

# SYNTHÈSE DES TRAVAUX EN COURS SUR LA ROTUNDONE :

un composé aromatique puissant responsable  
des notes poivrées dans les vins



AWRI

MARKUS HERDERICH  
AWRI



COOPERACIÓN COOPÉRATION  
TERRITORIAL TERRITORIALE  
2007-2013

*Invirtiendo en nuestro futuro*  
*Investir dans notre avenir*



# AUSTRALIAN Shiraz



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- **Volume, Quality & Value**

- 2012 vintage crush 379,925 tonnes
  - 45% of red grapes; 23% of total value 2011 approx. \$1.8b
  - 25.8% of domestic&exports

- **Heritage Clones**

- arrived 1832; no phylloxera
  - 165 y old vines (Barossa Valley, SA)
  - 149 y old vines (Victoria)
  - 124-146 y old (Hunter Valley, NSW)

- **Diversity of Styles**

- > *blends*: Shiraz x Cab Sauv, Grenache x Shiraz x Mouvedre,...
  - > *co-ferments*: Shiraz & Viognier
  - > sparkling *Shiraz*
  - => *terroir, regionality*



# Australian cool climate Shiraz



The Australian Wine Research Institute

## WINE REGIONS OF AUSTRALIA



### WESTERN AUSTRALIA

- 1 Swan District
- 2 Perth Hills
- 3 Peel
- 4 Geographe
- 5 Margaret River
- 6 Blackwood Valley
- 7 Pemberton
- 8 Manjimup
- 9 Great Southern

### SOUTH AUSTRALIA

- 10 Southern Flinders Ranges
- 11 Clare Valley
- 12 Barossa Valley
- 13 Eden Valley
- 14 Riverland
- 15 Adelaide Plains
- 16 Adelaide Hills
- 17 McLaren Vale
- 18 Kangaroo Island
- 19 Southern Fleurieu
- 20 Currency Creek
- 21 Langhorne Creek
- 22 Padthaway
- 23 Mount Benson
- 24 Wrattenbully
- 25 Robe
- 26 Coonawarra
- 27 Mount Gambier

### QUEENSLAND

- 28 South Burnett
- 29 Granite Belt

### NEW SOUTH WALES

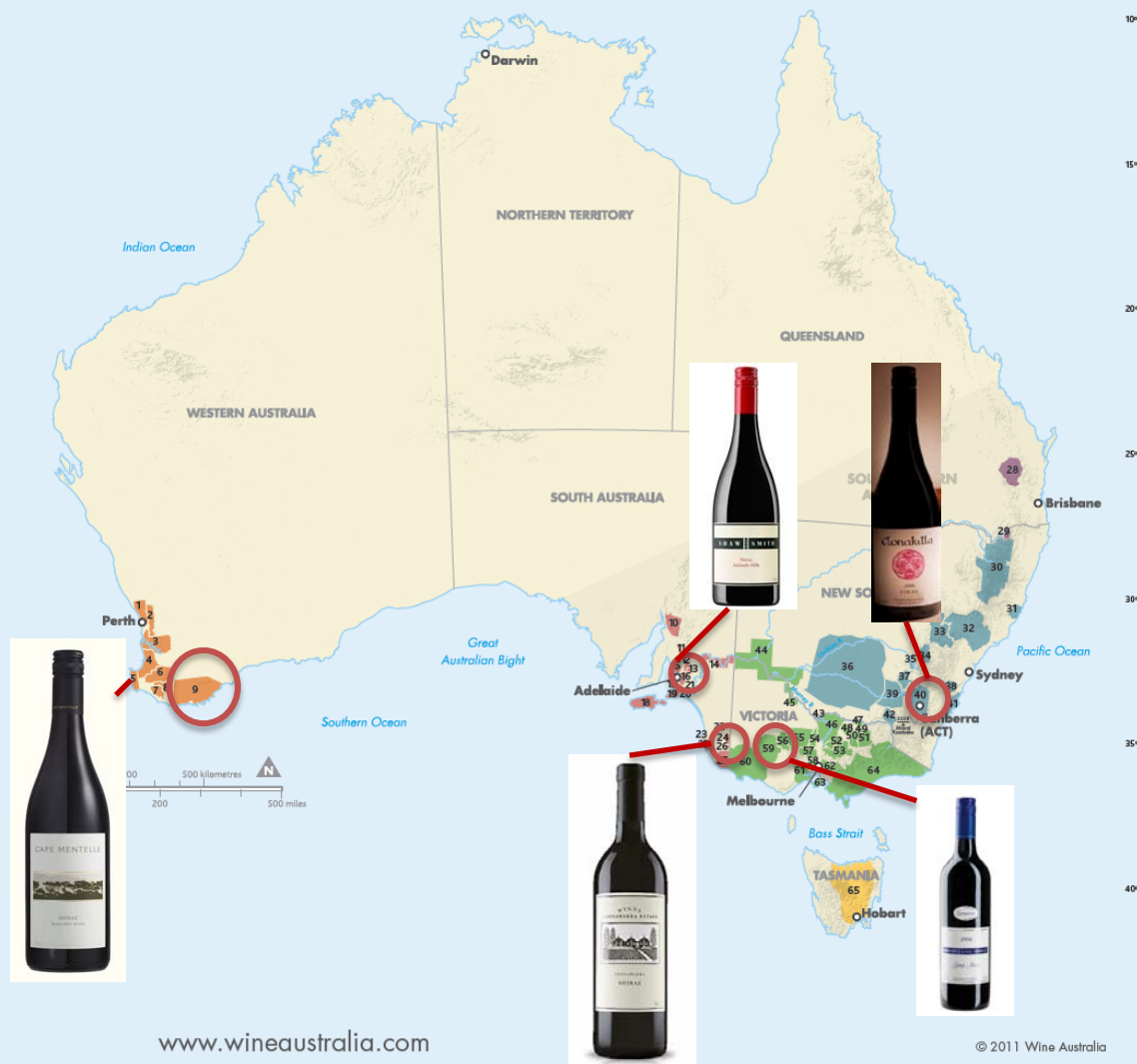
- 30 New England Australia
- 31 Hastings River
- 32 Hunter
- 33 Mudgee
- 34 Orange
- 35 Cowra
- 36 Riverina
- 37 Hilltops
- 38 Southern Highlands
- 39 Gundagai
- 40 Canberra District
- 41 Shoalhaven District
- 42 Tumbarumba
- 43 Perricoota

### VICTORIA

- 44 Murray Darling
- 45 Swan Hill
- 46 Goulburn Valley
- 47 Rutherglen
- 48 Glenrowan
- 49 Beechworth
- 50 King Valley
- 51 Alpine Valleys
- 52 Strathbogie Ranges
- 53 Upper Goulburn
- 54 Heathcote
- 55 Bendigo
- 56 Pyrenees
- 57 Macedon Ranges
- 58 Sunbury
- 59 Grampians
- 60 Henty
- 61 Geelong
- 62 Yarra Valley
- 63 Mornington Peninsula
- 64 Gippsland\*

### TASMANIA

- 65 Tasmania\*



\*South Eastern Australia and Gippsland are zones, Tasmania is a state.



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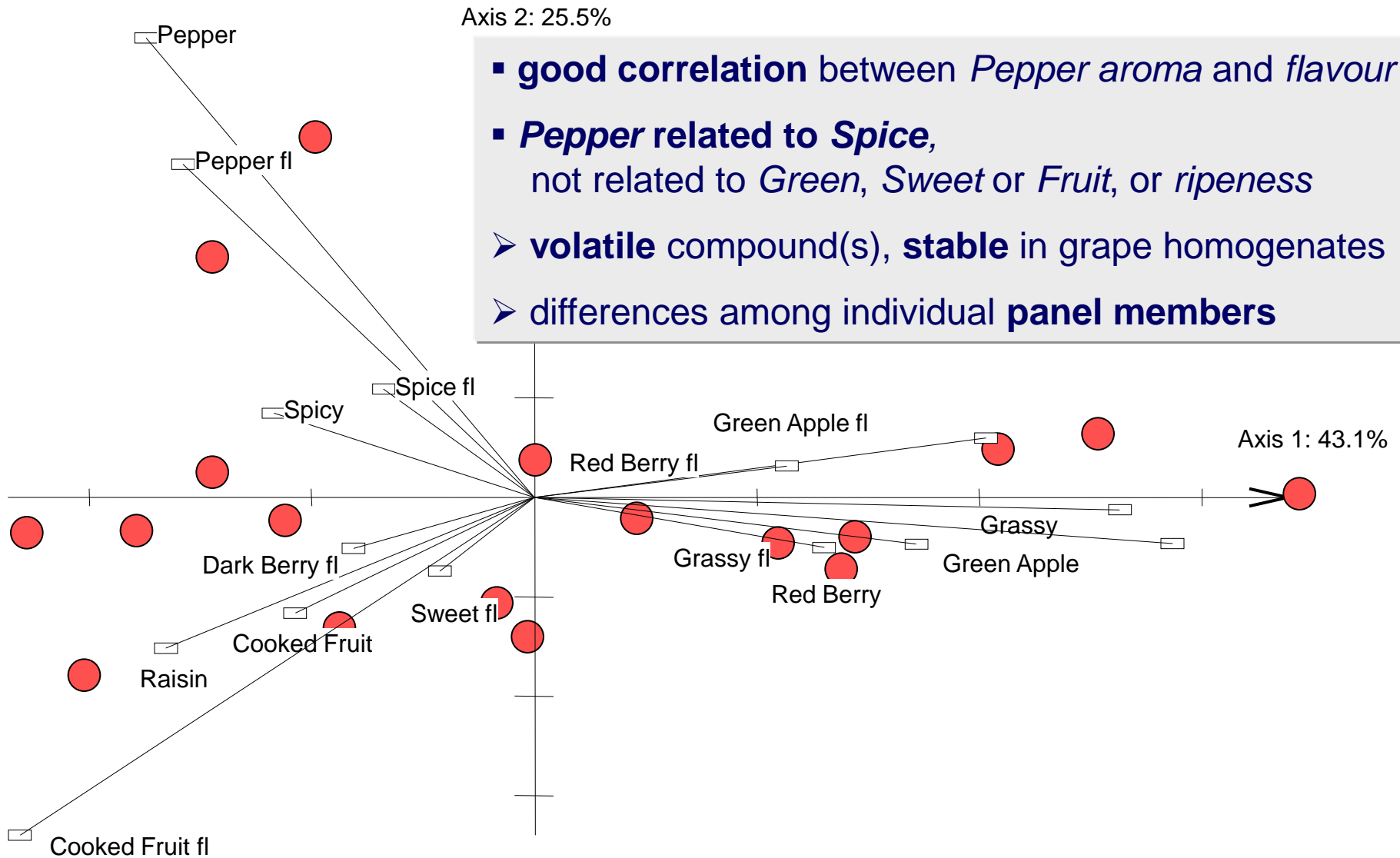
# Black pepper aroma in Shiraz

- A spicy, black pepper aroma is important to some key styles of high quality Australian Shiraz
- Described as ‘peppery’, ‘black pepper’, ‘white pepper’, ‘spicy’, ‘herbaceous’
- Shiraz
- Cool climate
- Significant variation between vineyards and seasons
- No peppery impact aroma compound known not for grapes, wine or pepper





# Sensory analysis of Shiraz grapes



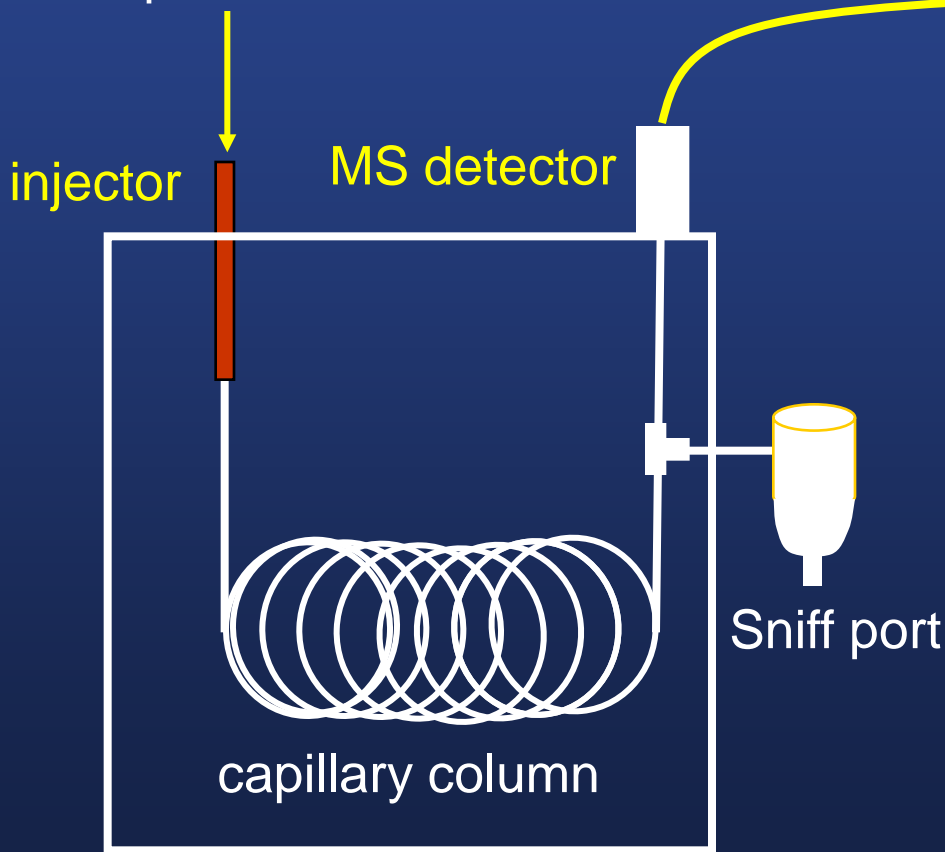
# Identification of peppery grape volatiles



