fondazione banfi
SANGUIS JOVIS
ALTA SCUOLA DEL SANGIOVESE

Particolarità compositive del Sangiovese e tecnica enologica

C3A CENTRO AGRICOLTURA ALIMENTI AMBIENTE

UNIVERSITÀ DI TRENTO

FONDAZIONE EDMUND MACH

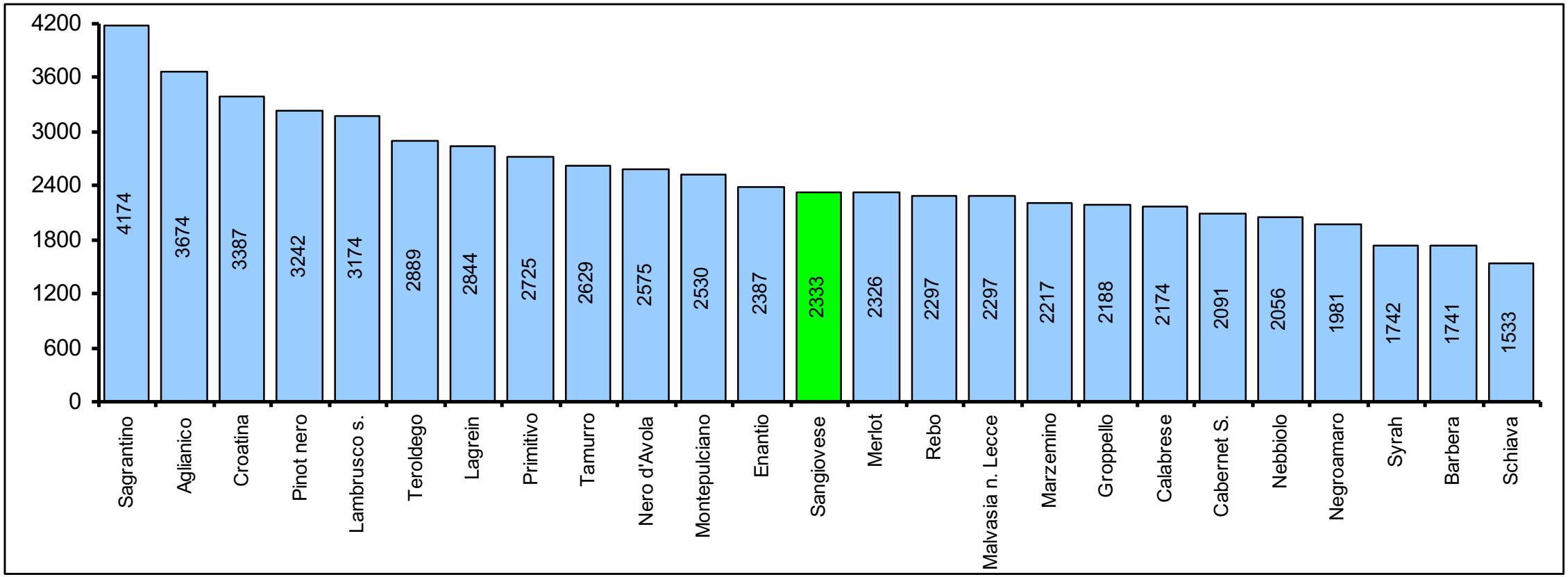
Fulvio Mattivi


1. Potenziale fenolico del Sangiovese
2. Cinetiche di estrazione da buccia e vinaccioli
3. Struttura del tannino del Sangiovese
4. Importanza di una corretta conservazione
Discussione


Cabernet S., Merlot,
Pinot noir,Syrah
Enantio, Lagrein,
Marzemino, Teroldego,
Rebo, Schiava
Barbera, Croatina, Groppello,
Marzemino, Nebbiolo
Lambrusco salamino
Montepulciano,
Sangiovese
Nebbiolo
Sangiovese
Montepulciano
Sagrantino, Sangiovese
Aglianico
Aglianico,
Tamurro
Calabrese, Nero d'Avola
Primitivo,
Malvasia nera
di Lecce,
Negroamaro

EXTRACTABLE POLYPHENOLS (FC) - 2000

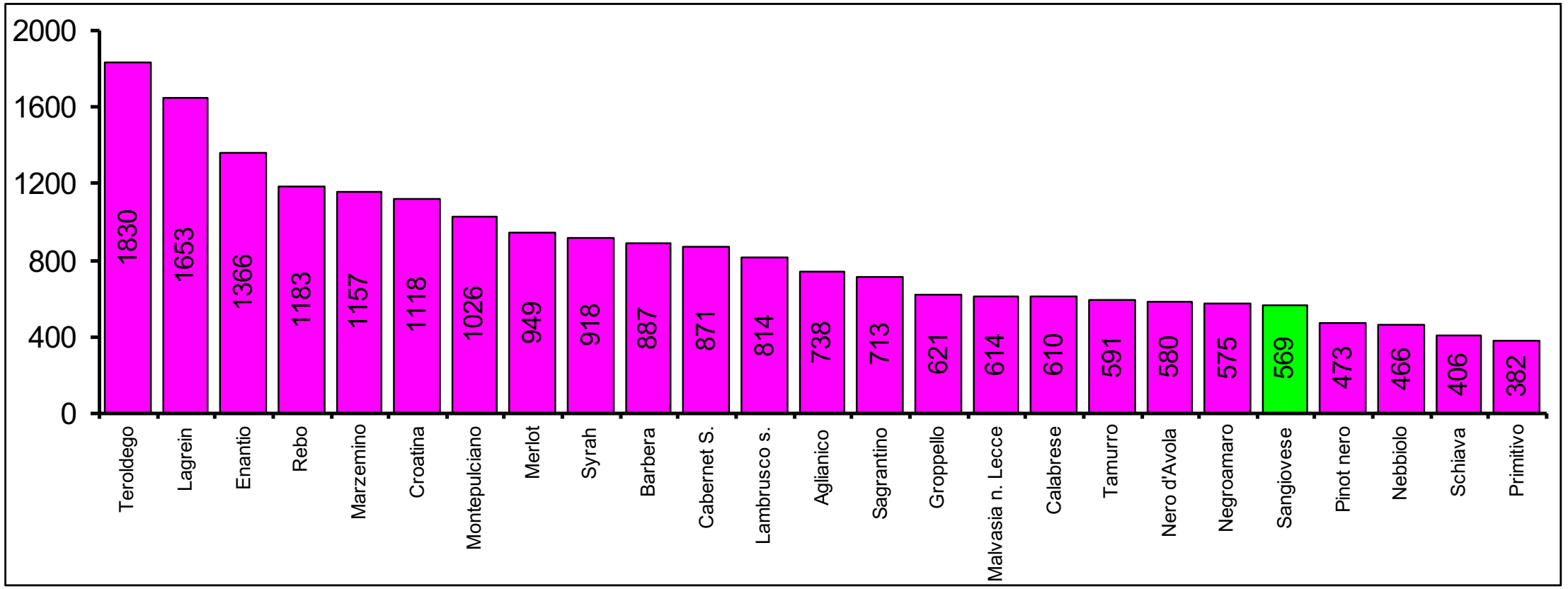
mean by variety, as (+)-catechin, mg/kg of grape



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

EXTRACTABLE ANTHOCYANINS (AT) - 2000

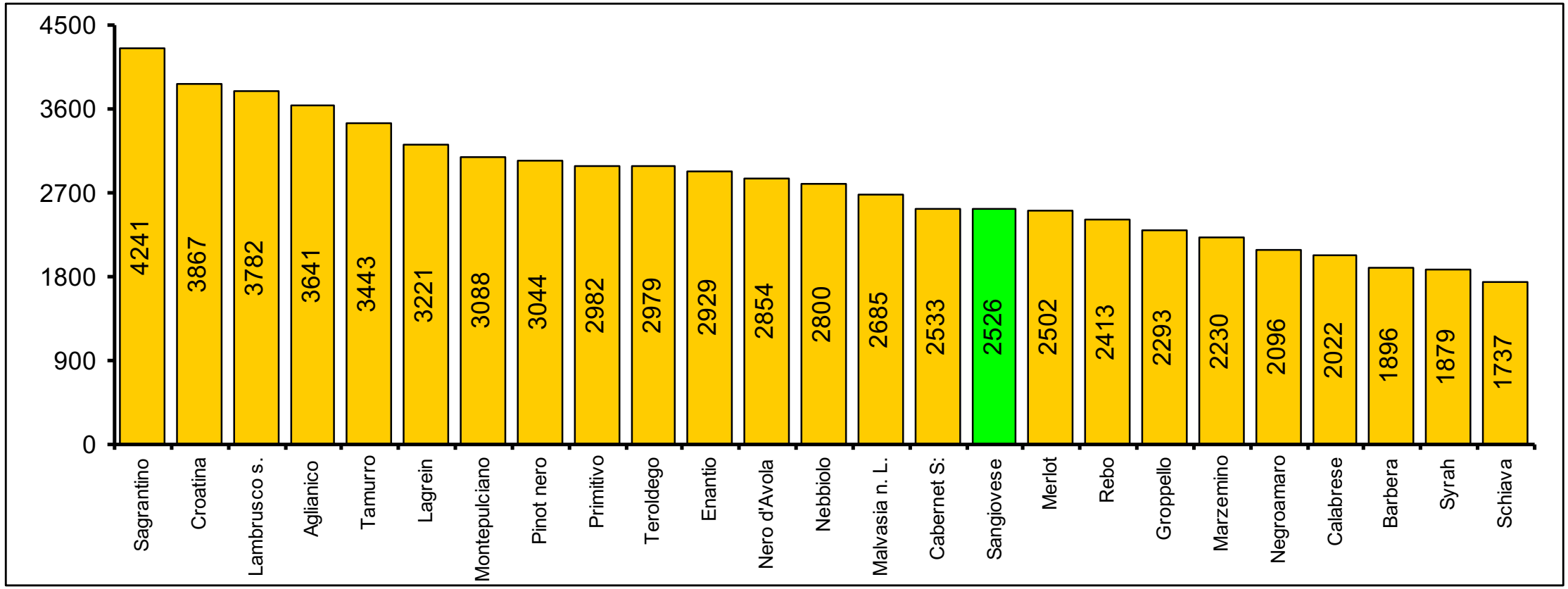
mean by variety, as malvidin 3-glucoside chloride, mg/kg of grape



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

EXTRACTABLE PROANTHOCYANIDINS (HMW, PROC) - 2000

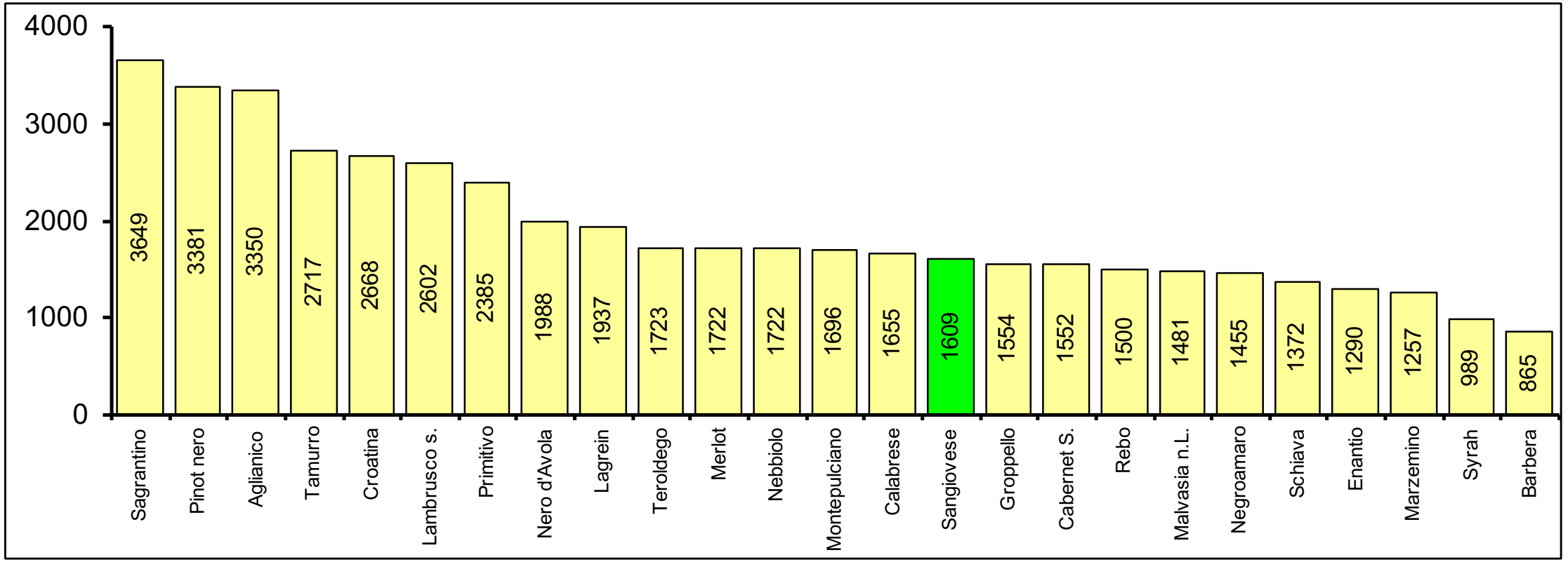
mean by variety, as cyanidin, mg/kg of grape



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

EXTRACTABLE CATECHINS AND LMW PROANTHOCYANIDINS (VAN) - 2000

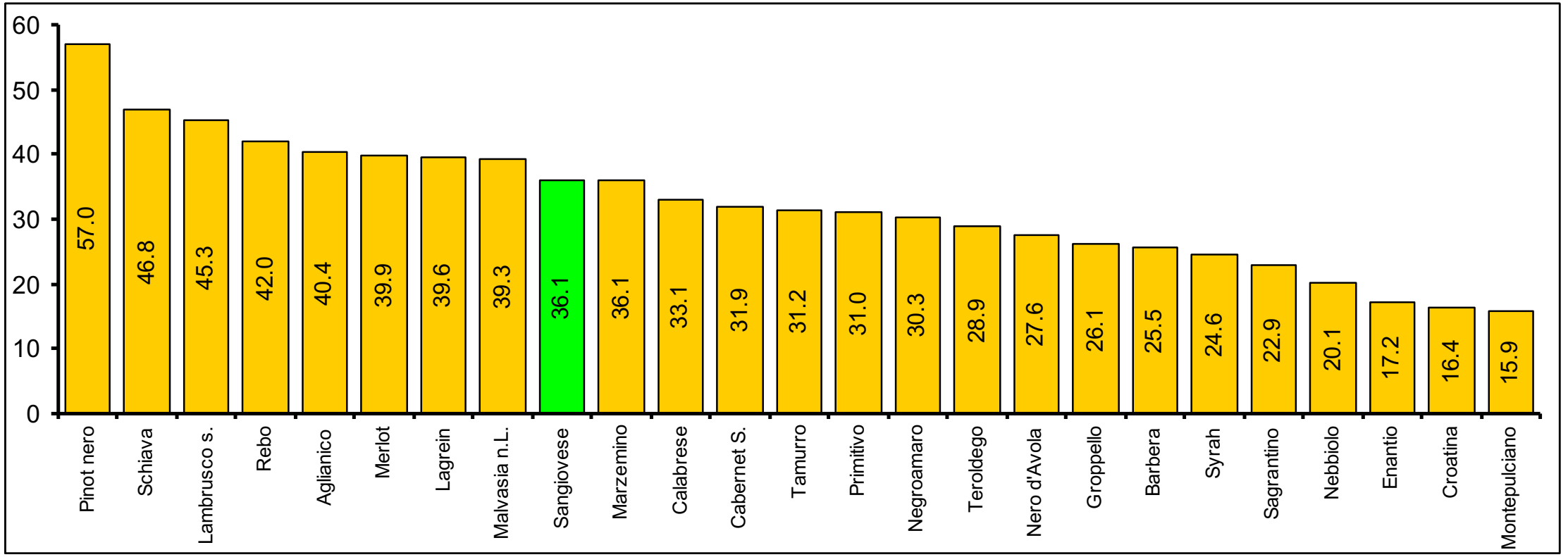
mean by variety, as (+)catechin, mg/kg of grape



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

LOCALISATION OF EXTRACTABLE PROANTHOCYANIDINS IN THE BERRY (PROC, 2000)

