

Phenolics in Cider Apples



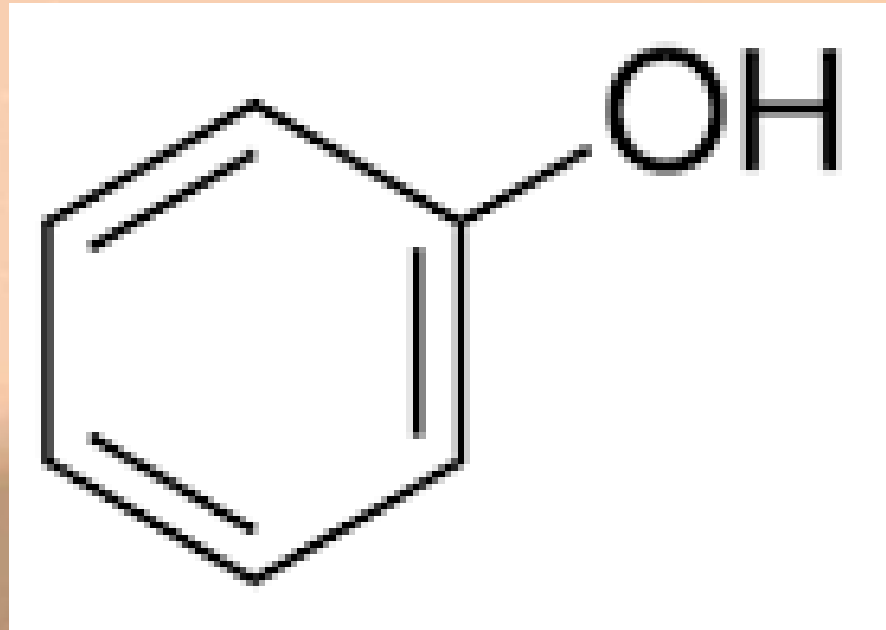
What do they mean for us?

*Presentation to Rocky Mountain
Cider Association*

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What is a phenolic?



The simple structure of phenol itself is not found free in plants. But [polyphenols](#) are widespread.