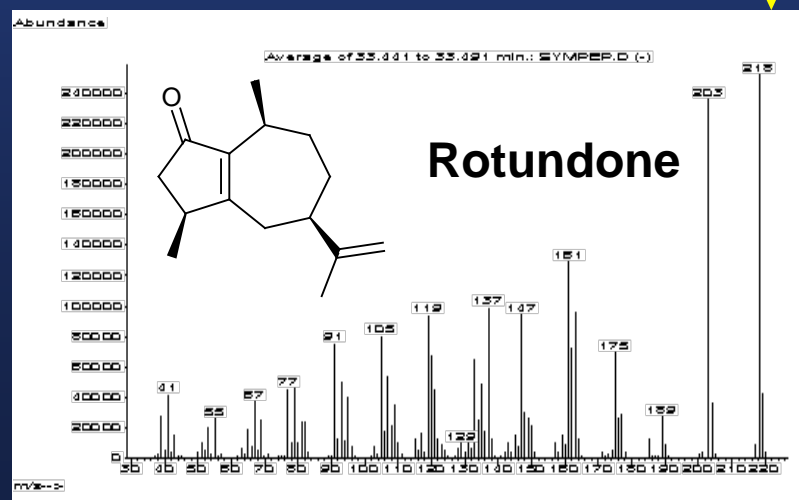
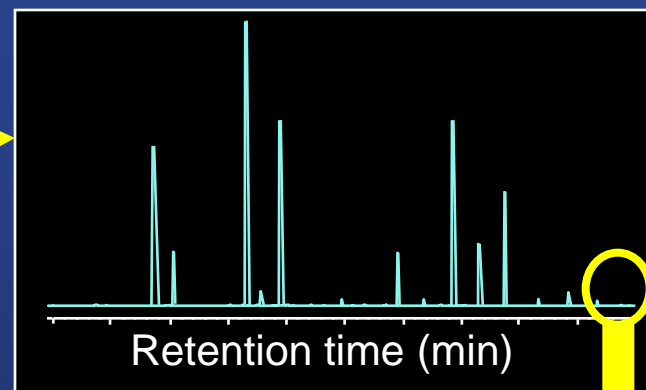
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Optimised extraction, purification and enrichment

Grape or wine extract



GC-MS chromatogram

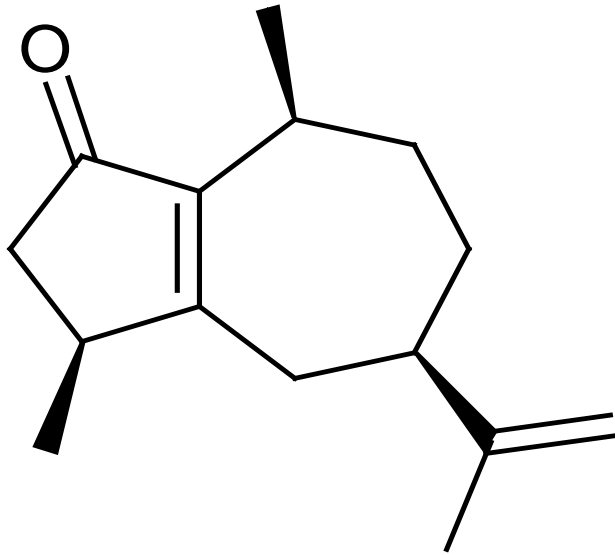


Mass spectrum

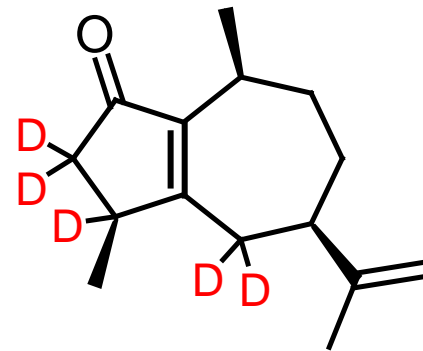
GC



# (-)-Rotundone identification



- **Identity:**  
confirmed with reference compound (Symrise)  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR, ORD  
GC-MS-O, coinjections
- **Quantification:**  
multidimensional GC-MS & stable isotope  
dilution analysis; LOQ 0.5 ng/L



➤ *Rotundone is the principal aroma impact compound for pepper aroma in grapes and wine.*



# How potent is rotundone?



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**8 ng/L in water**



**16 ng/L in red wine**

***20 to 25% of the panellists were anosmic to rotundone***

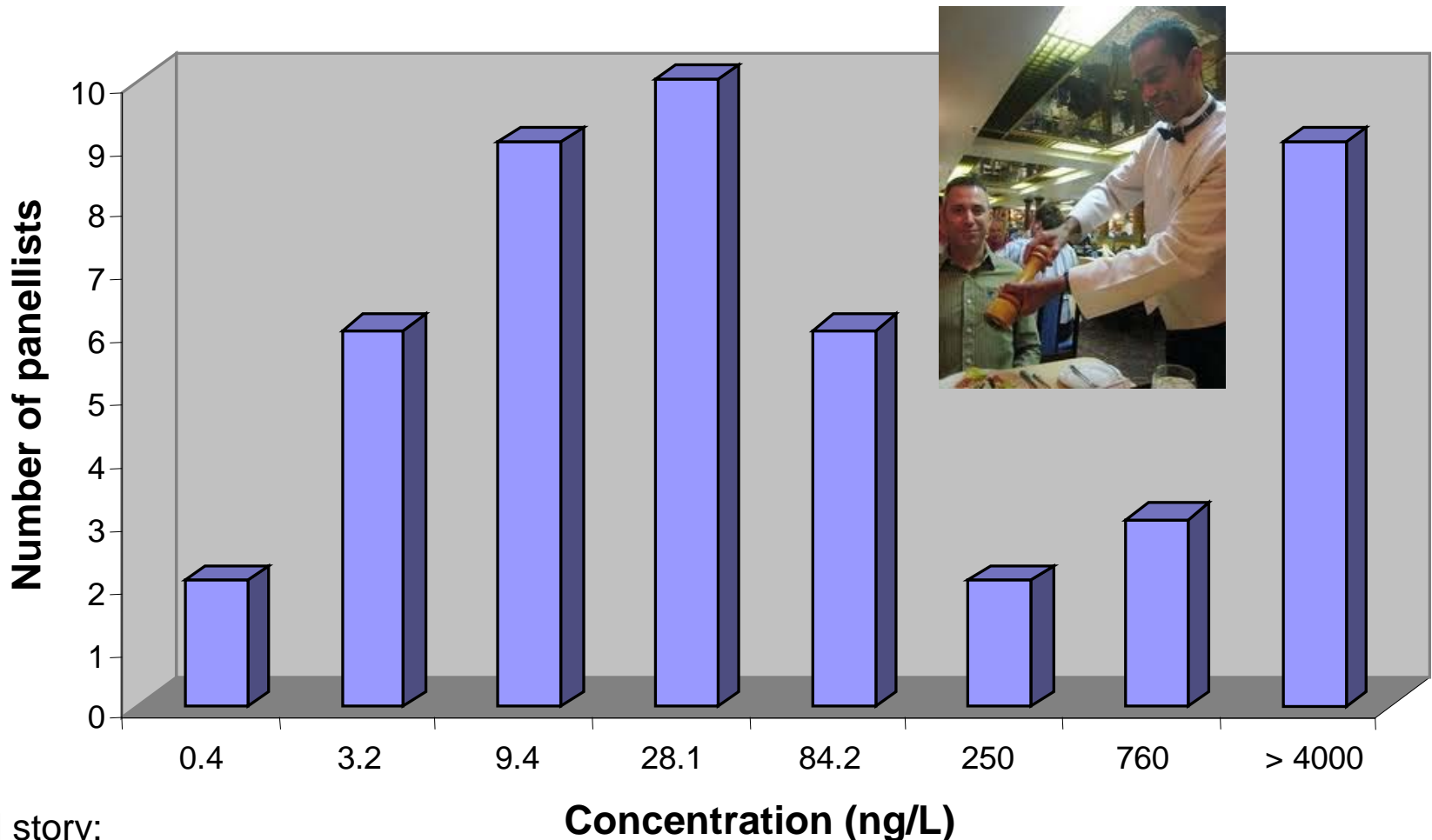




# How potent is Rotundone?

aroma threshold in red wine is 16 ng/L

~ 20% of panellists could not smell rotundone at the highest level tested



The full story:



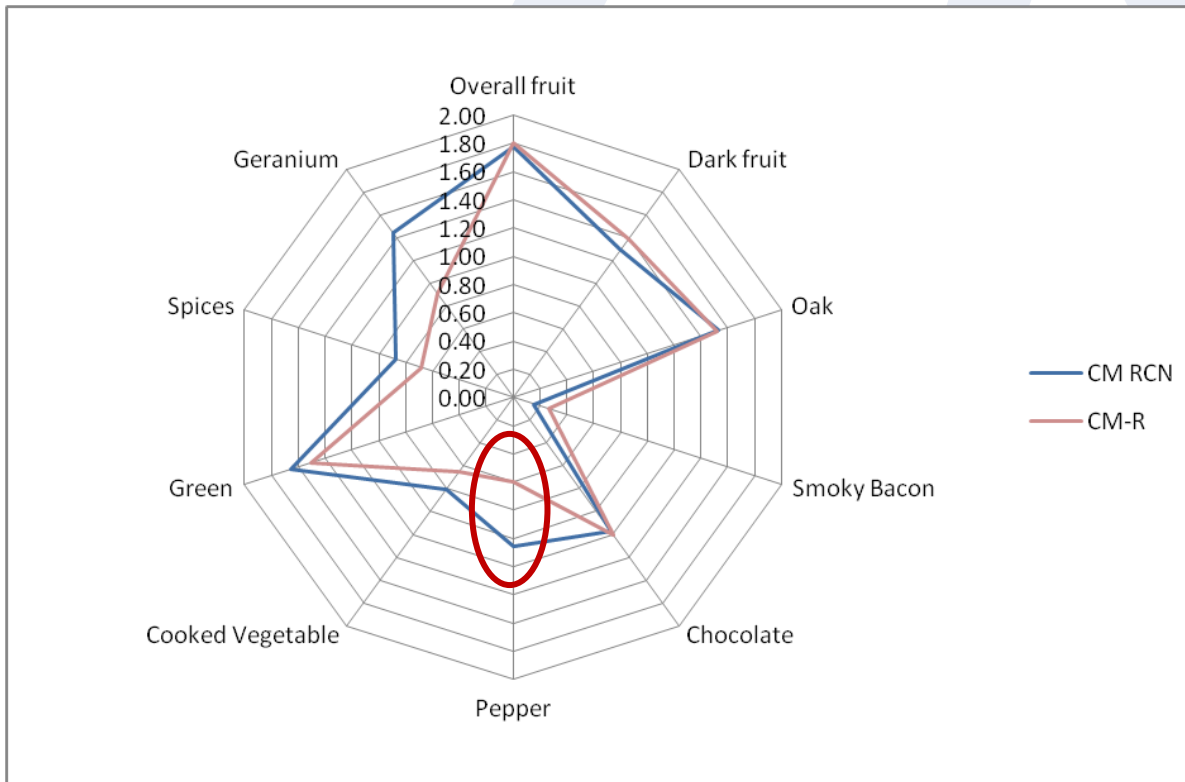
# How potent is Rotundone?

