

# Phenolics in Cider Apples



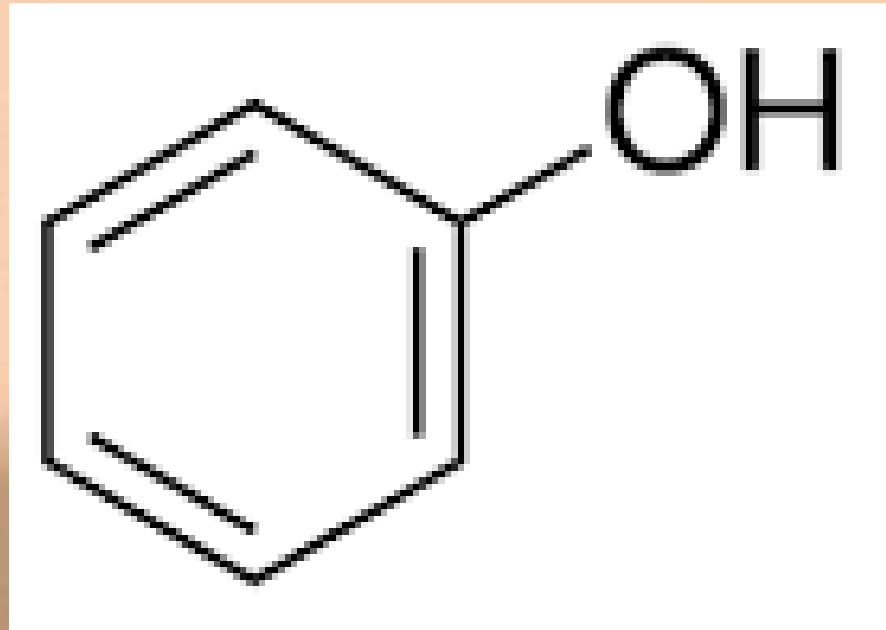
**What do they mean for us?**

*Presentation to Rocky Mountain  
Cider Association*

*April 2015*

**Andrew Lea**

# What is a phenolic?



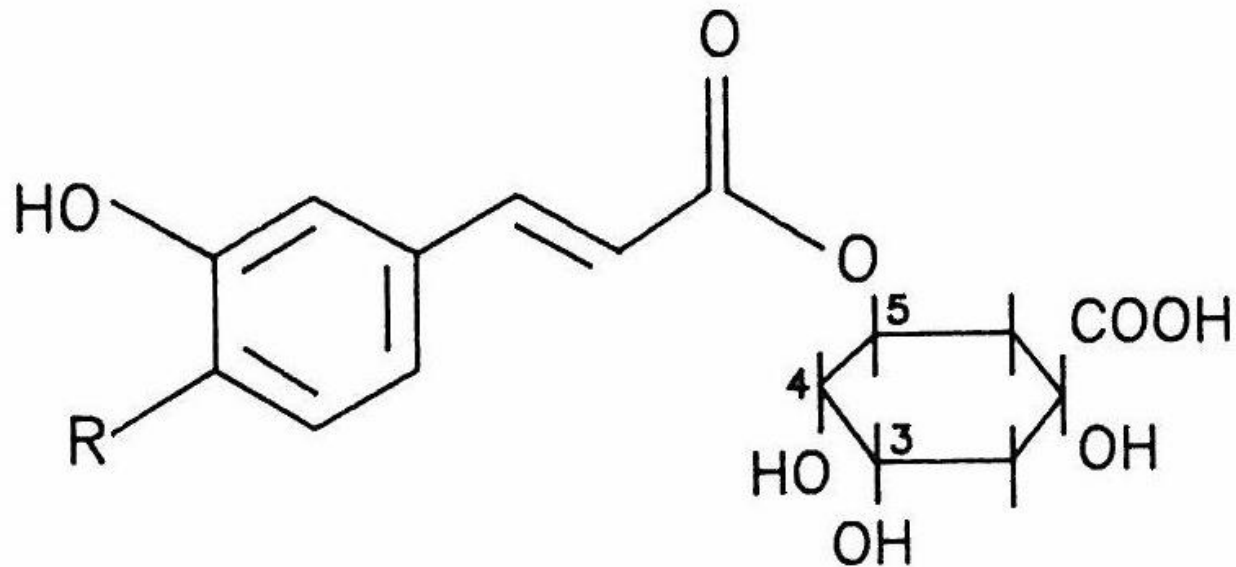
**The simple structure of phenol itself is not found free in plants. But [polyphenols](#) are widespread.**

