Organic viticulture and enology
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Hochschule Geisenheim University (HGU)

Organic/conventional viticulture Grape and Wine Composition

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www.oenoresearch.u-bordeaux.fr
www.isvv.fr

Organic (biodynamic)/ non-organic wines

Organic Wines :
Specific Label
Specific regulation in terms of additive
Total SO_2 (< 50 mg/L dry white wines or % less for red wines (i.e 100 mg/L) with regards to conventional wines) (UE 203/2012)
Specific use of additive, process…

Other labels (red wines)

- Nature and Progress 70 mg/L
- Demeter 70 mg/L
- Biodyvin 80 mg/L
- Natural Wine Association 30 mg/L

Non-organic Wines:
Conventional European regulation depending on produces wines
Ex red wines < 150 mg/L in total SO_2

Point on organic wines (without added sulfites)

- Sulfite
  - Used at least since 15th century
  - From 18th century beginning of wine ageing in cellars and aged wines due to use of sulphitizing
  - Meanwhile… losts of wines with taints in Pasteur period

  - Antioxidant, Anti-oxidative, antimicrobial, trapping carbonyles….

Point on organic wines (without added sulfites)

- Recent experiment in Bordeaux : red wines from 2016 and 2015 vintages
  - 2/3 of wines spoiled (oxidated, Brettanomyces taint, acetic character, …
  - 1/3 (mainly with limited ageing period in cellars… or very specific conditions which were satisfying

Magimel E., Barbe, 2019 ISVV

Main differences in terms of viticultural practices

Wine from organic viticulture : obtained from vines grown without chemical fertilizers, with pesticides (chemical origin but not synthetic), herbicide free.

Wine from conventional viticulture : obtained from vines that can be grown with chemical fertilizers, with synthetic chemical pesticides or non synthetic, eventually with herbicide.

Main differences in terms of viticultural practices

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Supplementary considerations

- ***Biodynamic wine (organic with adaptations)***

plant protection using plant extracts, quartz, with specific protocols and in relation to the moon cycles

- ***Biocontrol products (partially authorized in organic viticulture)***
- ***Biological control products***
- ***Low concern products***

Wine from conventional viticulture : obtained from vines that can be grown with chemical fertilizers, with synthetic chemical pesticides or non synthetic, eventually with herbicide.

What about viticultural impact choices on grape and wines quality and composition ?

… a gradual consideration associated with evolution of of pesticide use

1960 >1985
. Difficulties for alcoholic fermentation
. Developement of sensory defects

From 1985
. Residues in wines and commercial constraints

Development of risk assessment methods during homologation of pesticides

CEB Method 143 (France) (Commission Essais Biologiques)
1st version 1988
French Association of Plant protection

« Evaluation of unintended effects of pesticides on grape and wine component »
http://www.afpp.net

What about viticultural impact choices on grape and wines quality and composition ?

… a gradual consideration associated with evolution of of pesticide use

From 1993 . Modification of aromatic and polyphenolic and globally of grapes and wines quality

Development of risk assessment methods during homologation of pesticides

CEB Method 143 (France) (Commission Essais Biologiques)
2nd version 2000
3rnd version 2010

French Association of Plant protection

« Evaluation of unintended effects of pesticides on grape and wine component »
http://www.afpp.net

What about viticultural impact choices on grape and wines quality and composition ?

… a gradual consideration associated with evolution of of pesticide use

From 2000

. Analysis of microbial ecosystem on grape (after initial work in the 1970s)

. Residues and hygienical, sociological aspects

« We believe deeply, magically, we are what we eat, and exist a report of identity, analogy between us and what we eat … Then if we do not know what we eat, the risk is great no longer know what we are ».

Claude Fishler 1999 Du vin. Editions O. Jacob

Main parameters related to organic/conventional spraying in relation with grape and wine component

- Protection of vines against pathogens
- Pesticide (synthetic, not synthetic) and grape/wine composition, microbiological aspects
- Pesticide and grape/wine residues and their limitation

Main parameters related to organic/conventional spraying in relation with grape and wine component

- **Protection of vines against pathogens**
- Pesticide (organic, not organic) and grape/wine composition, microbiological aspects
- Pesticide and grape/wine residues and their limitation

Main vine pathogenic fungi and their consequences on grapes

Plasmopara viticola : downy mildew

Erysiphe necator (*Uncinula necator)* : powdery mildew

Botrytis cinerea : grey rot

. Alteration of vine physiology and loss of harvest

. Modification of grapes composition : proteins, aminoacid, vitamins, polyphenols, aroma compounds

. Non desire metabolites biosynthesis: volatile compounds, toxins…

1- Alteration of enological quality due to diseased grapes by **powdery mildew**

. Diminution of yield (berry weigh, juice) as % diseased grapes by powdery mildew

Type of cluster	Disease Intensity (%)	Juice weigh (Kg)	Average weigh of juice by cluster (g)	Juice loss (%) (compared to healthy cluster)
C_0	0	20.1	125.5	
C_1	< 25	10.6	99.7	21%
C_2	26-50	19.2	82.2	35%
C_3	50-80	21.0	72.5	42%
C_4	>80	9.6	61.1	51%

(notes during veraison)

Cabernet Sauvignon, 1999

Calonnec et al.Plant Path., 2004

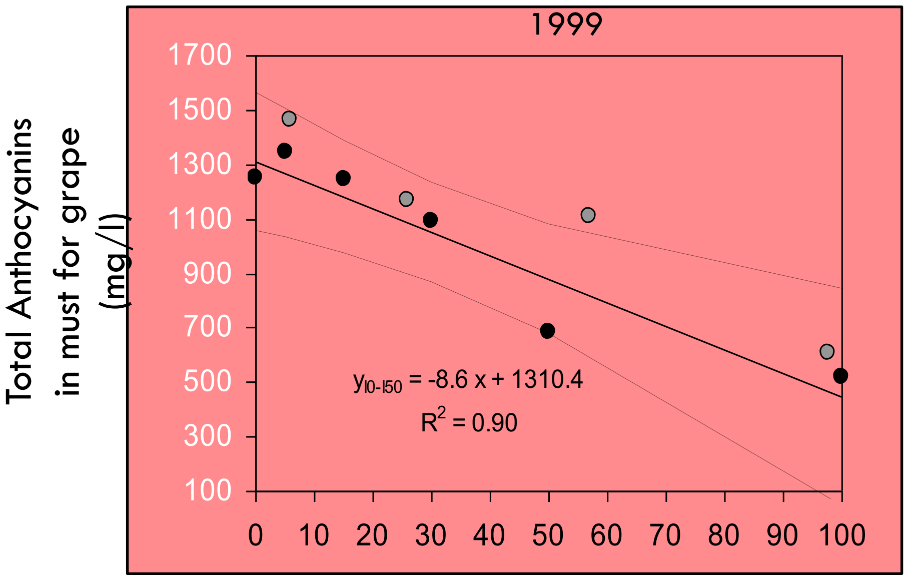
Collaboration with UMR 1065 INRA SAVE

Some characteristic of grapes and wines issued from diseased grapes by powdery mildew

. Sugar content in diseased clusters close to that measured in healthy grapes (Calonnec et al. 2004 Plant Dis. ; Stummer et al. 2003, 2005 Aust J Grape Wine Res)

Cabernet Sauvignon, 1999, 1998; Sauvignon 1999; Chardonnay 2000-2004

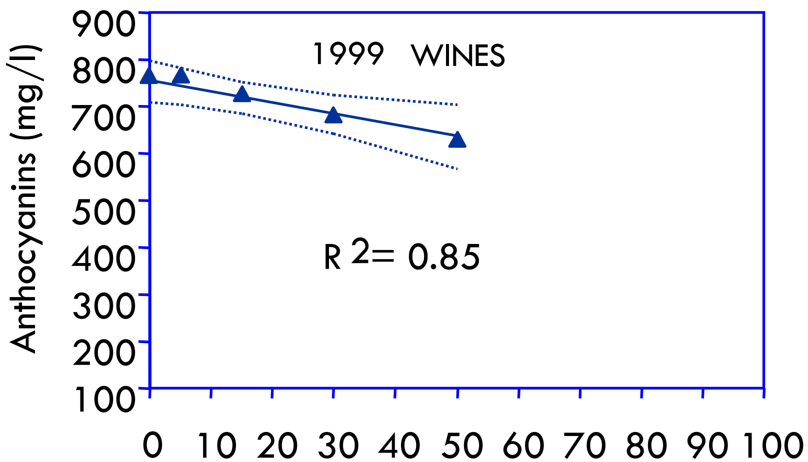
Cabernet Sauvignon GRAPES



% berries (black by W) and % clusters (grey) diseased by powdery mildew

. Diminution of anthocyanin concentration in grapes and wines in proportion of diseased grapes

