The Chemistry of Red Wine: pH, SO_2 and Phenolics

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What *is* wine ???????

"...bottled poetry."
Robert Louis Stevenson

"Liquid Music..."

"It puckers your mouth." –Art Buchwald

An expression of place

"the beverage of moderation"

Sunshine held together by water
-Galileo

The blood of Christ

A fate worse than death!
Susan B. Anthony

The most gentle and
efficaceous of medicines

"Wisdom and wit to the wise"
-Archimedes

"Wine is proof that God loves us and desires us to be happy."
Benjamin Franklin

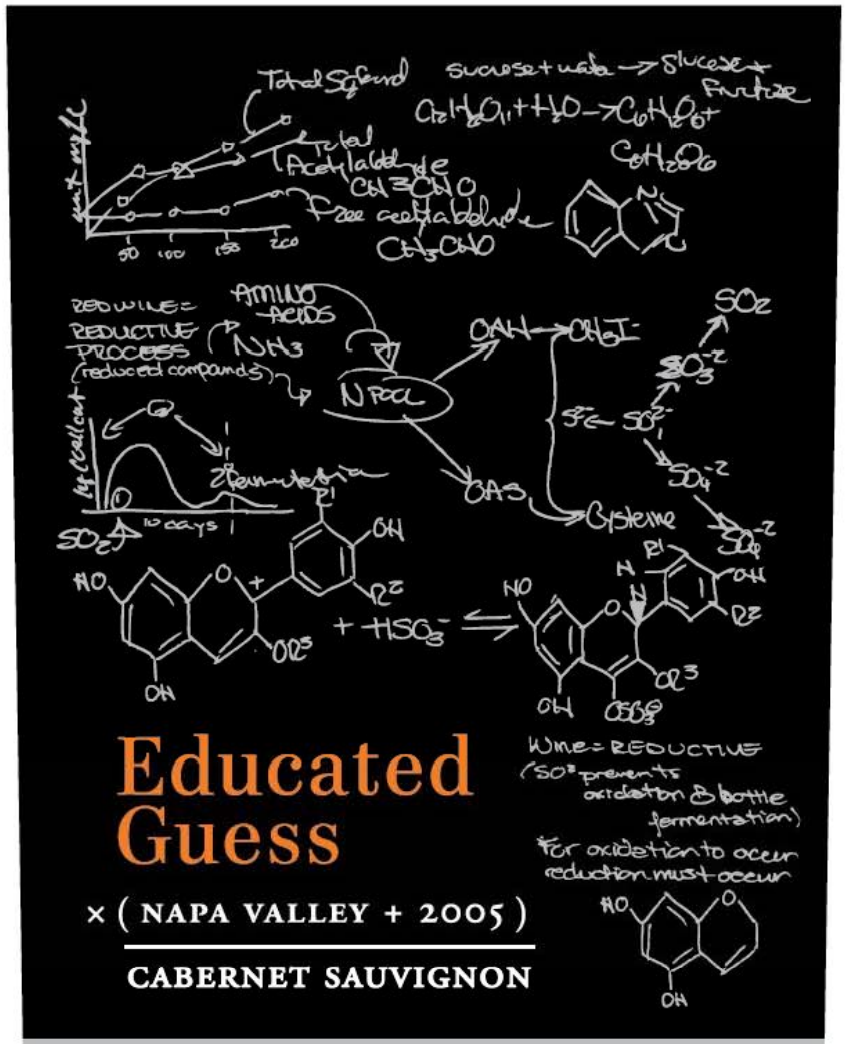
"It has a subtle nose, a long finish, strong body, and if you drink enough, you get absolutely pie-faced."

CHEMISTRY ON THE LABEL

Sulfur dioxide and enology: formation of acetylaldehyde in response to SO^2 in Fermentation. (Cornell University)

SO^2 and wine quality (reductive process graph) showing how SO^2 kills bacteria. SO^2 inhibits oxidation and bottle fermentation, and SO^2 blocks polymerization.

(Cornell University)



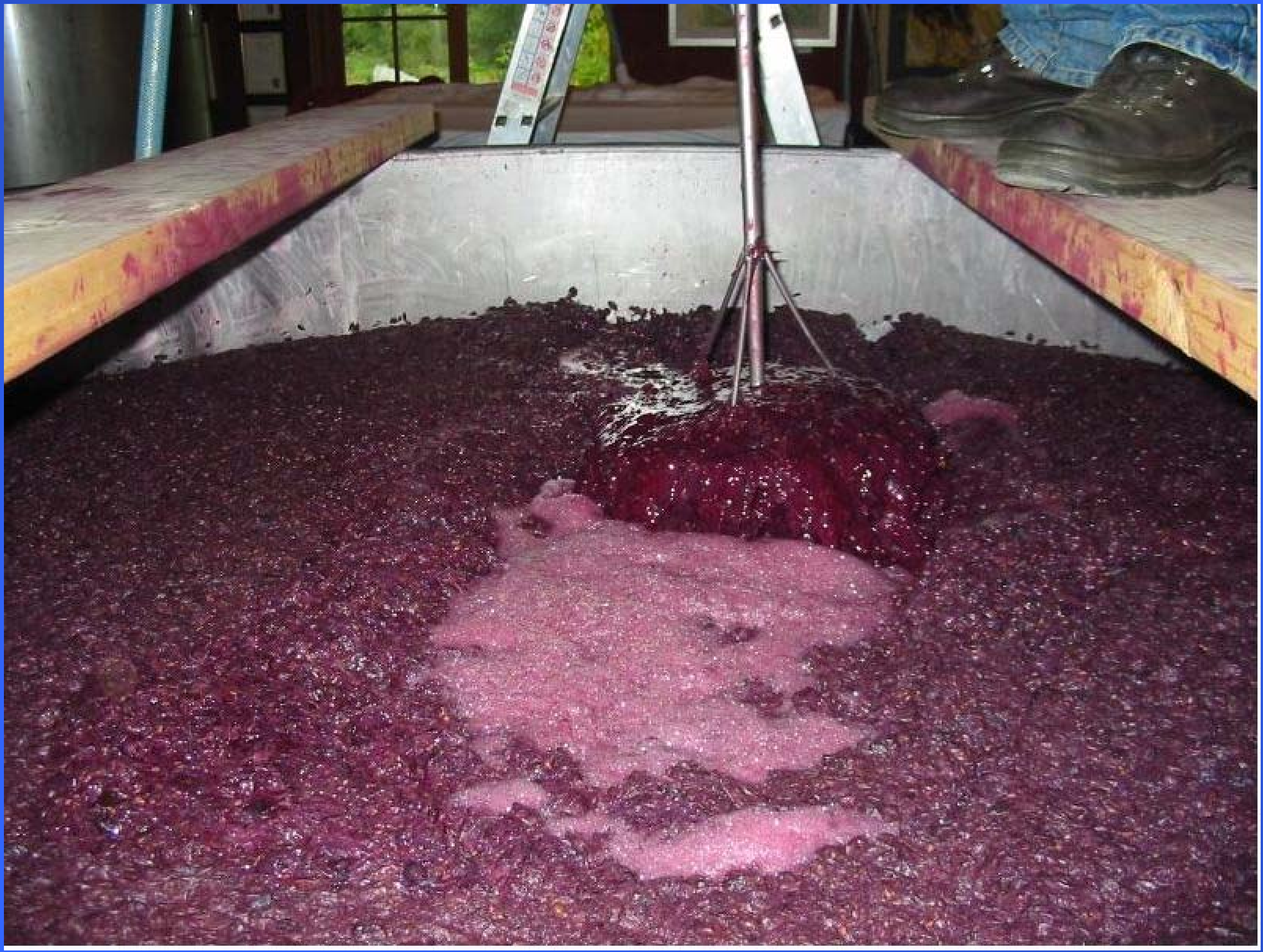
General Chemistry: Sucrose conversion to glucose and fructose, with structures.

(UC Davis)

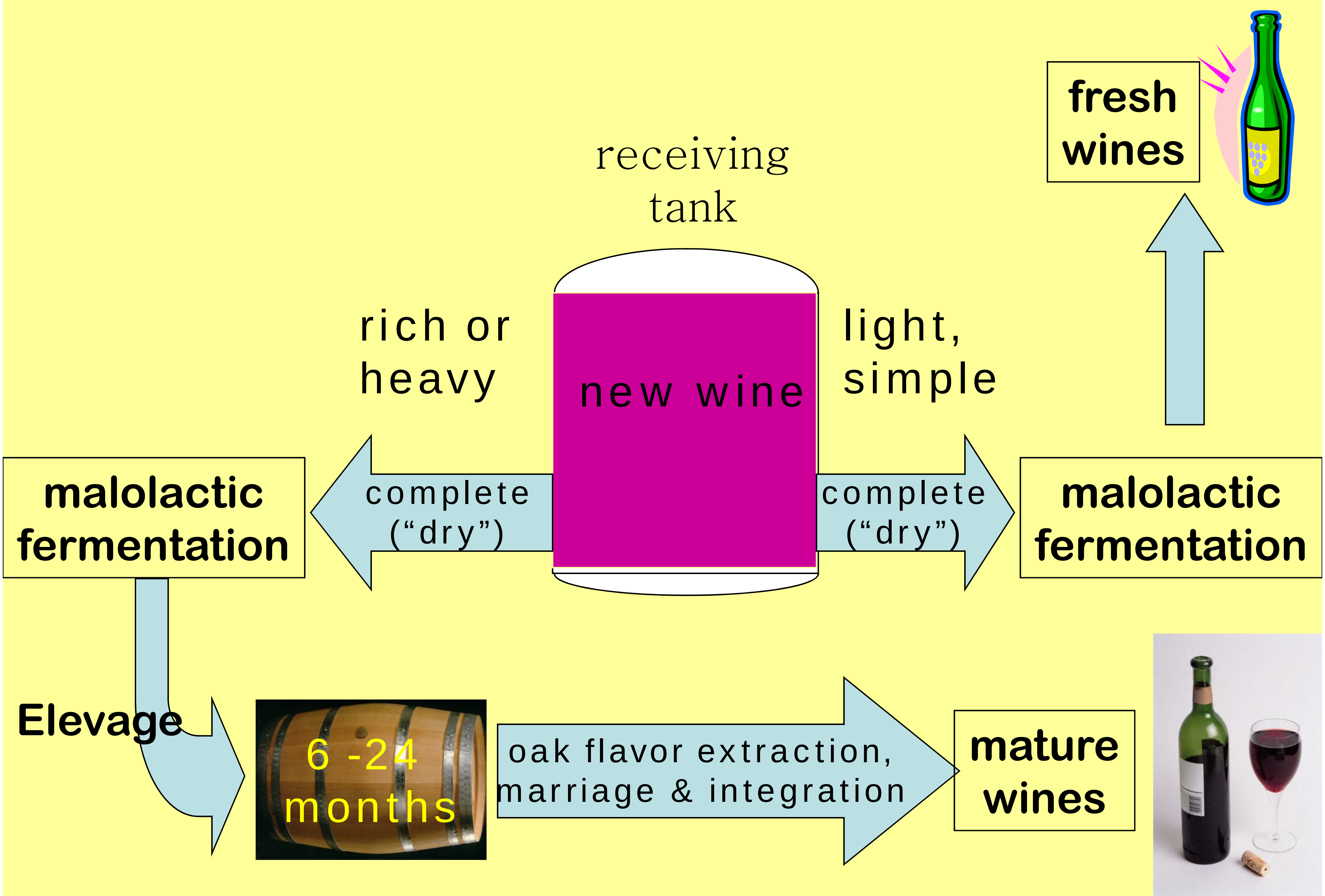
Sulfide production during fermentation. (Virginia Tech)