# Major (poly)phenols in apples



- **Phenolic Acids**
- **Phloridzins**
- **Anthocyanins (mostly skin)**
  
- **Catechins**
- **Procyanidins (“tannins”)**

# Phenolic Acids



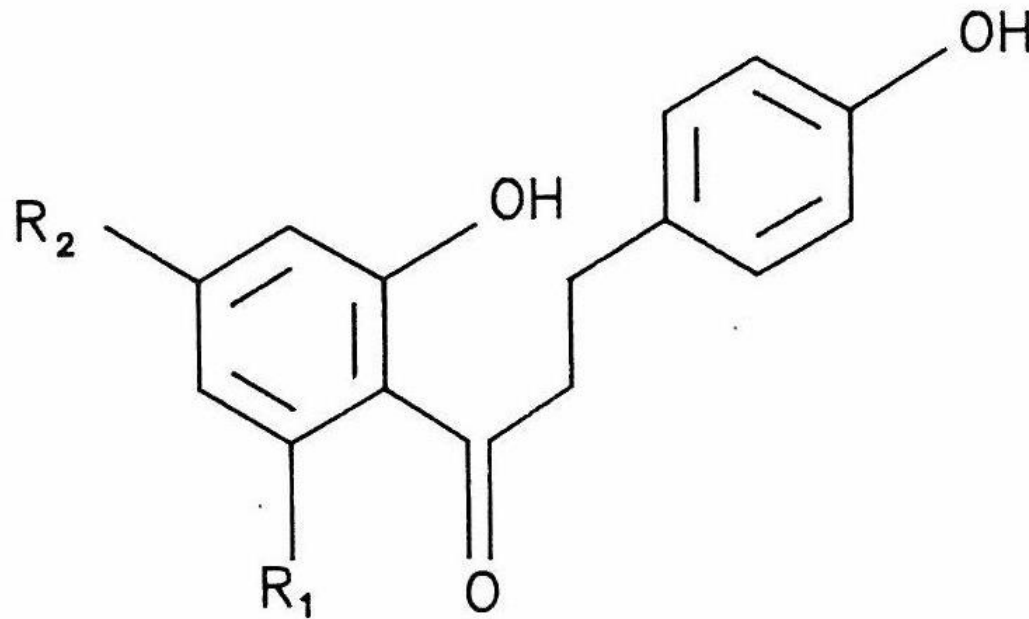
