



Cambiamenti climatici e profilo polifenolico: quali implicazioni nella stabilità dei vini.



Fulvio
Mattivi



Lettura suggerita

In general, one can divide the expected climatic changes during the grape-ripening period into two scenarios: **warmer and dryer** and **warmer and moister**, with **different responses for red and white grape varieties**

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Global Climate Change, Sustainability, and Some Challenges for Grape and Wine Production*

Hans R. Schultz^a

Climate change might be threatening our wines

- ✓ There's a number of ways through which warmer temperatures affect vineyards.
- ✓ The entire life cycle of the plants is shifted — they ripen faster and also wither quicker.
- ✓ Higher temperatures also favor pests and pathogens, making it much harder for the farmers to get rid of them.
- ✓ Climate change also brings more unpredictable weather and extreme events. A severe downpour or a hailstorm can ruin an entire year's harvest in mere hours, and this is starting to happen more and more.

<https://www.zmescience.com/science/climate-change-wine-31072017/>

Climate Change Might Not Get Our Wine



Daniel Kish, Negev

<https://www.greenprophet.com/2012/03/climate-change-wine/>

Climate change might make your favorite wine disappear

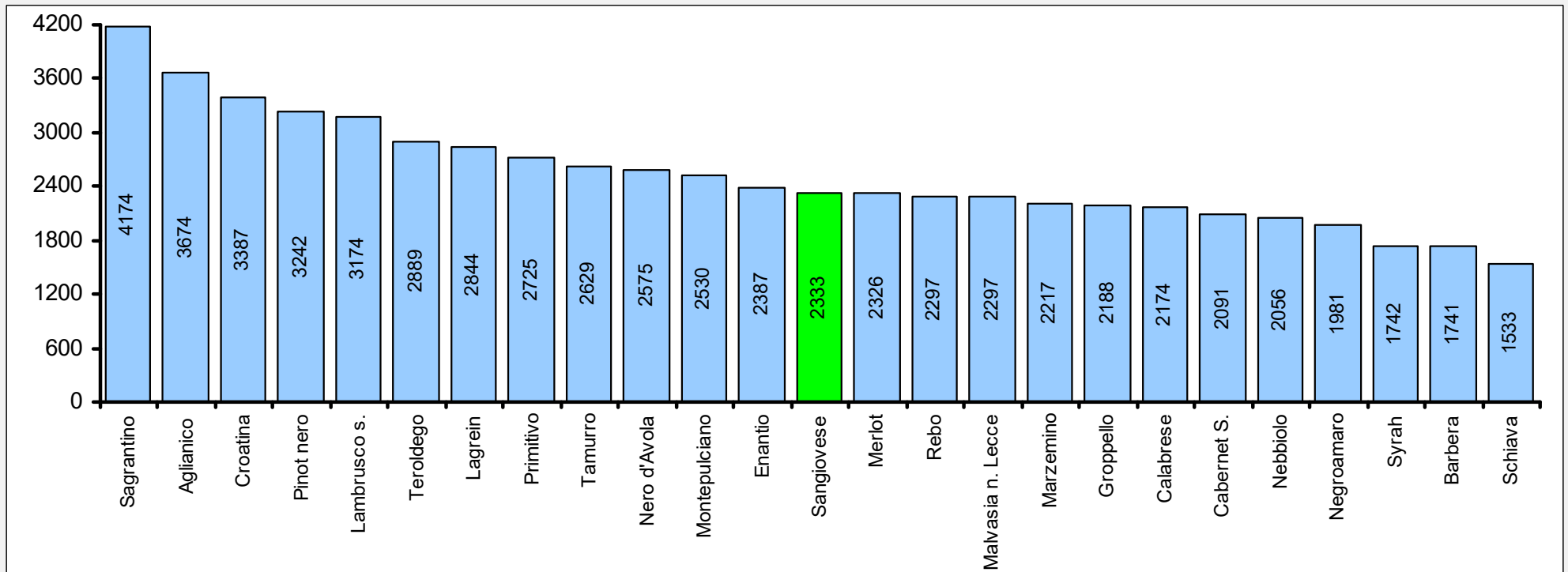
Wine quality is **only an indicator of future risk** and **we are only in the early stages of a massive ecological shift** that will require a different type of thinking about our environment.

<https://www.businessinsider.com/climate-change-might-make-your-favorite-wine-disappear-2015-7?IR=T>



EXTRACTABLE POLYPHENOLS (FC) - 2000

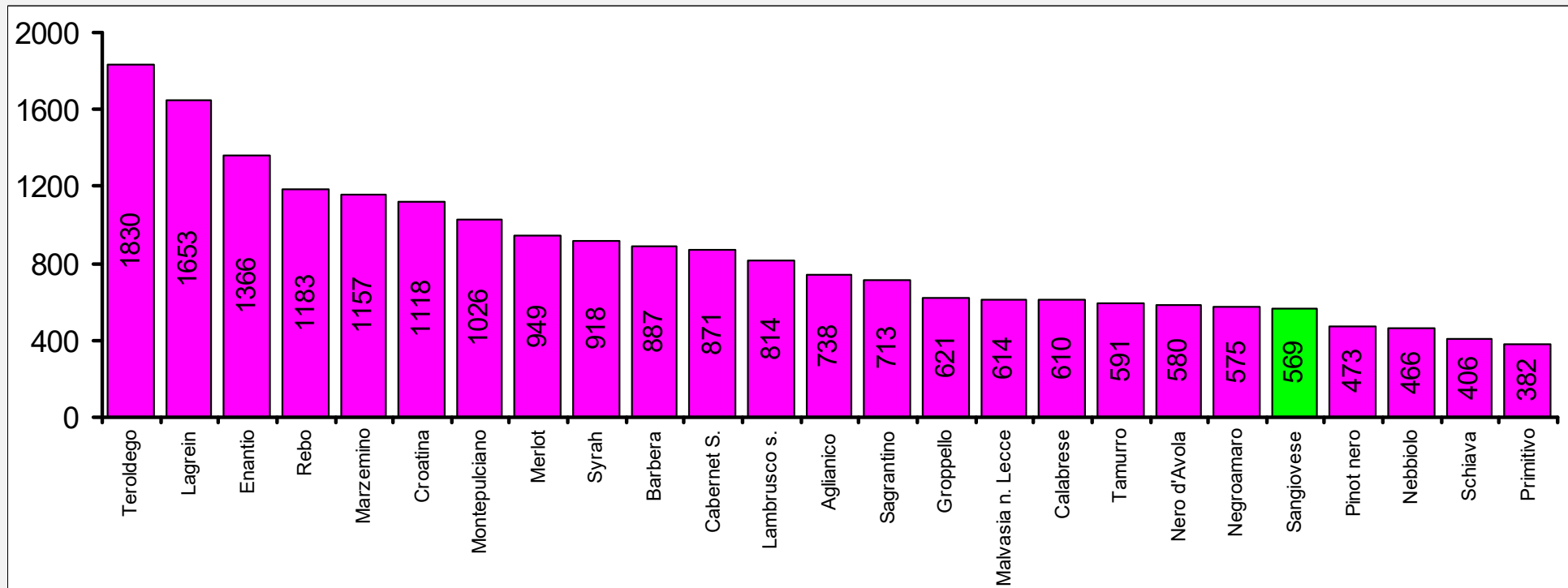
mean by variety, as (+)-catechin, mg/kg of grape



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

EXTRACTABLE ANTHOCYANINS (AT) - 2000

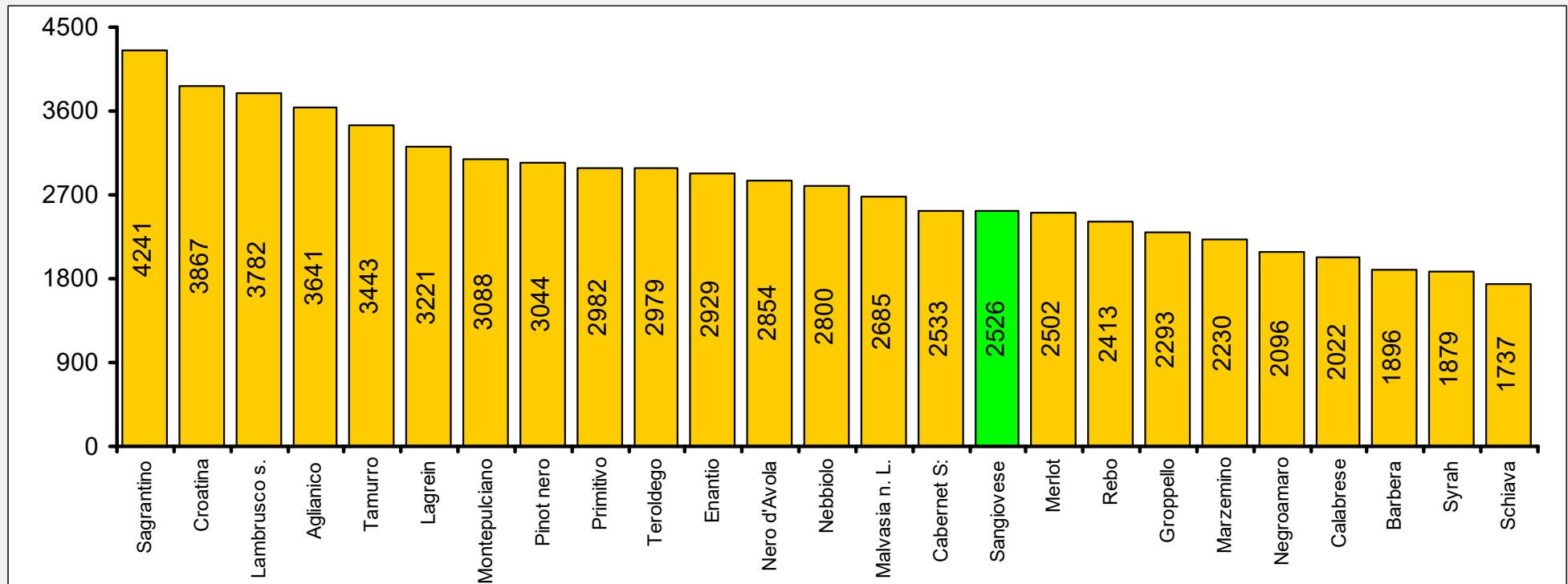
mean by variety, as malvidin 3-glucoside chloride, mg/kg of grape



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

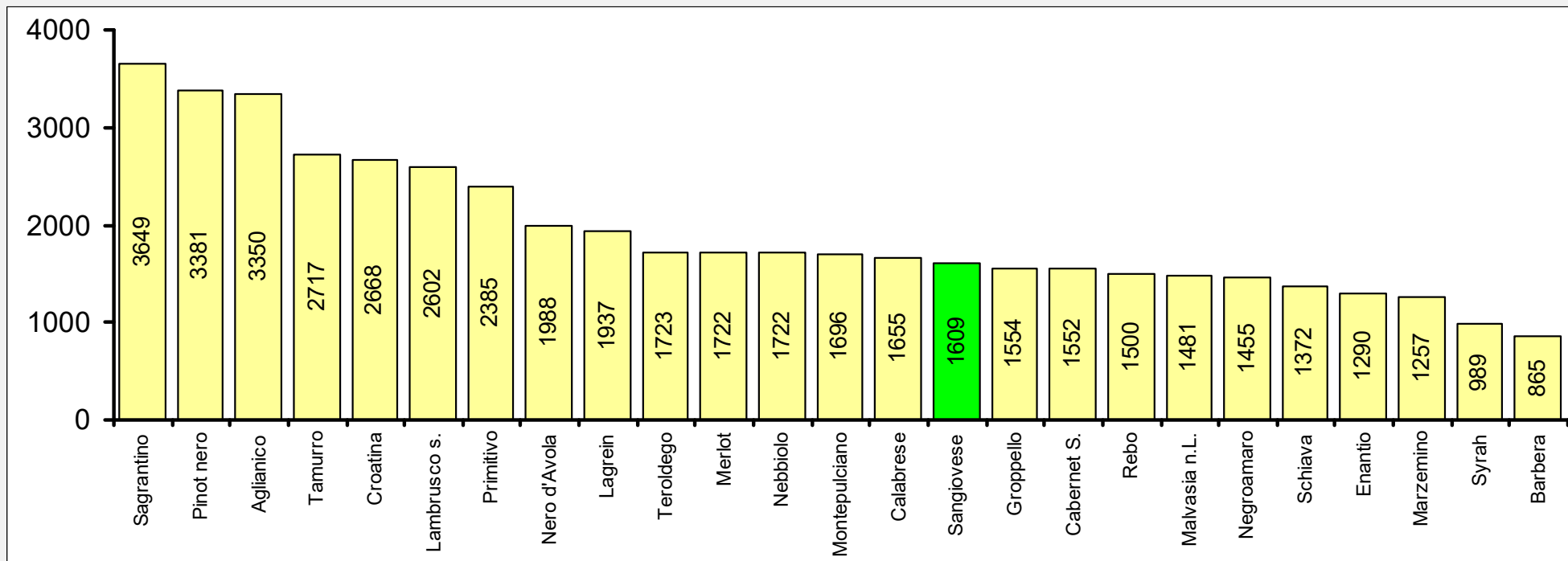
EXTRACTABLE PROANTHOCYANIDINS (HMW, PROC) - 2000