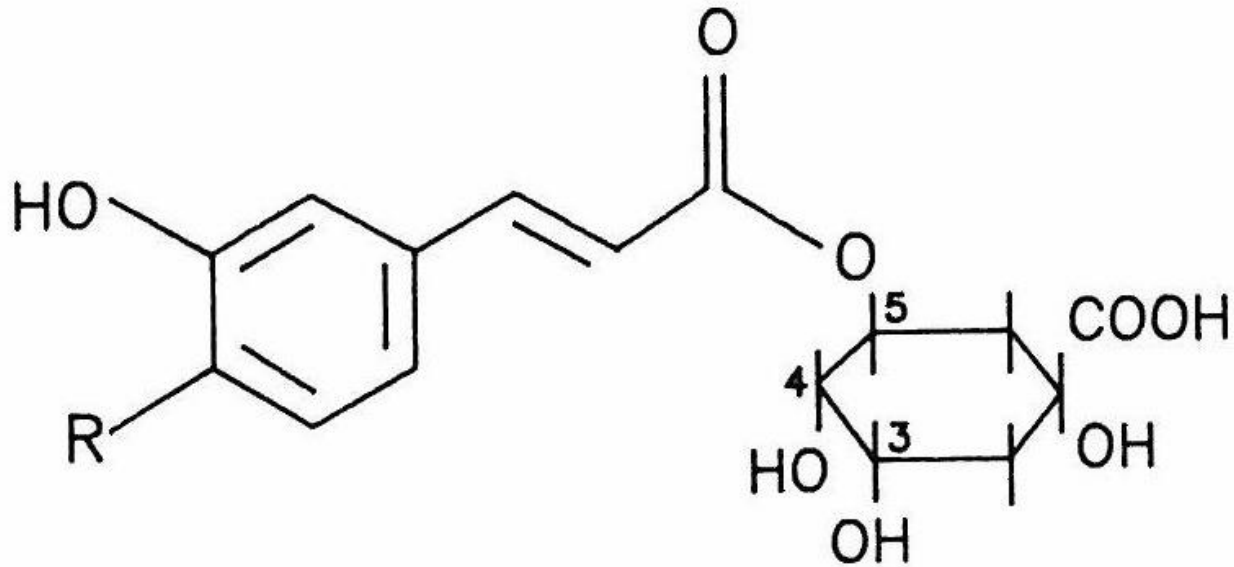
Major (poly)phenols in apples



- **Phenolic Acids**
- **Phloridzins**
- **Anthocyanins (mostly skin)**

- **Catechins**
- **Procyanidins (“tannins”)**

