at low temperatures, the young wine bouquet can be preserved for longer periods of time, while controlled higher storage temperatures can induce a bottle maturation character in wine in a far shorter period of time.

2.3 DISTILLATION METHODS

2.3.1 INTRODUCTION

In the preparation of spirits from wine the distillation technique is of fundamental importance in determining the organoleptic properties of the end product (Guymon, 1974a; Leaute, 1986; Postel and Adam, 1990a). Brandy congeners have varying boiling points and solubility in water thus exhibiting wide ranges of volatility as affected by the alcohol content of the liquid volatilized (Leaute, 1986). Many processes are used throughout the world for distilling wine into brandy. Continuous distillation in plate columns, discontinuous or batch distillation using pot stills (with and without rectifying columns) and even distillation apparatus involving both continuous and discontinuous aspects are used (Guymon, 1974a).

Discontinuous distillation enhances the aromatic qualities of the original wine, while the continuous process tends to give a much less aromatic end product, due to the alcoholic vapours undergoing rectification. Rectification is the separation of the constituents of a liquid mixture by successive distillations. With the discontinuous method it is very important to know the properties of the base wine and use only good quality raw material, avoiding the practice of using poor quality material on the assumption that it is to be distilled (Leaute, 1986).

2.3.2 COGNAC

In France, the most famous cognac brandy is distilled in simple, directly fired pot stills (**Figure 2.1**). The *Methode Charentaise* includes two successive distillations. In the first, wine is distilled into low wines (*brouillis*) containing 26-30% alcohol, or

approximately a threefold concentration. The low wines are redistilled, and three fractions are collected:

- A small heads cut amounting to about 1 vol % of the charge
- The brandy heart (alcohol content decreases from ± 80-60 %v/v, averaging 70%v/v)
- The tails to recover the remaining alcohol in the charge

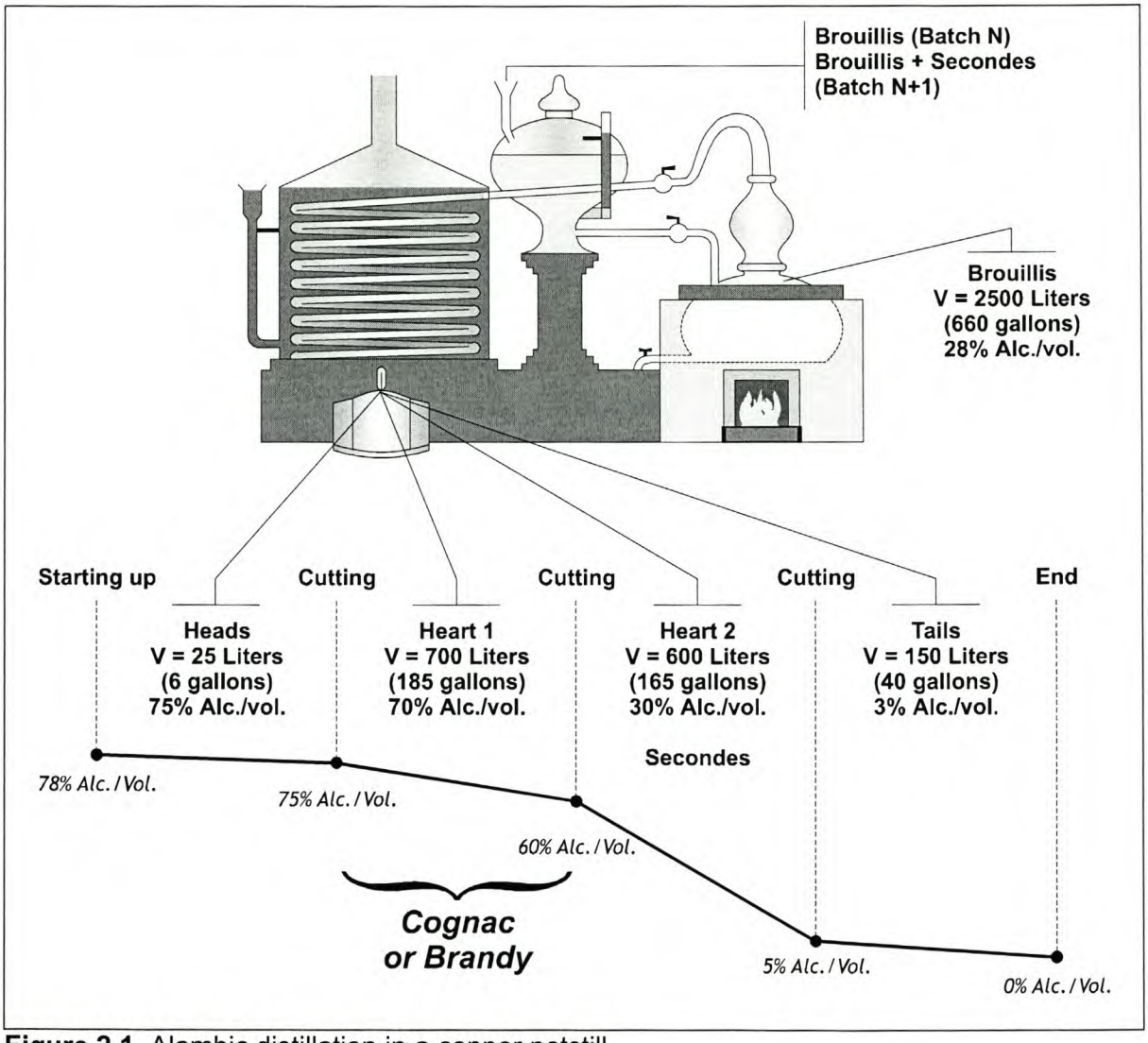


Figure 2.1 Alambic distillation in a copper potstill.

The heads and tails fractions are recycled to recover ethanol (Leaute, 1986). Acetaldehyde and almost all esters are low boiling point compounds that appear in the heads fraction of the distillate. Thus a strict separation of the heads from the heart-fraction, will not only remove the unwanted acetaldehyde, but also most of the sensorially favourable esters. Furfural, 2-phenyl ethanol, benzyl-alcohol, ethyl lactate and diethyl succinate typically appear in the tails-fraction of the distillate. Thus these compounds can be effectively removed from the heart fraction of the distillate (Leaute, 1986; Postel and Adam, 1990a).

2.3.3 ARMAGNAC

The Armagnac brandies are distilled in an apparatus known as the *Verdier systeme*. Wine, preheated by condensing vapour, flows continuously to the top of a short plate column and is partly stripped of alcohol as it transverses the column and flows into the top section of a two-tiered, directly fired boiler. The vapour generated in the lower section by the furnace bubbles through the liquid layer in the top section and up onto the plate column. Distillation columns are all fitted with horizontal plates along the inner length of the column. These plates allow for better contact between the gas and liquid phases during distillation so that a better separation may be obtained. Gaseous vapours thus move up the column and the liquids flow downwards to the base of the column. The resultant vapour reaching the top (feed) tray, is condensed by the pre-heater and condenser into a spirit containing 50-54 vol% alcohol. Intermittently, most of the spent wine in the lower level of the boiler is drawn off to waste, and then the same volume of liquid from the upper level is drawn to the lower part. Thus the process is both continuous and discontinuous (Guymon, 1974a).

2.3.4 CALIFORNIA

In California, distillation is usually carried out in a continuous single or split column unit (**Figure 2.2**). The brandy distillate, at a maximum of 85% v/v, is drawn as a liquid side-stream from a tray/horizontal plate in the middle or upper region of the concentrating section. A small portion of the overhead distillate from the vent condenser is withdrawn as a heads cut at a rate of 5-15% of the brandy rate to remove most of the low-boiling aldehydes, sulphites and esters. Some producers are also known to separate another small fraction (*ca.* 10-20%) of the product rate as low oils, or a high boiling stream from a level one or two trays below the brandy spirit tray to reduce the level of fusel oils in the product. The concentration of higher alcohols in the tray liquids of a concentrating section producing brandy at 83-85% v/v is usually at its maximum at two trays below the product level. This maximum concentration of higher alcohols is ± 2 to 2.5 times that of the product and occurs where the tray liquid indicates approximately 60 – 67% v/v. The disadvantage of this technique is that the volume of brandy is reduced by the volume of the low oils fraction removed. This is usually re-distilled to recover the alcohol as a neutral spirit (Guymon, 1974a).

In practice, perhaps two thirds of the trays lie between the feed and product tray, and the remaining one third of the trays at the top are used for concentrating the low boiling impurities into the heads cut. The trays are usually spaced 30 cm apart. The stripping or wine section typically contains 18-22 sieve or perforated trays with a 38-45 cm spacing. Direct or open steam is the standard heat source. Column diameters are usually 5-6 feet, although some larger and smaller ones can also be used. Feed rates to the stripping section are usually 11000 - 30000 litres per hour (Guymon, 1974a).

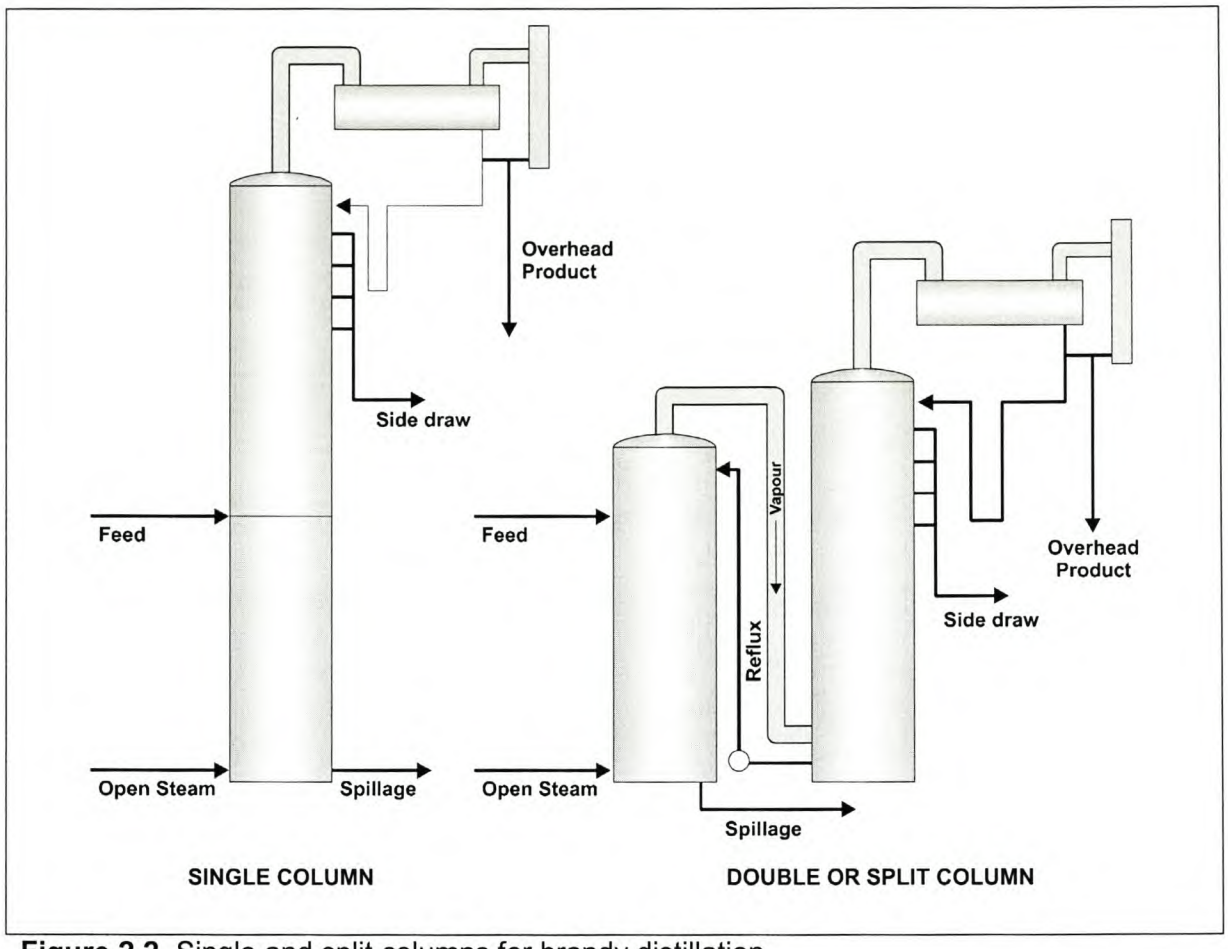


Figure 2.2 Single and split columns for brandy distillation.

2.3.5 SOUTH AFRICA

In South Africa, three brandy categories are produced using both column and potstill distillation. Neutral wine spirit at 96.4% v/v is produced during column still distillation whereas potstill brandy is produced using the *methode chartentais* of double distillation. The pot distilled brandy must then be matured for at least three years in oak barrels no larger than 340 litres (Weitz, 1997).

The three different brandy categories are:

1. Blended brandy (43% v/v). This is a blend comprising a minimum of 30% potstill brandy (matured for at least 3 years) and a maximum of 70% neutral wine spirit. These brandies are made to be enjoyed with mixers.
2. Potstill brandy (38% v/v) must contain a minimum of 90% pot distilled brandy, which has been matured for at least three years. A maximum of 10% neutral wine spirit may be added to the blend. These brandies are rich and full flavoured and are best savoured on their own or over ice.
3. Vintage brandy comprises a minimum of 30% wood matured potstill brandy, maximum 60% matured wine spirit and a maximum of 10% unmatured neutral wine spirit. The potstill and wood matured spirit must be of the same age and must be at least eight years old (Weitz, 1997).

2.3.6 PROOF AND VOLATILITY – AN IMPORTANT CONCEPT IN DISTILLATION

The behaviour of higher alcohols and fatty acid esters during distillation is clarified by the accompanying figures, prepared from vapour liquid equilibrium data (Williams, 1962) and illustrated graphically by Guymon (1974a). The volatility (concentration of a component in the vapour phase divided by that in the liquid phase at equilibrium) for several alcohols or esters added in small amounts (less than 1%) to various strengths of ethanol-water solutions, is shown as a function of alcohol concentration of the equilibrium liquid (**Figure 2.3** and **Figure 2.4**). A higher molecular weight and high boiling alcohol such as isoamyl alcohol is markedly less volatile than ethyl alcohol at high alcohol strengths since isoamyl alcohol is soluble in ethyl alcohol in all proportions. Normal binary solution behaviour for isoamyl-ethyl alcohol mixtures is exhibited. With water, however, in which isoamyl alcohol is only slightly soluble, the volatility of isoamyl alcohol is greatly enhanced, characteristic of a partially miscible binary system, which exhibits a minimum boiling point azeotrope (Guymon, 1974a).

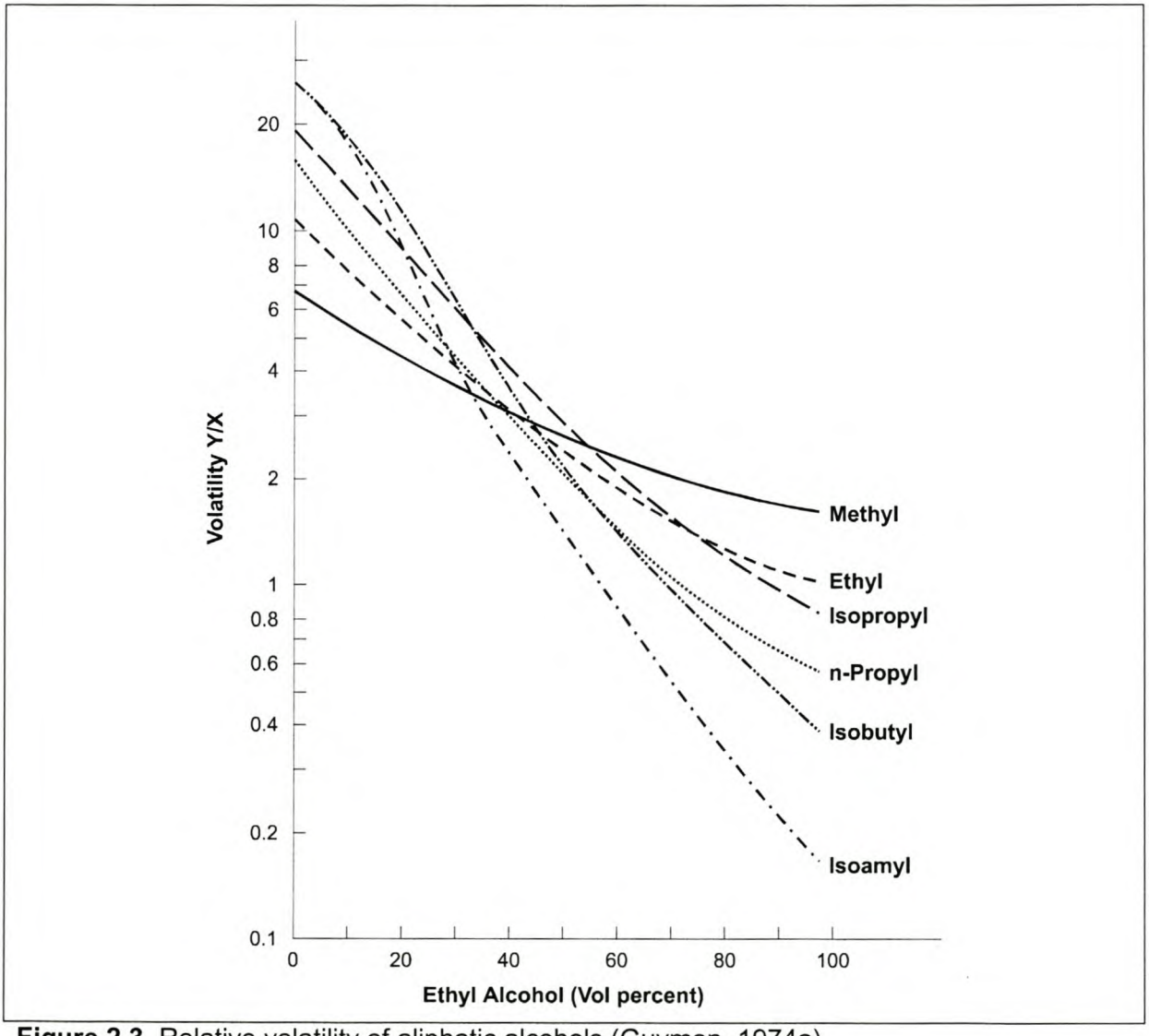


Figure 2.3 Relative volatility of aliphatic alcohols (Guymon, 1974a).

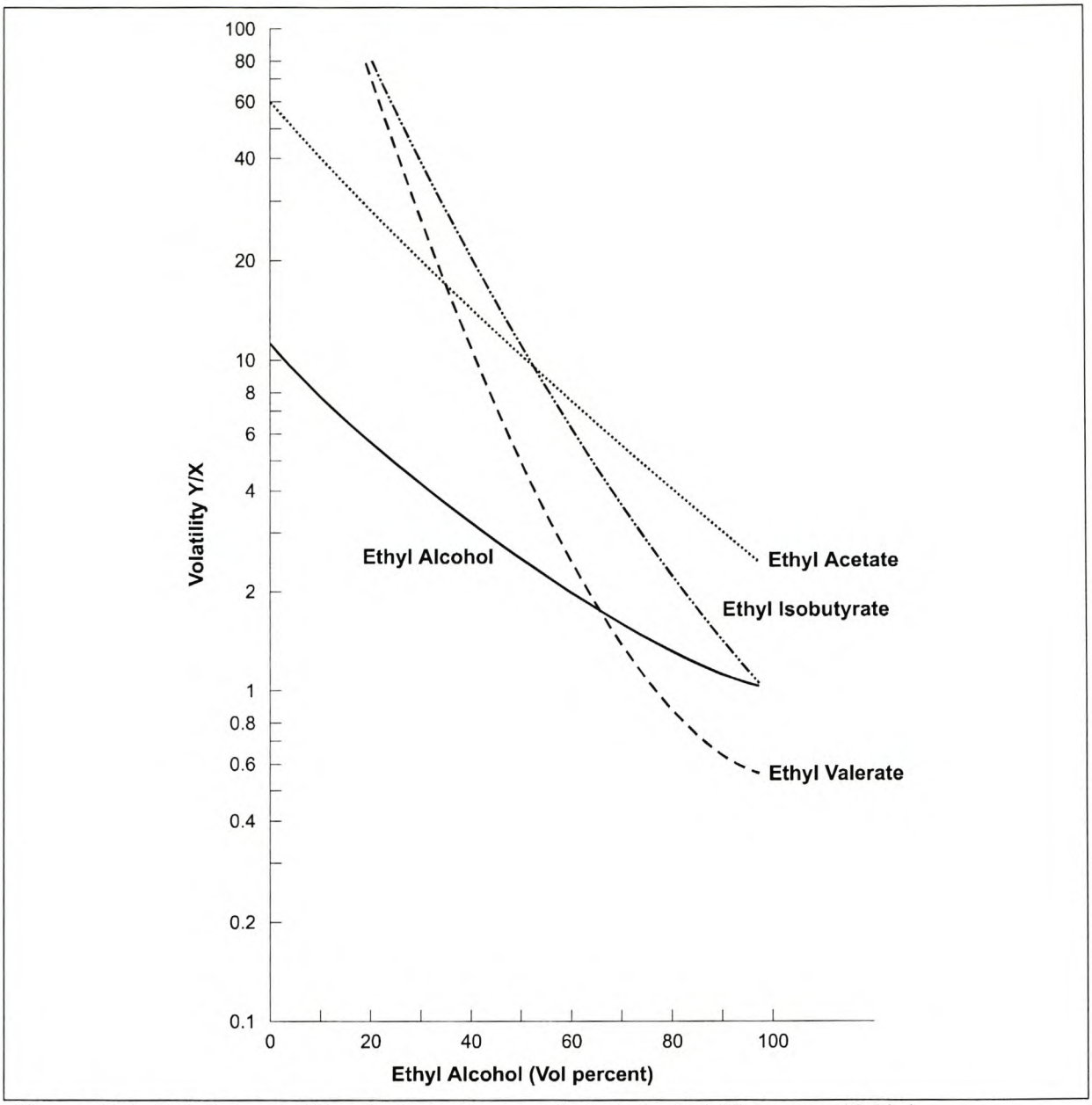


Figure 2.4 Relative volatility of ethyl esters and ethyl alcohol (Guymon, 1974a).

The proof strength at which the volatility curve of a particular component intersects that of ethyl alcohol indicates that proof at which the minor constituent will be concentrated in a fractionating column at the minimum condition of total reflux. For practical conditions, the maximum concentration of a particular congener or minor component occurs at a proof in the column at which its volatility is approximately equal to the internal reflux ratio (L/V where L is the molal liquid or overflow rate and V the molal vapour rate). This can be established by the technique of writing material balances or operating-line equations with respect to the particular congener, as well as the McCabe Thiele method in which molar liquid and vapour rates are assumed constant (Williams, 1962; Guymon, 1974a).

2.3.7 HIGHER ALCOHOL AND ETHYL ESTER CONCENTRATIONS AS AFFECTED BY THE DISTILLATION PROCESS

The reasons for the distillation behaviour of higher alcohols lie in their physical properties in relation to ethyl alcohol and water. A large number of the congener compounds present in wine, which distill over into brandy have boiling points above the maximum of 100 °C and therefore above the maximum boiling temperature in a continuous distillation column or in a pot still. This is only possible because of the thermodynamic properties and behaviour of solutions. A high boiling, distillable compound typically has a very limited solubility in water, but is generally mutually soluble with ethanol in all proportions.

The behaviour of isobutyl alcohol, a relatively minor compound of wine formed during fermentation and one of the major components of fusel oil, can serve as an example. Isobutyl alcohol has a boiling point of 108 °C at 1 atm. pressure, and has a solubility in water of ± 2 mol %, but is soluble in ethanol in all proportions. However, a boiling point compositon diagram for the binary system of isobutyl alcohol and water (which indicates the equilibrium between liquid and vapour phases at 1 atm for all binary compositions measured on the x-axis and temperatures plotted on the y-axis) represents one of a heterogenous azeotrope. Any mixture having an overall composition exceeding the solubility of water in isobutyl alcohol will distill at 90°C and the vapour will have a constant compositon of 33.5 mol %, the azeotrope. Since this vapour, if condensed, forms two equilibrium liquid phases, it is called a "heterogenous azeotrope". The behaviour of isobutyl alcohol in very dilute solution, where only a fraction of the alcohol is present, and hence all in solution in the water, is of particular interest to brandy distillation. Isobutyl alcohol has a greatly enhanced volatility, about 25 times more in the vapour than in the liquid phase at equilibrium (Guymon, 1974a).

Isoamyl alchohol behaves in a similar manner to isobutyl alcohol. It is mutually soluble with ethanol and has a higher boiling point of 132 °C, and so has a lower vapour pressure than ethanol (B.P 78.3 °C). The binary system of isobutyl and ethyl alcohols constitutes what is termed a normal system, so that the compound with the lower boiling point, ethanol, is more volatile than the isobutyl and isoamyl alcohol. Thus isobutyl and isoamyl alcohol are forced towards the bottom of the column in a fractional distillation in which ethanol is the other binary component. However, with water, isoamyl alcohol has a very limited solubility. The binary system of water-isoamyl alcohol is a partially miscible system, which yields a constant boiling mixture or azeotrope boiling at 92.5 °C. In water, or very dilute ethanol solutions, isoamyl-alcohol thus has an enhanced degree of volatility. This is manifested by the K-values or volatility constants of isoamyl alcohol in dilute solutions as a function of alcohol-water solutions (K-value is the ratio of the equilibrium concentration in the vapour phase to the liquid phase). The K-values for isoamyl alcohol as a function of alcohol proof are seen in **Table 2.1**.

Table 2.1 K-values for isoamyl alcohol as a function of alcohol proof (Guymon, 1974a)

Proof	0°	40°	80°	120°	160°	200°
K (isoamyl)	30	12	4	1.1	0.3	0.15

In summary, organic compounds must have some vapour pressure at the temperature of the brandy distilling process. However, a relatively high boiling point compound (B.P. 250 °C or more) will distill in appreciable quantities if it has a very low or insignificant solubility in water with the consequent tendency to form a heterogenous azeotrope and thus a markedly enhanced volatility in dilute ethanol solutions. Another example of interest is 2-phenyl ethanol, which has a very distinct rose-like aroma. Its boiling point (220 °C) is about the same as ethyl caprate, but 2-phenyl ethanol distills more weakly than the fatty acid esters because it has a greater solubility in water. Accordingly, little or no 2-phenyl ethanol is found in brandy as it distills over most abundantly in the late brandy fractions and in the tails. The ethyl esters of straight chain fatty acids, caprylic (C_8), capric (C_{10}) and lauric (C_{12}) are products of yeast metabolism and are rather abundant congeners of brandy and other distilled beverages. These fatty acid esters are similar in behaviour to isoamyl alcohol except that they have higher boiling points at lesser solubilities in water. In simple potstill distillates they distill over almost completely in the first fractions, more rapidly than the higher alcohols. The volatility of methanol exhibits the opposite behaviour. Whereas it is more volatile in high proof solutions, it is less volatile than ethanol in low proof solutions. Accordingly, methanol is more concentrated with respect to ethanol as successively lower proof fractions of distillates are collected from a simple pot distillation (Guymon, 1974a).

2.4 THE VOLATILE AROMA COMPOSITION OF WINE DISTILLATES

2.4.1 ESTERS

Esters are some of the most volatile compounds present in wine distillates and are known to contribute to their character and quality, even when they comprise in total only 9 to 14% of the total volatile compounds present. According to Postel and Adam (1990) one can expect to find at least 40 to 50 mg/ 100 ml A (A = absolute alcohol) of total volatile esters in finished brandies.

Von Adam *et al.* (1996) found that French and Italian distillates possess slightly higher total ester concentrations at 55 and 58 mg/100 ml A respectively (12 and 14% of total volatile compounds present), whilst German distillates possessed the lowest concentration at 10%. Spanish distillates possessed total volatile ester concentrations equal to those of French distillates.

Ethyl acetate and ethyl lactate particularly influence the total ester concentration in wine distillates. They can jointly comprise up to 90% of the total ester content. It is

thus important to consider the origin and factors that may influence the production of these two compounds in further detail.

2.4.1.1 Ethyl Acetate

As the dominant ester in all of the examined distillates, ethyl acetate concentrations vary between 5 to 115 mg/100 ml A, comprising percentage-wise, 22 to 94% of the total ester concentration (Von Adam *et al.*, 1996). Ethyl acetate levels can thus vary considerably in distillates. High concentrations of ethyl acetate are normally the results of undesirable microbial action taking place in the base wines (Postel and Adam; 1990a, 1990b), but can also be influenced by the distillation process.

In the *charentais* method of potstill distillation, ethyl actetate is a component that appears mainly in the heads fraction of the distillate. By increasing the volume of heads fraction collected, the ethyl acetate concentration can be reduced in the heart fraction of the distillate. In this manner, Von Adam *et al.* (1996) were able to reduce the ethyl acetate concentration in the 75% vol hearts fraction, from 67 mg/100 ml A (0.4 % of total volume separated as the heads fraction) to 13 mg/100 ml A (1.6 % of total volume separated as the heads fraction).

During continuous distillation (column with 10 plates running at equilibrium reflux) without separation of the heads fraction, the ethyl acetate concentration remains relatively constant in all alcoholic fractions drawn. These fractions may range from 20.3% to 94% vol of alcohol. With a 1% removal of the heads fraction in a column still with 20 plates, the ethyl acetate concentration in the 93% vol fraction, can be reduced by as much as 87% of its original concentration present in the base wine (Von Adam *et al.;* 1996). Thus, when column distillation takes place with rectification, the levels of ethyl acetate and other volatile compounds can be reduced to a greater degree than in a normal potstill distillation (Von Adam *et al.;* 1996).

In Italy an initial potstill distillation to produce low wine is performed, after which the second distillation (with removal of the heads and tails fraction) is performed in a column still (Von Adam *et al.*; 1996). Different distillation techniques can account for the varying levels of ethyl acetate in the different groups of wine distillates studied. German distillates (5 - 46 mg/100 ml A), Italian distillates (8.6 - 115 mg/100 ml A) and Spanish distillates (15 - 41 mg/100 ml A) showed large variations in their ethyl acetate concentrations (Von Adam *et al.*; 1996). Postel and Adam (1990) recommended that there be a minimum of 25 mg/100 ml A and a maximum of 85 mg/100 ml A ethyl acetate present in all wine distillates.

2.4.1.2 Ethyl lactate

Ethyl lactate is a tails fraction component (Leaute, 1986). Depending on the distillation technique used and the point at which the tails fraction is drawn, only 7 to 16% of the total ethyl lactate concentration is actually found in the heart fraction of the distillate (Von Adam *et al.*; 1996). Even when column distillation is employed, the levels of ethyl lactate are still very dependant upon the alcoholic cutoff point used

(Postel and Adam, 1992). The ethyl lactate concentration decreases dramatically after an alcoholic cutoff point of 85% has been reached (Von Adam *et al.*, 1996).

Malolactic fermentation, which can occur during storage of the base wine prior to distillation can strongly influence the presence of ethyl lactate (Du Plessis *et al.*, 2002). Thus concentrations above 25 mg/100 ml A usually point to microbially influenced base wine (Von Adam *et al.*, 1996). According to Cantagrel (1992), a wine distillate made from microbially spoiled wine, may contain as much as 60 mg/100 ml A ethyl lactate (described as sensorially poor and unfavourable), whereas one containing 22 mg/100 ml A was judged to be pleasant and of good quality. Of course, this cannot be purely ascribed to the samples' ethyl lactate contents. Of the 187 European samples analysed, ethyl lactate concentrations were found to vary between 0.4 to 42 mg/100 ml A (Von Adam *et al.*; 1996).

2.4.1.3 Ethyl esters of caproic, caprylic, capric, myristic, lauric and palmitic acid

Significant variation can exist in the levels of longer chain ethyl esters in wine distillates ranging from 0.3 to 10 mg/100 ml A (Von Adam *et al.*, 1996). These authors found that cognacs could be distinguished from other brandies on the basis of their high levels of longer chain ethyl esters. They also noted that, amongst the French distillates, the *Aquit jaune d'or* samples contain the highest relative levels of these esters, at an average of 7.2 mg/100 ml A. The *Aquit blanc* and armagnac distillates with average values of 3.9 and 3.6 mg/100 ml A respectively, were comparable to armagnacs (4.3 and 3.8 mg/100 ml A) and French brandies (4.0 mg/100 ml A). German wine distillates had concentrations in the same order of magnitude, with an average of 3.6 mg/100 ml A. Spanish wine distillates possessed a relatively high average concentration of 4.7 mg/100 ml A, while the Italian wine distillates possessed the lowest levels at an average value of 1.5 mg/100 ml A (Von Adam *et al.*, 1996).

Postel and Adam (1992) and Cantagrel (1992) showed that this particular ester fraction is influenced strongly by the amount of lees that is distilled with the wine. Of particular interest here is the ratio of ethyl caprate to ethyl caprylate (C_{10}: C_8). With increasing fractions of added lees, the concentration of ethyl caprylate increases significantly above that of ethyl caprate. Cantagrel (1992) found that the level of ethyl caprylate increased by a factor of 2.6 in samples with a large fraction of accompanying yeast lees (when compared to that with no or little accompanying yeast lees). The level of ethyl caprate increased by a factor of 4.6 in this instance. However, varying amounts of yeast lees fractions have no significant effect on the concentrations of ethyl acetate, ethyl lactate, diethyl succinate or the higher alcohols. He also reported that wine distillates resulting from distillation with a large fraction of yeast lees, had a higher number of organoleptically perceivable esters, adding a distinctly floral aroma to the samples. However, he stressed the importance of using fresh, good quality yeast lees, saying that old, poor quality lees could lead to wine

distillates with organoleptic defects (only fresh yeast lees must be used in the distillation process).

According to Von Adam *et al.* (1996), the C_6 to C_{16} esters behave differently in terms of their volatility and time of distilling over during the classical double distillation process. When the heads fraction was set at 1% of total distilling volume, and the heart fraction was swung to tails at 60% vol, the heart of the distillate showed a ± 34% decrease in ethyl caproate concentration, approximately 40% for ethyl caprylate, 50% for ethyl caprate and a 60% decrease for ethyl laurate, -myristate and –palmitate. However, during column distillation, ethyl caproate, caprylate, caprate and laurate all remained stable up to 87% vol. Ethyl myristate and palmitate remained stable until 84.6% vol (C_{10}: C_8 = 2.6 to 2.3). There was a strong decrease in all of the above-mentioned compounds at 90% vol. At this point the ratio of ethyl caprate to ethyl caprylate shifted to favour ethyl caprylate to 2.1 at 88% vol, 1.5 at 91% vol, and 0.5 at 94% vol (Von Adam *et al.*, 1996). Thus the ratio of ethyl caprate to ethyl caprylate can serve as a valuable indicator for the amount of yeast lees used during distillation. In distillates made from clarified wines, wines with very small lees fractions and wines distilled at a high cutoff value, higher levels of ethyl caprylate than ethyl caprate can be expected. With increasing yeast lees fractions, this ratio is reversed, favouring increased levels of ethyl caprate. Under normal distillation conditions, when a portion of the yeast lees is distilled with the wine, a ratio above 0.3 can be expected for ethyl caprate: ethyl caprylate (Cantagrel, 1992).

German distillates varied between 0.6 to 1.9 (mean = 1.1) in their C_{10}: C_8 ratios, *Aquit jaune d'or* distillates between 0.7 and 2.0 (mean = 1.4), *Aquit blanc* between 0.5 and 2.3 (mean = 1.0) and the armagnac distillates between 0.6 and 1.4 (mean = 0.8). The Italian distillates varied between 0.3 and 1.7 (mean = 0.6) and the Spanish distillates between 0.4 and 1.9 (mean = 1.2) (Von Adam *et al.,* 1996). Von Adam *et al.* (1996) thus concluded that the *Aquit jaune d'or* samples were produced using relatively large fractions of yeast lees in a potstill distillation. The remaining distillates seem to have been produced with very small lees fractions in a potstill (Italian samples) and with larger lees fractions in a column still (Spanish distillates).

Because of the filtration process that takes place on the finished brandy product, it is difficult to make a prediction as to what levels of these esters should be present in the wine distillates in order to enhance final product quality. Filtration has been shown to decrease the ethyl ester content in distilled products (Da Porto and Celotti, 2000). Von Adam *et al.* (1996) recommended, in conjunction with a sensory evaluation, a total longer chain ester (C_6: C_{16}) content of 2.0 mg/ ml A.

2.4.1.4 Ethyl propionate, diethyl succinate and ethyl butyrate

Ethyl propionate, diethyl succinate and ethyl butyrate are all so-called spoilage indicators which can be used to evaluate the distillate raw material (Postel and Adam, 1992). The concentration of ethyl propionate should not exceed

1.5 mg/100 ml A. Higher values are generally found in distillates made from microbially spoiled wines (Von Adam *et al.* 1996).

Diethyl succinate, which according to Cantagrel (1992) increases to a greater extent than ethyl lactate during storage of the wine (after 5 months more than 226%), could be found at levels between 0.05 to 3.2 mg/100 ml A in wine distillates (Von Adam *et al.* 1996). It possesses similar behaviour to ethyl lactate during distillation, and can thus be reduced by carefully controlling the point at which the tails fraction is begun. According to Postel and Adam (1992), levels above 2 mg/100 ml A indicate a microbially spoiled wine used for the distillation. Generally, where ethyl lactate concentrations are high, elevated levels of diethyl succinate will also be present (Von Adam *et al.*, 1996).

According to Cantagrel (1992), ethyl butyrate levels in distillates made from wines of good quality lie in the order of 0.1 mg/100 ml A. In distillates made from spoiled wines, this value may be as high as 4.0 mg/100 ml A. A noticeable organoleptic defect becomes apparent when ethyl butyrate is present in concentrations of 0.7 mg/100 ml A (Von Adam *et al.,* 1996).

2.4.1.5 Remaining esters

Ethyl formiate (n.d. – 3.8 mg/100 ml A), isoamylacetate (0.04 to 3.10 mg/100 ml A) and 2-phenethyl acetate (n.d. – 1.30 mg/100 ml A) show significant variations in their concentrations in wine distillates (Von Adam *et al.*, 1996). Other esters such as isoamyl esters of caproic, capric and caprylic acid, isobutyl- and butyl acetate, hexyl acetate and isoamyl lactate are present in concentrations less than 1 mg/100 ml A (Postel and Adam, 1990; Von Adam *et al.* 1996). Methyl esters of caprylic, caproic, capric, lauric, myristic and palmitic acids as well as the ethyl esters of heptanoic and nonanoic acids are only present in trace amounts (von Adam *et al.,* 1996).

2.4.2 HIGHER ALCOHOLS

The most abundant or important higher alcohols produced by yeasts during fermentation are 3-methyl butanol (isoamyl alcohol), 2-methyl butanol (active amyl alcohol), 2-methyl propanol (isobuanol) and 1-propanol (n-propanol). All distilled beverages whose aroma and flavour reflect those of their raw materials, such as brandy, contain significant levels of these higher alcohols.

The ideal concentrations in brandy have been subject to controversy for the past five decades (Warkentin, 1952; Guymon, 1972). Guymon (1972) stated that the problem with higher alcohols in brandy is mostly a question of too much rather than too little. Other researchers have suggested that the ratios of higher alcohols may be related to brandy quality (Reinhard, 1969; Hogben and Mular, 1976; Postel and Adam, 1980). Since the odour and taste effects of isoamyl and active amyl alcohols are not particularly pleasing, one might argue that fusel oil concentrations should be as low as possible. However, several compounds that exhibit somewhat unpleasant sensory characteristics in their pure states add complexity and interest when present

in dilute amounts. Warkentin (1952) speculated that this is true of higher alcohols. Traditionally, brandy or whisky flavours have been partly attributed to the higher alcohol components of the total congener content and it is said that they impart a sense of depth or body (Guymon, 1972). Furthermore, some of the higher alcohols will be esterified during ageing, and these esters are more aromatically pleasant than their fusel alcohol derivatives.

The range of higher alcohol contents in brandies is approximately 600 to 1200 mg/L. Warkentin (1952) classified those containing between 600 and 750 mg/L as light bodied, from 750 to ca. 900 mg/L as medium bodied and those containing more than 900 mg/L as full or heavy-bodied. A brandy distillate containing approximately 800 mg/L of higher alcohols was optimal. However, this optimum level of fusel alcohols in brandy remains a considerably subjective question, and depends on personal preferences and experience. A producer may choose to market a product that is light in body and designed to appeal to his concept of consumer preference. Another producer may adopt a policy of making a fuller-bodied brandy, one that may exhibit more aroma and flavour and which may well benefit from, even necessitate, a greater degree of ageing in wood. One refers to a degree of ageing rather than length of ageing for length of storage in itself is not as significant as the compositional changes occurring during ageing. These depend on the age and nature or activity of the wood, storage conditions and original composition of the distillate (Singleton, 1995).

In studying the role of cultivar and region on South African brandy quality, Hough (1985) found that the increased concentrations of isobutanol and isoamyl alcohol present in a distillate derived from Palomino grapes make it a less desirable cultivar for use in brandy production than Colombar. He found that, under South African conditions, Colombar produced an organoleptically more acceptable distillate. At the same degree of ripeness (measured in °Balling), Colombar has a much lower sugar/ acid ratio, which therefore makes it more suitable for brandy production. Palomino was also found to oxidize very quickly and resulted in brown, visually unpleasing wines (Hough, 1985). He made wines and distillates from four regions in South Africa, namely Vredendal, Robertson, Barrydale, and Worcester/ Rawsonville and observed that:

- The methanol concentration in Palomino was significantly higher (0.92 – 2.5 times) than that of Colombar in all regions in all vintages studied.
- Propanol values for Palomino were significantly lower than that of Colombar in all regions except for Robertson in both vintages, where no differences could be found.
- Brandies from the Robertson region had significantly higher concentrations of isobutanol and isoamyl alcohol for both cultivars and for all three vintages studied.

Other observations included,

i. The ratios of isoamyl alcohol to propanol as well as isobutanol to propanol were higher in Palomino than in Colombar with the exception of those from the Robertson region and one vintage from the Barrydale region.

ii. Robertson Colombar had higher isoamyl alcohol to propanol and isobutanol to propanol ratios than the other three regions for the same cultivar and vintage.

iii. Wines and distillates originating from Robertson tended to have higher total alcohol concentrations than the other three regions for both cultivars and all three vintages studied. This was statistically significant for two out of the three vintages.

iv. The tasting panel used preferred Colombar to Palomino from all regions and vintages, with only one exception, namely the Palomino from Worcester in 1983.

v. The organoleptic results showed a high correlation to the higher methanol and lower propanol concentrations present in Palomino when compared to Colombar

Hough (1985) thus concluded that the increased amounts of isobutanol and isoamyl alcohol in Palomino, as reflected by their respective ratios and total higher alcohol concentrations, make it a less desirable cultivar than Colombar for use in brandy production.

Hough's results (1985) confirmed the findings of Olschimke and Junge (1973), who set out a number of criteria for the evaluation of brandy. The ratio of isoamyl-alcohol to isobutanol must be at least 3:1 and that of isoamyl alcohol to propanol must be between 4:1 and 8:1 while the ratio of isobutanol to propanol should be between 1:1 and 2:1.

2.4.3 VOLATILE FATTY ACIDS

In wine distillates, the fractional composition of volatile fatty acids should not vary greatly from its base wine raw material, because all of the fatty acids containing 1-10 carbon atoms are volatile enough to be distilled over. The only other source of fatty acids could be the autolysis and thermal degradation of yeast cells during distillation (Sponholz *et al.*, 1990). In brandy production it is common practice to distill the base wine with a portion of its lees (Leaute, 1986). This factor is especially important when one considers the fatty acids with an even number of carbon atoms, ($C_2 - C_{10}$), which are products of the yeast biochemical metabolism (Von Adam, 1996).

The volatile acid composition, calculated as acetic acid, was reported by Suomalainen *et al.* (1965) to be as high as 70 mg/L A. Kain and Bandion (1968) reported 8-88 mg/L A in wine brandies. Nykänen (1986) reported that, without consideration of acetic and amino acids, octanoic and decanoic acids are the most prominent with a percentage composition of 30%, followed by hexanoic acid (8%)

and propionic, isobutyric, isovaleric acid which all comprise 3% of the total volatile fatty acids, respectively.

Sponholz *et al.* (1990) isolated volatile fatty acids from wine distillates, French and German brandy products and wine lees distillates. They confirmed that in all brandies, as is the case for wines, acetic acid is quantitatively the most prominent volatile acid. It was noted that a strong concentration effect in the volatile fatty acids did not take place from the first to the second distillate. The concentration of methionic acid remained almost constant at 36 mg/L in all samples. In the first distillate (low wine) the concentration of even chained fatty acids was found to be relatively high: 9.8 mg/L butyric acid, 8.6 mg/L hexanoic acid, 28 mg/L octanoic acid, and 11 mg/L decanoic acid. This confirmed that these compounds are partially yeast derived. A propionic acid concentration of 9.8 mg/L, which is in the same order of magnitude as the previously mentioned acids, was thought to be partially derived from lactic acid bacteria that may have been present in the base wine. The free fatty acids such as 2-methyl-propionic acid (3 mg/L), 2-methyl- (1.1 mg/L) and 3-methylbutyric acid (1.9 mg/L), which are derived from the amino-oxygen exchange mechanism, were quantitatively minor components (Sponholz *et al.*, 1990).

In the second distillate, Sponholz *et al.* (1990) found that hexanoic acid maintained its concentration levels, whereas the octanoic and decanoic acid concentrations increased, although not in the same proportion as that of the alcohol concentration in this process.

Sponholz *et al.* (1990) were able to distinguish German brandies from their French counterparts. Most noticeable was the significantly lower concentration of fatty acids, in particular those of even chain length, (predominantly yeast derived), in German brandies. This difference is most likely due to a difference in distillation separation techniques used during the second distillation (*i.e.* separation of head, heart and tail fractions), as the base wines used for brandy in both countries are known to be very similar. The practice of performing the first distillation in the presence of yeast lees is also common to both countries.

2.5 FACTORS INFLUENCING THE COMPOSITION AND QUALITY OF WINE DISTILLATES

The quality of a wine distillate depends on factors incorporated at every step of the production process, and include:

- Soil and geographical features of the origin of grapes used
- Grape maturity and grape variety
- Viticultural practices
- Vintage variation
- Vinification techniques (including yeast strain used)

- Storage of the wine prior to distillation
- Distillation technique

All of the above mentioned, except for the influence of viticultural practices will be discussed in further detail in this review. The manipulation of viticultural practices to influence the quality of wine distillates and ultimate brandy quality, which falls beyond the scope of this study.

2.5.1 REGIONAL EFFECTS

Climate may influence brandy quality by affecting mould and rot, especially in wet vintages and in cool climates. Where varietal aroma is not an important quality factor, however, climatic region may not have such a great effect. For example, with certain non-distinctive varieties it has been shown that crop level, usually an important consideration in varietal character, made no significant difference in general wine quality (Weaver *et al.*, 1961). Lafon (1964) in studying the less delicate brandies from warm vintages in Cognac, however, concluded that much of cognac's quality is due to the cool climate, which benefits the aroma constituents, the concentration of aroma with simultaneous lower alcohol production, and the storage of wine with low alcohol and no sulphur dioxide.

2.5.2 GRAPE MATURITY EFFECTS

As grapes approach maturity, the aroma level rises and berry aroma composition changes (Berg, 1953). It is generally assumed that higher must acidities yield higher quality wine aromas, better resistance to microbial spoilage, better flavour development, less yeast cell autolysis, less acetaldehyde production, less volatile acid and more aromatic principles due to a lower pH (Amerine and Joslyn, 1970). Thus a considerable debate has arisen as to the optimal level of maturity for grapes to be harvested and used in producing a high quality wine for brandy and cognac distillation. In comparing 24 years of tasting records from the Cognac district, Lafon (1964) observed that high quality distillates have never been made from wines with more than 10.5% alcohol. Amerine and Joslyn (1970) also recommended lower maturities in order to concentrate flavour volatiles. Wine acidity *per se* has been considered an important factor in brandy quality. Probably the most important effect is that resistance to bacterial spoilage in wines stored without SO_2 is increased, especially in the lower alcohol wines. Other effects can include increases in ester concentrations (due to lowered pH) or possible increased liberation of terpene-type compounds from acid induced hydrolysis during a long pot distillation (Amerine and Joslyn, 1970).

2.5.3 GRAPE CULTIVAR EFFECTS

There is still a considerable debate as to which cultivar possesses the most desirable fruit for producing high quality brandy distillates. No particular variety has been universally shown to be the best. Guymon (1967) recommended white or lightly coloured varieties with a moderately distinct and pleasing aroma, good tonnage, resistance to oxidation and resistance to mould and rot. Lafon *et al.* (1964) recommended the St Emillion cultivar (with its better resistance to *Botrytis cinerea* and higher acid content) to be replacing Folle Blanche and Colombard in the Cognac district.

French Colombard is an important variety in the Cognac district and its wine has a distinctive leafy or stemmy aroma (Quady and Guymon, 1973). It possesses a high natural acidity but, on the other hand, exhibits a greater tendency towards browning, which indicates that it has a high phenolic content. High tannin fruit was shown to result in poor quality distillates. These authors found that French Colombard made a wine with more distinctive aroma than Thompson Seedless. However, Thompson Seedless produced a significantly better distillate than French Colombard. It was concluded that quality from Thompson's Seedless was little affected by maturity, while that from French Colombard decreased with increasing maturity. Correlation coefficients indicated that better brandies were produced from wines with fruity, but not overripe or oxidized aromas. The better brandies were lower in ester, fusel oil and aldehyde concentrations and inexplicably higher in total acidities. Brandy quality was found to correlate positively with brandy acidity. Although volatile acidity in the wine correlates positively with brandy acidity, it does not correlate with brandy quality. The acids which affect brandy quality are thus not those accounted for in volatile acidity, and are predominantly also organic acids. Quady and Guymon (1973) thus speculated that this result may reflect the beneficial result of small amounts of fatty acids which can also influence brandy quality.

2.5.4 VINTAGE EFFECTS

Von Adam *et al.* (1996) attempted to ascertain whether brandies had changed both in chemical profiles as well as sensory characters in differing years of production. They studied samples from 1989 (the year before EU trade regulations were implemented determining minimum and maximum allowed levels of particular compounds present in brandies) through to samples from 1993. These brandies were selected so that they were all made from the same cultivar, wine distillation process and possessed the same wine extract and similar analytical composition. Thus, only the production year of the brandies varied amongst samples.

Difference tests with a ranking order were performed using 8 trained tasters and differences amongst samples were found to be very small. Significant sensory differences were thus still not noticeable even after the EU regulations governing brandy composition were changed (Von Adam *et al.,* 1996). Von Adam *et al.* (1996) concluded that regional effects and varying distillation effects are far more significant

in determining differences between wine distillates than the year of production. Hough (1985) in evaluating wine distillates made from Colombar and Palomino grapes in four South African wine growing regions, also concluded that cultivar and regional effects are more significant in determining distillate quality than vintage effects.

2.5.5 EFFECT OF WINEMAKING PROCESS ON VOLATILE COMPOSITION OF DISTILLATES

Carnacini and Di Stefano (1989) studied the effect of the winemaking process on the volatile content of distillates. They divided a batch of grapes into two lots. The first lot underwent soft pressing, cold settling with silica sol and gelatine, and underwent fermentation without SO_2 with non-sulphur dioxide producing yeasts. Upon completion of fermentation, the wine was allowed to settle and clarify. It was then further divided: The first batch came from the lower part of the tank and contained all yeast lees (wine A). The second was clear wine from the top of the tank (wine B)

The second lot of grapes was destemmed and crushed by being subjected to continuous pressing. The juice was fermented without SO_2 and was allowed to undergo a spontaneous, natural fermentation. The lees content was 8% (wine C). The resulting base wines showed significant differences in reduced extracts and total polyphenols. These differences can be attributed to the different lees content as well as the winemaking process used. The aromatic profiles of the wines were very similar, with only ten compounds showing statistically significant differences. Only three compounds, namely γ-butyrolactone, isovaleric acid and ethyl octadecanoate were found in lower quantities in the wine containing lees (Carnacini and Di Stefano, 1989).

The first distillation gave rise only to a concentration in alcohol and volatile compounds, and the low wines displayed significant differences in a considerable number of compounds. The lees content was noted to substantially influence the composition of the first distillate. Distillation of wine with no lees gave rise to a product especially rich in low boiling compounds. The highest concentrations of C_8 to C_{16} fatty acid ethyl esters were present in the first distillate of the wine containing the most lees. Furfural, the *trans*- and *cis*-forms of furanlinalool oxide, methylfurylketone, 5-methyl and 5-ethyl furfural, 1,1,6-trimethyl-1,2-dihydronaphthalene, actinidol, eugenol and neroldiol were formed during the first distillation due to the heating effect on the sugars, glucosides and norisoprenoid precursors (**Table 2.2**) (Carnacini and Di Stefano, 1989).

After the second distillation, when the heart of the distillate is separated from the heads and tails, only twelve compounds were found to be statistically the same in all three products. Five of these, namely isoamylacetate, 1-pentanol, 1-heptanol, diethyl succinate and ethyl octanoate were already present in equal amounts in the first distillates. The remaining seven compounds (isoamyl alcohol, ethyl pyruvate, 1-octanol, γ-butyrolactone, isovaleric acid, phenethyl alcohol and 4-ethyl phenol) were

present in considerably lower concentrations in the heart fraction, and were present in differing quantities in the head and tails fraction (**Table 2.3**). Comparison of the compounds having significant variation in the three spirits further confirmed that both the lees content and winemaking process influence the resulting distillate composition. Comparison of second distillates from the same wine but with different lees contents showed, as was already noted for the first distillates, that the lees containing distillate contained more high boiling compounds in its distillate than the distillate originating from wine without any lees. Furthermore, a decrease in the concentration of compounds was noted in the lees derived distillate. In the heart fraction, several substances appeared in significantly differing concentrations amongst the three treatments (Carnacini and Di Stefano, 1989). This again reaffirms the importance of base wine composition. An inadequate winemaking process will give rise to an inferior quality distillate and the lees content in a suitably processed wine can also give rise to distillates of differing aroma (Leaute, 1986).

Table 2.2 Result of tukeys test on the volatile compounds of three wines (Carnacini and Di Stefano, 1989) (Values not marked by a common letter differ at $\alpha = 0.01$)

Compound (mg/100 mLA)	Wine A	Wine B	Wine C
1-Heptanol	195 a	46 b	42 b
1-Octanol	53 a	17 b	14 a
Isoamylacetate	148 a	95 b	105 b
Gamma Butyrolactone	686 a	835 b	648 c
Isovaleric acid	301 a	456 b	436 c
Isoamyl decanoate	350 a	342 b	303 b
Benzyl alcohol	346 a	88 b	219 c
4-Ethyl-guaiacol	56 a	4 b	13 c
Ethyl-2-OH-3-phenylpropionate	183 a	84 b	87 b
Ethyl octadecanoate	6156 a	6526 b	7967 c

Unfortunately, Carnacini and Di Stefano (1989) did not include a sensory evaluation of the various products in their study. However, their study proves the importance of winemaking technique on end product characteristics and composition. Since most of the compounds will undergo modifications during aging, the decision as to exactly how much solid matter to include in the base wine will depend on the desired wood matured end product and the duration of wood maturation.

Table 2.3 Results of tukeys test on wines, low wine and heart volatile compound composition (Carnacini and Di Stefano, 1989)

Compounds	Wine A	Lw A	Heart A	Wine B	Lw B	Heart B	Wine C	Lw C	Heart C
1-Propanol	128 a	588 a	667 a	373 a	618 a	727 a	265 a	27a	35 a
1-Butanol	40 a	36 a	40 a	40 a	36 a	51 a	32 a	89a	182 b
Isoamyl alcohol	1153 a	2751 a		1712 a	4721 a		1202 a	1441 a	
Ethyl Lactate	1179 a	1008 a	812 a	1410 a	2017 a	1306 a	1029 a	746a	323 a
trans-3-hexenol	9a	7a	9a	6a	5a	38 b	7a	7a	16 a
cis-3-hexenol	36 a	31 a	29 a	35 a	37 a	51 a	33 a	28 a	36 a
Ethyl octanoate	165 a	651 a	884 a	138 a	291 a	385 a	145 a	12a	27 a
Benzaldehyde	39 a	651 a	72 a	30 a	68 a	109 a	35 a	34 a	51 a
Diethyl succinate	492 a	90 a		508 a	401 a		415 a	319 a	
Ethyl dodecanoate	620 a	452 a	897 a	441 a	416 a	249 a	470 a	371 a	8a
4-Ethyl guaiacol	56 a	806 a	2a	4a	11a	5a	13 a	7a	81 b
Ethyl hexadecanoate	202 a	35 a	674 b	178 a	291 a	247 a	204 a	21 a	123 a
Ethyl isobutyrate	72 a	306 b	344 b	212 a	251 a	338 a	151 a	41 a	121 a
2-Methyl-1-propanol	350 a	1108 a	1424 a	581 a	2194 a	1581 b	395 a	464 a	400 a
Isoamylacetate	68 a	136 a		42 a	125 b		36 a	48 a	
Ethyl hexanoate	111 a	173 a	143 a	97 a	300 b	539 c	89 a	91 a	42 a
Ethyl pyruvate	54 a	34 a		60 a	32 b		49 a	1 b	
1-Hexanol	236 a	519ab	621 b	269 a	793 b	1034 b	240 a	344 a	308 a
1-Heptanol	195 a	39 b		46 a	39 a		42 a	33 a	
Furfural	15 a	379 b	230 c	0	316 b	403 b	14 a	342 b	224 b
1-Octanol	53 a	22 b		17 a	8a		14 a	43 b	
Isoamyl alcohol	148 a	78 b	35 c	95 a	57 a	78 a	105 a	43 b	40 b
γ-butyrolactone	686 a	115 b		835 a	167 b		648 a	152 b	
Ethyl decanoate	56 a	1009 b	1465 b	53 a	133 a	454 a	50 a	1a	8a
Isoamyl octanoate	10a	32 b	50 c	10a	5a	24 b	9a	6a	8a
Isovaleric acid	301 a	28 b		456 a	36 b		436 a	57 b	
Isoamyl decanoate	350 a	77 b	74 b	342 a	8 b	16b	303 a	8 b	1 b
Benzyl alcohol	346 a	171 b	38 c	88 a	95 a	60b	219 a	36 b	28 b
2-Phenyl ethanol	627 a	970 a		794 a	1836 b		600 a	624 a	
Ethyl tetradecanoate	73 a	166 b	246 c	86 a	34 a		95 a	1 b	7 b
Isoamyl dodecanoate	22 a	767 b	376 c	13 a	751 b	533 b	14 a	497 b	81 a
4-Ethyl phenol	160 a	151 a		160 a	34 b		183 a	50 b	
4-Vinyl guaiacol	27 a	69 b	113 c	21 a	17 a	12a	23 a	1a	4a
Ethyl octadecanoate	6156 a	48 b		6526 a	50 b		7967 a	8b	

2.5.6 YEAST STRAIN EFFECTS

The effect of yeast strain and its influence on wine composition has been extensively studied, but relatively little work has to date been done on the influence of yeast strain on wine spirit composition.

Pronounced differences among strains of the same species, based on the quantitative analysis of volatile compounds and processing of analytical data have been reported. Soles *et al.* (1982) reported differences in the production of esters as a function of the yeast strain used, and Giudici *et al.* (1990) reported differences in the case of higher alcohols. These studies used strains from various vineyards, purchased collections or commercialised active dry wine yeasts.

Lurton *et al.* (1995) extensively studied 15 indigenous strains from the same area of production (a Cognac vineyard in France) which had been selected from a previous ecological survey (Versavaud *et al.*,1993). From their pulsed field chromosomal electrophoretic patterns and their mitochondrial DNA restriction profiles, these strains were clearly shown to be different. By quantifying the presence of 43 of the (what are believed to be) most actively participating organoleptic volatile compounds and a variance analysis, a highly significant effect of yeast strain was found for most of the 43 compounds as well as some of the higher alcohol ratios. The effect was particularly pronounced for propanol, butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and for the majority of fatty acid esters, acetaldehyde and linalool (**Table 2.4**).

One aspect of the strain differences was found to involve the relative production of higher alcohols. A principal component analysis was conducted on the same data (Lurton, 1995). The most interesting strains for the production of quality spirits were found in the plane area corresponding to a high ester concentration (along with low acetaldehyde and hexanol levels) combined with moderate to low levels of higher alcohols. Lurton (1995) thus concluded that yeast strain differences seem to be more prominent for the volatile aroma compounds than for conventional criteria such as volatile acidity, production of sulphur compounds and fermentation performance.

Riponi *et al.* (1996) evaluated the behaviour of 15 *Saccharomyces* strains, which were well known for wine production but had not yet been evaluated for brandy production (Suzzi *et al.*; 1985; Giudici *et al.*; 1990; Castellari *et al.*,1992). The yeasts were studied under the winemaking conditions commonly used for brandy (no SO_2 addition, no fining agents, using low sugar containing grapes with a high acidity) and were classified into three groups based on the properties exhibited in previous fermentation tests by other authors.

i. **SC1:**(all *S.cerevisiae*) These strains resulted in a maximum ethanol yield and a minimum total level of minor compounds such as glycerol, higher alcohols and acetic acid.

ii. **SC2**: (all *S.cerevisiae*). These strains were characterized as non-H_2S producing strains. They were distinctive for their high n-propanol and sulphite production

and low level of other minor compounds. They have a strong stabilising action on wines.

iii. **SB:** (*S.bayanus).* These strains were notably different from *S. cerevisiae* strains due to their different production ratio of minor compounds, higher levels of glycerol, succinic acid and higher alcohols (particularly 2-phenyl ethanol) and lower levels of acetic acid. They also synthesize malic acid instead of degrading it.

Table 2.4 Characterization of variables leading to the best discrimination between the 15 yeast strains studied on a small scale (Lurton; 1995)

Compound	Fobs	p(15,16> Fobs)
Propanol/Isobutanol	48.91	< 0.001
Ethyl stearate	37.41	< 0.001
Isoamylacetate	14.75	< 0.001
Isobutanol	13.17	< 0.001
Ethyl caprylate	12.86	< 0.001
Acetaldehyde	9.97	< 0.001
2MeBuOH/3MeBuOH	9.93	< 0.001
3-Methyl-1-butanol	7.83	< 0.001
Linalool	7.29	< 0.001
Ethyl lineolate	7.06	< 0.001
Ethyl caproate	6.11	0.001
Ethyl caprate	5.79	0.001
Hexyl acetate	5.23	0.001
cis-3-hexyl acetate	4.96	0.001
Higher alcohols	4.8	0.001
Propanol	4.56	0.002
2-phenethyl acetate	4.48	0.002
Ethyl lactate	4.45	0.003
2-Phenyl ethanol	4.37	0.003
1,1 diethoxyethane	3.69	0.007
Tetradecanol	3.47	0.009
Isoamyl caprylate	2.78	0.03
2-Methyl-1-butanol	2.34	0.05
Methanol	2.31	0.05
Hexanol	2.28	0.06
Ethyl laurate	2.01	0.09
beta-Damascenone	1.92	0.1
1-vitispirane	1.31	0.3
cis-3-hexenol	1.3	0.3
Ethyl acetate	1.21	0.35

In terms of higher alcohols, the differences were found to be independent of the above-mentioned yeast groups. In fact, the total higher alcohol content was a characteristic of each strain. n-Propanol was found to be the most variable alcohol, its concentration differing up to 30-fold. iso-Butanol showed high variability as almost every strain tested contained a statistically different amount of this compound. The SB group produced lower acetic acid concentrations and higher amounts of glycerol, succinic acid and malic acid with a correspondingly lower yield in ethanol. 2-Phenylethanol was also present in the largest amounts in this group of wines. They showed excellent microbial stability, which is probably due to their low pH and high acidity. The authors felt that group SC1 contained the most favourable distillation characteristics, since they exhibited the highest ethanol production and lowest levels of volatile compounds. Personally, I would view Riponi's SB group as potentially the most favourable since these yeasts produce little SO_2, acceptable alcohol levels and desirable flavour compounds such as 2-phenyl ethanol, which are all very desirable characteristics for a potential brandy yeast strain.

Steger and Lambrechts (2000) noted that the presence of yeast lees has a significant effect on the final concentrations of both higher alcohols and esters in the distillate. Highly elevated levels of ethyl acetate and isoamylacetate produced by one of the strains tested, were found to be sensorially undesirable in the wine distillate. Elevated levels of all esters present, not only the highly volatile ethyl acetate and isoamylacetate, were found in the sensorially most favoured distillates, as were slightly elevated levels of higher alcohols.

2.5.7 AROMATIC COMPOSITION OF WINE DISTILLATES AS A JOINT FUNCTION OF YEAST STRAIN AND DEGREE OF GRAPE MATURITY

Carnacini *et al.* (1993) studied the aromatic composition of wine distillates originating from Trebbiano grapes harvested at 2 different degrees of berry ripeness (9 and 10.5% v/v potential alcohol) using three different yeast strains, which were characterized by varying fusel oil metabolisms and their ability to produce SO_2. These wines were distilled and collected in nine separate fractions. Carnacini *et al.* (1993) found that statistical interaction between the effects of yeast strain and maturation degree influenced almost all of the compounds, especially in the first fractions of the heart. Yeast strain and grape maturity, when considered individually, could also exert an influence, particularly on the first fractions of the heart. In the first heart fraction of the distillate (35% of the whole heart), most of the non-alcoholic vapours are collected and this fraction also seems to be the point at which most differences in the end product are developed (Carnacini *et al.* 1993).

Wine composition was found to be dependant upon the initial degree of maturity of the grapes used, which in turn influenced a large number of compounds present in the distillate up to and including the fifth heart fraction drawn. Differences in concentrations of isoamyl alcohol, isobutylalcohol, ethyl alcohol and 2-phenyl ethanol

were found. Carnacini *et al.* (1993) found that the concentration of propanol is mainly influenced by yeast strain used for fermentation and this was confirmed by Riponi *et al.* (1996). The variation in higher alcohol concentrations remained constant in the first few fractions of the heart, especially the variation in n-propanol, isobutanol and isoamy lalcohol concentrations. 2-Phenyl ethanol exhibited a higher variation in its concentrations. This can be ascribed to the fact that it is a compound that is found primarily in the tails fraction of the distillate (Leaute, 1986).

Carnacini *et al.* (1993) observed that, while ethanol and higher alcohol concentrations decreased during distillation, the non-alcoholic compounds showed a great variability in their concentrations in the different fractions. They found that, when grapes are harvested late, wines with a high ethanol and low higher alcohol content are obtained. In this case, higher alcohols can be completely carried over during distillation by the hydro-alcoholic vapours that arise during distillation. When grapes are harvested early, wines with a lower ethanol content but increased higher alcohols content are obtained. In this case, during distillation, higher alcohols are distributed more homogenously in the distillation fractions and show a smaller correlation with ethanol. n-Propanol, 2-phenyl ethanol, and ethyl lactate were found to exhibit a high correlation with ethanol, consequently, the concentration of these compounds that may be present in the distillates will vary according to the length of the distillation process. Methanol did not correlate to ethanol concentrations, rather its concentration is dependant upon the vinification technique used (Carnacini *et al.*, 1993).

The concentration of ethyl esters was only influenced by the effect of yeast strain variation in the first fractions of the heart (Carnacini *et al.,* 1993). Riponi *et al.* (1996) confirmed this finding. The concentration of ethyl acetate was noted to be the one most influenced by the type of yeast strain used during base wine production. Relative concentrations of ethyl acetate present in the base wine, proved to be a good indicator of the relative concentrations to be expected in the distillate fractions.

Statistical analysis showed that acetoin, although not influenced by either the individual effect of yeast strain or degree of grape maturation, was indeed affected by the combined action of the two variables (Carnacini *et al.*; 1993).

The three distillates obtained from wines with 10.5 v/v using three different yeast strains did not exhibit significant organoleptic differences. The high degree of grape maturity seemed to nullify any differences that may have been brought about by the use of different yeast strains. Distillates obtained from wines with 9 % v/v showed slight differentiation on the basis of yeast strain (Carnacini *et al.*, 1993).

2.5.8 INTERACTIONS BETWEEN ETHYL ESTERS AND AROMA COMPOUNDS IN MODEL SPIRIT SOLUTIONS

For the assessment of flavour, distilled spirits are typically diluted to 22 or 23% ethanol by volume to reduce pungency. Dilution, however, changes the solubility of many volatile compounds that are more soluble in ethanol than water, such as the

ethyl esters of fatty acids. Furthermore, these esters are amphiphilic, with a polar head and a hydrophobic carbon chain, and may thus form agglomerates or miscelles in aqueous ethanolic solutions (Conner *et al.*, 1994a).

Salo *et al.* (1972) identified ethyl esters of fatty acids, notably those with even numbers of carbons between 6 and 12 in the hydrocarbon side chain, as major contributors to whisky flavour. Jounela-Erikson (1981) reported that significant addition to or depletion of these esters in spirits has negative effects on overall odour intensity.

Previous studies on the behaviour of ethyl esters in redistilled brandies have shown that tannic acid and oak wood extracts significantly reduce the activity of ethyl esters in solution (Piggot *et al.*, 1992). Conner *et al.* (1994b) found that ethyl dodecanoate and ethyl hexadecanoate are the primary components of agglomerates formed in diluted distillates. Addition of oak wood extract to esters in 23% ethanol was found to increase the proportion of esters in the agglomerate phase and decrease the concentration in solution (Conner *et al.*, 1994b).

Conner *et al.* (1994a) found that long chain aliphatic alcohols, aldehydes and esters have a limited solubility in 23% ethanol. In mixed solutions each compound was found to make an additive contribution to the final activity. Where a solubility limit was exceeded, excess solutes formed agglomerates containing a proportion of the alcohol or aldehyde.

Conner *et al.* (1994b) found that both wood extract and short chain aldehydes decreased the overall activity of ester solutions; for the latter this effect appeared to be a property of the aldehyde group. They thus proposed that the solubility behaviour of aldehydes has two components: a hydrophobic component due to the hydrocarbon chain and common to esters, alcohols and aldehydes; and an effect due to the aldehyde group. Changes in ester activity thus relate to the hydrophobicity of the aldehyde or alcohol co-solute, with short chain aldehydes and wood extracts decreasing overall activity. The effect of a wood extract may be due to the presence of aromatic aldehydes such as vanillin and syringaldehyde. Thus, for hydrophobic solutions in 23% v/v, activity and hence headspace concentration are not solely determined by concentration, but by the presence of other hydrophobic compounds in the spirit. Secondly, dissolution of wood extractives during wood maturation may alter the relative activities, and hence headspace concentrations, of certain solutes, with an effect also dependant upon spirit composition.

2.5.9 INFLUENCE OF YEAST LEES ADDITION DURING DISTILLATION

Increasing fractions of yeast lees present during distillation, lead to an increase in the concentration of ethyl caprate, -caprylate and -laurate. The ethyl esters of capric, myristic and palmitic acids, as well as acetoin also increase in concentration, but to a lesser extent. The yeast lees fraction, however, has no other effect on the concentration of any other compounds, such as the carbonyl compounds, alcohols and terpenes in the wine distillate. Storage of the base wine on its yeast lees, even

for as long as 5 to 10 months, has no noticeable effect on the concentration of the above-mentioned ethyl esters. This increase in concentration only takes place when the wine is distilled with a fraction of its lees (Guymon, 1974b; Carnacini and Di Stefano, 1989; Litchev, 1989).

Heptanoic and pentanoic acid ethyl esters, that are both responsible for a typical wine-like aroma, appear only in trace quantities in wine, brandy, wine spirit, lees-distilled distillates and even yeast oils. Even illegal yeast extract additions to brandy as well as unlawful distillation with too much yeast lees, will not lead to increased concentrations of these compounds (more than 0.1 mg/ 100ml A). Thus, any levels higher than 0.1 mg per 100 ml A, point to an unlawful addition of these esters during blending of the brandy in order to enhance its aroma and sensory appeal (Postel and Adam, 1990a).

2.5.10 INFLUENCE OF STORING THE BASE WINE PRIOR TO DISTILLATION

Studies performed on cherry "wine", the base for the resulting kirschwasser spirit, showed that it contains exceptionally high levels of propanol (480 - 2230 mg/100ml A). If the cherry "wine" is distilled immediately after alcoholic fermentation, the propanol concentration is much lower (80 - 100 mg/100 ml A). The longer the wine is stored prior to distillation, the more the concentration of propanol increases in the spirit. This is due to the metabolic action of bacteria that develop during storage of the wine. Butan-2-ol may also be formed by bacteria during wine storage. However, kirschwasser base wine containing more than 1000 mg/100ml A of propanol and 120 mg/100 ml A of butan-2-ol, was found to produce a sensorially more aromatic and complex spirit than a base wine containing <100 mg per 100ml A of propanol. Thus, in cherry spirits bacterial infection of wines during storage may not necessarily be detrimental to ultimate spirit quality. This is not the case for brandy spirit (Nykänen, 1986; Postel and Adam, 1990). Du Plessis *et al.* (2002) found that the likelihood of spontaneous malolactic fermentation taking place increased during extended periods of brandy base wine storage. This leads to increased concentrations of ethyl lactate and diethyl succinate in the resulting wine and distillate and detrimentally affects distillate quality.

2.6 WOOD MATURATION OF DISTILLED BEVERAGES

2.6.1 INTRODUCTION

Ageing in oak, while optional in the production of many fine wines, is a crucial element in the production of brandy. Although oak was used originally for purely practical reasons (oak being the most impermeable wood grown near the Cognac and Armagnac regions), it remains the ideal container for storing spirits (Robinson, 1994). During wood maturation of brandy, oak not only imparts specific flavour and colour substances, but also allows for slow oxygenation of the spirit. Indeed, the

balance between the original spirit and the qualities imparted by the oak is most important in determining the quality of the final product. The balance is a delicate one: the newer the wood in which the spirit is stored and the longer it remains in wood, the greater its influence (Robinson, 1994).

Thorough understanding of beverage maturation has been slow because of its complexity and difficulty of generalisation. Distilled beverages, such as brandy and whisky are usually matured in North American or European oak barrels of about 300 litre capacity for anything from 6 months to 3 or more years depending on the country of production. Bourbon whisky is matured for at least one and often up to 12 years in new, charred North American oak barrels. Scotch whisky is often matured in 300/barrels of North American oak, re-coopered and reused after Bourbon usage or sometimes after being used for sherry production. Cognacs spend three years or more in barrels of various ages and longer times in larger casks of European oak and may have oak extracts added. Brandies are often matured in reused bourbon or used wine barrels of varying ages, which are sanded and re-toasted before use (Boulton and Singleton, 1995). South African brandies must, by law, be matured in oak casks of no larger than 340 litres for a minimum of three years. French wood is used in the majority of instances.

The composition of oak wood is dependant upon a number of factors such as oak species (*Quercus robur* vs *Q. patrea* vs *Q. alba*), climatic conditions and soil fertility during growth, age of the trees, the position of the cut on the stem and the proportions of heartwood to sapwood (Weitz, 1997). Trees are usually cut down during the autumn or winter months when the sap is down. Logs of appropriate lengths are cut and then split into four lengthwise. The sapwood lies directly under the bark and is not suitable for the making of casks. The bark and sapwood are thus removed, leaving the heartwood, which is then cut from transversal rather than tangential sections of wood. European oak (traditionally used for brandy maturation in South Africa) could leak when sawn and must thus be split carefully following the grain of the wood (Robinson, 1994).

The composition of French oakwood is roughly as follows:

40-45% cellulose

25-30% hemi-cellulose

20-23% lignin

7-10% tannin

1-2% resins

0.5-1% minerals

The cellulose consists of long chains of ß-D glucose molecules. It is extremely hard and forms the structure of the wood, yet it is porous enough to allow gases such as oxygen to penetrate the wood. Cellulose is not soluble in water or alcohol and thus remains inert during brandy maturation. Hemi-cellulose, under the influence of water and acids, can be hydrolysed to sugars such as glucose. Lignin has a complex

composition and is probably the most important component in terms of its influence on flavour compounds, particularly aromatic aldehydes, during maturation. It is partially soluble in alcohol and forms an alcohol-lignin complex. Tannins are soluble or partially soluble in water and alcohol and impart colour and astringency to brandy (Weitz, 1997).

The chemical components of a distilled alcoholic beverage aged in wood can be classified as having their origin from one of three general sources:

a) Initially present in the distillate

b) Extracted from the oak wood of the barrel

c) Products of chemical reactions taking place during ageing.

Both external and internal factors may influence the extent to which wood compounds may be extracted. These factors include the type of wood used, drying method used for the wood, the extent of barrel toasting, relative humidity at storage as well as the oxidative conditions present in the barrel during maturation. Taking these factors into account, brandies can thus vary considerably in appearance and composition (Singleton, 1995).

Studies (as quoted by Singleton, 1995) have demonstrated that colour, acids, esters, furfural, solids and tannins all increase during the ageing process. Except for esters, the greatest change in congener concentration occurs during the first year. Thereafter the rate of change decreases with each year. Esters, on the other hand, are formed throughout the maturation period at a more or less constant rate. Of the congeners measured, the greatest change has been found in the ethyl acetate fraction. Acetaldehyde and acetals also increase (Onishi *et al.,* 1977).

From the standpoint of components extracted from the oak barrel, our present knowledge does not completely account for the remarkable flavour and aroma differences between brandies aged in American oak and those aged in French oak, particularly Limosin oak of the type used to age Cognac (Pocock *et al.,* 1994).

Odorous compounds must be relatively small and volatile. Tastable compounds, if they are not also odorous, are larger and non-volatile. Sensory analysis by profiling and statistical interrelation indicates that vanilla-like, oaky or woody, coconut, medicinal, burnt, smoky and spicy are flavour factors related to maturation of beverages in barrels (Pocock *et al.*, 1994). These aromas impart a harmony and complexity to products that the unmatured, raw components do not often possess, and therefore contribute significantly towards the style and character of brandy. However, it is important to bear in mind that complexity is a desirable flavour attribute, and will be defeated by excessive levels of any one flavour. Also, a number of flavourants at sub-threshold levels may combine to give a pronounced effect, but may be difficult to identify in synergistic circumstances (Pocock *et al.*, 1994).

2.6.2 SUMMARY OF REACTIONS TAKING PLACE DURING WOOD MATURATION

- Direct extraction of wood chemical compounds
- Decomposition of wood macromolecules and extraction of these into spirits
- Reactions between wood components and constituents of the raw distillate
- Reactions involving only the wood extractives
- Reactions involving only the distillate components
- Evaporation of volatile compounds through the cask
- Interaction between ethanol and water
- Formation of stable polymers and complexes

The extent to which these reactions may take place in aged spirits may vary. Ash and tannins appear in aged spirits purely through the phenomenon of extraction from the wood. However, ethanol lignin and aromatic aldehydes represent a type of extraction-reaction with the barrel and its contents. These reactions may include oxidation, hydroalcoholysis and interactions between compounds. Alcohols are oxidised to aldehydes, and these in turn to acids. These aldehydes may subsequently combine with other alcohols to produce acetals. In this literature study, the type and origin of compounds involved in the wood maturation of alcoholic beverages will be discussed prior to discussing the processes and factors that may influence the increased or decreased presence of these compounds.

2.6.3 WOOD CONGENERS INVOLVED IN BRANDY MATURATION

2.6.3.1 Lignin and tannin characteristics of oakwood

Oak heartwood is rich in lignin. Depending on the author and on extraction method, lignins account for 25 to 30% of the weight of dry wood (Vivas *et al.*, 1998). These lignins compounds impregnate the cell walls and are mainly localised in the primary wall. Lignins function to increase the mechanical strength and water repellency of wood. Lignins display heterogeneity and differ in structure and composition among and within species. They vary even according to their position in the wood tissues. Studies devoted to the structure of oak lignins do not necessarily reflect all oaks and often reflect the effects of sampling and the specific focus of the work (Vivas *et al.*, 1998).

Oak wood lignins, like those in other angiosperms, are three dimensional polymers formed by the co-polymerisation of two phenylpropenoic alcohols: hydroxy-4-methoxy—cinnamic alcohol (guaiacyl structure; coniferyl alcohol) and hydroxy-4-dimethoxy-3, 5-cinnamic alcohol (syringyl structure; sinapic alcohol) (Vivas *et al.*, 1998).

Puech (1981) analyzed several species of oak wood for their biochemical compositions in lignin and tannin. The selected samples of French oak wood from Troncais (*Quercus sessiflora),* Limosin and Gascony *(Quercus pedunculata)* were dried outdoors for five years. The methoxyl group content varied from 53-62 mg/g dry wood, showing some homogeneity between the woods. By contrast, there was high heterogeneity in the tannin levels (Puech, 1981). Therefore, depending on the wood used for manufacturing casks, brandy will contain more or less tannin, and, therefore, be light or tannic. American oakwood was found to have the lowest tannin content. However, further analyses on armagnac samples aged in these casks, showed that the percentages of extracted methoxyl groups ranged from 3 to 5.8%. In other words, a very small fraction of lignin is dissolved in the resulting brandy (Puech, 1981). Very long matured brandy has higher methoxyl content (and therefore more lignin) than does fresh oak extract, indicating a slow reaction (Puech and Moutonet, 1992).

Vivas *et al.* (1998) analysed three different types of lignin fractions in oak heartwood:

1. A low molecular weight fraction, corresponding to lignins, extractable in an aqueous and hydro-alcoholic medium
2. A fraction corresponding to native Braun's lignin, also called ethanol lignin, extractable with ethanol in an acid medium. Its formation is understood to be the result of alcoholysis and the breaking of certain links. The consequent depolymerisation makes them soluble.
3. The least degraded lignin fraction, which was extracted with hot dioxane (which does not react with lignin), thus allowing the study of in-tact *in situ* lignin structures.

The fractions have different molecular weights. Consistent with secondary lignification theory, Vivas *et al.* (1998) classified lignins broadly into 2 categories: soluble lignins (Ln) and extractable lignins (LE, LD). They did not isolate the linked or encrusted lignin fraction, but it can be obtained from cell wall residues by successive treatment with hot sulphuric acid. Purified lignins still contain non-lignins, which are difficult to eliminate. The high concentration of tannins in the heartwood can also be a source of contamination. The Ln was found to be particularly rich in free aldehydes, mainly vanillin and syringaldehyde, and also contains lyoniresinol (Vivas *et al.,* 1998). Currently, most of the elements that constitute the cell wall are thought be linked through ether, ester and glycosidic links. The Ln fraction was found to be contaminated with non-lignin phenolic compounds LE and LD.

LD fractions, *i.e.* high molecular weight (Mw) lignins from the heartwood are rich in syringyl units. Conversely, lignins of lower Mw, extractable when wines or spirits are being aged in the wood, are characterized by a balance between syringyl (S) and guaiacyl (G) units. Viriot *et al.* (1993) reported a 1.0 to 1.3 S/G ratio in a 30-year old cognac.

Various studies on lignin structure heterogeneity in wood tissues indicate that the solubilizing guaiacyl type lignins can result from the decomposition of the primary cell wall, whereas syringyl type lignins come from the secondary wall. This phenomenon might explain why lignins solubilize in wines and spirits, their structure thus being different from those lignins found in living trees.

LD was found to be the purest lignin fraction. Because the extraction protocol used in the study by Vivas *et al.,* (1998) mimics what happens in wines and spirits, the Ln and LE lignins are those most likely to end up in wines and spirits.

Only ethanol extracted lignin or Braun's native lignin representing the "sol" fraction of the cross-linked polymer is transferred to the brandy. Puech (1981) thus recommended that the "sol" fraction should be determined both on the wood before drying and on the same wood during drying to determine alterations induced by technological processes in order to optimize wood quality.

The oakwoods studied by Puech (1981) were found to contain 30% lignin, of which a minor fraction is extractable, whereas more than 50% of the tannins present in wood were dissolved in the resulting brandy. The tannin content in the woods was found to vary from 41 to 66%. American wood released the least amounts of tannin. He thus established that there is a clear relationship between the tannin content of wood and its extractable quantity for spirits.

2.6.3.2 Extraction mechanisms of lignin and lignin degradation products

Lignin is a three-dimensional, highly branched, polyphenolic molecule consisting of phenylpropane derivatives of guaiacyl (2-methoxyphenol) and syringyl (2,6-dimethoxyphenol) units substituted in the C_4 position with the aliphatic side chain and further crosslinked by oxidation. Lignin is hydrophobic, that is to say, it is almost a water repelling compound (Puech, 1981).

Although lignin itself is tasteless, it may contribute to the body and colour of long matured spirits. More importantly, the lignin degradation products are major contributors to aroma and taste characteristic compounds in brandy (Puech, 1981; Singleton, 1995).

Solvents such as ethanol can solubilize a portion of the lignin from the wood. However, the lignin present in oak matured spirits originates from the liberation of relatively free lignin fragments, leaving the milled wood lignin content of the stave unaffected by repeated use. Thus cask exhaustion is not accompanied by significant delignification (Conner *et al.* 1992).

According to Baldwin *et al.,* (1967) and Puech (1981), the following mechanisms of lignin degradation are active during spirit maturation:

1. Degradation of lignin to aromatic aldehydes with toasting or charring of oak
2. Extraction of monomeric compounds present in the free state and of native lignin by spirits
3. Formation of aromatics by ethanolysis of lignin
4. Further conversion of compounds extracted into spirits

Ethanol extraction and oxidation reactions as proposed by Reazin (1983) are illustrated below. The first one occurs in the wood and the second one in the hydroalcoholic phase. In the first example, lignin is extracted by ethanol to yield ethanol-lignin compounds, which are further degraded into simple phenolic compounds in spirits. In the second example, these phenolic compounds are formed previously in the wood.

Proposed Mechanisms for Aromatic Aldehyde Formation (Reazin, 1983)

Wood lignin_x + ethanol $\rightarrow$ wood lignin(x-n) + n ethanol lignin

Wood ligninx + ethanol $\rightarrow$ coniferyl alcohol + sinapic alcohol

Ethanol-lignin $\rightarrow$ ethanol + coniferyl alcohol + sinapic alcohol

Sinapic alcohol + O_2 $\rightarrow$ sinapaldehyde

Coniferyl alcohol + O_2 $\rightarrow$ coniferaldehyde

Sinapaldehyde + O_2 $\rightarrow$ syringaldehyde

Coniferaldehyde + O_2 $\rightarrow$ vanillin

Extraction from the wood by hydro-alcoholysis at room temperature leads to the formation of benzoic and cinnamic aldehydes. These benzoic and cinnamic aldehydes include syringaldehyde, sinapaldehyde, vanillin and coniferaldehyde, and can be oxidised to form aromatic acids. Of these aromatic acids, vanillic and syringic acids have been shown by Puech (1987) to be the most influential to typical brandy character.

Puech and Moutonet (1992) used high pressure liquid chromatography to identify and quantify the lignin derived acids and aldehydes in brandies. They noted that vanillin and syringaldehyde are the dominant aldehydes, whereas vanillic acid and syringic acid are the quantitatively most dominant acids present. Vanillin is present in lesser amounts than syringaldehyde, but is more odorous (Singleton, 1995). Singleton (1995) also observed that oxidation of vanillin to vanillic acid and syringaldehyde to syringic acid was accompanied by a subsequent loss of flavour in the brandy.

2.6.3.3 Presence of lignin and lignin degradation products in spirits

The maximum content of lignin in aged spirits may be as high as 800 mg/l, but with modern analysis 220 mg/l was found in very old cognac (Viriot *et al.* 1993). This lignin of old cognacs apparently had an average molecular weight of 780, suggesting tetrametric guaiacyl or syringylpropyl units. It was also higher in guaiacyl units relative to syringyl than in the wood. Syringyl/guaiacyl ratios were 2.0 in the wood and nearly constant at 1.3 to 1.0 in cognacs one to thirty years old. The content of free phenolic groups in the lignin of old brandy was much higher than in that of the wood, showing hydrolysis of phenolic ether linkages to release the lignin, but again this was observed to remain constant during ageing. This phenomenon indicates that further chemical alteration of the lignin is limited with neither depolymerization nor oxidative repolymerization taking place (Viriot *et al.*, 1993).

Kurdize *et al.* (1981) (as quoted by Sinlgeton, 1995) spectrophotometrically analyzed twelve lignins present in both oak fibre and brandies. They found that these lignins, and their subsequent degradation products, increased by 120% over the first 20 years of oak maturation of brandy. However, Somenko and Frolova (1981) (as quoted by Singleton, 1995) observed that in the fourth to sixth years of brandy maturation, the composition of these compounds present in the brandy, remained almost constant.

Dimers are the smallest unit that may be called "lignin", and it is interesting to compare optically active dimers resembling lignin. Different proportions of both isomers of lyoniresinol have been identified as glucoside or xyloside derivatives in oak wood and in brandy at 16.2 mg/l (Dada *et al.*, 1989). No comments were made as to any flavour contribution.

Henderson (1983) (as quoted by Singleton, 1995) tested the sensory effect of ethanol-lignin from barrel wood at 181 mg/l in 10 % (v/v) ethanol. After one year of storage, which would allow the breakdown of vanillin etc., there was no significant flavour difference from the model solution. A colour difference was, however, apparent. Furthermore, lignin prepared by peroxidase oxidation of coniferyl alcohol, and freed of residual coniferyl substrate, was tasteless (Henderson, 1983). Yet lignin may be significant to "body" and colour of long-matured spirits (Singleton, 1995).

2.6.3.4 Ligno-complex compounds in spirits

In 1981 Puech termed the degradation products of lignin the ligno-complex. He quantified the amounts of ligno-complex compounds and degradation products during the maturation of armagnac. Armagnac is aged in 400 litre Gascony or Limosin oak barrels and its maturation period may vary from 1 to 20 years. He aimed to identify aromatic aldehydes in the inner and outer surfaces of staves that had contained armagnac for 20 years. The inner surface was shown to be approximately seven times richer in vanillin and syringaldehyde, nine times richer in coniferaldehyde and 16 times richer in sinapaldehyde than the outer face. This proved that a fraction of oakwood lignin undergoes intense oxidation when in contact with spirit and oxygen (coming through wood pores), leading to aromatic aldehyde formation, and that these aromatic aldehydes are solubilized in armagnac.

Amounts of ligno-complex compounds in spirits are proportional to their methoxyl content. These compounds are further fractionated into extracted lignin (insoluble in water), volatile substances, and non-volatile substances that may be recovered in an ether-soluble fraction (Puech, 1981). He found that the volatile and non-volatile fractions represent respectively 2.4 to 7.3% and 8.1 to 15.8% of the total ligno-complexes and that there is equilibrium between these fractions with respect to ligno-complexes, even if maturation conditions (such as barrel quality and climatic conditions in the maturation storehouse) are changed. He found that the volatile, soluble ether fractions contain mainly aromatic aldehydes, and the non-volatile fractions contain mainly aromatic acids. Puech (1984b) then proceeded to quantify

the total concentrations of phenols and the ligno-complex in cognacs of varying ages. He found that the concentration of the lignin-complex was markedly higher in relation to the total phenol concentration in the matured cognacs, thus confirming this phenomenon of lignin degradation.

Gomes Cordoves *et al.* (1990) analysed brandies of low, medium and high quality and found that the lower quality brandies contained more vanillic acid, and subsequently less flavour than the high quality brandies. This confirms Singleton's postulation (Singleton, 1995) that the oxidation of vanillin results in a subsequent loss of flavour in brandy. Gomes Cordoves *et al.* (1990) thus concluded that the most important relationships defining a high quality brandy, are those in which vanillin participates. The gallic acid to vanillin ratio was shown to be high for the top quality brandies, however, this ratio may vary depending on the combined wood age used during maturation, as lower amounts of phenolic compounds will be extracted from old wood.

2.6.3.5 Tannins

Distillates contain no tannins and a little phenol, whereas commercially matured brandies reportedly contain up to 500 mg/l of tannin (Nykänen and Suomalainen, 1983). Wood that is rich in tannin will result in an astringent brandy, producing an unpleasant feeling of harshness on the tongue. However, too little tannin concentration in the wood, will result in a brandy with little or no body and mouthfeel. The tannin balance extracted from wood thus lies at a finely balanced, intermediate optimum level.

Tannins can be divided into two separate groups:

1. Hydrolysable tannins (including gallotannins and ellagitannins), which are easily hydrolysed enzymatically or in an acid or base solution; Tannins most important to brandy are the hydrolysable tannins (Singleton, 1995).
2. Non-hydrolysable tannins, including condensed tannins or proanthocyanidins. These are oligomers or polymers of flavonoid units, linked by carbon-carbon bonds that are not susceptible to hydrolysis (Singleton, 1995).

Hennig and Burkhardt (1987) (as quoted by Francis *et al.,* 1992) assigned oak tannins to the hydrolysable ellagitannin group. It was shown that the great preponderance of extractable wood phenols was not flavanoid in nature, contrary to the tannins found in grapes, but that ellagitannins comprised the highest proportion of extractable phenols in both American and European cooperage oaks.

Puech (1987) estimated that up to 55% of all wood tannins are dissolved by spirits, and that their solubility will generally decline with increasing molecular weight. Polymerisation is therefore likely to lead to a decrease in the level of soluble tannins. However, polymerisation is dependent upon how readily these tannins are oxidised.

Conflicting opinions exist concerning the aroma and taste impact of tannins on aged spirits. Du Penhoat *et al.* (1991a) felt that tannins contribute indirectly to the

taste of brandies through their complexing and reducing properties. Ventratarama *et al.* (1981) (as quoted by Du Penhoat *et al.*, 1991a) indicated that combinations of phenolic fractions of oakwood, when added to brandy improved the taste. However, Viriot *et al.* (1993) were of the opinion that ellagitannins do not play an important role in the maturation and aroma development of cognac and other spirits.

Not all ellagitannins present in oakwood are extractable, and the amount extracted varies with the alcohol content of the contained spirit. Puech (1987) found that maximum extraction of ellagitannins occurred at 55% (v/v) alcohol and that during wood maturation, ellagitannins may take part in the following reactions:

1. Solubilization by the grape spirit, followed by diffusion through the wood
2. Soluble ellagitannins may be hydrolysed, forming ellagic acid
3. They may be degraded without the formation of ellagic acid. This occurs when the hexahydroxydiphenol residue in ellagitannins is involved in an oxidative reaction.
4. Insoluble ellagitannins may also be hydrolysed, forming ellagic acid, which subsequently diffuses through the wood into the grape spirit.
5. Ellagic acid may possibly be further degraded, but the extent to which this may take place is very low, as ellagic acid is remarkably stable in an acidic- alcoholic solution.

There are several ellagitannins present. Castalagin, vescalgin, grandinin, roburins A - E, pedunculagin, castalin, and vescalin have been reported along with pentagalloyl glucose (Du Penhoat *et al.* 1991b). They differ from one another in molecular weight (about 900 to 2000), the number of galloyl moieties (2 per ellagic precursor, hexahydroxydiphenic acid), and the central glucose unit (glucose, xylose). Roburin A is a dimer of two vescalgins linked at the starred positions. Pentagalloyl glucose is a precursor for ellagitannins. They are all astringent, but weak to very weak compared to pentagalloyl glucose. They behave similarly and can be considered as part of one group.

Quercus robur and *Q. patrea* could not be discriminated based on these phenols, but *Q. rubra* had considerably higher gallic acid (Scalbert *et al.* 1986 as quoted by Singleton, 1995). Heartwood formation from sapwood entailed a seven to twenty-fold increase in ellagic and gallic acid units and individual trees vary greatly. The total ellagitannin content is about 10% of the dry heartwood, but the soluble portion increases from the periphery to the centre (Peng *et al.* 1991).

In matured distilled spirits the oak tannins become hydrolysed, and although the gallic acid survives, the ellagic derivatives have precipitated. It is thus clear that ellagitannins can be important to wine and spirit flavour and quality (Reazin, 1983, Viriot *et al.*, 1993). **Table 2.5** describes the tannin extract levels and percentage of total tannins extracted from woods of differing types (Puech, 1984). **Figure 2.5**

depicts the concentrational evolution of ellagitannins and lignin oligomers during brandy ageing (Viriot *et al.*, 1993).

Table 2.5 Tannins extracted and percentage of total tannins extracted from wood (Puech, 1984)

Type of Oak	Tannin Extract (mg/g dry wood)	% Tannins Extracted
Troncais	86	63.7
	62.6	65.2
	52.6	62.4
Limosin	29.9	41
	102	66.1
	59	66.5
Gascony	64.6	58.3
	82.3	54
	56.9	47.4
	60.8	57.7
	90.3	60.2
	48.3	60.7
	40	48.7
Bulgarian	39.5	49.9
Russian	58.3	55.5
White American	19.7	51

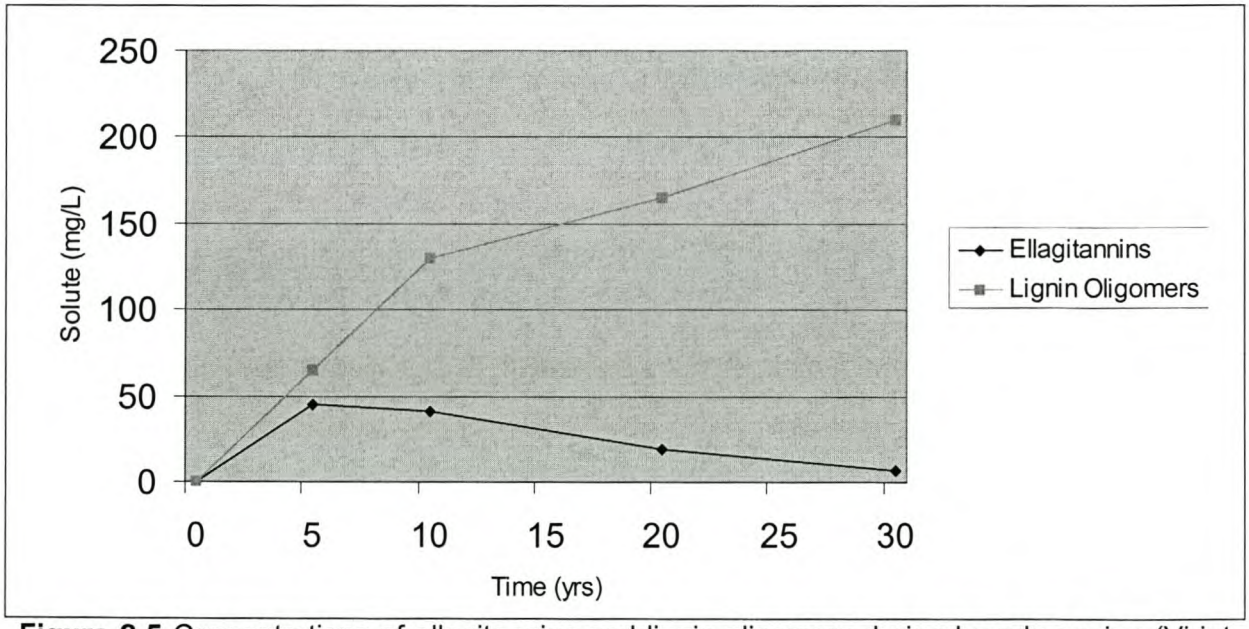


Figure 2.5 Concentrations of ellagitannins and lignin oligomers during brandy ageing (Viriot *et al.*, 1993).