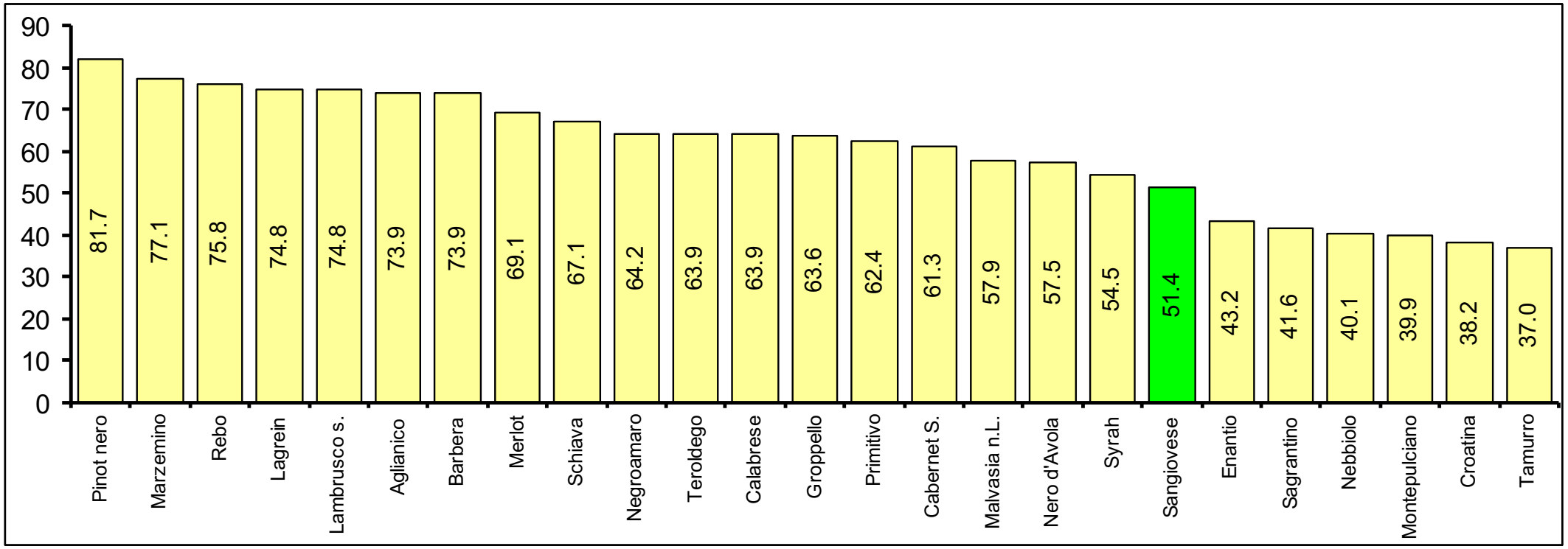
mean by variety, % in the seeds



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

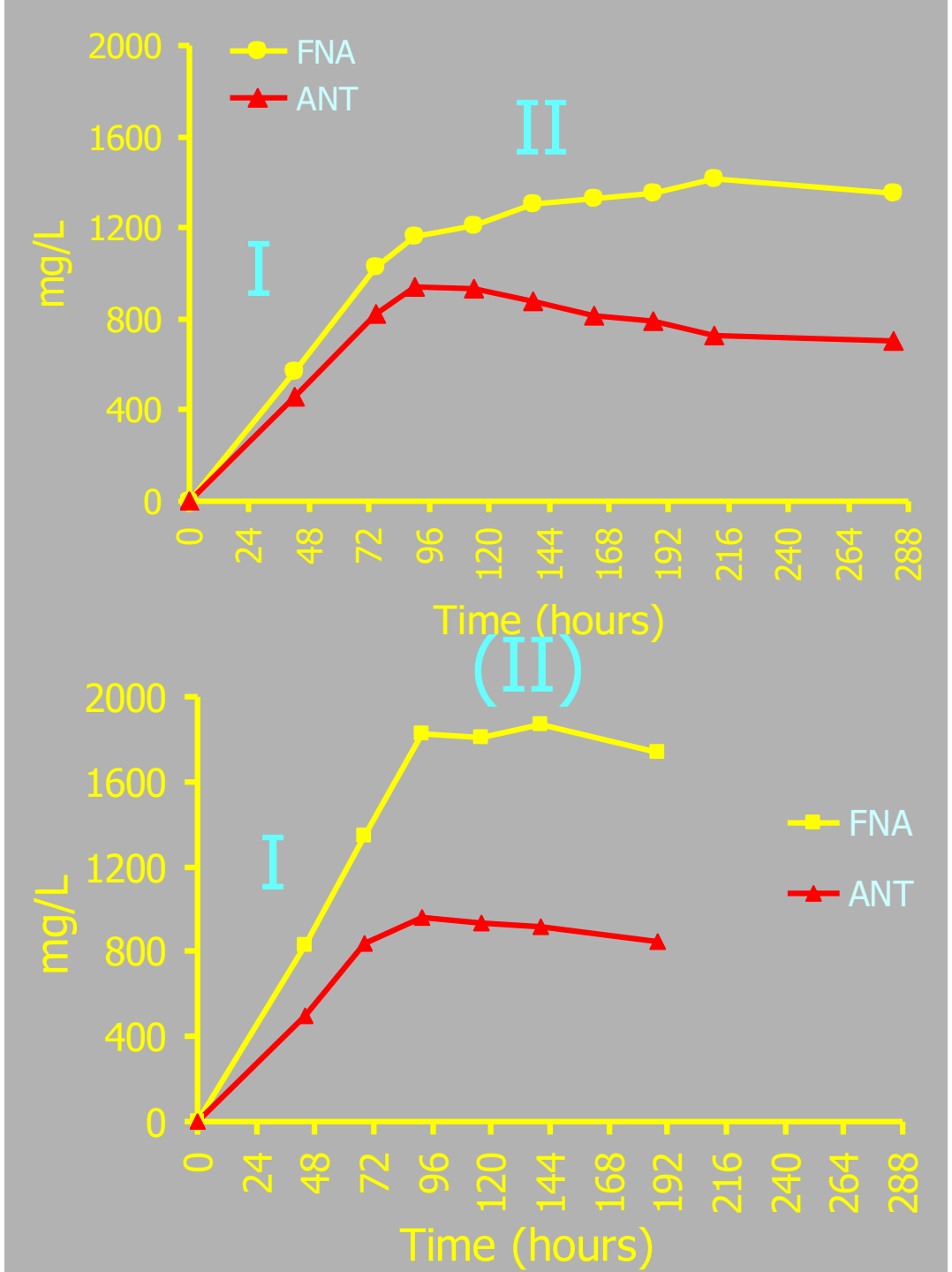
LOCALISATION OF EXTRACTABLE CATECHINS AND LMW PROANTHOCYANIDINS IN THE BERRY (PROC, 2000)

mean by variety, % in the seeds



from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

Why is the localisation of tannins in the berry important?



ENANTIO, less than 20% PROC in seeds

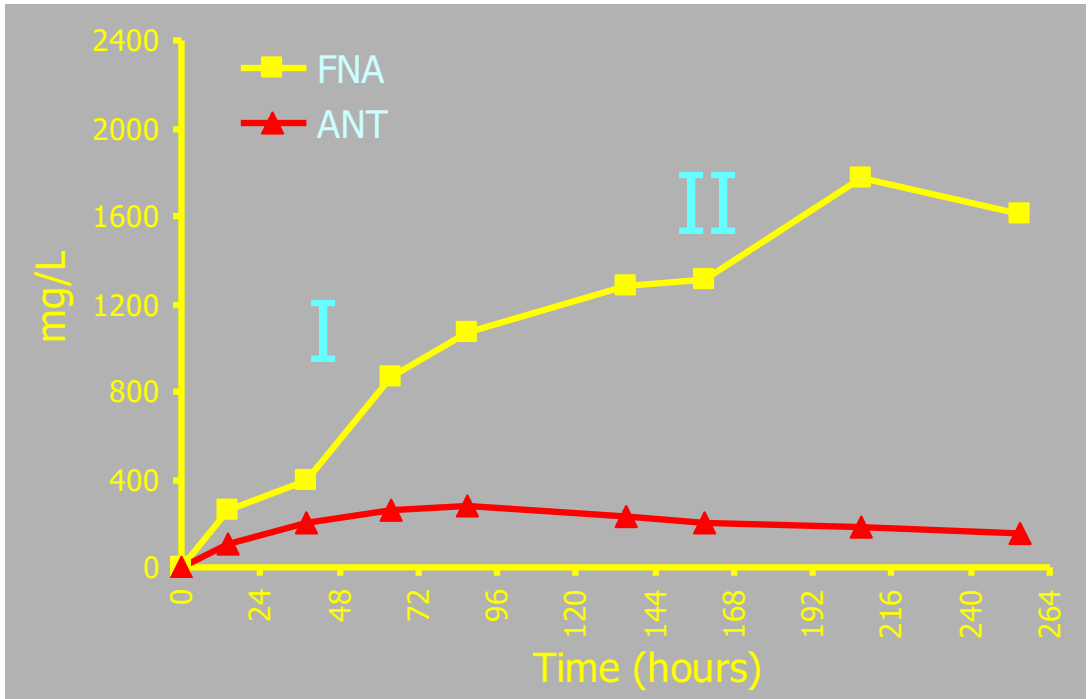
- **Experimental cellar**

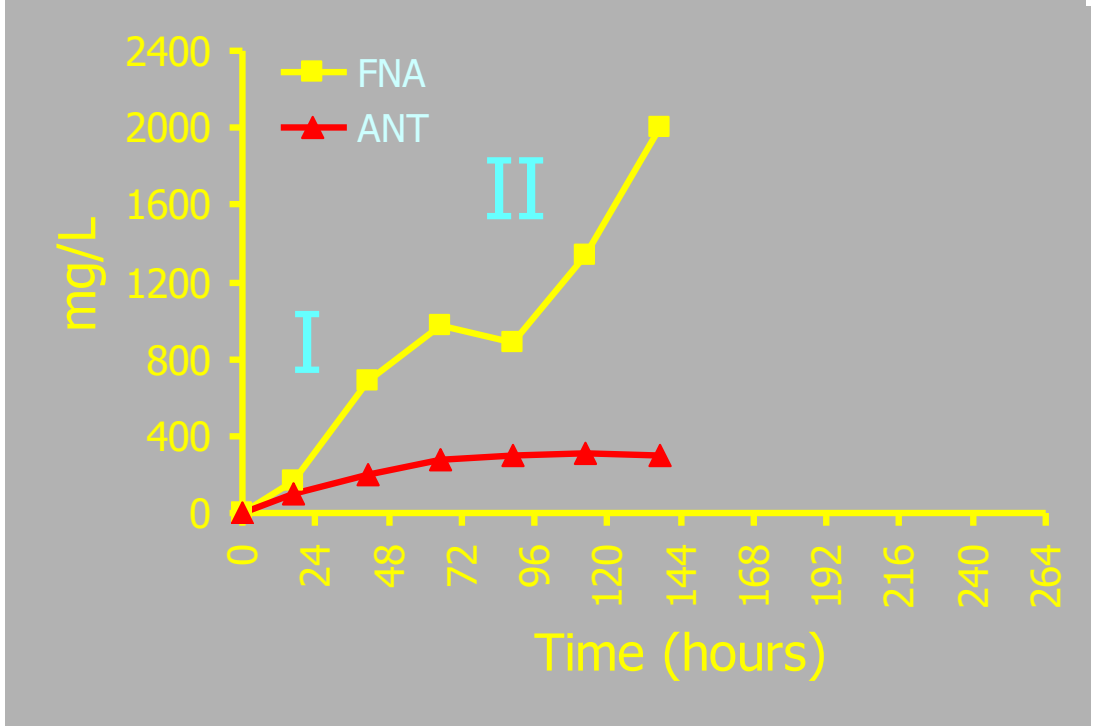
(100 kg, manual punching down, 2xday)

- **Winery scale**

(15 tons, seeds removed, automatic punching down, 12 x 1st day, 8 x 2nd, the 3 x day)

from Mattivi et al., NYAS 2002





PINOT NOIR (1), >55% PROC in the seeds

- **Experimental cellar**

(65 kg, manual punching down, 2 x day)

- **Winery scale**

(1.5 ton, conventional tank, pumping over 70% in v/v 2 x day)

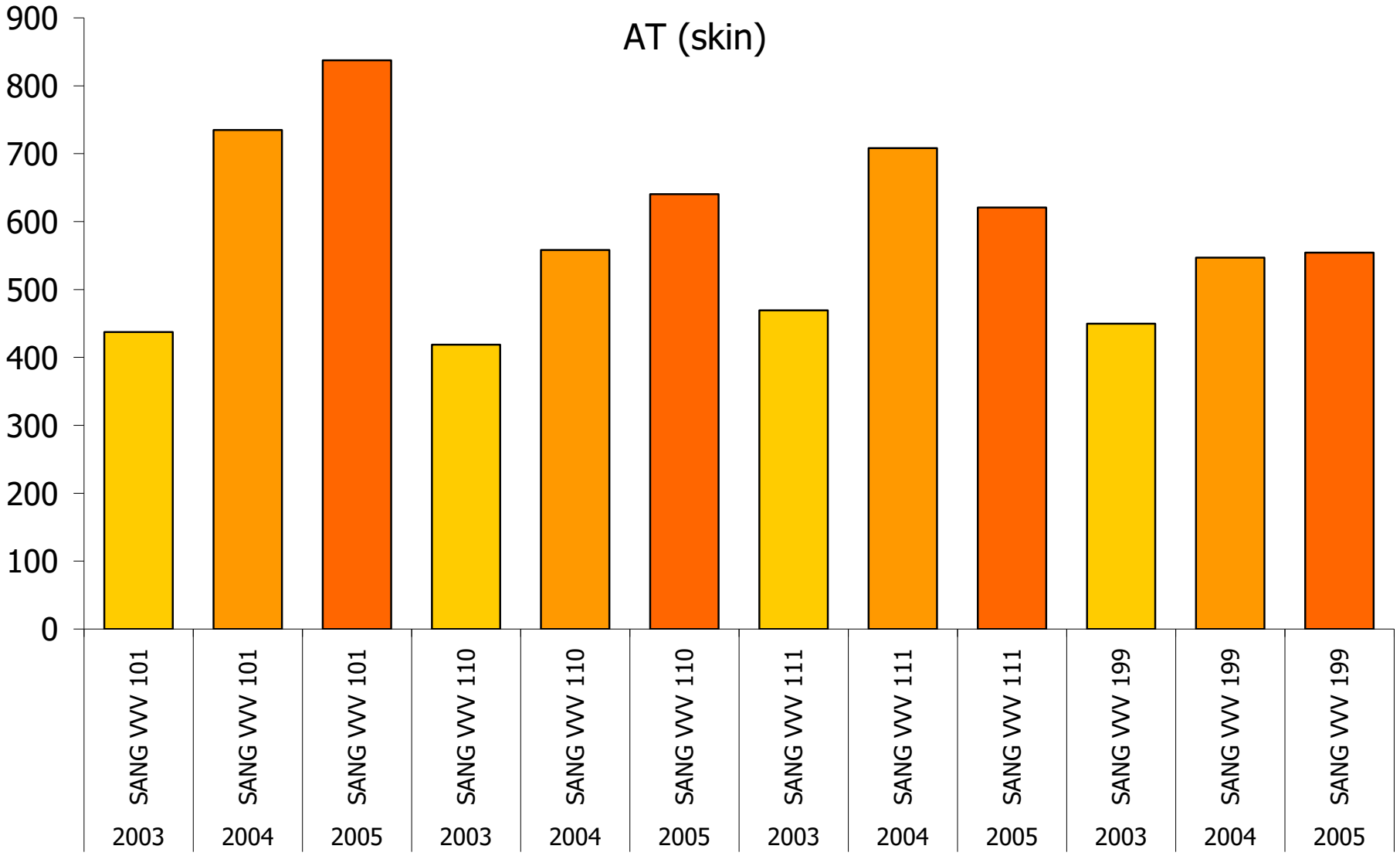
from Mattivi et al., NYAS 2002

VARIABILITY OF THE PHENOLIC POTENTIAL (in a single vineyard, with the same rootstock, and standardized agronomical practices)

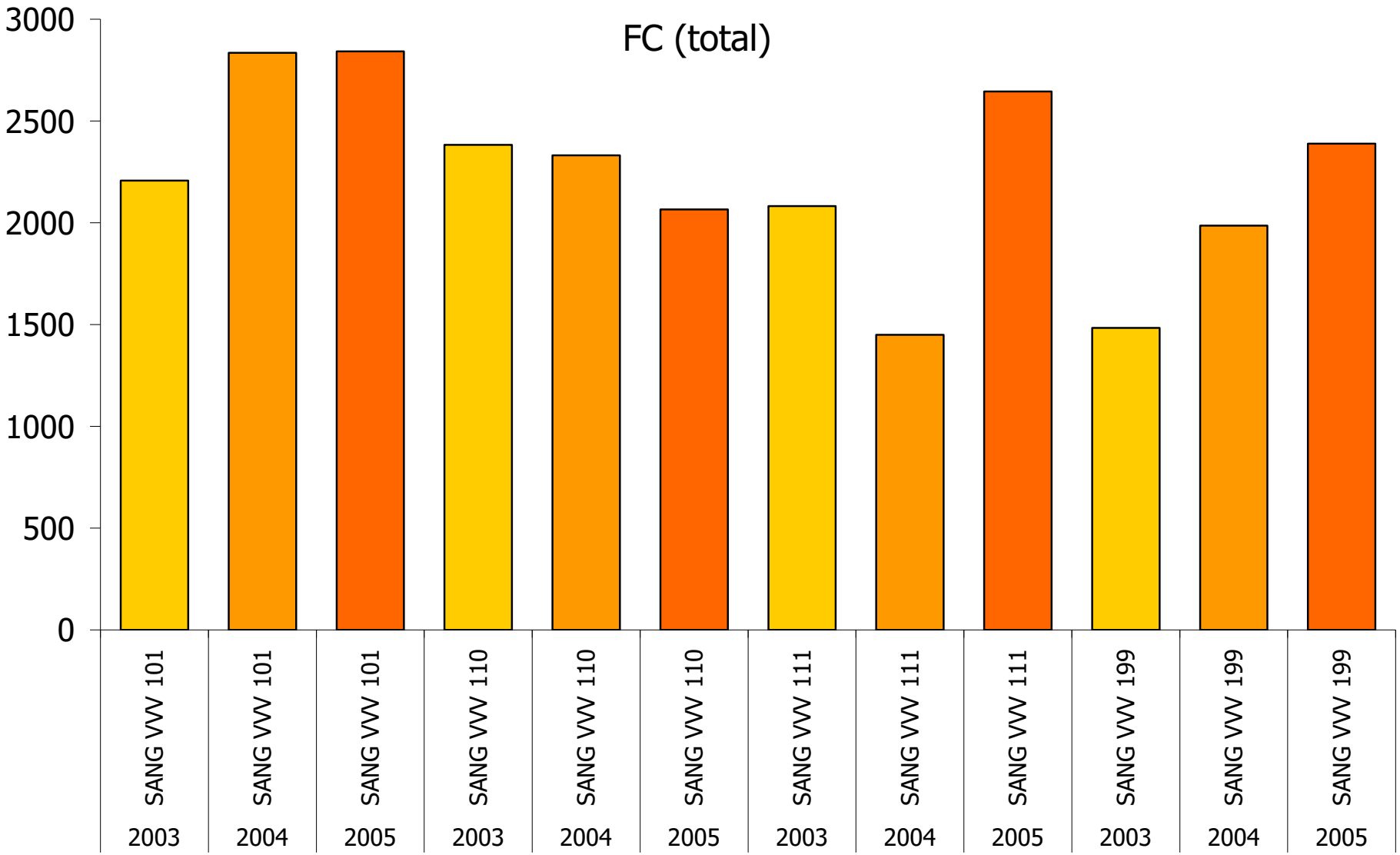
SANGIOVESE

- The phenolic potential of Sangiovese grape was studied during the vintages 2003-2005 in the frame of a project of clonal selection (VCR, Leonardo Valenti, Angelo Divittini).
- We investigated in depth the composition of four biotypes of Sangiovese (SANG VVV 101, SANG VVV 110, SANG VVV 111 and SANG VVV 199), which were selected from old vines growing near Modigliana di Romagna.
- The experimental vineyard was located in the "Fattoria del Cerro" (Saiagricola Spa, Montepulciano, Tuscany), and cultivated with spur pruned cordon trellis system (2,5 x 0,9 m), without grass covering.

