Flavour Development in the Vineyard

The Australian Wine Research Institute

Green Characters in Red Wine &

Tropical Characters in White Wine











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Background on Wine Aroma

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Complex with ~ 800 volatile compounds identified to date

Can be derived from numerous sources:

(either chemically or by enzymatic reactions)

- Grape berry itself: **e.g. terpenoids, MP's & C_6 compounds**
- Non volatile precursors in the grape being released during processing/storage: **e.g. varietal thiols & glycosides**
- Fermentation derived: **e.g. higher alcohols, ethyl esters & acetates**
- Oakwood contact: **e.g. oak lactones & vanillin**
- Oxidative & acid-catalysed reactions upon storage: **e.g. TDN & sotolon**
- Exogenous sources: **e.g. TCA**

Part 1: Known compounds involved in giving 'green' characters in wine

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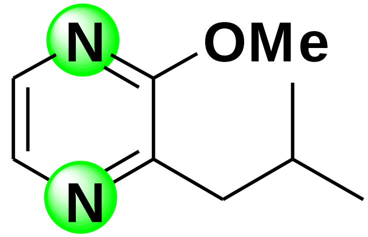
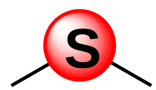
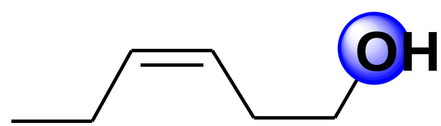
- Methoxypyrazines
  - **IBMP**, SBMP, IPMP
- Sulfur compounds
  - **DMS**, DES, DMDS
  - 2-Isobutylthiazole
- C6 compounds
  - **(*Z*)-3-Hexen-1-ol**
  - (*E*)-2-Hexenal
  - (*Z*)-3-Hexenal
  - Hexanal
  - 1-Hexanol
  - Hexyl esters



3-Isobutyl-2-methoxypyrazine (IBMP)



Dimethyl sulfide (DMS)



(*Z*)-3-Hexen-1-ol
(*cis*-3-Hexen-1-ol)

Sensory impact of IBMP

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- IBMP – capsicum, fresh green, asparagus, earthy; 2 ng/L threshold (extremely potent)
- Significant influence on wine aroma in white wine from 2 ng/L and red wine from 15 ng/L
- Found in wine up to
  - 50 ng/L in Sauvignon Blanc (Sth Af and NZ), 30 ng/L (Aus)
  - 56 ng/L in Cabernet Sauvignon (Aus)
  - 23 ng/L in Merlot (France)
  - 34 ng/L in Cab Franc (France)

Location of IBMP in grape berry

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Within berry

Skin: 95%

Seeds: 4%

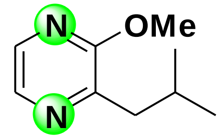
Pulp: <1%

Within cluster,

Stem accounts for ~50% of IBMP

Reference: Roujou de Boube, D. Thesis, University Bordeaux II, 2000

Modulating factors - IBMP



3-Isobutyl-2-methoxypyrazine (IBMP)

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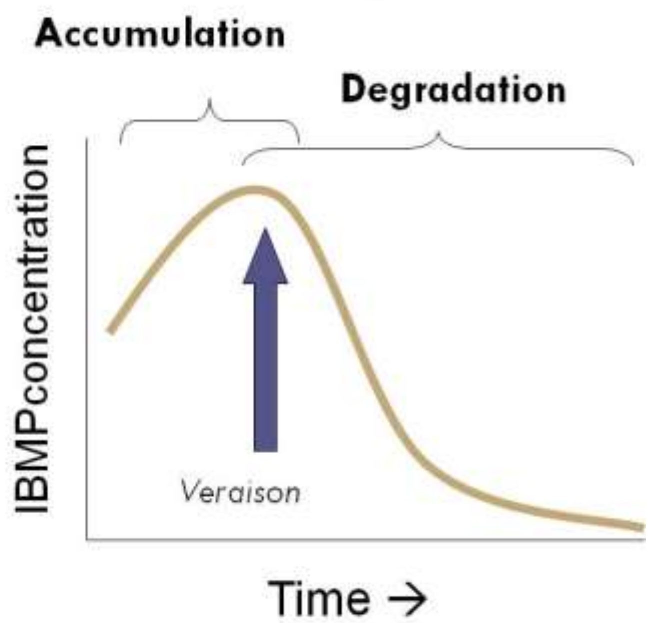
- Viticulture
  - Associated with Cabernet Sauvignon, Merlot, Cabernet Franc, Sauvignon Blanc
  - Berry maturity (MPs Accumulate pre-veraison and degrade post-veraison)
  - Vigour, canopy density (Less vine vigor reduces MPs)
  - Climate (Warmer regions reduces MPs)
  - Fruit exposure
    (Better cluster exposure – Lowers MPs)
  - Skin contact during winemaking
    (Increases during fermentation whilst on skins)
  - Green stalks



Bordeaux study
(van Leeuwen et al. 2004)

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- Best vintages where water supply to vine from flowering to harvest was most limiting
- Either soil effect or seasonal effect or both
- Water deficit prior to veraison → early cessation of shoot growth

Acknowledgment: Peter Dry

VAN LEEUWEN C., FRIANT Ph., CHONÉ X., TRÉGOAT O., KOUNDOURAS S. and DUBOURDIEU D., 2004. The influence of climate, soil and cultivar on terroir. *Am. J. Enol. Vitic.*, **55**, 207-217.

Cessation of shoot growth by veraison

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- Relationship between shoot vigour and concentration of methoxypyrazines (MP) in Cab Sauv fruit

- MP strongly correlated with pre-veraison shoot vigour
  - Independent of bunch exposure

(Lakso and Sacks (2010) Pract Winery and V'yard May/June 35-49, 73)

Acknowledgment:
Peter Dry

Jumilla, Spain

non-irrigated irrigated

Modulating factors - IBMP

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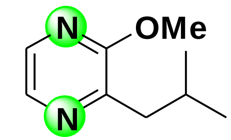
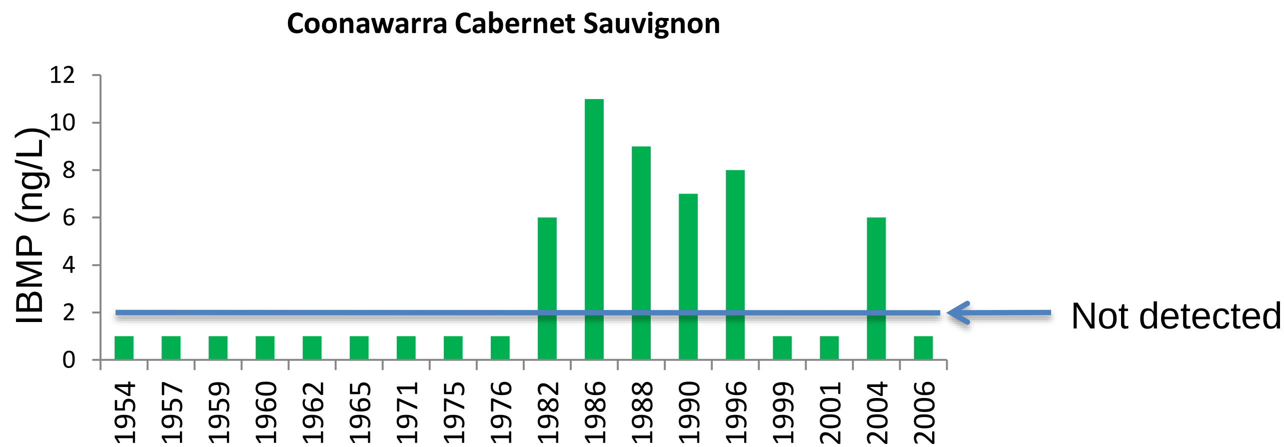