2.6.3.6 Carbohydrates

The content of sugars derived from wood during maturation can be high in spirits and represents a large fraction of the extracted solids. In wines stored for an equal

amount of time, sugar release by hydrolysis would be expected to be larger given the more aqueous and acidic medium. Most of these sugars are pentoses and low in sweetness, but glucose and even fructose have been found to be present on occasion (Sefton *et al.*, 1993).

Reazin (1983) found that arabinose, glucose, xylose, galactose and rhamnose were produced at a faster rate during the first year of maturation than in the following years, reflecting a hyperbolic curve. Fructose and glycerol formation rates followed a different pattern, their greatest rate of formation was at the end of the maturation period. This difference suggests that glycerol and fructose are produced from different substrates in the wood than are other sugars. Glycerol could possibly be a degradation product of glycerides in the wood (Reazin, 1983).

The "rich" flavour from oak maturation may lie with these sugars (Nykänen, 1986, Sefton *et al.*, 1993). Complete hydrolysis of *Q. alba* given as a percentage of oven dry wood yields 55% total carbohydrates, 36% glucose, 15% xylose, 2% galactose, 1.3% arabinose and 1.4% mannose (Conner *et al.,* 1982). Other woods were found to be roughly similar.

Presley (1978) (as quoted by Singleton, 1995) extracted Limosin and American chips and compared these to brandies aged (by Guymon and Crowell, 1970) in U.S. and French barrels. The ratio of arabinose to glucose was 2:1 in U.S. and 1:1 in most French products. Hydrolysis in the brandies increased the concentration of all sugars by 40% to 125%, with xylose increasing the most. One must, however, consider that:

- There are some extracted polymeric carbohydrates that should continue to hydrolyse.
- The comparisons of total extracted solids when corrected for tannins, lignins etc., will leave sizeable amounts unaccounted for.
- Concentrations of identified sugars in spirits are fairly high, but should be higher in wines.
- Hydrolysable tannins yield appreciable amounts of glucose.

There is scope for more detailed research on the contribution of carbohydrates from wood to matured wines and spirits, particularly in regard to a general richness of flavour (Sefton *et al.*, 1993; Singleton, 1995).

2.6.3.7 Volatile acids and esters

Several volatile acids, some already present in wines, are present in spirits as a result of maturation in oak. Brandy and other distilled spirits drop in pH from 5.0 to 4.0 in the early stages of barrel maturation owing to accumulation of acids, particularly acetic acid (Nykänen *et al.*, 1968). The rate of formation and conversion of esters depends largely on the pH of the distillate (Egorov *et al.,* 1994).

The major acid present is acetic acid (Onishi *et al.*, 1977). The amount in distilled beverages is significant, approximately 300 mg/l. A part of this increased acetic acid originates from direct hydrolysis and extraction from the wood. A much

larger part, comprising up to 4% of the wood, can be released by alkaline hydrolysis and somewhat less by acid hydrolysis, evidently from the hemicelluloses (Nishimura *et al.* 1983). Considerable amounts can also be released during pyrolytic toasting and more with charring, although it is driven off as pyroligenous acid during complete charring.

Reazin (1983) added C_{14} marked ethanol to ageing whisky and followed the marker in acetic acid and ethyl acetate. Based upon the relative specific activity, 27 to 55% of the acetic acid arose from oxidation of the ethanol to acetic acid by way of acetaldehyde. The rest originated from the wood.

It is believed that this ethanol oxidation is the result of coupled oxidation by hydrogen peroxide, which is produced when phenols such as gallic acid are oxidised (Wildenradt, 1974). This shows that rather strong oxidation does occur, and this can be explained by the fact that the spirit barrels are not topped and the dry top staves can then admit oxygen. The extracted phenols can react with oxygen entering via the liquid surface to produce hydrogen peroxide. Dissolved oxygen in brandy was shown to increase over one to three years of cask maturation and reached 50% or more of the saturation level (Mourget *et al.* 1973 as quoted by Singleton, 1995).

In spirits, with their high alcohol content, acetic acid partly esterifies to ethyl acetate. In wines, the high water content tends to favour hydrolysis of grape and fermentation esters, but in spirits, ethyl esters are favoured and tend to rise. Esters of other alcohols and of acids present in too small amounts will decrease with time. Fatty acids and their esters are present in distillates and have been reported to both rise and fall during oak ageing (Onishi *et al.*, 1977).

Egorov *et al.* (1994) found that the amount of ethyl acetate and other lower molecular weight esters increased somewhat when the cognac spirits were aged for up to 20 years, and then decreased slightly over 25 and 50 years of ageing. β-phenethyl acetate and diethyl succinate concentrations increased significantly with longer ageing times, most likely due to their being extracted from the oak wood by ethanol (**Table 2.6**) (Egorov *et al.,* 1994).

In the study by Reazin (1983) the ethyl esters of caproic through to myristic acid remained unchanged or showed small decreases. Ethyl caprate, palmitate, and linoleate all decreased significantly with maturation in oakwood barrels. Onishi *et al.* (1977) reported that acetate esters of isoamyl, n-hexyl and β-phenethyl alcohols decreased during ageing in oak barrels. The ethyl esters of caproic, caprylic and capric acids increased during ageing while ethyl laurate changed little or decreased slightly. Volatile esters have pleasant, fruity odours and have reasonably low thresholds. The amount formed in spirits by oak maturation should be significant to flavour, particularly when several esters combine to give an overall fruity impression (Nykänen and Suomalainen, 1983).

Piggot (1992) found that peak concentrations of ethyl hexanoate are associated with favourable, sweet, fruity and floral odours. Ethyl octanoate, decanoate and dodecanoate, as well as ethyl hexadecanoate tended to give rise to undesirable

characteristics in brandy. Their associated odours were found to be oily and soapy (Piggot, 1992).

Table 2.6 Content of various esters (mg/L) in cognac of different ages (Egorov *et al.*, 1994)

Ester	Ageing time (years)						
	0	3	7	15	20	25	50
Ethyl acetate	29.5	35.5	37.3	39.5	40.6	30.5	25.7
Diethyl acetate	22.7	25.6	28.5	26.1	28.8	26.7	30.5
Propyl acetate	3.6	4.5	4.9	3	3.5	3.5	4.5
Isobutyl acetate	8.5	9.7	11.6	-	13.5	11.7	8.7
Ethyl butyrate	6.4	8.5	10.7	10.9	-	9.5	8.1
Isoamylacetate	14.5	20.2	22.6	-	25.5	23.3	20.6
Hexyl acetate	3.3	3.9	4.3	4.9	-	4.4	4.2
Ethyl capronate	3.8	4.6	-	4	4.9	4.5	3.9
Ethyl lactate	20.6	26.6	25.7	-	-	22.3	25.5
Ethyl caprylate	3.2	3.5	-	3.9	3.7	3	3.5
Ethyl caprinate	4.4	-	4.9	5.5	4.8	5.5	5
Diethyl succinate	19.5	23.6	25.6	-	26	23.5	24.2
Hexyl caprylate	3.5	4.1	4.5	4.2	-	4	4.5
2-phenethyl acetate	12.8	15.2	18.1	20.3	23.5	25.5	28.6
Ethyl enanthate	3.7	4.1	4.5	-	4	4	4.5
Ethyl myristate	2.2	3	3.5	3	-	3	2.8
Ethyl palmitate	2.5	2.9	3	-	3	2	2.2
Ethyl linoleate	2.7	3	3.5	4	3.9	4	4.2

Both diethyl succinate and the monoethyl ester have been reported in grapes and wine. But, surprisingly, it has also been found to be a component extracted from oak. The absence of the ester in all unaged barrel fill materials studied, indicates that succinic acid is a normal component of oak which esterifies with ethyl alcohol during the ageing process. Small amounts of diethyl azelate have also been found in aged brandy (Onishi *et al.,* 1977).

2.6.3.8 Higher alcohols

Egorov *et al.* (1994) investigated the content and transformation rate of alcohols in cognac spirits aged for 3, 7, 15, 20, 25 and 30 years (**Table 2.7**). They found that the amount of low molecular alcohols decreased with up to 20 years of ageing, and then increased, but to a far lesser degree than the higher molecular weight alcohols, in particular β-phenethyl ethanol. Although this aromatic alcohol is formed during the process of alcoholic fermentation, it may also be extracted by the distillate from the oakwood itself.

Table 2.7 Concentration of alcohols (mg/L) during maturation of cognac spirits (Egorov *et al.*, 1994)

Alcohol	Ageing time (years)						
	0	3	7	15	20	25	50
n-Propanol	5.8	4.5	4	-	3.8	4	4.6
Butanol-2	5.3	4.6	3.9	3.2	-	4.3	5
Isobutanol	95.7	90	85.6	80.3	78.6	82.7	86.5
n-Butanol	5.5	4	3.5	3	3.5	3.9	4
Methyl-2-butanol-1	98.5	89.5	85.4	79.8	75.3	80.6	89
Methyl-3-butanol-1	335	325.5	316.8	305	309	311.6	325.3
Pentanol	7.6	6.8	6.5	5.4	-	6	6.5
Hexanol	6.5	5	4.6	4	4.6	4.5	4.8
Heptanol	5.8	4	3.5	3.3	3.6	3.5	1.9
Octanol	3.9	2.6	2	-	2.2	2.4	3.8
Nonanol	2.9	2.8	1.5	1.9	2	-	2.2
Decanol	3.2	2.2	-	1.5	1.8	2	3
β-Phenethanol	39.8	32.8	35.6	38.8	-	39	43.6
2,3-Butylene glycol	40.9	37.8	35.6	33.9	32.1	30.3	30

2.6.3.9 Volatile and other small phenols

By far the majority of research on this group has been devoted to vanillin and its relatives syringaldehyde, coniferaldehyde, sinapaldehyde, acetovanillone and acetosyringone (Wildenradt, 1974, Dubois, 1983; Francis *et al.*, 1992; Singleton, 1995). These compounds represent fragments of lignin and increase from hydrolysis, pyrolysis, or oxidative breakdown.

Vanillin is usually present in lesser amounts, but is more odorous than syringaldehyde. In old spirits, particularly if matured in new toasted barrels, vanillin clearly exceeds the threshold concentration and probably is augmented by its relatives (Dubois, 1983). The threshold of vanillin in water is about 2 mg/L, in 10% ethanol 0.05 mg/l and in 40% ethanol about 0.1 mg/l (Maga, 1985). Syringaldehyde, vanillic acid, and syringic acid thresholds in 10% ethanol are about 25 mg/l. Sinapaldehyde's threshold is 80 mg/l. Mixtures of these were shown to lead to an augmentation of flavour (Maga, 1985). The concentration of vanillin and its analogs can be well above sensory threshold and important to aroma of matured distilled spirits, particularly from new toasted stave barrels (Nykänen and Suomalainen, 1983).

Phenolic acids, especially gallic acid, are probably important to coupled oxidation reactions in spirits (Singleton, 1995). However, phenolic acids are not directly important to the flavour of wines and spirits (Nykänen and Suomalainen, 1983). As a further oxidation product of vanillin, vanillic acid, and syringic acid analogously, they actually represent a loss of flavour. **Table 2.8** lists the concentrations of the most abundant phenols in cognacs of various ages (Puech *et al.*, 1984). **Table 2.9** lists the

concentration of phenolic compounds found in armagnac aged in new and old barrels (Puech, 1981).

Table 2.8 Phenol concentration of cognacs of various ages (Puech *et al.*, 1984)

Constituent (mg/L)	1 Year	10 Years	30 Years
Total Phenols	92	553	833
Ellagitannins	10	31	4
Ellagic Acid	7	32	0.55
Gallic Acid	3	22	26
Lignins	12	127	219
Vanillin	0.6	5.8	7.2
Syringaldehyde	1.1	10.9	14.2
Vanillic Acid	0.9	3.1	5.4
Syringic Acid	0.8	4	6.4

Table 2.9 Phenolic compounds in armagnac traditionally aged in oakwood (Puech, 1981)

Constituent (mg/L)	New Barrel	Old Barrel
Total phenolic compounds	670	216
OCH3	79	35.2
Ligno-complex	814	363
Vanillic acid	1.3	0.6
Syringic acid	2	1.1
Vanillin	2.1	1.5
Syringaldehyde	3.5	2.5
Coniferaldehyde	1.5	0.4
Sinapaldehyde	0.3	0.1

Pyrolysis can form, from lignin and other compounds, small free phenols such as phenol itself, guaiacol, 2,6-dimethoxyphenol, catechol, resorcinol and hydroquinone. With sufficiently sensitive analysis, all these and others have been detected in aged distilled beverages. As a group, they have smoky, medicinal smells (Puech, 1981). The B-ring of flavonoids can break down with heat to give such compounds. This is suggested as a reason that red wines are less desirable for distillation than white (Puech, 1984).

Other phenols originally believed to be wood related are the 4-ethyl and 4-vinyl derivatives of phenol and guaiacol. 4-Ethyl phenol is described as unattractive, "animal-like", powerful, woody and phenolic in odour. Ethyl guaiacol has a slightly more attractive, complicated odour with spicy clove, medicinal, burnt nuances (Chatonnet *et al.*, 1995).

Malolactic fermentation can be a source for these two 4-ethyl phenols, since some of these bacteria can reduce the corresponding hydroxycinnamate and then

decarboxylate it. Although associated with contaminated barrels, these 4-ethyl phenols are evidently produced microbiologically. This is a particularly gratifying finding because the analog, with one less carbon, 4-methyl phenol (*p*-cresol), has a closely similar odour to the "barnyard" or "horsey" odour we associate with *Brettanomyces* spoilage (Chatonnet *et al.*, 1995).

The 4-vinyl derivatives also have primary sources other than barrel maturation. 4-Vinylguaiacol comes from ferulic acid and has more pleasant, clove-like odours with a threshold of about 10 μg/l in water. Standard fermentation yeasts have the variable ability to decarboxylate hydroxycinnamates to the 4-vinyl analogs. Since the free hydroxycinnamate is required for this enzymatic reaction, the grape's fetaric acid must first be hydrolysed. Thus, hydrolysis by esterases in added "pectinase" enzymes to release the ferulic acid, favours the production of 4-vinyl guaiacol. With further ageing, the vinyl group is partially converted to the 2-ethoxy saturated side chain with a decreased and less rank flavour (Etievant, 1981; Chatonnet *et al.*, 1995).

Eugenol, the remaining volatile phenol known to be of interest, does come from wood and appears to be readily extracted to a fairly characteristic level, depending on the original wood. American oak contains more eugenol than European oak (Vivas *et al.,* 1998). The concentration found in a cognac sample aged in European oak, was found to be 140 μg/l. Eugenol's sensory threshold is estimated at 11 μg/l in 10% ethanol and 50 μg/l in 20% ethanol. To be perceived as "cloves", unnaturally high concentrations are required.

2.6.3.10 Oak lactones and terpenoids

The two diastereomers known as "whisky" or oak lactones are (3S, 4S) *cis* and (3S, 4R) *trans* gamma lactones of 3-methyl-4-hydroxyoctanoic acid. The ratio in a sample of European oak was 77% *cis* and 23% *trans*. They occur in several deciduous oaks including those used for cooperage. Found first in whiskies in Finland and Japan by Nishimura and Masuda (1971), and in Californian brandy by Guymon and Crowell (1970, 1972). **Table 2.10** lists the amounts of *cis* and *trans* methyl octa-lactones (MO lactones) found in distilled liquors by Nykänen and Suomalainen (1983).

Outsuka *et al.* (1974) isolated and identified a precursor of these lactones as the ester between alcohol group on the branched non anionic acid and 3-hydroxyvanillic acid. This structure might well be a breakdown product of a lignin like ether in the polyphenol fatty part of suberin. The sizeable fraction of the total potential oak lactone present in the wood as a precursor, may explain some conflicting findings. There may be a liberation of the phenolic portion to give the free precursor, but there must be a hydrolysis of the gallic acid ester followed by lactonisation to produce active odorants. Moisture content, temperature, seasoning conditions, and pH play a role in this conversion and the equilibrium ratio between the lactone and the hydrolysed open ring (odourless form) (Outsuka *et al.*, 1974).

Table 2.10 Amounts of *cis* and *trans* MO-lactones in distilled liquors (Nykänen and Suomalainen, 1983)

Spirit		Grade	MO- Lactone *cis*	MO-lactone *trans*
Brandy	(Cognac)	***	0.14	0.17
		Napoleon	0.16	0.36
		Extra	0.22	0.43
Whisky	(Scotch)	Ordinary	0.26	0.7
		Medium	0.31	0.85
		High	0.75	1.42
	(Bourbon)		0.39	3.84
	(Canadian)		0.07	0.95
	(Irish)		0.21	0.58
Rum	(Jamaica)		0.05	1.12

The sensory threshold of the *trans* form was about 0.8 mg/l and the *cis* 0.07 mg/l. Starting with zero in the distillates, concentrations in brandies increased after five years in 30 litre barrels to 0.7 mg/l *trans* and 5.3 mg/l *cis* (Outsuka *et al.,* 1974). Commercial brandies had 0.14 to 0.22 mg/l *trans* plus 0.17 to 0.43 mg/l *cis.* Freshly harvested heartwood had 120 mg/kg of the *cis* and only 10 mg/kg of the *trans* form. During six years of stave ageing, the *cis* form increased to 580 mg/kg. A pH of 3.5 gave greater extraction than pH 2.5 or 4.5 on either plain or charred wood in 40% ethanol.

Conversion of the precursor seems to be more involved. Concentrations in a series of brandies ranged from traces to 0.68 mg/l of the *trans* and 0.13 to 1.54 mg/l of the *cis* lactone. Chips from various European regions ranged over 28 to 58 mg/kg of the *cis* isomer (**Table 2.11**) (Conner *et al.*, 1992). Charred barrel staves of American oak had maximum extractable colour within the char, but the maximum for other constituents was shifted toward the centre, more so with barrel use. Most compounds tested including the *trans* lactone, were maximal at 5 mm below fresh char, but the *cis* lactone was maximal at 15 mm, and both were mostly removed in the first use with bourbon (Conner *et al.*, 1992).

Table 2.11 Changes of *cis* and *trans* MO-lactones during ageing in oak barrels (Conner *et al.,* 1992)

Spirit Type	Ageing Period (years)	MO-lactone *cis*	MO- Lactone *trans*
Brandy	0.5	+	0.57
	1	+	1.04
	5	0.7	5.3
Whisky	0	-	-
	1	0.06	3.91
	2	0.11	8.05
	3	0.31	16.7

It is worrying that the odour of the oak lactones is best described as "coconut". There is, however, some evidence that the odour at lower concentrations is "woody". The best answer to date is that oak lactone plus some background from other components does account for the oak smell. Of great interest in a paper by Salo *et al.* (1972) is the very low odour threshold reported for β-methyl-γ- octalactone (0.05 mg/l), the lowest reported for any of 45 compounds which they studied, except diacetyl (0.02 mg/l).

Egorov *et al.* (1994) found that terpenoid concentrations decreased during prolonged ageing of the cognac spirits (**Table 2.12**). This can most likely be ascribed to their esterification, such as linalool to linalyl acetate. Oxidation by molecular oxygen may also occur, forming linalool-1-oxide.

Table 2.12 Contents of terpenes and lactones in aged cognac spirits (mg/L) (Egorov *et al.*, 1994)

Component (mg/L)	Ageing time (years)						
	0	3	7	15	20	25	50
Terpenoids							
Linalool	2.5	2.2	2	1.8	1.7	1.7	2
Linalyl acetate	0.5	0.7	0.9	-	1	1	1.1
Linalool-1-oxide	0.3	0.5	0.8	0.7	-	0.8	0.9
α-Ionone	1.9	1.7	1.6	-	1.5	1.7	1.8
β-Ionone	1.2	1	0.8	0.7	-	0.7	0.8
cis-Farnesol	2.5	2.2	2	-	2.1	2	2
trans-Farnesol	1.1	1.1	-	1	0.7	-	0.8
Lactones							
cis-oak lactone	0	1.2	1.9	2	2.5	2.6	2.5
trans- oak lactone	0	1.5	2	2.2	2.5	2.7	2.8

2.6.3.11 Furanic aldehydes

Furfural is clearly extracted from the oak barrel, where it is formed during the thermolysis of polysaccharides found in the wood during charring of the barrels. Rhamnose converts to 5-methyl furfural and hexoses are converted to 5-hydroxymethyl furfural. All these related furan derivatives have been found in barrel wood, increasing considerably with heat treatment (Onishi *et al.*, 1977).

Furfural originates in the constitutive pentoses of the hemicellulose in oak wood. When the temperature reaches 200°C, the glycosidic and C-C links of lyranose are broken. At 225°C molecular destruction begins, and at 290°C molecular fragments are dehydrated giving rise to furfural (Puech *et al.*, 1987). Furfural may also arise from distillation in a simple pot still as a result of prolonged heating of the distilling material (Leaute, 1986). Salo *et al.* (1972) reported an odour threshold for fufural as 5.8 mg/l and a very small odour contribution to the total odour. Similar thermolysis of

cellulose present in the wood leads to the formation of 5-hydroxymethylfurfural (5-HMF). At the low levels reported, it seems to have a negligible sensory effect when compared to furfural, which it resembles in odour.

The addition of caramel is another possible source of furanic aldehydes in brandies. The chemical composition of caramel is complex, due to the large number of substances produced as a result of pyrolysis in carbohydrates such as sucrose, glucose or starch. 5-Hydroxymethyl-furfural (5-HMF) has been shown by Badui Dergal (1981) (as quoted by Quesada-Granados *et al.*, (1996) to be present in much larger concentrations than furfural in caramel. Quesada-Granados *et al.* (1996) showed that the addition of caramel to brandies increased the concentration of 5-HMF, and also decreased the furfural/ 5-HMF ratio present in the brandy. They observed that the average concentration of furfural for a brandy aged in the traditional wood ageing system, was 0.99 mg/L, as opposed to 5.83 mg/L in the dynamic solera system. These values are lower than those obtained for 5-HMF, which were found to lie at 35.66 mg/L for the traditional system and 26.5 mg/L for the solera system. However, for the macerated mixtures of French and American oak to which caramel had not been added, Quesada-Granados *et al.*, (1996) found that the concentration of furfural is always higher than 5-HMF. These averaged 3.32 mg/L furfural and 0.3 g/L or 5-HMF in French oak, and 2.04 mg/L for furfural and 1.10 mg/L for 5-HMF in American oak (Quesada- Granados *et al.*, 1996). Any differences in American and European oak appear to arise from different heat treatments. An unaged distillate had 3 mg/l of furfural without detectable 5-hydroxymethyl furfural (Villalon Mir *et al.,* 1991).

Furfurals are believed to participate in the odour of caramelization and may contribute to "hotness" of spirits. Maltol and 2-hydroxy-3-methyl-cyclopentanone are also sugar degradation products with potentially desirable sweet, caramelized odours. They have been found at low levels in toasted, but not in untoasted oak and would therefore be associated with furfural production. (Nishimura *et al.,* 1983).

2.6.3.12 Miscellaneous compounds

Heterocyclic nitrogen compounds, certain pyrazines in particular, can provide burnt, nutty, roasted flavours at low thresholds. At least 18 have been identified in matured grain spirits. The primary source appears to be the Maillard sugar-amine browning reactions in the grain and malt processing (Piggot *et al.,* 1993). These reactions may also take place in wine.

Norisoprenoid compounds have been found in American oak wood near 12 mg/kg total, but are either absent or at low levels in French wood. Several terpenoids occur in distillates, so their contribution in oak maturation is uncertain. However, many terpene derivatives are quite odorous ranging from resinous, violets, lemon to leather smells. Considering American oak is more "oaky" in wines and spirits than European wood, and that "oak" lactone does not seem to fully account for "oakiness", some combination of compounds must be involved in this. The best

speculation is that it is perhaps a combination of oak lactone, eugenol and terpenoids (Schreier *et al.*, 1979). Sefton (1991) describes the norisoprenoid group as the most diverse and identified, in oak extract, precursors of compounds patented as flavour additives.

2.7 FACTORS INFLUENCING THE PRESENCE OF WOOD AND FLAVOUR CONGENERS DURING WOOD MATURATION

2.7.1 INFLUENCE OF OXIDATION PROCESSES ON THE DEVELOPMENT OF FLAVOUR OF WINE DISTILLATES

The flavour of brandy is based on a number of compounds, such as carbonyls, higher alcohols, esters, acetals, phenolic compounds, lactones, nitrogen-containing compounds and some microelements. The higher the activity of the processes of interaction and chemical conversion, the more strongly expressed is the role of these compounds in the development of a wood matured flavour in a product like brandy (Reazin, 1983; Puech, 1987; Sefton, 1993; Singleton, 1995). The presence of oxygen and oxidation reactions related to the extraction of some substances from the oakwood play a significant role in this complicated, and slow, process. Oxygen has a significant impact on the oxidation of the polyphenolic fractions of lignin and tannin substances, whereby the major products are aromatic aldehydes, sugars and other compounds affecting the taste and flavour of brandy (Wildenradt, 1974; Reazin, 1983).

Litchev (1989) proposed a non-enzymatic oxidation of the extracted oak wood lignin and its conversion into aromatic aldehydes via a chain radical mechanism. Firstly, molecular oxygen is activated by a cupric (Cu^{2+}) complex, whereby alkyl- and peroxy-radicals are obtained. After combining with an oxygen radical, an interaction with ethanol forms hydroxyhydroperoxide. Under the action of the copper complex, this is degenerated to alkoxy- and peroxy- radicals, which form the degenerate branching of the oxidation process. Acetaldehyde and acetic acid are produced along this pathway, and react with alcohol to form esters and acetals. The copper complex takes part in both the stage of activation of molecular oxygen and the stages of homolytic decomposition of the hydroxyhydroperoxide. Heavy metals such as copper, iron, manganese and molybdenum exert a catalytic effect on the oxidation processes. Some authors have even gone as far as to propose that the catalytic activity of copper ions is close to that of peroxidase, *i.e.*, one atom of copper can oxidize approximately 10^5 molecules of phenolic compounds (Singleton *et al.*, 1969). Thus, the oxidation reactions during aging of wine distillates in oak barrels proceed with the participation of tannin matter, lignin, metal catalysts and peroxy compounds.

In wine distillates, during oxidative degradation, lignin is converted to coniferyl alcohol, guaiacyl glycerol, 3-methoxy-4-hydroxy-phenylpyruvic acid, and other products, which through the oxidation of the hydroxyl group, form coniferyl aldehyde.

This is then oxidized at the double bond and is turned into vanillin (Litchev, 1989). The consumption of a larger amount of oxygen in the first stage of maturation is related to the active oxidative decay of the readily soluble compounds. Litchev (1989) found that at an oxygen content of 9 mg/L, the amount of oxidized tannin matter increases, reaching approximately 30% in the second and third years of aging. Simultaneously, the content of pyrogalloyl hydroxyl groups drops from 8.5% to 5.6% during first five years of distillate aging. As a result of the oxidative reactions occurring during maturation of the wine distillate, aldehydes increased from 34 to 67 mg/L, with the tannin matter and lignin contributing to their formation (Litchev, 1989). These findings indicate that oxygen is indeed an indispensable factor for the progress of all oxidation processes in wine distillates. Oxidation of the extracted substances of the distillate takes place both at the surface of the oakwood and in the bottom layers of the aging distillate. After three to five years of maturation, the entire volume of distillate in the barrel becomes an active zone for oxidative processes (Litchev, 1989).

2.7.2 THE INFLUENCE OF NON-VOLATILE CONSTITUENTS ON THE EXTRACTION OF ETHYL ESTERS FROM BRANDIES

Extracted wood components have secondary effects, other than their direct flavour contributions, which appear to be necessary for correct maturation of the beverage. They have been implicated with changes in sulphur compounds in whiskies, and in the development of structure in the beverage (Nishimura *et al.*, 1983).

Interactions involving phenols and purines that resulted in increased aqueous solubility and reduced headspace concentration of volatile flavour compounds have been reported by King and Solmes (1982). It is therefore possible that this or a similar mechanism operates in matured distilled beverages, and is at least partially responsible for their characteristic flavour.

Piggot *et al.* (1992) showed that wood derived material reduced the extraction of ethyl esters from diluted cognacs by dichloromethane, and thus increased their solubility in aqueous ethanol. The increased solubility reflected a reduction in the activity of the solute in the aqueous ethanol, relative to the dichloromethane, and indicated that an interaction between the components of the wood extract and the esters had indeed taken place. The degree of interaction was shown to increase with increasing acid chain length up to a maximum of 12-14 carbons. The observed reduction in solute activity can be expected to decrease their volatility and hence their headspace concentrations. Elution of ethyl octanoate to ethyl hexadecanoate was found to coincide with components giving rise to characteristics which are regarded as less desirable in matured spirits (sour, oily, soapy, etc). This suggested that esters or compounds of similar polarity give rise to such characteristics in distilled spirits. This also points to an important interaction between wood and distillate components in matured spirits. If the increased solubility reported were polarity dependent, as suggested by the aliphatic chain length dependance, the

effect would encompass components that would give rise to 'immature' characteristics. The increased solubility of such components and their subsequent reduction in headspace concentration would reduce their perception in the aroma of the matured spirit. They are thus there and quantifiable, but are merely masked in the sensory analysis, due to their reduced volatility and flavour activity (Piggot *et al.*, 1992).

2.7.3 OPTIMUM ALCOHOL CONTENT FOR EXTRACTION OF PHENOLIC COMPOUNDS

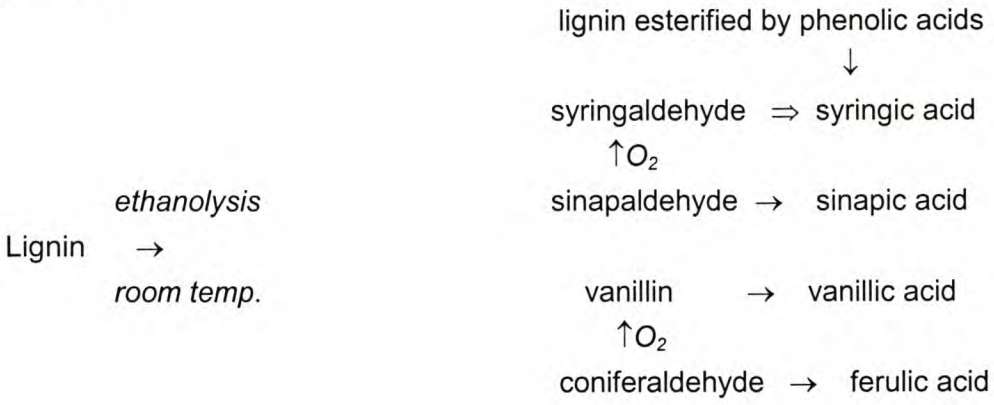
After distillation, brandy is transferred from the still into oak casks. Depending on the method of distillation employed, the alcohol content may vary from 55 to 70% (v/v) at this stage. Nykänen *et al.* (1985) found that maximum lactone extraction was obtained at about 60% v/v alcohol concentration. However, Maga (1985) found that maximum lactone extraction was obtained with 40% v/v, while Puech (1984) found that the optimum extraction levels of tannins and lignin by armagnac occurred at 55%v/v. If the alcohol content rises above approximately 60% v/v, then the extraction rate for colour, solids, tannins and volatile acids for all has been found to decrease. A number of authors have emphasised the effect that distillate strength can have on maturation speeds (Sharp, 1983; Maga, 1985). The reason for this variation is that while the hydrolytic reactions, such as the breakdown of polymeric material, require water, the solubility of degraded compounds improves with increasing alcohol concentration. Therefore, the highest rate of extraction will occur at the concentration where these two processes are most optimally balanced.

2.7.4 ETHANOLYSIS DURING WOOD MATURATION

Baldwin *et al.* (1967) studied the aromatic congener formation during the maturation of alcoholic distillates, in particular lignin derived congeners. They found a soluble substance, present in large amounts in all of the samples studied, including bourbons, ryes and aged spirits, and identified it as ethanol-lignin. It has a lower molecular weight than the parent lignin from which it is derived, and nitrobenzene oxidation experiments show that it is a true hardwood lignin. They postulated a pathway for its formation, and proposed that, under acidic conditions (pH 4 to 5) imposed by the barrel on whisky and other spirits, ethanol can react with lignin in the barrel wood to produce this alcohol soluble form of lignin. This process is known as ethanolysis. Since lignin can be converted to coniferyl alcohol, They felt it reasonable to assume that ethanol lignin can undergo a similar transformation.

A splitting of lignin into various building blocks under hydrogenation conditions can produce di-hydroconiferyl alcohol, which can originate from coniferyl alcohol. Moreover, Baldwin (1967) noted that nitrobenzene oxidation of ethanol lignin yielded syringaldehyde and vanillin, which can originate from sinapic alcohol and coniferyl alcohol, respectively.

Under the mild oxidising conditions present in the barrel, aromatic alcohols are slowly converted to the corresponding sinapaldehyde and coniferaldehyde. Further oxidation of these aldehydes at the olefinic bond produces vanillin and syringaldehyde respectively (Baldwin, 1967). Puech (1981) refined this postulated pathway:



Puech (1981) found that syringaldehyde and vanillin represent respectively 50% and 30% of the total aromatic aldehydes. Syringic acid was predominant in the studied armagnac samples and the syringic acid/ syringaldehyde ratio was shown to vary from 2 to 5. Syringic acid may form after hydrolysis of the lignin ester bonds. The vanillic acid/ vanillin ratio was found to lie close to one. Most of the vanillic acid originates from vanillin, and a small fraction may originate from coniferaldehyde, which yields vanillin, then vanillic acid, after oxidation of the double bonds. The ferulic acid/ coniferaldehyde ratio lay close to 0.2, indicating that only a small fraction of coniferaldehyde is converted to ferulic acid. Most vanillin is generated through oxidation of the coniferaldehyde double bonds.

2.7.5 CHARRING OR TOASTING OF BARRELS

The charring of casks dramatically affects the volatile composition of the oak wood, and increases the levels of many cask extractives. The extent to which lignin degradation takes place in spirits aged in charred or toasted oak barrels, is much greater than when spirits are aged in uncharred or untoasted barrels (Baldwin, 1967; Guymon, 1968; Puech, 1981; Chatonnet *et al.,*1992; Conner *et al.*, 1992).

John (1991) as quoted by Singleton (1995) claimed that slow, constant heating was preferred for the manufacture of barrels, but the duration of heating may range in time from 20-60 minutes, with many of the coopers offering their customers varying degrees of toasting. However, the toasting of barrels is usually an entirely empirical process, and therefore there is no objective ranking of toast between different coopers.

Toasting at medium intensity (35 minutes, 160 –170 °C) is carried out to obtain an increase in the quantity of phenolic aldehydes and acids without the production of phenol type compounds (such as guaiacol, dimethoxyphenol and cresol) which are characteristic of burnt wood (Cadahia *et al.*, 2001). The first phase of the toasting

process (120 – 165 °C) is characterized by the formation and increase of cinnamic aldehydes (sinapic and coniferylic aldehydes) and benzoic aldehydes (syringaldehyde and vanillin) or acids (syringic and vanillic acids), from the degradation of lignins (Monties, 1987). This mechanism works as follows: cinnamic aldehyde → benzoic aldehyde → benzoic acid, which involves the cleavage of α - β bonds of cinnamic aldehydes and the formation of benzoic acids (Sarni *et al.*, 1990). The second phase (165 – 195 °C) involves the thermolysis of aldehydes and acids into wood phenol type compounds (Sarni *et al.*, 1990; Chatonnet *et al.*, 1989). At the beginning of toasting there is a breakdown of celluloses that acts as the initiating stage in the degradation of lignins (Bourgois *et al.*, 1988). The breaking of hydrogen and covalent bonds between celluloses and lignins destroys the cohesion of the lignocellulose network and facilitates the depolymerisation by means of rearrangement of the terminal units of lignin (Monties, 1987). The formation of cinnamic aldehydes can be a result of the breaking of aryl ether bonds (α-O-4 and β-O-4), which are less stable than C-C bonds (Sarni *et al.*, 1990).

The important increase in furanic derivatives, mainly 5-(hydroxymethyl) furfural and 2-furanoic acid, in the toasted oakwood with respect to a non-toasted one reflects the degree of sugar degradation during toasting. The 5-(hydroxymethyl) furfural results from the degradation of aldohexoses of cellulose (Chatonnet, 1992). Furanoic acids could come from pentoses of hemicelluloses, which by thermodegradation, yield mainly furfural (Chatonnet, 1992). These compounds or their derivatives and other derivatives of sugar degradation products such as pentacyclic and hexacyclic ketones (Cutzach *et al.*, 1997; Cutzach *et al.*, 1999) can play an important role in the aroma of barrel aged wines and spirits. During wood toasting, a decrease in the content of ellagitannins, which produces ellagic and/or gallic acid by thermodegradation, is observed (Chatonnet *et al.*, 1992; Sarni *et al.*, 1990). However, this process does not always go with an increase in the quantities of these acids, due to the fact that they can be sensitive to heat treatment.

Phenolic compound quality and quantity are narrowly related to toasting intensity, but the particular characteristics of each wood species could determine the rate of modification in toasted wood (Nomdedeu *et al.*, 1988; Sarni *et al.,* 1990; Cadahia *et al.*, 2001).

The flavour derived from charring has long been thought favourable in whisky maturation. Many studies (Baldwin *et al.,* 1967; Singleton, 1974; Sarni *et al.,* 1990) have found that concentrations of furan and lignin degradation products are higher in spirits matured in charred casks. They found that the levels of lactones were proportional to the degree of cask charring and hypothesised that thermal lipid oxidation gives rise to lactones. They also found that the charring of wood eliminates ellagitannins from the extractive content. Patterson *et al.* (1994) noted that charring forms a layer of active carbon that may remove undesirable flavour congeners. Rejuvenating used casks by re-charring increases the amount of colour, solids, fixed acids, tannins and aromatic aldehydes that can be extracted, increasing the viability

of the cask. However, the same levels as those found in new casks will never be achieved and viability will once again decline with reuse.

Similar effects have been reported by studies done on toasting, although some apparently conflicting results have been obtained. Chatonnet *et al.* (1992) found that while toasting increases the levels of lignin degradation products and furan products, it decreases the levels of polyphenols and lactones. Marsal and Sarre (1987), also reported an increase in furan products, furfural and 5-hydroxymethyl furfural, and decreased levels of oak lactones extracted from toasted wood.

Nishimura *et al.* (1983) found that the optimum toasting temperature for producing the highest amount of aromatic aldehydes is 200 °C. Singleton (1995) found that oak wood chips heated for 1.5 hours at 150 °C provided the highest aldehyde content. Pyrolysis of lignins and other compounds during toasting or charring may lead to the formation of smaller phenolic compounds such as phenol itself, guaiacol, 2,6-dimethoxy phenol, catechol, resorcinol and hydroquinone. As a group these compounds possess smoky, medicinal aromas (Singleton, 1995).

2.7.6 WAREHOUSE HUMIDITY AND TEMPERATURE CONDITIONS

If the air of the warehouse is low in humidity, the rate of water loss is greater than that of alcohol and the alcohol concentration in the cask increases. Under conditions of high humidity, the diffusion of water is depressed by the significant vapour pressure of water vapour at the cask surface or in the air. In this instance the rate of diffusion of ethanol is not significantly affected and consequently the alcohol concentration inside the cask decreases (Singleton, 1995).

Compounds of comparatively high molecular mass, such as the fusel alcohols, which are less permeable through wood than ethanol or water, are slightly concentrated by maturation (Onishi *et al.,* 1977). In the absence of temperature control, more congeners are formed and extracted from casks in the top tier than in the bottom due to higher prevailing temperature and consequent increases in the rates of physical and chemical reactions (Reazin, 1983).

Venter *et al.* (1985) found that higher than average yields of the non-volatile phenols could be extracted from central French oak for the first 10 years of cask re-use at both a mean relative humidity of 80 and 60 percent. Thereafter these values decreased drastically and in 19 year old re-used casks these products were almost exhausted. Low ambient warehouse temperature was shown to inhibit the rate of chemical reactions taking place within the barrel. Thus certain oakwood extractives can be depleted sooner during maturation at high relative humidity compared to low relative humidity, whilst even higher levels of the non-volatile phenols can be extracted as the alcohol concentration proceeds towards the optimum extraction concentration of 55% v/v. Although Venter *et al.* (1985) observed chemical differences in their study, the effect thereof on the sensory quality of matured potstill brandy could not be determined. They noted the following in their study:

- Ethyl acetate was formed at a constant rate throughout the maturation period.

- Higher alcohol concentrations showed little change over the three year maturation period with the exception of used 10 and 19 year old casks. The latter reflected an increase in active amyl and isoamyl alcohol.
- Gallic acid showed a fairly constant increase in the amount extracted during maturation and a pronounced decrease in the total amount extracted as cask re-use exceeded 10 years.
- Procatechuic acid followed a pattern of extraction similar to that of gallic acid. With the exception of used 4 year old casks, no significantly greater amount was extracted at high relative humidity as opposed to low humidity.
- Syringaldehyde showed a pronounced increase between the first and the second year of maturation with significantly higher amounts extracted at high relative humidity. According to Puech (1981) syringaldehyde originates from the oxidation of sinapaldehyde, the latter being the product of lignin ethanolysis at room temperature. The low ambient temperature in the ventilated warehouse during winter might therefore be the cause of less lignin degradation with the resulting formation of less sinapaldehyde that can be converted to syringaldehyde.
- Syringic acid extraction increased with maturation and significantly higher levels were extracted from new to used 10 year old casks at high relative humidity.
- Ferulic acid extraction increased from the first to the second year of maturation and decreased somewhat towards the end of the third year of maturation. The pathway proposed by Puech (1981) for the extraction and evolution of lignin, proposed that ferulic acid originates from coniferaldehyde, yet with sufficient oxidation the preference would be for the formation of vanillin. This could account for the decrease in ferulic acid after the second year of maturation.
- Vanillin, the precursor of vanillic acid, increased significantly from the first to the second year of maturation and thereafter only increased slightly whilst vanillic acid continued to increase constantly throughout maturation. Vanillic acid was extracted at significantly higher levels at high relative humidity from new to used 10 year old oak casks. Vanillyl alcohol extraction from new to used 10 year old casks was similar. A statistically significant higher level of 4-hydroxy-3-methoxy-benzylalcohol was only extracted from one year used casks at high relative humidity.
- Syringaldehyde, syringic acid, vanillic acid and vanillyl alcohol were extracted at significantly higher levels at high relative humidity from new to re-used 10 year old casks.

It is unlikely that any optimum temperature exists in regard to maturation, as the organoleptic impact will differ for each of the components (Reazin, 1983). Extraction and formation of flavour congeners will generally occur more rapidly at 30 °C when compared to 20 °C (Reazin, 1983; Nykänen, 1986). The greatest increase was found

to be in aldehyde and fixed acid concentrations, while lactones and furfural levels appeared to be unaffected (Reazin, 1983; Nykänen, 1986).

2.7.7 PH AND ACIDITY

The pH may both influence and be influenced by the extractives of oakwood. Maga (1985) found that pH affected the degree of lactone extracted from wood by an alcohol solution. Peng *et al.* (1991) described how water reactions are more efficient at higher pH levels. The solution pH can also be influenced by the cask wood extractives, with acidification being characteristic of pyrolysed wood (Sarni *et al.;* 1990). Maga (1985) described how the pH declines during maturation of wine in wooden barrels, and this may in turn influence the for

2.8 THE AROMA COMPOUND COMPOSITION OF SOME COMMERCIAL BRANDIES

2.8.1 DEFINING A BRANDY OF QUALITY

Distillation control of brandies is usually aimed at achieving relatively low aldehyde and fusel oil concentrations. If specifications are set for these two characteristics, then the stillmaster can do little to control the ester content in both a continuous still and pot still operation. Ester loss, at least in part, is due to the considerable reduction of the aldehyde content, which is due to the removal of larger heads fractions (Guymon, 1974a). It is generally agreed that aldehydes, if excessive, give a brandy a hot, burning taste and it follows that the higher the aldehyde content, the longer the required ageing period to reduce this aldehyde content (Singleton, 1995). Extended ageing results in some flavour improvement through formation of acetals from aldehydes and alcohol (Guymon and Crowell, 1972b; Singleton, 1995).

Fusel oils are a loosely defined group of higher alcohols, mainly isoamyl, that contribute to the body of a brandy, and also, to some extent, its bouquet. If excessive, they are said to contribute to the "morning after" effects (Guymon, 1972a).

In 1952, Warkentin reported on the state and improvement of American brandies from pre- to post-war times spanning 30 years. Much of the post-war trends are still relevant for today. Warkentin (1952) basically divided good quality brandies into two broad classes:

i. The heavy, oak matured, cognac style brandies that are laden with fusel oils, esters and aldehydes.
ii. A lighter style brandy, that is easier to drink on its own, and that can also function as a successful mixer with other non-alcoholic beverages in that it does not completely overpower the taste of the mixing partner. There are many advantages to producing a lighter brandy. One of the most important is that a more uniform product can be made by removing the bulk of congeners. The other

advantage of producing a lighter brandy, which is low in aldehyde and fusel oil content, is that it requires less ageing to become palatable.

Both of these styles can also be achieved through the clever use of blending (for example, a standard brandy in South Africa is obtained by blending matured potstill brandy with neutral wine spirit to produce brandies in style ii). However, this style definition becomes more interesting when one considers 100% potstill brandies with differing flavour and aroma characteristics.

2.8.2 AROMA COMPOUND COMPOSITION OF COMMERCIAL EUROPEAN BRANDIES

The quantitative and qualitative aroma compound composition of spirits not only provides an indication as to the relationship between sensory attributes and chemical composition, but can also provide meaningful insight as to the technological processing and quality of raw materials used during spirits production. According to the EU regulations of 29 May 1989 regarding the composition and classification of spirits, EU brandies must contain at least 129 mg of volatile substances (excluding methanol) per 100 ml of pure alcohol (A). The methanol level may not exceed 200 mg/100ml A. This legislation, however, cannot control the addition of neutral fruit derived spirits to brandies, which is in fact illegal, as there are no stipulations on the maximum amount of other particular volatile substances allowed. This vague legislation therefore also exercises no control over the addition of trace amounts of aroma contributing substances, such as the addition of ethyl heptanoate, or the excessive rectification procedure during distillation, in order to mask bacterial spoilage defects present in the original base wines. Postel and Adam (1990) performed quantitative studies of European brandies from Germany, Italy and France (including Cognac and Armagnac), in order to ascertain whether and to what extent these products comply to the prescribed volatile compound composition regulations of the EU.

2.8.2.1 Cognac and armagnac

They reported a total amount of volatile substances in cognac of 590 mg/100ml A, with a variation of 540 – 652 mg/100ml A, and in armagnac 573 mg/100ml A, with similar levels of variation. Higher alcohols were found to comprise the majority of volatile substances present, comprising 79% of cognac, and 84% of armagnac volatiles. Methanol varied between 39-66 mg/ml A in cognac and between 50-62 mg/ml A in armagnac. These values were, on average, lower than what was found in German brandies. Armagnacs contained slightly higher levels of isoamyl alcohol and 2-phenylethanol than the cognacs, whereas the German brandies had the lowest concentration of these compounds.

As a measure of judging origin and quality in brandy, the ratio of 2-methyl-1-butanol (2MB) to 3-methyl-1-butanol (3MB) is often investigated. Singer (1987) (as

quoted by Postel and Adam, 1990) found that this ratio lay in the region of 0.19 to 0.24 for top quality brandies and varied from 0.24 to 0.26 in lower quality brandies. Postel and Adam (1990) found that the ratio lay between 0.21 to 0.23 in cognac, and between 0.23 to 0.26 in armagnac. German brandies had significantly higher ratios (0.32-0.34), even when compared to the remaining French, Italian and Spanish brandies.

The concentrations of linalool, α-terpineol, *cis*- and *trans*-linalool oxide were small, generally less than 0.01 mg/100ml A in both cognac and armagnac. Yet they were at all times quantifiable.

Carbonyl compounds and acetals comprised roughly 5% of the volatile components. Acetaldehyde made up the majority of this fraction, comprising an average of 23mg/100ml A in cognac and 19mg/100ml A in armagnac, around 10 mg/100ml A less than what was found in German brandies. Column distilled brandies contained less furfuraldehyde than pot distilled brandies and the cognacs contained significantly higher furfural concentrations (2.4-5.8 mg/100ml A) than the armagnacs (0.7-2.6 mg/100ml A).

Meisselhorn (1987) (as quoted by Postel and Adam, 1990) concluded that the 1,1-diethoxyethane content in brandy was not exclusively dependant on the alcohol and acetaldehyde concentration alone. This finding was confirmed by Postel and Adam (1990).

Esters comprised an average of 16% of the volatile constituents found in cognac, and 10.5% of those found in armagnac. The difference was quantitative and not qualitative. The ratio of ethyl caprate to ethyl caprylate was also significantly different. The ratio of ethyl caprylate to ethyl caprate was found to lie consistently below 1 in cognac, and consistently above 1 in armagnac. These results indicated that there are definitely differences in the amount of lees present during distillation in the two regions. In distillates distilled from wines with relatively little yeast lees, ethyl caprylate concentrations dominate over ethyl caprate. With increasing yeast lees, the concentration of both esters increase, and ethyl caprate begins to dominate over ethyl caprylate. Of course, the total ester concentration present in the distillates is also influenced by the method of distillation and the accompanying technological and control factors associated with this (Postel and Adam, 1990a).

2.8.2.2 Other French brandies

Postel and Adam (1990b) also investigated the aroma compound composition of other French brandies. The total concentration of volatile substances was found to lie between 393 to 554 mg/100 ml A, and was thus of the same order of magnitude as the German brandies studied previously. The same was apparent for the total higher alcohol concentrations. The concentration of total esters (excluding ethyl acetate) lay markedly below what was reported for cognac, armagnac, and of the same order of magnitude for German brandies. In most of the samples, ethyl acetate comprised 75-80% of the total ester fraction.

Whereas the methanol concentration in cognac, armagnac and German brandies lay significantly under 100 mg/100mlA, the majority of the French brandies analysed in this section of Postel and Adam's study (1990), contained 100-140 mg/100ml A. This was either due to the use of red grape cultivars in the base wine, or as a result of bacterially influenced wines, which, along with increased levels of other compounds, would then also contain increased levels of methanol. Most of these samples also possessed elevated levels of compounds such as acrolein, 1,1,3 triethoxypropane, allyl alcohol and ethyl propionate. This confirmed suspicions of various degrees of bacterial spoilage present and was thus also an indicator of lower quality brandy. The relatively high values for the ratio of 2-methyl-1-butanol to 3-methyl-1-butanol, lying in the region of 0.32, also confirmed these suspicions (Postel and Adam, 1990b). Further variations from the norm included: increased levels of 2-propanol, lower levels of 1-butanol and 2-phenyl-ethanol, trace amounts of furfural in almost all samples, elevated levels of 1,1-diethoxyethane and strongly diminished ethyl lactate levels. These values pointed to stringent rectification procedures used during distillation. However, all of these samples still met the specification requirements of the EU brandy regulations (Postel and Adam, 1990b).

2.8.2.3 Italian and Greek brandies

Next, Postel and Adam investigated the aroma compound composition of Italian and Greek brandies (Postel and Adam, 1990d). The Italian brandies contained high levels of total volatile compounds, including higher alcohols, similar in magnitude to German brandies. The total concentration of volatile compounds was found to lie between 287 and 503 mg/100ml A in 15 of the samples. Their ester composition profiles, however, were considerably different from those of their German and French counterparts. The levels of ethyl acetate were extremely low, as were the levels of longer chain fatty acid ethyl esters. This would indicate that strict rectification as well as pronounced separation of the heads and heart fraction took place in the Italian brandy production process. The levels of ethyl lactate, ethyl butyrate and diethyl succinate were notably higher in the Italian brandies. Four samples were noted to contain abnormally high levels of 1-propanol, 1-butanol and 1-hexanol, which would point to an addition of neutral fruit derived spirit. Ethyl heptanoate is an ester known for its rather 'wine-like' aroma and is usually only present in levels significantly lower than 0.1 mg/100ml A (Postel and Adam, 1990d). One sample contained an abnormally high amount of ethyl heptanoate, indicating that this had subsequently been added to the brandy in order to increase its aroma complexity. All of the Italian brandies showed, in lesser or greater concentrations, unusual levels of one or more of the following compounds: allyl alcohol, 2-butanol, 1-propanol, 2-propanol, acrolein, ethyl lactate, ethyl butyrate and diethyl succinate. This lead them to conclude that all of the samples contained a measure of bacterial spoilage in the original grapes or wine and were thus all considered to be of a lower quality than the French cognacs,

armagnacs and German brandies analyzed (Postel and Adam, 1990a, 1990b, 1990c).

Of the five Greek brandies studied, three possessed markedly lower levels of volatile compounds than the cognacs, armagnacs and German brandies. However, they still met the volatile compound requirements of the EU regulations. All Greek brandies studied had elevated levels of acrolein, and one possessed very high levels of 2-butanol, once again pointing to a measure of bacterial spoilage in the grapes or in the wine. One of the samples contained ethyl heptanoate at four times the level normally found in brandies, pointing to another unnatural addition in order to enhance aroma complexity.

2.8.3 CHEMICAL AND STATISTICAL CLASSIFICATION OF BRANDIES

Conditions prevalent during maturation such as initial distillate pH, ambient humidity, temperature, wood age (which affects the concentration of gallic acid and the relationship between cinnamic and benzoic aldehydes) as well as the total alcohol content (responsible for differences in the concentrations of acids and aldehydes, total polyphenols and tannins) all influence the concentration of phenolic compounds responsible for ageing (Gomez-Cordoves *et al.*, 1990). It thus follows that phenolic compounds can be used as indicators of brandy ageing (Guymon, 1972; Puech, 1984; Singleton, 1974) and the presence of certain coumarins, particularly scopoletin, is considered to be an index of genuine ageing in oak (Outsuka *et al.*, 1974).

Gomez-Cordoves *et al.* (1993) were able to classify Spanish brandies and cognacs according to quality by applying analysis of variance and principal component analysis to the results of simple chemical (pH, phenol content) and physical (colour) determinations and the relationships between them.

These brandies were classified according to the price-quality relationship where group 1 = good quality brandies, group 2 = medium quality brandies; group 3 = low quality or unbranded brandies, group 4 = 3-star brandies and VSOP cognacs. Analysis of variance revealed that significant differences existed between the total polyphenol values in the case of all three brandy categories, but not between the high quality brandies and the cognacs. However, the addition of extracts may also raise total polyphenol (TP) concentration in the lower quality brandies. Thus other ratios such as L (measure of brown or copper tones in aged distillates)/TP or L/(TP/C) where C = catechin concentration may also be employed to differentiate brandies of this type from genuinely aged brandies. The ratio L/(TP/C) was able to differentiate among all four groups, with some overlap between the groups of highest quality brandies. The ratio of pH/C was able to differentiate between the three brandy categories, but there was some overlap between the medium quality brandies and cognacs. Differences in pH were statistically significant for all of the brandy quality groupings.

Principal component analysis was applied to the results obtained in an attempt to verify the existence of definite groups according to brandy quality (using a total of 65 samples) and based on five parameter values (L, I, TP, C and pH). I represented colour intensity. From these, two components were selected, accounting for 83.02% of the total variance. Component 1, which could be defined as "colour" and mainly consisted of parameters I, L and C, differentiated the medium and good quality brandies. The greatest dispersion occurred in the group of low quality brandies which can be attributed to possible addition of wood extract instead of ageing in oak barrels).

2.8.4 INFLUENCE OF COMPLEX MEDIA COMPOSITION IN COGNAC ON THE CONCENTRATION OF VOLATILE SULPHUR COMPOUNDS

Many factors may affect the interactions of volatile sulphur products, particularly hydrogen sulphide and thiols. Natural chelating agents existing in alcoholic beverages such as polyphenols, organic acids (tartaric and citric acid) or amino acids may interact with volatile compounds and lead to the modification of flavour. In the case of French brandy or cognac, copper and caramel are two constituents which are known to interact with sulphur compounds (Nedjma, 1997). Double distillation in a copper pot still, may elevate the copper concentration in distillates from 0.3 – 5 mg/L (Leaute, 1986). These concentrations may be sufficient to chelate the volatile sulphur compounds, in particular the thiols, which are found in the mg/L range. He found that the presence of EDTANa (a chelating agent) considerably diminishes the concentration of free copper in the solution, which is then also accompanied by the decomplexation of thiols. He noted that 0.4 g/L of EDTANa was necessary for the complete removal of these thiols. Thus he proved that complexation of the -SH group in hydrogen sulphide, methanethiol and ethanethiol to copper present in brandies, does indeed occur. Similar results were also obtained with propanethiol, isopropanethiol, butanethiol and isobutanethiol (Nedjma, 1997).

The wood ageing process, as well as the colour adjustment process (through the addition of caramel), are two other important factors contributing to an increase in concentration of compounds like tannins and other carbonyl compounds (Singleton, 1995). These tannins and other carbonyl compounds (esters, acetals, aldehydes and alcohols) may also participate in interactions with sulphur compounds (Rauhut *et al.*, 1993). Nedjma's study (1997) showed that the addition of caramel does indeed lead to a decrease in the concentration of volatile sulphur compounds. Hydrogen sulphide, ethanethiol and methanethiol in particular are decreased considerably in the liquid brandy medium. A total loss of hydrogen sulphide was observed with 0.3% of caramel in the media (Nedjma, 1997).

Among the carbonyl compounds, ethanal and hydroxymethylfuraldehyde (HMF) are considered the most important in brandy. They are responsible for thiol fixation and their concentration in brandy and cognac varies from 5 to 100 mg/L for ethanal and <50 mg/L for HMF (Nykänen and Suomalainen, 1983). The fixation of various

thiols on the caramel may be explained by the formation of hemithioacetal, dithioacetal and other compounds with the carbonyl constituents of caramel. Nedjma (1997) demonstrated the importance of this medium effect on the detection of volatile sulphur compounds, particularly hydrogen sulphide and thiols and termed this the matrix effect, in which interactions exist between thiols and other substances contained in the brandy and cognac matrix.

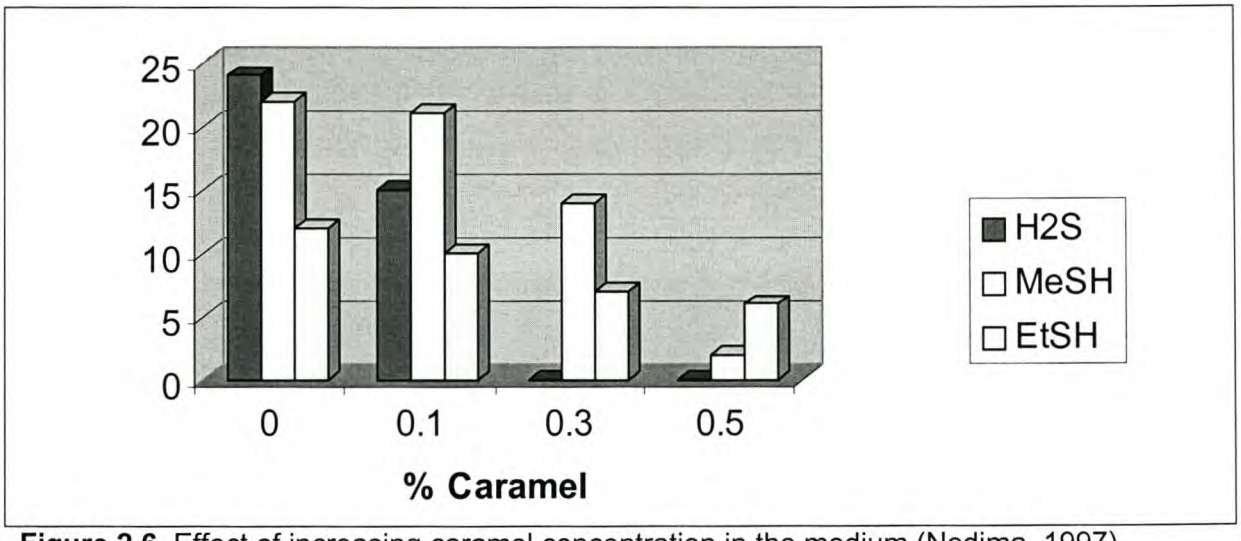


Figure 2.6 Effect of increasing caramel concentration in the medium (Nedjma, 1997).

2.8.5 AGGLOMERATION OF ETHYL ESTERS IN SPIRIT SOLUTIONS

Dissolution of wood components is thought to be of prime importance in the development of flavours inherent to brandies and whiskies. The character of Scotch whisky, for example, is closely related to its concentration of non-volatile compounds (Piggot *et al.*, 1992; Clyne *et al.*, 1993) and it has also been possible to predict sensory scores for mature characteristics from the quantification of non-volatile compounds (Piggot *et al.,* 1993).

Maturation also involves a reduction in the perception of undesirable, or immature characteristics. Losses of ethanol and water through the caskwood also increase the spirit conentrations of many volatile components during maturation (Reazin, 1983; Nishimura *et al.*, 1993).

Matured distilled spirits contain agglomerates or micelles that relate to sensory properties. These form when the spirits are diluted with water for sensory assessment, normally at 220 or 230 mL ethanol per litre (Hardy, 1969). Salo *et al.* (1972) showed that ethyl esters, particularly acetate, hexanoate, octanoate, decanoate and dodecanoate, make a major contribution to whisky odour and that both the addition or the depletion of these esters may have negative effects on whisky aroma. Thus, dilution for analysis will greatly affect the solubility of compounds, such as these ethyl esters, which are less soluble in water than in ethanol. Esters are amphiphilic with a polar head group and a hydrocarbon chain tail. These may thus form agglomerates or micelles in aqueous solutions, and model solutions containing ethyl esters in aqueous ethanol give similar “miscellar” diameters

as those found in matured spirits (Patterson *et al.*, 1994). In studies with a redistilled brandy, it was observed that tannic acid and oak extract significantly reduced the activity of ethyl esters, with reductions in extraction reaching a maximum of 12 to 14 carbons (Piggot *et al.*, 1992).

The activities of solutes may be determined directly by measuring the vapour pressure for the compound of interest. However, chromatographic quantifications of headspace concentrations are more readily obtained. These can then be compared with data from headspace concentrations above the pure solute (unit activity). Activity can then be related to the solution concentration by the following equation:

$$a = f X_a$$

Where a is the activity, f the activity coefficient and X_a the concentration of the solute expressed as mol fractions. For an ideal solution f = 1.

As a first step towards understanding how solute interactions, particularly those between volatile and non-volatile constituents, influence the sensory properties of distilled beverages, Conner *et al.* (1994a) examined the activity of ethyl esters in solutions and the effects of ester-ester interactions and dissolution of wood extracts.

They found that with solutions of individual esters, plotting activity against total solute concentration yielded a plateau as activity approached unity. There are alternate hypotheses that may explain this observation. The first is that a surface film forms as the esters are excluded from the solution, or alternatively, excess esters form agglomerates or micelles. However, measurements of ethanol activity showed no significant change with increasing ester concentration, which would be expected if a surface film were formed. Consequently, it was concluded that the esters were forming agglomerates or micelles.

Medium and long chain esters were found to have a limited solubility when model spirits and malt distillates were diluted to 230 ml ethanol per litre for sensory analysis. At concentrations above this critical level, the concentration of esters in solution remained constant, with the excess esters forming agglomerates. The saturated nature of the solution reduced the volatility of the other esters, with a proportion of these compounds also being partitioned into the agglomerate. This distribution was found to be proportional to the mol fraction of each ester and its activity coefficient. King and Solms (1982) reported interactions between many classes of volatile flavour compounds and purines. These interactions were attributed to plane-to-plane stacking resulting from hydrophobic and π-electron interactions. Compounds lacking an extended π-electron system were thus found unable to interact. In the ester studies by Conner *et al.* (1994a), the driving force for interaction appeared to be the hydrophobic effect, suggesting that other amphiphilic compounds may also be involved. Furthermore, they speculated that the presence of agglomerates might result in the solubilization of hydrophobic compounds in spirit solutions.

Conner *et al.* (1994) also found that the dissolution of wood extractives caused a number of changes in the solubility parameters of organic compounds; activity coefficients increased and both the concentration and activity at which agglomeration

occurred, were decreased. This resulted in lower solution concentrations with increased concentrations in agglomerates. When mixtures of three esters were analysed, addition of wood extract was found to decrease the ester in solution to a minimum, with the greatest effect being on the ester with the smallest hydrocarbon group. Estimating the distribution of ester between solution and agglomerate phases in matured distillate samples indicated that dodecanoate, tetradecanoate and hexadecanoate were primarily found in the agglomerate phase. Little difference was observed between cask types, though for ethyl decanoate a significantly higher proportion was found in the agglomerates for the newly charred casks. A plausible explanation for differences in extraction resulting from the presence of tannic acid and wood extract may lie in the stability of the esters in the agglomerate phase. It is also possible then, that in matured whisky samples, the stability of agglomerates is related to the concentrations of wood-derived non-volatile compounds. Conner *et al.* (1994) speculated that the reductions in free solution concentration due to the influence of wood-derived, non-volatile compounds could result in lower headspace concentrations and thus have a direct effect on the aroma and flavour of the matured spirit.

2.8.6 INFLUENCE OF FILTRATION ON ESTER CONCENTRATIONS IN BRANDIES

In order to prevent haziness in finished brandy products, the spirits are subjected to a cold filtration (-2 to 4 °C) just prior to bottling. The amount of cold stabilization as well as the filtration temperature required is determined by the concentration of C_6 to C_{16} ethyl esters present in the spirit. The concentration of the ethyl ester of capric acid is particularly important in this regard. The desired alcoholic strength of the finished product is also important to consider in this regard (Von Adam *et al.*, 1996).

The decrease in longer chain esters during the course of filtration depends on the actual chain length of the esters as well as their concentration. The shorter the chain length of the ester, the less likely it is to be removed during filtration. The converse is true for long chain esters. The degree to which this takes place is, however, directly influenced by the filtration temperature. Depending on their initial concentration and the filtration temperature employed, longer chain fatty acid ethyl acids may decrease by anything from 25 to 70% of their initial concentration prior to filtration (Von Adam *et al.*, 1996). As the filtration temperature decreases the proportion of esters remaining in the filtered product also decreases. The extent of this decrease is ester chain length dependant. Thus ethyl caproate (C_8) showed no decrease in concentration in the filtered product (Von Adam *et al.,* 1996).

2.9 NEGATIVE AND POSITIVE QUALITY INDICATORS IN DISTILLATES AND BRANDIES

In assessing the quality of a wine distillate, it is important to know which attributes are considered to be negative and positive and to have some indication as to their origin.

2.9.1 NEGATIVE QUALITY INDICATORS IN DISTILLATES

For negative attributes, detection of quality defects can generally involve:

i. Microbial analysis of wild yeasts, lactic acid bacteria, acetic acid bacteria, and *Botrytis cinerea* in the base wines.

ii. With *Botrytis cinerea* it has been noted that newly distilled spirits are richer in ethyl acetate, ethyl butyrate and the C_6 to C_{10} ethyl esters (Cantagrel; 1988).

iii. Determining the contamination threshold beyond which the quality of the spirit is adversely affected.

iv. Infected wines also exhibit organoleptic alterations that may have an adverse effect on the resultant distillate. These wines may exhibit the following characteristics, which can manifest themselves in the resultant distillate:

- loss in fruitiness
- instability of aromas arising from fermentation
- appearance of camphor, phenol and iodine like tastes
- appearance of a lactone, sotolon, with a note of honey, sugar or caramel [4,5-dimethyl-3-hydroxy-2-(5H)-furananone] (Cantagrel, 1988)
- formation of flavours typical of oxidation (heavy prune, maderized character)

Sensory analysis can detect acetic acid, acrolein, putrid, oxidation and maderized off-odours in wine distillates. Gas chromatographic analysis can also ascertain the following defects (Cantagrel, 1988):

i. Oxidation or maderization: acetaldehyde, acetal (1,1-diethoxytethane)

ii. Sourness or ascescence: ethyl acetate

iii. Pungency: correlated to the sum of ethanal and acetal (which varies from 50 – 200 mg/L)

iv. Stagnant and butyric: 1-butanol, 2-butanol and ethyl butyrate

v. Burnt plastic: acrolein and allyl alcohol

vi. Fermentation problems in the base wine if the propanol contents are higher than that of iso-butanol and acetoin

vii. Poor distillation: excess tails fraction in heart leads to excess ethyl lactate and 2-phenyl ethanol. Excess heads fraction inclusion in the heart leads to increased short chain ethyl esters, aldehydes and higher alcohols

viii. Initial tests on new spirits (Cantagrel, 1988) distilled in 1987-88 indicated the following taste thresholds, above which the spirits were judged to be defective:

- Acetaldehyde: 60 mg/L
- Acetal: 30 mg/L
- Ethyl acetate: 600 mg/L
- 1-Butanol: 6 mg/L
- 2-Butanol: 6 - 7 mg/L
- Ethyl butyrate: 4-5 mg/L
- 2,3-Butanediol: 3-20 mg/L, with an average of 8 mg/L. At a high level this compound and other tail products can mask floral, pungent and woody aromas.

2.9.2 POSITIVE QUALITY INDICATORS IN DISTILLATES

i. Fruity aromas: derived mainly from acetates of higher alcohols (especially isoamylacetate). Their concentration can vary from 0.3 to 10 mg/L. These compounds are hydrolyzed during ageing and disappear almost completely after about 10 years.

ii. Floral aromas: fatty acid ethyl esters (10 to 30 mg/L) are mainly responsible for this aroma.

iii. Grassy aromas reminiscent of cut grass are characterized by a high concentration of hexanol and 3-hexenol and usually correlate to the degree of ripeness of grapes.

iv. Buttery aromas: derived from the presence of diacetyl. Diacetyl at a concentration above 4 mg/L is undesirable as the subtle buttery aromas become too pungent and are perceived as a negative, rancid odour.

Research opportunities still exist for studying the above-mentioned flavour thresholds with greater accuracy, particularly by checking and comparing flavour thresholds over several years and performing the same tests on finished products. The effects of other constituents present in distillates also require more research.

2.9.3 THE EFFECT OF OFF-FLAVOURS IN DISTILLING WINE ON THE QUALITY OF BRANDY

David (1933) stated that "to make a good brandy one has to start with an exceptionally good distilling wine". In South Africa wines are made especially for distillation into brandy, commonly referred to as rebate wine due to the rebate on excise duty for brandy due to the alcohol losses incurred during wood maturation (Weitz, 1997). These wines are all evaluated organoleptically to check that they conform to the quality norms prior to being bought and brought into the distillery. In sensory evaluation of these wines, little or no foreign tastes or odours, including SO_2 may be present, while no indication of astrigency on the taste is allowed.

Wagener (1986) studied the effect of off-flavours and astringency in wines on the quality of the resultant brandy produced in South Africa. He found that, with good quality wines, high quality brandy distillates were obtained, which gradually developed into brandies with positive wood maturation aromas over the three year maturation period. One wine, which was described as being bitter and phenolic, produced an acceptable and fairly good brandy distillate, which later developed into a very good and soft product with good ageing characteristics after three years in wood. Three wines, which were described as being very rancid, produced brandy distillates with two distinct characteristics. One of these exhibited a strong rancid flavour and retained its very prominent rancid character right through the three-year wood maturation period. The panel judged this brandy to be of low quality and not potable. The other two distillates possessed a sharp, feints/ aldehyde character. Although these two distillates improved in quality with wood maturation, they still retained a slight aldehyde character at the end of maturation. Wagener (1986) speculated that there were two possible explanations for the occurrence or absence of rancidity in brandy distillates produced from rancid wines: Firstly, there are substances producing rancidity in wines, which distill over into the brandy distillate. And secondly, there are substances producing rancidity in wines, which are converted into non-rancid substances or are destroyed during the distillation process.

According to the then South African Brandy Board, oxidation was another objectionable off-flavour that could make wines unacceptable for brandy distillation. However, Wagener (1986) found that the brandy distillate made from heavily oxidized wine, produced a soft, well balanced distillate of very good quality, which retained its quality during maturation.

Wines possessing high levels of volatile acidity, sweet/ sour and organic characteristics, were, according to the then South African Brandy Board, also not suitable for distillation. However, Wagener (1986) found that, wines which were initially rated low in quality as a result of the above-mentioned characteristics, developed into brandies of fairly good to good quality after three years of wood maturation.

Wagener (1986) noted that distillates that were judged to be of low quality, contained the highest concentrations of higher alcohols while those with the highest quality rating contained the lowest higher alcohol concentrations. Although the aldehyde concentrations of these brandy distillates showed no definitive tendencies, the two brandies that received the highest quality rating possessed the lowest aldehyde concentrations. It is generally agreed that aldehydes, if excessive, give new brandy a hot, burning taste and the higher the aldehyde concentration the longer the required ageing period (Warkentin, 1952). Extended ageing does result in some improvement through the formation of acetals from aldehydes and alcohol. Wagener (1986) also observed that the ester, furfural and methanol concentrations present in the distillates could not be used as indicators of ultimate product quality. Thus he concluded that many off-flavours that may be present in brandy base wines will have

no effect on the quality of the resultant distillates. There are, however, definite indications that some specific off-flavours, such as rancidity, have a marked and lasting effect on the quality of the distillate. Wines with a rancid character that produce equally rancid distillates are not suitable for brandy maturation, although rancid wines that do not produce rancid distillates produce brandies with no trace of rancidity. Other off-flavours with wet feather and yeasty, organic, table-grape characteristics are also unsuitable for brandy distillation as they produce hard and unclean brandies (Wagener, 1986).

Guymon (1968) investigated the effect of the presence of SO_2 in brandy base wines and found that one could easily detect its organoleptic effect on the resultant brandy quality. Brandies distilled from wines containing added SO_2 possessed a characteristic acetal odour, devoid of any grapiness or fruit fragrance and had a hot and styptic aftertaste. Analysis showed that these brandies were high in fixed acids, aldehydes, ethyl acetate and metal ions and low in pH (Guymon, 1968).

Postel (1982) investigated the formation of n-butanol in wines and brandies and its correlation with the quality of these distilling wines and brandies. Although distilling wine, which was organoleptically rated as mousy, faulty, acetic and spoilt, showed butan-2-ol concentrations as high as 74 mg/ 100mL AA, its presence, even in such high concentrations, did not in any way contribute to the sensory qualities of these distillates. However, wines with off-characteristics in many instances have a negative effect on brandy quality.

Wagener (1986) analyzed wines containing different concentrations of polyphenols. He found that the wines containing increased concentrations of polyphenols possessed higher aldehyde concentrations and produced brandies with increased aldehyde, higher alcohol, total ester and furfural concentrations. Brandy distillates derived from wines with total polyphenols of 296 mg/L and higher were termed sharp and hard with a prominent aldehyde/ feints character. These undesired characteristics in the brandy distilled from a wine which contained 522 mg/L polyphenols did not even disappear after three years of wood maturation.

2.9.4 DISTILLATE INDICATORS OF BACTERIAL SPOILAGE IN WINE

The presence of acetic and/or lactic acid bacteria in the base wine will result in increased concentrations of ethyl lactate, ethyl propionate and ethyl acetate. One method of eliminating such undesirably high concentrations of these compounds is to perform a strict rectification during distillation. By removing a larger than normal share of the distillate heads, increased levels of ethyl acetate and ethyl propionate can be removed from the distillate heart. Similarly, by collecting a larger and earlier fraction of the distillate tails, increased levels of higher boiling ethyl lactate and diethyl succinate can be removed from the distillate heart (Postel and Adam, 1990). However, such rectification is inevitably coupled to a loss of desirable esters, as most of the desirable esters are lower boiling, soluble in alcohol and thus volatilize in the early hearts fraction. The total ester concentration (minus ethyl acetate) is comprised

mainly of the desirable esters such as ethyl caprylate, -caprate, and -laurate, as well as many other esters appearing only in trace amounts. This total is considered to be a good indication of brandy quality, and previous reports point to a generalised figure of 14-15 mg/100 ml A of this total ester concentration (minus ethyl acetate) for organoleptically good quality brandy (Postel and Adam, 1990a). Postel and Adam (1990), based on their quantitative studies on brandy distillates, concluded that a brandy made from healthy grapes and not undergoing any bacterial spoilage or harsh treatments during winemaking, should yield approximately 40 to 50 mg/100ml A of total esters. Values less than these, point toward either a strict rectification process during distillation, or to the addition of neutral alcohol, which will both strip a brandy spirit of its ester concentration.

Acrolein, which can be produced by bacteria in wine from glycerol, is the precursor to allyl-alcohol and 1,1,3-triethyl alcohol and is reportedly also useful as an indicator in determining the quality of the base wine that was used in brandy distillation (Postel and Adam, 1990).

2.9.5 RELATIONSHIPS BETWEEN PHENOLIC COMPOUNDS OF LOW MOLECULAR WEIGHT AS INDICATORS OF THE AGEING CONDITIONS AND QUALITY OF BRANDIES

The phenolic compounds of low molecular weight, aldehydes and acids have been considered indicators of wine and spirits aging in oak barrels by several authors (Outsuka *et al.*, 1974; Gomes Cordoves *et al.,* 1990; Singleton, 1995). It is believed that the presence of coumarines especially scopoletin, can be considered an index of the extent to which an authentic aging with oak has taken place in the spirit (Outsuka *et al.*; 1974).

Gomes-Cordoves and Bartolome (1993) classified Spanish brandies and cognacs according to quality by applying analysis of variance and principal component analysis (PCA) to the results of: alcohol content; distillate pH, phenol content, length of time spent in the cask, cask age, ambient conditions and colour determinations and/ or the relationships between all of these factors. They used a total of 65 samples based on five simple parameter values, namely absorbance, intensity, total polyphenols, catechins, and pH. The first component, which could be defined as “colour”, and mainly consisted of intensity, absorbance and catechin concentration as parameters, differentiated the medium and good quality brandies, although there was some overlap between certain brandies. This was thought to be attributable to differences in the quality standards applied by various distilleries to their high quality products and to production of several brands by each distillery. As expected, the greatest dispersion occurred in the group of low quality brandies.

Gomez-Cordoves *et al.* (1993), investigated the relationships between:

- Total syringyl compounds (Sr)/ Total vanillyl compounds (Vn)
- Syringaldehyde (S)/ Vanillin (V)

- Vanillin (V)/ Coniferaldehyde (C), which can be expressed as

  gallic acid (G)/ vanillic acid (V)

  vanillin (V)/ vanillic acid (Va)

  syringaldehyde (S)/ synapaldehyde (Sp)

  syringaldehyde (S)/ syringic acid (Sy)

  syringic acid (Sy)/ vanillic acid (Va)

By establishing a respective histogram for the statistically significant relationships, they noted the following:

Higher quality brandies **(Figure 2.7)**

- Have high Sr/Vn and S/V relationships
- The G/V is the most important relationship, almost half of the total and is very high for this category of brandies. This ratio can be lower if the aging takes place in barrels of very old wood, where the tannin concentration is lower.
- The other four relationships are very similar regarding compositional importance.
- Thus this compositional profile can be viewed as an indication of a genuine aging in oak wood.

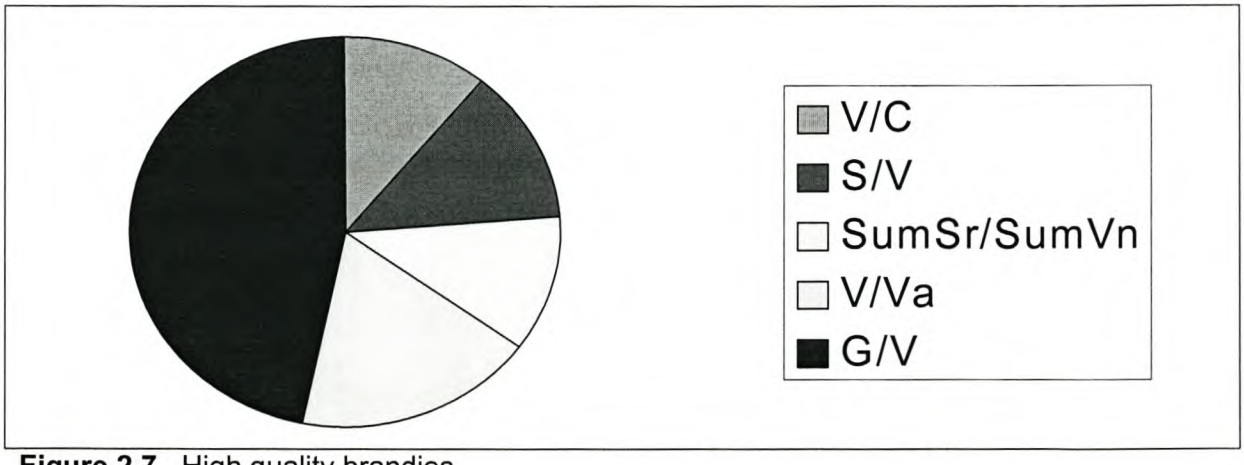


Figure 2.7 High quality brandies.

Medium quality brandies **(Figure 2.8)**

- Vanillin participates in all of the important ratios in this quality category.
- This observation may indicate the addition of materials other than oak, like almond shells, which have a high vanillin extract content, to the spirit in order to enhance brandy aroma in a more cost-effective manner.

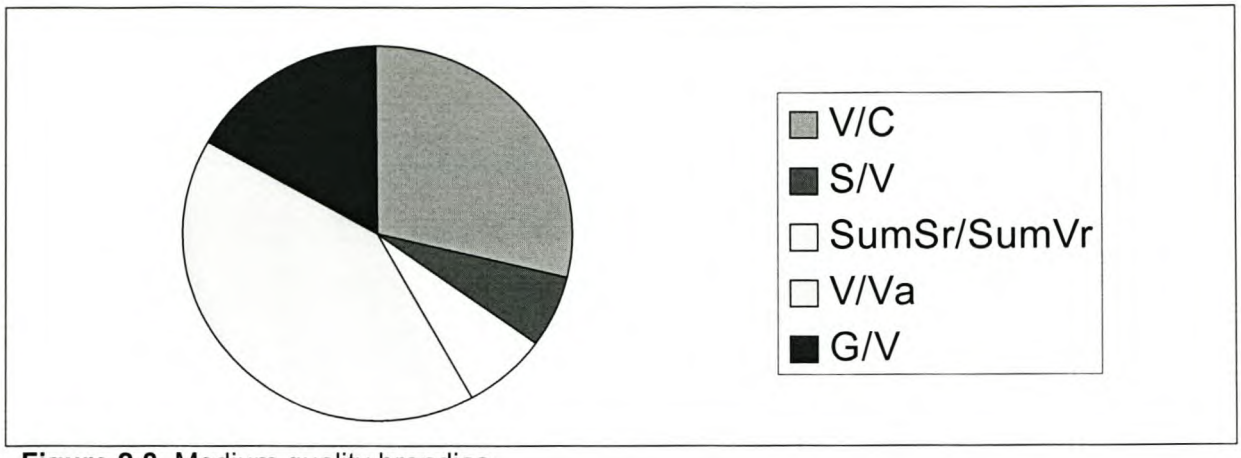


Figure 2.8 Medium quality brandies.

Low quality brandies **(Figure 2.9)**

- Here 97% of the samples, according to the studied relationships, consisted of vanillyl compounds, with an almost total absence of gallic acid and syringyl derivatives, which would indicate a large measure of spirit adulteration and an almost complete lack of oakwood aging.
- These brandies had the highest V/C ratios.
- They had the lowest Sr/Vn and S/V ratios

The scopoletin content, an indicator of aging with oak, presented a wide variety of values in the studied samples. This was thought to be due to the low concentrations in which it may have been extracted from the wood, as well as the influence of such factors as initial pH or barrel age (Gomes-Cordoves et al., 1990).

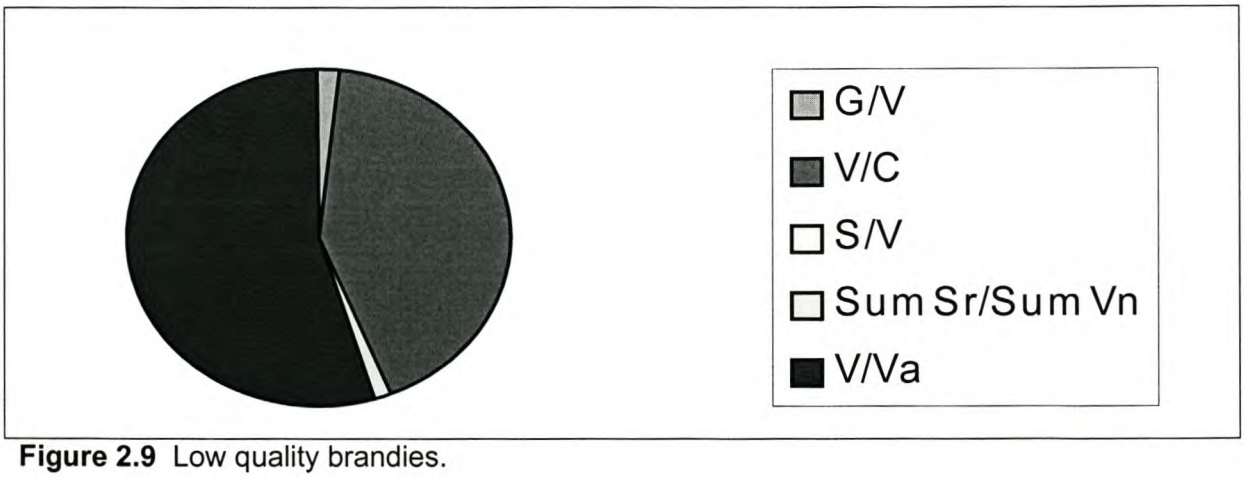


Figure 2.9 Low quality brandies.

2.10 CONCLUSION

Brandy production is a multi-stage process where the production of base wine, distillation technique and wood maturation phase all have a large influence upon the ultimate analytical profile and associated sensory quality of the brandy. Within each of these production phases, there are a multitude of factors that can influence the

presence and concentration of flavour and aroma compounds. This chapter has briefly highlighted the factors pertaining to distillation and oak maturation. However, many of the flavour and aroma compound interactions comprise complex, synergistic and antagonistic perception effects that are not necessarily linearly related to the compound concentration levels found in distillates and brandies. It is therefore difficult to view each of these factors, or for that matter, any one flavour compound, in isolation and hope to find a direct relationship to the perceived aroma and flavour quality of a brandy product.

Of importance is the fact that the presence and concentration of particular compounds in brandy can provide clues as to how the brandy was produced and matured.

South African brandies are produced from predominantly white cultivar grapes that grow in warm regions in predominantly alluvial soils. Much of the literature quoted in this chapter is based on studies done in other wine and brandy producing regions of the world (with different *terroir* and blending requirements) and thus, many of the indicated relationships between flavour compounds may have slightly different values than those quoted.

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CHAPTER 3

RESEARCH RESULTS

Yeast derived flavour compounds and their relationship to quality in young South African Chenin blanc wines

RESEARCH RESULTS

3. YEAST DERIVED FLAVOUR COMPOUNDS AND THEIR RELATIONSHIP TO QUALITY IN YOUNG SOUTH AFRICAN CHENIN BLANC WINES

ABSTRACT

Twenty-one volatile compounds were quantified in young, unwooded Chenin blanc wines entered into the South African Young Wine Show from 1998 to 2003. The results of the show were adjusted to create a 3-point scoring system, where gold and silver medal wines were awarded score 1, bronze medal wines score 2 and no medal wines a score 3. Using a two way ANOVA with vintage and score as independent variables, it was found that, although the concentration of compounds studied varied from vintage to vintage, no interaction between vintage and score could be found. This finding made it possible to perform a one way ANOVA on the volatile compound analyses using the score of the wines as independent variable. It was found that the concentration of isoamyl acetate, hexyl acetate, ethyl caprylate, ethyl caprate, 2-phenethyl acetate and octanoic acid was significantly higher in wines awarded gold and silver medals (score 1) and decreased significantly with subsequent decreases in quality categories. The concentration of decanoic acid, isoamyl alcohol, ethyl caproate and acetic acid exhibited the same pattern, however the difference between gold and silver medal wines (score 1) and bronze medal wines (score 2) was not significant for these compounds. Ethyl lactate exhibited the opposite pattern and the concentration of this compound was highest in the no medal wines. CART analysis confirmed many of the findings of the ANOVA and was also able to highlight the interactive behaviour taking place between some of the flavour compounds. Using MARS it was attempted to establish a quality predictor model based on the behaviour of the volatile compounds quantified in young Chenin blanc wines. The prediction accuracy of the MARS model was much better when having to predict the quality of wines made in the same vintage as it had been trained on, and was poorer when tested on a completely different vintage to the ones it had been trained on. Within the same sets of vintages, MARS was able to classify 40% of score 1 wines, 86% of the score 2 wines and 29% of score 3 wines correctly. Using data from a new vintage with adapted outputs MARS was able to correctly classify only 50% of score 1 wines, 57% of score 2 wines and 53% of score 3 wines.

3.1 INTRODUCTION

Chenin blanc plantings comprise 32.3% of the total white vine-plantings in South Africa and 30.2% of the total hectares under vine in South Africa as at 30 November 2002 (SAWIS statistics). It is the Cape's staple white grape, being a well adapted,

highly versatile variety that is related to the Loire Valley's famous Chenin blanc (Platter, 2002). Chenin blanc is easy to manage in the vineyard and has tremendous versatility in its application during winemaking, making a range of styles from sparkling wine to noble late harvest wines. Chenin blanc can yield between 20 to 23 tons/ha (with supplementary irrigation) and has moderate to strongly vigorous growth characteristics. Its ease of growing in the vineyard, relatively high yield and ability to produce a fresh, fruity, uncomplicated dry, white wine makes Chenin blanc the ideal cultivar for brandy base wine production in South Africa. Although De Villiers (1987) found that the flavour and bouquet of Chenin blanc differs from region to region and may vary from a fine, estery character to intense honey and even a strong guava aroma, the aroma of wines made from Chenin blanc grapes is predominantly fermentation derived. It is therefore not complicated by grape-derived components as is the case for Riesling and Sauvignon blanc, whose characteristic aroma is largely influenced by monoterpene and methoxypyrazine concentrations, respectively. This was confirmed when Augustyn and Rapp (1982) reported no measurable amounts of terpenoid components to be present in South African Chenin blanc grapes sourced from various origins. They speculated that local climatic conditions result in a poor terpenoid presence in the Chenin blanc grape leaf. Consequently, the concentration of the terpenoid components translocated to the berries was below the detection limits used in their study. On the other hand, the lack of measurable amounts of terpenoid components may well be the result of some form of physiological block that inhibits the translocation of terpenoid contents from the leaf to the berry (Augustyn and Rapp, 1982).

Young Chenin blanc wines in South Africa often have an aroma which is likened to that of the guava fruit. The reasons for occurrence and presence of this aroma have been studied in detail (Du Plessis, 1975; Du Plessis and Augustyn, 1981; Cosser *et al.*, 1980; Van Rooyen *et al.*, 1982; Van Rooyen *et al.*, 1984). The findings of these authors were based on multi-variate statistical techniques and either correlated sulphur-derived compounds, fermentation derived compounds (such as ethyl esters of C_4 to C_{10}, hexanoic acid and hexyl acetate) or grape skin derived compounds from pressing and ripening (eg. n-hexanol) to Chenin blanc wine quality and/ or origin in South Africa.

Chenin blanc and Colombar are the two most popular grape varietals used in the making of South African brandy base wine. As the absence of terpenoid compounds has not been proven in South African Colombar, it was decided to focus this study on Chenin blanc wines, whose dry white wine aroma is predominantly fermentation derived. The aim of this study was to identify those volatile flavour compounds that are correlated to wine quality and to try and establish a model of volatile flavour compound interactions taking place in young Chenin blanc wines. The reasons for doing so are two-fold. Firstly, this study forms part of a larger study on South African brandy flavour. Whereas brandy production is a multi-stage process involving winemaking, distillation and maturation, the production of unwooded Chenin blanc

wine only involves the first of these three steps. We wished to determine whether it is indeed possible to build a flavour compound model for a relatively simple process such as the making of a young Chenin blanc dry white wine before attempting the same exercise on the more complex process of brandy production. It must, however, be stressed that this study was performed on Chenin blanc table wines, which differ in composition to brandy base wines (these undergo no SO_2 addition or filtration prior to distillation). Secondly, a better understanding of the interactions taking place between flavour compounds, whether they be synergistic or antagonistic, and their effect on wine quality could aid in the optimisation of fermentation conditions desired flavour outcomes as well as the development of more tailored wine yeast breeding programs.

3.2 MATERIALS AND METHODS

3.2.1 WINE SELECTION

The Chenin blanc wines selected for this study comprised 416 wines entered in the unwooded Chenin blanc categories of the South African Young Wine Show from 1998 to 2003. These wines were all made in the same vintage as the year of the show and are expected to exhibit typical early-drinking, fruity and aromatic young, white wine characteristics, which are also desirable attributes of brandy base wine. These wines, according to the Chenin blanc judging panel convenor of 2003, characteristically fall into the first of five identified style categories for South African Chenin blanc. This category is termed “fresh and fruity” and typically comprises wines that have been made from grapes picked at under 23ºB, with a racy acidity and fresh aromas comprising predominantly fermentation ester characters. The remaining four categories, not included in this study are the rich and ripe wines (grapes picked at over 23ºB, structured, alcoholic), rich and ripe with wood influence, rich and ripe off dry and lastly sweet wines (special late harvest and noble late harvest wines).

3.2.2 GAS CHROMATOGRAPHIC ANALYSIS

This was performed using the method as described in Steger and Lambrechts (2000).

3.2.3 SENSORY ANALYSIS

The scores used as a basis for this study were those awarded by five trained and experienced Chenin blanc panel of judges at the Young Wine Show, based on a 20-point wine scoring system. Judges on the panel may have varied from year to year. Scores awarded to the wines by each judge are processed by an independent body and the results are released in medal format i.e. gold medal (average of 17 points and above); silver (average 16 points), bronze (average 15 points), no medal

(average 14 points and lower). Whereas final scoring of the wines from 1998 to 2002 was done by comparing the 20-point score of the five tasters, eliminating the highest or lowest score, and then taking the median of the remaining scores, scoring in 2003 was approached differently. Where there was reasonable consensus between judges, the average score was used. However, for those wines where the judges' scores differed significantly, the wines were presented for a second evaluation and a score was awarded for each wine through discussion and subsequent panel consensus. This may also have influenced the scores and the percentage distribution of the scores in 2003. Variation in terms of the judges used on the panel each year must also be taken into account. In total 66 wines were analysed from the 2003 show entries. There are rarely more than one or two gold medal winners in each class. This makes the statistical processing according to four quality categories very difficult, as the number of gold medal winners are too few to form a statistically representative set. Instead, a 3-point score system was used for this modelling exercise, where 1 = gold and silver medal winners, 2 = bronze medal winners and 3 = no medal awarded. The graphs of the ANOVA and CART analysis refer to this 3-point scoring system as SCORE2.

3.2.4 STATISTICAL ANALYSIS

Statistical analyses were preformed using STATISTICA version 6.0. A two-way analysis of variance (ANOVA), which tests for interactions between two categorical independent variables and also for effects of the variables separately, was performed using vintage and score as independent variables. A one way ANOVA, which tests the hypothesis that means for different groups are equal, was performed using the score as independent variable. The significance level used as a guideline for accepting or rejecting hypotheses was 5%. Where necessary, a Bonferroni *post hoc* test was carried out to determine the significance level of mean concentration differences for two particular scores. A factor analysis, classification and regression tree analysis (CART) and multivariate analysis of regression splines (MARS) was also performed on the data (chapter 4 and 5). The CART and MARS analyses were performed using software from Salford Systems.

CART analysis is able to divide the data into subsets based on a target variable and a selected set of predictor variables. The subsets are divided in such a way as to minimise the variance of the target variable (in this case the score allocated to the wine) within each subset. The result is a set of rules (based on the predictor variables) that characterise each of the subsets and a mean value for the target variable within each subset.

MARS is an extension of piecewise linear regression (Friedman, 1991). In a piecewise linear regression, more than one regression line is fitted to the data to account for non-linear relationships. Each of the regression lines operates on distinct non-overlapping regions of the independent variable space. The position where one regression line stops and the next line starts, is called a knot position. In the

traditional piecewise regression setting, the knot positions must be chosen beforehand. In the MARS analysis, the knot positions are derived from the data. MARS can also handle more than one predictor (independent) variable as well as combinations of categorical and continuous predictors. From a MARS analysis it is possible to determine the relative importance of predictor variables with respect to the target (dependent) variable. MARS can also be used in a binary classification setting. The binary response variable can be coded as 0's and 1's. The MARS model is fitted and estimated values for the response variable will typically lie between 0 and 1. A threshold (eg. 0.5) can then be chosen for classification purposes (Friedman, 1991; Hastie *et al.*, 2001).