Bleaching of Red Wine with excess sulphur dioxide, flavylium cation of anthocyanins. (Cornell University)

Maceration



How red wine is made




RAMON
Roqueta
2005
TEMPRANILLO
Ull de Llebre
CATALUNYA

Mosel Riesling	Cabernet Sauvignon
fresh	mature
pure	sexy
focused fruit	integrated voice
beautiful	profound
crisp	round
loves sunlight	loves firelight

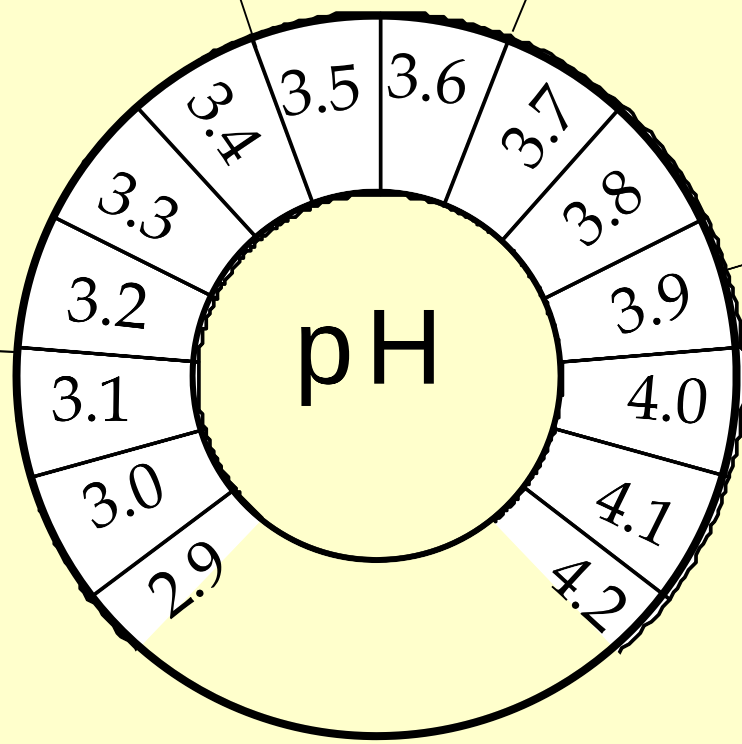
Sensible pH "Zones"

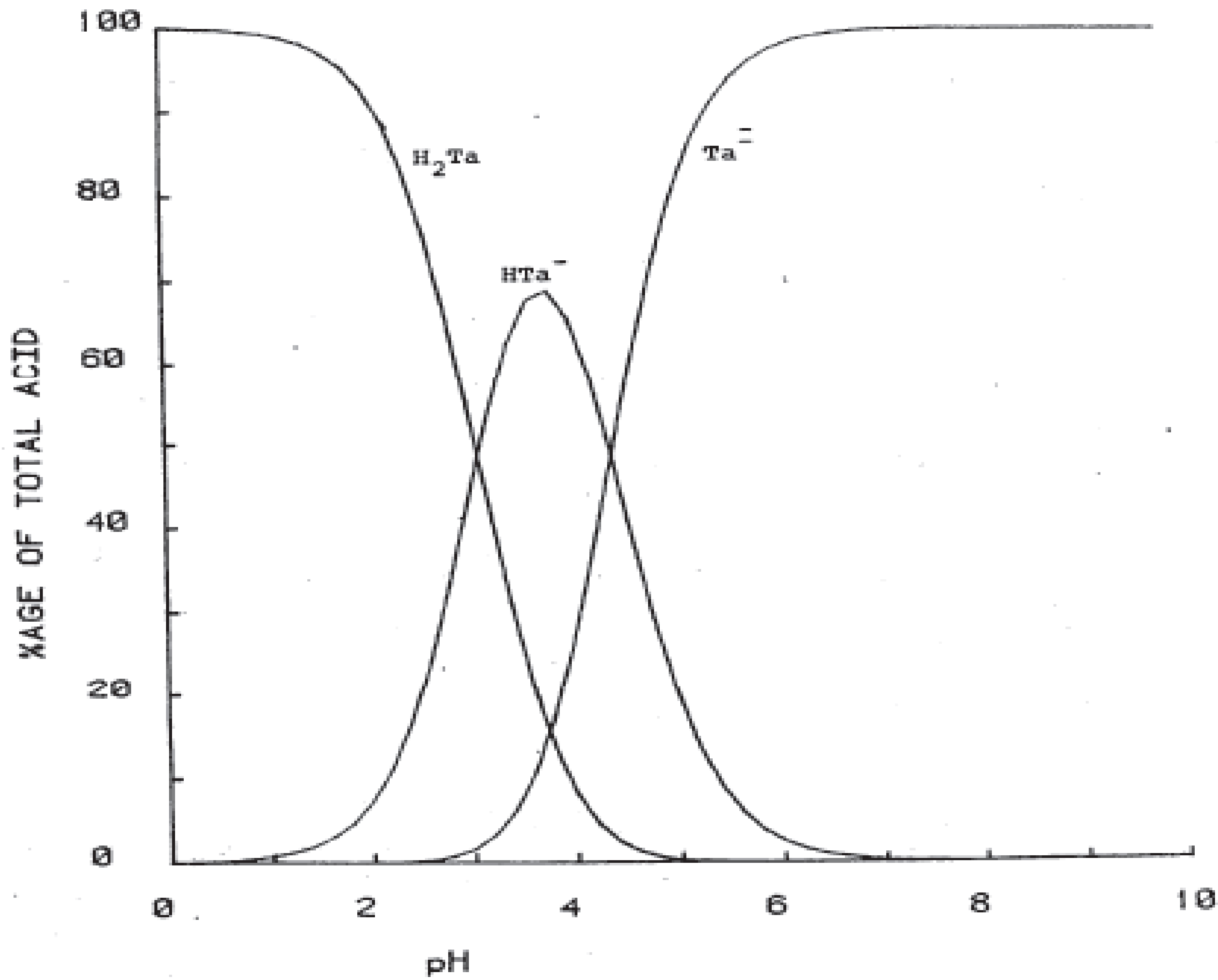
Fresh wine styles

- low tannin
- arrested ageing
- crisp acid taste

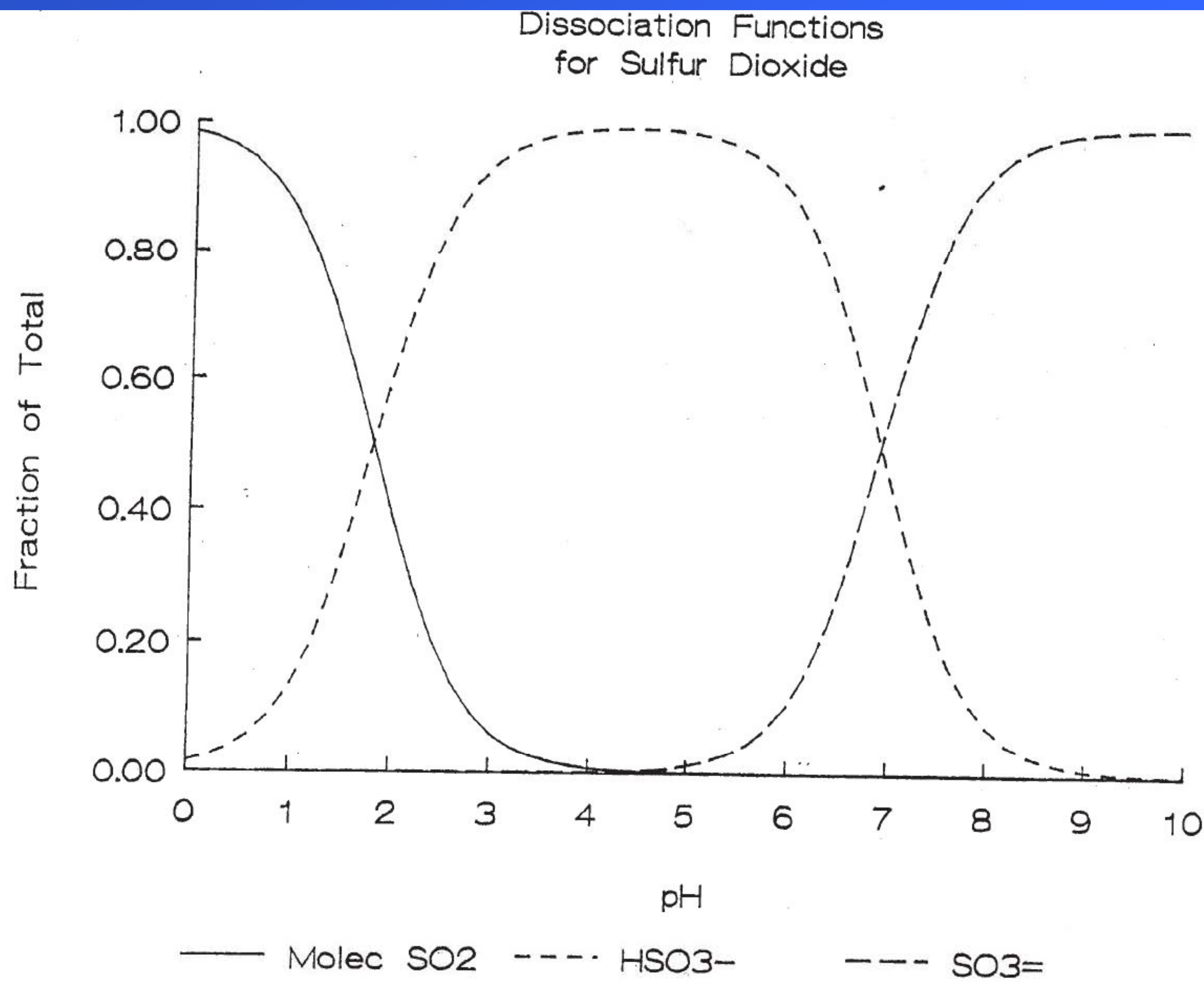
mature wine styles

- high tannin
- guided maturity
- soft acid taste





100
80
60
40
20
0
%AGE OF TOTAL ACID
H2Ta
HTa⁻
Ta⁼
0
2
4
6
8
10
pH


Dissociation Functions
for Sulfur Dioxide
Fraction of Total
1.00
0.80
0.60
0.40
0.20
0.00
0
1
2
3
4
5
6
7
8
9
10
pH
Molec SO2
HSO3-
SO3=