3-Isobutyl-2-methoxypyrazine
(IBMP)

Winemaking

- Quantitative extraction early during fermentation
- IBMP not modified during winemaking
- Bentonite fining, oak contact, pectinases and micro-ox have no effect
- Activated charcoal may reduce IBMP but is not specific



Storage

- IBMP may be affected by packaging type
- Greatest decrease with bag in box, then synthetic, then screw cap
- Natural cork retained the most IBMP
- Typically very stable over time

IBMP level in grapes correlates closely with IBMP in wine

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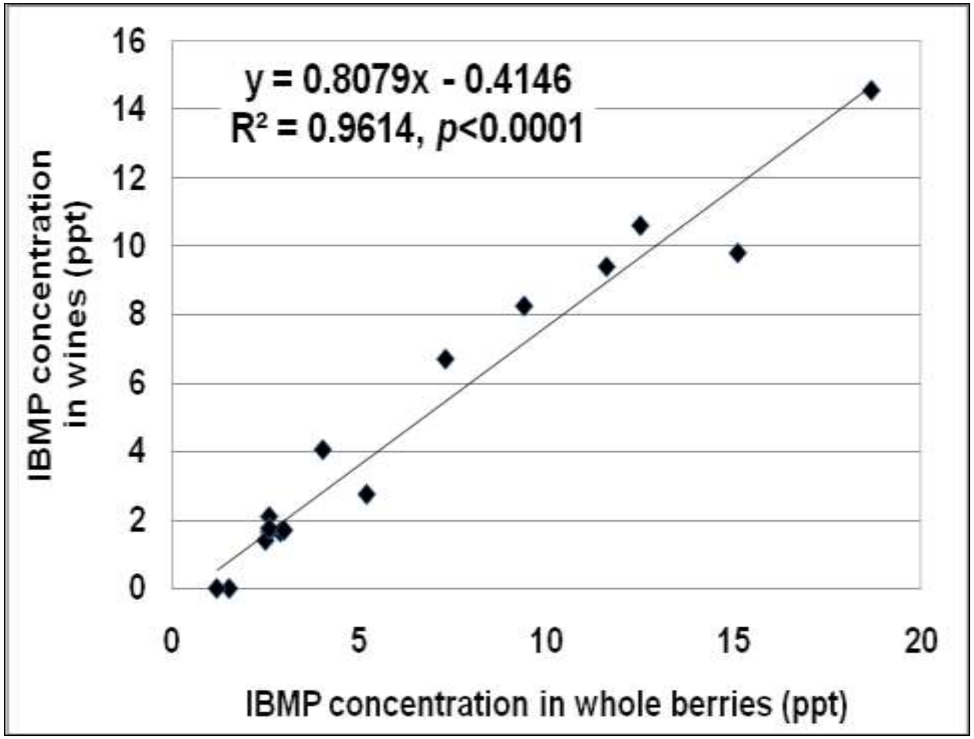
IBMP in wines vs. grapes for 16 small lot Cabernet franc fermentations



From
Gavin Sacks, Cornell University

They have also shown that IBMP is stable in the bottle

Ryona, Pan, Sacks (JAFC, 2009)

Silicone tubing selectively removes IBMP

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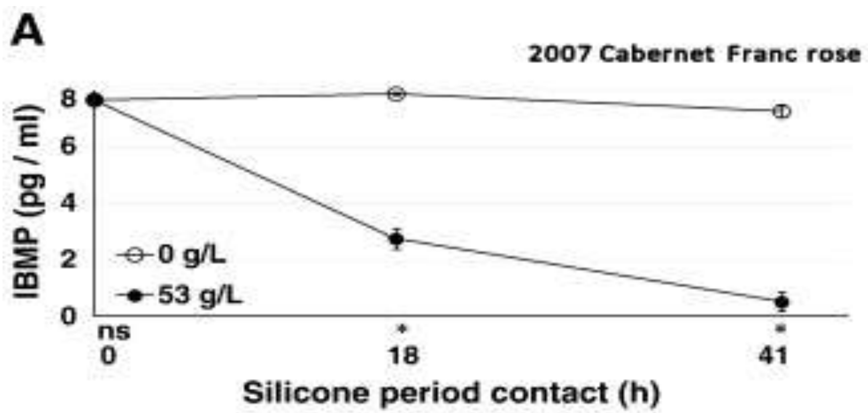

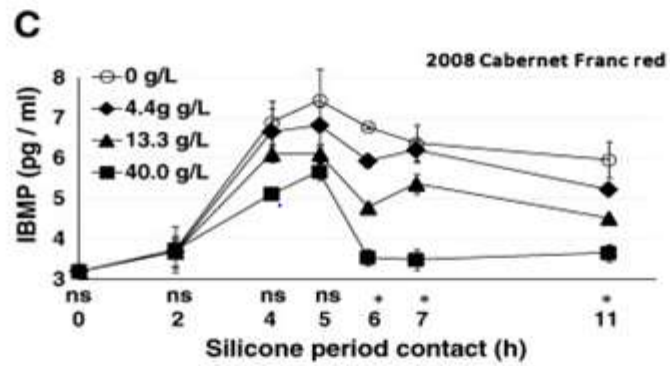

Generally, 50-90% reduction in MPs; no significant reduction of other wine volatiles (esters, fusel alcohols, most terpenoids, etc)

Fig. 2 Effects of pre-fermenation silicone treatment on A) IBMP in 2007 Cabernet Franc rosé without skin fermentation, and C) IBMP in 2008 Cabernet Franc red with skin fermentation

Reference: Treatment of grape juice or must with silicone reduces 3-alkyl-2-methoxypyrazine concentrations in resulting wines without altering fermentation volatiles. *Food Research International Volume 47, Issue 1 2012 70 – 79, Imelda Ryona , Johannes Reinhardt , Gavin L. Sacks, http://dx.doi.org/10.1016/j.foodres.2012.01.012*

Sensory impact of DMS

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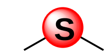

Dimethyl sulfide
(DMS)

- DMS – vegetal, canned corn, canned tomato, asparagus, black currant; 25 µg/L threshold
- Higher concentrations lead to vegetal characters, lower levels can enhance berry/fruity notes
- Can be beneficial to wine aroma perhaps below 100 µg/L; highly matrix-dependent but sound wines are typically well below this level
- Found in wine up to
  - 185 µg/L in Chardonnay
  - 37 µg/L in Riesling
  - 118 µg/L in Sauvignon Blanc
  - 380 µg/L in Cabernet Sauvignon
  - 235 µg/L in Merlot
  - 756 µg/L in Shiraz