R = OH

Chlorogenic Acid

R = H

p-Coumaroyl quinic acid

# Phloridzin



$R_1 = \text{Glucose}$

$R_2 = \text{OH}$

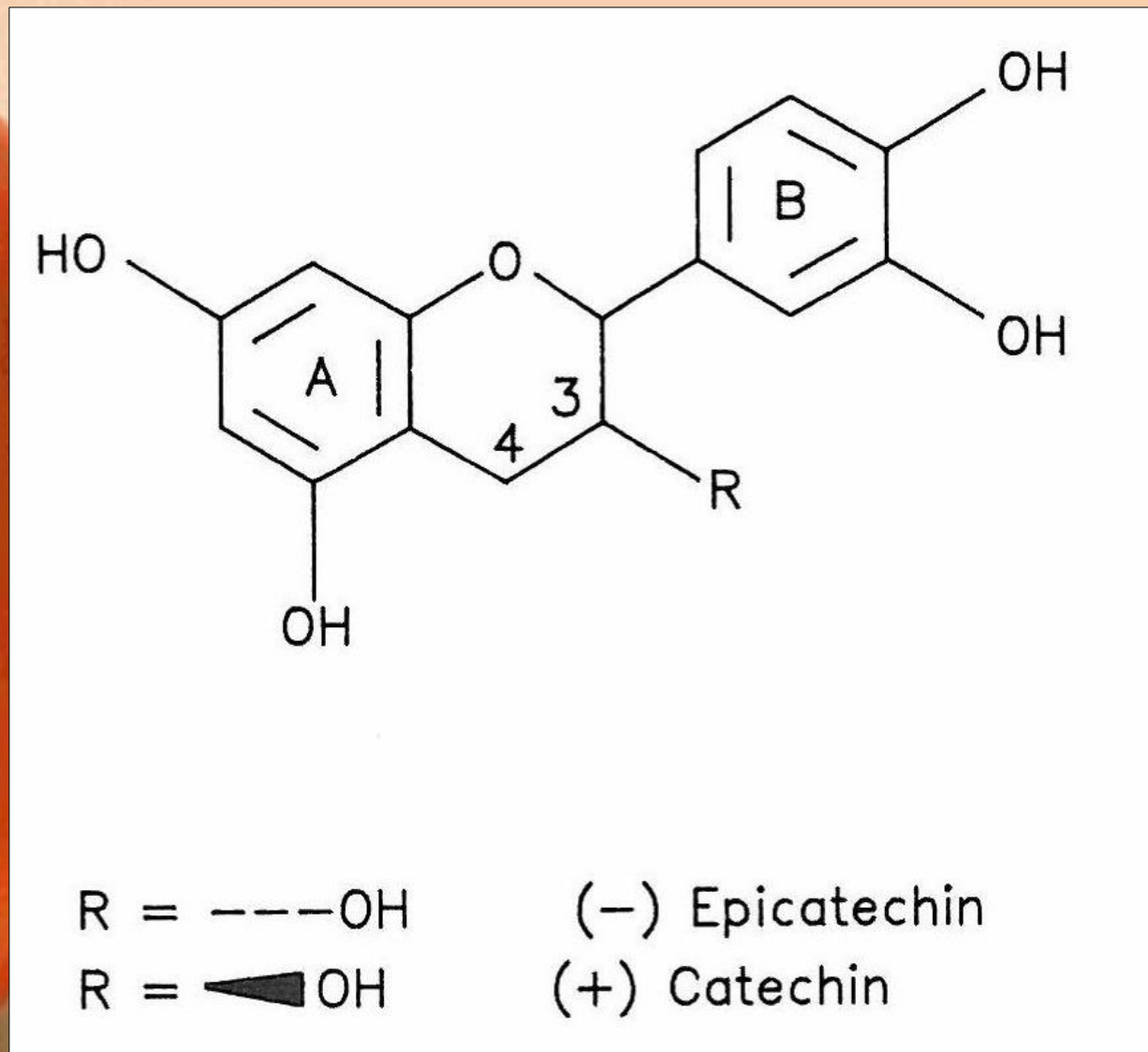
Phloridzin