3.3 RESULTS AND DISCUSSION

3.3.1 SCORE ANALYSIS

Refer to **Table 3.1** for the vintage mean score as well as the percentage distribution of scores 1, 2 and 3 from 1998 to 2002. When ranking the vintages according to quality on the basis of the mean score and the percentage distribution of score 1 per vintage, it is clear that both instances yield the same result, with the exception of vintages 2001 and 2002. However, in both instances, the basis for this difference between the 2001 and 2002 vintages, is very small.

Table 3.1 Percentage distribution and mean scores for unwooded young Chenin blanc wines entered into the Young Wine Show 1998-2002

Vintage	No. of wines	Score 1	Score 2	Score 3	Total	Mean Score	Ranking on vintage (% distribution score 1)	Ranking on vintage (mean score)
1998	106	47.2%	41.5%	11.3%	100%	1.64	1	1
1999	71	38.6%	50.0%	11.4%	100%	1.73	2	2
2000	68	23.5%	45.6%	30.9%	100%	2.07	3	3
2001	66	13.6%	45.5%	40.9%	100%	2.27	4	5
2002	39	12.8%	53.8%	33.3%	100%	2.21	5	4

3.3.2 SIGNIFICANCE OF VOLATILE COMPOUNDS IN DETERMINING YOUNG CHENIN BLANC WINE QUALITY

A two-way ANOVA using vintage and score as independent variables showed that, although the concentration of compounds studied varied from vintage to vintage, no interaction between vintage and score could be found (data not shown). This is an important, positive finding in a study of this nature. ANOVA results for the vintage differences from 1998 to 2003 are summarised in **Table 3.3**. The results of the one-way ANOVA on all of the 1998 to 2002 wines are summarised in **Table 3.2**. The

CART analysis confirmed the findings of those compounds where significant differences were found with the one way ANOVA. For the purposes of the discussion in section 3.2, **Table 3.3** refers only to vintage differences between vintages 1998 to 2002. The 2003 vintage comparison has been included in this same table, but is only of relevance to the discussion in section 3.5 of this chapter.

3.3.2.1 Ethyl acetate

Table 3.3 shows that the mean ethyl acetate concentration varied from vintage to vintage, with the concentration of ethyl acetate being significantly lower in the 1998 wines than the remainder of the vintages studied. Shinohara and Watanabe (1976) found that ethyl acetate concentrations varied from 28 to 261 mg/L (mean 97 mg/L) in French white wines and 19 to 84 mg/L (mean 46 mg/L) in Australian white wines. However, although this difference was not significant when compared to the wines awarded gold and silver medals (score 1), what was most interesting to note was that the mean concentration of ethyl acetate was lowest in wines awarded no medal (score 3) irrespective of vintage (**Table 3.2**).

3.3.2.2 isoAmyl acetate

The concentration of isoamyl acetate, which is known to have a banana-like aroma (Lilly *et al.,* 2000), was significantly higher in wines awarded gold and silver medals (score 1) and decreased significantly with subsequent decreases in quality categories (refer to **Figure 3.1** and **Table 3.2**). The mean concentration of isoamyl acetate was also significantly higher in wines from vintages 1998, 1999 and 2000 when compared to 2001 and 2002 (**Table 3.3**). The positive correlation between increased levels of isoamyl acetate and wine quality was also confirmed by the CART analysis (**Figure 3.2**).

Table 3.2 Volatile flavour compound composition in 1998 - 2002 Chenin blanc wines of differing quality

Compound	Score 1 (mg/L)	Score 2 (mg/L)	Score 3 (mg/L)	Overall p-value
Ethyl acetate	58.45ab	60.7a	54b	0.017
Ethyl caproate	3.05a	2.55a	1.75b	<0.001
Ethyl caprylate	3.13a	2.85b	2.24c	<0.0001
Ethyl caprate	3.15a	2.62b	2.06c	<0.0001
Ethyl lactate	5.5a	7a	11b	<0.0001
2-Phenethyl acetate	0.595a	0.5b	0.378c	<0.0001
Hexyl acetate	0.58a	0.475b	0.39c	<0.0001
isoAmyl acetate	10a	8.8b	7.5c	<0.001
Diethyl succinate	1.32a	1.26a	1.175a	0.145
n-Propanol	34a	37a	39a	0.102
n-Butanol	0.82ab	0.85a	0.7b	0.02
isoButanol	22.9a	22.85a	22a	0.851
isoAmyl alcohol	157a	144.5ab	135b	0.0004
n-Hexanol	1.5a	1.65a	1.65a	0.097
2 Phenethyl alcohol	17.35a	17a	16.38a	0.153
Acetic Acid	536a	480a	352b	<0.0001
isoButyric Acid	1.38a	1.43a	1.17a	0.138
Propionic acid	2.7a	2.495a	2.508a	0.443
Hexanoic Acid	8.8a	8.5a	7.6a	<0.0423
Octanoic acid	12.7a	11.3b	9.45c	<0.0001
Decanoic Acid	5.8a	5.18ab	4.4b	<0.0001

Table 3.3 Vintage differences for volatile flavour compounds in Chenin blanc wines

Compound	Mean 1998 (mg/L)	Mean 1999 (mg/L)	Mean 2000 (mg/L)	Mean 2001 (mg/L)	Mean 2002 (mg/L)	Mean 2003 (mg/L)
Ethyl acetate	45.88d	64ab	59.87ac	62.86a	72.82b	53c
Ethyl caproate	1.32ab	6.3c	2.07d	1.36a	1.63b	1.4a
Ethyl caprylate	3.62b	3c	1.91d	2.33a	2.44a	1.5e
Ethyl caprate	3.2b	4.21c	2.33d	1.3a	1.17a	0.7e
Ethyl lactate	7.77ab	6.25a	5.42a	7.27a	12.74b	7a
2-Phenethyl acetate	0.57a	0.51ab	0.48ab	0.42b	0.47ab	0.46b
Hexyl acetate	0.56a	0.56a	0.41bc	0.5b	0.31c	0.49ab
isoAmyl acetate	9.6a	9.63a	9.27ab	7.36c	7.38bc	6.9c
Diethyl succinate	1.2a	1.75d	1.01b	1.21ac	1.07bc	0.8e
n-Propanol	43.83a	39.88ab	28.47c	31.85bc	33.06bc	25.5c
n-Butanol	0.78a	1.09b	0.59c	0.94d	0.5c	0.72ac
isoButanol	25.17a	23.65ab	15.13c	22.37b	27.81a	20.8b
isoAmyl alcohol	179.73a	166.27ab	119.18c	125.35c	97.24d	162b
n-Hexanol	1.52ab	1.76a	1.42b	1.75ab	1.6ab	1.5ab
2 Phenethyl alcohol	18.2a	17.4ab	15.31bc	15.88bc	17.23ab	14.6c
Acetic Acid	472.66ab	466.29ab	461.41ab	411.23a	538.47b	275c
isoButyric Acid	1.25a	2.34d	0.88bc	0.96b	1.34a	0.75c
Propionic acid	1.93ab	6.12c	0.96d	1.42a	2.25bc	14e
Hexanoic Acid	9.1a	8.43ab	7.25b	9.68a	6.32c	5.5d
Octanoic acid	13.58a	12.69a	10.17c	8.53b	8.89b	7.5d
Decanoic Acid	6.29a	6.2a	4.32b	3.79bc	3.92bc	3.25c

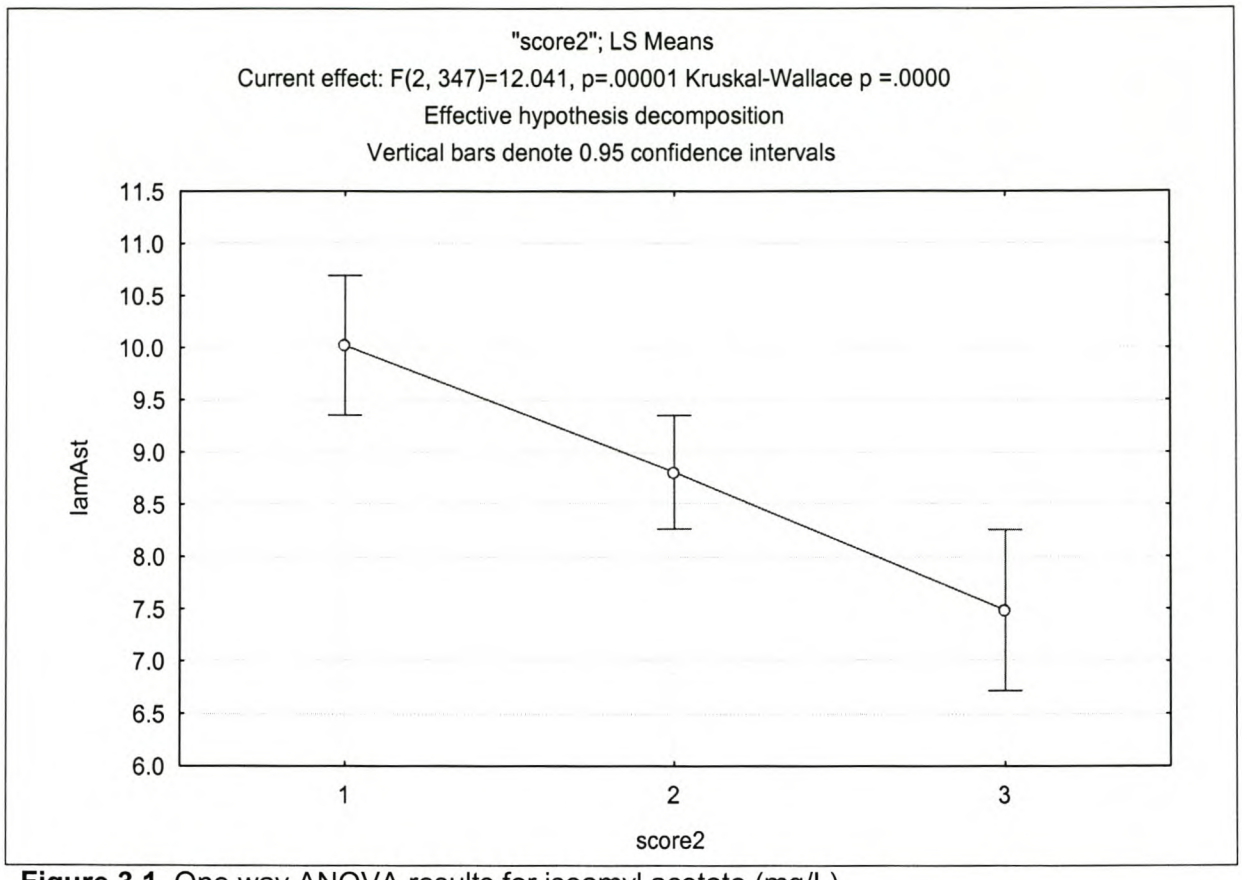

Figure 3.1 One way ANOVA results for isoamyl acetate (mg/L).

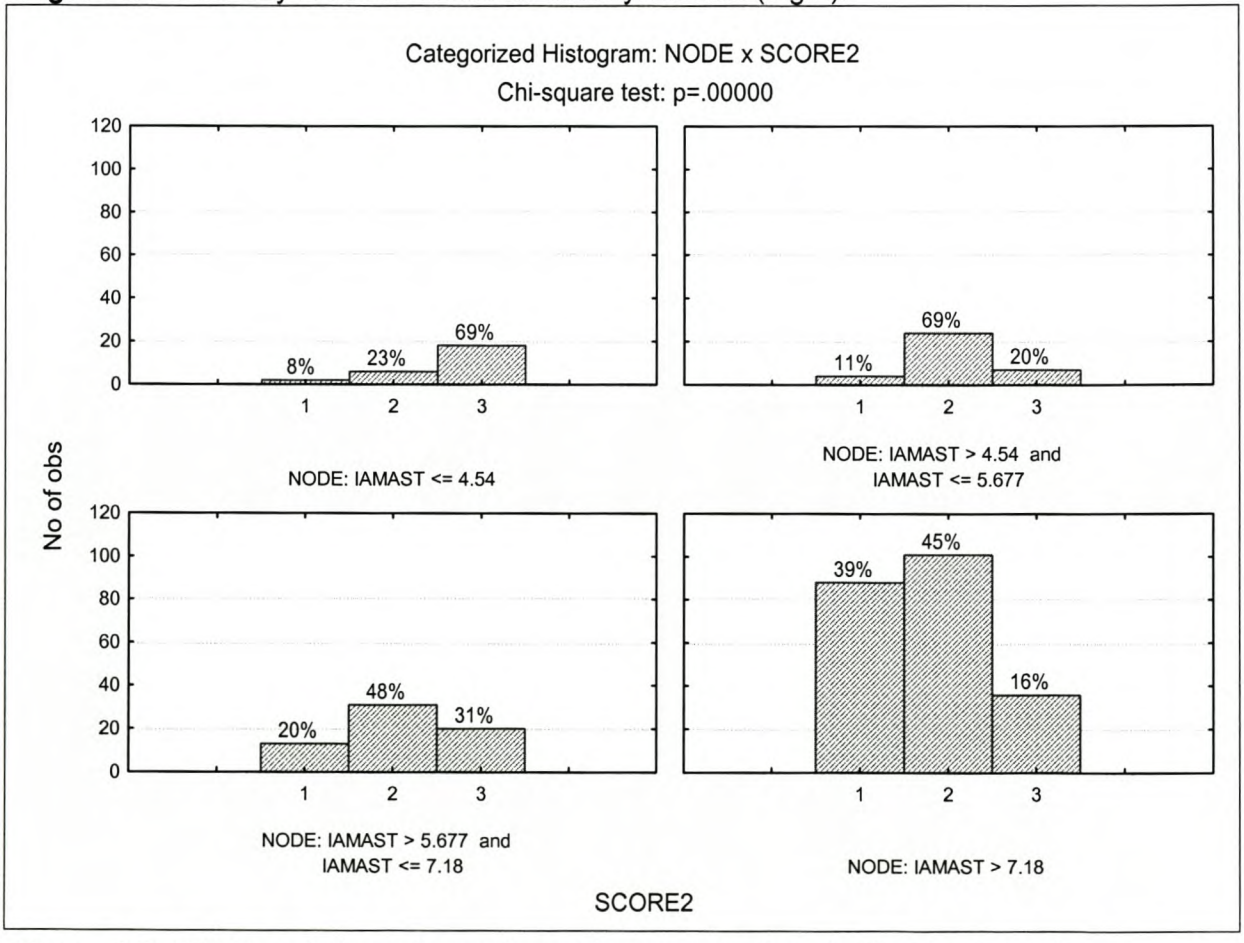

Figure 3.2 CART analysis on isoamyl acetate concentrations in Chenin blanc wines.

Van Wyk *et al.* (1979) found that isoamyl acetate, when present in relatively large concentrations, is the impact compound responsible for the typical fermentation bouquet of Pinotage. Ferreira *et al.* (2000) found that isoamyl acetate was one of 5 most important odorants in young Spanish wines made from Grenache, Tempranillo, Cabernet Sauvignon and Merlot. The other four compounds were beta-damascenone, ethyl caprylate (C_8), ethyl caproate (C_6) and isovaleric acid. It should, however, be noted that the concentration of isoamyl acetate decreases more rapidly at lower pH and at higher storage temperature (Garcia *et al.*, 1994). Garofolo (1994) expressed his concern at producing young, aromatic wines with a low pH, since at room temperature virtually total hydrolysis occurs after only 4 to 5 months, necessitating storage at approximately 0°C if the wine's sensory properties are to be maintained. This may explain why isoamyl acetate concentrations have such a high correlation to wine quality in these young Chenin blanc wines.

3.3.2.3 Hexyl acetate

The concentration of hexyl acetate decreased significantly with decreases in quality and was significantly different for each quality category ($p<0.02$ between scores 1 and 2 and $p<0.02$ between scores 2 and 3) (**Figure 3.3**). From **Table 3.3** it can be seen that hexyl acetate concentrations were significantly higher in wines from 1998 and 1999.

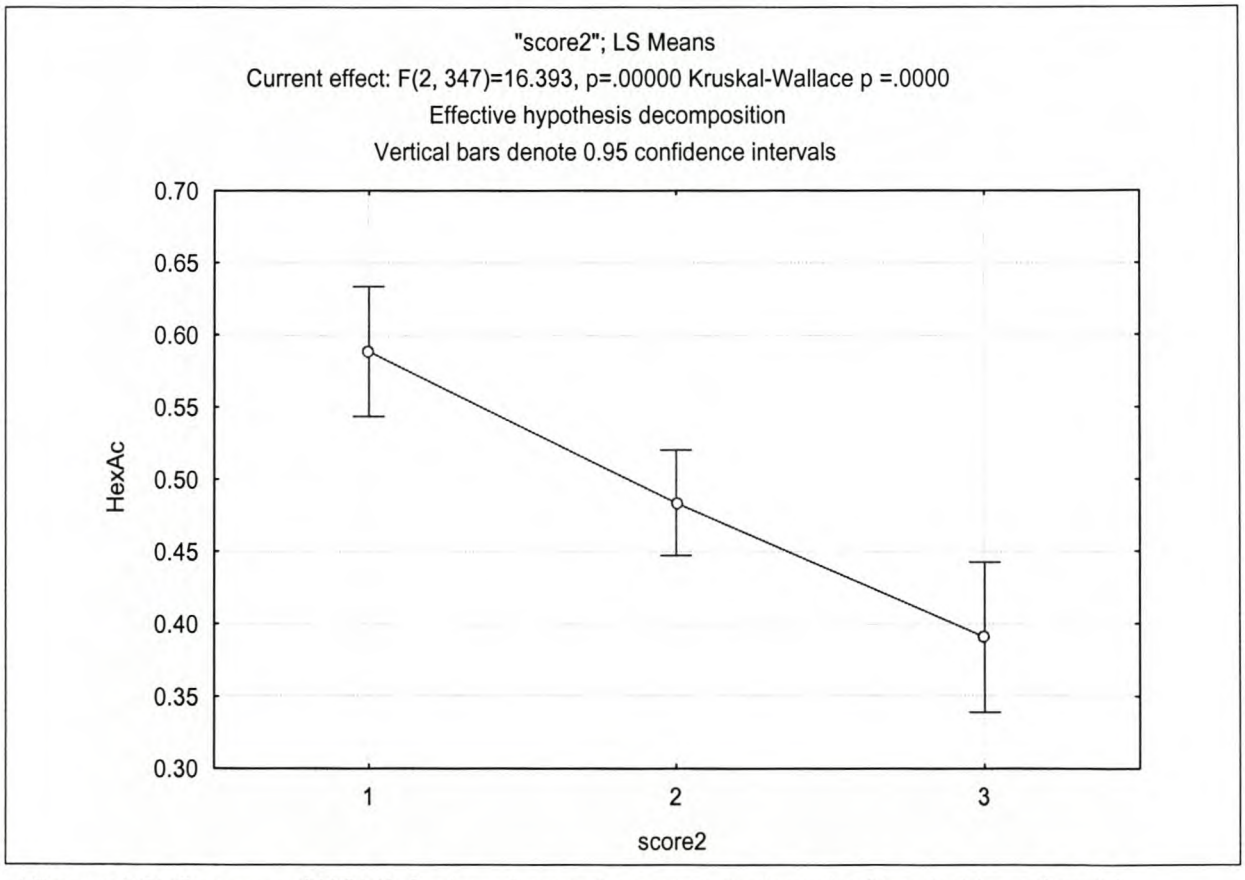

Figure 3.3 One way ANOVA for hexyl acetate concentrations in Chenin blanc (mg/L).

3.3.2.4 Ethyl caproate

The mean concentration of ethyl caproate was significantly lower in wines awarded no medal ($p<0.03$, **Table 3.2**). Although there were no significant differences in ethyl caproate concentrations between the gold, silver and bronze medal winners (scores 1 and 2), the same trend was noted as in the graphs of isoamyl acetate and hexyl acetate, showing that the concentration of ethyl caproate tends to decrease with concurrent decreases in quality. This was also confirmed by the CART analysis, where wines containing a concentration higher than 6.23 mg/L of ethyl caproate only fell into score categories 1 and 2 (**Figure 3.4**). Ethyl caproate is typically associated with an apple-like aroma (Lilly *et al.*, 2000) with a reported sensory threshold concentration of 0.08 mg/L in wine (Salo, 1970a).

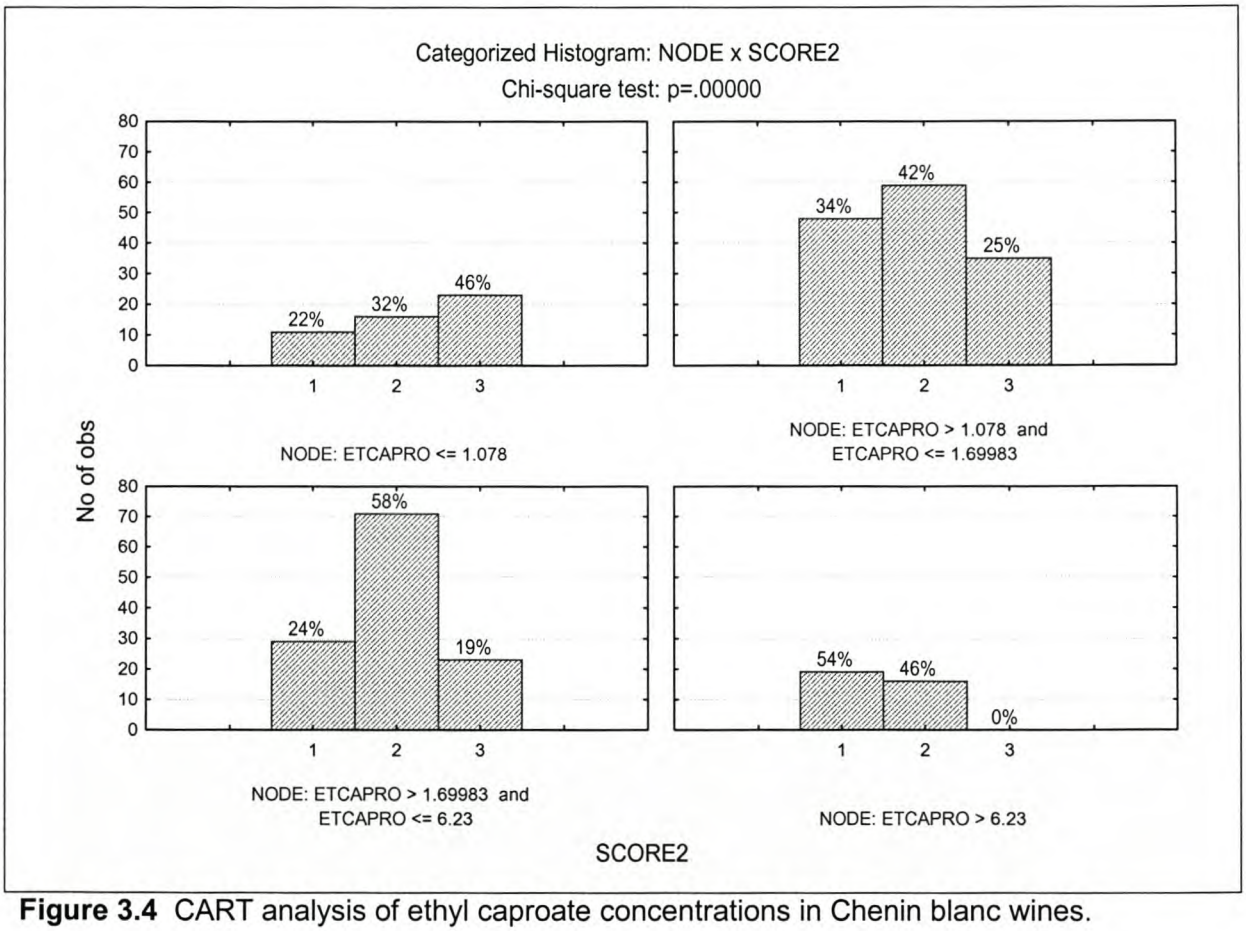

Figure 3.4 CART analysis of ethyl caproate concentrations in Chenin blanc wines.

3.3.2.5 Ethyl caprylate

As was the case for hexyl acetate, the concentration of ethyl caprylate decreased significantly with decreases in quality and was significantly different for each quality category ($p<0.03$ between scores 1 and 2 and $p<0.0001$ between scores 2 and 3, refer to **Table 3.2**). Lambrechts and Pretorius (2000) reported that ethyl caprylate has a pineapple and pear-like aroma with a sensory threshold value of 0.58 mg/L (Salo, 1970a; 1970b). From **Tables 3.2** and **3.3** it is evident that this compound was present in concentrations well above sensory threshold level.

3.3.2.6 Ethyl caprate

The concentration of ethyl caprate also decreased significantly with decreases in quality and was significantly different for each quality category ($p<0.005$ between scores 1 and 2 and $p<0.004$ between scores 2 and 3, refer to **Table 3.2**). Lambrechts and Pretorius (2000) reported that ethyl caprate has a sensory threshold value of 0.5 mg/L in wine, with a floral-like aroma. From **Tables 3.2** and **3.3** it is evident that ethyl caprate was also present in concentrations above sensory threshold in the wines studied.

3.3.2.7 2-Phenethyl acetate

The concentration of 2-phenethyl acetate also decreased significantly with decreases in quality and was significantly different for each quality category ($p<0.001$ between scores 1 and 2 and $p<0.0001$ between scores 2 and 3, refer to **Table 3.2**). For the vintages studied, the concentration range for this compound was very narrow (**Table 3.3**). 2-Phenethyl acetate is known to have a fruity, flowery aroma with a honey note (Lilly *et al.*, 2000). Guth (1997b) stated that the odour threshold value in 10% v/v alcohol solution was 0.25 mg/L. From **Table 3.2** and **3.3** it is evident that 2-phenethyl acetate is present in concentrations well above the sensory threshold value.

3.3.2.8 Ethyl lactate

Ethyl lactate shows the opposite tendency when compared to the above-mentioned esters. Concentrations are significantly higher in the no medal wines (**Table 3.2**) although there were no statistically differences between the bronze medal and silver/gold medal wines. There is a clear trend showing increasing ethyl lactate concentrations with a concurrent decrease in quality and this is confirmed in the CART analysis (**Figure 3.5**). From **Figure 3.5** it can be seen that only 14% of the wines containing ethyl lactate at less than 3.73 mg/L were awarded no medal, whilst only 15% of wines containing ethyl lactate concentrations greater than 8.05 mg/L were awarded gold and silver medals. What is interesting is the fact that the overall range of ethyl lactate concentrations is relatively low when compared to the concentration of ethyl lactate present in wines having undergone complete malolactic fermentation. Ethyl lactate concentrations in these wines varied from 4 to 16.5 mg/L, whereas the concentration of ethyl lactate present in brandy base wines which had undergone partial or complete malolactic fermentation varied from 25 up to as high as 139 mg/L in one instance (chapter 4, data not shown). Shinohara *et al.* (1976) (as quoted by Nykänen and Suomalainen; 1983) analysed over 200 wines for their ethyl lactate contents and reported that the ethyl lactate content ranged from a trace to 534 mg/L with an average of 116 mg/L in white wines. Du Plessis *et al.* (2001) found that in wine and unaged distillate samples where malolactic fermentation had occurred there was a loss in fruitiness and in the intensity of aroma. This implies that even at low concentrations of ethyl lactate, which would indicate a partial malolactic

fermentation, the presence of ethyl lactate in young, fruit-driven Chenin blanc table wines can have an impact on wine quality. From a vintage perspective, only 2002 wines contained significantly higher mean amounts of ethyl lactate (**Table 3.3**). This vintage was characterised by unusual rainfall during the harvest and an overall high incidence of downy mildew and berry rot as a result of these wet conditions, which could account for the difference.

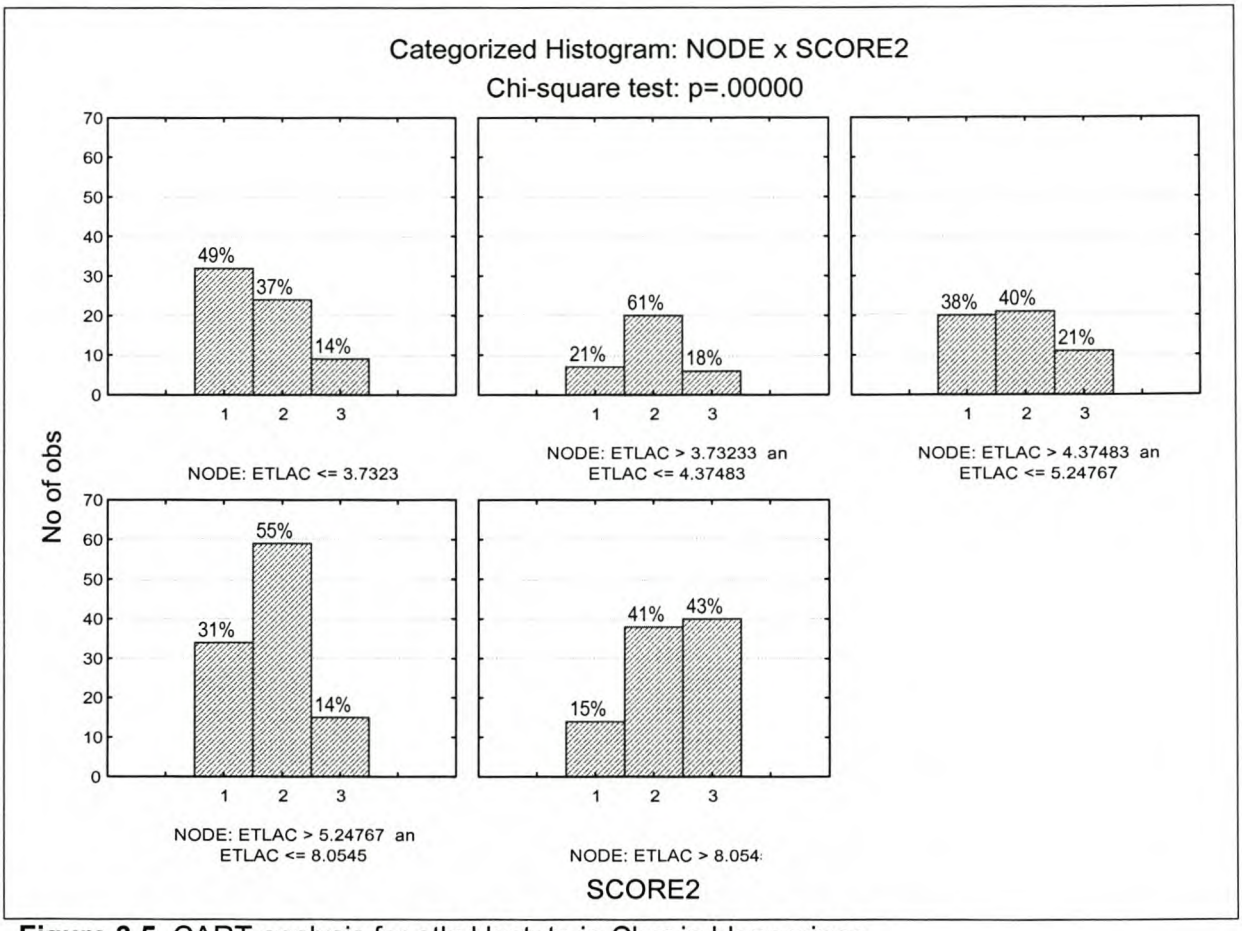

Figure 3.5 CART analysis for ethyl lactate in Chenin blanc wines.

3.3.2.9 Diethyl succinate

There were no significant differences in diethyl succinate concentrations between any of the quality categories. The range of diethyl succinate concentrations was also very small, varying from 0.8 to 1.40 mg/L. Reinhard (1972) found that diethyl succinate concentrations varied from 0.8 to 11 mg/L in Franconian wines. Postel *et al.* (1972a) reported that diethyl succinate contents vary from 0.9 to 3.6 mg/L in German wines of varying sweetness and Snyman (1977) reported 0.3 to 6.4 mg/L of diethyl succinate in wines.

3.3.2.10 n-Propanol

Although not significant, a tendency for increased n-propanol concentrations with concurrent decreases in quality was noted (**Table 3.2**).

3.3.2.11 isoAmyl alcohol

The mean concentration of isoamyl alcohol was highest in the silver/gold medal wines. As is evident from **Figure 3.6,** although the difference in concentration between scores 1 and 2 is not statistically significant, isoamyl alcohol concentrations decreased with decreases in quality and the concentration of isoamyl alcohol in silver/gold wines was significantly higher than in the no medal wines ($p<0.001$). Mean isoamyl alcohol concentrations per vintage also confirmed this observation (**Table 3.1** and **3.3**). Ribereau-Gayon *et al.*, (1999) classified isobutyl and isoamyl alcohol as the main fermentation higher alcohols which contribute to aromatic complexity of wine when present in concentrations lower than 300 mg/L. At higher concentrations their penetrating odours can mask a wine's aromatic finesse. From **Table 3.2** and **3.3** it is evident that the concentration of isoamyl alcohol was well below 300 mg/L in the wines studied. The higher alcohol content of wine varies according to fermentation conditions, especially the species of yeast used (Ribereau-Gayon *et al.,* 1999; Lambrechts and Pretorius, 2000). In general, factors that increase the fermentation rate (yeast biomass, oxygenation, high temperature and the presence of suspended matter in the must) also increase the formation of higher alcohols (Ribereau-Gayon *et al.*, 1999). Aznar *et al.* (2001) found that isoamyl alcohol was an effective and important contributor to wine aroma in Spanish Rioja red wine.

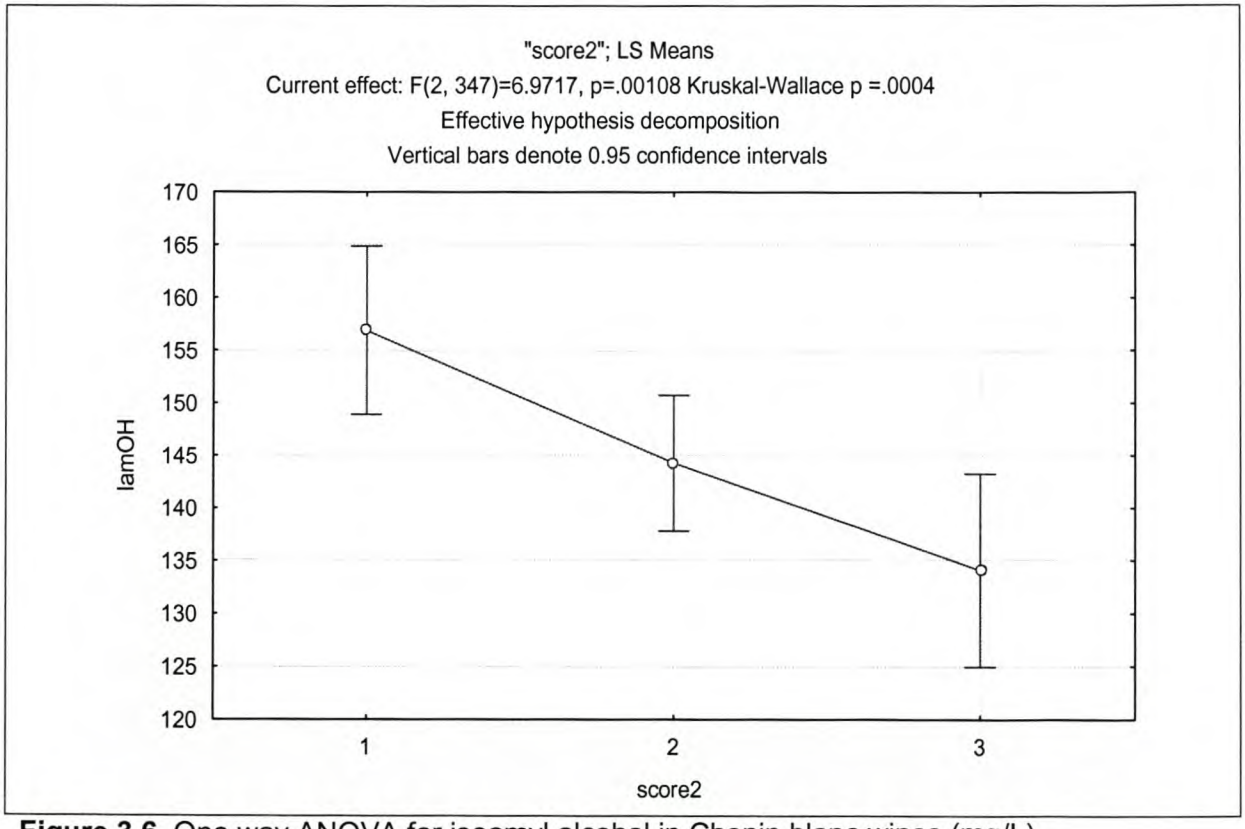

Figure 3.6 One way ANOVA for isoamyl alcohol in Chenin blanc wines (mg/L).

3.3.2.12 n-Hexanol

No statistically significant differences were noted between the three quality categories and, when one considers the range of n-hexanol concentrations (1.35 to

1.82 mg/L) present in these wines, there are effectively no differences in n-hexanol concentrations between these wines (**Table 3.2**). Postel *et al.* (1972b) found that n-hexanol concentrations ranged from 1 to 2 mg/L in German white wines and Rankine and Pocock (1969) reported a range of 1 to 4 mg/L in white wines. n-Hexanol is derived from plant tissues during crushing though a process of four enzymatic reactions, and has a grassy, herbaceous aroma (Ribereau-Gayon *et al.*, 1999).

3.3.2.13 isoButanol and 2-phenyl ethanol

No statistically significant differences were found between the three quality categories on the basis of isobutanol and 2-phenyl ethanol (**Table 3.2**). This even through 2-phenyl ethanol was present in concentrations above its threshold value of 7.5 mg/L and it known to have a floral, rose-like aroma (Lambrechts and Pretorius, 2000).

3.3.2.14 n-Butanol

The concentration of n-butanol was significantly lowest in the no medal wines (**Table 3.2**). There were however no significant differences between the gold/silver and bronze medal wines (score 1 and 2).

3.3.2.15 Acetic acid

Interestingly enough, the concentration of acetic acid was lowest in the no medal wines (**Table 3.2**), although there were no significant differences in acetic acid concentration between the silver/gold and bronze medal wines ($p<0.0001$ between scores 1 and 3; $p<0.003$ between scores 2 and 3). The CART analysis also confirmed this finding (**Figure 3.7**) where only 13% of the wines containing acetic acid concentrations greater than 420 mg/L were of score 3. Acetic acid concentrations varied from 245 mg/L to 570 mg/L, which is still far below the legal maximum of 1200 mg/L in South Africa and below the sensory threshold of between 700-1000 mg/L (Lambrechts and Pretorius, 2000). This finding confirms the long held theory that acetic acid, when present in small amounts can actually contribute towards increased aroma and flavour complexity. However, one must bear in mind that above legal limits for volatile acidity content (expressed as g/L of acetic acid), acetic acid will have a negative influence on the quality of wine.

3.3.2.16 Propionic and isobutyric acid

There were no significant differences in propionic and isobutyric acid concentrations between the 3 quality categories (**Table 3.2**). Guth (1997b) stated that the odour threshold value for isobutyric acid was 200 mg/L, which is considerably higher than the concentrations quantified in the wines studied. Both of these compounds are known to have a rancid, slightly pungent aroma when detectable (Lambrechts and Pretorius, 2000).

3.3.2.17 Hexanoic acid

The mean concentration of hexanoic acid decreased with concurrent decreases in wine quality, but was however, not statistically significant (**Table 3.2**). Guth (1997a) stated that the sensory odour threshold for hexanoic acid in 10% v/v ethanol/water was 3 mg/L, however Lambrechts and Pretorius (2000) stated that the threshold value was between 8 and 8.8 mg/L in an alcoholic grain spirit solution at approximately 9.4% w/w. From **Tables 3.2** and **3.3** it is evident that hexanoic acid is present in concentrations very close to the latter sensory threshold level. At concentrations above threshold hexanoic acid is known to have a rancid, sour, cheese-like aroma in isolation (Lambrechts and Pretorius, 2000). Hexanoic acid and its related ethyl ester (ethyl caproate) follow the same trend when comparing concentrations between quality categories (i.e. scores).

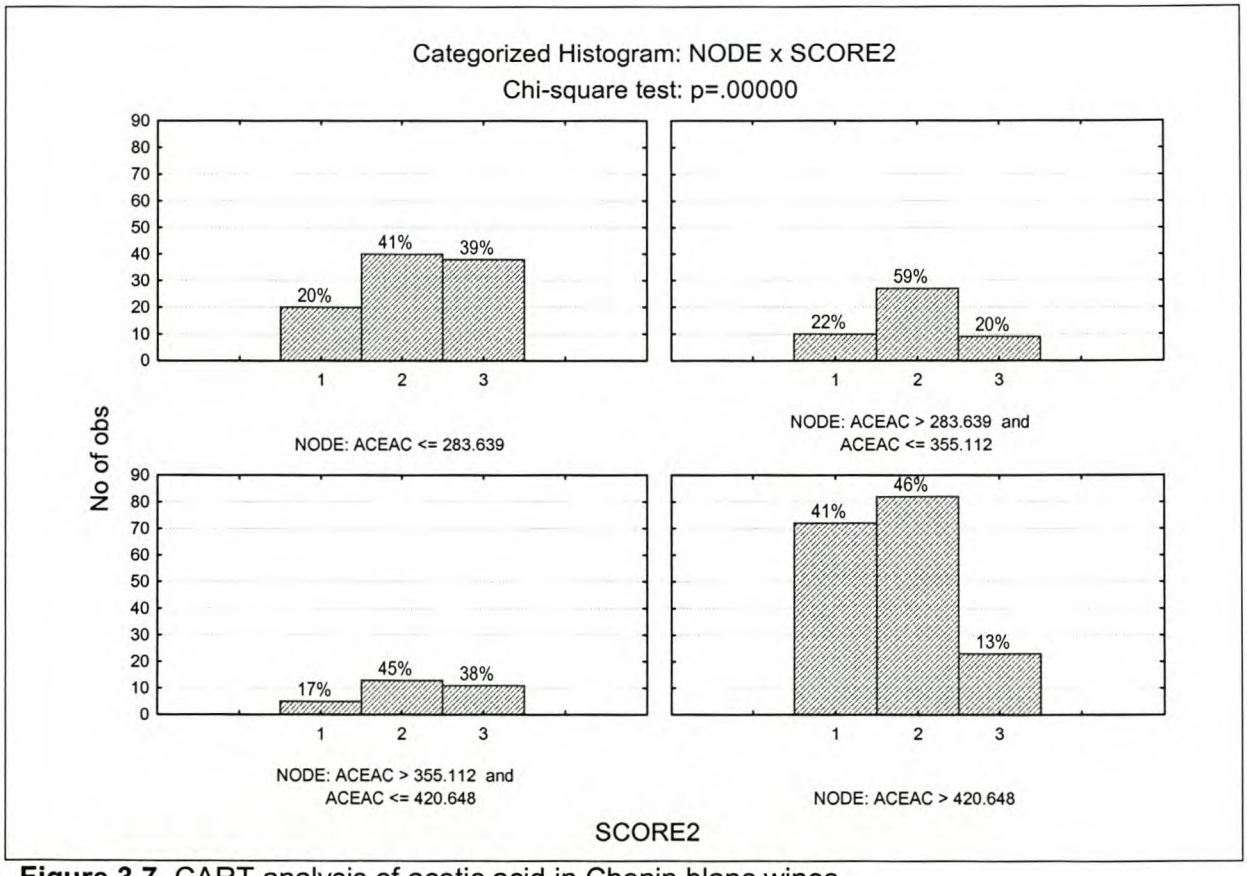

Figure 3.7 CART analysis of acetic acid in Chenin blanc wines.

3.3.2.18 Octanoic acid

The concentration of octanoic acid decreased significantly with concurrent decreases in wine quality (**Table 3.2**). This finding was also confirmed in the CART analysis (**Figure 3.8**). Only 11% of wines with an octanoic acid concentration of less than 9.1 mg/L were of score 1 (gold/silver medal), whilst only 3% of wines with an octanoic acid content greater than 13.71 mg/L were of score 3 (no medal). The sensory threshold level for this compound was 13 mg/L in an alcoholic grain spirit solution of approximately 9.4% w/w, and at concentrations above or on this level octanoic acid has an oily, fatty, buttery, soapy sweet aroma (Salo, 1970a). This would indicate that

the concentration of octanoic acid actually needs to be very close to or at threshold value in order for the probability of wine quality to increase. The concentration of octanoic acid and its related ethyl ester (ethyl caprylate) follow the same pattern when comparing concentrations between scores.

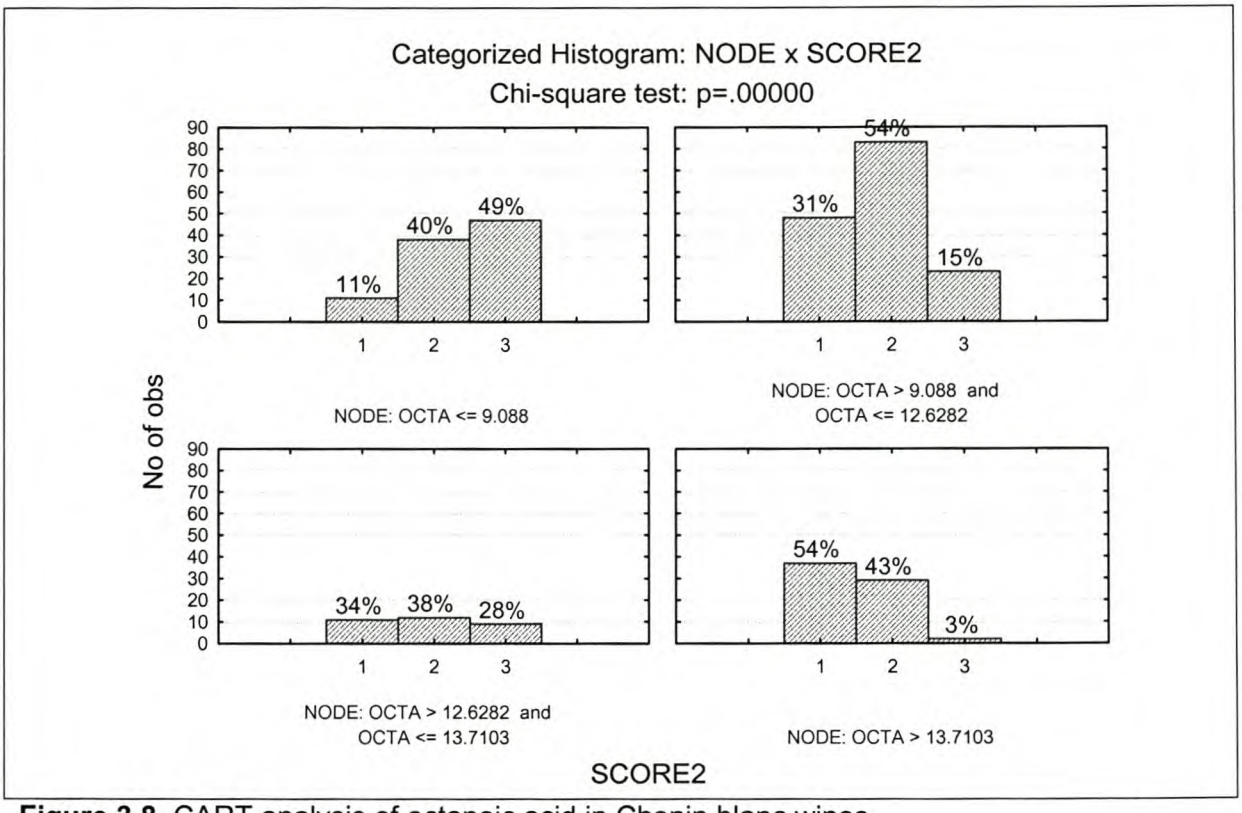

Figure 3.8 CART analysis of octanoic acid in Chenin blanc wines.

3.3.2.19 Decanoic acid

Decanoic acid exhibited the same trend as octanoic acid, although the difference between gold/silver and bronze medal wines was not as significant (**Table 3.2**). The CART analysis (**Figure 3.9**) also confirmed this finding. Guth (1997a) stated that the odour threshold concentration of decanoic acid in a 10% v/v wine solution was 15 mg/L, while Salo (1970a) found this value to be 10 mg/L in wine and 8.2 mg/L in a 9.4% w/w grain spirit solution. From **Table 3.2** and **3.3** it is evident that the decanoic acid concentration of wines used in this study, is well below the sensory threshold level. It is thus uncertain whether this compound acts directly on wine quality, or whether it acts as an indicator of other compounds which may also influence wine quality. One such example could be the effect of its related ethyl ester, ethyl caprate, which also followed the same pattern, as is evident from **Table 3.2**.

3.3.3 CART VARIABLE FACTOR IMPORTANCE AND OVERALL REGRESSION ANALYSIS

Table 3.4 lists the variable importance of each of the compounds as determined by the CART analysis. According to the CART analysis, these are the most important compounds used to predict the target variable, which in this case is quality or the

score allocated to each wine. From **Table 3.4** it can be seen that ethyl caprate (C_{10}), ethyl caprylate (C_8), and to a lesser extent octanoic-, hexanoic- and decanoic acid, isoamyl alcohol and isoamyl acetate are deemed the most important variables for CART analysis prediction. Guth (1997b) compared the odour of Gerwürztraminer wine model mixtures affected by the absence of one component and found that the absence of ethyl caproate (C_6) and ethyl caprylate (C_8) and acetic acid all significantly affected wine odour. As is to be expected with an aromatic grape variety, the remainder of compounds found to have a significant effect when absent were terpenoid compounds. However, the CART variable importance is merely a list of compounds that CART has identified as being important in being able to determine the subset target (in this case score) and predictor variables (in this case the volatile compounds). Using more than one volatile compound as a basis for prediction, CART was able to generate a number of rules to define a number of quality subsets (based on percentage distribution of scores) which can be seen in **Figure 3.10**. With the exception of ethyl acetate and n-propanol, the compounds used to define the subsets were all shown to correlate to wine quality in the one way ANOVA as discussed in section 2.3. Of particular interest is the middle graph in the second row, which appears to be a good indicator as to which ratios of compounds will yield a high probability of score 1 wines. It states that in those wines where the concentration of ethyl caprylate is greater than 2.34 mg/L and the concentration of isoamyl acetate is greater than 8.35 mg/L, whilst the n-propanol concentration remains below 35.82 mg/L then 78% of these wines are of score 1. The change in percentage distribution of scores from this graph to the following two in **Figure 3.10**, where hexyl acetate concentration is added as an additional "rule", confirms the long held view that the effect of volatile flavour compounds present in wine cannot be viewed in isolation. Complex relationships (which may lead to synergistic or antagonistic aroma effects) exist between volatile compounds in wine. It was attempted to apply this "rule" to the 2003 wine dataset to verify the validity of this rule under different vintage conditions. It was, however, not possible to apply this rule successfully. The main reason being the differing mean concentration of compounds in the 2003 dataset. None of the 2003 wines had an ethyl caprylate concentration higher than 2 mg/L. The difference in overall composition of the 2003 wines and this effect on model prediction is discussed in further detail in section 3.7.

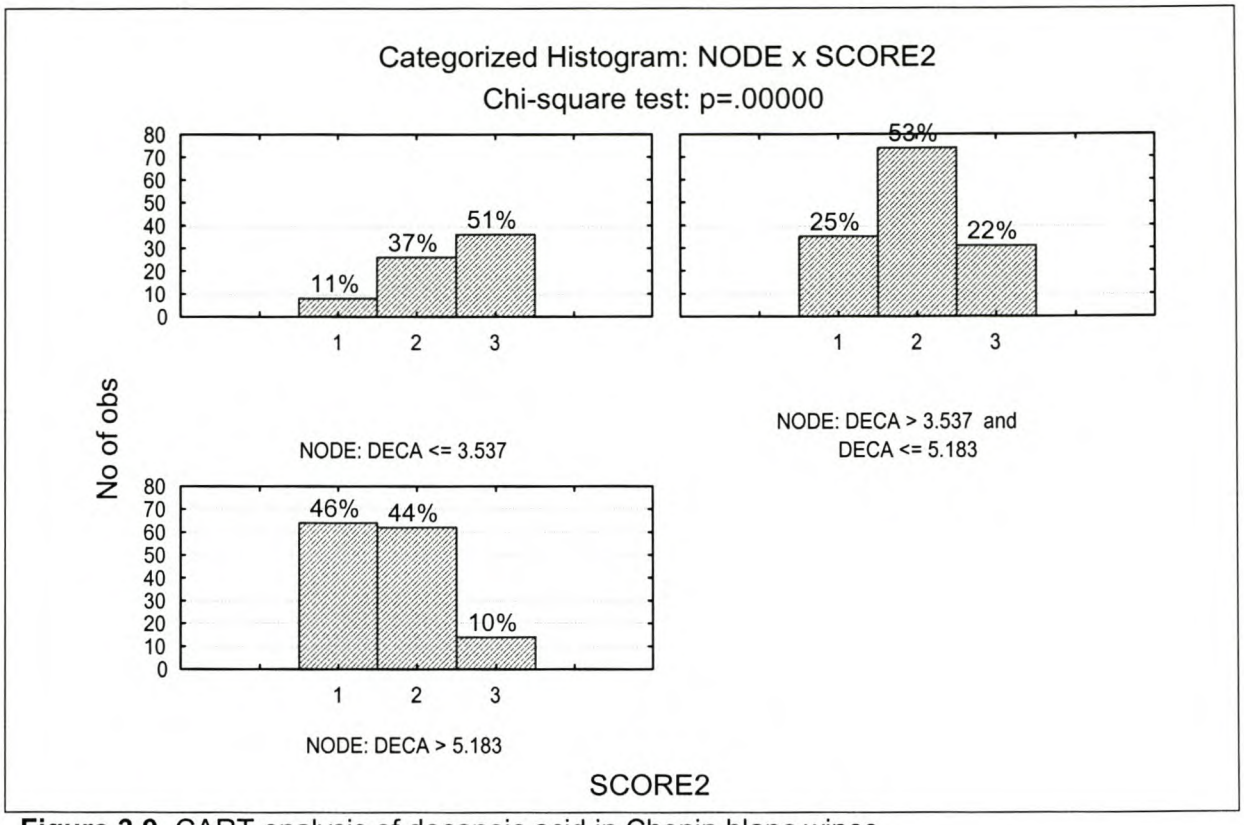

Figure 3.9 CART analysis of decanoic acid in Chenin blanc wines.

Table 3.4 CART variable importance analysis on Chenin blanc wines

Compound	Variable Importance %
Ethyl caprate	100
Ethyl caprylate	96.39
Octanoic acid	92.75
Hexanoic acid	73.7
Decanoic acid	72.05
isoAmyl alcohol	66.35
isoAmyl acetate	45.43
Hexyl acetate	42.08
2-Phenethyl acetate	39.44
n-Propanol	29.83
Ethyl acetate	28.14
Acetic acid	27.36
Ethyl caproate	13.09
Propionic acid	12.85
n-Butanol	11.77
2-Phenyl ethanol	6.93
n-Hexanol	2.13
isoButanol	0.36
isoButyric acid	0
Ethyl lactate	0
Diethyl succinate	0

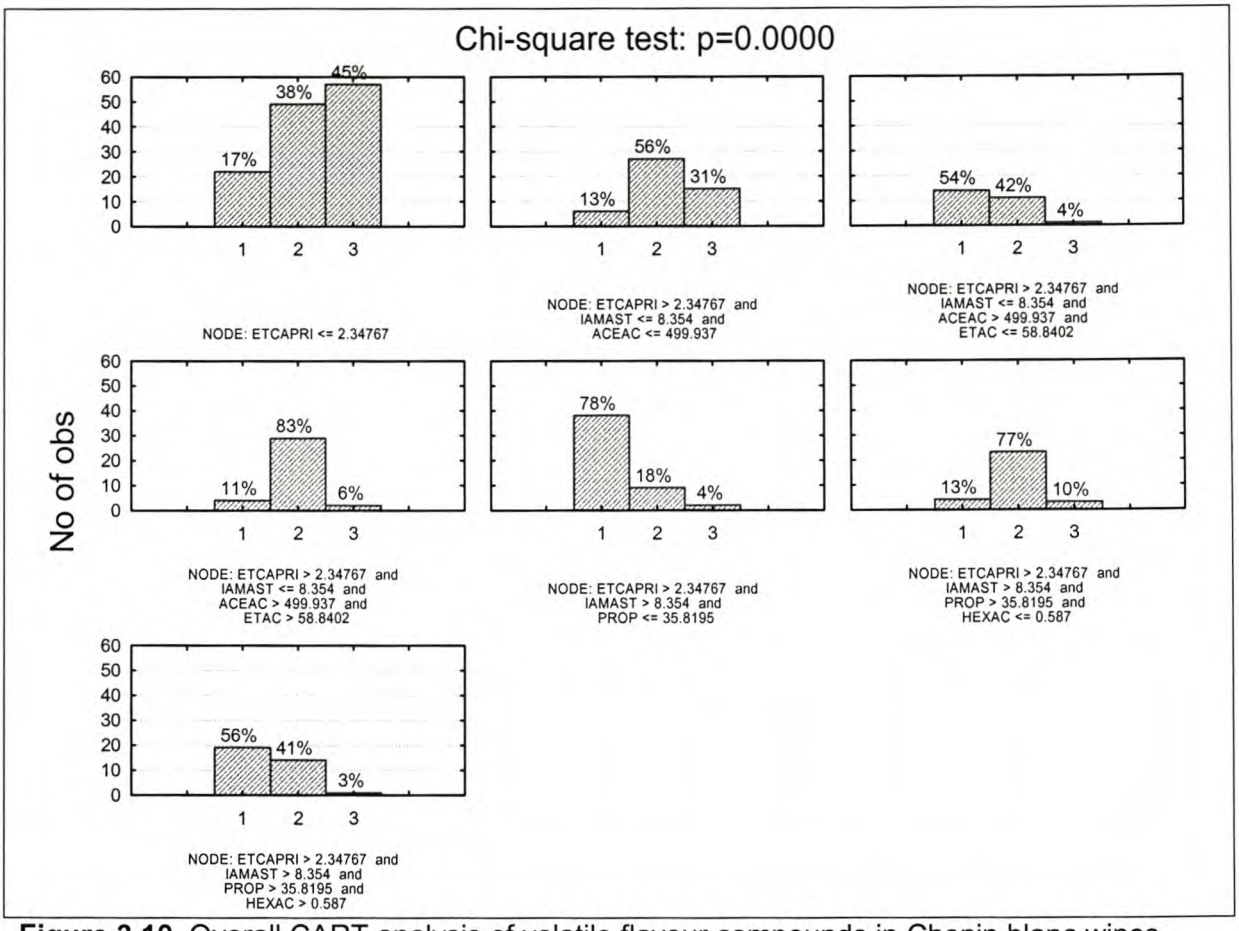

Figure 3.10 Overall CART analysis of volatile flavour compounds in Chenin blanc wines.

3.3.4 FACTOR ANALYSIS

A principal component factor analysis was also done on the data from 1998 to 2002. This analysis identified four factors, which accounted for 61% of the variation within the data. It also provides an indication as to the correlation structure of the variables or compounds. Factor 1, which accounted for 31.4% of the variation, positively correlated isoamyl alcohol, ethyl caprylate, isobutanol, 2-phenyl ethanol, octanoic and decanoic acid. These compounds, with the exception of isobutanol and 2-phenyl ethanol were all present in significantly higher concentrations in the silver/gold medal wines and their concentrations decreased significantly with concurrent decreases in wine quality. Isobutanol concentrations exhibited no significant differences between quality categories, although 2-phenyl ethanol tended to decrease with concurrently decreasing wine quality, although this was not found to be significant. Factor 2 only accounted for 12% of the variation and comprised n-propanol. Although not significant, n-propanol showed the opposite tendency and concentrations were found to be high when wine quality was low. Factor 3 accounted for even less of the variation at 9% and positively correlated ethyl caproate, propionic acid and isobutyric acid. Of these, only ethyl caproate was found to correlate to quality in the one way ANOVA and CART analysis.

3.3.5 QUALITY PREDICTOR MODEL

It was attempted to establish a quality predictor model based on the behaviour of the volatile compounds in the young Chenin blanc wines. Two approaches were employed. The first was to divide the data set of all the wines from 1998 to 2002 into two parts, a so-called training and a test set. Using MARS analysis, the volatile compound behaviour and its relationship to wine score was analysed in the training set and was then used to predict the score of the wine by studying the volatile compound behaviour in the test set. The fit of this model can be seen in **Table 3.5**. It is evident that MARS was able to correctly predict the score of all score 2 (bronze medal) wines in 86% of the cases, but was only able to predict the score 1 and 3 wines correctly with an accuracy of 40% and 29%, respectively. When one considers that this prediction is based on a subjective measurement taking place over a period of 5 years, and that the panel of judges may have varied from year to year, then the 86% prediction accuracy on the bronze medal wines can be considered high. Of course, a model such as this would find more practical application if one could accurately predict whether a wine will win a gold or silver medal rather than a bronze medal, which is more an indicator of compliance to average quality standards. The low prediction accuracy on the score 1 wines can be ascribed to the reduced number of wines or data points from which the model could learn, as only a handful of gold or silver medals are awarded to wines in this class each year.

Table 3.5 Model fit using 1998 to 2002 data

Score	Model 1	Model 2	Model 3	Grand Total	% Correct
Actual 1	8	9	3	20	40%
Actual 2	4	30	1	35	86%
Actual 3	1	11	5	17	29%
Grand Total	13	50	9	**72**	

The second approach taken was to use all of the wine analyses from 1998 to 2002 as the training set and to use the wine analyses from 2003 as the test set. In this instance the model fit was not as good. As can be seen from **Table 3.6**, MARS was not able to correctly predict any of the score 1 wines, correctly predicted 62% of the score 2 wines and 74% of the score 3 wines. MARS estimates for the scores are continuous values and need to be converted in some way back to discrete scores (scores 1, 2 and 3). For the first two attempts the output score was rounded off to the nearest whole number. A second approach was tried whereby the interval between the minimum and maximum estimated scores was divided into three non-overlapping segments in such a way that the percentage of correct classifications for each category (1, 2 or 3) is roughly the same. These boundaries were then used in subsequent predictions. This yielded reasonable results for the 1998 to 2002 data set, but gave unsatisfactory results when validated on the 2003 data. Subsequent analysis showed that if the model was used on the 2003 data it yielded consistently

higher estimates than for the training set. The first 20% of the 2003 data was then used to adapt the estimated scores for 2003 in the following manner: calculate the difference between the average of the 20% of the 2003 estimates and the training set estimates. Subtract this difference from all of the remaining 2003 estimates. Then use the adapted estimates to predict the scores. Far better predictions for 2003 were obtained in this manner, as can be seen from **Table 3.7**. However, the prediction accuracy was still not as good as it was using the 1998 to 2002 data as training and test set.

Table 3.6 Model fit using 2003 data as the test set

Score	Model 1	Model 2	Model 3	Grand Total	% Correct
Actual 1		10	7	17	0%
Actual 2	1	16	9	26	62%
Actual 3		6	17	23	74%
Grand Total	1	32	33	**66**	

Table 3.7 Model fit using adapted outputs as determined from the first 20% of 2003 data

Score	Model 1	Model 2	Model 3	Grand Total	% Correct	% Within 1
Actual 1	10	7	3	20	50%	85%
Actual 2	9	20	6	35	57%	
Actual 3	1	7	9	17	53%	94%
Grand Total	**20**	**34**	**18**	**72**		

The difference in model prediction between the 1998-2002 data set and the 2003 data set necessitated a more detailed analysis of the differences between the 2003 vintage and the previous five vintages. As is evident from **Table 3.3**, the 2003 wines differed significantly in the concentration of ethyl acetate, ethyl caprylate, ethyl caprate, diethyl succinate, acetic acid, propionic, octanoic and decanoic acid, with significantly lower concentrations of these compounds being present in the 2003 wines. A one way ANOVA on only the 2003 wine analyses showed that many of the mean concentrations for scores 1, 2 and 3 followed the same trend as was seen in the wines from 1998 to 2002 (section 3.3). However, the differences between the quality category concentrations for most of the compounds quantified, were not significant (**Table 3.8**). The lack of significant differences between the concentration of compounds in each quality category in the 2003 wines, when compared to significant differences in concentrations over quality categories using five vintages of data (1998 to 2002) could be as a result of two factors, or more likely a combination of these:

1. From **Table 3.3** it is evident that the concentration of ethyl acetate, n-propanol, isoamyl acetate, ethyl caproate, ethyl caprylate, isobutyric acid, acetic acid,

ethyl caprate, diethyl succinate, hexanoic acid, octanoic acid and decanoic acid are lower, in most cases significantly lower, in the 2003 wines when compared to 1998 - 2002. The range of concentrations for these compounds in the 2003 vintage is also very narrow, thus reducing the likelihood of significant differences. In addition, the lowered concentration of all of the above-mentioned compounds may also influence their sensory perception, and thus their effect on sensory quality.

2. Variation in scoring systems between the 1998-2002 and 2003 shows (refer to section 3.2.3).

Table 3.8 Volatile flavour compound composition in 2003 Chenin blanc wines of differing quality

Compound	Score 1 (mg/L)	Score 2 (mg/L)	Score 3 (mg/L)	Overall p-value
Ethyl acetate	54a	56a	50a	0.110
Ethyl caproate	1.35a	1.27a	1.2a	0.151
Ethyl caprylate	1.6a	1.5a	1.44a	0.075
Ethyl caprate	0.7a	0.7a	0.64a	0.165
Ethyl lactate	6.75a	5.9a	7.7a	0.130
2-Phenyl ethanol	0.49a	0.5a	0.43a	0.273
Hexyl acetate	0.58a	0.52a	0.38b	0.005
isoAmyl acetate	6.6a	7.6a	6.4a	0.237
Diethyl succinate	0.76a	0.84a	0.85a	0.710
n-Propanol	20.2a	24.5ab	30b	0.002
n-Butanol	0.7a	0.69a	0.8a	0.539
isoButanol	20.1a	21a	20.7a	0.858
isoAmyl alcohol	153a	166a	166a	0.062
n-Hexanol	1.5a	1.48a	1.5a	0.969
2 Phenethyl alcohol	14.3a	14.5a	15a	0.657
Acetic Acid	325a	285ab	225b	0.012
isoButyric Acid	0.78a	0.79a	0.73a	0.734
Propionic acid	13a	12a	17a	0.108
Hexanoic Acid	5.65a	5.58a	5.19a	0.321
Octanoic acid	7.78a	7.8a	7.2a	0.452
Decanoic Acid	2.65a	3.6a	3a	0.452

Thus, 2003 can be viewed as a vintage that differed significantly in both composition as well as scoring when compared to the previous five vintages. This may account for the lower prediction accuracy when using the 2003 wines as a test set for the model which was established on data from the 1998 to 2002 wines.

3.4 CONCLUSIONS

Using a two way ANOVA on the volatile compound analyses from young Chenin blanc wines with vintage and score as independent variables, it was found that although the concentration of compounds studied varied from vintage to vintage, no interaction between vintage and score could be found.

The one way ANOVA made it possible to determine the relationship between the concentration of volatile flavour compounds and the scores awarded to these wines over a period of five years at the South African Young Wine Show. The concentration of isoamyl acetate, hexyl acetate, ethyl caprylate, ethyl caprate, 2-phenethyl acetate was significantly higher in wines awarded gold and silver medals (score 1) and decreased significantly with subsequent decreases in quality categories. The concentration of octanoic acid also decreased significantly with concurrent decreases in wine quality, whilst the concentration of decanoic acid, isoamyl alcohol and ethyl caproate exhibited the same pattern, however, the difference between gold and silver medal wines (score 1) and bronze medal wines (score 2) was not significant. Ethyl lactate exhibited the opposite pattern and the concentration of ethyl lactate was highest in the no medal wines.

The CART analysis identified ethyl caprate, ethyl caprylate, and to a lesser extent octanoic, hexanoic and decanoic acid, isoamyl alcohol and isoamyl acetate as the most important variables used to predict the score of the wine. The ANOVA and CART analysis thus confirm that these compounds play a significant role in determining young Chenin blanc wine quality. The CART analysis was also able to establish a set of so-called "rules" or guidelines as to how the concentration of some of the volatile compounds can impact on the perception of wine quality and also highlighted the interactive behaviour taking place between some of the compounds (**Figure 3.10**). This confirms the long held view that flavour compounds in alcoholic beverages may exhibit synergistic or antagonistic relationships that can influence the perception of sensory character in wines. The results of the CART analysis in this chapter cannot be viewed as a definitive guideline for the ideal concentration of these volatile compounds in young Chenin blanc wines, but should rather be seen as a proof of concept. CART analysis can be used as a tool to better understand flavour compound relationships taking place in wine.

Using MARS it was attempted to establish a quality predictor model based on the behaviour of the volatile compounds quantified in young Chenin blanc wines. The model's prediction accuracy was much better when having to predict the quality of wines made in the same vintages as it had been trained on, and was significantly poorer when tested on a completely different vintage to the ones it had been trained on. As with any type of agricultural product that is influenced by its environment and climate during ripening, seasonal variations can affect wine composition and quality. Subsequent analysis showed that the 2003 vintage differed significantly in composition and also in the methodology of wine scoring when compared to the previous five years. This may have affected the model's performance. This modelling

exercise also highlighted the need for a sizeable dataset of wines on which to train such a model on. Unfortunately, establishing a wine database of ideal size for modelling purposes is rather difficult, due to vintage, cultivar and stylistic limitations. A wine database that is to be used for quality prediction must also incorporate wines of varying vintages in order to significantly reduce the impact of vintage variation on the model's performance. Intensive flavour and aroma research that has been carried out over the past few decades has led to the identification of more than 500 volatile compounds, additionally, taking non-volatile compounds into account, the number of identified compounds would be close to triple (Nykänen and Suomalainen, 1983). Only twenty-one volatile compounds were quantified in the wines used in this study and the limited number of aroma compounds used will also influence prediction accuracy.

Factors that may influence the production and concentration of the volatile compounds studied include grape and must composition (which in turn are influenced by climatic and vineyard management practices), fermentation conditions (such as pH, fermentation temperature and yeast strain used). The quality-concentration relationships as well as possible interactive relationships seen in the CART analysis could be useful in yeast breeding programmes and the optimisation of fermentation conditions. However, more importantly the resultant quality of a young Chenin blanc wine should be viewed more holistically and careful attention to grape and wine quality must be given at each point in the winemaking process.

It is recommended that this database be populated annually with analyses of each year's Young Wine Show results in order to establish a larger and hopefully seasonally more robust model that could be used for the prediction of young Chenin blanc wine quality.

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CHAPTER 4

RESEARCH RESULTS

The influence of vintage, region, cultivar, harvest time and yeast strain on the volatile composition of brandy base wines and their unaged potstill distillates

RESEARCH RESULTS

4. THE INFLUENCE OF VINTAGE, REGION, CULTIVAR, HARVEST TIME AND YEAST STRAIN ON THE VOLATILE COMPOSITION OF BRANDY BASE WINES AND UNAGED POTSTILL DISTILLATES

ABSTRACT

South African brandy production involves the making of a base wine, double distillation in copper potstills and maturation in oak casks for a minimum period of three years, all of which can impact on the flavour and character of the final product. In order to better understand the role of the first two mentioned factors on the quality of base wines and their unaged distillates, thirty-three and twenty-five brandy base wines were pot distilled on a commercial scale during 1999 and 2000, respectively. These wines were sourced from brandy base wine producers in four geographical regions of the Western Cape and one in the Northern Cape, South Africa. Twenty-seven volatile compounds present in these wines and resulting distillates were quantified using gas chromatography and the results were subjected to an analysis of variance (ANOVA), factor analysis and classification regression tree analysis (CART) using region, cultivar, harvest time, vintage and yeast strain as independent variables. ANOVA and CART showed that vintage, region, harvest time, choice of cultivar and yeast strain can have a significant influence on the volatile compound composition of brandy base wines and their resultant distillates. The concentration of ethyl lactate, acetic acid, n-hexanol, isobutanol and 2-phenyl ethanol increased significantly in the base wines with progression in harvest time. However, the concentration of acetate esters, ethyl caprate and –caprylate, n-propanol, n-butanol and the volatile C_6, C_8 and C_{10} acids in the base wines all decreased significantly with progression in harvest time. Wines made from table grapes contained significantly higher concentrations of ethyl butyrate, isoamyl acetate, n-hexanol and acetic acid. No distinct groupings of yeast strains could be made on the overall basis of volatile compounds in the base wines, although individual compound differences were noted for n-propanol and ethyl caprate. Wines originating from the Rawsonville region, contained significantly higher concentrations of hexyl acetate when compared to wines from the other regions.

4.1 INTRODUCTION

The quality of a wine and unmatured wine distillate depends on factors incorporated at every step of the production process. These factors include: soil, geographical and climatic features of the origin of grapes used, viticultural practices, grape maturity, grape variety, vintage variation, vinification techniques (including yeast strain used),

storage of wine prior to distillation and the distillation technique used (Guymon, 1974a; Marais and Pool, 1980; Soles *et al.*, 1982; Hough, 1985; Wagener, 1986; Steger and Lambrechts, 2000; Du Plessis *et al.*, 2002).

It is generally recognised that wines from cooler regions produce wines with more delicate, finer aromas and that the best wines from warm regions are often produced from slightly less mature grapes. Climate may influence brandy quality by affecting mould and rot, especially in wet vintages and cool climates. Where varietal aroma is not an important quality factor, however, climatic region might not have such a great effect. For example, with certain non-distinctive varieties it has been shown that crop level, usually an important consideration in varietal character, made no significant differences in general wine quality (Weaver *et al.*, 1961). Lafon (1964) studied the less delicate brandies from warm vintages in cognac and concluded that much of cognac's quality is due to the cool climate, which benefits the aroma constituents and leads to the concentration of aroma with simultaneous lower alcohol production, and benefits the storage of wine with low alcohol and no sulphur dioxide.

There is still a considerable debate as to the most optimal cultivar for the production of high quality brandy distillates. No particular variety has been universally shown to be the best. Guymon (1968) recommended white or lightly coloured varieties with a moderately distinct and pleasing aroma, good tonnage, resistance to oxidation, mould and rot. Lafon *et al.* (1964) recommended that the St Emilion cultivar (with its better resistance to *Botrytis* and higher acid content) replace Folle Blanche and Colombar in the Cognac district. French Colombar is an important variety in the Cognac district and its wine has a leafy or stemmy aroma (Quady and Guymon, 1973). It possesses a high natural acidity, but on the other hand, exhibits a greater tendency towards browning, which indicates that it has a high phenolic content. High tannin fruit was shown to result in poor quality distillates (Quady and Guymon, 1973). They found that French Colombar made a wine with a more distinctive aroma than Thompson Seedless. However, Thompson Seedless produced a significantly better distillate than French Colombar. They concluded that quality from Thompson's Seedless was little affected by maturity, while that from French Colombar decreased with increasing maturity. In South Africa, the majority of commercial brandy base wines are made from Chenin blanc and Colombar, with smaller quantities being made from St Emilion, Weisser and Emerald Riesling, Palomino and table grapes (Weitz, 1997). Hough (1985) studied the influence of cultivar and region on South African brandy quality, but focussed on comparing Palomino and Colombar. The increased concentrations of isobutanol and isoamyl alcohol present in a distillate derived from Palomino grapes made it a less desirable cultivar for use in brandy production when compared to Colombar (Hough, 1985). It was found that under South African conditions, Colobar produced an organoleptically more acceptable distillate. This study investigates the influence of cultivar and region on South African brandy quality using cultivars and regions currently in use for commercial production.

As grapes approach maturity, the aroma level rises and berry aroma composition changes (Boulton *et al.*, 1995). It is generally assumed that higher must acidities yield higher quality wine aromas with concurrently better resistance to microbial spoilage, better flavour development, enhanced lees cell wall autolysis, less acetaldehyde production, less volatile acid and more aromatic principles (Amerine and Joslyn, 1970). Thus a considerable debate has arisen as to the optimal level of maturity for grapes to be harvested and used in producing a high quality wine for use in brandy and cognac production. In comparing 24 years of tasting records from the Cognac district, Lafon (1964) observed that high quality distillates have never been made from wines with more than 10.5% v/v alcohol. Amerine and Joslyn (1970) also recommended lower grape maturities in order to concentrate flavour volatiles. Wine acidity, which is correlated to grape maturity, has been considered an important factor in brandy quality. Probably the most important effect is that the potential resistance to bacterial spoilage in wines stored without SO_2 is increased. Other effects can include increases in ester concentrations (due to lower pH) or possible increased liberation of terpene type compounds from acid induced hydrolysis during a long potstill distillation (Amerine and Joslyn, 1970). Correlation coefficients indicated that better brandies were produced from wines with fruity, but not overripe and oxidised aromas. The better brandies were lower in ester, fusel oil and aldehyde concentrations and inexplicably higher in total acidities (Quady and Guymon, 1973). Brandy quality was found to correlate positively with brandy acidity. Although volatile acidity in wine correlated positively with brandy acidity, it did not correlate with brandy quality. The acids, which affected the quality of these brandies, were thus not those accounted for in volatile acidity. Quady and Guymon (1973) thus speculated that these results reflect the beneficial result of small amounts of free fatty acids, which can influence brandy quality. The climate in South African brandy grape growing regions is considerably warmer than that of Cognac and generally, South African brandies, when compared to those from Cognac, have a warmer, riper, fruit driven aroma base that may well be the result of the warmer climatic growing conditions and riper berries. From past years of commercial data on base wines accepted for distillation, it is evident that South African brandy base wines possess between 10 and 12.5% v/v alcohol, with a total acidity in the range of 4 to 8 g/L (commercial data not shown). Optimal grape maturity and resultant alcohol contents for South African brandy can thus not be inferred from the findings of studies in cooler climate regions such as Cognac.

The effect of yeast strain and its influence on wine composition has been extensively studied (Lambrechts and Pretorius, 2000), but relatively little work has to date been done on the influence of yeast strain on wine distillate composition. Steger and Lambrechts (2000) noted that the presence of yeast lees has a significant effect on the final concentrations of both higher alcohols and esters in the distillate. Elevated levels of all esters, not only the highly volatile ethyl acetate and isoamyl

acetate, were found in the sensorially most favoured distillates, as were slightly elevated levels of higher alcohols (Steger and Lambrechts, 2000).

This study thus aims to investigate the effects of vintage, region, cultivar, harvest time and yeast strain on the composition and quality of brandy base wines and their resultant unaged distillates in a South African context. This chapter covers the effects on chemical composition of base wines and distillates using analysis of variance, classification and regression trees and principal component and factor analysis. Succeeding chapters will discuss the effects on sensory quality of the base wines and distillates followed by the effect of wood maturation on the chemical and sensory composition of these distillates.

4.2 MATERIALS AND METHODS

4.2.1 EXPERIMENTAL OUTLAY

Brandy base wines were sourced from brandy base wine producers in five geographical regions of the Cape, South Africa. These regions were: Worcester, Robertson, De Doorns, Rawsonville and the Northern Cape. Although Hough (1985) and Von Adam *et al.* (1996) both concluded that cultivar and regional effects are more significant in determining distillate quality than vintage effects, it was nevertheless felt that the results of this particular study would be more comprehensive if performed over two consecutive vintages. Thirty-three wines were distilled in 1999 and twenty-five wines were distilled in 2000. Wines were selected based on an initial chemical analysis and sensory evaluation to ensure that all of the wines used in the experiment met the South African legal specifications for brandy base wine. The specifications state: residual sugar < 4 g/L; total SO_2 less than 20 mg/L; volatile acidity less than 0.7 g/L; alcohol content = 10-12% v/v. Approximately 35 000 litres of each of the selected wines were then delivered to a commercial distillery in Worcester. Each wine was treated separately (i.e. separate storage and distillation) and the resultant distillates were also stored separately. Wine samples were drawn as soon as they had been offloaded from the road tanker into the storage tank after thorough mixing. Minimising the storage time of wine prior to distillation is a practical issue and depends on the volume of tank space available, tank cooling facilities and the daily distillation capacity of a commercial distillery. In this study, no tank cooling facilities were available at the distillery and all wines were therefore stored for no longer than three days prior to distillation in order to minimise the possibility of microbial infection in the base wines. Commercial scale double distillation took place in four identical copper potstills with a capacity of 2000 litres each.

Samples of the low wine (first distillate) and of the heads (every 5 minutes until the liquid temperature reached 82°C), heart (well-mixed sample from product receiving tank) and tails fraction (one sample every hour for the 8 hours of the tails

distillation) were taken for analysis. Although not covered in this chapter, the hearts fraction of each of these wines was then filled into six 340-litre French oak barrels to mature for three years, in compliance with the South African law on brandy. Winemakers of the base wines used in the study completed a detailed information sheet on each of these wines supplying details such as origin of grapes, cultivar/s used, date of harvest, skin contact time given, enzyme treatment (if any), yeast strain used, fermentation temperature, duration of fermentation (data not shown). This information was used in determining the independent variables needed for the analysis of variance (hereafter referred to as ANOVA) and classification and regression tree analysis (hereafter referred to as CART analysis), referred to in section 2.3.4 Independent variables used for the ANOVA and CART analyses).

4.2.2 GAS CHROMATOGRAPHIC ANALYSIS

4.2.2.1 Base wine analysis

Base wines were analysed using the method described in Steger and Lambrechts (2000). Twenty-eight volatile compounds were identified in the base wines. Among these 28 compounds, 21 were selected for statistical analysis because of their good extraction reproducibility (variation coefficient < 20%). For this reason, acetaldehyde, acetoin, methanol, diethyl succinate, n-butyric acid, isovaleric acid and n-valeric acid concentrations were removed for the purpose of statistical analysis.

4.2.2.2 Heart fraction analysis

This was performed using column gas chromatography. Five ml of the potstill distillate samples were mixed with 0.25 ml of a 2000 mg/L solution of 4-methyl-2-pentanol, which served as an internal standard. Samples were eluted using the method developed by M. Blom (Distell, 2000) and were run on a Hewlett Packard HP5890 gas chromatograph, coupled to an HP7673 auto sampler and injector, and an HP 3396A integrator. The same operating conditions were used as described in Steger and Lambrechts (2000). Injection volume: 1 µl. Twenty-seven volatile compounds were identified in the distillates. Among these 26 compounds, 21 were selected for statistical analysis because of their good extraction reproducibility (variation coefficient < 20%). For this reason, methanol, propionic acid, n-butyric acid, isovaleric and n-valeric acid were excluded from the statistical analysis. Acetoin and ethyl butyrate were not quantified. The highest coefficient of variation in the unaged distillate GC analysis was 16.95% for isobutyric acid in 2000. This compound also had the highest value in 1999, namely 14.06% (data not shown).

4.2.3 STATISTICAL ANALYSIS

The ANOVA and principal component factor analyses were performed using STATISTICA version 6.0. The significance level used as a guideline for accepting or

rejecting hypotheses was 5% (0.05). Classification and regression tree analysis was performed using the CART program from Salford Systems.

4.2.3.1 One way ANOVA

This analysis tool performs simple analysis of variance (ANOVA) to test the hypothesis that means for different groups are equal. The nul hypothesis used states that the means for all groups are equal. The alternative hypothesis to the nul hypothesis states that at least one of the means is different to the rest of the means of the remaining groups. In the one way ANOVA graphs included in this chapter, the p-values at the top of the graph reflect the level of significant differences between all of the variables on the graph. Where the p-value for individual differences was required, it was calculated separately using STATISTICA and are included in the text of the results and discussion.

4.2.3.2 Two way ANOVA

The two way ANOVA tests for interactions between two categorical independent variables and also for effects of the two variables separately. Prior to performing the two way ANOVA on the wine and distillate data, both sets of data were broken down into tables that showed where values were present and missing for all the combinations of two variables. Where there were no or too few data points in a particular combination (eg. region and yeast combinations), these were excluded from the interaction analysis.

4.2.3.3 Interpretation of data from CART program

Regression tree analysis divides the data into subsets based on a target variable and a selected set of predictor variables. The subsets are divided in such a way as to minimise the variance of the target variable within each subset. The result is a set of rules (based on the predictor variables) that characterise each of the subsets and a mean value for the target variable within each subset. In the simplest case, of one target variable (Y) and one predictor variable (X), where the data is split into two subsets, the two rules will be of the form: ($X \leq X_o$) and ($X > X_o$).

4.2.3.4 Independent variables used for the ANOVA and CART analyses

Independent variables used for both of the ANOVA and the CART analyses were:

Region: The base wines used in this study were classified according to five municipal/geographical regions of origin: Rawsonville (region 1), Robertson (region 2), Worcester (region 3), De Doorns (region 4) and the Northern Cape region (region 5). It is generally known that the Worcester, De Doorns and northern Cape region are warm to hot regions in summer, whereas Rawsonville is considered slightly cooler, with a considerably higher average rainfall during the course of the year. The Robertson region is also warm to hot in summer, but is prone to unexpected summer rain showers, although it is classified as a winter rainfall region. As this study was

based largely on commercial practice and commercially produced brandy base wines were selected for this study, it was in some cases not possible to obtain base wines from each region for each of the three harvest time intervals.

Cultivar: Chenin blanc (Ch), Colombar (Co), table grapes (TG), Chenin blanc/Colombar mix (CC) and "other" (O) (other includes varieties such as Cape Riesling, Weisser and Emerald Riesling, Saint Emilion and Clairette blanche) were used. There were not enough single varietal wines distilled of these last mentioned cultivars to warrant being placed into individual classes. This also reflects the current cultivar spread being used commercially for brandy base wine production in South Africa as well as the cultivar availability for brandy base wine production in each of the five regions. Thus, not all cultivars studied were available for use in brandy base wine production in all of the regions.

Harvest time: Harvest time refers to the time at which the grapes were harvested for vinification into brandy base wine. This was divided into three intervals, namely early, mid- and late season. Early refers to grapes harvested prior to the last week in February (early) , mid season refers to grapes harvested from the last week in February up to and including the middle of March (mid), and late season refers to those grapes harvested from the middle of March to the beginning of April (late).

Vintage: Distillations were performed in 1999 and 2000 to take seasonal variation into account.

Yeast strain: Eight yeast strains were used for vinification in these experiments. One additional category, entitled "other" (OY) was used as an overall category for other strains used in vinifying these wines. The number of "other" yeast strains were too few to be classified individually. The yeast strains used comprised commercially available strains (WE228, WE372, VIN13, VIN7, ICVD254, FAIEDV) as well as two experimental strains that have been shown to have desirable characteristics as brandy base wine strains (Steger and Lambrechts, 2000; unpublished data from ARC Nietvoorbij 1998). These were NT117 (a hybrid strain) and 20-2 (a VIN13 hybrid isolated at the Institute for Wine Biotechnology, Stellenbosch).

Table 4.1 summarises the occurrence of variable within each of the five regions studied.

Table 4.1 Summary of variable occurrence within the five regions studied

Region	Vintage	Cultivar	Harvest time	Yeast strain
1	1999, 2000	Ch, Co, CC, O	early, mid, late	VIN13, WE372, WE228, ICVD254,FAIEDV, NT117
2	1999, 2000	Ch, Co, CC, O	early, mid, late	ICVD254, WE228, VIN7, VIN13, NT117, OY
3	1999, 2000	Ch, Co, CC, O	early, mid	WE228, 20-2, ICVD254
4	1999, 2000	TG, O	late	OY, ICVD254, FAIEDV, VIN13, 20-2
5	1999, 2000	Ch, O	mid	WE228, VIN13, 20-2

4.3 RESULTS AND DISCUSSION

4.3.1 WINE AND DISTILLATE ANOVA AND CART ANALYSES

An ANOVA and CART analysis was performed on the data in order to determine the correlation between vintage, region, cultivar, harvest time as well as yeast strain and the volatile composition of the brandy base wines and unaged potstill distillates. **Table 4.2** lists the CART variable importance factors for each of the compounds quantified in the wines and distillates. The CART analysis identifies the most important predictor variable that aids in the determination of the target variable and this variable is designated as 100. All other predictor variables are then listed in relative importance to this one at 100. From **Table 4.2** it can be seen that the most important variable factors are the same in both wine and distillate for the following compounds: 2-phenethyl acetate, isoamyl alcohol, n-propanol (yeast strain); 2-phenyl ethanol (region); ethyl caprate, ethyl caprylate and isoamyl acetate (harvest). Variable importance differences between wines and distillates for the same compounds can be attributed to one of two possible reasons. Either the process of distillation causes significant changes to the concentration of a compound from wine to distillate, or it can be ascribed to normal variation occurring within the data. With the CART analysis, it is not possible to determine which reason is responsible, but some well-educated deductions can be made in those cases where enough research and findings are available on the origins and behaviour of particular compounds during distillation. Such deductions will be discussed in conjunction with the ANOVA results where possible. **Tables 4.3** and **4.4** list the ANOVA results for harvest time differences in both the wines and distillates. **Tables 4.5** and **4.6** list the ANOVA results for vintage differences in both the wines and distillates.

4.3.1.1 Acetaldehyde

Acetaldehyde was only quantified in the distillates. Yeast strains WE228, VIN13, WE372, FAIEDV, ICVD254, VIN7 and NT117 formed a group exhibiting similarly low (mean = 46 to 93 mg/L) concentrations of acetaldehyde. Strains 20-2 and OY formed a second group with higher acetaldehyde concentrations (mean = 112 and 900 mg/L, respectively). Radler (1992) and Romano *et al.* (1994) both found that the aldehyde content varies with the type of yeast strain used. More specifically, the amount of acetaldehyde that a yeast strain can produce is related to the activity of its pyruvate decarboxylase enzyme. A deficiency of nutrient substances during fermentation may also give rise to increased levels of acetaldehyde in wine, as the formation of ethanol is delayed. With a deficiency of amino acids, the path from the carbon source to the fusel alcohols is diverted to keto acids, which in turn are the chemical precursors to the aldehydes (Boulton *et al.*, 1995). Grape varieties differ from one another in the

amount of certain common amino acids (Hernandez-Orte *et al.*, 1999). The amino acid profile of juices from a given grape cultivar from the same location is generally similar from one year to another, but the concentration of amino acids varies from year to year (Huang *et al.*, 1990). This suggests that climatological conditions play a fundamental role in the amino acid content of the must. Their evolution during the ripening process has also been shown to be different (Hernandez-Orte *et al.*, 1999). In this study, distillates originating from wine made with Colombar grapes possessed the highest concentration of acetaldehyde ($p<0.01$) in both vintages. In both vintages acetaldehyde concentrations were significantly higher in distillates originating from wines made from grapes harvested late in the season, than those harvested in the early and mid season (**Figure 4.1**).

4.3.1.2 Ethyl acetate

The mean concentration of ethyl acetate was significantly higher in wines made from early harvested grapes, than from those made with mid and late harvested grapes (refer to **Table 4.3**). Ethyl acetate concentrations in distillates made from early harvested grapes were also significantly higher than in those from mid season grapes ($p=0.015$), although there was no significant difference between early and late harvest. However, distillates originating from region 1 showed the largest difference ($p<0.01$) between early and mid harvest (**Figure 4.2**). Wines fermented with strain VIN13 from region 1 possessed significantly higher concentrations of ethyl acetate than those wines made with WE228 and ICVD254. This was only observed in wines from region 1 (refer to **Figure 4.3**). There was no significant difference in ethyl acetate concentrations between wines made from these three strains in any of the other regions. Chenin blanc and Chenin/Colombar wines possessed significantly higher concentrations of ethyl acetate than wines made from Colombar, table grapes and other varieties ($p<0.01$, **Figure 4.4**). Although vintage differences were not found to be significant in the wines, the mean concentration of ethyl acetate in wines was also higher for 1999 than for 2000 (**Table 4.5**). However, the concentration of ethyl acetate was significantly higher in 1999 distillates than in the 2000 distillates (**Table 4.6**). The CART analysis was able to group four yeast strains together based on their similar concentrations of ethyl acetate in the distillates over both vintages (this was, however, not observed in their corresponding wines). Riponi *et al.* (1996) noted that the concentration of ethyl acetate present in distillates was most influenced by the type of yeast strain used during base wine production. CART was further able to identify another two groups within these using yeast strain, cultivar and region as distinguishing factors (**Table 4.7**).