Modulating factors - DMS

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Dimethyl sulfide (DMS)

- Origin
  - Methionine and *S*-methylmethionine (SMM) likely precursors
- Viticulture
  - Vine nutrient management and vineyard site affect amino acids
  - AA profiles vary greatly between grape varieties
  - Vintage differences also noticeable – similar pattern but variable concentrations
  - Shiraz potentially rich in precursors, Grenache not so
- Winemaking
  - Must nutrients and DAP addition
  - AA or SMM produced by yeasts
  - Yeast strain effects – *bayanus* vs *cerevisiae*
  - Wild and inoculated ferments

Sensory impact of *cis*-3-Hexen-1-ol

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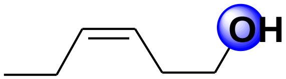

(*Z*)-3-Hexen-1-ol
(*cis*-3-Hexen-1-ol)

- *cis*-3-Hexen-1-ol – cut grass, herbaceous, leafy; 400 µg/L threshold
- Typically not found above threshold in most studies
- Found in wine up to
  - 650 µg/L in young red wines (highest in Tempranillo)
  - 800 µg/L in aged red wines
  - 75 µg/L in Gewurztraminer
  - 600 µg/L in some Italian and Spanish white wine varieties (Falanghina and Macabeo)

Modulating factors – *cis*-3-Hexen-1-ol

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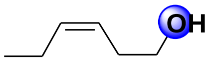

(*Z*)-3-Hexen-1-ol
(*cis*-3-Hexen-1-ol)

- Origin
  - Enzymatic formation via LOX pathway leads to C6 compounds
- Viticulture
  - Differs between varieties and during berry development (e.g. Riesling vs Cabernet Sauvignon)
  - Highest at pre-veraison in line with unsaturated fatty acid levels – decline in linolenic acid with ripening
  - Higher in skin (from press cake) than must at all ripening stages

Modulating factors – *cis*-3-Hexen-1-ol

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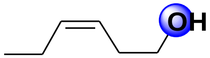

(*Z*)-3-Hexen-1-ol
(*cis*-3-Hexen-1-ol)

- Winemaking
  - Time and temperature of skin contact – similar extraction from 15-28 ºC with max after 10-15 h, continual increase during contact time at 10 ºC after 25 h
  - Relatively stable but SO_2 and enzymatic activity have effects – O_2 needed for formation
  - Presence of vine leaves has minimal impact – large release from leaves crushed in air as opposed to in must
  - Esterification to the acetate – from green (alcohol) to green/floral/fruity (ester)
- Storage
  - Not affected by storage in presence of oxygen
  - Minimal change with storage on lees for up to seven months
  - Unaffected by short-term oxidative storage in presence of phenolics
  - Slow decline with storage for 210 days but no impact from different SO_2 levels

Summary

- Green flavours in wine are caused by a number of different compound classes, with vastly different potencies
- Compound origins are in the grape, often in precursor form
- Viticultural practices and harvesting decisions can impact on green flavours
- Green flavours may be desirable, adding complexity or typicity to wine styles

Part 2: Tropical Flavours - Varietal thiols

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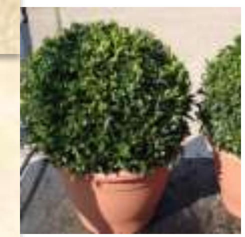
- Polyfunctional thiols are especially potent and have some of the lowest aroma thresholds of any food odorant
- Varietal thiols are important impact odorants in some wines e.g. Sauvignon Blanc

Thiol	Perception threshold	Aroma	OAV
4-MMP	3 ng/L	blackcurrant box tree passionfruit	Up to 30
3-MH	60 ng/L	grapefruit passionfruit	Up to 210
3-MHA	4 ng/L	passion-fruit box tree sweaty	Up to 195



Darriet et al. Flavour Fragr. 1995, 10, 385-392
Tominaga et al. Vitis 1996, 35, 207-210
Tominaga et al. Flavour Fragr. 1998, 13, 159-162

Volatile thiol sensory descriptors

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- Individual volatile thiols contribute *tropical* aromas to wine, 3-MH also *citrus* aroma
- Volatile thiol combinations had aromas of *tropical* & ***cooked green vegetal*** at both levels, and at high levels also *cat urine/sweaty*
- 4-MMP does not contribute any distinctive sensory properties at high levels
- At high concentrations 3-MHA is responsible for *cat urine/sweaty* aromas

Grape varieties containing volatile thiol compounds

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White varieties

Sauvignon Blanc
Chardonnay
Chenin Blanc
Colombard
Gewürztraminer
Gros Manseng
Koshu
Maccabeo
Muscat
Muscadet
Petit Arvine
Petit Manseng
Pinot Blanc
Pinot Gris
Riesling
Scheurebe
Semillon
Sylvaner
Tokay

Red varieties

Cabernet Franc
Cabernet Sauvignon
Grenache
Merlot
Pinot Noir

Volatile thiol concentrations in SAB wines from around the world

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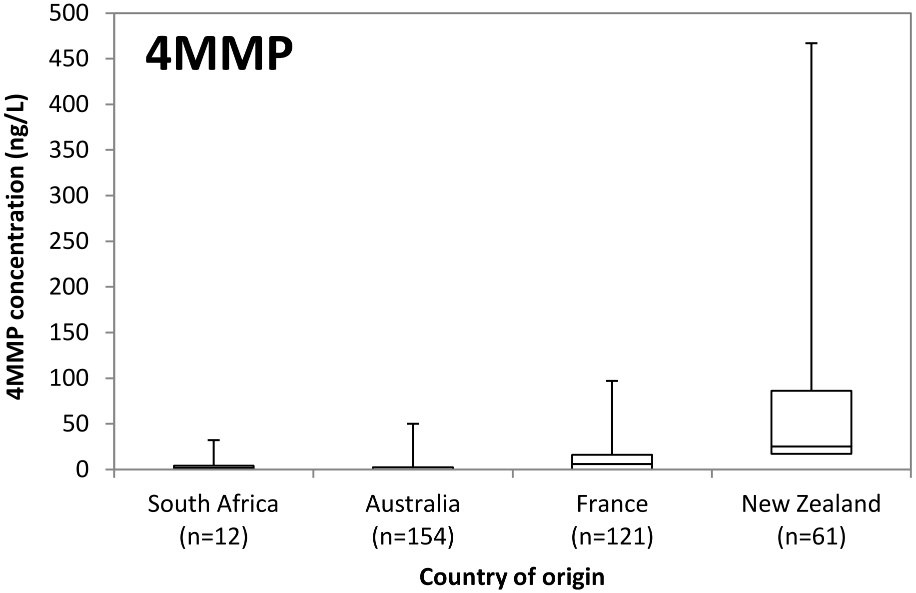