## reconstitution model of Shiraz flavour

### Cool climate Shiraz reconstitution model

42 volatiles; ethanol, water and tartaric acid; fructose, glucose, glycerol, succinic acid, malic acid, lactic acid, NaCl, K<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

**38 ng/L** ⇔ **0 ng/L rotundone** (aroma threshold in red wine 16 ng/L)

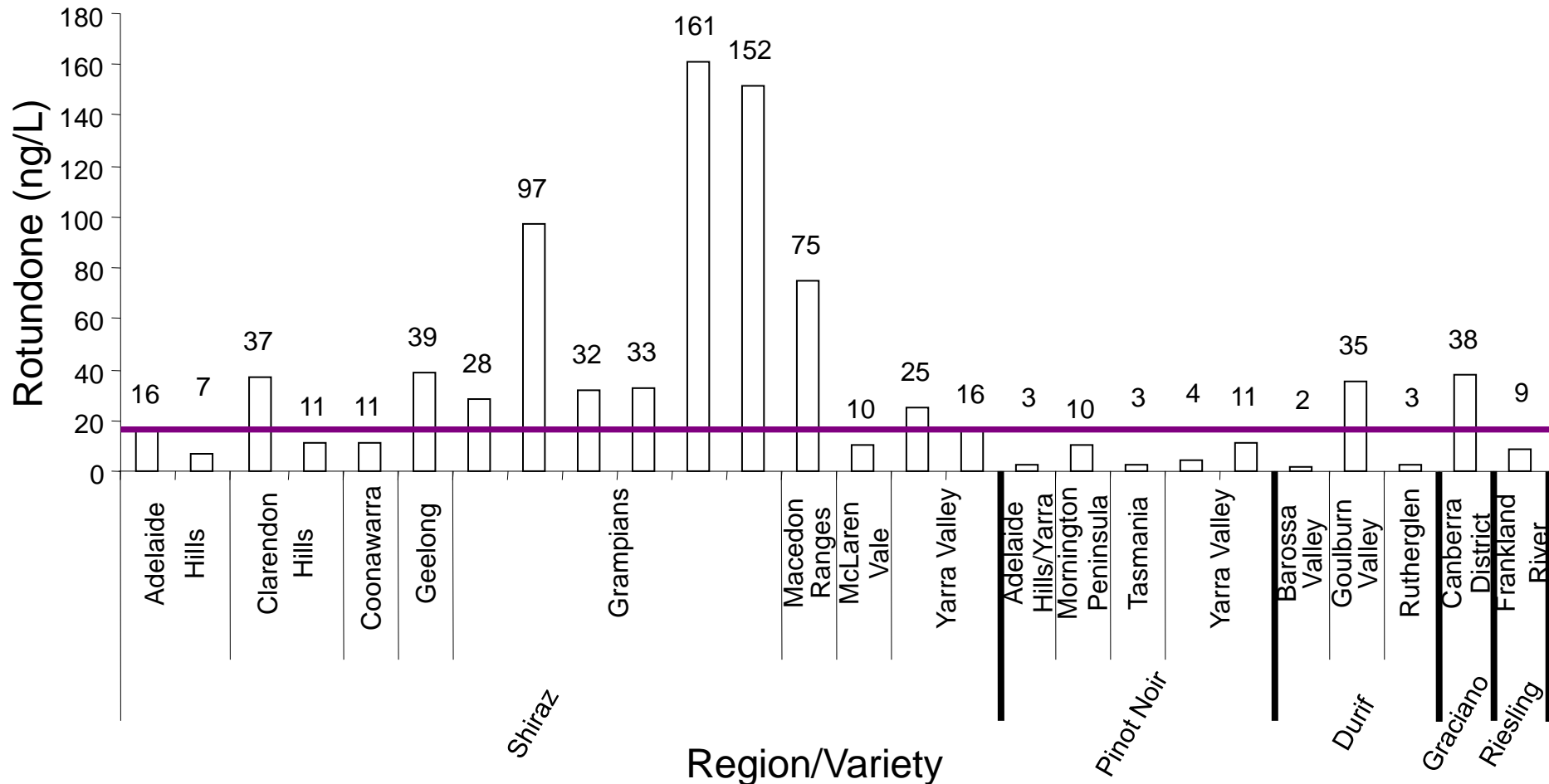


# Rotundone in Australian wines



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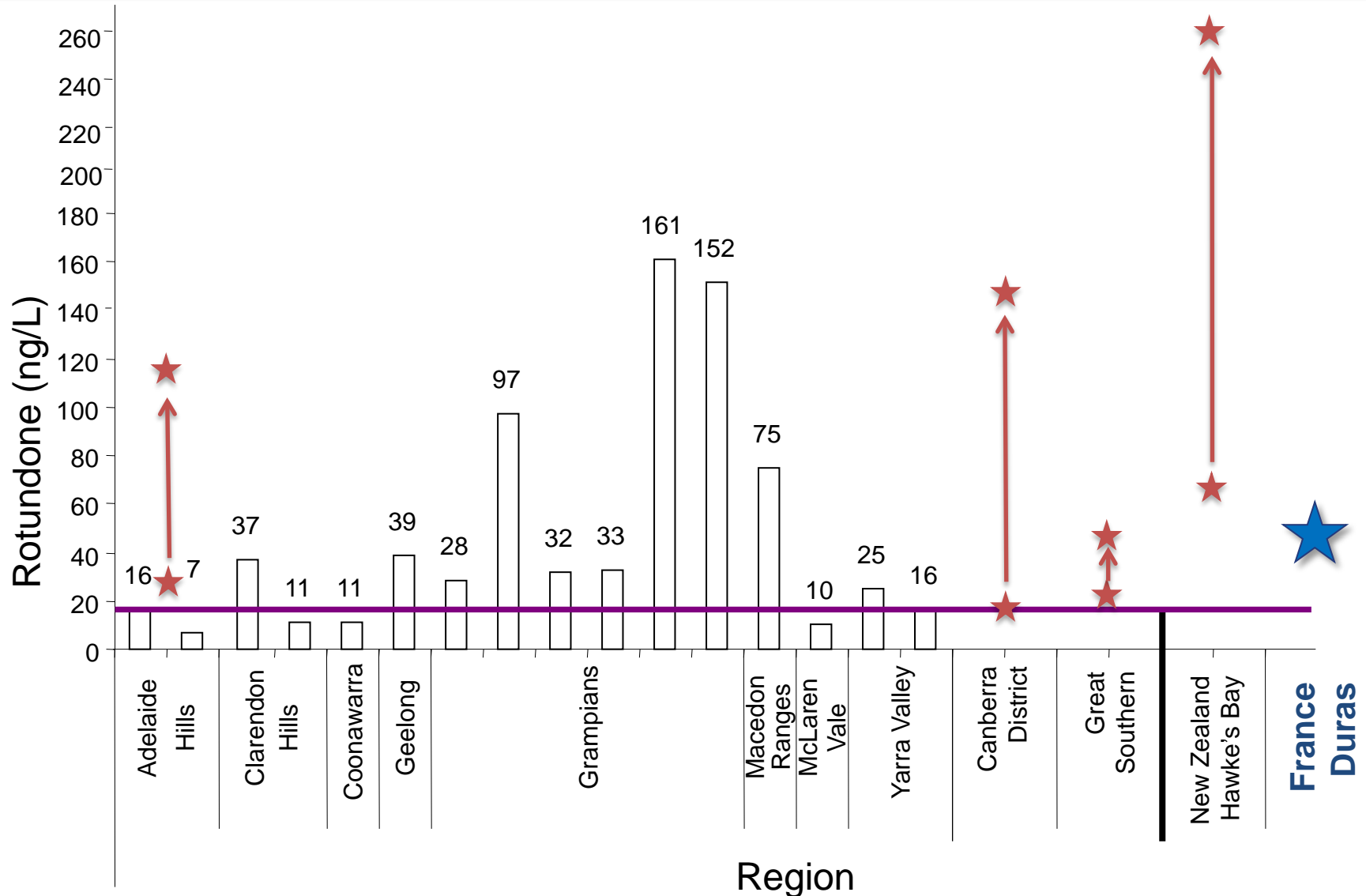
- We can now start to look at what influences rotundone levels
- A large survey of commercial wines was undertaken to guide us



# Rotundone in commercially available Shiraz wines; Duras from France



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# Rotundone in Duras, Graciano, Gamay & Pineau d'Auris wine

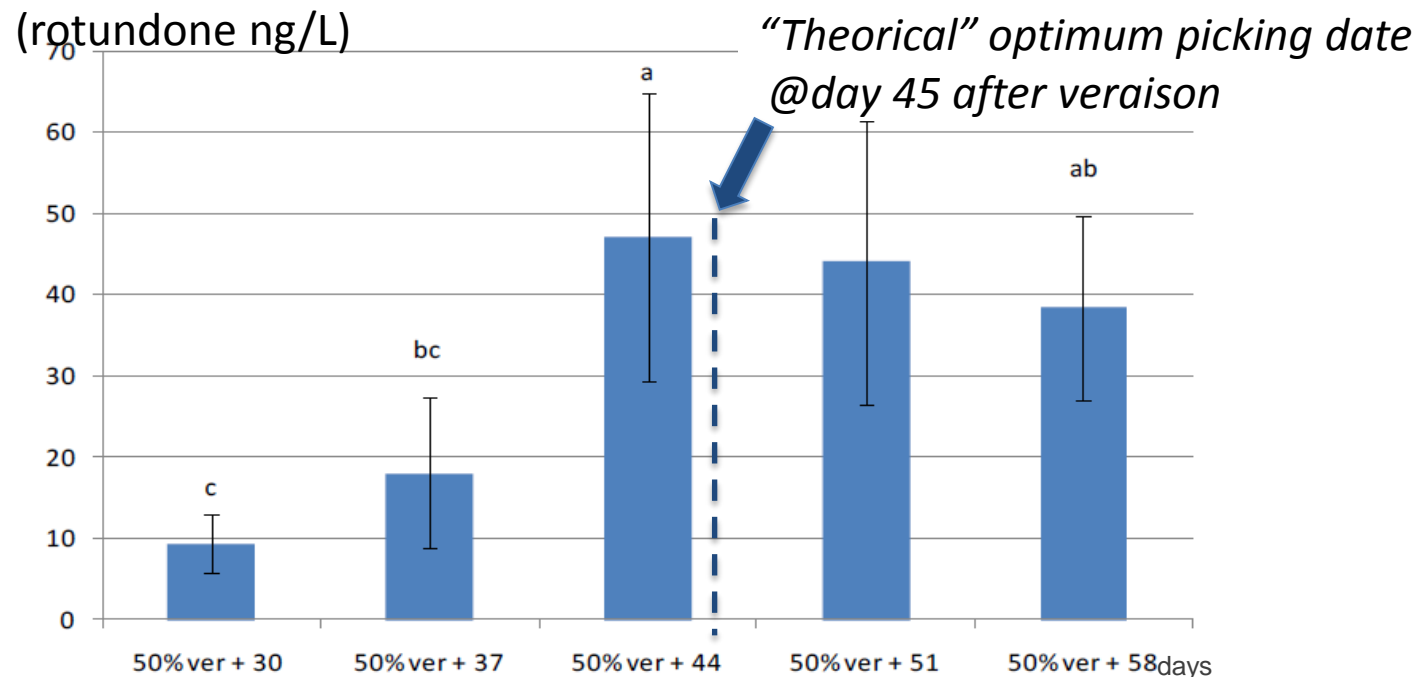
Olivier Geffroy, IFV Sud-Ouest



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2011 Graciano	17.5 & 11.3 ng/L
2011 Gamay	14.7 & 11.9 ng/L
2011 Pineau d'Aunis	65.6 & 200.0 ng/L
2012 Duras	26 ng/L

## 2011 Duras microvinification at 5 levels of maturity

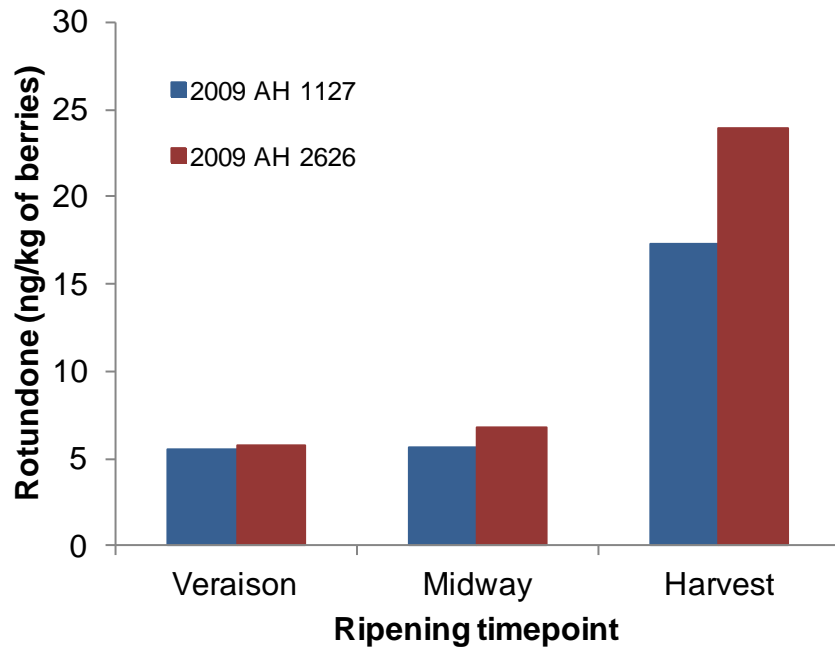


# Where and when does rotundone turn up in the berry?

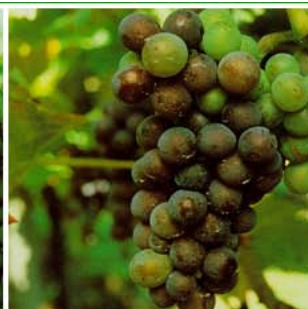
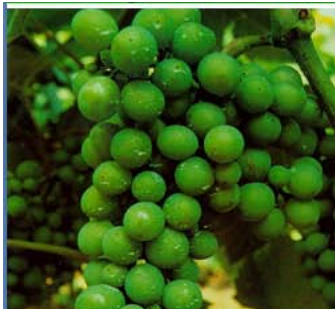
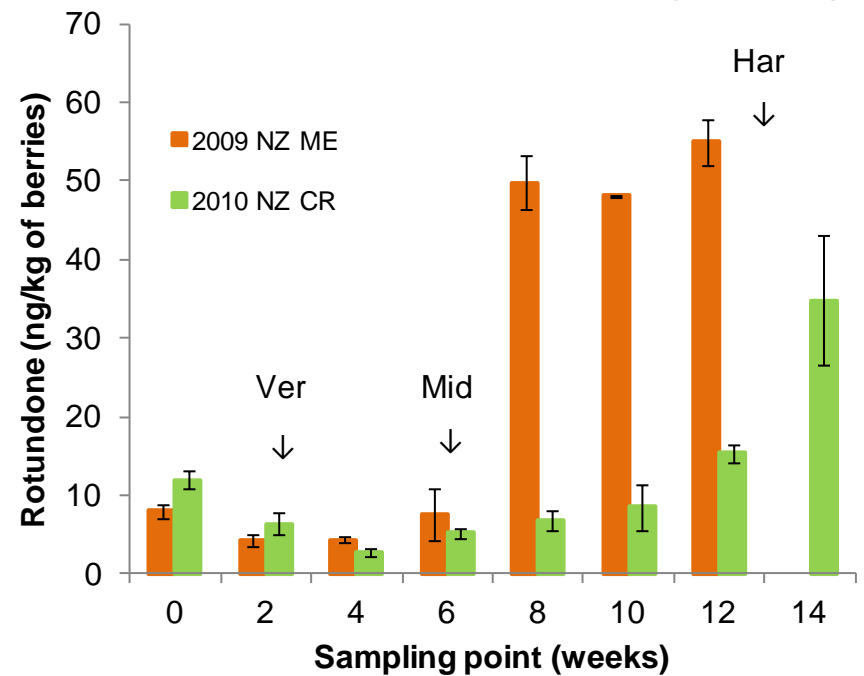