Cabernet Sauvignon

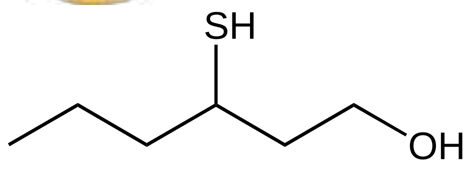


% berries (black byW) diseased by powdery mildew

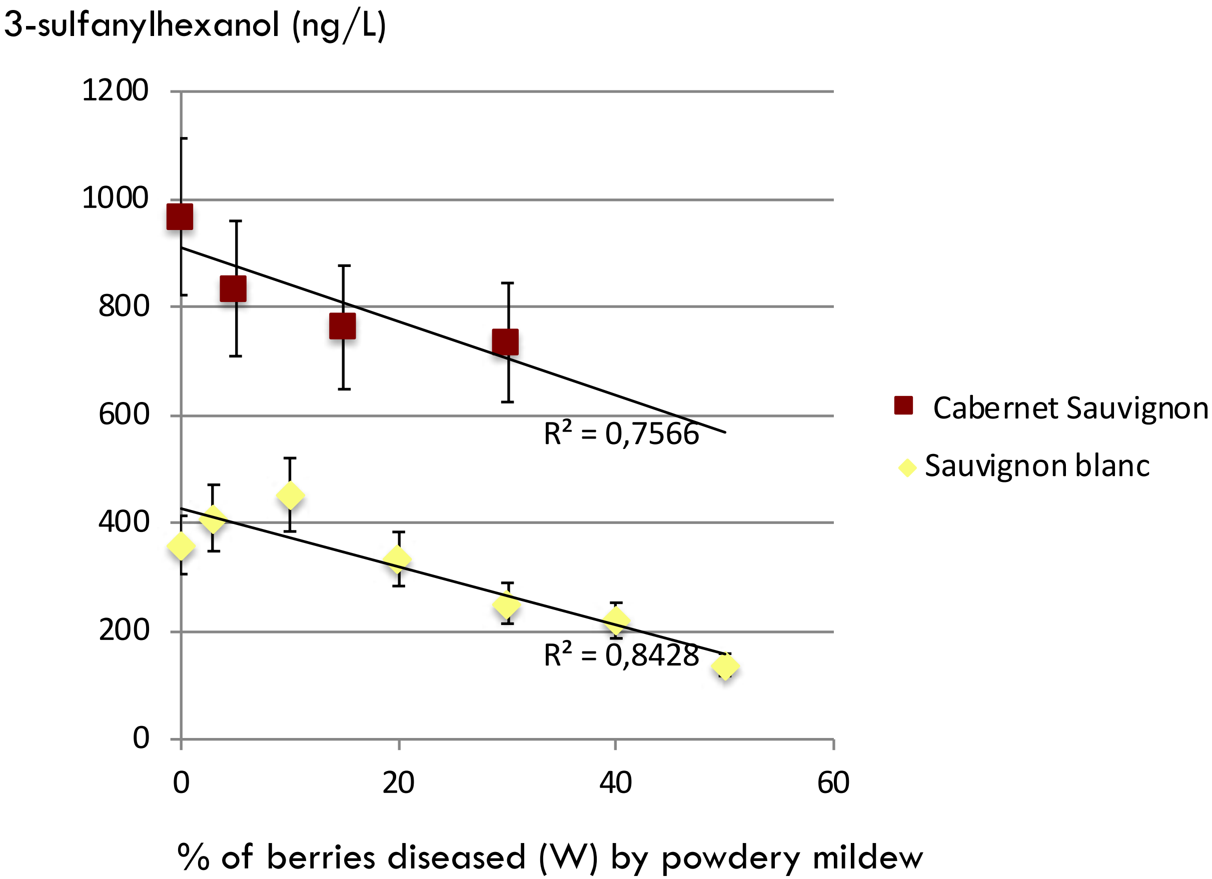
Calonnec et al. Plant Path. 2004

Some characteristic of grapes and wines issued from diseased grapes by powdery mildew

. Diminution of varietal aroma compounds (3-sulfanylhexan-1-ol) in Sauvignon blanc and Cabernet-Sauvignon wines



3-sulfanylhexan-1-ol



Cabernet Sauvignon, 1999,
Sauvignon 1999

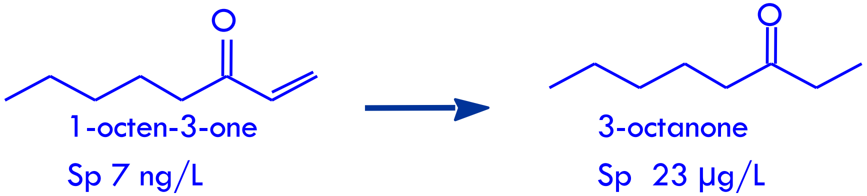
Calonnec et al. Plant Path. 2004

Some characteristic of grapes and wines issued from diseased grapes by powdery mildew

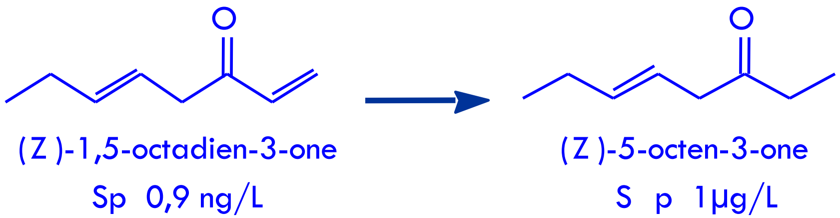
. Mushroom off-flavour of grapes specifically diseased by powdery mildew is less persistent in wines or not perceived

> Transformation of grape off flavor during wine-making

Fresh mushroom



Geranium leave odor

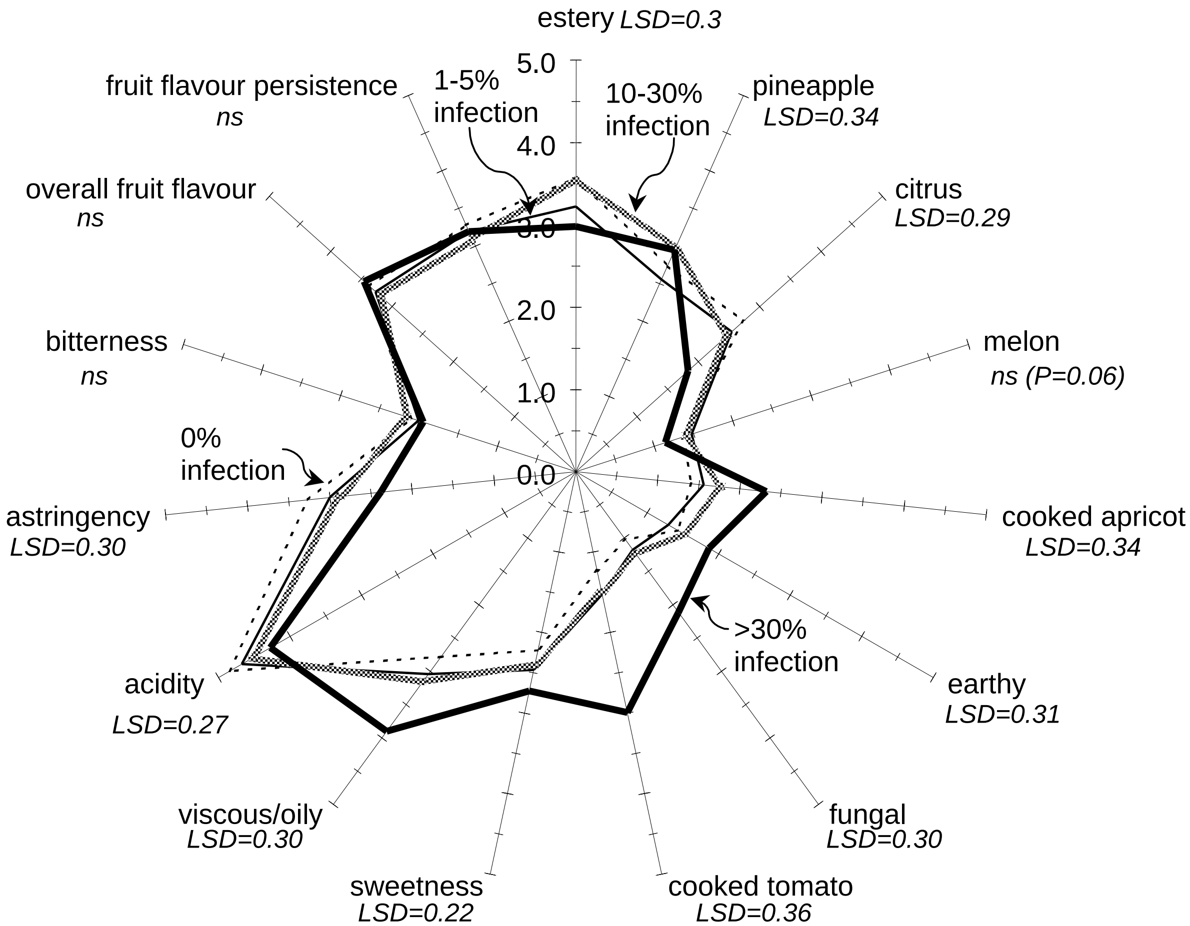


Wanner et al. 1998 Eur J Biochem.

Darriet et al. 2002; Vacher et al. 2008
confirmed by Stummer et al 2003, 2005

Specific context of complex rots : aroma precursors of 1-octen-3-one : release during fermentations

Sensory attributes of Chardonnay wines made from fruit with varied powdery mildew severity.



Stummer et al. 2003, 2005 J.Agric. Food Chem.