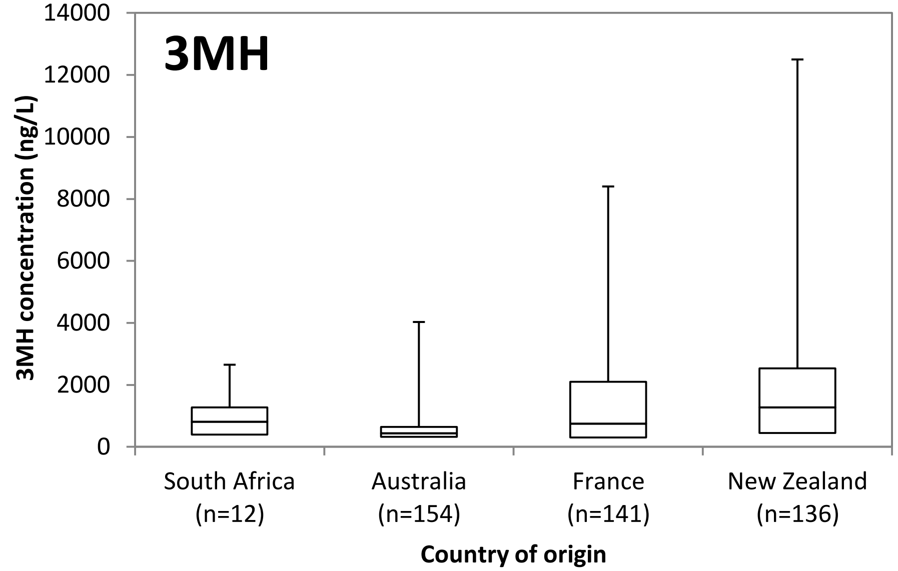

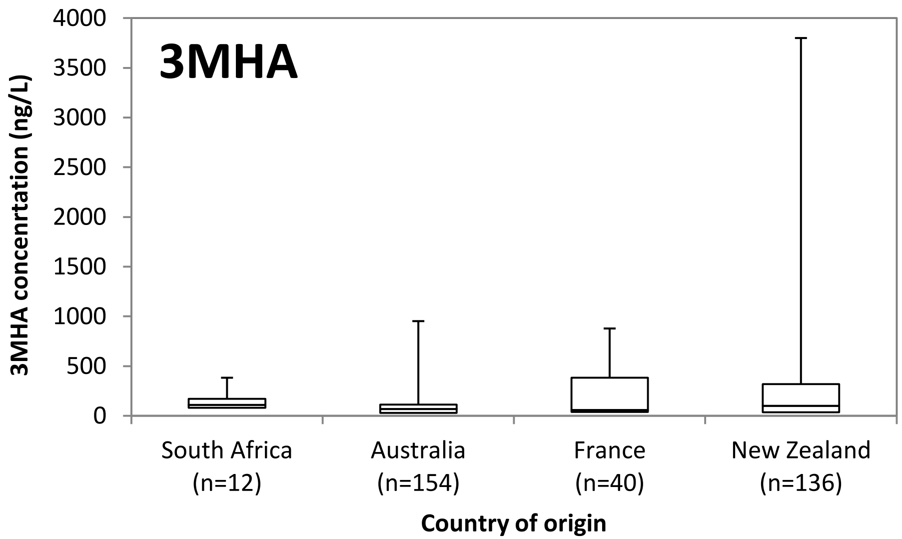

Varietal thiol formation

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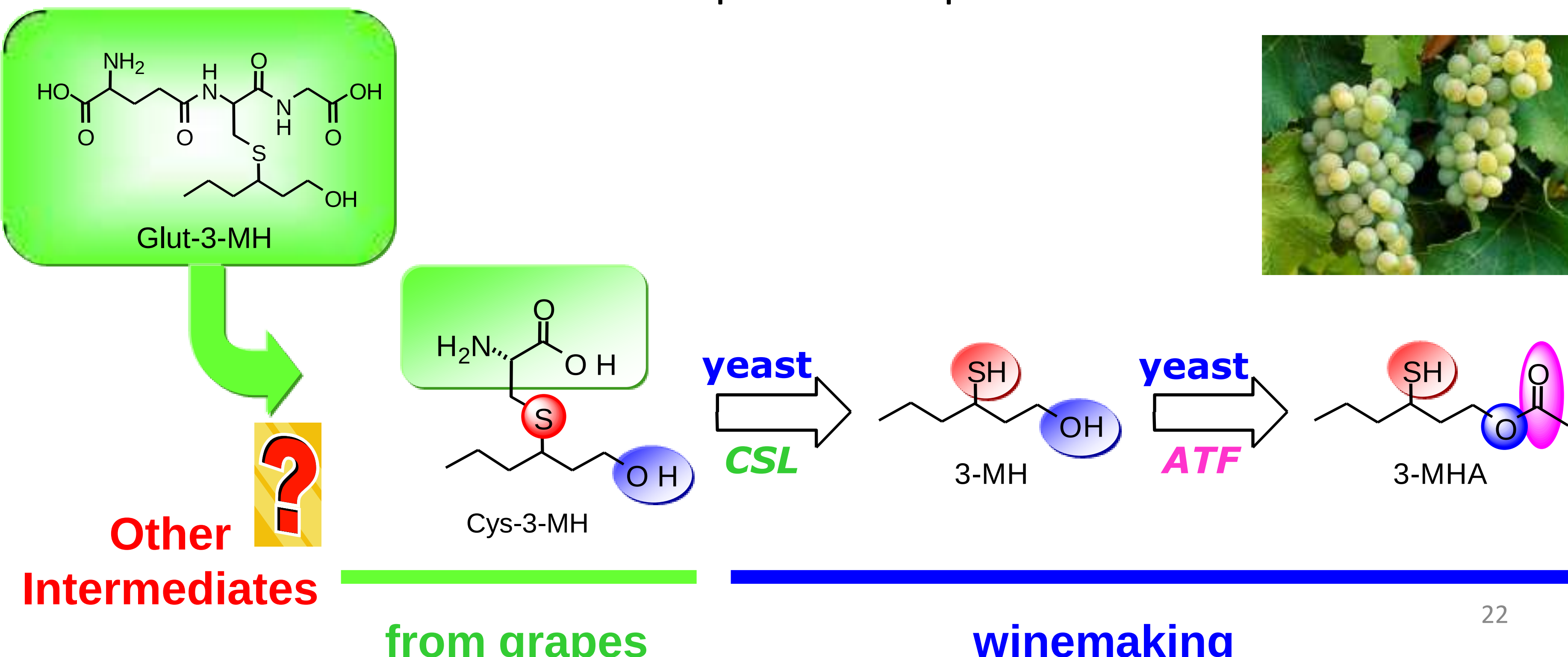
- Optimise formation and maximise stability of varietal thiols
- Need to further understand precursor formation

  (Stress response : Kobayashi et al)
- Yeast plays a key role in thiol release into wine
- Need to understand relationship between precursors and free thiols