Phenolic Acids



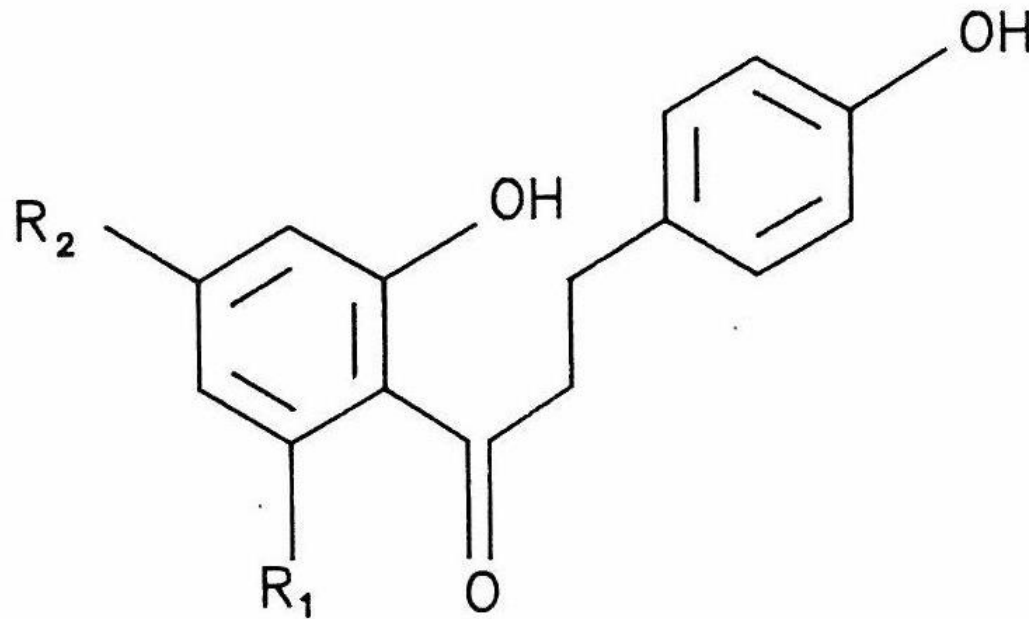
R = OH

Chlorogenic Acid

R = H

p-Coumaroyl quinic acid

Phloridzin



$R_1 = \text{Glucose}$

$R_2 = \text{OH}$

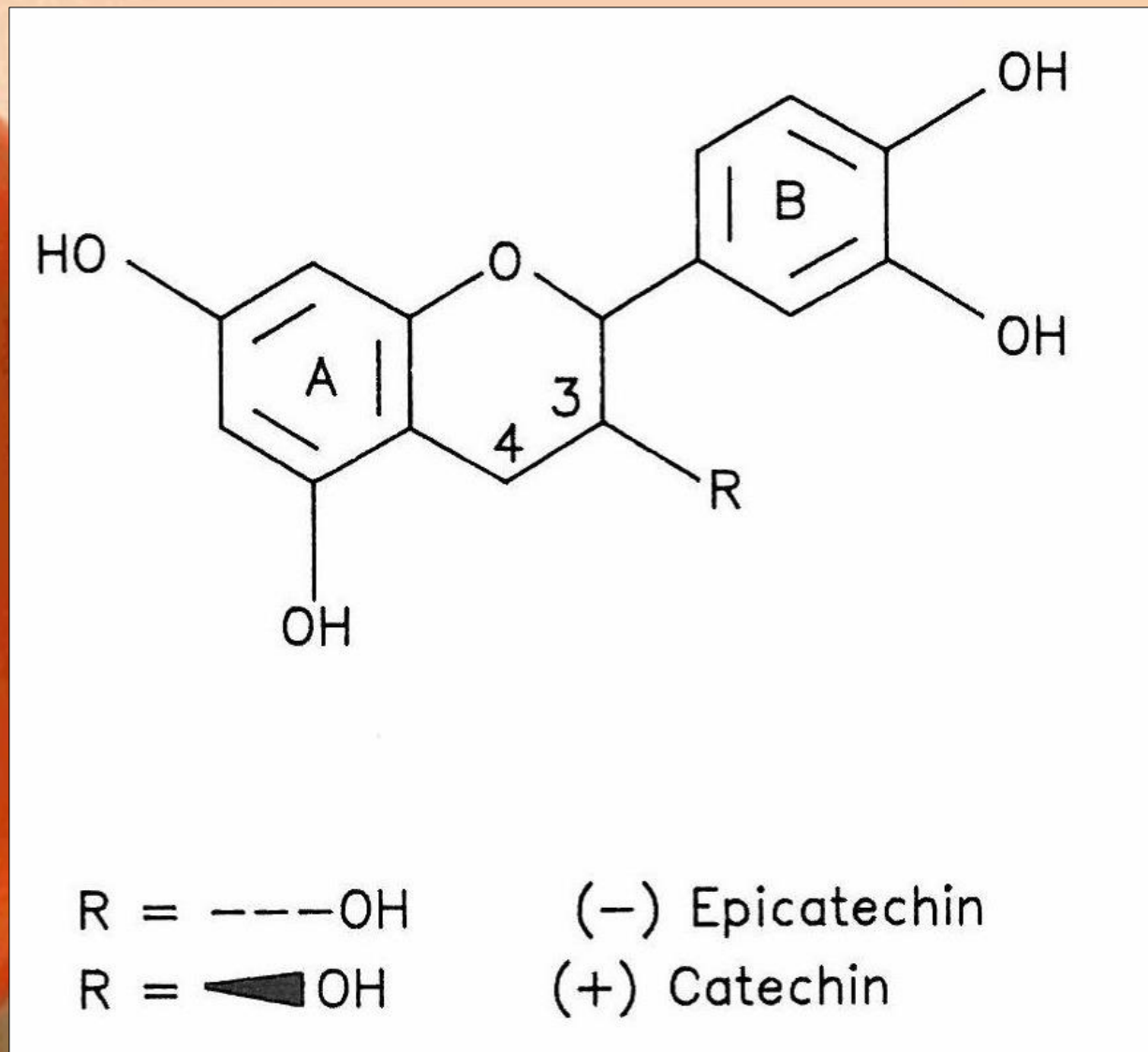