Table 4.2 CART variable importance in wines and distillates (the most important score has a value of 100 and all other scores are relative to this)

Compound (mg/L)	Type	Yeast	Cultivar	Region	Harvest	Vintage
Acetaldehyde	Distillate	**100**	10.69	29	17.66	5.96
Ethyl acetate	Wine	42.48	39.52	9.17	**100**	23.9
Ethyl acetate	Distillate	**100**	40.7	41.45	82.38	90.41
Ethyl butyrate	Wine	44.91	90.77	**100**	69.94	0
isoAmyl acetate	Wine	75.25	69.04	55.69	**100**	14.31
isoAmyl acetate	Distillate	65.29	44.44	64.98	**100**	0
Ethyl lactate	Wine	16.18	84.43	**100**	87.07	0
Ethyl lactate	Distillate	7.2	**100**	93.18	74.15	0
Ethyl caprate	Wine	41.94	48.16	18.35	**100**	0
Ethyl caprate	Distillate	32.36	27.15	19.48	**100**	9
Ethyl caproate	Wine	35.67	25.07	16.47	**100**	41.98
Ethyl caproate	Distillate	**100**	99.29	46.2	29.22	59.91
Ethyl caprylate	Wine	30	35.33	14.94	**100**	72.67
Ethyl caprylate	Distillate	27.61	62.86	38.39	**100**	0
2-Phenethyl acetate	Wine	**100**	88.83	23.92	47.83	16.78
2-Phenethyl acetate	Distillate	**100**	54.87	17.44	6.01	3.26
Hexyl acetate	Wine	32.99	98.87	89.04	**100**	8.17
Hexyl acetate	Distillate	78.68	**100**	49.89	31.84	0
Diethyl succinate	Distillate	6.36	**100**	63.68	30.38	77.94
Acetic acid	Wine	46.19	**100**	69.75	40.82	8.89
Acetic acid	Distillate	**100**	4.73	0.39	0.23	0
isoButyric acid	Wine	**100**	64.35	52.99	5.19	48.23
isoButyric acid	Distillate	19.79	31.54	11.33	10.28	**100**
Octanoic acid	Wine	16.94	67.7	27.98	**100**	13.37
Octanoic acid	Distillate	33.89	44.47	19.73	24.12	**100**
Hexanoic acid	Wine	61.25	47.57	**100**	28.18	0
Hexanoic acid	Distillate	**100**	61.12	26.02	83.8	68.13
Decanoic acid	Wine	25.93	42.67	12.17	**100**	14.65
Decanoic acid	Distillate	**100**	58.67	65.75	48.64	43.66
Propionic acid	Wine	57.97	**100**	59.92	59.61	10.83
isoButanol	Wine	**100**	64.35	52.99	5.19	48.23
isoButanol	Distillate	54.04	**100**	78.41	66.69	24.89
isoAmyl alcohol	Wine	**100**	23.76	8.76	8.58	36.65
isoAmy lalcohol	Distillate	**100**	65.54	68.23	39.31	0
n-Propanol	Wine	**100**	14.69	50.75	21.85	0
n-Propanol	Distillate	**100**	18.62	40.57	12.47	13.99
n-Butanol	Wine	89.96	65.44	15.5	**100**	4.95
n-Butanol	Distillate	97.12	**100**	79.93	70.76	24.79
n-Hexanol	Wine	37.25	**100**	68.08	53.43	28.88
n-Hexanol	Distillate	4.74	25.76	29.97	31.05	**100**
2-Phenyl ethanol	Wine	89.38	84.49	**100**	67.61	21.53
2-Phenyl ethanol	Distillate	19.68	80.15	**100**	70.41	3

Table 4.3 The effect of harvest time on the volatile compound composition of brandy base wines

Compound	Mean Early (mg/L)	Mean Mid (mg/L)	Mean Late (mg/L)	p Value	Decrease/ Increase
Decrease					
Ethyl acetate	170 a	100 b	89 b	<0.001	Decrease
isoAmyl acetate	10 a	5.3 b	1.7 c	<0.001	Decrease
Ethyl caprate	7.4 a	4.05 b	1.7 c	<0.001	Decrease
Ethyl caprylate	2.38 a	1.6 b	0.9 c	<0.001	Decrease
2-phenethyl acetate	0.32 a	0.26 a	0.165 b	<0.012	Decrease
Hexyl acetate	0.69 a	0.5 b	0.04 c	<0.001	Decrease
Octanoic acid	14.8 a	9.5 b	4.1 c	<0.001	Decrease
Hexanoic acid	7.4 a	5.6 b	2.9 c	<0.001	Decrease
Decanoic acid	11.9 a	5.9 b	2 c	<0.001	Decrease
n-Propanol	48 a	39.5 b	39.4 b	<0.017	Decrease
n-Butanol	1.13 a	0.7 b	0.68 b	<0.001	Decrease
Increase					
Ethyl lactate	4.5 a	10 b	77 c	<0.001	Increase
Acetic acid	262 a	330 a	540 b	<0.001	Increase
n-Hexanol	2.08 a	2.45 b	2.61 b	<0.001	Increase
isoButanol	22 a	27 b	30 b	<0.001	Increase
2-Phenyl ethanol	11 a	10 a	15.2 b	<0.001	Increase
Other					
Ethyl Butyrate	1.8 a	2.1 a	0.95 b	<0.001	
Ethyl caproate	2.9 a	1.3 b	1.7 b	<0.001	
isoButyric acid	1.25 a	1.31 a	1.24 a	0.57282	Not significant
isoAmyl alcohol	150 a	145 a	134 a	0.1302	Not significant
Propionic acid	2.15 a	1.84 a	1.78 a	0.34971	Not significant

Mean early = grapes harvested prior to last week in Feb; mean mid = grapes harvested last week in Feb to mid Mar; mean late = mid Mar to beginning Apr

Table 4.4 The effect of harvest time on the volatile compound composition of unaged potstill distillates

Compound	Mean Early (mg/L)	Mean Mid (mg/L)	Mean Late (mg/L)	p Value	Decrease/ Increase
Decrease					
Ethyl acetate	460 a	360 b	420 a	<0.002	Decrease
isoAmyl acetate	52 a	22 b	8 c	<0.001	Decrease
Ethyl caprate	23.5 a	12.5 b	12 b	<0.001	Decrease
Ethyl caproate	8.5 a	6.4 a	6 a	<0.02	Decrease
Ethyl caprylate	12.5 a	9 b	6.5 c	<0.001	Decrease
Hexyl acetate	1.75 a	1 b	0.3 c	<0.001	Decrease
Octanoic acid	25.7 a	21.5 a	16.5 b	<0.004	Decrease
Hexanoic acid	4.3 a	3 b	2.25 b	<0.001	Decrease
Decanoic acid	14 a	14.3 a	9 b	<0.003	Decrease
Increase					
Acetaldehyde	95 a	100 a	192 b	<0.02	Increase
Ethyl lactate	11 a	19 a	72 b	<0.001	Increase
Acetic acid	25 a	40 b	70 c	<0.001	Increase
Diethyl succinate	0.7 a	1.23 a	2.5 b	<0.004	Increase
isoButanol	144 a	188 b	216 c	<0.001	Increase
isoAmyl alcohol	995 a	980 a	1135 b	<0.017	Increase
n-Hexanol	14.5 a	11.5 a	22.5 b	<0.001	Increase
2-Phenyl ethanol	4.1 a	4.7 a	8.2 b	<0.001	Increase
Other					
2-phenethyl acetate	1.85 a	0.75 b	2.1 a	<0.005	
n-Propanol	360 a	292 b	380 a	<0.002	
n-Butanol	6.4 a	4.5 b	5.05 b	<0.001	
isoButyric acid	1.04 a	0.98 a	0.71 b	0.07883	Not significant

Table 4.5 The effect of vintage on the volatile compound composition of brandy base wines

Compound	Mean 1999 (mg/L)	Mean 2000 (mg/L)	p Value	Decrease/ Increase	% Increase or Decrease
Decrease					
isoAmyl alcohol	154.5	134.8	<0.005	Decrease	12.75%
n-Hexanol	2.46	2.19	<0.006	Decrease	10.98%
Propionic acid	2.2	1.6	<0.008	Decrease	27.27%
Ethyl lactate	22	10	<0.008	Decrease	54.55%
isoButanol	29.5	21	<0.001	Decrease	28.81%
isoButyric Acid	1.44	1.1	<0.001	Decrease	23.61%
Increase					
isoAmyl acetate	4.8	8.1	<0.001	Increase	68.75%
Ethyl butyrate	1.62	2.06	<0.004	Increase	27.16%
Hexyl acetate	0.43	0.61	<0.005	Increase	41.86%
2 Phenethyl alcohol	10.51	11.51	<0.021	Increase	9.51%
Decanoic Acid	5.6	9.45	<0.001	Increase	68.75%
Ethyl caproate	1.39	2.52	<0.001	Increase	81.29%
Ethyl caprylate	1.35	2.3	<0.001	Increase	70.37%
Hexanoic Acid	5.15	6.85	<0.001	Increase	33.01%
Octanoic acid	8.85	13	<0.001	Increase	46.89%
Other					
Ethyl caprate	4.65	5.2	0.173	Not significant	11.83%
2-Phenethyl acetate	0.26	0.28	0.553	Not significant	7.69%
n-Propanol	41.9	43	0.695	Not significant	2.63%
n-Butanol	0.78	0.92	0.045	Not significant	17.95%
Ethyl acetate	130	114	0.06	Not significant	12.31%
Acetic Acid	365	322	0.066	Not significant	11.78%

Table 4.6 The effect of vintage differences on the volatile compound composition of unaged potstill distillates

Compound	Mean 1999 (mg/L)	Mean 2000 (mg/L)	p Value	Decrease/ Increase	% Increase or Decrease
Decrease					
Ethyl acetate	445	345	<0.001	Decrease	22.47%
Hexanoic Acid	3.8	2.75	<0.001	Decrease	27.63%
isoButanol	190	161	<0.003	Decrease	15.26%
Ethyl lactate	27.5	17	<0.012	Decrease	38.18%
Decanoic Acid	14.5	12.5	<0.017	Decrease	13.79%
Ethyl caproate	8	5.7	<0.021	Decrease	28.75%
Increase					
2-Phenethyl acetate	0.8	1.93	<0.001	Increase	141.25%
isoAmyl alcohol	970	1045	<0.02	Increase	7.73%
Ethyl caprylate	9.25	10.46	<0.024	Increase	13.08%
Hexyl acetate	0.8	1.61	<0.001	Increase	101.25%
isoButyric Acid	0.67	1.34	<0.001	Increase	100.00%
Octanoic acid	15.3	30.5	<0.001	Increase	99.35%
isoAmyl acetate	22	41	<0.001	Increase	86.36%
Other					
n-Hexanol	19	15.91	0.45	Not significant	16.26%
Diethyl succinate	1.1	1.35	0.31	Not significant	22.73%
n-Butanol	5.08	5.3	0.54	Not significant	4.33%
Acetaldehyde	109	111.5	0.81	Not significant	2.29%
2-Phenyl ethanol	5.19	4.74	0.195	Not significant	8.67%
n-Propanol	332	316	0.407	Not significant	4.82%
Ethyl caprate	16.5	15.5	0.488	Not significant	6.06%
Acetic Acid	40	37.7	0.644	Not significant	5.75%

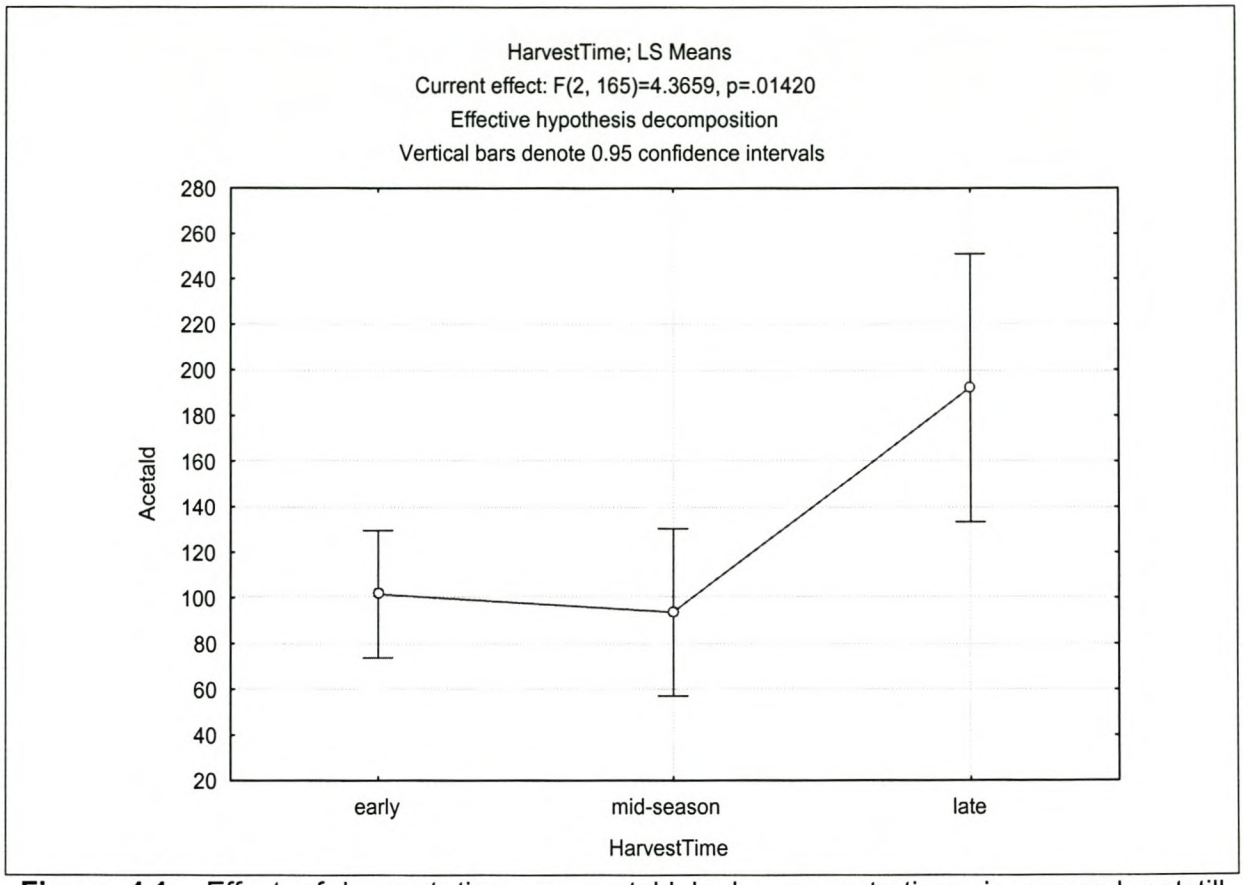

Figure 4.1 Effect of harvest time on acetaldehyde concentrations in unaged potstill distillates (mg/L).

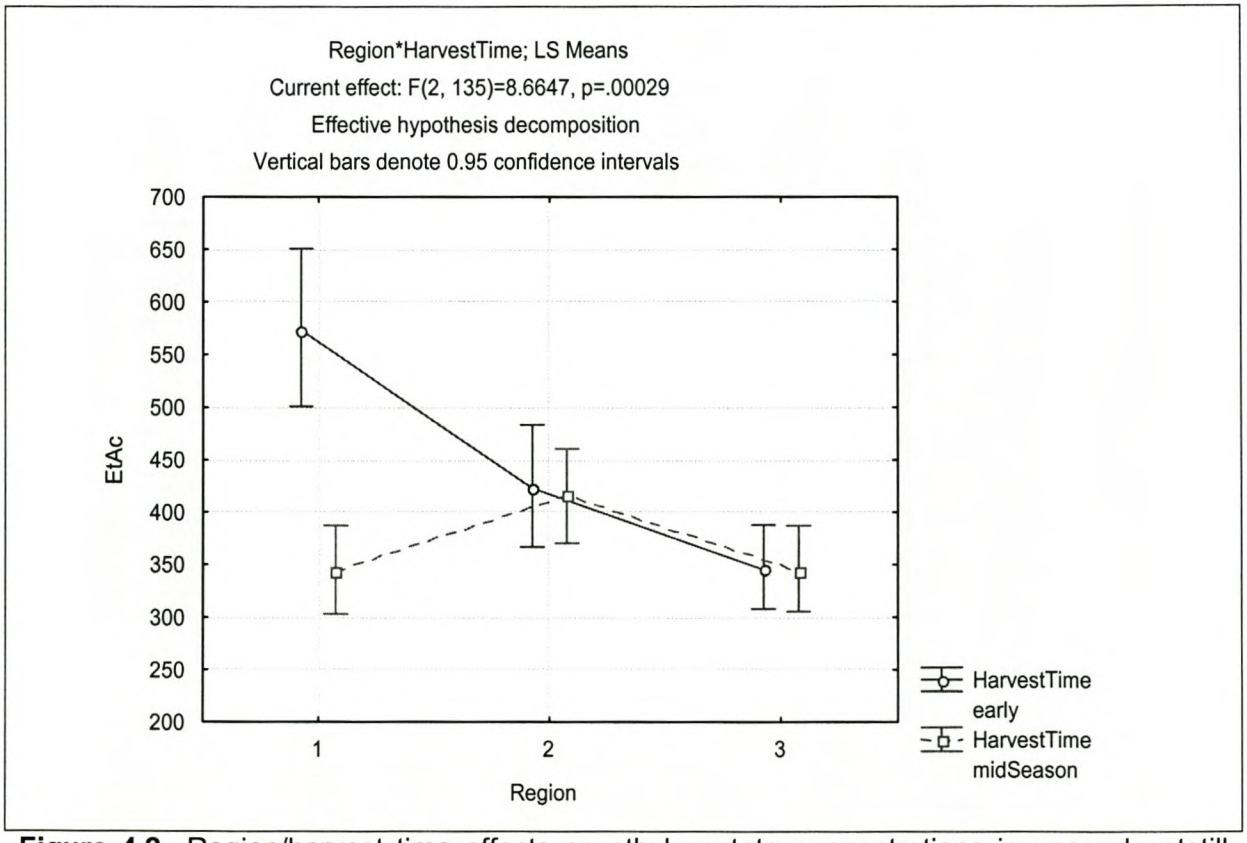

Figure 4.2 Region/harvest time effects on ethyl acetate concentrations in unaged potstill distillates (mg/L).

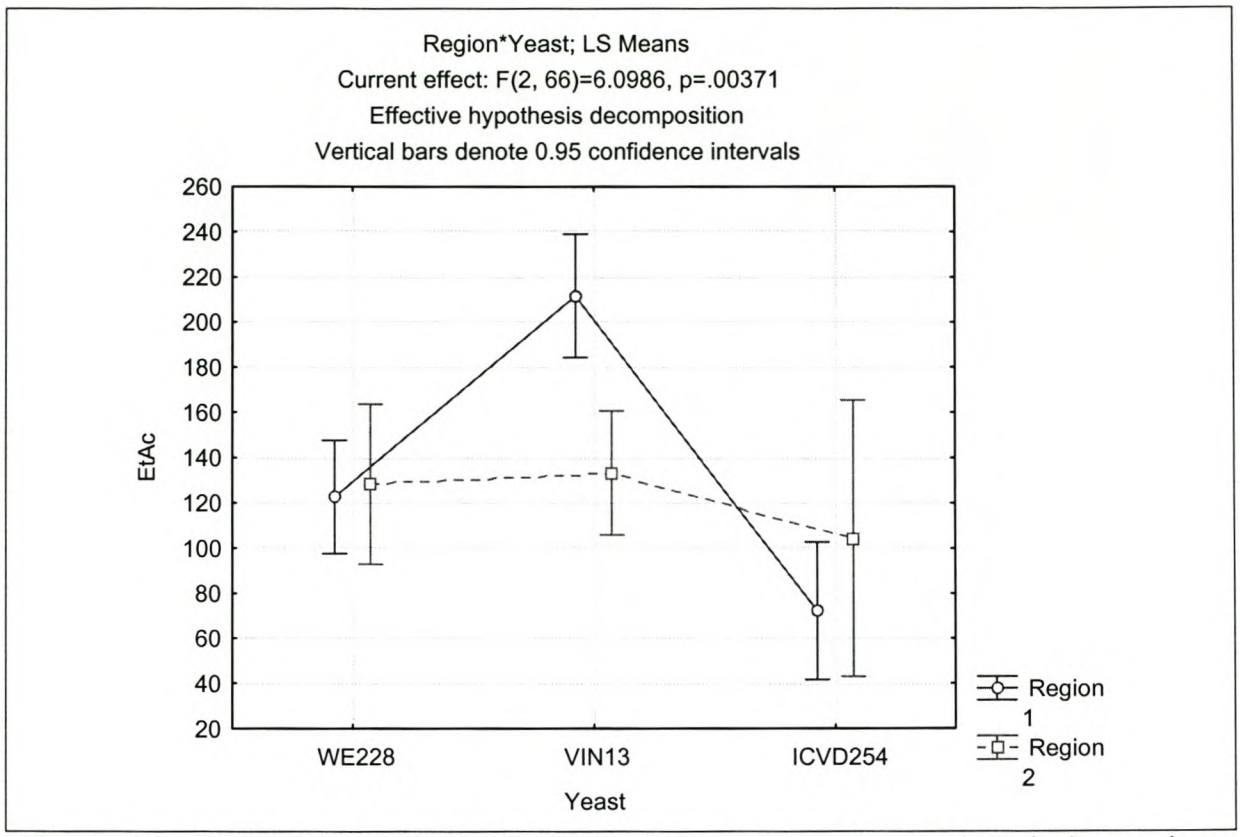

Figure 4.3 Region/ yeast strain effects on ethyl acetate concentrations in base wines (mg/L).

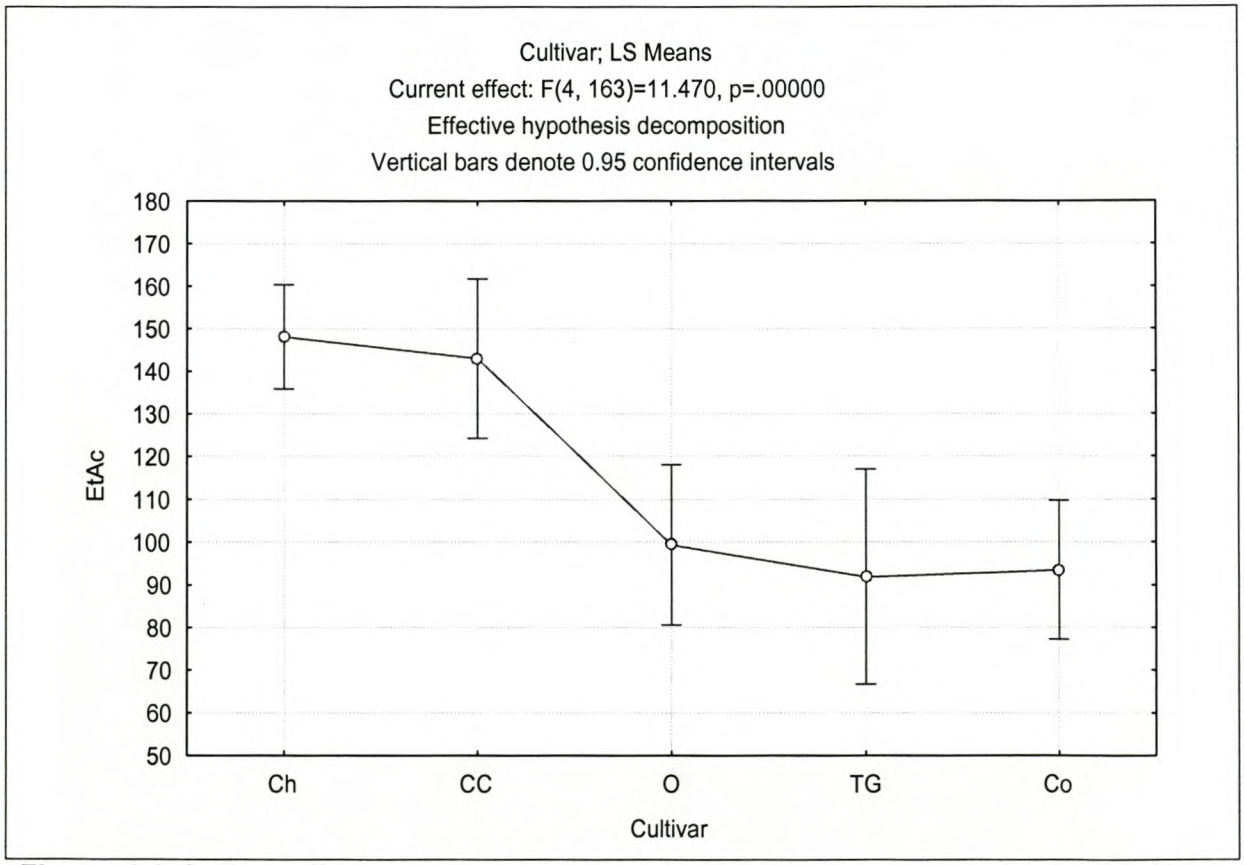

Figure 4.4 Cultivar effects on ethyl acetate concentrations in base wines (mg/L) (Ch = Chenin blanc; CC = Chenin blanc/Colombar; O = other varieties; TG = table grapes; Co = Colombar).

Table 4.7 CART classification rules for ethyl acetate concentrations in distillates

Rule	Mean (mg/L)
If Vintage = 2000 and Yeast = WE228, ICVD254, FAIEDV, NT117	275.287
If Vintage = 1999 and Yeast = WE228, ICVD254, FAIDEV, NT117	401.861
If Cultivar = Colombar, Table grapes and Yeast = WE372, Vin13, Vin7, OY, 20-2	400.45
If Region = 2, 3, 5 and Cultivar = Chenin, Chenin/ Colombar, Other and Yeast = WE372, Vin13, Vin7, OY, 20-2	446.213

4.3.1.3 Ethyl butyrate

The concentration of ethyl butyrate was significantly lower in 1999 wines than in 2000 wines ($p<0.01$, refer to **Table 4.5**). The concentration of ethyl butyrate was significantly higher in wines made from early and mid season harvested grapes ($p<0.01$) than those made from late harvested grapes, which confirms the correlation observed in the factor analysis of these wines (refer to factor analysis results and **Table 4.3**). In both vintages wines made from table grapes originating in region 4 contained the lowest concentration of ethyl butyrate when compared to the other regions ($p<0.01$, **Figure 4.5**). As confirmation, the CART analysis determined that region of origin was the most important variable in determining the concentration of ethyl butyrate in the base wines, followed by cultivar and then harvest time (**Table 4.2**). This is very similar to the variable importance factors identified for ethyl lactate. Postel and Adam (1992) referred to ethyl butyrate and ethyl lactate as spoilage indicators in the evaluation of distillate raw material. However, in this study, the relationship between ethyl butyrate and ethyl lactate was found to be an inverse one. The concentration of ethyl butyrate was significantly higher in wines made from early and mid season harvested grapes, whereas the concentration of ethyl lactate was highest in wines made from grapes harvested late in the season. This inverse relationship was also confirmed in the factor analysis (section 4.3.2.1).

4.3.1.4 isoAmyl acetate

Vintage and harvest time had a significant effect on isoamyl acetate concentrations (**Tables 4.3, 4.4, 4.5** and **4.6**). This difference was largest when comparing wines and distillates made from grapes harvested early and in mid season in region 1 (wine $p<0.01$; distillate $p<0.01$) (**Figure 4.6**). In mid to late season wines and distillates, the CART analysis was able to distinguish two distinct groups (**Table 4.8**). Daudt and Ough (1973) found that the type of yeast strain used definitely influences the amount of esters formed, although the amount of individual esters formed is not affected equally by the specific yeast. The formation of esters was also found to be dependent

on the grape variety used and it follows that the composition of the grape juice also contributes greatly to the total amount of esters formed (Daudt and Ough, 1973). Wines and distillates originating from region 4 had significantly lower concentrations of isoamyl acetate when compared to the regions 1, 2 and 3 [p (wines)<0.001; p (distillates)<0.02]. All of the table grapes originated from region 4. As was noted for ethyl acetate, wines fermented with strain VIN13 from region 1 possessed significantly higher concentrations of isoamyl acetate than those wines made with WE228 and ICVD254. However, contrary to what was noted for ethyl acetate, this was also observed in wines from region 2. Marais *et al.* (1981) found that isoamyl acetate is a statistically sensitive parameter with regard to classifying white wines by origin.

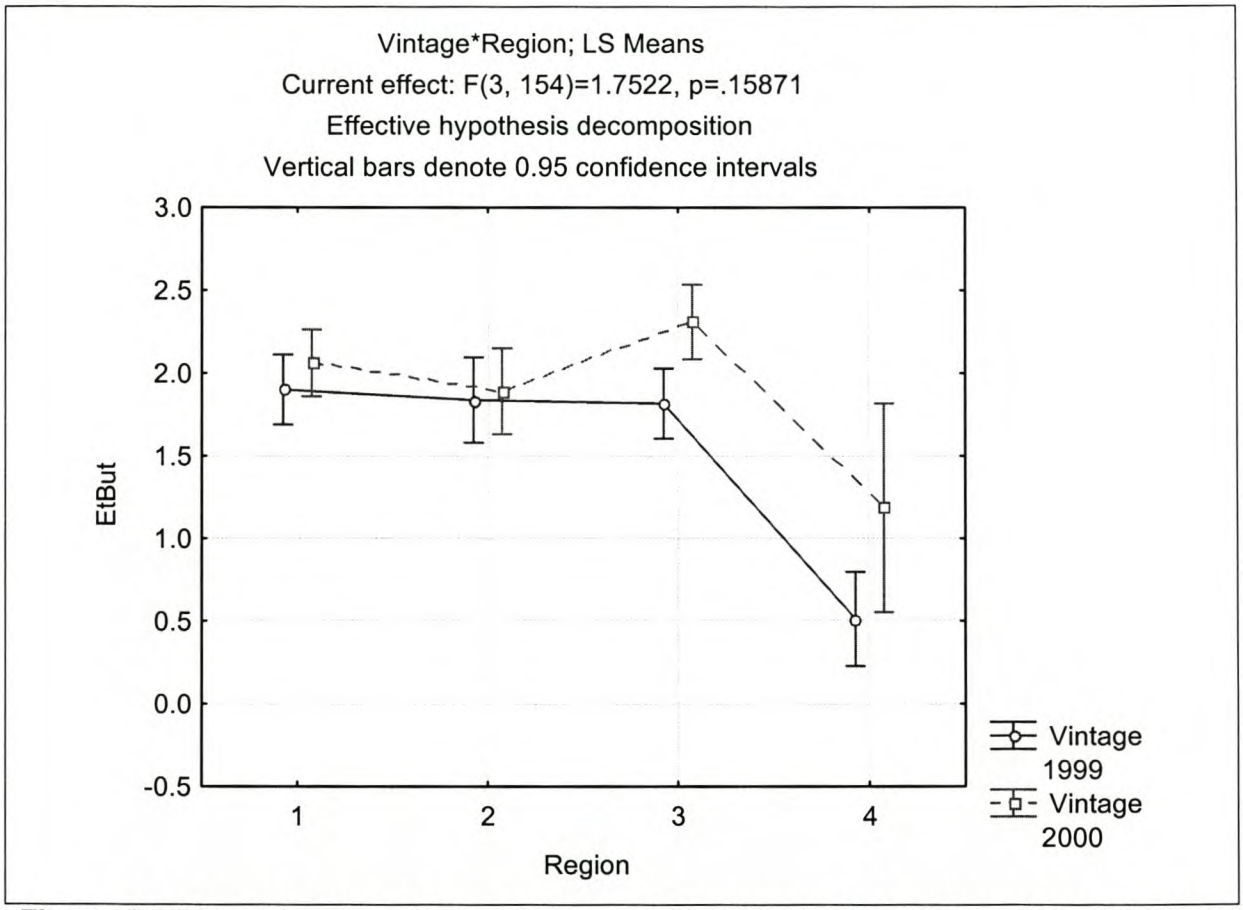

Figure 4.5 Vintage/ region effects on the concentration of ethyl butyrate in brandy base wines (mg/L).

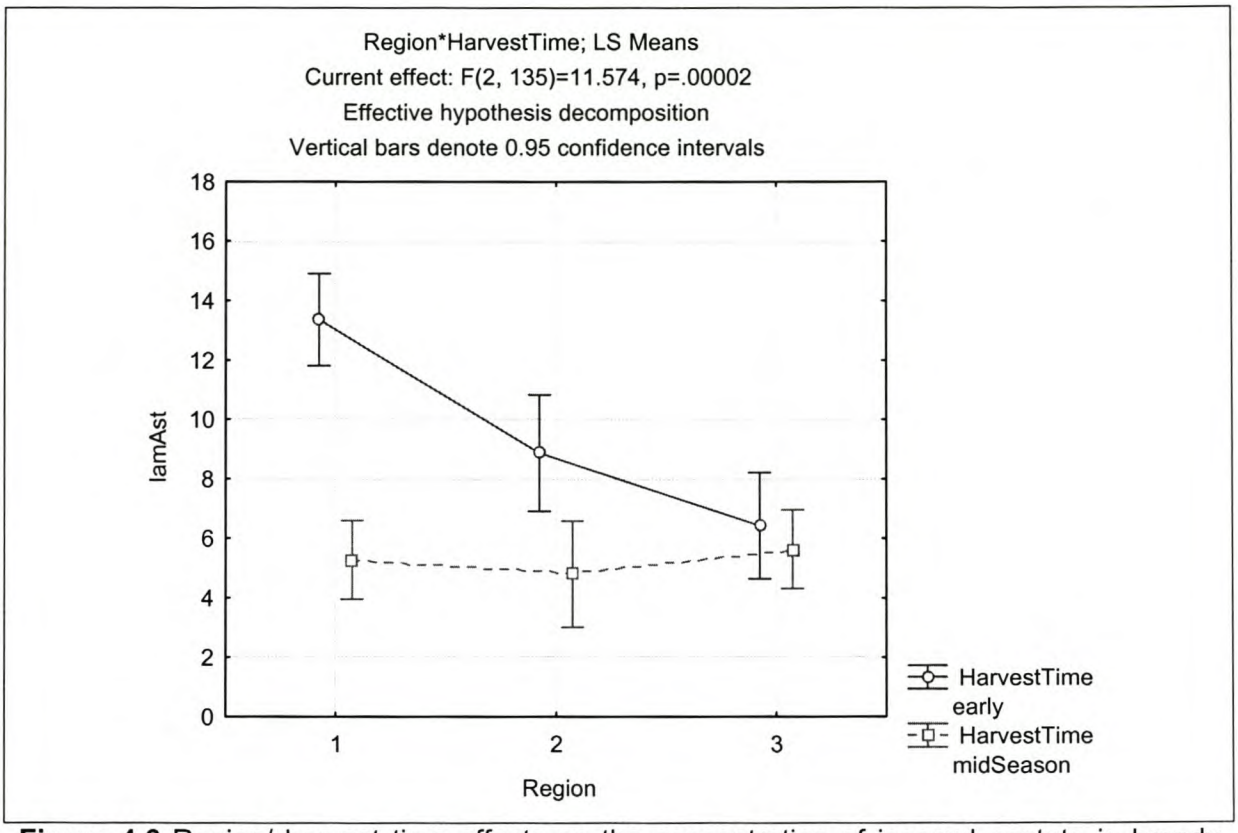

Figure 4.6 Region/ harvest time effects on the concentration of isoamyl acetate in brandy base wines (mg/L).

Table 4.8 CART classification rules for iso amyl acetate concentrations in wines and distillates

Wine Rules	**Mean (mg/L)**
If Cultivar = Table grapes, Other and Harvest = mid season, late	1.8061
If Vintage = 1999 and Cultivar = Chenin, Colombar, Chenin/ Colombar and Harvest = mid season, late	4.384
Distillate Rules	**Mean (mg/L)**
If Cultivar = Table grapes, Other and Harvest = mid season, late	8.256
If Yeast = WE372, WE228, ICVD254, FAIEDV, OY and Cultivar = Chenin, Colombar, Chenin/ Colombar and Harvest = mid season, late	21.27
If Yeast = Vin 13, Vin7, 20-2, NT117 and Cultivar = Chenin, Colombar, Chenin/ Colombar and Harvest = mid season, late	41.76

4.3.1.5 Ethyl lactate

ANOVA results showed that ethyl lactate levels were significantly higher in wines and distillates originating from grapes harvested late in the season ($p<0.01$, refer to **Tables 4.3** and **4.4**). Wines and distillates made from table grapes in region 4 possessed significantly higher levels of ethyl lactate than wines and distillates

originating from the remaining four regions and cultivars ($p<0.01$). The mean of ethyl lactate concentrations was lower in 2000 than in 1999 for both wines and distillates (refer to **Tables 4.5** and **4.6**). What is interesting is that cultivar, region and harvest time were all identified as being of high importance in both the wines and distillates in the CART analysis (**Table 4.2**). Thus all three of these factors play an integral role in the concentration of ethyl lactate in both the base wines and distillates. This correlates well with the findings of Du Plessis *et al.* (2002). They showed that the concentration of ethyl lactate increases during the course of the harvest season, when grapes become more susceptible to microbial infection and this is further encouraged due to the fact that brandy base wines are not permitted sulphur treatment during storage.

4.3.1.6 Ethyl caproate

Ethyl caproate values were significantly lower in 1999 wines than in those from 2000 ($p<0.001$, **Table 4.5**). However, this trend was reversed in the distillates, where the distillates from 1999 were found to have a significantly higher mean concentration than those in 2000 ($p<0.021$, **Table 4.6**). CART showed that the discrepancy between wine and distillate trends for this compound could be ascribed to those distillates originating from regions 1 and 3. (**Table 4.9**). The concentration of ethyl caproate present in wines made from early harvested grapes was significantly higher than those made from mid and late harvested grapes ($p < 0.001$, **Table 4.3**). Although not as significant, the same trend was observed in the distillates (**Table 4.4**).

Table 4.9 CART classification rules for ethyl caproate concentrations in distillates

Rule	Mean (mg/L)
If Region = 2, 4, 5 and Yeast = WE372, WE228, ICVD254, FAIEDV, NT117	2.95
If Vintage = 2000 and Region = 1, 3 and Yeast = WE372, WE228, ICVD254, FAIEDV, NT117	4.8
If Cultivar = T/ grapes, Colombar, Other and Vintage = 1999 and Yeast = WE372, WE228, ICVD254, FAIEDV, NT117	5.5
If Cultivar = Chenin blanc, Chenin/ Colombar and Vintage = 1999 and Region = 1, 3 and Yeast = WE372, WE228, ICVD254, FAIEDV, NT117	9.22

4.3.1.7 Ethyl caprylate

The mean of the ethyl caprylate values was higher in the 2000 wines and distillates (refer to **Tables 4.5** and **4.6**). Time of harvest has a significant effect on the concentration of ethyl caprylate present in wines and distillates. The concentration of ethyl caprylate is highest in wines and distillates originating from grapes harvested

early ($p<0.001$, **Tables 4.3** and **4.4**). Houtman *et al.*, (1980) showed that the concentration of ethyl caproate and ethyl caprylate in wine is correlated to the initial sugar content present in the grape juice and thus also the degree of ripeness of the grapes at harvest. From the ANOVA results, it is evident that table grapes and "other" varieties from regions 4 and 5 possess significantly lower concentrations of ethyl caprylate (refer to **Figure 4.7** for wines; $p_{(distillates)}<0.01$). Postel and Adam (1992) and Cantagrel *et al.* (1992) found that the concentration of C_6 to C_{10} esters present in distillates is strongly influenced by the amount of lees that is distilled along with the wine. Of particular interest here is the ratio of ethyl caprate to ethyl caprylate (C_{10}:C_8). With increasing fractions of added lees, the concentration of ethyl caprylate increases over-proportionately to the level of ethyl caprate. In this study, emphasis was placed on performing identical distillations (in terms of cutoff points and lees content). A portion of roughly 3% lees by volume was added to the wines during distillation. This is also evident in the values obtained from the ratio of ethyl caprate to ethyl caprylate. The ratio of ethyl caprate to ethyl caprylate was found to vary between 1.9 and 2.5, with the exception of two distillates, which had ratios of 3 and 4.1 respectively. Cantagrel *et al.*, (1992) found that, under normal distillation conditions, when a portion of yeast lees is distilled with the wine, a ratio above 0.3 can be expected for ethyl caprate: ethyl caprylate. In the study by Cantagrel *et al.* (1992), the level of ethyl caprylate increased by a factor of 2.6 in the samples with a large fraction of accompanying yeast lees (when compared to those with little or no accompanying yeast lees). The level of ethyl caprate increased by a factor of 4.6. Thus, with the exception of one of the distillates (ethyl caprate: ethyl caprylate = 4) the amount of yeast lees present in each distillation remained relatively constant. Cantagrel *et al.,* (1992) also found that varying amounts of yeast lees present have no significant effect on the concentrations of ethyl acetate, ethyl lactate, diethyl succinate or the higher alcohol concentrations.

4.3.1.8 Ethyl caprate

Harvest time has by far the largest impact on the concentration of ethyl caprate present in the wines and distillates. The concentration of ethyl caprate is highest in wines and distillates made from early harvested grapes and decreases with progression in harvest time (**Table 4.3** and **4.4**). The variable importance of harvest time was also confirmed by the CART analysis (**Table 4.2**). Wines made from table grapes and "other" cultivars, possessed significantly lower concentrations of ethyl caprate than those made from Chenin, Colombar and Chenin/Colombar ($p<0.01$). The yeast strains WE372, VIN13, VIN7 and 20-2 produced higher concentrations of ethyl caprate in both wines and distillates when compared to the remaining strains.

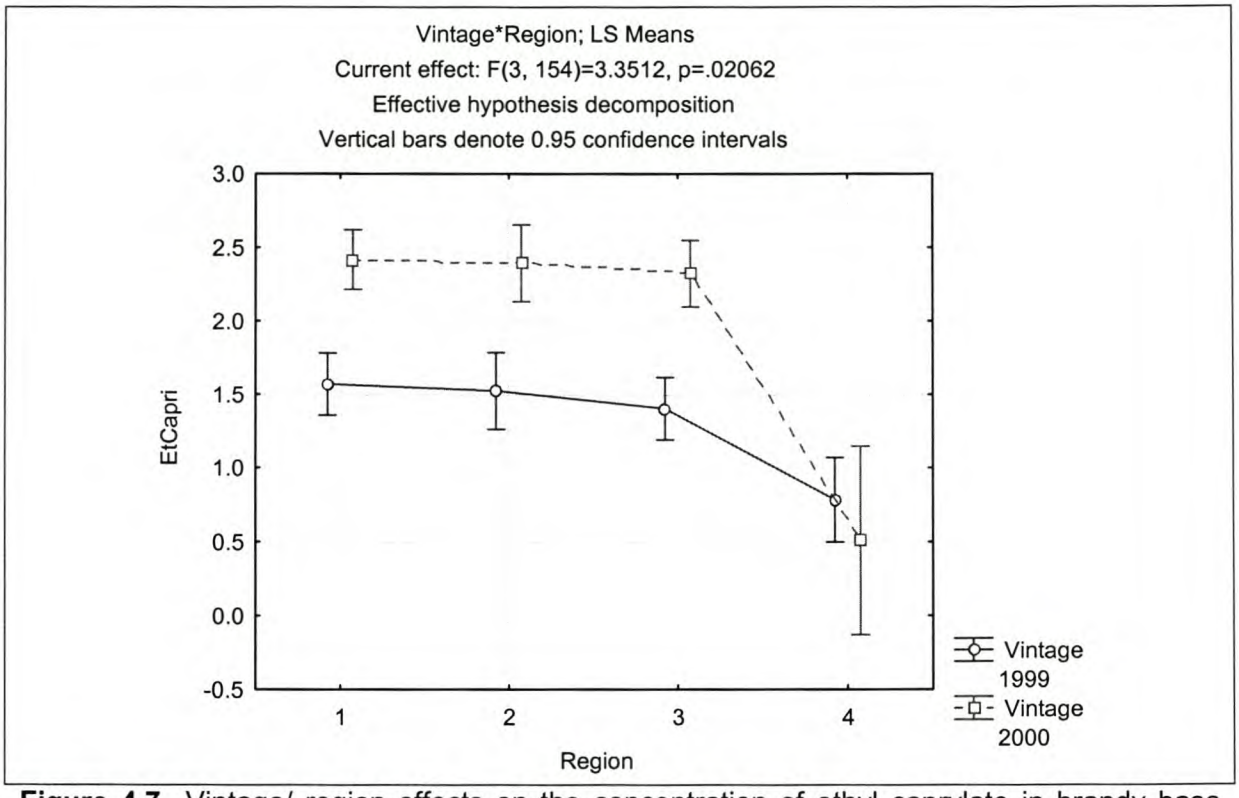

Figure 4.7 Vintage/ region effects on the concentration of ethyl caprylate in brandy base wines (mg/L).

4.3.1.9 2-Phenethyl acetate

Distillates from 1999 possessed significantly lower concentrations of 2-phenethyl acetate than those from 2000 (**Table 4.6**). The same trend was observed in the wines, although this was not found to be significant. The concentration of 2-phenethyl acetate tended to decrease in wines with progression in harvest time (**Table 4.3**). Wines fermented using yeast strains WE372, VIN13, VIN7 and NT117 possessed significantly higher concentrations of 2-phenethyl acetate than the remainder of the strains ($p<0.01$). Distillates originating from wines fermented with strains VIN13 and NT117 consistently contained higher levels of 2-phenethyl acetate, but this was also influenced by cultivar type. Where VIN13 and NT117 were used on Colombar, Chenin/Colombar and "other" cultivars, the mean concentration was 1.49 mg/L. Where VIN13 and NT117 were used on Chenin blanc and table grapes, the mean was 4.2 mg/L. The importance of yeast strain in determining the concentration of 2-phenethyl acetate in both wines and distillates is confirmed in **Table 4.1**.

4.3.1.10 Hexyl acetate

The concentration of hexyl acetate is significantly influenced by vintage and harvest time, decreasing significantly with harvest time (**Table 4.3, 4.4, 4.5** and **4.6**). Both wines and distillates made from table grapes and "other" varieties possessed significantly lower concentrations of hexyl acetate than wines made from Chenin blanc, Colombar and a Chenin/Colombar mix ($p<0.01$) (**Figure 4.8**). Wines fermented with WE372 and NT117 possessed significantly higher concentrations of hexyl acetate when compared to the remainder of the strains ($p<0.01$). Wines and

distillates originating from region 1 possessed significantly higher concentrations of hexyl acetate when compared to the remaining regions ($p<0.01$, **Figure 4.9**).

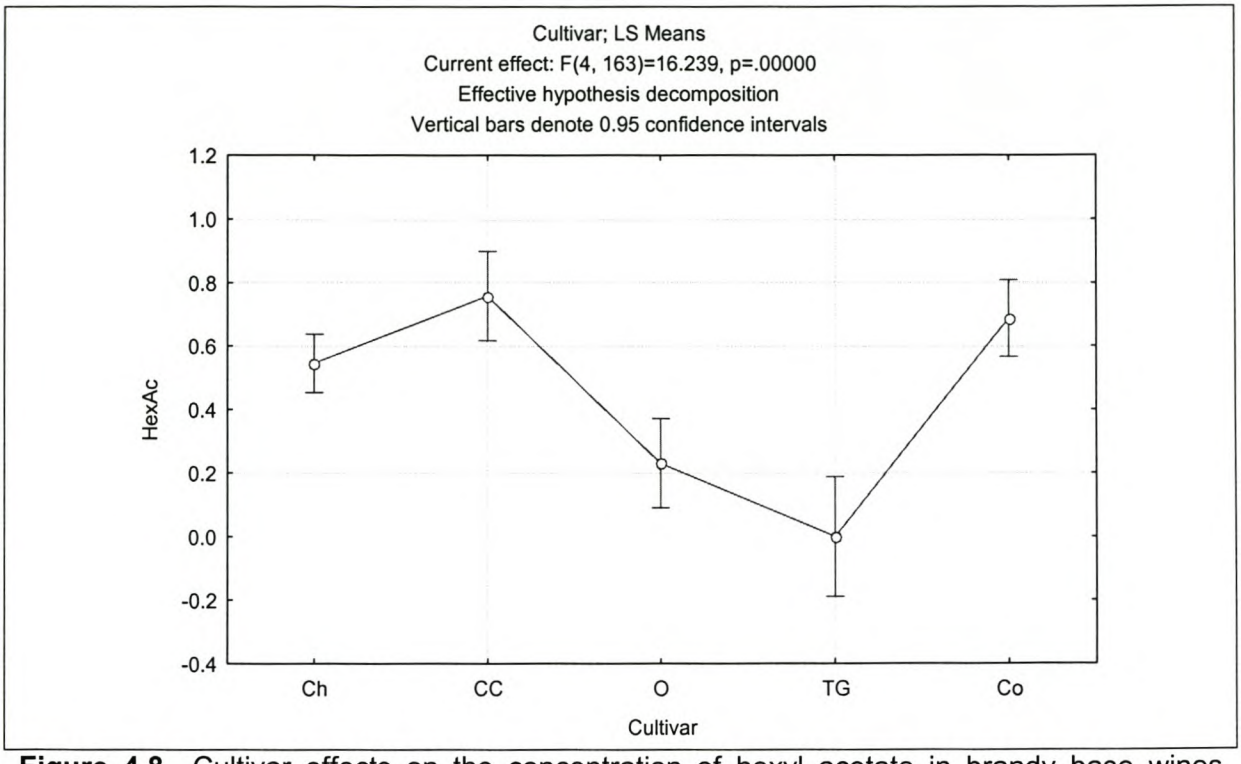

Figure 4.8 Cultivar effects on the concentration of hexyl acetate in brandy base wines (mg/L)(Ch = Chenin blanc; CC = Chenin blanc/ Colombar; O = other varieties; TG = table grapes; Co = Colombar).

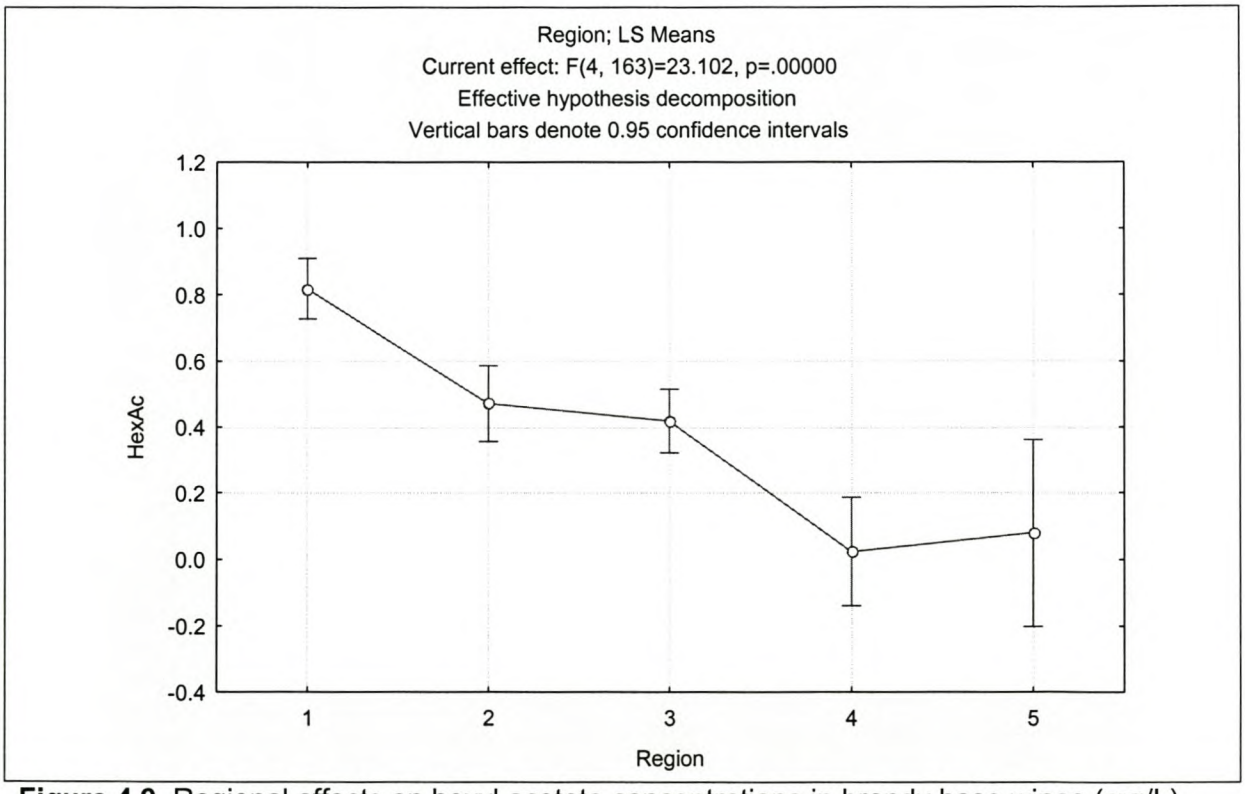

Figure 4.9 Regional effects on hexyl acetate concentrations in brandy base wines (mg/L).

4.3.1.11 Diethyl succinate

This compound was only quantified in the distillates. Distillates originating from wines made using table grapes and "other" varieties produced significantly higher concentrations of diethyl succinate than distillates made from Chenin blanc, Colombar and Chenin/Colombar ($p<0.01$). In distillates originating from Chenin blanc, Colombar and Chenin/Colombar, CART was further able to distinguish two distinct groups on the basis of yeast strain used. The first comprised distillates originating from base wine fermentation with ICVD254, 20-2 and NT117 and had a mean concentration of 1.11 mg/L. The second group had lower mean than the former and comprised those whose wines were originally fermented with WE372, WE228, VIN13, VIN7, FAIEDV and OY strains at a mean concentration of 0.63 mg/L (data not shown). The time of harvest also has an effect on the concentration of diethyl succinate, increasing with progression in harvest time (**Table 4.4**). The same trend was observed in ethyl lactate concentrations. Von Adam *et al.* (1996) noted that, where ethyl lactate concentrations are high, elevated levels of diethyl succinate can also be expected.

4.3.1.12 Acetic acid

Wines made from table grapes in region 4 possessed the highest mean concentration of acetic acid in both wines and distillates when compared to the other regions. Houtman *et al.*, (1980) and Delfini and Cervetti (1991) noted that the production of large amounts of acetic acid by yeasts during alcoholic fermentation occurred particularly in free run grape musts that were immediately separated from skins. Both authors hypothesised that there are unidentified nutrient factors concentrated in the clarified must that stimulate yeast cells to restrict and/or to avoid the release of acetic acid into the medium, and thus the concentration of these nutrient factors might vary from cultivar to cultivar. The concentration of acetic acid increased in both wines and distillates with progression in harvest time. Although the increase between early and mid harvest is not significantly different, the increase from early and mid harvest to late harvest is very significant (**Table 4.3** and **4.4**). As with lactic acid, acetic acid is produced in small quantities by yeasts through the oxidation of acetaldehyde (Boulton *et al.*, 1995). Although acetaldehyde concentrations were not determined in the base wines, from **Table 4.4** it can be seen that the acetaldehyde concentrations in the distillates also increased significantly when originating from wines made with grapes from early and mid to late harvest. The CART analysis found that yeast strain used in fermentation of the base wine is the most important factor in determining the concentration of acetic acid present in these distillates (**Table 4.10**). Acetic acid production levels were shown by Ravaglia and Delfini (1993) to be different for various strains of *S. cerevisiae.* Du Plessis *et al.* (2002) showed that acetic acid concentrations increase in wine and distillate samples that have undergone malolactic fermentation. Thus, the greater predisposition to malolactic fermentation late in the season could also account for the increased acetic

acid concentrations in wines and distillates made from grapes harvested late in the season.

Table 4.10 CART classification rules for acetic acid in distillates

Rule	Mean (mg/L)
If Cultivar = Chenin blanc, Colombar, Chenin/ Colombar and Yeast = WE372, WE228, VIN13, VIN7	24.77
If Cultivar = T/ grapes, Other and Yeast = WE372, WE228, VIN13, VIN7	38.27
If Yeast = ICVD254, NT117	49.51
If Yeast = FAIEDV, 20-2, Other	101.41

4.3.1.13 isoButyric Acid

Isobutyric acid concentrations were significantly higher in wines made in 1999 than in 2000. However, this trend was reversed in the distillates (**Table 4.5** and **4.6**). As isobutyric acid is a compound with relatively high molecular weight, it can be speculated that a significant portion of isobutyric acid is distilled over into the tails fraction, rather than the heart fraction. In both wines and distillates, those made from a mix of Chenin/Colombar grapes possessed significantly higher concentrations of isobutyric acid than those wines and distillates originating from Chenin blanc and Colombar grapes (**Figure 4.10**).

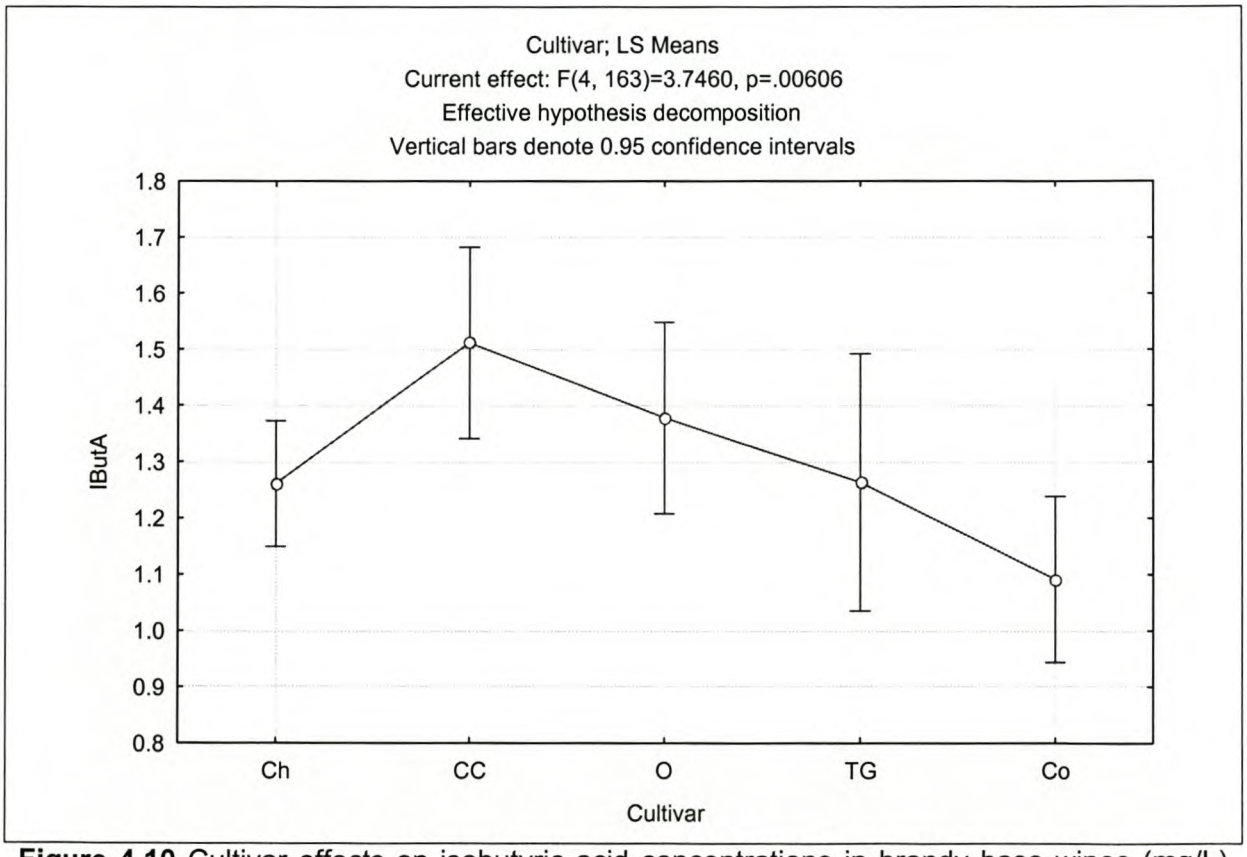

Figure 4.10 Cultivar effects on isobutyric acid concentrations in brandy base wines (mg/L) (Ch = Chenin blanc; CC = Chenin blanc/ Colombar; O = other varieties; TG = table grapes; Co = Colombar).

4.3.1.14 Hexanoic acid

The concentration of hexanoic acid was significantly lower in wines from 1999 than those from 2000. On the other hand, the concentration of hexanoic acid was significantly higher in 1999 distillates than those from 2000 (**Table 4.5** and **4.6**). The CART analysis found that the discrepancy arises in mid and late season values and not from the early harvest values (**Table 4.11**). Both the wines and distillates showed a decrease in the concentration of hexanoic acid with progression in harvest time (**Table 4.3** and **4.4**). Wines made using table grapes and "other" grape varieties possessed the lowest concentrations of hexanoic acid ($p<0.001$), whereas wines made from Colombar grapes possessed higher concentrations of hexanoic acid than those from table grapes and "other" varieties, but were still significantly lower than those wines made from Chenin blanc and Chenin/Colombar grapes (**Figure 4.11**). Although not as statistically significant as the wine data, this trend was the same for the distillate data. The two way ANOVA showed that the concentration of hexanoic acid was significantly lower in wines made from Colombar in region 1 when compared to regions 2 and 3 (**Figure 4.12**).

Table 4.11 CART classification rules for hexanoic acid in wines and distillates

Wine Rules	**Mean (mg/L)**
If Region = 4, 5	0.038
If Yeast = WE372, WE228, FAIEDV, OY, NT117 and Region = 2, 3	0.3
If Yeast = VIN13, VIN7, ICVD254, 20-2 and Region = 2, 3	0.64
If Yeast = WE228, VIN7, ICVD254, OY, 20-2 and Region = 1	0.62
If Yeast = WE372, VIN13, FAIEDV, NT117	1.04
Distillate Rules	**Mean (mg/L)**
If Vintage = 2000 and Harvest = mid season, late	1.6
If Yeast = WE372, VIN13, FAIEDV, 20-2, NT117 and Vintage = 1999 and Harvest = mid season, late	1.77
If Cultivar = Chenin blanc, T/ grapes, Other and Yeast = WE228, VIN7, ICVD254, Other and Vintage = 1999	3.57
If Cultivar = Chenin/ Colombar, Colombar and Yeast = WE228, VIN7, ICVD254, OY and Vintage = 1999 and Harvest = mid season, late	5.54
If Harvest = early	4.38

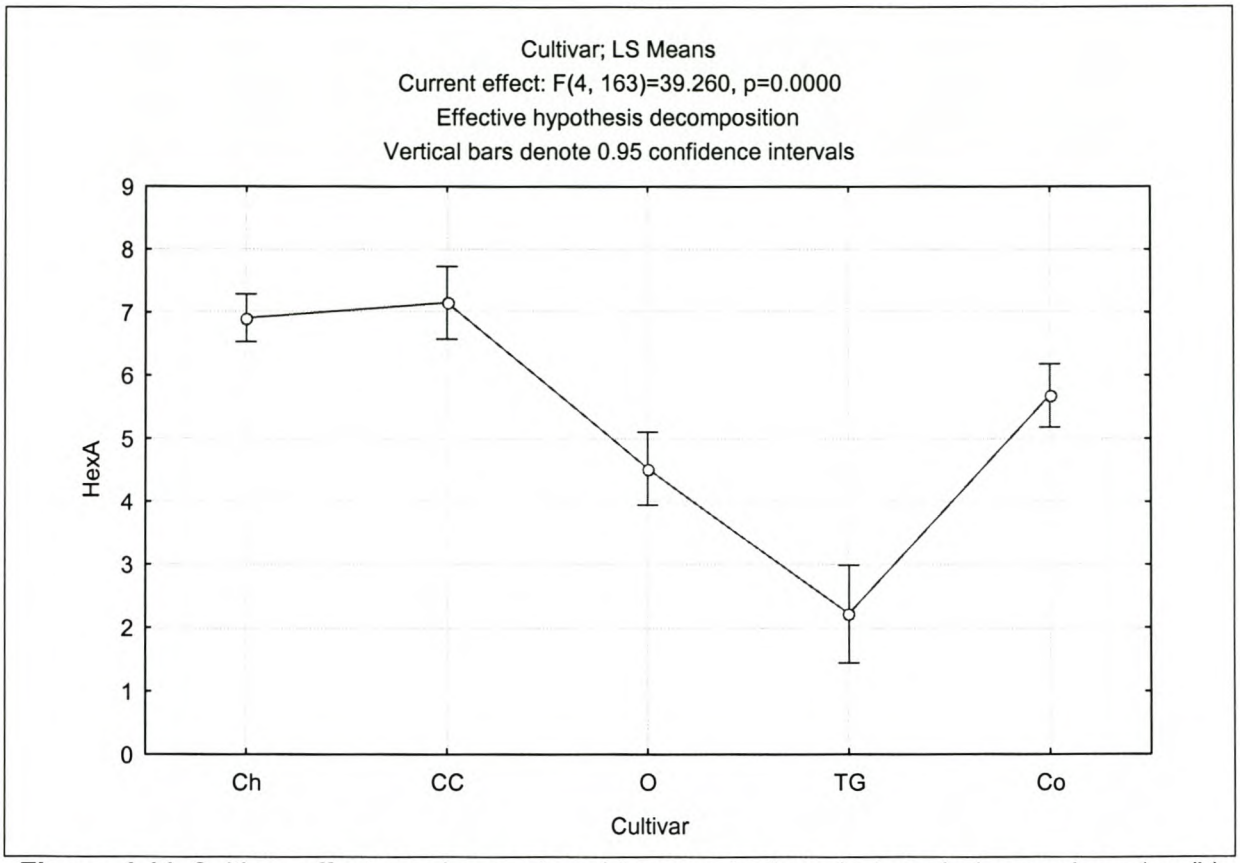

Figure 4.11 Cultivar effects on hexanoic acid concentrations in brandy base wines (mg/L) (Ch = Chenin blanc; CC = Chenin blanc/Colombar; O = other varieties; TG = table grapes; Co = Colombar).

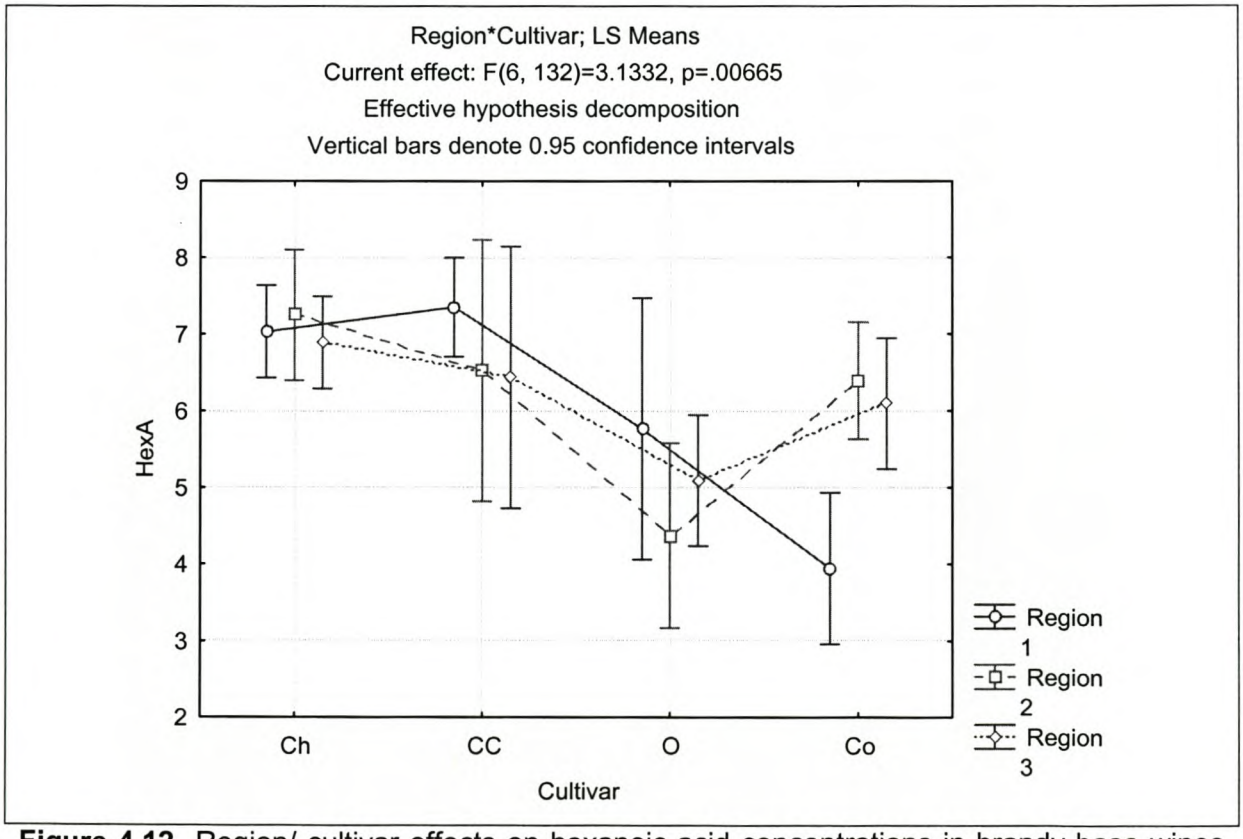

Figure 4.12 Region/ cultivar effects on hexanoic acid concentrations in brandy base wines (mg/L) (Ch = Chenin blanc; CC = Chenin blanc/Colombar; O =other varieties; Co = Colombar).

4.3.1.15 Octanoic Acid

The concentration of octanoic acid decreased significantly with progression in harvest time. For wines, there was a significant difference between those made from grapes harvested early and in mid-season than those harvested late in the season (**Table 4.3**). The same trend was observed in the distillates, however there was only a significant difference between those distillates originating from wines made with early and late harvested grapes (**Table 4.4**). Wines made from Chenin blanc and Chenin/Colombar grapes possessed the highest concentrations of octanoic acid, followed by those made from Colombar, table grapes and "other" varieties. (**Figure 4.13**). Although the differences were not as significant as in the wines, the same trend was observed in the distillates. Wines and distillates originating from regions 1, 2, and 3 possessed significantly higher concentrations of octanoic acid than those from regions 4 and 5 ($p<0.001$).

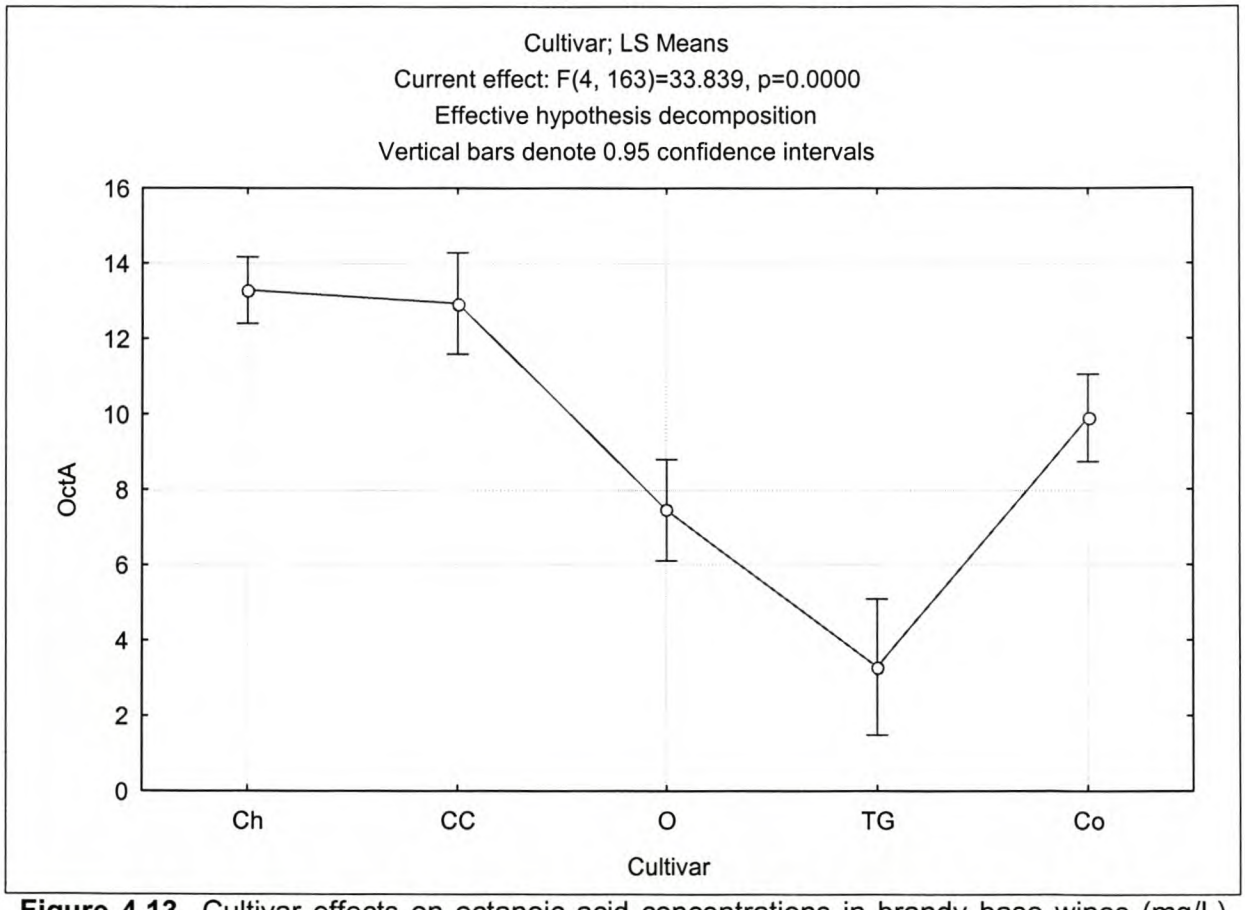

Figure 4.13 Cultivar effects on octanoic acid concentrations in brandy base wines (mg/L) (Ch = Chenin blanc; CC = Chenin blanc/ Colombar; O = other varieties; TG = table grapes; Co = Colombar).

4.3.1.16 Decanoic acid

In wines, decanoic acid showed a 68.75% increase in concentration from 1999 to 2000, whereas octanoic acid showed a 46.89% increase in mean concentration from 1999 to 2000. However, in the distillates, the mean average concentration of

decanoic acid only increased by 13.79% from 1999 to 2000 whilst the mean octanoic acid concentration increased by 99.35% (**Tables 45** and **4.6**). As decanoic acid has a high boiling point, it is likely that the concentration of decanoic acid present in the distillates is influenced by distillation and that not all of the decanoic acid is distilled over into the heart fraction. In both wines and distillates, those made using table grapes originating from region 4 possessed the lowest concentrations of decanoic acid when compared to the other four regions ($p=0.002$). The concentration of volatile compounds present in the distillates is influenced by the yeast lees present as well as the relative volatility and concentration of these compounds in the wine during distillation. Relative volatility and concentration will especially influence those compounds that can distill over into the heads and heart (low boiling point compounds) as well as the heart and tails fraction (higher boiling point compounds), whereas yeast lees can have a significant effect on the concentration of esters. Although the yeast lees content present during distillation is maintained at approximately 3%, it was not possible to control this percentage to an exact figure, due to the commercial scale of the distillations as well as the equipment used for storage and distillation of these products. The potstills used for this study are connected to a SCADA system that offers the continuous viewing of both the vapour and liquid temperature in the potstills during distillation for enhanced control. However, the steam feed, which will determine these temperatures, was manual and thus slight differences in distillation temperature profiles of the 58 distillations in total may have arisen. As far as possible, the operators attempted to keep the temperature profiles the same and these graphic profiles were checked for major differences, which were not found to exist.

Wines and distillates made using Chenin blanc grapes possessed the highest mean concentration of decanoic acid. As was the case with hexanoic acid, the two way ANOVA showed that the concentration of decanoic acid was significantly lower in wines made from Colombar in region 1 when compared to regions 2 and 3. Wines and distillates originating from late harvested grapes also showed significantly lower concentrations of decanoic acid than those made from early and mid season harvested grapes (**Tables 4.3** and **4.4**). Wines and distillates originating from fermentation using yeast strain WE372 possessed the highest concentrations of decanoic acid in both cases (**Figure 4.14**).

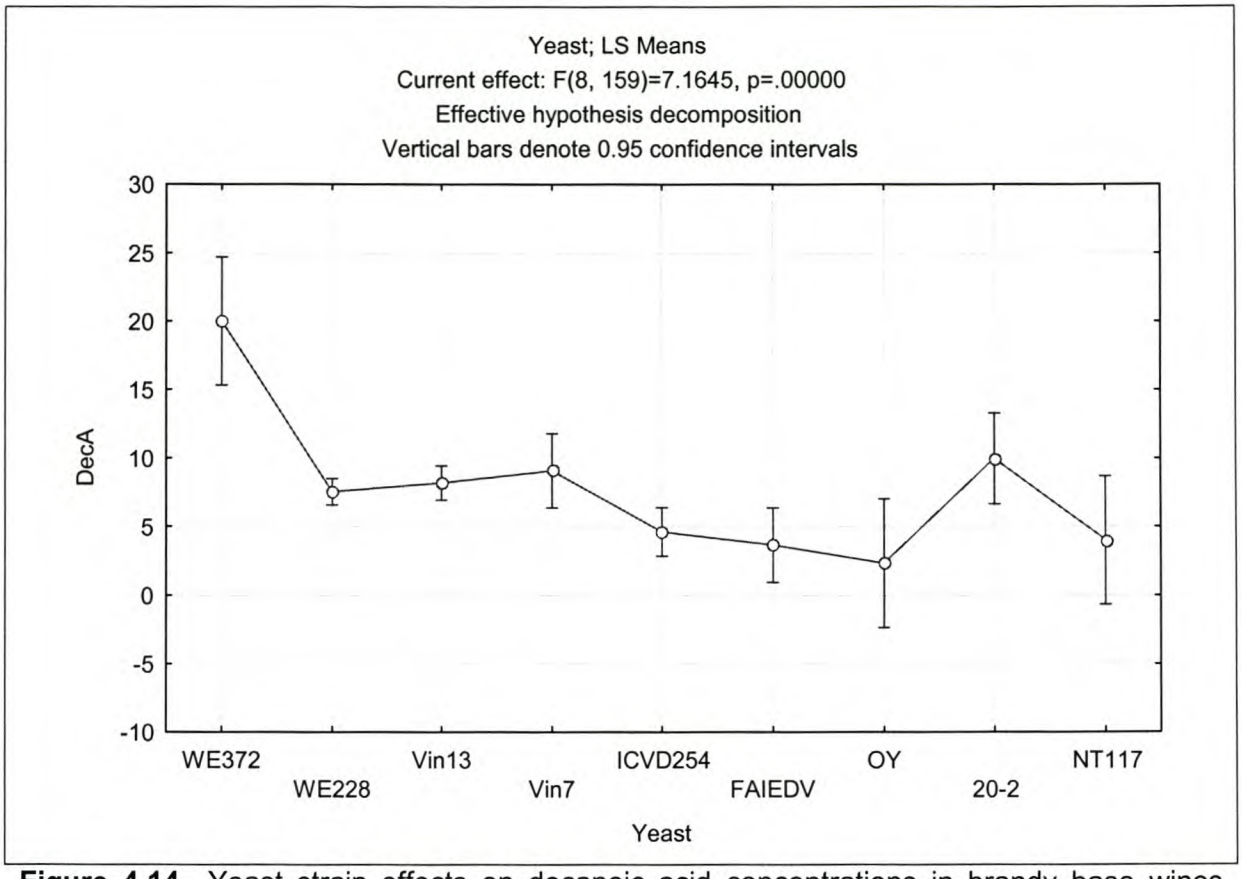

Figure 4.14 Yeast strain effects on decanoic acid concentrations in brandy base wines (mg/L).

4.3.1.17 Propionic acid

This compound was only quantified in the wines. The concentration of propionic acid was significantly higher in wines made in 1999 than in those from 2000 (**Table 4.5**). Sponholz *et al.* (1990) speculated that propionic acid is partially derived from lactic acid bacteria that may be present in the base wine. In this study, the mean concentration of ethyl lactate was higher in both wines and distillates in 1999, which is in agreement with Sponholz's (1990) findings. However, no significant harvest time differences were noted (**Table 4.3**) in wines even though the concentration of ethyl lactate was significantly higher in wines made from late harvested grapes, which was not observed in Sponholz's study (1990).

4.3.1.18 isoButanol

The concentration of isobutanol was significantly higher in 1999 wines and distillates than in those from 2000 (**Tables 4.5** and **4.6**). The concentration of isobutanol also increased significantly in both wines and distillates as the harvest time of the grapes used progressed (**Tables 4.3** and **4.4**). The amino acids in a medium are among the most important factors that influence fusel alcohol formation. They are able to alter the yield of fusel alcohols in several different ways (Schulthess and Ettlinger, 1978). Firstly amino acids contribute to the total nitrogen content of the medium and the amount of fusel alcohols formed by the anabolic pathway (from carbohydrates) depends to a great extent on the nitrogen level. Secondly, amino acids can influence

the anabolic formation of their corresponding higher alcohols by inhibiting the biosynthetic enzymes. This has been shown for the formation of iso-butyl, active amyl and isoamyl alcohol on the biosynthetic pathway of valine, isoleucine and leucine (Boulton *et al.*,1995). Thirdly, amino acids can also be converted directly into higher alcohols. This catabolic pathway is known as the Ehrlich mechanism. Giudici *et al.* (1993) observed that the differences in the amount of higher alcohols in various wines, irrespective of the yeast strain used to ferment the original juice, could be due in general to the must composition or, in particular, to the differences in amino acid content of the juices. Giudici *et al.* (1993) found that despite the fact that low amounts of amino acids were present with respect to the quantity of corresponding higher alcohols formed (via the Ehrlich reaction), amino acids could indeed play a role in controlling the pathways of their own formation and could therefore influence the anabolic formation of the higher alcohols. This was shown to be the case for isobutanol, active amyl and isoamyl alcohol by Schulthess and Ettlinger (1978). Abundance of assimilable nitrogen has a tendency to suppress the formation of higher alcohols, although in complex media there is no simple relationship between the nitrogenous nutrient level and the total yield of higher alcohols (Suomalainen and Nykänen, 1972). In this study, one could deduce that harvest time and region have the largest impact on must amino acid composition. Wines and distillates made from Chenin blanc, Colombar and Chenin/Colombar possessed significantly lower concentrations of isobutanol than those made from table grapes and “other” varieties ($p < 0.001$ for wines and distillates). Riponi *et al.* (1996) found that isobutanol is a highly variable alcohol, and almost every strain tested in his study showed a statistically different amount of this compound. In this study, wines fermented using yeast strains FAIEDV and NT117 had significantly different concentrations of isobutanol (**Figure 4.15**).

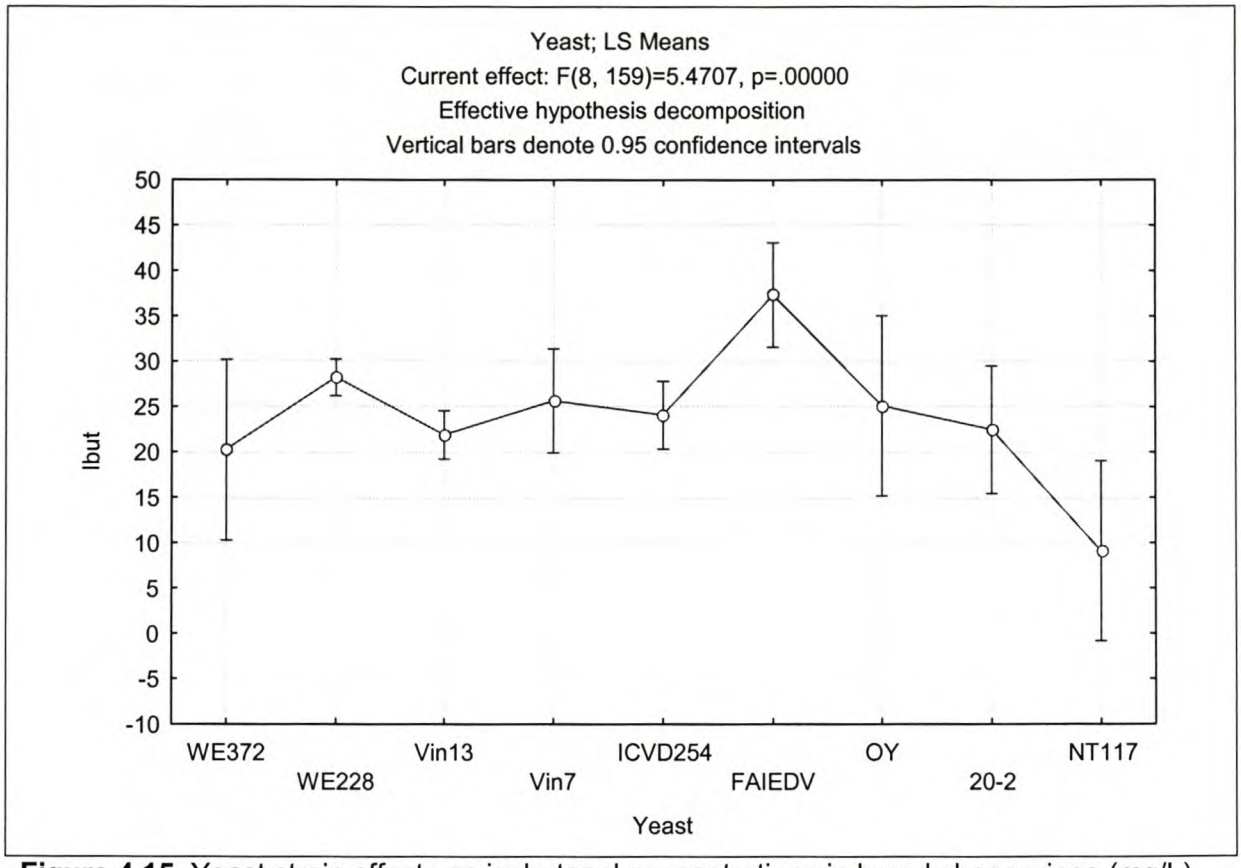

Figure 4.15 Yeast strain effects on isobutanol concentrations in brandy base wines (mg/L).

4.3.1.19 isoAmyl alcohol

The concentration of isoamyl alcohol was significantly higher in 1999 wines than in 2000 wines, although the opposite was observed in the distillates (**Tables 4.5** and **4.6**). Although no significant difference in concentration was noted for progression in harvest time in the wines, there was a significant increase in isoamyl alcohol concentration between those distillates originating from wines made from early and mid-season grapes and those originating from grapes harvested late in the season (**Table 4.4**). As is apparent from **Figure 4.16**, the yeast strain effect on wines could be clustered into two distinct groups. The first group possessed a higher mean concentration of 150 - 160 mg/L and comprised strains WE372, WE228, VIN13 and VIN7. The second group had a lower mean concentration of 110 - 120 mg/L and comprised the remaining strains (ICVD254, FAIEDV, OY, 20-2 and NT117). This confirms the variable importance of yeast strain also identified in the CART analysis for wines and distillates (**Table 4.2**). Distillates originating from region 4 were found to have the highest mean concentration of isoamyl alcohol when compared to the remaining regions.

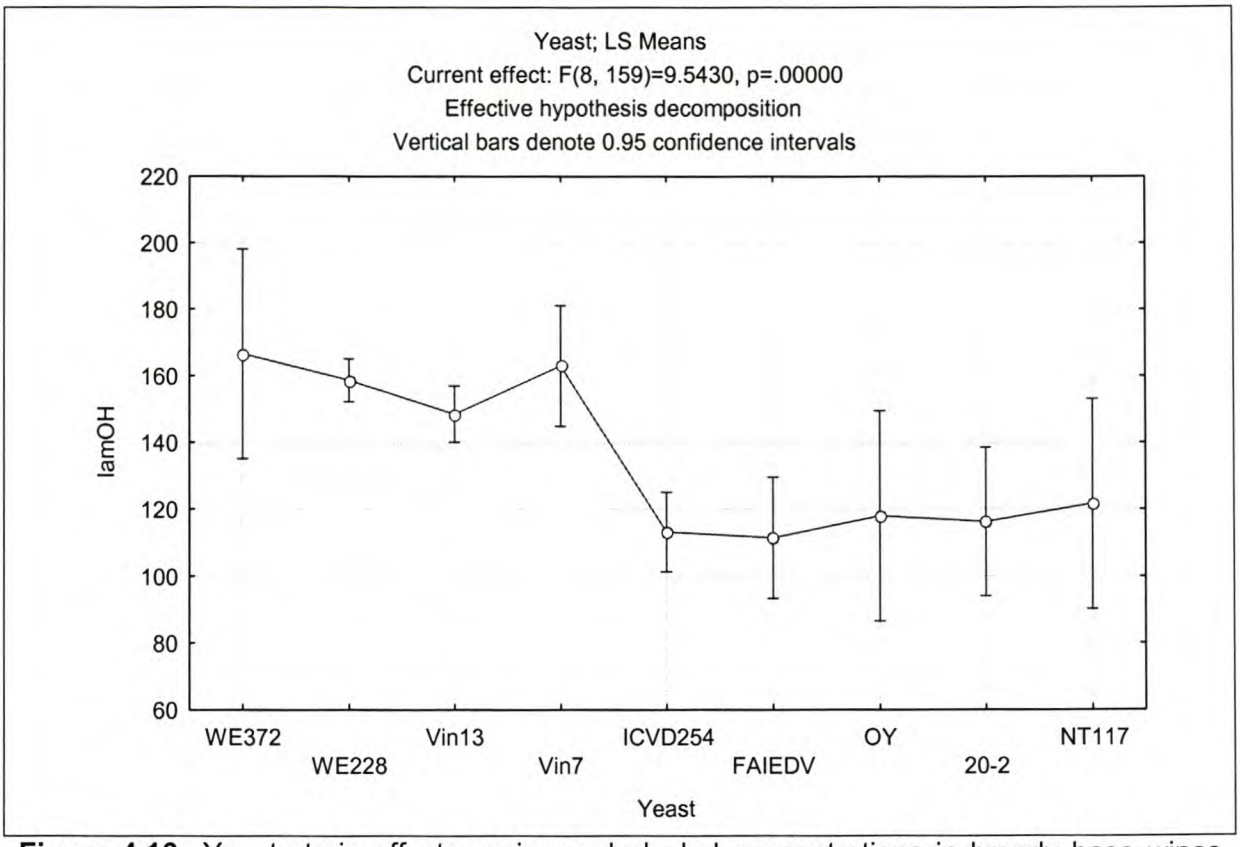

Figure 4.16 Yeast strain effects on isoamyl alcohol concentrations in brandy base wines (mg/L).

4.3.1.20 n-Propanol

Wines and distillates originating from region 5 possessed significantly higher concentrations of n-propanol [$p_{(wines)}$= 0.02 (**Figure 4.17**), $p_{(distillates)}$< 0.001]. Wines and distillates made with yeast strain 20-2 possessed the highest mean concentration of n-propanol while those fermented with strain NT117 possessed the lowest concentration of n-propanol in wines and distillates and were significantly different ($p<0.001$). Riponi *et al.* (1996) showed that high SO_2 producing strains can produce high concentrations of n-propanol, and that the concentration of n-propanol in wines can be highly variable due to the fact that yeast strains can influence n-propanol production. The significance of yeast strain as a discriminating factor for n-propanol concentrations in both wines and distillates was also confirmed by the CART analysis in **Table 4.2**. The concentration of n-propanol was significantly higher in wines made from early harvested grapes than wines made from mid and late season grapes. This was however not the case for the distillates, where the n-propanol concentration was lowest in mid season harvested distillates than those from early and late harvest (**Tables 4.3** and **4.4**). From the CART analysis it was found that distillates distilled in 2000 and originating from regions 1, 3, 4 and 5, fermented originally with WE228, VIN13 and 20-2, had a mean concentration of 429 mg/L. The distillates from 1999 originating from the same regions and using the same yeast strains, had a mean concentration of 552.245 mg/L, which supports the tendency seen in the ANOVA that the n-propanol concentration tended to be higher in the 1999 distillates than in those from 2000.

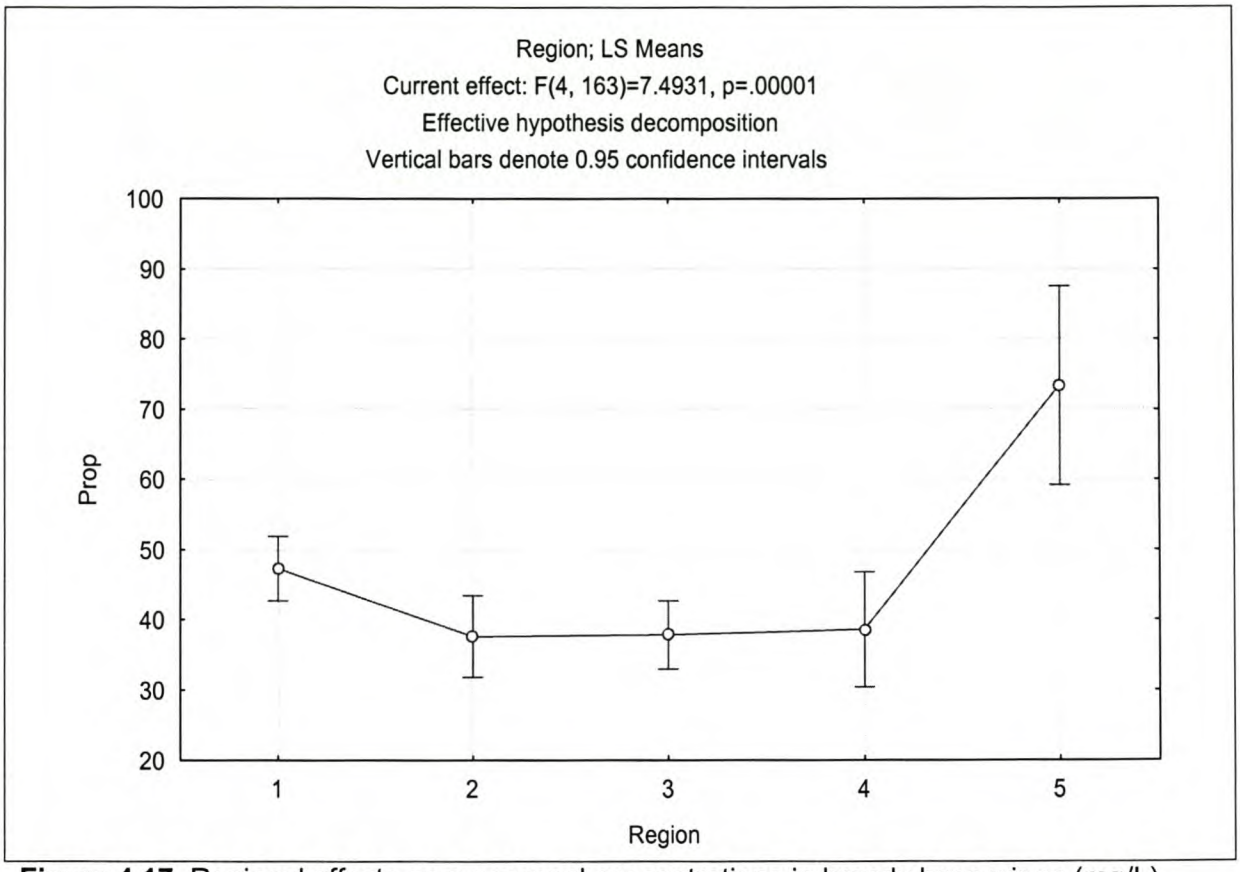

Figure 4.17 Regional effects on n-propanol concentrations in brandy base wines (mg/L).

4.3.1.21 n-Butanol

The concentration of n-butanol in wines and distillates originating from early harvested grapes was significantly higher than those originating from mid and late harvested grapes (**Tables 4.3** and **4.4**). Table grapes had the lowest mean n-butanol concentration in both wines and distillates whilst wines and distillates made with Chenin blanc and Chenin/ Colombar had the highest mean concentration of n-butanol. Large variations (as much as two-fold) in higher alcohol formation have been noted between grape varieties handled under parallel conditions. This can be attributed to the amino acid composition of the grape in question (Boulton *et al.,* 1995). Maturity of fruit, region and soil type may also play an interrelated role, although their exact influence has, to date, been difficult to determine (Boulton *et al.*, 1995). Wines and distillates originally fermented with strains NT117 and OY had the highest mean n-butanol concentration, whilst those made with FAIEDV had the lowest concentration of this compound (**Figure 4.18**). From the CART analysis it was found that wines and distillates fermented with VIN13 had significantly higher concentrations of n-butanol when originating from region 1 than when coming from region 2 (data not shown). This difference was not apparent in any of the other strains.

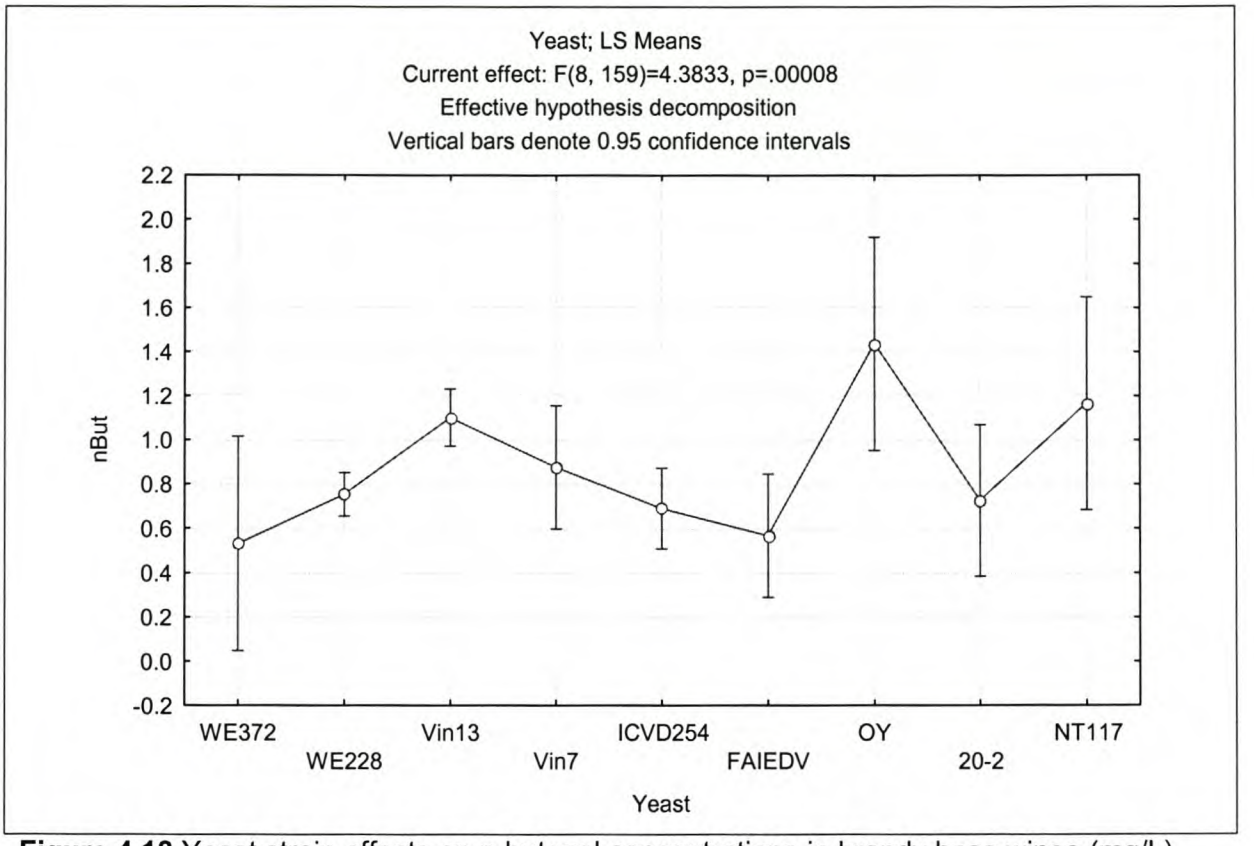

Figure 4.18 Yeast strain effects on n-butanol concentrations in brandy base wines (mg/L).

4.3.2.22 n-Hexanol

Both vintage and time of harvest were shown to have a significant effect on n-hexanol concentrations in base wines and distillates (**Tables 4.3, 4.4, 4.5** and **4.6**). Wines and distillates originating from table grapes were found to have the highest mean concentration of n-hexanol and this was significantly higher than those originating from the remaining cultivars ($p<0.001$), whilst wines made from Chenin blanc and Colombar had the lowest mean concentration of n-hexanol in both wines and distillates. From a regional perspective, wines originating from region 2 possessed the lowest concentrations of n-hexanol ($p<0.001$) and this also followed through to the distillates. Falque and Fernandez (1996) found that n-hexanol and its acetate are very origin specific in concentration. Its concentration can also be related to skin contact time, and has been found to increase in concentration with increases in skin contact time. All of the wines used in this study, received less than 5 hours of skin contact time. Thus region of origin plays a greater role in n-hexanol concentration in this study and this was verified in the CART and ANOVA analyses (data not shown). n-Hexanol has a herbaceous aroma.

4.3.1.23 2-Phenyl ethanol

2-Phenyl ethanol has a floral, rose-like aroma and is present in grape berries, where it exists in a free and bound form. Falque and Fernandez (1996) found that the concentration of 2-phenyl ethanol is also related to skin contact time. In this study all wines received less than 5 hours of skin contact time. This could explain why cultivar,

region and harvest time, which can be traced back to berry composition, have such high variable importance scores in the CART analysis (refer to **Table 4.2**). As is the case for n-hexanol, the concentration of 2-phenyl ethanol was significantly higher in wines and distillates originating from late harvested grapes than from mid to early harvested grapes (**Tables 4.3** and **4.4**). Wines and distillates originating from table grapes exhibited significantly higher concentrations of 2-phenyl ethanol than those originating from the remaining cultivars ($p<0.001$). Both ANOVA and CART noted two distinct groupings according to region of origin. Wines and distillates originating from region 2 and 4 possessed significantly higher concentrations of 2-phenyl ethanol ($p<0.001$) than the remainder of the regions.

4.3.2 FACTOR ANALYSIS ON WINE AND DISTILLATE COMPOUNDS

Table 4.12 and **4.13** lists the factor loadings obtained from the principal component factor analysis for wines and distillates respectively. Where factor loadings are positively correlated, it implies that the concentration of compounds within a factor will increase or decrease concurrently. Where there is a negative correlation, the relationship between these compounds is an inverse one.

4.3.2.1 Wine factor loadings

Factor 1: Positively correlated ethyl caproate (C_6) ethyl caprylate (C_8), ethyl caprate (C_{10}), hexanoic (C_6), octanoic (C_8) and decanoic (C_{10}) acid. The above-mentioned ethyl esters are derived from their respective acids. These acids are esterified in the presence of ethanol, forming the respective ethyl esters (Nykänen and Suomalainen, 1983).

Factor 2: Positively correlated ethyl butyrate and negatively correlated ethyl lactate and acetic acid. Malolactic acid bacteria metabolize malic acid to lactic acid. Lactic acid then further reacts with ethanol to produce ethyl lactate. Thus, the presence of ethyl lactate is highly correlated to the presence of lactic acid bacteria in the base wine (Du Plessis *et al.*, 2002). Acetic acid is also produced in small quantities by yeasts and in more significant quantities by acetic acid bacteria. Thus, the presence of elevated concentrations of acetic acid (above 700 mg/L) and ethyl lactate (above 10 mg/L) in wine are an indication of spoilage micro-organisms having been present in the wine prior to distillation. Conversely, ethyl butyrate is an ethyl ester that yields fruity aromas. This factor analysis indicates that ethyl butyrate concentrations are very low in wines that show the presence of spoilage bacteria, and very high in wines not affected by spoilage bacteria. The ANOVA showed that the concentrations of ethyl lactate and acetic acid both increase significantly with progression in harvest time whereas the concentration of ethyl butyrate decreases significantly with progression in harvest time. This finding contradicts that of Postel and Adam (1992), unless one considers the absence of ethyl butyrate concentrations to be an indicator for spoilage.