Each value is the mean score from duplicate fermentation replicate wines that were presented to 16 assessors in two replicate sessions. LSD: Least significant difference (P=0.05), ns: not significant

2- Alteration of enological quality due to diseased grapes by downy mildew

Some characteristic of grapes and wines issued from diseased grapes by downy mildew (*Plasmopara viticola)*

withered berries and necrosis of pedicels

Grapevine at maturity and infected berries

Brown rot : withered berries

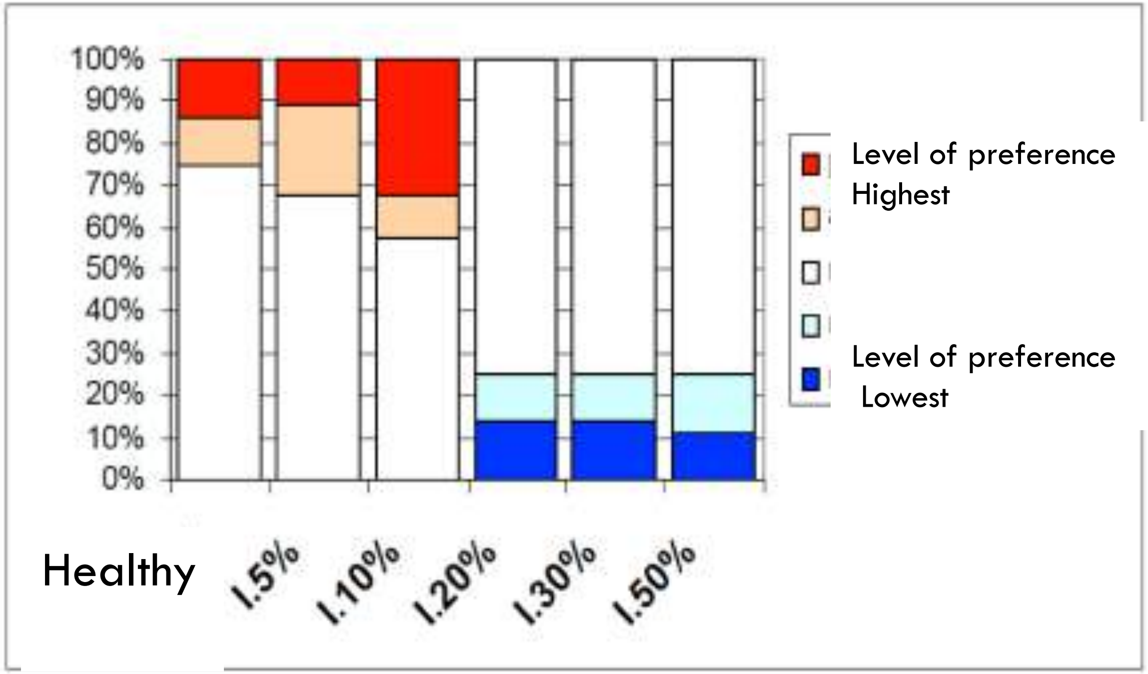
. Diminution of yield

. Increased titratable acidity (pH diminution)
. No significant impact on sugar content

. Alteration of wine's aromatic component
  . Modification of wine's fruity : less fresh fruit, more heavy, jammy fruit
  . Increased herbaceous expression, particularly during ageing

Organoleptic impact related to the incorporation of harvest diseased by brown rot

Millésime 2008

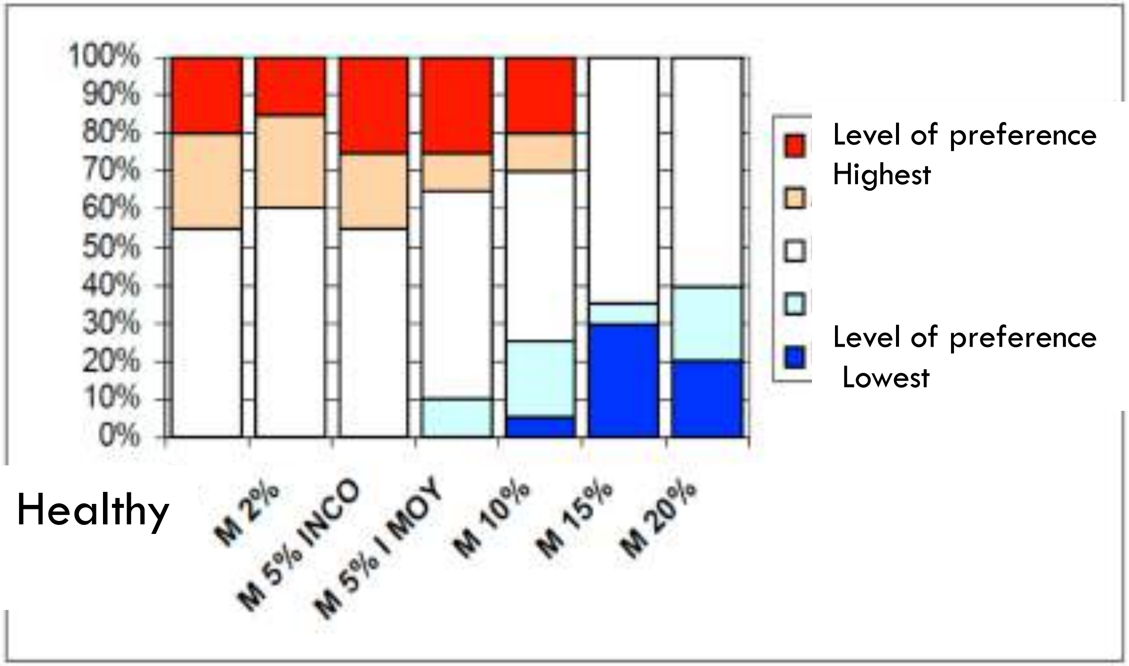


Ludivine Davidou, Jean-Christophe Crachereau
Chambre d'Agriculture de la Gironde - Service Vigne et Vin - Blanquefort - France.

Rev Oenol. 2011

Organoleptic impact related to the incorporation of harvest diseased by brown rot

Millésime 2009



Ludivine Davidou, Jean-Christophe Crachereau
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Rev Oenol. 2011

Interpretation of wine aroma modification in relation with downy mildew on grapes (Merlot)

Effect of maceration (M) and alcoholic fermentation (AF) of media supplemented or not with withered berries infected by *P. viticola* on the formation of cooked fruit and herbaceous nuances.

Treatments[a]	Descriptors[b]	
	Cooked fruit	Herbaceous
AF-	–	–
M+/AF–	–	+
M+/B– AF+	–	+
B+ AF+	+++	+++

[a] (AF) synthetic must after alcoholic fermentation; (M+/AF–) synthetic wine supplemented with withered berries (maceration 5 d, 24 °C); (M+/B– AF+) synthetic must supplemented with withered berries (maceration 5 d, 15 °C) and removed before inoculating the media with yeast; (B+ AF+) alcoholic fermentation with withered berries.

[b] Intensity of aromas perceived by two assessors: - no intensity, + weak, ++ medium, +++ strong intensity.

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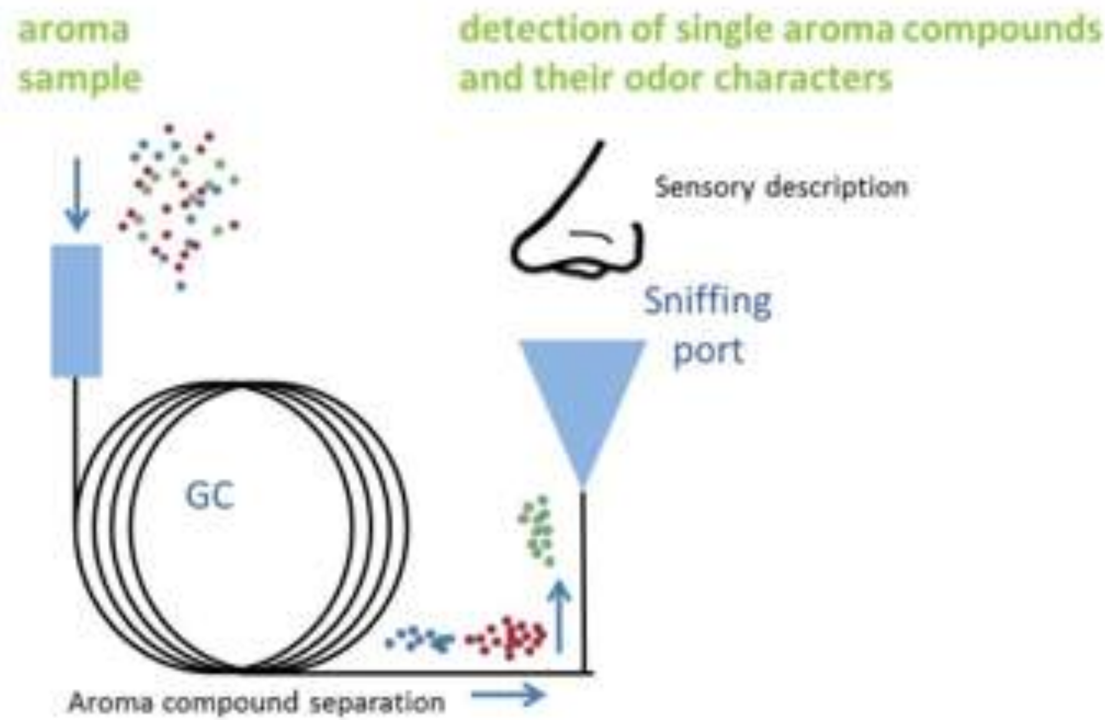
Interpretation of wine aroma modification in relation with downy mildew on grapes/wines



Interpretation of wine aroma modification in relation with downy mildew on grapes (Merlot) : strongly odorous compounds

- **Herbaceous expression : Various origins**

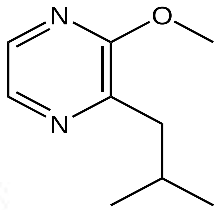
Increased proportion of 2-**methoxy-3-isobutylpyrazine (IBMP)** in wines

Increased proportion of **1,5-octadien-3-one** / **1,5-heptadien-3-one**

Main odorant zones detected by GC-O during analysis of red Merlot wine made or not with berries infected by *P.viticola.*

Odorant zone	Descriptors	LRI		Compounds	Wine[c]	
		BPX5	BP20		Control	Control + brot[d]
OZ1	Geranium	880	1260	(*Z*)-1,5-heptadien-3-one[a]	–	++
OZ2	Geranium	950	1376	(*Z*)-1,5-octadien-3-one[b]	–	+++
OZ3	Green, bell pepper	1144	1552	3-isobutyl-2-methoxypyrazine[b]	+	+++

[a] tentatively identified on the basis of odor similarity and IRL found in literature: IRL_{polar} 1278 (Lorber et al., 2014).
[b] Identified by comparison with IRL found in literature and co-injection of pure compound.
[c] odor intensity: – not detected, + weak, ++ medium, +++ high intensity.
[d] berries infected by *P. viticola*.



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FranceAgriMer

Interpretation of wine aroma modification in relation with downy mildew on grapes (Merlot)

- **Herbaceous expression : Various origins**

Increased proportion of 2-**methoxy-3-isobutylpyrazine (IBMP)** in wines

Increased proportion of **1,5-octadien-3-one / 1,5-heptadien-3-one**

Incidence of increasing concentrations of withered berries infected by *P. viticola* on volatile compounds concentration in Merlot wines. (n = 3).

