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**SANGUIS JOVIS**

ALTA SCUOLA DEL SANGIOVESE

Panagiotis Arapitsas  
Summer School Sanguis  
Jovis 2018  
Climate Change e vite

# Titolo della presentazione

Σύλλογος μεγάλος δεν υπάρχει άλλος  
δεν υπάρχει άλλος πιο δυναμικός  
και χιλιάδες φίλοι, μόλις δουν τριφύλλι,  
"ζήτω!", λένε, "ο Παναθηναϊκός!"

Παναθηναϊκέ-Παναθηναϊκέ

Παναθηναϊκέ μεγάλε και τρανέ.

Παναθηναϊκέ-Παναθηναϊκέ

πρωταθλητή σ' όλα τα σπορ παντοτινέ.

πρωταθλητή σ' όλα τα σπορ παντοτινέ.

Σ' έχουνε δοξάσει οι γνωστοί σου άσσοι  
που λεβέντες είναι όλοι με καρδιά.

Χαίρεται η Ελλάδα που 'χει τέτοια ομάδα,  
που της νίκης έχει πάντα τα κλειδιά.

Παναθηναϊκέ-Παναθηναϊκέ

Παναθηναϊκέ μεγάλε και τρανέ.

Παναθηναϊκέ-Παναθηναϊκέ

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ALTA SCUOLA DEL SANGIOVESE



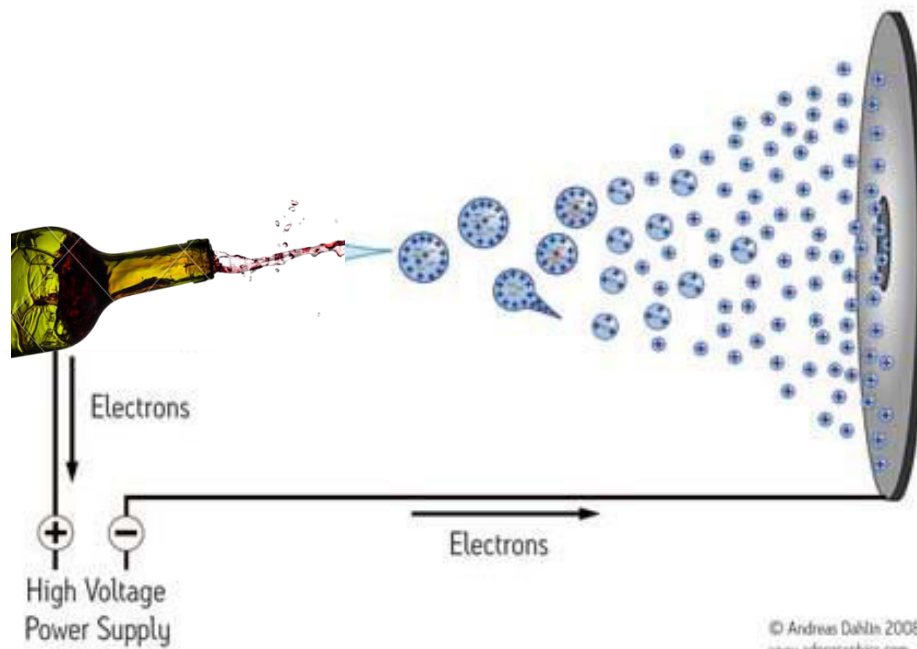
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**CENTRO RICERCA  
& INNOVAZIONE**



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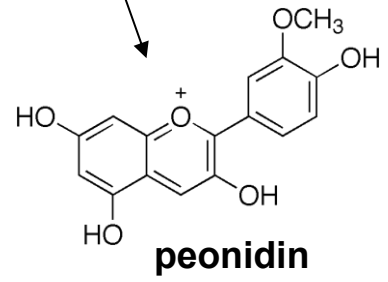
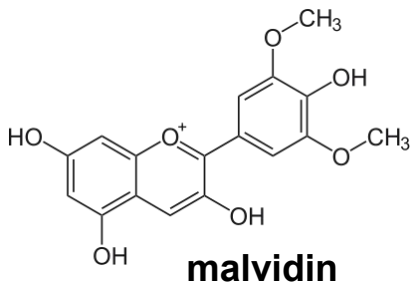
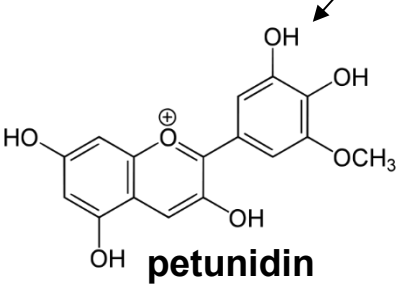
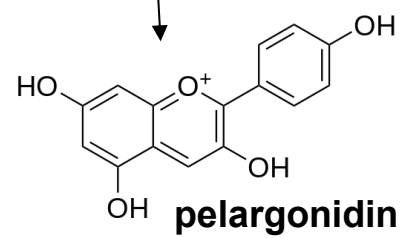
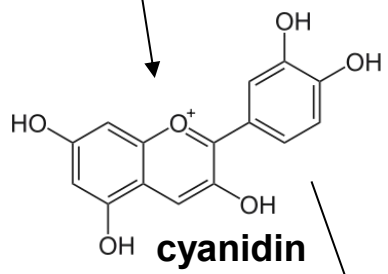
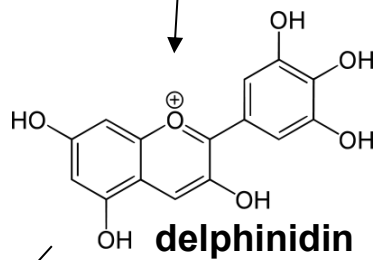
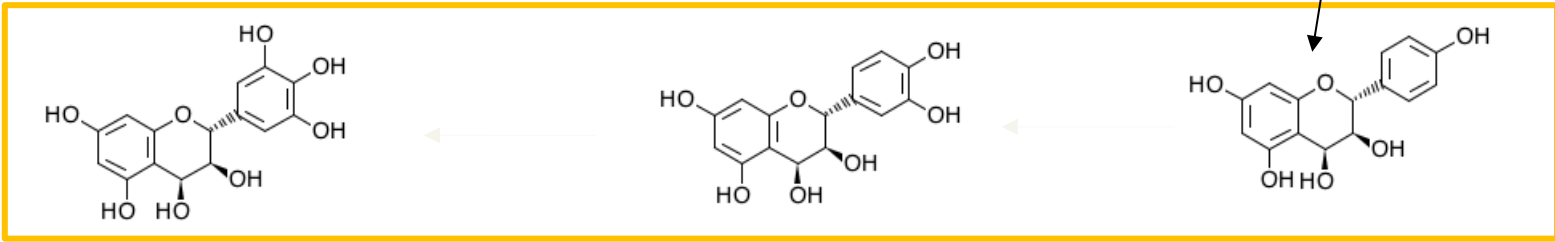
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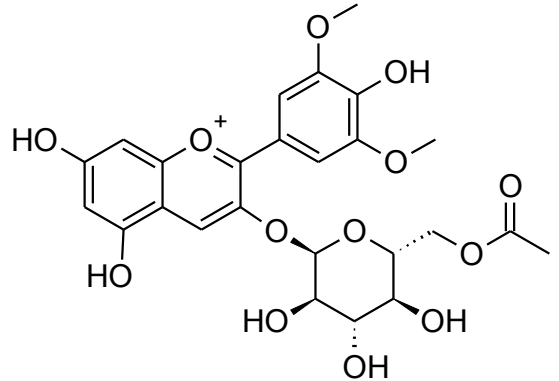
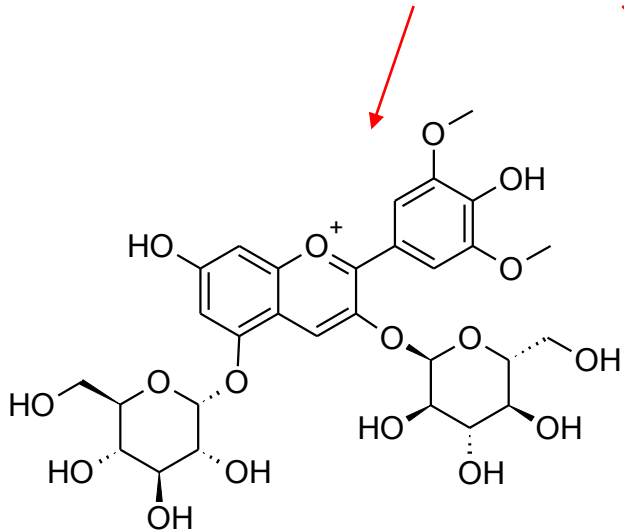
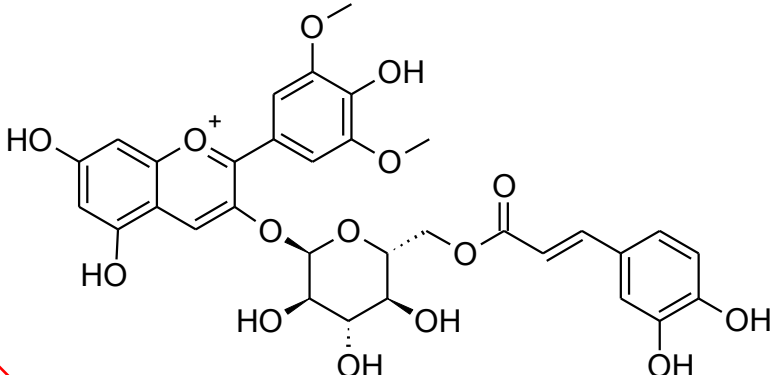
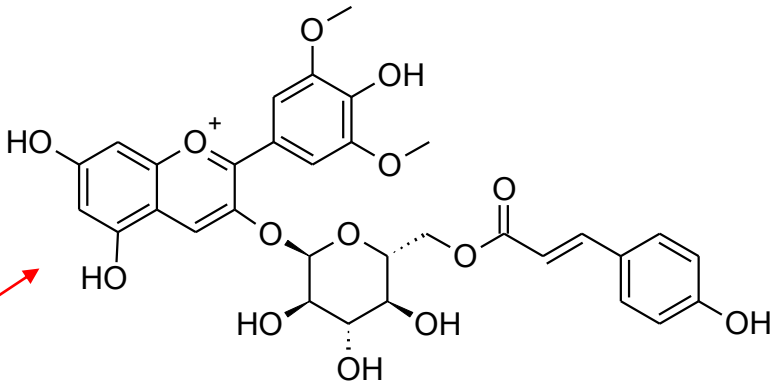
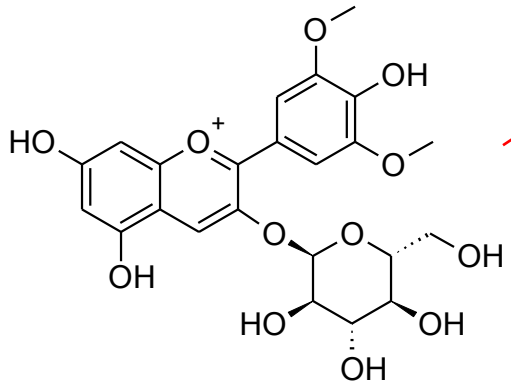
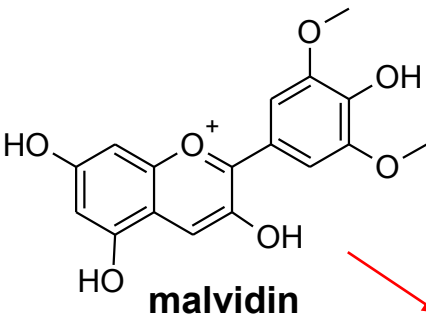
**Wine chemistry**





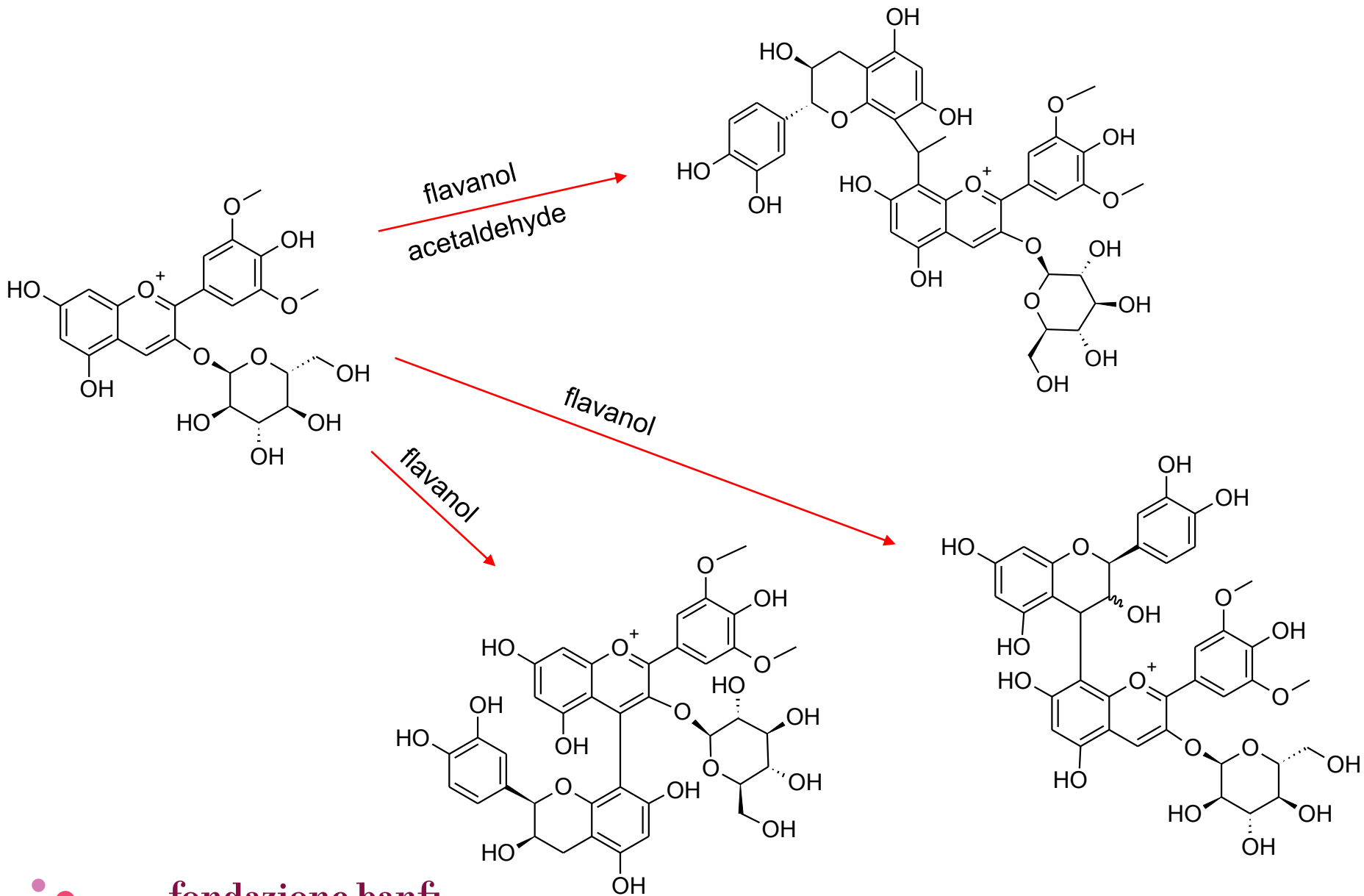
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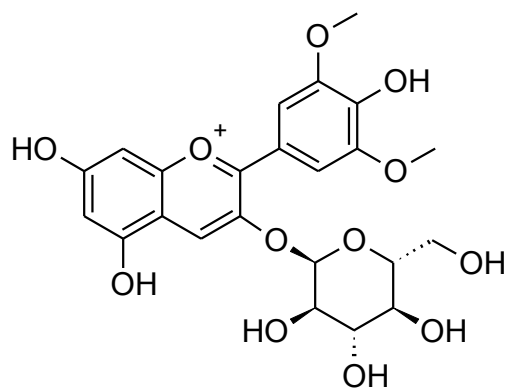
**Wine pigments**