Modulation of volatile thiol precursors

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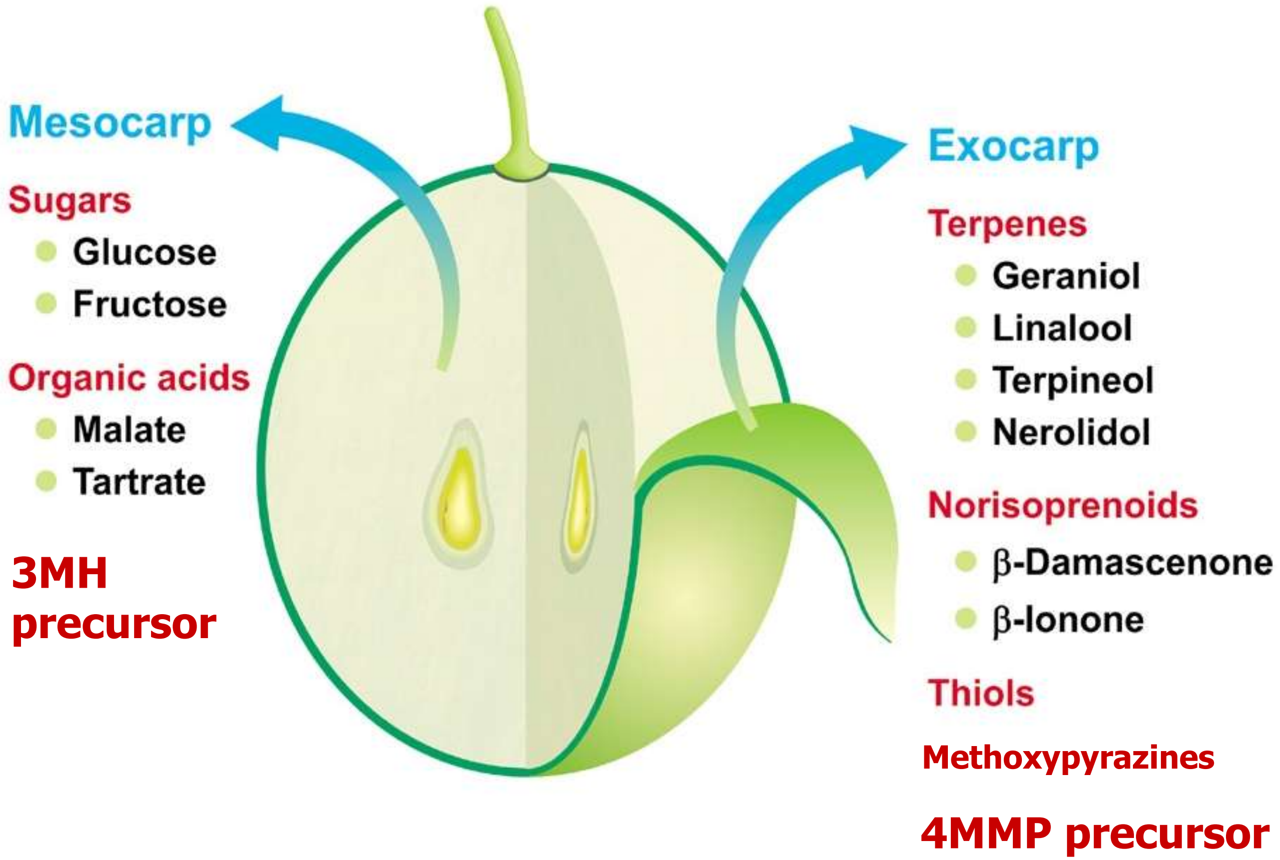

- 3MH precursors are mainly found in the skins of grape berries
- 4MMP precursors are mainly found in the flesh of grape berries

HPLC-MS/MS analysis of precursors

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- Amount of precursors measured in SAB juice:

Cys-3-MH	**21 – 55 µg/L**
Glut-3-MH	**245 – 696 µg/L**

- Also found precursors in other varieties (in the juice) generally:

Sauvignon Blanc > Pinot Gris > Chardonnay > Riesling

Capone et al. JAFC 2010, 58, 1390-1395

Precursor and thiol studies

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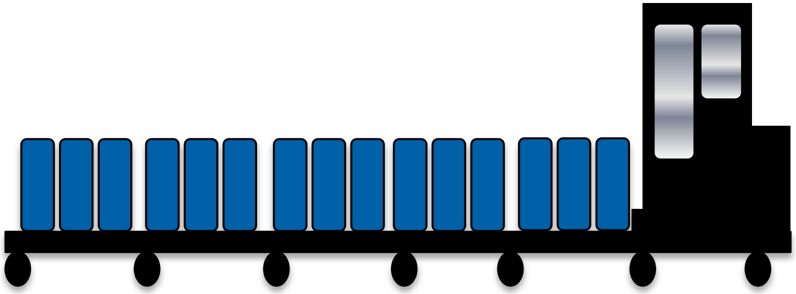
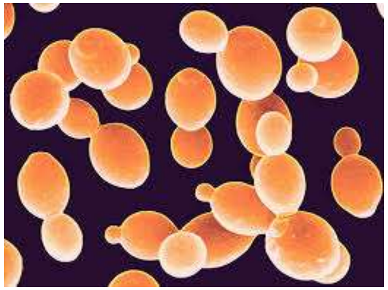
- **Ripening**



- **Transportation / Holding**

- **Yeast Selection**




Amount of 3-MH precursors during ripening

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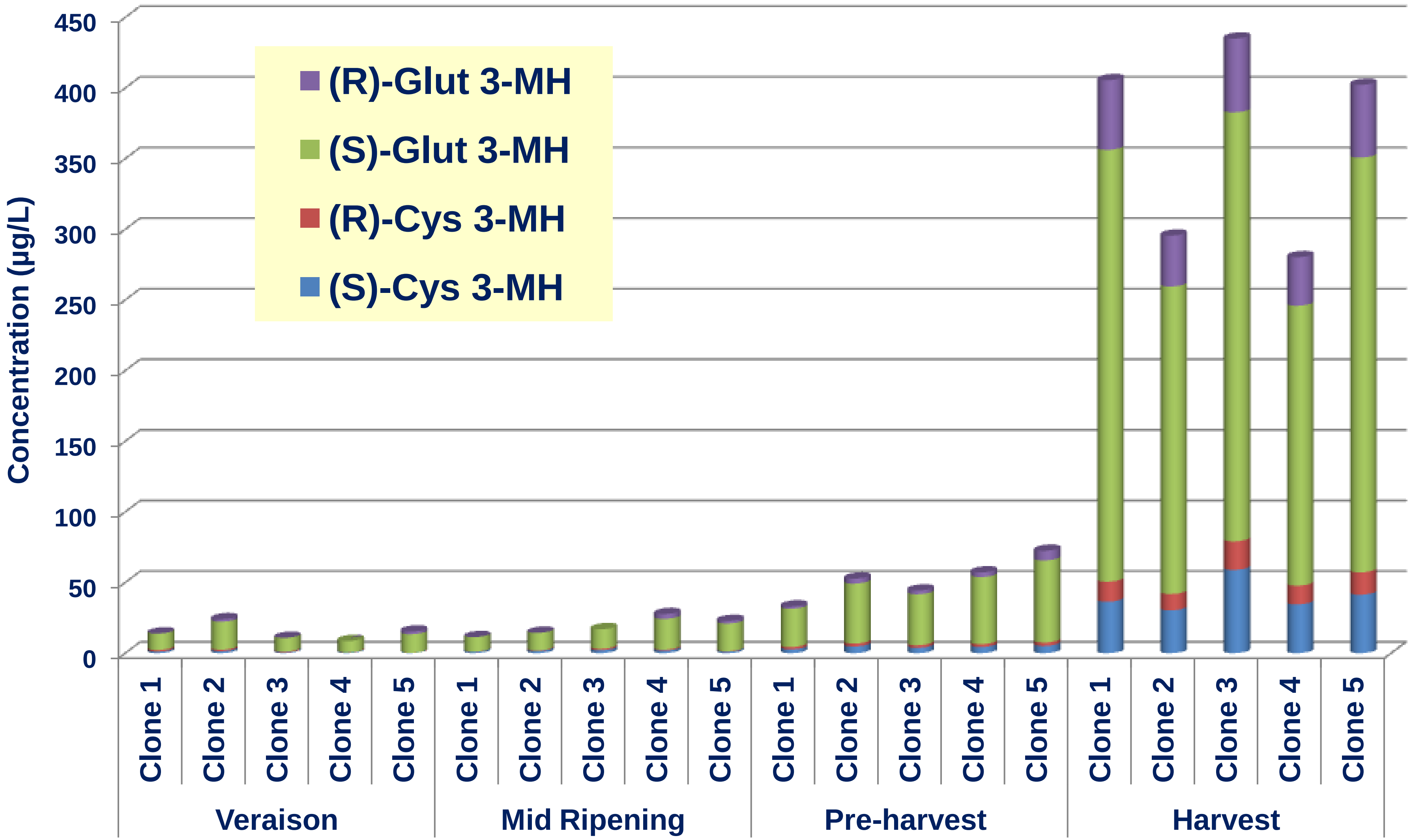