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### Adelaide Hills Shiraz berries during ripening



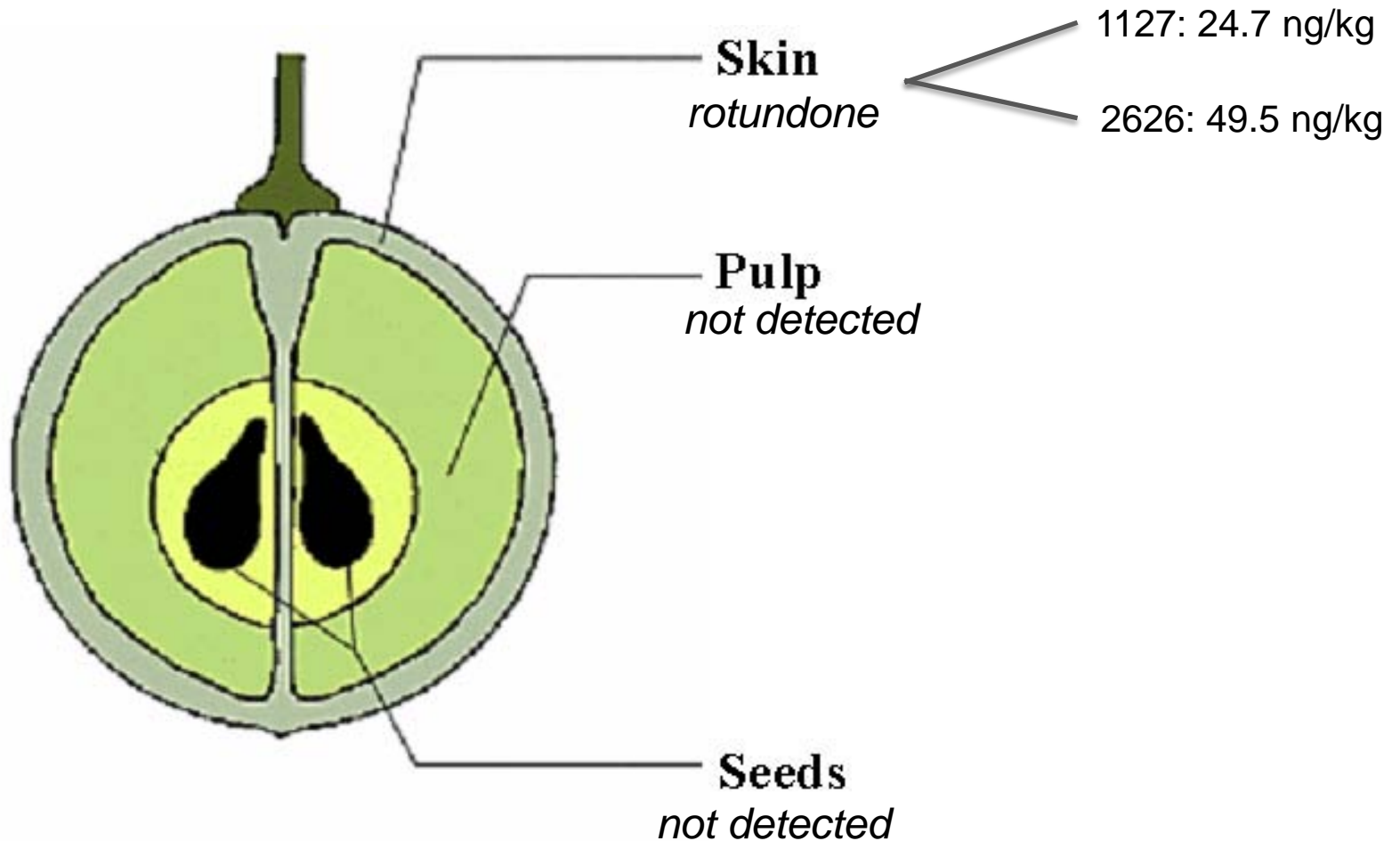
### NZ Hawke's Bay Syrah berries during ripening



# Where and when does rotundone turn up in the berry?

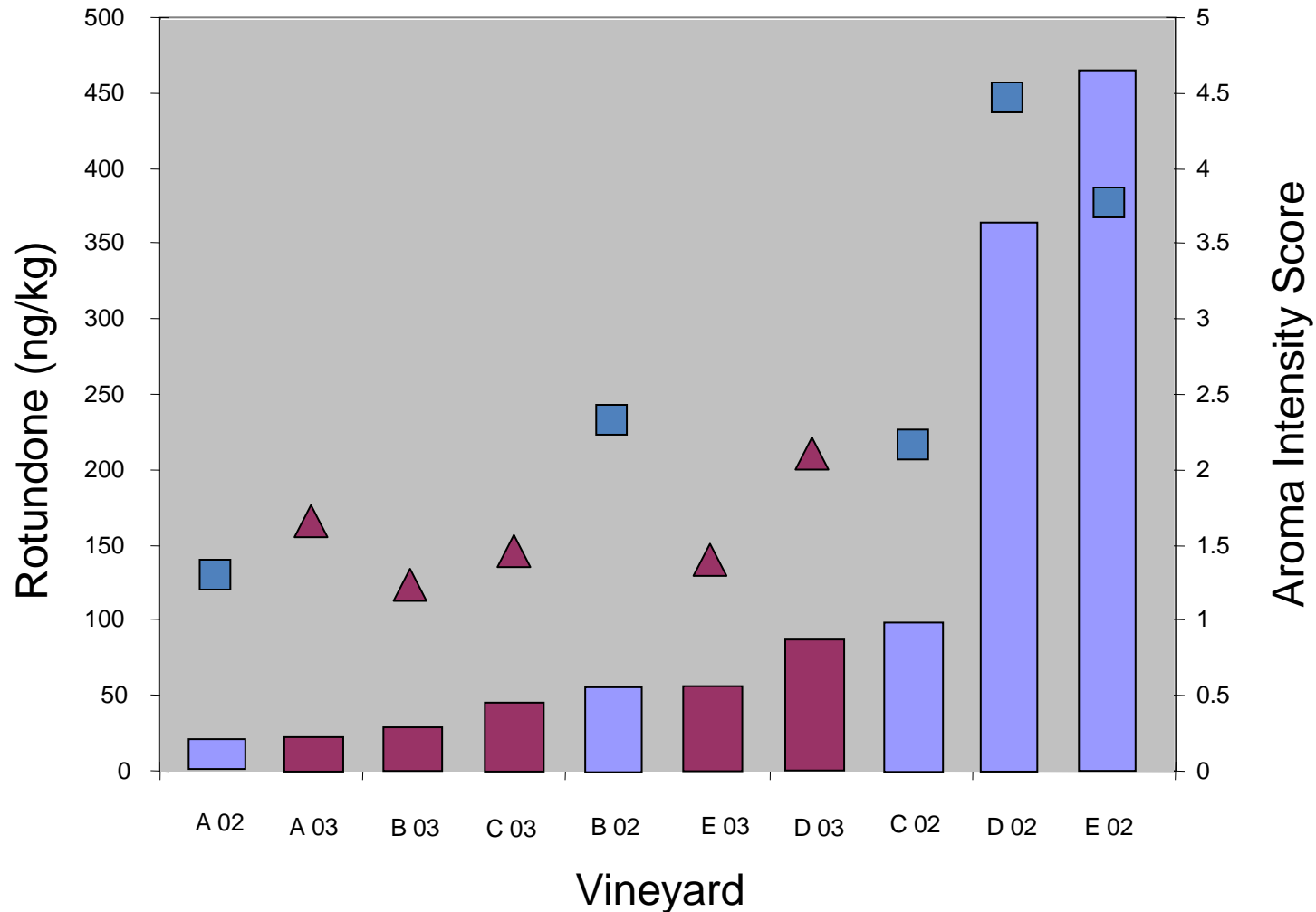


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# Concentration of rotundone and aroma of Australian Shiraz grapes



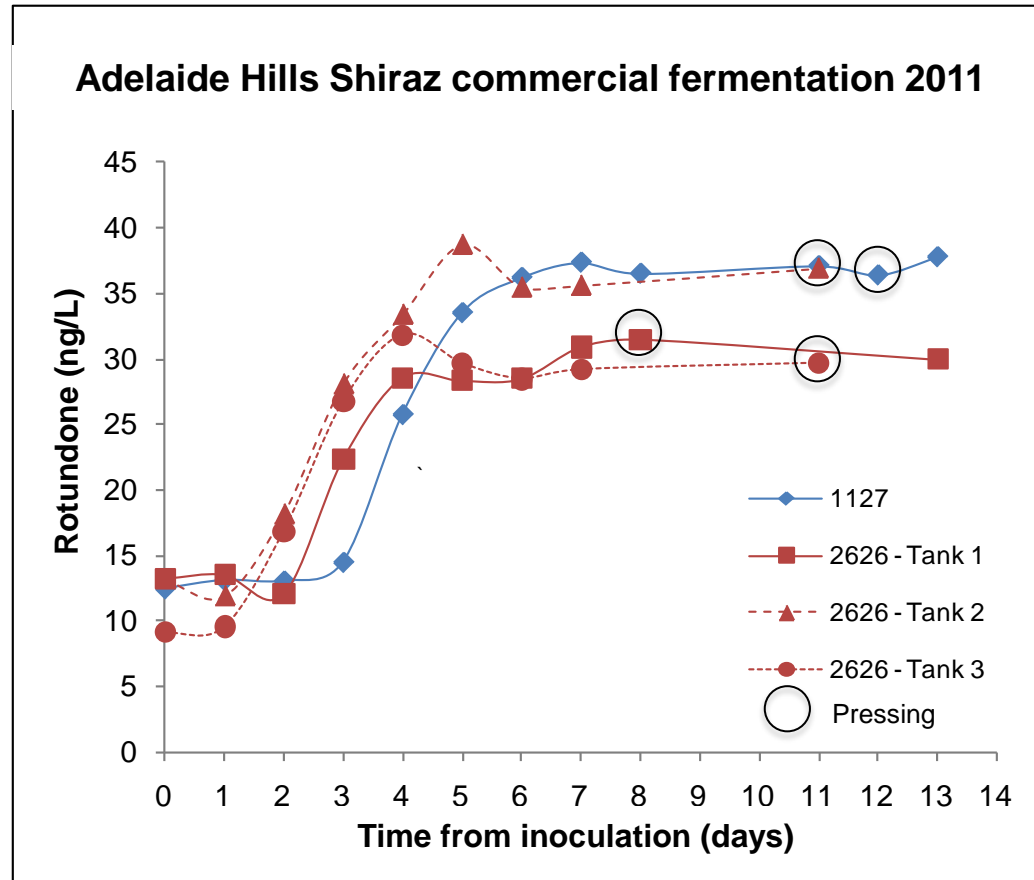
5 vineyards  
over 2 vintages

- 2003
- 2002
- Aroma 2003
- Aroma 2002

# Rotundone extraction from berries during winemaking



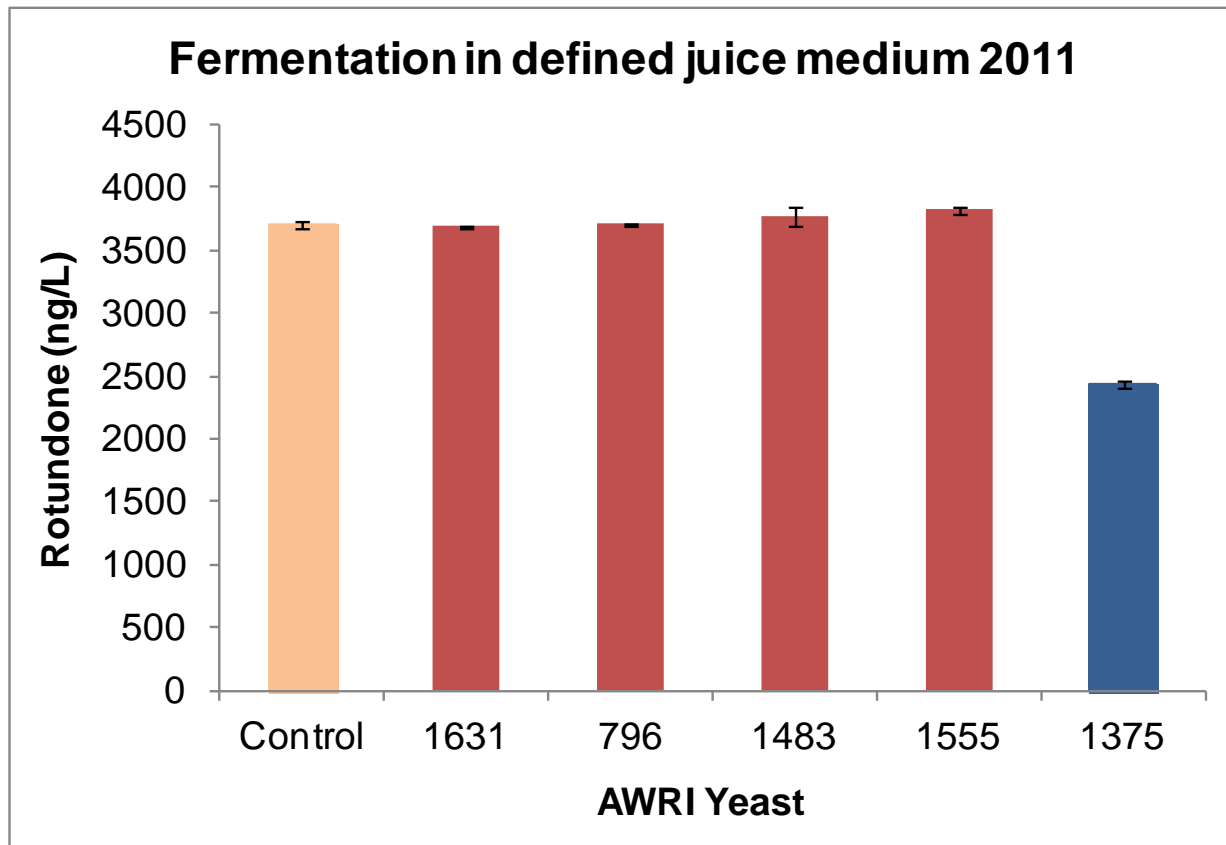
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# Can yeast affect rotundone levels during fermentation?