Factor 3: The third factor is isoamyl alcohol.

Factor 4: The four factor is n-butanol, which was found to decrease in concentration with progression in grape harvest time in this study.

Table 4.12 Principal component factor analysis on all base wines

Factor	Compound	Loading
Factor 1	Ethyl caprylate	0.864
	Ethyl caprate	0.836
	Ethyl caproate	0.806
	Hexanoic acid	0.832
	Octanoic acid	0.932
	Decanoic acid	0.934
Factor 2	Acetic acid	-0.773
	Ethyl lactate	-0.741
	Ethyl butyrate	0.701
Factor 3	isoAmyl alcohol	0.838
Factor 4	n-Butanol	0.781

Table 4.13 Principal component factor analysis on all distillates

Factor	Compound	Loading
Factor 1	isoButyric acid	-0.737
	Octanoic acid	-0.75
	n-Hexanol	0.849
Factor 2	Ethyl acetate	0.752
	isoAmyl acetate	0.799
	Ethyl caprylate	0.732
	Ethyl caprate	0.801
Factor 3	isoAmyl alcohol	-0.722
	2-Phenyl ethanol	-0.692
Factor 4	Acetic acid	0.909
	Acetaldehyde	0.855

4.3.2.2 Distillate factor loadings

Factor 1: n-Hexanol showed a positive correlation, whereas isobutyric acid and octanoic acid showed a negative correlation. The ANOVA analysis showed that the concentrations of isobutyric and octanoic acid decreased significantly with progression in harvest time and were significantly higher in the 2000 distillates. On the other hand, the concentration of n-hexanol was shown to increase with progression in harvest time and was highest in the 1999 distillates.

Factor 2: Positively correlated the following esters: ethyl acetate, ethyl caprate, ethyl caprylate and isoamyl acetate. These all have low sensory thresholds and contribute

fruity and floral aromas. All of these esters were shown to decrease significantly with progression in harvest time.

Factor 3: Positively correlated isoamyl alcohol and 2-phenyl ethanol. The concentration of both of these alcohols was shown to increase significantly with progression in harvest time. These two alcohols might contribute to the so-called flavour body of distillates.

Factor 4: Acetic acid and acetaldehyde were positively correlated in this factor. These are both highly volatile compounds and should be highly correlated as the time duration allowed prior to cutting off the heads fraction will influence the concentration present in the heart fraction of the distillate. Both of these compounds were also shown to increase significantly with progression in harvest time. However, no significant vintage differences were noted for these compounds.

4.4 CONCLUSIONS

Using analysis of variance as well as classification and regression tree analysis it has been shown that vintage, region, harvest time, choice of cultivar and yeast strain can have a significant influence on the volatile compound composition of brandy base wines and their resultant distillates.

A number of volatile compounds showed significant increases or decreases in concentration from 1999 to 2000. The most significant increases from 1999 to 2000 in the brandy base wines were noted for isoamyl acetate, octanoic and decanoic acid, whereas ethyl lactate showed the most significant decrease in concentration from 1999 to 2000. Du Plessis *et al.* (2002) showed that lactic acid bacteria populations varied between the 1998, 1999 and 2000 vintages studied and consequently affected the predominance of spontaneous malolactic fermentation taking place in brandy base wines.

The concentration of ethyl lactate, acetic acid, n-hexanol, isobutanol and 2-phenyl ethanol increased significantly with progression in harvest time in the base wines. The base wine concentration of acetate esters (ethyl acetate, isoamyl acetate, 2-phenethyl acetate and hexyl acetate), ethyl caprate and –caprylate, n-propanol, n-butanol and the volatile C_6, C_8 and C_{10} acids all decreased significantly with progression in harvest time.

Wines originating from region 1 contained significantly higher concentrations of hexyl acetate when compared to wines from the other regions. More specifically, wines from region 1 fermented with yeast strain VIN13 showed significantly higher concentrations of ethyl acetate and isoamyl acetate than those fermented with WE228 and ICVD254 from the same region. Wines made from Colombar grapes in region 1 contained significantly lower concentrations of hexanoic and decanoic acid than Colombar wines originating from regions 2 and 3.

Some interesting cultivar differences were noted. Wines made from table grapes had significantly lower concentrations of ethyl butyrate, isoamyl acetate and the

highest concentrations of n-hexanol and acetic acid. Wines made from table grapes and "other" varieties had significantly lower concentrations of ethyl caprate, hexyl acetate, hexanoic and octanoic acid than those made from Chenin blanc, Colombar and a mix of Chenin/ Colombar, whilst the latter had significantly lower concentrations of isobutanol and diethyl succinate. Wines made from Chenin blanc possessed the highest concentrations of decanoic acid, whilst wines made from Chenin blanc and a mix of Chenin and Colombar had significantly higher concentrations of ethyl acetate.

No distinct groupings of yeast strains could be determined on the overall basis of volatile compounds. However, grouping of yeast strains based on similar concentrations of a particular compound was possible in some instances. Here the most notable differences were between strains NT117 and 20-2 on the basis of n-propanol concentration and strains WE372, VIN13, VIN7 and 20-2 whose wines and distillates contained significantly higher concentrations of ethyl caprate when compared to those made with the remaining strains. The CART analysis also proved to be a powerful tool in identifying groups of yeast strains within certain vintage, cultivar and region parameters.

In both vintages, distillates originating from Colombar wines had the highest concentration of acetaldehyde, which was only quantified in the distillates. In many instances, influences of harvest time, vintage and cultivar followed the same trend in both the wines and distillates. There are, however, exceptions and these discrepancies in the CART variable importance and ANOVA results between wines and distillates are not easily explained. Possible reasons for these discrepancies could be attributed to the amount of yeast lees present during distillation as well as the relative volatility of compounds studied.

Although it has been shown that vintage, region, cultivar, harvest time and yeast strain can have a significant influence on the volatile compound composition of brandy base wines and distillates, their influence of these factors on the sensory quality of the brandy base wines and unaged distillates, as well as their effect on composition and quality after wood maturation will also need to be determined.

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CHAPTER 5

RESEARCH RESULTS

The influence of demographic and production factors as well as volatile aroma compound composition on the sensory quality of brandy base wines and their unaged potstill distillates

RESEARCH RESULTS

5. THE INFLUENCE OF DEMOGRAPHIC AND PRODUCTION FACTORS AND VOLATILE AROMA COMPOUND COMPOSITION ON THE SENSORY QUALITY OF BRANDY BASE WINES AND THEIR UNAGED POTSTILL DISTILLATES

ABSTRACT

South African brandy production is a multi-step process that involves the making of a base wine, double distillation in copper potstills and maturation in oak casks for a minimum period of three years. All of these steps can impact on the flavour and character of the final product. In order to better understand the role of the first two mentioned factors on the quality of base wines and their unaged distillates, fifty eight brandy base wines and their unaged distillates were evaluated by a panel of expert brandy judges to assess the sensory quality of these products. The distillate quality assessment led to the selection of six distillates from each vintage for sensory descriptive analysis (SDA) using the South African Brandy Aroma Wheel. Analysis of variance (ANOVA), principal component analysis (PCA) and classification and regression tree analysis (CART), were used to study the effect of production factors (growing region, cultivar, harvest time, vintage and yeast strain) and volatile aroma compound composition on the sensory quality of base wines and their unaged distillates. Base wines studied exhibited the same quality trends over both vintages in terms of region, cultivar and time of harvest. There is a clear relationship between time of harvest and base wine and distillate quality. Products made from early harvested grapes were of significantly higher quality. Although wines made from Chenin blanc and a mix of Chenin and Colombar were consistently of higher quality, these differences were not as significant in the distillates. The volatile aroma compound composition was found to differ significantly between the two vintages studied, irrespective of the exclusion of those samples that had undergone partial or complete malolactic fermentation. Consequently, quality indicating compounds may vary from vintage to vintage depending on the composition of the base wines and thus also the distillates. Ethyl caprate was found to be a quality indicator in the 1999 distillates (irrespective of the influence of malolactic fermentation). Hexyl acetate was found to be a quality indicator in the 2000 distillates as well as in the 1999 distillates not affected by malolactic fermentation. Using SDA it was found that the differences in profile between the good and average distillates were small. There were, however, significant differences between the good and poor quality distillate profiles. Good quality distillates are characteristically intense in the 'fruity' aroma descriptor, whilst poor quality distillates show 'herbaceous' as the most intense aroma. Increased levels of ethyl lactate were found to exert a negative influence on distillate quality and were highest in the poor quality samples whilst the concentration of n-propanol,

isoamyl acetate and hexyl acetate were found to be highest in the good quality distillates over both vintages.

5.1 INTRODUCTION

The intensive research that has been carried out world-wide in the field of flavour and aroma, particularly wine and other alcoholic beverages, has shown that both of these can be attributed to a complex, non-linear system of interactions between many hundreds of compounds present in the beverage. Whereas flavour refers to the effects of both odour and taste, aroma is purely associated with odour and is thus brought about by the interactive effects of volatile compounds.

Extensive research has been done on investigating the substances that may contribute to the aroma of brandies. Bandion (1972), in his research on the chemical components of brandies and wines for distillation, was not able to find a correlation between brandy quality and the sole concentration of esters and other major components such as higher alcohols. He concluded that the organoleptic evaluation of brandies by a competent and qualified panel is the most accurate way to assess quality. A study by Williams (1975) concluded that none of the compounds he studied were singly responsible for a specific aroma, but taken together, are essential in forming brandy aroma. Similar results were obtained by Guymon (1974), although he indicated that some of the quantitatively major components such as the higher alcohols to some extent do affect brandy quality.

Goranov (1983) studied the influence of aroma compounds on the quality of wines and spirits. He showed that significantly higher concentrations of higher alcohols lead to an increase in “roughness” or “harshness” on the palate and makes an unbalanced wine. He emphasised that it is difficult to numerically quantify the relationships between aroma compounds that lead to a positive effect on the quality of wines as one cannot ignore the influence of other remaining key constituents in the beverage matrix, in the case of wines these would include organic acids, phenolic and nitrogen containing compounds. He found that the poorest quality wines had a significantly higher concentration of higher alcohols and a lower concentration of esters, with ethyl acetate as the quantitatively most dominant ester. The wines with the highest sensory score were characterised by a complex aroma and had significantly higher concentrations of short and medium chain fatty acid ethyl esters. The concentration of isoamyl and active amyl alcohol was of the same order of magnitude as the remaining higher alcohols and the overall ratio of esters to higher alcohols was significantly higher in this group of wines. He concluded that not only is the relative concentration between types of aroma compounds (eg. esters and higher alcohols) important, but that the relative concentration between compounds within a specific group (eg. iso-butyl and isoamyl alcohol) are also important in determining the aroma and quality of wine. Goranov (1983) showed that esters with a high sensory threshold (such as isoamyl acetate, hexyl acetate, ethyl caproate and ethyl

caprylate) exhibit a stronger influence upon the quality of wine aroma, whereas esters with a low sensory threshold (such as ethyl formiate, ethyl acetate and amyl acetate) contribute less to the overall sensory quality of the wine. In cases where there are markedly higher concentrations of these low threshold compounds present, a negative influence on wine quality was observed.

The aroma and flavour of an alcoholic beverage decisively determines the sensory quality of the product and may be influenced by factors incorporated at every step of the production process. These factors include: soil, geographical and climatic features of the origin of grapes used, viticultural practices, grape maturity and grape variety, seasonal (vintage) variation, vinification technique (including yeast strain used), storage of wine prior to distillation and the distillation technique used. All of these factors have been shown to exert a direct influence on the chemical composition of the wine and distillates (Berg, 1953; Weaver *et al.*, 1961; Lafon, 1964; Guymon, 1968; Amerine and Joslyn, 1970; Quady and Guymon, 1973; Hough, 1985; Von Adam *et al.*, 1996). However, much research still needs to be carried out on quantifying the complex aroma and flavour compound interactions and their relationships to the above-mentioned factors in wine and alcoholic beverages.

This study is part of a programme to investigate the effects of grape growing region, cultivar, harvest time, vintage and yeast strain on the composition and quality of brandy base wines and their resultant distillates in a South African context. Chapter 4 discussed the effects of the above-mentioned factors on the composition of brandy base wines and their resultant distillates. This study discusses the effects of the above-mentioned factors on the sensory quality of brandy base wines and their resultant distillates.

5.2 MATERIALS AND METHODS

5.2.1 EXPERIMENTAL OUTLAY

Refer to chapter 4 for the experimental outlay. The brandy base wines and distillates were evaluated by a panel of expert brandy judges (with many years of experience in the South African brandy industry) to assess the sensory quality of these products. This distillate quality assessment was then used to select six distillates for aroma profiling using the South African brandy aroma wheel (Jolly and Hattingh, 2001) and sensory descriptive analysis, using a panel of trained tasters at the ARC Infruitec-Nietvoorbij (The Fruit, Vine and Wine Institute of the Agricultural Research Council). All samples were evaluated blind, in a random order and the distillates were evaluated at 20% v/v through dilution with distilled water. Analysis of variance, principal component analysis and multivariate adaptive regression splines (MARS) were used, to study the relationship between sensory quality (including aroma profile) of base wines and distillates and production factors (growing region, cultivar, harvest

time, vintage and yeast strain) as well as the volatile compound composition of these base wines and distillates.

5.2.2 GAS CHROMATOGRAPHIC ANALYSIS

5.2.2.1 Base wine analysis

Refer to chapter 4.

5.2.2.2 Heart fraction analysis

Refer to chapter 4.

5.2.3 SENSORY ANALYSIS

All of the sensory evaluations were performed by two judges who both have extensive commercial experience in the evaluation of brandy base wines and unaged distillates, having worked in the South African brandy production industry for a number of years. In conventional research studies that involve the process of sensory evaluation, it is best practice to work with a larger panel of judges, in order to reduce the variation that may arise as a result of judging differences. However, this study is based on commercial practice within a large brandy producing company in South Africa. Steger and Lambrechts (2000) showed that three large brandy producing companies differed in their sensory evaluation of brandy base wines and distillates, due to the inherent brandy style differences between the three companies. It was therefore not possible to involve external judges in this evaluation as the aim of the study was to specifically focus on the style of brandies desired and produced by Distell. From a commercial perspective within Distell there are only two judges who perform these evaluations on a regular basis as part of production quality control checks. These are the two judges used for all of the sensory quality evaluations in this study.

5.2.3.1 1999 Base wines

The base wines used in 1999 were evaluated on nine separate occasions. Samples were presented blind in a random order and appeared in triplicate in each of the tasting sessions. Due to the fact that brandy base wines are legally not allowed to contain more than 20 mg/L of total SO_2, no reference sample could be kept for use in each of the sessions. A 5-point scale was used to evaluate the samples, where 0 = unacceptable, 1 = poor, 2 = average, 3 = good and 4 = outstanding.

5.2.3.2 2000 Base wines

The base wines used in 2000 were evaluated on nine separate occasions. No reference sample was available for inclusion in each of the sessions. A 10 cm line scale, where 0 was unacceptable and 10 was outstanding, was used for the

evaluation. Samples were presented blind, in a random order and appeared in triplicate in each of the tasting sessions.

5.2.3.3 1999 Unaged distillates

The 1999 unaged distillates were evaluated using a 5-point scale where 0 = unacceptable, 1 = poor, 2 = average, 3 = good, 4 = outstanding. The samples were evaluated in one session and were presented blind, in a random order. All of the samples were evaluated in triplicate.

5.2.3.4 2000 Unaged distillates

The 2000 unaged distillates were evaluated on four separate occasions. A reference sample was included in each of the four sessions. Seven distillates (1 reference, 6 distillates) were evaluated in each session. A 10 cm line scale, where 0 was unacceptable and 10 was outstanding, was used for the evaluation. Samples were presented blind, in a random order and appeared in triplicate. An ANOVA on the scores awarded to the reference sample in each of the four sessions was performed. The ANOVA showed that there was a significant difference between the score awarded in session 1 and sessions 2 to 4 ($p<0.001$). The mean score for session 1 was 6.25 and the mean score for the remaining sessions was 7.72. Adapted scores were calculated by adding 1.47 to all session 1 scores. Thus only the scores of session 1 have changed in the adapted score.

5.2.4 SENSORY DESCRIPTIVE ANALYSIS

A sensory descriptive analysis was performed on twelve distillates using six from 1999 and six from 2000. These distillates were selected based on the results of the sensory analysis for quality by the two judges. In each year two poor quality, two average and two good quality distillates were selected for the full descriptive analysis (SDA). The SDA was performed by a panel of eleven judges at the ARC Infruitec-Nietvoorbij. The analysis was performed using the South African brandy aroma wheel (Jolly and Hattingh, 2001). This brandy aroma wheel was developed using standardised descriptive aroma terminology (descriptors) for South African brandy aroma. The terminology was developed to be applicable at all stages of brandy production and, consequently, only small sections of the listed descriptors are likely to be used at any one stage. Negative descriptors are also incorporated to describe faults that may occur during the production process. The positive descriptors have been arranged in a progression from aromas that occur most frequently in young distillates ('herbaceous', 'fruity', 'smooth associated') to more mature aromas ('sweet associated', 'nutty' and 'spicy'). The fruity aromas are arguably the most important in brandy and make it uniquely different and distinguishable from other distilled products such as whisky and rum (Jolly and Hattingh, 2001). The 'muscat' and 'floral' notes are particularly prominent in brandies made from aromatic Muscat type varieties. 'Woody' and 'toasted' notes are those derived from maturation in oak wood (Jolly and

Hattingh, 2001), which do not apply to the samples profiled in this particular study. The eleven judges were trained on nosing standards for six sessions prior to evaluating the distillates. The samples were presented blind. Each judge was asked to mark the aroma intensity of the following overall descriptors: fruity, herbaceous, smooth associated, floral, sweet associated and spicy as well as negative aromas (heads, tails, musty, solvent/ chemical), using a 10 cm line scale, where 0 indicated "not detectable" and 10 indicated "very prominent". An average score was then calculated from the scores of the eleven judges and was plotted graphically.

5.2.5 STATISTICAL ANALYSIS

The analysis of variance (ANOVA) and principal component analyses (PCA) were performed using STATISTICA version 6. A significance level of 5% (0.05) was selected as a guideline for accepting or rejecting hypotheses. The CART analyses were performed using software from Salford Systems. Refer to chapter 4 for an explanation regarding the approach of these two types of analyses.

5.2.5.1 ANOVA

Four one-way ANOVA's were performed using vintage, yeast strain, harvest time, region of origin and cultivar as independent variables and the score from the sensory evaluation as dependent variable. ANOVA was done using 1999 and 2000 base wine and distillate data. Refer to chapter 4 for the independent variables used in both of the ANOVA analyses and CART analyses. Where necessary, *post hoc* tests were carried out between individual values of the above-mentioned variables using the non-parametric Bootstrap 95% confidence interval test as well as the Bonferroni test. The following abbreviations were used to denote cultivars used in this study: Ch = Chenin blanc; CC = Chenin blanc/Colombar mix; Co = Colombar; TG = table grapes; O = other varieties.

5.3 RESULTS AND DISCUSSION

5.3.1 THE INFLUENCE OF REGION, CULTIVAR, HARVEST TIME AND YEAST STRAIN ON THE SENSORY QUALITY OF BRANDY BASE WINES

The base wines were found to exhibit the same quality trends over both vintages in terms of region, cultivar and time of harvest. Base wines originating from region 4 were scored significantly lower than those from the remaining regions ($p<0.001$ in 2000 and $p<0.001$ in 1999, data not shown). Although there was no significant difference between the scores for wines from regions 1, 2 and 3, the mean score for region 1 was highest, followed by region 2 and then region 3.

No significant differences in sensory quality were noted in the 1999 base wines in terms of yeast strain used. However, in the 2000 base wines, wines fermented using strain VIN13 were scored significantly higher than those made with WE228, ICVD254

and NT117 (p=0.01) (**Figure 5.1**). Wines fermented with strain 20-2, an experimental VIN13 hybrid, had a higher mean score than those made from WE228, ICVD254 and NT117, however, the mean score of these wines was still lower than those wines fermented with VIN13 (**Figure 5.1**).

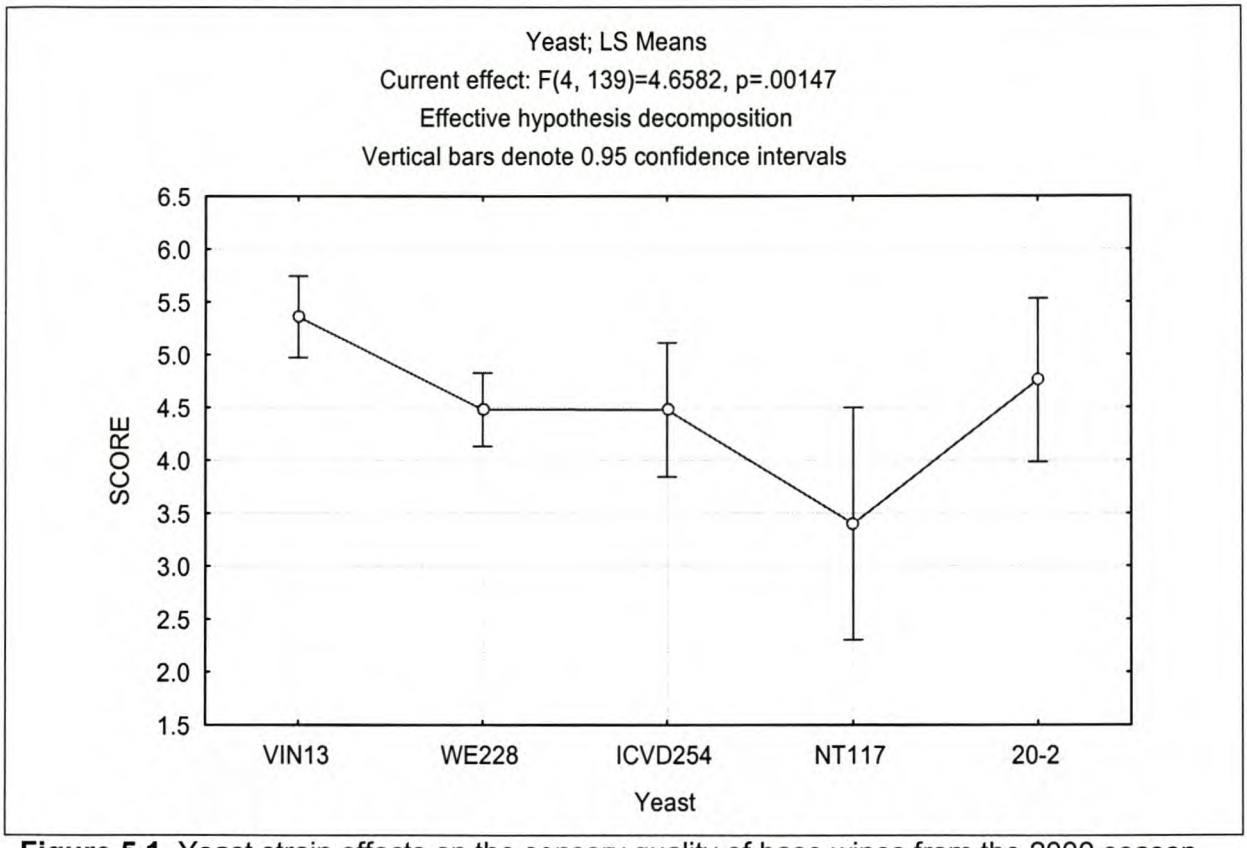


Figure 5.1 Yeast strain effects on the sensory quality of base wines from the 2000 season.

In both vintages, wines made from early harvested grapes were scored significantly higher than those made from middle and late harvested grapes. In fact the scores were significantly different between early, mid and late harvest (p<0.001) (**Figure 5.2**). This clearly illustrates that base wine quality is directly related to the time of harvest and decreases with progression in harvest time. One of the factors that could contribute to this observation is the incidence of malolactic fermentation. Only 5.3% of the wines made from early harvested grapes underwent partial malolactic fermentation, whereas 30% and 71% of the mid- and late harvested wines, respectively, underwent either a full or partial malolactic fermentation.

In both vintages, wines made from Chenin blanc and Chenin/Colombar were consistently awarded the highest scores, significantly higher than those made with Colombar, table grapes and "other" varieties. Wines made with table grapes consistently received the lowest scores (**Figure 5.3a** and **5.3b**). Chenin blanc is an early ripening cultivar, whilst Colombar ripens slightly later. There may thus be interaction taking place between cultivar and harvest time. For this reason a two way ANOVA was performed using cultivar and harvest time as independent variables and sensory score as dependent variable. It was found that in wines made from early harvested grapes, and a mix of Chenin/Colombar were scored significantly higher

than those made from Chenin blanc or Colombar (p_{1999}=0.041; p_{2000}<0.0022 in **Figure 5.4**). When looking at trends from the mid season wines, it was found that the 2000 wines showed no significant differences between Chenin blanc, Chenin/Colombar and Colombar. However, in the 1999 wines, wines made from Chenin/Colombar were scored significantly higher than those made only from Colombar (p=0.021 in **Figure 5.5**).

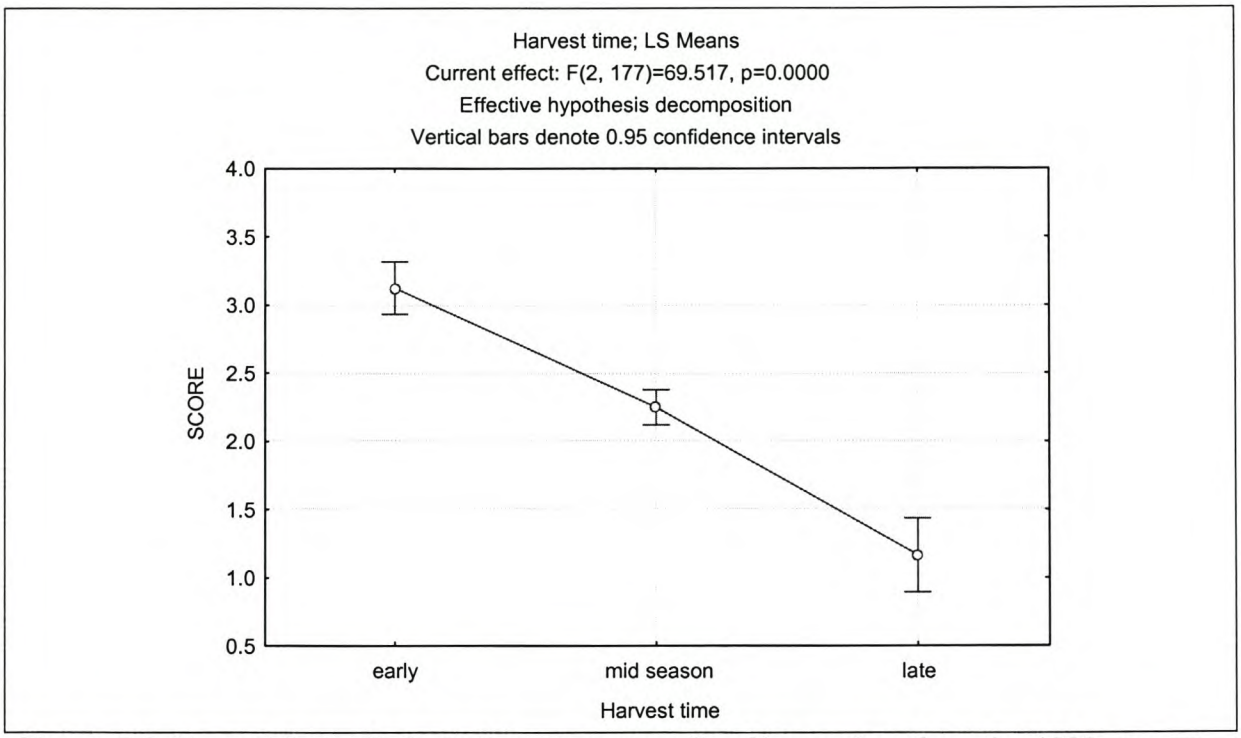


Figure 5.2 Harvest time effects on the sensory quality of base wines from the 1999 season.

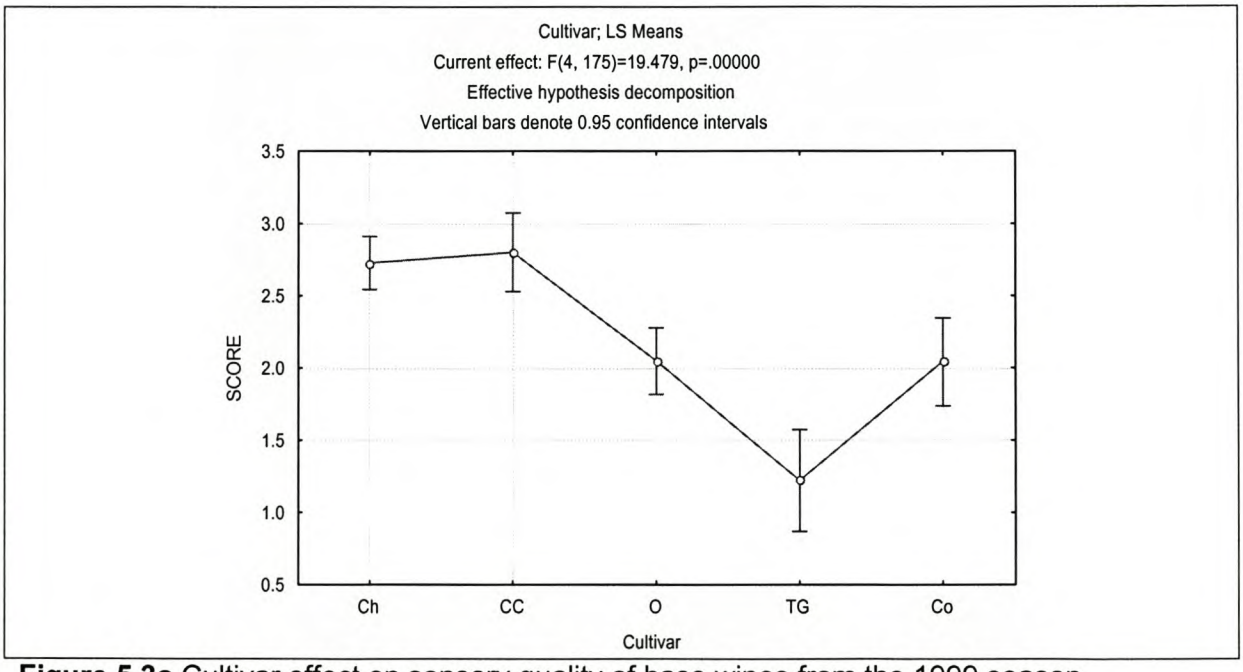


Figure 5.3a Cultivar effect on sensory quality of base wines from the 1999 season.

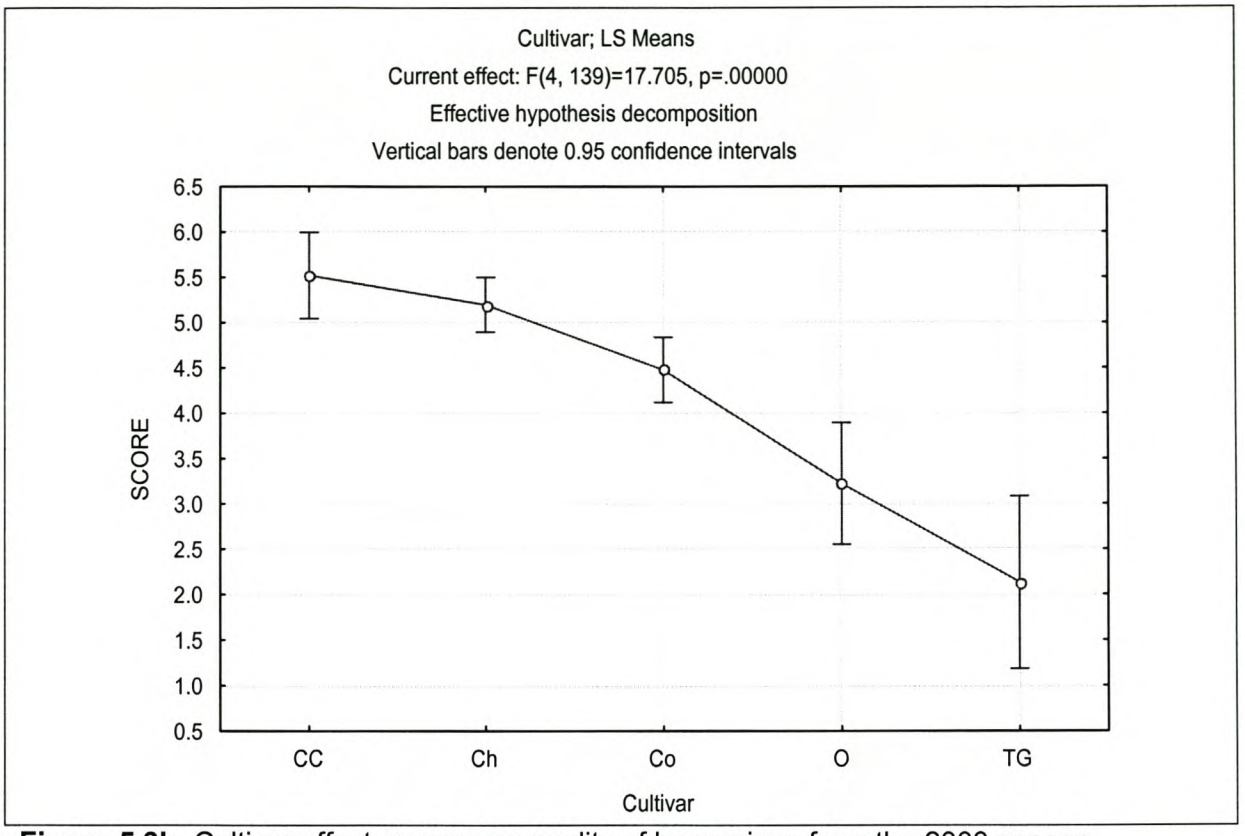


Figure 5.3b Cultivar effect on sensory quality of base wines from the 2000 season.

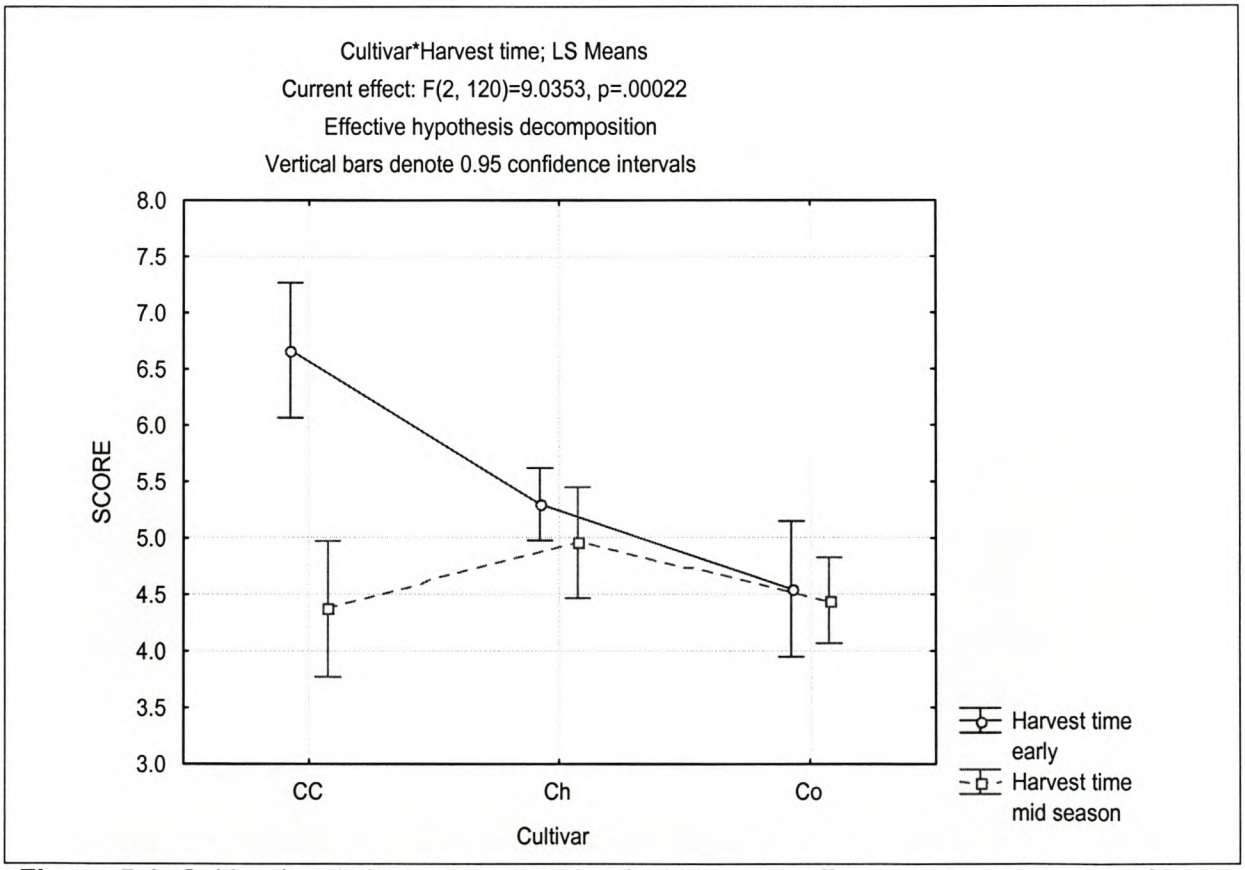


Figure 5.4 Cultivar/ early harvest and cultivar/ mid harvest effect on sensory quality of base wines from the 2000 season.

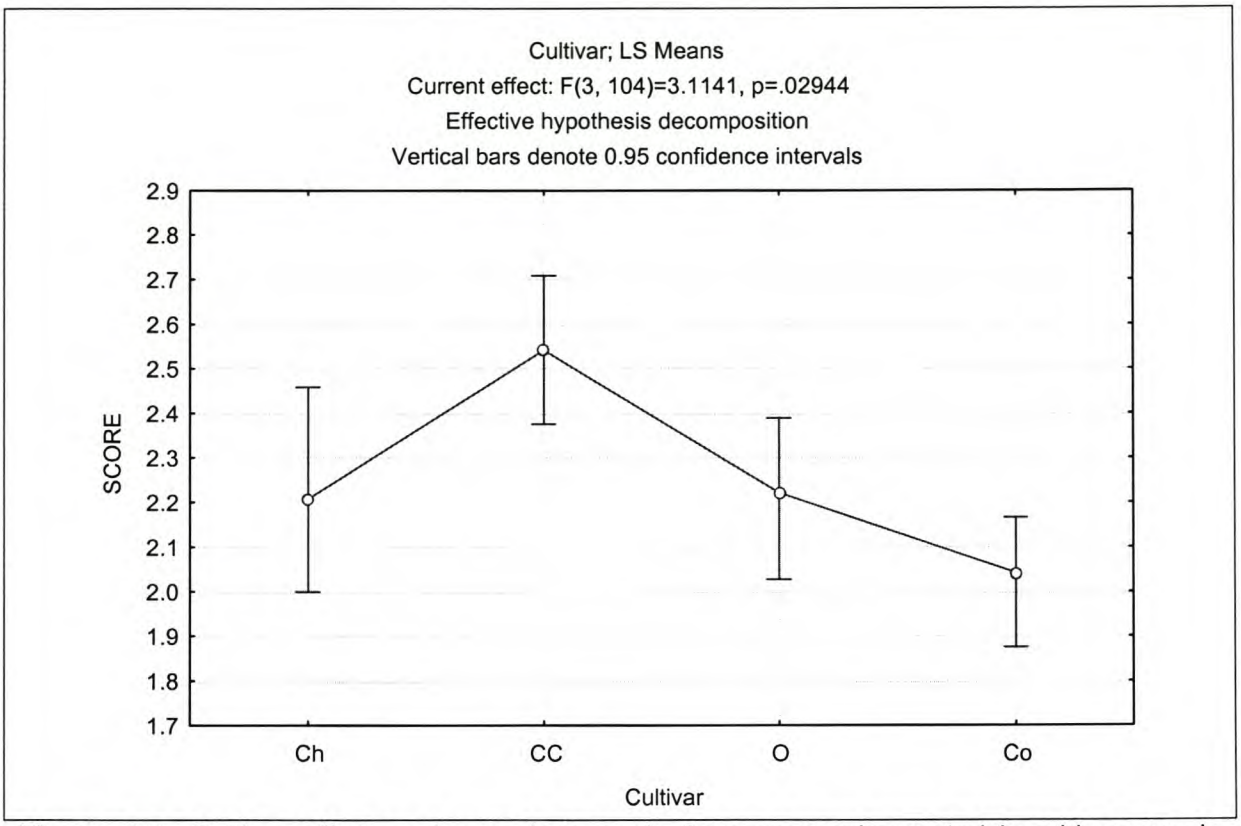


Figure 5.5 Cultivar effect on base wines made from grapes harvested in mid-season in 1999.

5.3.2 THE INFLUENCE OF REGION, CULTIVAR, HARVEST TIME AND YEAST STRAIN ON THE SENSORY QUALITY OF UNAGED POTSTILL DISTILLATES

Sensory data on the distillates followed trends similar to those noted for the wines. Distillates originating from region 4 were scored lowest in terms of quality than those originating from the remaining regions ($p<0.001$) in both vintages. In 1999, distillates originating from region 1 were scored highest, significantly higher than those originating from regions 2, 3 and 5. However, there was no significant difference between regions 1 and regions 2, 3 and 5 in the 2000 distillates, although the mean average of region 1 was slightly higher. No significant differences in scores were noted based on yeast strain used.

As was noted in the wines, in both vintages the distillates originating from wines made using table grapes were scored significantly lower than those originating from Chenin blanc, Colombar and Chenin/Colombar ($p<0.001$). It was interesting to note that the quality score gap between distillates made with Colombar grapes and those made with Chenin blanc and Chenin/Colombar was much smaller in the distillates than in the wines. In both vintages there was no significant difference between distillates made from Colombar, Chenin blanc and Chenin/Colombar grapes (data not shown).

As was seen in the base wines, distillate quality is also clearly related to time of harvest and decreases with progression in harvest time. In the 1999 distillates there was a significant difference between early, mid and late harvest ($p<0.001$), whereas

in 2000 there was a significant difference between early and mid to late harvest. (p=0.02) (**Figure 5.6a** and **5.6b**).

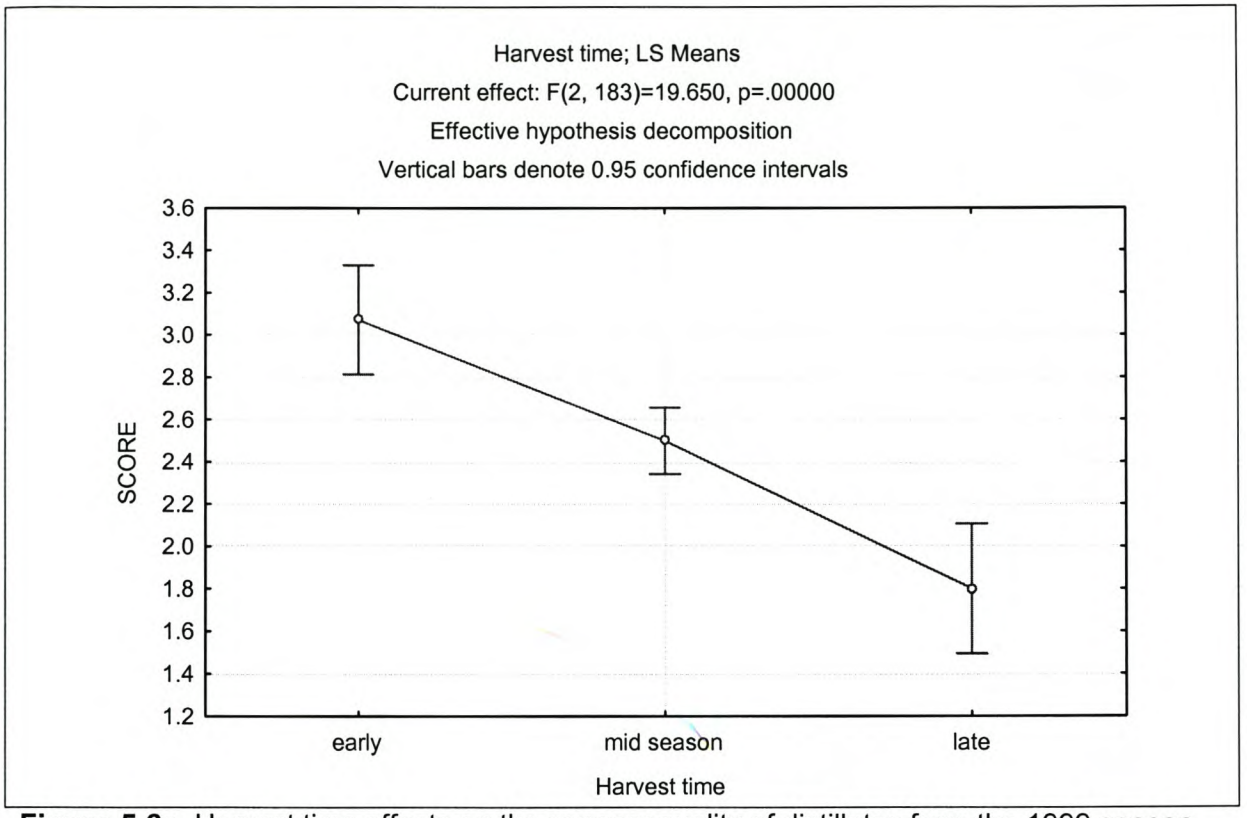


Figure 5.6a Harvest time effects on the sensory quality of distillates from the 1999 season.

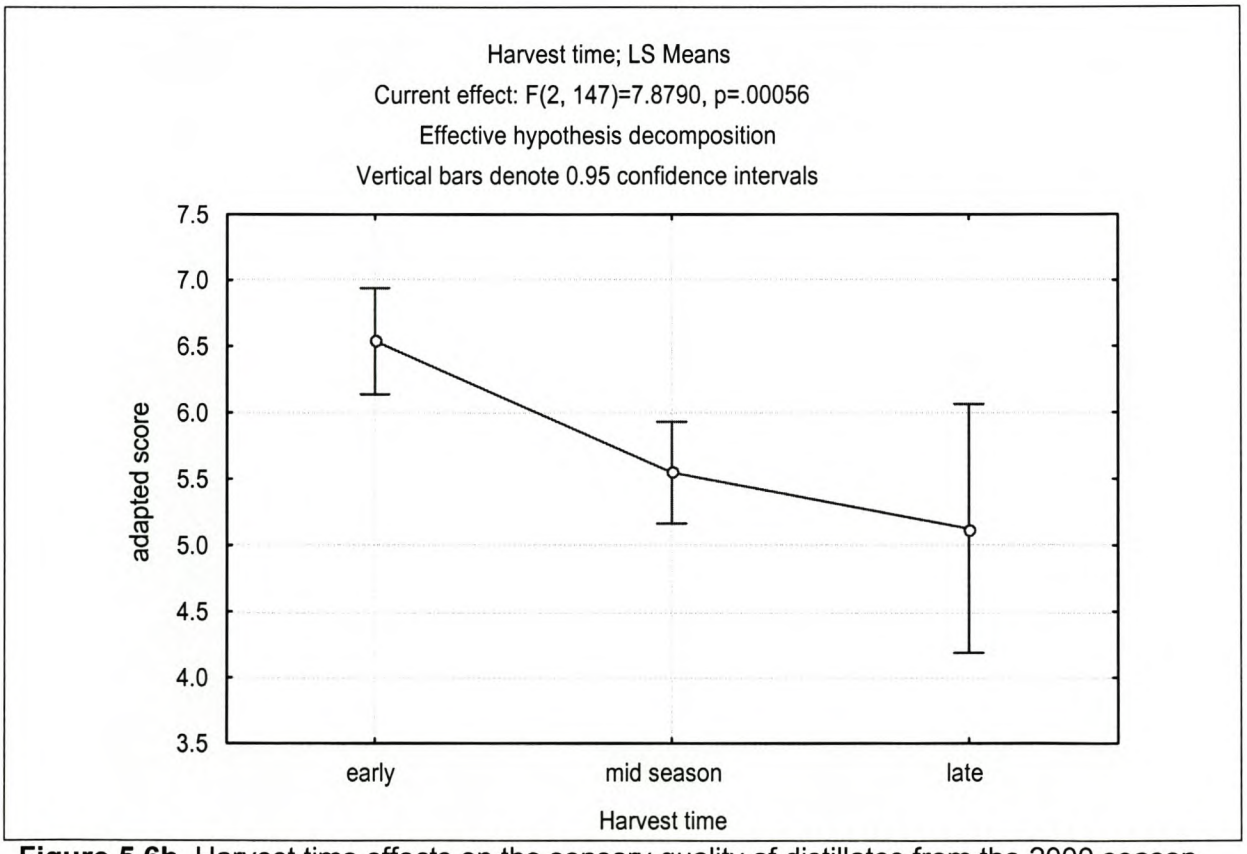


Figure 5.6b Harvest time effects on the sensory quality of distillates from the 2000 season.

5.3.3 DETERMINATION OF QUALITY INDICATING VOLATILE COMPOUNDS IN BASE WINES AND UNAGED DISTILLATES USING CART ANALYSIS

CART analysis was used to try and identify those volatile compounds that act as indicators of quality in brandy base wines and distillates. **Table 5.1** lists the relative variable importance scores according to the CART analysis. The 1999 and 2000 base wines had decanoic acid, octanoic acid, ethyl caprate, isoamyl acetate, and hexanoic acid in common as important variables identified in the CART analysis, although these did not appear in the same order of relative importance. Both ethyl lactate and acetic acid feature in the 1999 distillate variable importance analysis, yet neither of these compounds are deemed important in the 2000 distillates. In chapter 4 it was shown that the mean concentration of ethyl lactate was higher in both the 1999 wines and distillates (ethyl lactate: $mean_{1999\ wines}$ = 22 mg/L, $mean_{2000\ wines}$ = 10 mg/L, $mean_{1999distillates}$ = 27.5 mg/L, $mean_{2000distillates}$ = 17 mg/L). Du Plessis *et al.* (2002) found that the lactic acid bacteria population present in grape juice and in base wines varied in cell numbers from 1998 to 2000. Seasonal variations and their effect on naturally occurring populations of micro-organisms could possibly account for this difference.

Table 5.1 Comparison of volatile compounds identified as important in being able to define quality subsets in the CART analysis (relative to the score of 100)

1999 Wines		1999 Distillates		2000 Wines		2000 Distillates	
Decanoic acid	100	Ethyl lactate	100	Ethyl caprylate	100	Hexyl acetate	100
Octanoic acid	91.18	Ethyl caprate	85.81	Hexanoic acid	83.19	Ethyl caproate	82.08
Ethyl caprate	80.22	n-Hexanol	67.6	Ethyl caprate	68.06	2-Phenyl ethanol	63.66
isoAmyl acetate	78.67	Acetic acid	58.55	isoButanol	64.37	isoButanol	61.71
Hexanoic acid	76.75	Diethyl succinate	56.71	Octanoic acid	58.14	Ethyl caprylate	37.7
Hexyl acetate	48.48	2-Phenyl ethanol	46.78	Decanoic acid	46.94	isoAmyl acetate	15.66
n-Butanol	29.48	Ethyl caprylate	46.69	isoAmyl acetate	33.52	Acetaldehyde	15.04
Ethyl butyrate	23.04	isoAmyl acetate	42.51	n-Propanol	27.71	isoAmyl alcohol	10.56
Ethyl lactate	20.17	Decanoic acid	32.99	Propionic acid	27.46		

Due to the significantly higher concentration of ethyl lactate present in the 1999 wines and distillates, it was decided to repeat the CART analysis on only those wines that did not undergo a significant partial or full malolactic fermentation. This database yielded an ethyl lactate wine mean concentration of 5.7 mg/L in 1999 and 6.35 mg/L in 2000, and ethyl lactate mean distillate concentration of 12.5 mg/L in 1999 and 14.5 mg/L in 2000. It was hoped that, by eliminating the wine and distillate samples that had undergone varying degrees of MLF, the CART analysis would yield a greater overlap in variable importance between the two vintages. The results are listed in **Table 5.2**. The compounds marked with a * also appear in the CART variable importance of **Table 5.1**.

Table 5.2 Comparison of volatile compounds identified as important in being able to define quality subsets in the CART analysis done on those wines and distillates that did not undergo MLF (relative to the score of 100)

1999 Wines		1999 Distillates		2000 Wines		2000 Distillates	
Decanoic acid*	100	Ethyl caprate*	100	isoAmyl acetate*	100	Ethyl acetate	100
Ethyl caprate*	91.99	2-phenyl ethanol*	61.46	isoButanol*	76.97		
n-Butanol*	82.54	2-phenethyl acetate	46.93	Ethyl caprylate*	57		

Irrespective of the inclusion or exclusion of samples that underwent malolactic fermentation, decanoic acid remained the most important variable in the 1999 base wines. Ethyl caprate and n-butanol show an increase in variable importance in the 1999 non-MLF wines. Although the 2000 non-MLF base wine variable importance analysis comprises three compounds that also appear in **Table 5.1**, their relative importance has changed. However, the distillate analysis yielded more surprising results. When comparing **Tables 5.1** and **5.2**, it is clear that the higher incidence of partial or full malolactic fermentation in 1999 has an effect on the variable importance of the 1999 distillates. Where ethyl lactate was listed as the most important variable in 1999 distillates in **Table 5.1**, it did not even appear in **Table 5.2**. The 2000 distillates, which showed a lower overall incidence of partial or full malolactic fermentation, yielded completely differing results for the CART variable importance analysis in **Tables 5.1** and **5.2**. Ethyl acetate was the only volatile compound identified in the 2000 non-MLF variable importance analysis.

The main function of the CART analysis is to divide the data into subsets based on a target variable (in this case the score of the wines or distillates) and a selected set of predictor variables (in this case a selected set of the quantified volatile compounds). The subsets are divided in such a way as to minimise the variance of the score (target variable) in each subset. The result is a set of rules (based on the predictor variables) that characterise each of the subsets and a mean value for the score within each subset. The above-mentioned CART variable importance is merely a list of compounds that CART has found important in being able to determine these subset target and predictor variables. Thus, a compound listed as important in the variable importance analysis will not necessarily be a predictor variable for any of the rules generated by CART. The rules generated by CART for each vintage of wines and distillates are depicted in **Figures 5.7a** & **5.7b, 5.8a** & **5.8b, 5.9a** & **5.9b** and **5.10a** & **5.10b**. Key: NBUT= n-butanol, OCTA = octanoic acid, ETLAC = ethyl lactate, ETCAPRI = ethyl caprylate, PRAC = propionic acid, IAMST= isoamyl acetate, IAMOH = isoamyl alcohol, PROP = n-propanol, DECA = decanoic acid, HEXAC = hexyl acetate, ETAC = ethyl acetate, ACEAC = acetic acid.

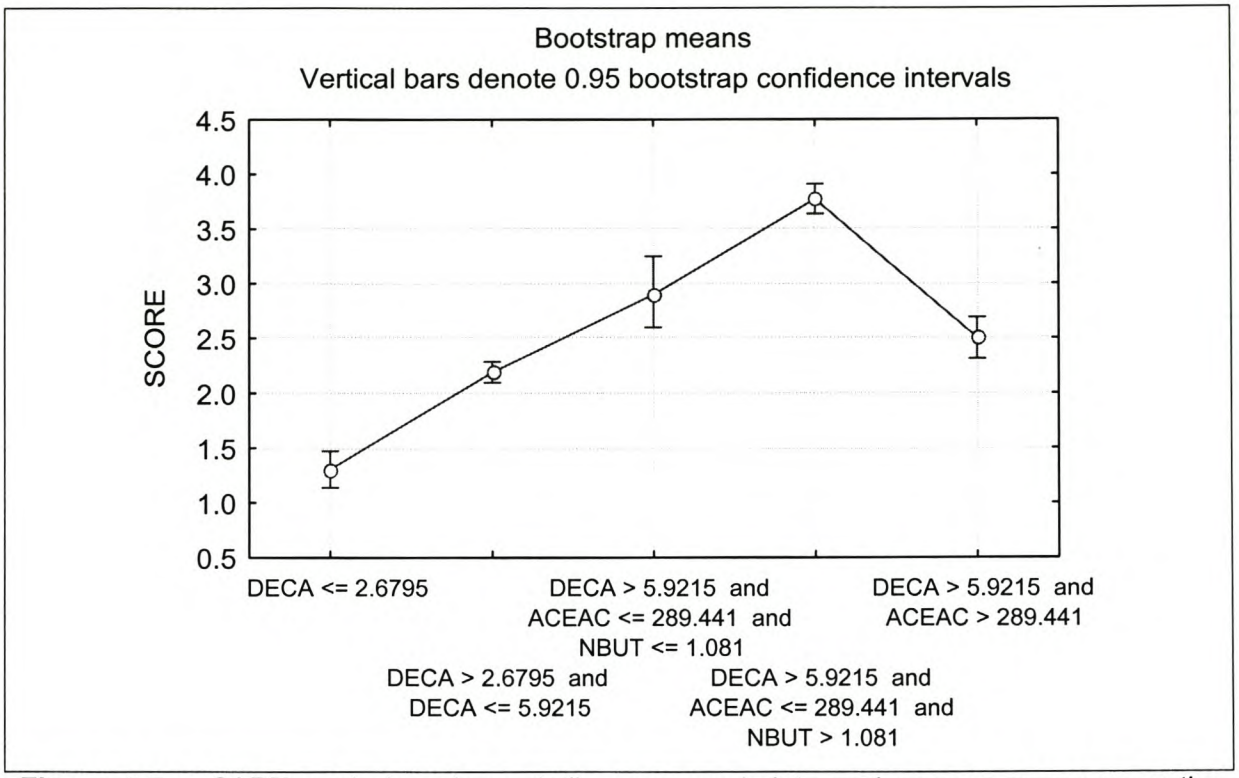


Figure 5.7a CART analysis using volatile compound data and sensory score on entire dataset of 1999 base wines (i.e. including those that underwent MLF).

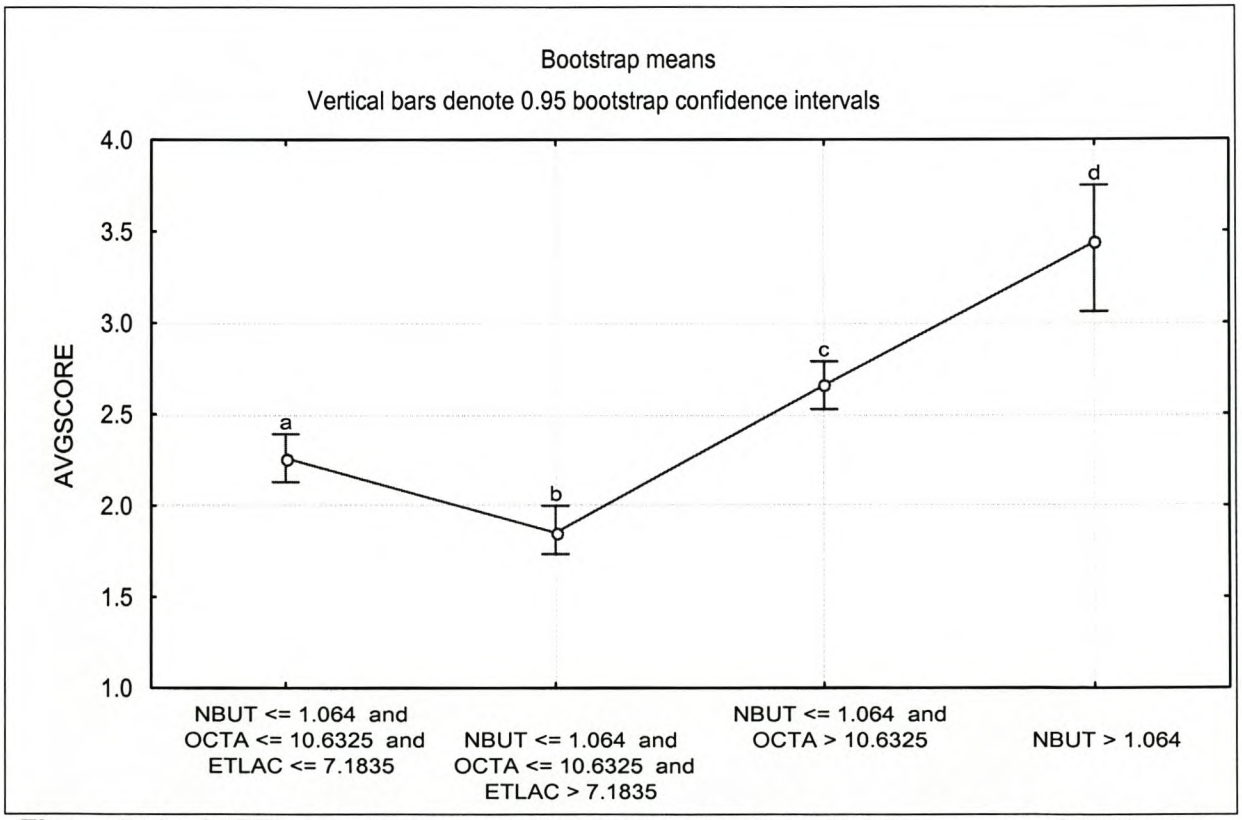


Figure 5.7b CART analysis using volatile compound data and sensory score of 1999 wines that did not undergo MLF.

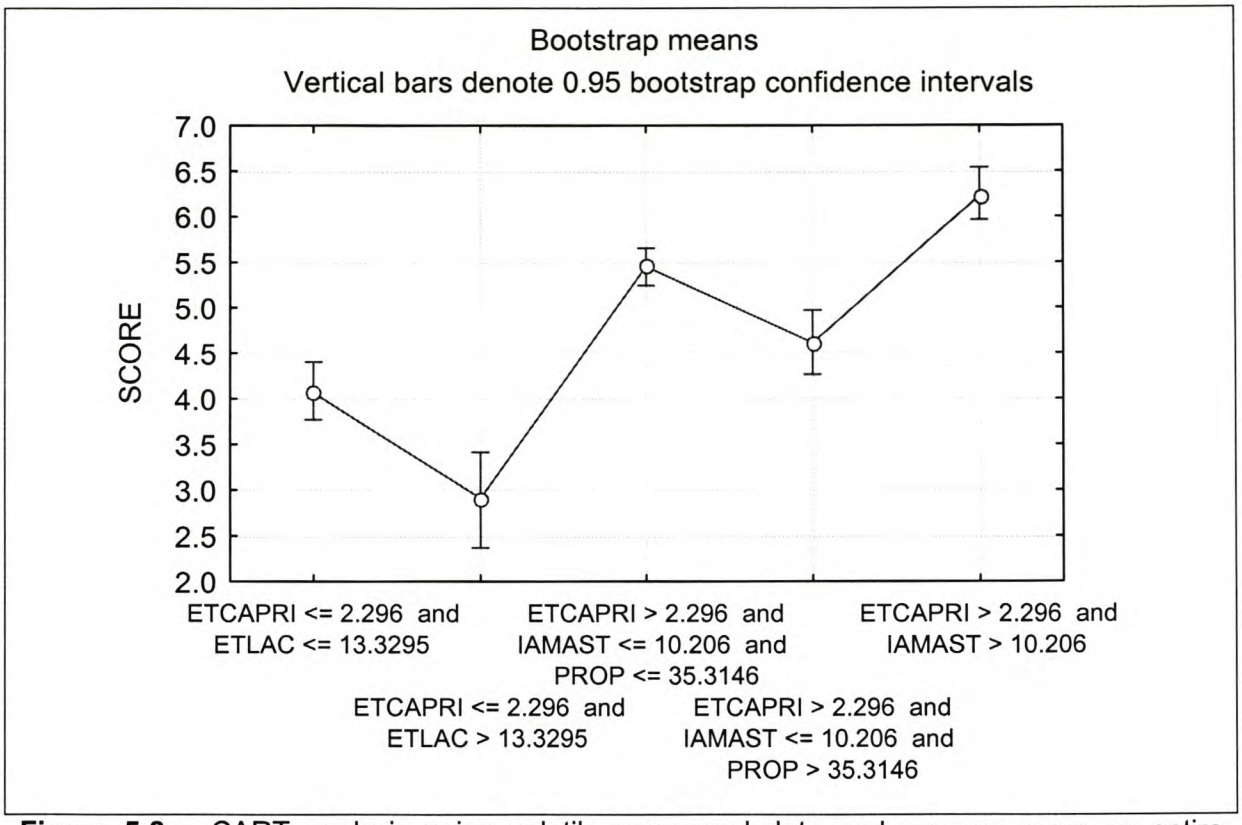


Figure 5.8a CART analysis using volatile compound data and sensory score on entire dataset of 2000 base wines (i.e. including those wines that underwent MLF).

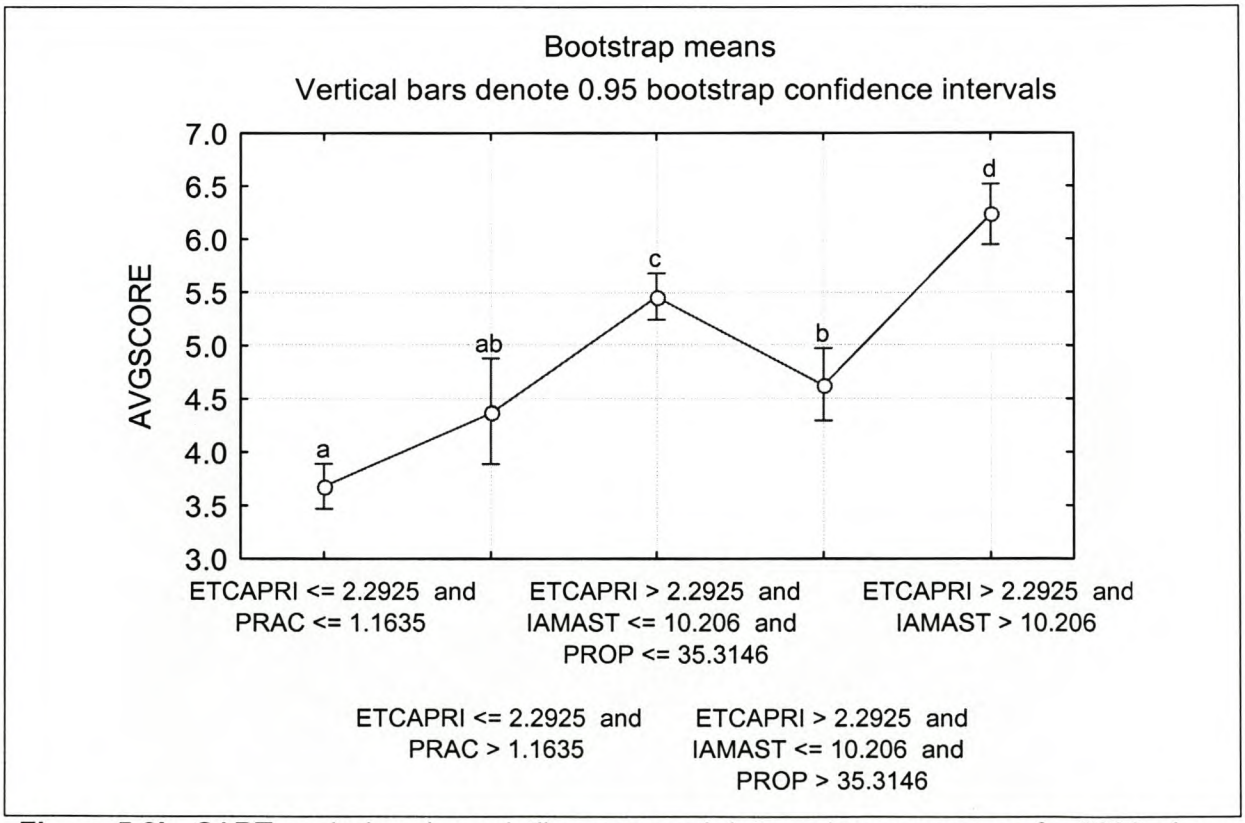


Figure 5.8b CART analysis using volatile compound data and sensory score for 2000 wines that did not undergo MLF.

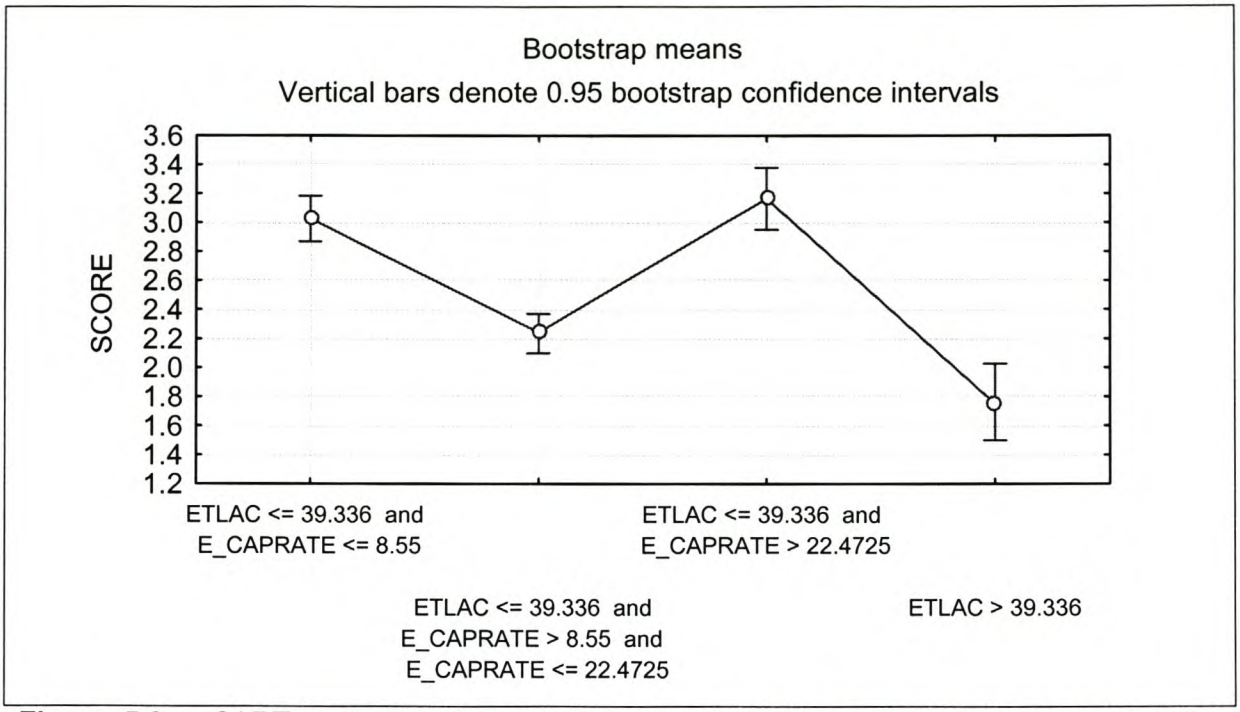


Figure 5.9a CART analysis using volatile compound data and sensory score of entire dataset of 1999 unaged distillates (i.e. including those that did not undergo MLF).

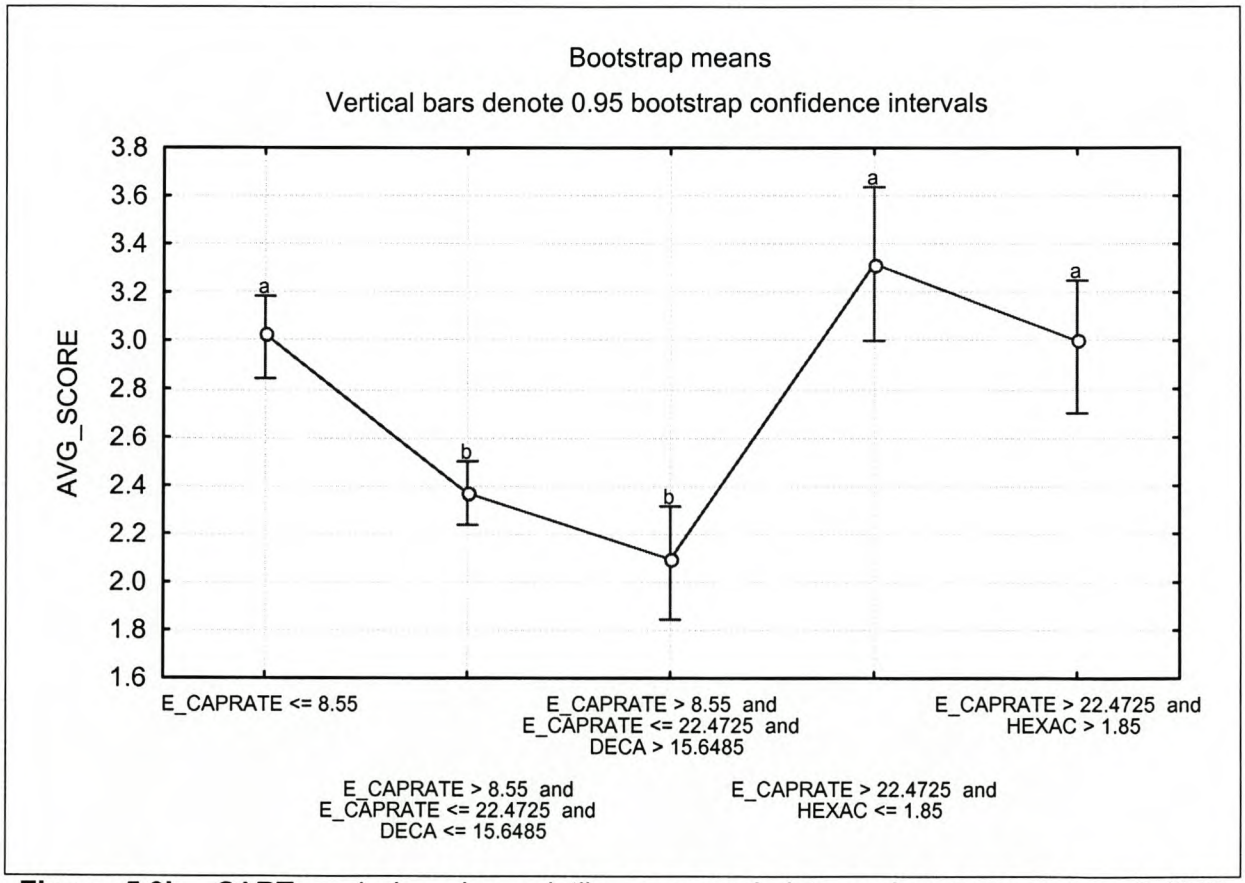


Figure 5.9b CART analysis using volatile compound data and sensory score of 1999 distillates that did not undergo MLF.

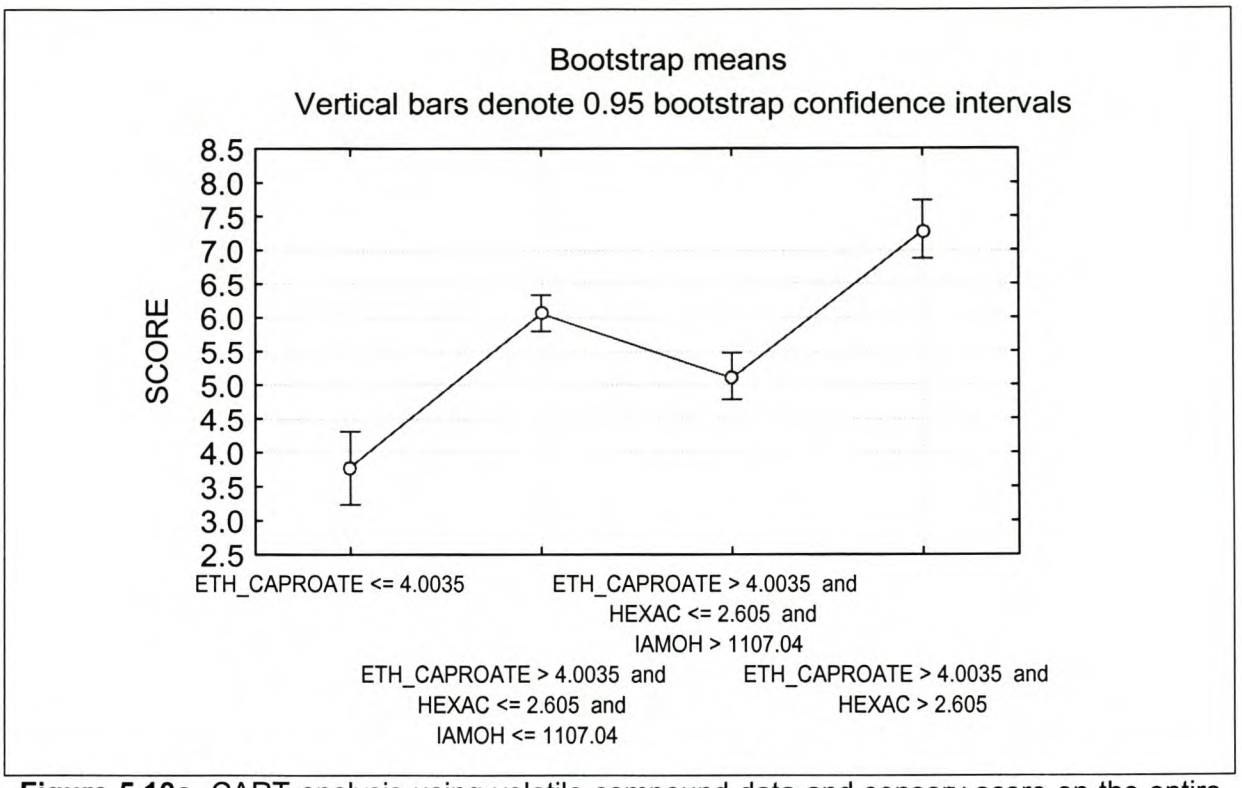


Figure 5.10a CART analysis using volatile compound data and sensory score on the entire dataset of 2000 unaged distillates (i.e. including those that underwent MLF).

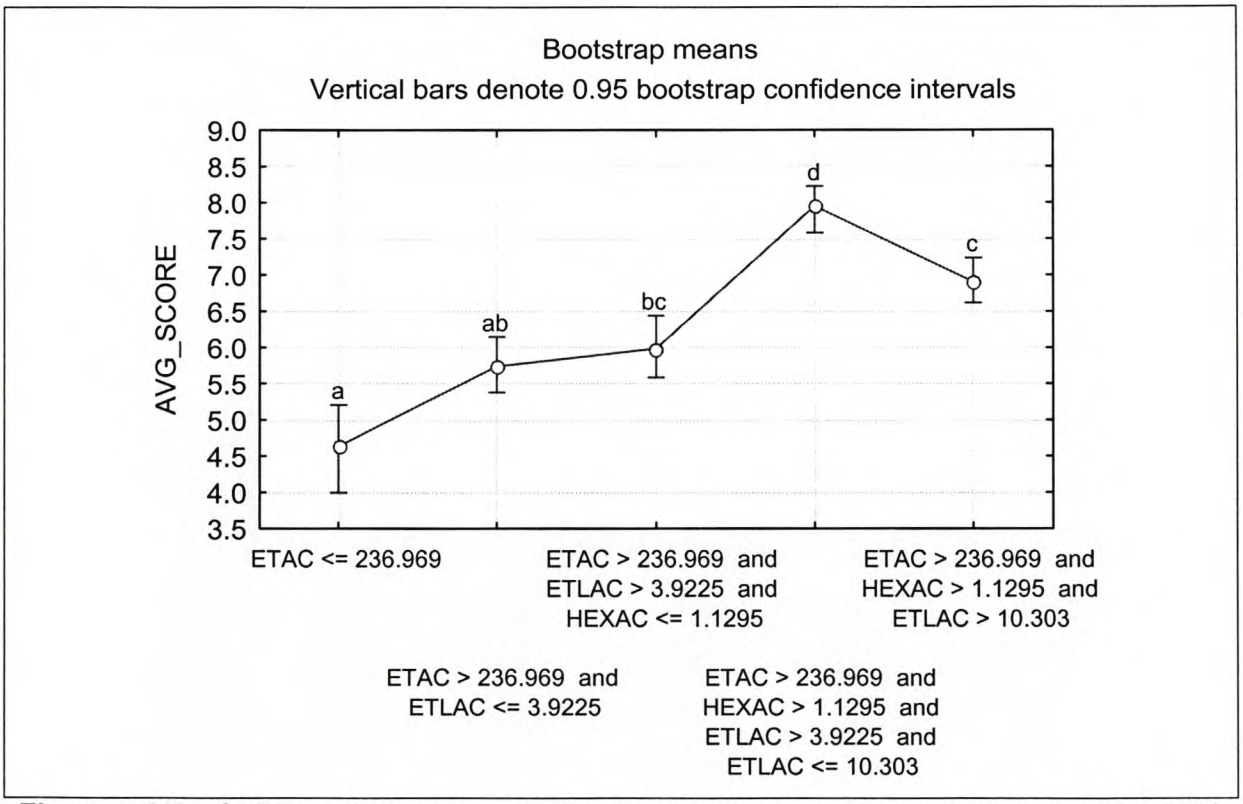


Figure 5.10b CART analysis using volatile compound data and sensory score on for 2000 distillates that did not undergo MLF.

Figure 5.7a depicts the rules generated by the CART analysis on the entire dataset of 1999 base wines, while **Figure 5.7b** depicts the rules generated by CART in those 1999 wines that did not undergo a partial or full malolactic fermentation.

When comparing these two figures it is interesting to note that only n-butanol features as a predictor variable in both datasets. **Table 5.3** lists the mean concentration and significant differences in concentration between 1999 and 2000 for the entire set of wines as well as the dataset comprising only those wines not affected by MLF. The letters indicating significance are only relevant to the particular dataset i.e. a level of significance was determined separately for each of the two datasets. The p-values refer only to the non-MLF dataset. The p-values for compounds within the complete dataset (i.e. including wines that had undergone partial or full MLF) can be found in chapter 4. In both **Figures 5.7a** and **5.7b**, the correlation between the concentration of n-butanol and wine quality remains the same. In chapter 3 it was found that the concentration of n-butanol increases with concurrent increases in Chenin blanc wine quality. The mean concentration of acetic acid was lower in the non-MLF dataset and also very close to the predictor variable concentration of 289 mg/L, which is seen in **Figure 5.7a**. The fact that the non-MLF wines had an acetic acid concentration very close to or less than this value, may account for the absence of acetic acid as a predictor variable in **Figure 5.7b**. In chapter 3 it was found that the concentration of decanoic and octanoic acid was correlated to Chenin blanc wine quality. This is confirmed in **Figures 5.7a** and **5.7b,** respectively, where the concentration of these compounds increases with concurrent increases in wine quality. Why decanoic acid appears in **Figure 5.7a** and octanoic acid in **Figure 5.7b** is unknown, especially as there was no significant change in the concentration of these two compounds in the complete and non-MLF dataset (**Table 5.3**). It is also interesting to note that in **Figure 5.7a**, ethyl lactate is not a predictor variable, even though the range of ethyl lactate concentrations is much larger in the entire dataset (ethyl lactate concentrations varied from 1.3 mg/L to 180 mg/L). In the ANOVA performed on those unaged distillates that underwent SDA (refer to section 5.3.6. and **Tables 5.5** and **5.6)** it is also evident that ethyl lactate concentrations are significantly higher in poor quality distillates. In chapter 3 it was found that ethyl lactate concentrations increase with concurrent decreases in young Chenin blanc wine quality. One could speculate that this compound was not able to aid in the definition of a number of subsets that are divided in such a way as to minimise the variance of the score. Had ethyl lactate been included as a predictor variable, it may have led to the definition of only two subsets, one with a higher and one with a lower mean score with a relatively large variance within the mean score. The inclusion of ethyl lactate as a predictor variable in **Figure 5.7b** may be due to the reduced concentration range of this compound in the non-MLF dataset (ethyl lactate concentrations varied from 1.3 mg/L to 18 mg/L). **Figure 5.7b** confirms the observation noted in chapter 3 regarding the correlation between ethyl lactate concentration and wine quality.

From **Figure 5.8a** and **5.8b** it is evident that the only change in predictor variable when excluding the MLF wines in the 2000 vintage, was ethyl lactate, which was replaced by propionic acid as a predictor variable. **Figure 5.8a** confirms the correlations noted in chapter 3, where it was found that the concentration of ethyl

caprylate and isoamyl acetate increased with increasing young Chenin blanc wine quality. Although not significant, n-propanol concentrations tended to increase with decreasing wine quality (chapter 3). **Figures 5.8a** and **5.8b** largely confirm these findings, but highlights the long held belief of volatile compounds being able to act either synergistically or antagonistically and affect wine quality though their differing relative concentrations. This is illustrated in the relationship between ethyl caprylate, isoamyl acetate and n-propanol in both **Figures 5.8a** and **5.8b**.

Table 5.3 Vintage differences in volatile compound composition between 1999 and 2000 base wines (including and excluding wines that underwent malolactic fermentation)

Compound	1999 Wine Mean (mg/L)	2000 Wine Mean (mg/L)	1999 non-MLF Wine Mean (mg/L)	2000 non-MLF Wine Mean (mg/L)	p-Value non-MLF
Ethyl acetate	130a	114a	135a	120a	0.0777
Ethyl butyrate	1.62a	2.06b	1.86a	2.1a	0.038
Ethyl caprylate	1.35a	2.3a	1.48a	2.4b	<0.0001
Ethyl caproate	1.39a	2.52b	1.21a	2.7b	<0.0001
Ethyl caprate	4.65a	5.2a	5.26a	5.6a	0.404
Ethyl lactate	22a	10b	5.7a	6.35a	0.638
isoAmyl acetate	4.8a	8.1b	5.75a	8.9b	0.0001
Hexyl acetate	0.43a	0.61b	0.52a	0.685b	0.007
2-Phenethyl acetate	0.26a	0.28a	0.27a	0.28a	0.057
Acetic acid	365a	322a	288a	294a	0.46
isoButyric acid	1.44a	1.1b	1.45a	1.1b	0.002
Propionic acid	2.2a	1.6b	1.9a	1.7a	0.187
Hexanoic acid	5.15a	6.85b	5.7a	7.1b	<0.0001
Octanoic acid	8.85a	13b	9.9a	13.6b	<0.0001
Decanoic acid	5.6a	9.45b	6.4a	10b	<0.0001
n-Propanol	41.9a	43a	42a	44.5a	0.997
n-Butanol	0.78a	0.92a	0.79a	0.97a	0.122
isoButanol	29.5a	21b	29.3a	20.7b	<0.0001
isoAmyl alcohol	154.5a	134.8b	159a	134.5b	<0.0001
2-Phenyl ethanol	10.51a	11.51b	9.75a	11a	0.003
n-Hexanol	2.46a	2.19b	2.46a	2.18a	0.002

From **Tables 5.3** and 5.**4,** it is evident that wine and distillate composition varied significantly between the 1999 and 2000 vintages, even when excluding those samples that underwent malolactic fermentation. This may explain the relatively low level of overlap in predictor variables seen in **Figures 5.7** and **5.9** when compared to **Figures 5.8** and **5.10,** respectively. With the exception of ethyl butyrate, ethyl lactate, propionic acid and 2-phenyl ethanol, the same compounds found to be significantly different in concentration between 1999 and 2000 in the entire dataset, remain significantly different in concentration in the dataset of non-MLF wines. This illustrates that wine composition can vary from season to season. Houtman and Du Plessis (1981) found that the concentration of ethyl caprate, ethyl caprylate, isoamyl acetate, 2-phenethyl acetate, 2-phenyl ethanol and isobutanol are all significantly

influenced by the choice of yeast strain used to ferment settled Chenin blanc juice. Ravaglia and Delfini (1993) found that the concentration of hexanoic, octanoic and decanoic acid are all significantly influenced by choice of yeast strain. Medium chain fatty acids are produced by yeasts as intermediates in the biosynthesis of long chain fatty acids, rather than as a result of acid catabolism. However, the amount and proportion of medium chain fatty acids released into the fermentation medium is strictly dependant upon yeast strain, the composition of the medium, and the fermentation conditions such as pH, temperature and degree of aeration during fermentation (Miranda-Lopez *et al.*, 1992). The production of higher alcohols such as n-butanol, n-propanol and isoamyl alcohol during fermentation is most significantly influenced by the must amino acid composition, irrespective of whether this synthesis takes place via anabolic or catabolic metabolism or via the Ehrlich mechanism (Schulthess and Ettlinger, 1978). Temperature, must turbidity and pH as well as choice of yeast strain can also influence the concentration of higher alcohols in wine (Rankine, 1963, 1968; Crowell and Guymon, 1969; Houtman and du Plessis, 1981). Thus the observed differences in wine composition and CART predictor variables between 1999 and 2000 can be ascribed to seasonal variations which result in differences in must composition and which in turn can also influence yeast strain activity.

Table 5.4 Vintage differences in volatile compound composition between 1999 and 2000 unaged distillates (including and excluding distillates that underwent MLF)

Compound (mg/L)	1999 Distillate Mean	2000 Distillate Mean	1999 non-MLF Distillate Mean	2000 non-MLF Distillate Mean	p-Value non-MLF
Acetaldehyde	109a	111.5a	85a	120b	0.0003
Ethyl acetate	445a	345b	445a	350b	0.0002
Hexyl acetate	0.8a	1.61b	0.96a	1.73b	<0.0001
Ethyl caproate	8a	5.7b	8.7a	5.9b	0.025
Ethyl caprate	16.5a	15.5a	17a	16.2a	0.624
Ethyl caprylate	9.25a	10.46b	9.8a	10.75a	0.09
Ethyl lactate	27.5a	17b	14.5a	12.9a	0.326
isoAmyl acetate	22a	41b	25a	43.5b	<0.0001
2-Phenethyl acetate	0.8a	1.93b	0.5a	1.85b	<0.0001
Diethyl succinate	1.1a	1.35a	0.68a	1.1a	0.494
Acetic acid	40a	37.7a	28.5a	36b	0.231
isoButyric acid	0.67a	1.37b	0.65a	1.38b	<0.0001
Hexanoic acid	3.8a	2.75b	4a	2.76b	0.003
Octanoic acid	15.3a	30.5b	16.6a	31b	<0.0001
Decanoic acid	14.5a	12.5b	16.1a	12.5b	<0.0001
n-Propanol	332a	316a	313a	322a	0.932
n-Butanol	5.08a	5.3a	4.95a	5.45a	0.357
isoButanol	190a	161b	187a	151b	0.0004
n-Hexanol	19a	15.91a	16.5a	15a	0.235
isoAmyl alcohol	970a	1045b	945a	1023a	0.044
2-Phenyl ethanol	5.19a	4.74a	4.52a	4.5a	0.456

Table 5.5 Volatile compound composition differences between 1999 unaged distillates used in the SDA

Compound (mg/L)	Mean Good	Mean Average	Mean Poor	p-value
Acetaldehyde	70a	70a	545b	0.0145
Ethyl acetate	450a	405a	555b	0.211
isoAmyl acetate	28a	7.5b	2b	<0.001
Hexyl acetate	0.85a	0.27b	0.05c	<0.001
Ethyl lactate	31a	24a	62b	<0.001
Ethyl caproate	9.4a	11a	9.8a	0.887
Ethyl caprylate	11a	7ab	6.2b	0.016
Ethyl caprate	15a	13a	7b	0.074
Diethyl succinate	0.7ab	0.5b	0.79a	0.034
2-Phenethyl acetate	0.52a	0.38ab	0.13b	0.011
n-Propanol	445a	250b	310b	<0.001
isoButanol	170a	255b	231b	0.02
n-Butanol	5.2a	3.9a	7.1a	0.132
isoAmyl alcohol	952a	900a	875a	0.615
n-Hexanol	19a	12.8b	21.7c	0.0002
2-Phenyl ethanol	4a	6.9b	6.6b	0.0015
Acetic acid	40a	42a	140b	0.0007
isoButyric acid	0.58a	0.72a	0.88a	0.432
Hexanoic acid	4.5a	2.7b	2.75b	0.0151
Octanoic acid	13.5a	17.7b	5.5c	<0.001
Decanoic acid	8.2a	18b	6.7a	<0.001

Table 5.6 Volatile compound composition differences between 2000 unaged distillates used in the SDA

Compound (mg/L)	Mean Good	Mean Average	Mean Poor	p-value
Acetaldehyde	100ab	115a	80b	0.0098
Ethyl acetate	385a	315a	270a	0.054
isoAmyl acetate	70a	43b	24c	0.0003
Hexyl acetate	2.7a	1.5b	0.9b	0.0002
Ethyl lactate	6.6a	8.5a	40b	0.0002
Ethyl caproate	6.4a	7.2a	4.3b	0.0013
Ethyl caprylate	11.9a	12.7a	8.8b	0.0139
Ethyl caprate	18a	21a	16a	0.3727
Diethyl succinate	0.4a	0.5a	4b	0.0009
2-phenethyl acetate	5.3a	1.6b	2b	0.0023
n-Propanol	410a	285ab	250b	0.0105
isoButanol	117a	149ab	212b	0.003
n-Butanol	6a	5.1a	4a	0.2841
isoAmyl alcohol	1020a	970a	1150a	0.0931
n-Hexanol	15.2a	13.3a	19.5b	0.003
2-phenyl ethanol	3.8a	4.75ab	5.9b	0.0814
Acetic acid	26a	28.4a	29a	0.773
isoButyric acid	1.05a	1.35a	1.25a	0.073
Hexanoic acid	3.5a	3.8a	3.35a	0.754
Octanoic acid	28a	31.5a	29.5a	0.578
Decanoic acid	9.1a	10.8a	12.05a	0.164

In **Figures 5.9a** and **5.10b** it is evident that increased concentrations of ethyl lactate also exert a negative influence on brandy distillates. In **Figure 5.9a** it is interesting to note that at intermediate concentrations of ethyl caprate, the perceived quality of the distillates actually decreases. This indicates a non-linear relationship between the concentration of volatile aroma compounds that are associated with positive effects on beverage quality (such as ethyl esters of shorter chain fatty acids) and the sensory quality of brandy distillates. This is confirmed in **Figure 5.9b**. Although the difference is not shown to be significant, the effect of decanoic acid on distillate quality tends to oppose what was observed in the base wines and distillates. As decanoic acid is a compound with a relatively high molecular mass, a large amount of this compound is removed during the fractionation between heart and tails during the second distillation. Rancid, buttery and soapy aromas are negatively associated to brandy quality (Jolly and Hattingh, 2001) and in a solution of higher alcohol concentration, decanoic acid could contribute to these undesirable aromas if present in higher concentrations.

Figures 5.9b and **5.10a** and **5.10b** share only hexyl acetate as a common indicator for determining the quality of distillates and in all three instances higher concentrations of this compound exhibit a positive effect on distillate quality. **Figure 5.10a** illustrates the positive contribution of increased ethyl caproate concentrations to distillate quality. From **Figure 5.10a**, the concentration of isoamyl alcohol seems to have a cut-off or maximum value at which its contribution to sensory quality is positive. In the complete dataset of distillates, the concentration of isoamyl alcohol was significantly higher in the 2000 distillates (**Table 5.4**). The concentration of ethyl acetate was significantly lower in the 2000 distillates (including and excluding the MLF samples) (**Table 5.4**). In chapter 3 it was observed that the concentration of ethyl acetate was lowest in young Chenin blanc wines judged to be of lowest quality, although this difference was not proven to be significant. **Figure 5.10b** also indicates that very low concentrations of ethyl acetate lead to lower sensory quality. However, it should be stressed that the overall concentration of ethyl acetate in the distillates studied is low (**Table 5.4**). Cantagrel (1988) indicated a threshold of 600 mg/L for ethyl acetate above which spirits are found to be defective.

5.3.4 SENSORY DESCRIPTIVE ANALYSIS ON TWELVE SELECTED UNAGED POTSTILL DISTILLATES FROM 1999 AND 2000

5.3.4.1 Good quality distillates

The good quality distillates all had 'fruity' as their most intense aroma descriptor (**Figures 5.11** and **5.12**). In both years, the good quality distillates were scored very similarly in terms of 'smooth associated' aromas. 'Herbaceous' aromas were also found to be present in both years, although the intensity of this descriptor varied between samples. In both years, 'spicy' was the other positive aroma detected in

these distillates. The panel detected a negative aroma component in one 2000 distillate, this was identified as a 'solvent/ chemical' type of aroma.

