Questions

- Where in the grape berry do most of the important phenolic compounds in wine come from?
- How are skin tannins different from seed tannins
- Why are Pinot noir wines generally lighter in color than other red wines?

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Dr. Richard Smart Seminar

Improving Wine Quality in the Vineyard
Vine Vigor and Wine Quality

Jessica M. Cortell, Ph.D
J. Cortell Consulting
Vitis Terra Vineyard Services
Northwest Viticulture Center, Instructor

North West Viticulture Center, Salem, OR
June 16, 2010

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Tamar Pilot Winery Research Group

Phil using the small lot press

Gail

Fiona

3

Tamar Pilot Winery Research Group

L to R Gail, (summer intern) Fiona (PhD student), Phil (summer intern), Bob Danbergs (Senior Research Wine Chemist), Angela Sparrow and Richard Smart

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Today

- Review of phenolic compounds in grapes
- Research on vine vigor and fruit and wine chemistry in Pinot noir
- Canopy management influences on Pinot noir aroma and flavor compounds

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Phenolic Compounds in Wine

Anthocyanins – Provide color properties to wine as anthocyanins and derived pigments

Flavan-3-ols - Contribute bitterness

Proanthocyanidins (tannins) - Provide astringency /mouth feel

Flavonols – Contribute to white wine color and co-pigmentation in red wines

All have associated health benefits

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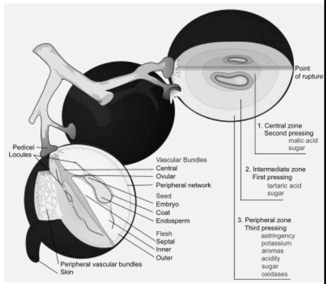
The Grape Berry
(after Coombe, 1987)
• Skin (anthocyanins, tannins, aroma and flavors)
• Pulp (water, sugars, organic acids, mineral salts, aroma and flavors)
• Seeds (tannins)
• Stems (tannin, aroma and flavors)



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Flavonoid (Phenols) Biosynthesis

- Accumulation of phenolic compounds is an integral part of berry ripening
- External stimuli such as microbial infections, ultraviolet radiation, and chemical stressors induce their synthesis.
- Phenolic compounds are plant-based materials, phytochemicals.
- Under conditions of low water and nutrient availability (especially nitrogen) plants can reduce growth and shift into producing more secondary plant metabolites.

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Phenolic Compounds

- Phenolic synthesis begins early during berry development; each group differs in berry location, in changes during ripening, and potential impact on wine quality
- Each variety has its own unique set of compounds and pattern of accumulation

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Phenolic Compounds Flavonoids

- Flavonoids comprise about 85% of the total phenols in winegrapes; flavonoid content is moderate to high in the skins, low in the juice, and high in the seeds.
- Aside from seed phenolics, both red and white grapes contain most of their phenolics in the skin.
- Primary source of grape phenolics in most wines come from skins.

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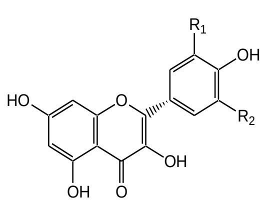
Flavonols



Flavonol	R_1	R_2
kaempferol	H	H
quercetin	OH	H
myricetin	OH	OH

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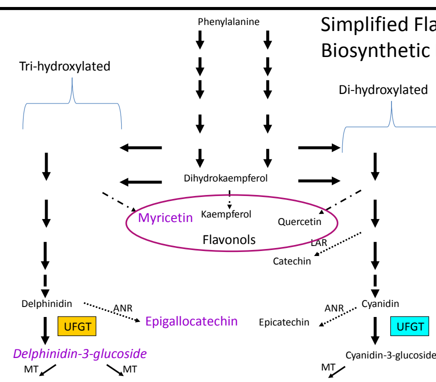
Simplified Flavonoid Biosynthetic Pathway



Cortell & Kennedy, J. Agric Food Chem, 54, 8510-8520

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Phenolic Compounds
Flavonols

- Found only in skin tissue.
- The predominant flavonol in *V. vinifera* is kaempferol while in *V. labrusca*, quercetin appears to predominate.
- Glyconsidically linked to glucose, rhamnose or glucuronic acid.
- Responds to sunlight exposure in the vineyard, plays a UV screening protective role.
- Contributes to color in white wines, plays a role in copigmentation in red wines.

