

Enzymatic Browning and Spoilage Reactions

Enzymes

- Enzymatic browning may occur in many fruits and vegetables.
- When the tissue is cut or peeled it rapidly darkens on exposure to air as a result of conversion of phenolic compounds to brown melanins (mushrooms, banana, apple).
- The enzymes involved in browning reaction;

Monophenol monooxygenase or TYROSINASE

Diphenol oxidase or catechol oxidase POLYPHENOL
OXIDASE

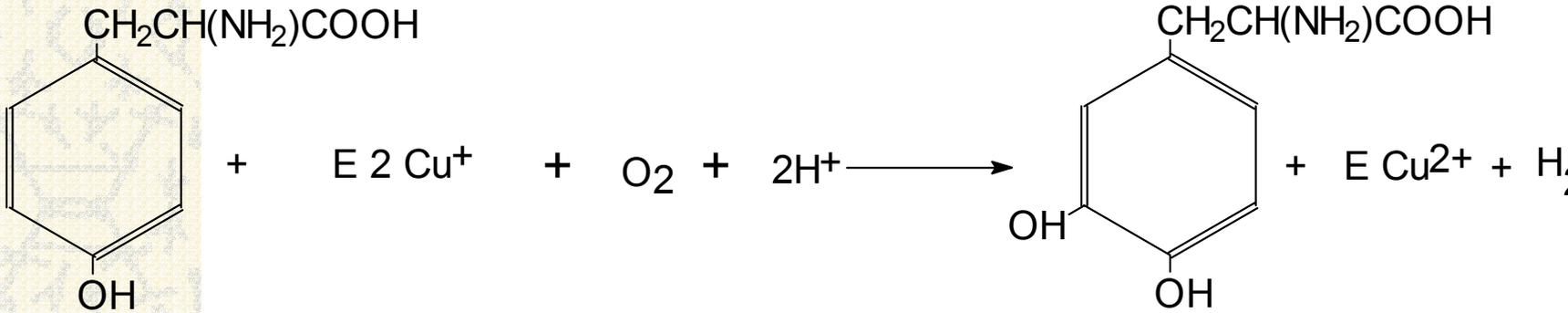
Laccase

Enzymes

- Polyphenol oxidase requires copper and oxygen!
- It is an oxido-reductase class of enzyme with oxygen functioning as hydrogen acceptor.
- The substrates of polyphenol oxidase are phenolic compounds.
- It catalyzes two types of reaction.

Reaction types

Cresolase Activity: This reaction involves hydroxylation of monophenols to *o*-diphenols.



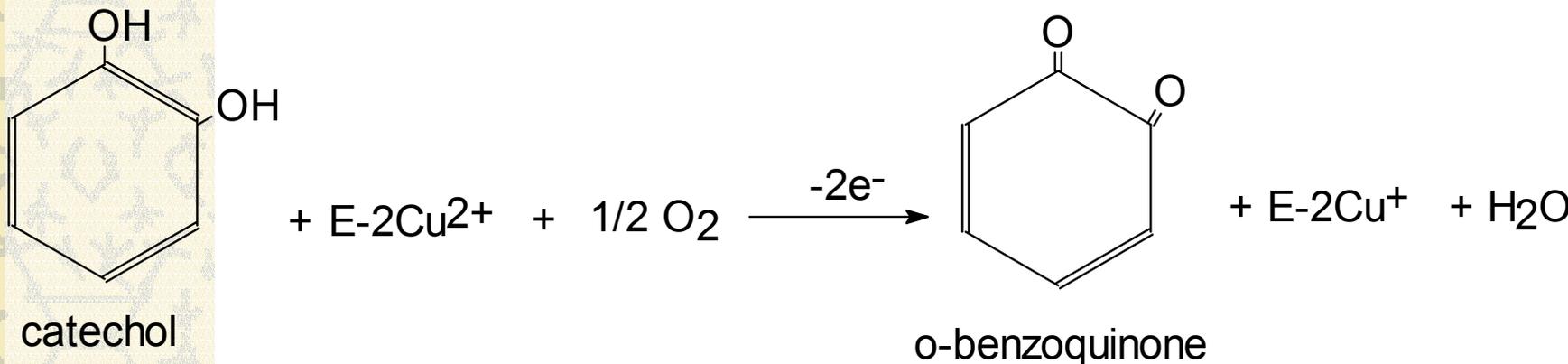
L-tyrosine

3,4-dihydroxyphenylalanine

DHPA

Reaction types

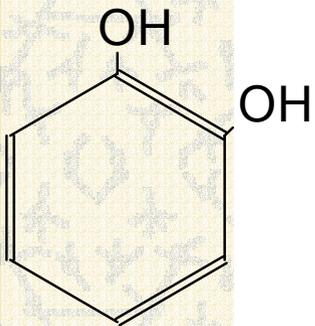
Catecholase or diphenolase reaction:



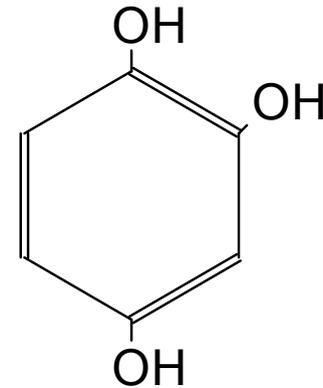
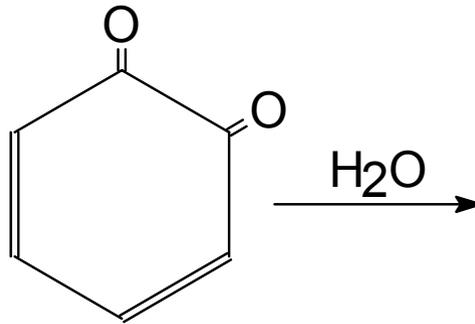
Quinone formation is both dependent on enzyme and oxygen.

Once the reaction starts, the subsequent reactions occur spontaneously and no longer depend on the presence of oxygen or polyphenol oxidase.

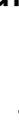
Brown Melanin Formation



OR



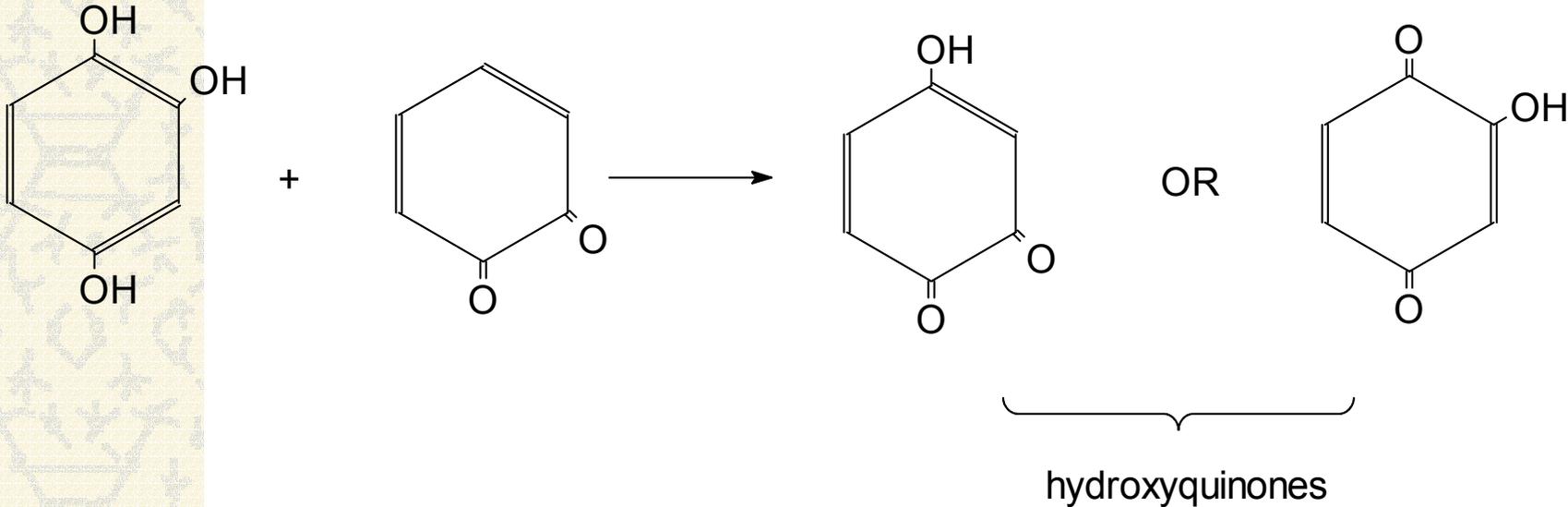
Triphenolic
trihydroxybenzene



interacts with *o*-quinone to
form hydroxyquinones 6

The first reaction is thought
to be a secondary
hydroxylation of *o*-quinone.

Brown Melanin Formation



Undergo polymerization and are progressively converted to red and red-brown polymers, finally to brown melanins.