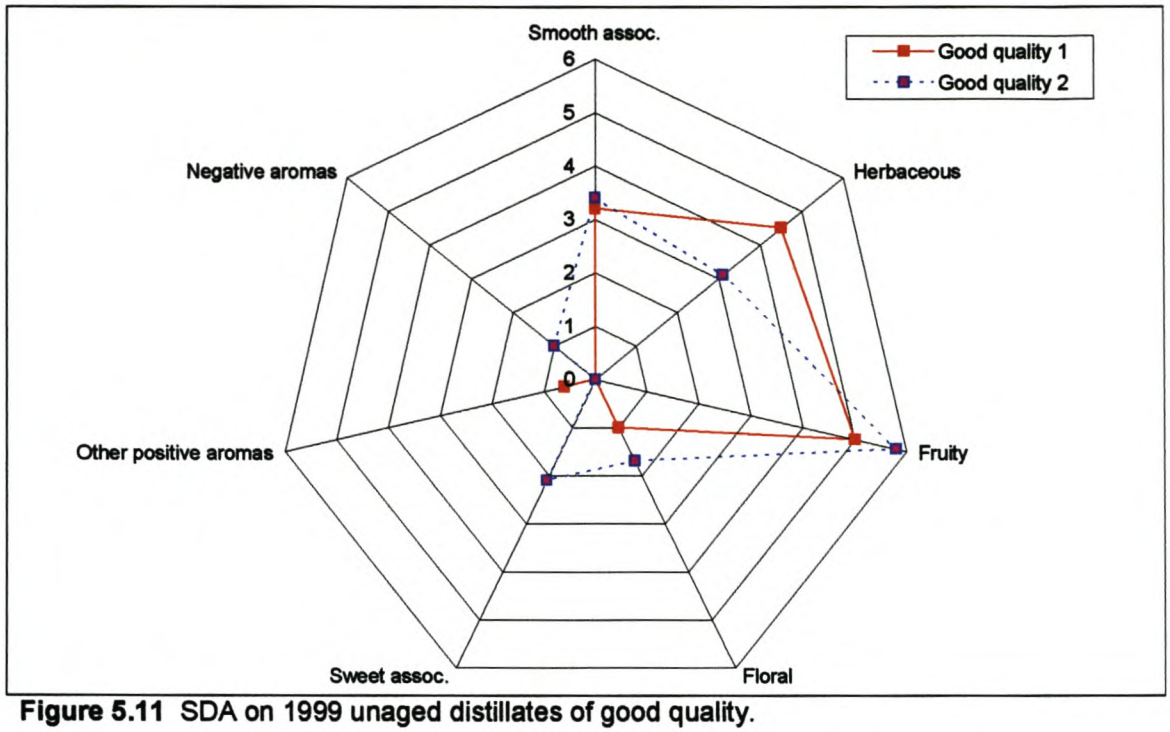


Figure 5.11 SDA on 1999 unaged distillates of good quality.

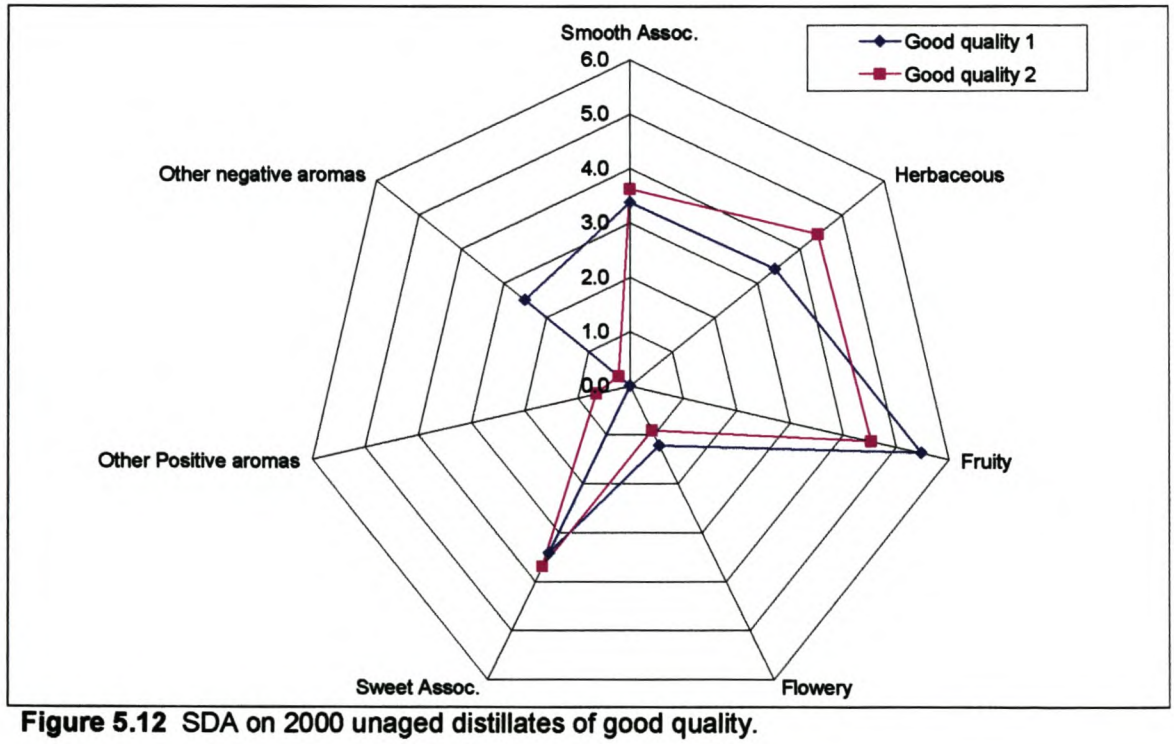


Figure 5.12 SDA on 2000 unaged distillates of good quality.

5.3.4.2 Average quality distillates

In the 1999 distillates, the 'fruity' and 'sweet associated' components were somewhat lower in the average quality distillates than in the good quality distillates (**Figures 5.13** and **5.14**). This difference was not as marked in the 2000 distillates. 'Herbaceous' and 'smooth associated' aromas were detectable in both vintages of average quality distillates.

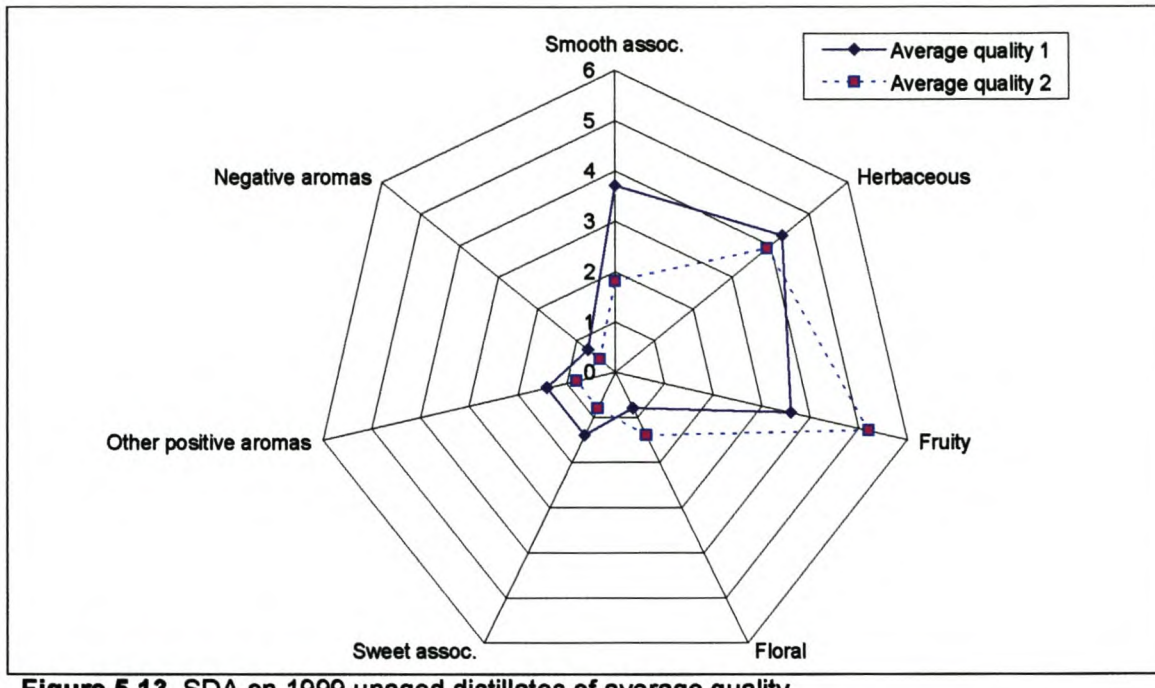


Figure 5.13 SDA on 1999 unaged distillates of average quality.

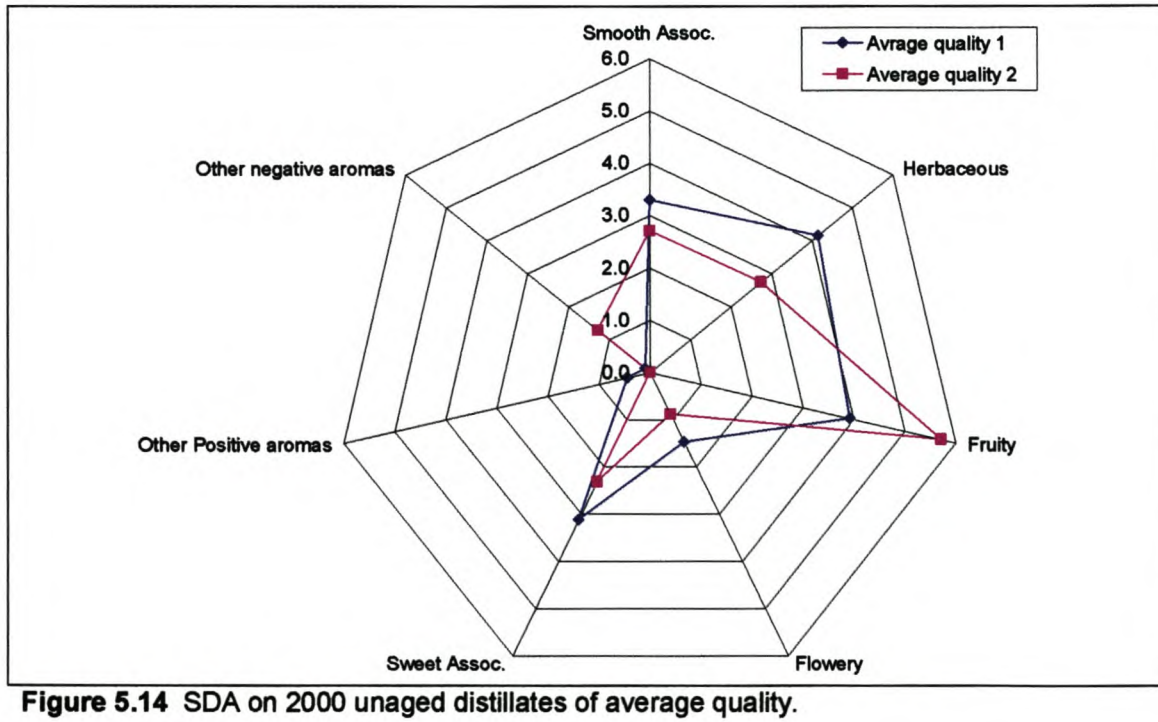


Figure 5.14 SDA on 2000 unaged distillates of average quality.

5.3.4.3 Poor quality distillates

The main descriptor that distinguishes poor quality distillates from those of good and average quality, is the 'herbaceous' descriptor (**Figures 5.15** and **5.16**). In poor quality distillates, over both vintages, 'herbaceous' is the descriptor of highest intensity. In the 1999 distillates, the panel also detected a 'solvent/ chemical' character as well as traces of 'heads' aromas as a negative aroma. In 2000, the same negative aromas were found in sample 1, although sample 2 was found to have a molasses character which falls under the 'sweet associated' aroma descriptor.

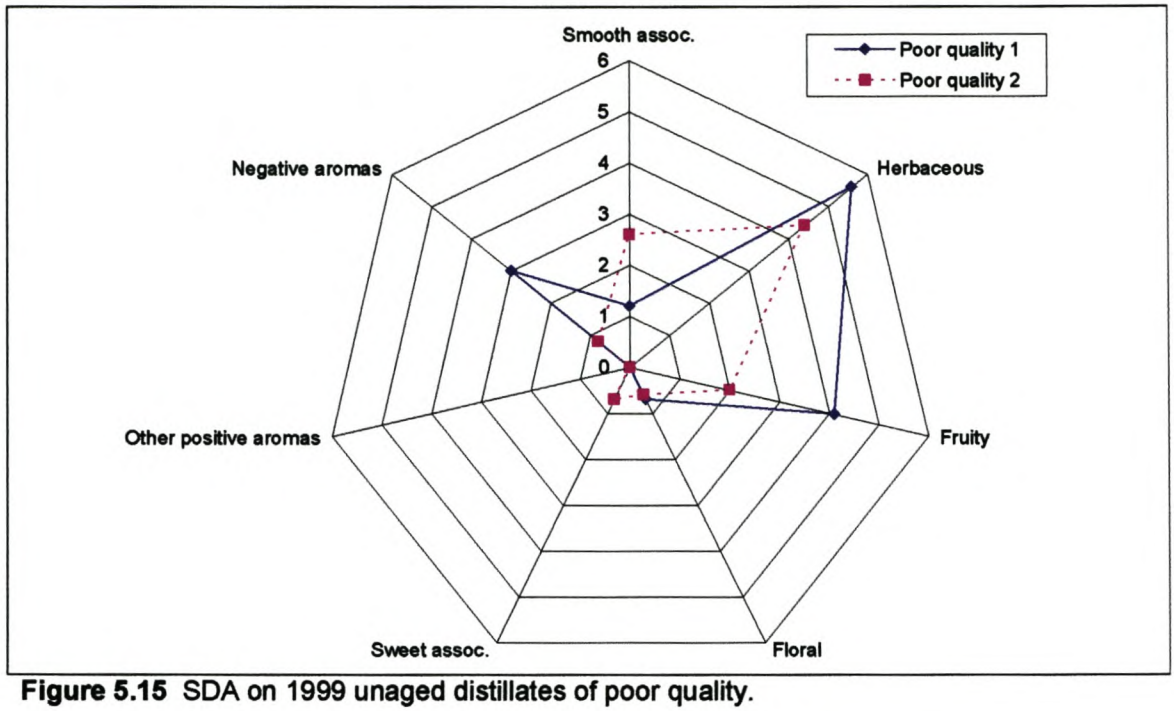


Figure 5.15 SDA on 1999 unaged distillates of poor quality.

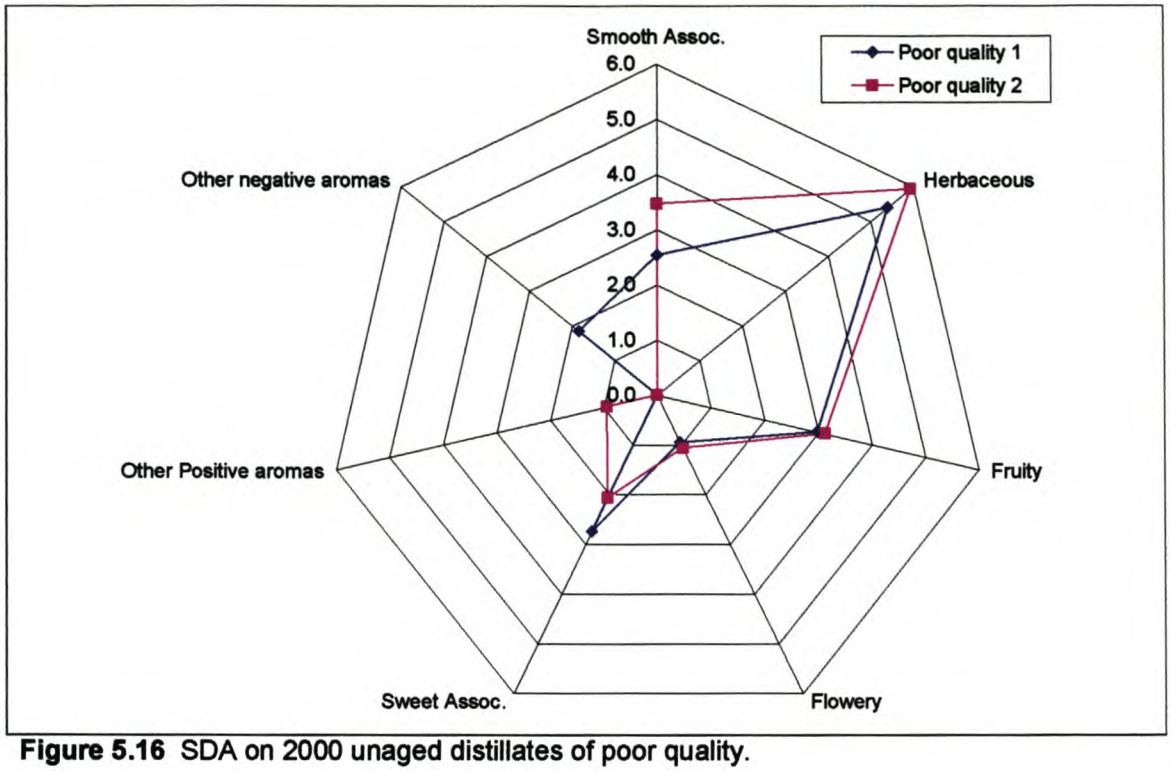


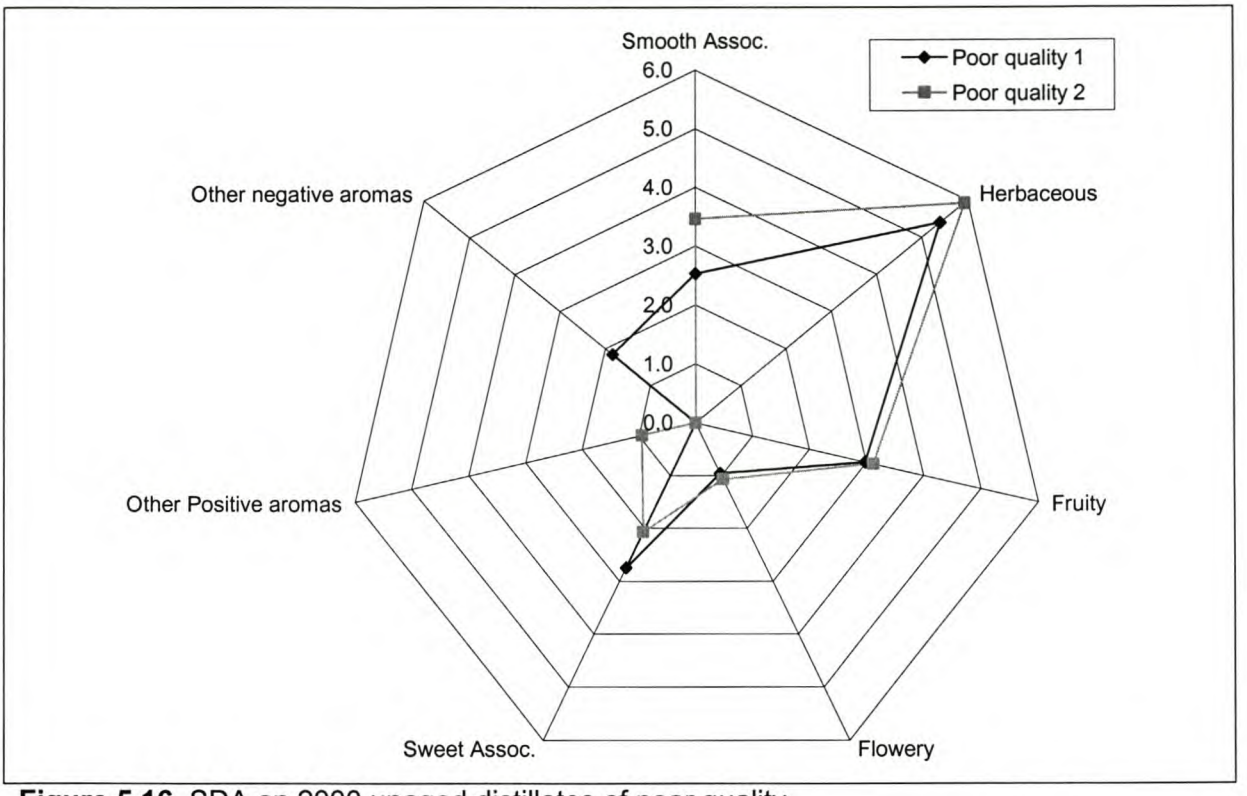
Figure 5.16 SDA on 2000 unaged distillates of poor quality.

5.3.5 VOLATILE COMPOUND COMPOSITION DIFFERENCES BETWEEN DISTILLATES PROFILED USING SENSORY DESCRIPTIVE ANALYSIS

5.3.5.1 1999 Distillates

Table 5.5 lists the mean values and p-values for the 1999 distillate ANOVA. The concentration of acetaldehyde, ethyl lactate and acetic acid was highest in the poor quality samples, significantly higher than the good and average quality samples. This could be correlated to the 'solvent/chemical' aroma that the SDA panel detected. Cantagrel (1988) found that spirits which contain concentrations of ethyl acetate higher than 600 mg/L are organoleptically defective. As can be seen from **Table 5.5,** the mean concentration of ethyl acetate in poor quality distillates in 1999 was 555 mg/L. Poor quality distillate number one of 1999, which was judged to be of the lowest quality, contained 784 mg/L of ethyl acetate, which accounts for its poor quality rating (data not shown).

The concentrations of n-propanol, isoamyl acetate, hexyl acetate, ethyl caprylate and hexanoic acid were highest in the samples of good quality, significantly higher than those of average and poor quality (**Table 5.5**). The higher concentrations of acetate (hexyl, isoamyl and 2-phenethyl acetate) and $C_6 - C_{10}$ ethyl esters present in good quality distillates (**Table 5.5**) can account for the high intensity fruity descriptor noted in these samples (Boulton *et al.*, 1995). Although relatively little work has been done on the aroma effect of esters in distilled beverages, Van Rooyen (1984) found that, of all the esters he considered in his study, isoamyl acetate and ethyl hexanoate were those that played a major role in the aroma of young white wines. Similar



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conclusions were made by Romano *et al.* (1994). They showed that a simple linear model could explain the intensity of caramel, apple, acetate notes of Chardonnay as a function of their acetate content, mainly isoamyl acetate. However, the model did not explain the perception of tropical fruit notes, which are attributed to ethyl esters of fatty acids. The reason why these results do not offer any definitive conclusion may be due to the complex interactions that take place between these and other aroma compounds, and even among them and various matrix compounds. Piggot and Findlay (1984) showed by means of a study on binary mixtures of esters, that at certain concentrations there are synergistic or antagonistic relationships between these compounds. The interactions between these compounds and ethyl acetate (Van der Merwe and Van Wyk, 1981; Bertuccioli *et al.*, 1983) and ethanol (Williams, 1962) have also been studied. 2-Phenyl ethanol appeared in significantly lower concentrations in the good quality samples compared to the poor and average quality samples (**Table 5.5**). Although 2-phenyl ethanol has a floral, rose-like aroma and is found in grape berries, where it exists in free and bound form, it is a precursor to 2-phenethyl acetate, which is produced during fermentation (Boulton *et al.*, 1995). The concentration of 2-phenethyl acetate is significantly higher in the good quality distillates when compared to the average and poor quality distillates, and thus confirms this relationship. Isobutanol concentrations were significantly higher in average and poor quality distillates ($p=0.02$). Ethyl caprylate concentrations decreased concurrently with decreases in quality, although this decrease was only significant between the good and poor quality distillates (**Table 5.5**). Ethyl caprylate is associated with fruity, floral aromas reminiscent of pineapples and pears, while 2-phenethyl acetate is associated with a floral, rose-petal and honey-like aroma (Boulton *et al.*, 1995).

Octanoic and decanoic acid concentrations were highest in the samples of average quality, significantly higher than those of both good and poor quality. The n-hexanol concentration in the average quality samples was significantly lower than in good and poor quality distillates (**Table 5.5**). n-Hexanol is described as having a grassy, herbaceous aroma (Boulton *et al.*, 1995) and the higher concentrations of n-hexanol in good and poor quality distillates could account for the herbaceous aromas detected in these distillates. 3-Hexenol is also commonly associated with a grassy herbaceous aroma, but could not be quantified in this study. In terms of accounting for n-hexanol's effect on the overall quality of the distillates, one can speculate that, in good quality distillates (shown to have higher concentrations of congeners such as isoamyl acetate, hexyl acetate, ethyl caprylate and hexanoic acid), the grassy, herbaceous aroma of n-hexanol is balanced by the positively associated aromas of the other congeners present. Similarly, the poor quality distillates with their high concentration of congeners with negatively associated brandy aromas (ethyl lactate, acetic acid and acetaldehyde) and lower concentrations of positively associated aromas could have accentuated the grassy, herbaceous

aromas of the n-hexanol present, and led to the perception of an unbalanced product.

5.3.5.2 2000 Distillates

Table 5.6 lists the mean values and p-values for ANOVA on the 2000 distillates. The concentrations of ethyl lactate and diethyl succinate were highest in the poor quality samples, significantly higher than the good and average quality samples (refer to **Table 5.6**). The concentrations of n-propanol, isoamyl acetate, hexyl acetate and 2-phenethyl acetate were highest in the samples of good quality, significantly higher than those of average and poor quality. This same trend was observed for n-propanol, isoamyl acetate and hexyl acetate in the 1999 good quality distillates. In studying the role of cultivar and region on South African brandy quality, Hough (1985) found that Colombar made an organoleptically more acceptable distillate than Palomino. He noted that, over both vintages studied, n-propanol values were significantly higher in Colombar distillates when compared to Palomino distillates originating in all regions except Robertson, where the values were found to be similar. Hough (1985) also noted that the ratios of isoamyl alcohol to n-propanol and isobutanol to n-propanol were higher in Palomino than in Colombar with the exception of those from the Robertson region and one vintage from the Barrydale region. In this study the mean ratio of isobutanol to n-propanol was 0.33 in good quality distillates, 0.80 in average quality distillates and 0.82 in poor quality distillates. The mean ratio of isoamyl alcohol to n-propanol was 2.4 in good quality distillates, 3.95 in those of average quality and 4.03 in poor quality distillates. This finding thus confirms Hough's conclusion that increased amounts of isobutanol and isoamyl alcohol, as reflected by ratios and total higher alcohols, have a detrimental impact on the quality of brandy distillates.

As was the case with the 1999 distillates, 2-phenyl ethanol appeared in lower concentrations in the good quality samples than when compared to the poor and average samples (although this was not significant). However, the concentration of 2-phenethyl acetate was significantly higher in the good quality distillates (**Table 5.6**), which was also observed in the 1999 distillates. Isobutanol ($p=0.003$) and n-hexanol ($p=0.003$) concentrations were significantly higher in the poor quality distillates than in those of good quality. Ethyl caprylate concentrations showed the opposite trend and were significantly lower in poor quality distillates, when compared to those of good and average quality (**Table 5.6**). Ethyl caproate concentrations exhibited the same behaviour ($p=0.001$). Contrary to what was observed in 1999, no significant concentration differences were noted for acetic, octanoic and decanoic acid.

5.4 CONCLUSIONS

In summary, base wines studied exhibited the same quality trends over both vintages in terms of region, cultivar and time of harvest. Base wines and distillates originating

from region 4 were of significantly lower quality than those from the remaining regions. There is a clear relationship between time of harvest and base wine and distillate quality and products made from early harvested grapes were of significantly higher quality. This could be attributed to the lowered incidence of microbial spoilage and grape rot early in the season as well as lowered ripeness or over-ripeness of grapes harvested at this time. Although wines made from Chenin blanc and a mix of Chenin and Colombar were consistently of higher quality, it is interesting to note that these differences were not as significant in the distillates. Any significant differences observed due to yeast strain in the base wines did not follow through to the distillates. The distillation process as well as the amount of yeast lees present during distillation may mask this effect.

The volatile aroma compound composition was found to differ significantly between the 1999 and 2000 wines and distillates, irrespective of the exclusion of those samples that had undergone partial or complete malolactic fermentation. Consequently, quality indicating compounds may vary from vintage to vintage depending on the composition of the base wines and thus also the distillates. Due to the observed differences between the two vintages studied, it is recommended that this study be continued over a further number of vintages in order to determine more robust quality indicating compounds. The limited number of volatile compounds determined in this study can also influence this variability, as there are other quality indicating compounds present which have not been determined.

The complexity of the relationships existing between volatile flavour compounds was highlighted using a CART analysis. The relationship between the quality of brandy base wines and the concentration of n-butanol, isoamyl acetate, ethyl lactate, ethyl caprylate, octanoic- and decanoic acid was the same as that reported in chapter 3 for young Chenin blanc wines. In the case of unaged distillates, increased levels of ethyl lactate also exert a negative influence on distillate quality. Ethyl caprate was found to be a quality indicator in the 1999 distillates (irrespective of the influence of malolactic fermentation). Hexyl acetate was found to be a quality indicator in the 2000 distillates as well as in the 1999 distillates not affected by malolactic fermentation.

Using sensory descriptive analysis (by means of a trained panel using the South African brandy aroma wheel), an aroma profile for good, average and poor quality distillates was established. Although the differences in profile between the good and average distillates were small, there were significant differences between the good and poor quality distillate profiles. Good quality distillates are characteristically intense in the 'fruity' aroma descriptor, whilst poor quality distillates show 'herbaceous' as the most intense aroma. It is interesting to note that even though relatively small differences in 'fruity', 'floral' and 'sweet associated' aroma intensity were noted, there were significant differences in the concentration of aromatically important esters such as isoamyl acetate, hexyl acetate and 2-phenethyl acetate between the good and average quality distillates. As unaged potstill distillates are

merely an intermediate of the brandy production process, it is important to bear in mind that the properties and relationships observed at this stage may be subject to change after the distillates have spent three years in oak maturation.

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CHAPTER 6

RESEARCH RESULTS

The influence of wood maturation on the composition of potstill brandy distillates

RESEARCH RESULTS

6. THE INFLUENCE OF WOOD MATURATION ON THE COMPOSITION OF POTSTILL BRANDY DISTILLATES

ABSTRACT

Fifty-eight potstill brandy distillates were placed into maturation in oak casks for three years. Each distillate was placed into six casks, of differing ages to comprise an average cask age of 12 years per lot. These lots were stored under the same conditions in the same warehouse. Samples were drawn and analysed at one, two and three years. Using repeated measures analysis of variance the changes in distillate volatile compound composition taking place during wood maturation as well as the changes in distillate volatile compound composition as a result of maturation in casks of differing ages, were studied. Classification and regression tree (CART) analysis was used to determine whether demographic and production factors still exert an influence on the volatile compound composition of the distillates after three years of wood maturation. The concentration of 2-phenethyl acetate, ethyl caprate, ethyl lactate, isobutanol, n-butanol and n-propanol did not vary significantly during the course of maturation. The concentration of acetic acid, diethyl succinate, ethyl caprylate, 2-phenyl ethanol, octanoic and decanoic acid increased during wood maturation. Differences on the basis of region and vintage were also evident during the course of and after wood maturation. The mean concentration of isoamyl acetate and hexyl acetate remained highest in distillates originating from the Rawsonville region. Isoamyl acetate, ethyl caprylate and octanoic acid concentrations remained lowest in distillates originating from the De Doorns region, whilst n-hexanol and 2-phenyl ethanol concentrations remained highest in distillates from this region. Distillates from the De Doorns region developed notably higher concentrations of ethyl acetate when compared to the remaining regions during wood maturation. The mean concentration of acetaldehyde, ethyl acetate, ethyl caproate, ethyl caprate, ethyl caprylate acetic acid and decanoic acid was found to be higher during the course wood maturation in new block barrels. The mean concentration of hexyl acetate and 2-phenethyl acetate was found to be lowest in distillates matured in the new block barrels. No significant differences in volatile compound concentration were observed in the distillates matured in the remaining barrel ages. After three years of wood maturation it was still possible to divide the distillates into two groups on the basis of acetaldehyde content, according to the yeast strains used to ferment the base wine. Yeast strain groupings were also identified on the basis of ethyl acetate. Three-year old distillates made from grapes harvested early in the season using yeast strain VIN13 for the base wine fermentation, contained significantly higher concentrations of isoamyl acetate than the remaining distillates. Distillates made from mid and late harvested grapes contained significantly lower concentrations of ethyl

caprate than those made with early harvested grapes. Isoamyl alcohol concentrations were significantly higher in three-year old distillates made from grapes harvested in mid and late season. Three-year old distillates made from table grapes contained significantly higher concentrations of isobutanol. Some differences in the concentration of medium chain fatty acids were noted between distillates. However, no clear trend for the effect of wood maturation on the medium chain fatty acids was evident. The mean concentrations of selected wood lactones, furanic aldehydes, volatile phenols and phenolic acids and aldehydes indicate that distillate maturation in the new block barrels imparts more wood maturation character than in the remaining barrels.

6.1 INTRODUCTION

Ageing in oak, while optional in the production of many wines, is a crucial element in the production of brandy. During wood maturation of brandy, oak not only imparts specific flavour and colour substances, but also allows for slow oxygenation of the spirit (Robinson, 1994). South African potstill brandies must, by law, be matured in oak casks of no larger than 340 litres for a minimum of three years (Weitz, 1997).

Thorough understanding of beverage maturation has been slow due to its complexity and difficulty of generalisation. The composition of oakwood used in brandy production is dependent upon a number of factors which include: oak species used, climatic conditions and soil fertility during growth, age of the trees, position of the cut on the stem and the proportion of heartwood to sapwood (Weitz, 1997). Accordingly oakwood composition, even amongst those oaks of the same species, can vary considerably. In addition, the chemical components of a distilled alcoholic beverage aged in wood can be classified as having their origin from one of three general sources. They are either: initially present in the distillate, extracted from the oakwood of the barrel or are the products of chemical reactions taking place during wood maturation. Both external and internal factors may influence the extent to which wood compounds may be extracted and may react. These factors include the type of wood used, wood drying method, the extent of barrel toasting, relative humidity at storage as well as the oxidative conditions present in the barrel during wood maturation (Singleton, 1995). Studies (Singleton, 1995; and references therein) have demonstrated that colour, acids, esters, furanic aldehydes, solids and tannins all increase during the ageing process.

Investigating the influence of all of the above-mentioned factors is beyond the scope of this study. It was decided to base this study on commercial brandy production practice within Distell. The focus is on the influence of oak maturation on the composition of potstill brandy distillates during the first three years of maturation. This chapter will only consider chemical changes taking place during maturation. The sensory effect of wood ageing on these distillates is discussed in chapter 7. Thus the aims of this study are to:

1. Investigate the volatile compound changes taking place within 58 distillates (chapter 4) on a yearly basis over three years.
2. Monitor the volatile compound differences arising from maturation in barrels of differing ages.
3. Determine whether the influence of vintage and region (demographic factors) as well as cultivar, harvest time and yeast strain (production factors), as described in chapter 4, on the volatile composition of potstill distillates after three years of oak maturation is still present and whether this is related to the findings in chapter 4 in the corresponding unaged distillates.

6.2 MATERIALS AND METHODS

6.2.1 EXPERIMENTAL OUTLAY

Refer to chapter 4 for the experimental outlay regarding base wine selection and potstill distillation. The South African Liquor Products Act requires that potstill brandies must be matured in oak casks no larger than 340 litres for a minimum period of three years. The thirty-three and twenty-five potstill distillates from 1999 and 2000, respectively, were placed into French oak casks for wood maturation over a period of three years. Each of the 58 distillates was placed into six oak casks of differing ages. These six oak casks per distillate will be referred to as lots. All 58 of the distillates used in this study were matured in the same warehouse under identical storage conditions in French oak casks. Exact origin (i.e. species and forest origin) of each barrel is unknown in commercial brandy production. All barrels initially underwent a medium toast at the start of their lifetime as a brandy barrel. The barrel ages selected were identical in each of the lots and were selected based on commercial practice whereby the average age of each commercial lot must amount to 12 years This average age was reached by using the following lot composition:

1 kol barrel: 3 year-old barrel (i.e. filled once previously with potstill brandy for three years)

2 kol barrel: 6 year-old barrel (i.e. filled twice previously with potstill brandy)

4 kol barrel: 12 year-old barrel (i.e. filled four times previously with potstill brandy)

N/blok barrel: Once a brandy barrel has been filled four times with potstill brandy it undergoes a form of rejuvenation. This is done by adding 80 oak blocks each with a dimension of 14 mm × 14 mm which have been toasted for two hours at 160°C. Hence the term *new blok* barrel.

5 kol blok barrel: This barrel is the oldest barrel that can possibly be used for brandy maturation. It has been filled with potstill brandy four times without blocks and four times with blocks. It is thus twenty-one years old when being filled with brandy for the last three year period.

Two *5 kol blok* barrels were used, whilst only one of the above-mentioned barrels was used in each lot. The term *kol* originates from the fact that the side of each barrel is painted with a white circle for every three-year cycle that it is used to mature potstill brandy. This enables the distilleries to easily identify the age of each barrel in stock. *Kol* is the Afrikaans term used for this white circle. Samples were drawn from each barrel after one, two and three years of wood maturation. These were then analysed for volatile aroma compounds (using gas chromatography), medium chain fatty acids (using GC) and phenolic compounds [using GC and high pressure liquid chromatography (HPLC)]. A composite sample comprising equal volumes of each of the samples drawn from the six barrels was also made up and analysed. This composite sample reflects commercial practice whereby all barrels within the lot are emptied into one tank to make up a composite sample of the lot. This composite sample then also underwent sensory evaluation and classification to determine its end use in commercial products.

6.2.2 ANALYSIS OF VOLATILE COMPOUNDS

The method as described in chapter 4 was used for distillate volatile compound analyses.

6.2.3 ANALYSIS OF MEDIUM CHAIN FATTY ACIDS

Underivatised C_{12} to C_{16} fatty acids were analysed by means of capillary gas chromatography. Ten mL of the distillate solution was used in a liquid-liquid extraction procedure with 5 mL of pentane and 0.4 mL of a 500 mg/L solution of pentadecanoic acid as the internal standard. Samples underwent continuous liquid-liquid extraction at 60 rpm in a rotary evaporator (without vacuum) for 30 minutes before removing 1 ml of the upper pentane layer for subsequent analysis. Samples were eluted on an HP6890 series gas chromatograph with an HP 7683 series autosampler using ChemStation as the integrating unit. Column type: HP-Innowax Polyethylene Glycol (capillary column); Dimensions: 30 m × 0.25 mm I.D. × 0.5 µm; Carrier gas flows: He (column) 1.9 mL/min (constant flow mode), He (make-up) 20 mL/min, H_2 30 mL/min, synthetic air 275 mL/min; Detector (FID) temperature: 280°C; Injector temperature: 250°C; Split ratio: 15:1; Split flow: 28.5 mL/min; Injection volume: 3 µL; Oven program: 120°C for 1 minute thereafter increasing to 250°C for 15 minutes at 10°C/minute.

6.2.4 ANALYSIS OF WOOD PHENOLS AND FURANIC ALDEHYDES BY GC

Neutral wood phenols were analysed by capillary gas chromatography. Six mL of the distillate solution was added to 4 mL of deionised water, 5 mL of diethyl ether and 0.4 mL of a 2-phenethyl acetate alcohol solution at 100 mg/L. Samples underwent continuous liquid-liquid extraction in a rotary mixer at 60 rpm (no vacuum) for 30 minutes before removing 1 mL of the upper diethyl ether layer for subsequent

analysis. Samples were eluted on an HP 5890 series II gas chromatograph with an HP 7673 injector couples to an HP 3396A integrator. Column: LabAlliance polyethylene glycol (capillary column); Dimensions: 60 m × 0.32 mm ID × 0.5 µm. Injector temperature: 200°C; Detector (FID) temperature: 250°C; Gas flows: H_2 (column) 3 – 5 ml/min, N_2 (make-up) 30ml/min, H_2 (FID) 30mL/min; synthetic air 300mL/min; Oven program: 80°C increasing to 210°C at 3 °C/min and thereafter up to 230°C at 10°C/min; Split flow: 10 mL/min; Column head pressure: 14 psi; Injection volume: 5 µL.

6.2.5 ANALYSIS OF PHENOLIC ACIDS AND RELATED ALDEHYDES BY HPLC

Phenolic acids and related aldehydes were determined using an Agilent 1100 high pressure liquid chromatograph. Column: Phenomenex Luna 5µm C18(2); Dimensions: 150 m × 4.60 mm × 5 µm; Oven temperature: 40°C; Column flow: 1mL/min; Stop time: 36 minutes; Post time: 9 minutes; Solvents: A = 100% acetonitrile; B =0.1% perchloric acid; Solvent A = 100 – (solvent B); Wavelength: 280 nm.

Table 6.1 Timetable (gradient) for HPLC run.

Time (minutes)	Solvent B	Flow	Pressure
0.00	100.00	1.00	250
28.00	60.00	1.00	250
29.00	0.00	1.00	250
35.00	0.00	1.00	250
36.00	100.00	1.00	250
44.00	100.00	1.00	250
45.00	100.00	1.00	250

6.2.6 STATISTICAL ANALYSIS

Repeated measures analysis of variance and non-parametric bootstrap *post hoc* tests were done using STATISTICA version 6.0. Classification and regression tree analysis was done using the CART program from Salford Systems. For details as to the theory of CART analyses please refer to chapter 4. In this instance the results of the CART analysis were subjected to a non-parametric bootstrap *post hoc* test. In the graphs generated by these two analyses, results are statistically significantly different when the 95% confidence intervals show no overlap.

6.3 RESULTS AND DISCUSSION

6.3.1 BEHAVIOUR OF VOLATILE COMPOUNDS DURING WOOD MATURATION IN COMPOSITE POTSTILL SAMPLES

In chapter 4 and 5 it was shown that the volatile aroma compound composition in unaged distillates can vary significantly and that seasonal (vintage), regional, cultivar and harvest time differences as well as the yeast strain used during fermentation can also affect the concentration of volatile compounds present. The quantitative volatile compound data from the unaged distillates and the composite samples of the one, two and three-year old wood matured distillates was used in a repeated measures analysis of variance. This analysis determined the influence of wood maturation on the concentration of volatile compounds present in the distillates after one, two and three years of wood maturation. In this manner, the changes in concentration for each of the volatile compounds studied over time could be plotted separately for each of the 58 distillates. This would have made discussion of the results and trends noted very laborious. Instead it was decided to view the data in terms of vintage and region. The vintages used were 1999 and 2000 (chapter 4 and 5). Regional division was done using the same regions as described in chapter 4. However, it was only possible to use four of the five regions as described in chapter 4 due to a missing set of analyses from the second year of maturation in region five, which made the dataset for this region incomplete.

6.3.1.1 Acetaldehyde

The concentration of acetaldehyde remained relatively constant over the three-year maturation period for all regions except region 4. In region 4 the mean concentration increased from 180 mg/l in year one to 290 mg/L in year two, thereafter decreasing slightly to a mean of 265 mg/L in year three (**Figure 6.1**). The mean acetaldehyde concentration, initially found to be higher in the 1999 unaged distillates, remained higher in the 1999 samples than in the 2000 samples over all three years.

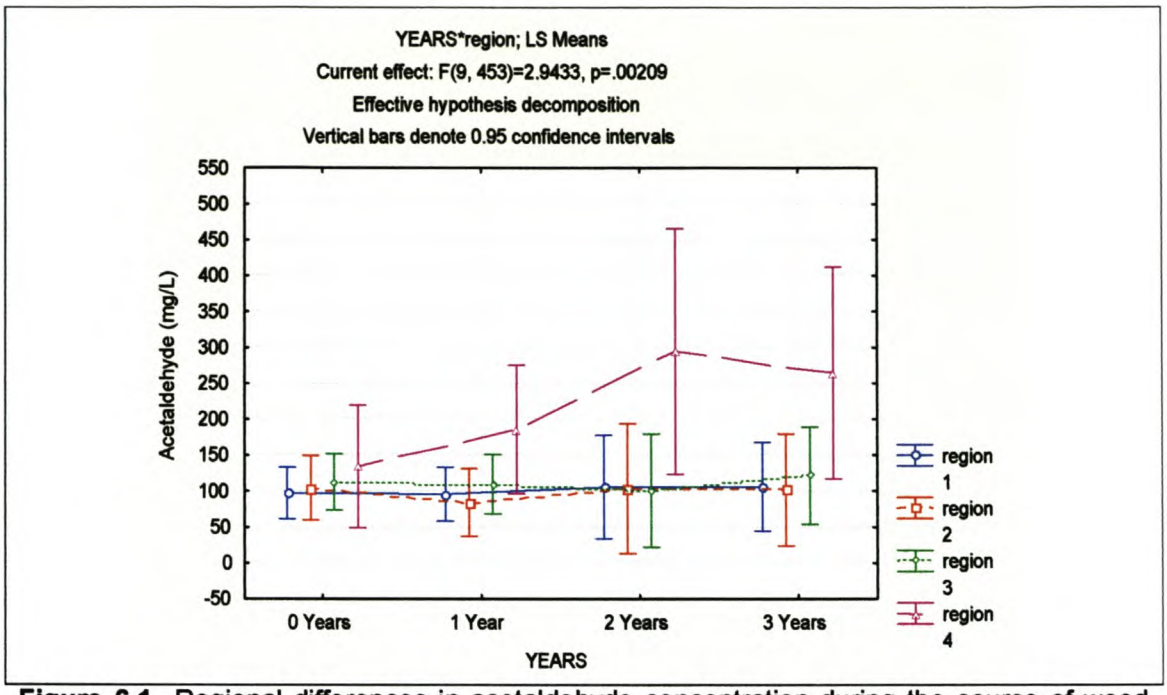

Figure 6.1 Regional differences in acetaldehyde concentration during the course of wood maturation in 1999 and 2000 distillates.

6.3.1.2 Ethyl acetate

Although the concentration of ethyl acetate was found to be significantly higher in the 1999 unaged distillates (chapter 4), this difference was not noted after one, two and three years of wood maturation (**Figure 6.2**). It is interesting to note that the ethyl acetate concentrations notably decreased in the first year of maturation, thereafter increasing somewhat during the following two years of wood maturation (**Figure 6.2**). Although there were no significant differences in ethyl acetate concentrations between regions in the unaged distillates, samples from region four developed notably higher concentrations of ethyl acetate when compared to the remaining regions during wood maturation (data not shown). Distillates from region four had a mean concentration of 425 mg/L ethyl acetate when compared to an overall mean of 310 mg/L in the remaining regions after three years of wood maturation.

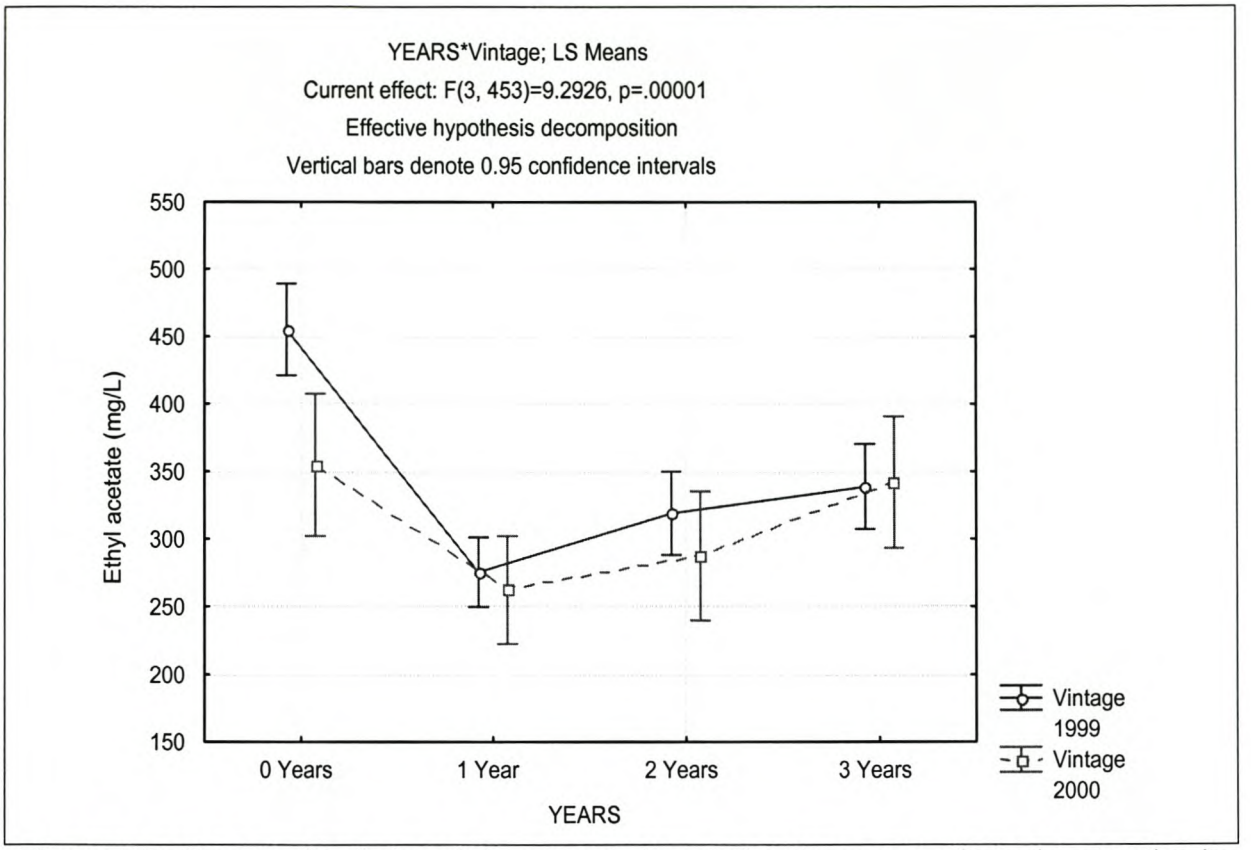

Figure 6.2 Changes in ethyl acetate concentration during the course of wood maturation in 1999 and 2000 distillates.

6.3.1.3 isoAmyl acetate

Isoamyl acetate concentrations remained significantly higher in the 2000 distillates over time even though the concentration of isoamyl acetate tended to decrease during the course of wood maturation in both vintages (data not shown). Onishi *et al.* (1977) found that the concentration of isoamyl acetate decreased during wood maturation. The mean concentration of isoamyl acetate remained highest in samples from region one and lowest in samples from region four in both vintages (**Figure 6.3**).

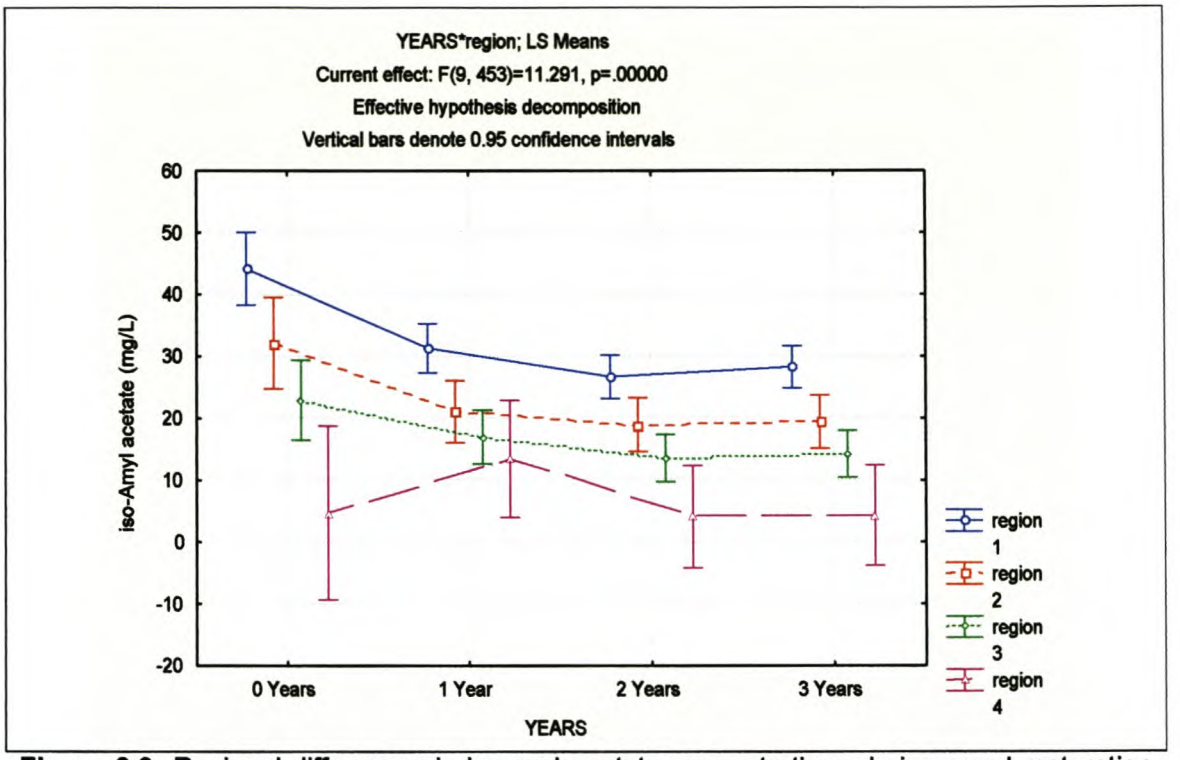

Figure 6.3 Regional differences in isoamyl acetate concentrations during wood maturation in 1999 and 2000 distillates.

6.3.1.4 Ethyl caproate

Although in chapter 4 it was shown that the concentration of ethyl caproate was significantly higher in the 1999 distillates, these differences were found to decrease with time and after three years of wood maturation, the concentration of ethyl caproate showed a near identical concentration of approximately 7 mg/L. The largest changes in concentration occurred in year one, where the mean concentration in the 1999 samples decreased by 3 mg/L whilst the mean concentration increased by 2 mg/L in the 2000 samples. From a regional perspective, no noticeable differences in mean concentration were noted over time in the composite samples.

6.3.1.5 Ethyl caprylate

In chapter 4 no significant vintage differences in unaged distillate ethyl caprylate concentrations were reported. This pattern continued over the three years of wood maturation. However, where the concentration of ethyl caproate was not found to increase with wood maturation, the concentration of ethyl caprylate tended to increase during the course of wood maturation (**Figure 6.4**). The concentration of ethyl caprylate remained significantly lower in samples originating from region 4 (**Figure 6.4**).

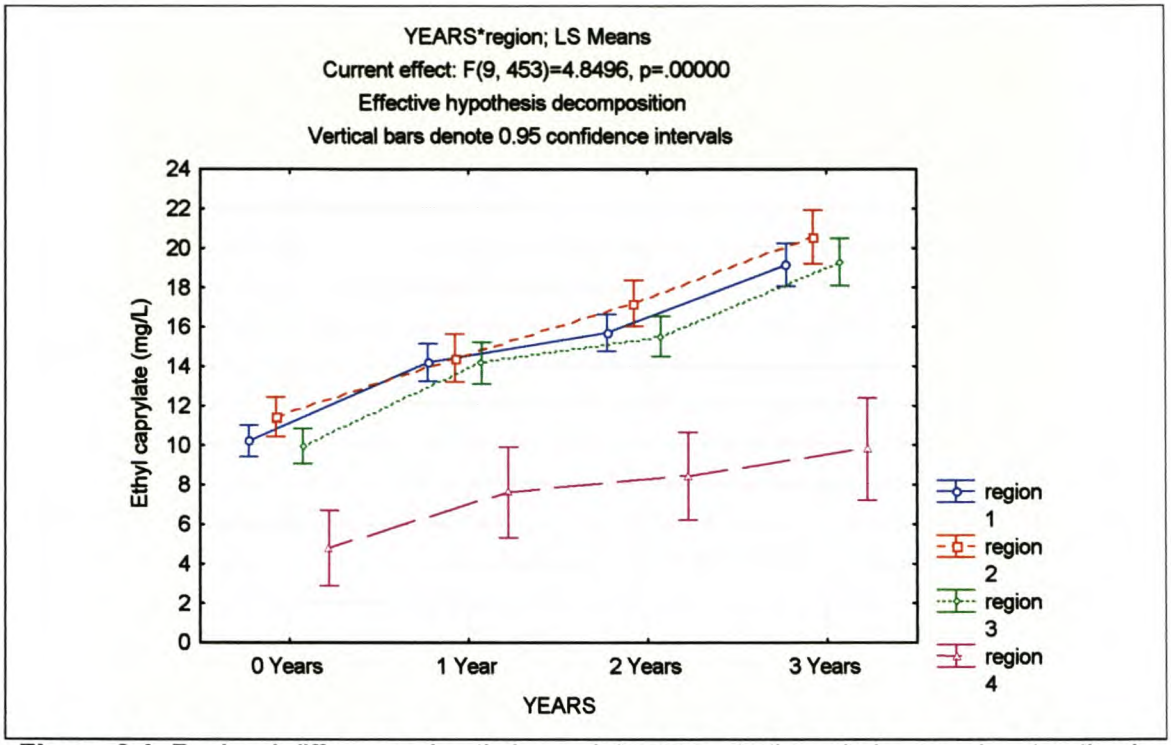

Figure 6.4 Regional differences in ethyl caprylate concentrations during wood maturation in 1999 and 2000 distillates.

6.3.1.6 Ethyl caprate

Although no significant changes in ethyl caprate concentrations were noted during the course of wood maturation, the 1999 distillates did contain significantly higher concentrations of ethyl caprate than the 2000 distillates after three years of wood maturation (data not shown). However, the mean concentration of ethyl caprate in samples from region 4 tended to decrease with time, whilst the mean concentration of ethyl caprate tended to increase with time in the remaining regions. This resulted in a significantly lower ethyl caprate concentration in samples from region 4 after three years when compared to the remaining regions (data not shown).

Conflicting results have been published regarding the behaviour of the three above-mentioned fatty acid ethyl esters. Reazin (1983) found that ethyl caprate concentrations decreased significantly during maturation in oak barrels, while the ethyl esters of caproate through to myristate remained unchanged or showed small decreases. Egorov *et al.* (1994) found that these lower molecular weight ethyl esters increased somewhat when cognac spirits were aged for up to 20 years, and then decreased slightly after 25 to 30 years of ageing. Onishi *et al.* (1977) noted that the ethyl esters of caproic, caprylic and capric acid, increased during ageing while ethyl laurate changed little or decreased slightly.

6.3.1.7 Ethyl lactate

Ethyl lactate concentrations remained constant during the course of wood maturation and remained significantly higher in those samples originating from region 4.

6.3.1.8 Diethyl succinate

Diethyl succinate concentrations tended to increase with time and were significantly higher after three years of wood maturation when compared to the concentration present in unaged distillates (data not shown). Samples from region 4 still possessed significantly higher concentrations of diethyl succinate over the three-year period. Onishi *et al.* (1977) discovered that diethyl succinate is a component that can be formed during oak ageing of distilled alcoholic beverages. Onishi *et al.* (1977) indicated that succinic acid is a normal component of oak, which esterifies with ethyl alcohol during the ageing process.

6.3.1.9 Hexyl acetate

The concentration of hexyl acetate showed a slight increase in concentration after one year of maturation, but decreased again after year two and remained relatively constant during the remainder of the three-year period (data not shown). Chapter 4 noted that unaged distillates from region one contained significantly higher concentrations of hexyl acetate. This remained the case after three years of wood maturation. Onsihi *et al.* (1977) found that the concentration of hexyl acetate tended to decrease during wood maturation.

6.3.1.10 2-Phenethyl acetate

The concentration of 2-phenethyl acetate was significantly higher in the 2000 unaged distillates (chapter 4) and remained significantly higher during the course of wood maturation. The concentration of 2-phenethyl acetate remained relatively constant during the course of wood maturation, although the mean concentration of samples in year one was lower than in the unaged, two and three year old samples (data not shown). Onishi *et al.* (1977) found that 2-phenethyl acetate concentrations decreased during oak ageing.

6.3.1.11 n-Propanol

No significant differences in n-propanol concentrations were noted on the basis of region or vintage during the course of wood maturation (data not shown).

6.3.1.12 isoButanol

The concentration of isobutanol remained relatively constant in samples from all regions excepting region four, which showed a significant increase in concentration after the second and third year of maturation (**Figure 6.5**). This was also noted for isoamyl alcohol concentrations (in the 2000 samples from region four) as well as the 2-phenyl ethanol concentrations in samples from region four (irrespective of vintage).

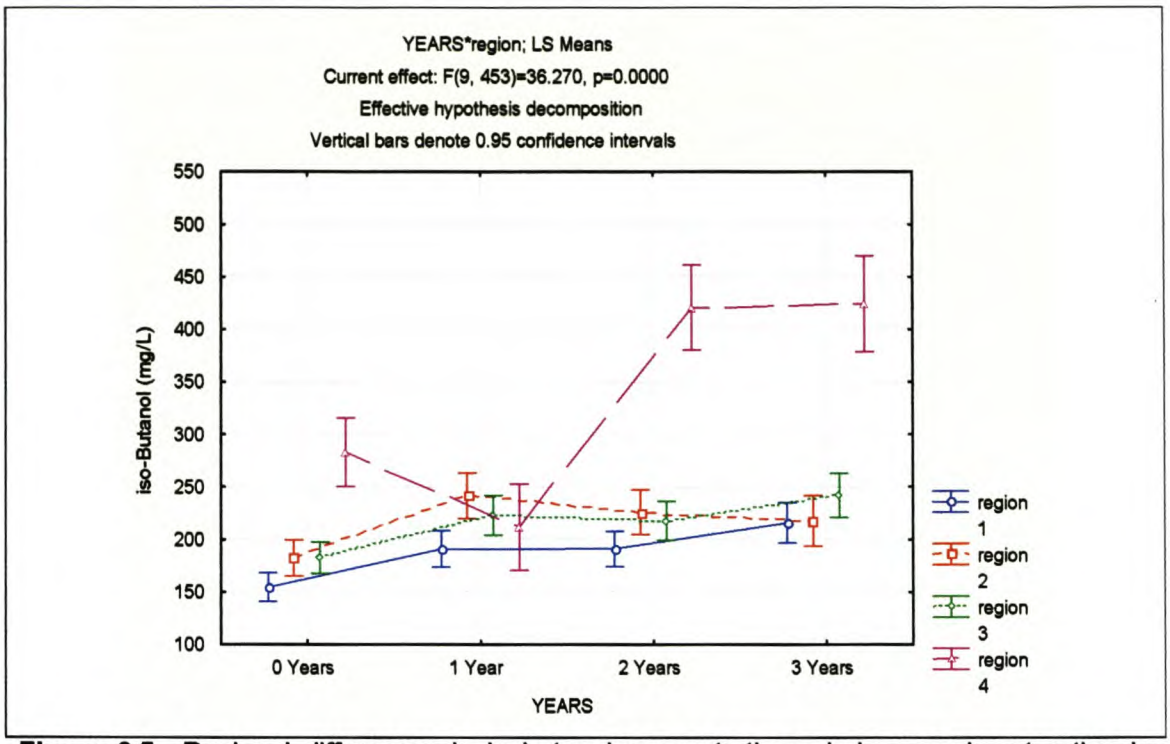

Figure 6.5 Regional differences in isobutanol concentrations during wood maturation in 1999 and 2000 distillates.

6.3.1.13 n-Butanol

No significant differences in n-butanol concentrations on the basis of region or of vintage were noted during the course of maturation (data not shown).

6.3.1.14 isoAmyl alcohol

Figure 6.6 depicts the vintage and regional differences in isoamyl alcohol concentrations from unaged to after three years of wood maturation. It is evident that the two vintages followed differing concentration patterns. Whereas the concentration of isoamyl alcohol in the 1999 distillates tended to decrease during the course of wood maturation, the 2000 distillates showed the opposite pattern. The concentration of isoamyl alcohol in distillates originating from region four in 2000 was significantly higher than the remaining regions after two and three years of wood maturation, whereas no significant differences were noted for this region in 1999.

6.3.1.15 n-Hexanol

In chapter 4 it was noted that n-hexanol concentrations were highest in the unaged distillates made from table grapes. These originate from region 4. The regional differences observed in n-hexanol concentrations in chapter 4 continued to be significant during the course of wood maturation. Although not significant, the mean concentration of n-hexanol after three years of wood maturation was higher than in the unaged distillates, irrespective of region (data not shown).

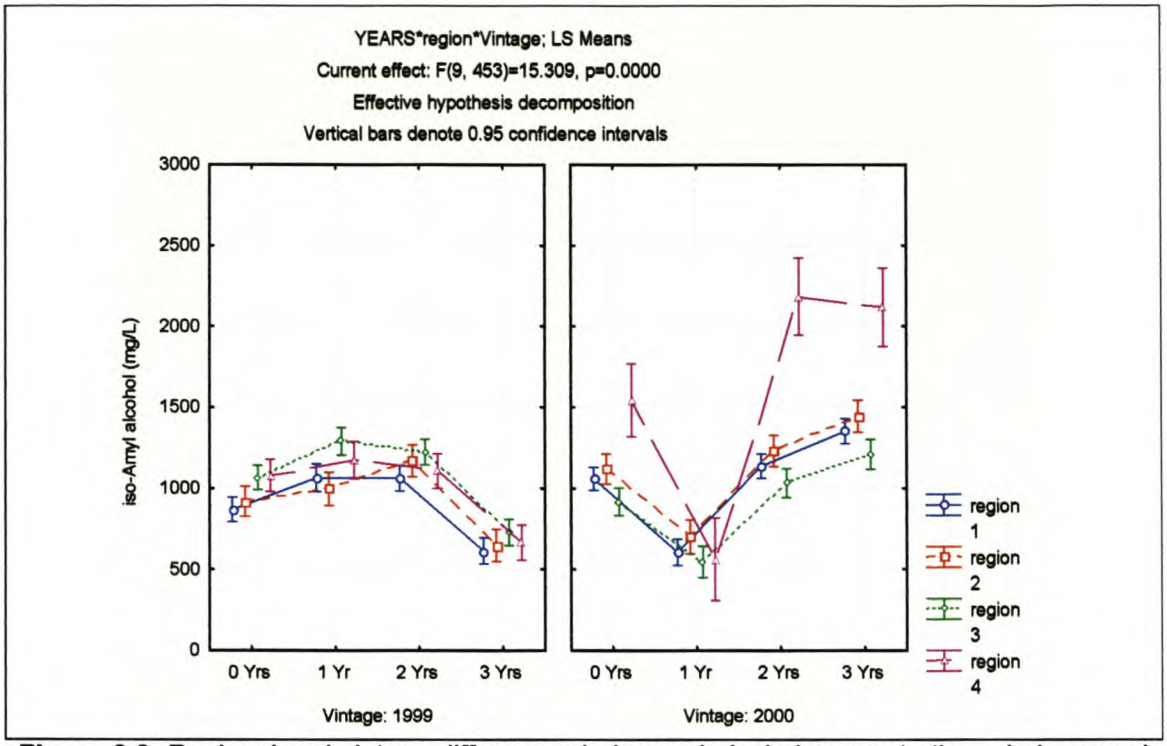

Figure 6.6 Regional and vintage differences in isoamyl alcohol concentrations during wood maturation for 1999 and 2000 distillates respectively.

6.3.1.16 2-Phenyl ethanol

After three years of wood maturation, region four followed by region two possessed significantly higher concentrations of 2-phenyl ethanol. This was also observed in the unaged distillates in chapter 4. The mean concentration of 2-phenyl ethanol tended to increase from unaged to three years old (**Figure 6.7**). Egorov *et al.* (1994) investigated the content and transformation rate of alcohols in cognac spirits aged for 2, 7, 15, 20, 25 and 30 years. They found that the amount of low molecular weight alcohols decreased with up to 20 years of ageing, and then increased, but to a far lesser degree than the higher molecular weight alcohols, in particular 2-phenyl ethanol. Although this alcohol is formed during alcoholic fermentation, it can also be extracted by the distillate from the oakwood during maturation.

6.3.1.17 Acetic acid

Acetic acid concentrations increased during the course of wood maturation. Although no significant differences were noted in acetic acid concentrations in the unaged distillates, the 1999 distillates contained significantly higher concentrations of acetic acid after three years of wood maturation. From **Figure 6.8** it is apparent that the mean concentration of acetic acid in samples from region 4 was significantly higher than that of the remaining regions after three years of maturation. Reazin (1983) added C_{14} marked ethanol to ageing whisky and followed the marker in acetic acid and ethyl acetate. Based upon the relative specific activity, 27% to 55% of the acetic acid arose from oxidation of the ethanol to acetic acid by way of acetaldehyde. The

rest originated from the wood. This wood-derived acetic acid can either originate from direct hydrolysis and extraction from the wood. A much larger part, comprising up to 4% of the wood, can be released via alkaline hydrolysis and somewhat less by acid hydrolysis, which is evidently derived from the wood hemicelluloses (Nishimura *et al.*, 1983).

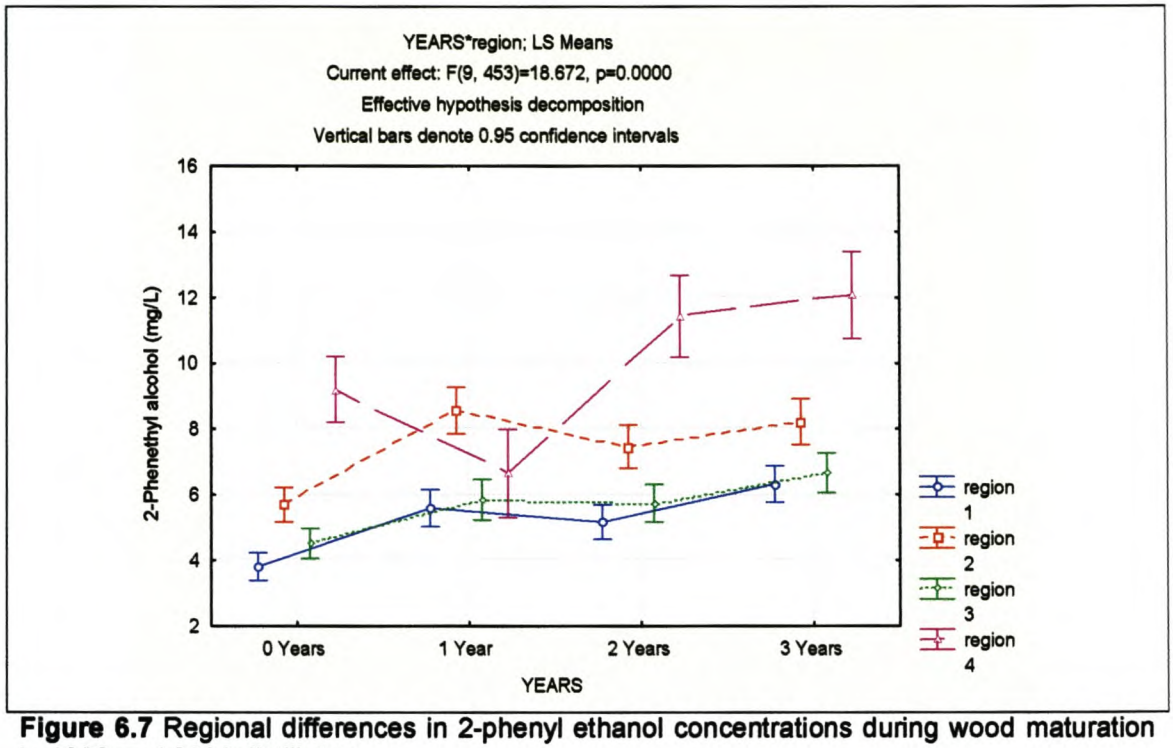

Figure 6.7 Regional differences in 2-phenyl ethanol concentrations during wood maturation in 1999 and 2000 distillates.

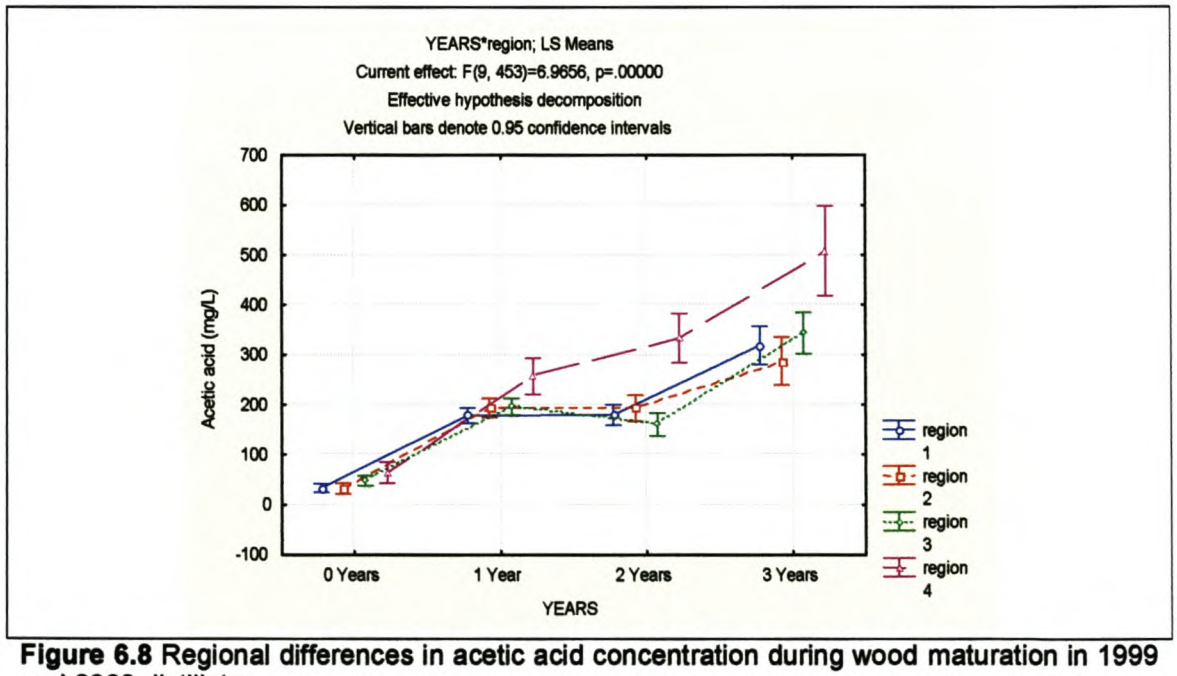

Figure 6.8 Regional differences in acetic acid concentration during wood maturation in 1999 and 2000 distillates.

6.3.1.18 Hexanoic acid

The mean concentration of hexanoic acid tended to increase during the three years of wood maturation, although this increase was not significant over the three-year period (data not shown).

6.3.1.19 Octanoic acid

The regional differences in octanoic acid concentration noted in the base wines and unaged distillates (chapter 4) were also noted after three years of wood maturation. Distillates originating from region 4 still contained significantly lower concentrations of octanoic acid after three years of wood maturation than those from the remaining regions. Although not significant, the concentration of octanoic acid tended to be higher in the distillates after three years of maturation when compared to the concentrations in the unaged distillates (data not shown).

6.3.1.20 Decanoic acid

As was noted in the unaged distillates, table grapes originating from region four continued to possess the lowest mean concentrations of decanoic acid during wood maturation although these differences were not significant after three years of wood maturation (**Figure 6.9**). The mean concentration of decanoic acid was higher after three years of wood maturation when compared to the unaged distillate concentrations. This could be ascribed to the 1999 samples, which showed significantly higher concentrations at three years of wood maturation (**Figure 6.10**).

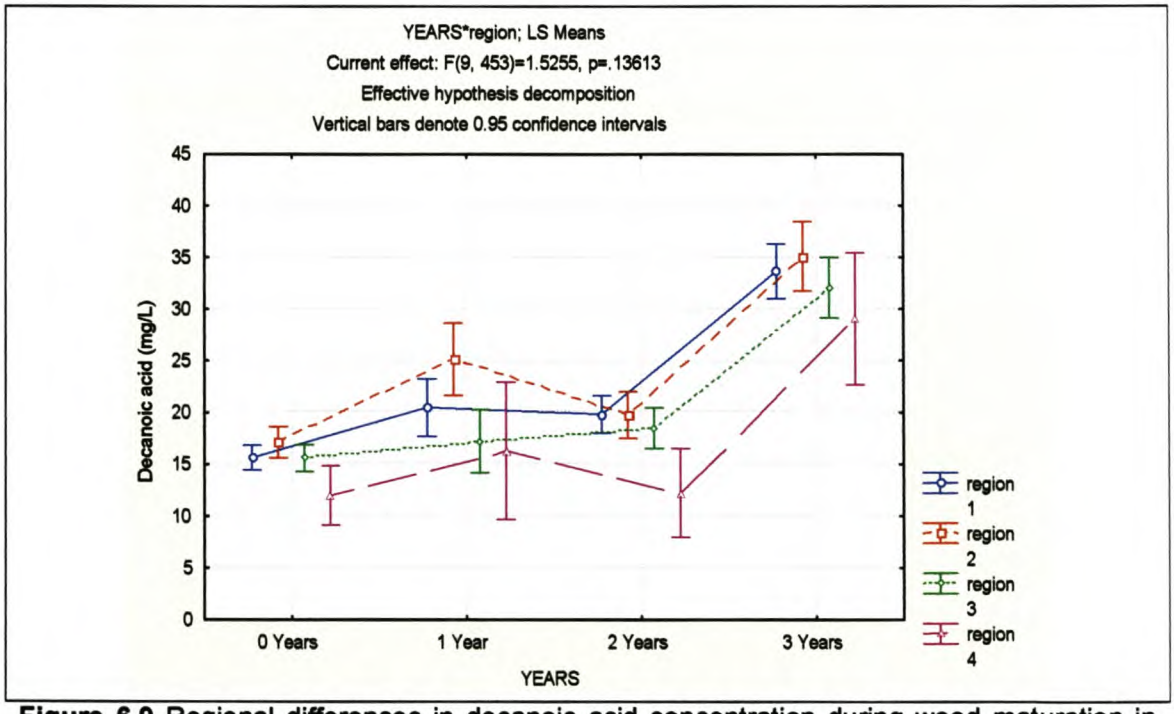

Figure 6.9 Regional differences in decanoic acid concentration during wood maturation in both 1999 and 2000 distillates.

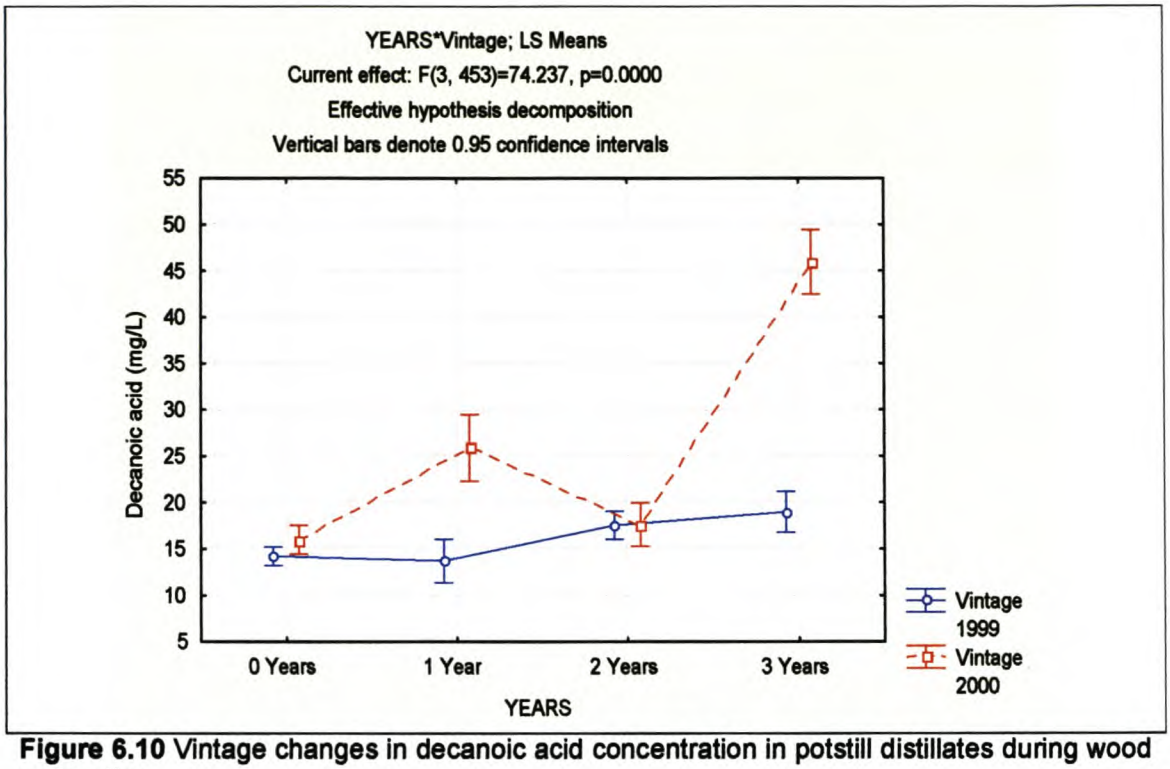

Figure 6.10 Vintage changes in decanoic acid concentration in potstill distillates during wood maturation.

6.3.2 COMPARISON OF VOLATILE COMPOUND BEHAVIOUR IN BARRELS OF DIFFERING AGES

Differences in distillate volatile compound concentrations between barrels of differing ages were also investigated using a repeated measures analysis of variance. Few differences in distillate volatile composition were noted between the *1 kol, 2 kol, 4 kol* and *5 kol* block barrels. However, the new block barrels (*N/blok*) did exhibit differences in volatile compound concentration when compared to the remaining barrel ages. The mean concentration of acetaldehyde (**Figure 6.11**), ethyl acetate (**Figure 6.12**), ethyl caproate (**Figure 6.13**), ethyl caprate, ethyl caprylate (**Figure 6.14**), acetic acid (**Figure 6.15**) was found to be higher with wood maturation progression in new block barrels. Nishmura *et al.* (1983) found that considerable amounts of acetic acid can also be released from wood during pyroligenous toasting. As these new block barrels contain freshly toasted oak blocks, this may account for the increased concentration of acetic acid when compared to the remaining barrels. The increased presence of acetic acid could also account for the increased presence of ethyl acetate, which is formed by esterification of acetic acid in the presence of ethyl alcohol (Egorov *et al.*, 1994). The mean concentration of hexyl acetate (**Figure 6.16**) and 2-phenethyl acetate (**Figure 6.17**) was found to be lower in the new block (*N/blok*) barrels when compared to the remaining barrels.

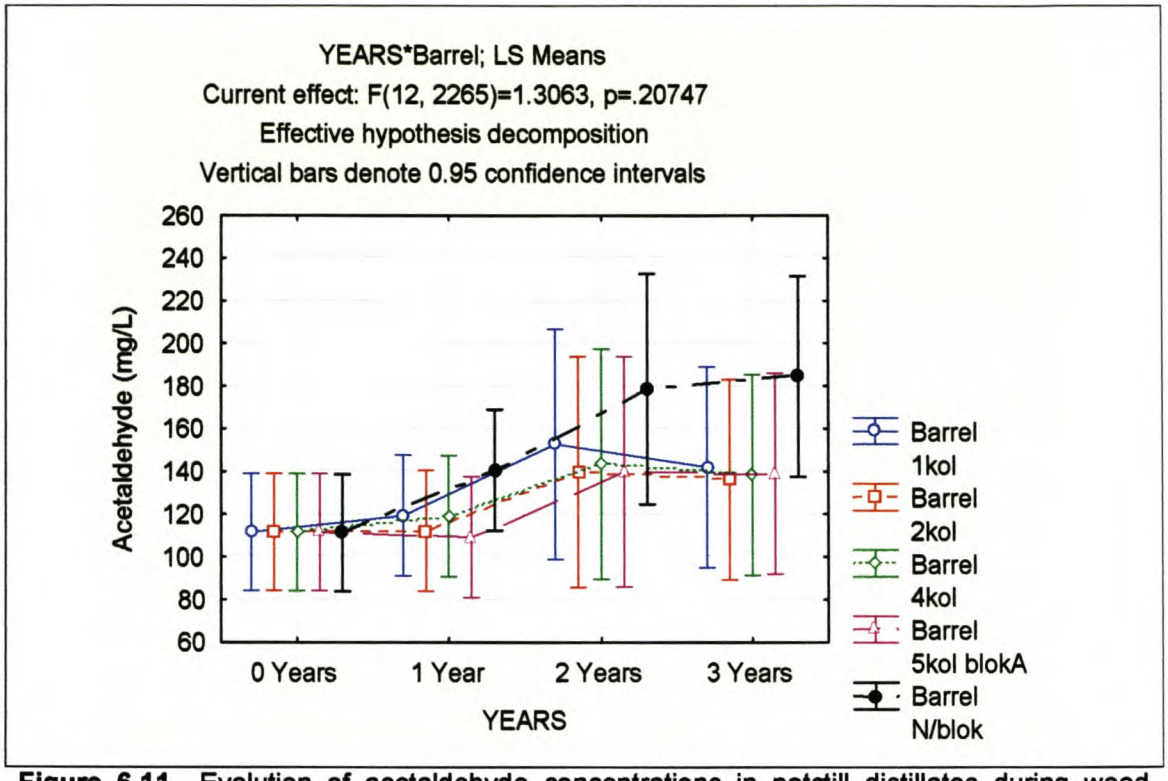

Figure 6.11 Evolution of acetaldehyde concentrations in potstill distillates during wood maturation in barrels of differing ages.

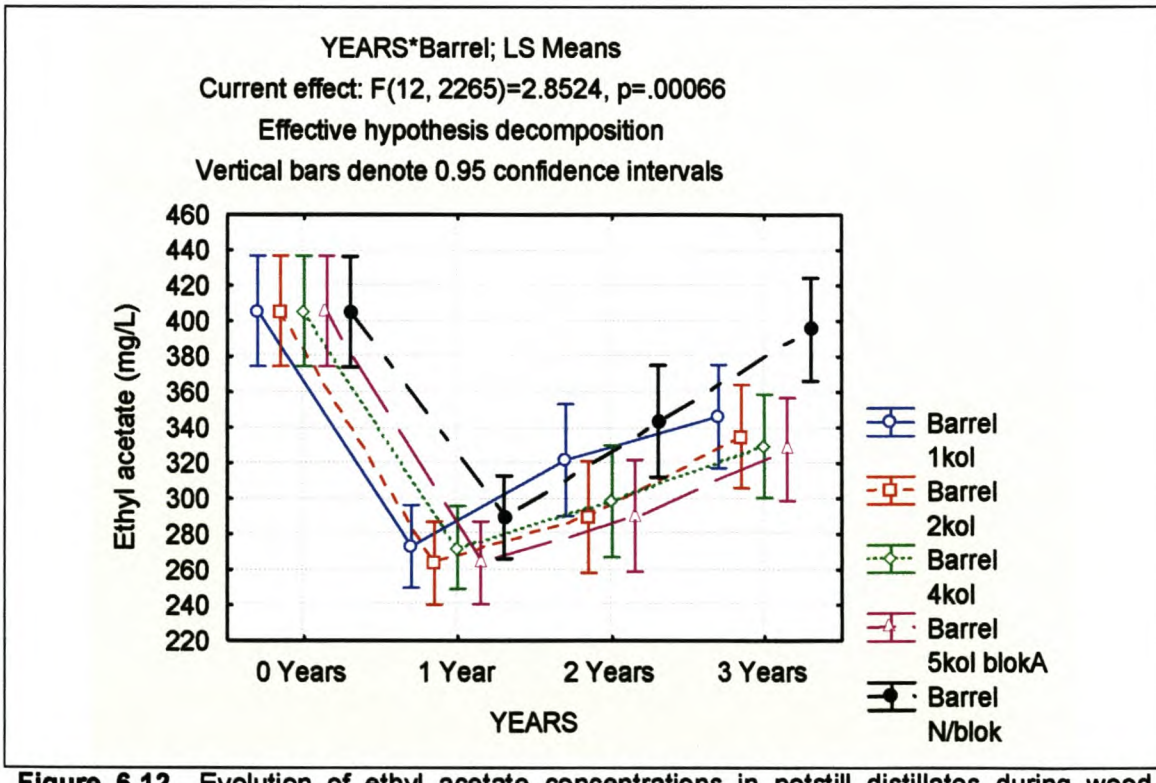

Figure 6.12 Evolution of ethyl acetate concentrations in potstill distillates during wood maturation in barrels of differing ages.

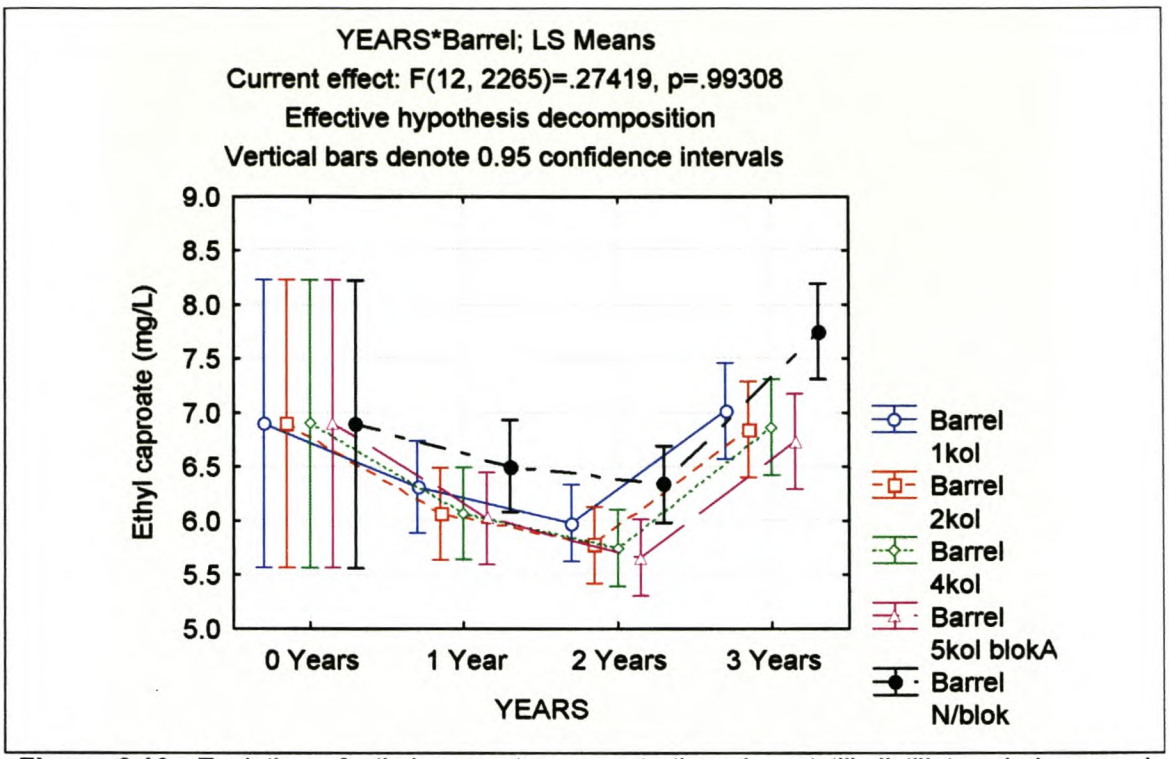

Figure 6.13 Evolution of ethyl caproate concentrations in potstill distillates during wood maturation in barrels of varying ages.

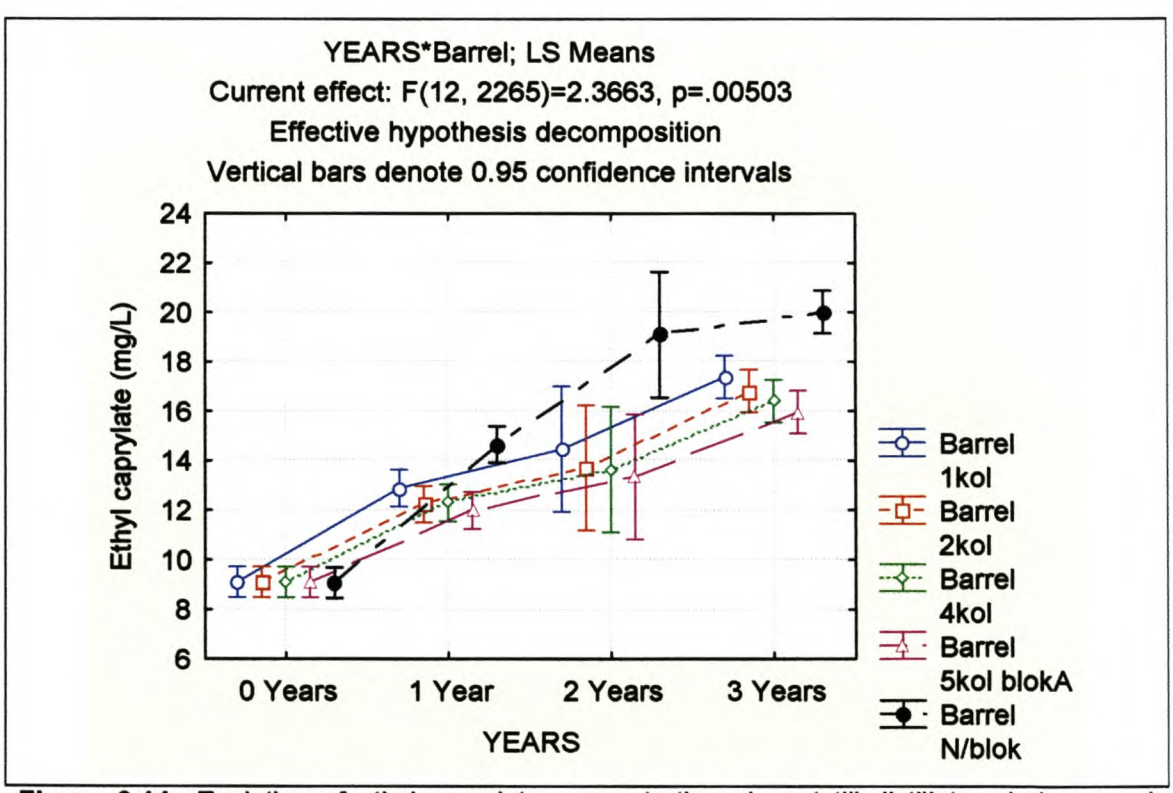

Figure 6.14 Evolution of ethyl caprylate concentrations in potstill distillates during wood maturation in barrels of differing ages.

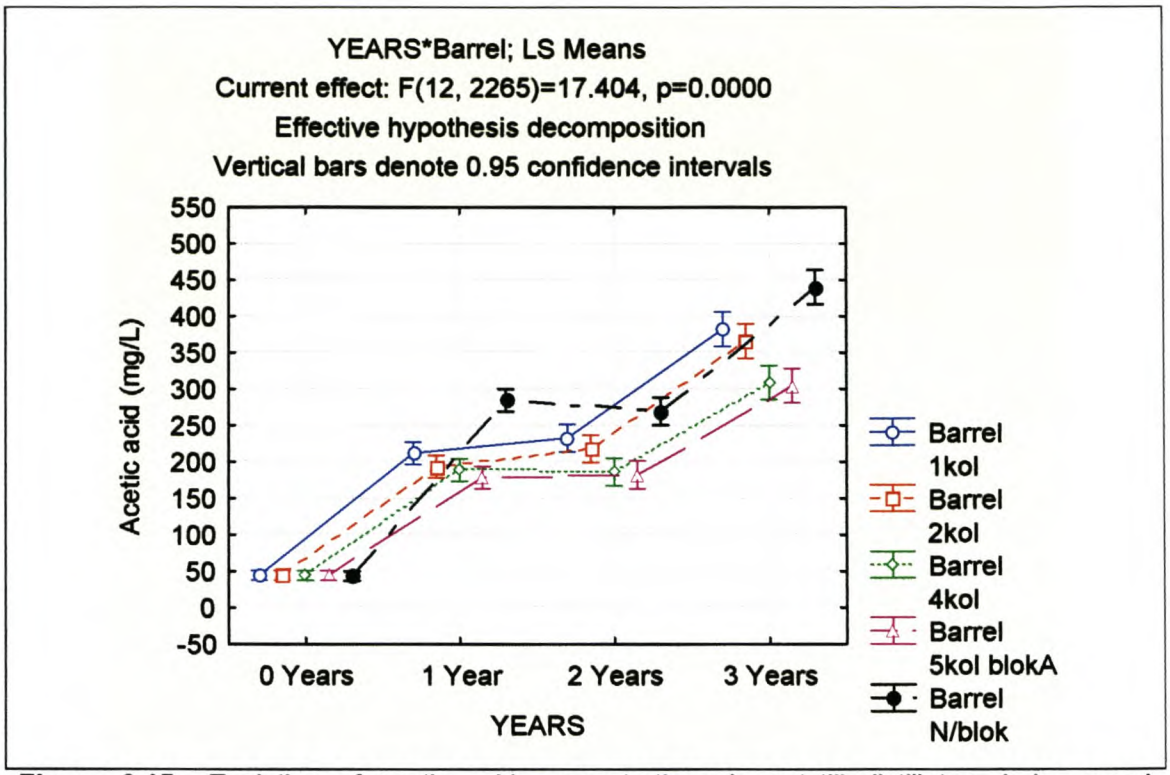

Figure 6.15 Evolution of acetic acid concentrations in potstill distillates during wood maturation in barrels of differing ages.

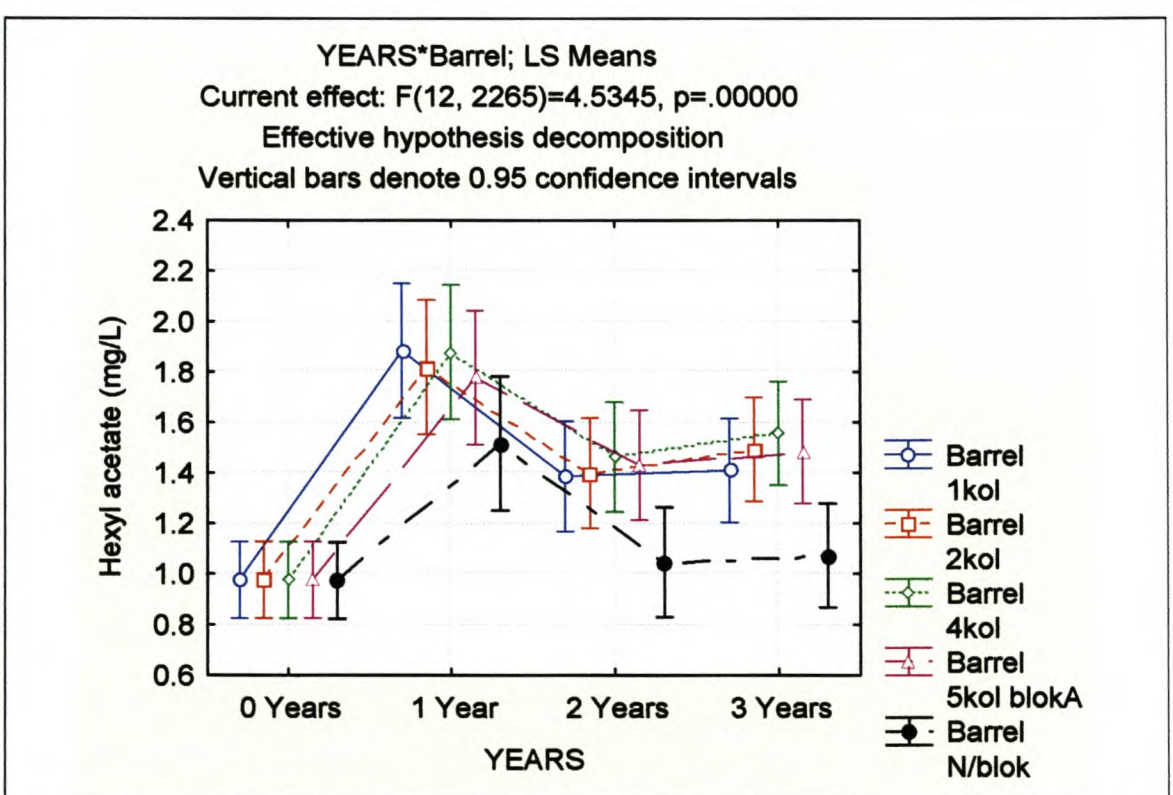

Figure 6.16 Evolution of hexyl acetate concentrations in potstill distillates during wood maturation in barrels of differing ages.