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



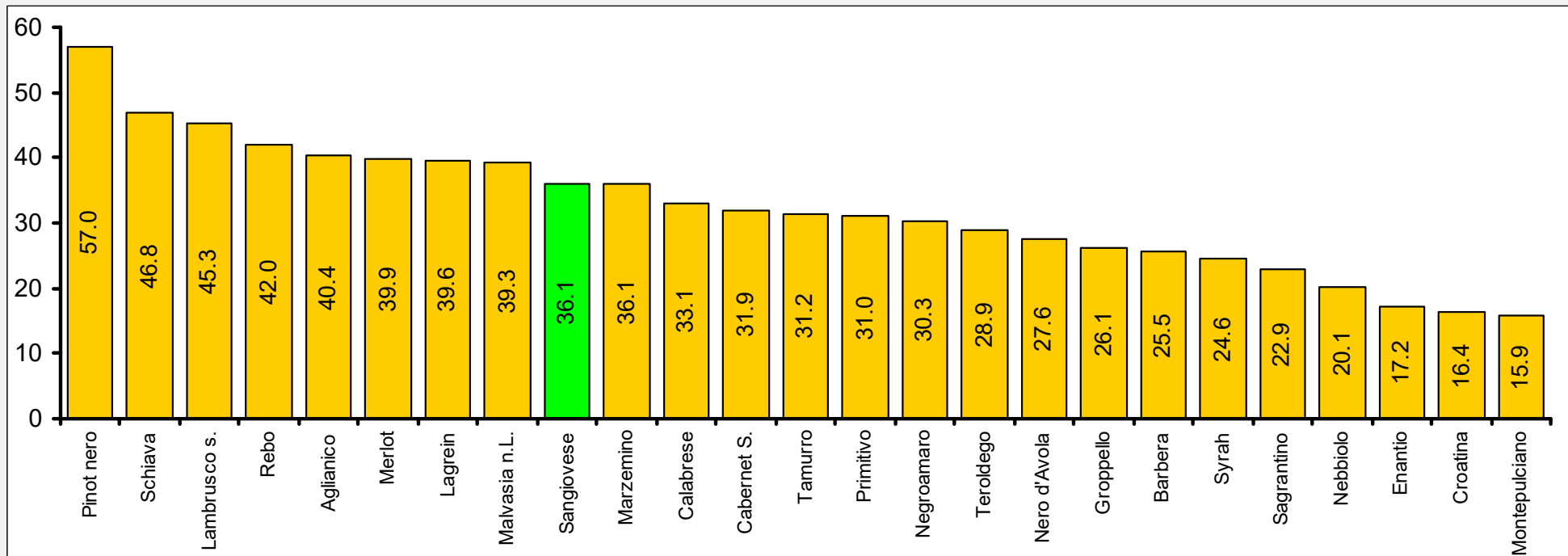
from Mattivi, Prast, Nicolini e Valenti, L'Enologo, 2003, 10, 105-114

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

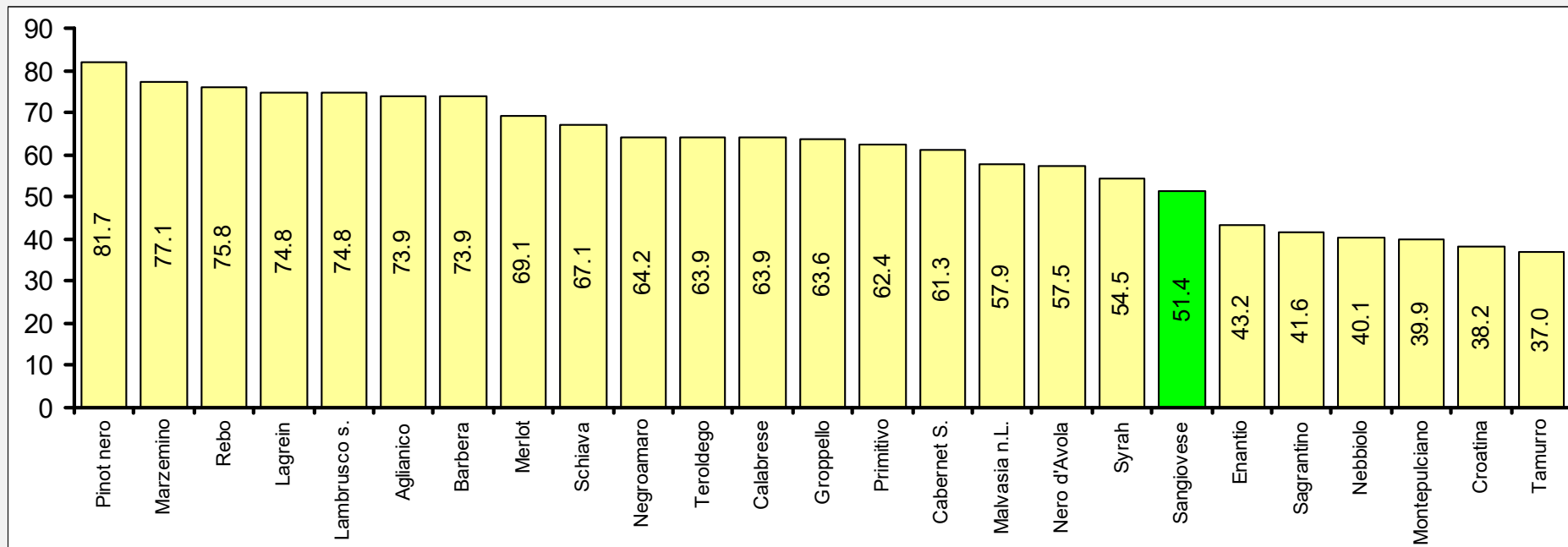
LOCALISATION OF EXTRACTABLE PROANTHOCYANIDINS IN THE BERRY (PROC, 2000) mean by variety, % in the seeds



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

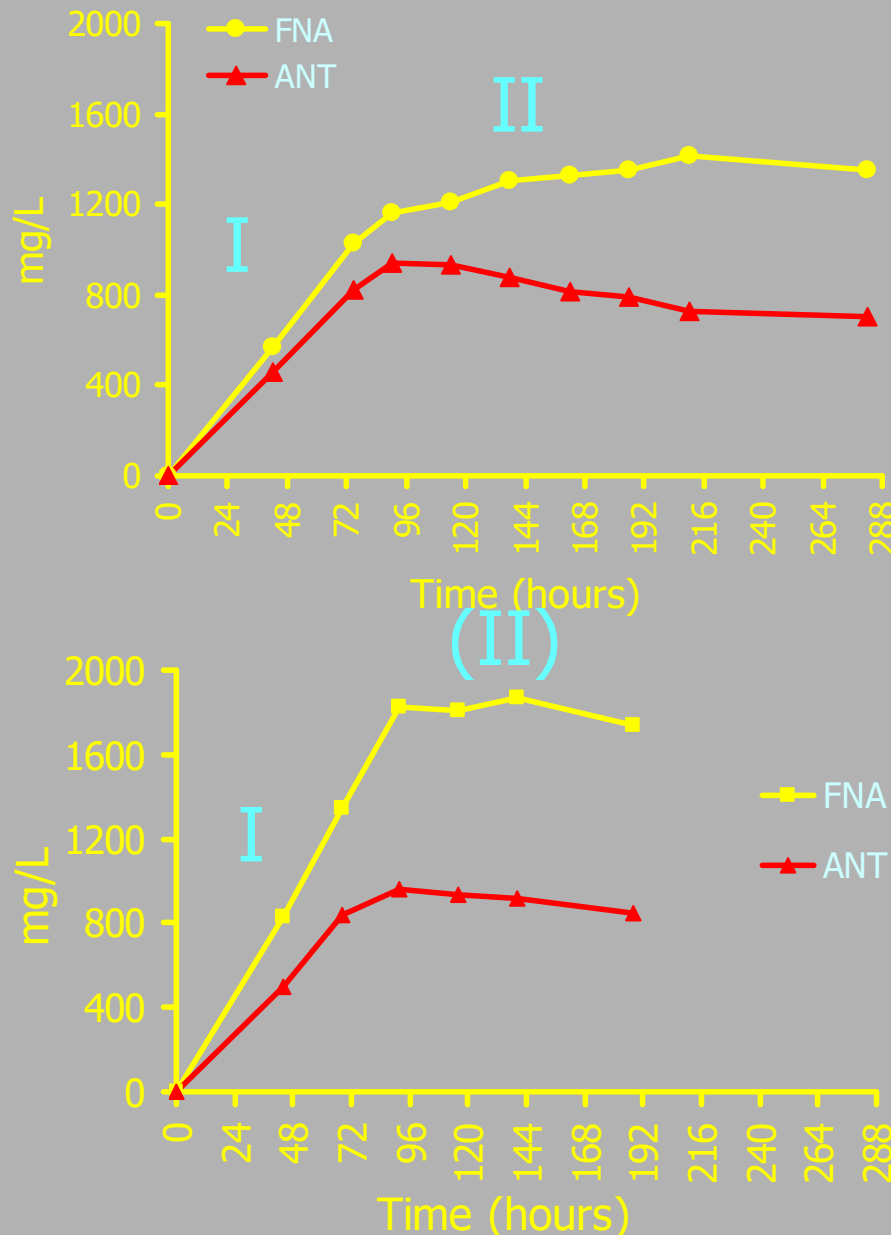
- **Experimental cellar**

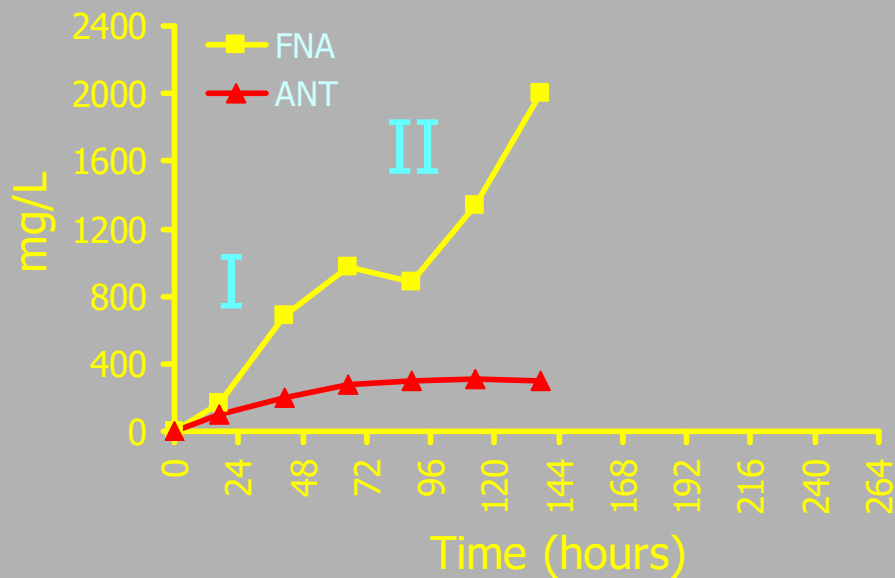
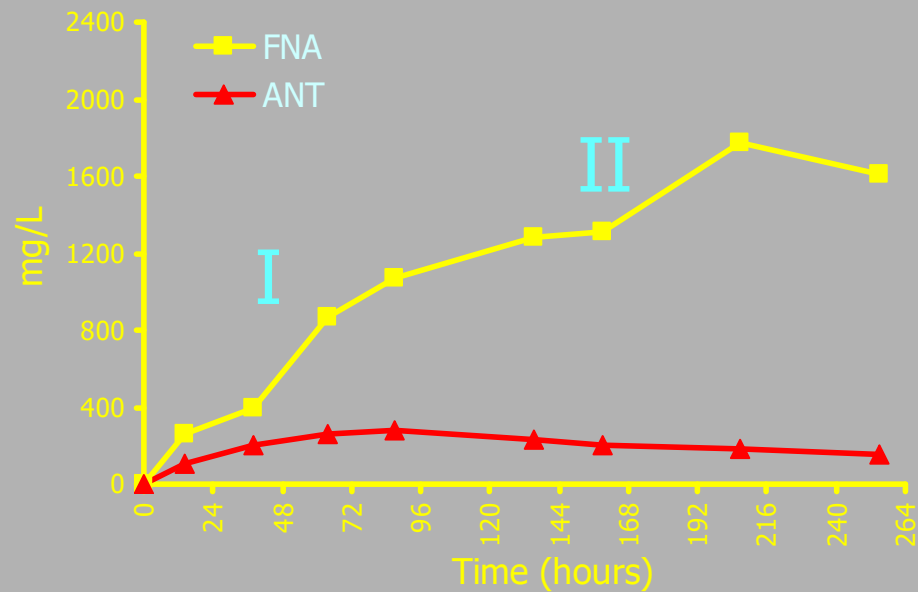
(100 kg, manual punching down, 2xday)

- **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)