	Detection threshold[a]	Must	Wines							
			Treatments (g/75 mL)							
			0	1	2	5	8	10	10[c]	
IBMP (ng/L)	15	5.8	6.11 (0.9)	8.51 (0.8)	**15.24 (0.8)**	**24.70 (3.4)**	**31.65 (6.8)**	**33.29 (5.2)**	**27.1 (3.3)**	**0.930**

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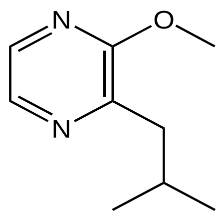
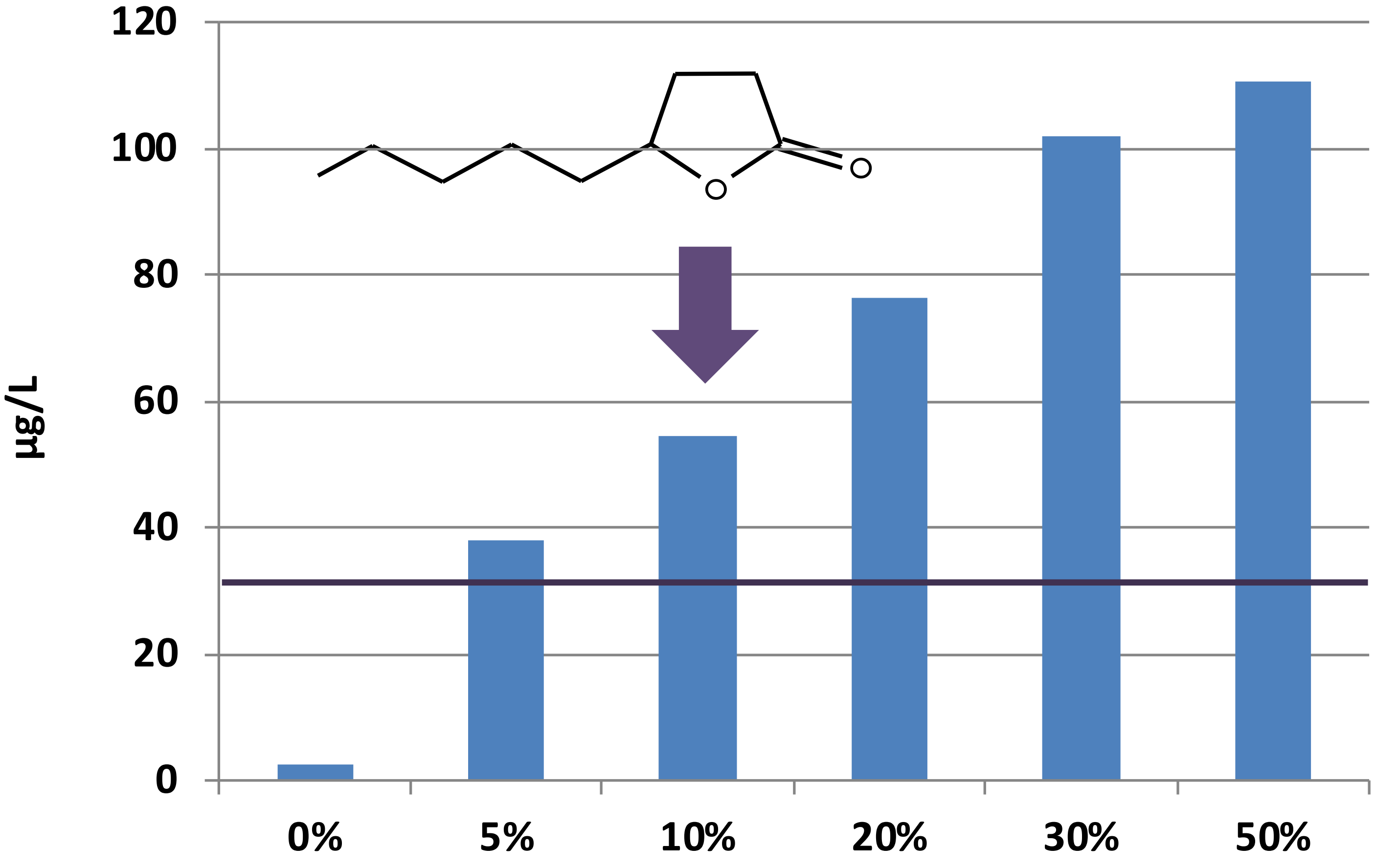


Interpretation of wine aroma modification in relation with downy mildew on grapes

- **Modified fruity expression : Increased proportion of some lactones**



γ-nonalactone olfactory detection threshold

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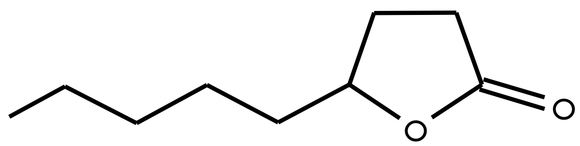
Merlot, 2008 Bordeaux

γ-Nonalactone

(Fruity, coconut, almond)



❖ Identified in apricot (Tang, 1968), peach (Bayonove, 1988), natural sweet wines (Cutzach, 1999)

❖ Results from the oxidation of some unsaturated fatty acids (linoleic acid) (Tressl, 1980)

❖ Compound found naturally in red wine 5-30 µg / L (increased values in wines from overmatured grapes/grapes diseased by *Botrytis cinerea* …)

Detection olfactory threshold in alcoholic solution 27 µg / L, in a red wine 60 µg / L

Pons et al. Œno 2011, Dunod 2012
Pons et al. 2014
Pons et al. 2017

Interpretation of wine aroma modification in relation with downy mildew on grapes

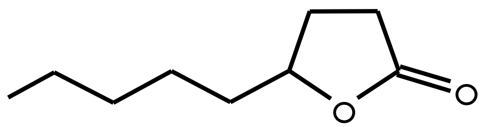
- **Fruity expression : Increased proportion of some lactones and MND** (3-methyl-2,4-nonadione)

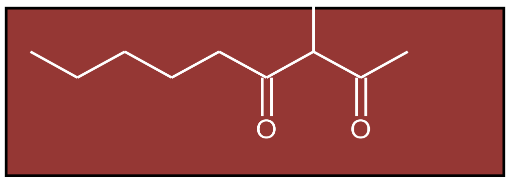
- Both derivatives of lipidic compounds

Incidence of increasing concentrations of withered berries infected by *P. viticola* on volatile compounds concentration in Merlot wines. (n = 3).

	Detection threshold[a]	Must	Wines							r[d]
			Treatments (g/75 mL)							
			0	1	2	5	8	10	10[c]	
γ-octalactone (μg:L)	7	tr[b]	4.11 (1.1)	5.52 (0.5)	6.14 (1.5)	**10.21 (1.9)**	**11.60 (2.2)**	**14.15 (2.5)**	2.1 (0.6)	**0.991**
γ-nonalactone (μg/L)	27	tr	5.82 (0.6)	**30.55 (1.5)**	**52.47 (3.3)**	**96.41 (7.9)**	**111.90 (12.8)**	**133.54 (13.3)**	12.3 (2.2)	**0.975**
γ-decalactone (μg/L)	0.7	tr	**2.70 (0.3)**	**4.34 (0.2)**	**4.92 (0.3)**	**7.11 (0.4)**	**7.71 (0.5)**	**8.56 (0.5)**	2.1 (0.7)	**0.964**
γ-undecalactone (μg/L)	60	tr	tr	0.71 (0.2)	1.41 (0.3)	2.01 (0.3)	2.13 (0.3)	2.55 (0.3)	tr	**0.924**
γ-dodecalactone (μg/L)	7	tr	1.80 (0.5)	2.15 (0.6)	2.12 (0.7)	2.94 (0.3)	2.84 (0.7)	3.21 (0.8)	tr	**0.942**
MND (ng/L)	16	8	16.2 (2.1)	17.5 (1.9)	**18.5 (2.1)**	**35.2 (2.1)**	**44.1 (3.3)**	**61.1 (8.4)**	**32.1 (3.4)**	**0.983**
IBMP (ng/L)	15	5.8	6.11 (0.9)	8.51 (0.8)	**15.24 (0.8)**	**24.70 (3.4)**	**31.65 (6.8)**	**33.29 (5.2)**	**27.1 (3.3)**	**0.930**

[a] (Gemmert, 2003).
[b] Traces.
[c] Concentrations in hydroalcoholic solutions supplemented with withered berries kept for 5 days at 24 °C (n = 2).
[d] Pearson correlations in bold were significant for α = 0.05. For each compound, concentration in bold corresponds to OAV > 1.