Capone et al. 2011, JAFC. 59: 4649-4658

Effect of transportation on precursor concentration

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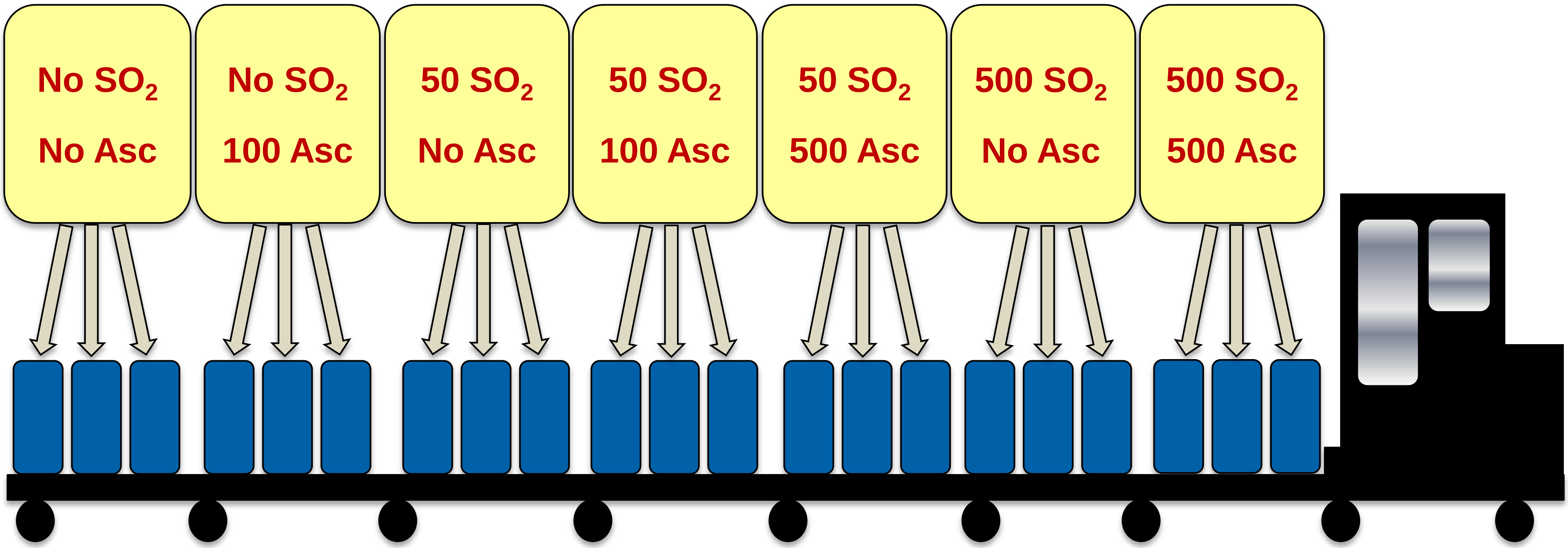

Analysed shortly after machine harvesting then ……..


Arafura Sea
Torres Straits
N
Timor Sea
Darwin
Gulf of
Carpentaria
Coral Sea
Cairns
Northern
Territory
Western Australia
South Australia
794 km
New South Wales
Indian
Ocean
Perth
Great
Sydney
Canberra
Victoria
Adelaide
Melbourne
South
Pacific Ocean
Hobart
Tasmania

Effect of transportation on precursors

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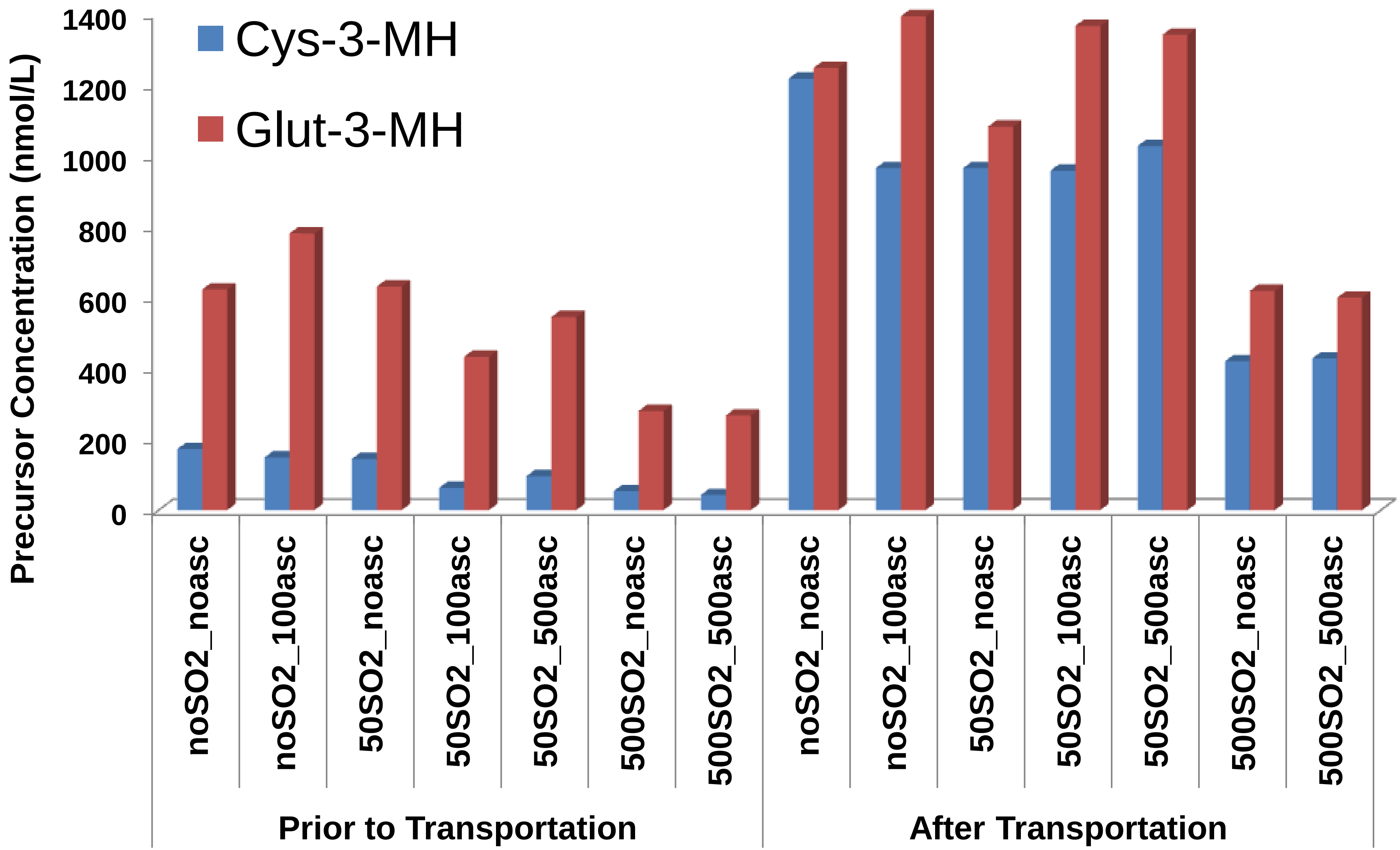