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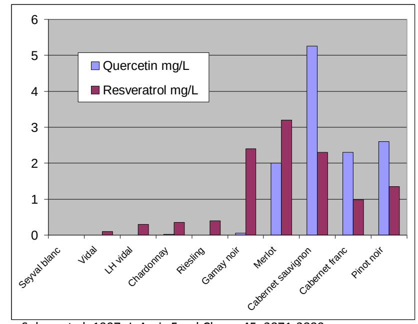
Wine varietal differences in quercetin and resveratrol (mg/L)



Soleas et al. 1997, J. Agric Food Chem. 45, 3871-3880

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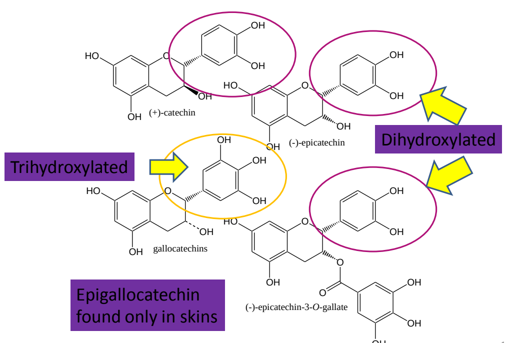
Flavan-3-ols



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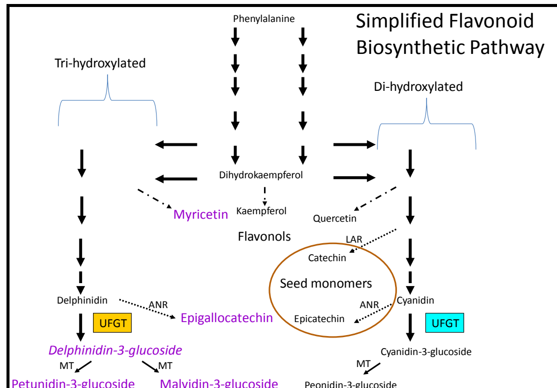
Simplified Flavonoid Biosynthetic Pathway



Cortell & Kennedy, J. Agric Food Chem, 54, 8510-8520

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Phenolic Compounds
Flavan-3-ol

- Present in seeds, skins and stems.
- Building blocks for tannins (flavonoid polymers).
- Seed flavan-3-ol monomer accumulation was shown to have a rapid increase 1-2 weeks after veraison followed by a decline leading to harvest.
- (-)-epicatechin and catechin account for the major proportion of monomers.

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Phenolic Compounds
Flavan-3-ols

- Difference between varieties exist
  - P. noir – (70% C & 30% EC); Shiraz (30% C and 70% EC); C. Sauvignon (50% C & 50% EC).
- Low MW, tend to be bitter in water solutions.
- Epicatechin was found to be 2X more bitter than catechin.

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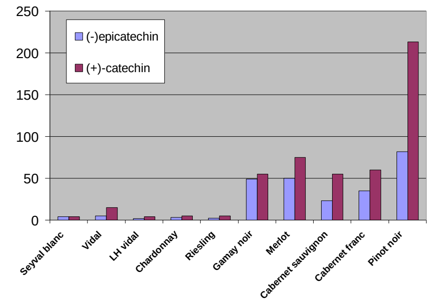
Wine varietal differences in flavan-3-ols (+)-catechin and (-)-epicatechin (mg/L)



Soleas et al. 1997, J. Agric Food Chem. 45, 3871-3880

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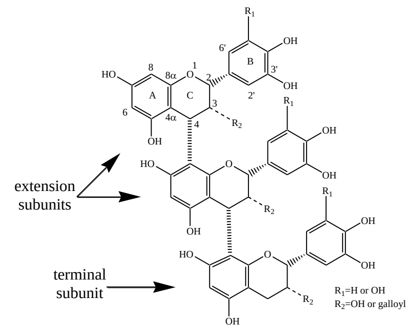
Proanthocyanidins (tannins)