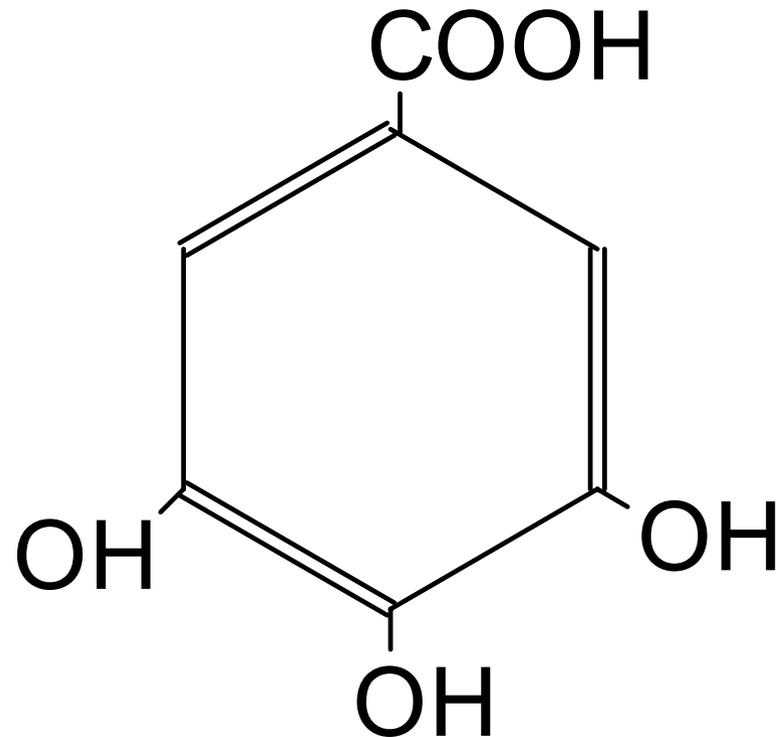
Phenolic Compounds in Foods

Phenolic compounds in foods may be classified into three groups;

- + Simple phenols
- + Cinnamic acid derivatives
- + Flavonoids

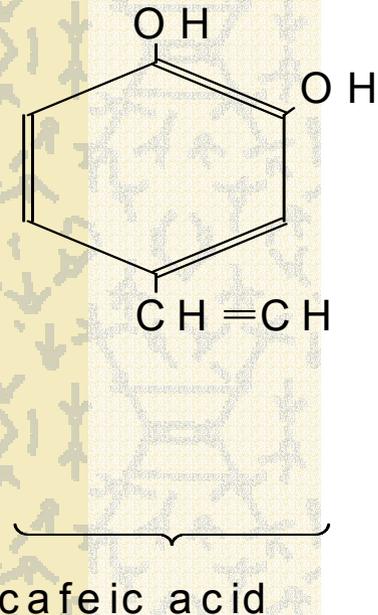
Phenolic Compounds: Simple Phenols

- Monophenols.
 - L-tyrosine
 - o-diphenols
- Gallic acid in tea.
 - A tea flavonoid



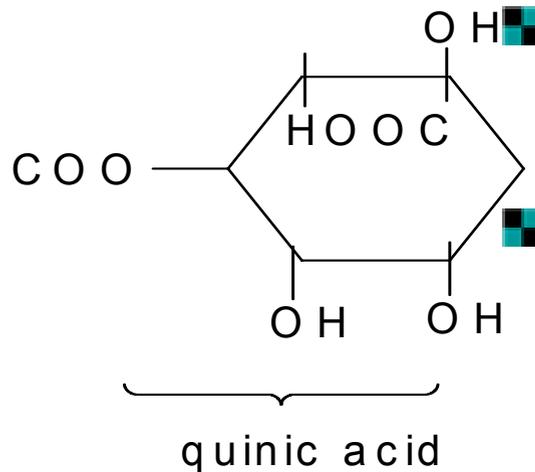
Gallic acid

Phenolic Compounds: Cinnamic acid derivatives

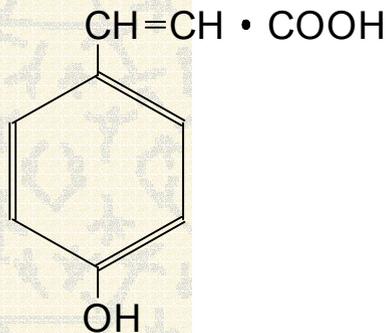


Chlorogenic acid

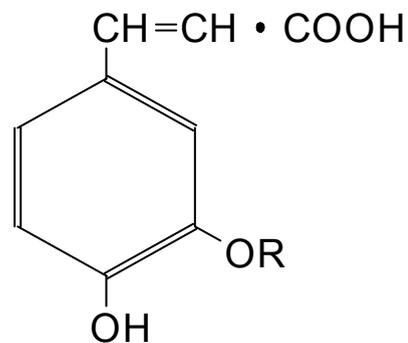
- It is the key substrate in apples and pears.
- It is responsible for gray color formation upon standing of boiled potatoes.
- It is attributed to oxidation of complexes formed between iron and caffeic acid and chlorogenic acids.