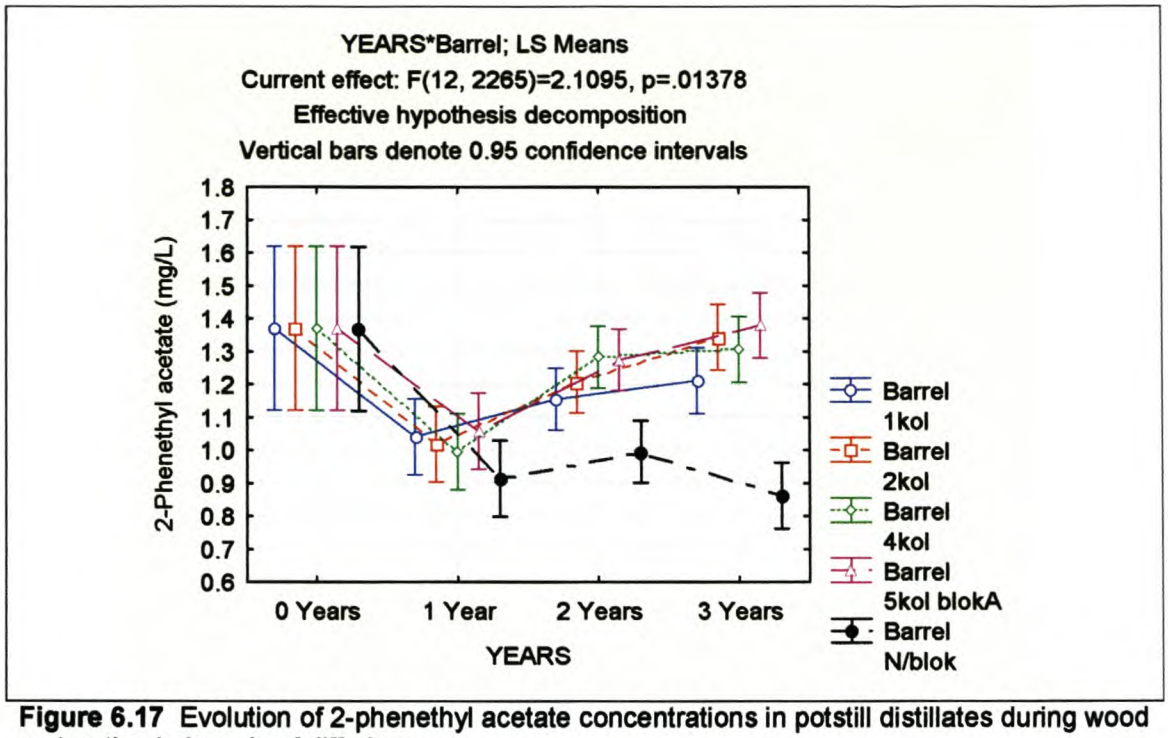

Figure 6.17 Evolution of 2-phenethyl acetate concentrations in potstill distillates during wood maturation in barrels of differing ages.

6.3.3 CART ANALYSIS OF DEMOGRAPHIC AND PRODUCTION VARIABLES ON VOLATILE COMPOUND COMPOSITION OF THE THREE-YEAR OLD COMPOSITE POTSTILL SAMPLES

In chapter 4 the influence of vintage, region, cultivar, harvest time and yeast strain on the volatile composition of brandy base wines and unaged distillates was studied. As the three-year old composite potstill sample is the final product in brandy production prior to blending, it was decided to investigate whether any of the above-mentioned, so-called demographic and production factors have a significant influence on any of the volatile compounds quantified after three years in maturation. Due to the complexity of interaction that may take place between these factors, it was decided to use a CART analysis, verified by a bootstrap *post hoc* test for this purpose, rather than an analysis of variance.

6.3.3.1 Acetaldehyde

In chapter 4 it was possible to divide the yeast strains into two groups on the basis of low and high acetaldehyde production in the resulting unaged distillates. After three years of wood maturation, it was still possible to divide the distillates into two groups according to the yeast strains used to ferment the base wine on the basis of acetaldehyde production. In this instance, distillates made with yeast strains 20-2, OY and FAIEDV contained significantly higher amounts of acetaldehyde when compared to the remaining strains (mean high acetaldehyde producing yeasts = 450 mg/L; mean low acetaldehyde producing yeasts =100 mg/L).

6.3.3.2 Ethyl acetate

In the unaged distillates (chapter 4) an increase in ethyl acetate concentration in those distillates made from VIN13 and from region 1 was noted. Differences based on cultivar, vintage and yeast strain were also noted in the unaged distillate CART analysis (chapter 4). After three years of wood maturation, CART was able to distinguish three significantly different groups of distillates based on their ethyl acetate concentrations (**Figure 6.18**). Distillates made with yeast strains 20-2, OY and NT117 comprised the group with the highest ethyl acetate concentration. Strains 20-2 and OY also comprised the group with the highest ethyl acetate concentration in the unaged distillates. However, strain NT117 formed part of the two lowest ethyl acetate containing groups in the unaged distillates. In spirits, such as these brandy distillates, with their high alcohol content (68-70% v/v), acetic acid is partially esterified to ethyl acetate (Egorov *et al.,* 1994). Thus, this reaction which takes place during wood maturation can also influence the concentration of ethyl acetate in the three-year old distillates and could explain the discrepancy between the unaged and three-year old CART results.

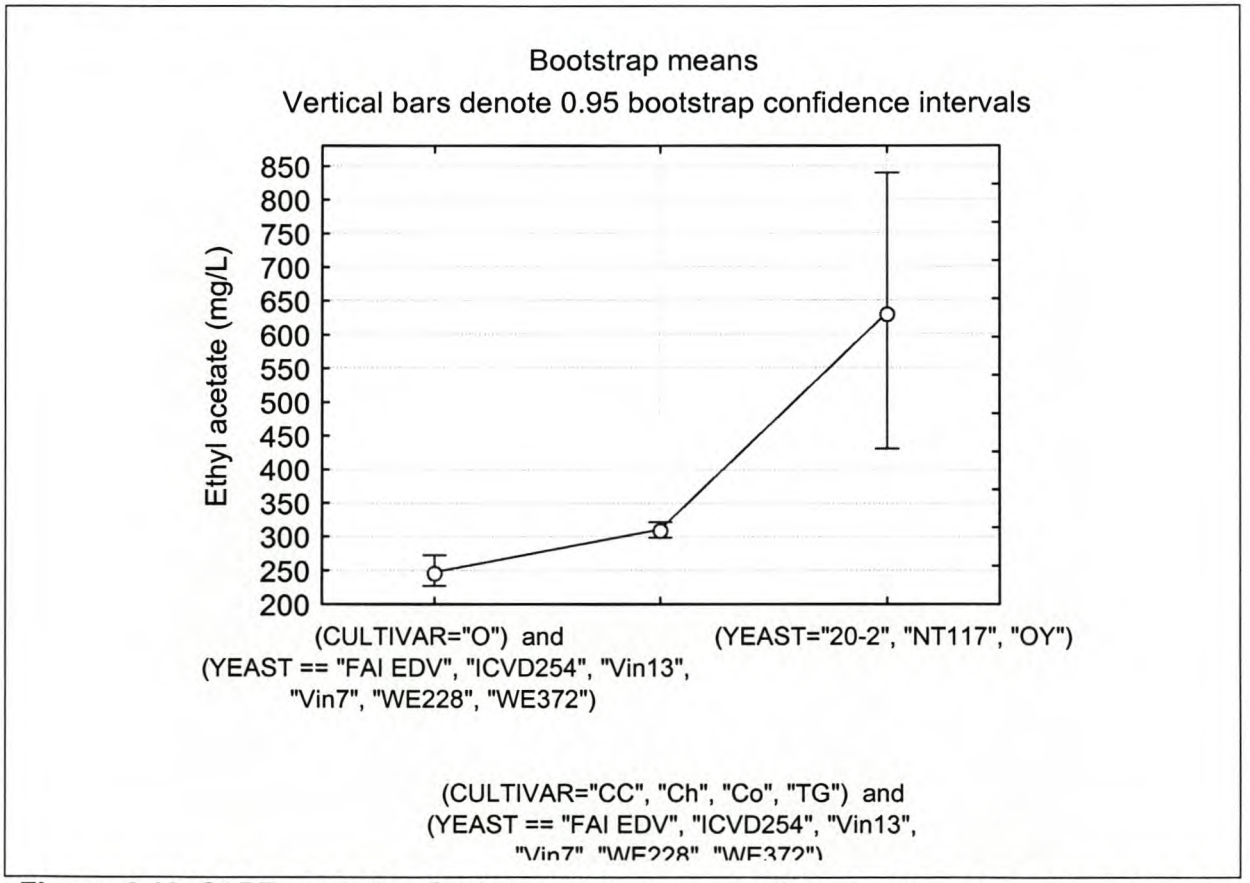

Figure 6.18 CART analysis of ethyl acetate concentrations in three-year old composite distillates based on demographic and production variables (Key: O = other varieties; CC = Chenin blanc/ Colombar; Ch = Chenin blanc; Co = Colombar; TG = table grapes).

6.3.3.3 isoAmyl acetate

After three years of wood maturation, distillates made from grapes harvested early in the season using yeast strain VIN13 contained significantly higher concentrations of

isoamyl acetate than the remaining distillates. Harvest time was found to be the largest discriminating factor for isoamyl acetate concentrations at this point. Those three-year old distillates made from grapes harvested in mid or late season contained the lowest concentration of isoamyl acetate (**Figure 6.19**). In chapter 4 it was also noted that unaged distillates made with strain VIN13 from regions 1 and 2 contained significantly higher concentrations of isoamyl acetate than those made from WE228 and ICVD254 in the same regions. They also noted that isoamyl acetate concentrations were higher in wines made from early harvested grapes in regions 1, 2 and 3. Although there is no discrimination of isoamyl acetate concentrations on the basis of region after three years of wood maturation, the yeast strain differences between these three strains are still evident.

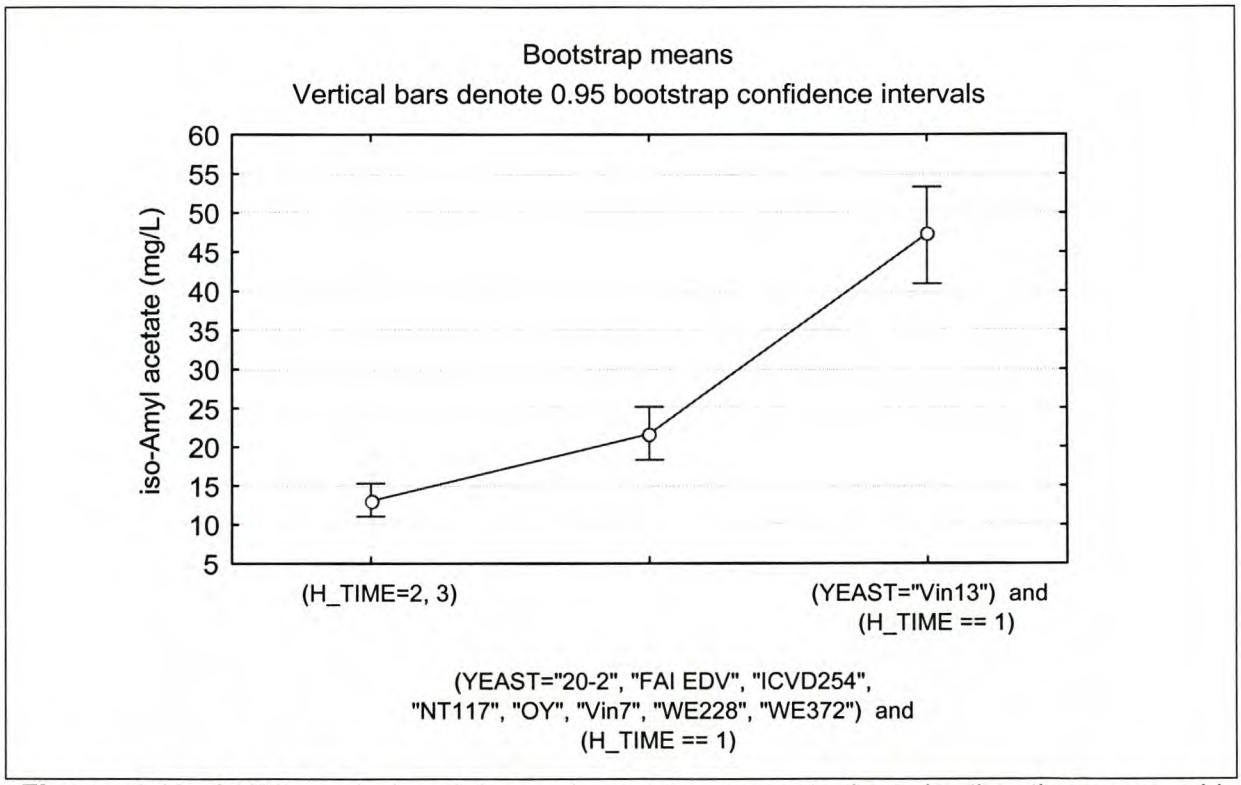

Figure 6.19 CART analysis of isoamyl acetate concentrations in the three-year old composite distillates based on demographic and production variables.

6.3.3.4 Ethyl lactate

As was noted in chapter 4, distillates originating from region 4, made using table grapes possessed significantly higher concentrations of ethyl lactate than three-year old distillates from other regions and made with other cultivars. Harvest time differences were not noted in the other regions and cultivars (data not shown).

6.3.3.5 Ethyl caproate

Three-year old distillates made from table grapes possessed the lowest concentration of ethyl caproate, followed by those distillates made from "other" varieties. Within those distillates originating from Chenin blanc, Colombar and a mix of Chenin/Colombar, it was further possible to differentiate ethyl caproate

concentrations on the basis of yeast strain. With these cultivars, three-year old distillates originally made with strains 20-2 and VIN7 possessed the highest concentrations of ethyl caproate (**Figure 6.20**).

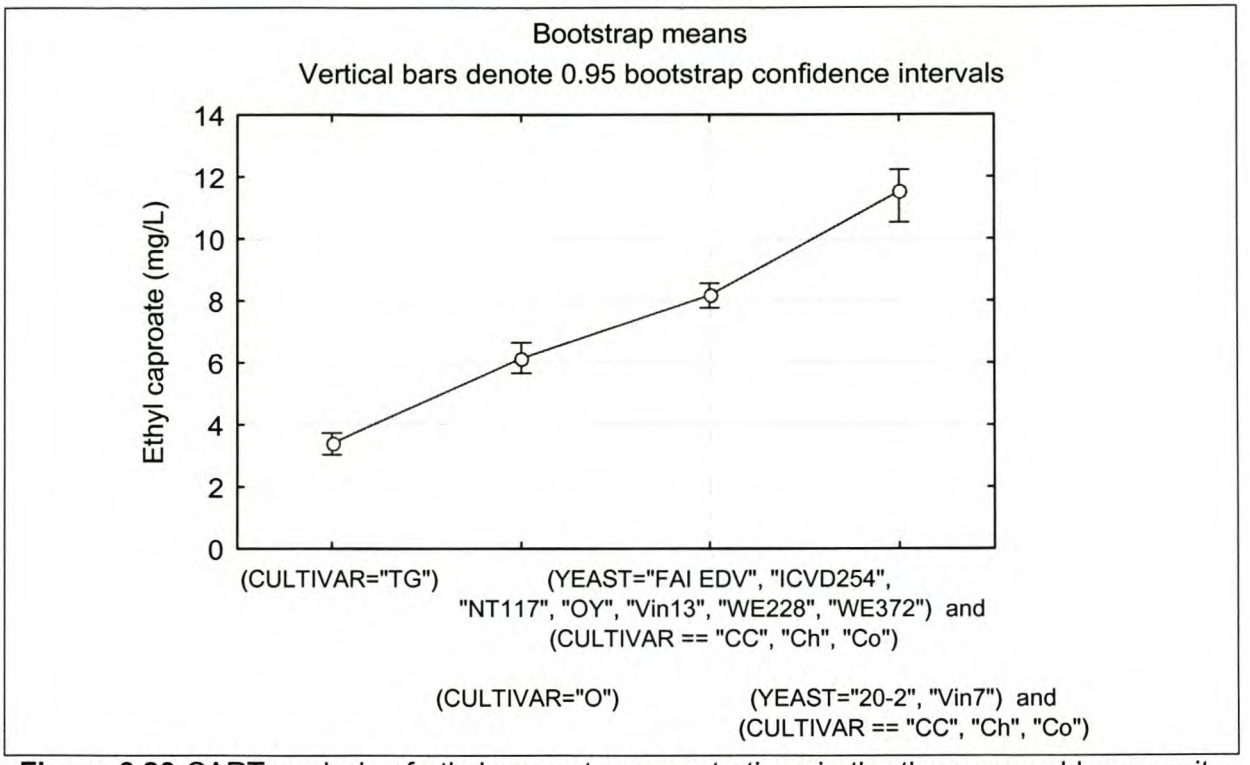

Figure 6.20 CART analysis of ethyl caproate concentrations in the three-year old composite distillates based on demographic and production variables (Key: O= other varieties, TG = table grapes; CC = Chenin blanc/Colombar; Co = Colombar).

6.3.3.6 Ethyl caprylate

As was noted in chapter 4 in the unaged distillates, grapes and "other" varieties from regions 4 and 5 continued to possess significantly lower concentrations of ethyl caprylate after three years of wood maturation. After three years of wood maturation, those distillates originating from regions 1, 2 and 3 originally fermented with strains 20-2, VIN7, VIN13 and WE372 contained significantly higher concentrations of ethyl caprylate (data not shown).

6.3.3.7 Ethyl caprate

As was noted in chapter 4, harvest time continued have the largest impact on the concentrations of ethyl caprate after three years of wood maturation. Those distillates made from mid and late harvested grapes contained significantly lower concentrations of ethyl caprate than those made from early harvested grapes. Within those distillates made from early harvested grapes, those originally fermented with strains VIN13, 20-2 and VIN7 contained significantly higher concentrations of ethyl caprate when compared to the remainder of the strains after three years of maturation (data not shown).

6.3.3.8 2-Phenethyl acetate

In chapter 4 it was shown that unaged distillates made with strains VIN13 and NT117 consistently contained higher levels of 2-phenethyl acetate, however, this was also influenced by cultivar type. After three years of wood maturation, those distillates made with strains NT117 and VIN13 still contained significantly higher concentrations of 2-phenethyl acetate, although there was no further discrimination within this group on the basis of region (data not shown).

6.3.3.9 Hexyl acetate

As was noted in chapter 4 in the unaged distillates, those originating from table grapes and "other" varieties still contained significantly lower concentrations of hexyl acetate after three years of wood ageing. However, where the CART analysis on the unaged distillates highlighted distillates from region 1 as containing significantly higher concentrations of hexyl acetate, no differences on the basis of region were observed after the three-year ageing period. Those distillates made from Chenin blanc. Colombar and a mix of Chenin/Colombar using strains NT117 and VIN13 contained significantly higher concentrations of hexyl acetate than those distillates made from the remaining yeast strains (data not shown). In chapter 4 it was noted that wines made from strains WE372 and NT117 contained significantly higher concentrations of hexyl acetate. However, this was not observed in the unaged distillates.

6.3.3.10 Diethyl succinate

No significantly different groups of diethyl succinate could be found on the basis of demographic and production variables (data not shown). This can be attributed to the fact that diethyl succinate is also formed during the maturation process when ethyl alcohol and succinic acid (naturally present in oakwood) undergo an esterification reaction (Onishi *et al.*, 1977).

6.3.3.11 n-Propanol

CART was not able to identify significantly different groups of n-propanol concentrations on the basis of vintage, as was the case for the unaged distillates in chapter 4. However, the influence of region as well as yeast strain in determining significantly different groupings of n-propanol concentrations in the three-year old distillates was still evident (**Figure 6.21**). This confirms the finding by Riponi *et al.* (1996) that the type of yeast strain used can significantly influence n-propanol concentrations.

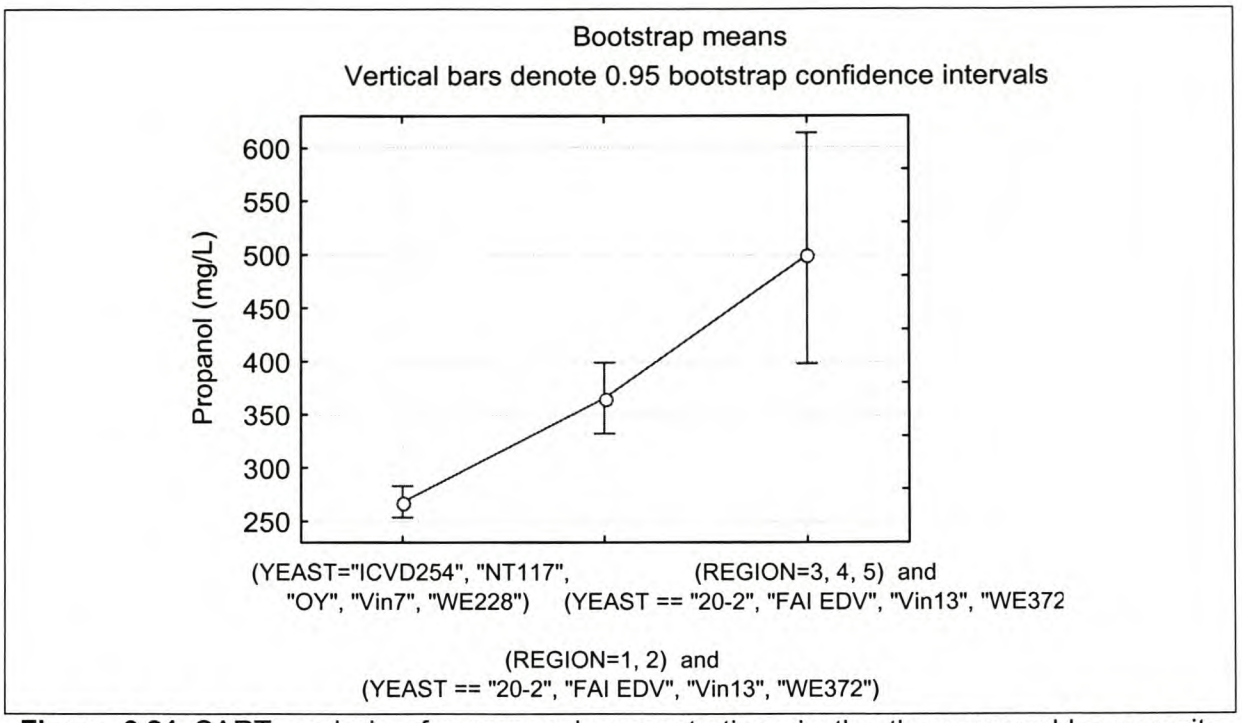

Figure 6.21 CART analysis of n-propanol concentrations in the three-year old composite distillates based on demographic and production variables.

6.3.3.12 isoAmyl alcohol

As was noted in chapter 4, the concentration of isoamyl alcohol remained significantly lower in the 1999 distillates when compared to those from 2000 after three years of wood maturation. As was also noted in the unaged distillates, isoamyl alcohol concentrations were significantly higher in distillates made from grapes harvested in mid and late season after three years of wood maturation. However, this was only significant within those distillates from the 2000 vintage. Vintage differences in isoamyl alcohol concentration were also noted in section 3.1.14. As is evident from **Figure 6.22**, isoamyl alcohol concentrations were also significantly higher in those distillates originating from regions 2 and 4 when compared to the remaining mid to late harvested distillates in 2000.

6.3.3.13 n-Butanol

CART was no longer able to distinguish significantly different groups of n-butanol concentrations on the basis of harvest time, as was the case in chapter 4. However, some similarities in terms of yeast strain and region were found to be present. Three-year old distillates originating from region 1, made using strains NT117, OY, VIN13 and VIN7 contained significantly higher concentrations of n-butanol (data not shown). In chapter 4 it was noted that unaged distillates made with strains NT117 and OY contained the highest mean n-butanol concentration. They also noted that unaged distillates originating from region 1 originating from wine fermented with yeast strain VIN13 contained significantly higher concentrations of n-butanol than when originating from region 2.

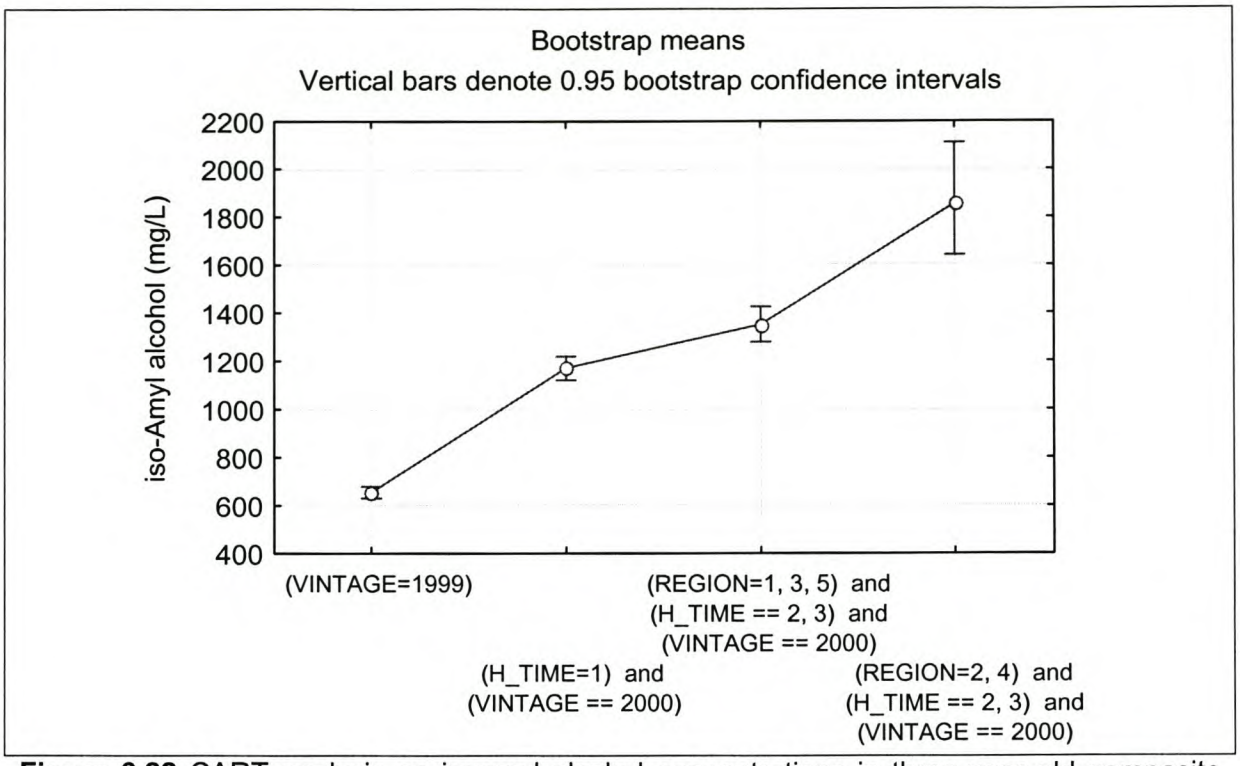

Figure 6.22 CART analysis on isoamyl alcohol concentrations in three-year old composite distillates based on demographic and production variables.

6.3.3.14 isoButanol

After three years of wood maturation, distillates made from table grapes contained significantly higher concentrations of isobutanol (**Figure 6.23**). Differences on the basis of cultivar were also noted in unaged distillates in chapter 4. However in the unaged distillates, table grapes and "other" varieties formed a group with significantly higher isobutanol concentrations.

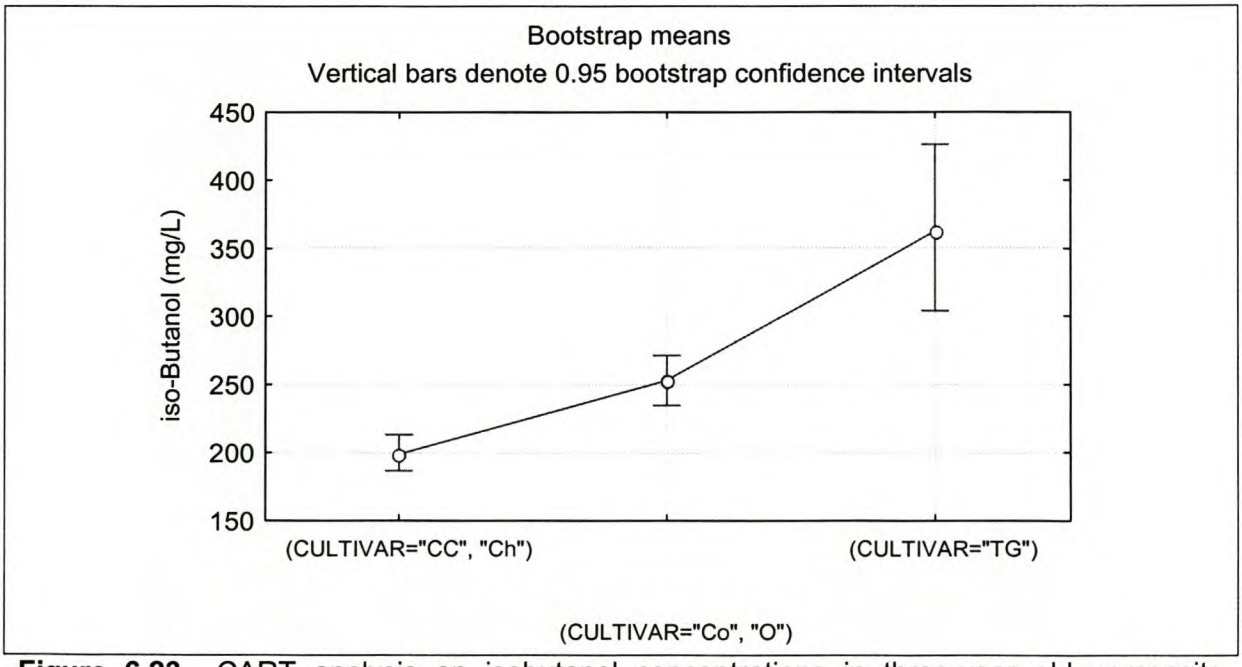

Figure 6.23 CART analysis on isobutanol concentrations in three-year old composite distillates with demographic and production variables (Key: O = other varieties, Ch = Chenin blanc; CC = Chenin blanc/Colombar; Co = Colombar; TG = table grapes).

6.3.3.15 n-Hexanol

As was noted in chapter 4, vintage, harvest time and region were shown to have a significant effect on the concentration of n-hexanol, even after three years of wood maturation. Those distillates made from mid and late harvested grapes from regions 1 and 4 contained significantly higher concentrations of n-hexanol. This was also found to be vintage dependant, and distillates from 2000 contained significantly higher concentrations of n-hexanol within this group when compared to the 1999 distillates (data not shown).

6.3.3.16 2-Phenyl ethanol

Although in chapter 4 it was found that the concentration of 2-phenyl ethanol was influenced by cultivar, region and harvest time, after three years of wood maturation the distillates could only be grouped according to cultivar for this compound. This may be due to the fact that 2-phenyl ethanol concentrations can also increase during wood maturation as a result of the naturally occurring presence of this compound in oak wood. As is evident from **Figure 6.24**, distillates originating from Colombar, table grapes and "other" varieties contained significantly higher concentrations of 2-phenyl ethanol than those made from Chenin blanc and a mix of Chenin/Colombar.

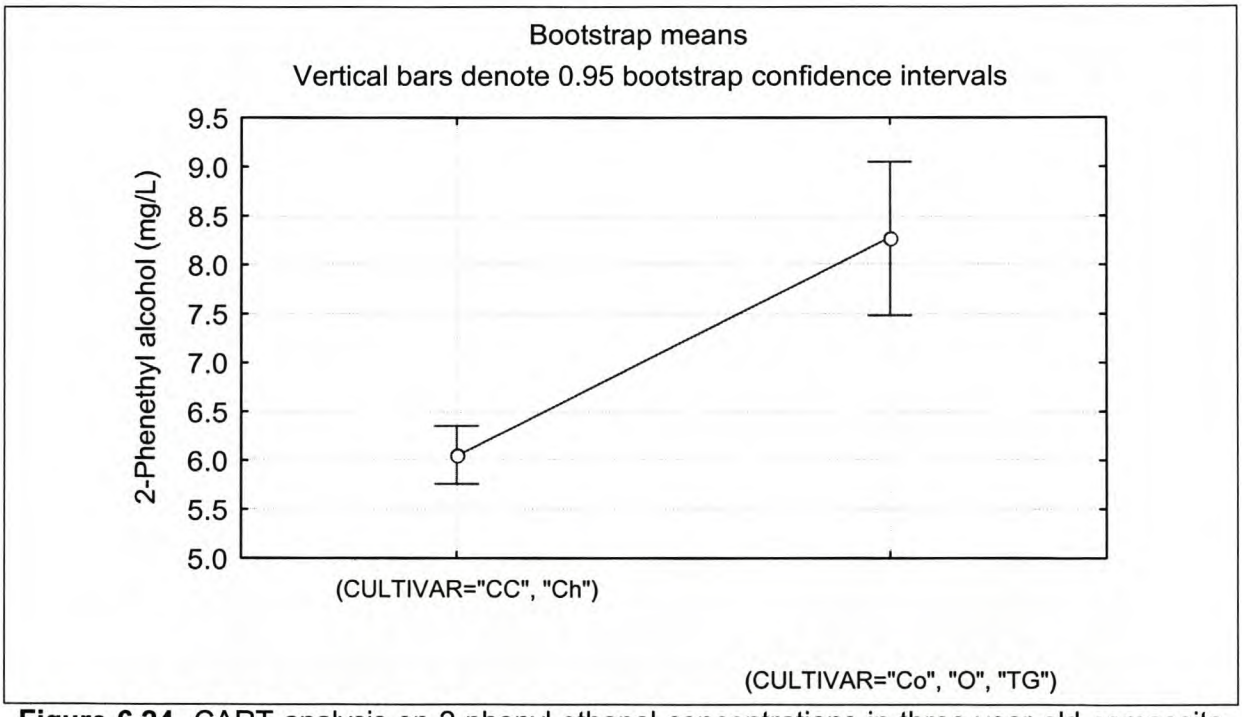

Figure 6.24 CART analysis on 2-phenyl ethanol concentrations in three-year old composite distillates with demographic and production variables (Key: O = other varieties; Ch = Chenin blanc; CC = Chenin blanc/ Colombar; Co = Colombar; TG = table grapes).

6.3.3.17 Acetic acid

Three-year old distillates made from table grapes contained significantly higher concentrations of acetic acid than those from originating from the remaining cultivars. The same observation was made in the base wines and unaged distillates (chapter 4).

6.3.3.18 Hexanoic acid

As was observed in chapter 4, the concentration of hexanoic acid was significantly higher in the 1999 distillates than in those from 2000, even after three years of wood maturation. Within the 1999 three-year old distillates, those originating from regions 1, 2 and 3 contained significantly higher concentrations of hexanoic acid (data not shown).

6.3.3.19 Octanoic acid and decanoic acid

CART was only able to establish significantly different groups of octanoic and decanoic acid on the basis of vintage in the three-year old distillates. The concentration of both octanoic and decanoic acid was significantly higher in the 1999 distillates. This difference in concentrations was reversed in the unaged distillates (chapter 4). Regional differences in octanoic acid concentrations were only evident in the 1999 three-year old distillates. Here the same pattern was observed as was noted in chapter 4 in the unaged distillates, whereby the concentration of octanoic acid was significantly lower in distillates originating from regions 4 and 5.

6.3.4 THE CONCENTRATION OF MEDIUM CHAIN FATTY ACIDS IN POTSTILL DISTILLATES DURING THE COURSE OF WOOD MATURATION

The mean concentration of C_{12}, C_{14} and C_{16} fatty acids in unaged, one, two and three year old samples as well as the mean concentrations for each of the respective barrel types are listed in **Table 6.2**. As is evident from **Table 6.2**, the mean concentrations of dodecanoic (lauric) acid were slightly higher in the 1999 samples, whilst the mean concentration of tetradecanoic (myristic) and hexdecanoic (palmitic) acid tended to be slightly higher in the 2000 samples. Due to the analytical variance present in this quantitative determination it was not possible to determine whether these vintage differences were significant. No trend for the effect of wood maturation on these fatty acids is evident either. In terms of differences between barrel types, there appear to be no notable differences, with the exception of the new block barrels. In the 2000 distillates, the mean concentrations of lauric and palmitic acid in the new block barrels in years one, two and three tend to be higher than in the remaining barrel types. This trend is also evident in the 1999 mean concentrations. However, the differences are only worth mentioning at two and three years of age. Fatty acids and their esters were reported by Onishi *et al.* (1977) to be present in distillates and they reported that these can both rise and fall in concentration during oak ageing.

Table 6.2 Mean concentrations of C12 to C16 fatty acids (mg/L)

Age	Barrel Type	1999			2000		
		C12	C14	C16	C12	C14	C16
Unaged	Average	7.23	2.35	6.49	4.91	3.54	7.08
Year 1	Average	7.47	1.85	6.07	6.49	2.19	7.06
Year 2	Average	8.48	1.57	5.10	6.30	2.39	8.24
Year 3	Average	7.86	1.53	5.69	6.64	2.08	7.45
Year 1	1 kol	7.73	1.86	6.75	5.86	2.58	6.81
Year 1	2 kol	7.58	1.90	5.91	6.12	2.29	6.70
Year 1	4 kol	7.17	1.80	5.72	5.93	1.65	6.64
Year 1	5 kol blok	6.88	1.72	5.64	6.47	2.15	6.66
Year 1	N/blok	7.94	1.99	6.17	8.01	2.45	8.24
Year 1	Composite	7.54	1.86	6.23	6.56	2.02	7.32
Year 2	1 kol	8.35	1.47	4.86	5.45	2.82	7.93
Year 2	2 kol	8.20	1.65	5.08	6.38	2.13	8.23
Year 2	4 kol	8.44	1.59	4.84	5.80	2.30	7.97
Year 2	5 kol blok	7.93	1.50	5.12	6.37	2.44	7.58
Year 2	N/blok	9.41	1.66	5.53	7.54	2.44	9.64
Year 2	Composite	8.56	1.58	5.20	6.27	2.24	8.09
Year 3	1 kol	8.04	1.62	5.54	6.13	2.37	7.08
Year 3	2 kol	7.46	1.49	5.38	5.95	2.25	6.79
Year 3	4 kol	7.62	1.51	5.51	6.18	2.04	7.02
Year 3	5 kol blok	7.07	1.44	5.66	6.77	1.78	7.13
Year 3	N/blok	8.81	1.47	6.32	8.03	2.29	8.79
Year 3	Composite	8.16	1.67	5.71	6.78	1.73	7.90

6.3.5 MEAN CONCENTRATION OF WOOD LACTONES, FURANIC ALDEHYDES AND VOLATILE PHENOLS IN THREE YEAR OLD POTSTILL DISTILLATES MATURED IN BARRELS OF DIFFERING AGES

Table 6.3 lists the mean concentration of wood lactones, furanic aldehydes and volatile phenols quantified in the three-year old distillate samples matured in barrels of differing ages. It is evident that the distillates matured in new block barrels contain the highest concentration of 5-methyl furfural, 2,6-dimethoxy phenol, hydroxymethyl furfural and vanillin. There are surprisingly fewer differences between the values of distillates matured in the 1 kol, 2 kol 4 kol and 5 kol block barrels. The composite samples were made up by taking equal volumes of distillate from each of the six barrels (one barrel of each kol type except the 5 kol block barrels, where two barrels were included in each lot). Thus the composite sample concentration values reflect the values that are typically present in a commercial three-year old potstill distillate at Distell.

Table 6.3 Mean concentration of wood lactones, furanic aldehydes and volatile phenols in three-year old composite brandy distillate samples (mg/L)

Compounds	1 Kol block Barrel	2 kol Block Barrel	4 kol Block Barrel	5 kol Block Barrel	New Block Barrel	Composite
Furfural	1.03	1.102	1.238	1.186	1.256	1.29
5-Methyl furfural	0.733	0.471	0.975	0.814	2.857	1.03
Guaiacol	1.173	1.165	1.212	1.181	0.9854	1.17
c-Lactone	0.348	0.302	0.475	0.381	0.4828	0.31
Ethyl guaiacol	0.402	0.494	0.362	0.499	0.517	0.33
Eugenol	0.814	0.577	0.578	0.575	0.586	0.48
2,6 di-Methoxy phenol	2.36	2.177	1.574	0.982	3.336	2.72
5-Hydroxy methyl furfural	2.426	1.502	1.829	1.514	31.65	9.28
Vanillin	2.62	1.978	2.517	2.121	4.84	3.84

6.3.6 MEAN CONCENTRATION OF PHENOLIC ACIDS AND ALDEHYDES IN THREE YEAR OLD POTSTILL DISTILLATES MATURED IN BARRELS OF DIFFERING AGES

Table 6.4 lists the mean concentration of phenolic acids and aldehydes quantified in the three-year old distillates matured in barrels of differing ages. These values indicate the magnitude of concentration that can be expected from wood maturation in these barrels for three years. As is to be expected, the distillates matured in the new block barrels contain the greatest concentration of phenolic acids and aldehydes, followed by the 1 kol block barrels. These were also the only distillates in which the concentration of catechin and coniferaldehyde could be quantified.

Table 6.4 Average concentration of phenolic acids and aldehydes in composite three-year old potstill brandy distillates (mg/L)

Compounds	1 Kol Block Barrel	2 Kol Block Barrel	4 Kol Block Barrel	5 Kol Block Barrel	New Block Barrel	Composite
Gallic acid	6.037	4.55	5.003	4.596	17.054	7.29
Catechin	nd	nd	nd	nd	15.189	nd
Vanillic acid	3.393	2.973	2.8	2.97	10.17	4.97
Syringic acid	1.77	1.195	1.25	1.314	21.15	4.76
Syringaldehyde	3.941	2.94	2.689	2.74	14.55	4.75
m-Coumaric acid	0.323	0.33	0.209	0.329	1.129	0.303
Ellagic acid	24.14	19.85	20.71	29.067	134.15	44.51
Coniferaldehyde	nd	nd	nd	nd	1.677	nd
Sinapaldehyde	2.927	3.739	2.809	2.583	41.38	7.11

6.4 CONCLUSIONS

Differences in the concentration of volatile compounds were noted in potstill distillates during the course of and after three years of wood maturation. The concentration of acetaldehyde remained relatively constant over the three-year period for all regions except region 4, which showed an increase over time. The concentration of 2-phenethyl acetate, ethyl caprate, ethyl lactate, isobutanol, n-butanol and n-propanol did not vary significantly during the course of maturation. The concentration of acetic acid, diethyl succinate, ethyl caprylate, 2-phenyl ethanol, octanoic and decanoic acid increased with wood maturation. Differences on the basis of region and vintage were also evident during the course of and after wood maturation. Isoamyl acetate concentrations remained significantly higher in the distillates from 2000 even though the concentration of isoamyl acetate tended to decrease with time in wood. The mean concentration of isoamyl acetate and hexyl acetate remained highest in distillates originating from region 1. Isoamyl acetate, ethyl caprylate and octanoic acid concentrations remained lowest in distillates originating from region 4, whilst n-hexanol and 2-phenyl ethanol concentrations remained highest in distillates from this region. Distillates from region 4 developed notably higher concentrations of ethyl acetate when compared to the remaining regions during wood maturation.

Differences in volatile compound concentrations in distillates matured in barrels of varying ages were studied using a repeated measures analysis of variance. The mean concentration of acetaldehyde, ethyl acetate, ethyl caproate, ethyl caprate, ethyl caprylate acetic acid and decanoic acid was found to be higher with wood progression in new block barrels. The mean concentration of hexyl acetate and 2-phenethyl acetate was found to be lowest in the distillates matured in new block barrels. No significant differences in volatile compound concentration were observed in the distillates matured in the remaining barrels of differing ages.

It was decided to investigate whether the demographic and production factors that were shown in chapter 4 to have an effect on base wine and unaged distillate composition still have an effect upon the composition of the distillates after three years of wood maturation. After three years of wood maturation it was still possible to divide the distillates into two groups on the basis of acetaldehyde content, according to the yeast strains used to ferment the base wine. Yeast strain groupings were also identified on the basis of ethyl acetate. Three-year old distillates made from grapes harvested early in the season using yeast strain VIN13 for the base wine fermentation, contained significantly higher concentrations of isoamyl acetate than the remaining distillates. As was noted in chapter 4 in the unaged distillates, harvest time continued to have the largest impact on the concentration of ethyl caprate after three years of wood maturation. Distillates made from mid and late harvested grapes contained significantly lower concentrations of ethyl caprate than those made with early harvested grapes. It was possible to determine significantly different groupings of n-propanol concentrations using region and yeast strain as discriminators. As was noted in the unaged distillates (chapter 4) isoamyl alcohol concentrations were

significantly higher in distillates made from grapes harvested in mid and late season after three years of wood maturation. Three-year old distillates made from table grapes contained significantly higher concentrations of isobutanol. Thus, demographic and production factors do still exert an influence on the volatile composition of potstill distillates after three-years of wood maturation and in most instances exerted the same or similar effect as was noted in the unaged distillates.

Some differences in the concentration of medium chain fatty acids were noted between the distillates from 1999 and 2000. However, no clear trend for the effect of wood maturation on the medium chain fatty acids was evident. This supported the observation by Onishi *et al.* (1977) that the concentration of medium chain fatty acids can both rise and fall during the course of wood maturation.

The mean concentrations of selected wood lactones, furanic aldehydes, volatile phenols and phenolic acids and aldehydes indicate that distillate maturation in the new block barrels imparts more wood maturation character than in the remaining barrels, which is to be expected as these can be viewed as rejuvenated, new brandy casks. There were however, surprisingly little differences in the concentrations of these wood maturation related compounds in the remaining barrels, as was also noted for the volatile compound composition. Future studies of this nature should focus on the joint influence of these volatile compounds studied as well as those compounds that are wood derived to determine their joint effect on the composition on the quality and character of potstill distillates. As many of these wood derived compounds are not volatile, it can be speculated that compounds such as furfural may have an effect on the taste perceptions of the product.

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CHAPTER 7

RESEARCH RESULTS

The influence of wood maturation on the sensory character and quality of potstill brandy distillates

RESEARCH RESULTS

7. THE INFLUENCE OF WOOD MATURATION ON THE SENSORY CHARACTER AND QUALITY OF POTSTILL BRANDY DISTILLATES

ABSTRACT

The volatile compound composition and sensory quality were analysed and evaluated in fifty eight three-year old potstill brandy distillates from two successive vintages. Using analysis of variance (ANOVA), regression analysis, Pearson correlation, Spearman rank order correlation as well as classification and regression tree (CART) analyses, the relationship between sensory quality of the three-year old distillates, demographic and production factors, volatile compound composition as well as routine base wine analyses was determined. Sensory descriptive analysis using the South African brandy aroma wheel was used to monitor the aroma profile changes taking place after one, two and three years of wood maturation. It was found that, with the exception of the 2000 base wine score and the 2000 three-year old distillate score, there is a significant correlation between the score of the base wine, unaged distillate and three-year old wood maturated distillates. Even after three years of wood maturation, demographic and production factors can still influence the sensory quality of the distillates. Three-year old distillates that were scored lowest in terms of sensory quality all originated from the De Doorns region, irrespective of harvest time or cultivar. The next most important factor to influence the sensory quality of these distillates was found to be harvest time in the remaining regions. Distillates originating from grapes harvested early in the season were all awarded the highest scores. Isoamyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, n-butanol, octanoic acid, ethyl caprate and decanoic acid showed some positive correlation to the quality of the three-year old distillates. Isobutanol, ethyl lactate, acetic acid, acetaldehyde and ethyl acetate showed a significant negative correlation to three-year old distillate quality. Many of these findings were also confirmed in the analysis of variance performed on selected distillates of varying quality, which were profiled using sensory descriptive analysis. The routine analyses performed on the brandy base wines, whether viewed individually or as a group, showed little statistical correlation to the sensory quality of the base wines, unaged and three-year old distillates. The style classification was not influenced by the sensory quality of the distillates. However demographic and production factors as well as volatile compound composition were found to exhibit an influence. All distillates originating from region 4 were classified as style 3. The remaining regions did not provide such clear cut style relationships. Ethyl caproate and octanoic acid were found to be the most important volatile compounds in determining the style classification of the three-year old distillates.

7.1 INTRODUCTION

The flavour and aroma constituents of aged brandy are derived from each successive stage of the production process. Many chemical compounds thus far identified in brandy are either present in the grape raw material or, more importantly, are produced by yeast during the fermentation process. However, ageing of brandy in oak barrels produces additional compositional changes. Both alcohol and water are lost as a result of diffusion through the oak stave and barrel-head and subsequent evaporation into the atmosphere. As ethanol has a molecular weight approximately 2.5 times that of water, ethanol diffuses more slowly than water except under high humidity conditions (Onishi *et al.*, 1977). Compounds of comparatively high molecular weight, less permeable than alcohol or water, such as the fusel alcohols are somewhat concentrated by ageing. Aromatic aldehydes and acids, sugars, tannins and other chemical compounds are either extracted from oak or are produced by the action of alcohol on the macro-chemical structure of oak lignin (Belchior *et al.*, 1972; Guymon and Crowell, 1968; Guymon and Crowell, 1970; Singleton, 1995). The porous barrel also allows certain oxidative reactions to occur, although it is difficult to prove to what extent these occur (Onishi *et al.*, 1977). All of these reactions not only affect the composition of brandy distillates, but also profoundly affect colour and aroma. “Fruity” aroma notes are arguably the most important in brandy and make it uniquely different and distinguishable from other distilled products such as the different kinds of whiskies and rum (Jolly and Hattingh, 2001). ”Woody” and “toasted” notes are those derived during maturation form oakwood and prior treatment of the barrels, respectively (Jolly and Hattingh, 2001). The “nutty”, “sweet associated” and “spicy” aroma notes are often associated with older brandies, usually fifteen years and older (Venter, 1994).

In chapter 6 some of the chemical changes taking place during three years of wood maturation in medium toasted oak casks of varying ages were studied. This study investigates the sensory changes taking place during three years of wood maturation in these casks. More specifically, the aims of this study are to:

1. Determine whether wood maturation significantly alters the sensory quality of potstill distillates as originally determined in the base wines and unaged distillates.
2. Determine whether demographic and production factors as well as volatile compound composition are related to the sensory quality of potstill distillates after three years of wood maturation.
3. Determine the changes taking place in the sensory profile of the potstill distillates after one, two and three years of wood maturation.
4. Determine whether the original so-called routine analyses performed on each incoming base wine are at all an indicator of quality in the base wines, unaged distillates or three-year old distillates.

5. Determine whether demographic and production factors, volatile compound composition as well as the sensory quality of the three-year old distillates have any influence on the ultimate style classification of these matured distillates.

7.2 MATERIALS AND METHODS

7.2.1 EXPERIMENTAL OUTLAY

Refer to chapters 4 and 5 for the experimental outlay.

7.2.2 STATISTICAL ANALYSIS

Regression, Pearson correlation and Spearman rank order correlation analyses as well as analysis of variance (ANOVA) were performed using STATISTICA version 6.0. Classification and regression tree analysis was performed using the CART program from Salford Systems. For a background summary of the methodology and purpose of the CART analysis please refer to chapter 4. Where there is no overlap between the 95% confidence intervals in the CART analysis graphs, the results are considered significantly different. For a description and classification of the demographic and production factors used in this study, please refer to chapter 4.

7.2.3 SENSORY ANALYSIS

All of the sensory evaluations were performed by two judges who both have extensive commercial experience in the evaluation of three year old wood matured potstill brandies (refer to chapter 5). The distillates were only evaluated after three years of wood maturation, as the South African liquor law states that potsill brandies must be matured for at least three years in oak casks no larger than 340 litres. Thus the one and two year old products were of no commercial value and did not warrant a sensory quality evaluation. Only the composite sample, comprising equal volumes of distillate drawn from each of the six casks as described in chapter 6 were used in the sensory evaluations, which emulates commercial practice. The 1999 and 2000 three-year old potstill brandies were evaluated over four and three separate occasions, respectively. A reference sample was included in each of these sessions. Scores were adapted for any session differences that may have existed by using the score of the reference sample in each of the evaluation sessions relative to its score in session one. This was done by adding the difference between the score of the reference sample in session one and the score of the reference sample in each of the other respective evaluation sessions to each of the remaining sample scores per session. Thus, if the score of the reference sample was 9.1 in session one and 8.5 in session two then 0.6 was added to the score of all of those sample evaluated in session two. The largest difference in the sensory score of the reference sample between session one and any of the remaining sessions was 0.6. A 10 cm line scale,

where 0 was unacceptable and 10 was outstanding, was used for these evaluations. Samples were presented blind, in a random order and appeared in triplicate and were diluted to 20% v/v with distilled water.

7.2.4 SENSORY DESCRIPTIVE ANALYSIS

A sensory descriptive analysis was performed on the composite barrel sample of the same twelve distillates (six from 1999 and six from 2000), as discussed in chapter 5. These distillates were evaluated after one, two and three years of wood maturation. The sensory descriptive analysis (SDA) was performed using a panel of 11 judges at the Agricultural Research Centre, Stellenbosch. The 11 judges were trained on nosing standards for 6 sessions prior to evaluating the distillates. The analysis was performed using the South African brandy aroma wheel (Jolly and Hattingh, 2001, chapter 5). All samples were diluted with distilled water to an alcoholic strength of 20% v/v for all of the tasting sessions. The samples were presented blind in a random order and each judge was asked to mark the aroma intensity on a 10 cm line scale. The following descriptors were used: fruity, herbaceous, floral, woody, nutty, toasted and other positive (eg. sweet associated, smooth associated and spicy) as well as negative aromas (eg. heads, tails, musty, solvent/ chemical). The lowest end of the scale stated "not detectable" and the highest end stated "very prominent". An average score was then calculated from the scores of the 11 judges and this was plotted graphically.

7.2.5 CLASSIFICATION OF THREE YEAR OLD BRANDIES INTO COMMERCIAL STYLES

The three year old brandies were also classified according to Distell's three year old potstill brandy classification. Only the composite sample, comprising equal volumes of distillate drawn from each of the six casks as described in chapter 6 were used in the style classification. From a commercial perspective, this classification enables the company to determine which product a commercial three-year old potstill brandy can be used in. The classification is based on an organoleptic evaluation of the product on nose, and more particularly on palate. There are five possible categories or styles that are differentiated by varying degrees of smoothness and hardness on the palate. Flavour body and intensity also play a role in this classification. The three-year old samples were presented five at a time, blind and in a random order to the trained and experienced panel that carries out all of the commercial classifications at Distell. The panel comprises six judges. As is commercial practice, the samples are always judged using reference standards for the three styles and judges compared degrees of hardness or smoothness as well as flavour body and intensity with the reference samples. The three styles can be defined as:

style 1 = smooth and rounded on the palate

style 2 = intermediate in terms of hardness, not hard, but not as smooth as style 1

style 3 = hard on the palate, full bodied

7.3 RESULTS AND DISCUSSION

7.3.1 CORRELATING WINE TO UNAGED DISTILLATE TO THREE YEAR OLD DISTILLATE QUALITY

A non-parametric Spearman rank order correlation test was performed using the sensory scores of the base wines, unaged distillates and three-year old potstills in order to determine whether there was any significant correlation between these scores. A correlation is significant at a p-value of less than 0.05. As is evident from **Table 7.1**, a significant correlation was found in five of the six relationships, the exception being the correlation between the 2000 base wine and three-year old potstill scores. The five significant correlations were all found to be positive.

Table 7.1 Spearman rank order correlations on sensory data

Pair of Variables	Valid N	Spearman R	t(N-2)	p-Value
1999 wine score & 1999 distillate score	33	0.563	3.7944	<0.001
1999 wine score and 1999 3 yr score	33	0.375	2.2543	0.031
1999 distillate score and 1999 3 yr score	33	0.439	2.7245	0.01
2000 wine score & 2000 distillate score	25	0.412	2.171	0.04
2000 wine score & 2000 3 yr score	25	0.214	1.052	0.3
2000 distillate score & 2000 3 yr score	25	0.51	2.844	0.009

7.3.2 CART ANALYSIS ON THREE YEAR OLD COMPOSITE SAMPLES

7.3.2.1 CART analysis using demographic and production variables and score

A CART analysis was performed on the composite three-year old potstill samples in order to determine the relationship between the demographic and production variables (refer to independent variables used in ANOVA and CART analyses in chapter 4) and the score of these three year old distillates. The results appear in **Figure 7.1**. **Figure 7.1** clearly indicates that the lowest quality three-year old distillates all originate from region 4, irrespective of harvest time or cultivar. As was mentioned in chapter 4, all of the distillates made from table grapes originate from region 4. The next most important factor to influence the sensory quality of the three-year old distillates is harvest time. Those distillates from the remaining regions made from grapes harvested in the middle and end of the season, were scored significantly higher than those originating from region 4, but these scores were still significantly lower than those distillates made from grapes harvested early in the season. Distillates originating from grapes harvested early in the season were all awarded the highest sensory score. Although no significant differences were noted between

cultivars in those distillates originating from early harvested grapes, those made using a mix of Chenin/Colombar did possess a higher mean score (**Figure 7.1**).

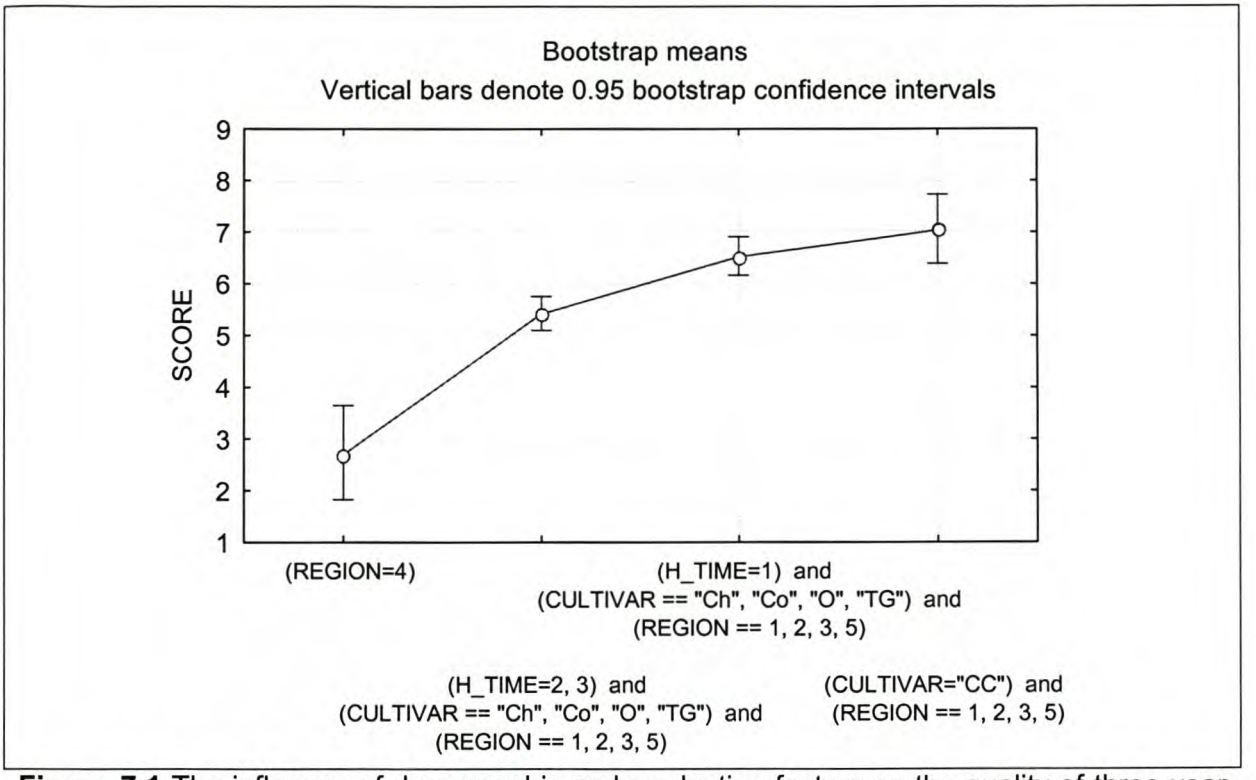

Figure 7.1 The influence of demographic and production factors on the quality of three-year old distillates (Key: Ch= Chenin blanc, Co = Colombar; CC = Chenin blanc/ Colombar; O = other varieties; TG = table grapes; H_TIME = harvest time).

7.3.2.2 CART analysis using volatile compounds and score

A CART analysis was performed using the volatile aroma compound analyses for the composite three-year old potstill samples of both vintages in order to determine the relationship between these volatile compounds and the score awarded to these distillates. The first two columns in **Table 7.2** list the CART variable importance established for the combined vintage analysis and **Figure 7.2** depicts the resulting subsets defined by "rules" for this CART analysis. From **Figure 7.2** it is evident that concentrations of ethyl caprylate and 2-phenethyl acetate above 12.6 mg/L and 0.38 mg/L respectively positively contribute to three year old distillate quality, but that isobutanol can have a synergistic or antagonistic effect on this relationship, depending on its concentration. In chapter 5 it was not possible to perform a CART analysis using the combined volatile compound data and scores for the two vintages in the unaged distillates due to the difference in scoring scales between these two years. As considerable differences in the unaged distillate CART analyses were found to exist between the two vintages, it was decided to investigate whether there were still differences in the results of the CART analysis after three years of wood maturation. The CART variable importance analysis for these two separate vintages is tabulated in the third to sixth column of **Table 7.2** and the corresponding CART analysis figures are depicted in **Figures 7.3** and **7.4**. When one compares these to the unaged CART analyses in chapter 5, it is evident that there are considerable

differences. In chapter 6 it was shown that the volatile composition of distillates can alter during the course of maturation. This could account for some of the differences. Those variables identified by CART as being important in determining defined quality subsets with predictor variables in all three analyses are marked in bold. These compounds are isobutanol, ethyl acetate and n-propanol. However, from **Table 7.2** it is evident that although the individual CART variable importance analyses between 1999 and 2000 differ, there are compounds in each of the separate analyses that appear in the combined vintage variable importance analysis. In addition, all of the predictor variable rules generated by CART in **Figures 7.2, 7.3** and **7.4** are also listed in the combined vintage CART variable importance (**Table 7.2 and Figure 7.2**). The concentrations of isoamyl acetate, 2-phenethyl acetate and ethyl caprate were all significantly higher in the 2000 three-year old distillates when compared to those of 1999 (chapter 6). Although not significant, the mean n-propanol concentration was also highest in the 2000 three-year old distillates. However, isobutanol, ethyl acetate and ethyl caprylate concentrations showed no significant differences between these two vintages (chapter 6). It is interesting that ethyl acetate appears as a predictor variable in both of the individual CART vintage analyses (**Figures 7.3** and **7.4**), but does not appear in the overall CART analysis (**Figure 7.2**), although it is listed in the combined vintage variable importance analysis in **Table 7.2**.

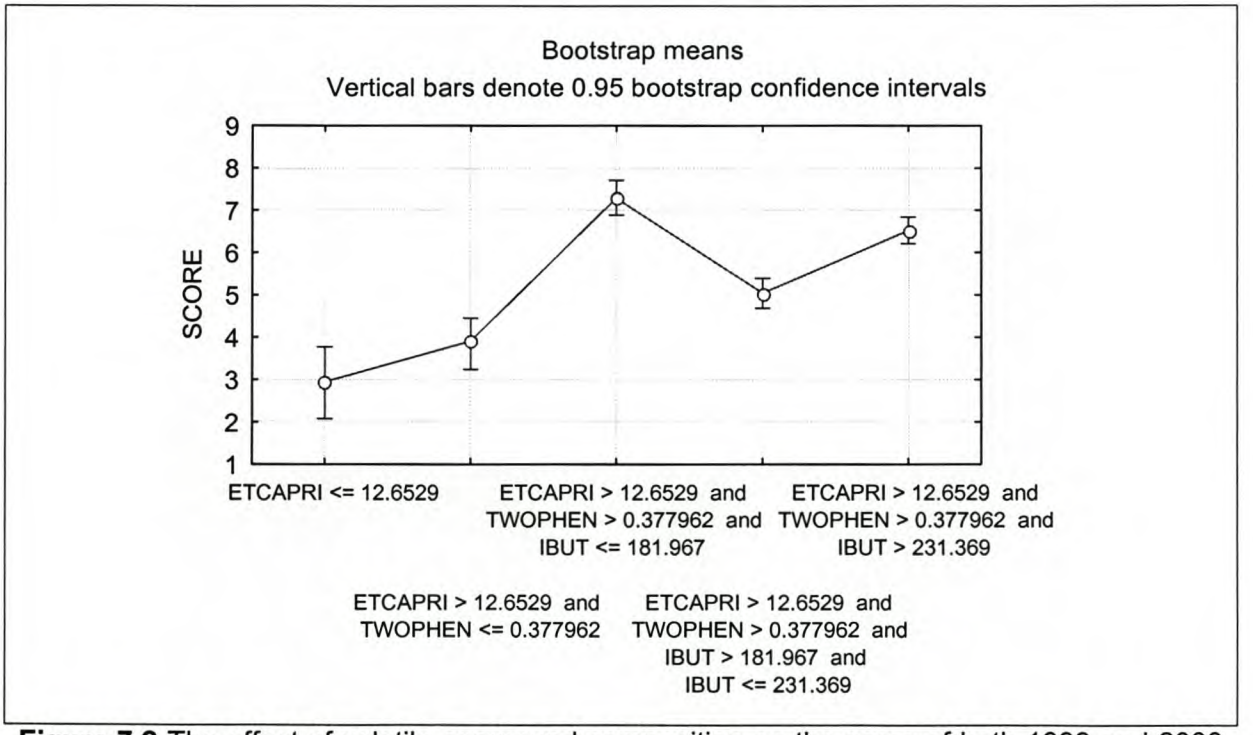

Figure 7.2 The effect of volatile compound composition on the score of both 1999 and 2000 three-year old composite distillate samples (Key: ETCAPRI = ethyl caprylate; TWOPHEN = 2-phenethyl acetate; IBUT = isobutanol).

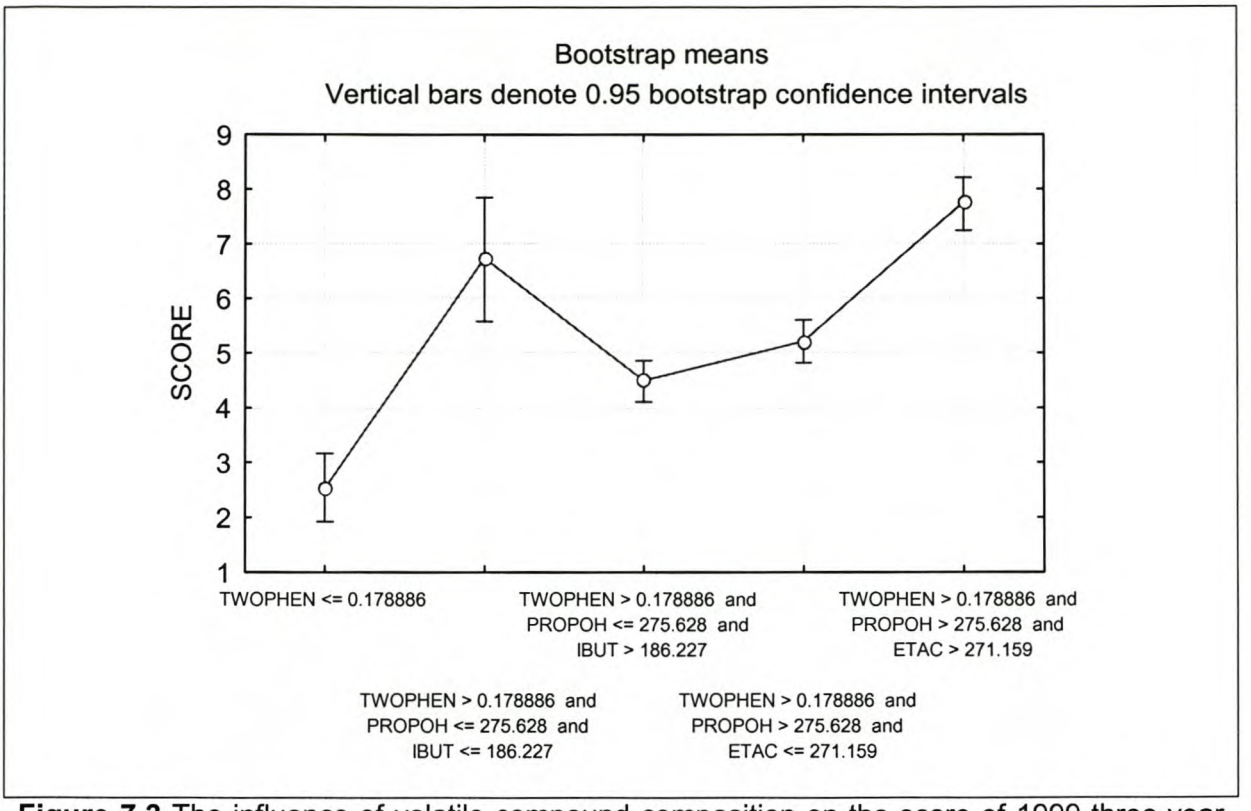

Figure 7.3 The influence of volatile compound composition on the score of 1999 three-year old composite distillates (Key: TWOPHEN = 2-phenethyl acetate; PROPOH = n-propanol; IBUT = isobutanol; ETAC = ethyl acetate).

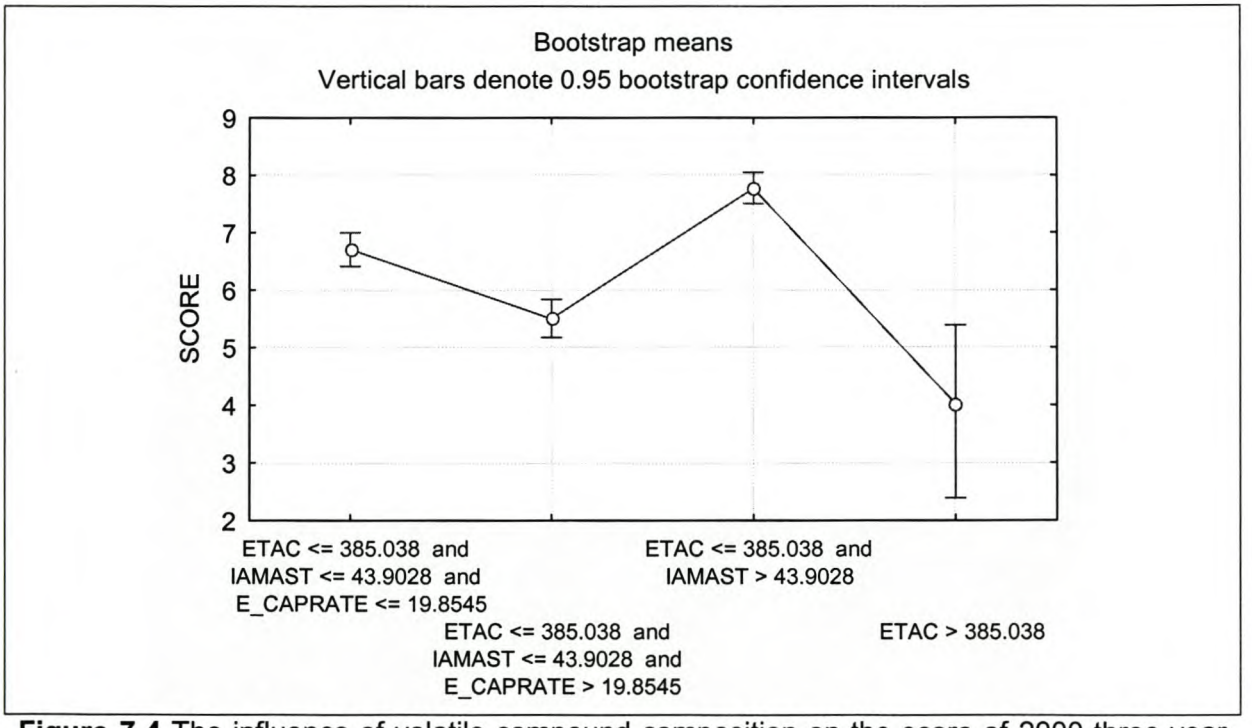

Figure 7.4 The influence of volatile compound composition on the score of 2000 three-year old composite distillate samples (ETAC = ethyl acetate; IAMAST = isoamyl acetate; E_CAPRATE = ethyl caprate).

In summary it is therefore evident that the "rules" generated by CART to define particular quality subsets based on volatile compound composition, can vary from vintage to vintage in three-year old brandy distillates. This can be ascribed to volatile

compound compositional differences, which were found to exist between the two vintages. However, it is evident from **Table 7.2** and **Figures 7.2, 7.3** and **7.4** that there is a measure of overlap in the variable importance analysis and the "rules" generated for both individual vintages and in the combined analysis. This was not evident in the individual vintage analysis of unaged distillates (chapter 5). This could be as a result of reduced variation in the three-year old sensory evaluations between the two vintages. As a three-year old potstill distillate is commercially considered to be an end-product in the brandy production process, the judges are more accustomed to evaluating three-year old brandy distillates in terms of quality and style than they are evaluating unaged brandy distillates. This could possibly account for the greater degree of overlap in variable importance as well as CART rules when compared to the unaged distillate CART analysis in chapter 5.

Table 7.2 CART variable importance on volatile compounds vs score (relative to score of 100)

1999 and 2000 CART importance		1999 CART importance		2000 CART Importance	
Ethyl caprylate	100	2-Phenethyl acetate	100	isoButanol	100
isoButanol	63.62	Ethyl acetate	66.39	Ethyl acetate	47.21
2-Phenethyl acetate	50.59	isoButanol	63.57	Hexyl acetate	45.93
Ethyl lactate	49.21	n-Propanol	47.97	isoAmyl acetate	32.09
Ethyl caproate	38.04	n-Hexanol	45.78	n-Butanol	19.77
Acetaldehyde	34.35	Acetaldehyde	35.13	Hexanoic acid	17.88
Ethyl acetate	32.29	Ethyl caproate	23.68	Ethyl caprate	17.88
Ethyl caprate	30.55	Hexyl acetate	14.4	Decanoic acid	16.82
isoAmyl acetate	19.77	Ethyl lactate	14.2	n-Propanol	7.33
n-Hexanol	10.64	Ethyl caprylate	11.62		
n-Propanol	9.76	Decanoic acid	8.87		

7.3.3 STATISTICAL CORRELATION BETWEEN VOLATILE COMPOUNDS AND SCORE IN BOTH VINTAGES

Table 7.3 lists those volatile compounds in decreasing order of correlation up to ethyl acetate which were found to have a statistically significant correlation to the score at $p<0.05$ using a Pearson correlation analysis. Thus, the listed compounds all showed a significant correlation, although in some instances the degree of correlation was not high. A 100% correlation would be tabulated as one or minus one. As is evident from **Table 3** isoamyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, n-butanol, octanoic acid, ethyl caprate, and decanoic acid show some positive correlation to the quality of the three-year old composite samples, measured as the score. Isobutanol, ethyl lactate, acetic acid, acetaldehyde and ethyl acetate show some significant negative correlation to quality. It is evident that all eleven compounds listed in the combined vintage variable importance in **Table 7.2** are listed in **Table 7.3**.

Table 7.3 Statistical correlation between volatile compound concentration and sensory score awarded to the matured distillates from 1999 and 2000

Variable	Correlation to score
isoAmyl acetate	0.42
isoButanol	-0.39
Hexyl acetate	0.39
Ethyl lactate	-0.34
Ethyl caproate	0.33
Acetic acid	-0.29
Acetaldehyde	-0.28
Ethyl caprylate	0.25
n-Butanol	0.24
Octanoic acid	0.22
Ethyl caprate	0.22
Decanoic acid	0.18
Ethyl acetate	-0.17
n-Hexanol	-0.15
2-Phenethyl acetate	0.13
isoAmyl alcohol	0.09
2-Phenyl ethanol	-0.08
n-Propanol	0.05
Hexanoic acid	0.05
Diethyl succinate	-0.01

7.3.4 VOLATILE COMPOUND CONCENTRATION DIFFERENCES BETWEEN DISTILLATES PROFILED USING SENSORY DESCRIPTIVE ANALYSIS

An analysis of variance was performed on the volatile compound data of each of the six composite distillates profiled using sensory descriptive analysis. This was done in order to determine significant differences in the concentration of these compounds between the good, average and poor quality distillates after one, two and three years of wood maturation. The distillates were classified as good, average and poor quality as unaged distillates, however, as is also proven in section 7.3.1, distillates retained their sensory quality rating after three years of wood maturation when they were organoleptically evaluated again. As the sensory evaluation scale was a 10 cm line scale, scores below 4 were regarded as being poor quality, between 4 and 7 as average quality and above 7 as good quality.

7.3.4.1 1999 Distillates

Good quality distillates contained significantly higher concentrations of isoamyl acetate over all three years of wood maturation (**Table 7.4**). Although not significant after year one of wood maturation, the concentration of ethyl caproate in the good quality distillates was significantly higher than in the average and poor quality distillates after two and three years of wood maturation. The ethyl caproate concentration was also significantly higher after three years when compared to the

two-year old good quality sample. Although not significant, the mean concentration of ethyl caprylate was higher in the good quality samples in all three years. The ethyl caprate concentration was significantly higher in the good and average quality distillates when compared to the poor quality distillates in all three years. Hexyl acetate concentrations, although not significantly different between good and average quality samples in year one, were significantly higher in the good quality distillates after two and three years of wood maturation. Good quality samples contained significantly lower concentrations of isobutanol and 2-phenethyl alcohol over all three years. In the Pearson correlation analysis (**Table 7.3**) isoamyl acetate, ethyl caproate, ethyl caprylate, ethyl caprate and hexyl acetate show a significant positive correlation to quality, whereas isobutanol and 2-phenyl ethanol were found to have a significant negative correlation to quality, even if the level of correlation was low.

Table 7.4 Mean volatile compound concentration differences in 1999 SDA distillates profiled over three years of wood maturation (mg/L)

Compounds	Year 1			Year 2			Year 3		
	Good	Ave-rage	Poor	Good	Ave-rage	Poor	Good	Ave-rage	Poor
Acetaldehyde	113a	83a	585b	60a	83a	1183b	68a	68a	991b
Ethyl acetate	249a	222a	578b	236a	233a	790b	280c	236a	735b
isoAmyl acetate	20a	6b	1.9c	15.4a	3.8b	1.8c	15a	4.5b	2.5c
Ethyl caproate	5a	3.8a	3.1a	6.3b	4.5a	4a	7.7c	5.9a	4.6a
Ethyl caprylate	13.6a	10.5ab	8.4b	14.3a	12.9ab	9.7ab	16.9c	16abc	11.3ab
Ethyl caprate	16.5a	13.4a	8.9b	19.3a	18.3a	10.7b	14.4a	15a	9.5b
Hexyl acetate	1.5a	0.9a	0d	1.2a	0.5b	0d	1.1a	0.3c	0d
Ethyl lactate	19a	22.7a	55b	31a	25a	58.5b	30a	22a	57.7b
Diethyl succinate	1.7a	1b	1.97a	2.4a	2.8a	2.6a	1.5a	1.2b	1.6a
2-Phenethyl acetate	0.8a	0.8a	0.09b	0.6a	0.7a	0b	0.5a	0.9a	0b
n-Propanol	303a	224b	260c	280ac	218b	272c	357a	216b	259c
isoButanol	191a	300b	266b	184a	302b	275b	150a	230ab	280b
n-Butanol	5.3a	4a	6a	4.1a	4.2a	5.5a	5.8a	4.4a	6.6a
isoAmyl alcohol	1115a	1099a	1029a	1026a	1064a	998a	625b	598b	576b
n-Hexanol	18.5a	14b	21a	17.8a	13.5b	20.5a	18.8a	13.6b	21.3a
2-Phenyl ethanol	6a	8.7b	7.3b	5.2c	8.4b	7b	5.2c	7.5b	7b
Acetic acid	165a	169a	325b	81.5c	216ab	502b	345b	317b	933d
Hexanoic acid	8.3a	8.4a	9.5a	7.4a	6.1b	2.8c	6.1b	6.7a	3.9d
Octanoic acid	15a	18.3a	8.3b	19.5a	22.1a	9.1b	17.6a	17.4a	12.2ab
Decanoic acid	8.4a	21b	8.2a	12c	17.1b	9.3a	13.4c	19.2b	11.4a

The average quality samples possessed the lowest mean concentration of n-propanol and n-hexanol over all three years, significantly lower when compared to the good and poor quality samples. Average quality samples possessed significantly

higher concentrations of decanoic acid when compared to the good and poor quality samples. Isoamyl acetate concentrations were significantly lower than in the good quality distillates, but were significantly higher than in the poor quality distillates over all three years of wood maturation. Although not significant, the mean concentration of ethyl caproate and ethyl caprylate was lower than in the good quality samples yet higher than in the poor quality samples over all three years.

Acetaldehyde, ethyl acetate, acetic acid and ethyl lactate concentrations were significantly higher in the poor quality distillates over all three years. All of the above-mentioned compounds showed a significant negative correlation to quality in the Pearson correlation analysis (**Table 7.3**). Acetic acid showed a significant increase in concentration in the third year of maturation in the poor quality samples (**Table 7.4**). Isoamyl acetate and 2-phenethyl acetate concentrations were lowest, whilst hexyl acetate was not detected in the poor quality samples. Although no significant differences in hexanoic acid concentration were noted after the first year of maturation, the concentration of hexanoic acid decreased significantly in the second and third year of maturation. Conversely, the concentration of octanoic acid was significantly lower in the poor quality samples after one and two years of maturation, however in year three, poor quality octanoic acid concentrations were only significantly lower than those present in the good quality samples (**Table 7.4**).

7.3.4.2 2000 Distillates

The concentration of isoamyl acetate was significantly higher in the good quality distillates over all three years of wood maturation (**Table 7.5**). This was also observed in the 1999 samples. Ethyl caproate concentrations were significantly higher than those of the average and poor quality distillates after the first year of wood maturation. However, after three years of wood maturation, there were no significant differences in ethyl caproate concentration between the good and average quality distillates, only between the fore-mentioned and the poor quality distillates. The concentration of ethyl caprylate in the good quality distillates was significantly higher than that of the poor quality distillates throughout the three years of wood maturation (**Table 7.5**). The concentration of hexyl acetate was significantly different for each of the three quality categories over the three-year period and the good quality distillates contained the highest concentration of hexyl acetate. Good quality distillates contained the lowest mean concentrations of isobutanol as well as n-butanol over all three years. This is interesting as the Pearson correlation analysis (**Table 7.3**) found that isobutanol has a significant negative correlation to quality but that n-butanol has a significant positive correlation to quality, which contradicts the tendency noted in the SDA distillates, although the Pearson analysis was performed using data from all fifty eight distillates, whilst this section only compares data from six distillates.

Table 7.5 Mean volatile compound concentration differences in 2000 SDA distillates profiled over three years of wood maturation (mg/L)

Compounds	Year 1			Year 2			Year 3		
	Good	Ave-rage	Poor	Good	Ave-rage	Poor	Good	Ave-rage	Poor
Acetaldehyde	75a	86a	78a	88a	112b	70a	99b	116b	83a
Ethyl acetate	254a	222a	220a	286a	278a	294a	330a	306a	306a
isoAmyl acetate	39.7a	20b	21b	37a	20b	10c	38a	20b	9.5c
Ethyl caproate	7.6a	6.7b	5.9b	6.3b	7.6a	3.9c	7.8a	8.4a	4.9c
Ethyl caprylate	16.6a	14.6ab	11.3b	17.6a	17.6a	12b	22c	21c	13b
Ethyl caprate	18.6a	16.3a	27a	24a	23a	24a	28.3a	24a	23.5a
Hexyl acetate	4.5a	1.7b	0.3c	3.2a	1.3b	0.4c	5.2a	1.9b	0.3c
Ethyl lactate	12a	16a	67b	14a	21.3a	80b	15.5a	20.7a	78b
Diethyl succinate	1.2a	1.2a	6.9b	1.7a	2.4c	9.2b	2.5c	2.6c	10.5b
2-Phenethyl acetate	0.98a	1.2a	1a	1.1a	1.2a	2.4a	1a	1.2a	2.1a
n-Propanol	313a	182b	264a	347a	220b	256ab	378a	232b	256b
isoButanol	147a	183a	169a	164a	216b	384b	181a	219b	374b
n-Butanol	2.9a	3.8b	4.3c	3.2a	4.6bc	4.8bc	3.8b	6.5d	4.4c
isoAmyl alcohol	577a	501a	585a	1199b	1113b	1692c	1346d	1157b	1651c
n-Hexanol	14.5a	11.7a	17.8a	16a	14a	24a	17.6a	14a	24a
2-Phenethyl alcohol	4.9a	4.7a	6b	6ab	6.2ab	11.2c	7b	7.4b	12c
Acetic acid	171a	298a	227a	166a	224a	222a	272a	304a	295a
Hexanoic acid	3.2a	3a	4.7b	3.3a	3.1a	3.3a	4.2b	3.9b	4b
Octanoic acid	20a	25a	22a	19.6a	24.5a	13.6b	33c	36c	26a
Decanoic acid	18a	21a	32b	16.7a	22.5a	15.5a	44c	46cd	52d

The average quality samples possessed the lowest mean concentration of n-propanol, although this was not significantly different to the poor quality n-propanol concentration after the second and third year of maturation. The mean concentration of octanoic acid was highest in the average quality samples over all three years and lowest in the two and three year-old poor quality samples.

Contrary to what was noted in the 1999 distillates, the poor quality distillates from 2000 did not contain significantly higher concentrations of acetaldehyde, ethyl acetate or acetic acid when compared to the average and good quality distillates. In fact the mean acetaldehyde concentration was highest in the average quality distillates throughout the three years of wood maturation. Poor quality samples possessed the lowest concentration of isoamyl acetate. The concentration of this compound was significantly lower after two and three years of maturation when compared to both the average and good quality distillates. Hexyl acetate concentrations were also lowest in the poor quality distillates over all three years. As was noted for the 1999 samples, the concentration of ethyl lactate was significantly higher in the poor quality samples. Diethyl succinate concentrations were also

significantly higher in the poor quality samples of 2000, as were the 2-phenethyl alcohol and isoamyl alcohol concentrations in all three years and in years two and three respectively.

7.3.5 SENSORY DESCRIPTIVE ANALYSIS ON SELECTED ONE, TWO AND THREE YEAR OLD POTSTILL DISTILLATES

A sensory descriptive analysis was performed on those distillates analysed in section 7.3.4 in order to gain a better idea of the impact of the volatile compound concentration differences on the sensory aroma characteristics of these distillates throughout the three-year maturation period.

7.3.5.1 Good quality distillates

1999 Good quality distillates one year in maturation

Fruity and woody aromas were most intense in sample one, more so than in sample two (**Figure 7.5**). This is interesting as sample one exhibited a lower fruity aroma intensity as an unaged distillate (chapter 5). However, sample two is characterised by equally intense herbaceous and fruity aromas, with less intense woody aromas. The remaining descriptors were found to have nearly equal intensity in both of the samples. Woody aromas were probably not as detectable in sample two to a more equal balance of the remaining positive aromas. Negative aromas were not detected in either of these samples.

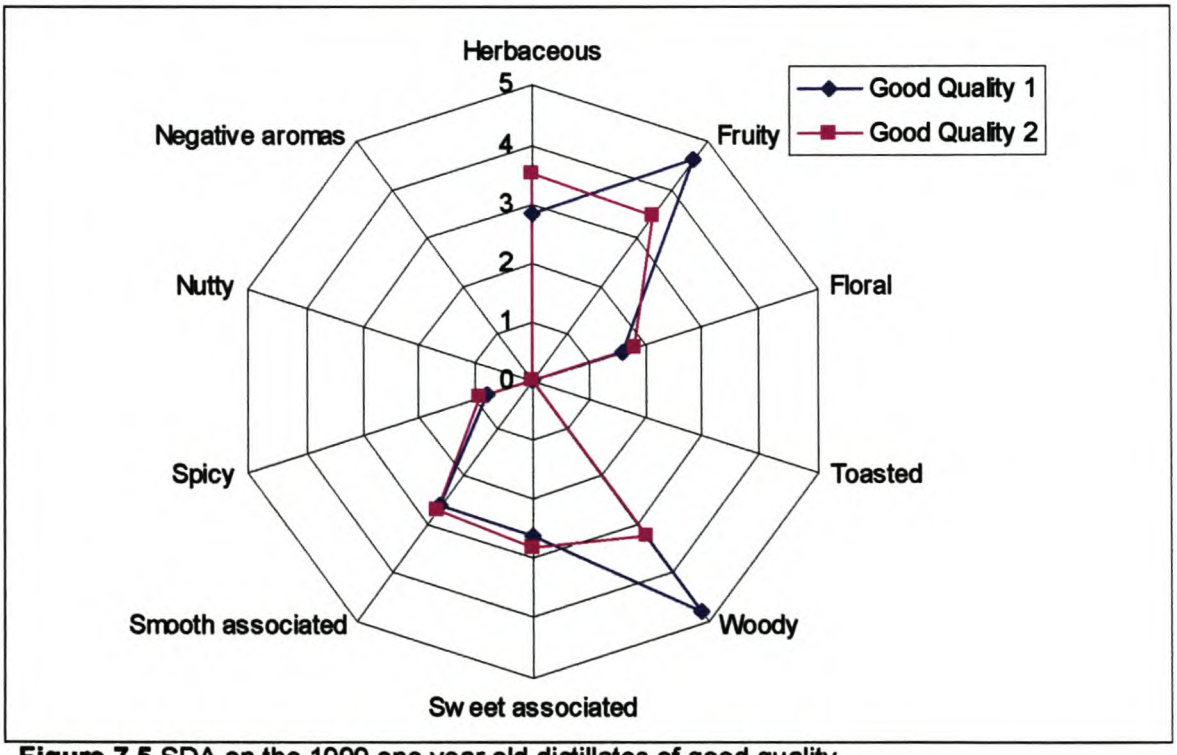

Figure 7.5 SDA on the 1999 one year old distillates of good quality.

1999 Good quality distillates two years in maturation

After two years of wood maturation, the fruity and woody aromas were still found to be more intense in sample one than in sample two (**Figure 7.6**). Sample two still had a greater intensity of herbaceous aromas. However, the remaining positive descriptors, particularly toasted, nutty, floral and smooth associated aromas now differed in intensity between the two samples. As toasted and nutty aromas are typically associated with wood maturation, it follows that the more prominent woody aromas detected in sample one are closely correlated to these other positively associated aromas.

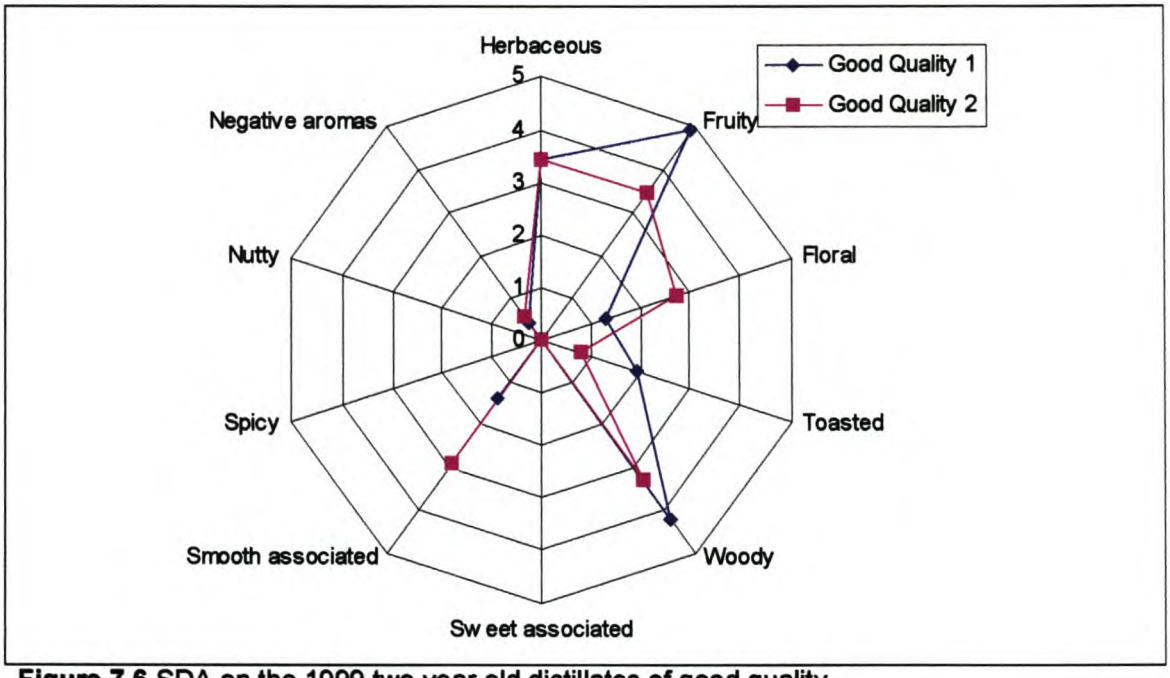

Figure 7.6 SDA on the 1999 two year old distillates of good quality.

1999 Good quality distillates three years in maturation

After three years of wood maturation the aroma profiles of both samples had become remarkably similar (**Figure 7.7**). Fruity aromas were the most intense in both of the samples, while the herbaceous and woody aromas were significantly lower in intensity. The lower intensity of the woody aroma would indicate that the flavours of these samples have now integrated to produce a fruit-driven product that is not dominated by either woody or herbaceous aromas.

2000 Good quality distillates one year in maturation

The most prominent descriptor for both samples was fruity, which was found to be almost equally intense in both samples (**Figure 7.8**). However, sample two was found to have a more intense herbaceous and woody aroma than sample one. A slight floral aroma was also detected in both samples.

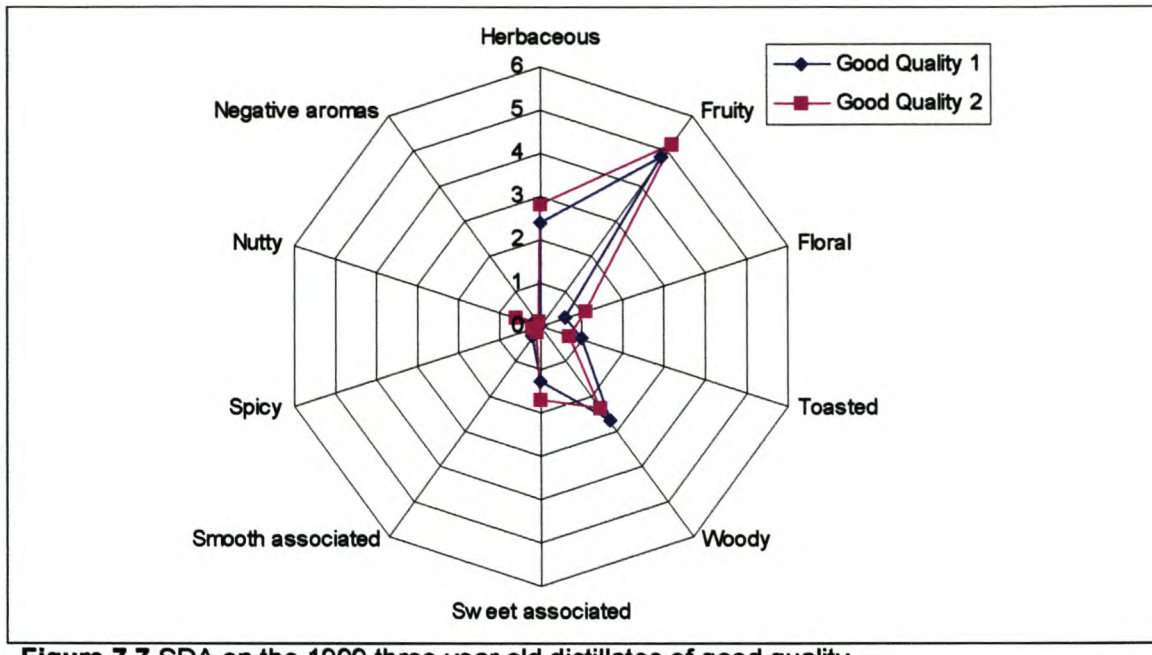

Figure 7.7 SDA on the 1999 three year old distillates of good quality.

