

LES THIOLS VARIETAUX:

Point sur les voies de biogenèse et incidence des itinéraires de production et d'élaboration



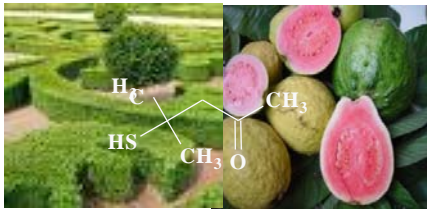
RÉMI SCHNEIDER
IFV Rhône Méditerranée



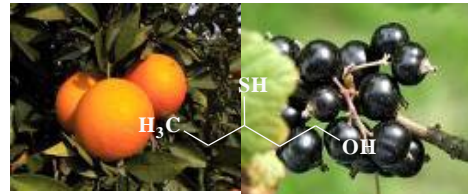


Contribution of varietal thiols to wine aroma

- 3 varietal thiols have been identified as key aroma compounds



4-mercapto-4-methylpentan-2-one
0,8 ng/L



3-mercaptohexan-1-ol
60 ng/L

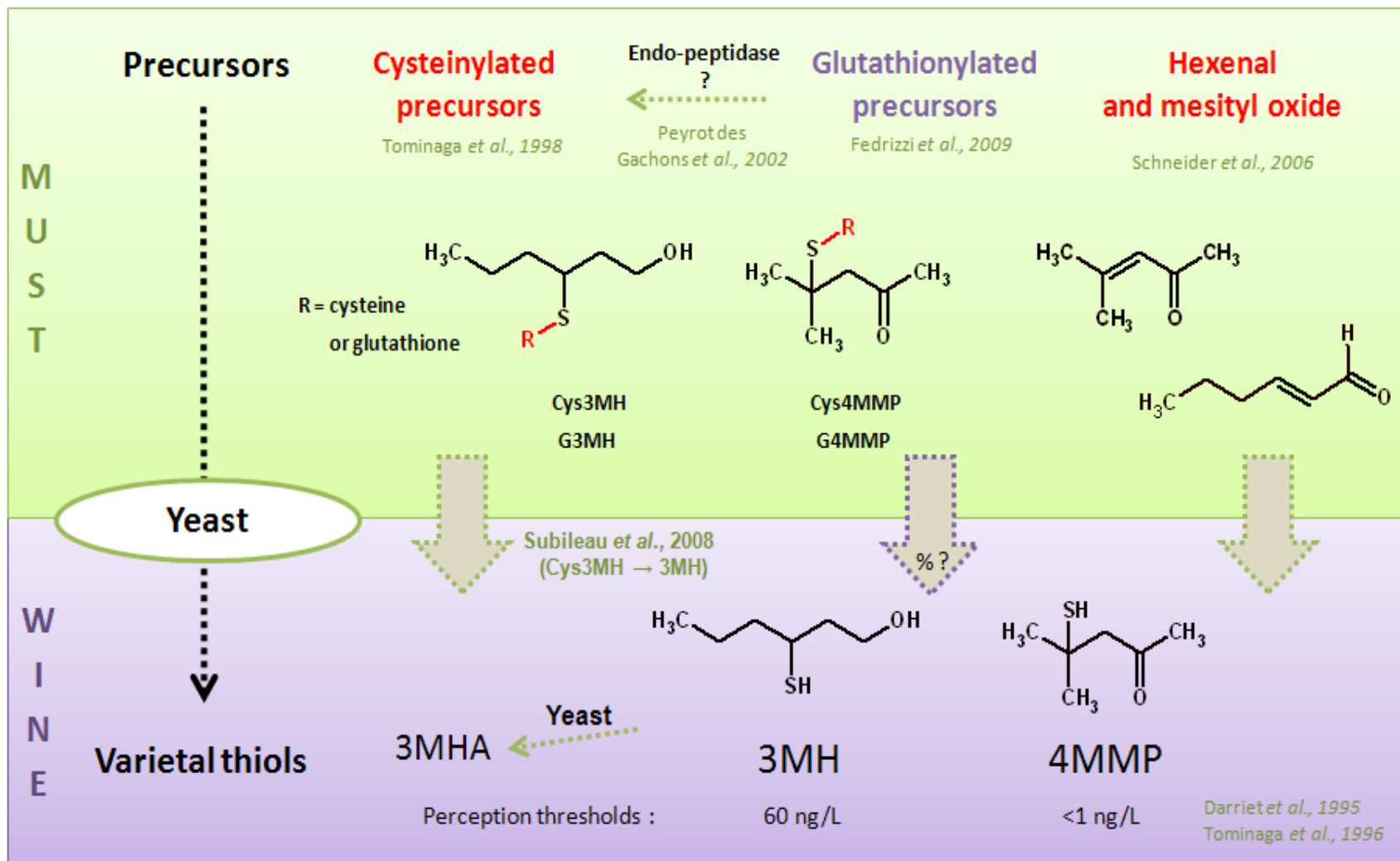


3-mercaptohexyl acetate
4 ng/L

- Occurrence in several white, rosé and some red wines :
 - ✓ Sauvignon, Colombard, Petite Arvine, Manseng, Muscadet,...
 - ✓ Grenache, Syrah, Merlot and Cabernet,



State of the art : thiols biogenesis in wine



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Levels of thiol precursors in grapes ($\mu\text{g/L}$)

refs	variety	3MH precursors		4MMP precursors	
		Cys	G	Cys	G
Dubourdiou <i>and coll.</i> , 2000	SB	20 - 100	-	0.2 - 2.5	-
Frey <i>and coll.</i> , 2008	Petite Arvine	30 - 85	-	-	-
Schneider <i>and coll.</i> , 2008	SB	11-35	-	-	-
Dubourdiou <i>and coll.</i> , 2010	SB et Semillon	4-80^(a) 520 – 2000^(b)	- -	- -	- -
Jeffery <i>and coll.</i> , 2010	Various	10 - 55	140 - 640	-	-
Suzuki <i>and coll.</i> , 2010	Koshu	22 - 50	6 - 18	-	-
Schneider <i>and coll.</i> , 2010	Various	6 - 130	1 - 10	3 - 20	0.2 - 1



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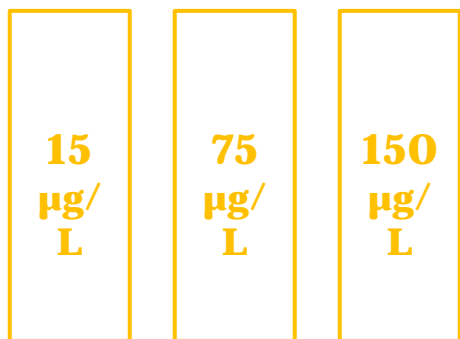
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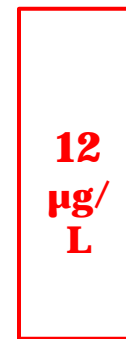
G3MH a precursor of 3MH ?

