

The compositional basis of the aroma of Riesling and unwooded Chardonnay wine

Heather Eunice Smyth

**School of Agriculture and Wine, Faculty of Sciences
The University of Adelaide**

The Australian Wine Research Institute

**A thesis submitted in fulfilment of the requirements for the degree
of Doctor of Philosophy**

January 2005

TABLE OF CONTENTS

Table of contents	i
Abstract	iii
Dedication	v
Declaration	vii
Acknowledgements	ix
Publications and Presentations	xi
Chapter 1 General introduction	1
1.1 Volatile compounds important to white wine aroma	2
1.2 Sensory analysis of wine aroma	8
1.2.1 Aroma recombination models	10
1.2.2 Sensory descriptive analysis of wine	12
1.3 Relating volatile composition to wine aroma with multivariate data analysis	13
1.3.1 Principal component analysis	15
1.3.2 Partial least squares regression	16
1.3.3 Interpretation of multivariate prediction models	19
1.4 Aims of this project.....	20
Chapter 2 Development of analytical methods	21
2.1 Introduction	21
2.1.1 Stable isotope dilution analysis.....	21
2.1.2 Development and application of analytical methods	22
2.2 Results and discussion	23
2.2.1 Fermentation-derived compounds	23
2.2.2 Diacetyl and trans-ethyl cinnamate.....	28
2.2.3 Various other yeast, grape- and oak-derived compounds.....	30
2.2.4 Low molecular weight sulfur compounds.....	31
2.3 Conclusion	31
2.4 Materials and methods.....	32
2.4.1 General Instrumental analysis	32
2.4.2 Method for the analysis of fermentation-derived compounds.....	34
2.4.3 Method for the analysis of diacetyl and trans-ethyl cinnamate.....	39
2.4.4 Method for the analysis of grape- and oak-derived compounds	40
2.4.5 Method for the analysis of 4-vinylguaiacol and 4-vinylphenol	42
2.4.6 Method for the analysis of methionol	43
2.4.7 Method for the analysis of low molecular weight sulfur compounds	43
Chapter 3 The compositional basis of Riesling wine aroma	47
3.1 Introduction	47
3.2 Results and discussion	47
3.2.1 Sensory descriptive analysis	49
3.2.2 Volatile chemical analysis.....	58
3.2.3 Multivariate analysis of sensory and chemical data	69
3.3 Conclusion	83
3.4 Materials and methods.....	84
3.4.1 Wines.....	84
3.4.2 Sensory descriptive analysis	84

3.4.3 Volatile chemical analysis	86
3.4.4 Statistical and multivariate data analysis	87
Chapter 4 The compositional basis of unwooded Chardonnay wine aroma	89
4.1 Introduction	89
4.2 Results and discussion	90
4.2.1 Sensory descriptive analysis	92
4.2.2 Volatile chemical analysis	99
4.2.3 Multivariate analysis of sensory and chemical data	109
4.3 Conclusion	121
4.4 Materials and methods	122
4.4.1 Wines	122
4.4.2 Sensory descriptive analysis	122
4.4.3 Volatile chemical analysis	123
4.4.4 Statistical and multivariate analysis	124
Chapter 5 Comparison of data for Riesling and unwooded Chardonnay.....	125
5.1 Introduction	125
5.2 Results and discussion	125
5.2.1 Comparison of routine chemical data between varieties	125
5.2.2 Comparison of sensory descriptive data between varieties	126
5.2.3 Comparison of volatile chemical data between varieties	130
5.2.4 Relationships between sensory and wine composition for each variety	135
5.3 Conclusion	142
Chapter 6 Prediction of wine sensory properties using rapid instrumentation.....	145
6.1 Introduction	145
6.2 Results and discussion	148
6.2.1 Mass spectrometry based electronic nose	148
6.2.2 Visible and near infrared spectroscopy	149
6.2.3 Comparison of MS Enose and VIS-NIR	151
6.2.4 Combined MS Enose and VIS-NIR	153
6.2.5 Prediction of sensory properties using combined MS Enose and VIS-NIR spectral data ...	154
6.3 Conclusion	160
6.4 Materials and Methods	161
6.4.1 Mass spectrometry based electronic nose	161
6.4.2 Near Infrared spectroscopy	161
6.4.3 Multivariate data analysis	162
Chapter 7 Study of wine lactone	165
7.1 Introduction	165
7.2 Results and discussion	167
7.2.1 Synthesis of racemic wine lactone (1a/1b and 6a/6b)	167
7.2.2 Synthesis of enantiomerically pure wine lactone (1a)	168
7.2.3 Analytical method development	171
7.2.4 Hydrolytic and chiral study	173
7.3 Materials and methods	176
7.3.1 General	176
7.3.2 Synthesis of enantiomerically pure wine lactone	176
7.3.3 Preparation of samples for hydrolytic study	178
7.3.4 Analytical method for the determination of wine lactone	178
Appendices	181
References	199