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No yeast



*S. cerevisiae*

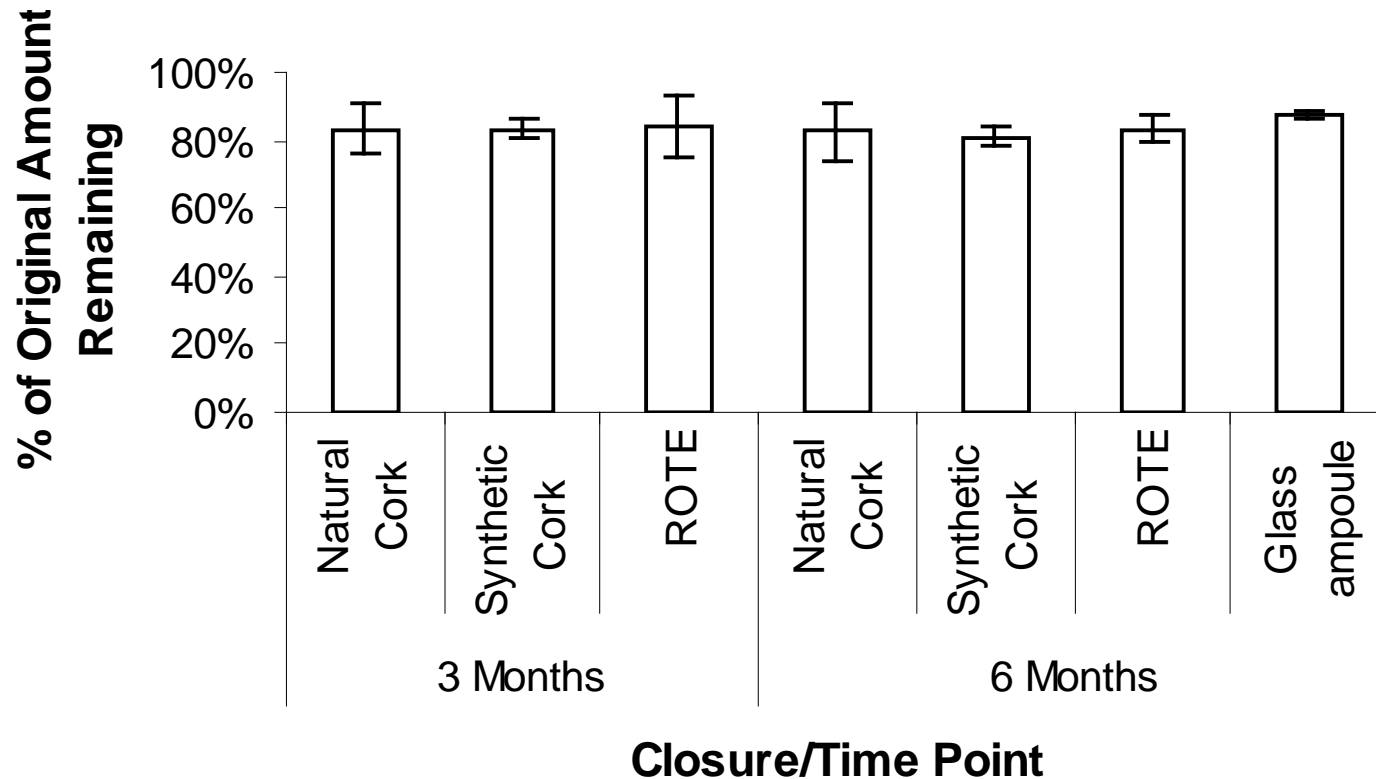


*S. bayanus*



# Stability and scalping of rotundone: no obvious effects

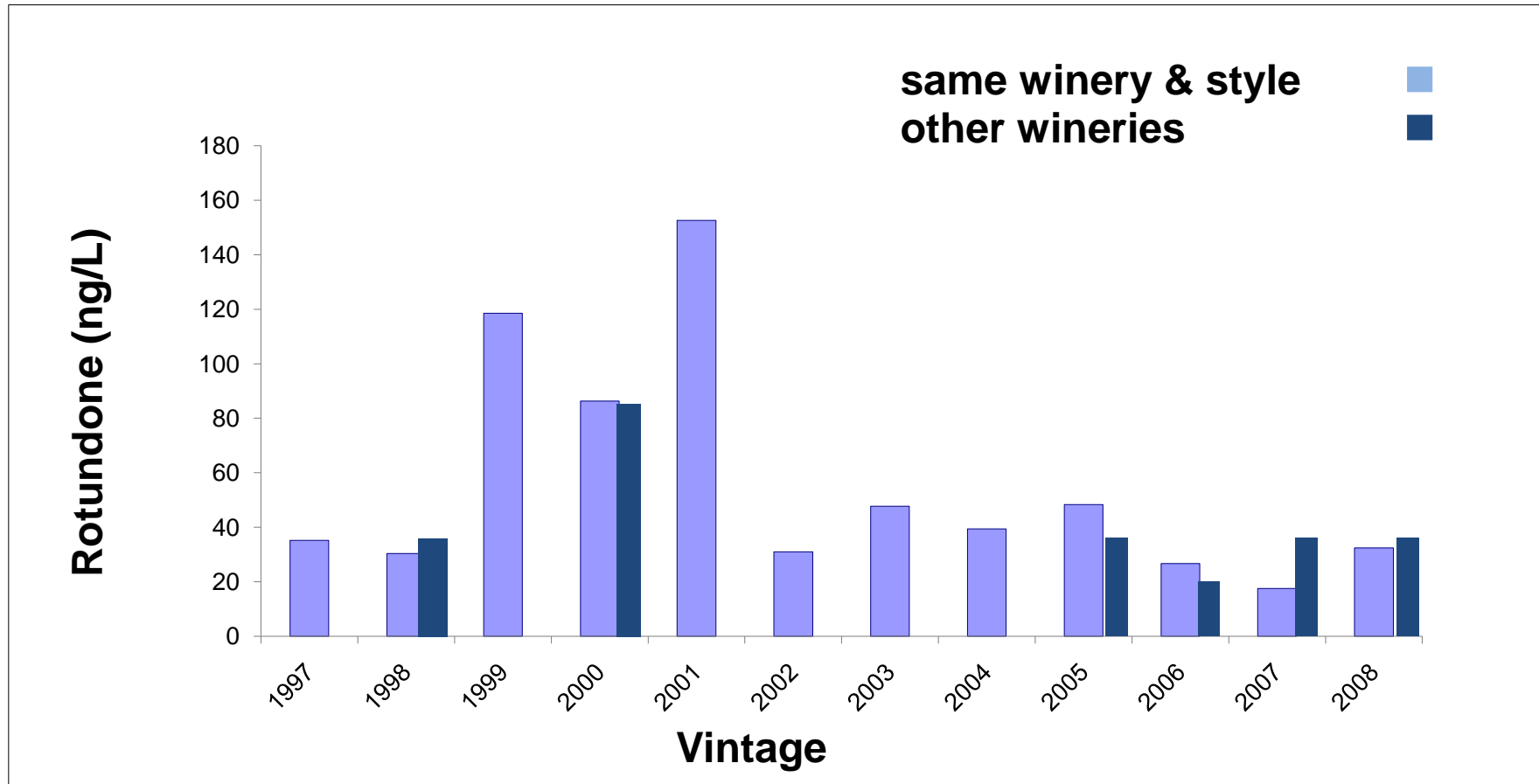
## Scalping of Rotundone by Closures



# Variability across the vineyard & vintages: Shiraz/Viognier wines - Canberra District



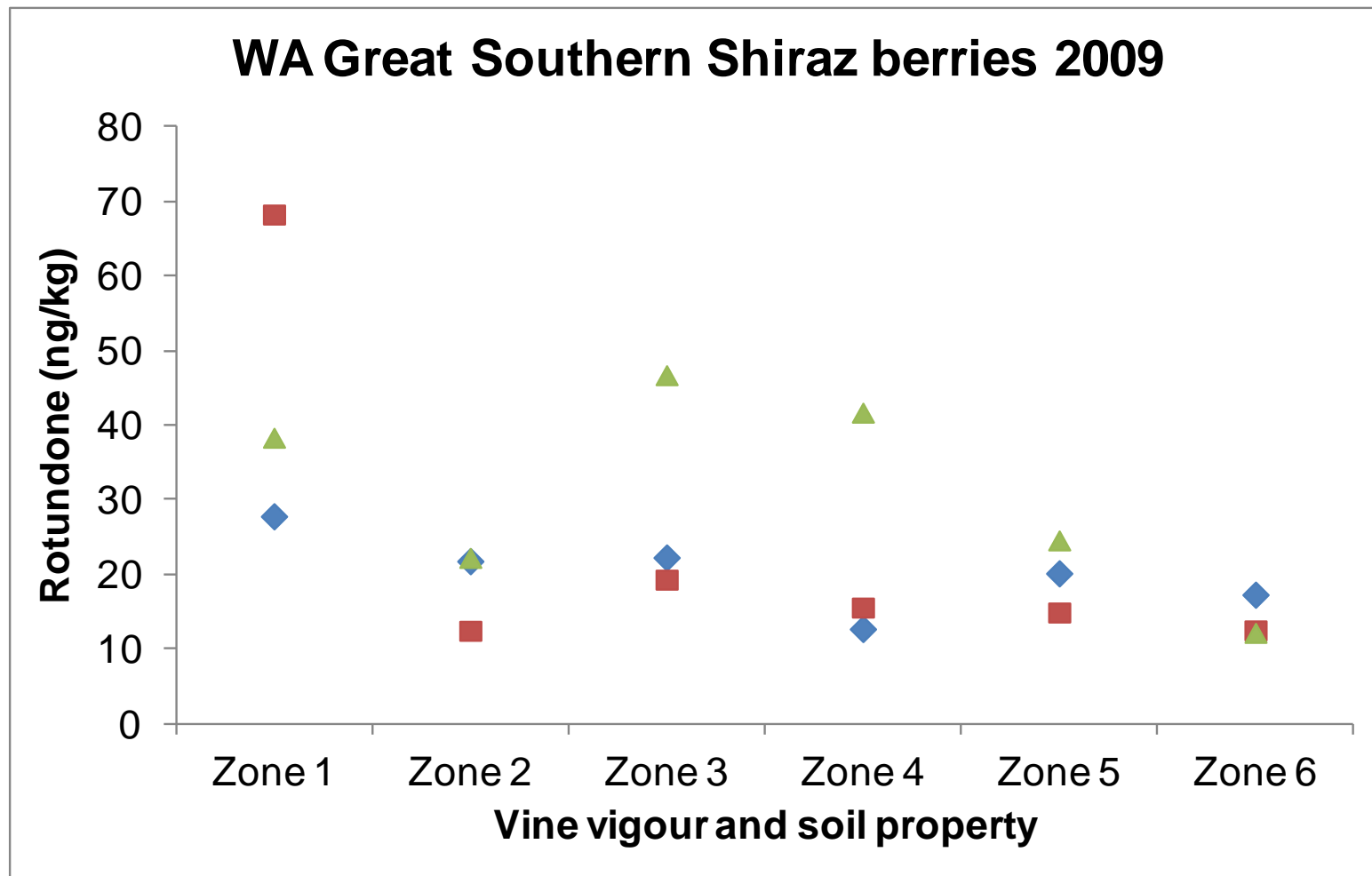
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# Variability across the vineyard & vintages: Great Southern



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# Rotundone variability across a vineyard: 2012 Grampians Shiraz

Nathan Scarlett, Mount Langi; Rob Bramley, CSIRO; Pangzhen Zhang, University of Melbourne



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rotundone in grapes  
74 – 1081 ng/kg  
distinct spatial pattern

uniform TSS, TA, colour





# Summary I: rotundone - the key to peppery aromas in Duras and Syrah wine

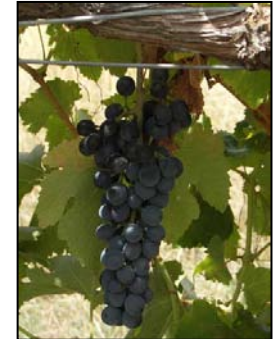


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- vineyard **site & vintage** key to rotundone in grapes & wine
- significant **vine-to-vine variation** in uniform sites
- **Shiraz - viticulture & rotundone concentration:**
  - ✓ ripening
  - clone, vigour, water stress, leaf removal & crop load (Gerard Logan, Uni Auckland)
- **Duras - viticulture & rotundone concentration in wine:**
  - ✓ Ripening

**2012 – IFV trials (Olivier Geffroy):**

  - ✓ irri / elicitor / crop thinning      => 29-36 ng/L
  - ✓ control      => 27 ng/L
  - ✓ leaf removal      => 12 ng/L

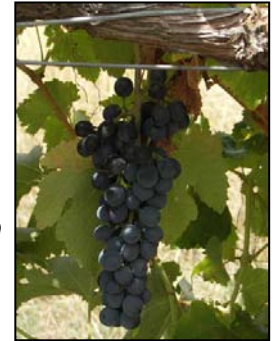


# Summary II: rotundone - the key to peppery aromas in Duras and Syrah wine



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- Limited options to lower rotundone & pepper aroma in the winery:
  - yeast?
  - skin contact and cap extraction?  
no effect: *machine picked, crushed, de-stemmed & open fermentation*  
*vs hand picked & whole bunch open fermentation*



- How can we manage our vineyards to increase or decrease rotundone in fruit, or to reduce variability?