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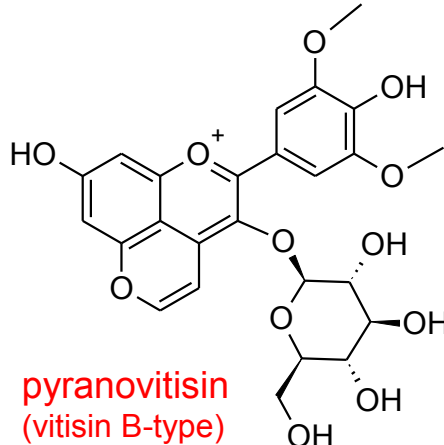
**Wine pigments**





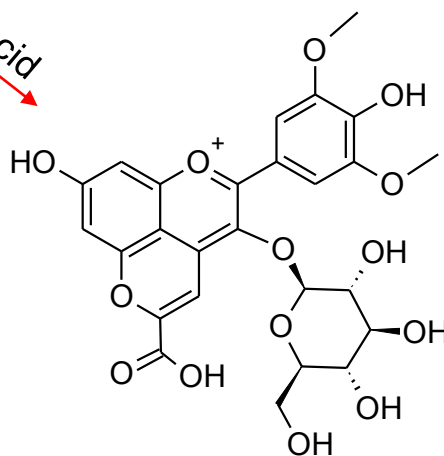
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pyranovitisin  
(vitisin B-type)

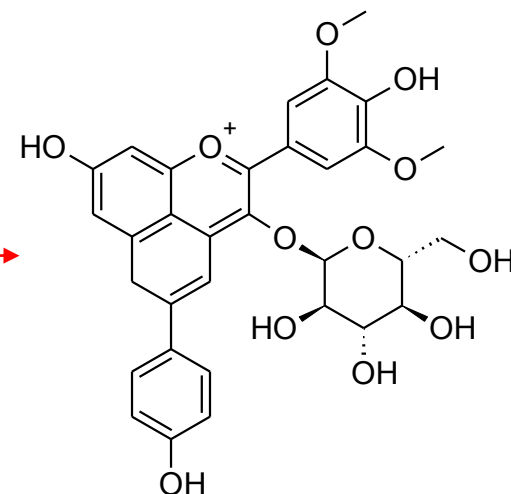


*p*-coumaric acid

pyruvic acid



carboxypyranovitisin  
(vitisin A-type)



Pinotin type

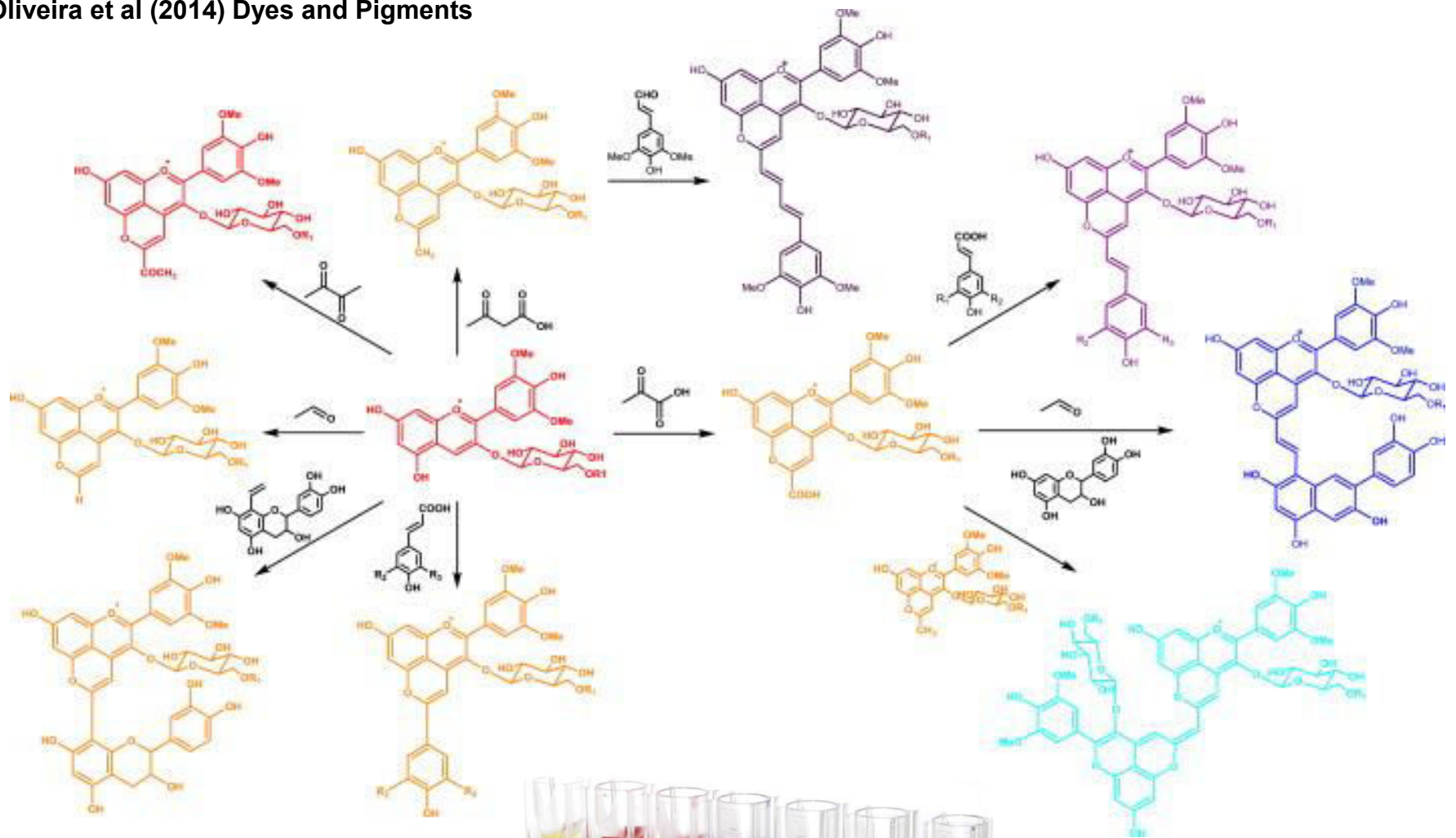


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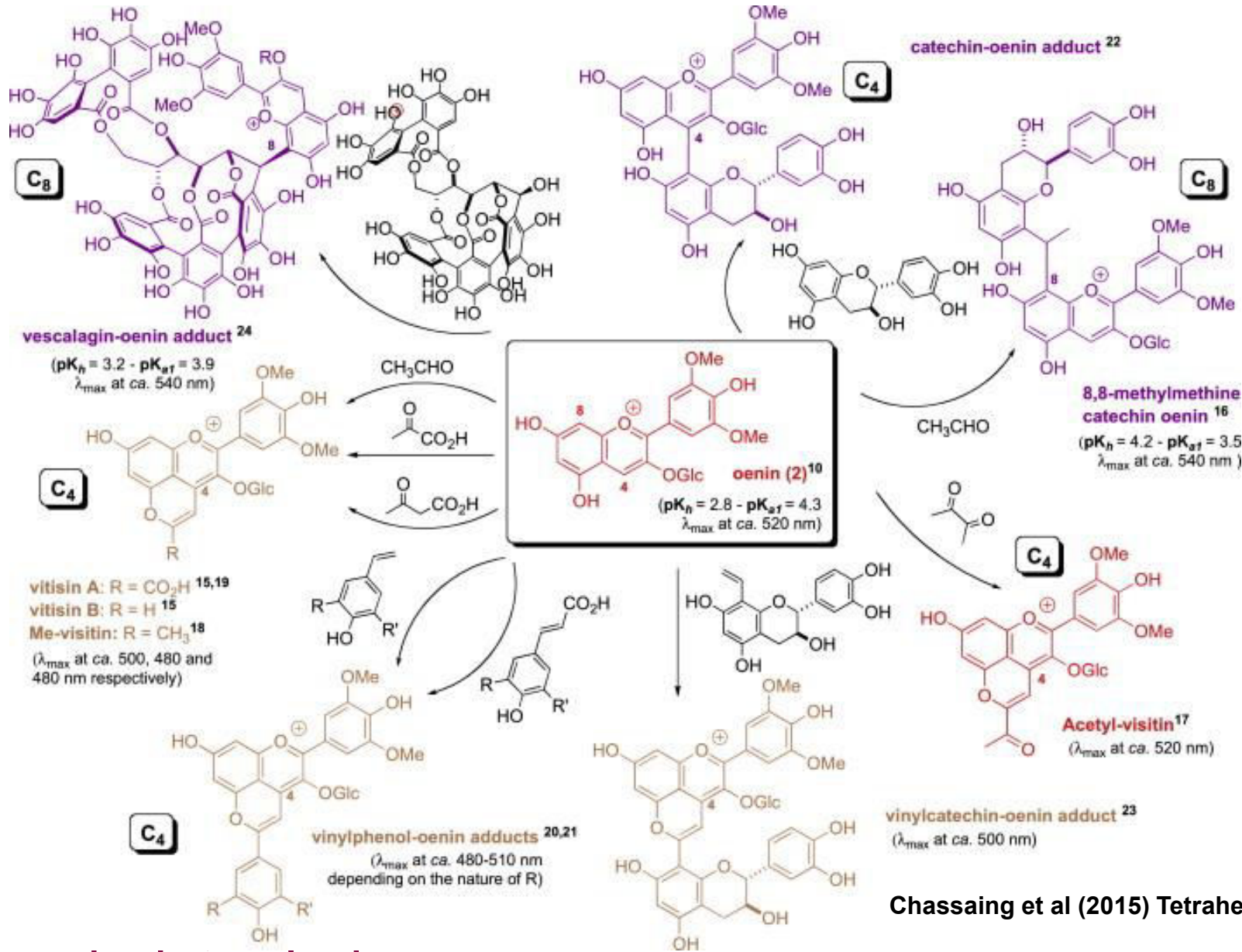
Wine pigments





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**Wine pigments**



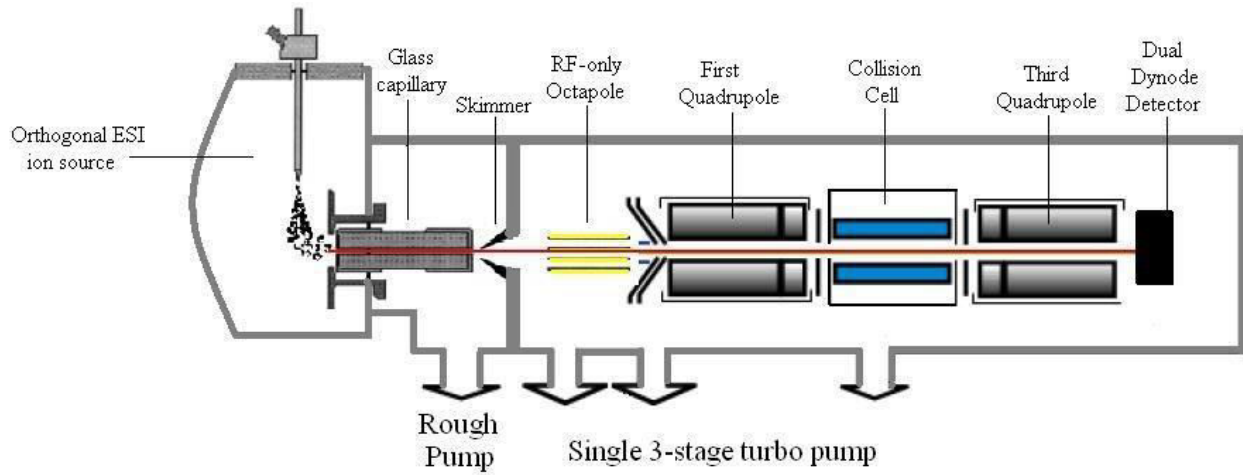
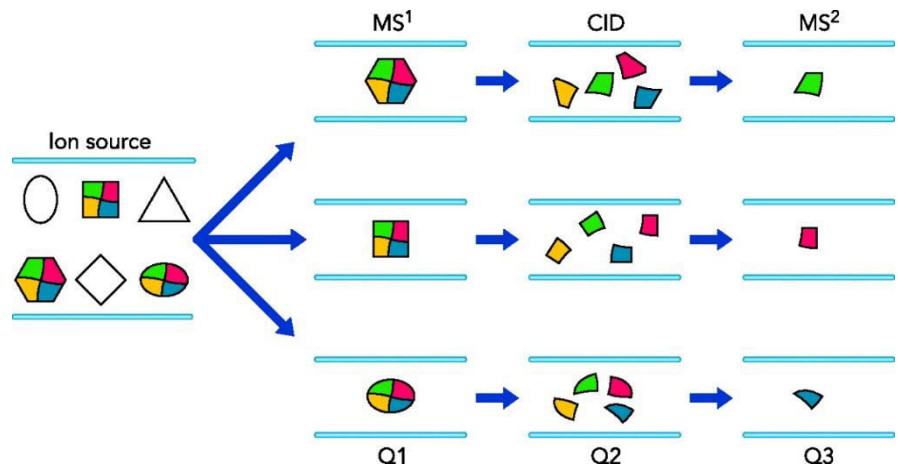
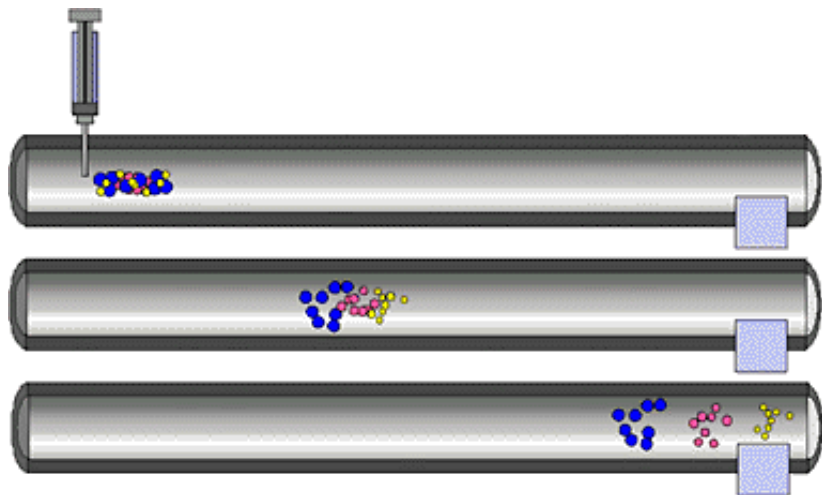
Chassaing et al (2015) Tetrahedron



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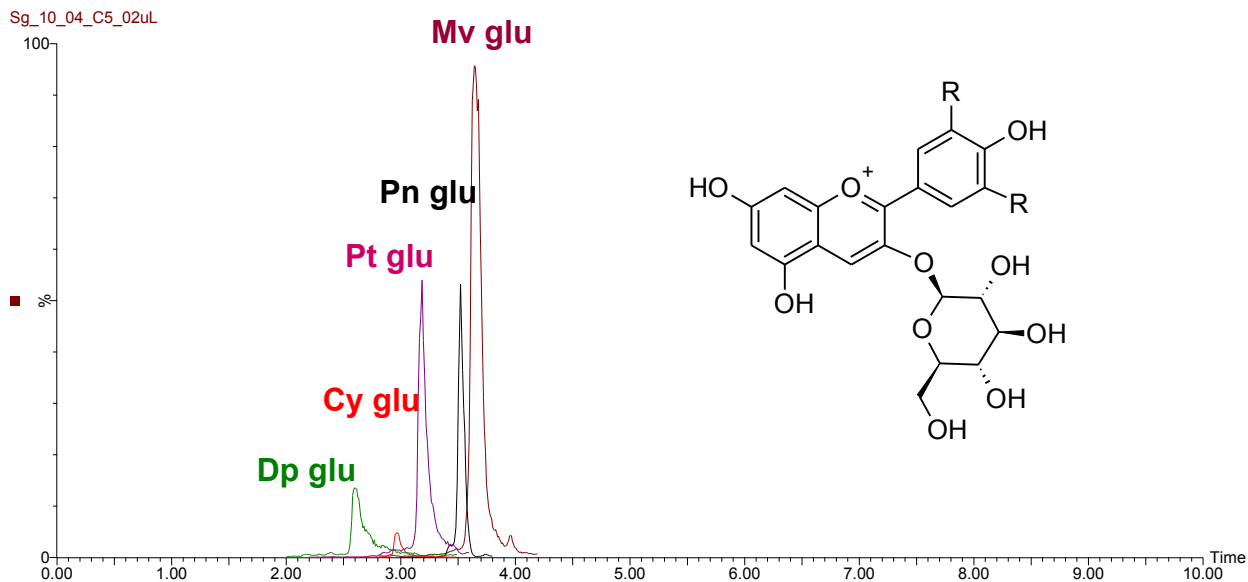
**Wine pigments**