- Synthetic must



Spiking of G3MH d₂/d₃
in synthetic must at
laboratory scale

- Sauvignon Blanc must



Spiking of G3MH d₂/d₃
in Sauvignon Blanc must
at laboratory scale

Alcoholic fermentation (yeast strain: VIN13)

Production of labeled 3MH in resulting wines ?

Roland *et al.*, 2010, Food Chem., 121, 847-855

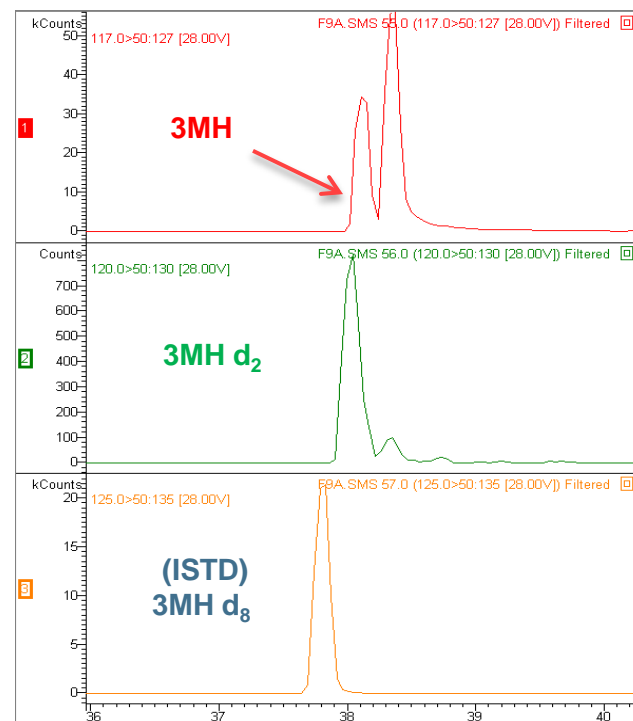
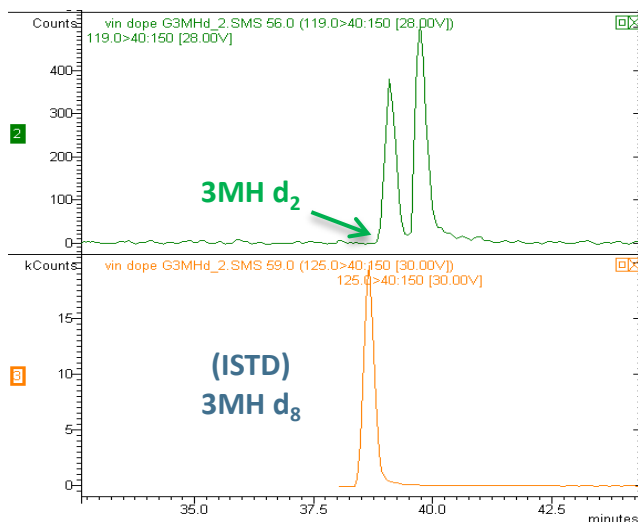


G3MH a precursor of 3MH ?

- Analysis of resulting wines by GC-MS/MS :

Sauvignon Blanc wines

Synthetic wines



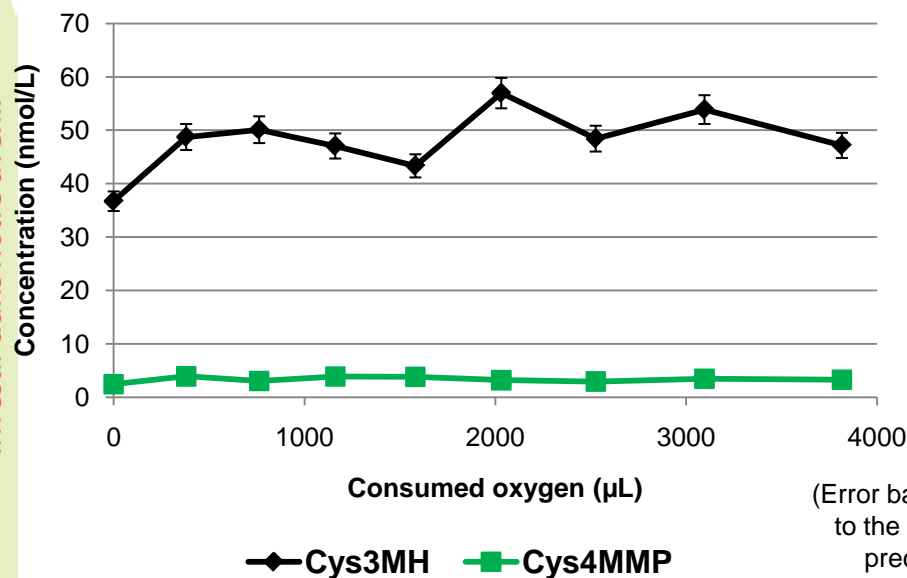
Formal proof of relationship between G3MH and 3MH

(Roland *et al.*, 2010, Food Chem., 121, 847-855)



G3MH as a varietal and pre-fermentative aroma precursor

Cysteinylated precursors

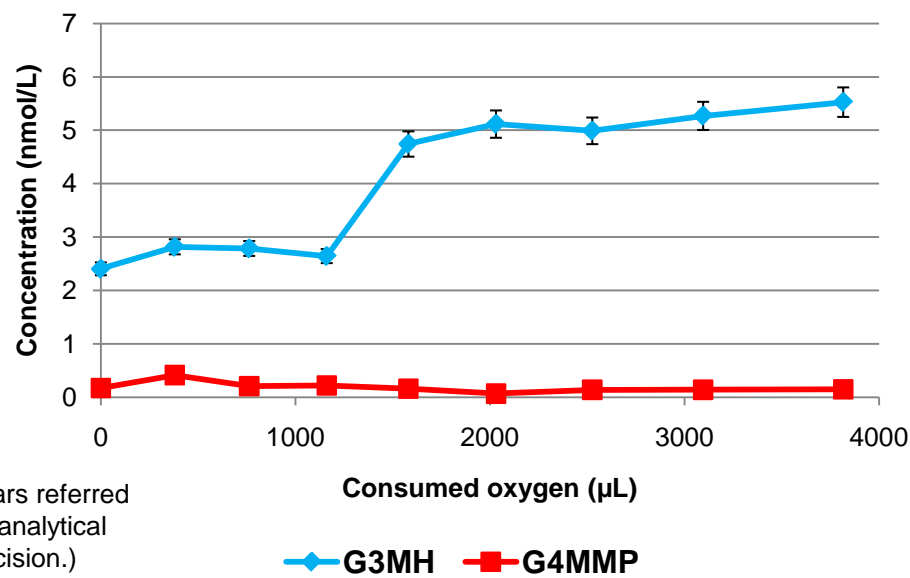


◆ Cys3MH ■ Cys4MMP

No influence of oxygen on cysteinylated precursor

Thioether bond stable under oxidative conditions

Glutathionylated precursors



◆ G3MH ■ G4MMP

No influence of oxygen on G4MMP

Huge production of G3MH (+140%)

