Browning Reactions

- ✓ Maillard browning

reducing sugar + amine ⟶ brown pigments + flavors

- ✓ Caramelization

sugar —high temps⟶ brown pigments + flavors

- ✓ Enzymatic browning

phenolics —polyphenoloxidase⟶ brown pigments + flavors

Caramelization

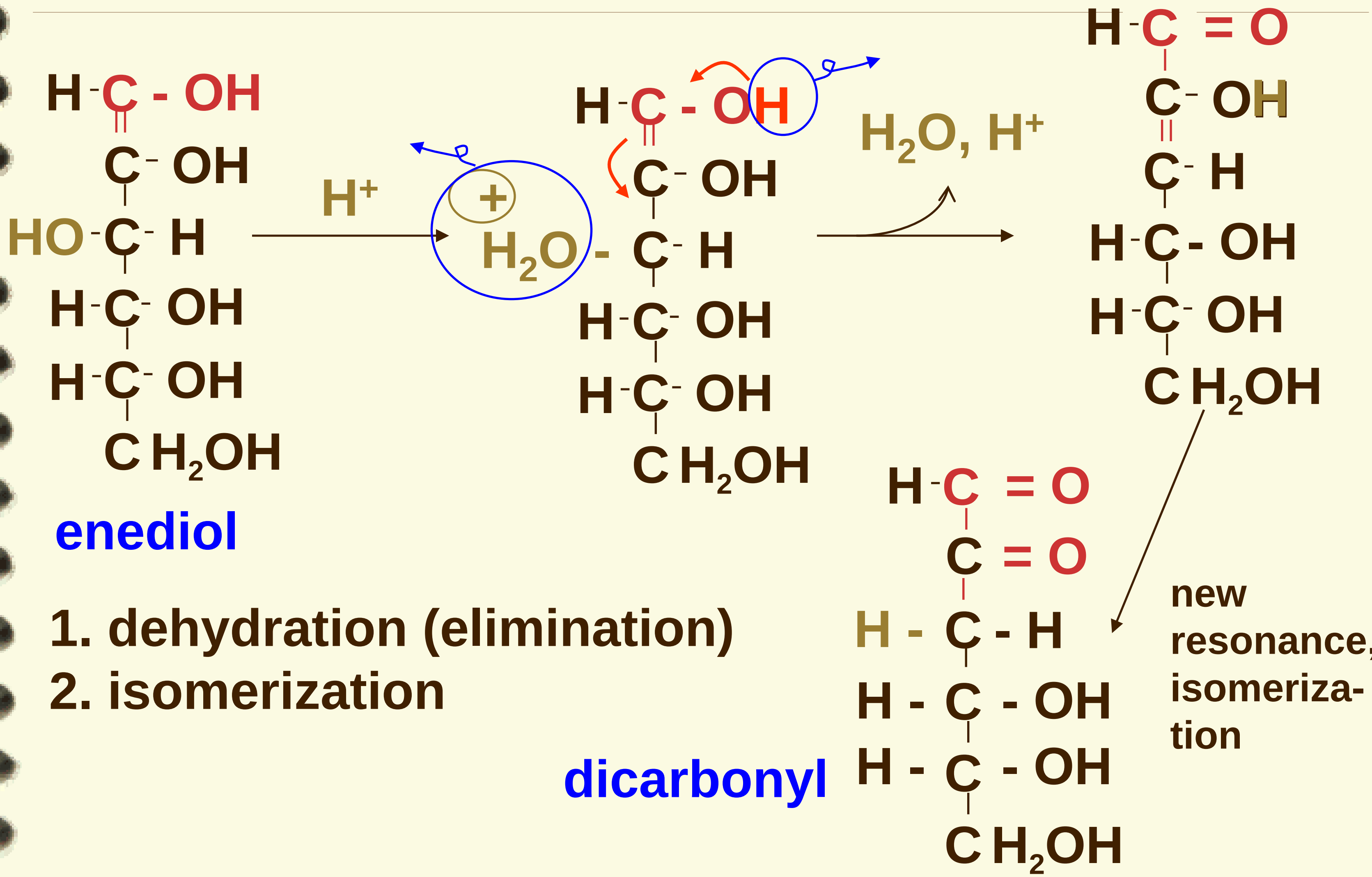
- ✓ At high temperatures, sugar reactions are accelerated
  - Isomerization
  - Water elimination
  - Oxidation
- ✓ Caramelization occurs at
  - High temperatures (~150˚C)
  - Low water content/high sugar