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**Mv** : malvidin  
**Pn** : peonidin  
**Pt** : petunidin  
**Cy** : cyanidin  
**Dp** : delphinidin



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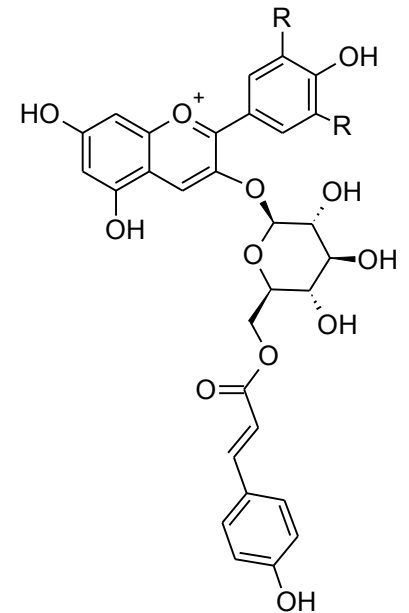
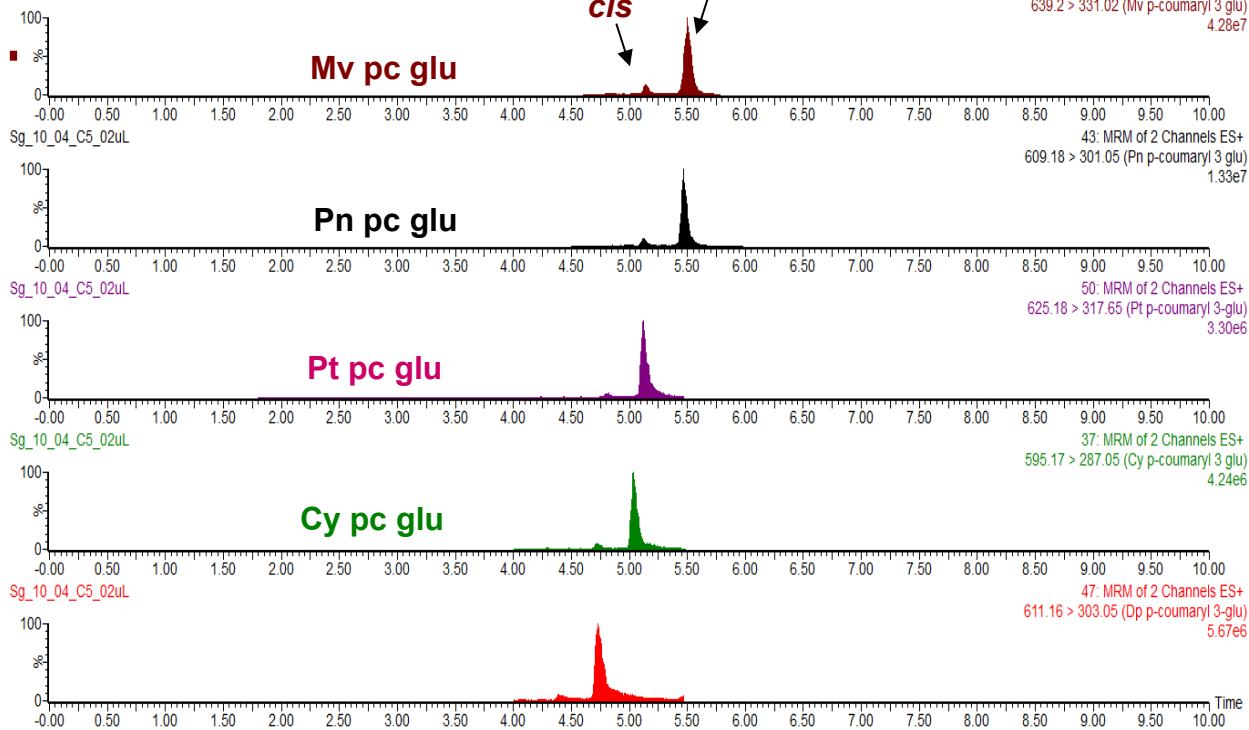
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**Wine pigments UPLC-MS/MS**



Sagrantino 2010 - Thesis 01 - Conc x5 - Inj 02 uL

Sg\_10\_04\_C5\_02uL



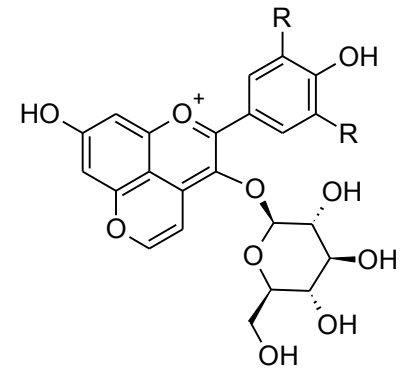
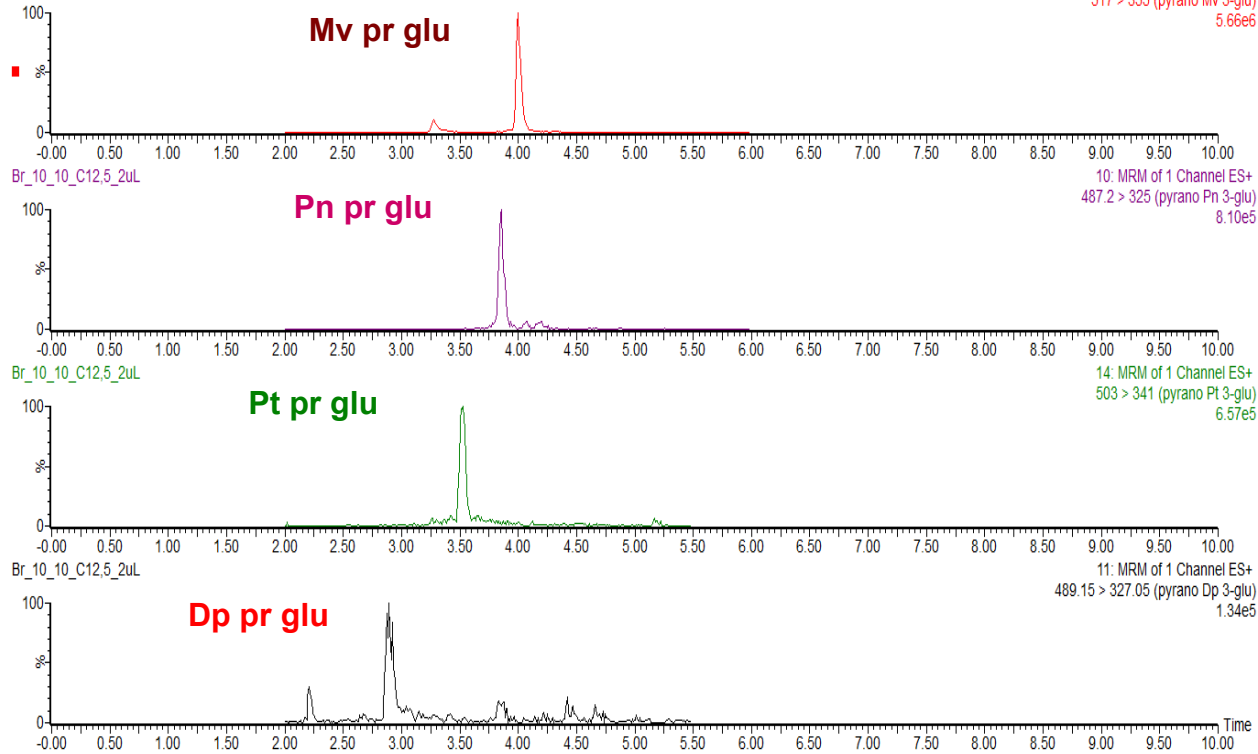
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**Wine pigments UPLC-MS/MS**



Brunello 2010 - Thesis 10 - Conc x12.5 - Inj 02 uL

Br\_10\_10\_C12,5\_2uL



vitisins B-type



fondazione banfi

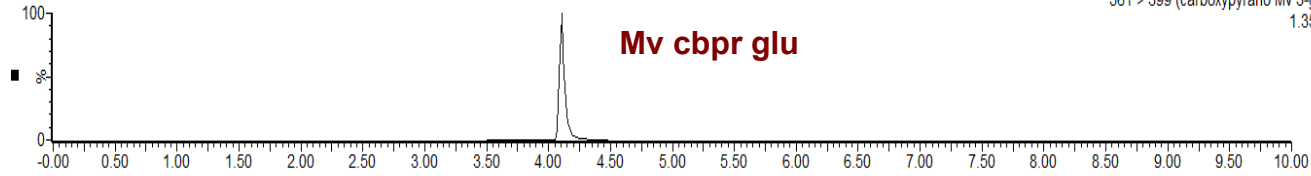
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Wine pigments UPLC-MS/MS

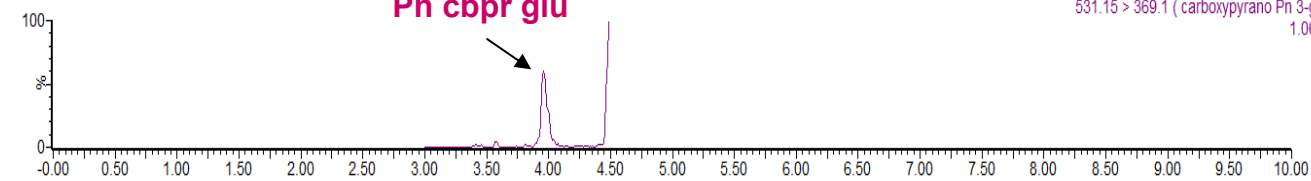


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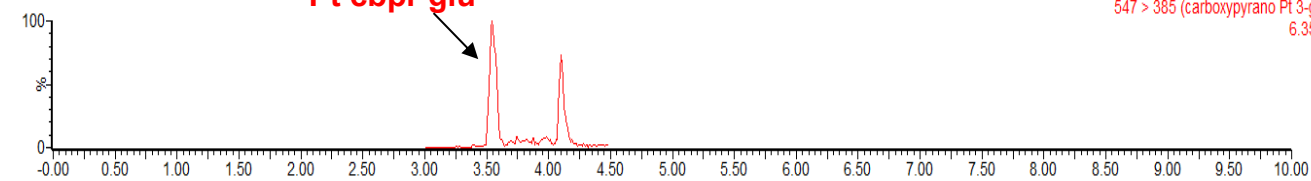
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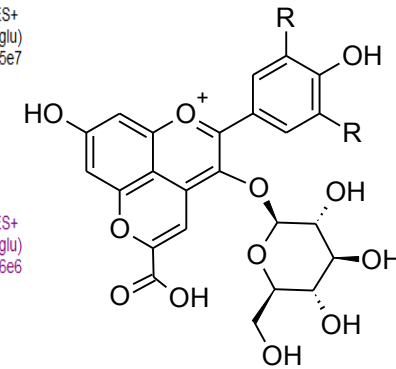
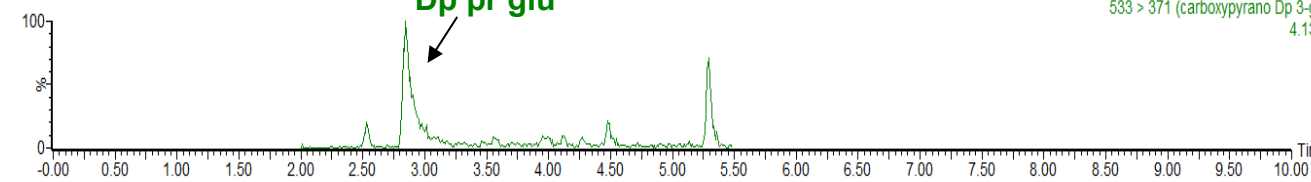
Sg\_10\_05\_C5\_02uL



Sg\_10\_05\_C5\_02uL



Sg\_10\_05\_C5\_02uL



vitisins A-type



fondazione banfi

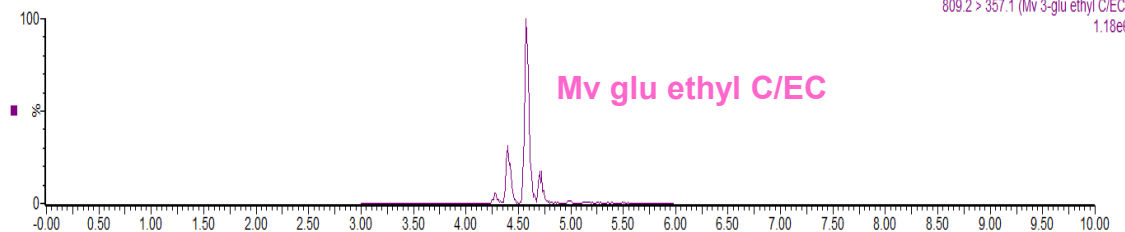
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Wine pigments UPLC-MS/MS

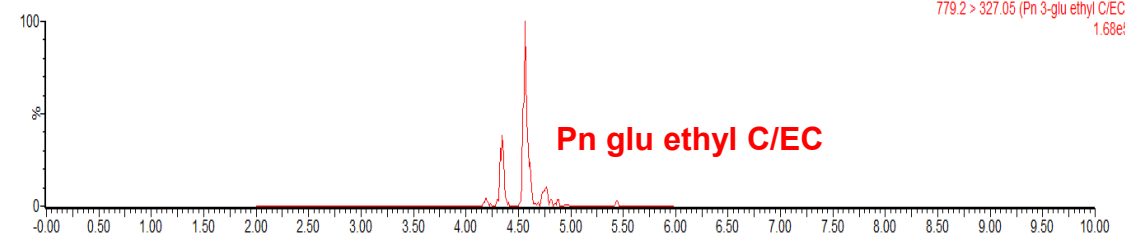


Sagrantino 2009 - Thesis 02 - Conc x5 - Inj 02 uL

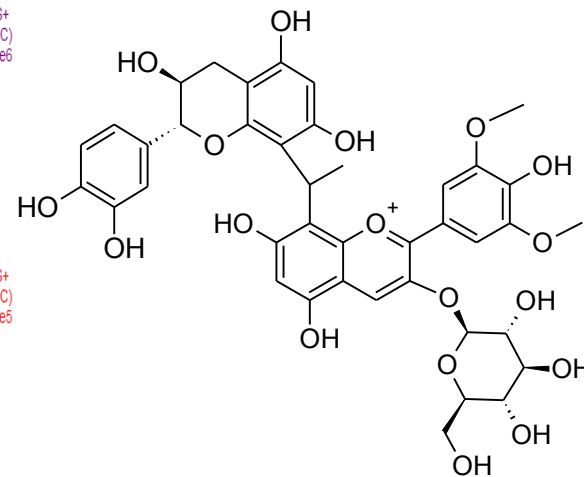
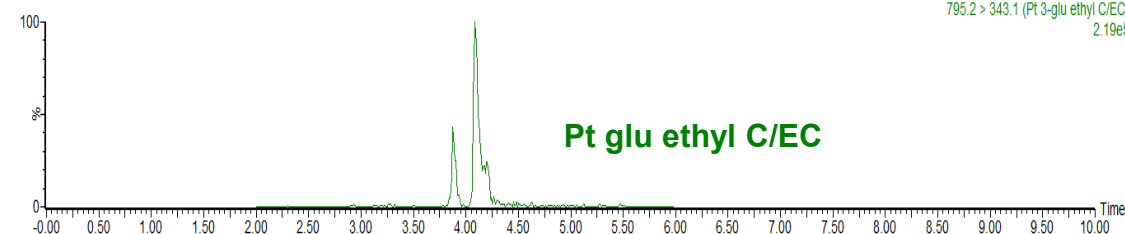
Sg\_09\_02\_C5\_02uL