- Why does rotundone occur in ***Shiraz*** and ***Duras*** compared to other cultivars, ie role of ***grapevine genome?***  
what are the ***environmental factors*** that cause high rotundone in some grapevines & some seasons?

- What ***biological function*** does rotundone serve?



# Acknowledgements



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## Australian wine industry collaborators

- Nathan Scarlett, Dan Buckle, Damien Sheehan (Mt Langi Ghiran)
- Darryl Catlin, Winemaker, and the winery and laboratory staff of Shaw and Smith Wines
- Frank van de Loo, Mt Majura Vineyard
- Jim Lumbers, Lerida Estate
- Dr Ayalsew Zerihun, Curtin University of Technology
- Allen and Andrea Hart (Fosters Group), Inca Pearce, Martin Wirper (Orlando Wyndham), Sue Hodder (Wynns Coonawarra Estate)

## Symrise, Germany

## AWRI

- Tracey Siebert, Mango Parker & Claudia Wood
- Flavour & Sensory Teams (past & present members)
- Radka Kolouchova

## New Zealand collaborators

- Gerard Logan,  
The University of Auckland & EIT Hawke's Bay  
Craggy Range Vineyards, Mission Estate Wines

## France

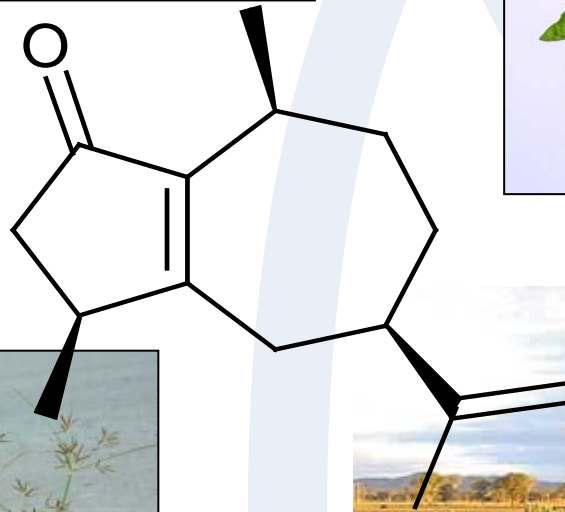
- IFV Sud-Ouest  
Olivier Geffroy



The AWRI, a member of the Wine Innovation Cluster in Adelaide, research is financially supported by Australia's grape growers and winemakers through their investment body the Grape and Wine Research and Development Corporation, with matching funds from the Australian Government.



# Thank you!





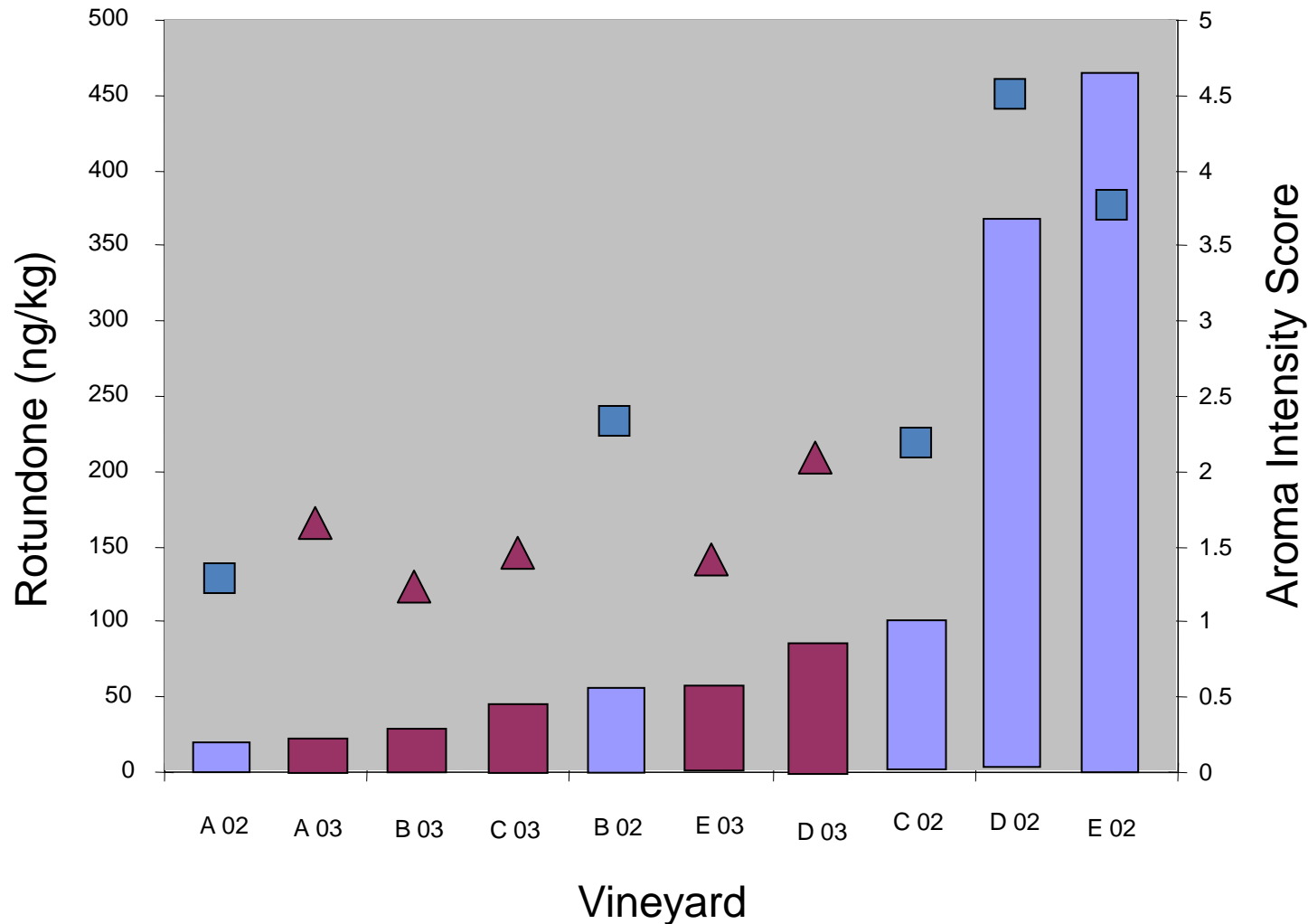
**Stand by**



# Concentration of rotundone and aroma of Australian Shiraz grapes



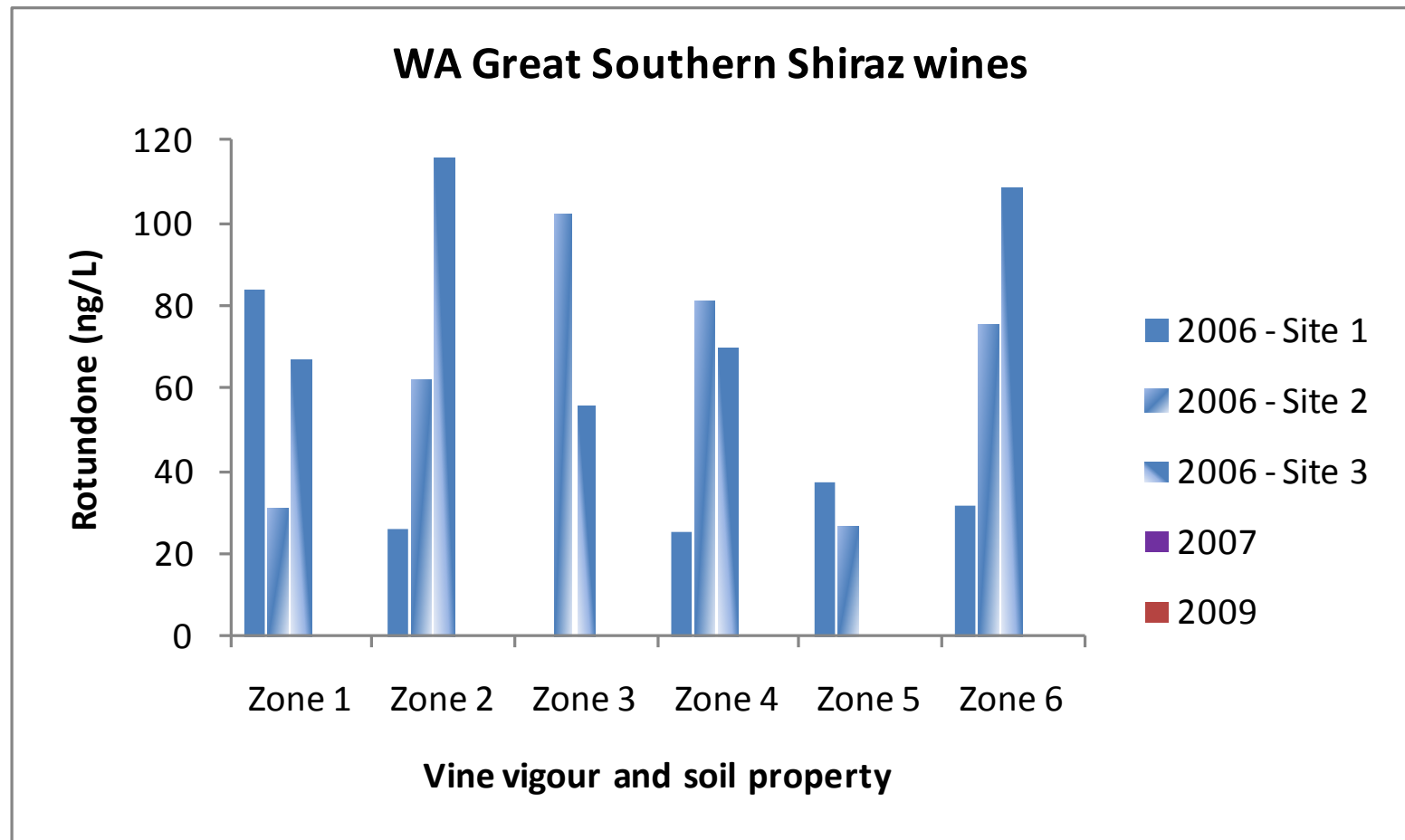
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# Variability across the vineyard & vintages: Shiraz wine from Great Southern, WA