Distribution of free SO_2 at various pH's

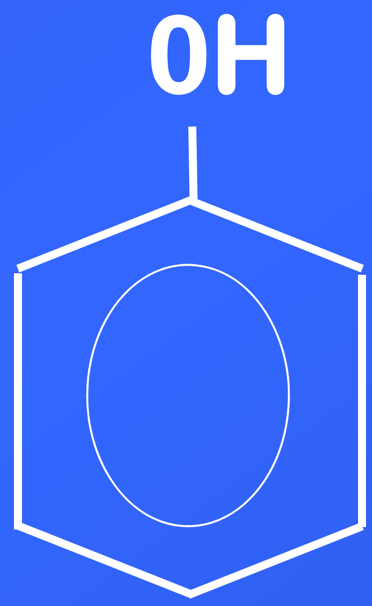
pH	% SO_2 (m)	% HSO_3^-	% SO_3^{-2}	Free SO_2 to obtain 0.8 ppm molecular SO_2
2.9	7.5	92.5	.009	11 ppm
3.0	6.1	93.9	.012	13
3.1	4.9	95.1	.015	16
3.2	3.9	96.1	.019	21
3.3	3.1	96.8	.024	26
3.4	2.5	97.5	.030	32
3.5	2.0	98.0	.038	40
3.6	1.6	98.4	.048	50
3.7	1.3	98.7	.061	63
3.8	1.0	98.9	.077	79
3.9	0.8	99.1	.097	99
4.0	0.6	99.2	.122	125

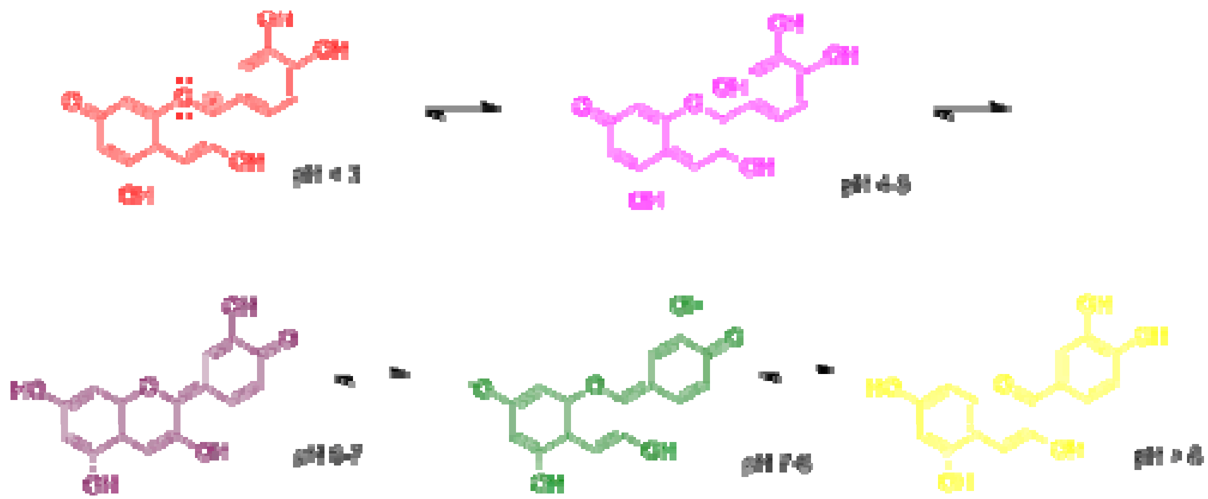
Why do some big red wines fail to age?

- Oxidized flavors (poor reductive strength)
  - Vinegar (nail polish, sour finish)
  - Aldehyde: sherry, nutty, lacking freshness
  - Caramel, pruney, baked, dull
- Over-polymerized tannins (poor structure)
  - Dry, grainy, dirty mouthfeel
  - Precipitation of structure
  - Aromatic disintegration unbalances flavors

Phenolic:

Any compound containing a benzene ring which carries an -OH.

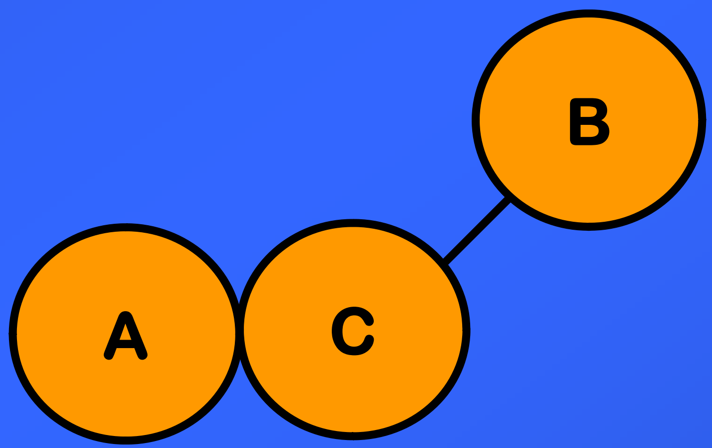




The stability of anthocyanidins is dependant on pH. At a low pH (acidic conditions), colored anthocyanidins are present, whereas at a higher pH (basic conditions) the colorless chalcones forms are present.

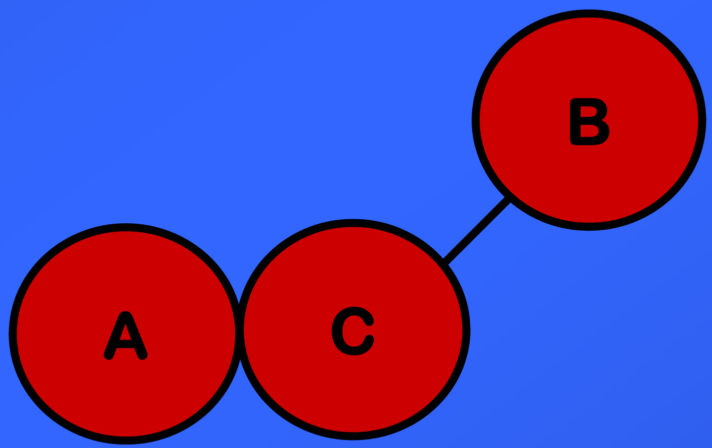
Flavonoid:

Any of the class of three-ringed phenolics extractable from skins



Anthocyanin:

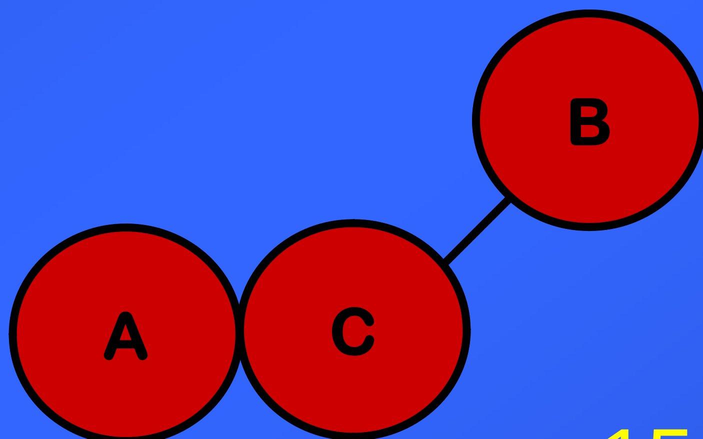
Any of the five red-colored flavonoid monomers



Malvadin, Delphinidin, Peonidin,

Flavilium ion:

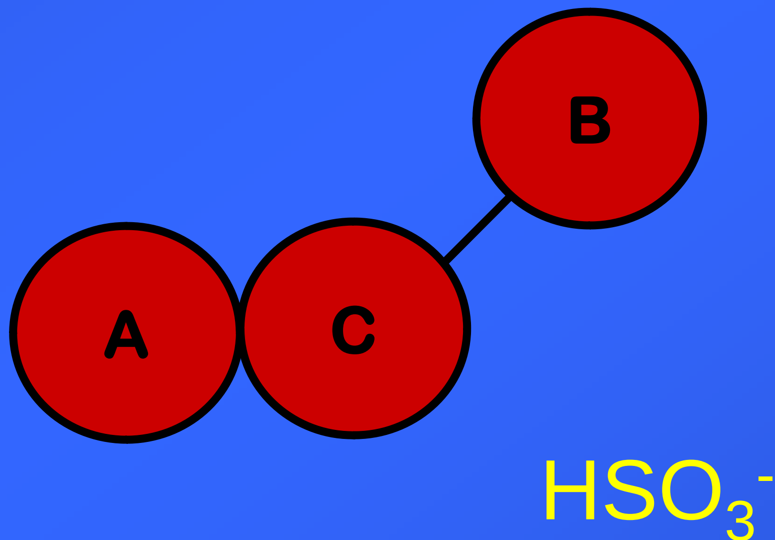
Low pH red-colored form
of an anthocyanin



15 – 30% visible
at wine pH

Anthocyanin monomers:

Subject to
bisulfite bleaching



Good Stuff about monomeric anthocyanins:

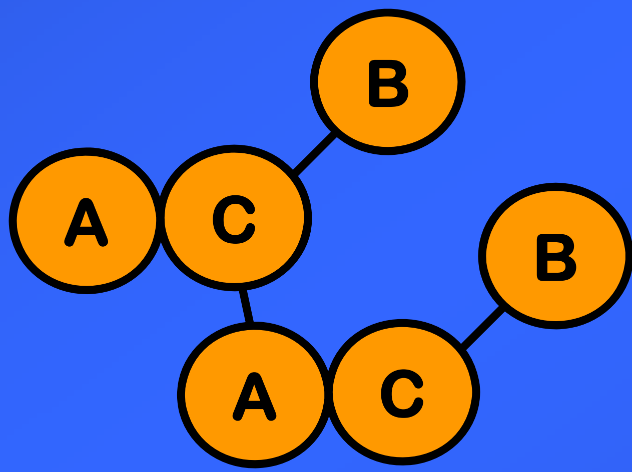
- Reactive: capable of improving structure

Bad Stuff:

- Nearly insoluble in 13% alcohol
- Colored only at low pH: 15-30% visible in wine
- Bleachable by SO_2
- Vulnerable to attack by enzymes
- Vulnerable to oxidation

Monomer:

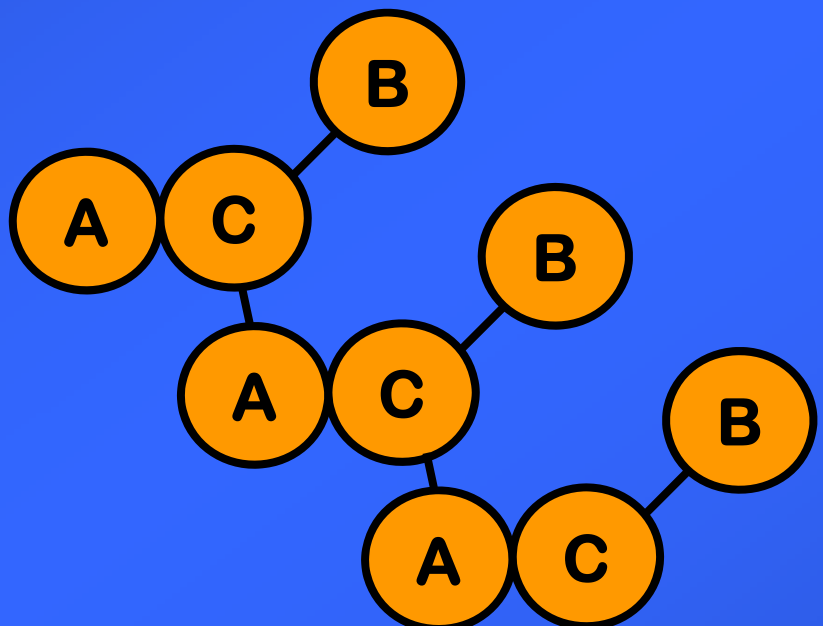
A discrete small molecule which can serve as a building block for a macromolecule