Sg\_09\_02\_C5\_02uL



Sg\_09\_02\_C5\_02uL



ethyl-linked  
flavano-anthocyanins



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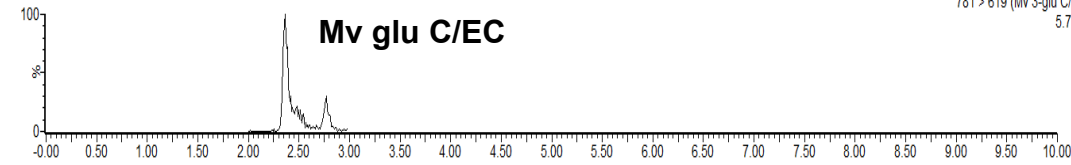
**Wine pigments UPLC-MS/MS**



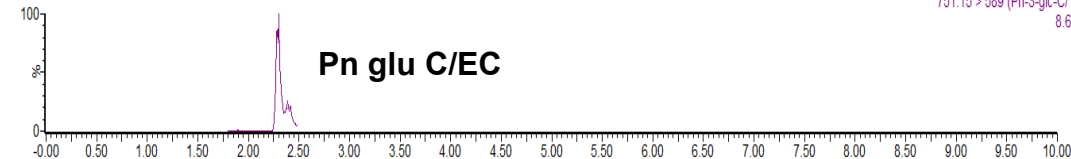


Sagrantino 2009 - Thesis 07 - Conc x5 - Inj 02 uL

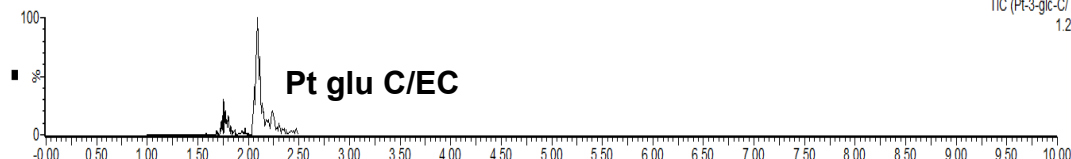
Br\_10\_02\_C12,5\_2uL



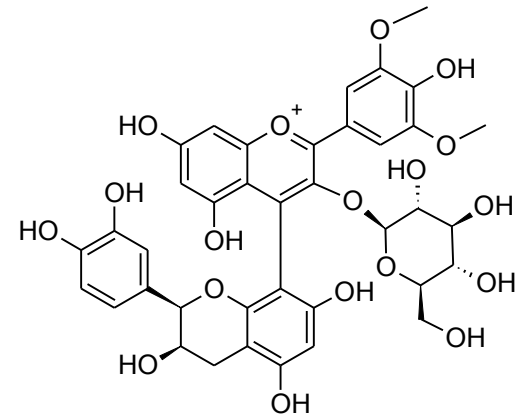
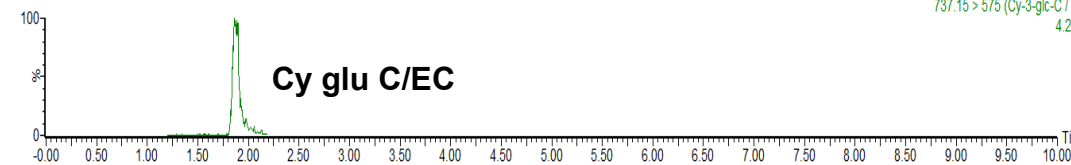
Br\_10\_02\_C12,5\_2uL



Sg\_09\_07\_C5\_02uL



Br\_10\_02\_C12,5\_2uL



direct linked  
flavano-anthocyanins



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**Wine pigments UPLC-MS/MS**

## Study of Sangiovese Wines Pigment Profile by UHPLC-MS/MS

Panagiotis Arapitsas,<sup>†</sup> Daniele Perenzoni,<sup>†</sup> Giorgio Nicolini,<sup>‡</sup> and Fulvio Mattivi<sup>\*†</sup>

<sup>†</sup>Research and Innovation Centre, Food Quality and Nutrition Department, and <sup>‡</sup>Technology Transfer Centre, Fondazione Edmund Mach, via E. Mach 1, 38010 San Michele all'Adige, Italy

### Supporting Information

**ABSTRACT:** The metabolic pigment composition of Sangiovese wines produced from grapes harvested at 20 different vineyards in Montalcino over three consecutive years (2008–2010) on a semi-industrial scale and of 55 commercial Brunello di Montalcino wines (2004–2007) was studied, using a targeted method capable of analyzing 90 pigments in an 11 min UHPLC-MS/MS chromatographic run. Interesting correlations were shown between various pigments formed during wine aging and those present in Sangiovese grapes. Vitisin B-like pigment and vitisin A-like pigment concentrations would seem to have a good correlation with ethyl-linked and direct-linked flavanol–anthocyanin concentrations, respectively. Moreover, the anthocyanic pattern recognition, genetically controlled by the plant variety, was shown to be inherited by the pigments formed during wine aging.

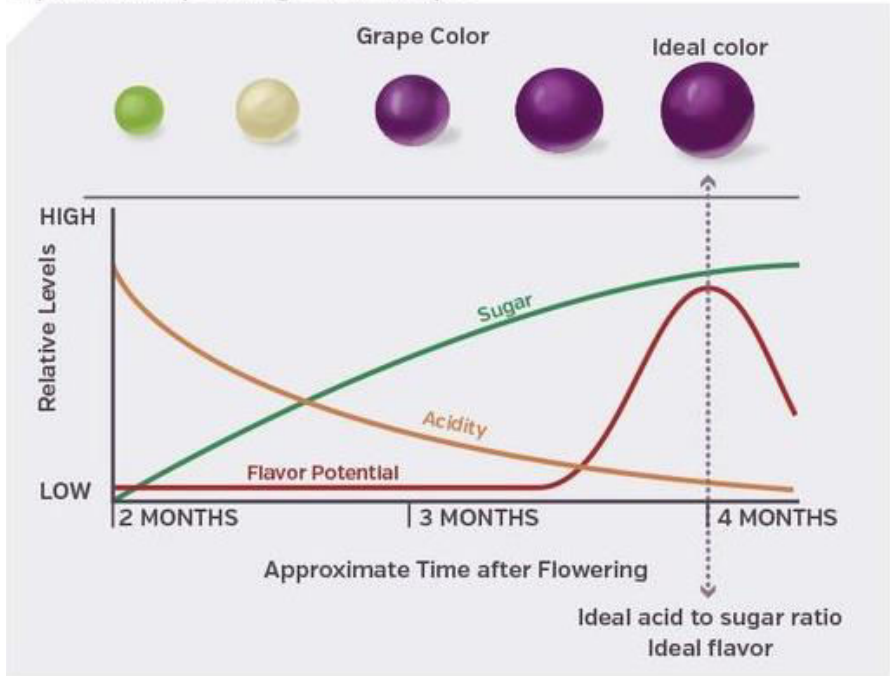
**KEYWORDS:** UHPLC, tandem mass spectrometry, anthocyanins, traceability, wine aging, Sangiovese



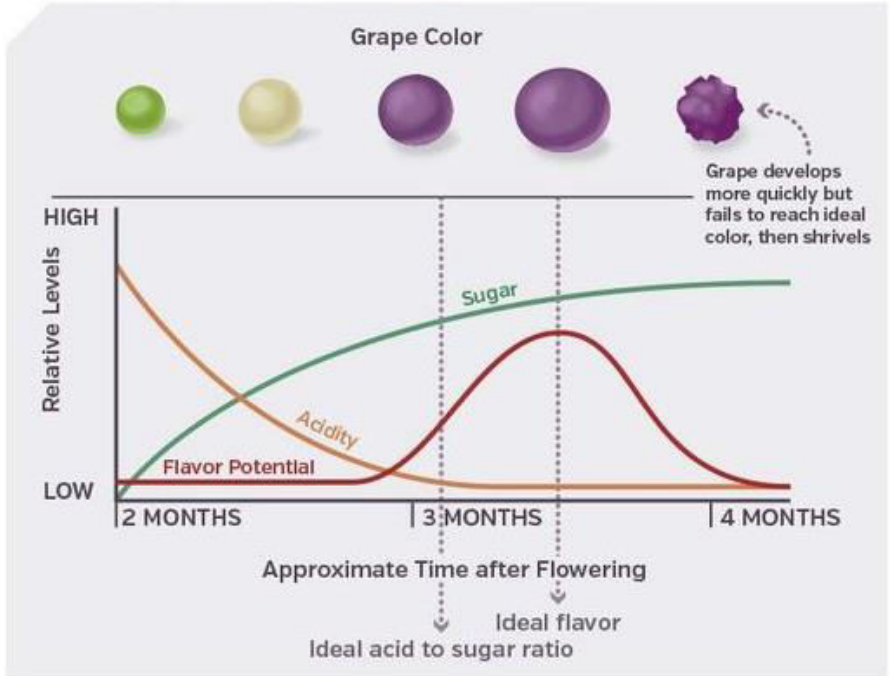
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### Optimal Ripening of a Grape



### Same Grape under Warmer Conditions





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Short communication

### Do white grapes really exist?

Panagiotis Arapitsas <sup>a,\*</sup>, Joana Oliveira <sup>b</sup>, Fulvio Mattivi <sup>a</sup>



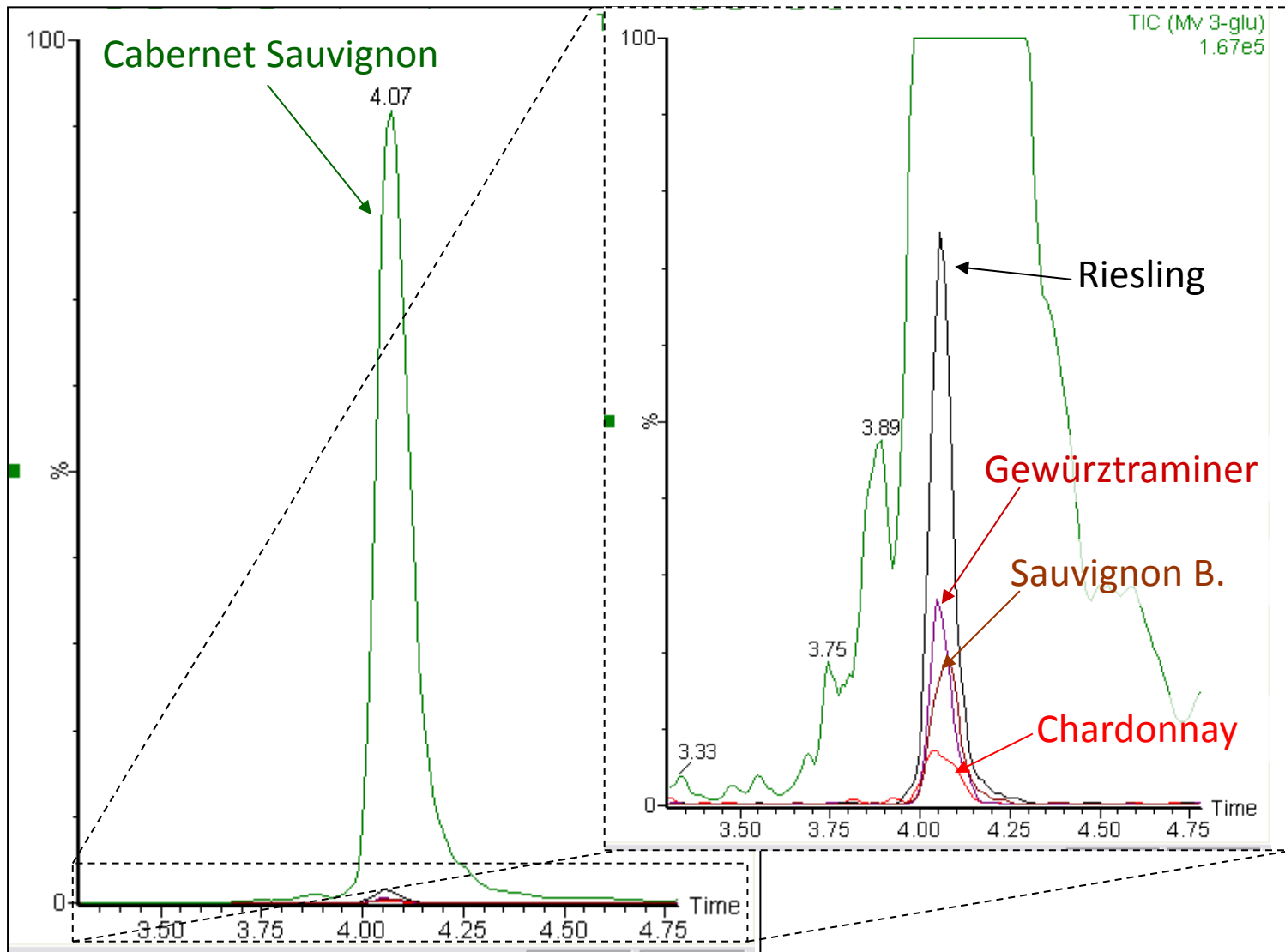
<sup>a</sup> Department of Food Quality and Nutrition, Research and Innovation Centre, Fondazione Edmund Mach (FEM), Via E. Mach 1, 38010 San Michele all'Adige, Italy

<sup>b</sup> Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal



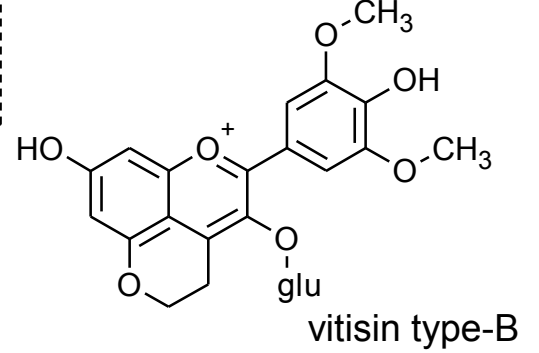
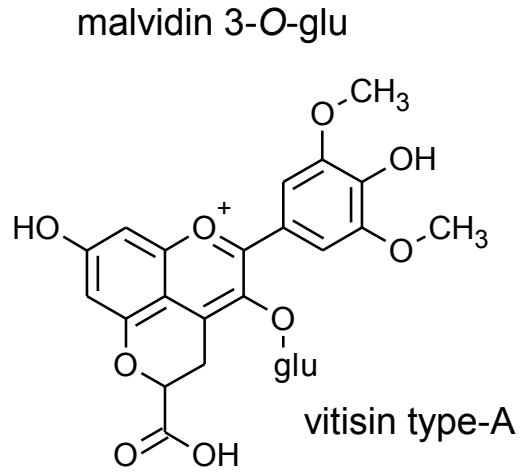
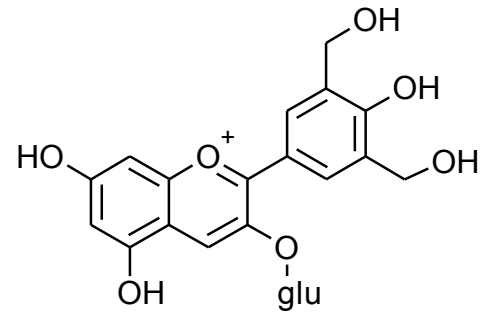
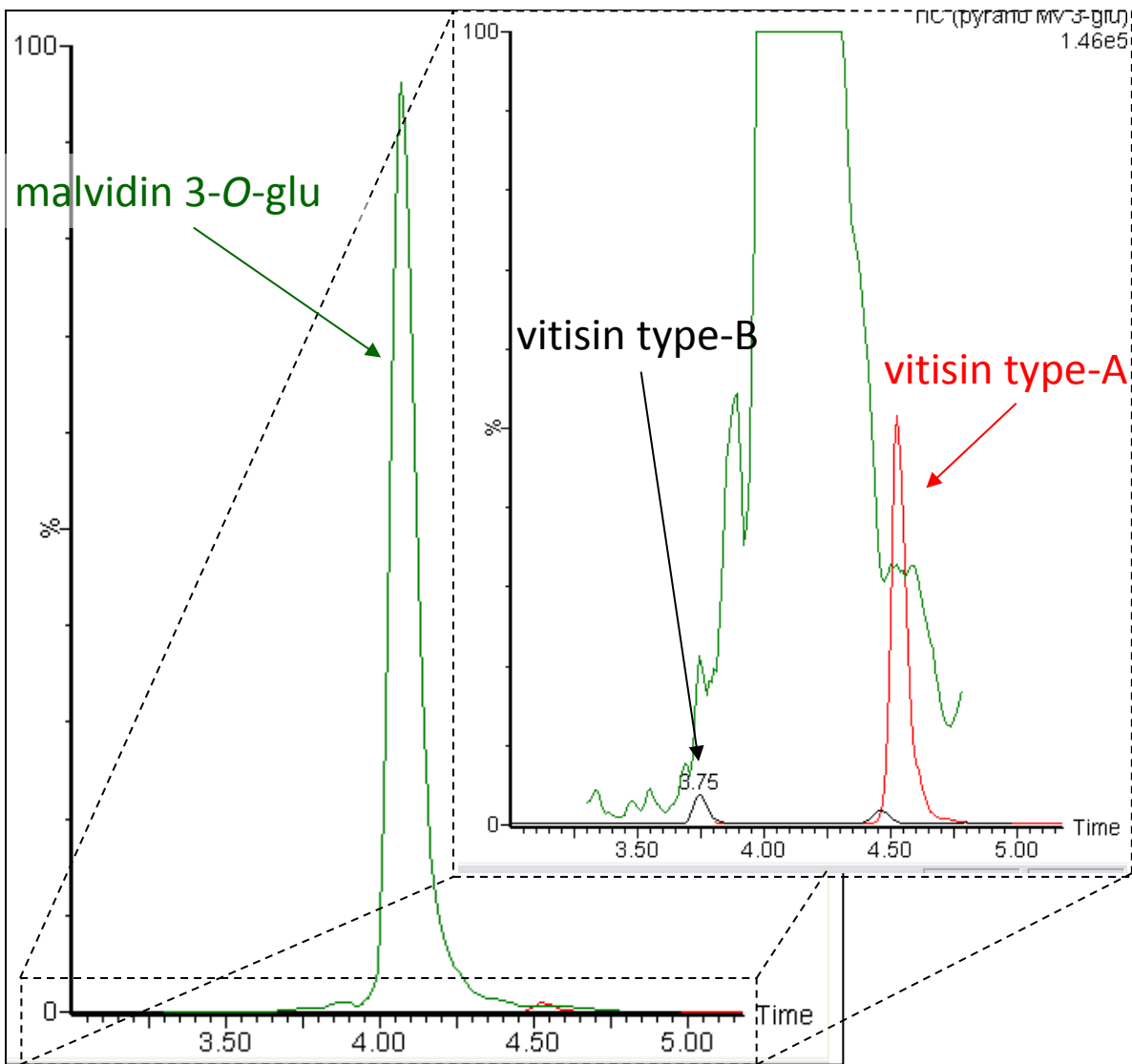
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**Grape pigments**