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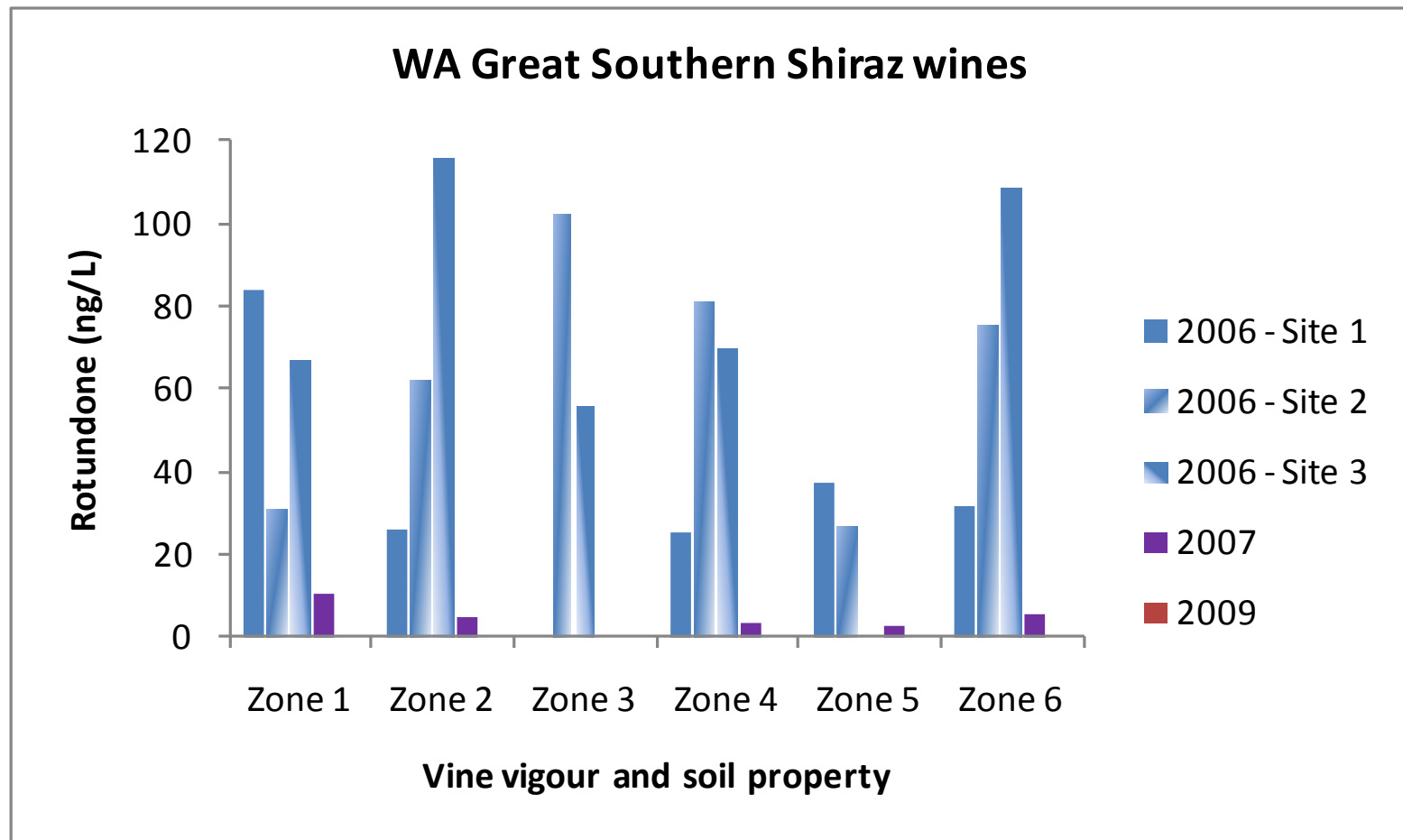




# Variability across the vineyard & vintages: Great Southern



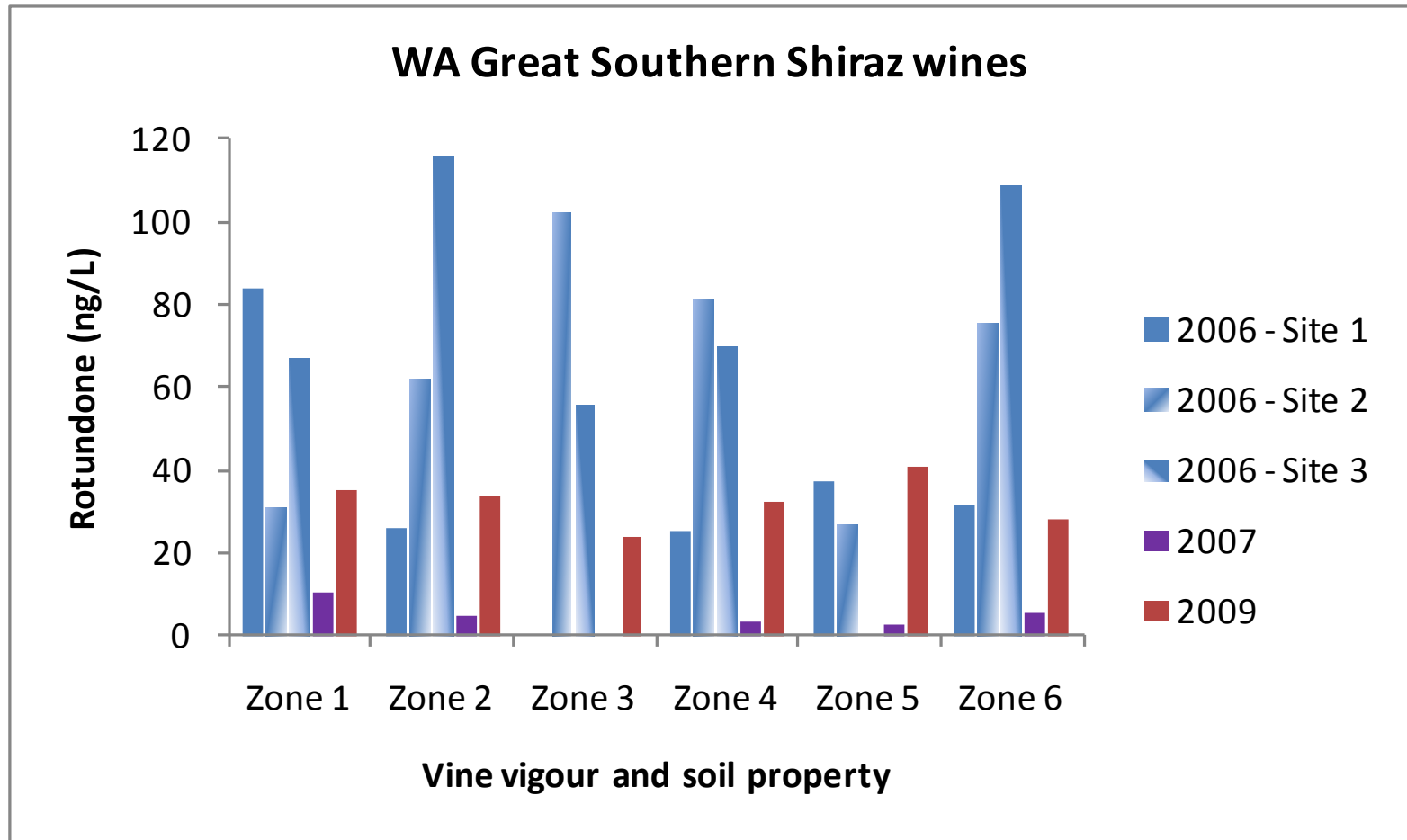
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# Variability across the vineyard & vintages: Great Southern



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# A few facts about Syrah / Shiraz

- **ancient variety**

Mondeuse blanche x Dureza  
Northern Rhone Valley, 100AD

- **1980s only 10.000 ha**

- **140,000 ha in 2004/2005**

one of world's top six grape varieties  
along with Merlot, Cabernet Sauvignon, Pinot Noir,  
Sauvignon Blanc and Chardonnay



- **World styles**

France:

Côte-Rôtie, Hermitage

South Africa:

Boekenhoutskloof Syrah

New Zealand:

Craggy Range Le Sol Syrah

Chile:

Matetic Vineyards EQ Syrah

Washington, USA:

Gramercy Cellars "John Lewis"

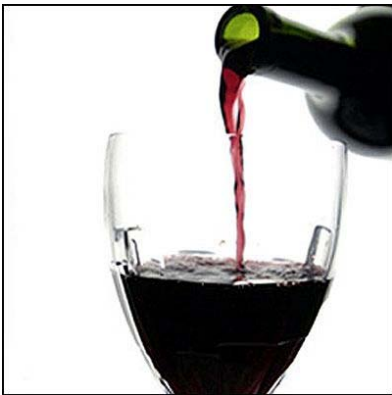
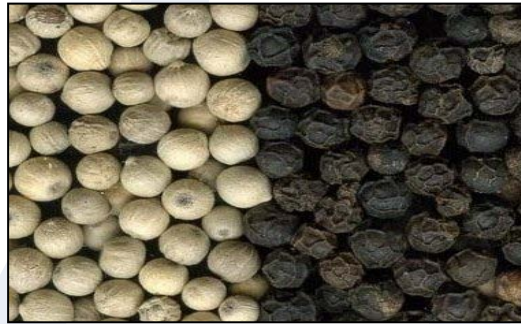
Walla Walla Valley Syrah

California, USA:

Saintsbury Rodgers Creek Carneros Syrah

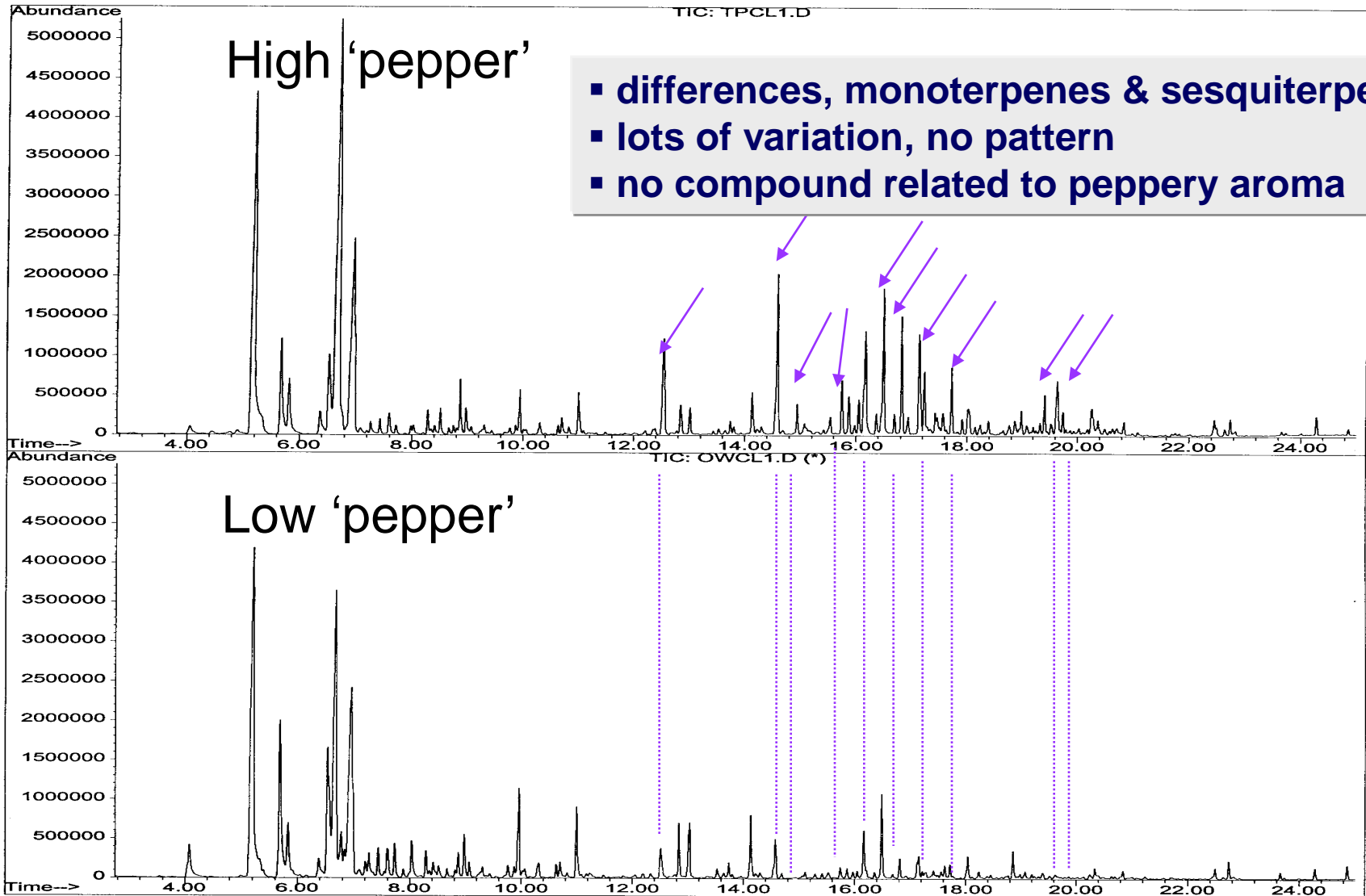


# Rotundone is widely found in plants and plant products





# Comparison of grape volatiles by GCMS





# The search for 'pepper markers': untargeted metabolomics experiment

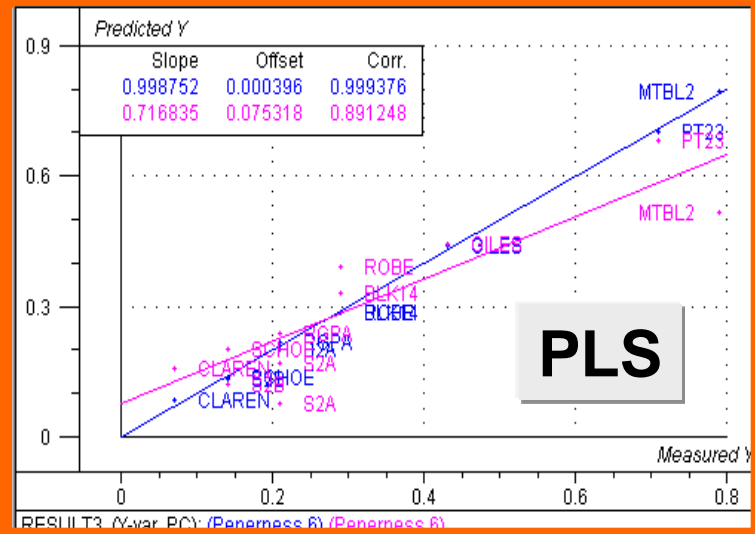
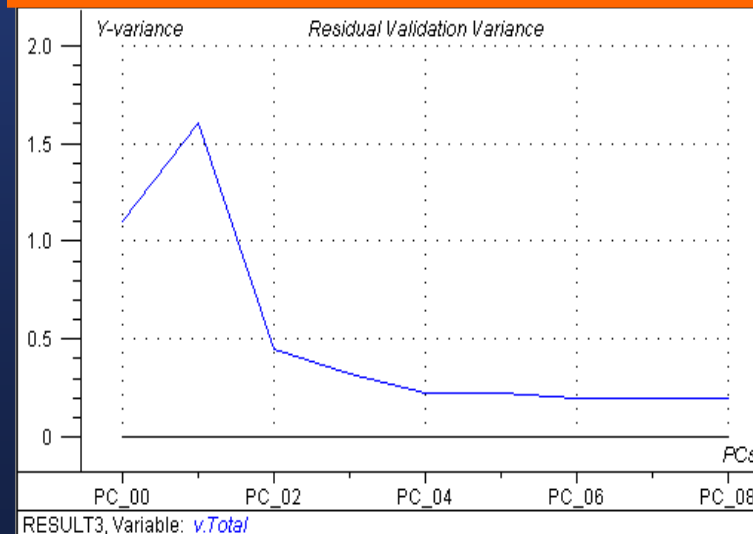
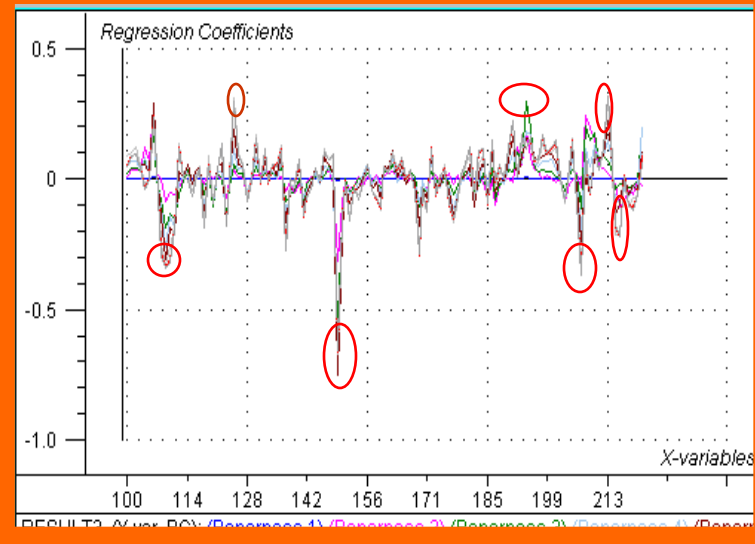
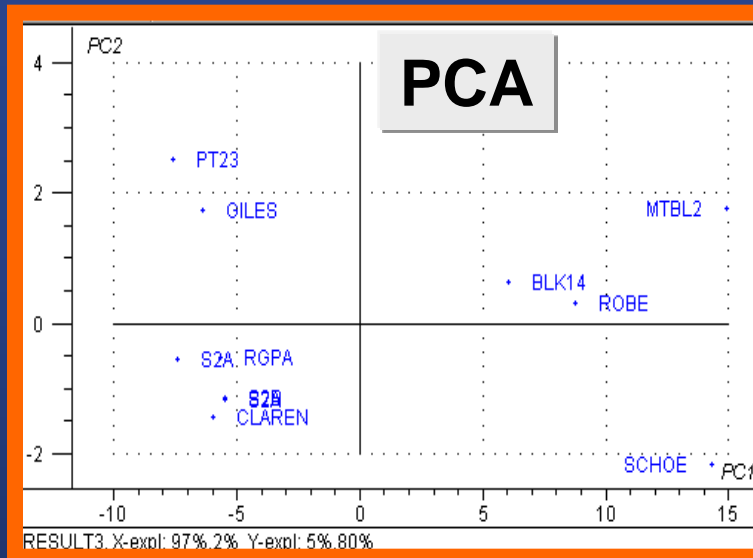
## THE IDEA:

- compare quantitative sensory data (n=22)  
*with*  
comprehensive volatile profiles  
(entire headspace-GC-MS datasets, 12000 mass spectra/sample)
- ❑ to look for **correlations** among data sets
- ❑ to identify **marker substances** in peppery grape samples
- ❑ to identify **key peppery aroma** compounds

# The search for 'pepper markers': untargeted metabolomics experiment



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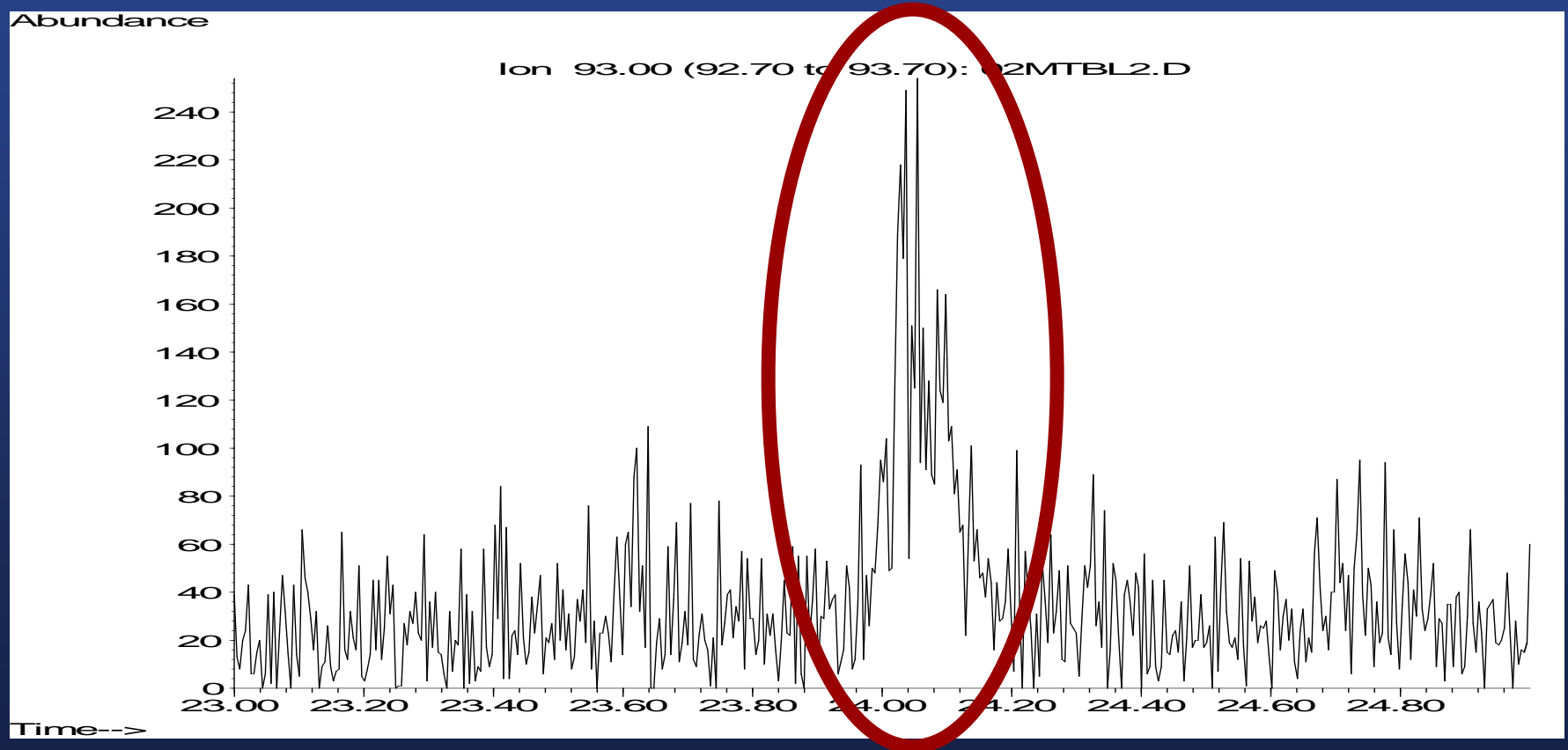


mass spec versus pepper rating

# GC-MS data allow prediction of 'pepper' aroma new biomarker - sesquiterpene ylangene



AWRI

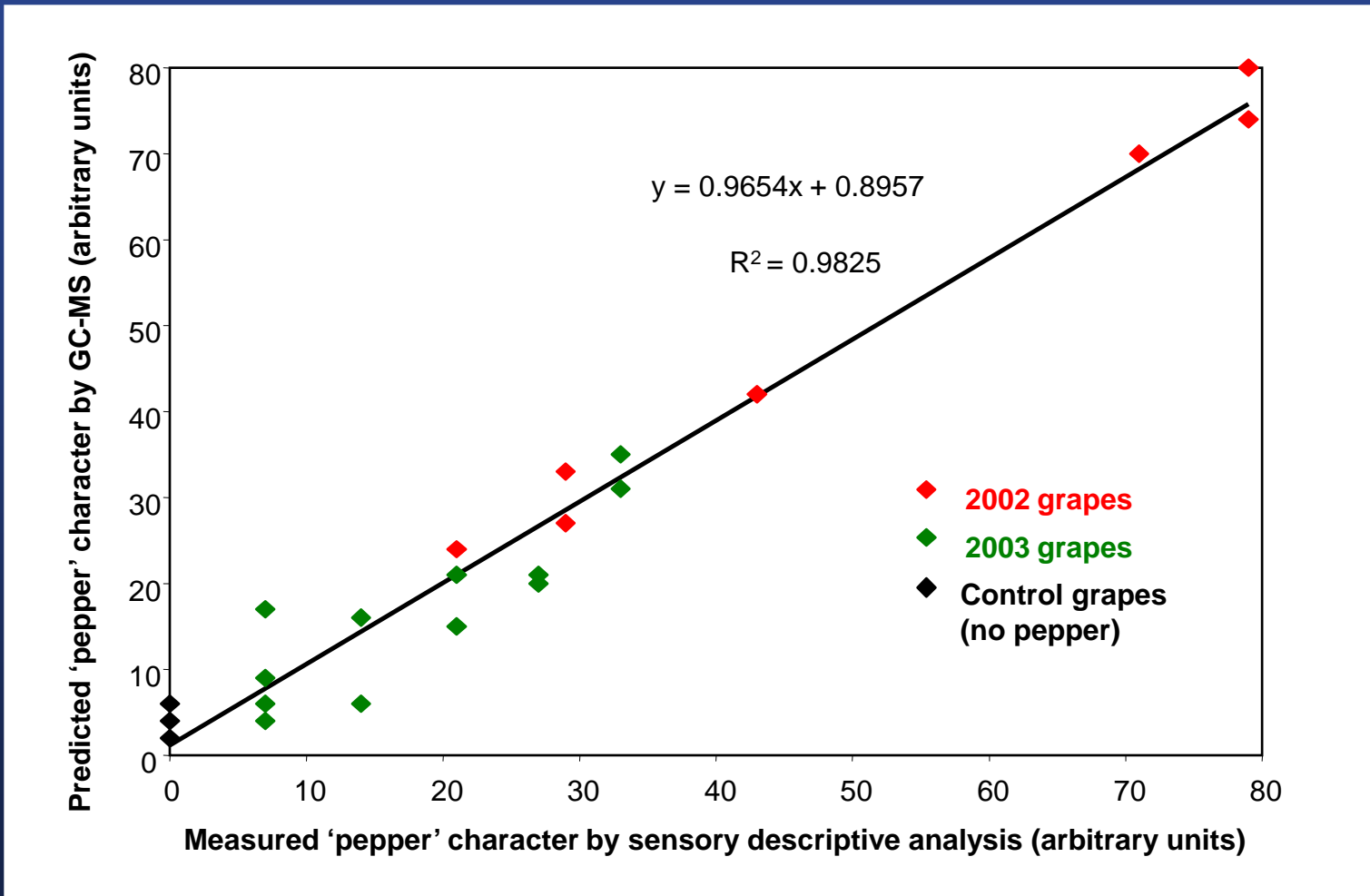




# GC-MS data allow prediction of 'pepper' aroma



AWRI

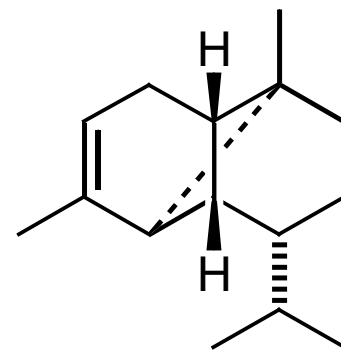




# The search for 'pepper markers': untargeted metabolomics experiment

- identified  **$\alpha$ -ylangene** (a tricyclic sesquiterpene) as a new compound in grapes
- **quantified**  $\alpha$ -ylangene with  $\alpha$ -copaene as I.S.
- good correlation of  $\alpha$ -ylangene with 'pepper'

➤ *marker compound:*  
 **$\alpha$ -ylangene has no peppery aroma**



# Identification of peppery grape volatiles: GC-MS-Sniff in action



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# How potent is Rotundone?

aroma threshold in red wine is 16 ng/L

1 drop of rotundone is enough to make an Olympic size swimming pool smell peppery!



1 g of rotundone is enough to make the entire Australian annual crush smell peppery!