C4 – C8

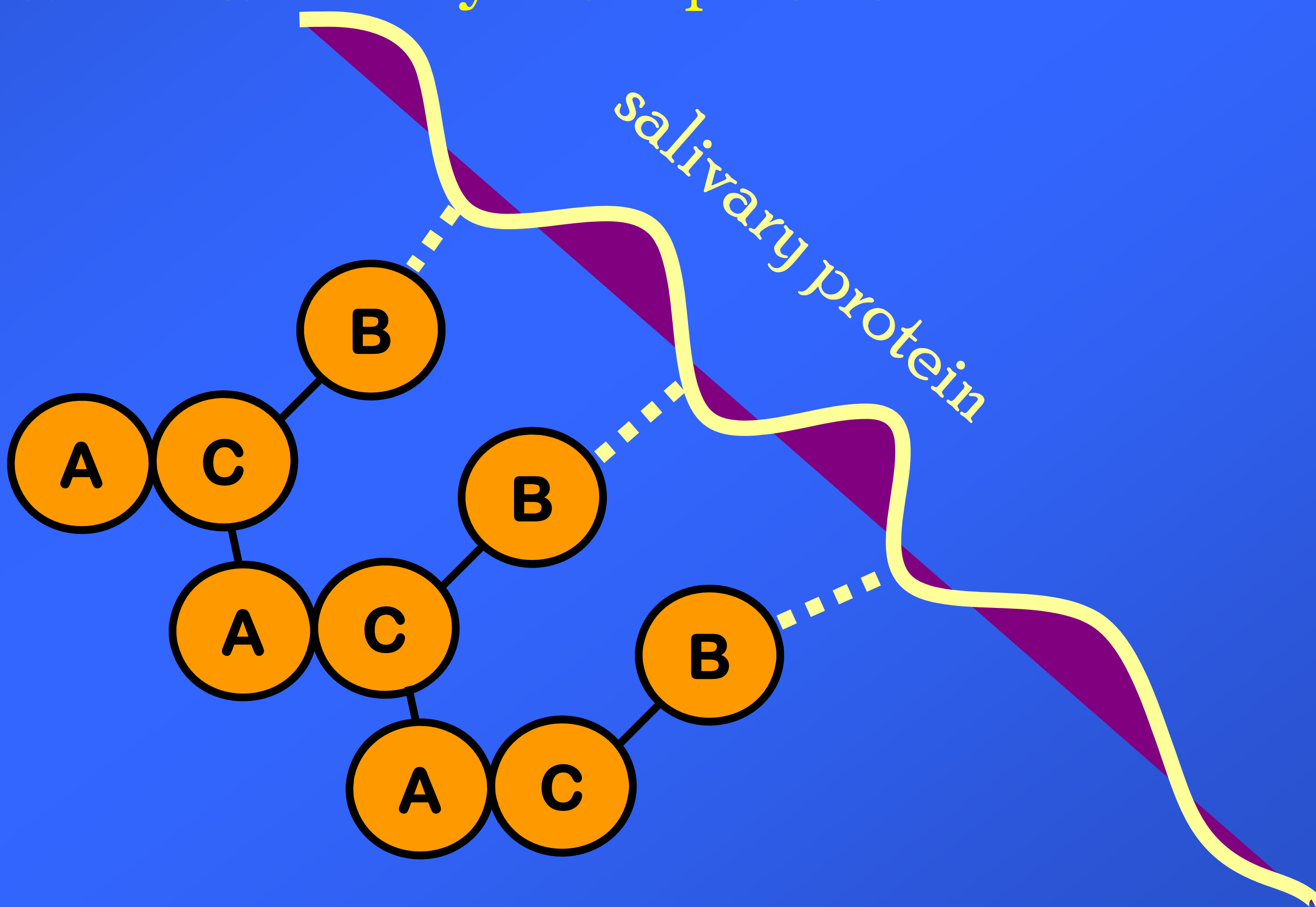
Polymer:

A macromolecule created by linking monomers together.



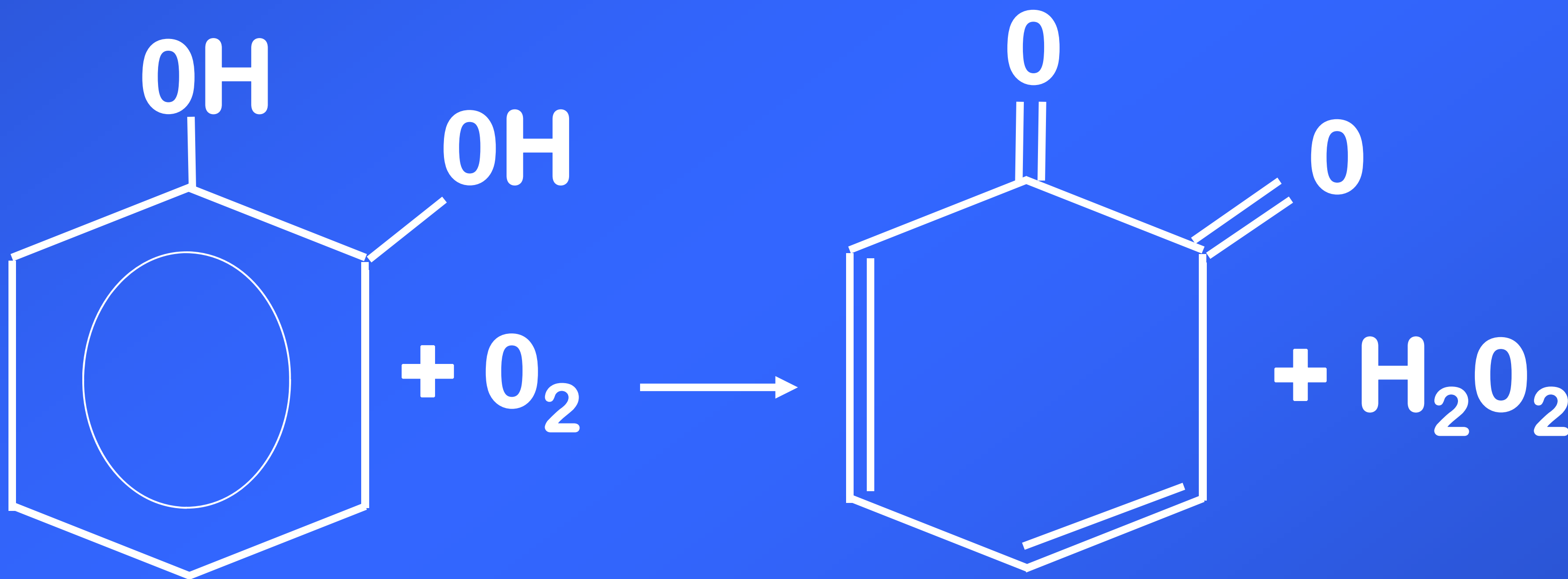
Tannin:

A polyphenol
with affinity for protein.



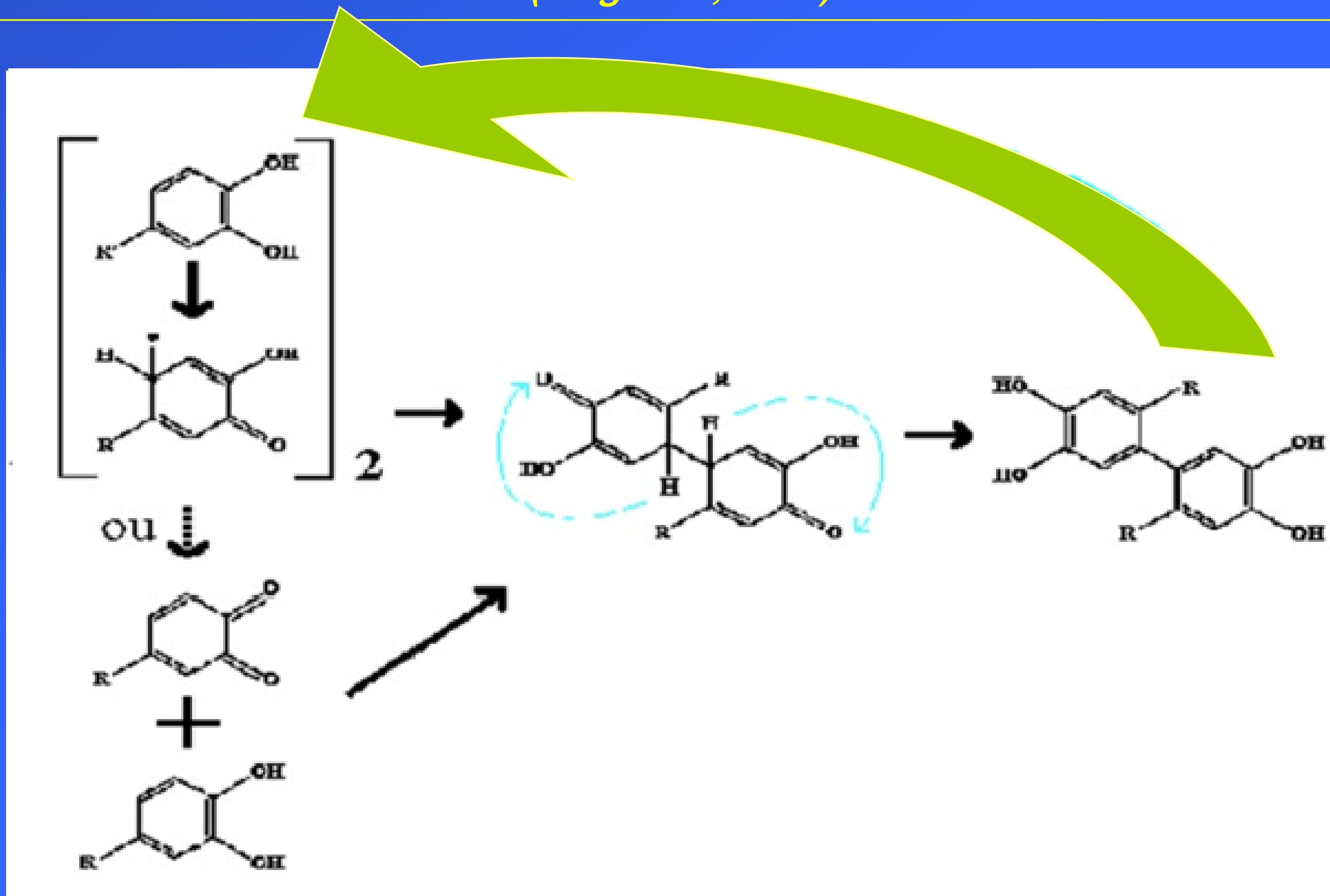
Interpretation of principle of oxydation of di-phenols