(Error bars referred to the analytical precision.)
n=3

Roland *et al.*, 2010, *J. Agric. Food Chem.*, 58, (7), 4406-4413

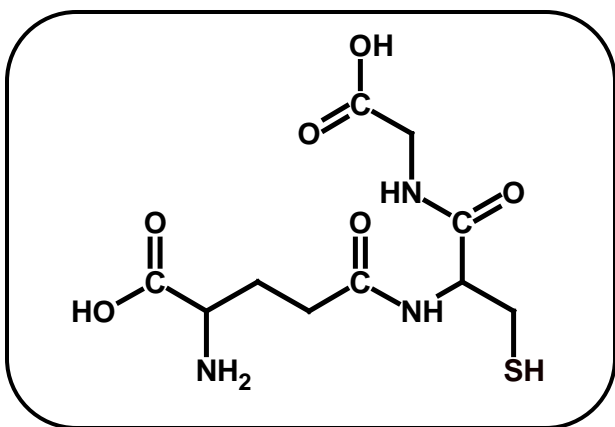


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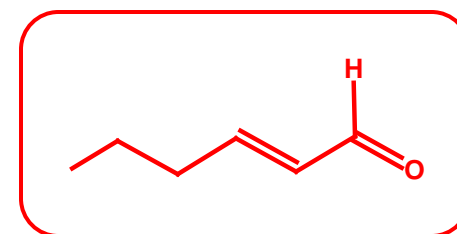
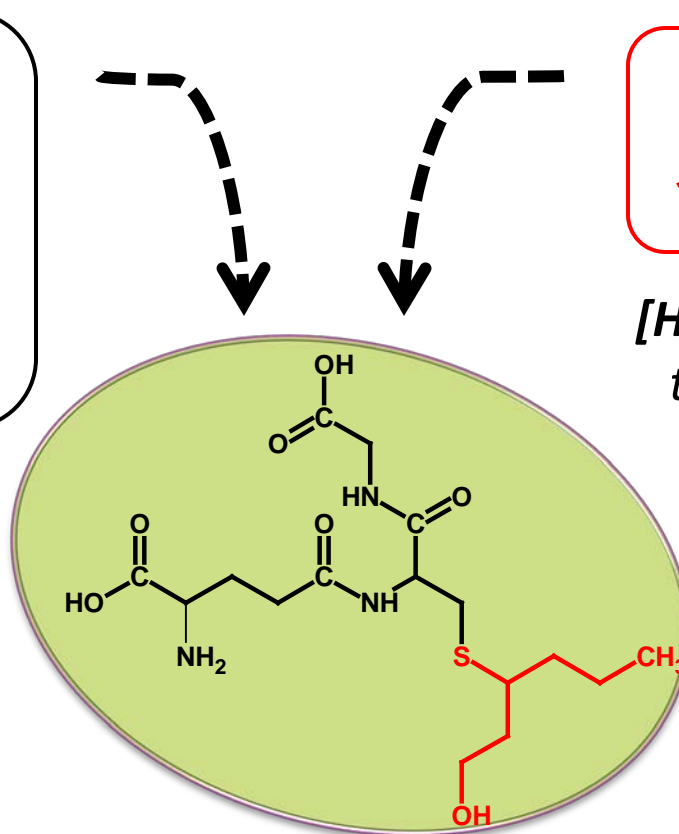




Hypothesis of G3MH formation during winemaking



GSH extracted from berries at the beginning of the crushing



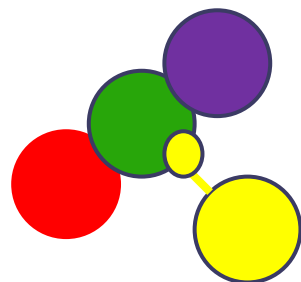
[Hexenal] increases at the end of crushing

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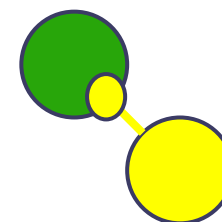


Relationships between the precursors ?



Glutathionylated conjugates

Fedrizzi et al, 2010
Roland et al, 2010



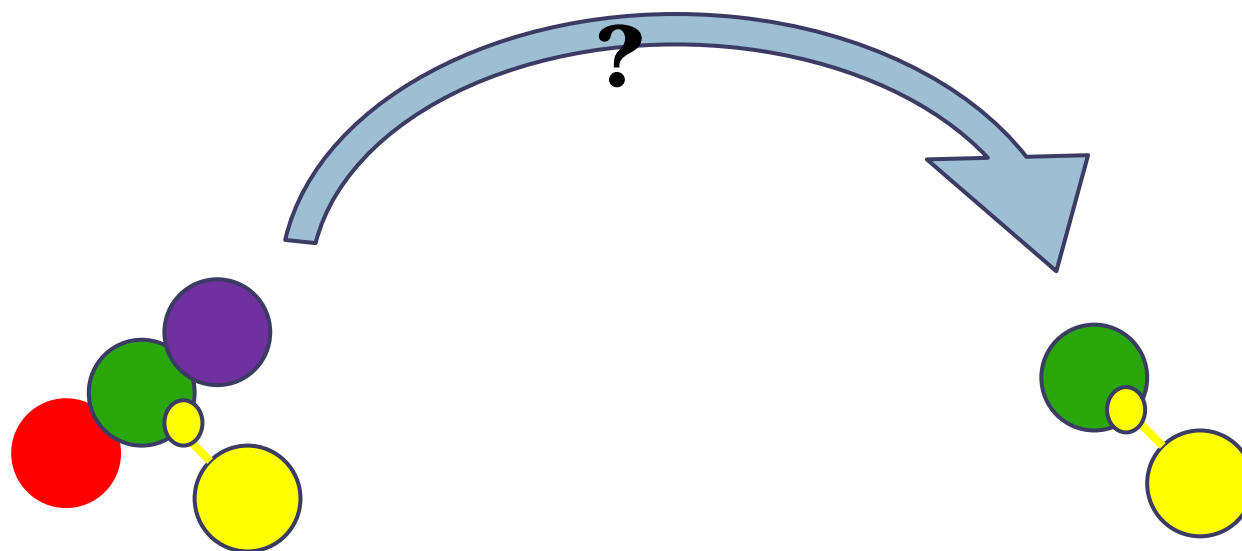
Cysteinylated conjugates

Tominaga et al, 1998



Relationships between the precursors ?