→ **no amines**

- ✓ Formation of
  - Enediols
  - Dicarbonyls

→ ***Caramel flavors and pigments***

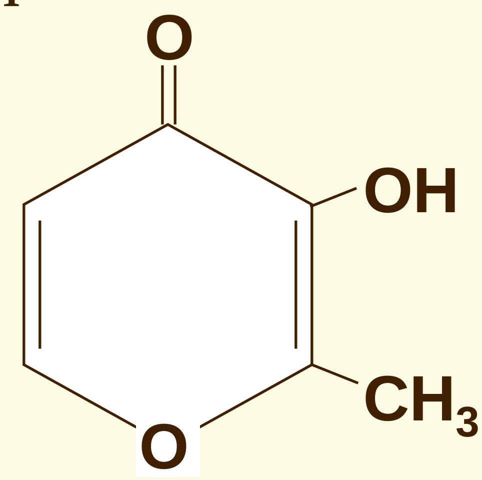
Dehydration mechanism



1. dehydration (elimination)
2. isomerization

Caramelization: Consequences

- ✓ Leads to nice flavors and colors in many foods
  - Caramel aroma, coffee
  - Beverage colors, beer
  - Maltol one important flavor (produced by Maillard rxns also)



- ✓ Can also lead to undesirable flavors and colors
  - "burnt-sugar" smell

Maillard Reaction

Maillard Reaction

- ✓ Non-enzymatic browning
- ✓ Complex set of reactions between amines, usually from proteins, and carbonyl compounds, generally sugars.
- ✓ The consequences:
  - – formation of many products, most of which have some impact on the flavor and appearance of the cooked food.

Effects of Maillard Reaction

- ✓ **Desirable:**
  - Color - bread crust, syrup, meat
    Flavor - coffee, cocoa, meats
    Antioxidants
- ✓ **Undesirable**
  - Color - changes in color during storage
    Flavor - changes during processing and storage
    Nutritional loss - essential amino acids,
    Vitamins (vit c), palatability and digestibility