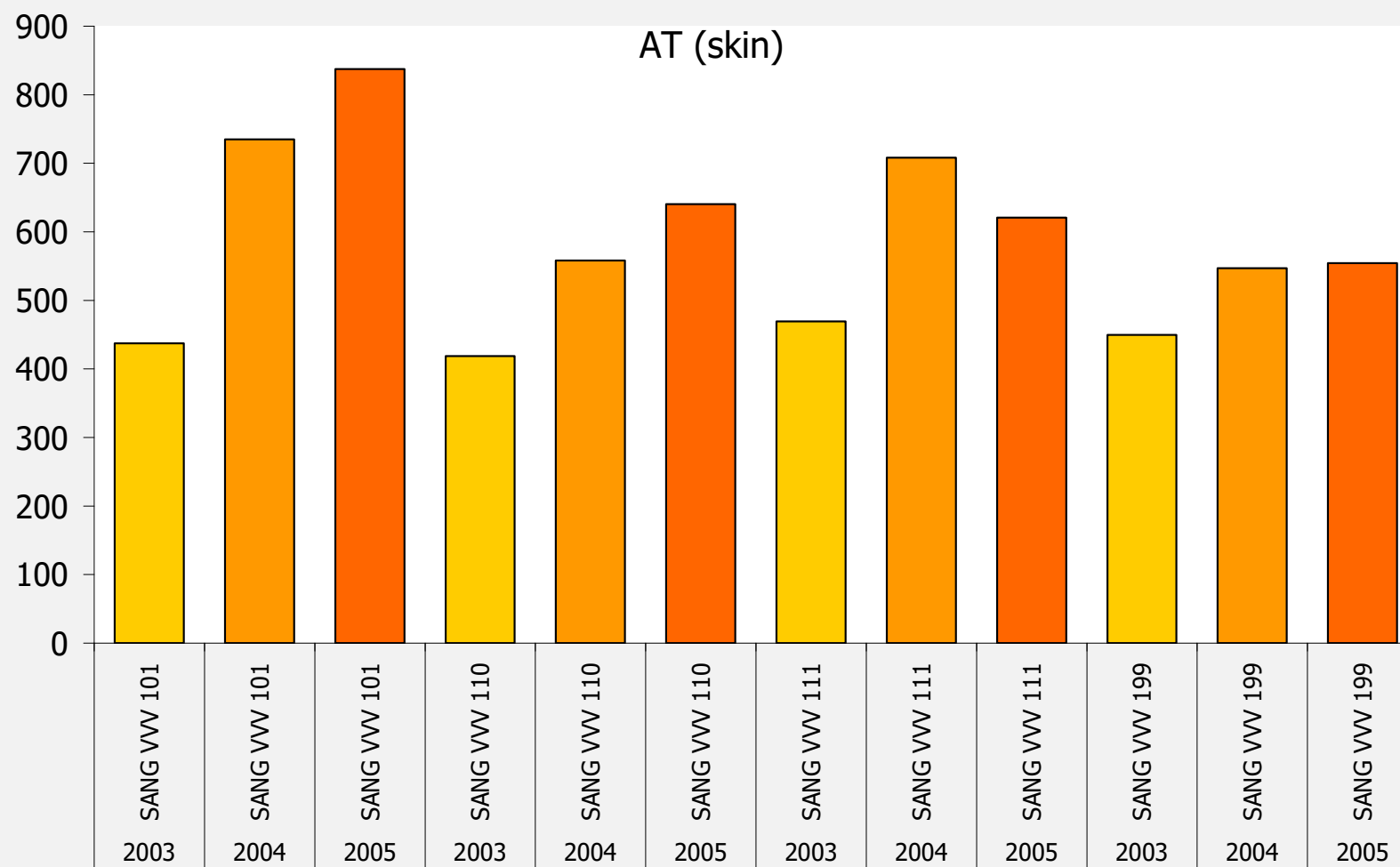
from Mattivi et al., NYAS 2002

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

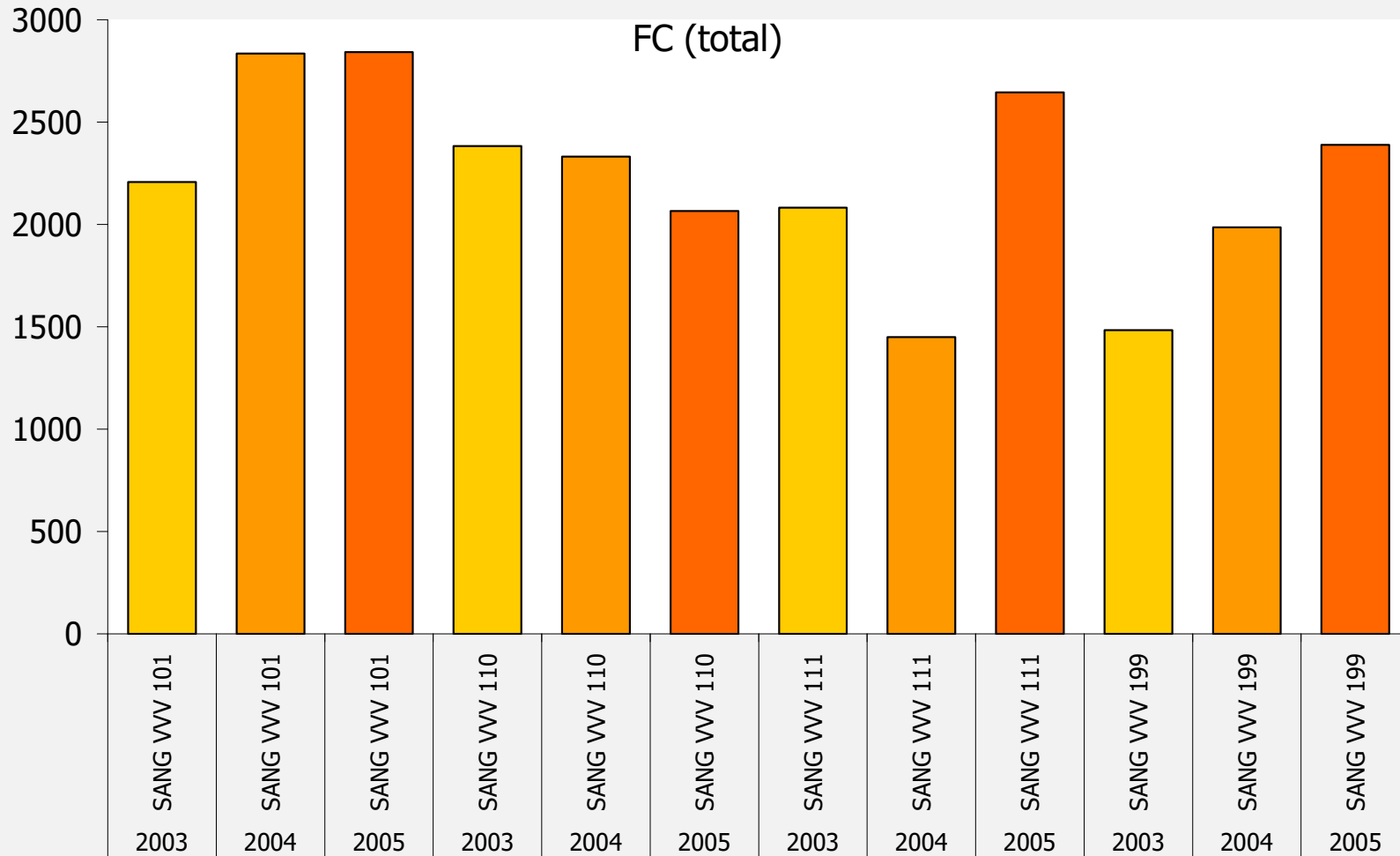
SANGIOVESE

- 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.

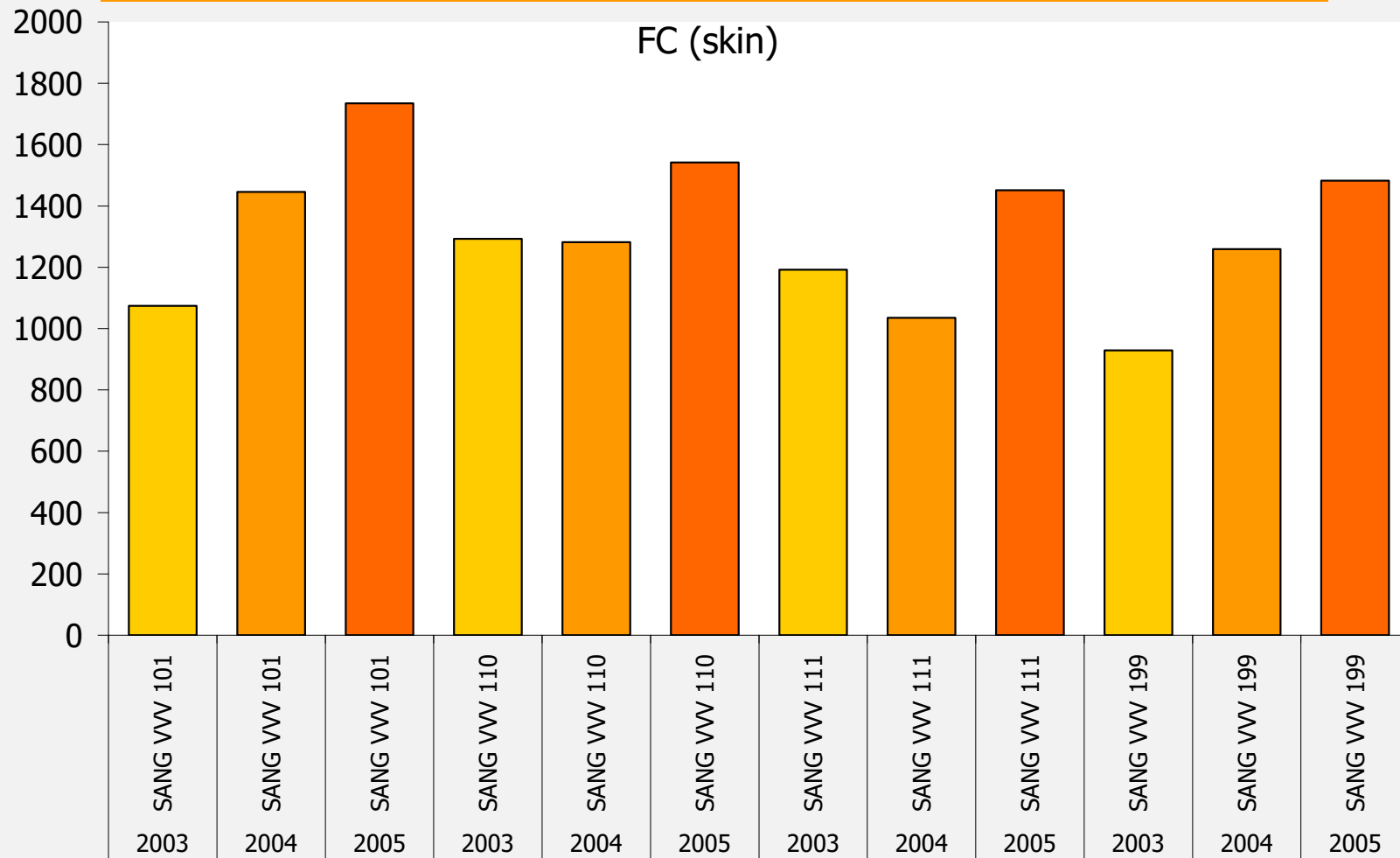
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



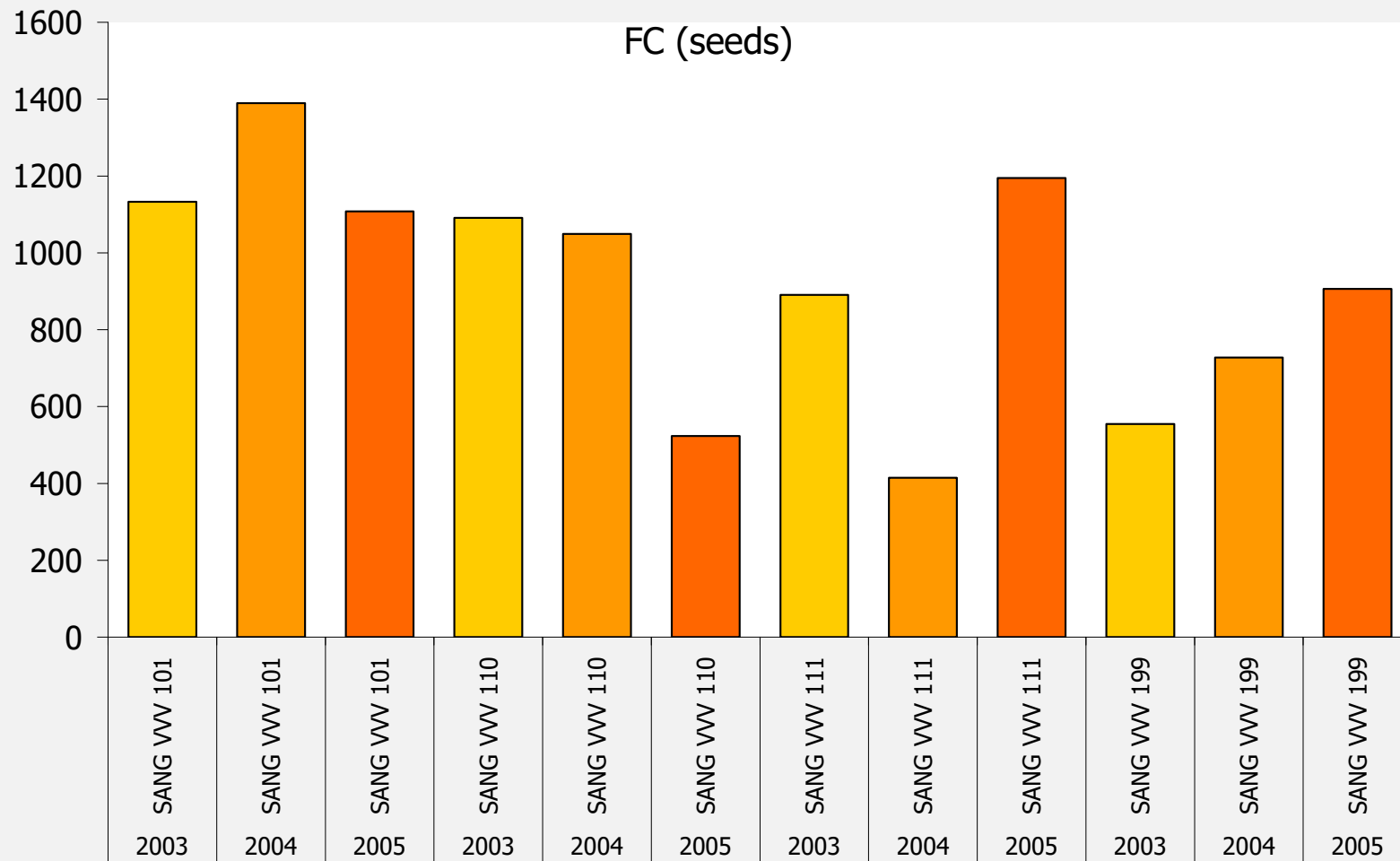
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