Peyrot des Gachons et al, 2002



Glutathionylated conjugates

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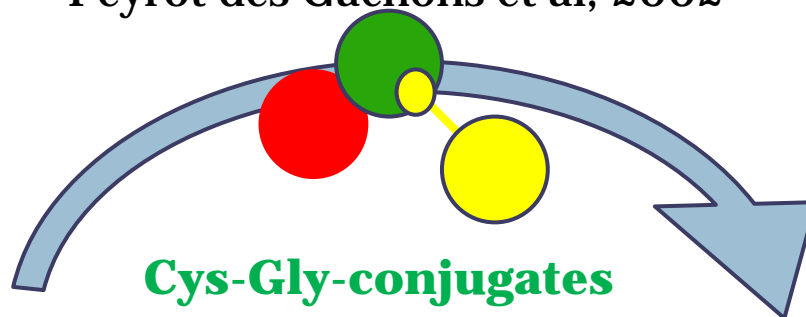
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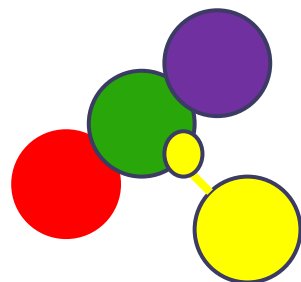


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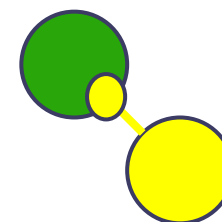


Capone et al, 2010



Glutathionylated conjugates

Fedrizzi et al, 2010
Roland et al, 2010



Cysteinylated conjugates

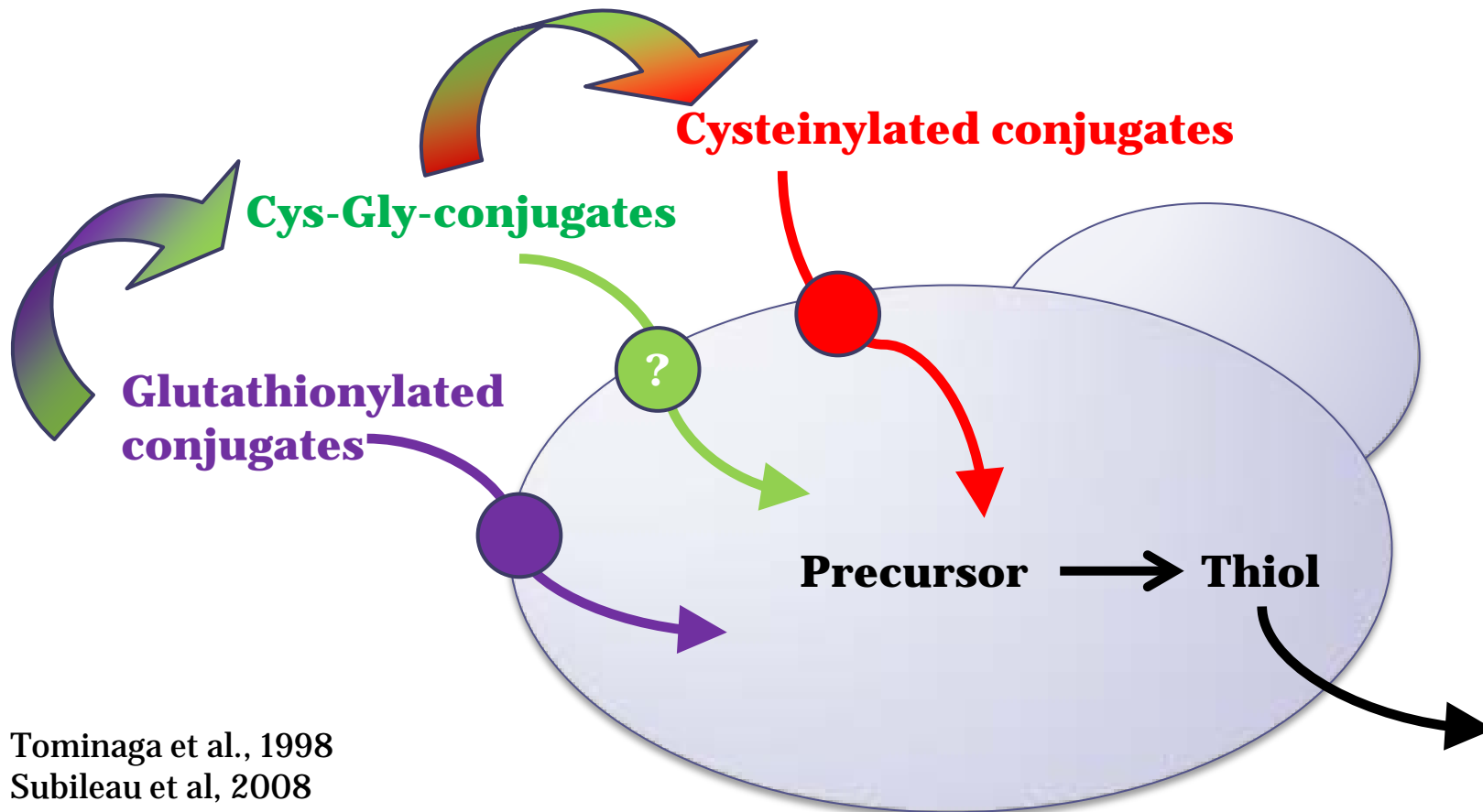
Tominaga et al, 1998

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Which kind of conversion for G-precursors ?