    Toxicity/mutagenicity

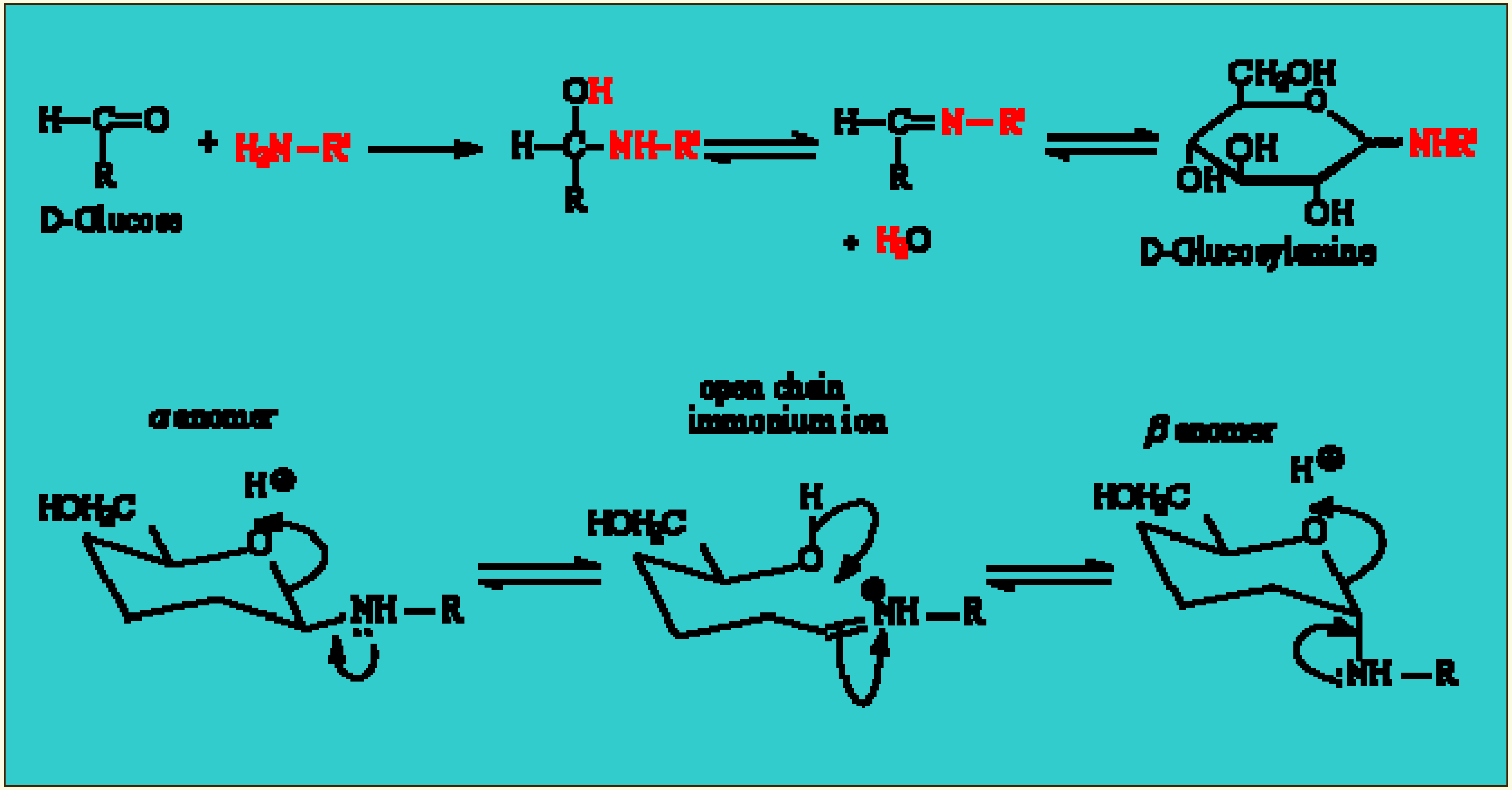
Steps

- ✓ Condensation - amine/carbonyl
- ✓ Rearrangement - enolization
- ✓ Fragmentation
- ✓ Strecker degradation
- ✓ Polymerization - brown color

Initial Step

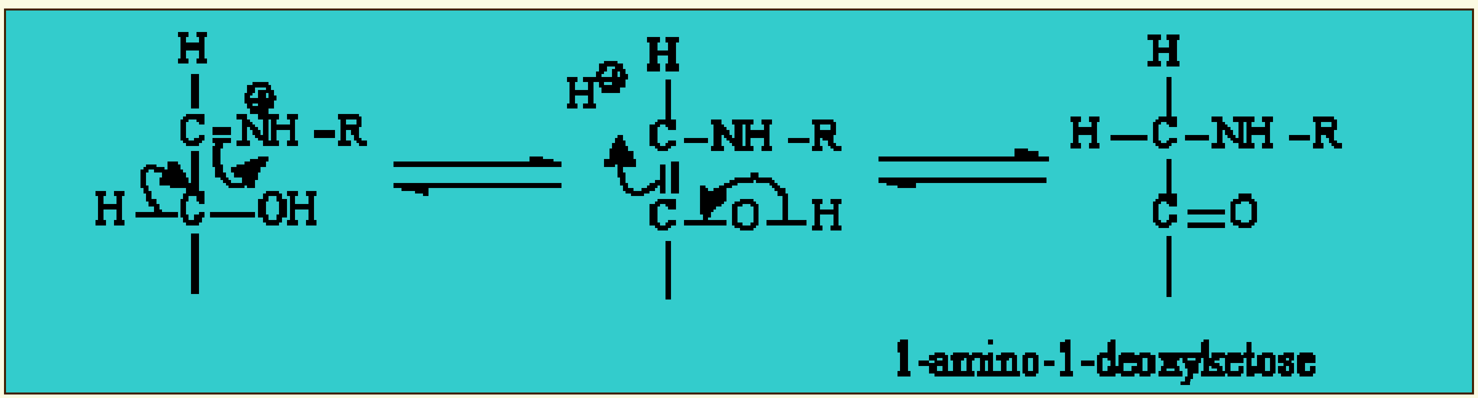
- ✓ Reaction between a reducing sugar and a primary amino acid.
- ✓ Loss of water from this molecule produces an imine that is able to cyclise, resulting in the formation of an N glycoside (a sugar attached to an NR_2 group).