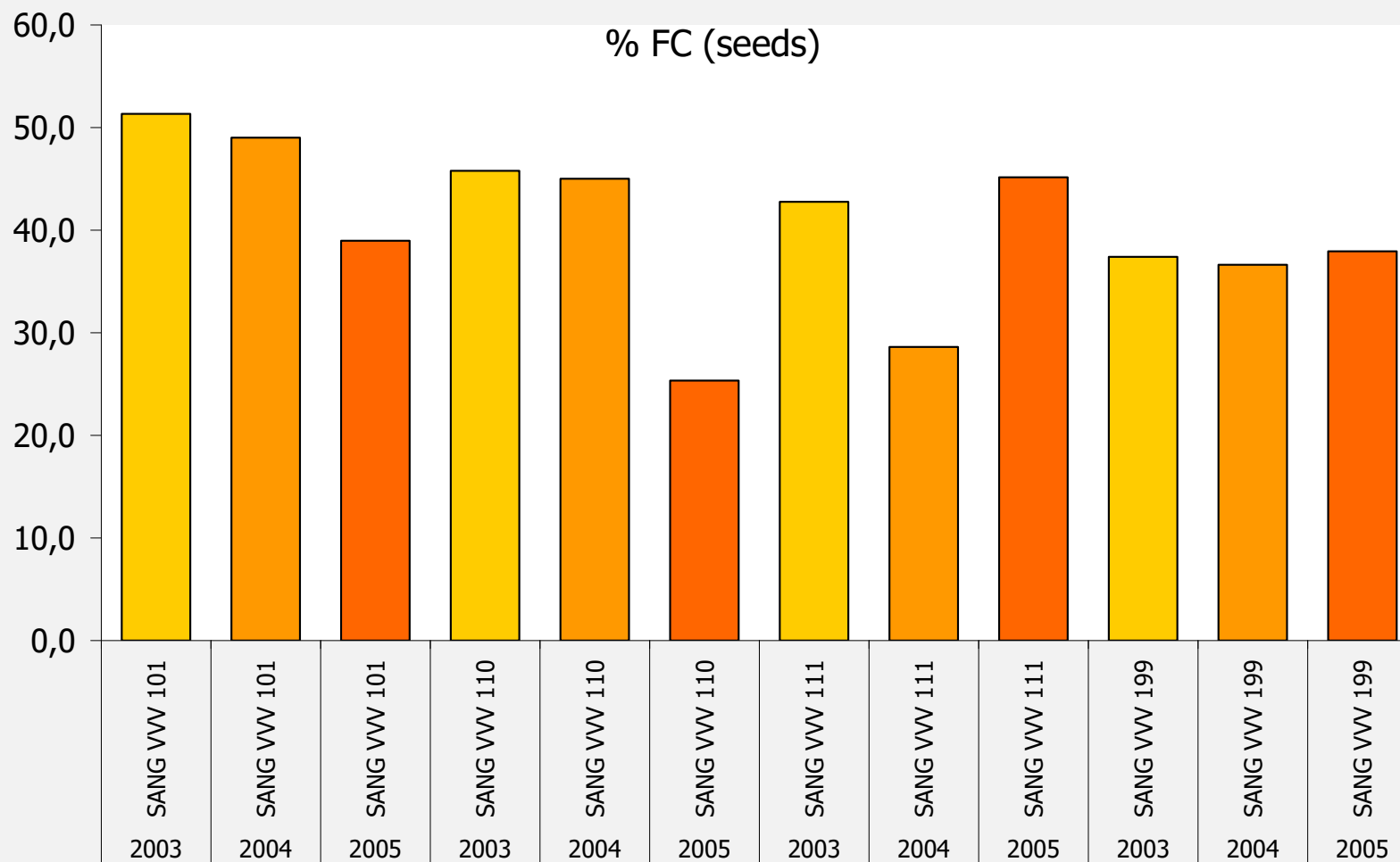
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



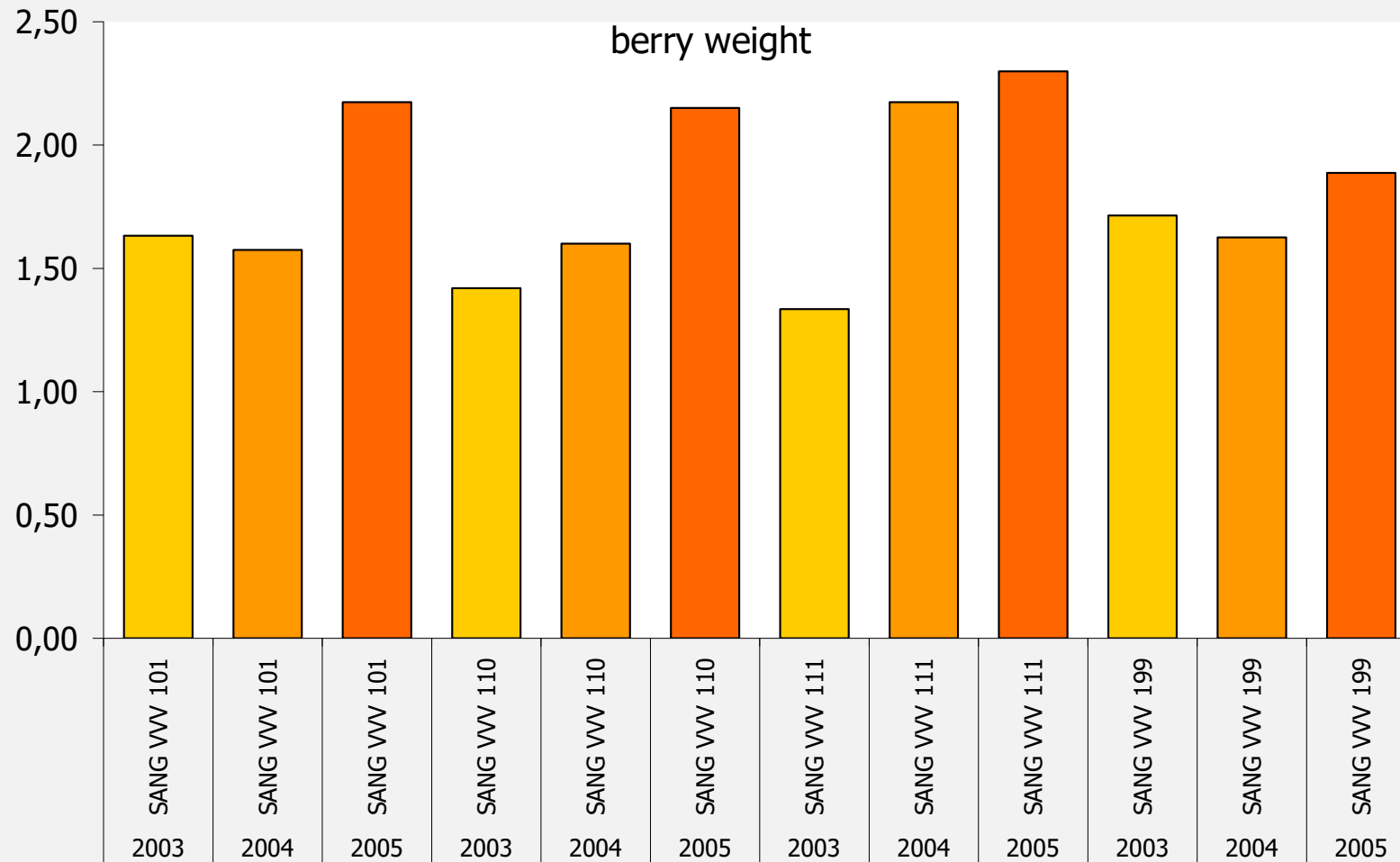
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



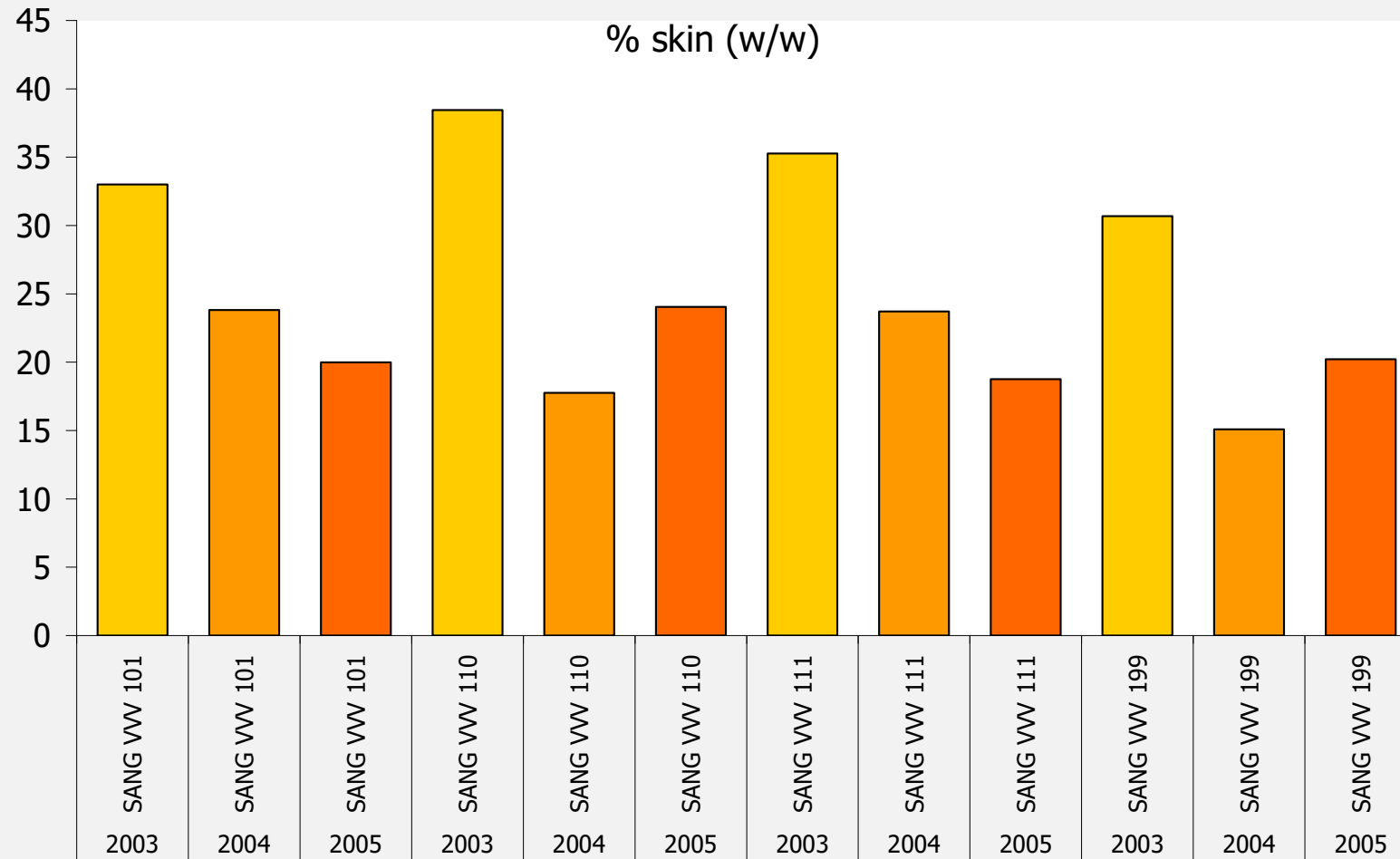
Variability of the phenolic potential in the grape of Sangiovese clones (vintages 2003-2005)



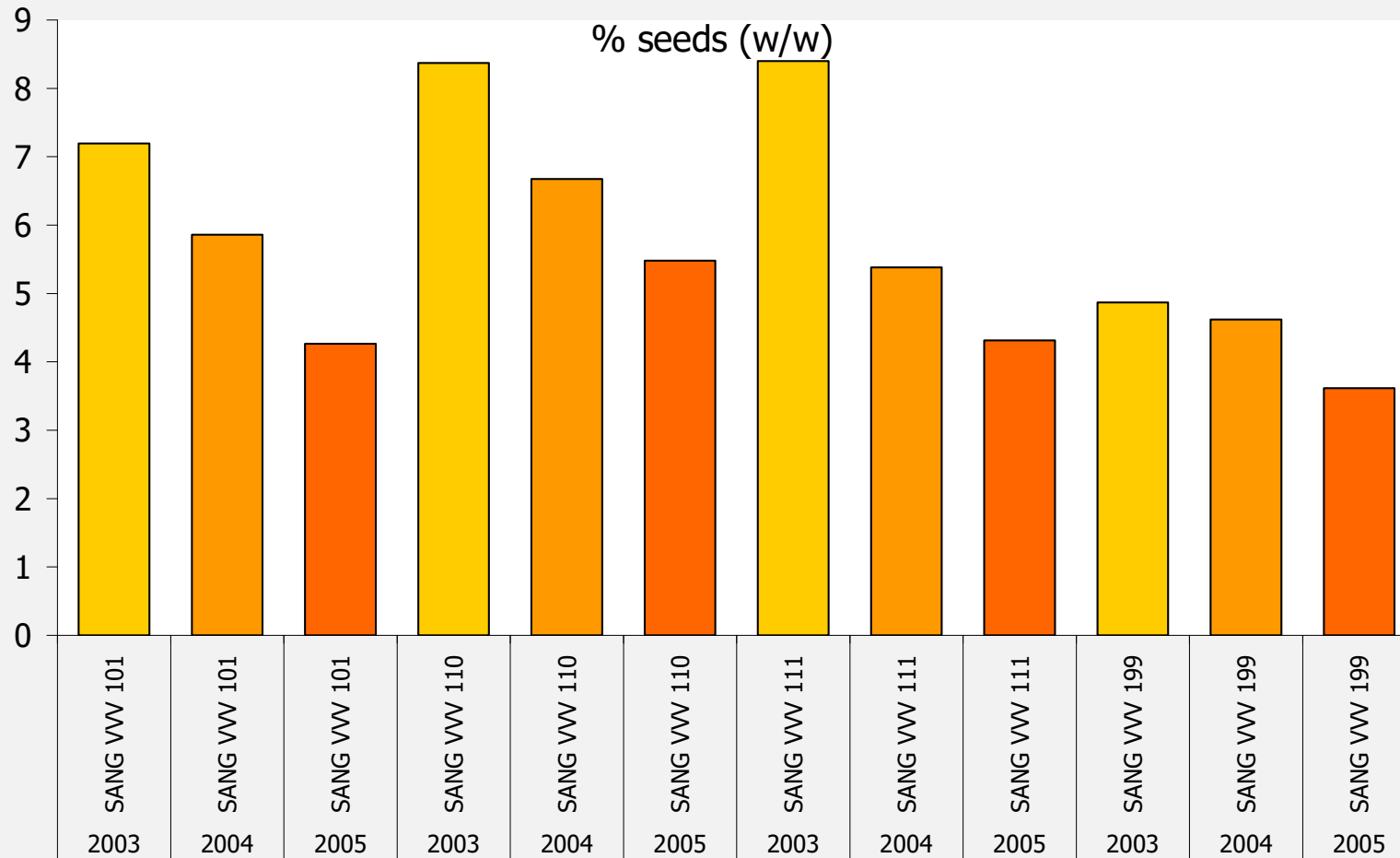
Variability of the berry weight in the berries of Sangiovese clones (vintages 2003-2005)



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)