3-methyl-2,4-nonanedione
Anis, dried herb
Detection threshold 16ng/L

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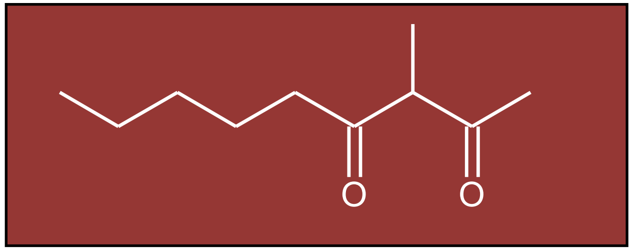
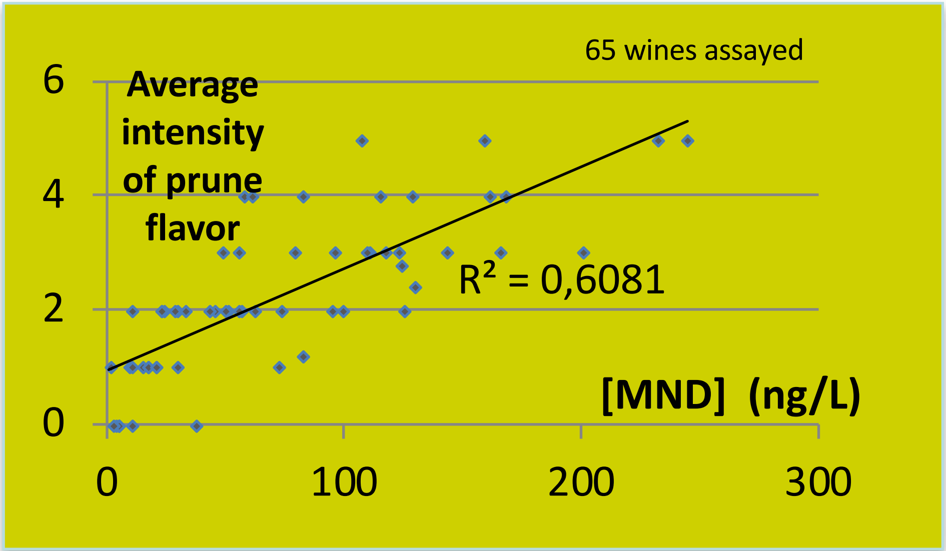
3-methyl-2,4-nonanedione marker of prematurely red wines oxidative flavor



3-methyl-2,4-nonanedione (MND)
Anis, dried herb
Detection threshold 16ng/L

- Correlation of MND concentrations with the intensity of prune and fig flavor in wines



➨ Supplementation of MND in red wines diminish their fresh fruity aromas

➨ Precursors of MND identified, currently assayed in grapes and wines

Incidence of increasing concentration of withered berries infected by *P. viticola* on herbaceous/cooked fruit odor intensity in young and aged Cabernet Sauvignon and Merlot wines.

Vines		Aging time (years)	Sum of ranks					
			% berries					
			0	2	5	10	15	20
Merlot	T0	1	19	21	32	51	64	65
	T1	6	12	30	33	42	39	54
Cabernet-Sauvignon	T0	0.7	25	27	32	42	/	54
	T1	3	20	24	25	37	/	44

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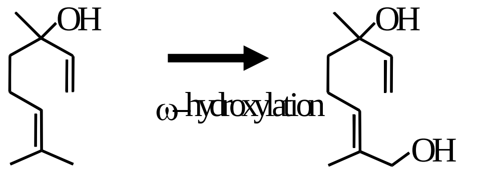
3- Alteration of enological quality due to diseased grapes by *Botrytis cinerea* and complex rots

. *B. cinerea* laccase activity (polyphenol oxidase) oxidating grapes and wines polyphenols (anthocyanins, tanins) Dubernet, Ribereau-Gayon (1975); Mayer A.M. (2000); Ky et al. 2012

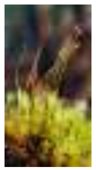
. Hydrolysis of fatty acid ethyl esters contributing to the fermentative aroma by B. cinerea esterase Dubourdieu et al. (1985)

. Enzymatic hydroxylation of monoterpenes (linalol, geraniol…) contributing to Muscat type aroma to less odoriferous compounds Boidron (1978); Bock et al. (1986)

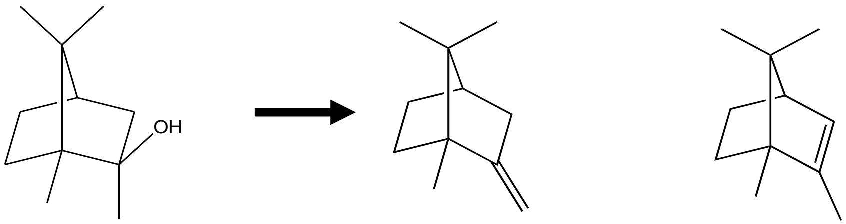


Linalol 8-Hydroxylinalol

. Contribution generally to some off flavours (Bayonove et al. 1999) but usually not very stable and intense (La Guerche et al. 2006)



Ex:



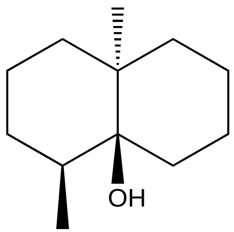
2-methylisoborneol 2-methylenebornan 2-methylbornene

Characteristics of harvests partially spoiled grapes with bunch rot complexes

. not always easily distinguishable because rot situated inside the bunch
. with wet conditions before and during harvesting (100 mm precipitation)
. persevering morning mists
. berries wounded due to insects and hail

Secondary rot, Rot complexes

Secondary bunch rot implicating *B cinerea* with various saprophytic fungi : production of potent off-flavors



(-)-geosmin

Olfactory detection threshold in wine
40 ng/L
Concentration up to 500 ng/L)

- powerful compound : damp earth, beetroot
- terpene synthesized by *Streptomyces* sp. and various *Penicillium* sp.

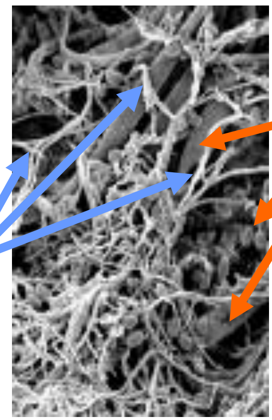
- From the 2000th, the proportion of vineyards concerned is more important (France, Europe)
- Grape varieties concerned : Gamay, Pinot noir, Cabernet Sauvignon, Chardonnay, Sémillon, Chenin

- Grapes containing (-)geosmin are associated with bunch rot complexes implicating with *Botrytis cinerea* various *Penicillium* sp. particularly *P.expansum*

Darriet et al. 2000 J Agric Food Chem., 2001,Eur J Food Res Techn
La Guerche et al. 2006 J Agric Food Chem.

Model for formation of (-)geosmin on grapes : implicating with *Penicillium* sp., and *Botrytis cinerea* metabolisms

electronic microscopy of an earthy berry



Penicillium sp.

Spores and large myceli a of *B. cinerea*

Botrytis cinerea

degrades

produces

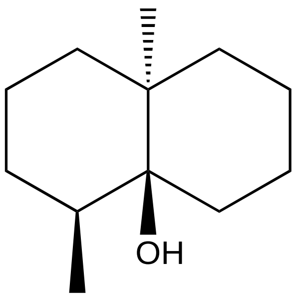
aminoacids

mannitol

Penicillium sp. particularly P.expansum

Low aw-value (0.92)

Unsaturated fatty acids (skin berry)



(-)-Geosmin

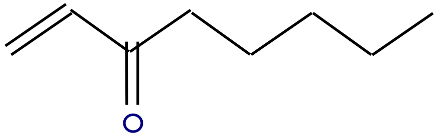
(olfactory detection threshold 40 ng/L)

Concentration up to 500 ng/L)

Collaboration with UMR 1065 INRA SAVE
D Blancard, P Sauris

La Guerche et al. 2004, 2005, 2007 Ant Van Leuw. Int J Microb 2006 J Agric Food Chem; Morales-Valle et al. 2011 Food Microbiol

Other story - Secondary bunch rot implicating *B cinerea* with various saprophytic fungi : production of potent off-flavors

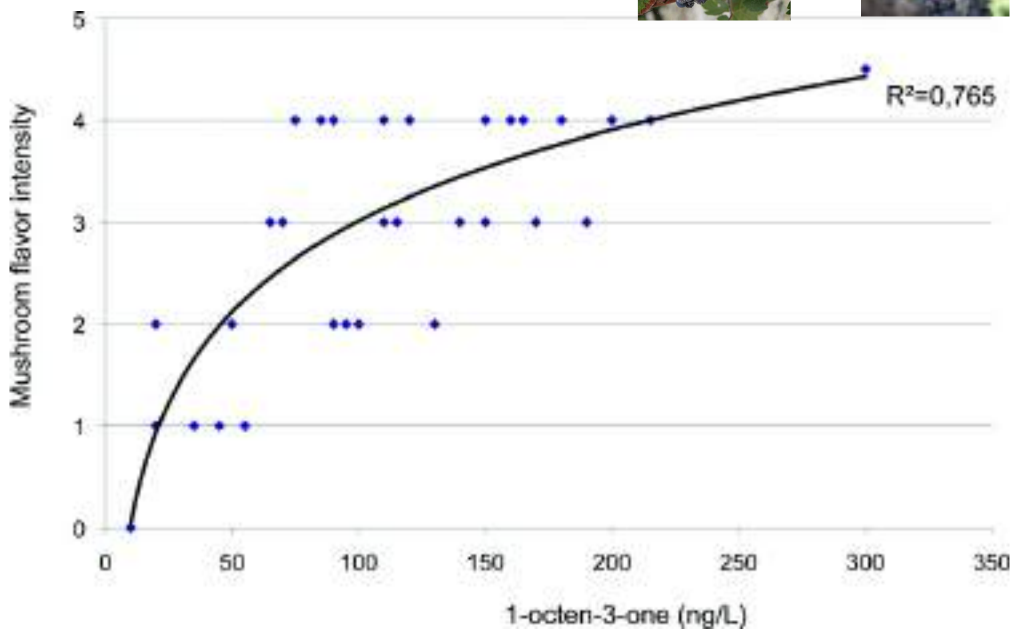


1-octen-3-one

Olfactory detection threshold 30 ng/L
Concentration up to 350 ng/L)

1-nonen-3-one

Olfactory detection threshold 8 ng/L
Concentration up to 160 ng/L)

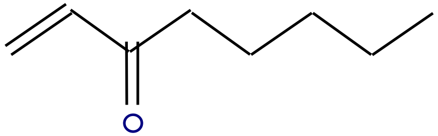


Wine sample	1-octen-3-one (ng/L)	1-nonen-3-one (ng/L)	1-octen-3-ol (µg/L)	Fresh Mushroom flavor
Pinot gris 2007	20 ± 3	23 ± 3	17	weak
Pinot gris 2007	115 ± 10	20 ± 2	5	Intense
Pinot meunier 2006	106 ± 10	31 ± 3	2	Intense
Pinot meunier 2006	120 ± 10	20 ± 2	5	Intense