$R_1 = \text{OH}$

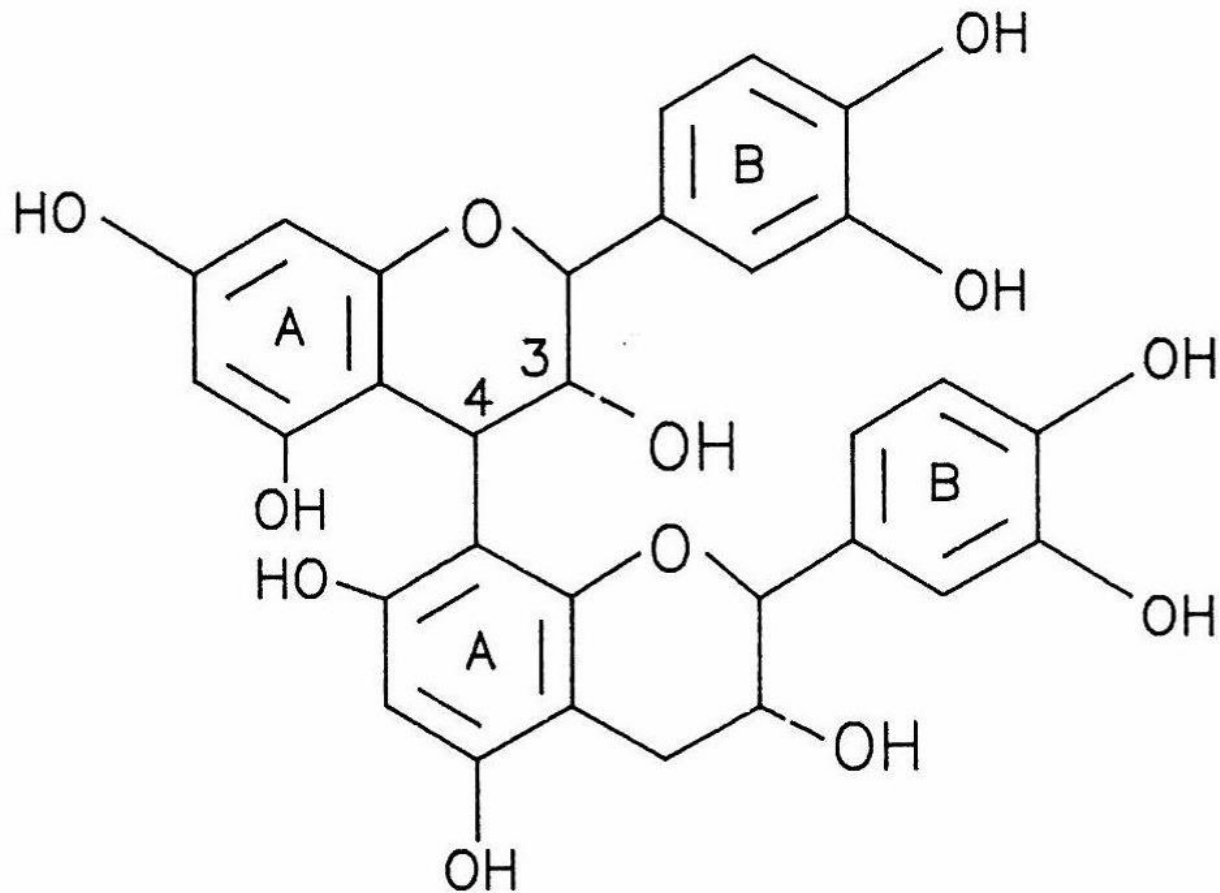
$R_2 = \text{Glucose}$

Sieboldin

# Catechins

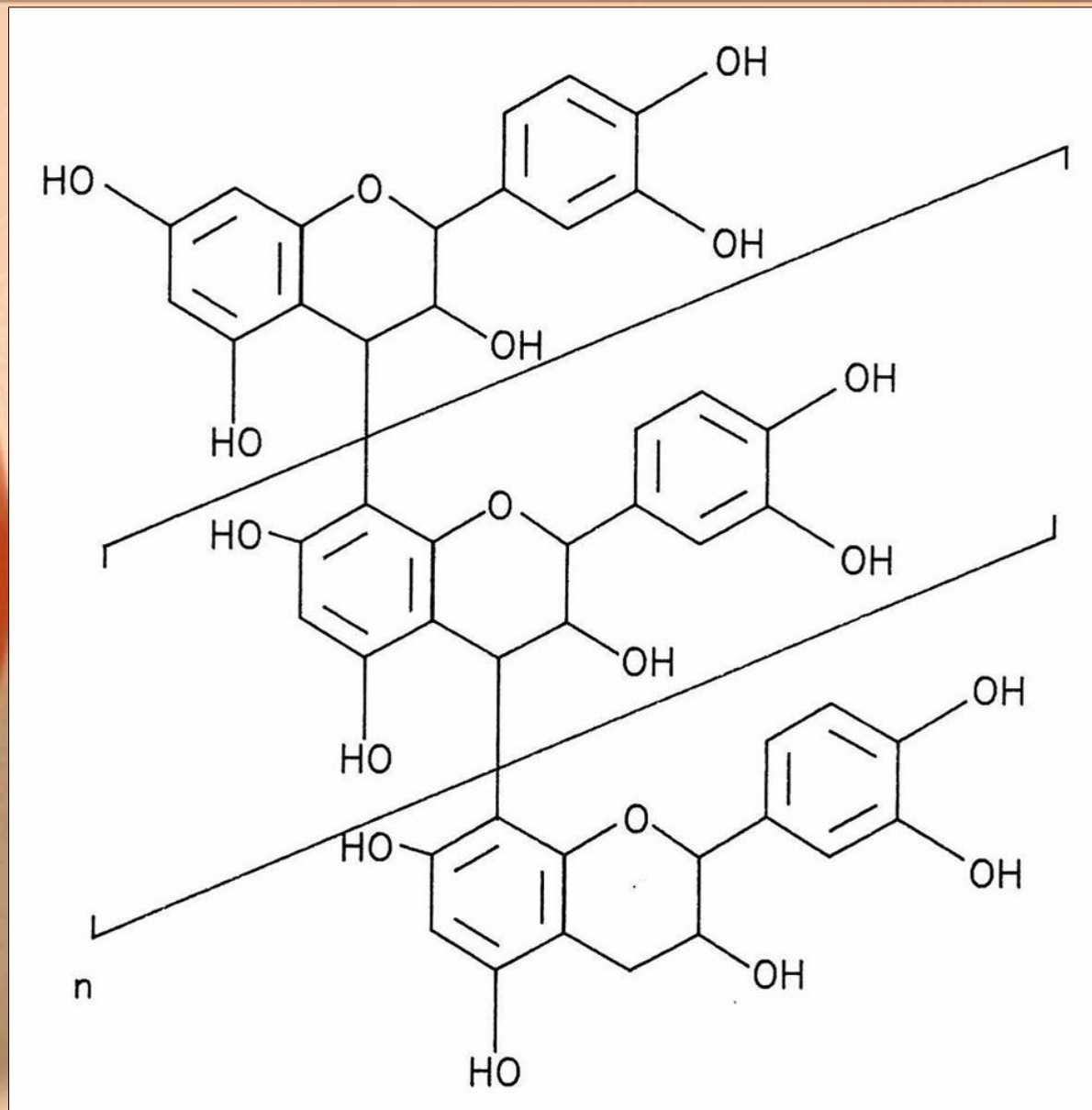
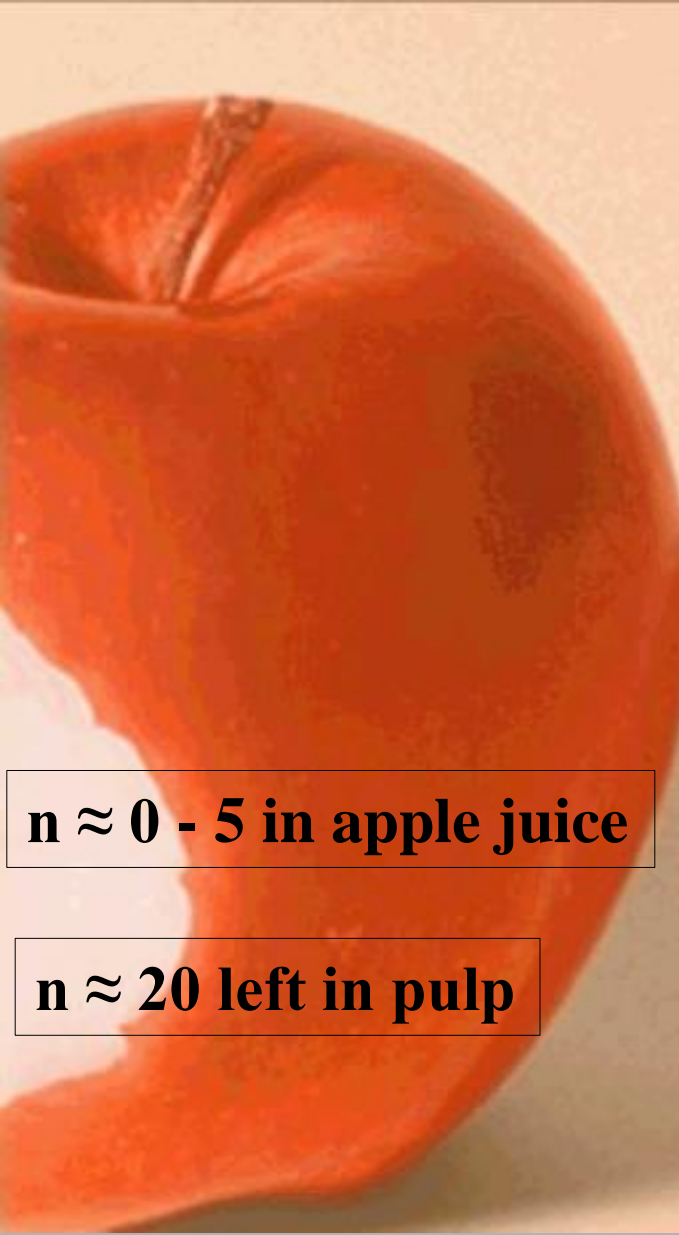