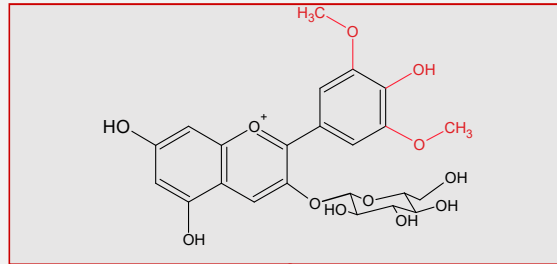


Conclusions - I

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"

Cyanidin

Peonidin

"TRI"

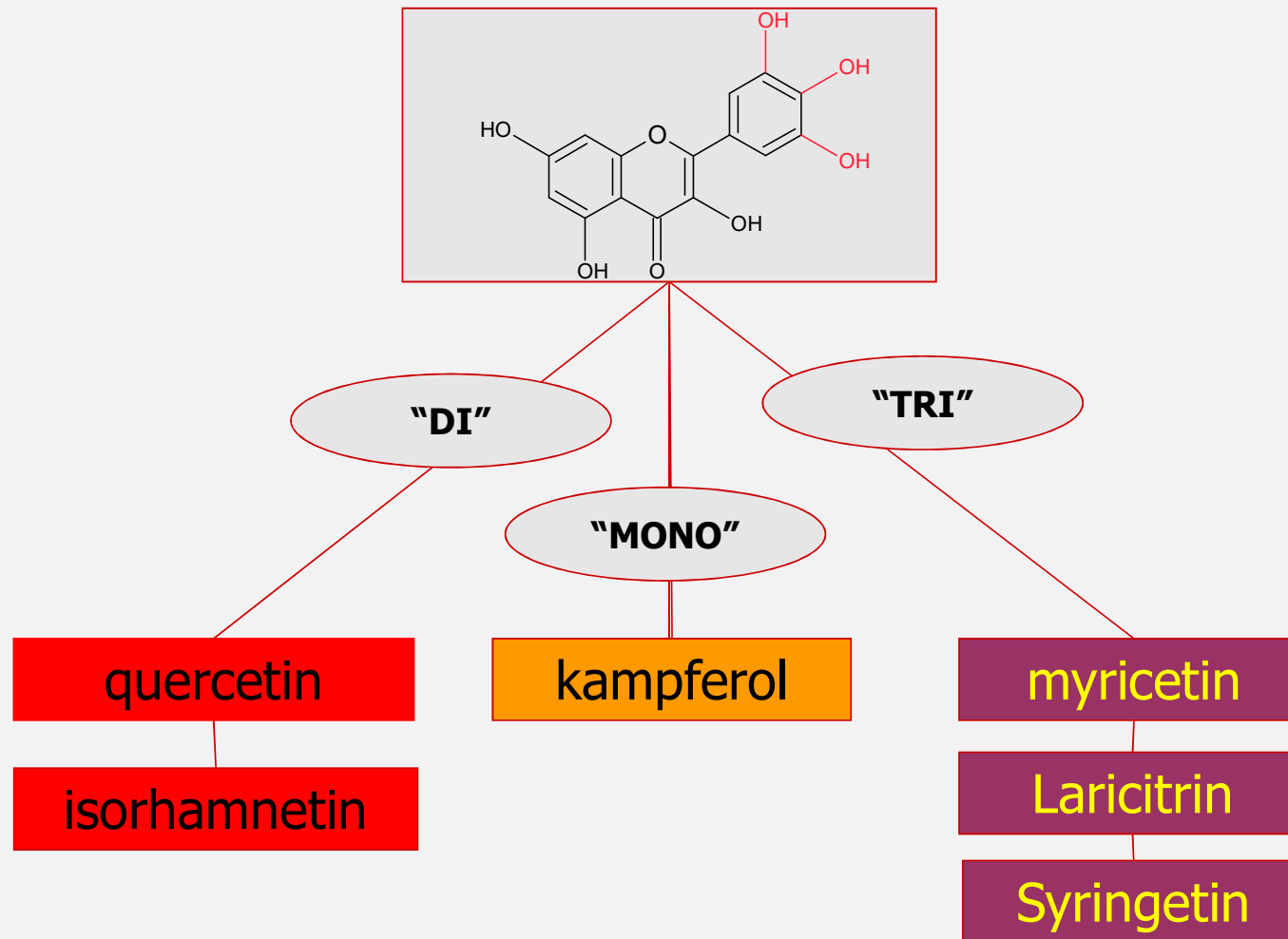
Delphinidin

Petunidin

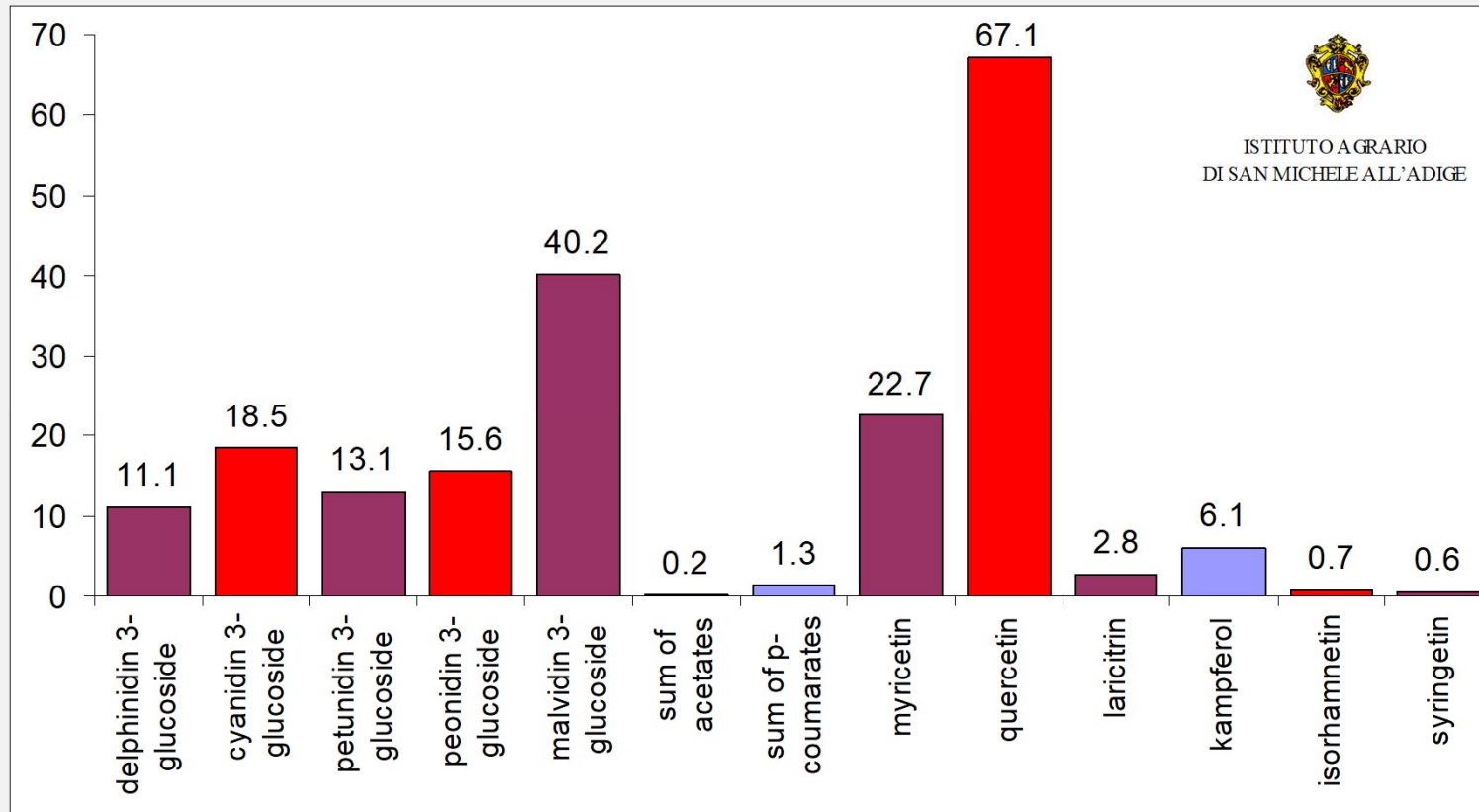
Malvidin

free glucoside, acetate,
p-coumarate.

Grape flavonols



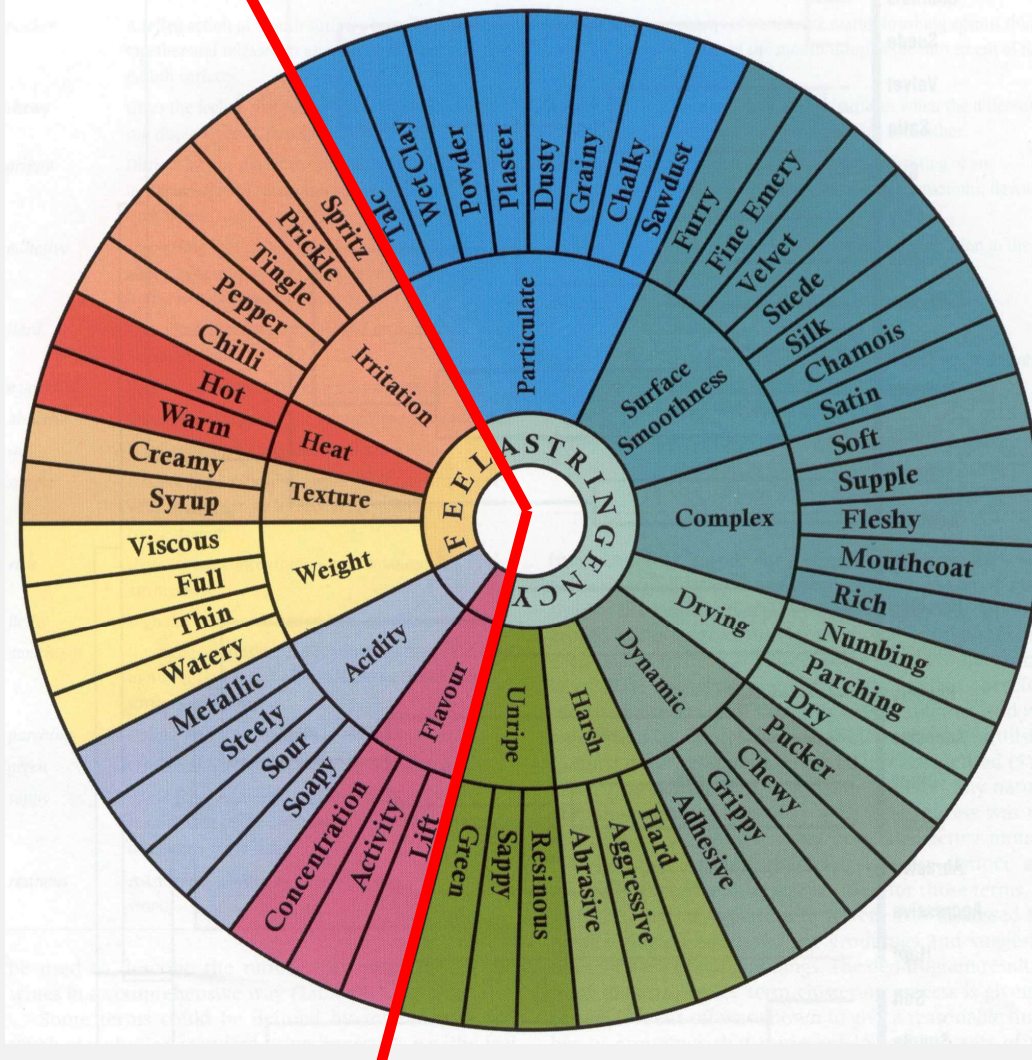
Anthocyanins and flavonols in Sangiovese grape



(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 (**talca, 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 desiccation 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**)

Taste compounds in red wine (sensomics)

Hufnagel & Hofmann, JAFC 2008, 56, 1376-1366

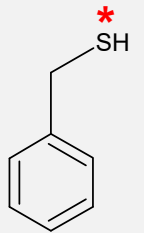
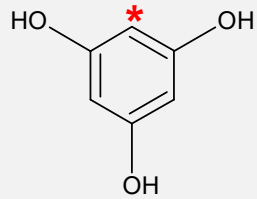
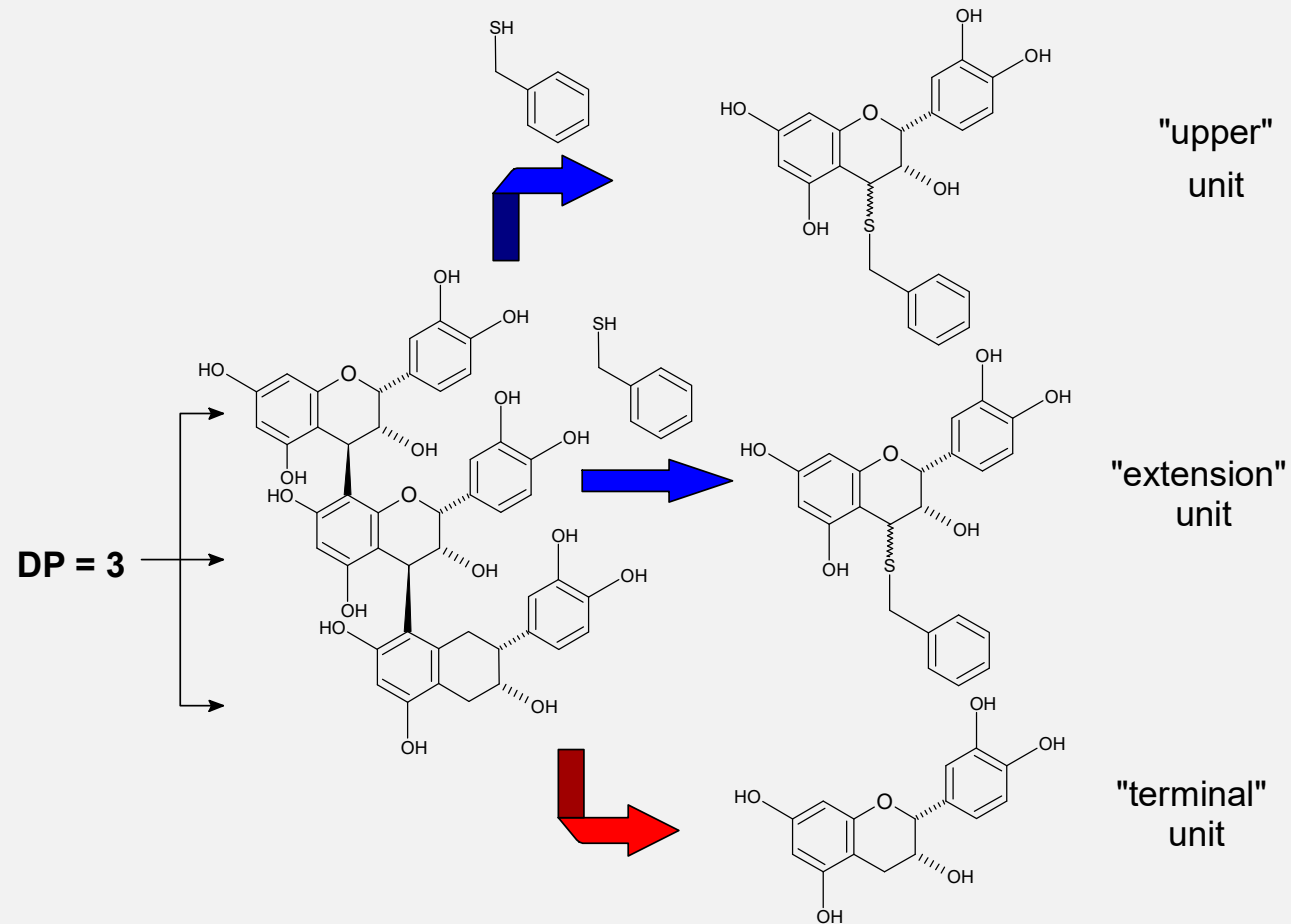
Table 4. Human Taste Recognition Thresholds of Compounds Isolated from Red Wine