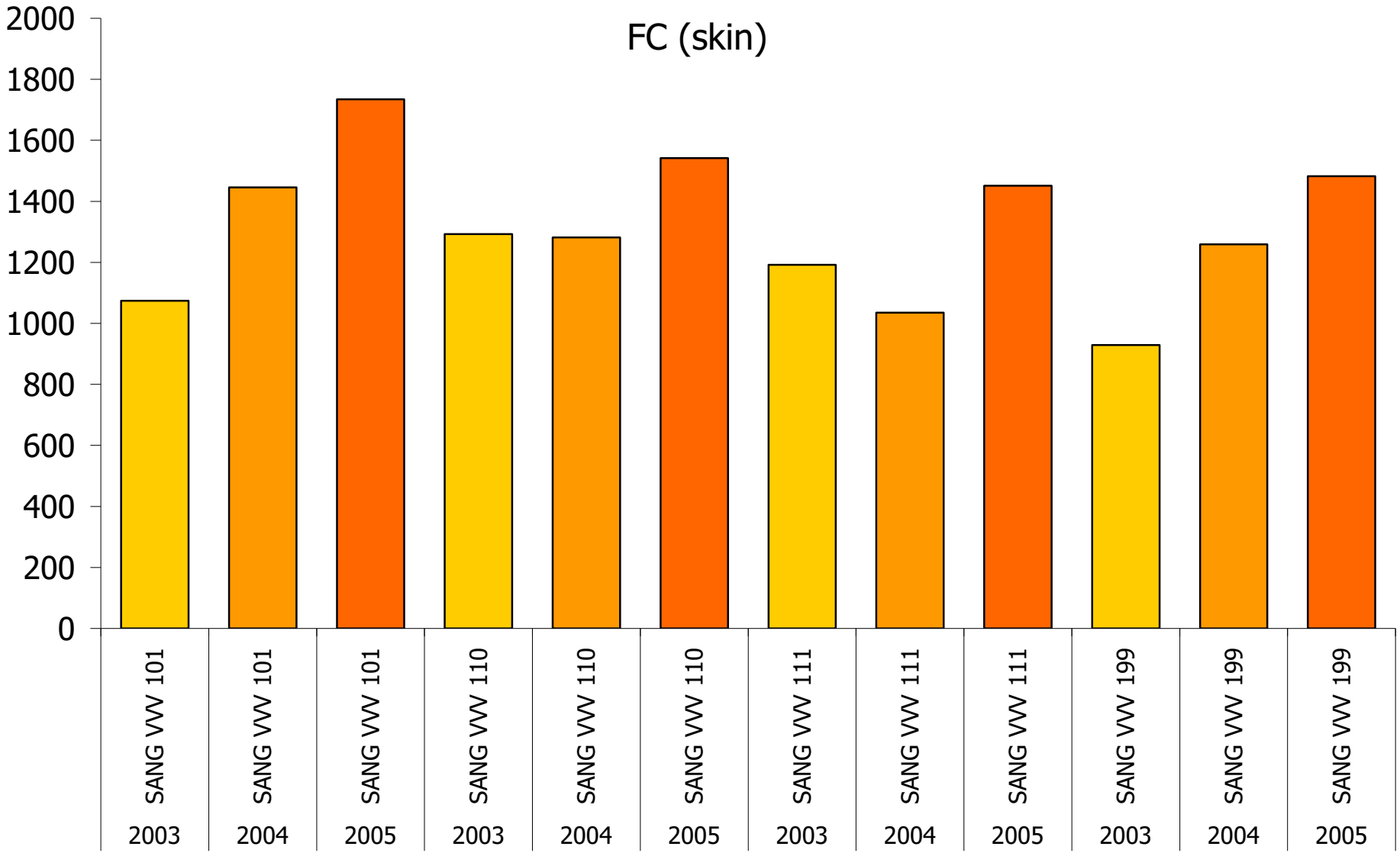
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



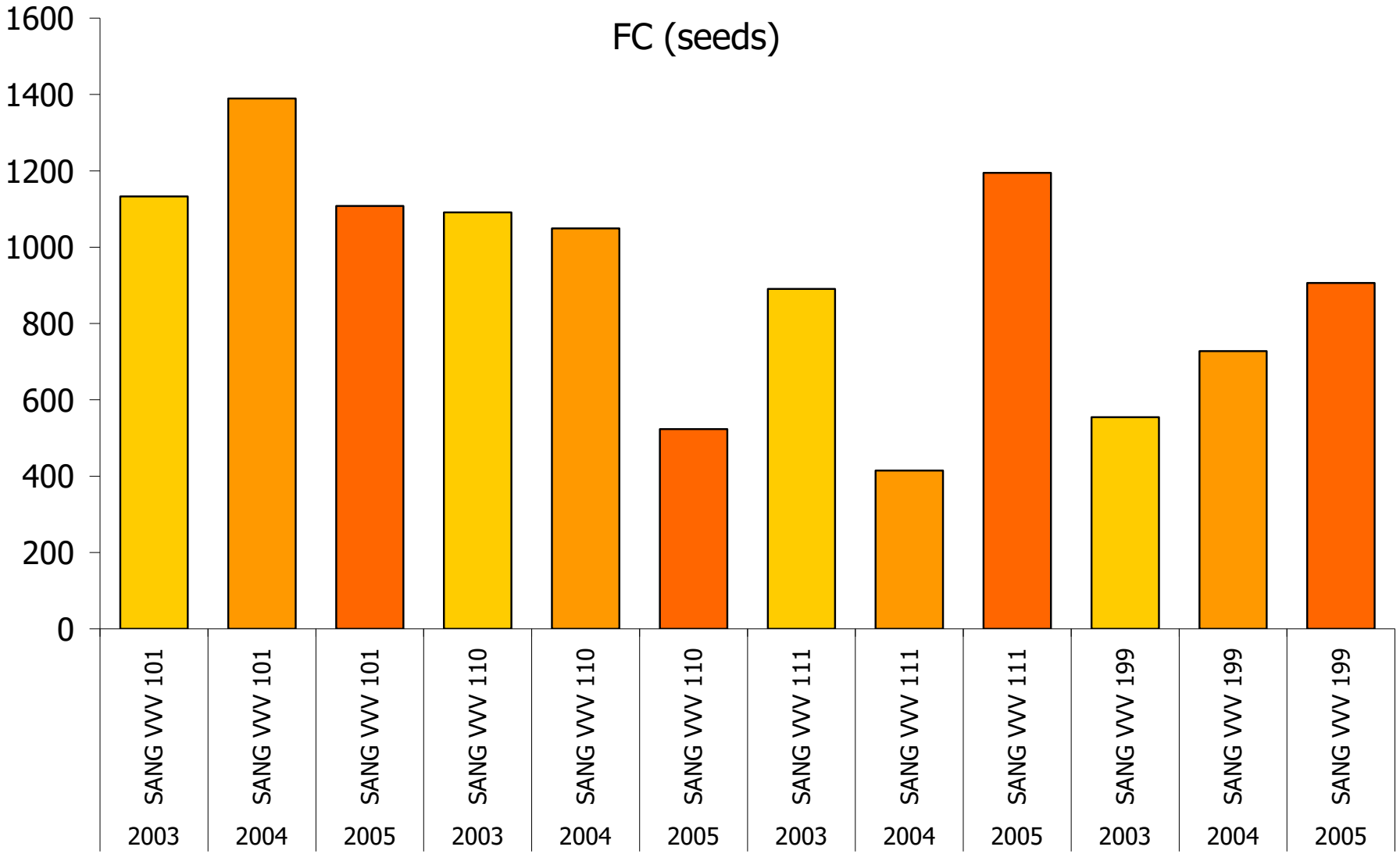
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



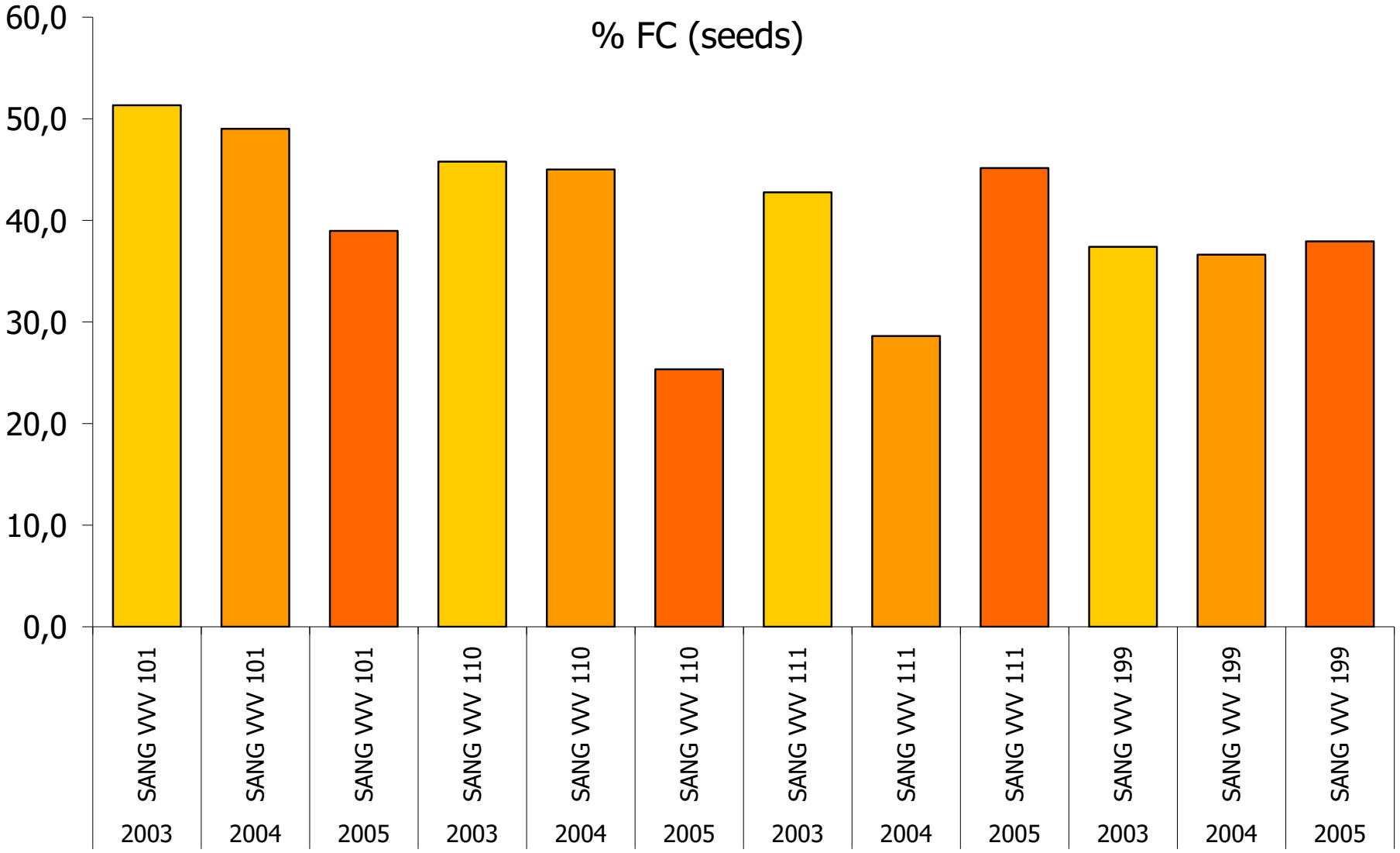
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



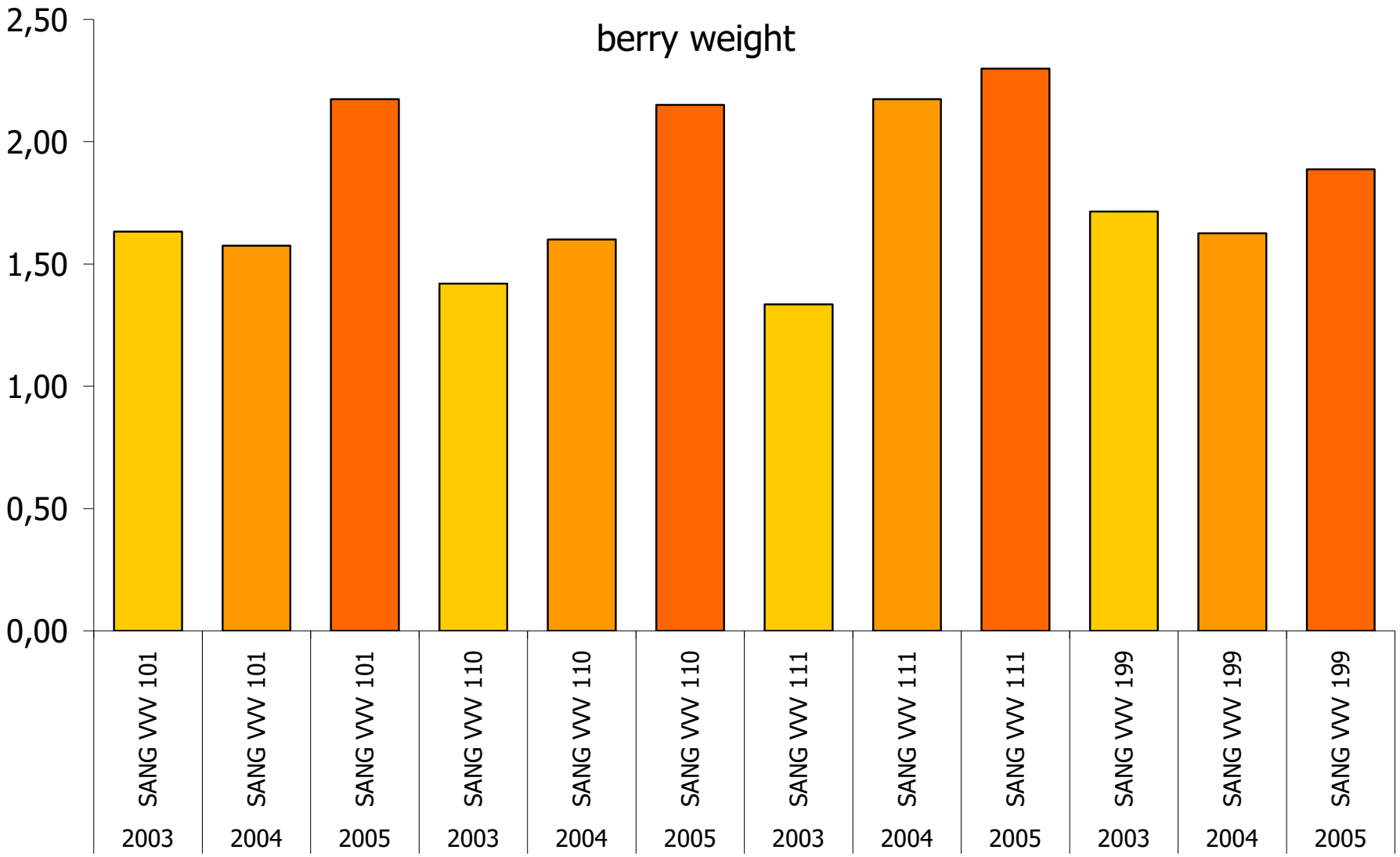
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



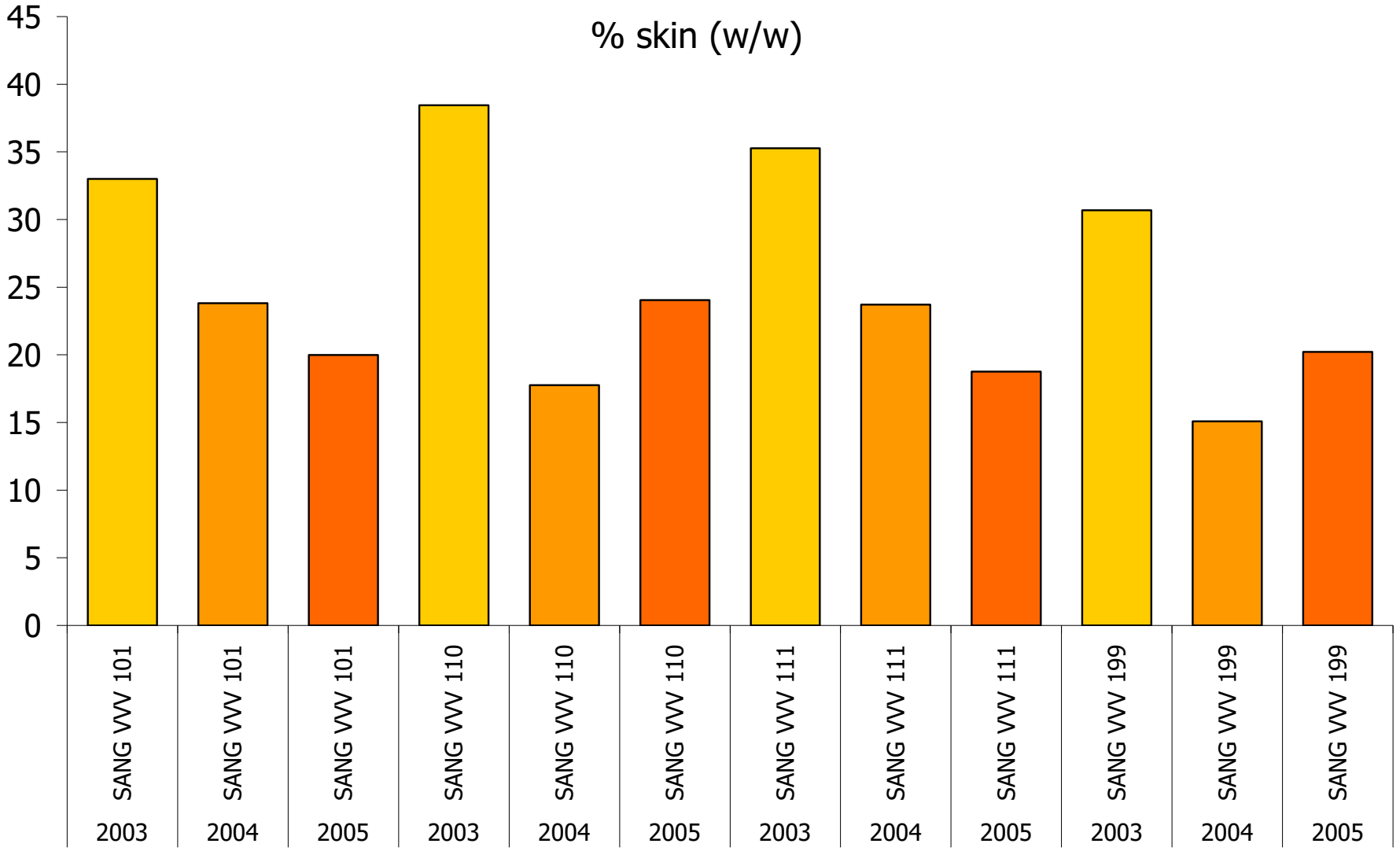
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



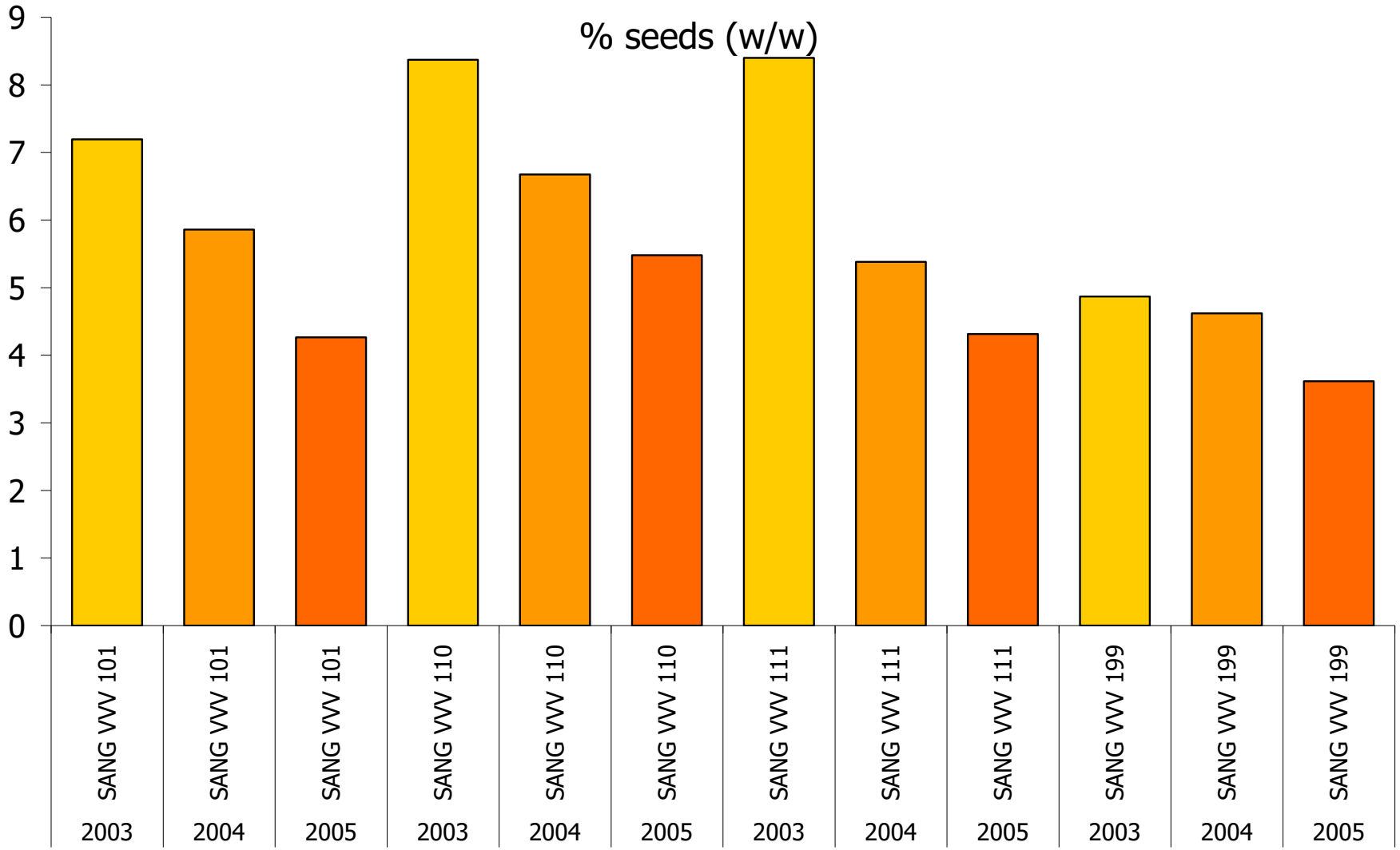
Variability of the berry weight in the berries of Sangiovese clones (vintages 2003-2005)



Variability of the amount of skin in the berries of Sangiovese clones (vintages 2003-2005)



Variability of the amount of seeds in the berries of Sangiovese clones (vintages 2003-2005)

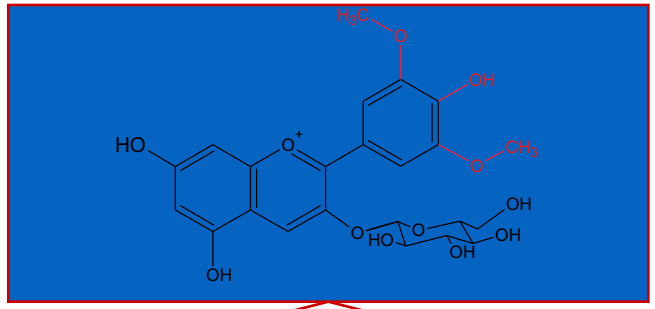


Conclusions - I

This study of the phenolic potential in the Sangiovese grape in the years (2003-2004-2005) highlighted the variability of expression of this grape variety in different vintages, evidencing as main weak points the amount of anthocyanins in the skin and sometimes the amount of seed tannins.