# Procyanidins – a major dimer



Procyanidin B2

# Procyanidin oligomers - tannins



$n \approx 0 - 5$  in apple juice

$n \approx 20$  left in pulp



# Polyphenol roles



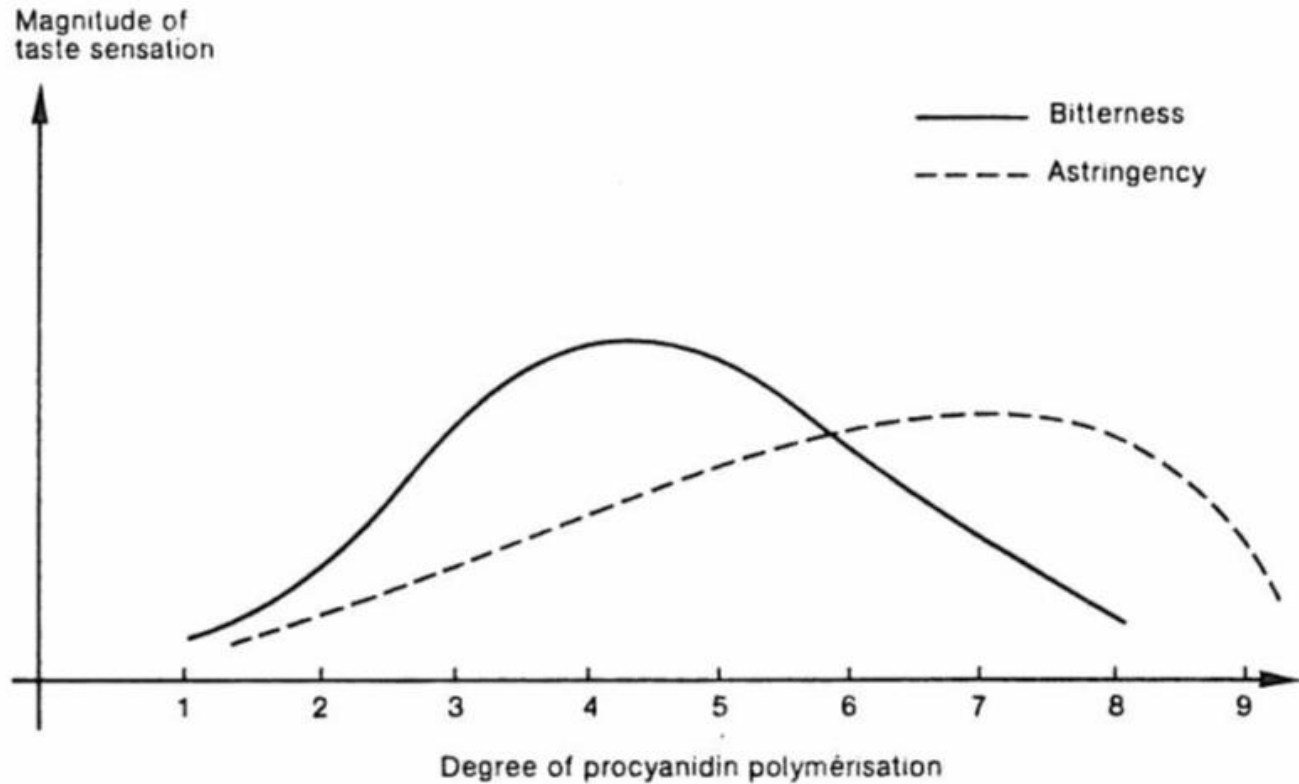
- **Mouthfeel**
- Volatile aroma precursors
- Colour formation
  