compound ^a (no.)	taste threshold ^b for			
	astringency		bitterness	
	$\mu\text{mol/L}$	mg/L	$\mu\text{mol/L}$	mg/L
Velvety Astringent Compounds				
dihydrokaempferol-3-O- α -L-rhap (18)	4.8	2.1	nd	nd
dihydroquercetin-3-O- α -L-rhap (13)	3.7	1.7	nd	nd
isorhamnetin-3-O- β -D-glcp (17)	2.4	1.1	nd	nd
quercetin-3-O- β -D-glcp (12)	2.0	1.0	nd	nd
quercetin-3-O- β -D-galp (22)	0.4	0.2	nd	nd
syringetin-3-O- β -D-glcp (15)	0.2	0.1	nd	nd
Puckering Astringent Compounds				
vanillic acid (11)	315	53	nd	nd
gallic acid (1)	292	50	nd	nd
syringic acid (4)	263	52	nd	nd
protocatechuic acid (2)	206	32	nd	nd
<i>p</i> -coumaric acid (8)	139	23	nd	nd
ferulic acid	67	13	nd	nd
caffeic acid (3)	72	13	nd	nd
(<i>E</i>)-caltaric acid (16)	16	5	nd	nd
(<i>Z</i>)/(<i>E</i>)-aconitic acid (27) ^c	0.5	0.1	nd	nd
polymeric fraction (>5 kDa)		22	nd	nd
Bitter and Astringent Compounds				
(-)-epicatechin (26)	930	270	930	270
(+)-catechin (23)	410	119	1000	290
procyanidin C1 (7)	300	260	400	347
caffeic acid ethyl ester (19)	277	58	1100	229
procyanidin B1 (24)	240	139	400	231
procyanidin B3 (25)	200	116	500	289
procyanidin B2 (5)	190	110	485	280
gallic acid ethyl ester (6)	185	37	2200	438
<i>p</i> -coumaric acid ethyl ester (10)	143	27	715	137
vanillic acid ethyl ester (20)	125	25	1500	294
ferulic acid ethyl ester (9)	67	15	710	158
protocatechuic acid ethyl ester (14)	49	9	1000	182
syringic acid ethyl ester (21)	18	4	576	130

^a The structures of the compounds are displayed in Figure 3. ^b Taste threshold concentrations were determined in bottled water by means of a triangle test for bitterness and by means of the half-tongue test for astringency. ^c Taste threshold for sour is 500 $\mu\text{mol/L}$.

Caratterizzazione mediante HPLC delle proantocianidine, mediante tioacidolisi o floroglucinolisi

Rottura acido catalizzata del legame interflavanico in presenza di nucleofili quali toluene- α -tiolo o floroglucinolo, permette di ottenere una depolimerizzazione (completa o sequenziale, a seconda delle condizioni), distinguendo le unità terminali da quelle "superiori"

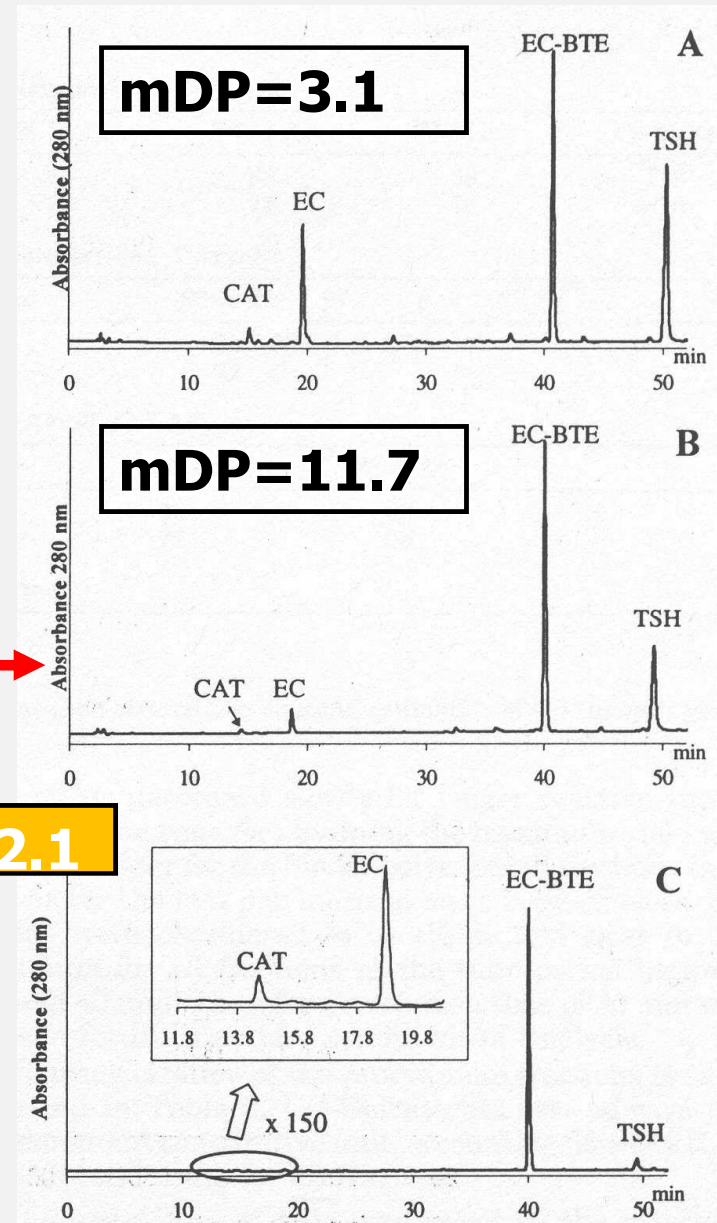


I prodotti ottenuti con tioacidolisi possono essere direttamente iniettati in HPLC:

$$\text{mDP} = \frac{[\text{terminali}] + [\text{benziltioeteri}]}{[\text{terminali}]}$$

dove $[\text{terminali}] = [\text{cat}] + [\text{epi}]$

(esempio di applicazione alle procianidine della mela)



Guyot, Marnet & Drilleau, J. Agric. Food Chem. 2001, 49, 14-20

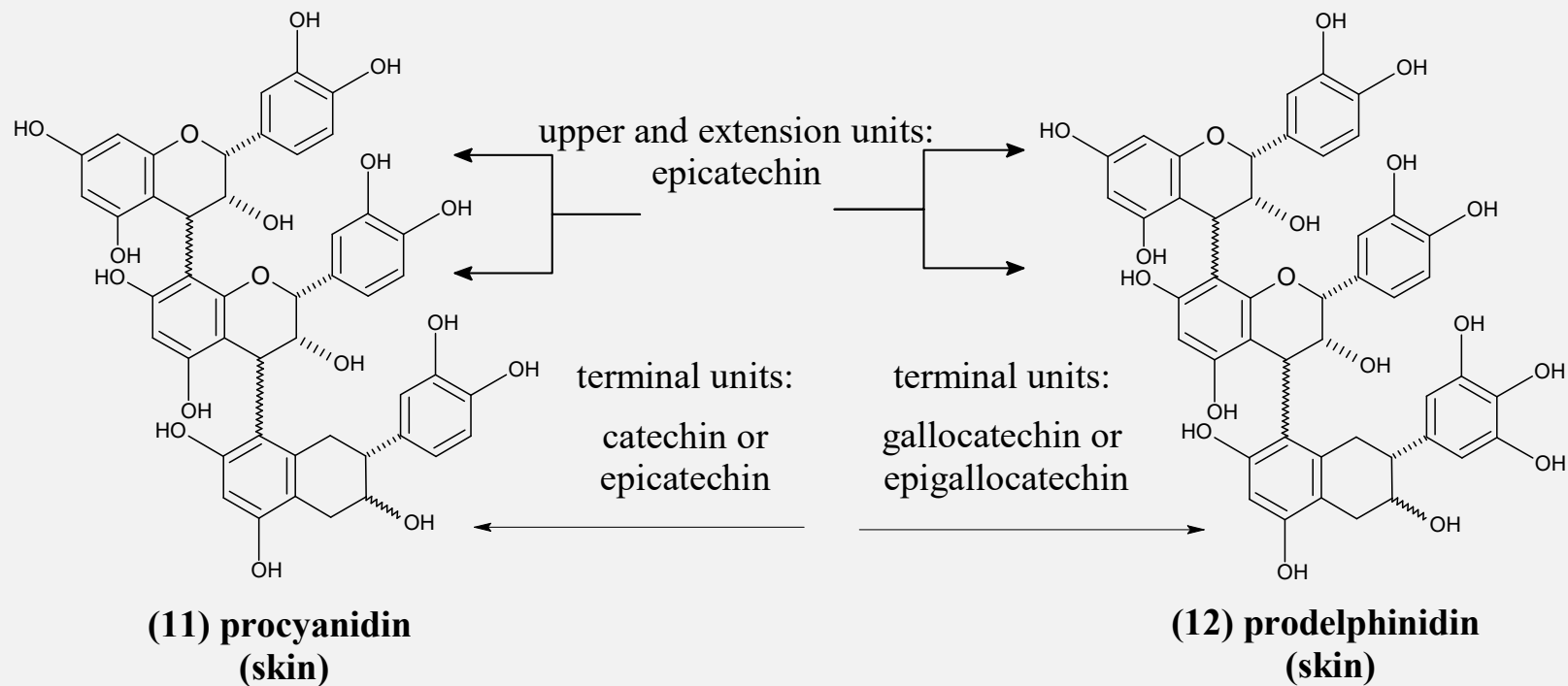
Numero di strutture possibili per DP=n, nei semi

- ✓ 3 monomeri (catechina, epicatechina, epicatechina gallato)
le possibili combinazioni sono 3^n
- ✓ si legano principalmente in due modalità (4→8 e 4→6)
le possibili combinazioni sono $2^{(n-1)}$
- ✓ numero di combinazioni totali = $3^n \times 2^{(n-1)}$

DP	3 monomeri	2 modalità di legame	possibili modalità di combinazione
2	9	2	18
3	27	4	108
4	81	8	648
5	243	16	3.888
6	729	32	23.328
7	2.187	64	139.968
8	6.561	128	839.808
9	19.683	256	5.038.848
10	59.049	512	30.233.088
20	3.486.784.401	524.288	1.828.079.220.031.490
30	205.891.132.094.649	536.870.912	110.536.959.860.367.000.000.000

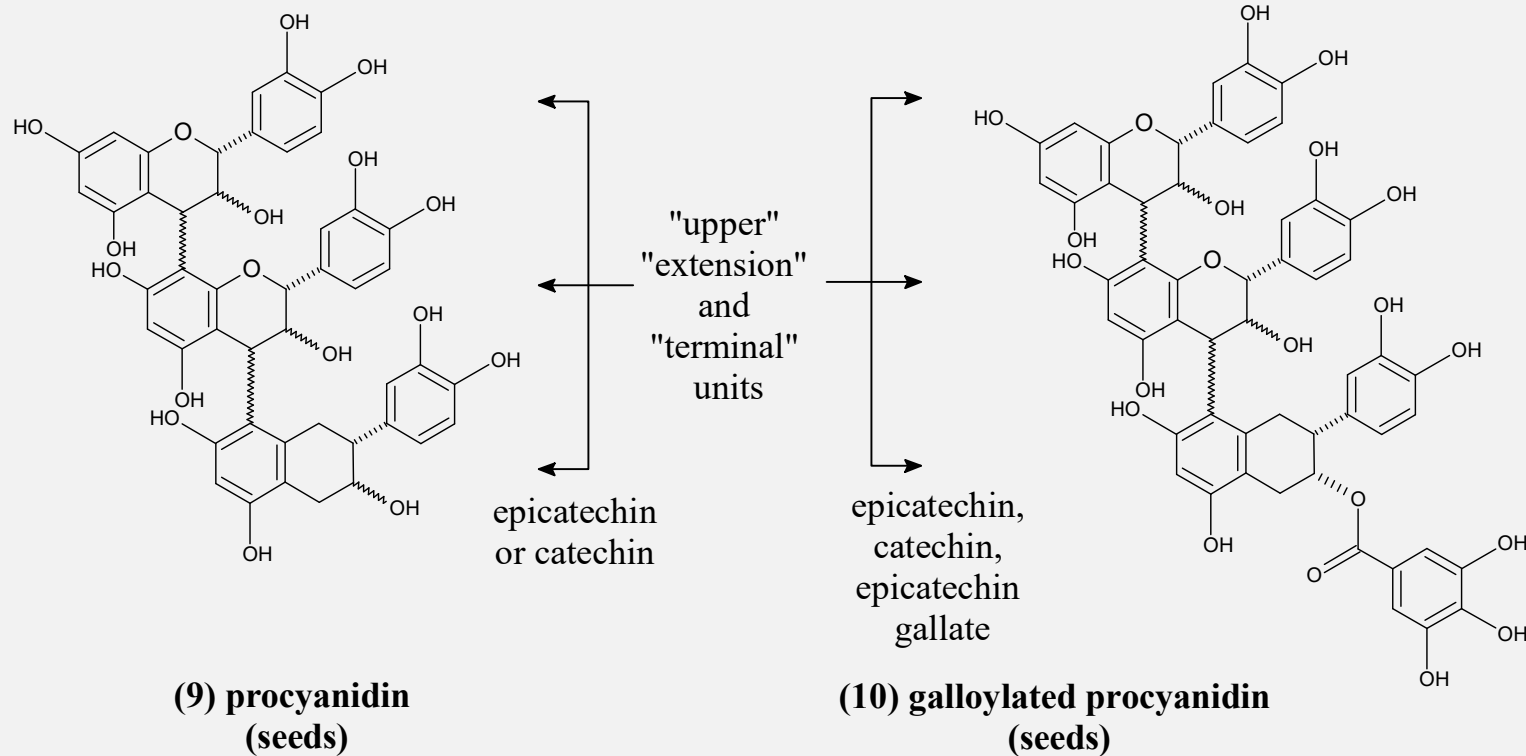
Proantocianidine da buccia di uva

"struttura generale"