The high variability of the phenolic potential in different vintages explains why the design of the winemaking (number and intensity of pumping over, duration of the skin contact, temperature, etc.) should be very flexible: winemaking can be rather challenging in the worst vintages!

Grape anthocyanins



"DI"

"TRI"

Cyanidin

Peonidin

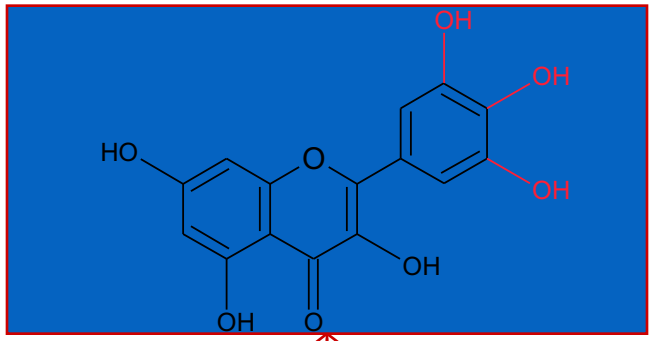
Delphinidin

Petunidin

Malvidin

free glucoside, acetate, p-coumarate.

Grape flavonols



"DI"

"MONO"

"TRI"

quercetin

isorhamnetin

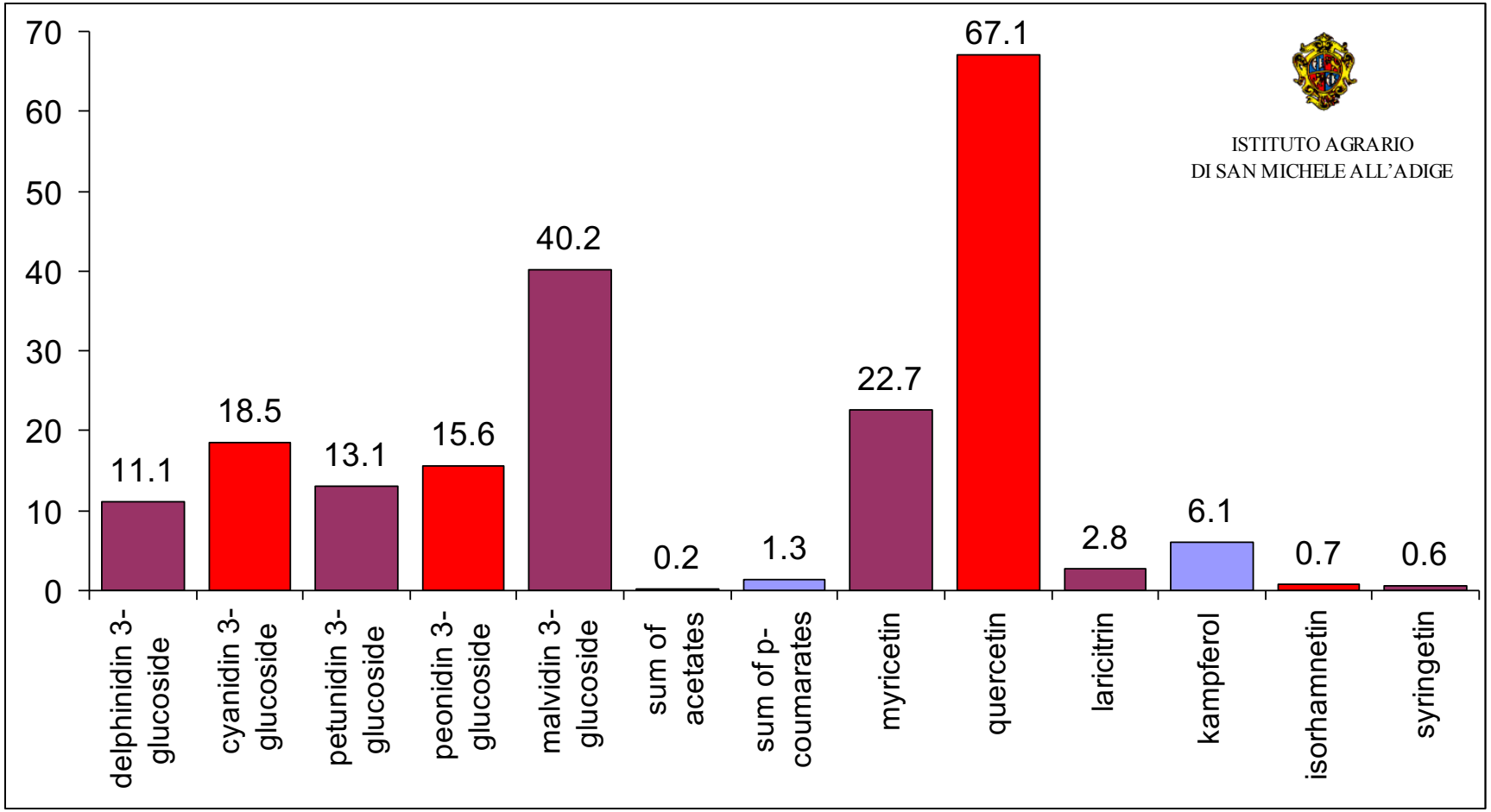
kampferol

myricetin

Laricitrin

Syringetin

Anthocyanins and flavonols in Sangiovese grape

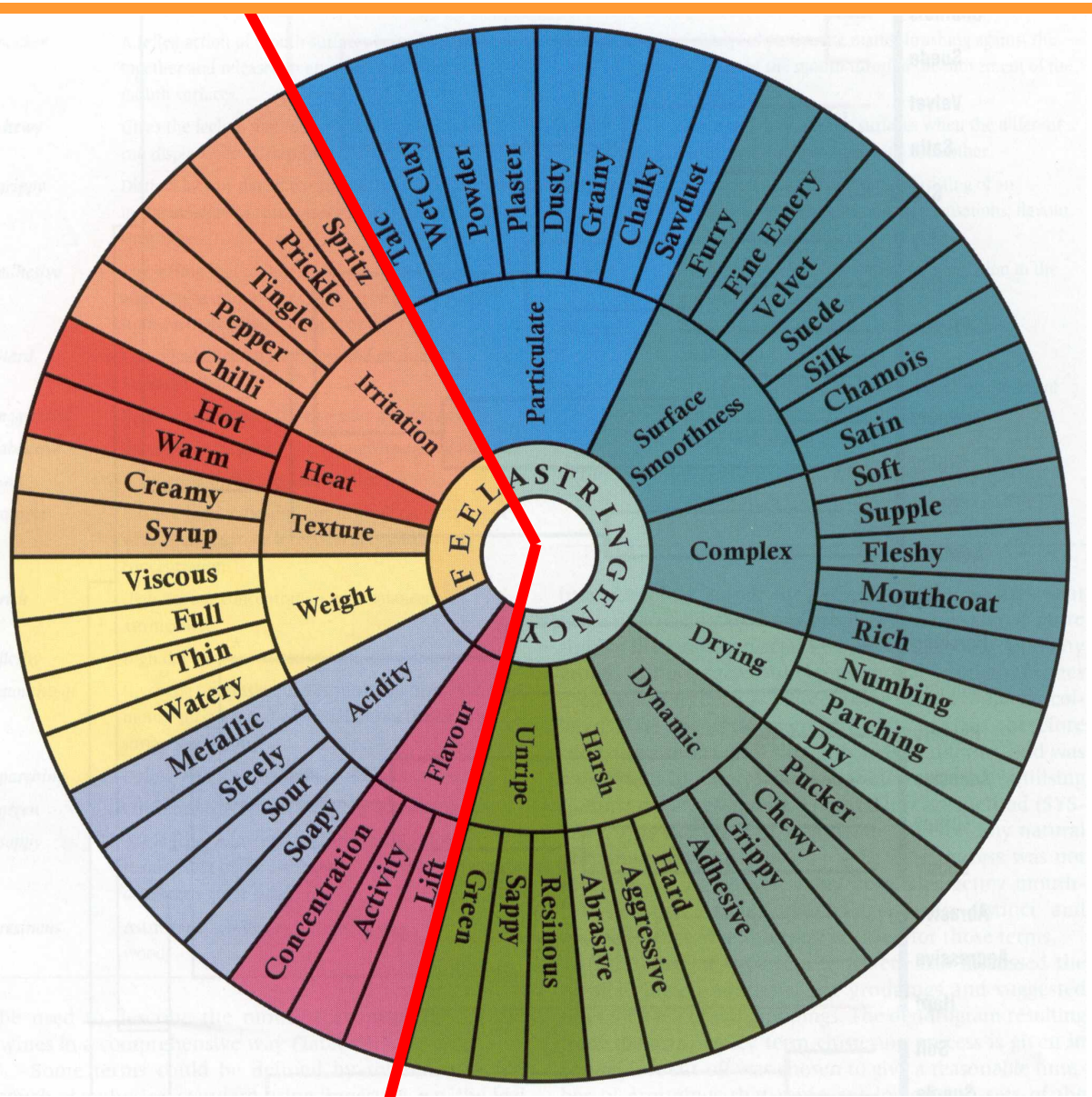


(anthocyanins=765.11 and flavonols=24.56 mg/kg of berries)

A new frontier: structural differences among tannins could explain the different mouth-feel of red wines

non-astringency terms

astringency terms



Red wine mouth-feel terminology
Gawel et al, Australian J. Of Grape and Wine Research, 2000, 6, 203-207

- **particulate**: feelings of particulate matter brushing the surfaces of the mouth through the movement of the wine (talc, wet clay, powder, plaster, dusty, grainy, chalky, sawdust)

- **surface smoothness**: textures felt on mouth surfaces when the different surfaces come in contact with each other (furry, fine emery, velvet, suede, silk, chamois, satin)

- **complex**: a positive hedonic grouping consisting of an amalgam of pleasing astringency sensations, flavour and balanced acidity (soft, supple, fleshy, mouthcoat, rich)

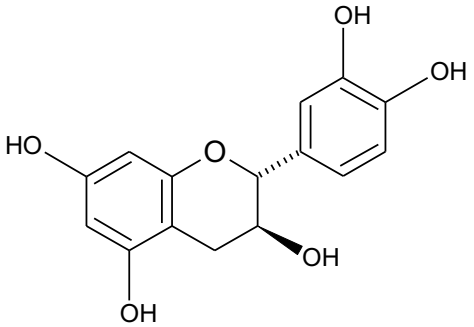
- **drying**: feelings of lack of lubrication or dessiccation in the mouth (numbing, parching, dry)

- **dynamic**: sensations involving some form of mouth movement (pucker, chewy, grippy, adhesive)

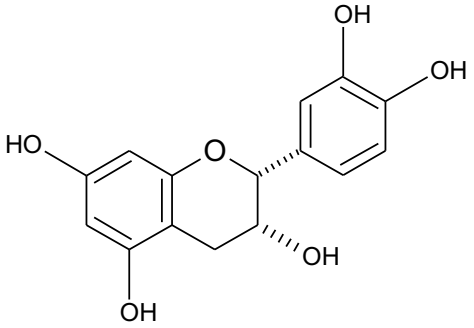
- **harsh**: a negative hedonic grouping suggesting aspects of excessive unbalanced astringency, excessive roughness and/or bitterness (hard, aggressive, abrasive)

- **unripe**: a negative hedonic grouping consisting of an astringent feel associated with excessive acidity and associated green flavour notes (resinous, sappy, green)