N-Glycosylation



Amadori Re-arrangement

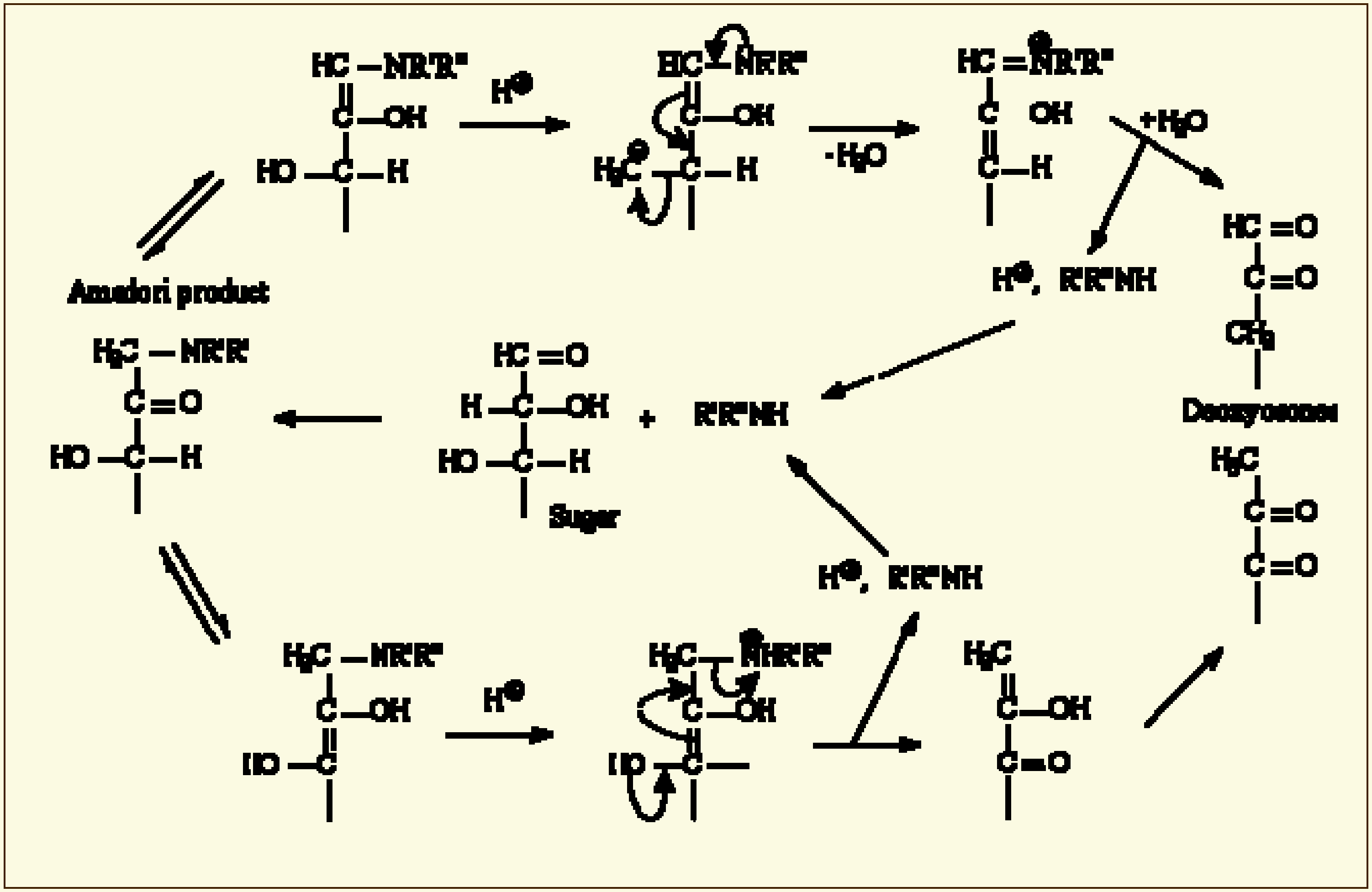
✓ Instead of cyclisation of the immonium ion, an Amadori rearrangement may take place. Alkali catalysed isomerisation reaction.



Fragmentation

- ✓ Glycosylamines and Amadori products are intermediates formed during the course of the Maillard reaction.
- ✓ The concentration of these intermediates depends upon the reaction conditions (pH, temperature and time).
- ✓ In the pH range 4-7, Amadori products undergo degradation to give 1- and 3-deoxydicarbonyl compounds (deoxyosones).