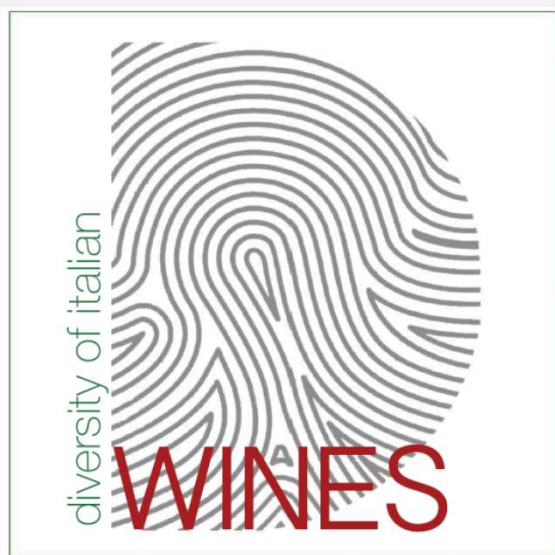
Proantocianidine da semi di uva

"struttura generale"



CAMPIONAMENTI:

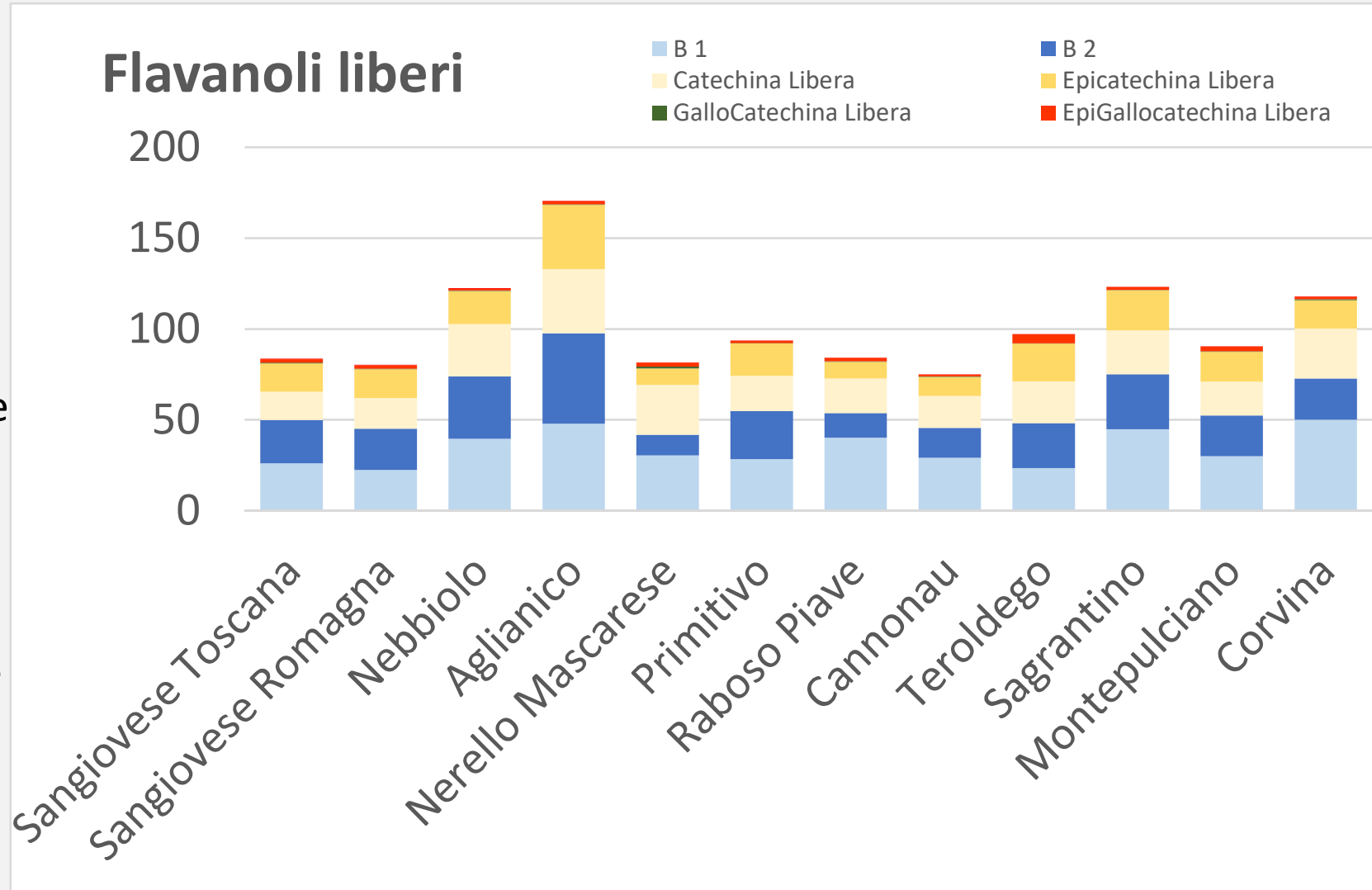
- ✓ 2016
- ✓ Annate precedenti comprese tra il 2012 e il 2015
- ✓ Solforosa libera standardizzata a 50 mg/L dopo il campionamento da vasca



RISULTATI

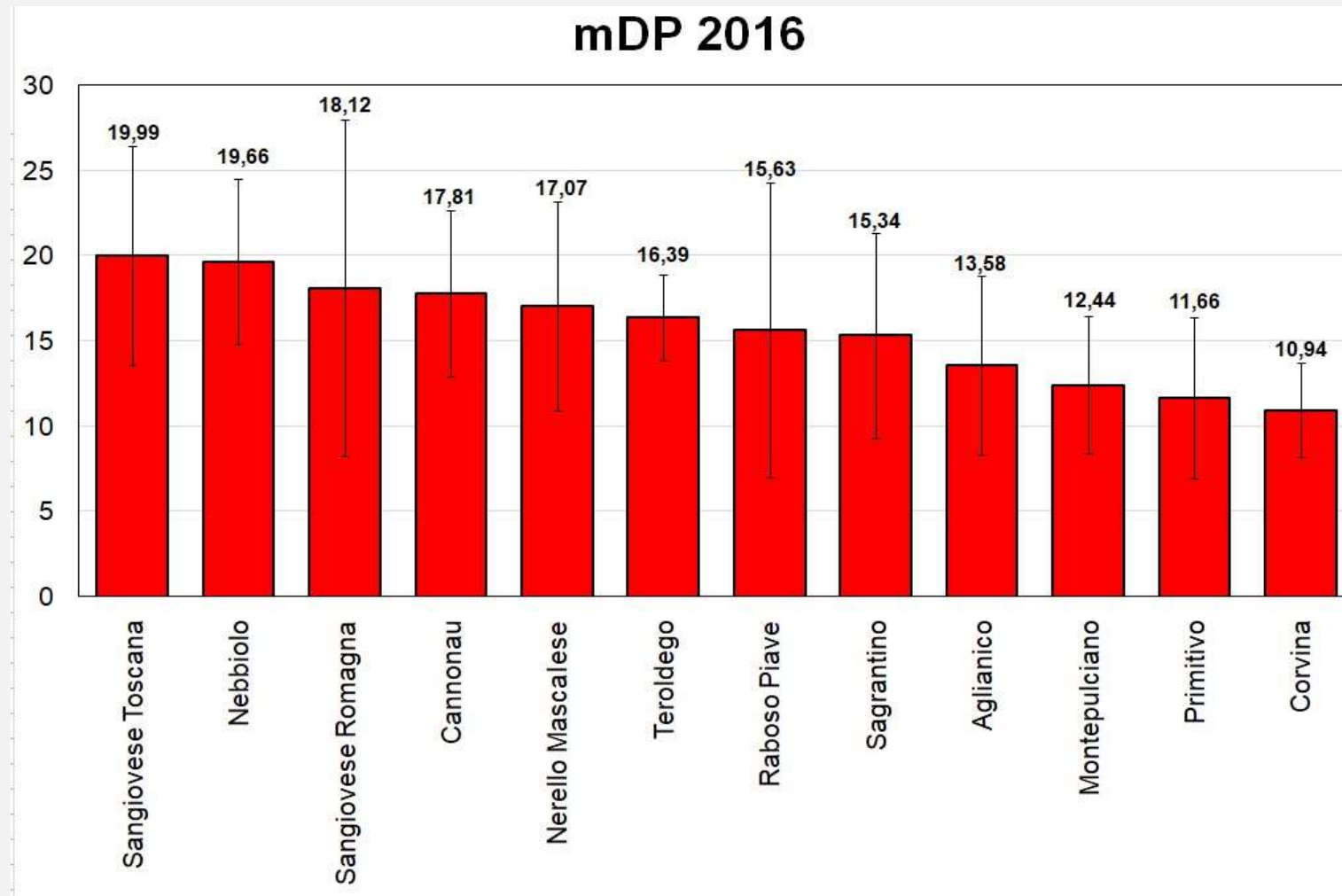
Flavanoli liberi

- ✓ procianidine B1 e B2 sono quelle più rappresentative in entrambe le varietà
- ✓ rapporto può essere decisamente a favore della B1 (Nerello Mascalese e Raboso Piave)
- ✓ rapporto circa equivalente per Primitivo, Aglianico e Sangiovese
- ✓ Aglianico varietà più ricca e Cannonau varietà più povera.



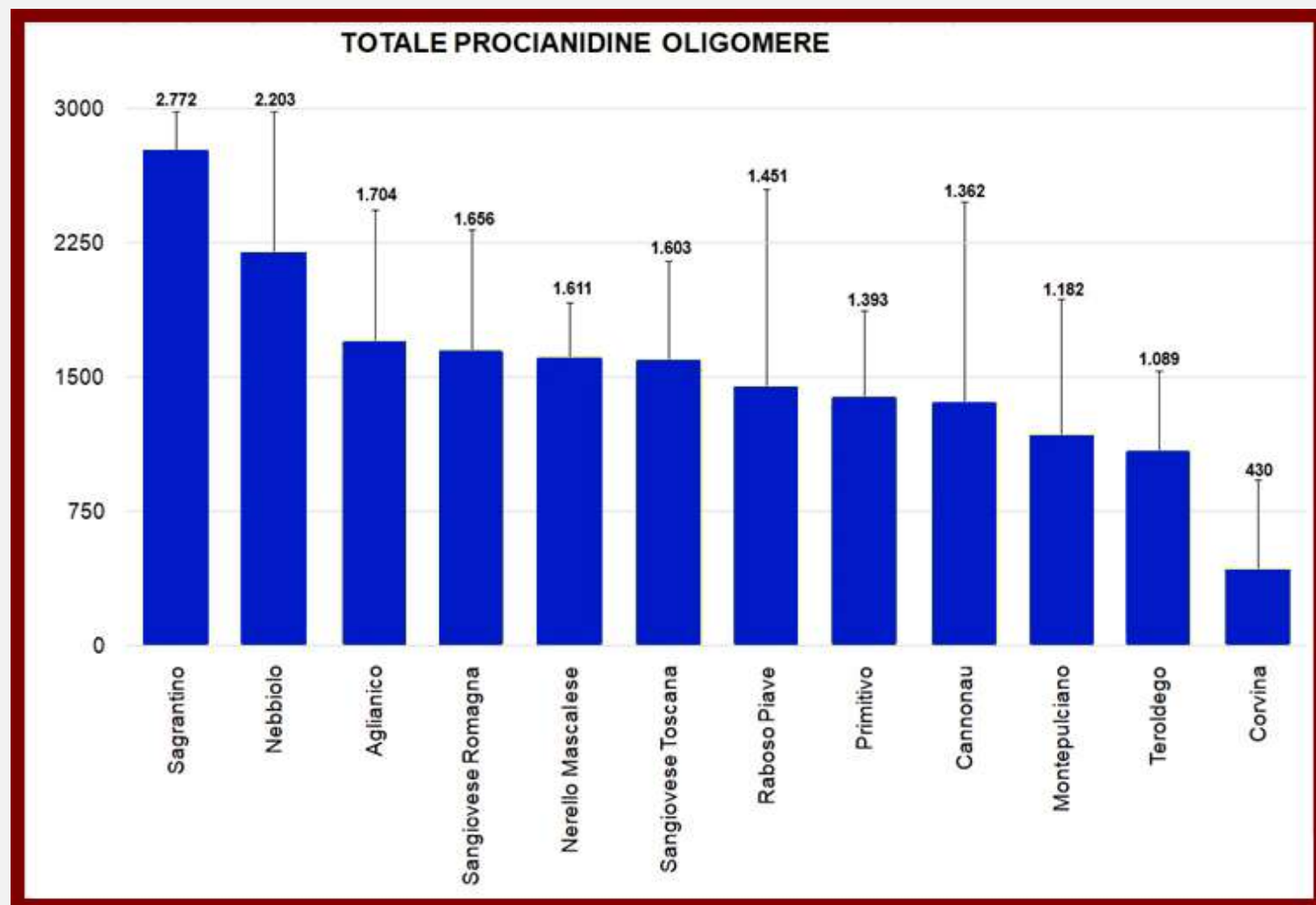
Grado medio di polimerizzazione (mDP)

- ✓ Primo elemento di diversità: la taglia media dei tannini (2x)
- ✓ Sangiovese e Nebbiolo composti da pigmenti polimerici di taglia media molto più grande rispetto alla Corvina e al Primitivo.
- ✓ E' atteso che la differenza sia tale da impattare sulla interazione con le proteine salivari.