Tominaga et al., 1998
 Subileau et al., 2008
 Roland et al., 2010
 Capone et al., 2010

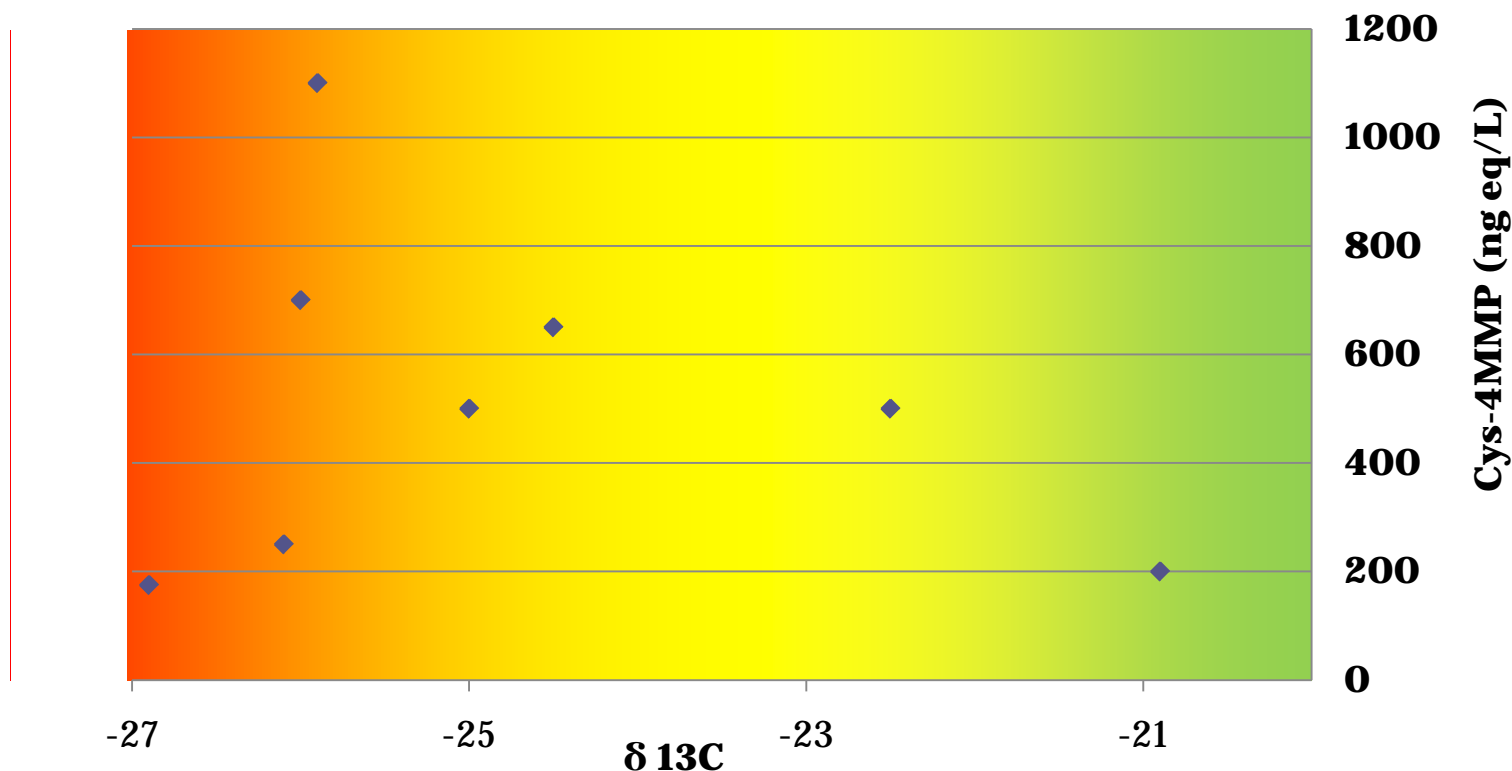
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Key factors of management for grapegrowners (1/3)

✓ Water status

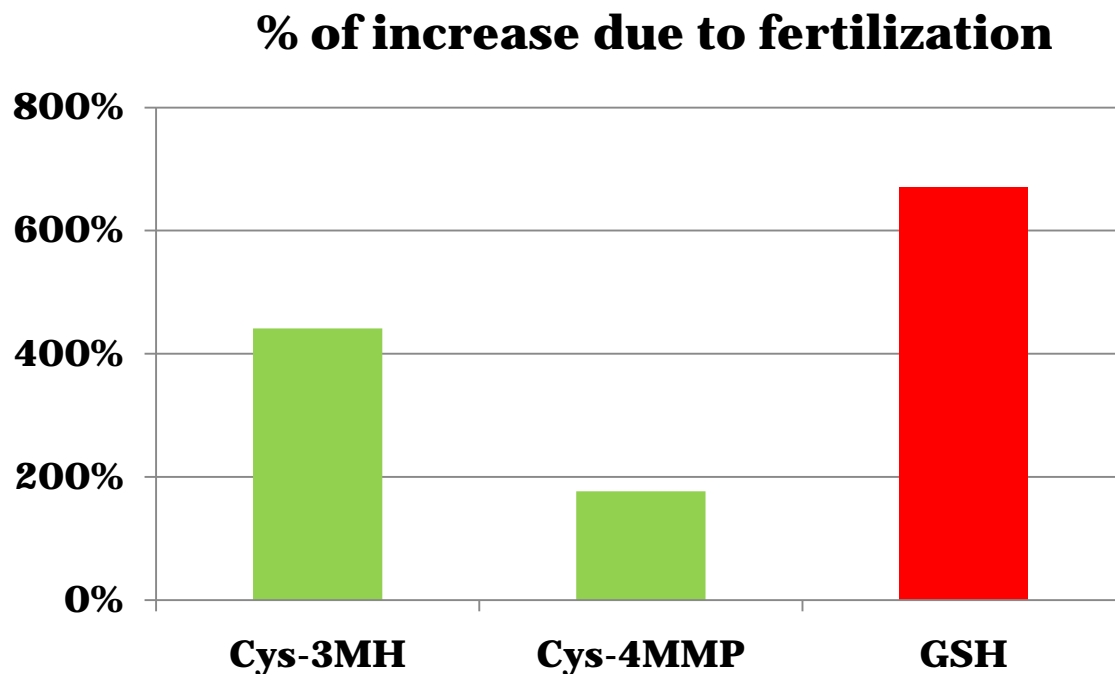


Peyrot des Gachons et al., 2005



Key factors of management for grapegrowers (2/3)