Grape varieties : Pinot meunier, Pinot gris, Pinot noir, Chenin, Sauvignon…

Pons et al. J Agric Food Chem, 2011

Other story - Secondary bunch rot implicating *B cinerea* with various saprophytic fungi : production of potent off-flavors



1-octen-3-one

Olfactory detection threshold in white wine 40 ng/L
Concentration up to 350 ng/L)

1-nonen-3-one

Olfactory detection threshold in 8 ng/L model media close to wine
Concentration up to 160 ng/L)

. Particularity of the situation

➢Formation of 1-octen-3-one and 1-nonen-3-one during Alcoholic Fermentation from aroma precursors

. In the vineyard

➢Grape bunch complexes with *Penicillium* sp., *Clonostachys* sp., *Trichothecium roseum*, *Verticillium* sp., and *Trichoderma* sp. (Vacher et al. 2008)

Grape varieties : Pinot meunier, Pinot gris, Pinot noir, Chenin, Sauvignon …

Pons et al. J Agric Food Chem, 2011

Main parameters related to organic/conventional spraying in relation with grape and wine component

- Protection of vines against pathogens
- **Pesticide (organic, not organic) and grape/wine composition, microbiological aspects**
- Pesticide and grape/wine residues and their limitation

Enological risks related to the application of pesticides on vine

. Difficulties for alcoholic fermentation
. Development of sensory defects

. Modification of aromatic components, polyphenolic the quality of grapes and wines
. Modification of grape microflora

Enological risks
related to the application of pesticides
on vine

Related to

-Impact of pesticide residues on grape/wine composition

- through direct chemical reactivity during alcoholic fermentation and ageing (potential organic/conventional viticulture) (persistence of residue on grape)
- through modification of grape physiology

-Impact of pesticides on grape physiology with systemic pesticides (conventional viticulture)

1-Historical subjects related to difficulties for **alcoholic fermentation**

- **Inhibition of yeast populations:**

Phthalimide (captan, folpet)
Sulfonamides (Dichlofluanid)
Phthalic derivative (chlorothalonil)

- **Difficulties to completion of alcoholic fermentation:**

Triazoles, Imidazoles (triadimefon, Flusilazole ...)
Carbamic acid derivative (thiophanate-methyl)

- **Little inhibitory effects of MLF**

- **Limited impact of copper residues on alcoholic fermentation development**

2-Sulfur olfactory defects sulfur in wines related to the application of pesticides

Active ingredient	Type	Commercial name	Sulfur off odors
Lannate	Insecticide	Méthomyl	CH_3SH, CH_3-S-S-CH_3
Acephate	Insecticide	Orthène	CH_3SH, CH_3-S-S-CH_3
Dithiocarbamate	Fungicide	Mancozèbe, Manèbe… Thirame	H_2S CS_2 COS
Sulfur	Fungicide		H_2S
Folpet	Fungicide	Folpel, Folpet…	CS_2 COS

3-Modification of aromatic components, polyphenolic the quality of grapes and wines

Impact of cupric protection on copper residues and the impact on wine varietal aroma

Copper reactivity with sulfur compounds : thiols or Sulfanyl

Due to reactivity of residue on aroma component during alcoholic fermentation

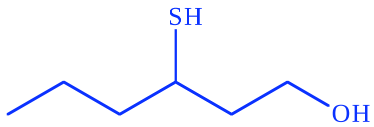
Thiol compounds or sulfanyl

- Some thiols responsible for off-flavors (CH_3SH, CH_3CH_2SH)
- Antioxydative compound of grape and wines : glutathione
- Highly volatile thiol compounds frequently presenting powerful and penetrating aromas contributing to the specific flavor of numerous wines (white, red, dessert wines)

Varietal thiols content in the wines of various grape varieties

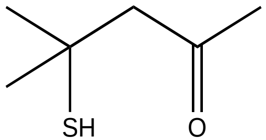
Sauvignon

	4MSP	3SH	3SHA
Champagne wines	nd	250-640	
Colombard	nd	400-1100	20-60
Gewürztraminer	4-15	1000-3300	0-10
Macabeo	nd	nd	15-20
Merlot (rosé wines)	nd	0-7000	nd
Muscadet	nd	50-450	nd
Muscat	5-30	100-900	nd
Negrette	1-4	800-1500	8-22
Petit Manseng	nd	500-5000	50-150
Pinot Blanc	0-1	90-250	nd
Pinot Gris	0-2	310-1050	2-50
Riesling	2-10	400-1000	0-10
Sauvignon Blanc	5-60	250-15000	10-1000
Semillon	0-5	100-2000	10-100
Botrytised wines	0-100	1000-20000	nd
Sylvaner	0.2-0.5	60-150	nd
Verdejo	nd	nd	40-50



3-sulfanylhexanol (3SH)

(grapefruit)



Olfactory perception threshold: 0,8 ng/l

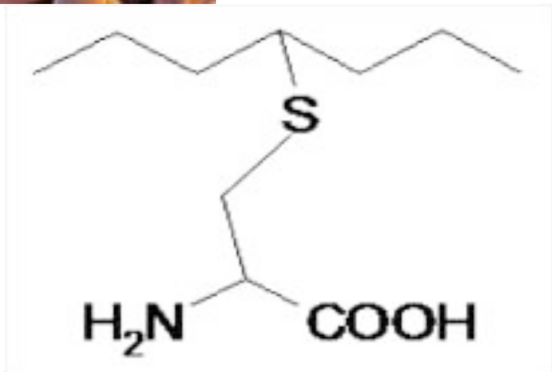
4-sulfanyl-4-methylpentan-2-one

Cabernet Sauvignon

Varietal thiols release during alcoholic fermentation by *S.cerevisiae* from aroma precursors

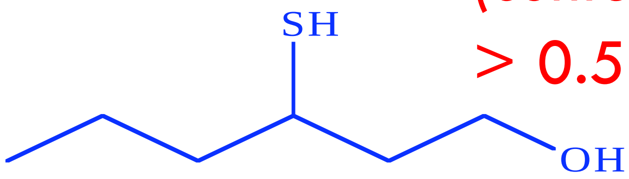
Saccharomyces cerevisiae

Trapping by Cu^{+} (content residue > 0.5-1 mg/L)



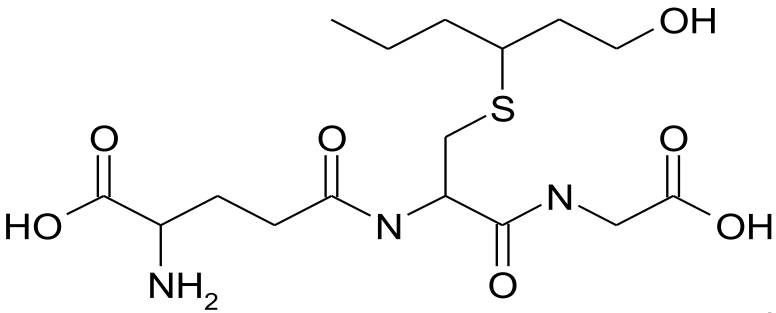
S-3-hexan-1-ol-L-cystein (P3MH)