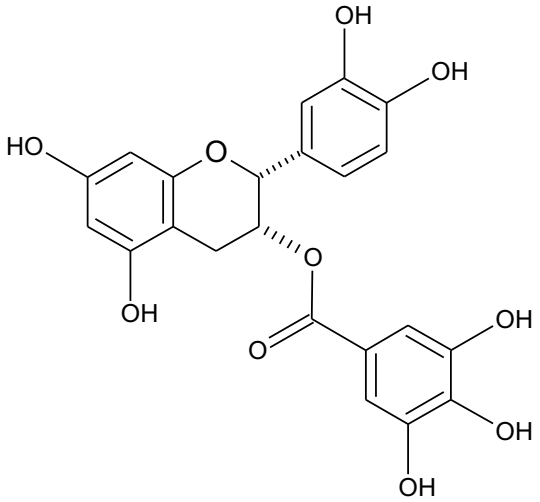
Structure of free flavanols in grape



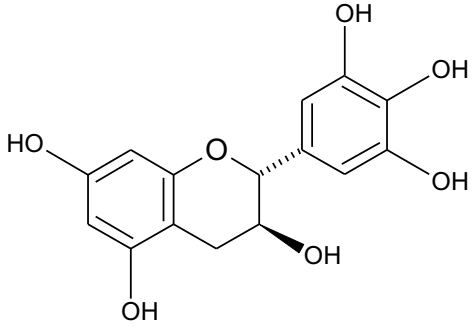
(1) catechin



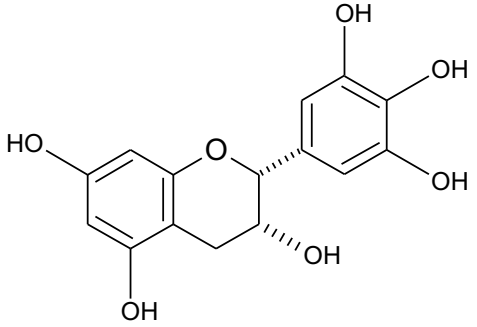
(2) epicatechin



(3) epicatechin gallate

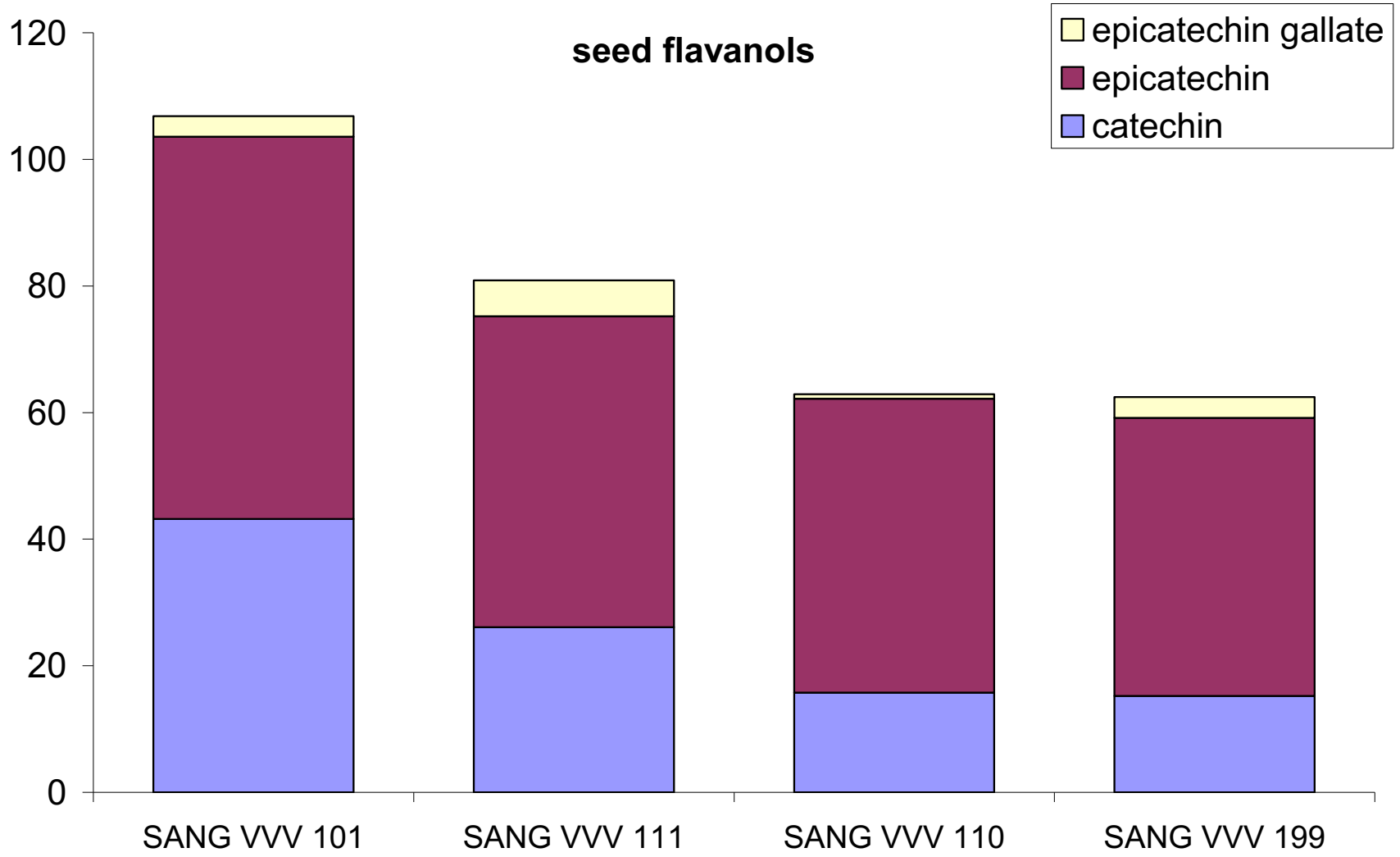


(4) gallocatechin

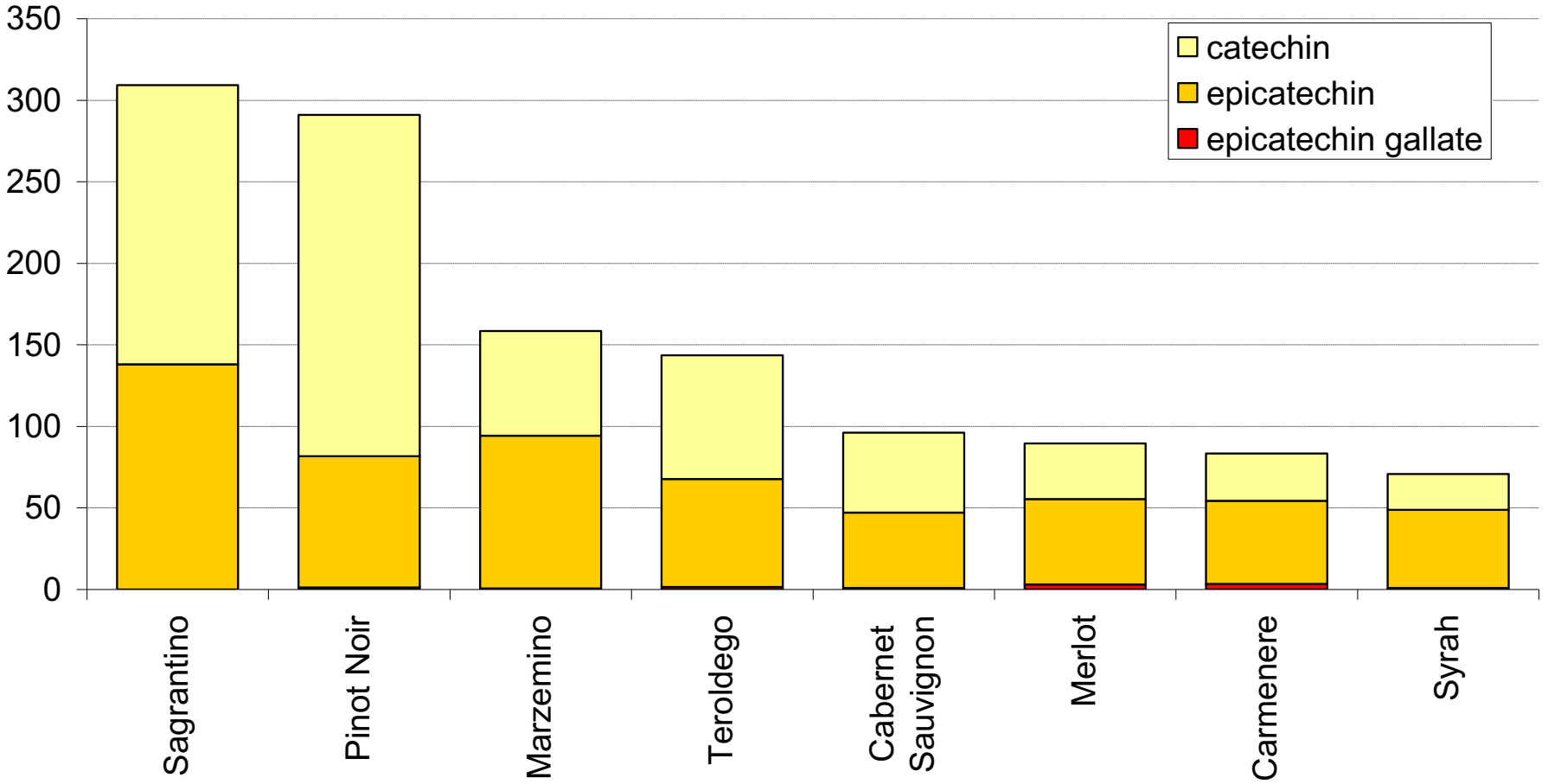


(5) epigallocatechin

Amount of free flavanols extracted from Sangiovese seeds (mg/kg)

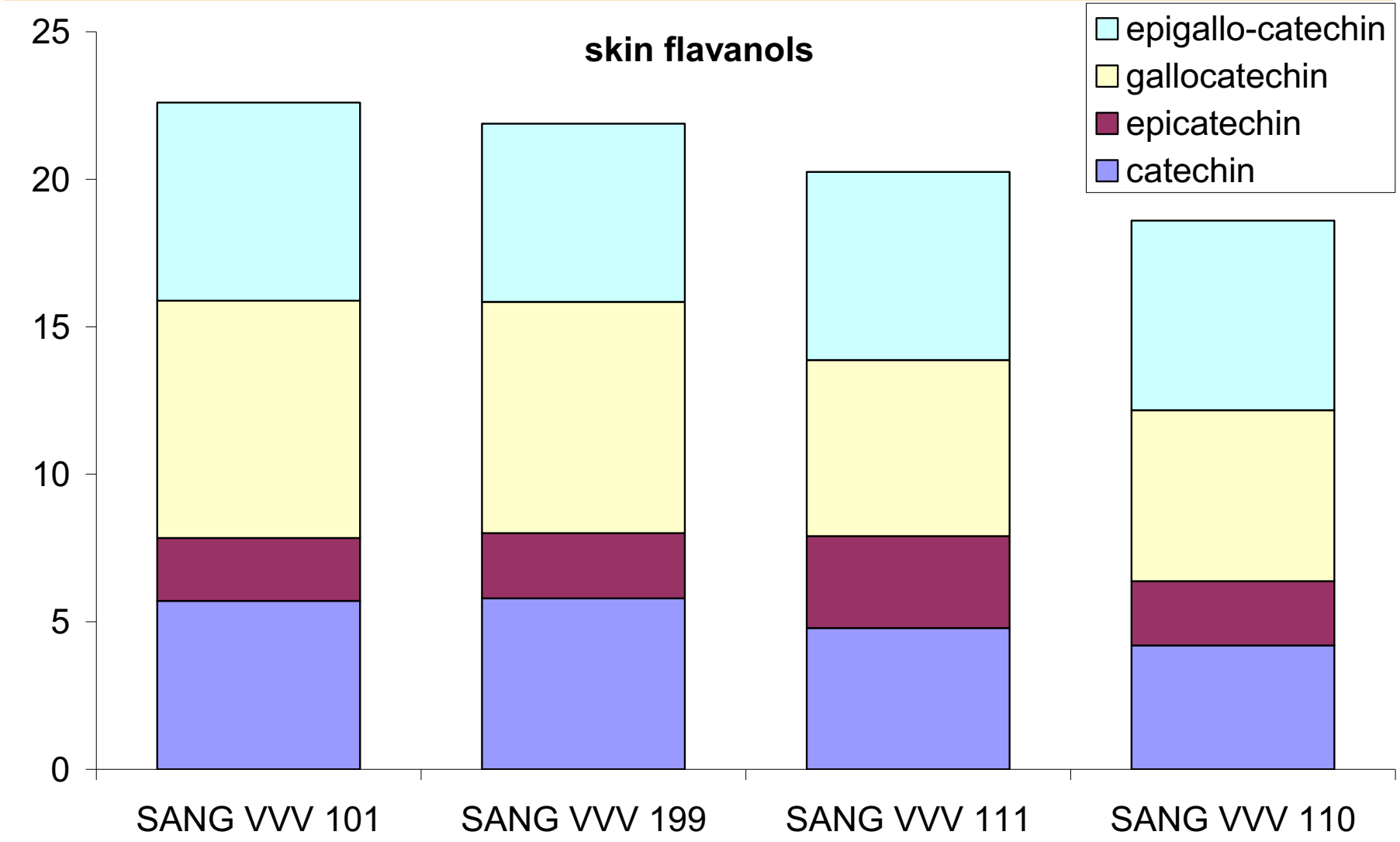


Amount of free flavanols (seeds)



from Mattivi et al, AJGWR 2009

Amount of free flavanols extracted from Sangiovese skins (mg/kg)



Conclusions - II

Sangiovese grape extracts contain 80-130 mg/kg of "flavanol monomers"

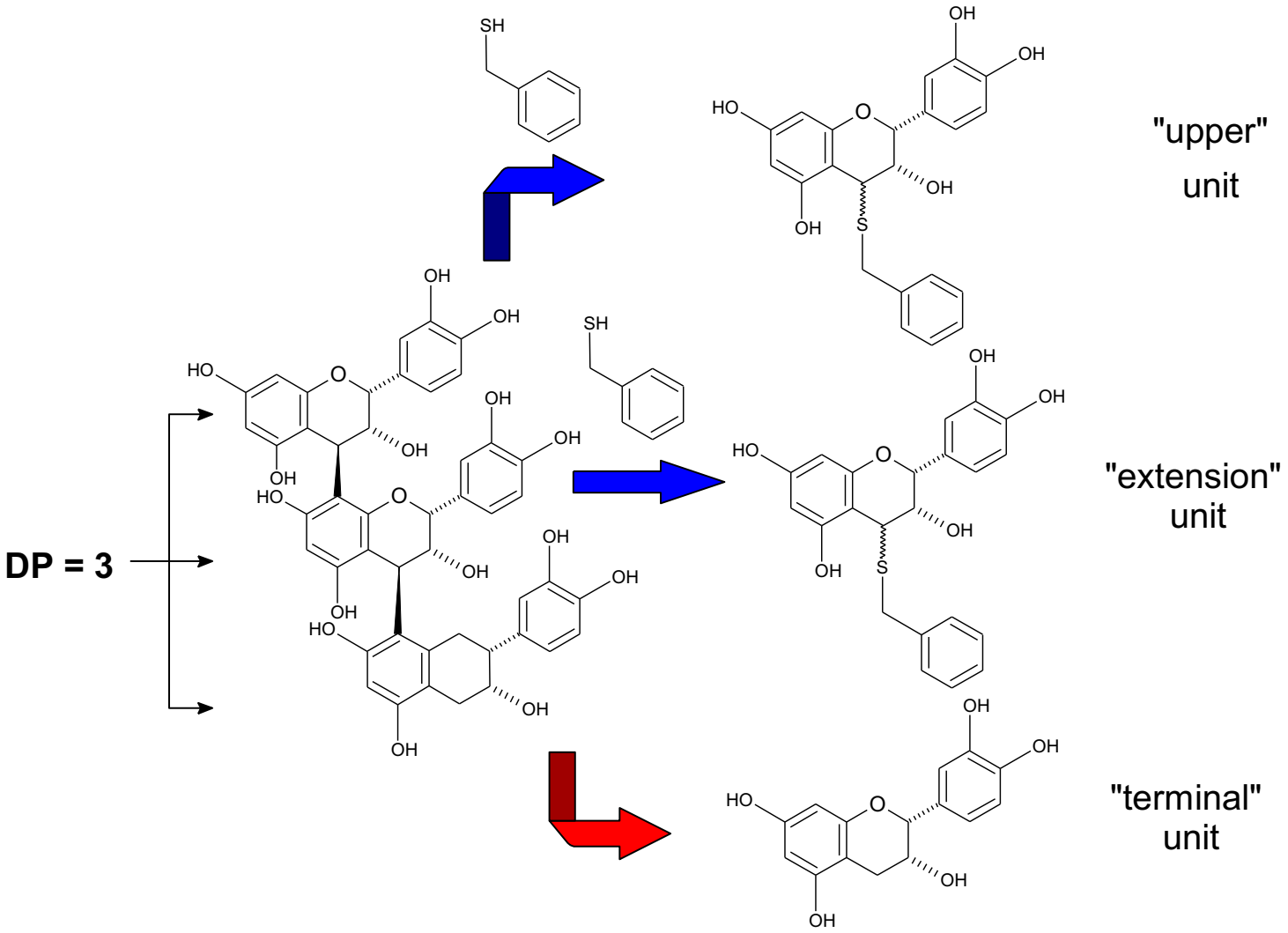
Grape seeds extracts contain, in decreasing order,

- epicatechin (56-74%) & catechin (24-32%)
- epicatechin gallate (1-7%).

Grape skins extracts contain four monomers,

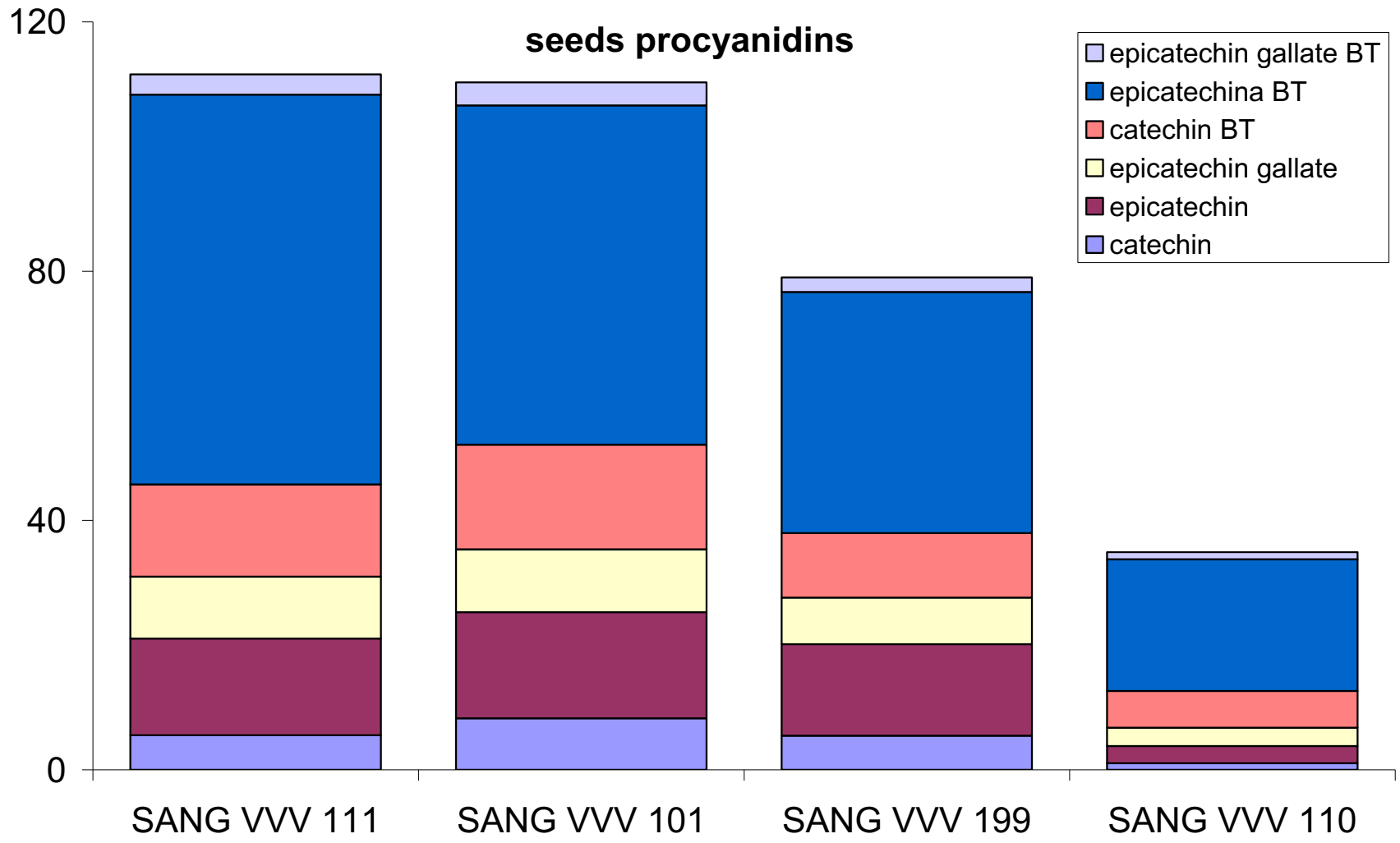
- gallocatechin (29-36%) & epigallocatechin (28-35%)
- catechin (22-26%) and epicatechin (9-12%).

Characterisation of the structure of grape proanthocyanidins by thiolysis



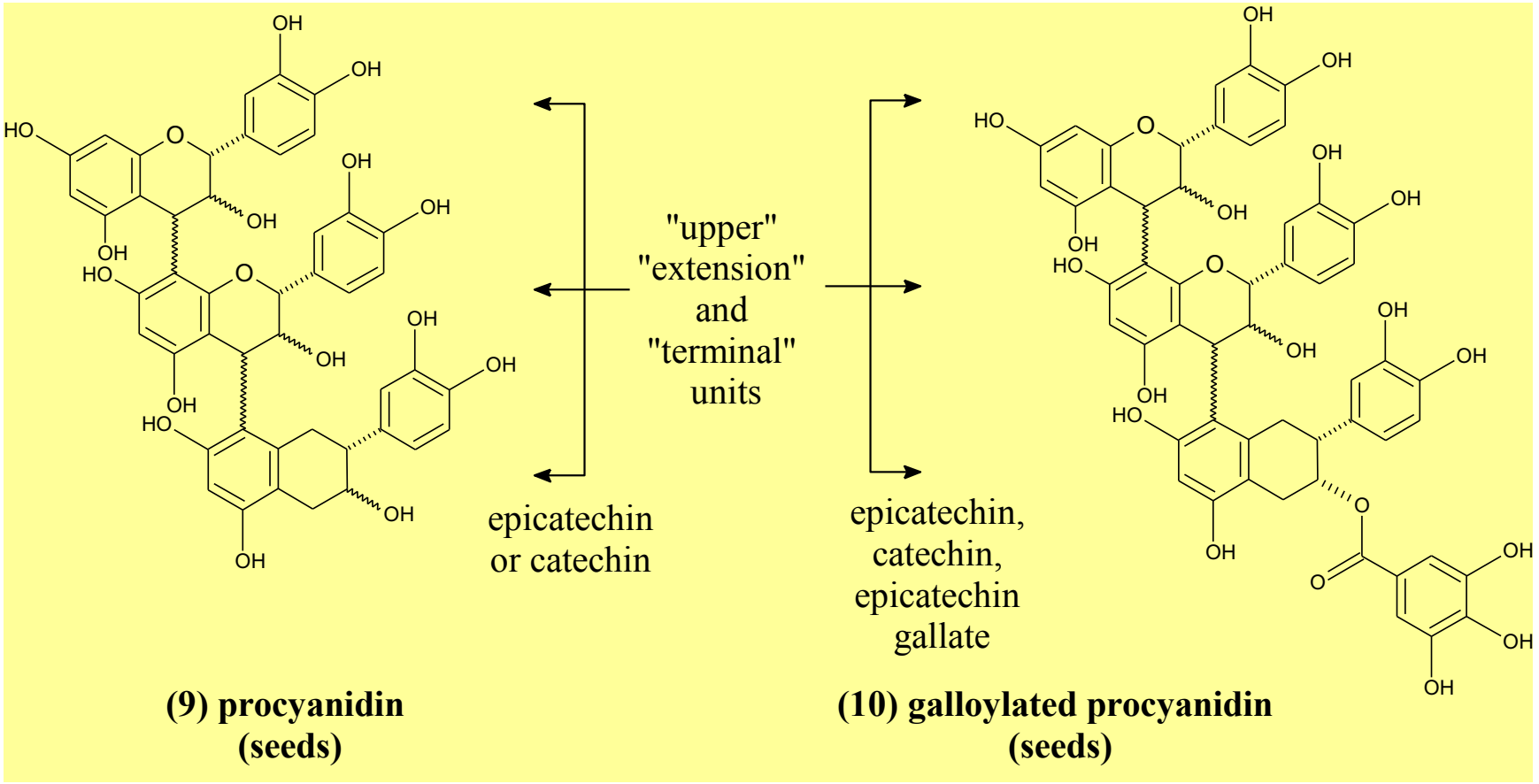
Proanthocyanidins in the berry seeds

(mg/kg)



