

# SYNTHESIS OF ALLENIC KETONES AND THE ROLE OF YEAST IN THEIR CONVERSION TO DAMASCENONE

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*A Thesis Submitted for the  
Degree of Doctor of Philosophy*

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**October 2013**



## ***Dedication***

*This Thesis is dedicated to my dad, Robert Lloyd who passed away (03/10/1941 – 16/11/2009) and my wonderful mom, Maxine and brother, Ryan who are always there to support me. I am so grateful to have both of you in my life.*

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## ***Abstract***

The thesis describes the formation of damascenone during fermentation conditions from potential ketone precursors. An introduction to the thesis and aims of the study are described in Chapter 1, the synthesis of the precursors is detailed in Chapter 2, identification of the precursors as natural products and hydrolysis studies are included in Chapter 3, fermentation studies are detailed in Chapters 4 and the damascenone stability studies are in Chapter 5.

Chapter 2 describes the synthesis of megastigma-4,6,7-triene-3,9-dione (**26**) and 3-hydroxymegastigma-4,6,7-trien-9-one (**27**) from the common starting material, 4-oxoisophorone as well as the synthesis of 9-hydroxymegastigma-4,6,7-trien-3-one (**28**) from diketone **26**. The allene 3-*tert*-butyldimethylsilyloxy-9-hydroxymegastigma-4,6,7-triene (**29**) was synthesised first and this was then used to produce ketones **26** and **27**. The synthesis of **26** occurred in two steps from the silylated allene diol **29** which involved deprotection, followed by a Dess-Martin oxidation. The synthesis of ketone **27** was achieved by a Dess-Martin oxidation of the silylated allene diol **29** followed by deprotection using TBAF. The ketone **28** was synthesised by a selective reduction of **26**.

Chapter 3 covers the identification of the ketones **26** and **28** as natural products. It describes the hydrolysis studies performed with ketone **27** in model wine and includes a discussion as to why **27** was not seen in grape juice or honey extracts, in contrast to the analogues **26** and **28**.

The fermentation study involving the synthesised ketones **26**, **27** and **28** is discussed in Chapter 4. The fermentation studies demonstrate that damascenone can be formed by the action of yeast during fermentation, from precursors **26**, **27** and **28**. The results emphasise that the presence of yeast is essential for the conversion. The concentration of damascenone at the end of fermentation was also shown to be dependent on the yeast strain. Yeast strain AWRI 796 showed to be more efficient in the formation of damascenone compared to yeast strain AWRI 1537.

The final section of the thesis (*Chapter 5*) details the stability of damascenone during fermentation. A substantial loss of damascenone was observed during fermentation and the factors involved were further explored. The possible contributing factors included the loss of damascenone through the action of yeast metabolism, loss from reaction with components in the model or real juice and loss via evaporation of damascenone via the ferment flask during fermentation.

## ***Declaration***

I, Natoiya Dee Rayette Lloyd certify that 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 has been made in the text.

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Natoiya Dee Rayette Lloyd



## *Acknowledgments*

There are many individuals who have helped me throughout my PhD, some who have been there since the beginning and some who came on board mid way through. Over the years my supervisors included Prof. Dennis Taylor, Dr. Mark Sefton, Dr. Chris Curtin, Dr. Gordon Elsey, Dr. Maurizio Ugliano and Dr Martin Johnston and I can't express how appreciative I am for all of the help and guidance you all gave me.

I want to particularly thank the Grape and Wine Research and Development Corporation for providing the funding for my PhD project and also enabling me to attend the 9<sup>th</sup> Wartburg Flavour Symposium 2010, in Eisenach, Germany. Thank you to Flinders University, The University of Adelaide and The Australian Wine Research Institute for providing me the opportunity to work on such a great project with access to outstanding facilities and a friendly and supportive working environment.

I particularly want to thank Dennis for all his enthusiasm and positive encouragement in regard to every aspect of my project giving me the tools to continue forward and to always strive to achieve great results. Thanks so much for all of your guidance and support.

I want to especially thank Mark Sefton for your supervision from the very beginning of the project. You helped me in many ways and you were always keen to chat with me about my research providing me with many ideas that would strengthen my work. I learnt a lot from you and always appreciated your feedback especially when the results were sometimes overwhelming. The time you gave towards my work will always be remembered and I am forever grateful.

I want to especially thank Dr. Dimitra Capone. Your help throughout my PhD was endless even at your busiest moments. You have been great to work with over the years and I have learnt so much from you. I can't thank you enough for your help, guidance and encouragement to finish.