- Post bottling haze
- Antioxidant and pro-oxidant properties

# Mouthfeel



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

# Bitterness and Astringency

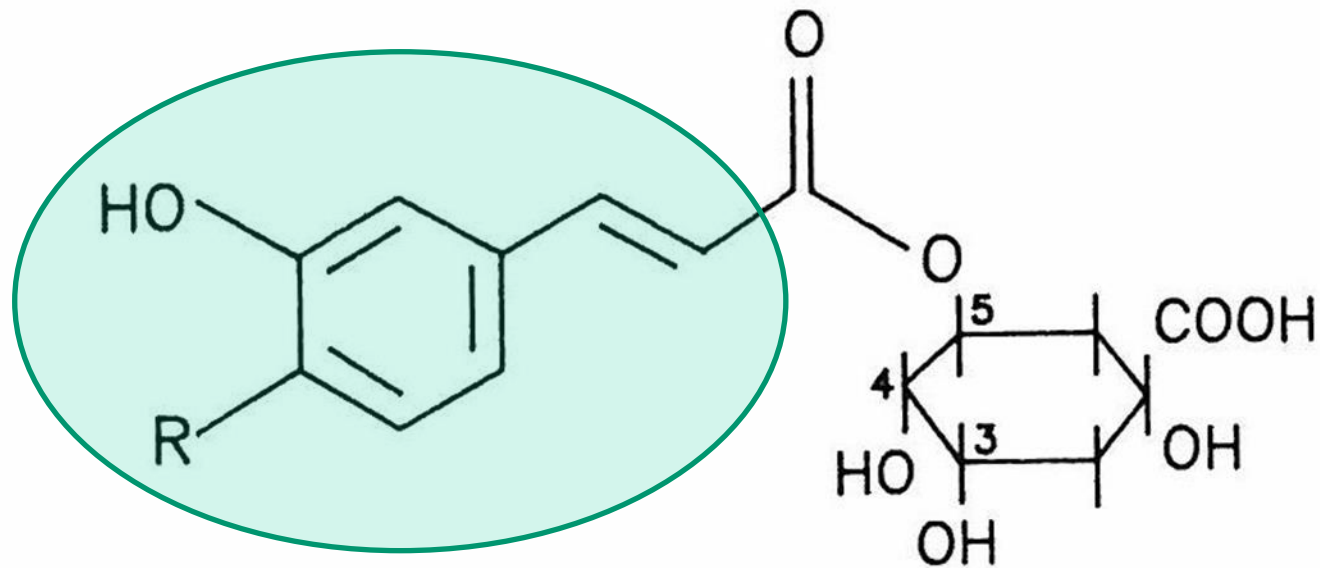


# Polyphenol roles



- 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

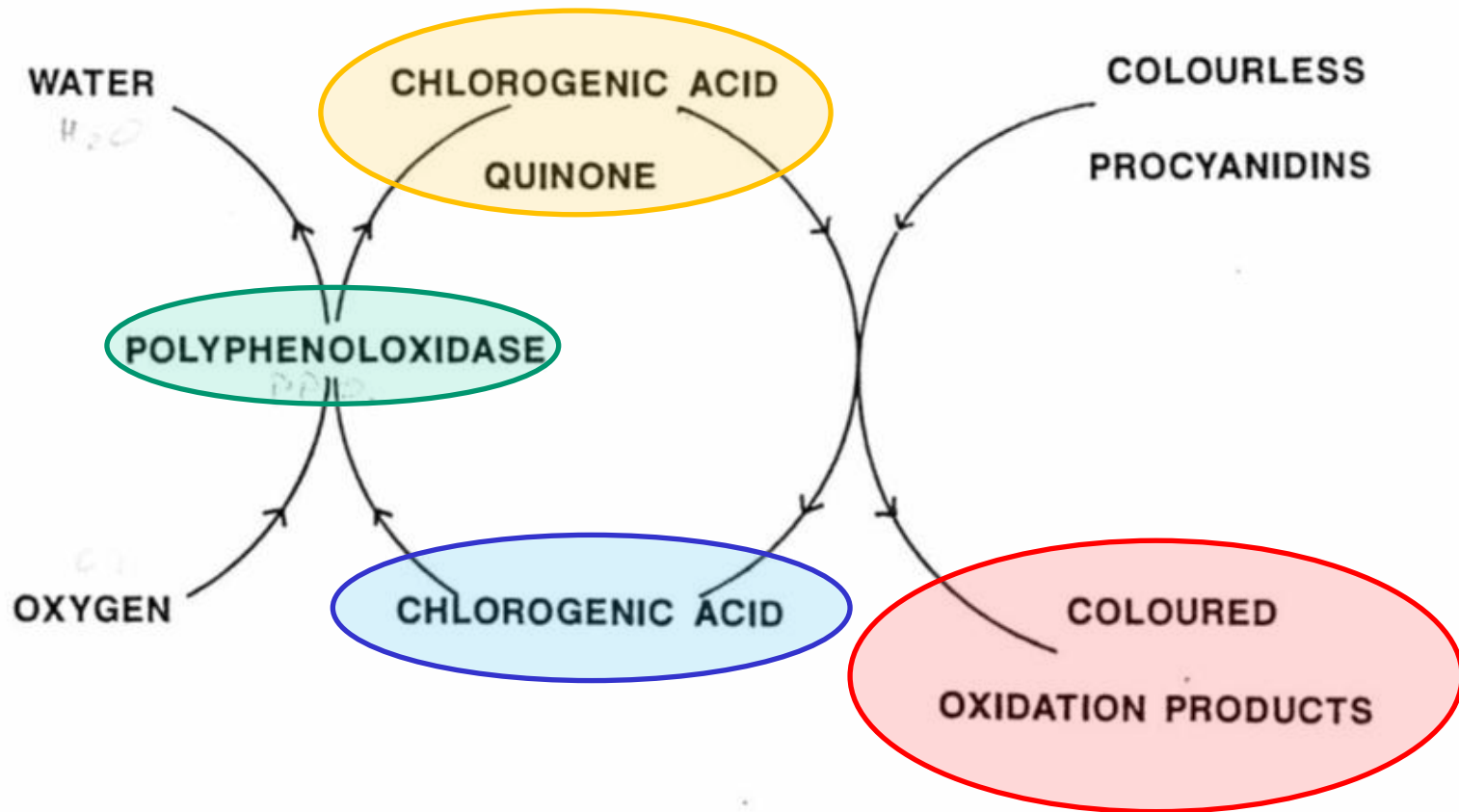
# Colour formation



- 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’