Singleton , 1987

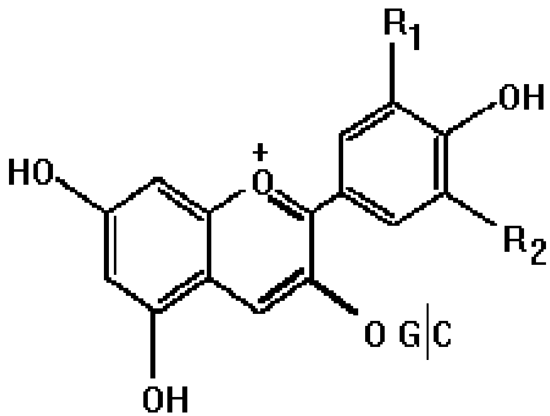


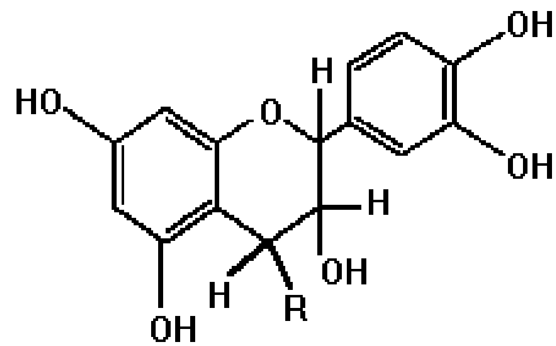
Example of polymerative regeneration

(Singleton, 1986)



Building Blocks of Red Wine Structure





Anthocyanin
(color)

Contains no
vicinal diphenol

(terminates
polymer)

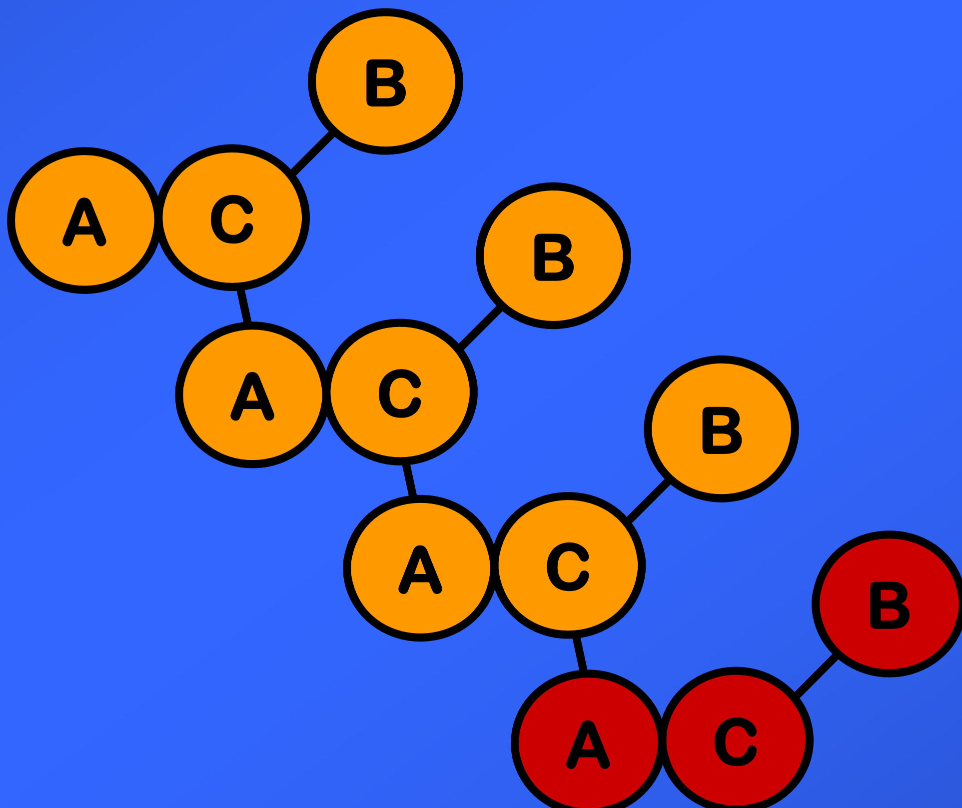
Flavanol
(tannin)

Contains a
vicinal diphenol

(can oxidatively
polymerize)

Polymeric Pigment:

Stable, unbleachable color which is the basis of refined texture.



The Importance of Color

- Wine appearance itself
- Key indicator of ripeness
- Declines during ripening
- Polymerization chemistry:

  pigment is critical to wine texture

Acknowledgements

Clark Smith, WineSmith

Mike Riddle, Fickle Fermenters

Tom Webber, Seguin-Moreau Copperage

George Shanks, Peripolli

U California Davis, Viticulture & Enology

Napa Valley Community College, V&E De

Q&A

or

Shall We Get a Glass of Wine?

Reading List

Technical

Concepts in Wine Chemistry, Y. Margalit (1997);
Concepts in Wine Technology, Y. Margalit (200X)
Wine Analysis and Production, B.W. Zoecklin et.al.(1999);
Introduction to Wine Laboratory Practices and Procedures, J.L. Jacobson (2010).
Wine Science: Principles and Application, R. Jackson (2007)
Principles and Practices of Winemaking, R.B. Boulton et.al.
Handbook of Enology, Vol 1(2000a) & 2(2000b), Ribereau e
The University Wine Course, M. Baldy (1997)

Encyclopedia

The Sotheby's Wine Encyclopedia , Tim Stevenson (2007)

General

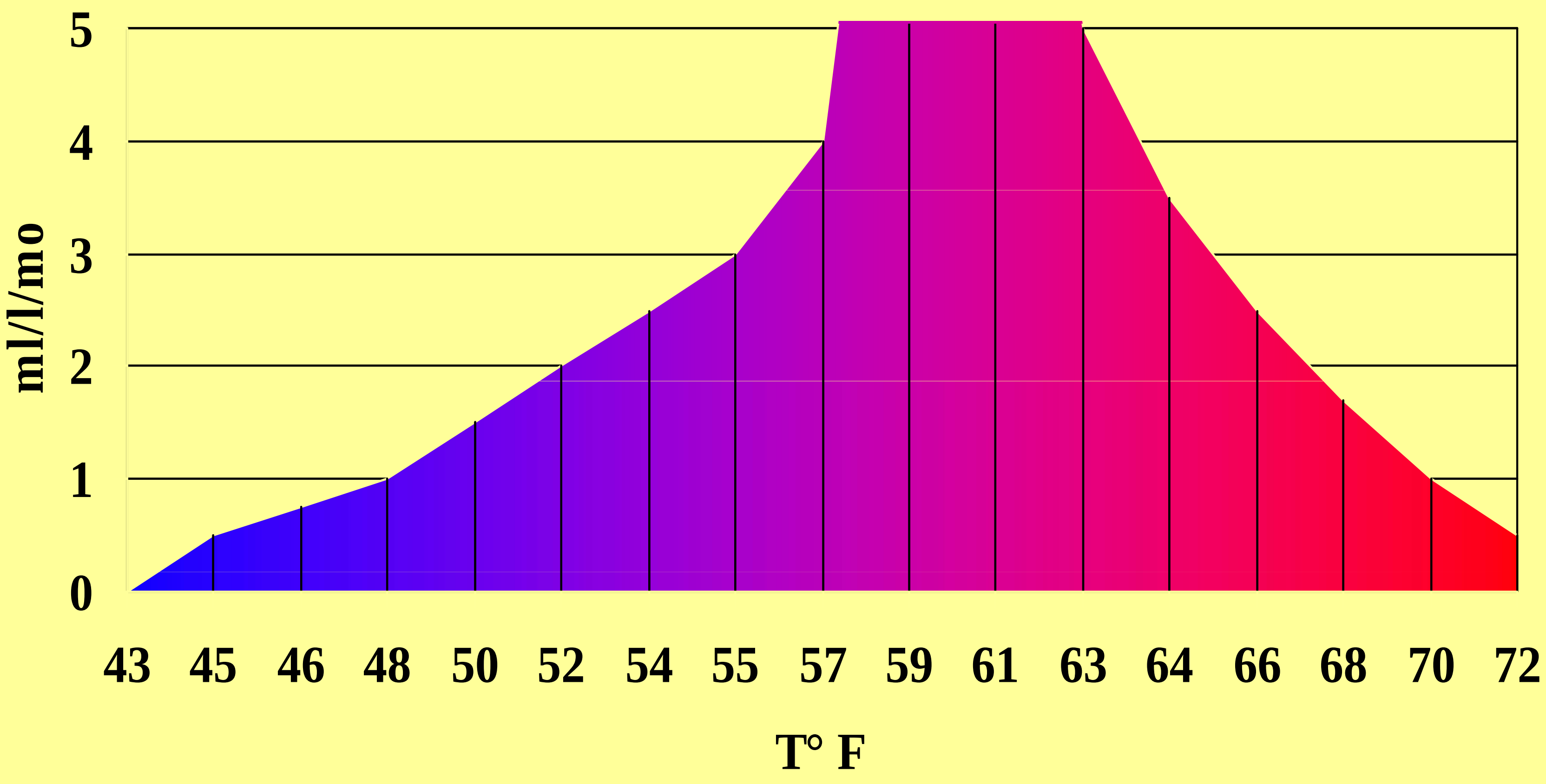
An Ideal Wine, David Darlington (2011)
The Judgement, George Taber (2011)

Articles Cited

1. "Vintage Chemistry" S.L. Rovner, C&EN p.30-32 May 1
2. "The Chemistry of a 90+ Wine" D. Darlington, N.Y. Tim 39, August 7, 2005
3. "Wine Sniffers Are Inconsistent" K.M. Reese, C&EN p. December 3, 2001

TEMPERATURE
as a major limiting factor

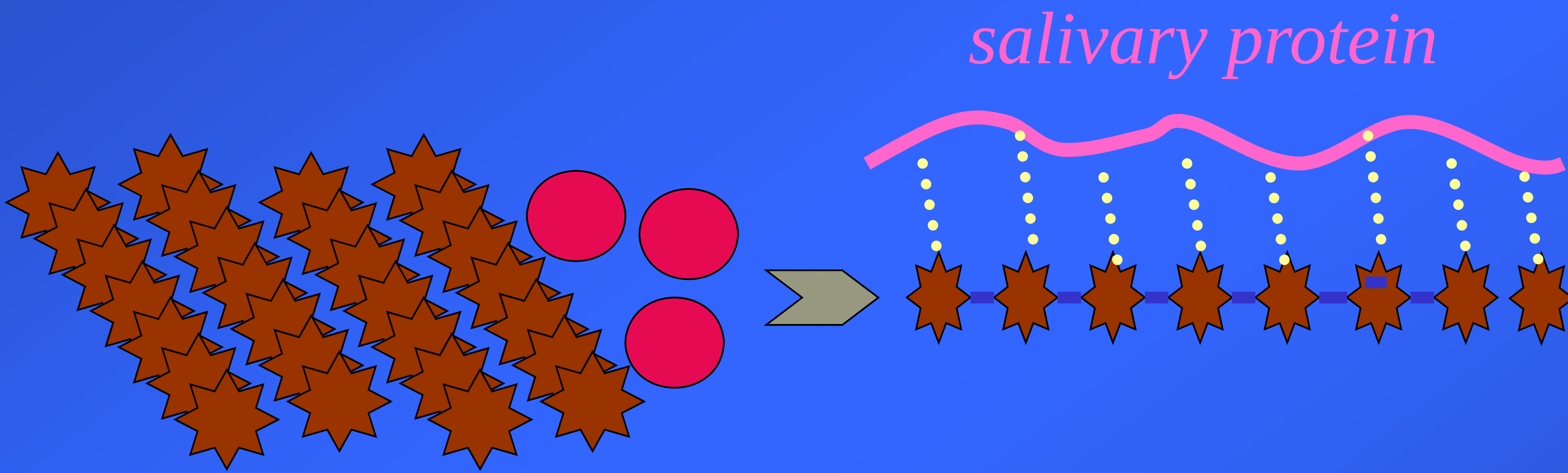
Maximum micro-oxygenation dose in clear wine