Structure by Jim Kennedy

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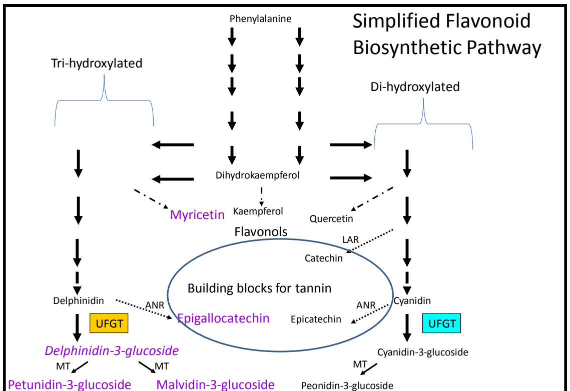

Cortell & Kennedy, J. Agric Food Chem, 54, 8510-8520

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Phenolic Compounds Tannins

- Tannins are found in the skins, seeds and stems
- All are astringent and bitter and MW. ranges from 1,000-4,000 corresponding to polymers of 3-40+ monomer units.
- In solution tannins can interact with protein to form precipitates.
- Astringency is a tactile (touch) sensation resulting from the interaction and precipitation of proteins in the saliva with tannins.

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Phenolic Compounds Skin Tannins

- Skin tannins increase to a maximum early in berry development and then tend to decrease in concentration.
- As skin tannins decrease in concentration they increase in size (mean degree of polymerization) in the later stages of ripening.
- PN skin tannins were found to have a mDP of 27-42 units.

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Phenolic Compounds Skin Tannins

- Skin tannins contain 33% epigallocatechin which is not found in seeds.
- Skin tannins are also associated with cell wall material such as pectin and anthocyanins and they become more easily extractable at the later stages of ripening.
- Skin tannin modified with pectin may moderate astringency.

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Phenolic Compounds
Seed Tannins

- Seed tannins increase to a maximum concentration up to veraison and then tend to decrease moderately.
- Seed tannins decrease in both solubility and extractability which leads to lower bitterness and astringency and a reduction in tannins
- Seeds have mDP of 5-9 subunits in Pinot noir
- Seed tannin contain high levels of epicatechin-gallate compared to skin tannins.

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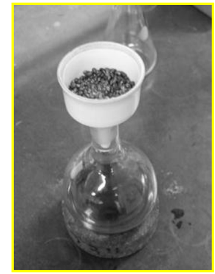
Phenolic Compounds
Seed Tannins

- Reduction in seed tannins appears to be due to oxidation as the tannins become fixed to the seed coat which parallels the color change from green to brown seeds.



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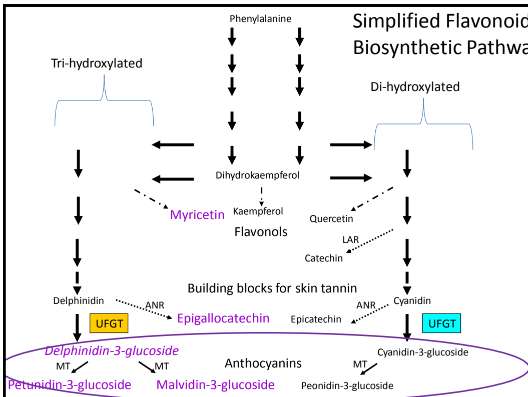
Simplified Flavonoid Biosynthetic Pathway



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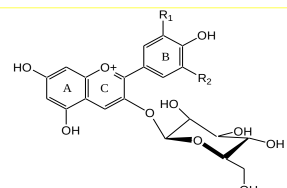
Pinot noir Anthocyanins



Anthocyanidin	R_1	R_2
cyanidin	OH	H
peonidin	OCH_3	H
delphinidin	OH	OH
petunidin	OCH_3	OH
malvidin	OCH_3	OCH_3

Pinot noir: glucosides of delphinidin, cyanidin, petunidin, peonidin and malvidin
Other varieties can have up to 20 different anthocyanins
Anthocyanin profile can affect color and color stability of wines

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Phenolic Compounds
Anthocyanins

- Begin accumulating in grape skins at veraison
- Continue to accumulate up until about 24 Brix.
- All genes leading to the production of anythocyanins are expressed as early as 10 weeks post flowering except for UFGT which is specific to anythocyanins.
- Regulation of UFGT is under different controls than the other genes in the pathway.

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Phenolic Compounds
Anthocyanins

- At veraison synthesis and accumulation begins in the skin epidermal layers and are contained in vacuoles within the skin cells.
- Anthocyanin synthesis generally reaches a maximum on a per berrry basis with maximum sugar accumulation and then the concentration tends to decline slightly.
- Synthesis is stimulated by light and good sun exposure of the clusters in the canopy; very high temperatures can degrade them (<90°F).