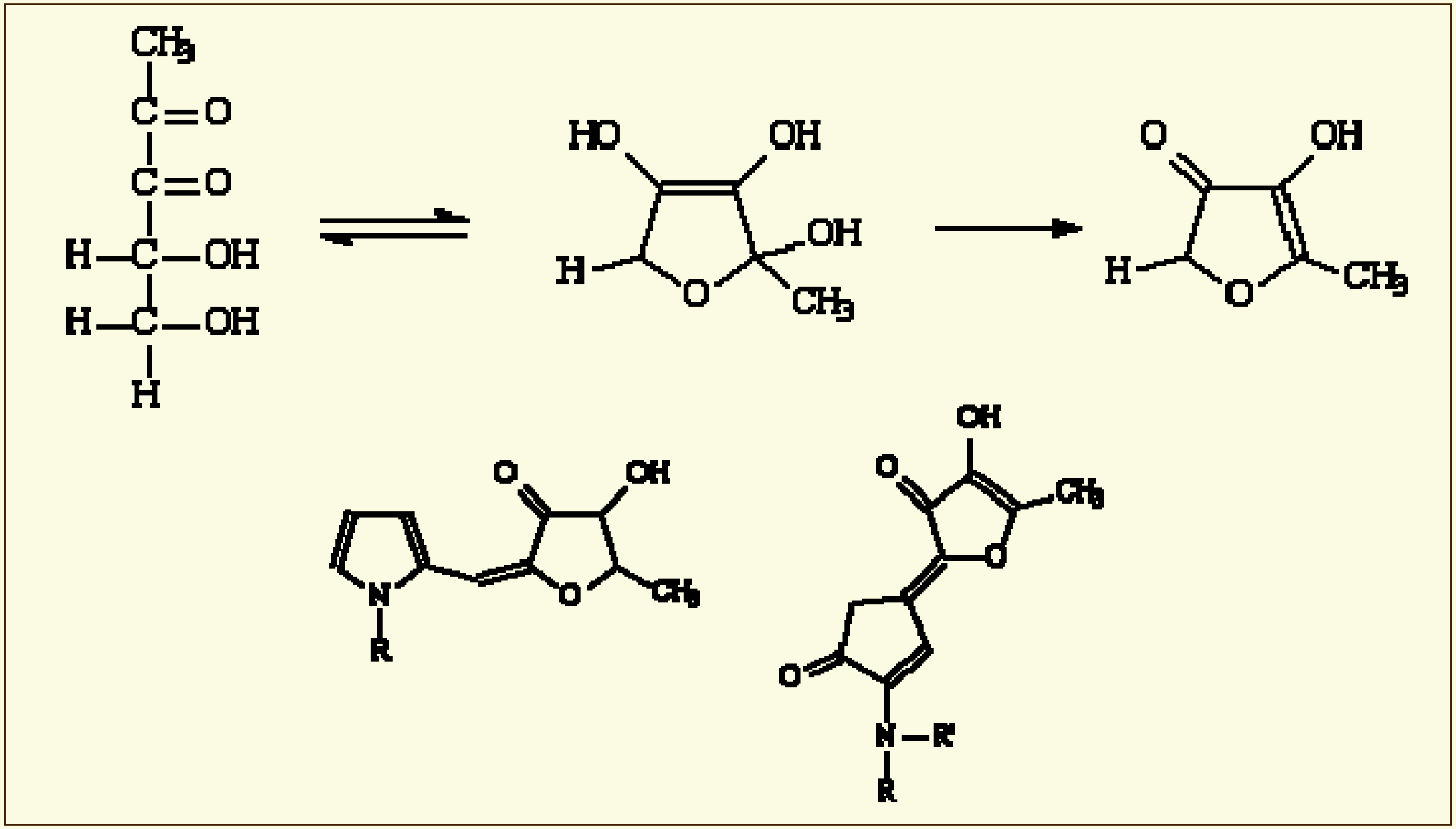
Fragmentation



Formation of Aroma Compounds

- ✓ Deoxyosones are reactive α–dicarbonyl compounds and give rise to other, secondary products.
  - From 1-deoxyosone, the secondary products include furanoses (important aroma compounds), pentoses and hexoses.
  - Secondary products from 3-deoxyosone include pyrroles, pyridines and formylpyrroles.