$\alpha\beta$ elimination :
ß-lyase



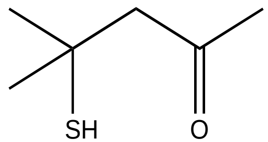
3-sulfanylhexan-1-ol

$\alpha\beta$ elimination :
ß-lyase



carboxypeptidase
glutamyltranspeptidase

S-3-hexan-1-ol-glutathione

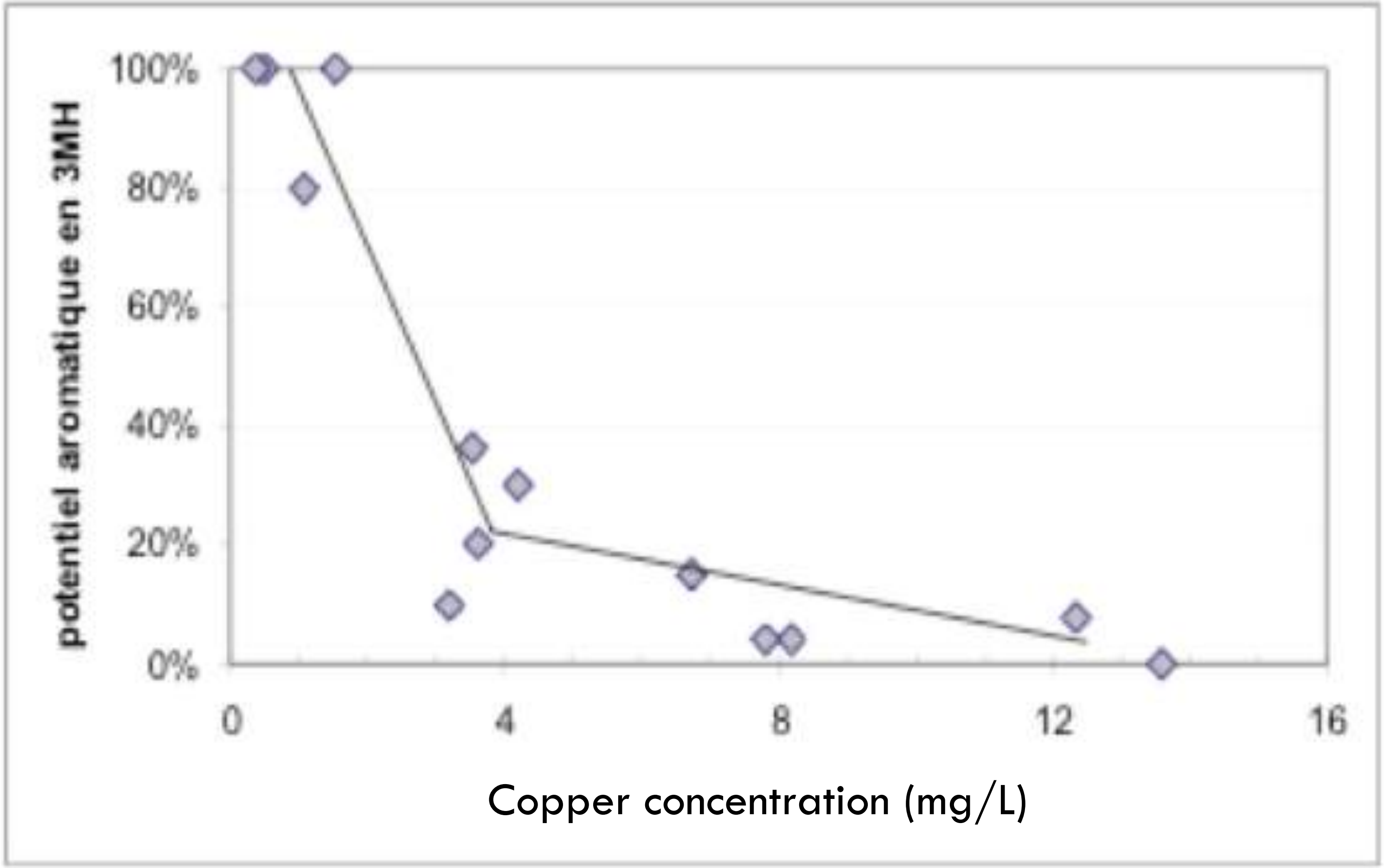


Olfactory perception threshold: 0,8 ng/l

4-sulfanyl-4-methylpentan-2-one

Tominaga et al. 1998
Murat et al. 2001, Hatzidimitriou et al 1996

Consequences of copper treatments on the content in 3-sulfanylhexanol (3SH) in wines Colombard related the residue of copper (2001-2003)



ITV Gaillac, Serrano et al. 2004

Incidence of localized protection of fungicide on foliage on the residue of grape juices

	Copper (mg/L)	
	Conv spraying	Spraying on leaves
Cabernet Sauvignon Margaux (1997)	13,6	2,4
Cabernet Sauvignon Margaux (1998)	11,6	1,4
Merlot Pomerol (1997)	16,7	3,8
Merlot Pomerol (1998)	6,4	2,3
Sauvignon blanc Entre-deux-Mers (1997)	7,3	3,5

Vitis 40 (2) 93-99, 2001

Limited impact of copper spraying only directed on the leaves

		3-mercaptohexanol (ng l^{-1}) 1996	1997	1998	
Cabernet Sauvignon					
CS (1)	none[b]	519 (100)	930 (100)	2137 (100)	A
CS (2)	3 x 3000[c]	-	340 (37)	136 (6)	-
CS (3)	2 x 3000	30 (6)	340 (37)	152 (7)	B
CS (4)	3000	206 (40)	590 (63)	467 (22)	B
CS (5)	3000 (grapes protected)	-	1087 (117)	1770 (82)	-
Merlot					
M (1)	none[b]	293 (100)	4550 (100)	357 (100)	A
M (2)	2 x 3000[c]	120 (41)	980 (22)	117 (33)	B
M (3)	3000	397 (135)	1870 (41)	173 (49)	AB
M (4)	3000 (spraying leaves only)[d]	-	5370 (118)	286 (80)	-

Vitis 40 (2) 93-99, 2001

The copper treatments of the vine and grape composition and wine

- Decreased of content in thiols in wine associated with treatment of vine with copper
- **Impact from the « grape closure » stage**
- No enological damage **with treatments selectively applied to the foliage at veraison**
- Depends on the **dose of copper applied during the vegetative stage**

3-Modification of aromatic components, polyphenolic the quality of grapes and wines

Other effects of copper sprayings due to **phytotoxic properties**

Impact on berry size (smaller berries)
Impact on sugar content (diminished)
Impact on anthocyanin concentrations (diminished)

Under specific conditions of increased copper sprayings

…but non longer at spraying treatments < 1kg cu/ha

Vitis 40 (2) 93-99, 2001

3-Modification of aromatic components, polyphenolic the quality of grapes and wines

Other examples of fungicide impacts

Treatment with various fungicides and impact on wine fermentative aroma (Molina et al. 1999)

-Treatments with sterol and impact on composition monoterpene composition (Aubert et al., J.Sci.Vigne Vin, 1997)

No information currently concerning Low Concern Products : basic substances (Example: willow bark (wicker), horsetail, nettle... used for specified preparation methods

4) Fungicide treatments and limitation of grape microflora

Negative correlation between copper concentrations and bacterial density

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Grape berry bacterial microbiota: Impact of the ripening process and the farming system

Guilherme Martins [a,b,*], Cécile Miot-Sertier [a], Béatrice Lauga [c], Olivier Claisse [a], Aline Lonvaud-Funel [a], Guy Soulas [a], Isabelle Masneuf-Pomarède [a,b]

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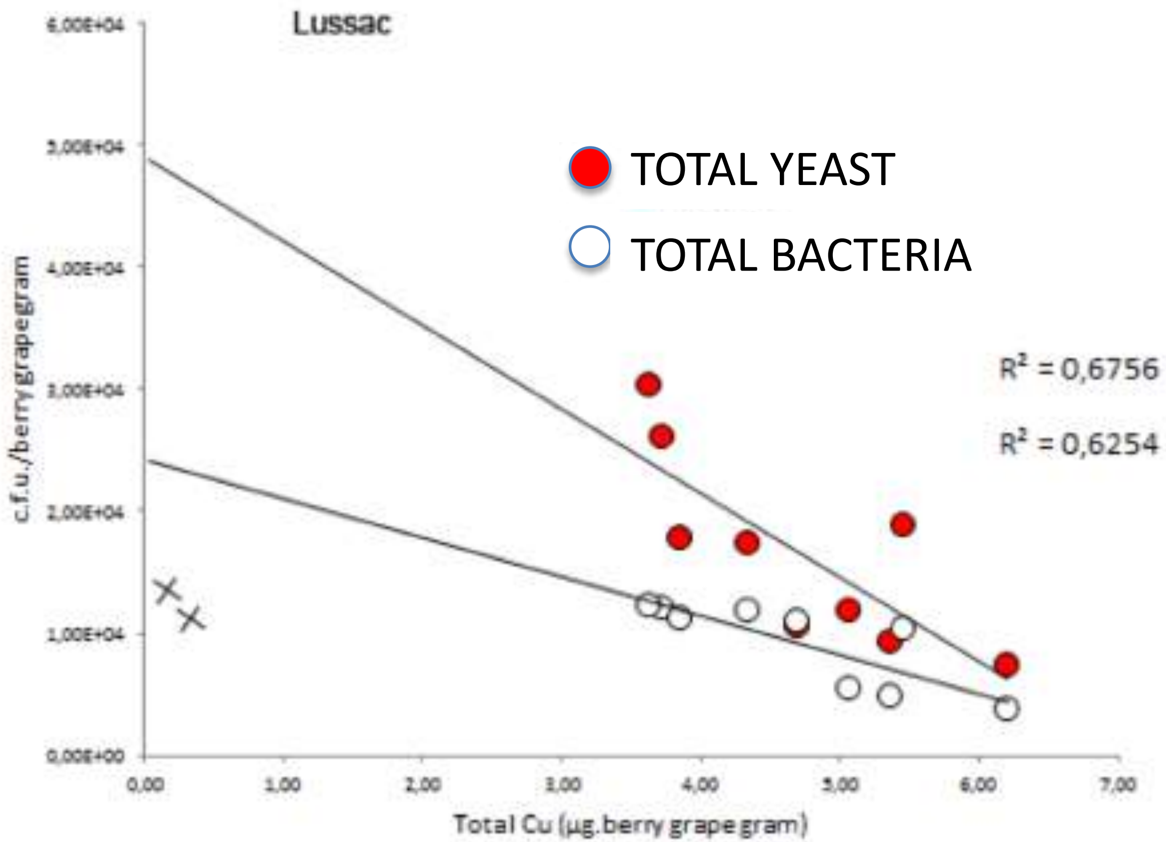
Correlation of copper content on grapes with diminution of microbial population density at veraison



Martins, G., Vallance, J., Mercier, A., Albertin, W., Stamatopoulos, P., Rey, P., et al. (2014). Influence of the farming system on the epiphytic yeasts and yeast- like fungi colonizing grape berries during the ripening process. *Int. J. Food Microbiol*. 177, 21–28.

Main parameters related to organic/conventional spraying in relation with grape and wine component

- Protection of vines against pathogens
- Pesticide (organic, not organic) and grape/wine composition, microbiological aspects
- **Pesticide and grape and wine residues and their limitation**

Parameters influencing fungicide residues on grapes

- Number of treatments
- Waiting delay between the last application and harvest and kinetics of degradation of the fungicide
- Persistence of the product
- Location of phytosanitary treatment (all vegetation, grapes, only the foliage …)
- Type of vinification

Impact of the waiting period on the residue (ancient families of fungicides)

Type fungicide	Nb applications	during Last spraying (mg/Kg)	20 days after (mg/Kg)	50 days after (mg/Kg)
mancozèbe	6 à 8	14 à 29	3,6 à 10	3,4 à 10,2
dichlofluanide	6 à 8	12,8 à 44	7 à 19,6	1,7 à 12
Folpel	6 à 8	5,8 à 40,5	2,4 à 20,5	2,6 à 12,8
vinchlozoline	5	2,7 à 6,2	1 à 2	0,3 à 1,6
iprodione	5	2,0 à 6,7	1,3 à 4	0,6 à 3
procymidone	5	4,4 à 8,7	2,2 à 4,4	1 à 4,4
Soufre	6	14 à 25	6 à 7	5 à 8

Lemperle (1989)