Phloridzin

$R_1 = \text{OH}$

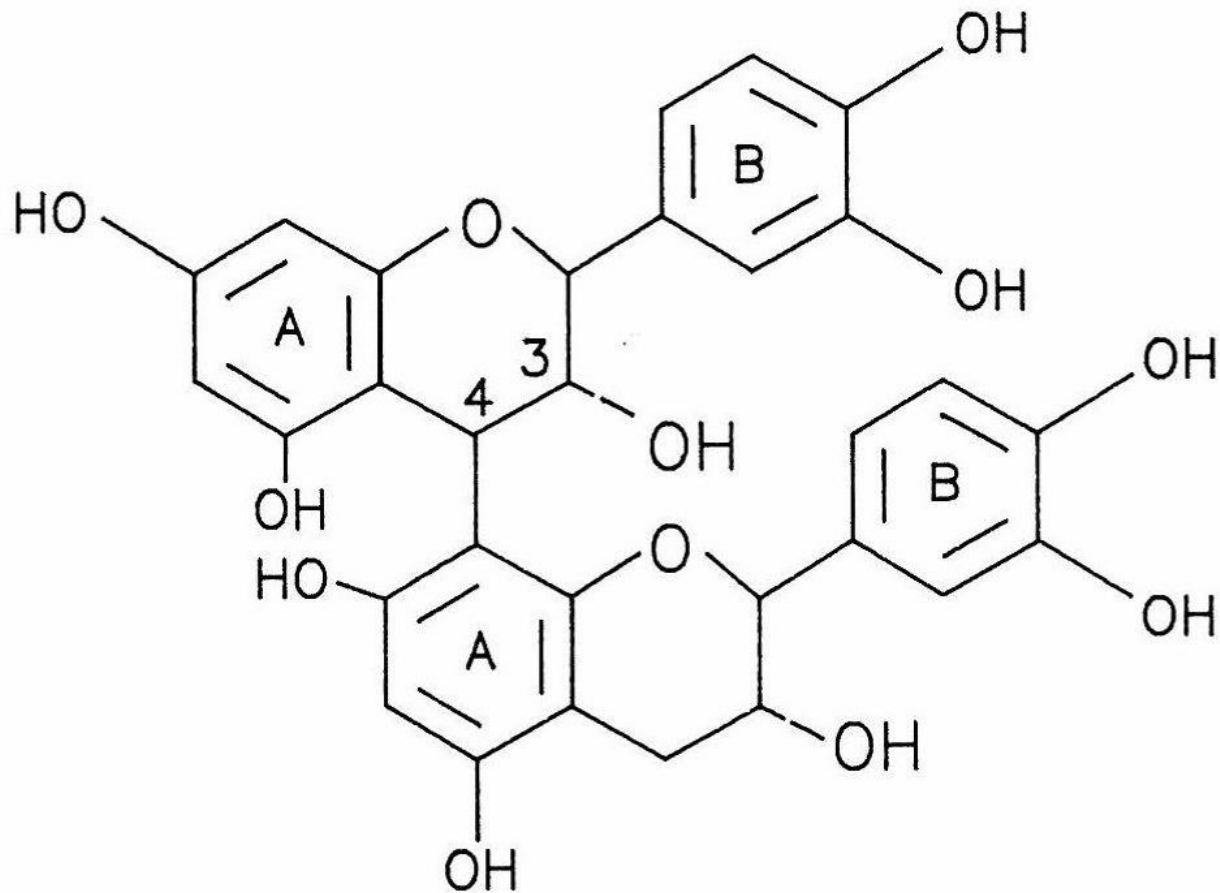
$R_2 = \text{Glucose}$

Sieboldin

Catechins

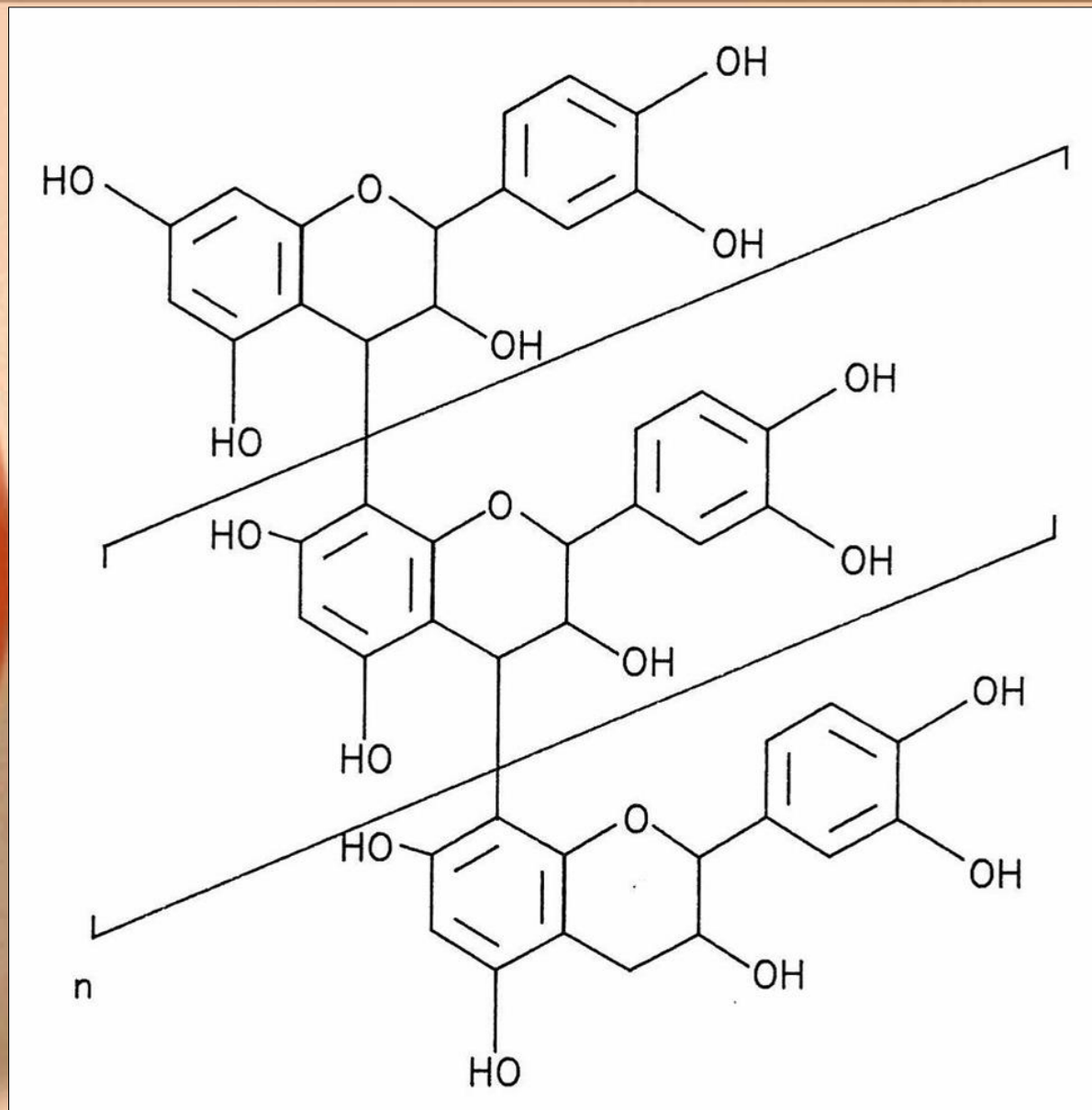
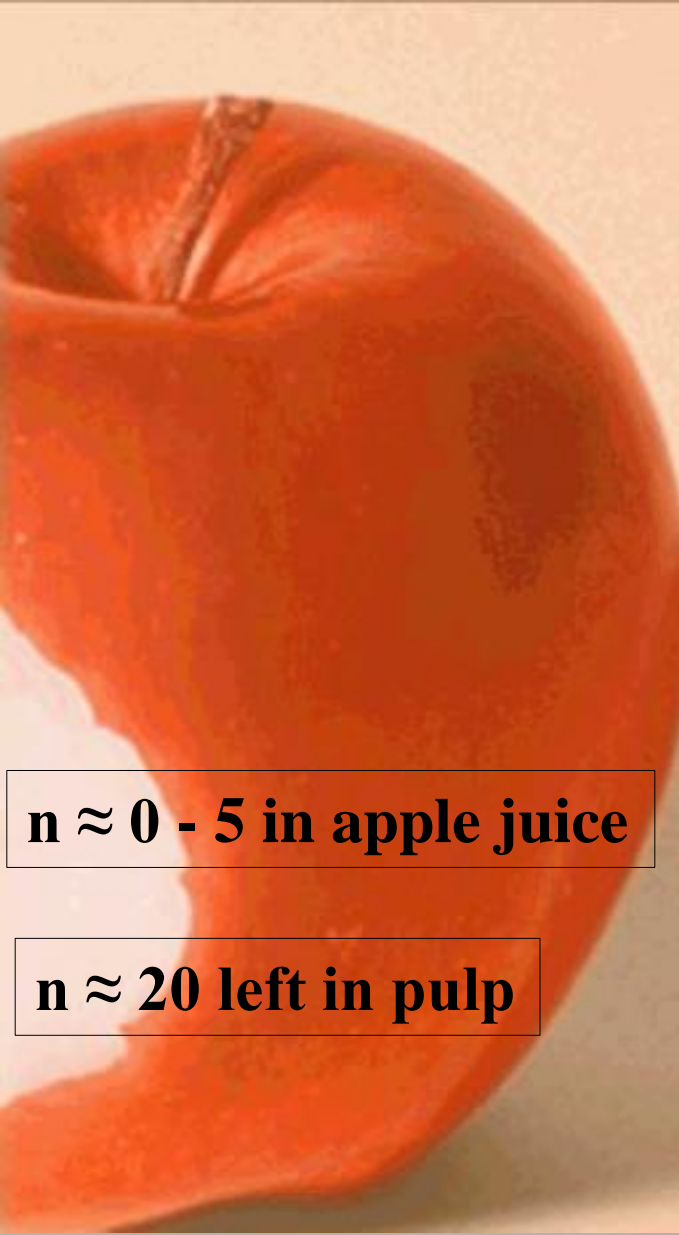