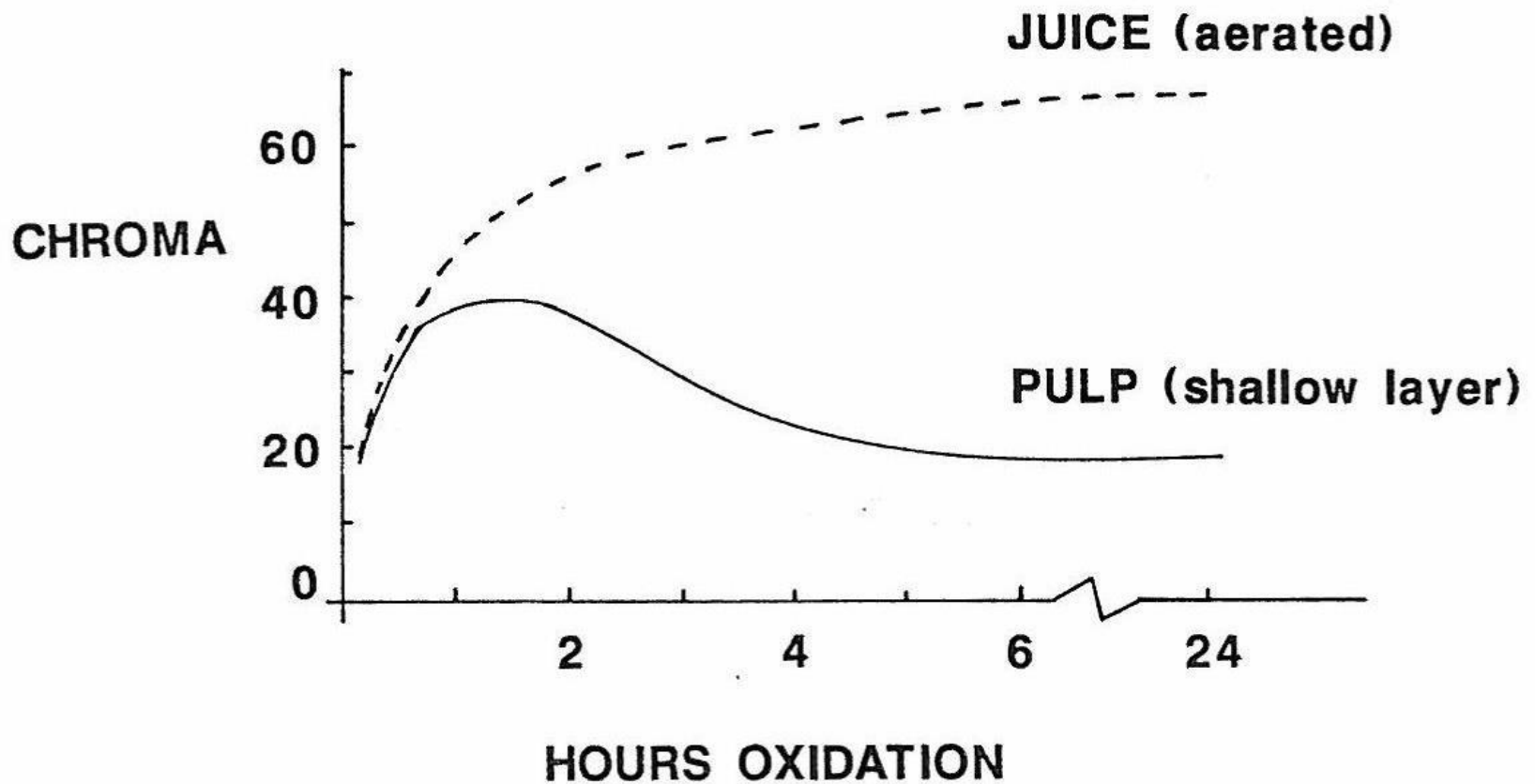


# Coupled oxidation in apples



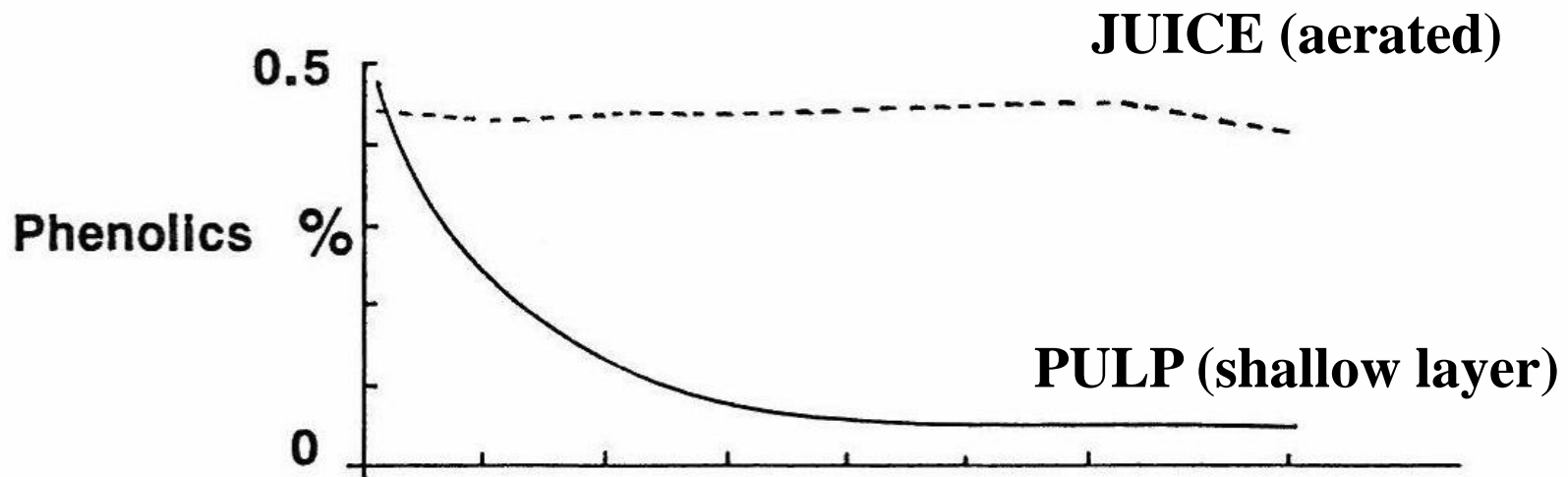
# Colour changes

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  $\text{SO}_2$



# 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!