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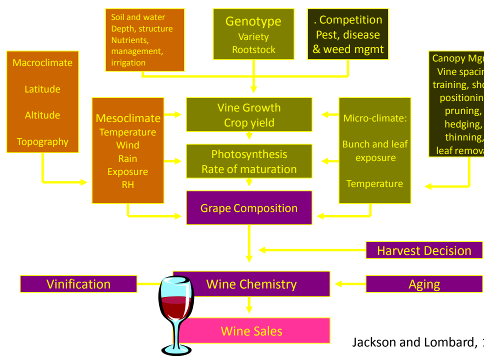
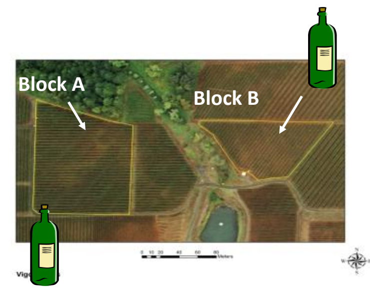
Vineyard / Winery Management System



Jackson and Lombard, 1993

Pinot Noir Phenolic Potential?

$75/bottle



$38/bottle

Map by Mike Halbleib

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Research Objectives

To investigate the influence of vineyard site environment and vine vigor on yield components, fruit chemical analyses, and wine chemical analyses

To determine the extent of variation in phenolic compounds in fruit

To explore relevant environmental factors in the system

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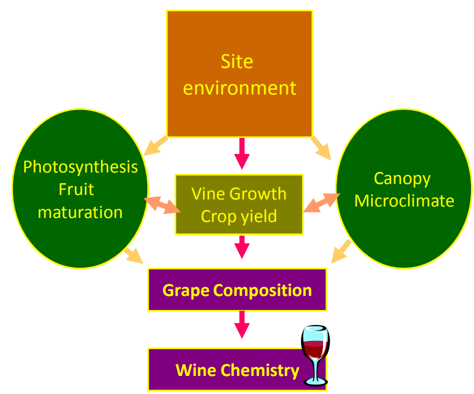

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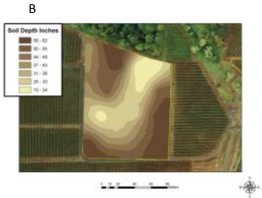
Soil Maps

A. Digital image of Block 6
B. Soil depth (inches)
C. Calculated water holding capacity (inches) – Andy Gallagher, Red Hills Soils, maps by Mike Halbleib

A

B



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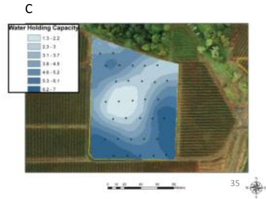

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Vine Vigor

- Vine vigor is NOT the same as VINE SIZE!!
- Vine vigor reflects a vine out of balance in one direction or another:
  - High vine vigor – too much vegetation relative to fruit production
  - Low vigor – Not enough vegetation relative to fruit load

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Vine Vigor

- Vine vigor is related to the amount of shoot and lateral growth
- Low vigor = minimal shoot growth and few laterals, small diamater shoots, small leaves and light green colored leaves
- High vigor = Excessive shoot and lateral growth, heavy shoots, large leaves and dark green leaves

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Influence of Low to Moderate Vigor on Phenolic Accumulation in the Vineyard

- High phenolics
  - High sun exposure
  - Lower levels N
  - Low soil moisture
  - Moderate canopy size
  - Moderate crop load
  - Low soil fertility
  - Small berry size

Jackson and Lombard, 1993

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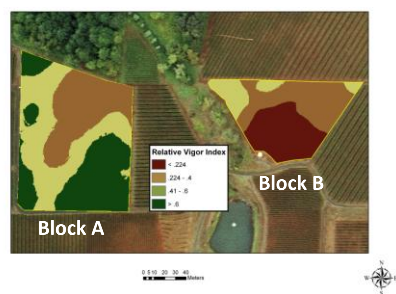
Influence of High Vigor on Phenolic Accumulation in the Vineyard