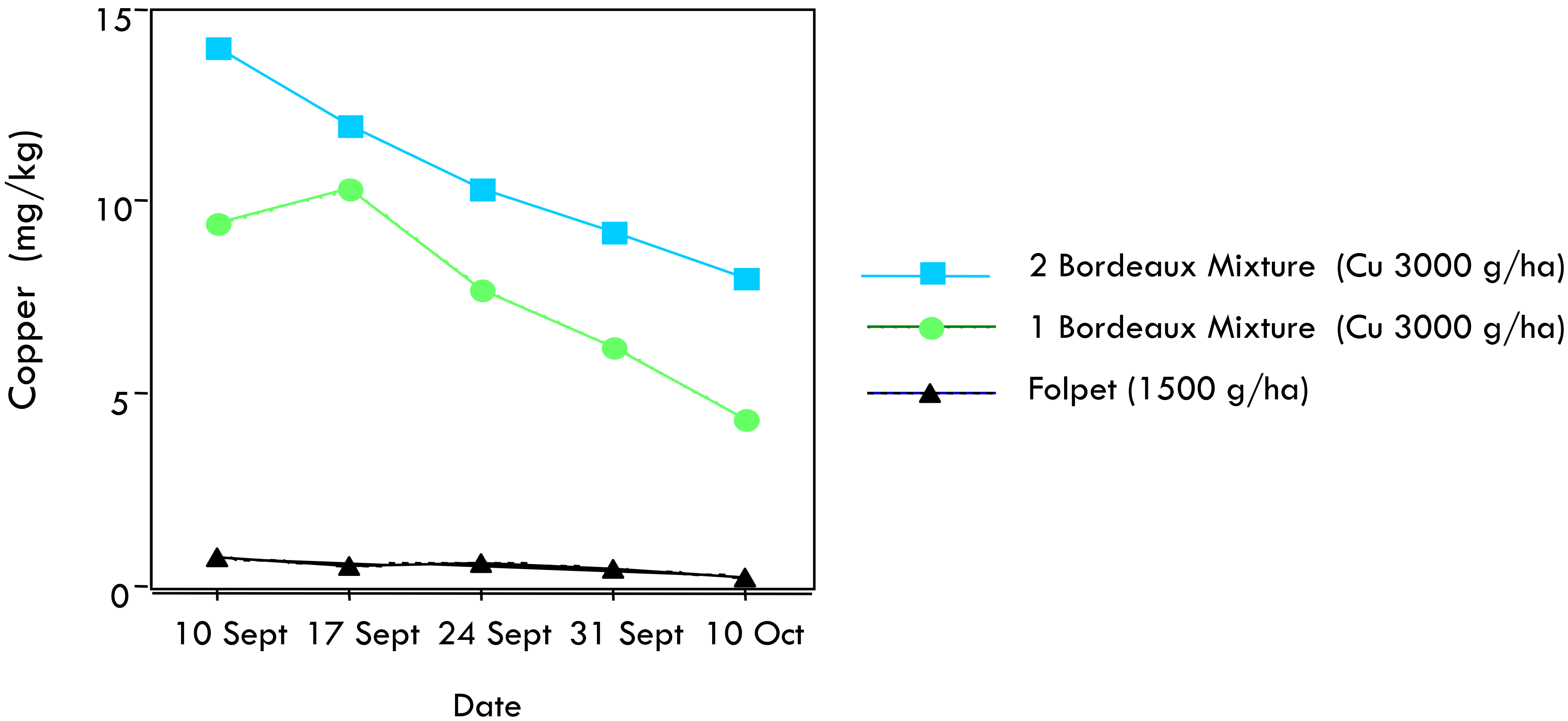
Big concern on fungicides with Carcinogenic, Mutagens, Reprotoxics and endocrine disrupters pesticides

Impact of the waiting period on the residue (more recent families of fungicides)

	interval of days after the last application					
	0-1	6 à 7	14	21	28	Time Half life
azoxystrobine (mg/kg)	0,5	0,31	0,23	0,19		15,2 days
cyprodinil (mg/kg)	5,54	2,27	1,69	1,08	1,03	12 days
fluazinam (mg/kg)	1,21	0,51	0,15	0,04		4,3 D
fluodioxonil (mg/kg)	1,8	1,6	1,46	1,2	0,78	24 D
kresoxim-methyl (mg/kg)	0,15	0,08	< 0,01	<0,01		
pyrimethanil (mg/kg)	1,6	1,3	1,24	1,2	1,1	57 D
tebuconazole (mg/kg)	4,8	3,16	2,7	0,7	0,4	4,8 D

Lemperle (1989)

Evolution of the copper content at the surface of the berries during grape maturation



Cabernet Sauvignon

Vitis 40 (2) 93-99, 2001

Evolution of the copper content at the surface of the berries during grape maturation

Name of active ingredient[a]	Chemical formula
Basic copper sulfate	$CuSO_43Cu(OH)_2$
Basic copper carbonate	$CuCO3Cu(OH)_2$
Copper chloride	$CuCl_2$
Copper hydroxide	$Cu(OH)_2$
Copper oxide	Cu_2O
Copper oxychloride	$3Cu(OH)_2CuCl_2$
Copper oxychloride sulfate	$(Cu_4(OH)6(SO_4))$
Copper sulfate pentahydrate[2]	$CuSO_45H_2O$

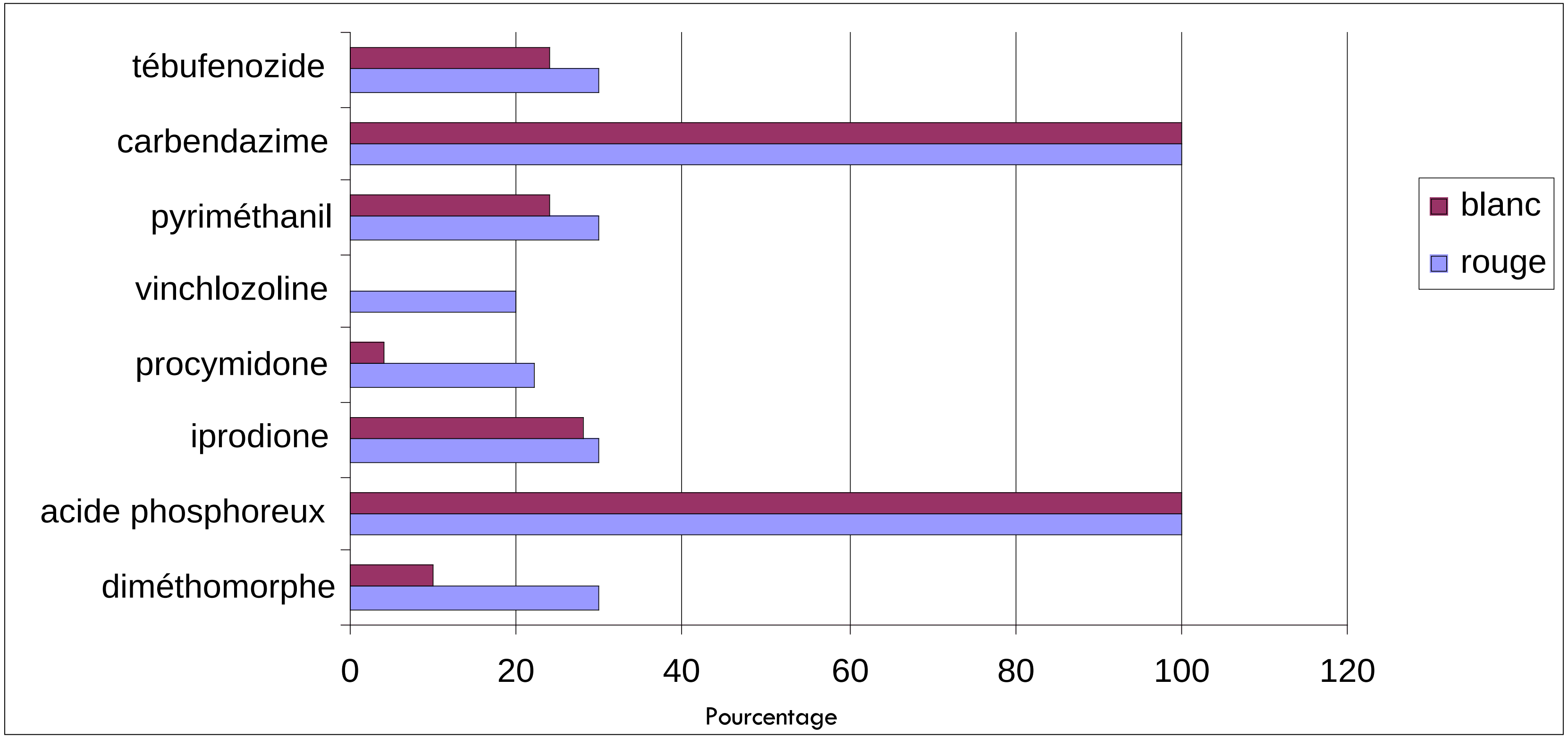
DIFFERENCE ON RESIDUES DEPENDING ON COPPER FORM

Copper spraying depending on the type of fungicide

	Copper residues (mg/L)	
	B.B. industrial	B.B. extemporaneous
Cabernet Sauvignon Entre-deux-Mers	24.1	9.2
Cabernet Sauvignon Margaux	17.9	5.3
Merlot Pomerol	9	8.3
Sauvignon blanc Entre-deux-Mers	8.4	5

2 copper sprayings (3000 g/ha)

Type of vinification and transfert of pesticide residues
Grape wine



Cantagrel, BNIC

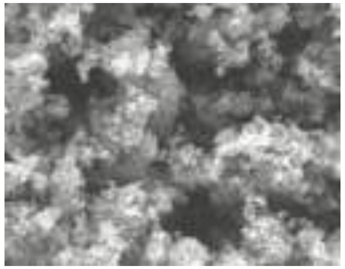
Strategies for limiting grape fungicide residues

- Cleaning grape bunches : not much efficient with water/ acidified water…

- Adsorption of grape residues from musts/wines

    - **Vegetal micronized fibers** (50 à 95 % residues removal, in particular
    - anti-botrytis ones)

    - Zeolithes



- Crystalline aluminosilicates of natural origin or synthesized from silica and aluminium (synthetic zeolites).
- Development of regular-sized pores in the microporous range (< 2 nm).

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