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**Grape pigments**

**Table 2.** Anthocyanins concentration in red berries expressed in mg/Kg of grape

	Sangiovese		Cabernet Sauvignon		Merlot	
	2011	2012	2011	2012	2011	2012
	mg/Kg (%CV)		mg/Kg (%CV)		mg/Kg (%CV)	
Dp 3-glu	142.325 (16)	84.507 (19)	323.664 (10)	118.683 (10)	135.812 (15)	116.543 (20)
Cy 3 glc	85.017 (15)	43.041 (17)	23.463 (19)	5.071 (12)	26.263 (17)	8.584 (23)
Pt 3-glu	77.391 (11)	48.817 (13)	134.140 (9)	33.842 (6)	58.784 (16)	35.580 (13)
Pn 3-glc	66.499 (11)	54.577 (17)	129.499 (19)	34.979 (6)	87.036 (16)	27.852 (13)
Mv 3-glc	163.243 (10)	126.62 (13)	815.296 (14)	193.910 (8)	285.486 (18)	137.371 (14)
Pl 3-glc	0.403 (6)	0.349 (23)	1.190 (14)	0.281 (12)	0.813 (13)	0.114 (30)
B-type vitisin	0.035 (16)	0.003 (28)	0.053 (6)	nd	0.042 (18)	nd
A-type vitisin	4.286 (20)	0.509 (17)	29.607 (7)	0.451 (11)	6.421 (18)	nd
total acylated	55.220 (12)	16.465 (14)	1607.174 (7)	299.997 (10)	882.531 (14)	267.493 (9)
<b>Total</b>	<b>594.419 (11)</b>	<b>374.888 (16)</b>	<b>3064.086 (12)</b>	<b>687.214 (8)</b>	<b>1483.188 (11)</b>	<b>593.537 (17)</b>

Dp: delphinidin; Cy: cyanidin; Pt: petunidin; Pn: peonidin; Mv: malvidin; Pl: pelargonidin; glu: glucoside; nd: not detected



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**Grape pigments**

**Table 4.** Pyranoanthocyanins ( $\text{mg L}^{-1}$ ) in musts and wines as related to different leaf removal treatments: UN, untreated (control); PF, pre-flowering leaf removal; BS, berry-set leaf removal; VE, véraison leaf removal; CM, cold maceration; AF, alcoholic fermentation; YWAP, young wine after pressing

	CM	4 days AF	8 days AF	YWAP
<b>Vitisin a</b>				
UN	$4.0 \pm 0.53$	$19.9 \pm 1.36c$	$20.2 \pm 1.00b$	$18.9 \pm 0.64b$
PF	$4.0 \pm 0.19$	$26.5 \pm 0.39a$	$26.1 \pm 2.44a$	$26.4 \pm 1.10a$
BS	$3.3 \pm 0.80$	$25.5 \pm 0.22ab$	$26.1 \pm 2.11a$	$24.7 \pm 1.48a$
VE	$3.4 \pm 0.12$	$24.3 \pm 0.33b$	$22.1 \pm 1.18b$	$24.0 \pm 4.29a$
Sign. <i>F</i>	NS	***	**	*
<b>Pyrano malvidin-3-glucoside</b>				
UN	$0.1 \pm 0.05$	$0.9 \pm 0.07c$	$0.8 \pm 0.15$	$0.9 \pm 0.06$
PF	$0.1 \pm 0.01$	$1.3 \pm 0.04a$	$1.1 \pm 0.19$	$1.1 \pm 0.14$
BS	$0.1 \pm 0.05$	$1.1 \pm 0.12bc$	$1.1 \pm 0.34$	$1.1 \pm 0.10$
VE	$0.1 \pm 0.03$	$1.1 \pm 0.04b$	$1.1 \pm 0.03$	$1.2 \pm 0.12$
Sign. <i>F</i>	NS	**	NS	NS

Data were processed through ANOVA and means separated using the SNK test ( $P < 0.05$ ) (NS, not significant).

\*  $P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$ ). Means followed by the same letter or no letters are not significantly different.



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## Study of Sangiovese Wines Pigment Profile by UHPLC-MS/MS

Panagiotis Arapitsas,<sup>†</sup> Daniele Perenzoni,<sup>†</sup> Giorgio Nicolini,<sup>‡</sup> and Fulvio Mattivi<sup>\*,†</sup>

<sup>†</sup>Research and Innovation Centre, Food Quality and Nutrition Department, and <sup>‡</sup>Technology Transfer Centre, Fondazione Edmund Mach, via E. Mach 1, 38010 San Michele all'Adige, Italy

**S** Supporting Information

**ABSTRACT:** The metabolic pigment composition of Sangiovese wines produced from grapes harvested at 20 different vineyards in Montalcino over three consecutive years (2008–2010) on a semi-industrial scale and of 55 commercial Brunello di Montalcino wines (2004–2007) was studied, using a targeted method capable of analyzing 90 pigments in an 11 min UHPLC-MS/MS chromatographic run. Interesting correlations were shown between various pigments formed during wine aging and those present in Sangiovese grapes. Vitisin B-like pigment and vitisin A-like pigment concentrations would seem to have a good correlation with ethyl-linked and direct-linked flavanol–anthocyanin concentrations, respectively. Moreover, the anthocyanic pattern recognition, genetically controlled by the plant variety, was shown to be inherited by the pigments formed during wine aging.

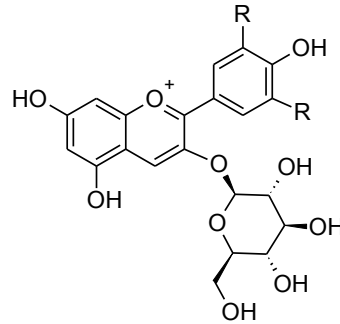
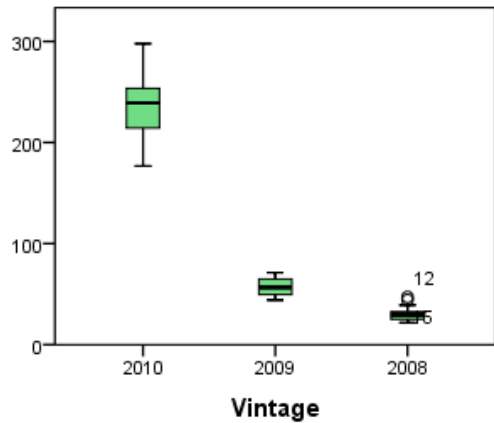
**KEYWORDS:** UHPLC, tandem mass spectrometry, anthocyanins, traceability, wine aging, Sangiovese



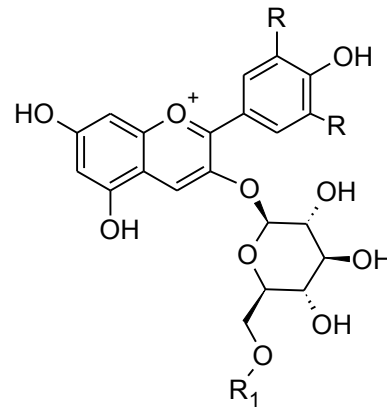
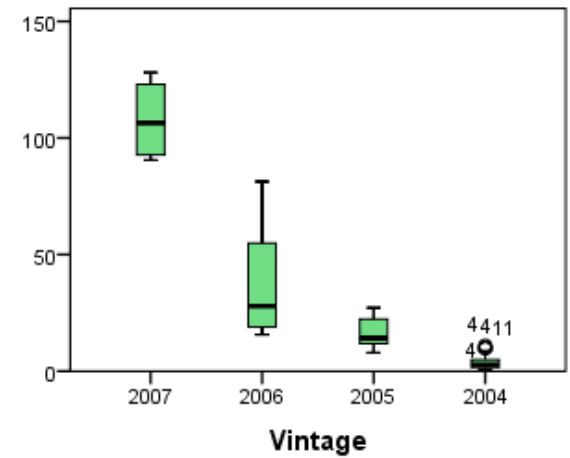
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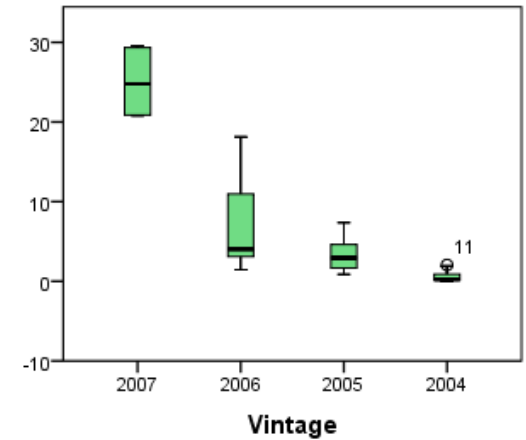
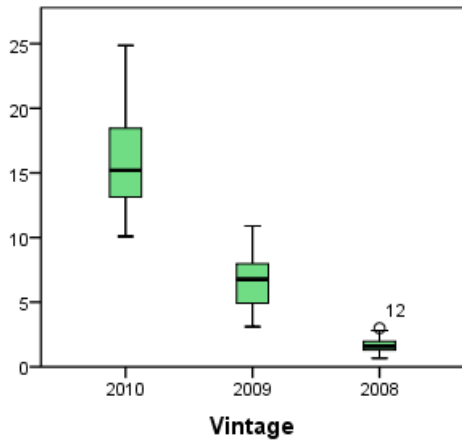
## Experimental wines



## Commercial wines



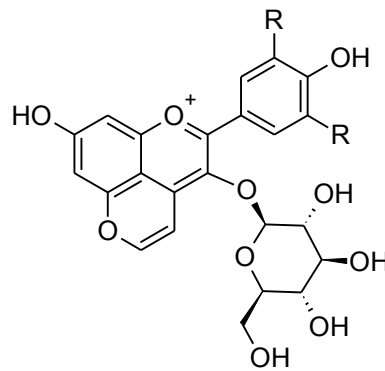
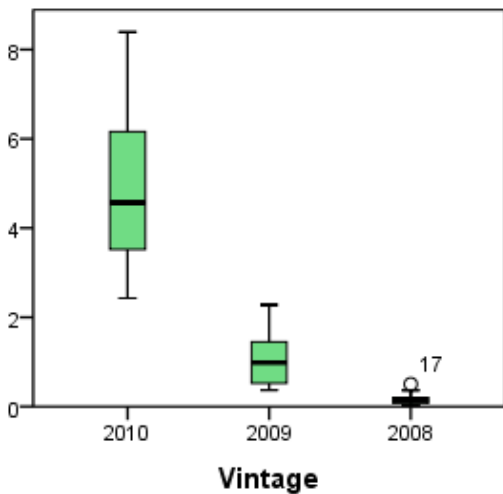
R1 = *p*-cumaroyl or acetyl



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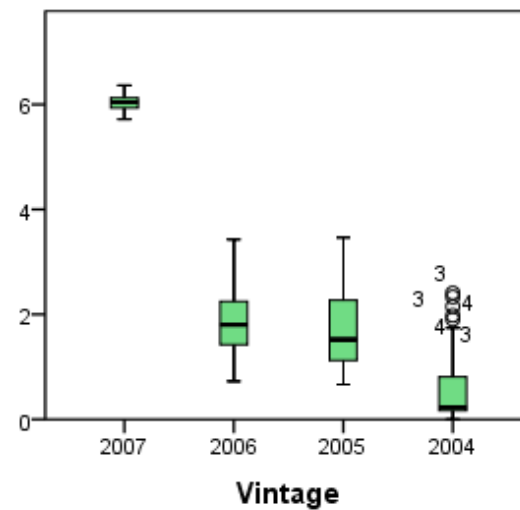
**Wine pigments during aging**

## Experimental wines

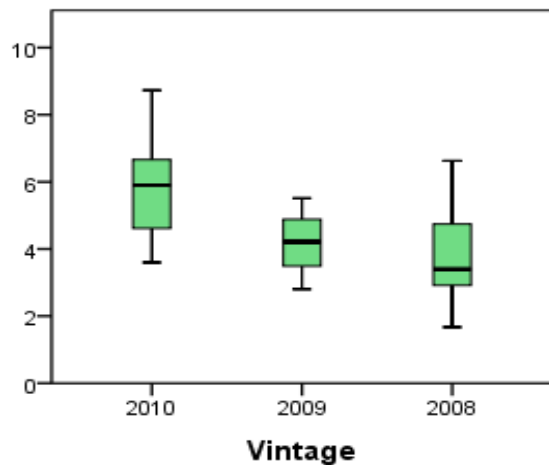


vitisins B-type

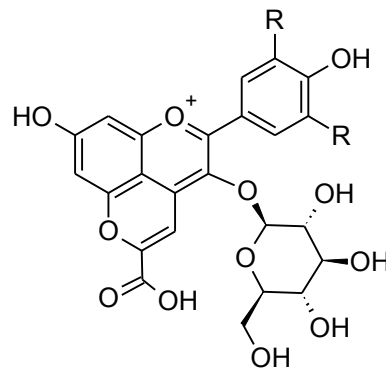
## Commercial wines



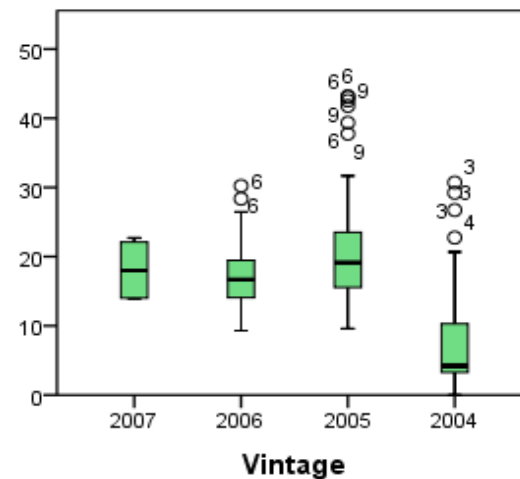
Vintage



Vintage



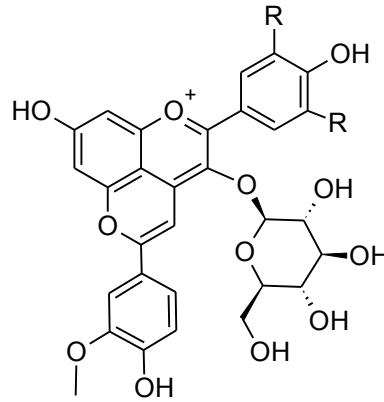
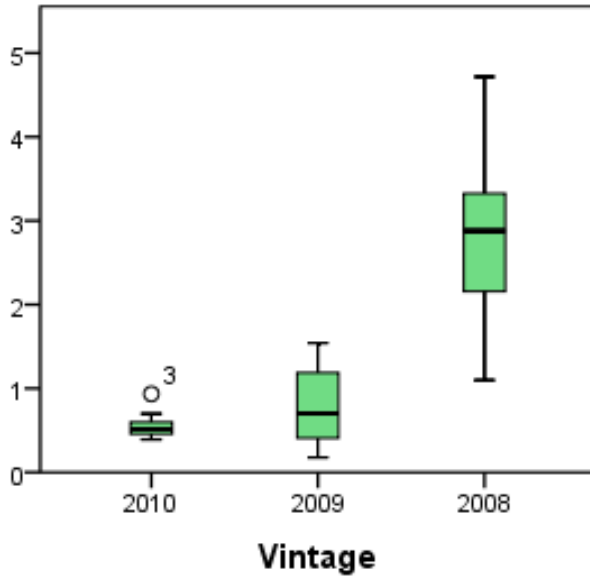
vitisins A-type