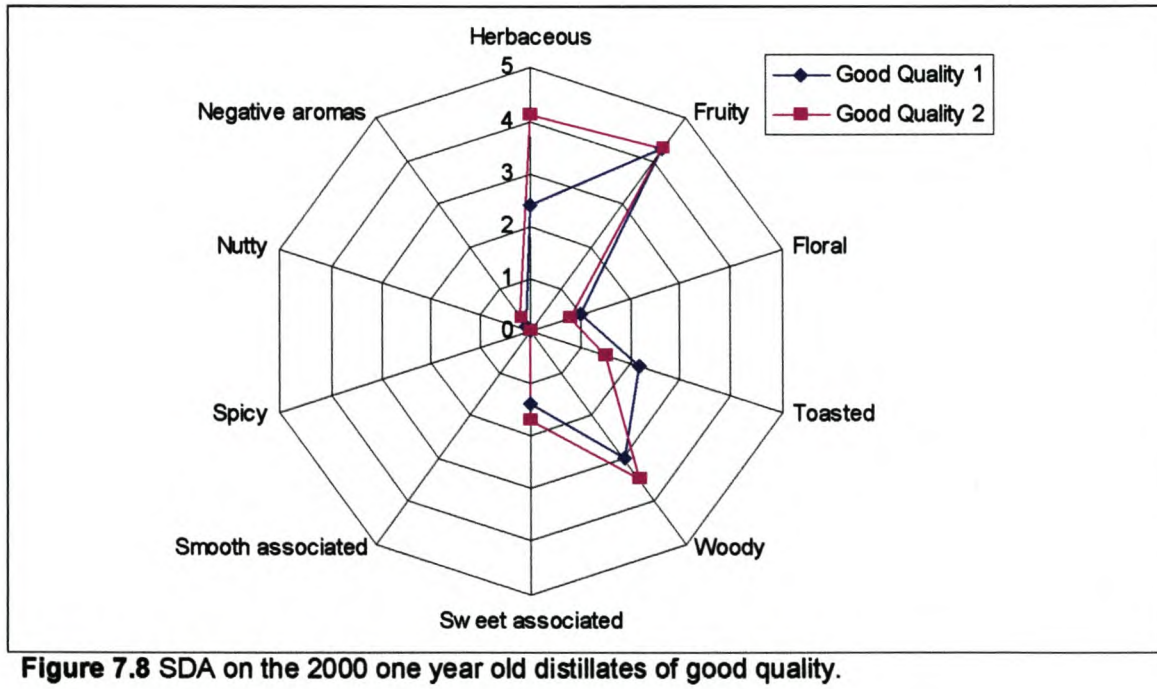

Figure 7.8 SDA on the 2000 one year old distillates of good quality.

2000 Good quality distillates two years in maturation

After two years in wood maturation, both samples exhibited very similar aroma profiles with very few differences in intensity for most of the descriptors (**Figure 7.9**). The herbaceous aroma detected in sample one after one year of wood maturation had decreased somewhat in intensity. Also interesting is the fact that the woody aroma had decreased in intensity after two years of wood maturation when compared to year one. Other positive aromas such as smooth, spicy and nutty were barely detectable. Sample one was found to have a slightly negative aroma attribute.

2000 Good quality distillates three years in maturation

Except for the floral and negatively associated aroma attributes detected, both samples exhibited very similar aroma profiles for the remaining descriptors at three years of age (**Figure 7.10**). Sample one was found to exhibit less of a floral aroma and had retained its slightly negative, solvent/chemical aroma attribute. The aroma profile of both three-year old samples is very similar to that after two years of wood maturation, however, after three years the woody and toasted aroma was found to be more intense. Toasted and sweet associated aromas are also present in both samples hinting at an integrated wood maturation character with some complexity.

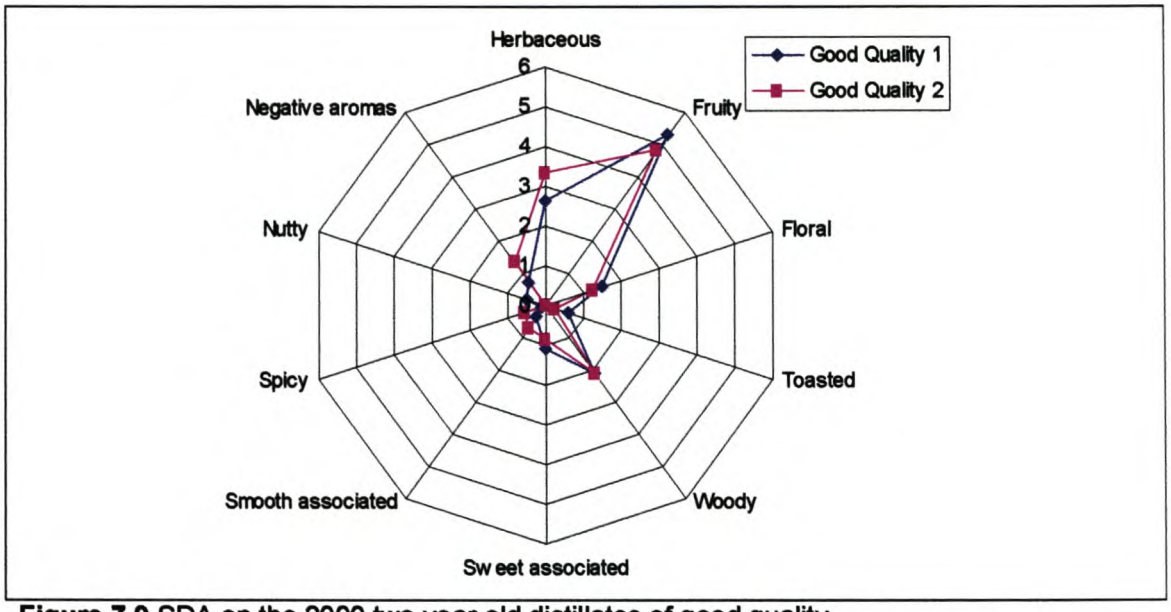

Figure 7.9 SDA on the 2000 two year old distillates of good quality.

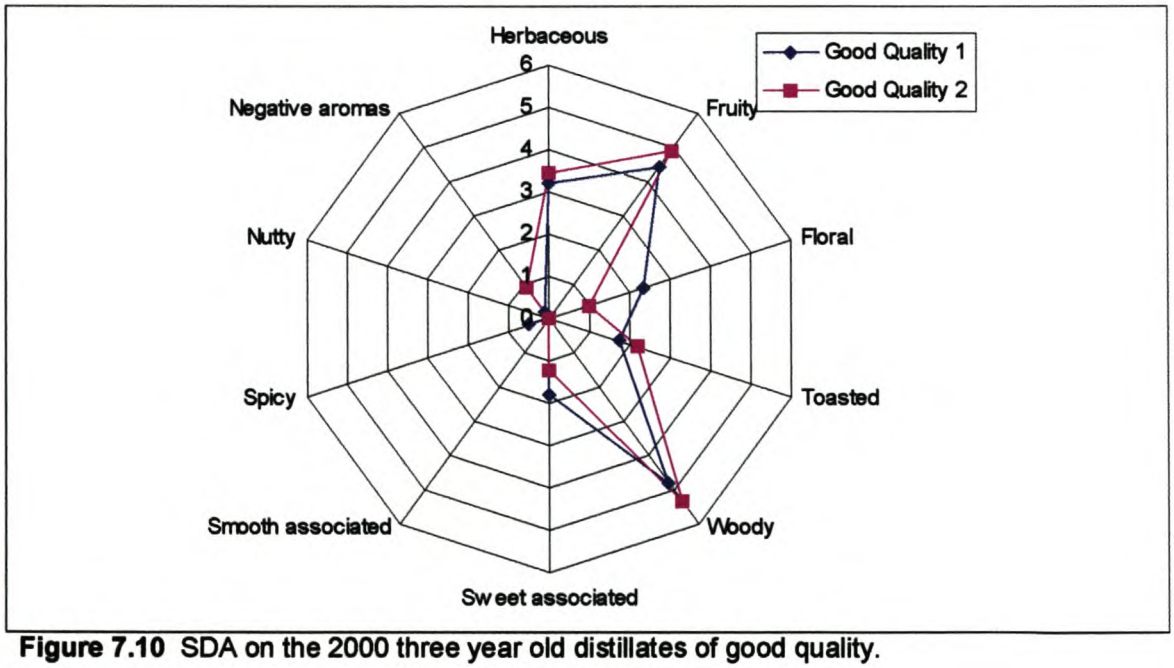

Figure 7.10 SDA on the 2000 three year old distillates of good quality.

From the above-mentioned descriptions, one can conclude that the sensory aroma profile of good quality distillates throughout maturation is typically characterised by prominent fruity aromas that are balanced by herbaceous and woody aromas, with sweet associated and floral aromas adding subtle complexity. After three years of wood maturation, the woody aromas are less prominent or of equal intensity as the fruity aromas resulting in an integrated, balanced aroma profile. These distillates already had fruity as their most intense aroma descriptor as unaged products (chapter 5). Already in the unaged product, the panel had detected a negative aroma component in sample one of the good quality 2000 distillates, which was also identified as a solvent/ chemical type of aroma (chapter 5).

7.3.5.2 Average quality distillates

1999 Average quality distillates one year in maturation

Herbaceous aromas were the most prominent in sample two followed by fruity and woody aromas, whereas woody aromas closely followed by fruity aromas were most prominent in sample one (**Figure 7.11**). Smooth associated aromas were equally prominent in both samples. Floral, sweet associated and spicy aromas were also detected in both samples.

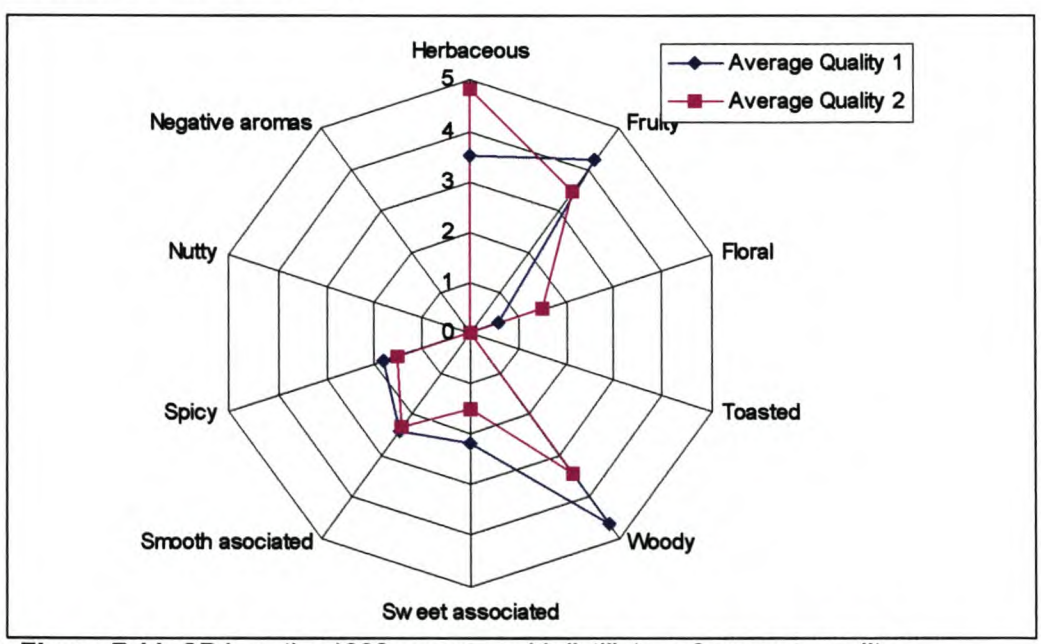

Figure 7.11 SDA on the 1999 one year old distillates of average quality.

1999 Average quality distillates two years in maturation

After two years of wood maturation, the aroma profile of both 1999 distillate samples was very similar, with the same descriptors being used for both sets of distillates. However, all of the aromas were slightly more intense in sample one (**Figure 7.12**). In sample one the herbaceous and woody aromas were the most prominent aromas and were almost equal in intensity, whereas the herbaceous aroma was slightly more

prominent in sample two. Small amounts of nutty, toasted and sweet associated aromas were detectable in both samples. Floral aromas were also found to be present in both samples.

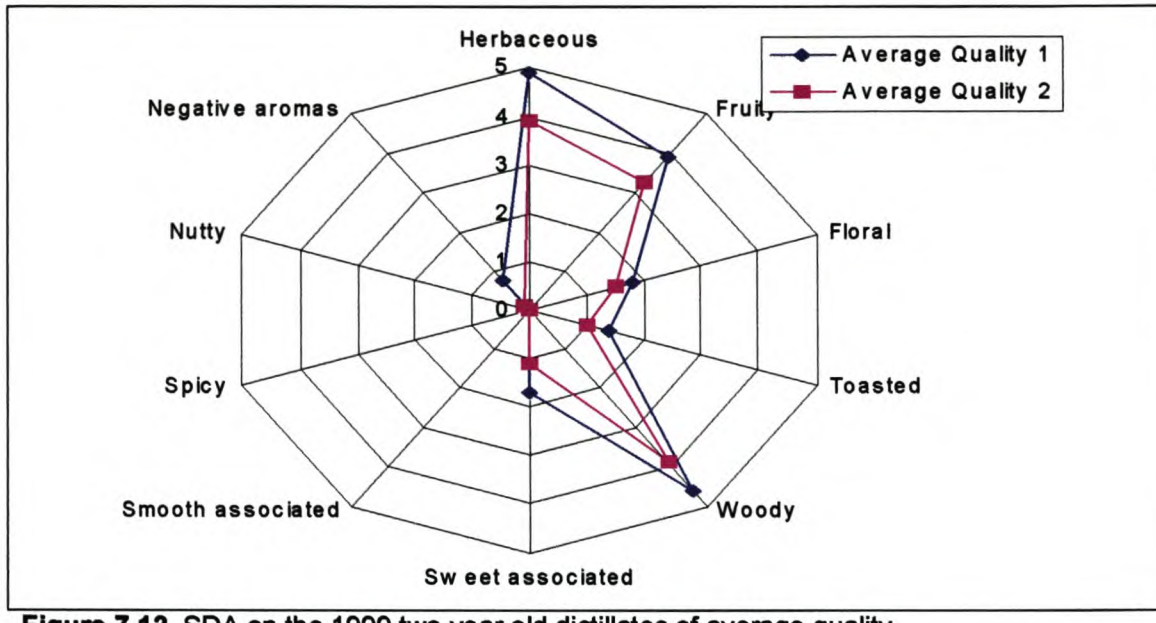

Figure 7.12 SDA on the 1999 two year old distillates of average quality.

1999 Average quality distillates three years in maturation

After three years of wood maturation, the aroma profile of the both distillates had changed somewhat and the profile of the two distillates became similar (**Figure 7.13**). Fruity aromas were the most prominent in both samples followed by woody and herbaceous aromas of almost equal intensity.

2000 Average quality distillates one year in maturation

In this instance, the fruity aroma was most prominent in sample one, followed by woody and then herbaceous aromas (**Figure 7.14**). However, sample one exhibited more prominent herbaceous aromas. Sweet associated aromas were also detected in both samples. Both samples also exhibited some toasted and floral aromas.

2000 Average quality distillates two years in maturation

After two years of wood maturation, fruity remained the most prominent aroma in sample two, whilst herbaceous aromas were still found more prominent than the woody aroma in this sample (**Figure 7.15**). Sample two was also found to exhibit an interesting spicy aroma. Sample one, on the other hand, exhibited more intense herbaceous than fruity aromas, also with less prominent woody aromas.

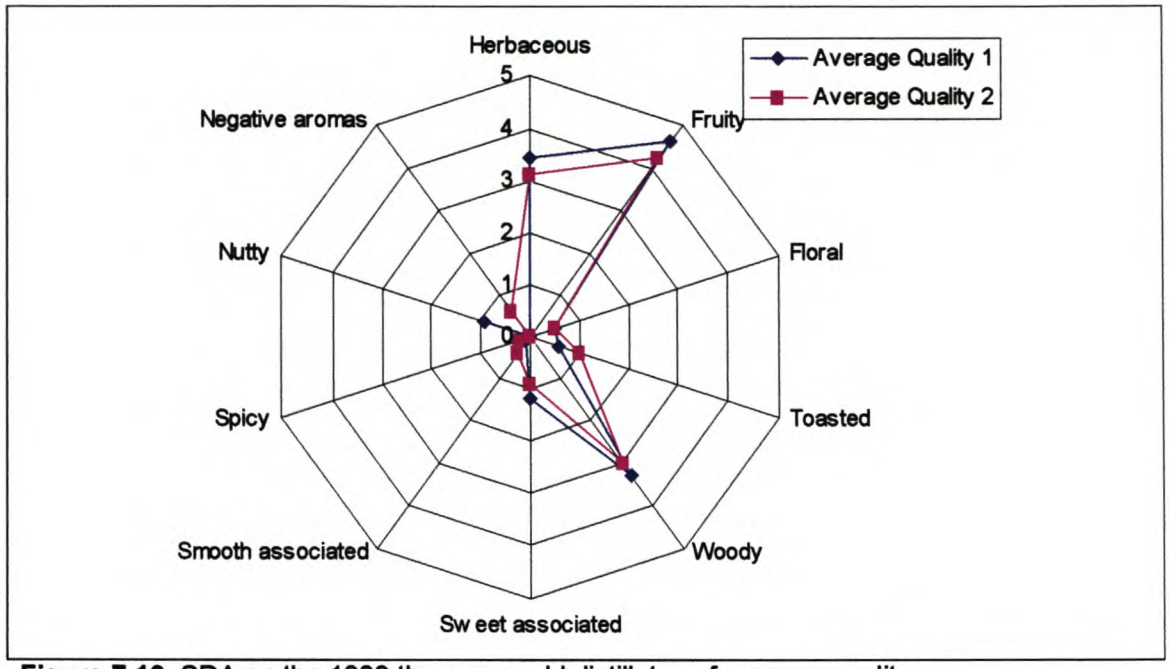

Figure 7.13 SDA on the 1999 three-year old distillates of average quality.

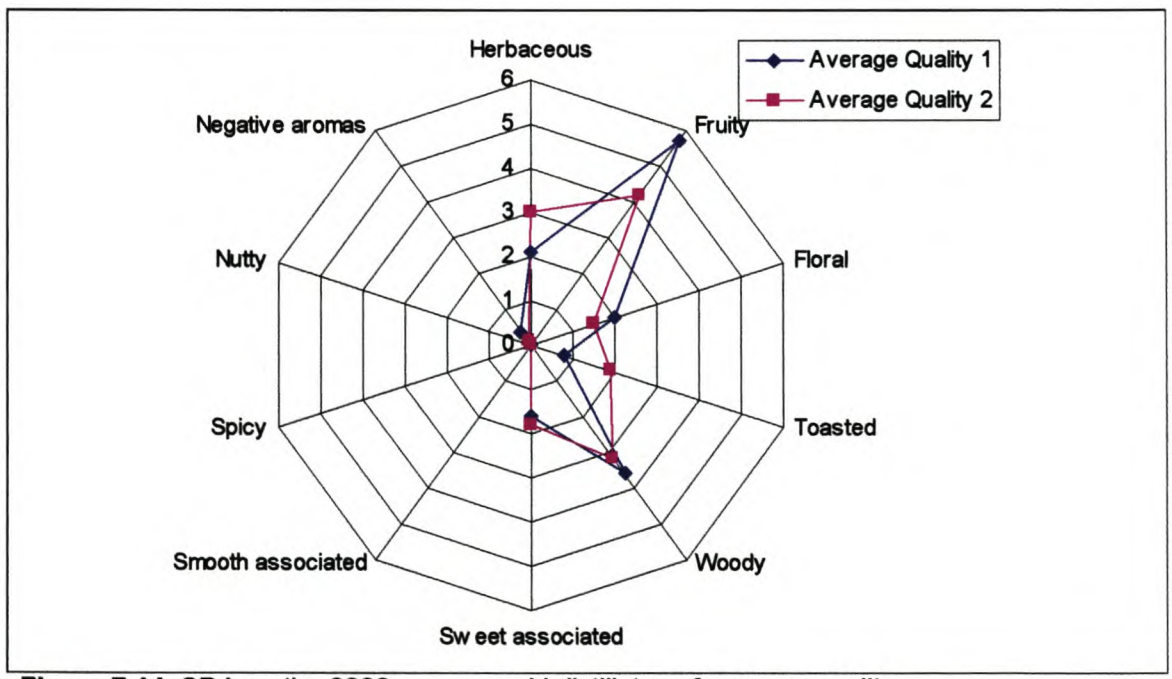

Figure 7.14 SDA on the 2000 one year old distillates of average quality.

2000 Average quality distillates three years in maturation

After three years of wood maturation, the aroma profile of the both distillates had changed and both samples were found to exhibit a similar aroma profile (**Figure 7.16**). Woody aromas were the most prominent in both samples. Fruity and herbaceous aromas were in both instances almost equal in intensity and toasted aromas also added a new dimension to the aroma profile. The spicy aroma detected

in sample two at two years of age was no longer detectable, however, a spiciness was detected in sample one.

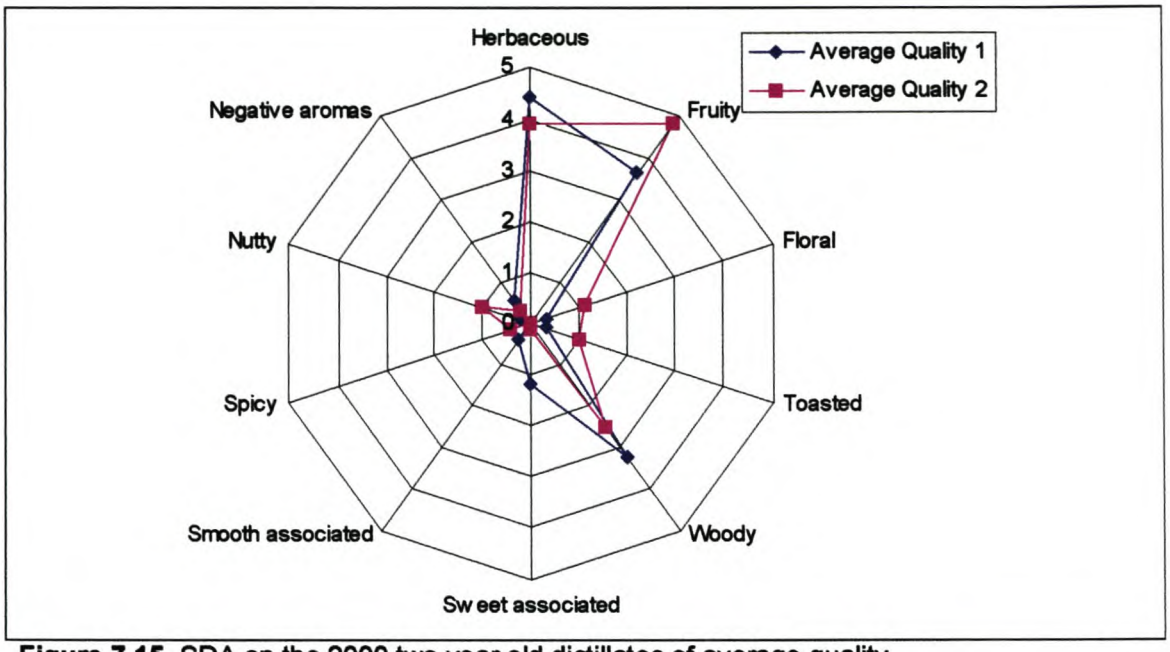

Figure 7.15 SDA on the 2000 two year old distillates of average quality.

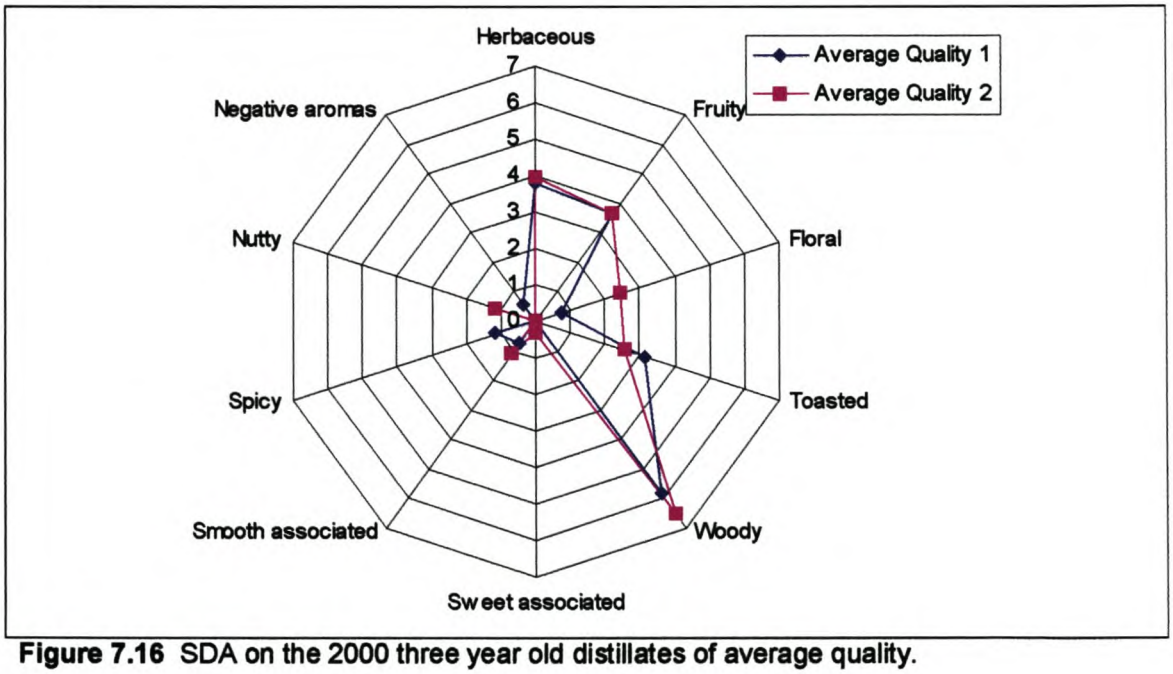

Figure 7.16 SDA on the 2000 three year old distillates of average quality.

When one compares the aroma profiles of the three-year old good and average quality distillates there are few differences amongst the 1999 samples. However, the 2000 average quality distillates have distinctly more wood-driven aromas (woody and toasty) than their 2000 good quality, fruit-driven counterparts. In these average

quality distillates, herbaceous and fruity aromas are also of equal intensity, whereas the good quality 3-year old distillates exhibited less prominent herbaceous aromas.

7.3.5.3 Poor quality distillates

1999 Poor quality distillates one year in maturation

Herbaceous aromas were found to have the highest intensity in sample two followed by woody aromas (**Figure 7.17**). Fruity aromas were detected but were of low intensity, as were spicy, smooth and sweet associated aromas. However, sweet associated aromas, described by the panel as acetaldehyde, port and sherry like, and then, to a lesser extent, fruity aromas, dominated the aroma profile of sample one.

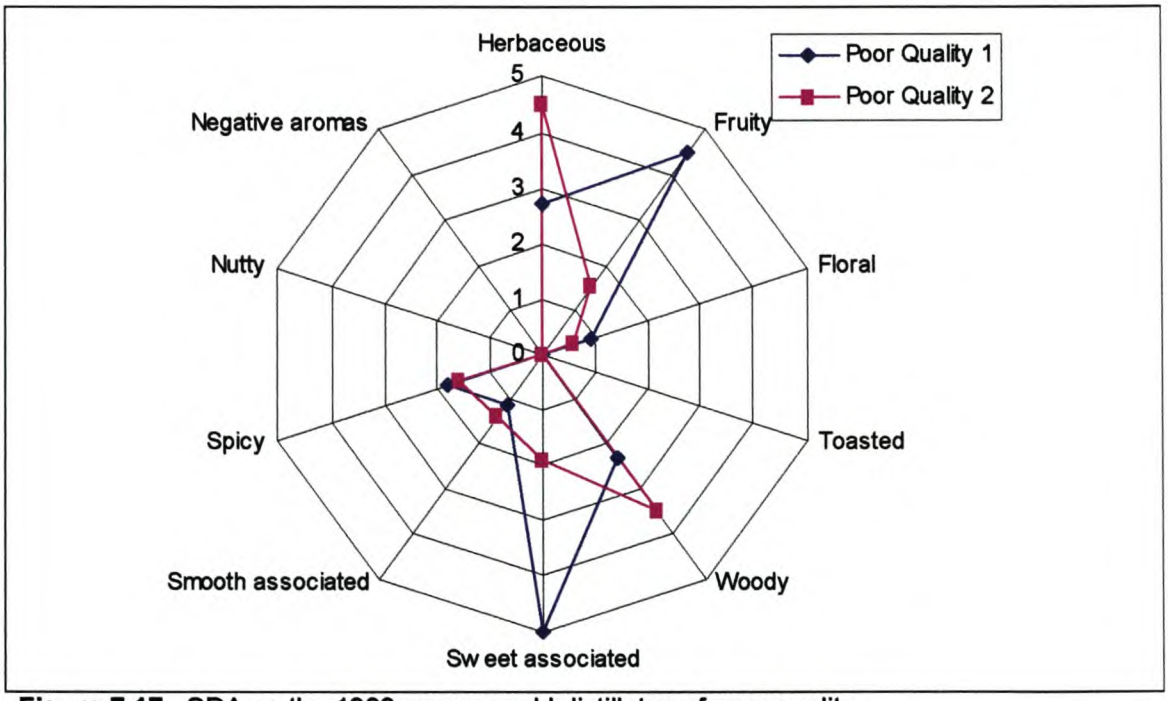

Figure 7.17. SDA on the 1999 one year old distillates of poor quality

1999 Poor quality distillates two years in maturation

The same sweet associated aromas were present after two years of maturation in sample one, but the panel now also detected prominent negative aromas reminiscent of solvents, chemicals and a heads fraction (**Figure 7.18**). Woody aromas were the most prominent in sample two, however, these were closely followed by herbaceous and fruity aromas. Sample two also exhibited some toasted aromas after two years of wood maturation.

1999 Poor quality distillates three years in maturation

After three years of wood maturation, the panel detected faint, sweet associated aromas in both samples (**Figure 7.19**). Prominent negative and herbaceous aromas now characterised sample one, whereas sample two had prominent herbaceous and

woody aromas. Although present, fruity aromas were lower in intensity than the herbaceous aromas in both samples. Some negatively associated aromas were also detected in sample two, although these were perceived to be of low intensity when compared to sample one. The prominent negative aroma in sample one was once again described as being of a solvent/ chemical and heads fraction nature.

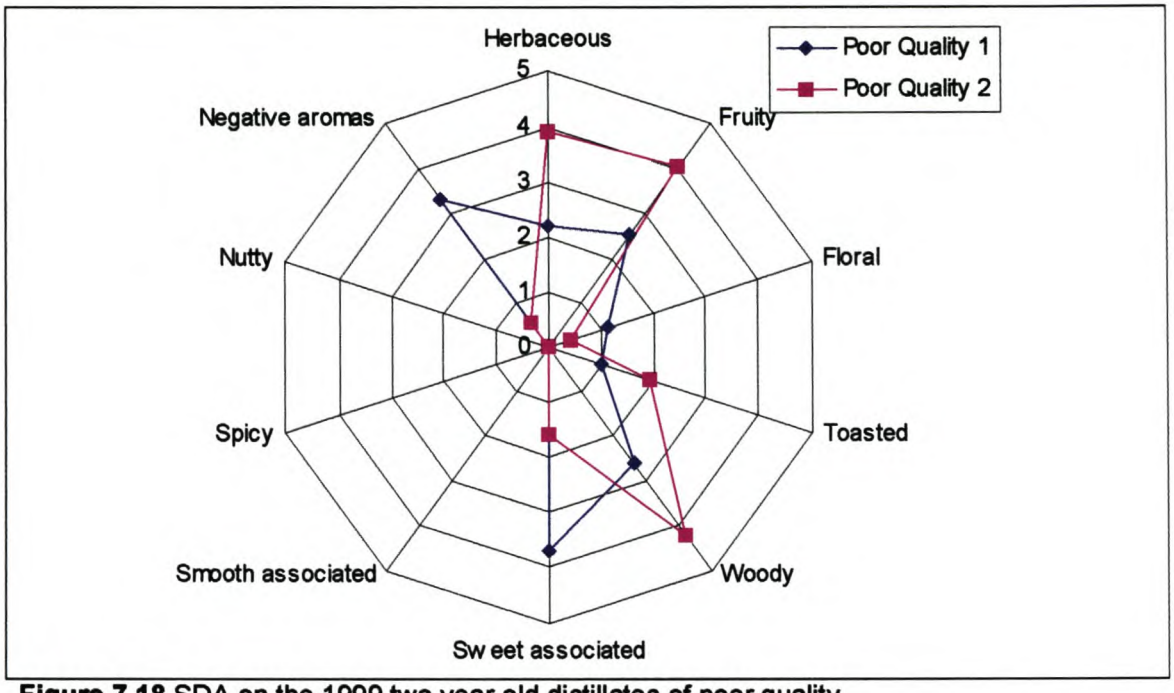

Figure 7.18 SDA on the 1999 two year old distillates of poor quality.

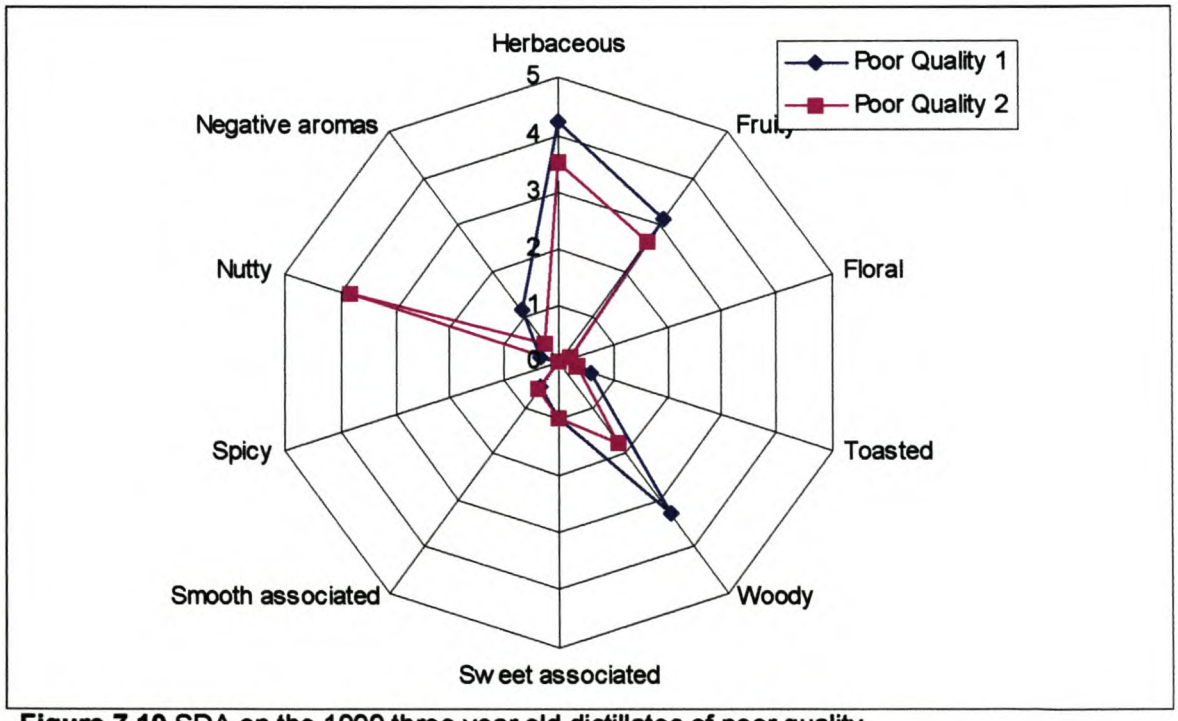

Figure 7.19 SDA on the 1999 three year old distillates of poor quality.

2000 Poor quality distillates one year in maturation

Contrary to the 1999 poor quality distillates at one year of age, these samples exhibited rather similar aroma profiles (**Figure 7.20**). Herbaceous aromas were found to be highest intensity in sample two, followed by sweet associated and woody aromas. Floral and sweet associated aromas were more prominent in sample two. The sweet associated aroma in sample two was described as being sherry-like. Slight negative aromas (heads) were also detected in both samples by the panel with sample one having more prominent negative and toasty aromas.

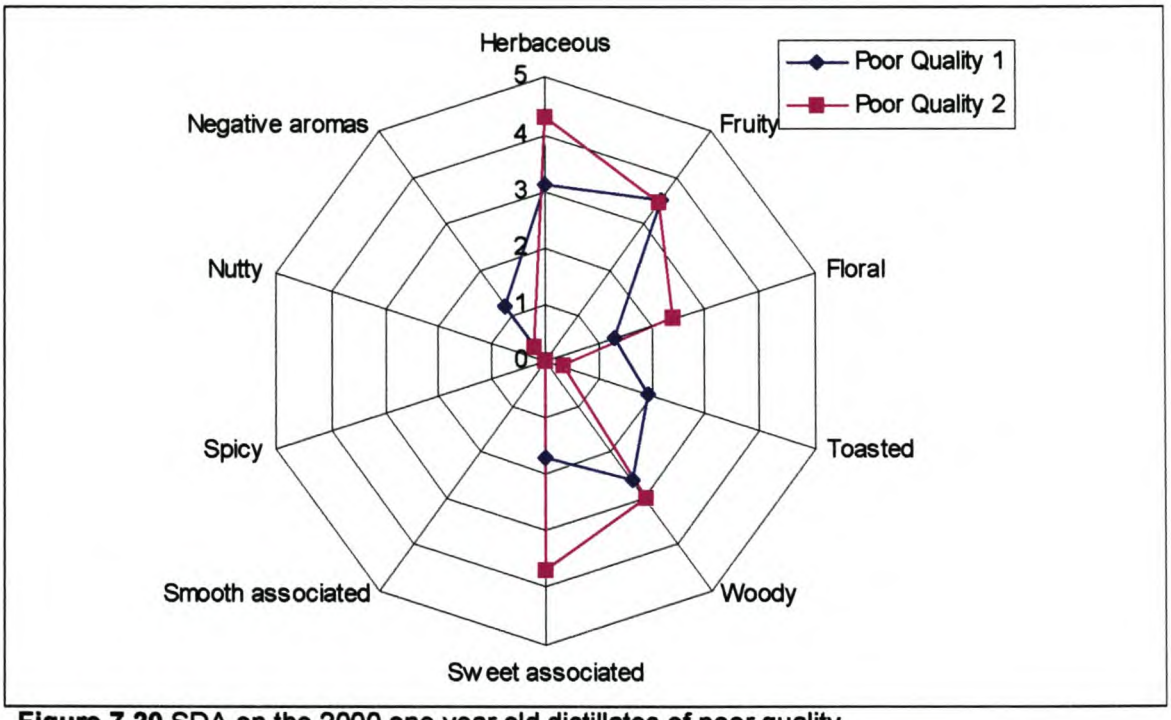

Figure 7.20 SDA on the 2000 one year old distillates of poor quality.

2000 Poor quality distillates two years in maturation

After two years of wood maturation, herbaceous aromas were most prominent in both of the samples (**Figure 7.21**). Negative aromas were still prominent in sample one whilst sample two had more prominent fruity, sweet and smooth associated aromas than negative aromas. Woody aromas were prominent in both samples

2000 Poor quality distillates three years in maturation

After three years of wood maturation, both samples had equally prominent herbaceous and woody aromas (**Figure 7.22**). Negative aromas (heads) were still detected in sample one, whereas sample two exhibited some fruity aromas. Toasted aromas were also present at almost equal intensity in both samples. After three years of wood maturation, the main descriptor that distinguishes poor quality distillates from those of good and average quality is the herbaceous descriptor, which was found to be the most intense aroma in both vintages of poor quality distillates.

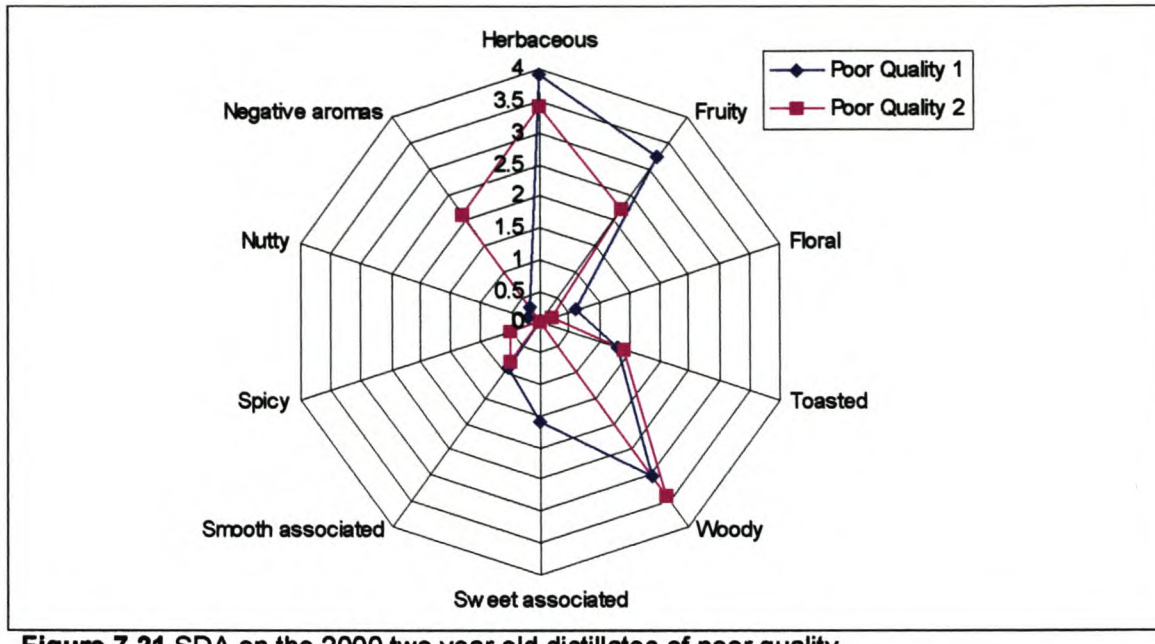

Figure 7.21 SDA on the 2000 two year old distillates of poor quality.

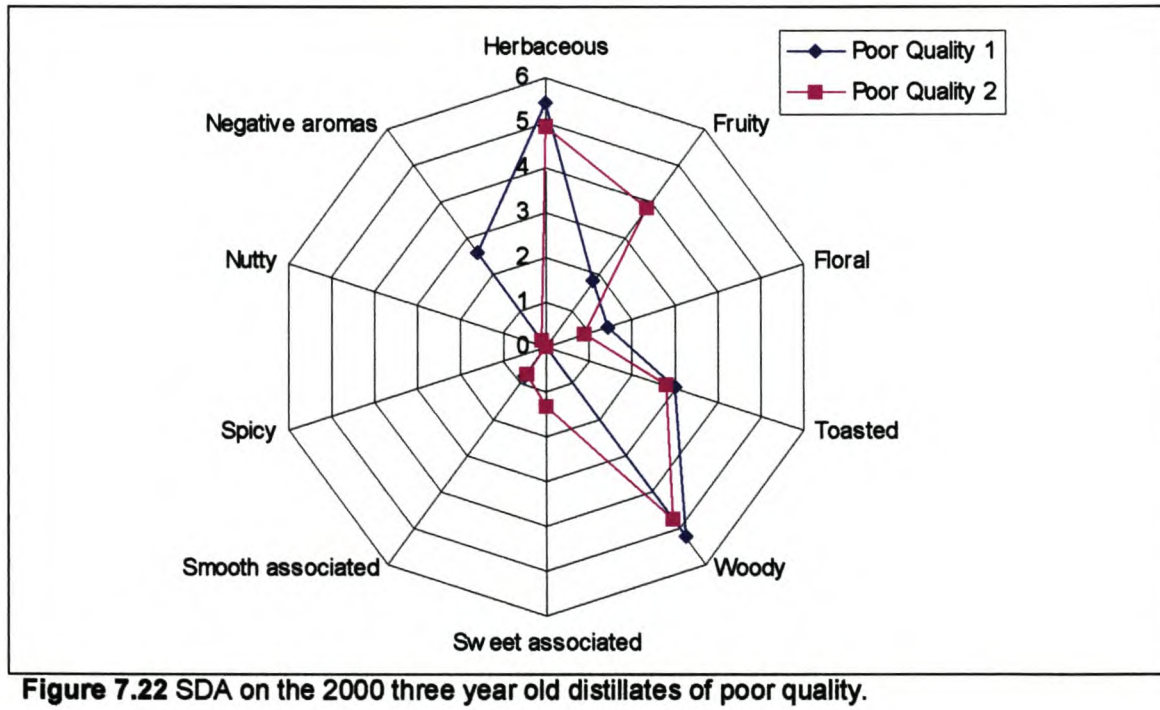

Figure 7.22 SDA on the 2000 three year old distillates of poor quality.

In summary, after three years of wood maturation, the aroma profile of poor quality distillates can be characterised by prominent herbaceous and woody aromas, which are more intense than the fruity aromas. In chapter 4 it was found that herbaceous was the most intense aroma in the unaged poor quality distillates. In this instance, negatively associated aromas were detected on two of the samples from both vintages. In the 1999 distillates, the panel detected a solvent/ chemical character as well as traces of heads aromas as negatively associated aromas. In 2000, the same negatively associated aromas were present in sample one, whilst

sample two was found to have a molasses character that was categorised as a sweet associated aroma. As all samples in this project underwent the same wood maturation process (equal times and equal barrel age composition), one can speculate that the combination of less prominent fruity aromas and more prominent herbaceous aromas may serve to accentuate the woody aromas in the poor quality samples.

Although few distinctive differences in aroma profiles were found to exist between the good and average quality distillates, there were distinct differences between the good quality and poor quality aroma profiles throughout the course of maturation. In chapter 4 the same observation was made on the unaged distillates. Although aroma profiles may have differed between the two samples in each category at one and two years of maturation, it is interesting to note that, after three years of maturation, the profiles became markedly similar. Where woody aromas were prominent at one and two years of maturation in the good and average quality distillates, the woody aroma became less prominent and more integrated into the aroma profile after three years of wood maturation. This was however not the case for the poor quality distillates. The distinct differences in the aroma profile of the poor quality distillates, when compared to those of good and average quality after all three years of oak maturation indicate that wood maturation does not significantly alter the perceived aroma profile of a poor quality distillate. The undesirable characteristics originally present are still present, even if at lower intensity than in the unaged product. This implies that a poor quality, unmatured distillate will not significantly improve in quality with three years of wood maturation. Similarly, a good quality unmatured distillate, on condition that it is not matured in a faulty barrel or under incorrect conditions, will retain its quality throughout maturation, although it is difficult to distinguish between a distillate of good and average quality after three years of wood maturation. This correlation is largely confirmed in the Spearman rank order correlation analysis in **Table 7.1**.

7.3.6 REGRESSION ANALYSIS USING SENSORY SCORE AS DEPENDENT VARIABLE ON ROUTINE BASE WINE ANALYSES

It is commercial practice to do a so-called routine analysis on each brandy base wine that is presented to the distillery for purchasing. This analysis has its origin with the South African liquor law and the dates back to the time when the South African Brandy Board had legislative power to control the quality of wines used for brandy distillation. Although there are currently no more technical specifications for a brandy base wine that are prescribed by law, and the activities of the South African Brandy Board have been disbanded, Distell continues to adhere to these technical specifications as a guideline in the selection of base wines to be purchased. It is important to bear in mind that a brandy base wine is not merely purchased based on the results of this routine analysis, rather the final purchasing decision is based on its passing of a sensory evaluation. Thus, a base wine presented to the distillery for purchasing may pass the technical requirements and may not be purchased if its

sensory character is displeasing. Although a base wine that fails the analytical criteria will not be purchased even if it is sensorially acceptable. The following analyses form part of this routine analysis:

Residual sugar less than 4 mg/L

Volatile acidity less than 0.7 mg/L

Alcohol approximately between 10 – 12 %v/v

Total SO_2 less than 20 mg/L

Total polyphenol content less than 250 mg/L

As these routine analyses already form part of the analytical infrastructure for brandy production, it was decided to investigate whether any one of the above-mentioned analyses might yield an indication as to the expected quality of the base wine, unaged distillate and/or the three-year old matured potstill distillate. All base wines used for this study met the above-mentioned criteria. Thus, it was hoped to find an indication of sensory quality within these analytical parameters. This was done using single and multiple regression analysis.

Table 7.6 summarises the R_2 and p-level values for a single regression analysis for each of the six analyses that comprise the routine analysis. The dependant variable used was as an indication of quality was the average score of the 1999 base wines. As is evident from **Table 7.6**, only the total polyphenol content showed any significant relationship to base wine quality in 1999. From **Figure 7.23** it is evident that, even though all of the base wines had a polyphenol content less than or just equal to 250 mg/L (the maximum value of this specification), there is a tendency that as polyphenol concentrations increase, the quality of the 1999 base wines decrease. Although not deemed significant, total acidity and wine score yielded the same trend i.e. as the total acidity increases, so too did the average 1999 wine score (data not shown). A multiple regression analysis, which tries to establish the inter-relationship between all six of the routine analyses and 1999 wine quality showed that no significant inter-relationships existed in this dataset (data not shown).

Table 7.6 Relationship between individual routine base wine analysis and 1999 average wine score

Independent Variable	R2	p-level
Alcohol	0.001	0.850
Residual sugar	0.090	0.102
Volatile acidity	0.046	0.245
Total acidity	0.110	0.069
Total SO2	0.003	0.771
Free SO2	0.090	0.108
pH	0.048	0.234
Polyphenols	0.187	0.015

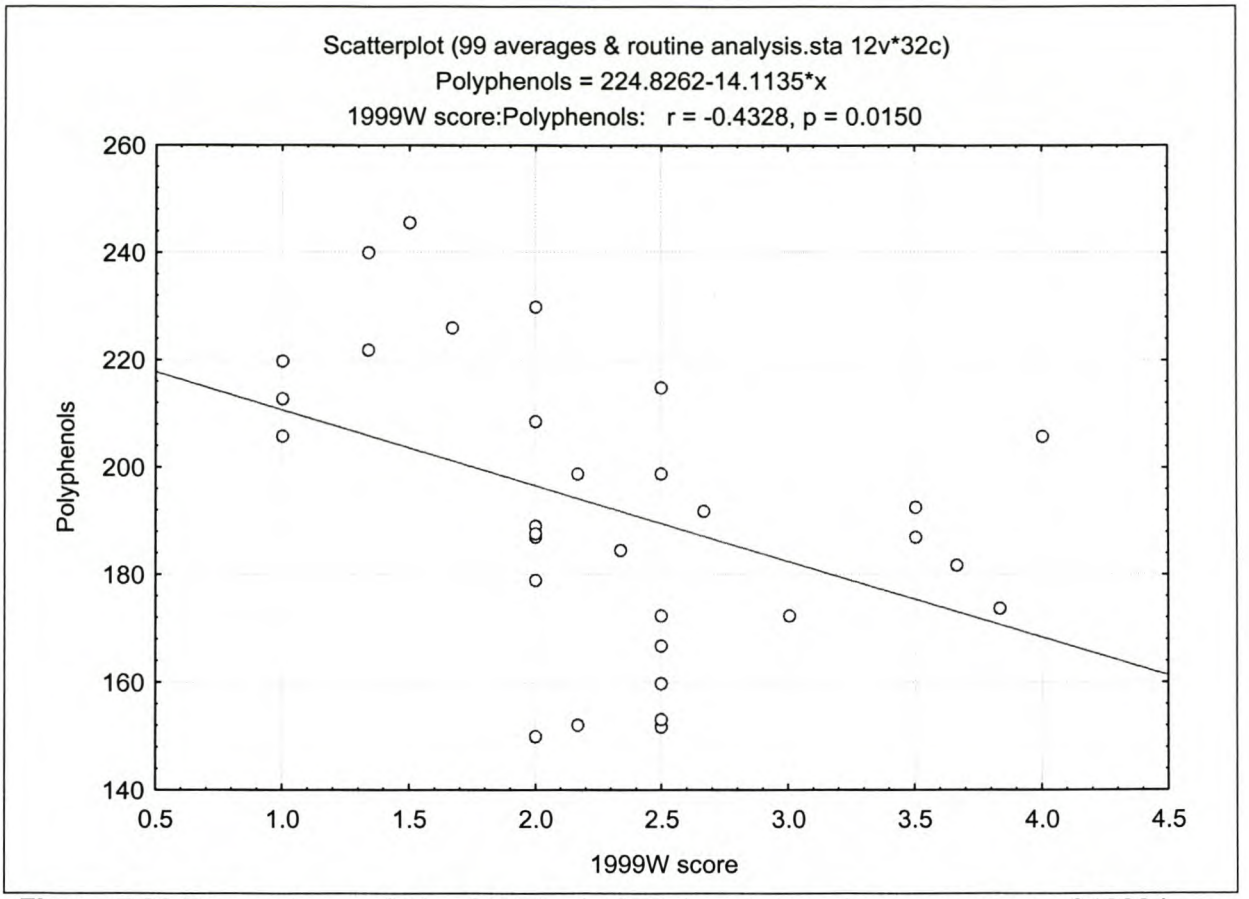

Figure 7.23 Regression analysis of total polyphenol content and average score of 1999 base wines.

Table 7.7 summarises the R_2 and p-level values for a single regression analysis using each of the six analyses individually and the 2000 average wine score as the dependant variable. As is evident from **Table 7.7**, none of the p-levels showed statistical significance (i.e. p less than 0.05). However, the quality of the 2000 base wines tended to decrease as polyphenol concentrations increased, as was observed in the 1999 wines. Wine quality in 2000 also tended to decrease as volatile acidity levels increased. There was, however, no clear pattern for total acidity in the 2000 base wines (data not shown).

Table 7.7 Relationship between individual 2000 routine base wine analysis and 2000 base wine score

Independent Variable	R2	p-level
Alcohol	0.032	0.391
Residual sugar	0.023	0.472
Volatile acidity	0.128	0.080
Total acidity	0.010	0.630
Total SO2	0.037	0.356
Free SO2	0.117	0.094
pH	0.097	0.129
Polyphenols	0.134	0.072

From **Table 7.8** it is evident that the only significant relationship found in the 1999 unaged distillates was that of base wine alcohol content and distillate quality (**Figure 7.24**). This relationship was also confirmed in the multiple regression analysis (**Table 7.9**). Although not significant, the 2000 unaged distillates exhibited the same trend with quality tending to increase as the alcohol concentration of the base wine increased. There were no significant relationships between 2000 unaged distillate quality and any of the six analyses (**Table 7.10**). However, polyphenol concentrations exhibited the same trend as discussed for the 1999 and 2000 base wines. Base wine pH also tended to decrease as distillate quality increased (data not shown).

Table 7.8 Relationship between individual 1999 routine base wine analysis and 1999 unaged distillate score

Independent Variable	R2	p-level
Alcohol	0.160	0.026
Residual sugar	0.037	0.302
Volatile acidity	0.066	0.164
Total acidity	0.017	0.481
Total SO2	0.001	0.844
Free SO2	0.004	0.746
pH	0.032	0.338
Polyphenols	0.087	0.107

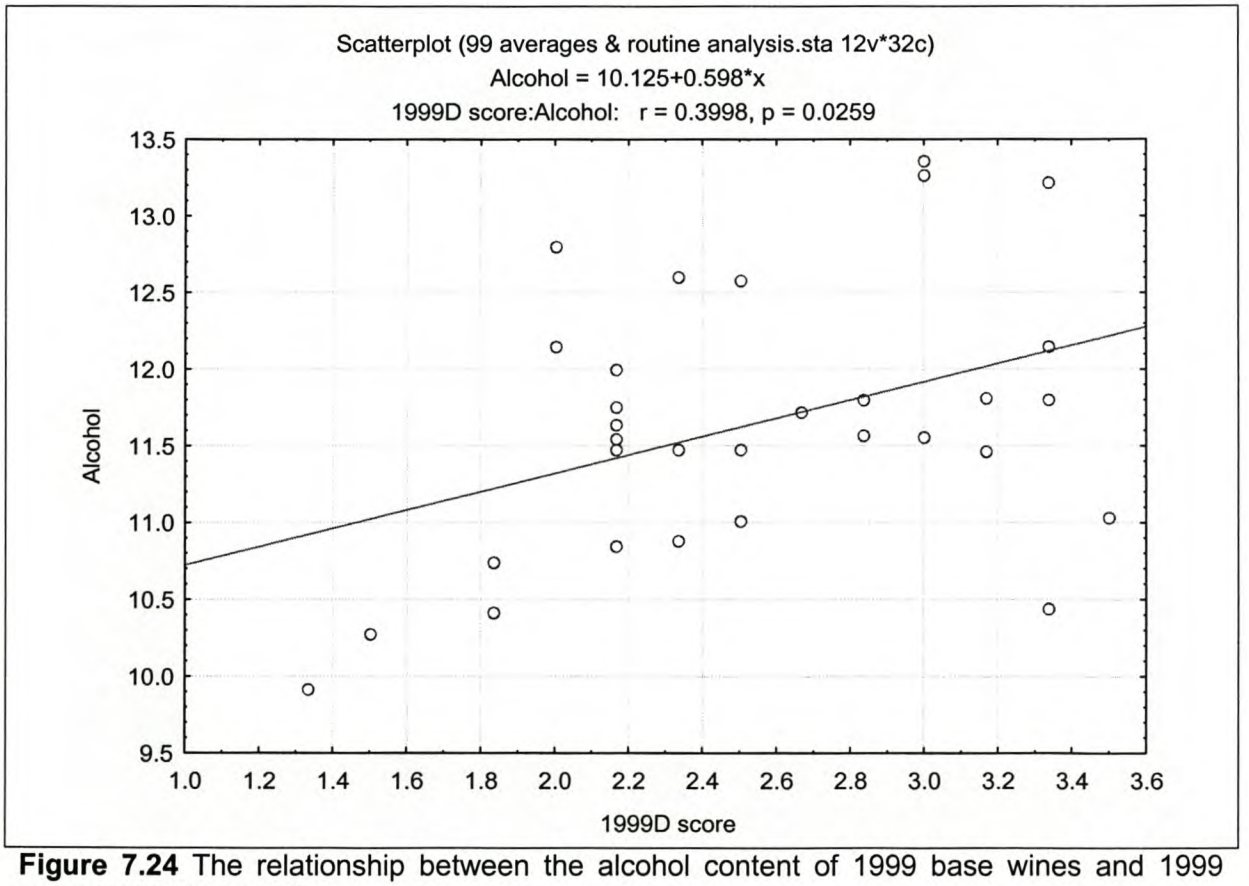

Figure 7.24 The relationship between the alcohol content of 1999 base wines and 1999 unaged distillate quality.

Table 7.9 Relationships between 1999 routine base wine analyses and 1999 unaged distillate score. Multiple regression summary for dependant variable 1999 distillate score R2 =0.27294 P<0.47436

	Beta	Std.Err.	B	Std.Err.	t(21)	p-level
Intercept			0.354	3.543	0.100	0.921
Alcohol	**0.519**	**0.218**	**0.342**	**0.144**	**2.383**	**0.027**
RS	0.022	0.215	0.010	0.097	0.100	0.921
VA	-0.105	0.215	-0.480	0.979	-0.491	0.629
TA	0.298	0.242	0.151	0.123	1.230	0.232
TSO2	-0.091	0.213	-0.032	0.074	-0.426	0.674
FSO2	0.075	0.198	0.013	0.035	0.379	0.708
pH	-0.195	0.218	-0.637	0.710	-0.897	0.380
Polyphenols	0.014	0.251	0.000	0.005	0.056	0.956

Table 7.10 Relationship between individual 2000 base wine analyses and 2000 unaged distillate score

Independent Variable	R2	p-level
Alcohol	0.042	0.324
Residual sugar	0.068	0.207
Volatile acidity	0.082	0.165
Total acidity	0.026	0.441
Total SO2	0.030	0.409
Free SO2	0.000	0.941
pH	0.122	0.087
Polyphenols	0.084	0.160

No significant relationships were found to exist between the 1999 three-year old potstill quality scores and any of the six analyses (data not shown). However, base wine alcohol content and the 2000 three-year old distillate score exhibited a significant relationship (**Figure 7.25**). There was a tendency for the score of the 2000 three-year old distillate to increase as the value for base wine pH and volatile acidity decreased (data not shown). The multiple regression analysis using the 2000 three-year old potstill score yielded no significant results (data not shown).

7.3.7 THREE YEAR OLD POTSTILL DISTILLATE STYLE CLASSIFICATION

7.3.7.1 Relationship between sensory quality and style classification of the three-year old distillates

An analysis of variance (ANOVA) was performed in order to determine whether the style classification of three-year old distillates is in any way correlated to their sensory quality or that of the respective unaged distillates and base wines. ANOVA showed that there were no significant differences between the quality of these three products and the style classification of the three-year old potstills. Using ANOVA it was also

established that there is no relationship between any of the routine analysis values and the style classification of the three-year old distillates (data not shown).

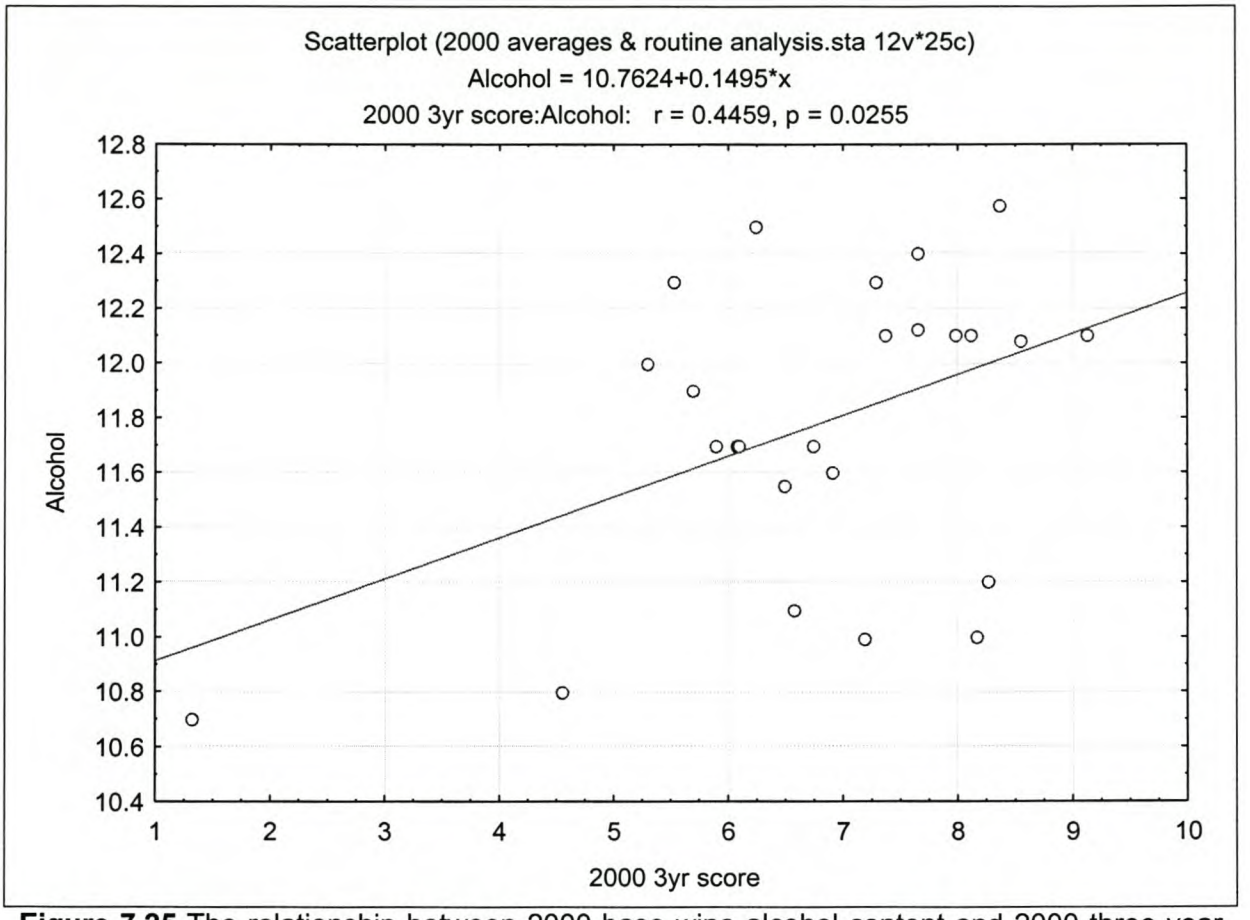

Figure 7.25 The relationship between 2000 base wine alcohol content and 2000 three year old distillate score.

7.3.7.2 Relationship between demographic and production factors and style classification of the three-year old distillates

CART analysis was used to determine the relationship, if any, between demographic and production factors (chapter 4) and the style classification of the three-year old potstill distillates. From **Figure 7.26** it can be seen that all of the three-year old distillates originating from region 4, were classified as style 3. Eighty-three percent of those distillates originating from regions 2 and 5 and were originally made using Colombar and table grapes were also classified as style 3. However, 63% of those distillates originating from the same region but made with Chenin blanc, "other" varieties and a mix of Chenin blanc/Colombar were classified into style 2. Fifty one percent of those distillates originating from regions one and three were classified into style 1.

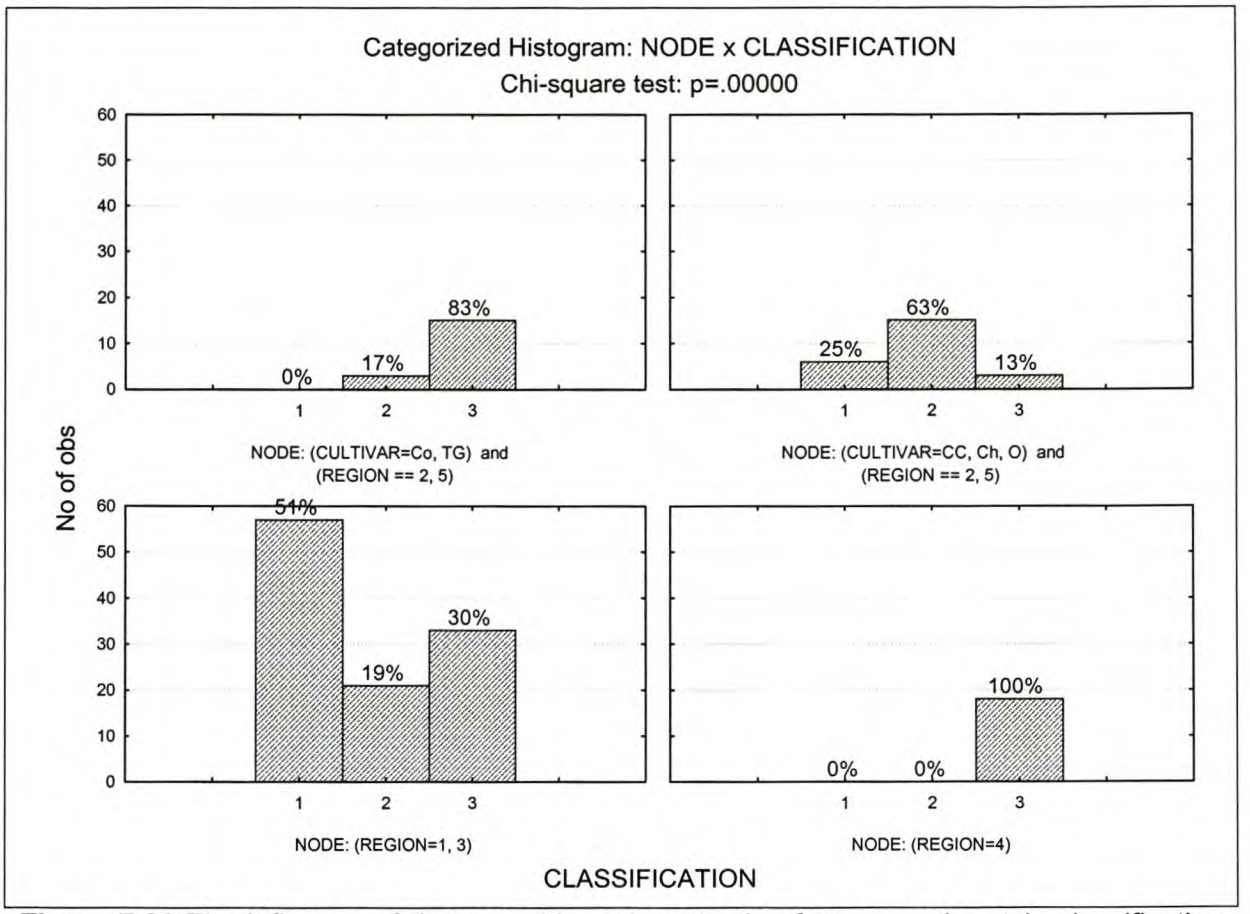

Figure 7.26 The influence of demographic and production factors on the style classification of three-year old potstill distillates.

7.3.7.3 Relationship between volatile compound composition and style classification of the three-year old distillates

Using CART analysis it was attempted to determine the relationship between the volatile compound composition and the style classification of the three-year old potstill distillates. **Table 7.11** lists the variable importance analysis that was generated by CART and **Figure 7.27** depicts the categorized histogram that was generated in the CART analysis. Ethyl caproate and octanoic acid were identified by CART as being the most important variables used to determine the subsets or rules generated by CART in this analysis. These two variables also comprise the predictor variables that are used in the subset rules. From **Figure 27** it is evident that 100% of those distillates that contained an ethyl caproate concentration less than 4.7 mg/L were classified as style 3. In distillates with ethyl caproate concentrations between 4.7 and 5.4 mg/L, 71% were classified as style 2 whilst 29% were classified as style 1. At ethyl caproate concentrations above 5.4 mg/L, the concentration of octanoic acid also seems to play a role. In this instance, 58% of the distillates that contained less than 34.8 mg/L of octanoic acid were classified as style 1. Whereas those distillates which contained octanoic acid concentrations greater than 34.8 mg/L were predominantly classified as style 2 or 3, with only 8% of these distillates being classified as style 1. There is thus a relationship between certain volatile compounds

and the style classification of potstill distillates, which implies that these compounds can also affect the taste of the product, in terms of smoothness or harshness.

Table 7.11 CART variable importance analysis for the relationship between volatile compound composition and three-year old distillate style classification (importance relative to 100)

Compound	Variable Importance
Ethyl caproate	100
Octanoic acid	71.83
Ethyl caprylate	63.03
isoButanol	56.63
Decanoic acid	48.26
Ethyl caprate	43.47
Ethyl lactate	31.54
2-Phenyl ethanol	25.16
isoAmyl alcohol	25.13
n-Propanol	20.68
isoAmyl acetate	15.3
Acetaldehyde	13.3

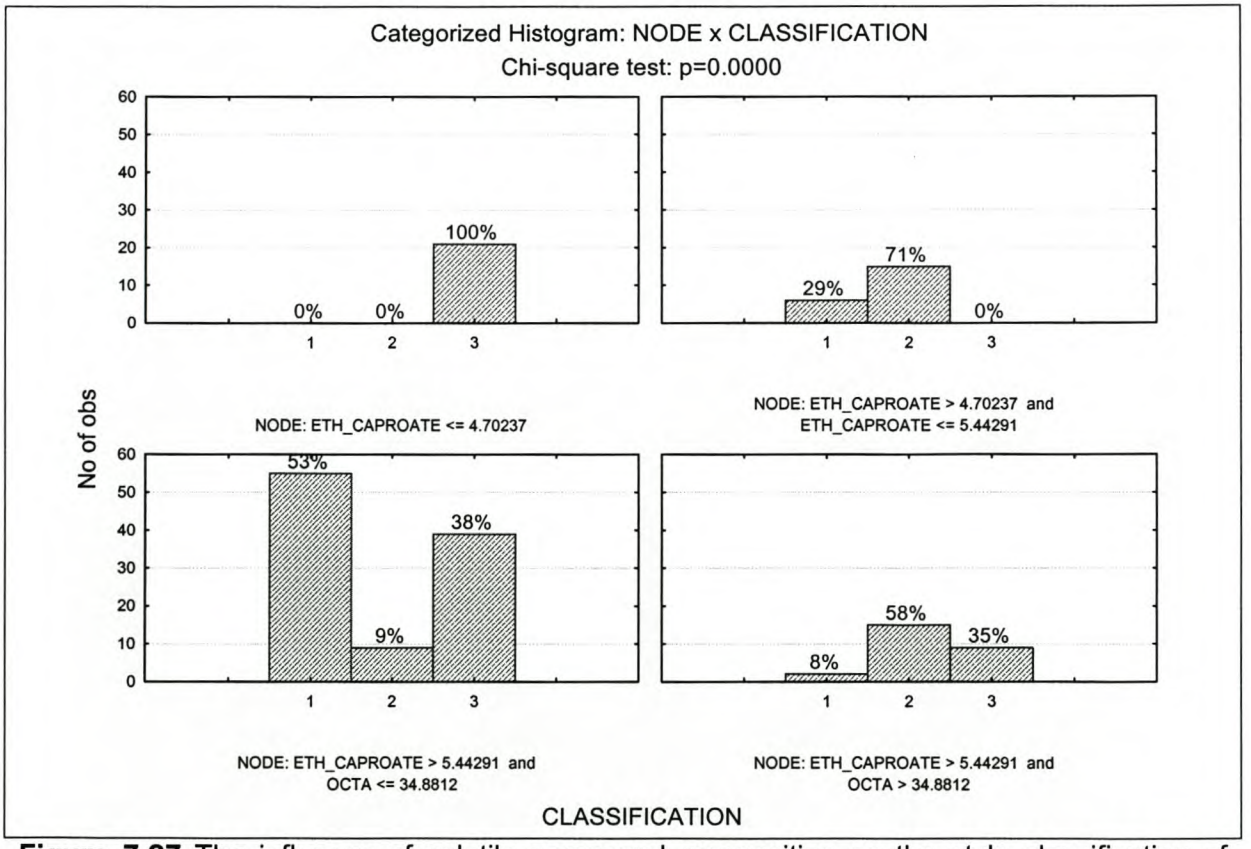

Figure 7.27 The influence of volatile compound composition on the style classification of three-year old potstill distillates.

7.4 CONCLUSIONS

In conclusion, it was found that, with the exception of the 2000 base wine score and the 2000 three-year old distillate score, there is a significant correlation between the score of the base wine, unaged distillate and three-year old wood maturated distillates. Thus, three years of wood maturation do not significantly alter the perceived sensory quality of potstill distillates as originally determined in their unaged distillates and in the case of the 1999 distillates also as originally determined in their base wines.

Even after three years of wood maturation, demographic and production factors can still influence the sensory quality of the distillates. Three-year old distillates that were scored lowest in terms of sensory quality all originated from region 4, irrespective of harvest time or cultivar. The next most important factor to influence the sensory quality of the three-year old distillates was found to be harvest time in the remaining regions. Distillates originating from grapes harvested early in the season, were all awarded the highest sensory scores.

The volatile compound composition of the distillates was also found to correlate to the sensory quality of the three-year old distillates. Isoamyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, n-butanol, octanoic acid, ethyl caprate and decanoic acid showed some positive correlation to the quality of the three-year old distillates. Isobutanol, ethyl lactate, acetic acid, acetaldehyde and ethyl acetate showed a significant negative correlation to three-year old distillate quality. Many of these findings were also confirmed in the analysis of variance performed on selected distillates of varying quality, which were profiled using sensory descriptive analysis. Although few distinctive differences in aroma profiles existed between the good and average quality distillates profiled over three years of wood maturation, there were distinct differences between the good quality and poor quality aroma profiles throughout the course of maturation. Where woody aromas were prominent at one and two years of wood maturation in the good and average quality distillates, the woody aroma was found to become less prominent and more integrated into the aroma profile after three years of wood maturation. This was however not the case for poor quality distillates. After three years of wood maturation, the aroma profile of poor quality distillates can be characterised by prominent herbaceous and woody aromas, which are more intense than the fruity aromas.

The routine analyses performed on the brandy base wines, whether viewed individually or as a group, showed little statistical correlation to the sensory quality of the base wines, unaged and three-year old distillates. The exceptions were total polyphenol concentration and base wine quality, wine alcohol content and 1999 unaged distillate quality as well as 2000 three-year old distillate quality. Thus, when already within the required specification, these analyses cannot provide a clear guideline as to the expected quality of the base wines, unaged and three-year old distillates.

From a commercial perspective, the style classification of a three-year old potstill distillate is of crucial importance. It determines which brand or product these distillates will be used in. It was found that there is no correlation between sensory quality and the style classification of these distillates. However demographic and production factors as well as volatile compound composition were found to exhibit an influence. All distillates originating from region 4 were classified as style 3. The remaining regions did not provide such clear cut style relationships, however, 63% of those distillates originating from regions 2 and 5 and originally made using table grapes and "other" varieties, were also classified as style 3. Ethyl caproate and octanoic acid were found to be the most important volatile compounds in determining the style classification of the three-year old distillates.

It is important to bear in mind that this study has focussed on relatively few compounds and only volatile compounds in determining their relationship to wood matured potstill distillate quality. Those compounds derived from the wood maturation process may also play a role in this relationship. In future studies, these should also be taken into account. Steger and Lambrechts (2000) showed that three large brandy producing companies within South Africa differed in their sensory evaluation of brandy base wines and distillates, due to differences in preferred brandy styles. Thus, the findings of this study are closely related to Distell's perception of base wine and distillate quality in the style of brandies that are produced by the company. Thus findings of this nature may be different for other brandy producing companies, depending on the style of brandy desired.

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CHAPTER 8

GENERAL DISCUSSION AND CONCLUSION

GENERAL DISCUSSION AND CONCLUSIONS

8.1 CONCLUDING REMARKS AND OTHER PERSPECTIVES

Brandy production is a multi-step process that involves harvesting of grapes, fermentation of the brandy base wine, distillation, wood maturation and blending to produce a final commercial product. Within each of these steps of the production process there are a number of factors that can influence the composition and resultant quality of the base wine, unaged and wood matured distillate. These factors include geographic and climatic features of the origin of grapes used, viticultural practices, grape maturity, grape variety, vintage variation, vinification techniques (eg. fermentation temperature and type of yeast strain used), storage of the base wine prior to distillation, distillation technique, age and origin of oak wood used for maturation and barrel toasting levels.

There has been much research into the flavour and aroma of alcoholic beverages over the past five decades. A major stimulus has been the recognition that aroma in itself invariably has a profound effect on the quality of an alcoholic beverage. A second reason for the active research has clearly been the rapid improvement in methods of analysis and aroma compound quantification. Intensive flavour and aroma research over the past few decades has led to the identification of more than 500 volatile compounds. Taking non-volatile compounds into account, the number of identified compounds would be close to triple (Nykänen and Suomalainen, 1983). Accordingly, the composition of flavour is extremely complex in beer, wine and distilled beverages such as whisky, rum and brandy. Due to the fact that a multitude of compounds can take part in the formation of flavour, it is rare that a particular compound, that is solely responsible for nuances of a specific flavour, is identified. Thus, taking brandy production factors and the nature of aroma and flavour into account, it is clear that thorough understanding of the complexities affecting the perception of quality in brandy is difficult.

In commercial brandy production, standard operating procedures do not allow for the separate distillation of different brandy base wines. Due to the size of the charger tanks and the number of wine producers that can be delivering approved brandy base wines to the distillery at any day, base wines from each producer are not stored separately. Thus mixing of the base wines occurs. However, a considerable amount of time goes into the analysis and approval of individual brandy base wines prior to purchasing. The aim of this study is to determine whether there is any merit in storing and distilling brandy base wines from different producers and regions separately, by determining the influence of brandy base wine composition on the quality of the respective unaged potstill distillates as well as the ultimate style and quality of the three-year old wood matured potstill distillates.

For this purpose, four potstills with a capacity of 2000 L each were isolated and used for commercial scale distillations of 33 and 25 brandy base wines in 1999 and 2000 respectively at the Distell distillery in Worcester. Brandy base wines were selected from

current brandy base wine producers delivering to Distell from brandy base wine producing regions in South Africa throughout the course of the harvesting season. The experimental outlay used in the study closely emulated Distell's standard operating procedures for commercial brandy production in terms of: the distribution of brandy base wines received from each region and at each harvest time interval, brandy base wine storage time at the distillery, percentage of lees content present during distillation, distillation and maturation method as well as organoleptic evaluation and classification of the intermediate and final products.

Chenin blanc and Colombar are the two most popular grape varietals used in the making of brandy base wine in South Africa. As the absence of terpenoid compounds has not been proven in South African Colombar, it was decided to focus the first part of the study on South African Chenin blanc wines, whose dry white wine aroma is predominantly fermentation derived. The aim of this part of the study was to identify those volatile flavour compounds that are correlated to wine quality and to try and establish a model of volatile flavour compound interactions taking place in young Chenin blanc wines that had been entered into the South African Young Wine Show from 1998 to 2003. It was found that the concentration of isoamyl acetate, hexyl acetate, ethyl caprylate, ethyl caprate, 2-phenethyl acetate and octanoic acid was significantly higher in wines awarded gold and silver medals (score 1) and decreased significantly with subsequent decreases in quality categories. The concentration of decanoic acid, isoamyl alcohol and ethyl caproate exhibited the same pattern, however, the difference between gold and silver medal wines (score 1) and bronze medal wines (score 2) was not found to be significant. Ethyl lactate exhibited the opposite pattern and the concentration of ethyl lactate was highest in the no medal (score 3) wines. As confirmation of these findings, a classification and regression tree (CART) analysis also identified ethyl caprate, ethyl caprylate and to a lesser extent octanoic, hexanoic and decanoic acid, isoamyl alcohol and isoamyl acetate as the most important variables used to predict the score of these wines. The CART analysis was also able to generate a set of "rules" as to how the concentration of some of the volatile compounds can impact on the perception of wine quality and also highlighted the interactive behaviour taking place between some of the volatile flavour compounds. This analysis also confirmed the long held view that flavour compounds in alcoholic beverages may exhibit synergistic or antagonistic relationships that can influence the perception of sensory character in wines. CART analysis can thus be used as a tool to better understand flavour compound relationships in beverages such as wine. A quality predictor model based on the behaviour of 21 volatile compounds quantified in the young Chenin blanc wines was established using MARS. It was found that the model's prediction accuracy was much higher when having to predict the quality of wines made in the same vintages as it had been trained on. It was significantly poorer when tested on a completely different vintage of wines to the ones it had been trained on. As with any type of agricultural product that is influenced by its environment and climate during ripening, seasonal variations can affect wine composition and quality. Subsequent analysis showed that the wines from 2003 (the

separate vintage test set used to test the prediction accuracy of the model) differed significantly in composition and also in wine scoring methodology when compared to the previous vintages. In addition, a mere 21 volatile compounds were used in this model. Thus the limited number of compounds quantified as well as the limited number of wines available for analysis in each vintage, can also affect the prediction accuracy. In order to build a seasonally more robust model, the analyses of subsequent vintages of young Chenin blanc wines should be added to the model database and the number of relevant volatile compounds quantified should also be expanded.

The second part of this study focussed on the quantification of twenty-seven volatile compounds in 33 and 25 brandy base wines and their unaged distillates from 1999 and 2000 respectively. Using analysis of variance (ANOVA) and CART analysis it was found that vintage, region, harvest time, choice of cultivar and yeast strain can have a significant influence on the volatile compound composition of brandy base wines and their resultant distillates. The most significant increase in base wine concentration from 1999 to 2000 was noted for isoamyl acetate, octanoic and decanoic acid, whereas ethyl lactate showed the most significant decrease in concentration from 1999 to 2000. In the base wines, the concentration of ethyl lactate, acetic acid, n-hexanol, isobutanol and 2-phenyl ethanol increased significantly with progression in harvest time. The base wine concentration of acetate esters (ethyl acetate, isoamyl acetate, 2-phenethyl acetate, and hexyl acetate) ethyl caprate and –caprylate, n-propanol, n-butanol and the volatile C_6, C_8 and C_{10} acids were all found to decrease significantly with harvest time. Wines originating from region 1 contained significantly higher concentrations of hexyl acetate when compared to wines from the other regions. More specifically, wines from region 1 fermented with yeast strain VIN13 showed significantly higher concentrations of ethyl acetate and isoamyl acetate than those fermented with WE228 and ICVD254 from the same region. Wines made from Colombar grapes in region 1 contained significantly lower concentrations of hexanoic and decanoic acid than Colombar wines originating from regions 2 and 3. Wines made from table grapes had significantly lower concentrations of ethyl butyrate, isoamyl acetate and the highest concentrations of n-hexanol and acetic acid. Wines made from table grapes and "other" varieties had significantly lower concentrations of ethyl caprate, hexyl acetate, hexanoic and octanoic acid than those made from Chenin blanc, Colombar and a mix of Chenin/Colombar, whilst the latter had significantly lower concentrations of iso-butanol and diethyl succinate. No distinct groupings of yeast strains could be determined on the overall basis of volatile compounds. However, grouping of yeast strains based on similar concentrations of a particular compound was possible in some instances. Here the most notable differences were between strains NT117 and 20-2 on the basis of n-propanol concentration and strains WE372, VIN13, VIN7 and 20-2 whose wines and distillates contained significantly higher concentrations of ethyl caprate when compared to those made with the remaining strains. The CART analysis also proved to be a powerful tool in identifying groups of yeast strains within certain vintage, cultivar and region parameters. In both vintages, distillates originating from Colombar wines had the highest concentration of

acetaldehyde, which was only quantified in the distillates. In many instances, influences of harvest time, vintage and cultivar followed the same trend in both the wines and distillates. There are, however, exceptions and these discrepancies in the CART variable importance and ANOVA results between wines and distillates were not easily explained. This could possibly be attributed to the presence of yeast lees during distillation as well as the relative volatility and concentration of these compounds in the wine during distillation.

The third part of this study involved determining the influence of vintage, region, cultivar, harvest time and yeast strain as well as the volatile compound composition on the sensory quality of the brandy base wines and their unaged potstill distillates. It was found that the base wines studied exhibited the same quality trends over both vintages in terms of region, cultivar and time of harvest. Base wines and distillates originating from region 4, which predominantly cultivates table grapes, were of significantly lower quality than those from the remaining regions. There was a clear relationship between time of harvest and base wine and distillate quality and products made from early harvested grapes were of significantly higher quality. This could be attributed to the lowered incidence of microbial spoilage and grape rot early in the season as well as lowered ripeness or over-ripeness of grapes harvested at this time. Although wines made from Chenin blanc and a mix of Chenin and Colombar were consistently of higher quality, these differences were not as significant in the distillates. Any significant differences observed due to yeast strain in the base wines did not follow through to the distillates and it can be speculated that the distillation process as well as the amount of yeast lees present during distillation may influence this effect. The volatile aroma compound composition was found to differ significantly between the 1999 and 2000 base wines and distillates, irrespective of the exclusion of those samples that had undergone partial or complete malolactic fermentation. Consequently, quality indicating compounds may vary from vintage to vintage and it is thus recommended that this exercise be continued over a further number of vintages in order to determine more robust quality indicating compounds for brandy base wines and unaged distillates. As was noted in the study on young Chenin blanc wines, the limited number of volatile compounds determined can also influence this variability, as there certainly are other quality indicating compounds present which have not been determined. The relationship between the quality of brandy base wines and the concentration of n-butanol, isoamyl acetate, ethyl lactate, ethyl caprylate, octanoic- and decanoic acid was the same as that reported in young Chenin blanc wines in this study. In the case of unaged distillates, increased levels of ethyl lactate also exert a negative influence on distillate quality. Ethyl caprate was found to be a quality indicator in the 1999 distillates (irrespective of the influence of malolactic fermentation). Hexyl acetate was found to be a quality indicator in the 2000 distillates as well as in the 1999 distillates not affected by malolactic fermentation. An aroma profile for good, average and poor quality distillates was established using sensory descriptive analysis and the South African brandy aroma wheel (Jolly and Hattingh, 2001). Although the differences in profile between the good and average distillates were found to be small, there were significant differences

between the good and poor quality distillate profiles. Good quality unaged distillates are characteristically intense in the 'fruity' aroma descriptor, whilst poor quality unaged distillates show 'herbaceous' as the most intense aroma. Even though relatively small differences in 'fruity', 'floral' and 'sweet associated' aroma intensity were noted, there were significant differences in the concentration of aromatically important esters such as isoamyl acetate, hexyl acetate and 2-phenethyl acetate between the good and average quality distillates.

In the fourth part of this study, the influence of wood maturation on the composition of these potstill distillates was investigated. Volatile compound concentration differences were noted during the course of and after three years of wood maturation. The concentration of acetaldehyde remained relatively constant over the three-year period for all regions except region 4, which showed an increase over time. The concentration of 2-phenethyl acetate, ethyl caprate, ethyl lactate, iso-butanol, n-butanol and n-propanol did not vary significantly during the course of maturation. The concentration of acetic acid, diethyl succinate, ethyl caprylate, 2-phenyl ethanol, octanoic and decanoic acid was found to increase during wood maturation. Differences on the basis of region and vintage were also evident during the course of and after wood maturation. The mean concentration of isoamyl acetate and hexyl acetate remained highest in distillates originating from region 1. Isoamyl acetate, ethyl caprylate and octanoic acid concentrations remained lowest in distillates originating from region 4, whilst n-hexanol and 2-phenyl ethanol concentrations remained highest in distillates from this region. Distillates from region 4 developed notably higher concentrations of ethyl acetate when compared to the remaining regions during wood maturation. Differences in volatile compound concentrations in distillates matured in barrels of varying ages were also studied. The mean concentration of acetaldehyde, ethyl acetate, ethyl caproate, ethyl caprate, ethyl caprylate acetic acid and decanoic acid was found to be higher with wood progression in new block barrels. The mean concentration of hexyl acetate and 2-phenethyl acetate was found to be lowest in the distillates matured in new block barrels. No significant differences in volatile compound concentration were observed in the distillates matured in the remaining barrels of differing ages. It was decided to investigate whether the demographic and production factors that were shown to have an effect on base wine and unaged distillate composition in this study still have an effect upon the composition of the distillates after three years of wood maturation. Yeast strain groupings on the basis of acetaldehyde and ethyl acetate were possible in the three-year old distillates. Those distillates made from grapes harvested early in the season using yeast strain VIN13 for the base wine fermentation, contained significantly higher concentrations of isoamyl acetate than the remaining three-year old distillates. As was noted in the unaged distillates, harvest time continued to have the largest impact on the concentration of ethyl caprate after three years of wood maturation. Distillates made from mid and late harvested grapes contained significantly lower concentrations of ethyl caprate than those made with early harvested grapes. As was noted in the unaged distillates isoamyl alcohol concentrations were significantly higher in distillates made from grapes

harvested in mid and late season after three years of wood maturation. Three-year old distillates made from table grapes contained significantly higher concentrations of iso-butanol. Thus, demographic and production factors do still exert an influence on the volatile composition of potstill distillates after three-years of wood maturation and in most instances exerted the same or similar effect as was noted in the unaged distillates. Although some vintage differences were noted in the concentration of medium chain fatty acids, no clear trend for the effect of wood maturation on the medium chain fatty acids was evident. The mean concentrations of selected wood lactones, furanic aldehydes, volatile phenols and phenolic acids and aldehydes indicate that distillate maturation in the new block barrels imparts more wood maturation character than in the remaining barrels, which is to be expected as these can be viewed as rejuvenated, new brandy casks. However, surprisingly few differences in the concentrations of the above-mentioned compounds were noted in the remaining barrel ages, as was also noted for the volatile compound composition.

The last part of this study focussed on the influence of wood maturation on the sensory character and quality of these potstill brandy distillates. With the exception of the 2000 base wine score and the 2000 three-year old distillate score, a significant correlation between the score of the base wine, unaged distillate and three-year old wood matured distillates was found. Thus, three years of wood maturation do not significantly alter the perceived sensory quality of potstill distillates as originally determined in their unaged distillates and in the case of the 1999 distillates also as originally determined in their base wines. After three years of wood maturation, demographic and production factors were found to still influence the sensory quality of the distillates. Three-year old distillates that were scored lowest in terms of sensory quality all originated from region 4, irrespective of harvest time or cultivar, as was noted in the unaged distillates. The next most important factor to influence the sensory quality of the three-year old distillates was found to be harvest time in the remaining regions. Distillates originating from grapes harvested early in the season, were all awarded the highest sensory scores. The volatile compound composition of the distillates was also found to correlate to the sensory quality of the three-year old distillates. Isoamyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, n-butanol, octanoic acid, ethyl caprate and decanoic acid showed some positive correlation to the quality of the three-year old distillates. Iso-butanol, ethyl lactate, acetic acid, acetaldehyde and ethyl acetate showed a significant negative correlation to three-year old distillate quality. Many of these findings were also noted in the young Chenin blanc wines as well as the base wines and resultant unaged distillates. The same selected distillates of varying quality, which were profiled as unaged distillates using sensory descriptive analysis were profiled after one, two and three years of wood maturation. As was the case in the unaged distillates, few distinctive differences in aroma profiles existed between the good and average quality distillates profiled over three years. There were, however, distinct differences between the good quality and poor quality aroma profiles throughout the course of maturation. Where woody aromas were prominent at one and two years of

wood maturation in the good and average quality distillates, the woody aroma was found to become less prominent and more integrated into the aroma profile after three years of wood maturation. This was however not the case for poor quality distillates. After three years of wood maturation, the aroma profile of poor quality distillates can be characterised by prominent herbaceous and woody aromas, which are more intense than the fruity aromas.

The routine analyses performed on the brandy base wines as part of the standard operating procedure for brandy production within Distell, whether viewed individually or as a group, showed little statistical correlation to the sensory quality of the base wines, unaged and three-year old distillates. The exceptions were total polyphenol concentration and base wine quality, wine alcohol content and 1999 unaged distillate quality as well as 2000 three-year old distillate quality. As the base wines used in this study and for brandy production within Distell already comply to the required specification, these analyses, when within specification, cannot provide a clear guideline as to the expected quality of the base wines, unaged and three-year old distillates.

From a commercial perspective, the style classification of a three-year old potstill distillate is of crucial importance as it determines which brand or product these distillates will be used in. It was found that the style classification is not influenced by the sensory quality of these distillates. However demographic and production factors as well as volatile compound composition were found to exhibit an influence on the distillate style classification. All distillates originating from region 4 were classified as style 3. However, the remaining regions did not provide such clear cut style relationships. 63% of those distillates originating from regions 2 and 5 and originally made using table grapes and "other" varieties, were also classified as style 3. Ethyl caproate and octanoic acid were found to be the most important volatile compounds in determining the style classification of the three-year old distillates.

In summary, vintage, region, cultivar, harvest time and choice of yeast strain have a significant influence on the volatile composition of brandy base wines, their unaged and three year old potstill distillates, which in turn affects the sensory quality of these products. These effects cannot be viewed in isolation as they jointly exert an influence on the composition and quality of brandy base wines, unaged and three year old distillates. In such instances, classification and regression tree analysis is a powerful tool that can be used to study these non-linear relationships. From a commercial perspective, this study has provided an indication as to which production and demographic factors can influence the quality and style of potstill brandy. Thus, future brandy base wine intake should, as far as possible, take place in such a manner to allow base wines originating from the same cultivar or region or harvest time or combination thereof (and to a lesser extent yeast strain) to be received simultaneously at the distillery for distillation. This practice will result in distillates of differing quality, which can then be further managed and utilised in different brandy products. For example, a distillate of good quality, which has been shown to exhibit prominent fruity aromas, may be more suitable for wood maturation over a period of 10,

12, 15 or 20 years. The prominence of wine-derived aromas in potstill distillates become critical to quality when being wood matured for so many years, as the product must at all times retain its balance between fruit and wood aromas to be of good quality. This becomes harder as the wood maturation period becomes longer. Poor quality distillates could also be blended into determined amounts of better quality distillates to ensure homogenous quality. Managing base wine intake in this manner will also increase the probability of obtaining a particular style classification of three-year old distillate. This is important in ensuring the sustainable and continuous supply of all three desired styles for the key brandy brands within Distell. Currently the style classification has only been possible after three years of maturation and it has not been known what determines this style classification. Although further work to confirm these exact influences is recommended, the results of this study do provide an indication as to the probability of obtaining one of the three styles based on demographic and production factors as well as volatile compound composition. As the changes in volatile compound composition during the course of wood maturation are now known, it may be possible to predict, or at least gain some indication as to the expected style classification of the three-year old distillate, by studying its origin and composition as an unaged distillate. This could facilitate the planning of brandy style requirements three years into the future.

As has been previously mentioned, the number of compounds used in this study as well as the limited number of vintages studied can also influence the results obtained. As brandy production in South Africa is a process that takes a minimum of three years, it is not a field of study in which complete results are generated quickly. It is recommended that the study be continued in successive vintages to determine whether the current findings are robust enough to accommodate possible vintage differences in grape and resultant wine, unaged and three year old distillate composition. It must also be borne in mind that the results generated in this study relate specifically to the style and quality of brandy desired by Distell. As brandy producers must produce varying styles of brandy to cater for all consumer requirements, this style may differ from company to company, as was proven by Steger and Lambrechts (2000).

It is recommended that the number of compounds quantified in future studies of this nature be expanded to include other possible quality and style relevant compounds. The influence of compounds present in distillates as a result of wood maturation also warrants more detailed investigation, as these may also influence the aroma and flavour of the wood matured distillates. It would be interesting to monitor the evolution of wood derived compounds in potstill distillates matured in barrels of differing ages after one, two and three years of wood maturation. Comparisons of sensory character and quality of potstill brandy distillates matured in these barrels of different ages should also be investigated. Although, from a commercial perspective, the composite distillate sample, arrived at by adding equal volumes of each barrel within a lot, is the final product to be used in brandy blending, the above-mentioned recommended investigations may lead to a more optimal lot composition for potstill brandy maturation. In this study, the volatile composition of the

distillates was only significantly different for the new block barrels. This was also noted in the mean concentration of the wood derived compounds after three years of maturation. Should this finding be confirmed in a more detailed investigation, as well as a sensory comparison of the distillates from these barrels of differing ages, it might not be necessary to comprise a maturation lot with each of these barrel ages. Instead, any older brandy barrel could be used in a lot along with a determined percentage of new block barrels to impart the desired amount of wood maturation character to the brandies.

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