Colored Products

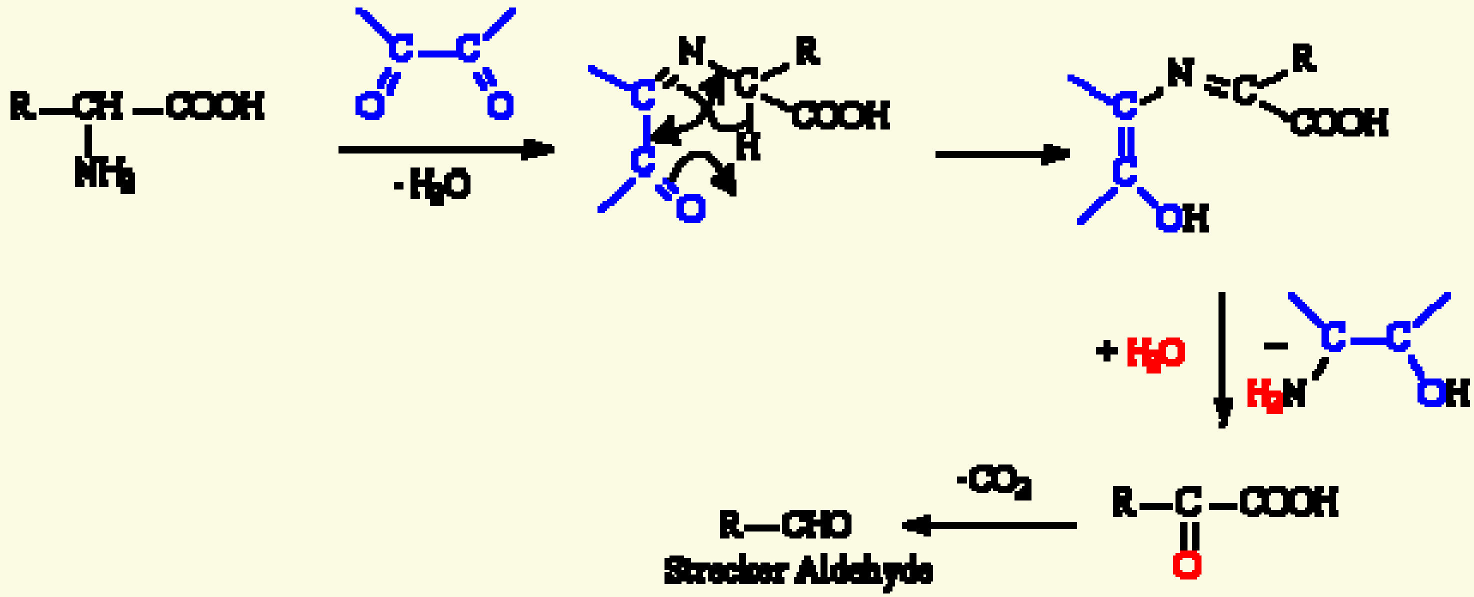


Pentoses may further react with amines to give orange dye products, influencing the color of the food.

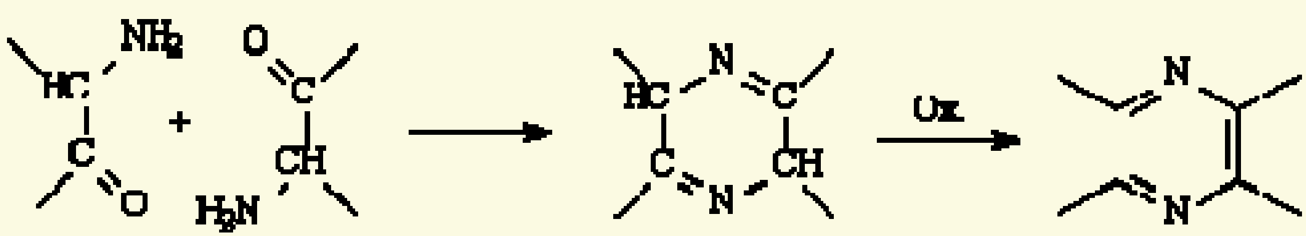
Strecker Reaction

- ✓ Reactions between α– dicarbonyl compounds, such as the deoxyosones formed in the Maillard reaction, and amines.
- ✓ The reaction involves transamination and yields aminoketones, aldehydes and carbon dioxide.