Vintage

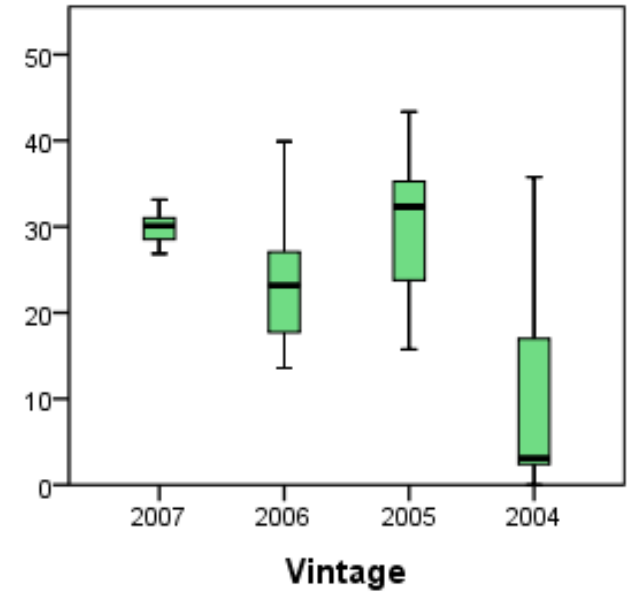


## Experimental wines

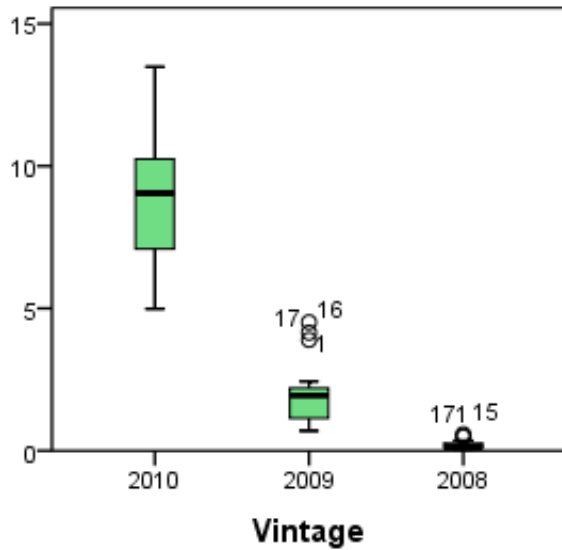


pinotins

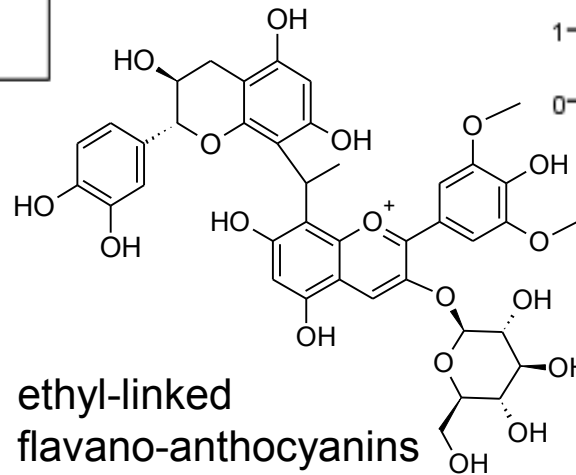
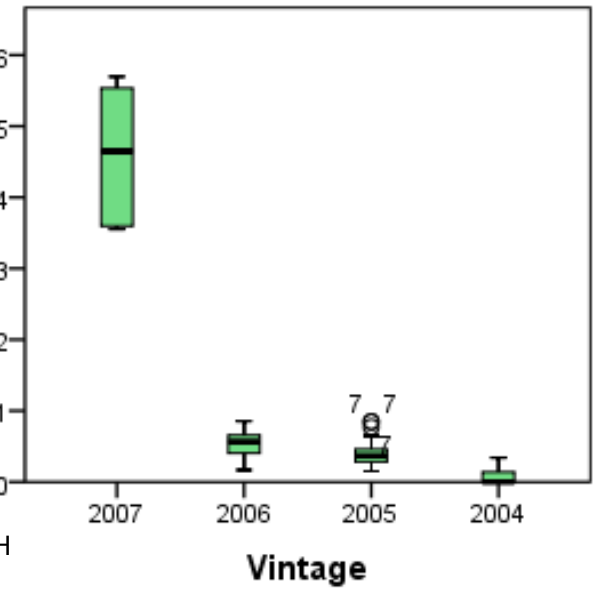
## Commercial wines



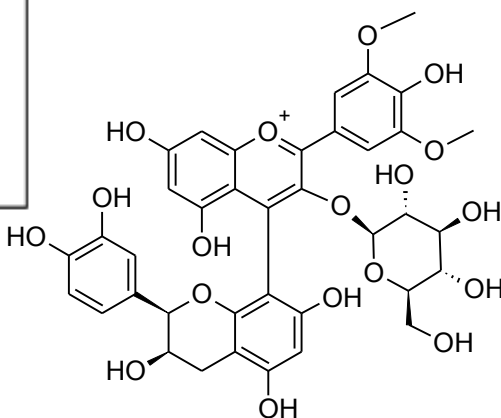
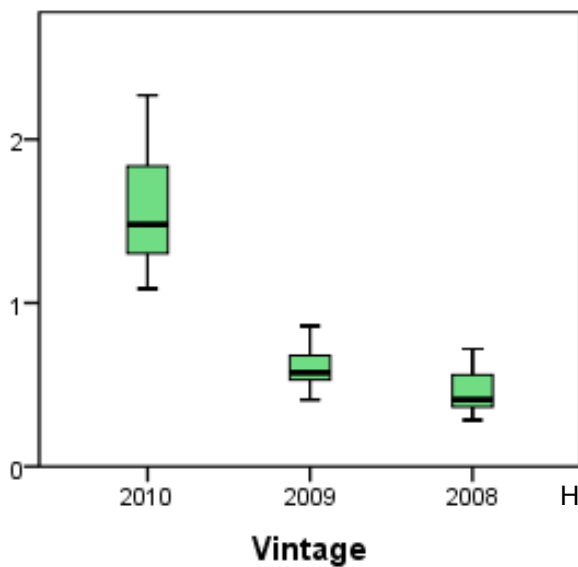
## Experimental wines



## Commercial wines

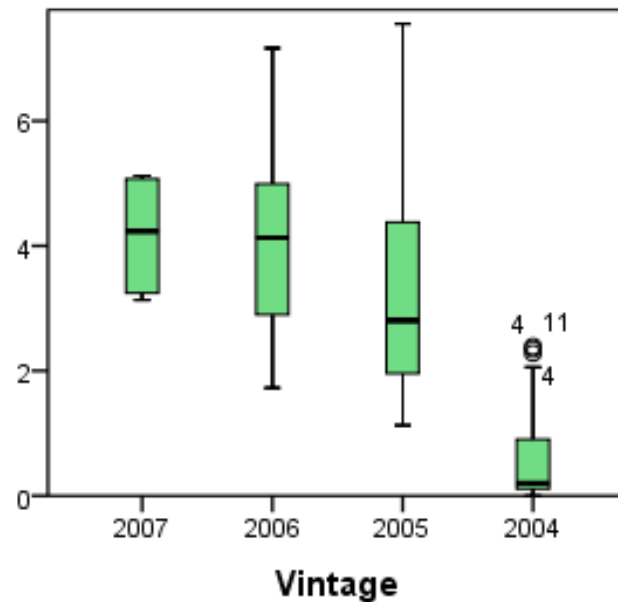


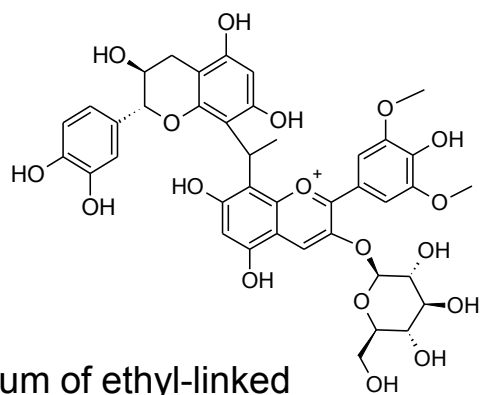
## Experimental wines



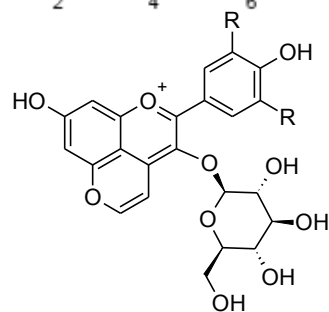
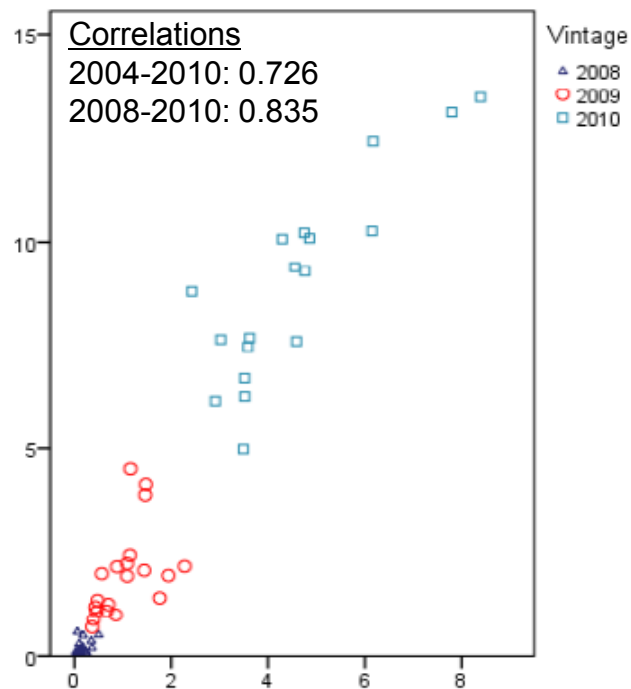
direct linked  
flavano-anthocyanins

## Commercial wines





sum of ethyl-linked flavano-anthocyanins



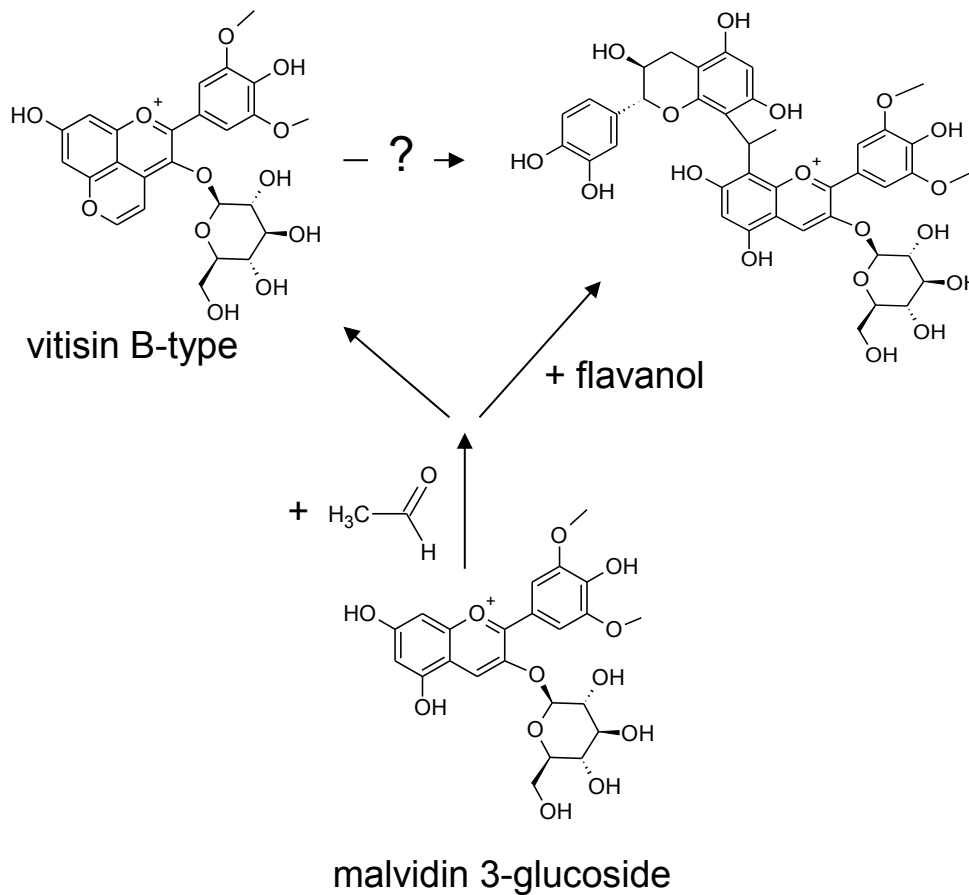
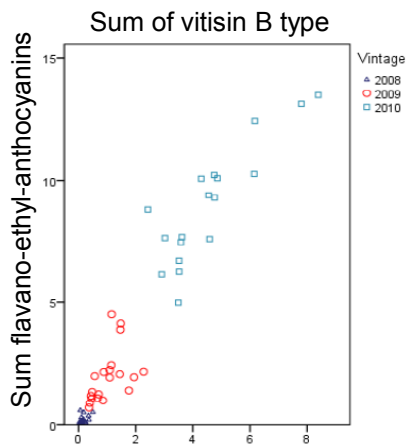
Sum of vitisins B-type



Correlations

2004-2010: 0.726

2008-2010: 0.835



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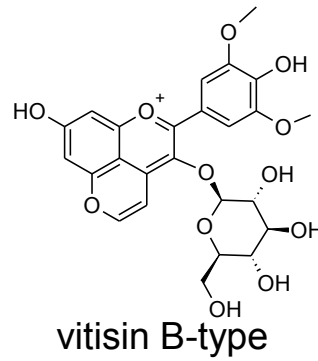
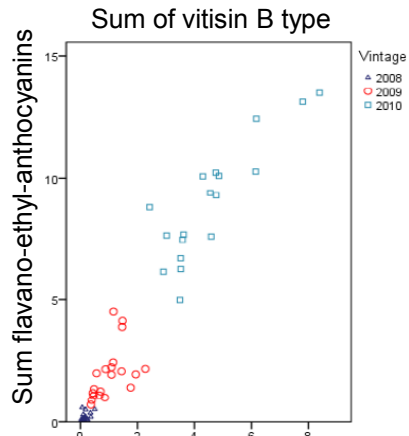
**Wine pigments during aging**