Seeds proanthocyanidins

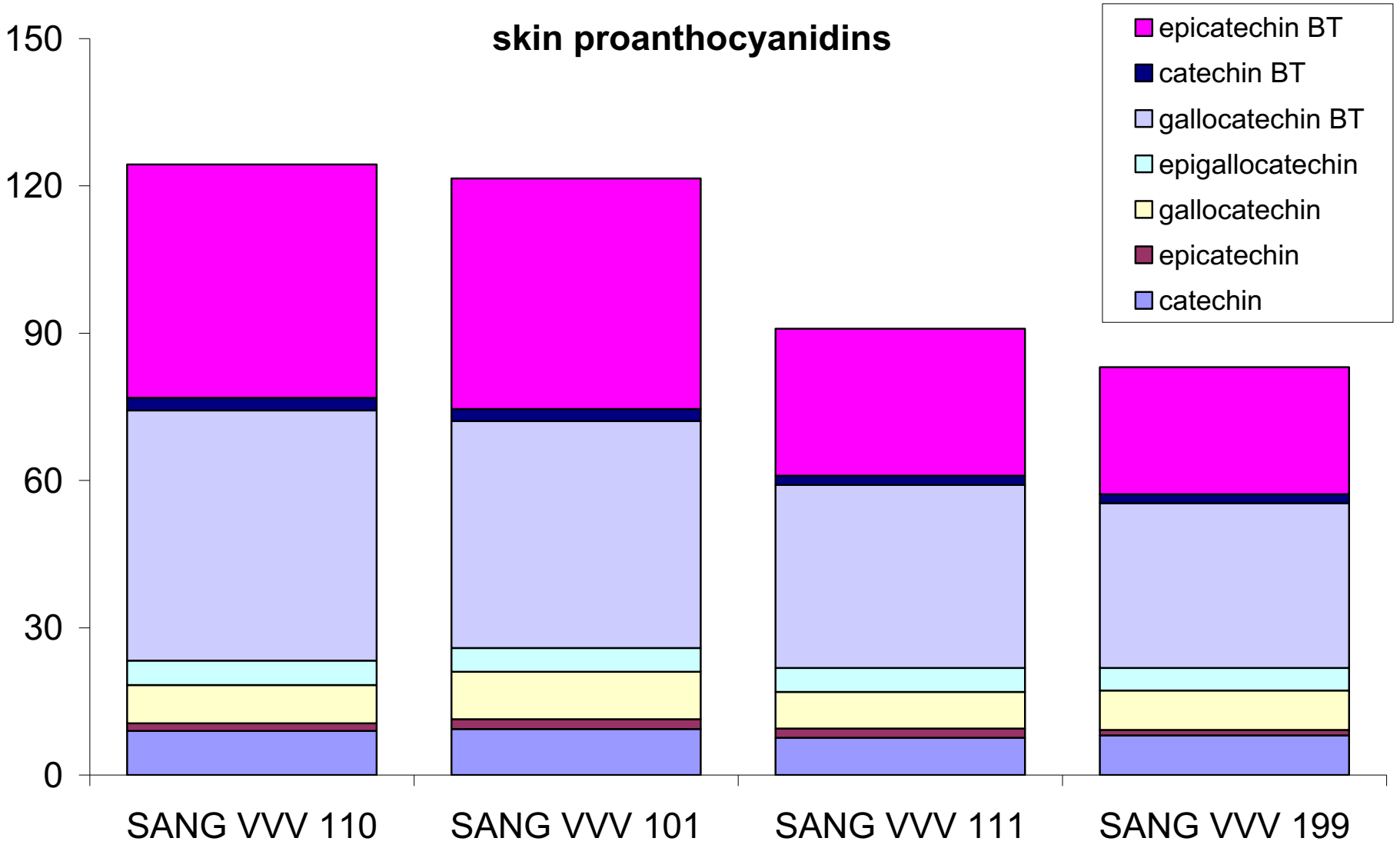
"general structure"



Conclusions - III

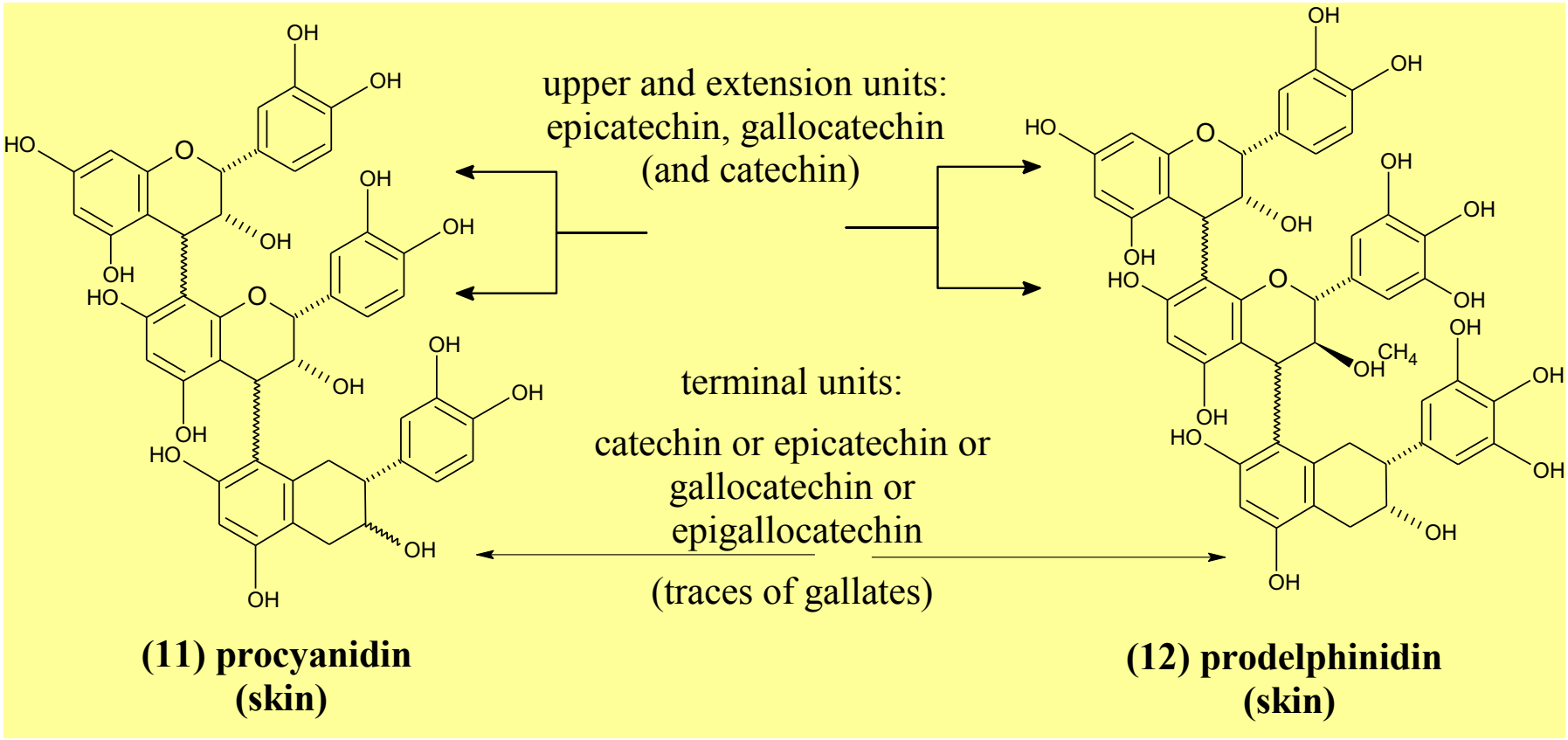
- Grape seeds procyanidins in the Sangiovese grape are characterized by a very large presence of epicatechin gallate in the terminal units (27-43%), which also contain epicatechin (41-53%) and catechin (15-23%).
- The upper and extension units of seeds procyanidins are mainly rich in epicatechin (72-78%), with a lower presence of catechin (18-22%) and lower amounts of epicatechin gallate (4-5%).

Proanthocyanidins in the berry skins
(mg/kg)



Skins proanthocyanidins

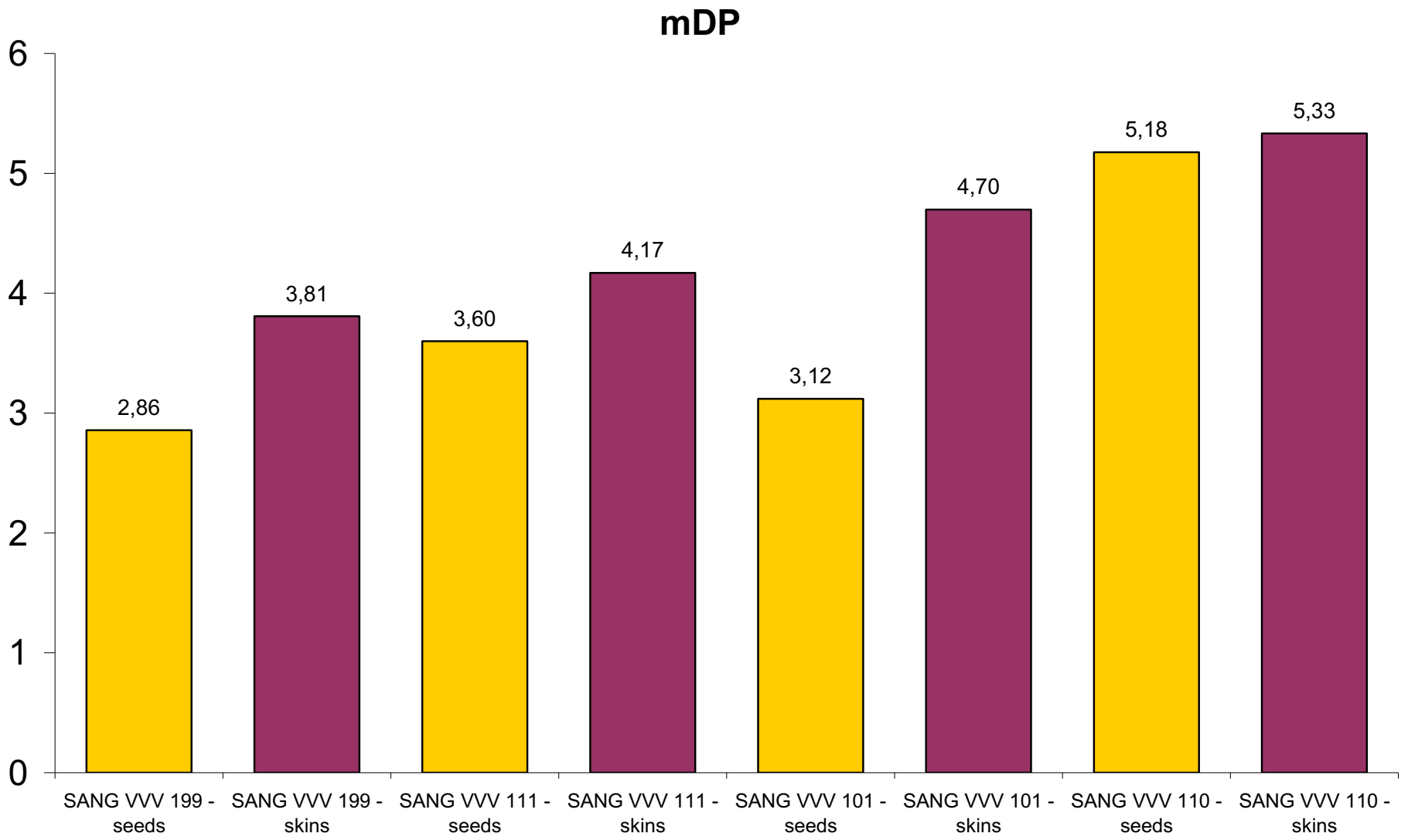
"general structure"



Conclusions - IV

- Grape skins tannins are a mixture of procyanidins and prodelphinidins.
- The prodelphinidin units (gallocatechin and epigallocatechin) constitute more than 50% of both the terminal and the upper-extension units in the skins tannins.
- The procyanidins consist mainly of catechin in the terminal units and of epicatechin in the upper and extension units.
- BOTH SEEDS AND SKIN TANNINS SHOWED THE SAME PATTERN OF COMPOSITION IN ALL THE CLONES

Sangiovese: mean polimerization degree (mDP < 6; seeds=3.7; skins=4.50)



The differences in the structure are likely to influence the biochemical properties of the wines

- Increasing percentages of galloylated PAs and of prodelphinidins are expected to increase the antioxidant potential of the wine, since there is an unequivocal linear relationship between the number of reactive hydroxyls and the antioxidant capacity of the flavanols and PAs (Bors and Michel, 2002).

- Galloylated PAs from seeds are a source of free gallic acid in the wine, which is the wine polyphenol with the highest bioavailability (Manach et al., 2005).

- The extent of galloylation affects both bitterness and astrigency (Lesschaeve and Noble, 2005).

Conclusions V

The biosynthesis of anthocyanins, flavonols, flavanols and PAs in the grapes appear to be highly regulated at the level of the variety, leading to differences in the amount and in the structure that are likely to play a significant role in the nutritional and sensorial (color & taste) properties of the wines.

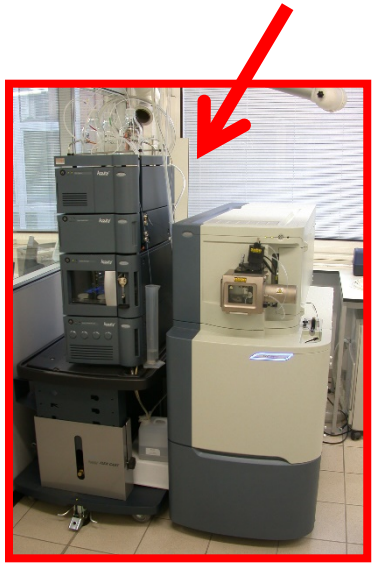
These different are relevant for the color, astringency, and durability of the wines!

Untargeted metabolomics (at FEM)

Adding value to the food chain

DEPARTMENT OF FOOD QUALITY AND NUTRITION

Shared facility,
online booking, operative 24/7



UPLC-Q-Tof
GCxGC-Tof

Orbitrap

GC-MS/MS

1. Storage

the effect of temperature on wine composition

The **“chemical age”** can significantly differ from the vintage written in the label

Your wine could became much older if not properly stored!

Strictly controlled temperature
15–17 °C

Temperature adjusted to human well-being
20–27 °C
fluctuating with the seasons

Standard **HKQAA** for **fine wines**
Temperature 11–17 °C
Fluctuation daily, max 3%
Fluctuation annual,max 5%
humidity 55%–80%

Standard **HKQAA** for **commercial wines**
Temperature 22 °C
Fluctuation daily, max 5%
Fluctuation annual, max 10%
humidity >50%

Wines: cv. Sangiovese, harvest 2009

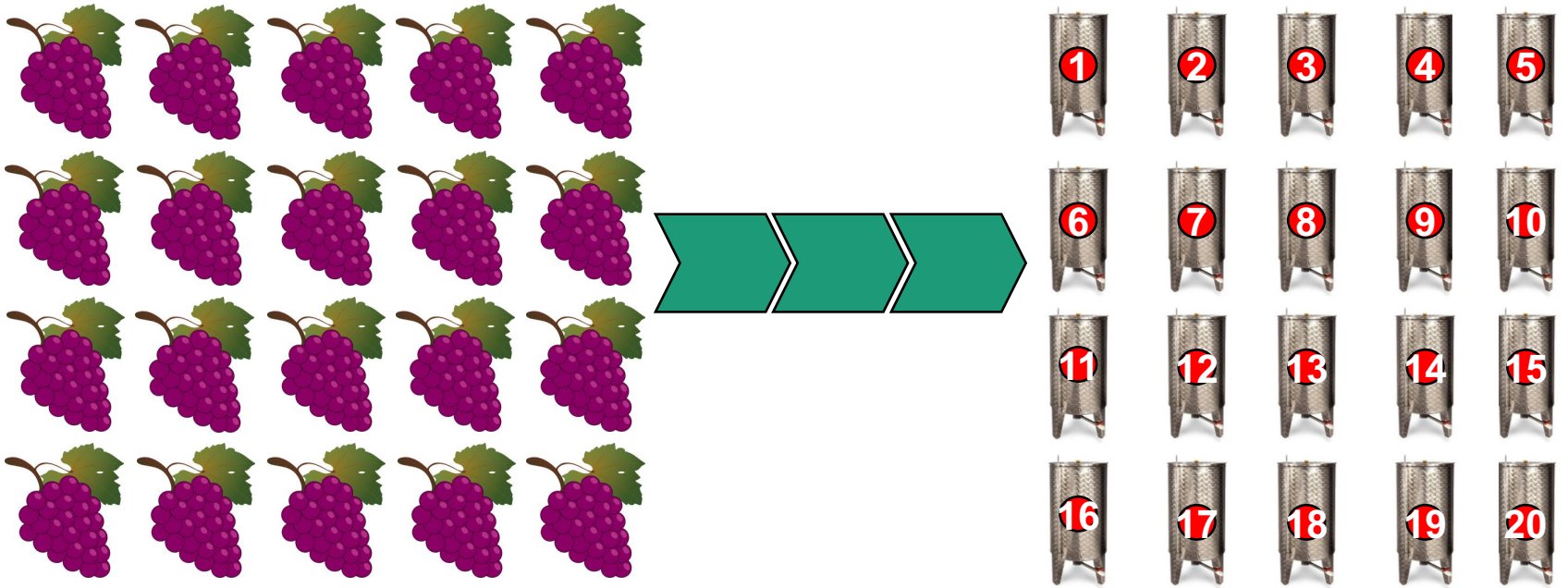
(20x20 -> 400 bottles, 375 ml, natural cork stoppers)

2009

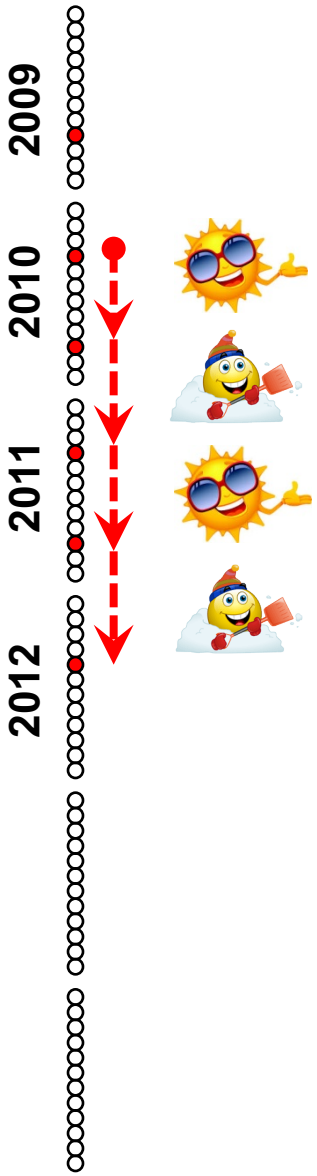
Montalcino (Tuscany)