Procyanidins – a major dimer



Procyanidin B2

Procyanidin oligomers - tannins



$n \approx 0 - 5$ in apple juice

$n \approx 20$ left in pulp

Polyphenol roles



- **Mouthfeel**
- Volatile aroma precursors
- Colour formation

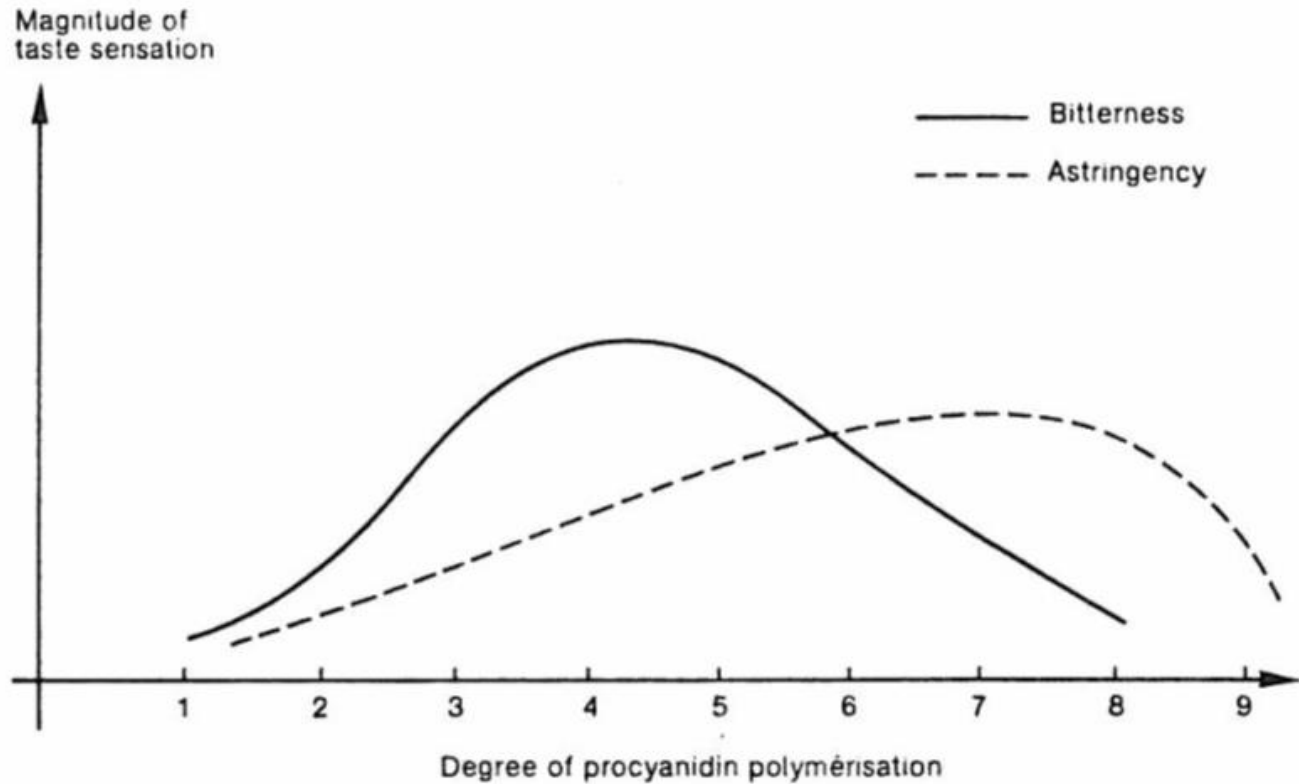
- Post bottling haze
- Antioxidant and pro-oxidant properties

Mouthfeel



- Non-specific mouthfeel from phenolic acids
- Bitterness and astringency from procyanidins
 - Bitterness – smaller oligomers
 - Astringency – larger oligomers

Bitterness and Astringency



Effect of Cultivar



Soft tannin vs hard tannin

Q. Why is Tremlett's more bitter (**hard**) than Dabinett (**soft**) for the same phenolic level?

A. Because it contains relatively more lower molecular weight procyanidins.

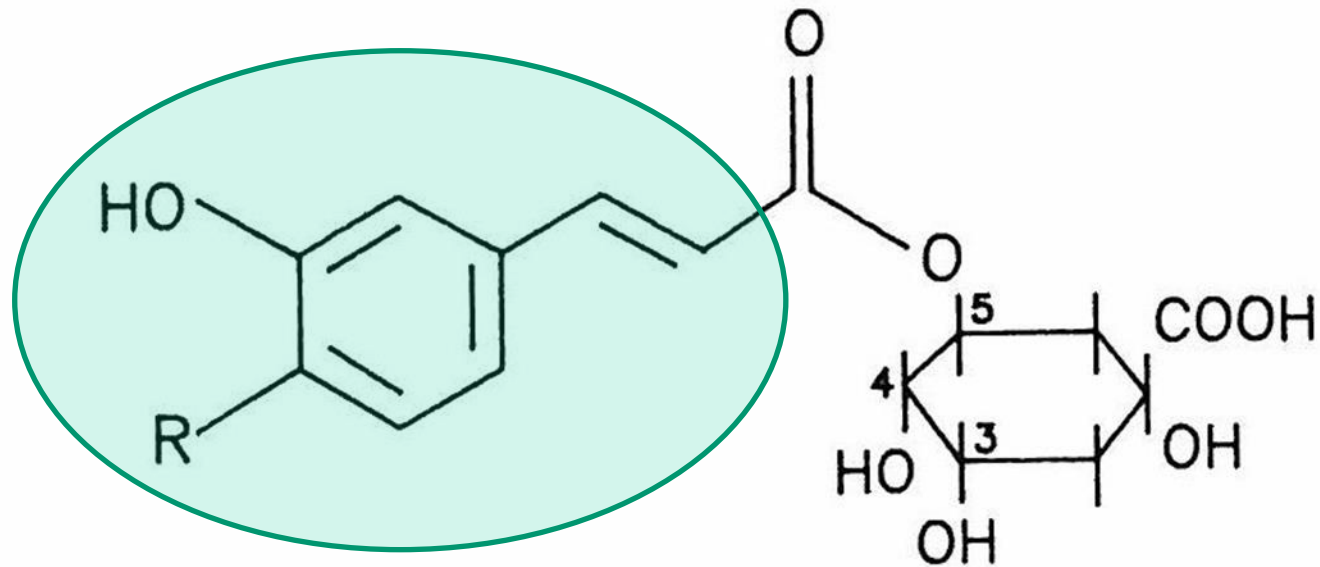
Polyphenol roles



- Mouthfeel
- **Volatile aroma precursors**
- Colour formation

- Post bottling haze
- Antioxidant and pro-oxidant properties

Breakdown of phenolic acids



R = OH

Chlorogenic Acid

R = H

p-Coumaroyl quinic acid

Formation of 'phenolic' aromas



- Action of *Lactobacilli* or *Brettanomyces* on phenolic acids
- Yields 'spicy', 'leathery', 'old horse' aromas
- Ethyl phenol, ethyl catechol ..
 - Prized in low amounts
 - Taints at high levels
 - Transition ~ 1 ppm
 - Conversion rate is very low