Capone et al. 2011, JAFC. 59: 4659-4667

Storage of grape must increases 'tropical' precursor levels

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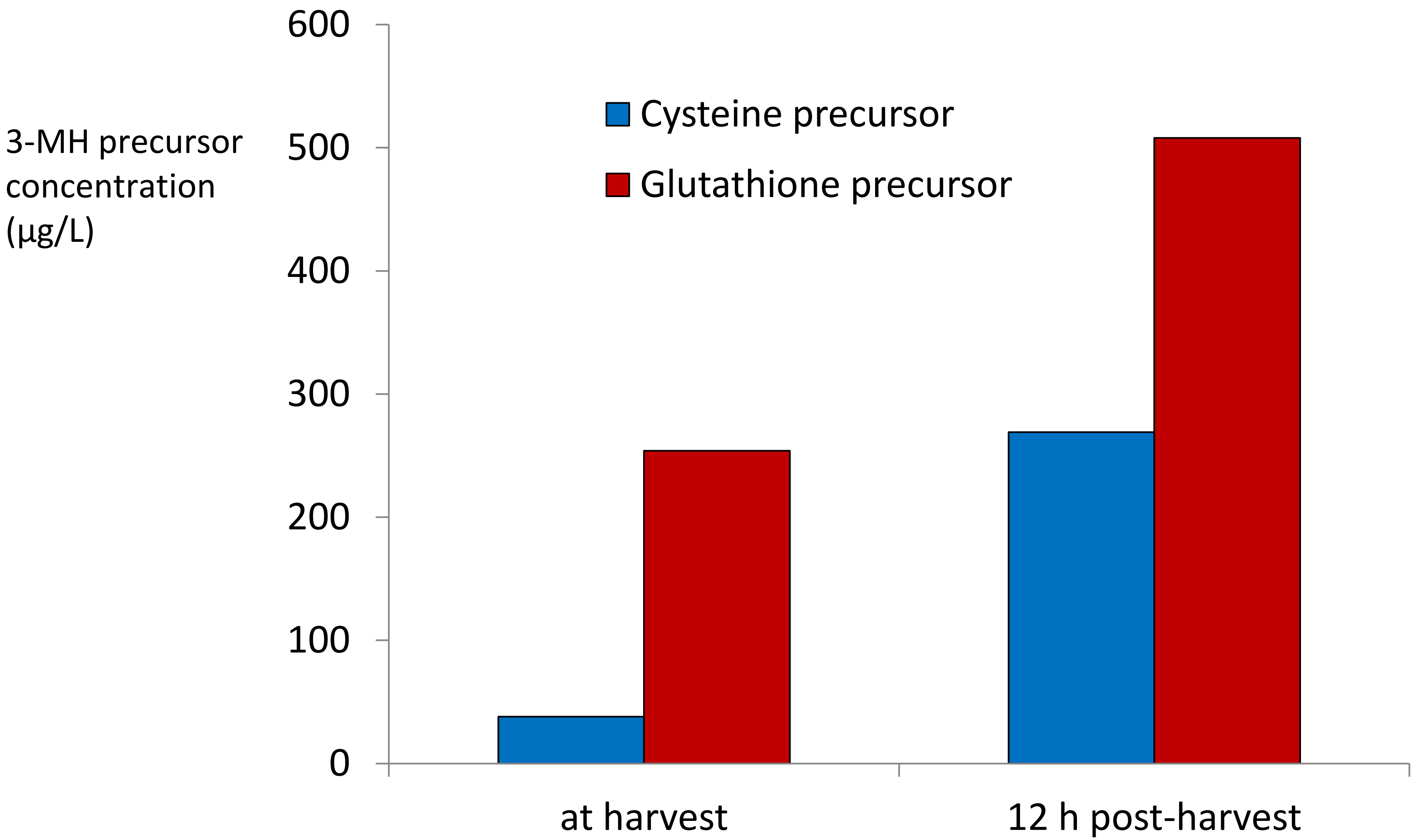