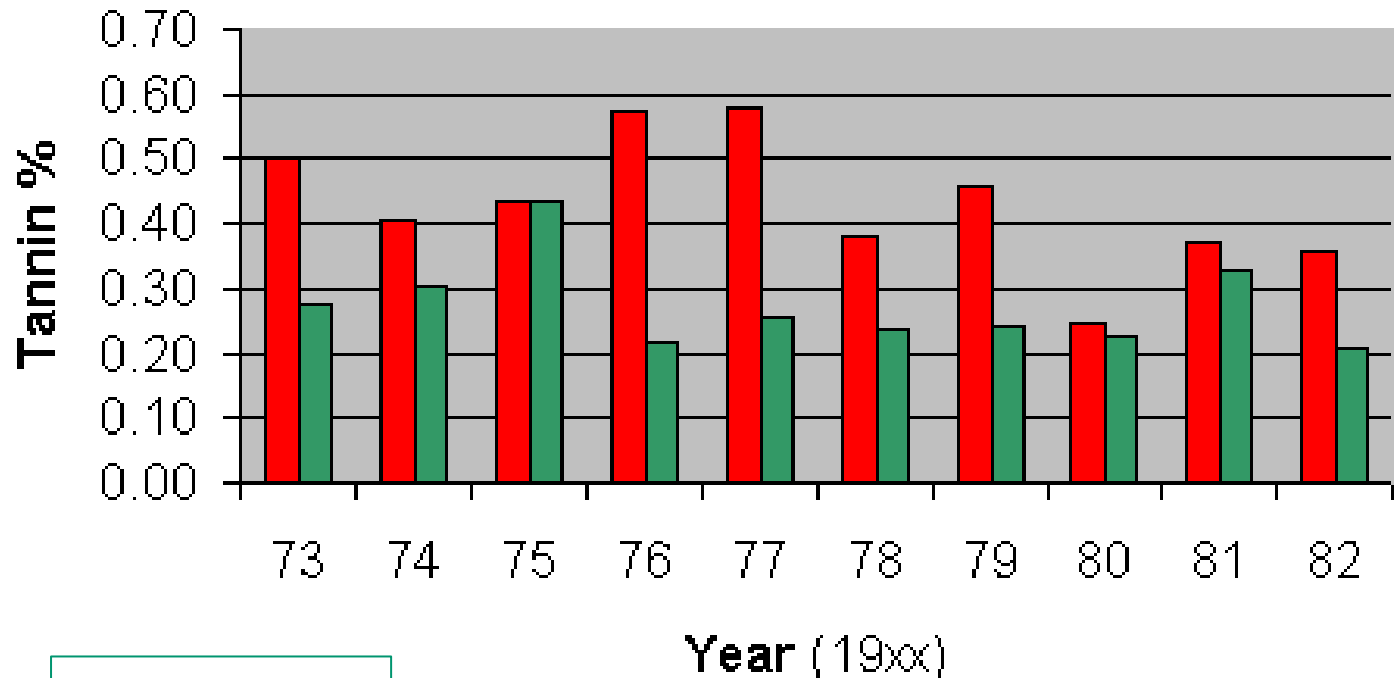
A sliced apple core is shown on the left side of the slide, partially cut and hollowed out, with a stem at the top. The apple is a reddish-orange color.

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