San Michele all'Adige (Trento)

samples from 20 vineyards to produce 20 experimental wines



2-years storage



Protocols for wine analysis

1. UPLC-Q-TOF MS untargeted, ESI+ and ESI- (Synapt HDMS QTOF MS)

→Arapitsas P. et al., Metabolomics 2014

"Untargeted metabolomics"

2. UPLC-MS/MS targeted for wine pigments (Xevo TQ MS)

→Arapitsas P. et al., JAFC 2012, 10461–10471

"Targeted metabolomics"

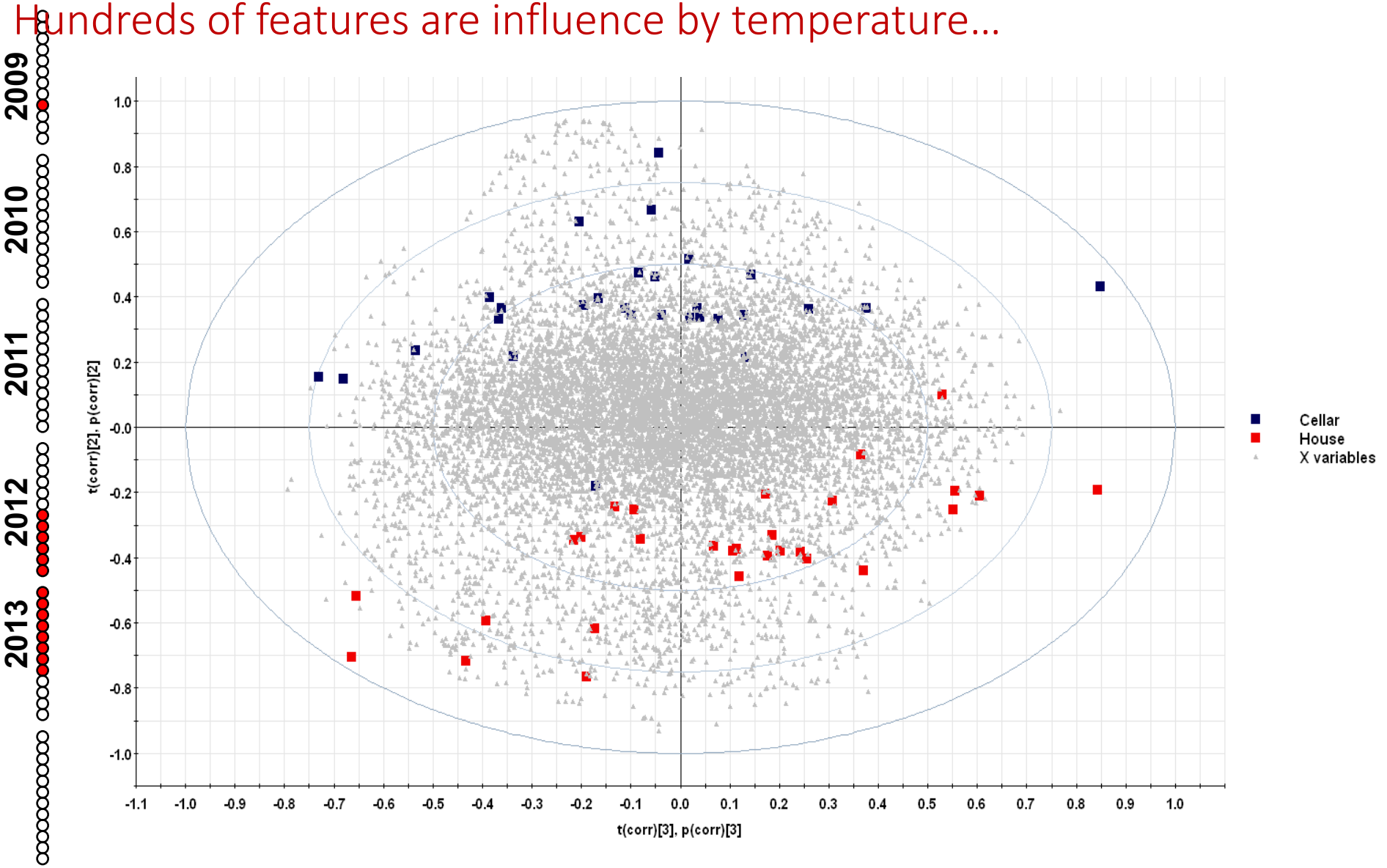
3. UPLC-MS/MS targeted for common phenolics (Xevo TQ MS)

→Vrhovsek U. et al., JAFC 2012, 8831–8840

"Open data"

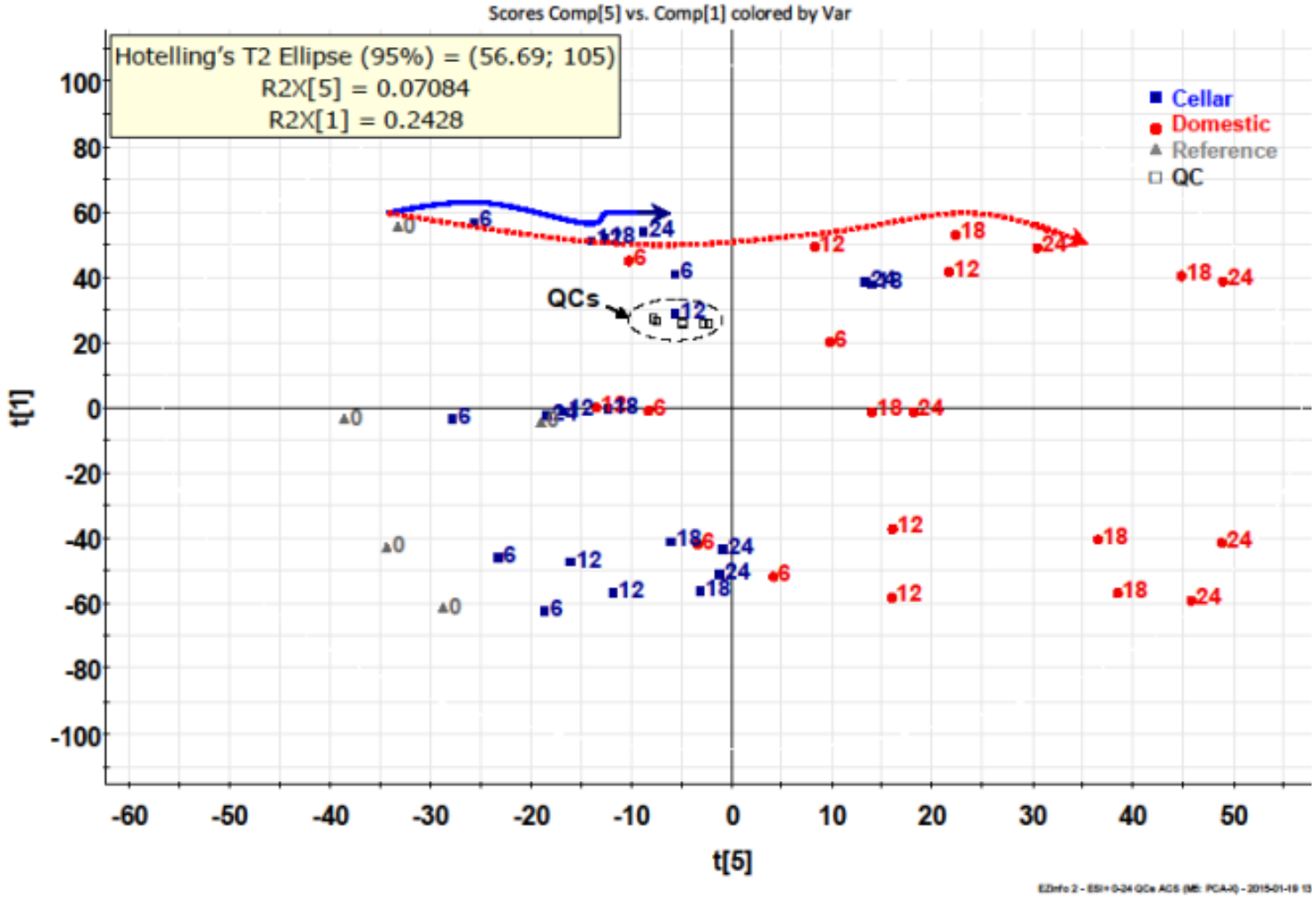
→http://www.ebi.ac.uk/metabolights/altMTBLS55

Untargeted analysis by HPLC-Q-Tof (ESI+ and ESI-) reveals 10k features.
The large majority of wine compounds is stable (expected!).
Hundreds of features are influence by temperature…



Arapitsas P. et al. Metabolomics 2014

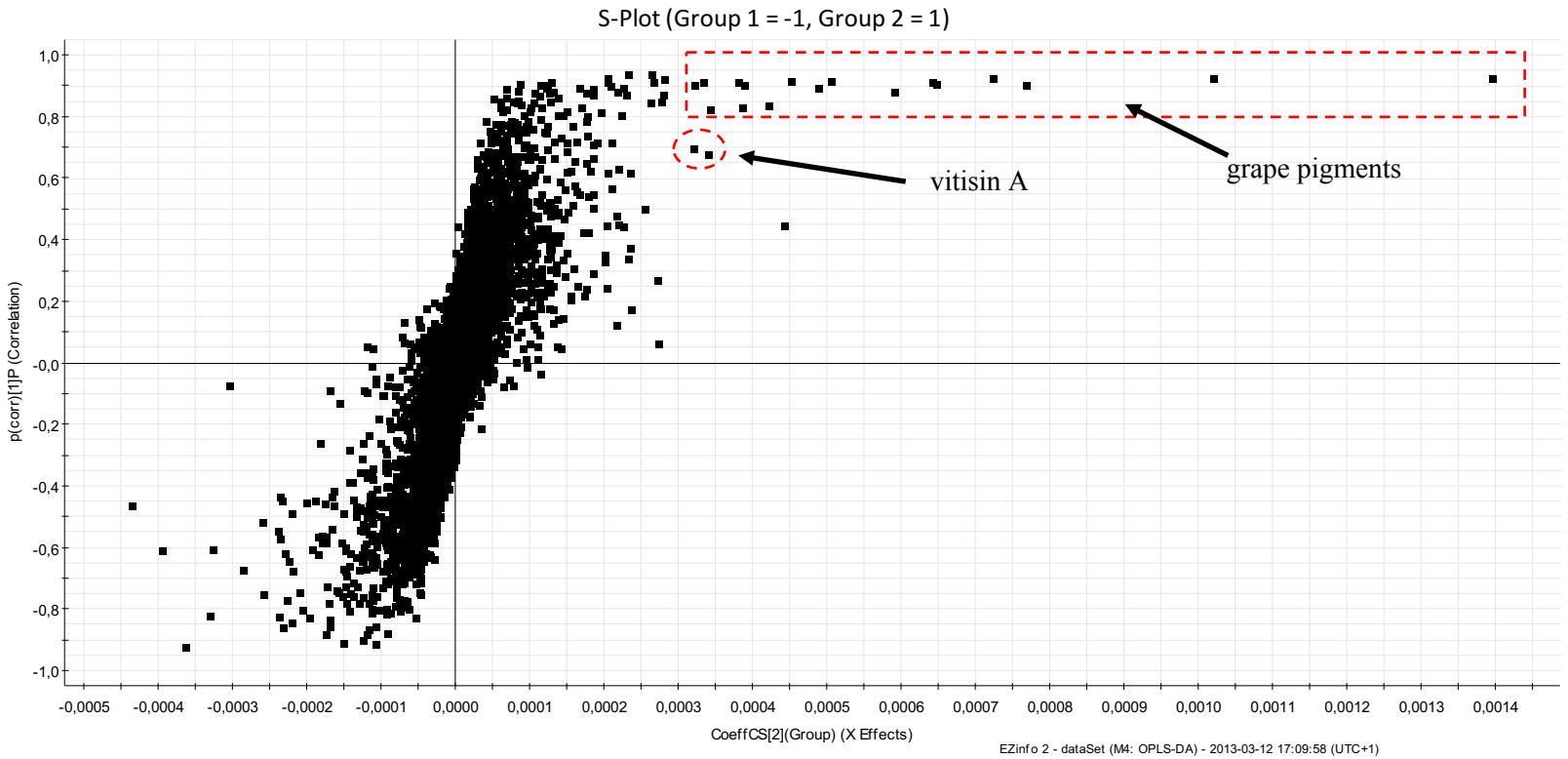
Considering the overall composition, wines stored in typical domestic conditions developed approximately 3-4 times faster



Mattivi et al., 2015 (in Advances in Wine Research)

S-plot of OPLS-DA analysis for feature selection from ESI+ data in the two storage conditions (24 months)

LC-MS ESI+



Arapitsas P. et al. Metabolomics 2014

Average change of chromatographic area of selected compounds during storage in the two conditions

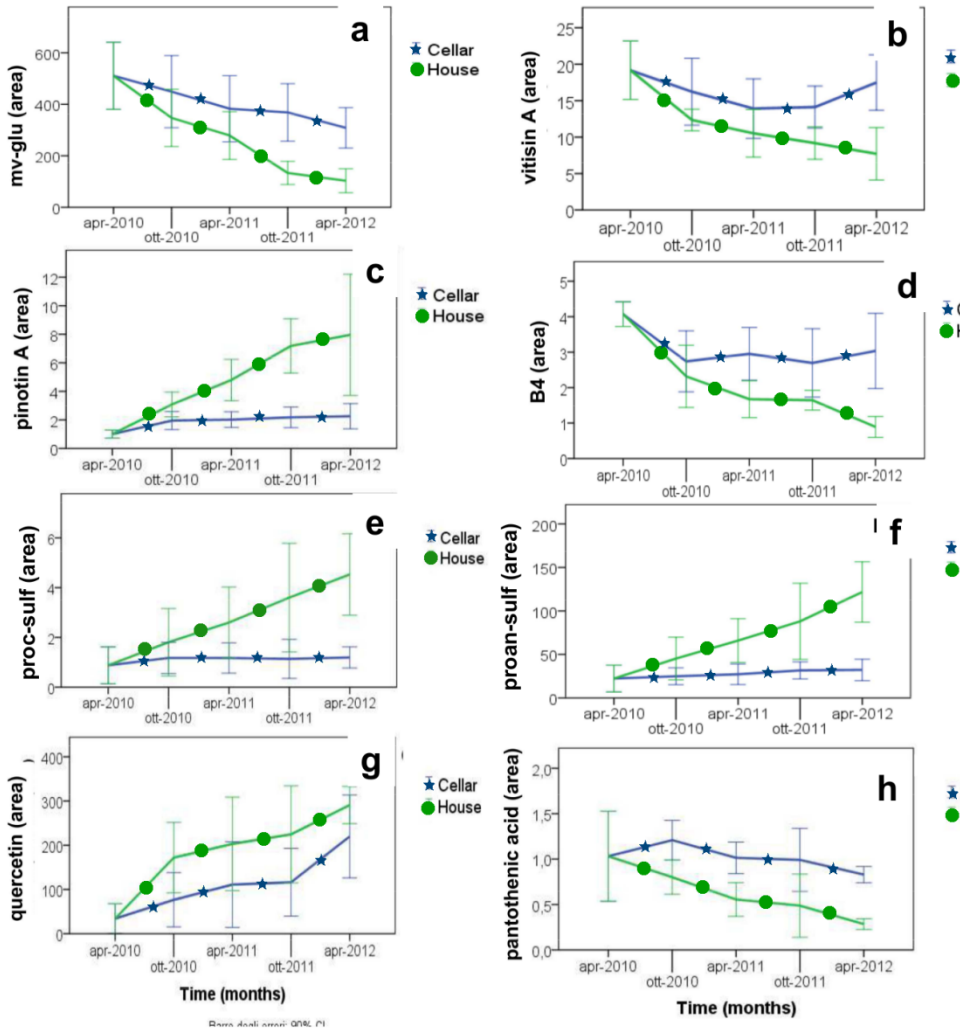
2009 2010 2011 2012 2013

a) malvidin 3-glucoside

c) pinotin A

e) sulfonated procyanidin

g) quercetin



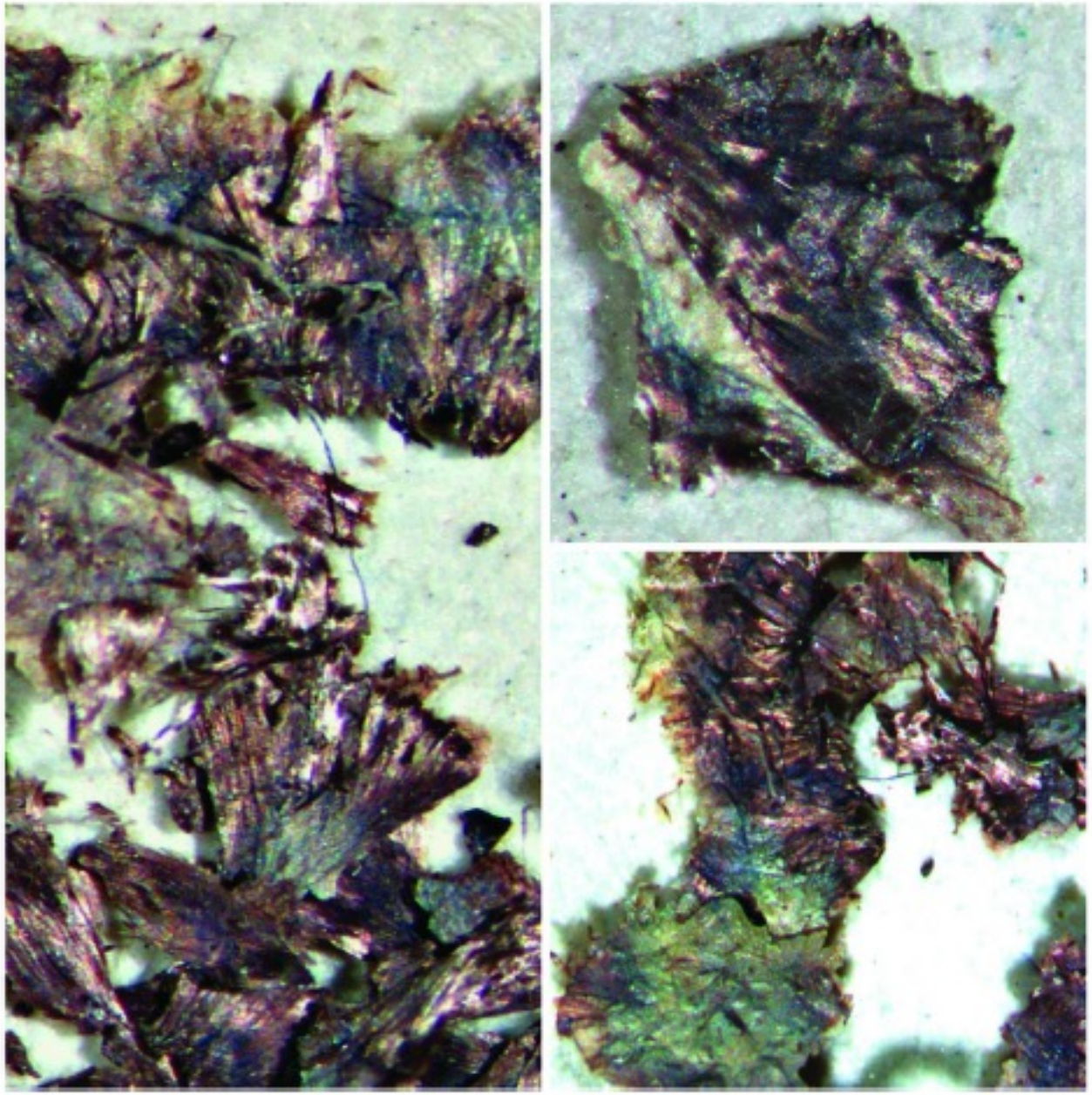
b) vitisin A

d) procyanidin B4

f) sulfonated proanthocyanidin

h) pantothenic acid

Arapitsas P. et al. Metabolomics 2014

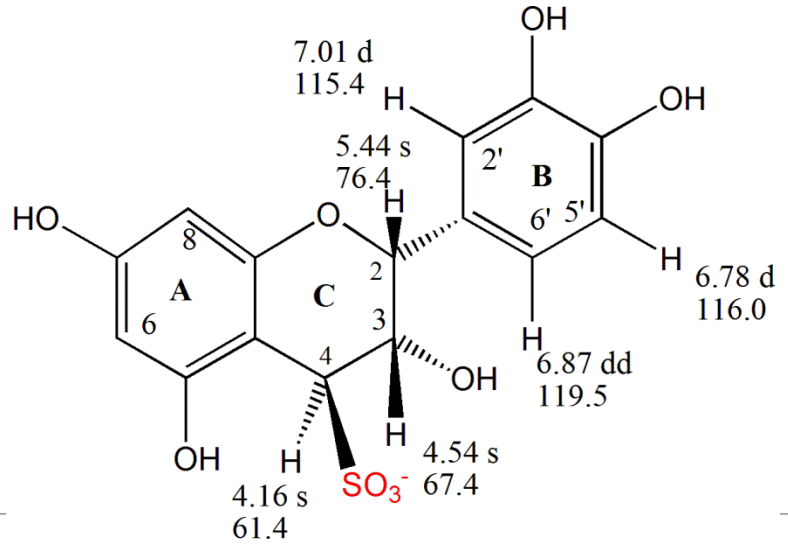


Floating flakes isolated from a Sangiovese wine, and consisted mainly of quercetin and other flavonols in minor amounts.