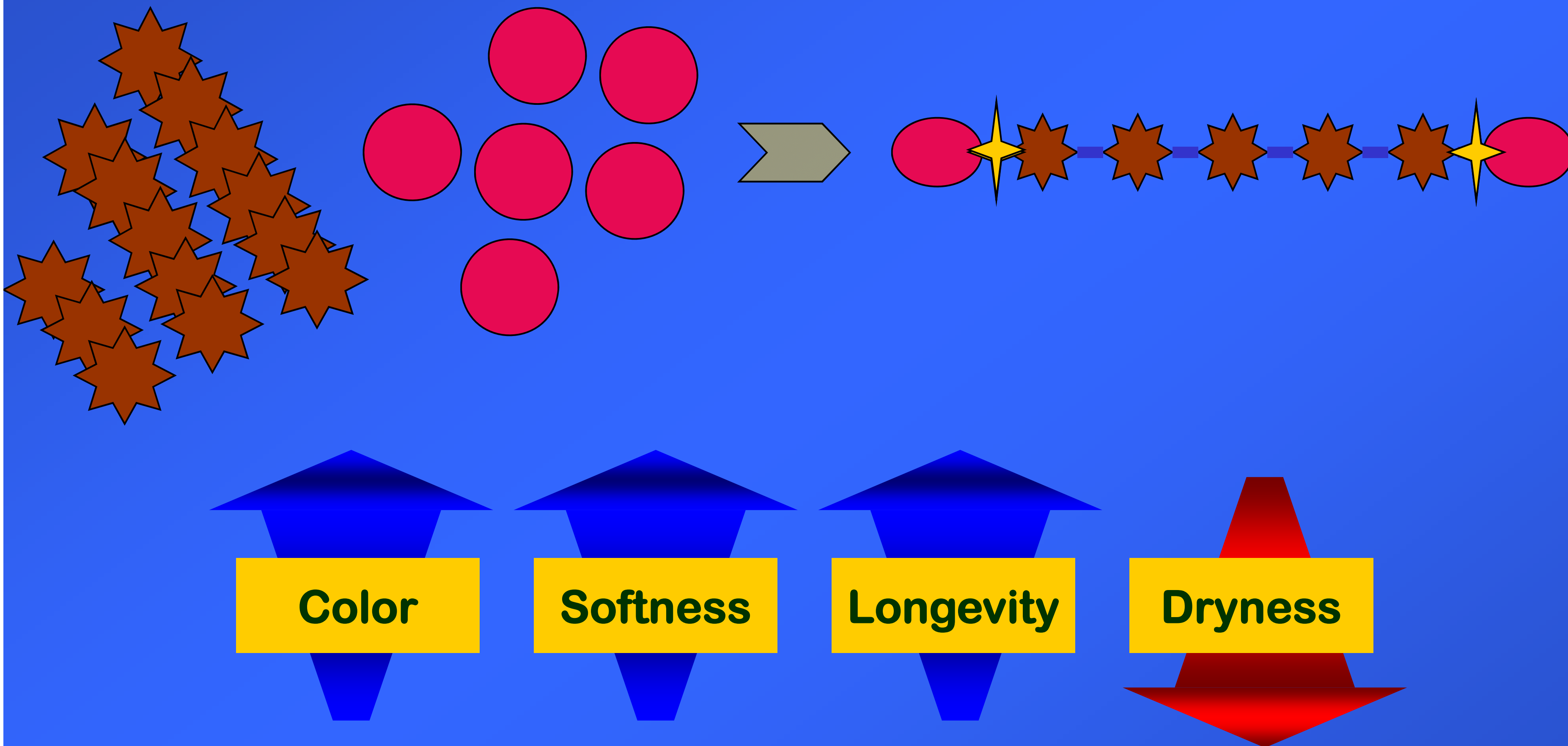
WINE ACIDS AND THEIR CHARACTERISTICS

NAME	STRUCTURE (acidic protons italicized)	WEIGHT PER MOLE	WEIGHT PER EQUIVLENT	pKa's	SOLUBILITY	INDUSTRIAL SOURCE	PROPERTIES
ACETIC	CH_3COOH	60	60	4.8	Complete **	Bacteria & Yeast	Vinegar Taste (Smell is Ethyl Acetate, formed by yeast & bacteria from Acetic Acid & Ethanol)
LACTIC	COOH | HO - C - H | CH_3	90	90	3.8	Complete **	N/A	Produced by malolactic bacteria from malic acid. Illegal to add.
MALIC	COOH | HO - C - H | H - C - H | COOH	134	67	3.5, 5.0	Easy	Apples	Weaker acid than tartaric. Not microbially stable.
TARTARIC	COOH | HO - C - H | H - C - OH | COOH	150	75	3.0, 4.2	Reluctantly dissolves in wine. Hot water helps.	Grapes	Most expensive. Gives most pH shift for a given T.A. rise. Microbially stable in wine.
FUMARIC	H COOH \ / C | C / \ HOOC H	116	58	3.0, 4.4	Sparing. Takes effort to exceed legal limit of 0.3 gm/L.	Fungal	Kills malolactic bacteria.
CITRIC	H_2C - COOH | HC - COOH | H_2C - COOH	176	58.7	3.1, 4.7, 5.0	Easy	Citrus	Inexpensive. Chelating agent: prevents metal casse. Shines stainless. Only legal acid additive in France. Some bacteria may convert to acetic.

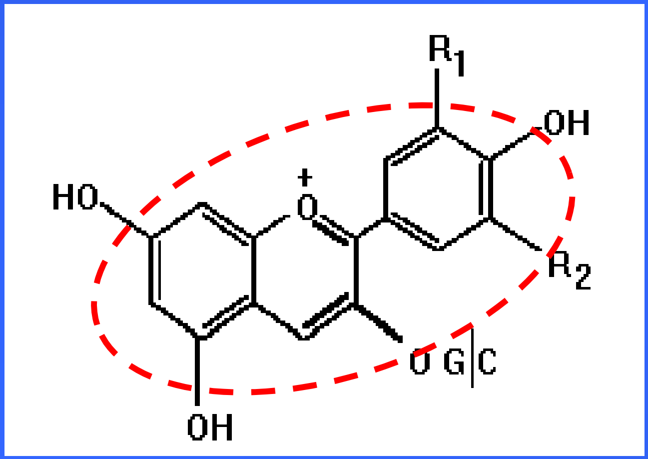
Poor anthocyanins lead to long, dry polymers



High anthocyanins lead to short, soft polymers



Flavilium Anthocyanin



520 nm
when protonated
(low pH)

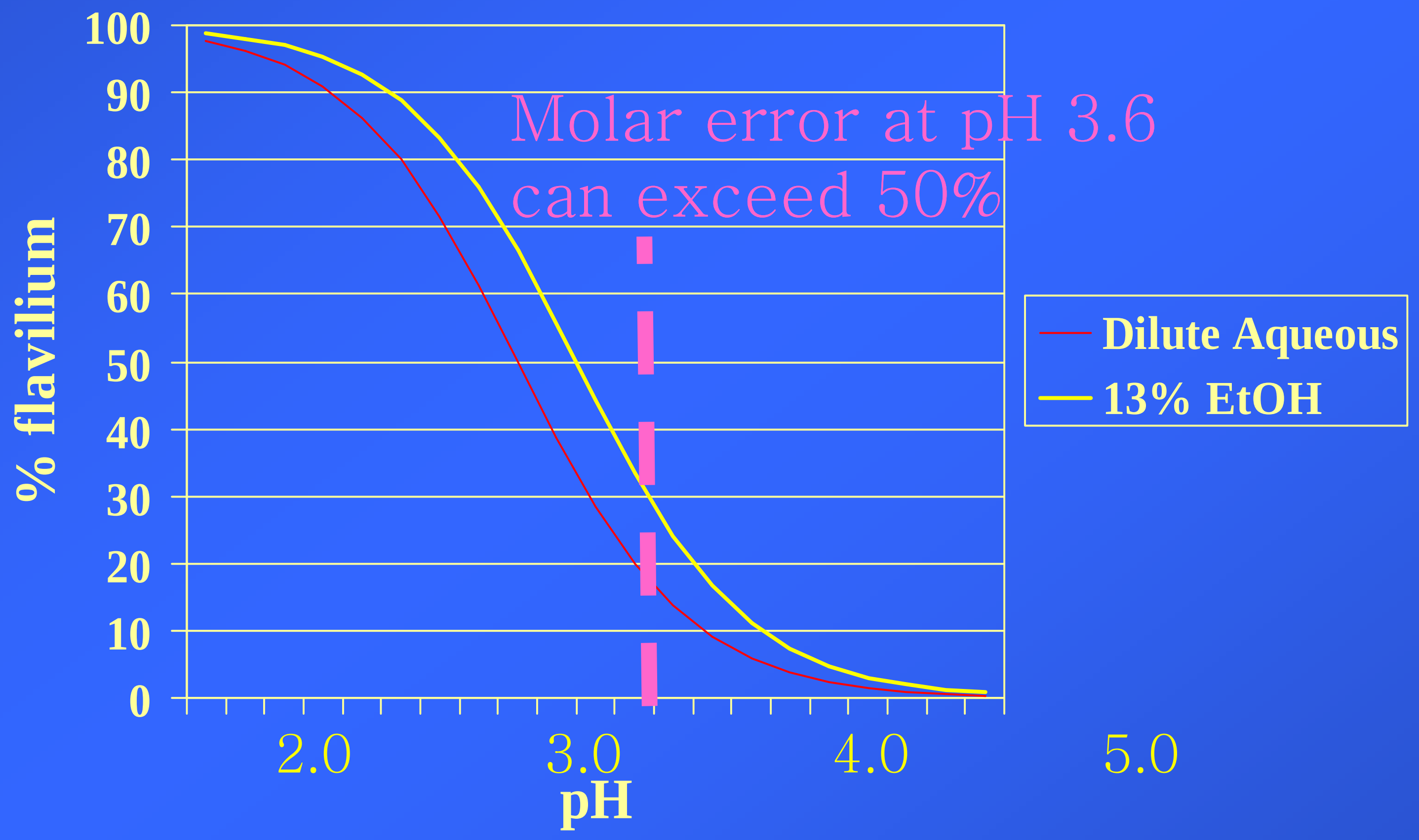
Boulton-modified Somers

- Good measure of visible flavilium at wine pH
- Poor anthocyanin molar estimator