- Low phenolics
  - Shading
  - Higher leaf N
  - High soil moisture
  - Excessive vegetation
  - High crop load
  - High soil fertility
  - Large berry size

Jackson and Lombard, 1993

Vine Vigor Index



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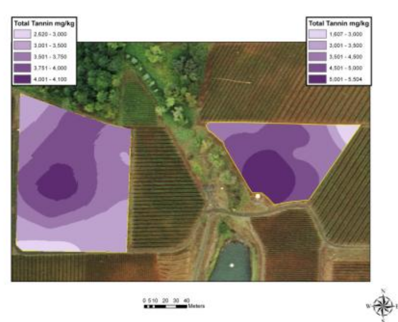
Vine Growth Parameters used in Delineating the Vigor Zone Wines

Block	Vigor zone	Shoot length (cm)	Trunk cross sectional area (cm^2)	Leaf chlorophyll (SPAD units)	Relative vigor index
A	High	122 a	8.6 a	45.4 a	.82 a
A	Med	108 b	8.9 a	41.6 b	.64 b
A	Low	99 c	7.3 b	40.1 b	.44 cd
B	High	108 b	7.2 b	40.3 b	.49 c
B	Med	91 c	7.2 b	38.6 c	.35 d
B	Low	73 d	5.0 c	34.2 d	.09 e
ANOVA	*p*-value	<0.0001	<0.0001	<0.0001	<0.0001

Values sharing the same letter within each column are not significantly different at α ≥ 0.05.

Total Fruit Tannin



Cortell et al. 2005, J. Ag. Food Chem. 53, 5798-5808

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Tannin in Seeds

Block	Vigor zone	# seeds per berry	Tannin (nmol/seed)
6	High	1.31^{a}	7939^{a}
6	Med	1.37^{ab}	7785^{a}
6	Low	1.56^{a}	7666^{ab}
19	High	1.45^{abc}	6489^{b}
19	Med	1.50^{ab}	7653^{ab}
19	Low	1.59^{a}	7082^{ab}

Values sharing the same letter within each column are not significantly different at $\alpha \geq 0.05$

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Skin Tannin (mg/berry)

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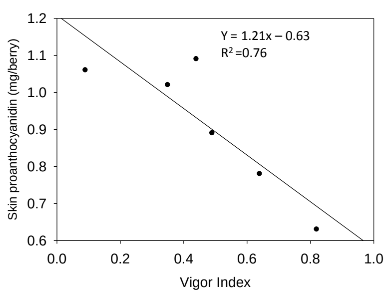
Relationship between the Vigor Index and Skin Tannin



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Fruit Summary – Reduction in Vine Vigor

- ↓ Flavan-3-ol monomers
- ↑ (+)-catechin relative to (-)-epicatechin
- ▬ Seed tannin
- ↑ Skin tannin
- ↑ Anthocyanin mg/berry

Cortell et al. 2005, J. Ag. Food Chem. 53, 5798-5808

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Wine flavan-3-ol monomers

Block	Vigor zone	Total monomers (mg/L)	(+)-catechin (%)	(-)-epicatechin (%)
A	High	53.6 a	77.3 c	22.7 a
A	Med	50.5 ab	75.7 c	24.3 a
A	Low	46.1 b	77.6 c	22.4 a
B	High	38.9 c	83.9 b	16.1 b
B	Med	36.2 c	86.6 a	13.4 c
B	Low	35.6 c	88.0 a	12.0 c
	p-value	<0.0001	<0.0001	<0.0001

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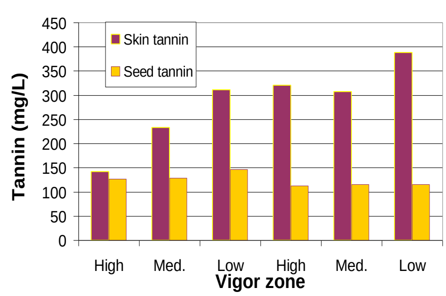
Extraction of Skin and Seed Tannin into Wine