Yeast strains can release differing levels of volatile thiols

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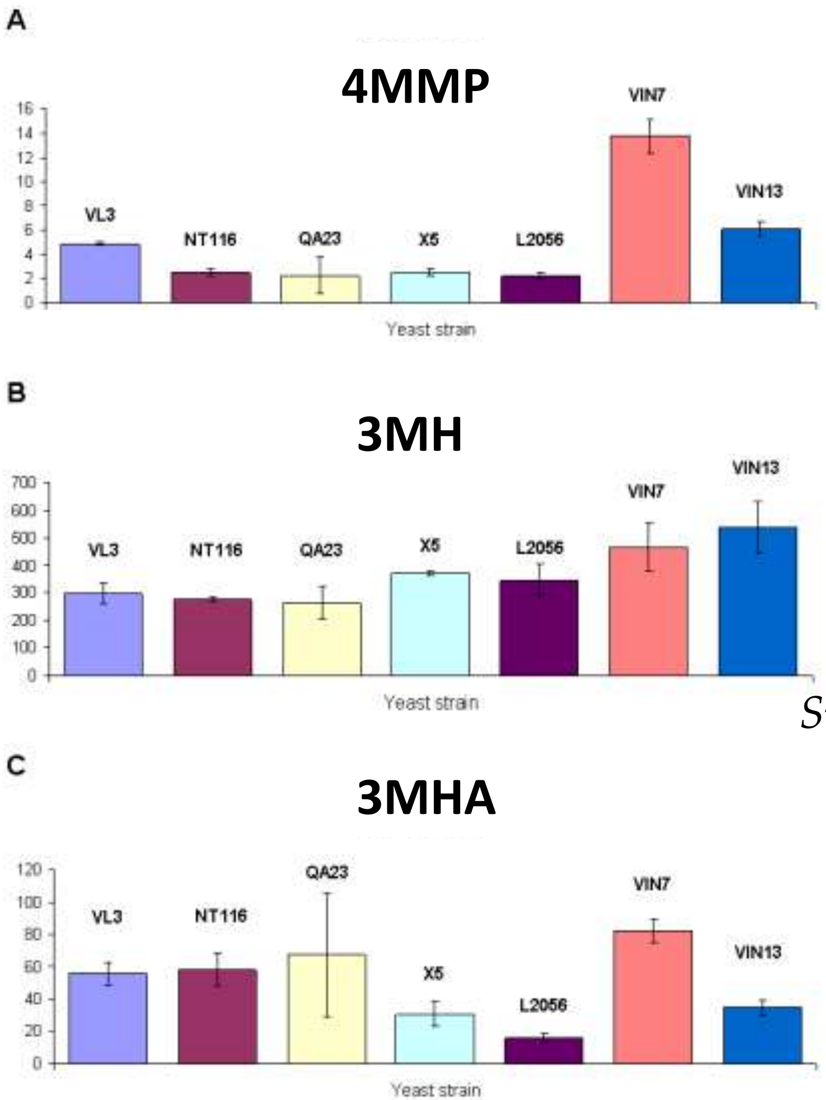

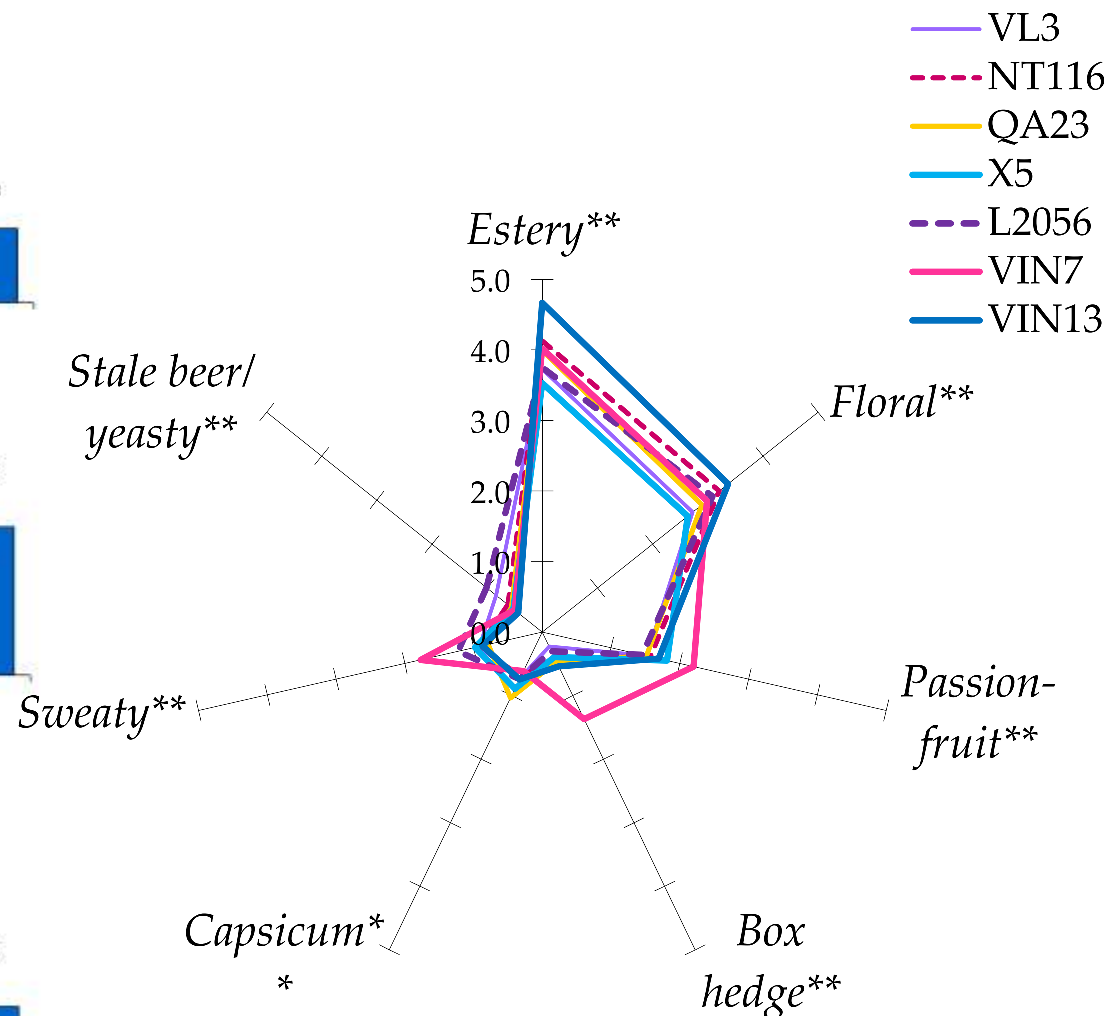

Modified from Swiegers et al. (2009)

Further modulating factors for varietal thiols

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- Higher fermentation temperatures increased volatile thiol levels (20°C compared to 13°C)
- 3MH decreased during malolactic fermentation and barrel ageing
- The addition of Sulfur dioxide stabilised 3MH and 4MMP levels in wine
- Cork closures decreased the levels of 3MH and 3MHA in wine
- 3MHA levels decreased dramatically within the first year of bottling
- Addition of Copper as a wine fining agent decreased volatile thiol levels
- In-mouth release of volatile thiol precursors by saliva bacteria

Current work – Varietal thiols in Chardonnay

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- Predominance of varietal thiols in Commercial Australian Chardonnay
  - 106 Commercial bottles purchased
- Predominance of thiols in Chardonnay across Australia
  - 18 Sites selected from major wine growing areas
  - Standardised winemaking on each juice sample
  - Wines have just been bottled and awaiting:
    - Sensory analysis
    - Analysis of both thiol precursors in the juice and free thiol analysis in the finished wine

Concluding remarks

- 3-MH precursor and free 3-MH concentration can be significantly affected by
  - Ripening
  - Transportation / Storage of grapes
  - Harvest type: Machine versus Hand Picking
  - Yeast selection

Flavour optimisation – the future

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❖ Be able to predict concentrations of volatiles from:

Acknowledgements

The Australian Wine Research Institute

Green Project

- Dr Leigh Francis (AWRI)
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- Ellie King (AWRI)
- Dr David Jeffery (UA)
- Dr Mark Sefton (UA)

THE UNIVERSITY OF ADELAIDE AUSTRALIA

Industry Partners

Australia's grapegrowers and winemakers through their investment body, the Australian Grape and Wine Authority, with matching funds from the Australian government

Australian Government

Australian Grape and Wine Authority