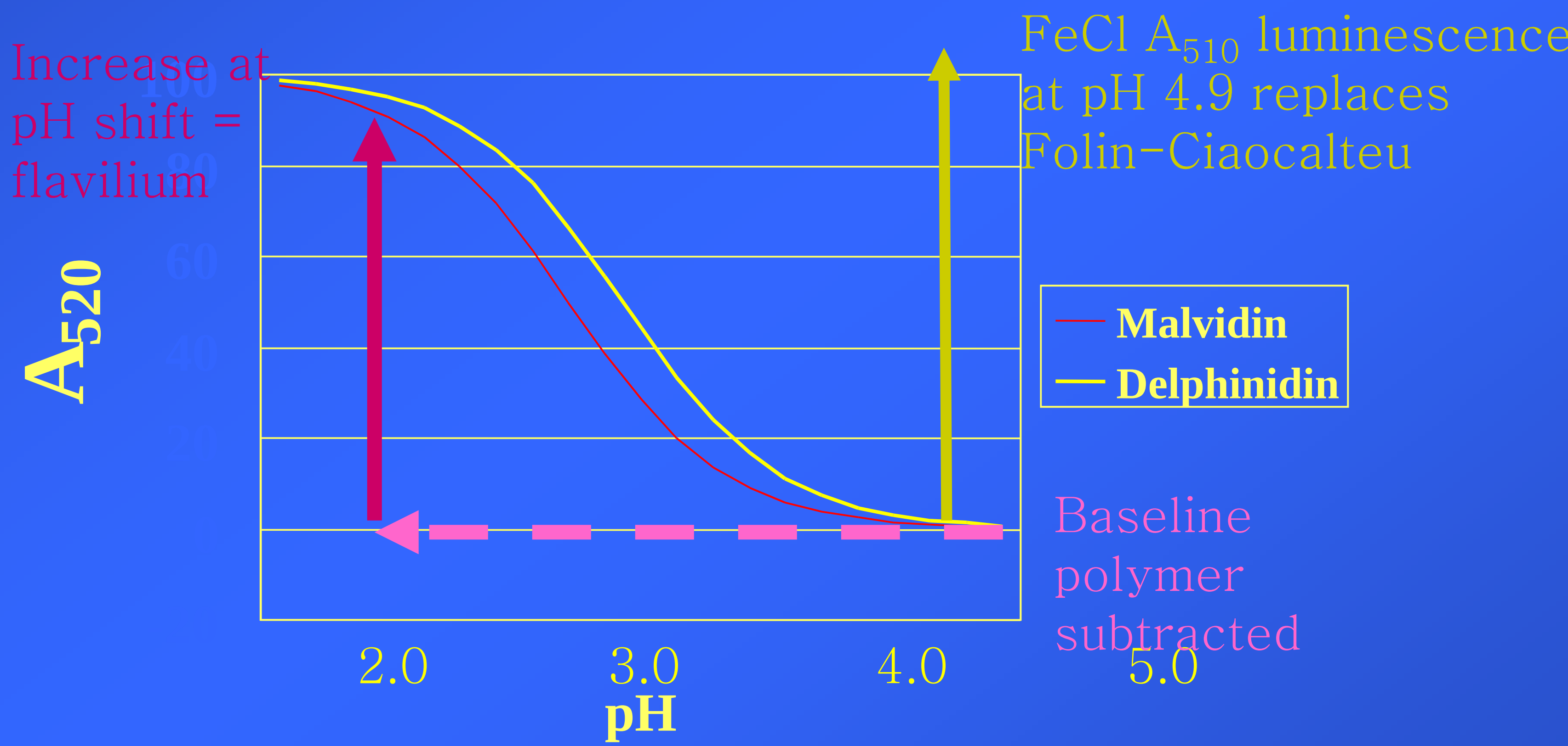
Adams BSA precipitation / FeCl complexing

- Total phenol determination at A_{510}
- Discriminates protein-precipitable polymer
- Good anthocyanin molar estimator

Malvidin-3 Glucoside Ionization



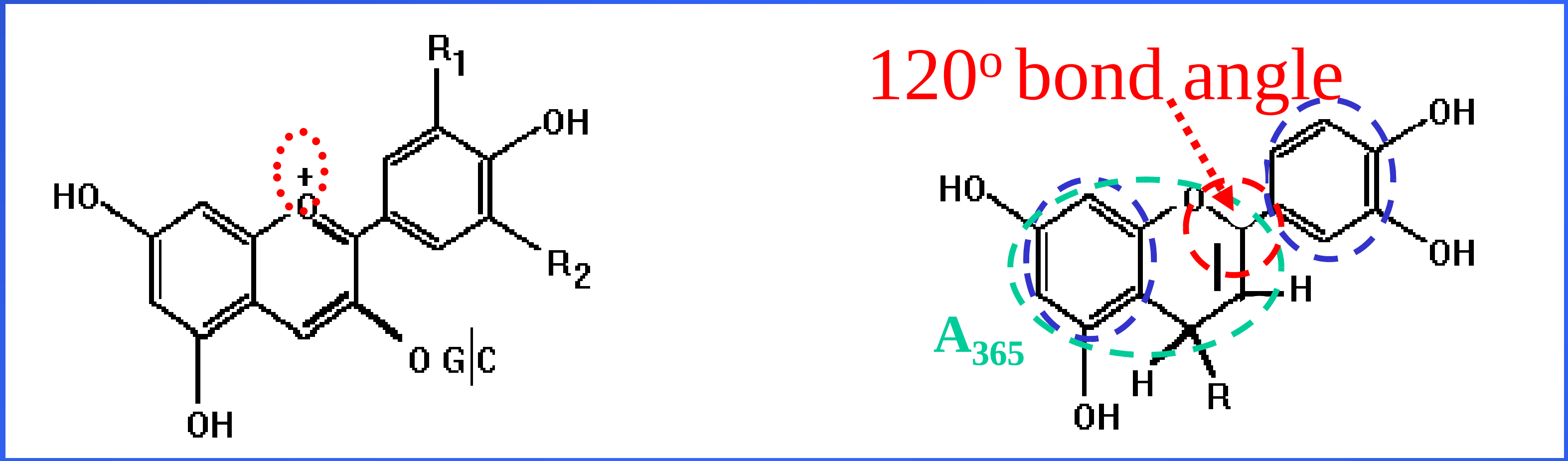
Adams method for molar estimation of ionizable anthocyanin



Maturity criteria for optimum wine quality

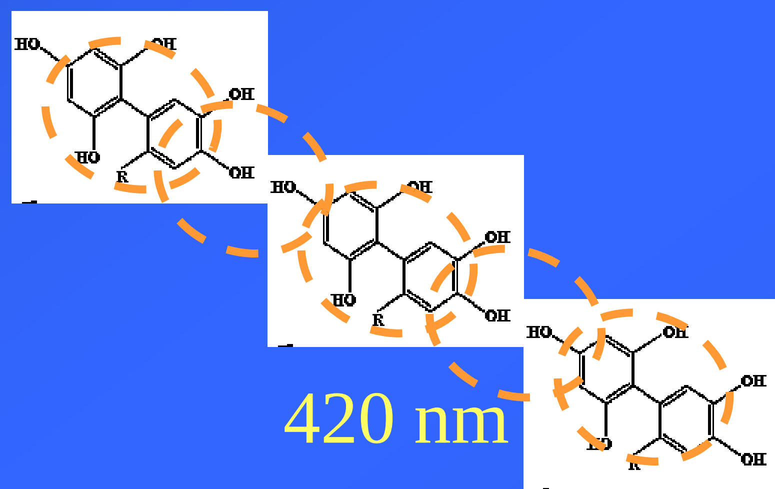
- Berry inspection and tasting
- Skin anthocyanins (A_{520})
- Co-factor potential (A_{280} and A_{365})
- Browning from rot or oxidation (A_{420})

Co-Pigmentation during Red Wine Fermentation



Anthocyanin (color)	**<u>Tannins</u>**
	Flavanols (A280) & Super-Cofactor Flav<u>o</u>nols (A_{280} & A_{365})
Apolar rings (Sparingly soluble)	**Uncharged**
Positively Charged (repel each other, so cannot stack)	**(can stack between anthocyanins to create colloids)**

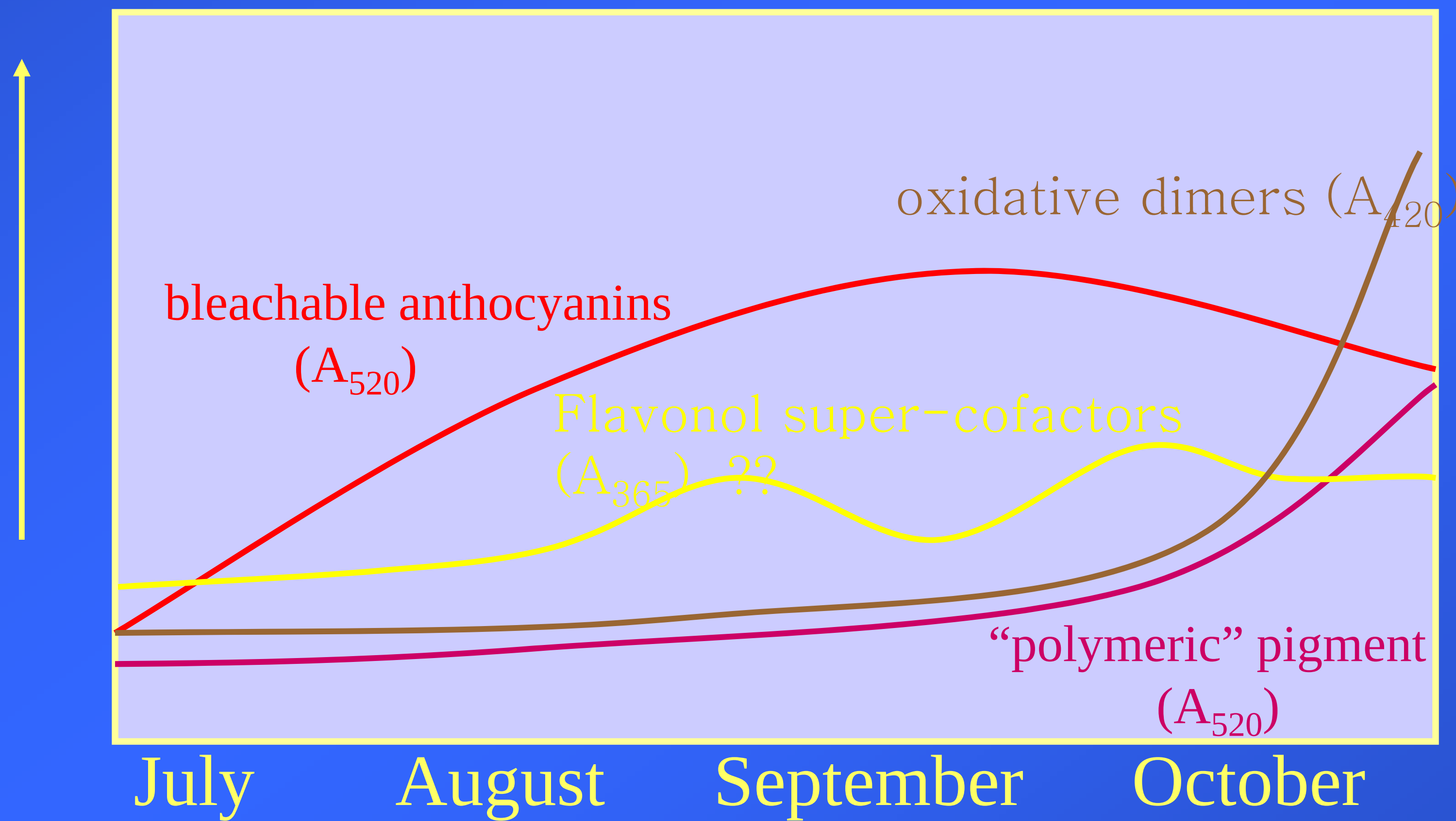
Oxidative dimer cross-linkages:



correlates with browning,
i.e. general visible light
absorption by polyphenols

Winegrape Phenolic Maturity

(Northern Hemisphere)