✓ Nitrogen fertilization

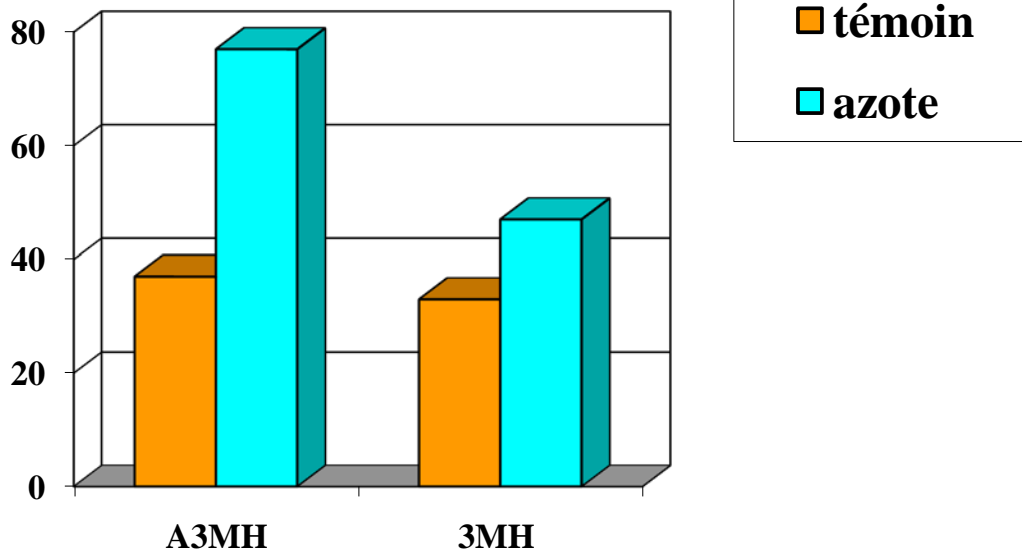


Choné et al., 2006



Key factors of management for grapegrowers (3/3)

✓ Nitrogen foliar spraying



Colombard 2004



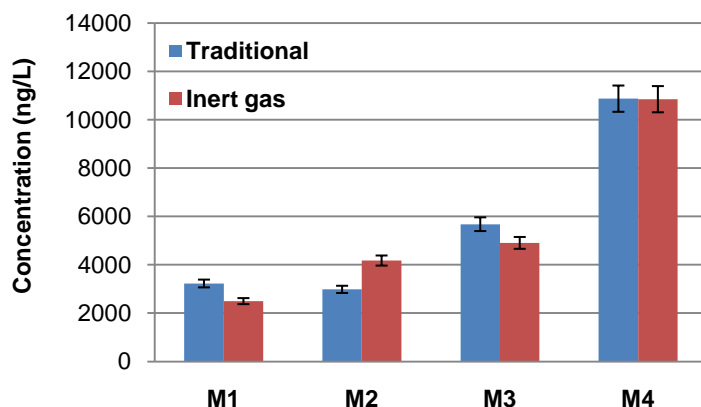
Parcelle à faible vigueur
[N assimilable < 100mg/L]

IFV Midi-Pyrénées



Key factors of management for enologists (1/5)

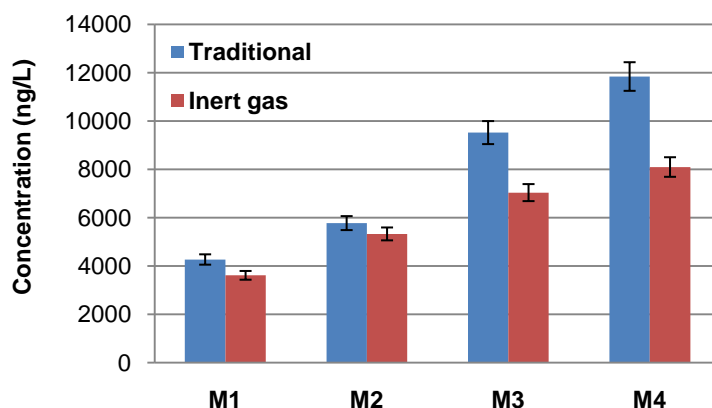
Influence of pressing on **Cys3MH** concentration



✓ **Kind of press**

No significative difference between traditional and inert gas process on Cys3MH concentration

Influence of pressing on **G3MH** concentration



Lower levels of G3MH in juices obtained under inert gas



In coherence with the concept of pre-fermentative G3MH production

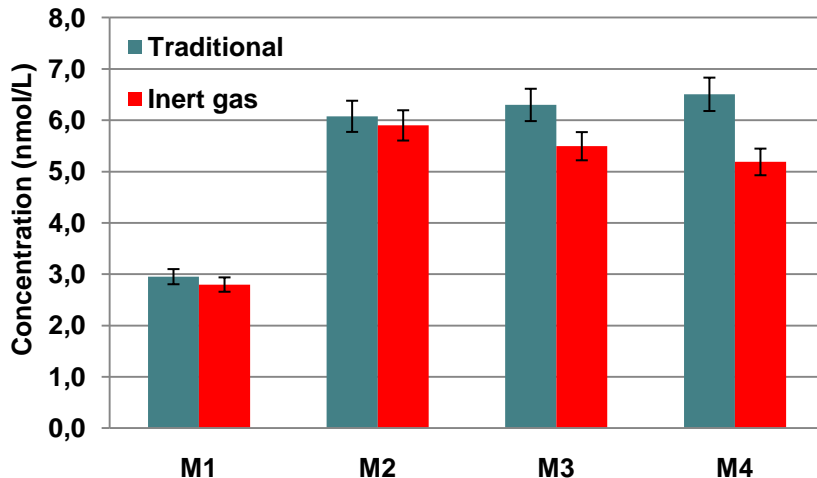
(Roland *et al.*, 2010, *J. Agric. Food Chem.*, 58, (7), 4406-4413)



Key factors of management for enologists (2/5)

✓ Kind of press

Influence of pressing on Eq3MH concentration

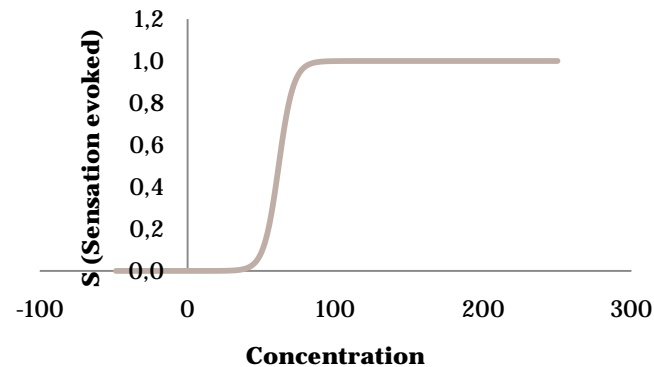


Tasting wines by 13 trained panelists:

No significative difference found



Stevens' law



Until 25% of Eq3MH losses in wines obtained from inert gas juices

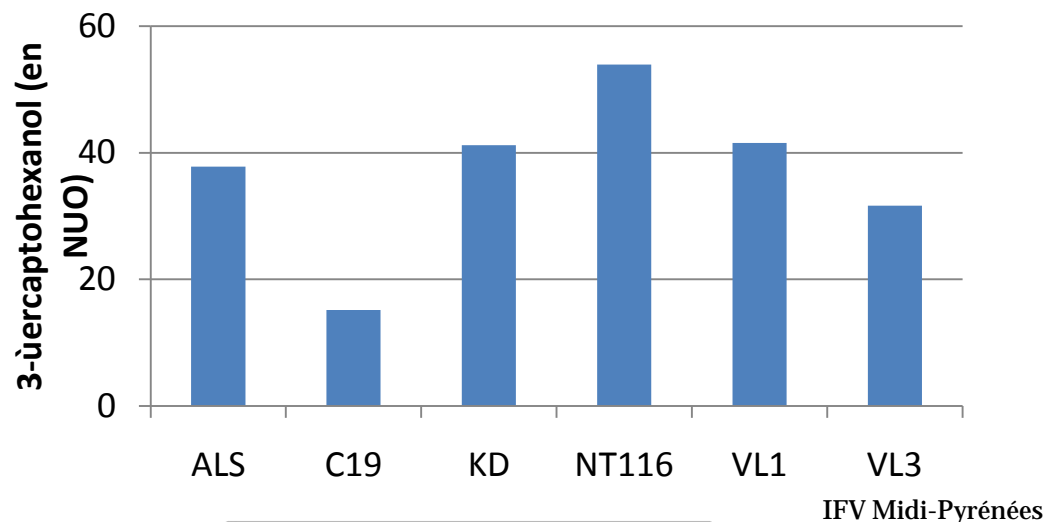
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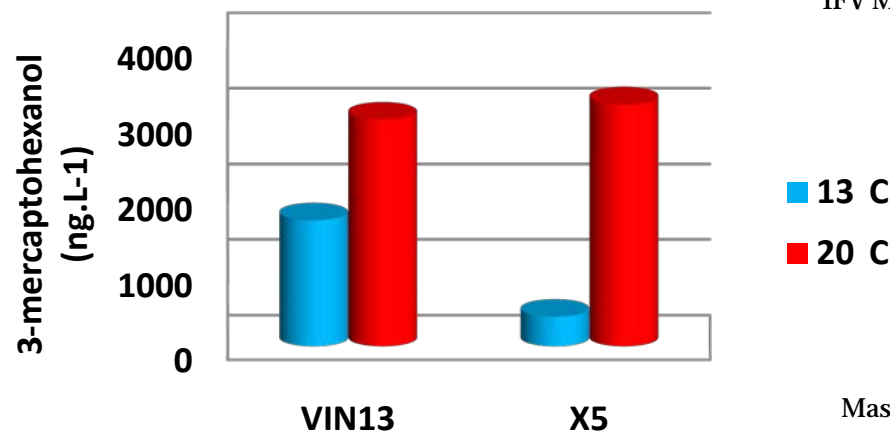


Key factors of management for enologists (3/5)

✓ Yeast strain



✓ Fermentation temperature



Masneuf et al., 2006

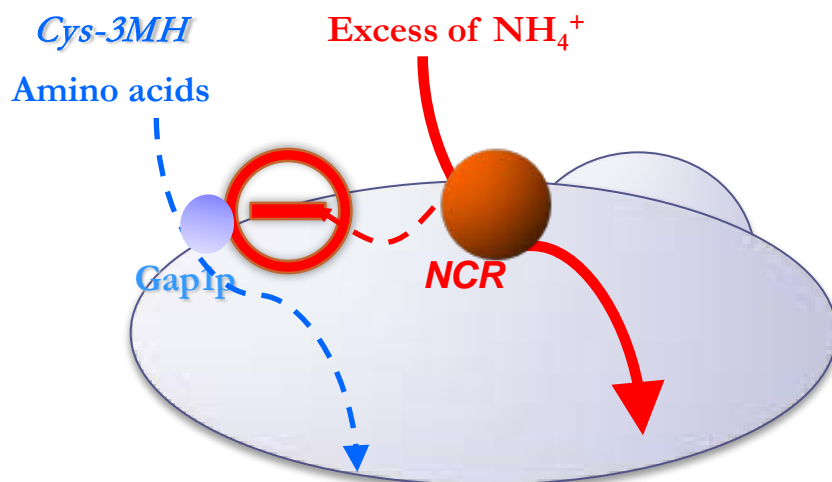
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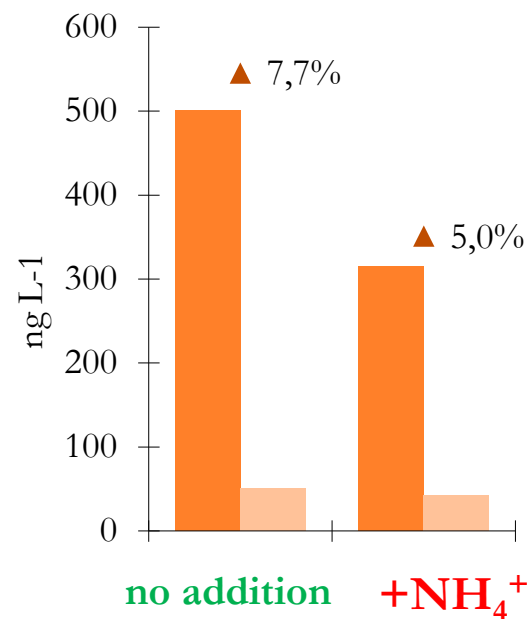


Key factors of management for enologists (4/5)