Mattivi et al., 2015 (ACS Book Chapter, Advances in Wine Research)

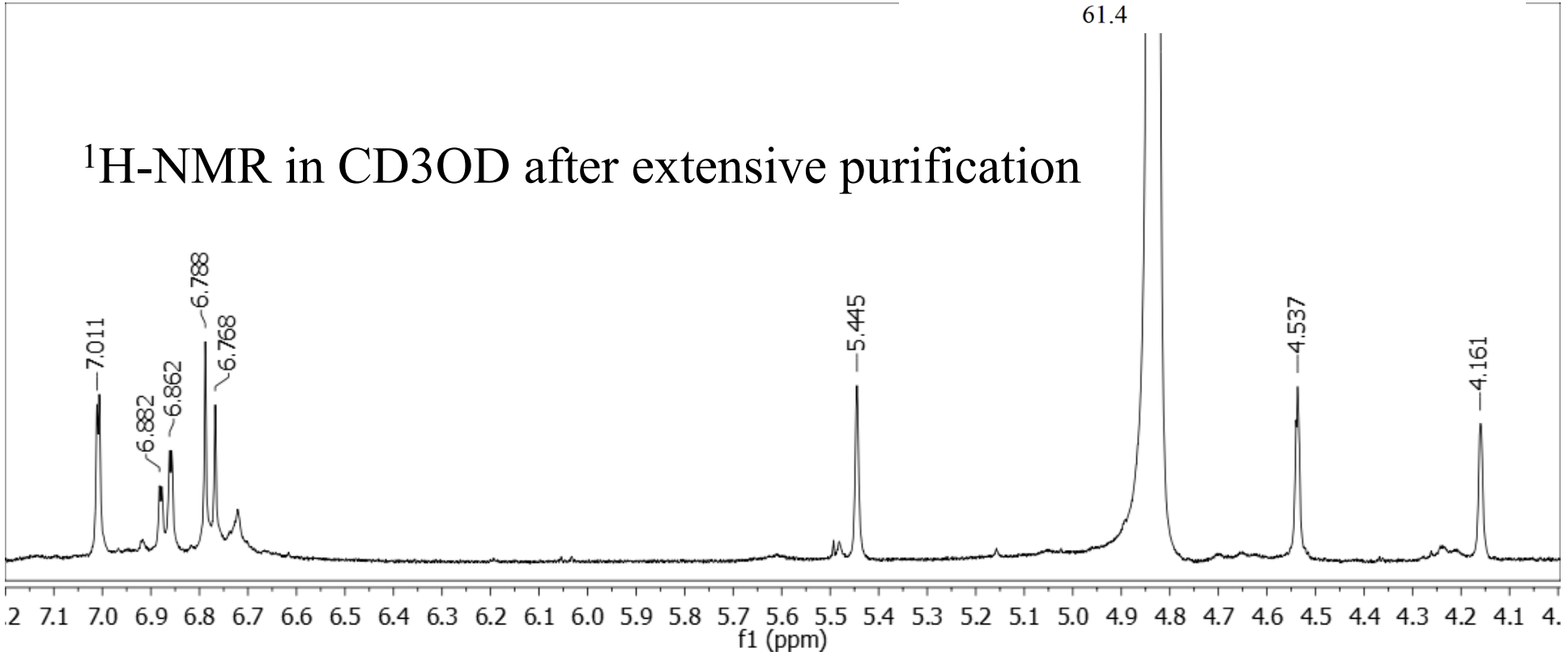
A very specific reaction

epicatechin-(4β)-sulfonate



Structure further supported by ^{1}H-^{13}C 2D correlations

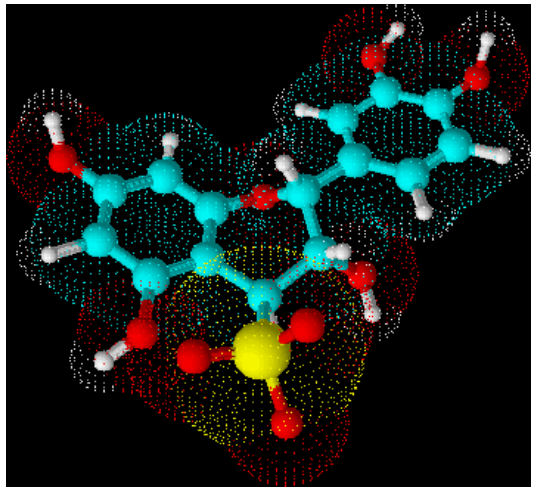
^{1}H-NMR in CD3OD after extensive purification

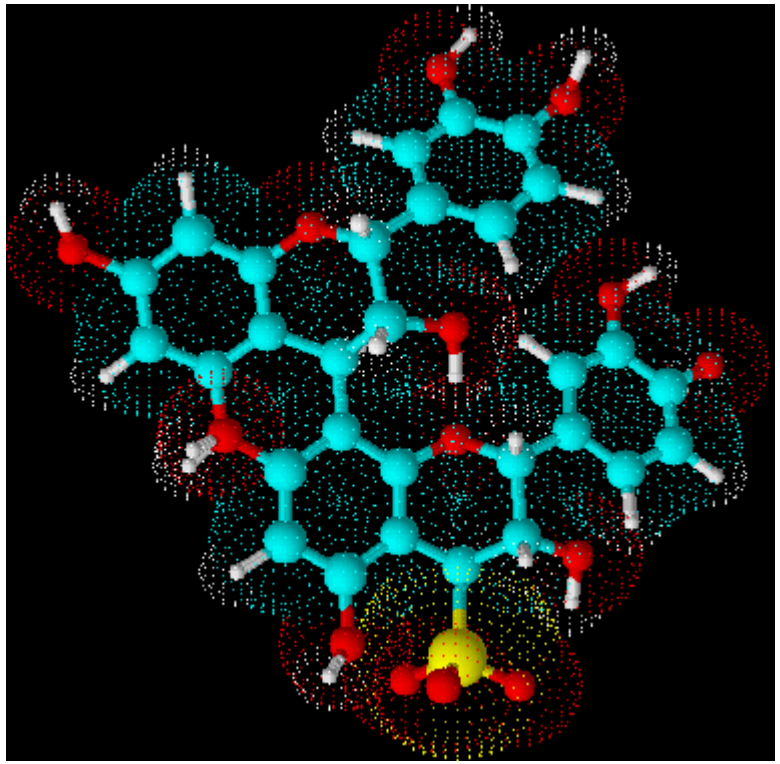


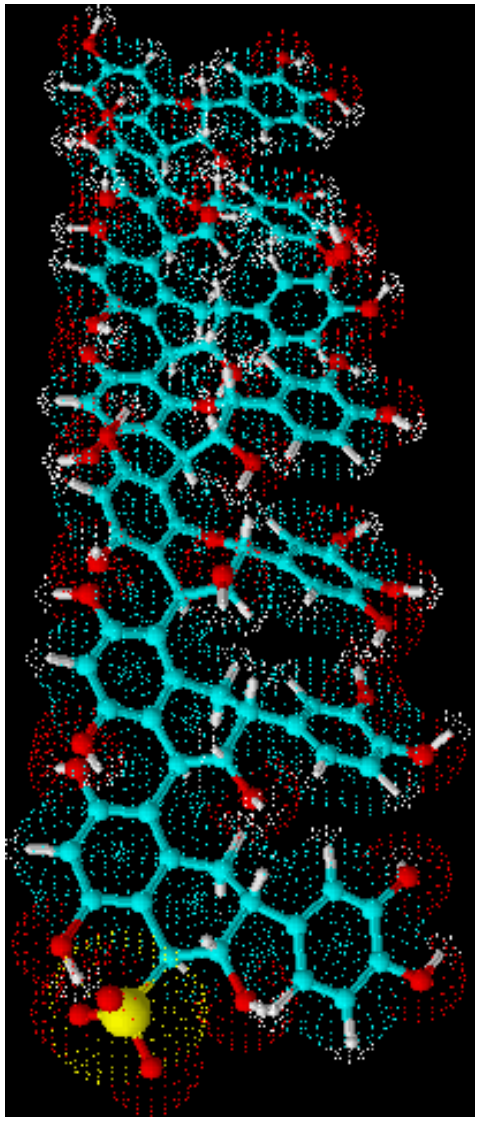
Mattivi et al., 2015 (ACS Book Chapter, Advances in Wine Research)

sulfonated flavanols in wine

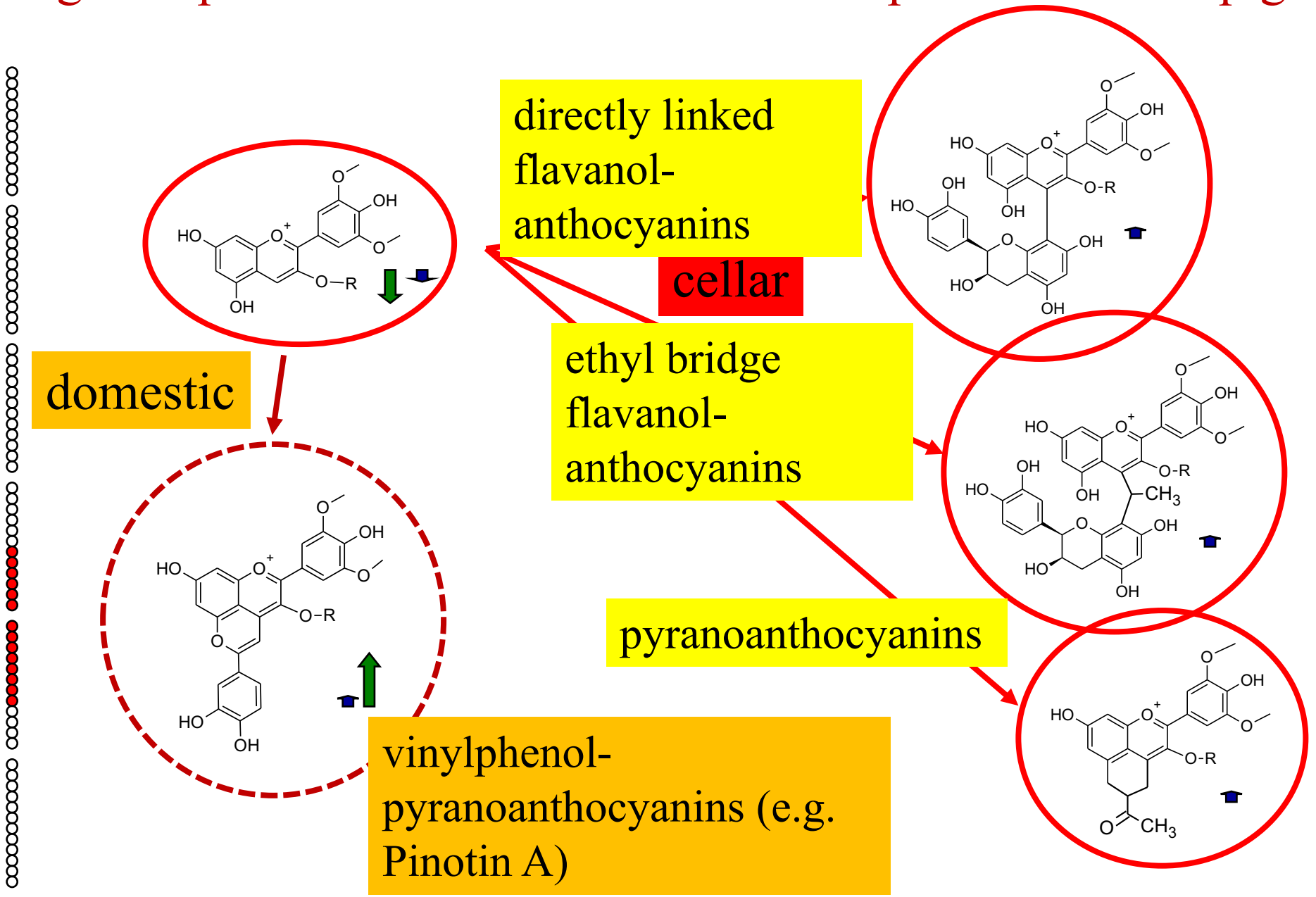
- hydrophilic compounds with increased solubility
- In part produced via cleavage of larger oligomers
- Cannot be involved in inter-flavanic linkages at their terminal C4 (reduced mDP of wine tannins)
- Putative markers of inappropriate storage





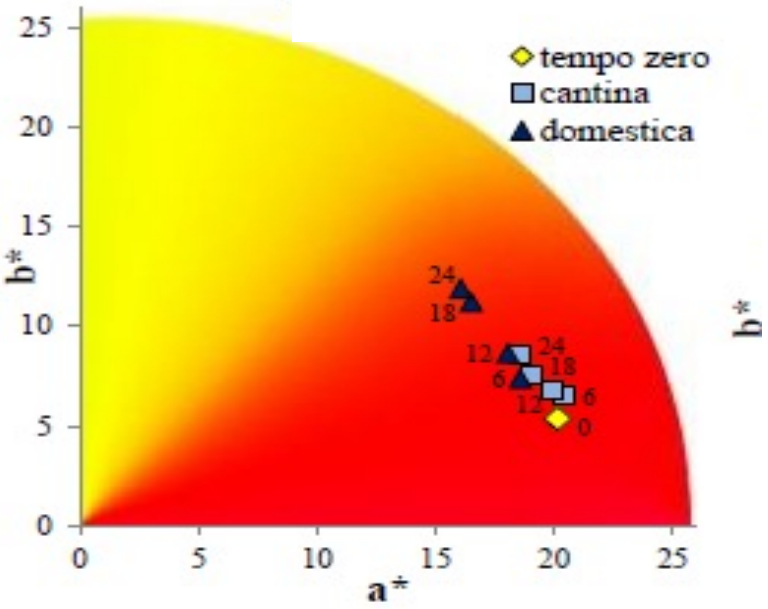


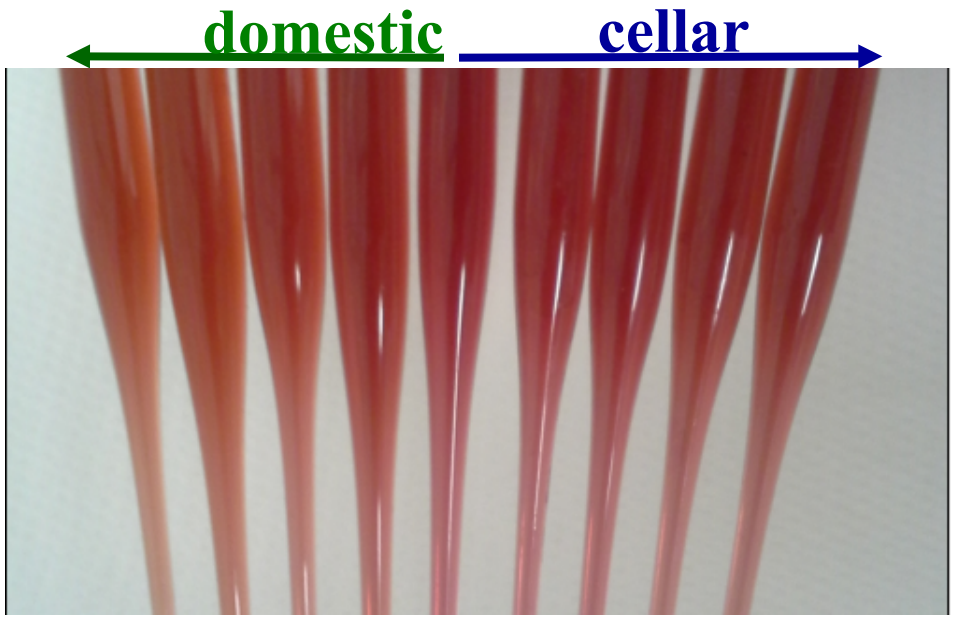
Storage temperature affects concentration & pattern of wine pigments…..



Arapitsas et al. Metabolomics 2014

… and the colour of wine





Arapitsas P. et al. Metabolomics 2014

Per chi volesse saperne di più…

- ✓ Arapitsas P., Speri G., Angeli A., Perenzoni D., Mattivi F. (2014) *The influence of storage on the "chemical age" of red wines*. Metabolomics, 10, 816–832;
- ✓ Mattivi F., Angeli A., Perenzoni D., Guella G. (2015) *Influence of storage conditions on the composition of red wines.* In "Advances in Wine Research", ACS Books, 2015
- ✓ Speri G. (2015) Evoluzione fenolica in bottiglia del Sangiovese in funzione delle condizioni di conservazione. Università degli Studi di Udine, Corso di Laurea Triennale in Viticoltura ed Enologia, AA 2013-14.

fondazione banfi

SANGUIS JOVIS

ALTA SCUOLA DEL SANGIOVESE

Grazie!