Maturity criteria for optimum wine quality

- Berry inspection and tasting
- Skin anthocyanins (A_{520})
- Browning potential (A_{280} and A_{365})
- Browning from rot or oxidation (A_{420})
- Hue = $\dfrac{\text{Browning from rot or oxidation } (A_{420})}{\text{decline in } A_{520}}$
- Brix x berry weight detects sampling errors

Viewing List

A Walk in the Clouds (1995)

– K. Reeves, A. Sanchez-Gijon, A. Quinn

Sideways (2004)

– P. Giamatti, T. Hayden Church, V. Mad

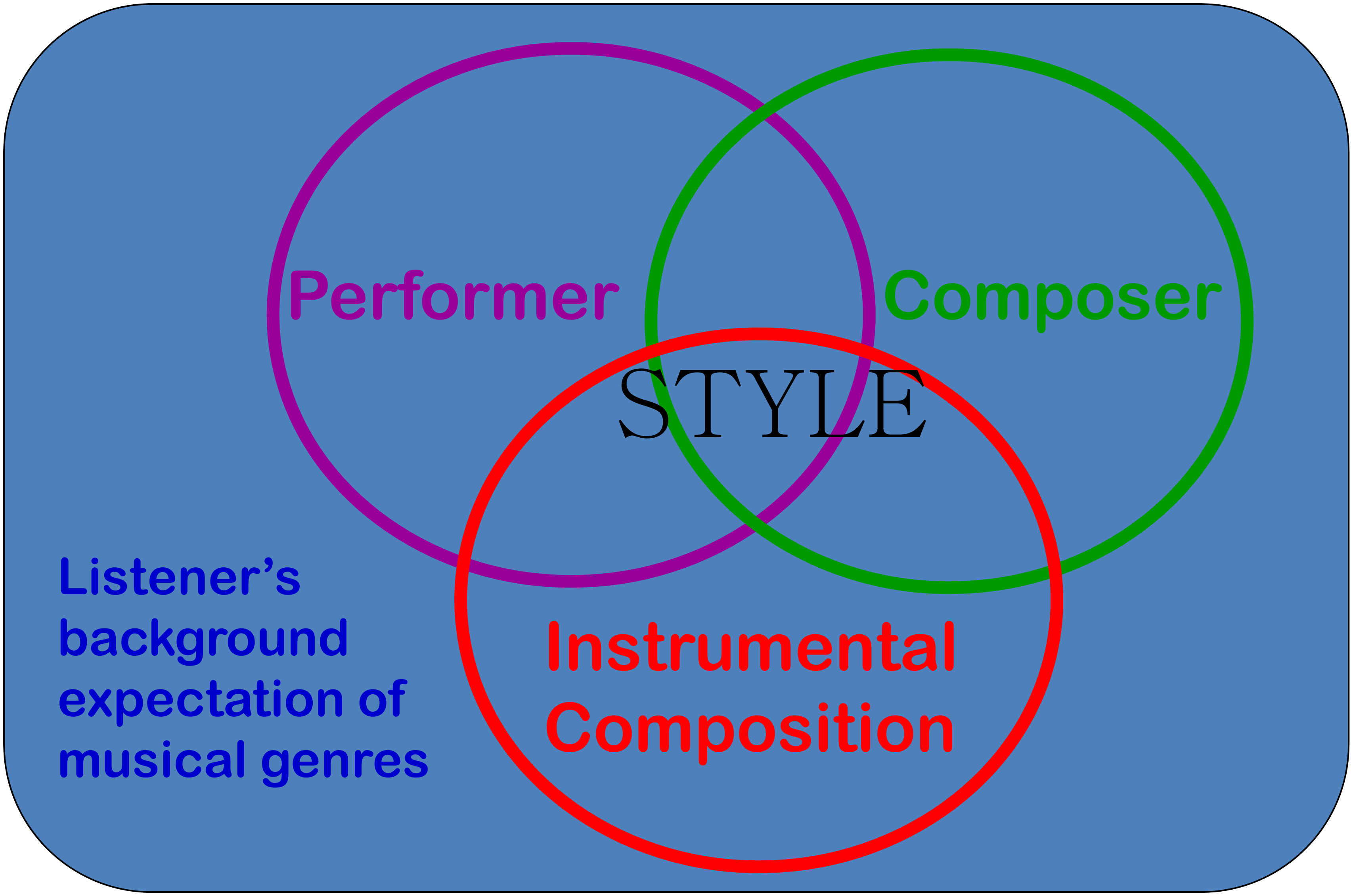
A Good Year (2006)

– R. Crowe, M. Cotillard, A. Finney

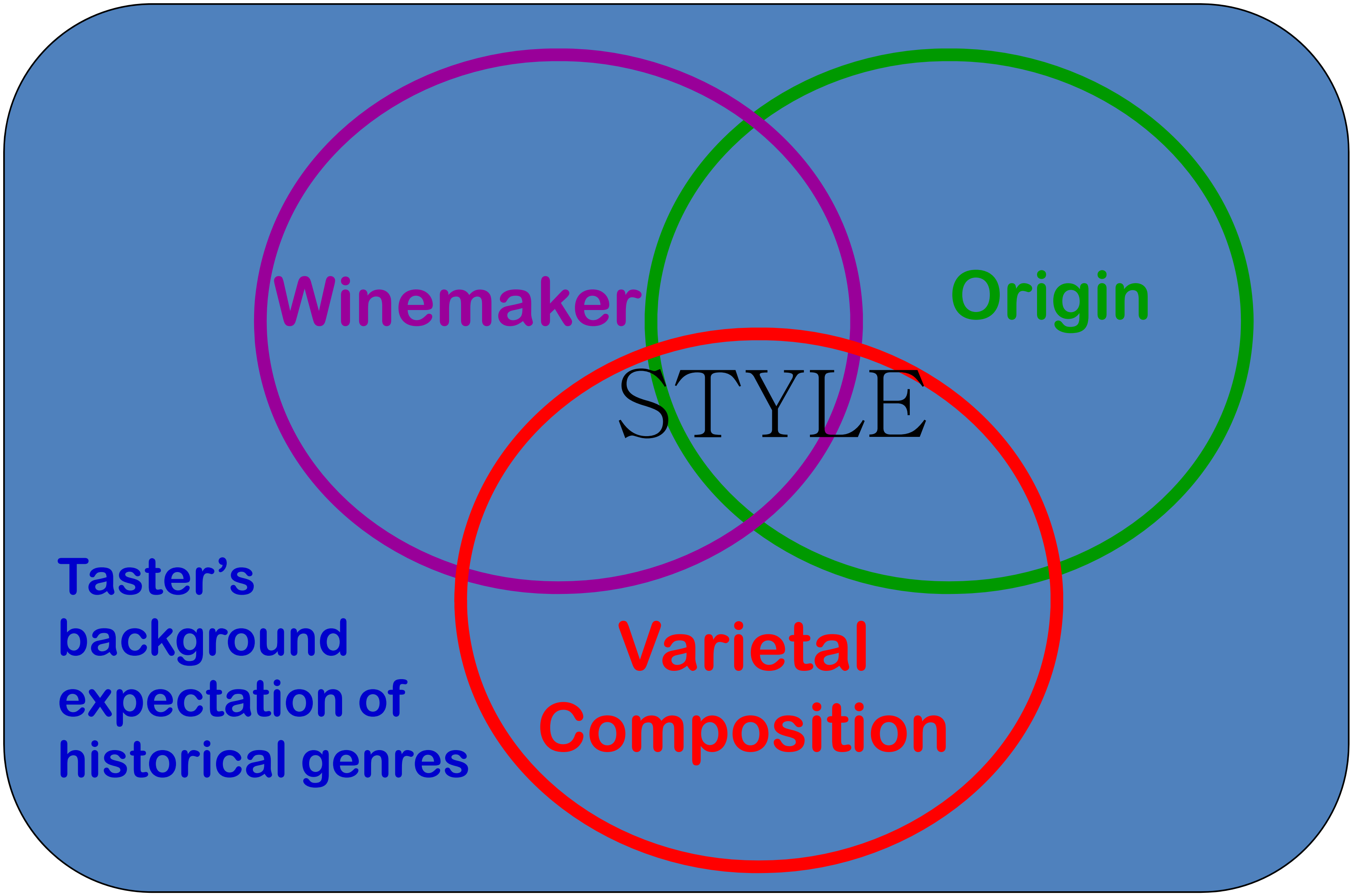
Bottleshock (2008)

– C. Pine, A. Rickman, B. Pullman

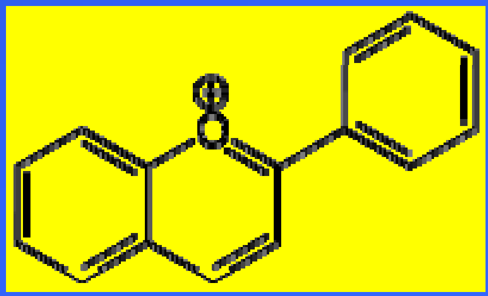
MUSICAL APPRECIATION



WINE APPRECIATION

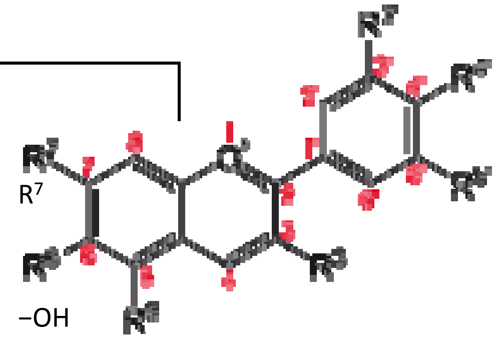


Flavylium Ion



Madrona Vineyards

Selected anthocyanidins and their substitutions



Anthocyanidin	$R^{3'}$	$R^{4'}$	$R^{5'}$	R^3	R^5	R^6	R^7
Aurantinidin	−H	−OH	−H	−OH	−OH	−OH	−OH
Cyanidin	−OH	−OH	−H	−OH	−OH	−H	−OH
Delphinidin	−OH	−OH	−OH	−OH	−OH	−H	−OH
Europinidin	$-OCH_3$	−OH	−OH	−OH	$-OCH_3$	−H	−OH
Luteolinidin	−OH	−OH	−H	−H	−OH	−H	−OH
Pelargonidin	−H	−OH	−H	−OH	−OH	−H	−OH
Malvidin	$-OCH_3$	−OH	$-OCH_3$	−OH	−OH	−H	−OH
Peonidin	$-OCH_3$	−OH	−H	−OH	−OH	−H	−OH
Petunidin	−OH	−OH	$-OCH_3$	−OH	−OH	−H	−OH
Rosinidin	$-OCH_3$	−OH	−H	−OH	−OH	−H	$-OCH_3$