Polyphenol roles



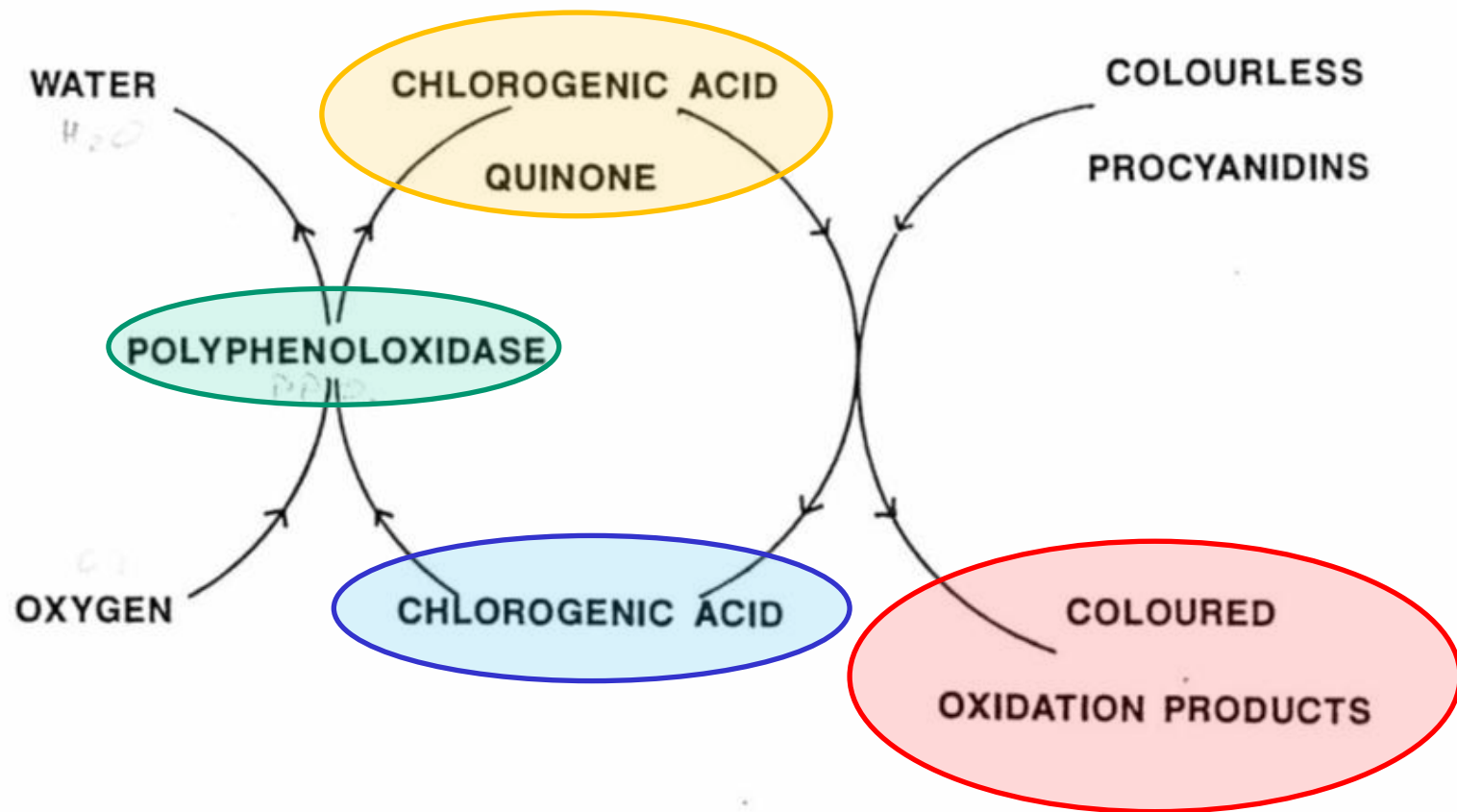
- Mouthfeel
- Volatile aroma precursors
- **Colour formation**
- Post bottling haze
- Antioxidant and pro-oxidant properties