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Wine Color Differences

Block A

High vigor | Med. vigor | Low vigor

Block B

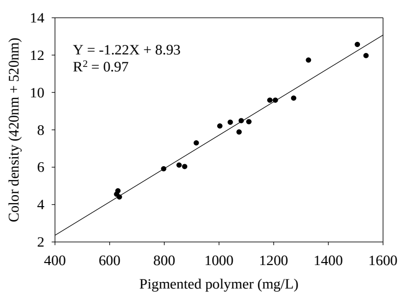
High vigor | Med. vigor | Low vigor

Wine Color

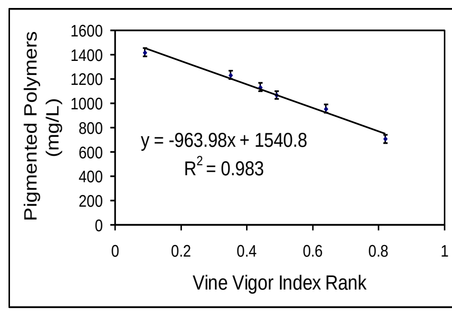
Block	Vigor zone	ACY (Mg/L)	Pigmented polymers (mg/L)	Sulfite resistant pigments (%)	Color density (520nm + 420nm)	Hue (420nm/ 520nm)
A	High	143.9 d	632 e	36.9 c	4.5 e	0.78 a
A	Med	199.7 a	844 d	37.7 c	6.0 d	0.77 a
A	Low	159.7 c	1090 b	41.6 b	8.2 c	0.68 b
B	High	204.8 a	989 c	33.3 d	8.0 c	0.67 bc
B	Med	162.3 c	1223 b	43.7 ab	9.6 b	0.64 cd
B	Low	177.6 b	1459 a	44.3 a	12.1 a	0.62 d
	p-value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

Values sharing the same letter within each column are not significantly different at α ≥0.05

Relationship between Pigmented Polymers and Wine Color Density



Relationship between Vine Vigor and Wine Pigmented Polymers



Wine Summary – Reduction in Vine Vigor

- ⬇ Flavan-3-ol monomers
- ▬ Seed tannin
- ⬆ Skin tannin
- ⬆ Pigmented polymers
- ⬆ Skin extraction

Cortell et al. 2005, J. Ag. Food Chem. 53, 5798-5808

Vineyard Exposure Experiment

- In low vigor zone of Block 6
- Two clusters on one shoot installed in box and two labeled outside
- All clusters treated the same
- Fruit harvested at véraison and harvest

Boxes Courtesy of Dr. Mark Downey

Model Extractions

10 reps of 300 g of berries

Run through roller

Used 300 ml 40% ethanol v/v with 100 ppm SO_2

Extracted on shaker table for 48 hours at 38°C

Pressed, weighed and analyzed

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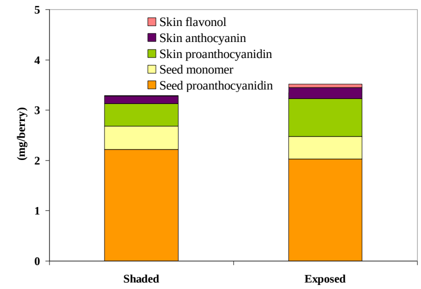
Total Accumulation of Phenolics in Shaded and Exposed Fruit at Harvest



Cortell & Kennedy, Journal of Agric. Food Chem., 2006

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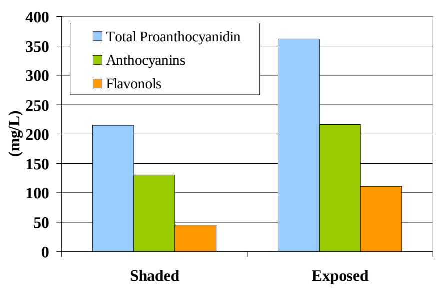
Model Extraction Phenolic Profile



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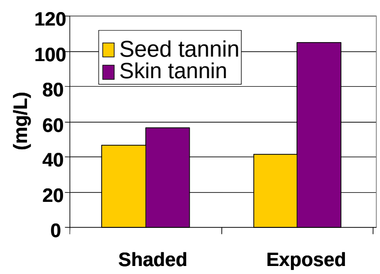
Extraction of Skin and Seed Tannin



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Summary-Exposed Fruit

- ↓ Flavan-3-ol monomers
- ▬ Seed tannin
- ↑ Skin tannin
- ↑ Pigmented polymers
- ↑ Skin extraction

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Summary-Exposed Fruit

- ↑ Flavonols
- ▬ Anthocyanins (fruit)
- ↑ Anthocyanins (model extract)

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Conclusions

- Vine vigor did not have an impact on seed tannin in fruit or wine
- Vine vigor differences influenced the accumulation of skin tannin, flavonols and anthocyanins
- Skin tannin and the percent skin tannin extraction were higher in low vigor zone wines
- Pigmented polymers were higher in wines made from low vigor zones

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Development of Aroma and Flavor

- Several hundred different chemicals are involved with grape aroma and flavor including hydrocarbons, alcohols, esters, aldehydes, ketones, and other compounds often present at small concentrations of ppm and ppt.