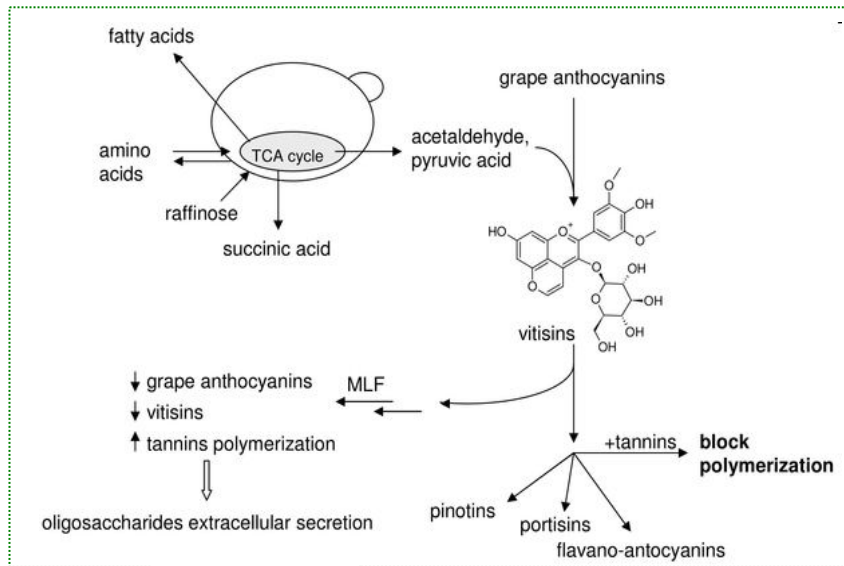
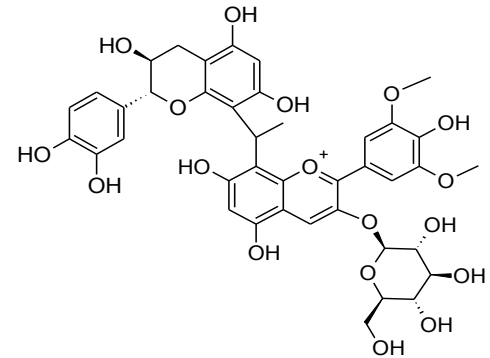
Correlations

2004-2010: 0.726

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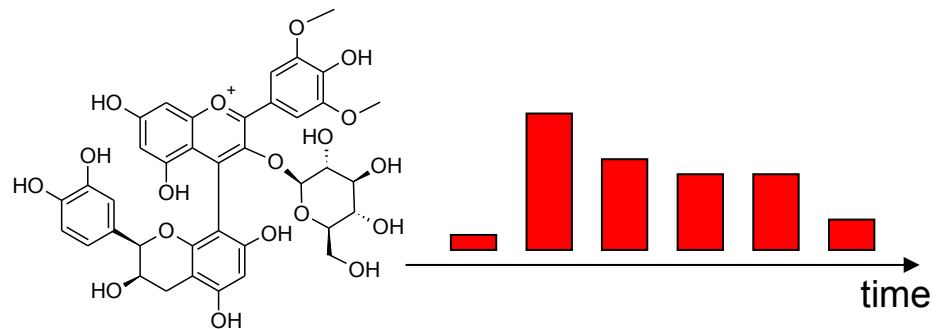
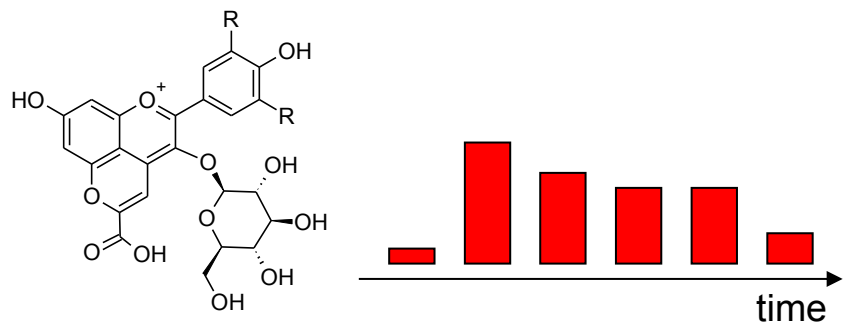
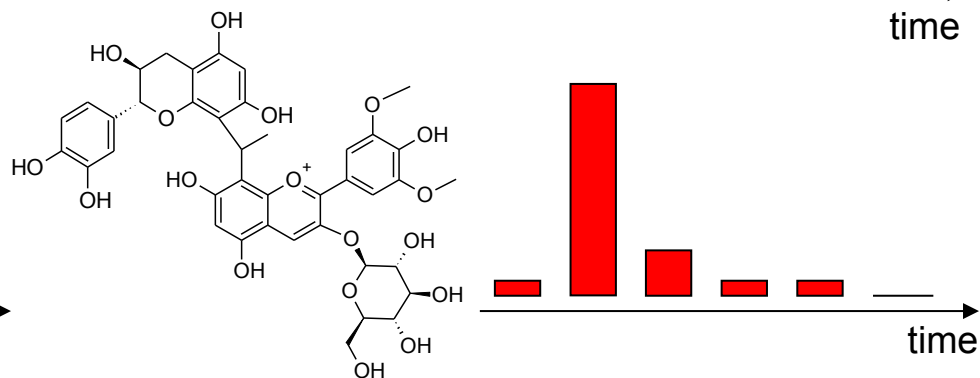
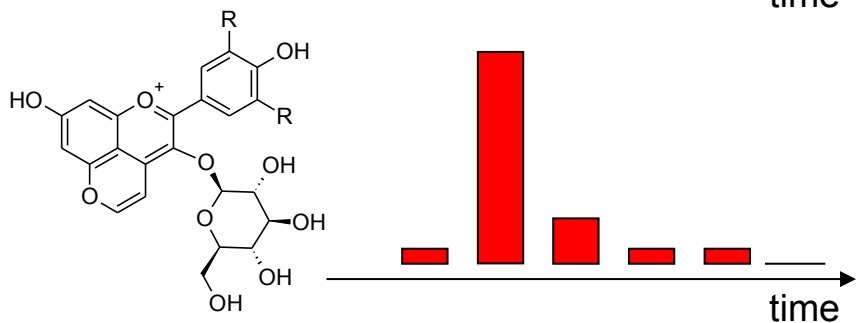
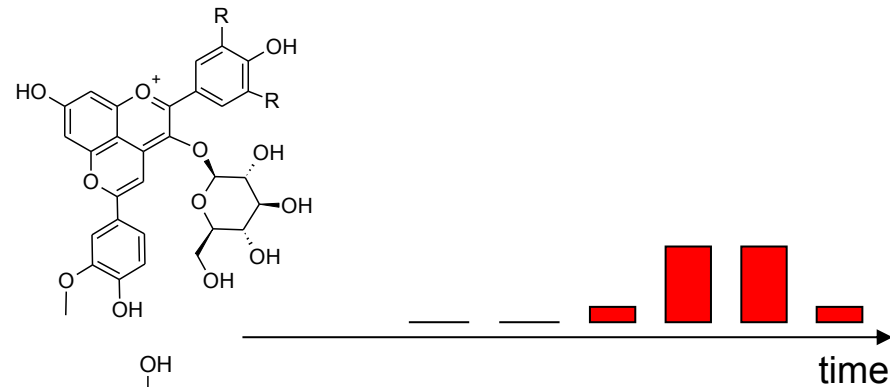
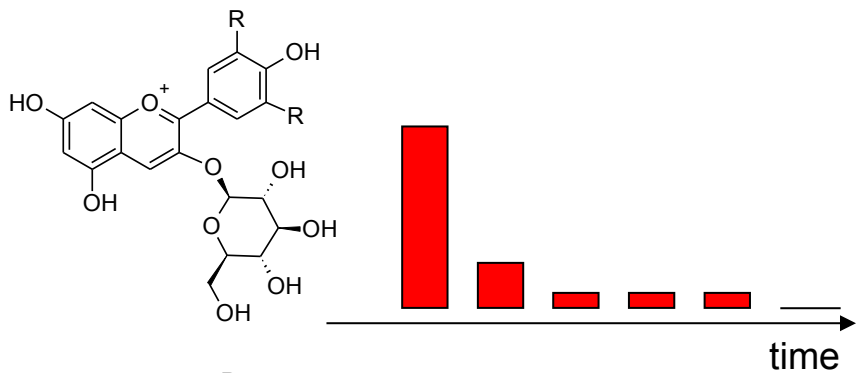


Arapitsas et al (2012) PLoS ONE



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Arapitsas et al. J Agric Food Chem 2012



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**Wine pigments during aging**

Metabolomics (2014) 10:816–832

DOI 10.1007/s11306-014-0638-x

ORIGINAL ARTICLE

# The influence of storage on the “chemical age” of red wines

Panagiotis Arapitsas · Giuseppe Speri ·  
Andrea Angeli · Daniele Perenzoni ·  
Fulvio Mattivi



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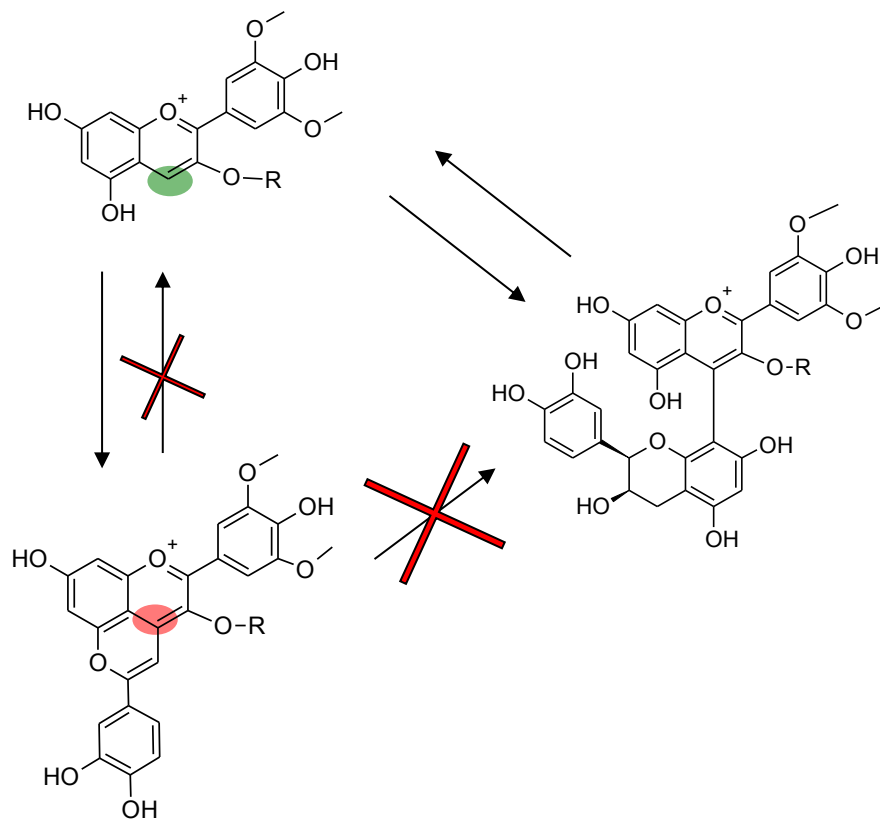
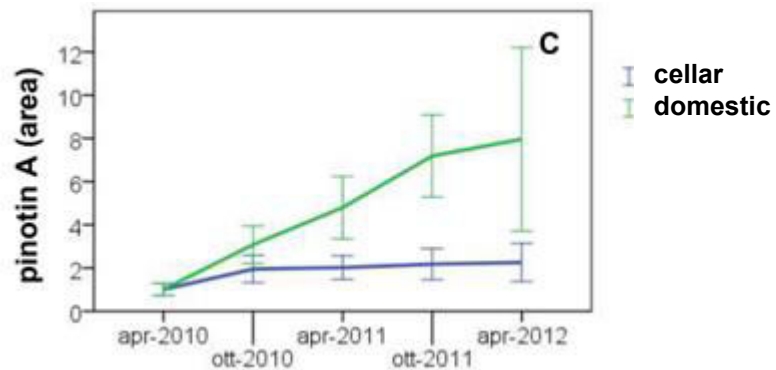
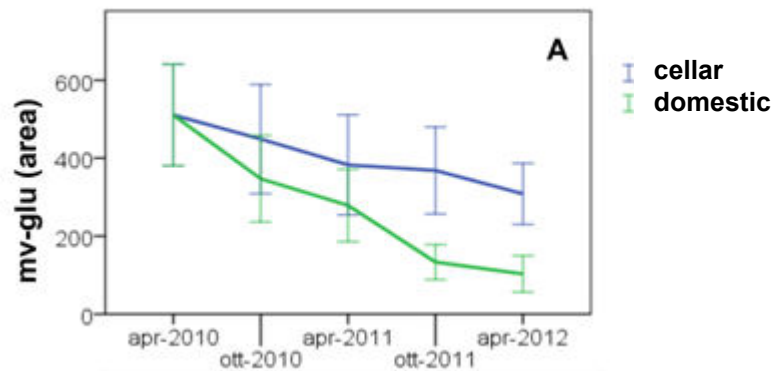


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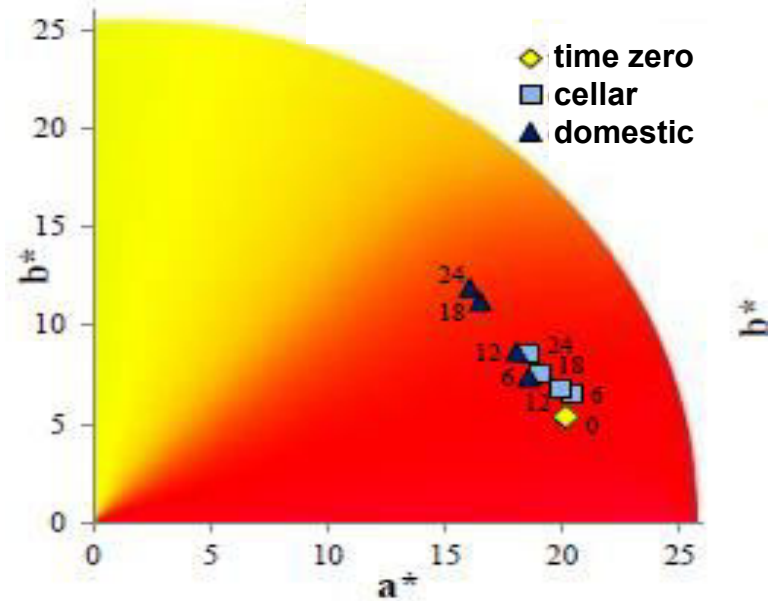
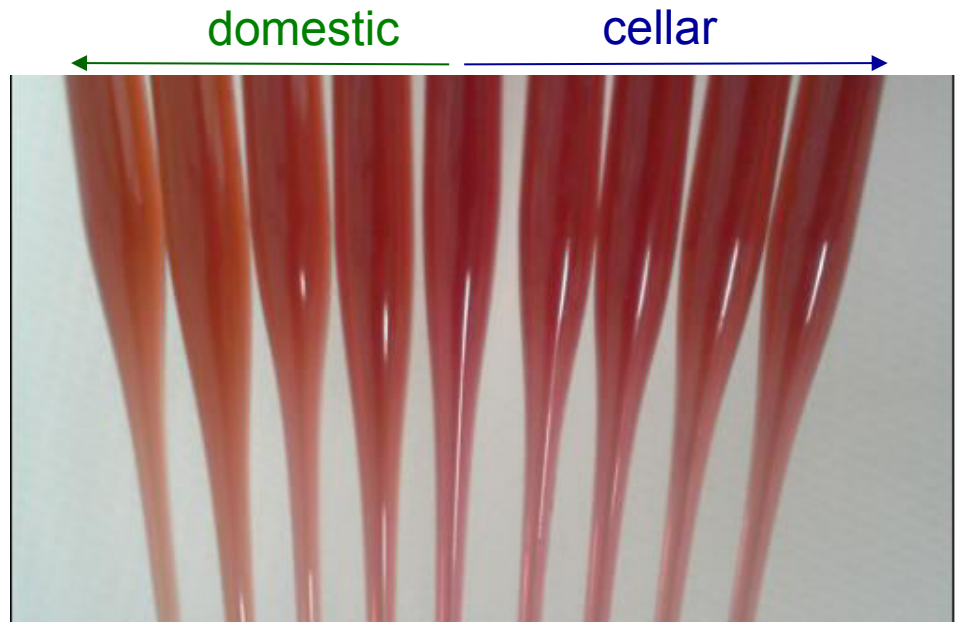
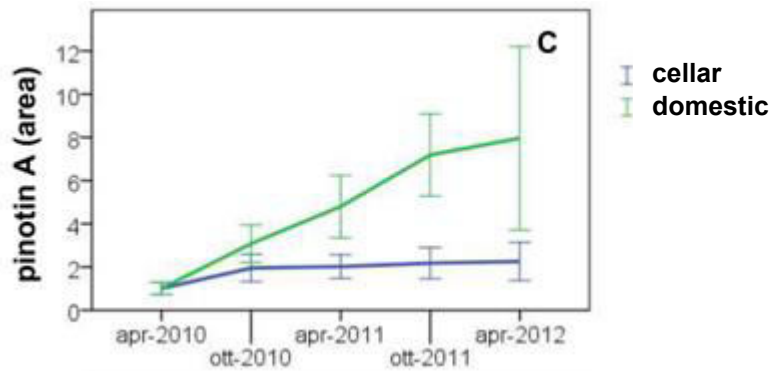
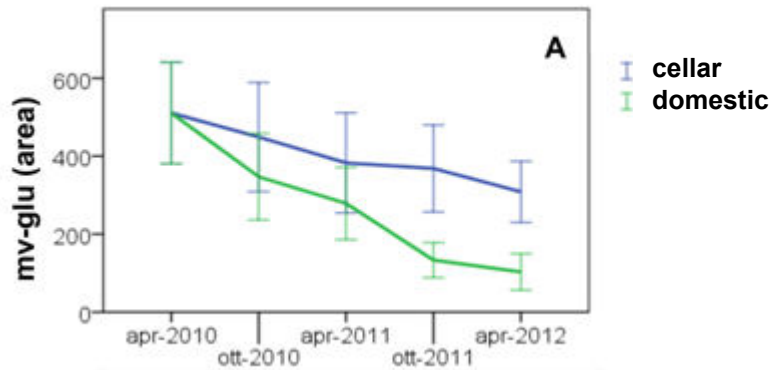