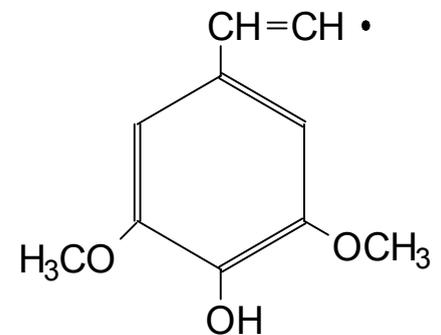
Phenolic Compounds: Cinnamic acid derivatives



p-coumaric acid

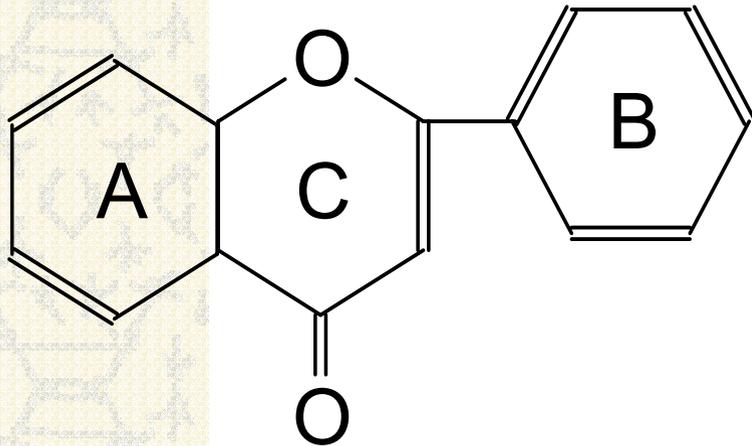


R=H caffeic acid
R=CH₃ ferulic acid



Sinapic acid

Phenolic Compounds: Flavonoids



Flavone structure

All compounds are structurally related to flavone.

Important flavonoids are:

- Catechin (important in tea leaves)
- Leucoantocyanidins (called as tannins)
- Antocyanins (color of plants from purple to red)

● Flavonols

Inhibitors of polyphenol oxidase

- 1) Some compounds structurally related to *o*-diphenols do not function as substrates of polyphenol oxidase (Substrate analogs-Competitive inhibition).
- 2) Polyphenol oxidase is a metalloprotein in which copper is prosthetic group, it is inhibited by chelating agents. (Diethyl dithio carbonate - cannot be used in foods-toxic).

● Methods to Control Enzymatic Browning

Exclusion of oxygen

- ◆ It is the simplest method of controlling enzymatic browning.
- ◆ For instance, immersing the peeled product such as potato in water prior to cooking.
- ◆ This procedure is used on a large scale for the production of potato chips and French fries or using ascorbic acid to use up surface oxygen.

● Methods to Control Enzymatic Browning

Application of heat to denature enzyme:

- Polyphenoloxidase can be inactivated by subjecting food to high temperatures.
- Hot water blanching is a major unit operation in processing potatoes.
 - This process retards enzymatic browning but also results in the leaching of reducing sugars.
 - It also reduces sugar content, which in turn produces a lighter color and a more attractive product.

● Methods to Control Enzymatic Browning

pH treatment:

- Application of acids to control enzymatic browning is used extensively (citric, malic, phosphoric, and ascorbic acid).
 - Lowering pH reduces enzymatic browning.
 - The optimum pH of most polyphenol oxidases lies between pH 4.0 - 7.0 with little activity below pH 3.0 .
- A particular effective inhibitor of polyphenol oxidase is ascorbic acid.
 - It does not have a detectable flavor nor have a corrosive action on metals.

● Methods to Control Enzymatic Browning

Application of sulfurdioxide & sulfites

- + Powerful inhibitors of polyphenol oxidase enzyme.
- + Be employed as either gaseous sulfurdioxide or a dilute solution of the sulfite.
- + Particularly useful where heating would result in unfavorable texture and off-flavor changes in product.
- + Also a preservative used against molds.

It's mechanism:

1. The formation of colorless addition products between sulfite and quinones.
2. Change in protein conformation (polyphenol oxidase)