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Development of Aroma and Flavor

- Nearly all compounds identified are present in most varieties even those that do not have specific distinctive varietal aromas.
- For certain varieties the characteristic aromas result from a limited number of specific compounds.

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Pinot noir Aroma and Flavor Compounds

- Very complex involving a large number of compounds.
- Different proportions of these compounds give rise to different perceived odors.
- Concentration of these aroma compounds and their balance in the wine matrix will affect the quality of Pinot noir wines.
- Differences could be related to clones, growing conditions, climate, etc.

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Pinot noir Aroma and Flavor Compounds

Compound	Level found	Treshold	Aroma/flavor
Phenyl ethanol	24-37 mg/L	1 mg/L	Rosy & honey
Guaiacol	70 -200 mg/L	20 ppb	Smoky, spicy, medicinal
Eugenol & 4-ethyl guaiacol		ug/L	Smoky, spicy (fault at high levels)
linalool		ug/L	Floral, cherry aroma
geraniol		ug/L	Floral, cherry aroma
nerol		ug/L	Floral, cherry aroma
citronellol		ug/L	Floral, cherry aroma
Β-damascanone	5-10 ug/L	0.002 ug/L	Exotic fruit, apple, rose, honey
Β-ionone	0.2 – 0.6 ug/L	0.007 ug/L	Berry and violet aroma
Λ - nonalactone	10-18 ug/L	N/A	Cocconut, peach

J. Agric. Food Chem. 2006, 54, 8567-8573

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More Pinot noir Aroma and Flavor compounds

- 3-methylbutyl acetate — Banana
- ethyl hexanoate — Sweet Fruity
- ethyl 3-(methylthio)propanoate — Vegetable
- ethyl octanoate — Green fruity floral
- whisky lactone — Green floral
- ethyl dihydrocinnamate — Fruity
- methyl and ethyl vanillate — Green tea
- ethyl cinnamate — Fruity, Cinnamon

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Changes in Pinot noir Aroma Compounds in Wine from Different Grape Maturities

- For most short-chain fatty acid esters, there were no obvious trends with grape maturity, however, the concentrations of ethyl 2-methylpropanoate and ethyl 3-methylbutanoate consistently decreased with grape maturity.
- The decreasing trend was also observed for other esters including ethyl cinnamate, ethyl dihydroxycinnamate, and ethyl anthranilate, with the exception of ethyl vanillate.

J. Agric. Food Chem. 2006, 54, 8567-8573

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Changes in Pinot noir Aroma Compounds in Wine from Different Grape Maturities

- The C13 norisoprenoids, monoterpenes, and guaiacols had increasing trends with grape maturation.
- These include norisprenoids - B – damascanone and B –ionone
- Monoterpenes – geraniol, linalool and nerol
- Guaiacol and eugenol

J. Agric. Food Chem. 2006, 54, 8567-8573

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Changes in Pinot noir flavorants during ripening

Vegetation *Plant matter* → **Herbaceousness** *Straw, herb, vegetal, tobacco,* → **Unripe fruit** *Green apple, mint, green tea* →

→ **Red Fruit** Cherry, strawberry, raspberry, cranberry → **Black fruit** *Plum, blackberry, black cherry, floral, black tea* → **Jam** *Prune, date, raisin*

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Vigor Management

Input → Process → Output

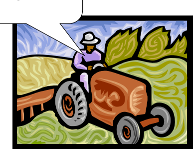
High vigor — Harvest — Wine Quality

Vineyard adjustments

What can I do in the vineyard to reduce the vine vigor……

The Team!

This wine has poor color, harsh tannins, not what I am looking for…



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Applications

- Manage vineyard zones differently
- Harvest vineyard zones separately
- Use zones to target fruit for premium wines

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Don't Just Grow a Vine, Grow Wine!"

Thank-you!!

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