ABSTRACT

The aim of this research project was to explore, in detail, the relationship between volatile composition and wine aroma for two white wine varieties, namely Riesling and unwooded Chardonnay, so that the most influential volatile aroma compounds to the aroma of these two varieties could be identified. Twenty Australian commercial wines of each variety were analysed by quantitative sensory descriptive analysis and targeted for the chemical analysis of more than 45 volatile compounds. The compositional and sensory data sets were related using multivariate methods (e.g. PCA and PLS), and aroma volatiles were identified that related to the specific sensory properties of each variety. Most of the Riesling and several of the unwooded Chardonnay sensory properties were well predicted by the compositional data and several compounds were identified as important to the aroma of each variety. The unwooded Chardonnay wines were higher in concentration of various fermentation-derived compounds than were the Riesling wines, and these volatiles played an important role in the sensory properties of this variety. The Riesling wines were higher in concentration of grape-derived compounds including the monoterpenes, norisoprenoids, and dimethyl sulfide. These compounds, and also many of the fermentation-derived compounds, were identified as important contributors to the aroma of the Riesling wines. The results from this study have greatly advanced our understanding of the complex interactions between volatile compounds and the role that they play in the specific aroma nuances of white wines.

The prediction of sensory properties of the Riesling and unwooded Chardonnay wines was investigated using rapid instrumental techniques, namely mass spectrometry based electronic nose (MS Enose) and visible and near infrared (VIS-NIR) spectroscopy. A combination of MS Enose and VIS-NIR gave the best predictive results compared to either method alone. Promising results were achieved for many of the sensory properties indicating that this technique shows good potential for application.

The so-called 'wine lactone' (3a,4,5,7a-tetrahydro-3,6-dimethylbenzofuran-2(3H)-one) is known to be an important white wine odorant. The formation of wine lactone was investigated from two potential precursors, namely (E)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid and the glucose ester of this acid, in model wine at room temperature and 45°C. The hydrolytic results show that the rate of formation of wine lactone is too slow for either the acid or the glucose ester to be major precursors to wine lactone in young white wine. Therefore, different precursors are most likely responsible for the formation of wine lactone in young white wine.

DEDICATION

I dedicate this thesis to my Lord God, who made my heart, mind and soul, and who is and forever will be, my only audience.

Whatever you do, work at it with all your heart, as working for the Lord, not for men, since you know you will receive an inheritance from the Lord as a reward. It is the Lord you are serving. Colossians 3:23

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made.

I consent to this copy of my thesis, when deposited in the University Library, being made available for photocopying and loan.

Signed

Date

ACKNOWLEDGEMENTS

I thank the Grape and Wine Research and Development Corporation and the Cooperative Research Centre for Viticulture for providing funding that allowed me the privilege of pursuing a PhD and for the opportunity to attend and present my research at conferences in Australia and overseas.

I am very grateful to the many wine producers and wine makers across Australia who provided generous support of this research through the contribution of wine and through openly providing detailed information about the wines included in this study.

I thank my supervisors Drs Leigh Francis, Mark Sefton and Markus Herderich for the opportunity to work under their supervision and for their valued guidance, support and advice throughout my PhD. I also thank Dr Daniel Cozzolino, who has been an integral part of the success of this project, for his mentorship and friendship. I also thank Professors Peter Høj, Sakkie Pretorius and the staff and students at The Australian Wine Research Institute for their on-going support and encouragement throughout my time at the Institute.