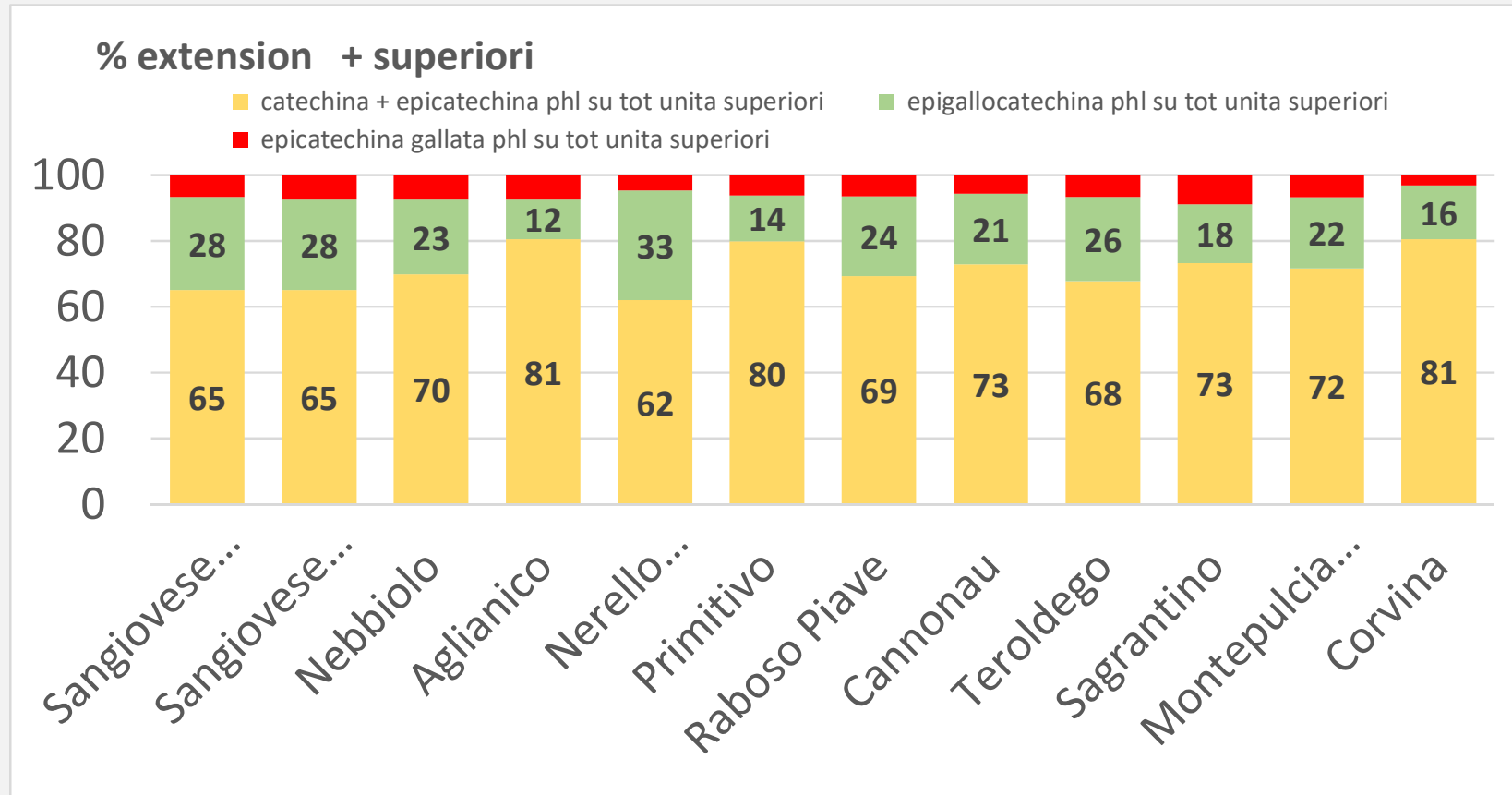
Procianidine oligomere

- ✓ Secondo elemento di diversità: la quantità (7x)
- ✓ varietà con una maggiore quantità di procianidine è il Sagrantino mentre quella più povera risulta essere la Corvina;
- ✓ Attenzione al ruolo della vinificazione (diversi stili di vino rosso!)



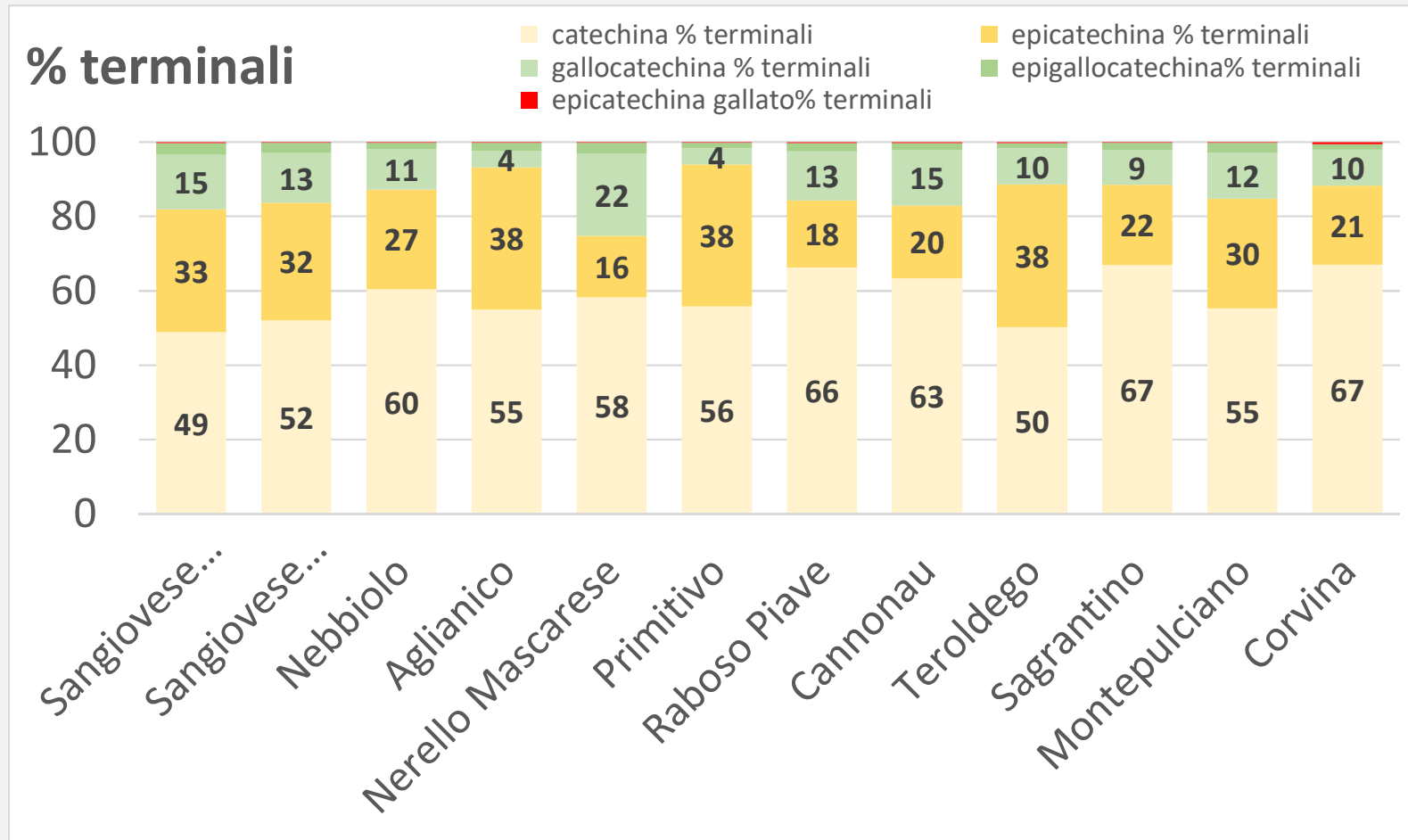
% Unità di estensione

- ✓ Terzo elemento di diversità: rapporto fra i flavanoli monomeri;
- ✓ % di catechina ed epicatechina sono dominanti in tutte le varietà (62-81%);
- ✓ epigallocatechina (12-33%)
- ✓ epicatechina gallata (3-9%)



% Unità terminali

- ✓ Quarto elemento di diversità: le unità terminali;
- ✓ % di catechina dominante in tutte le varietà;
- ✓ epicatechina (16-38%)
- ✓ gallocatechina (4-22%)

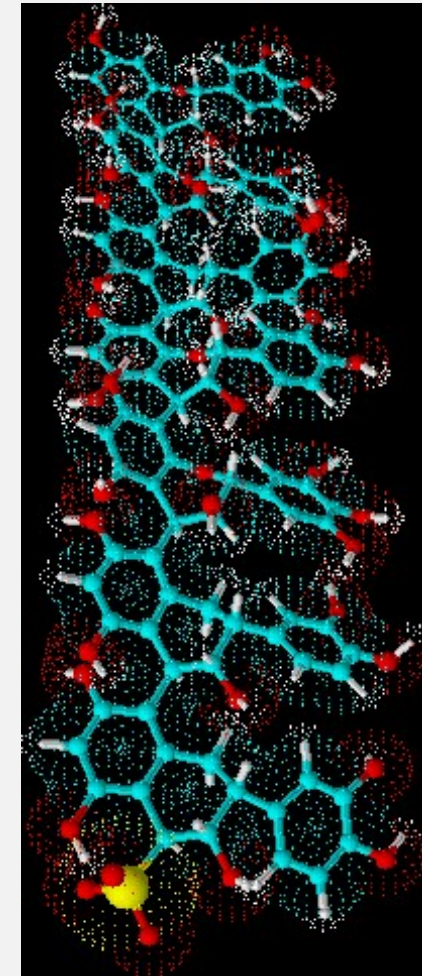
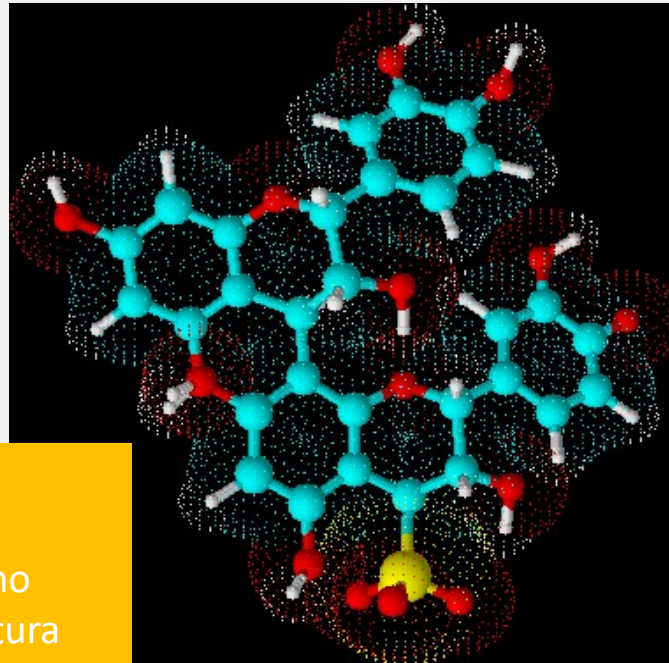
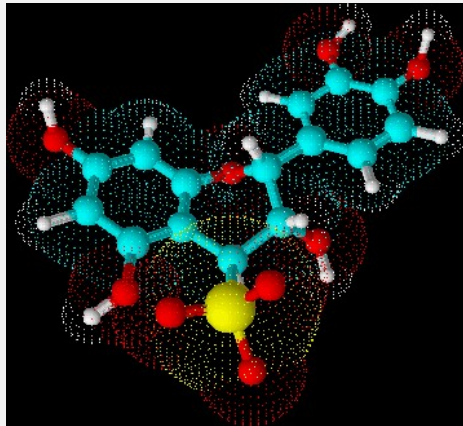


OPEN The impact of SO₂ on wine flavanols and indoles in relation to wine style and age

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Accepted: 22 December 2017

Panagiotis Arapitsas¹, Graziano Guella^{2,3} & Fulvio Mattivi^{1,2}

Flavanoli C-solfonati nel vino



- ✓ Composti idrofili con aumentata solubilità
- ✓ Prodotti anche via idrolisi degli oligomeri
- ✓ Sono attesi ridurre mDP dei tannini del vino
- ✓ Formazione lenta, dipende dalle temperatura

Conclusioni

Tramite floroglucinolisi è possibile avere delle informazioni quantitative molto dettagliate sulla composizione dei tannini dei vini rossi.

Il quadro complessivo che deriva dalla comparazione dei vini aziendali del 2016 ci mostra come esistano delle differenze marcate tra le varietà per

- i) concentrazione;**
- ii) dimensione;**
- iii) rapporti tra le unità costituenti i tannini.**

E' ragionevole ipotizzare che queste grandi differenze compositive tra i tannini contribuiscano in maniera non trascurabile a conferire un profilo gustativo particolare/identitario associato a ciascuna varietà.



Grazie!



Maurizio Ugliano

Daniele Perenzoni
Panagiotis Arapitsas

Camilla Berlato

A tutte le Cantine che hanno
collaborato ai campionamenti