Colour formation



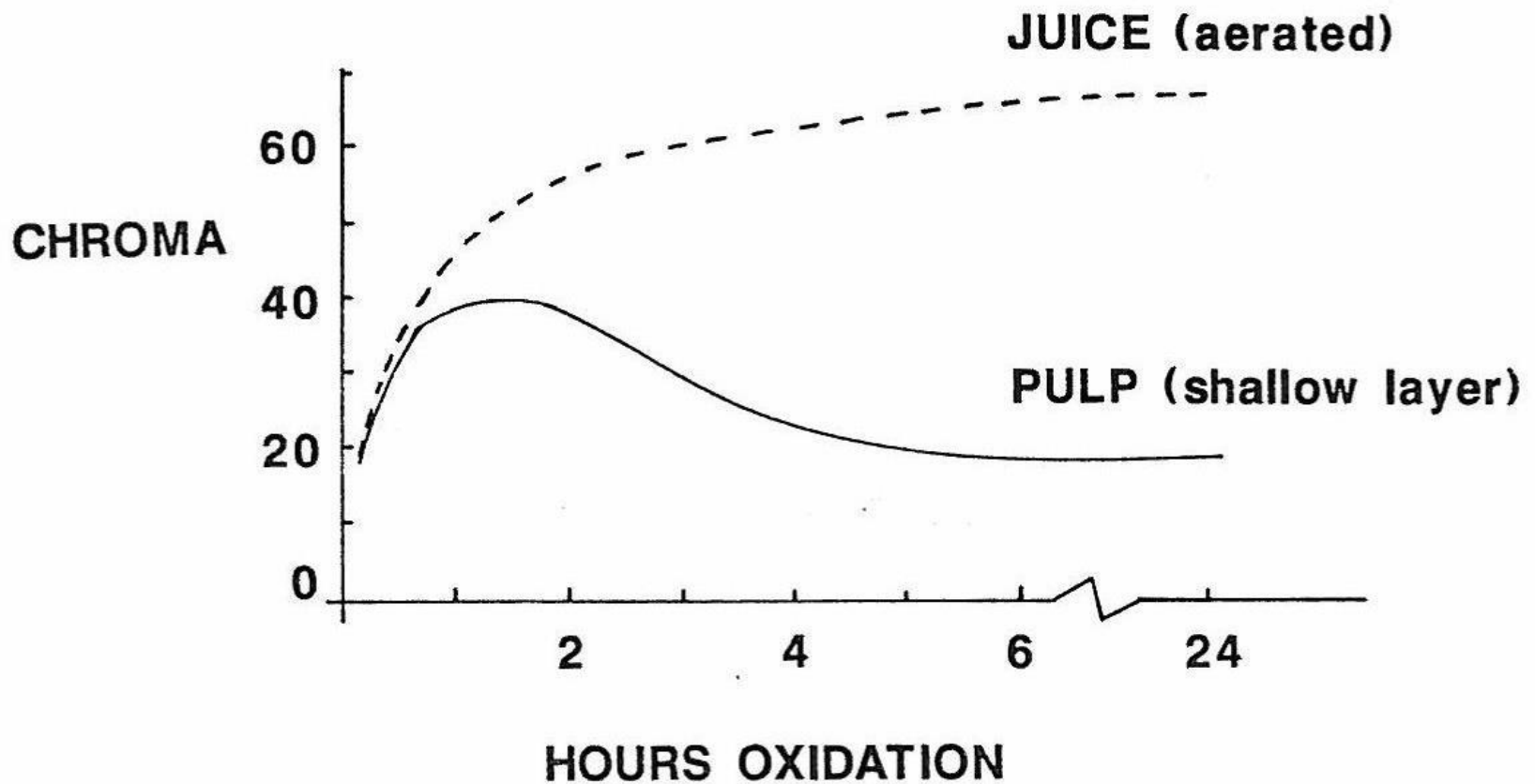
- Oxidation of phenols to form coloured ‘quinones’
- Mediated in pulp / juice system by polyphenol oxidase enzyme (PPO)
- Is more complicated than it might appear
 - ‘coupled oxidation’

Coupled oxidation in apples



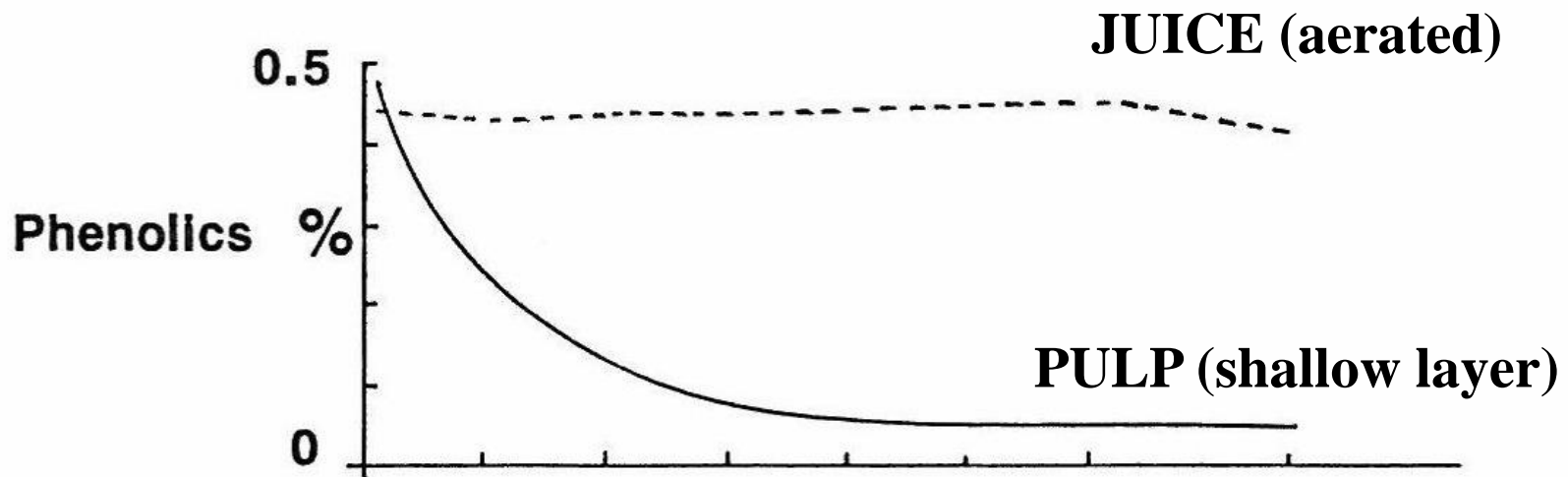
Colour changes

Measured in oxidised juice, and in juice made from oxidised pulp



Phenolic changes

Measured in oxidised juice, and in juice made from oxidised pulp



Pulp oxidation



- A place to gain or lose colour
- A place to lose phenolics (mostly ‘tannins’)
- Affected by apple cultivar (pH, PPO and phenolic levels)
- Colour changes are partly reversed by ‘reductive’ yeast activity during fermentation