In particular, I acknowledge Tracey Siebert, Dr Alan Pollnitz, Dr Kate Howell, Dr Markus Herderich and Dr Mark Sefton for their participation in the development of the analytical method for fermentation-derived compounds and Dr George Skouroumounis for his advice on the synthetic component of this project. I also acknowledge those who were involved with developing the various analytical methods that were used by the author, including Tracey Siebert, Dr Alan Pollnitz, Dimitra Capone, Katryna van Leeuwen, Dr Gordon Elsey and Geoff Cowey. I thank Dr Aggie Cox (nee Janusz) for analysing the study wines for TPB.

For their assistance and expertise with the sensory analysis of the study wines I thank Dr Leigh Francis and Kate Lattey, and also the staff and students of the AWRI for their involvement as panellists.

I thank Dr Daniel Cozzolino for his expert advice on multivariate data analysis and for his direction over the rapid instrumental component of this project. I acknowledge Dr. Weis Cynkar for her assistance with the electronic nose work. I also thank Dr Vicente Ferreira for his comments and advice for the project, particularly in the area of multivariate analysis and the grouping of chemical variables.

For the wine lactone work, I thank Dr Gordon Elsey, Anders Hakansson, Kevin Pardon, and Dr George Skouroumounis who provided expert advice and assistance with the synthetic part of this study. Dr Gordon Elsey made significant contributions by synthesising bulk

deuterium labelled and unlabelled wine lactone that was used for analytical method development and Kevin Pardon assisted by separating wine lactone isomers **1a** and **1c** by chromatography. I also thank Dimitra Capone who provided expert advice and assistance with analytical method development, Katryna van Leeuwen who assisted in the preparation of samples for the hydrolytic study and Dr Mark Sefton who provided outstanding supervision and direction for this project.

I thank all those who provided comments and feedback on my thesis, including my supervisors, Dr Daniel Cozzolino, Dr Alan Pollnitz, my father Daryll Pain and my husband Graeme Smyth. I also thank the wonderful Ingrid Oates and the team from the JFM Library for providing me fast and easy access to all of the journal articles and books that I needed to conduct my research.

I thank my friends, in particular my fellow postgraduate students and my church family (NEVC), for their friendship, support and encouragement in the good times and the tough times throughout my PhD studies.

I especially thank my parents, Daryll and Hazel Pain, for their unconditional love and support, and for giving me so many opportunities in life to pursue my dreams. I also gratefully thank my husband, Graeme John Smyth who continues to love me, and believe in me, in everything I do.

PUBLICATIONS AND PRESENTATIONS

The following publications were derived from this research:

Refereed Papers:

Cozzolino, D.; Smyth, H.E.; Lattey, K.A.; Cynkar, W.U.; Janik, L.; Damberg, R.G.; Francis, I.L.; and Gishen, M., *Relationship between sensory analysis and near infrared spectroscopy in Australian Riesling and Chardonnay wines*. *Analytica Chimica Acta*, 2005. In press.

Siebert, T.E.; Smyth, H.E.; Capone, D.L.; Neuwöhner, C.; Pardon, K.; Skouroumounis, G.; Herderich, M.J.; Sefton, M.A.; and Pollnitz, A.P., *Stable Isotope Dilution Analysis of wine fermentation products by HS-SPME-GC-MS*. *Analytical and Bioanalytical Chemistry*, 2005. 381: 937-947.

Cozzolino, D.; Smyth, H.; and Gishen, M., *Feasibility study on the use of visible and near infrared spectroscopy together with chemometrics to discriminate between commercial white wines of different varietal origins*. *Journal of Agricultural and Food Chemistry*, 2003. 51: 7703-7708.

Papers and posters presented at conferences:

Cozzolino, D.; Smyth, H.E.; Lattey, K.A.; Cynkar, W.U.; Janik, L.; Damberg, R.G.; Francis, I.L.; and Gishen, M., *Relationship between sensory analysis and near infrared spectroscopy in Australian Riesling and Chardonnay wines*. *Near Infrared Spectroscopy: Proceedings of the 12th International conference, Auckland, NZ Vic, 10 - 15th April 2005*. Paper Accepted.