✓ Nitrogen composition of must



**Sauvignon
Languedoc 2004**



Subileau et al., 2008

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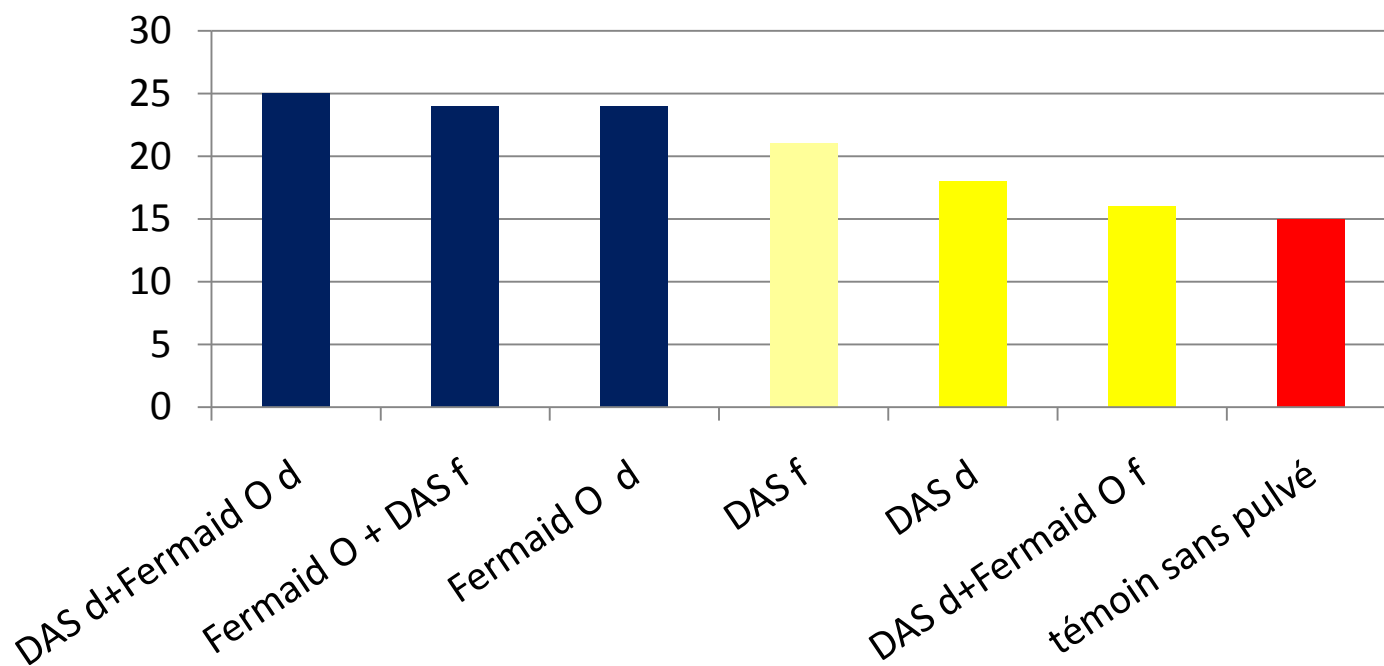
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Key factors of management for enologists (5/5)

✓ The time of addition of nitrogen nutrients in fermentation

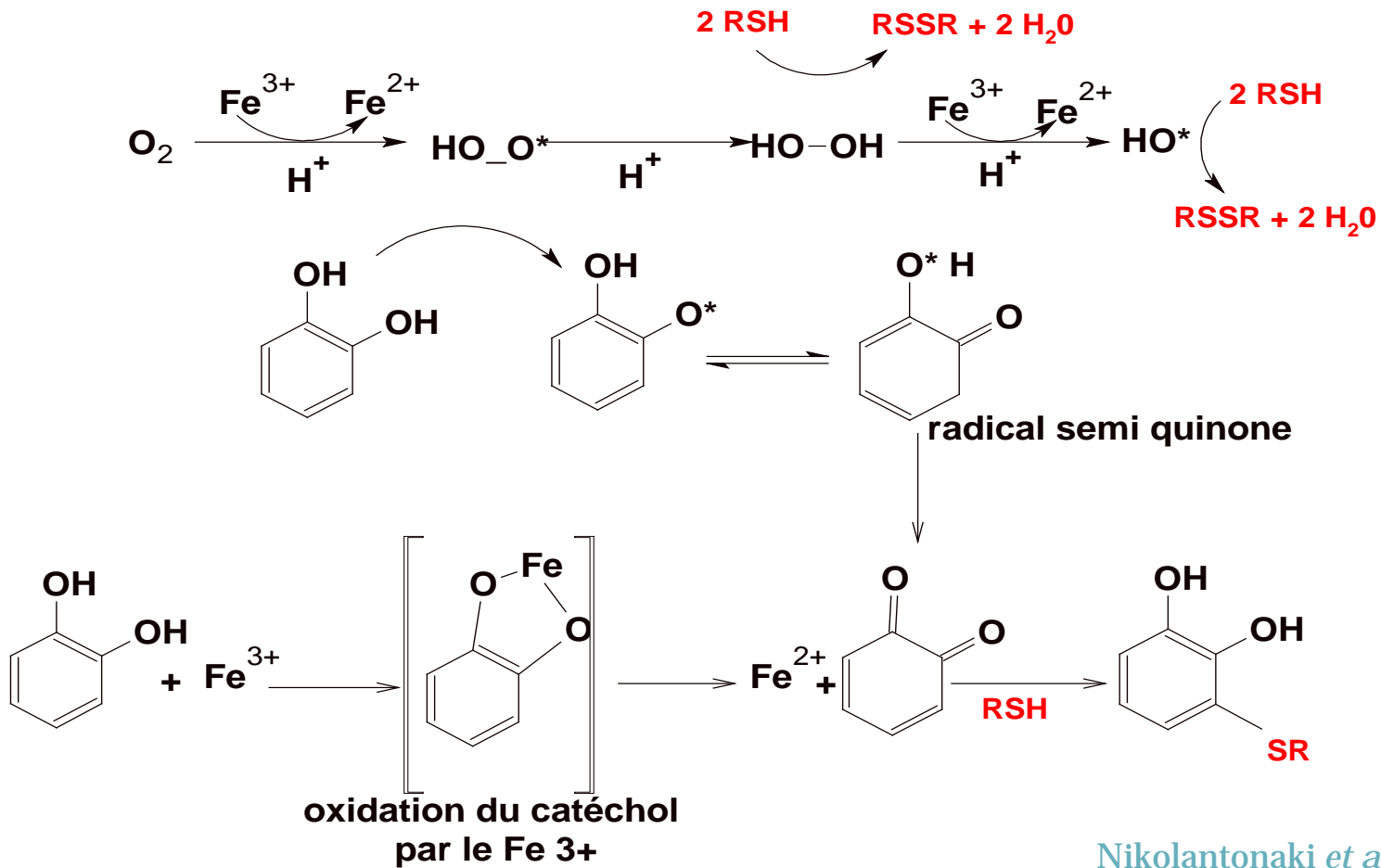
Total of 3MH and A3MH (nmol/L)





Key factors of management for enologists (3/4)

✓ Management of oxygen and related factors after fermentation



Nikolantonaki et al., 2009



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Key factors of management for enologists (3/4)

✓ Management of oxygen and related factors after fermentation

- free SO₂
- ascorbic acid or other anti-oxydant (GSH)
- polyphénols quantities (finning)
- limiting Iron and Copper (PVPP-PVI)
- dissolved oxygen between end of AF and bottling
- free oxygen in the headspace at bottling
- OTR of the stopper



Conclusion

- **The management of thiols levels in wine is a multifactorial approach, thus complex**
- **Adaptation of the production techniques are required**
 - Viticultural technical process
 - Must elaboration
 - Fermentation conditions (yeast strains, nitrogen nutrition, temperature)
 - Storage and bottling conditions
- **In favor to integrated processes from the vine to the bottle**



Aknowledgments



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