Polyphenol roles



- Mouthfeel
- Volatile aroma precursors
- Colour formation
- **Post bottling haze**
- Antioxidant and pro-oxidant properties

Post bottling haze



- Polymerisation of procyanidins
 - amongst themselves
 - together with protein
 - with acetaldehyde
- Often manifests as chill haze which becomes permanent
- Can be prevented with finings or Polyclar

Polyphenol roles



- Mouthfeel
- Volatile aroma precursors
- Colour formation

- Post bottling haze
- **Anti-oxidant and pro-oxidant properties**

Phenolics are antioxidants



- But in some cases they can generate **hydrogen peroxide** as a by-product
- This can oxidise **ethanol** to **acetaldehyde**
- Cause of ‘sherry-like’ aromas in ciders affected by air
- Chemical, not microbial
- Inhibited by SO_2

Are antioxidants good for you?




- Most apple phenolics cannot cross into the plasma at physiologically relevant levels to act as antioxidants
- Any effect is more likely due to mediating the up- and down-regulation of gene synthesis in the body

How much is there?



- Difficult to measure all the components individually
- A fair assumption for apples
 - Non tannins 40 – 60 %
 - Tannins 60 – 40 %
- **Absolute** data is usually by Folin or Lowenthal methods as “total polyphenols” in juice

Finally some figures!

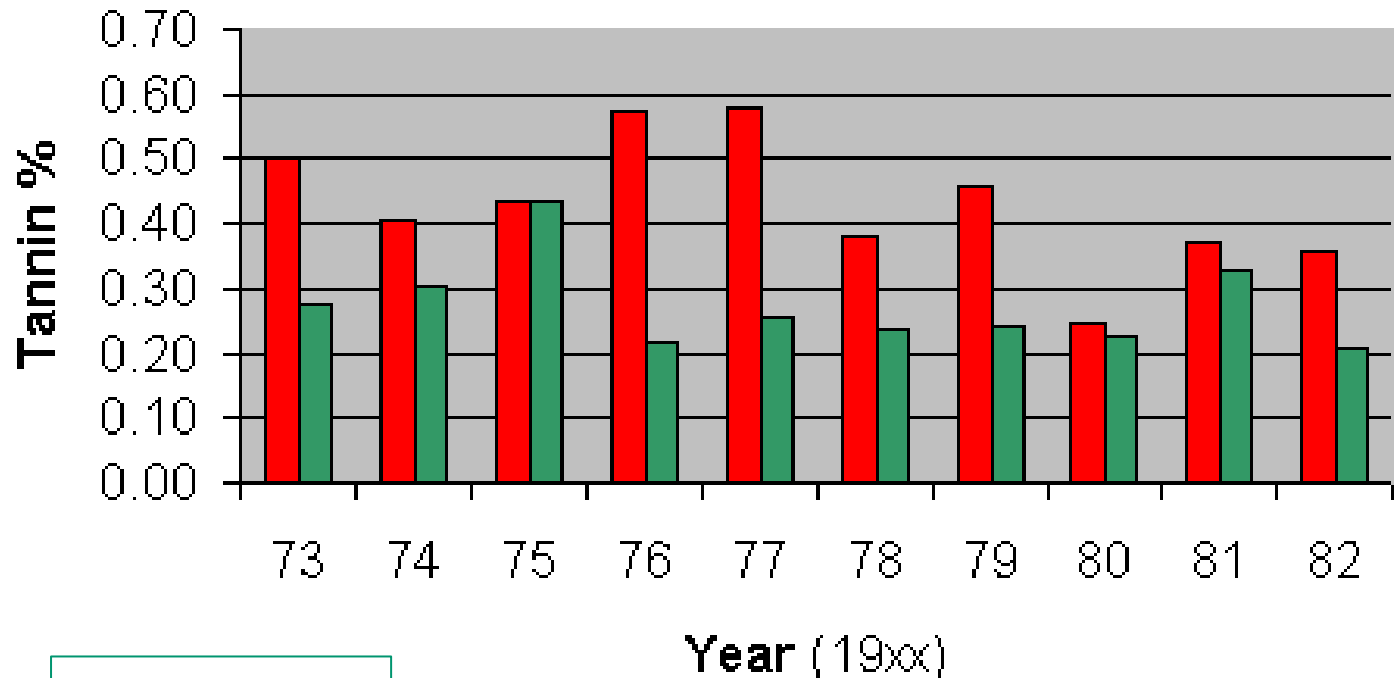
A sliced apple core is shown on the left side of the slide, partially cut and hollowed out, with a stem at the top. The apple is a reddish-orange color.

Cultivar	Polyphenol (mg/L)
Golden Delicious (VA)	240
Fuji (VA)	220
Idared (VA)	230
Granny Smith (VA)	360
Harrison (VA)	930
Golden Russet (NY)	900
Redfield (NY)	1500
Michelin (NY)	1100
Yarlington Mill (UK)	2200
Dabinett (NY)	2000

Seasonal Variation

Tannin Variation over Ten Years

(Exact same trees)



CV ca 25%

■ Tremletts ■ Dabinett