Smyth, H.E.; Cozzolino, D.; Herderich, M.; Sefton, M.A.; Francis, I.L., *Relating volatile composition to wine aroma: identification of key aroma compounds in Australian white wines*. *Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004*. Paper presented.

Cozzolino, D.; Smyth, H.E.; Damberg, R.G.; Gishen, M., *Multivariate analysis (chemometrics): a novel approach in modern interdisciplinary sciences*. *Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004*. Paper presented.

Cozzolino, D.; Smyth, H.E.; Lattey, K.A.; Cynkar, W.U.; Francis, I.L.; Damberg, R.G.; and Gishen, M., *A preliminary investigation of the potential of near infrared spectroscopy to predict sensory attributes in white wine*. *Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004*. Poster presented.

Cozzolino, D.; Smyth, H.E.; Francis, I.L.; Cynkar, W.U.; Janik, L.; Damberg, R.G.; and Gishen, M., *White wine varietal discrimination using near infrared reflectance spectroscopy*. *Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004*. Poster presented.

Siebert, T.E.; Smyth, H.E.; Herderich, M.; Sefton, M.A.; Pollnitz, A.P., *Quantification of 31 important fermentation-derived aroma compounds in wine*. *Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004*. Poster presented.

Lathey, K.A.; Smyth, H.E.; D-Costa, N.E.; Liebich, B.K.; Francis, I.L., *Consumer acceptability and sensory properties of a set of commercial Australian Riesling and unwooded Chardonnay wines*. Proceedings of the 12th Australian Wine Industry Technical Conference, Melbourne Vic, 25 - 29th July 2004. Poster presented.

Smyth, H.E.; Cozzolino, D.; Herderich, M.; Sefton, M.A.; Francis, I.L., *Identification of key aroma compounds in Australian Riesling and unwooded chardonnay wines*. Proceedings of the 7th Wartburg Symposium on Flavor Chemistry & Biology, Eisenach, Germany 21st - 23rd April, 2004. Poster presented.

Smyth, H.E.; Cozzolino, D.; Herderich, M.; Sefton, M.A.; Francis, I.L., *Riesling wine aroma: Relating volatile to sensory data using PLS regression models*. Proceedings of the 6th annual scientific meeting of the Australasian Association for ChemoSensory Science (AACSS), Rutherglen Vic, 2nd - 4th October 2003. Paper presented.

Smyth, H.E.; Cozzolino, D.; Francis I.L., *Identification of key aroma compounds in Australian Riesling wines*. Proceedings of the Australian Society of Viticulture and Oenology: Viticulture and Oenology Seminars, Tanunda SA, July 10 - 11th 2003. Paper presented.

External presentations:

Smyth, H.E., *Key aroma compounds in white wine*. Oral presentation for the Department of Dairy and Food Science, The Royal Veterinary and Agricultural University, Copenhagen, Denmark. 26th April 2004

Smyth, H.E., *Key aroma compounds in white wine*. Oral presentation for the Department of Analytical Chemistry, University of Zaragoza, Zaragoza, Spain. 29th April 2004

Press / media interviews:

Goodness, does wine really smell like this? Great drop with fine bouquet of kerosene. By Zac Milbank, The Advertiser, Wednesday December 15th 2004, p 33.

On the nose with a hint of bubblegum. By Rebecca DiGirolamo, The Australian, Wednesday February 11th 2004, p 31.

Choose your own wine aroma. ABC Radio Riverland, Rural Report by Alice Plate, Thursday, 5th February, 2004.

Technology traces essential aromas. Australian Vignerons Volume 3, Number 5, January/February 2004, p 53-55.

The sweet smell of honey, passionfruit and lemon – Uncovering the key aroma compounds. Cooperative Research Centre for Viticulture Newsletter, November-December 2003, Volume 9, Number 6, p 5-7.

Sense of smell drives search for key aroma compounds. Australian and New Zealand Wine Industry Journal: September/October 2003 Volume 18, Number 5, p 82.

Smells OK? It must be the ethyl propanoate. Tim White, The Australian Financial Review: July 19-20th 2003, p 69.