Gordon, you were there at the beginning of my PhD project and I will never forget all of the things I have learnt from you over the years. I always looked up to you and I will take what you have taught me and use it throughout my chemistry career. I want to thank Kevin for your endless help in the lab, you taught me a lot and it was always very enjoyable to work with you.

Thank you to Maurizio for all his assistance with the biochemistry aspects of my project. Your direction and support throughout my PhD will always be valued. I want to thank Dr. Chris Curtin for becoming involved in my PhD work as a supervisor and always being interested in the work and results I obtained. I really appreciate the contributions you made and the time you gave to help me finish. I want to also thank Dr. George Skouroumounis for all of his inspiring ideas towards my work which created some major turning points in my research.

I would have not made it through to the end without the people that surrounded me on a day to day basis. I want to thank my fellow PhD students both at Flinders University, the University of Adelaide and my work colleagues at the AWRI. I especially want to thank Josh, Jo, Kerry, Anthea, Nicole, Stacey, Pete, Dave, Taryn, Simon, Rachel, Bek, Andrew, Angus, Caroline, Radka, Jane, June, Jenny, Ally, Ruyi, Xin, Mao and Anson.

Lastly, I cannot forget my beautiful family who I love so much, who wish me well in anything I do and always believe in me. My mum, the best mum in the world, I want to thank you for your endless support. My brother Ryan I thank you for all your words of encouragement to get through and finish and a big thank you for the awesome coffee machine to help me daily particularly near the end of my PhD. My dad, I love you so much. I think of your positive words often and will always cherish our time together.

Matt, you mean the world to me and have been there since I started my PhD. You have always been there for me, respected, and supported me during my research. Thanks for cooking me awesome dinners every night and supporting me in whatever I needed. You truly are one of a kind.

# ***Publications***

## ***Refereed Publications***

1. Lloyd, N. D. R.; Capone, D. L.; Ugliano, M.; Taylor, D. K.; Skouroumounis, G. K.; Sefton, M. A.; Elsey, G. M., Formation of damascenone under both commercial and model fermentation conditions. *J. Agric. Food. Chem.* **2011**, 59, (4), 1338-1343.
2. Lloyd, N. D. R.; Capone, D. L.; Ugliano, M.; Taylor, D. K.; Skouroumounis, G. K.; Sefton, M. A.; Elsey, G. M. The role of yeast in the generation of the odorant damascenone in wine. *Proceedings of the 9<sup>th</sup> Wartburg Symposium on Flavor Chemistry and Biology*, Eisenach, Germany, 13 – 16<sup>th</sup> April, **2010**, pp. 447 – 451.

## ***Symposia***

1. Lloyd, N. D. R.; Capone, D. L.; Ugliano, M.; Taylor, D. K.; Sefton, M. A.; Elsey, G. M. The role of yeast in the generation of damascenone in wine. Crush Conference, Adelaide, South Australia, **2011**.
2. Lloyd, N. D. R.; Capone, D. L.; Ugliano, M.; Taylor, D. K.; Sefton, M. A.; Elsey, G. M. The role of yeast in the generation of the odorant damascenone in wine. 14<sup>th</sup> Australian Wine Industry Technical Conference, Adelaide, South Australia, **2010**.
3. Lloyd, N. D. R.; Capone, D. L.; Ugliano, M.; Taylor, D. K.; Elsey, G. M. The formation of damascenone under fermentation conditions. The 23<sup>rd</sup> RACI Organic Division Conference, 'Organic 08', Hobart, Tasmania, **2008**.

## ***Abbreviations***

CDGJ medium	Chemically defined grape juice medium
CDMW	Chemically defined model wine (made from CDGJ medium)
COSY	Correlation spectroscopy
DCM	Methylene chloride
DMAP	4-Dimethylaminopyridine
DMSO	Dimethylsulfoxide
EIC	Extracted ion chromatogram
EtOAc	Ethyl acetate
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum coherence
hr	Hour
Hz	Hertz
KI	Kovats Index
LAH	Lithium Aluminium Hydride
MeOH	Methanol
mM	millimolar
NaOMe	Sodium methoxide
ppb	parts per billion, $\mu\text{g/L}$
ppm	parts per million, $\text{mg/L}$
ppt	parts per trillion, $\text{ng/L}$
RT	Room temperature
sat. aq.	Saturated aqueous
TBAF	Tetrabutylammonium fluoride
TBDMS	<i>tert</i> -Butyldimethylsilyl
TBDMSCl	<i>tert</i> -Butyldimethylsilyl chloride
THF	Tetrahydrofuran
TIC	Total ion chromatogram
TLC	Thin layer chromatography
$\mu\text{M}$	micromolar

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