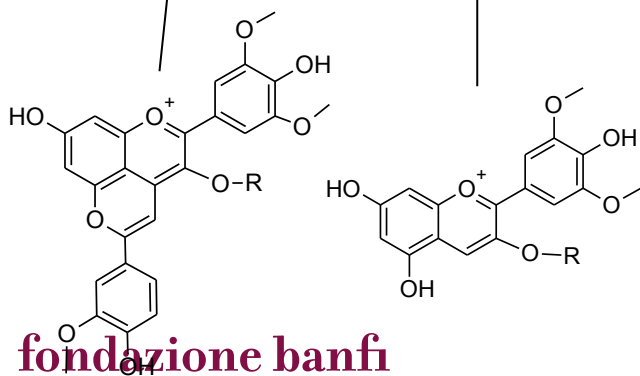
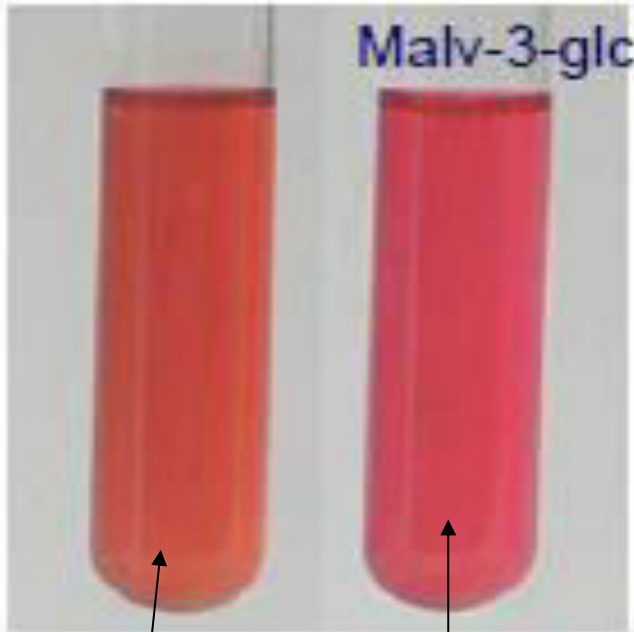
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**Wine pigments during storage**



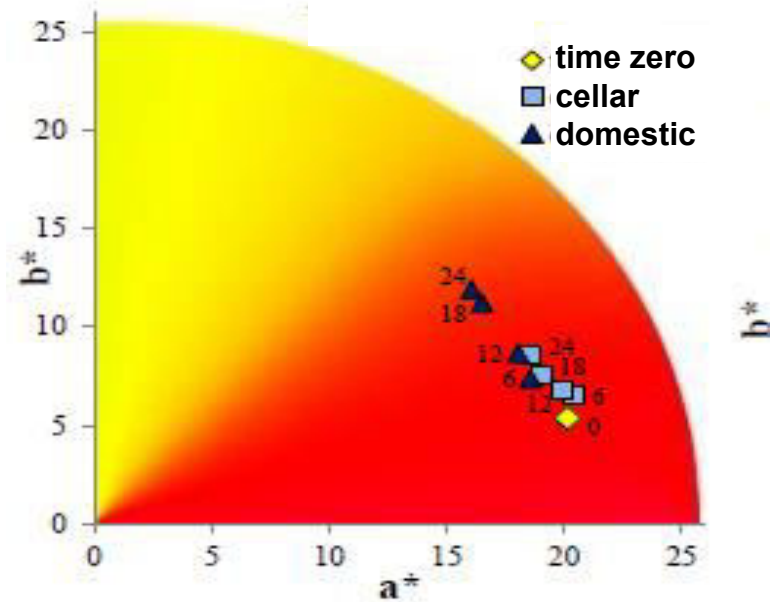
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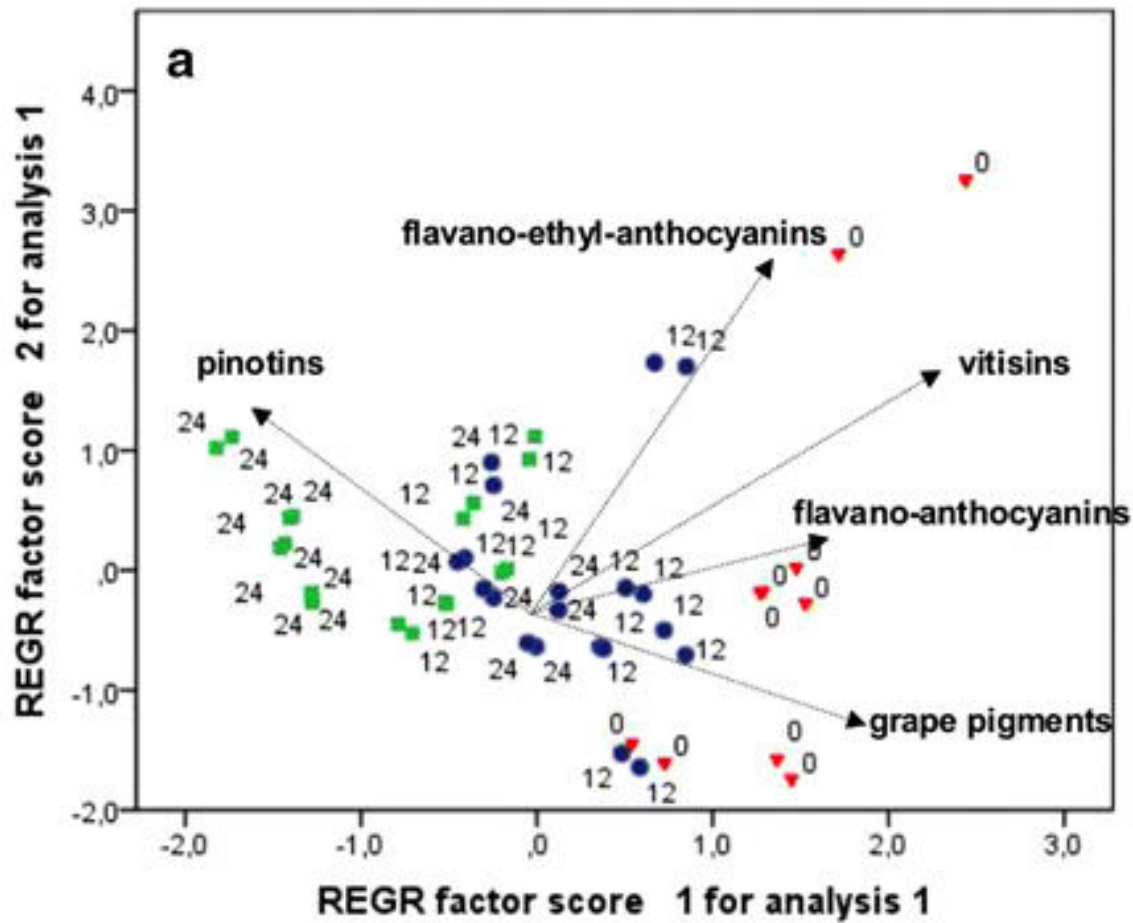
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domestic

cellar



**Wine pigments during storage**

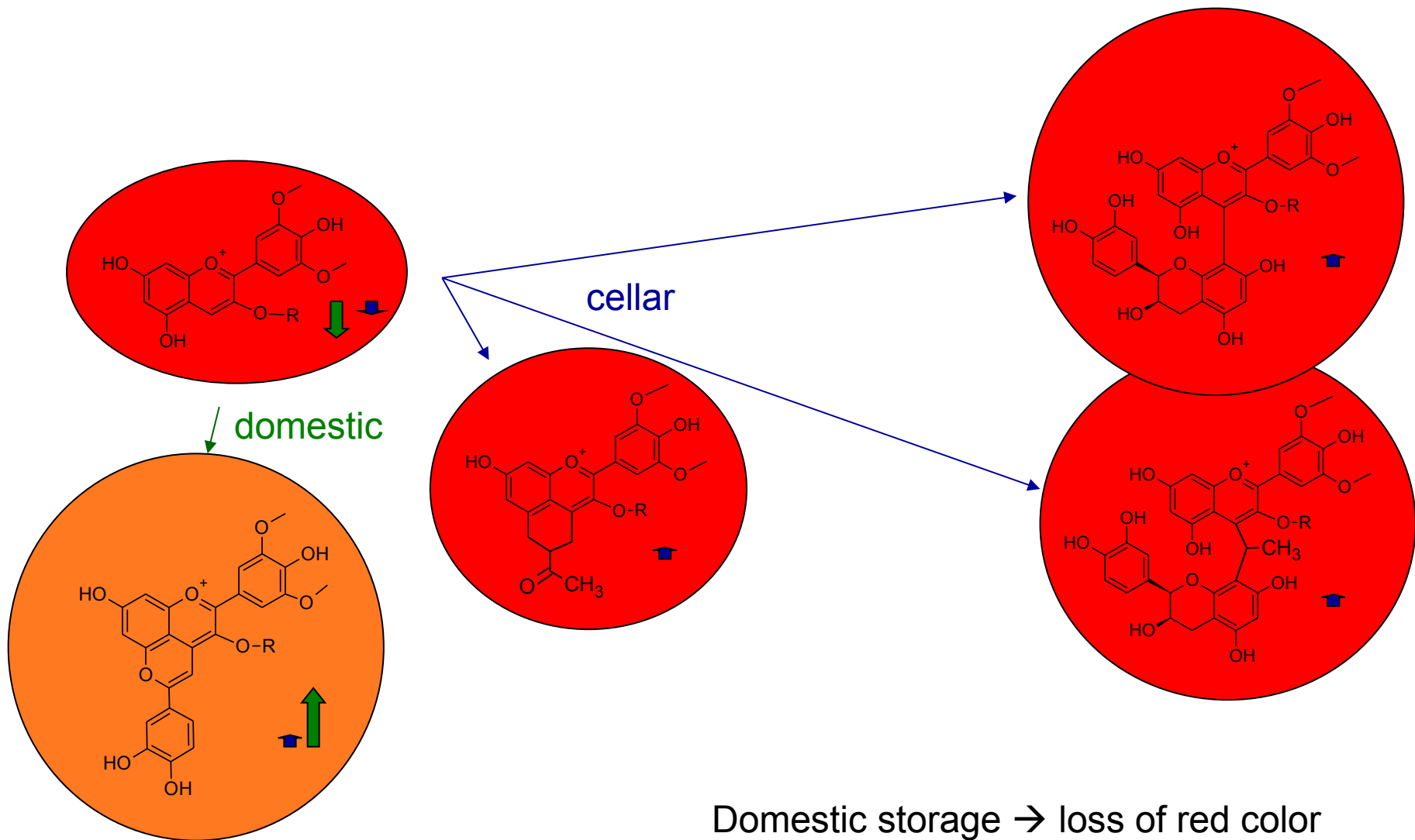


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Wine pigments during storage





Domestic storage → loss of red color  
 Pinotins → possible markers of bad storage





**C3A**  
CENTRO  
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ALIMENTI  
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DI TRENTO



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EDMUND  
MACH

**Fulvio Mattivi**



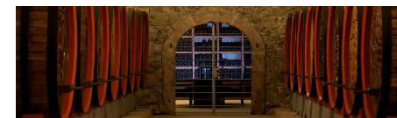
FONDAZIONE  
EDMUND  
MACH  
CENTRO RICERCA  
e INNOVAZIONE

**Daniele Perenzoni  
Andrea Angeli  
Giuseppe Speri**



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**Tomas Roman  
Mario Malacarne  
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**Winery  
Fondazione E. Mach**



University of Porto

**Joana Oliveira**



**Melita Sternad Lemut**



**Consorzio  
Brunello di Montalcino**



**CREA-NUT**



CONSORZIO  
**TUSCANIA**

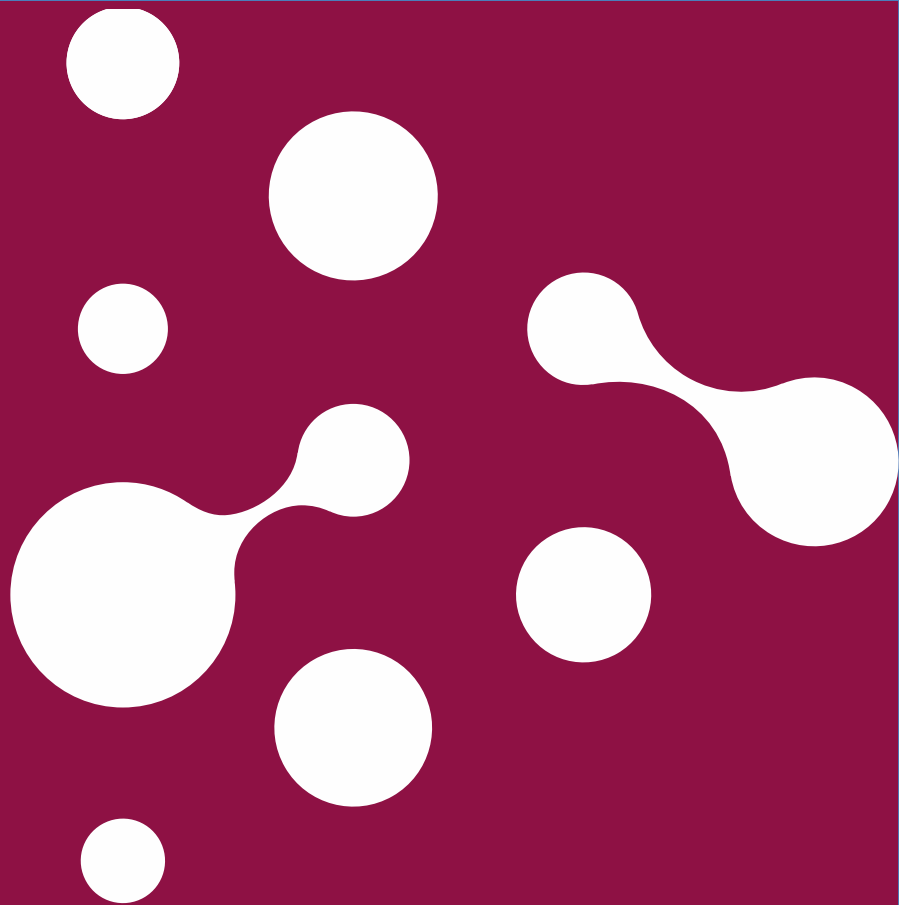


MINISTERO DELLE POLITICHE AGRICOLE  
ALIMENTARI E FORESTALI  
**ICQRF**  
SPETTACOLO CENTRALE DELLA TUTELA DELLA QUALITÀ  
E REPRESSIONE FRODI DEI PRODOTTI AGRICOLI ALIMENTARI



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