Strecker Degradation



Pyrazine Formation

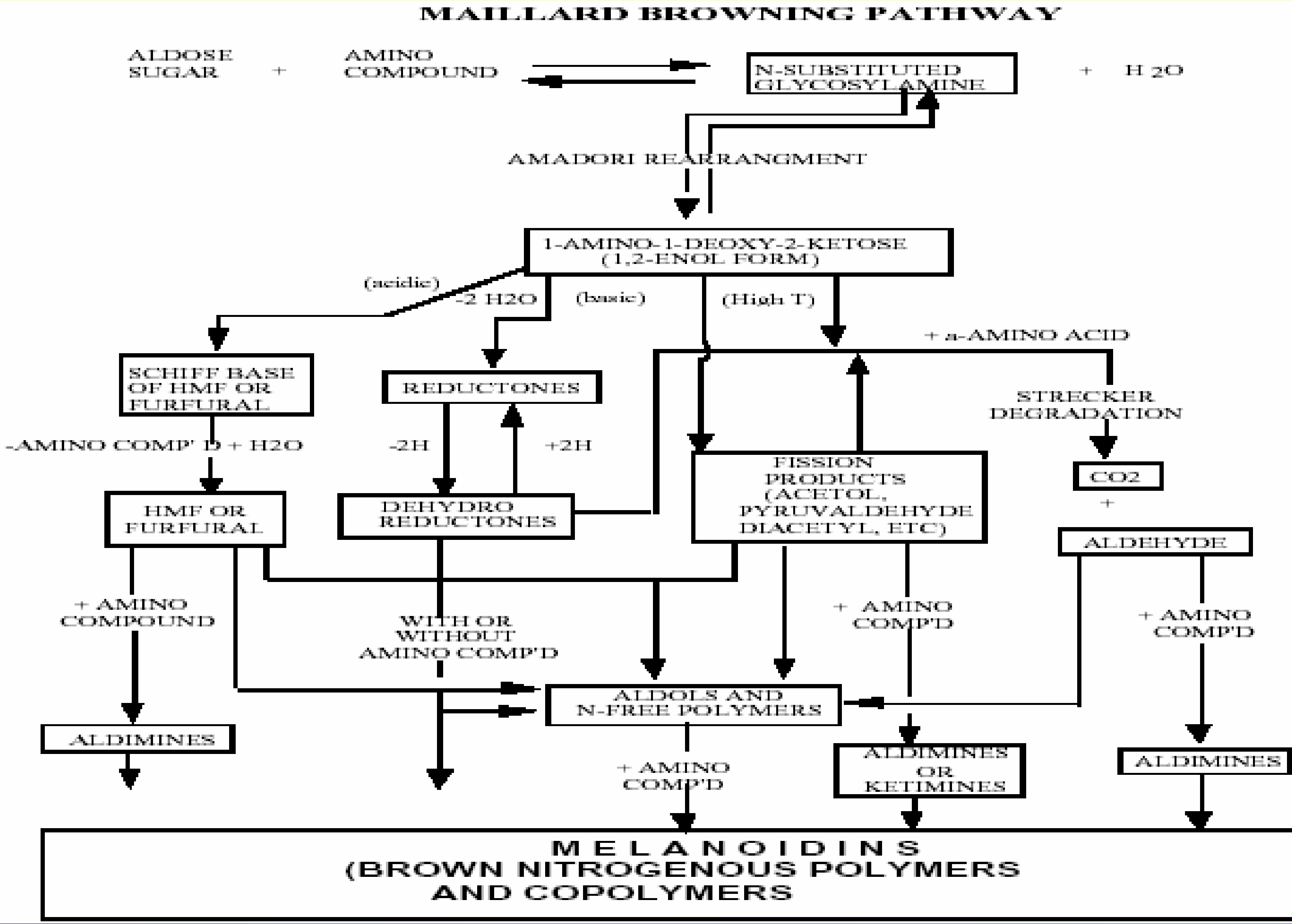


Strecker Degradation

- ✓ The aldehyde (referred to as a Strecker aldehyde) and aminoketone gives rise to strong odors.
- ✓ Common Strecker aldehydes include ethanal (fruity, sweet aroma), methylpropanal (malty) and 2-phenylethanal (flowery/honey like aroma).
- ✓ Condensation of two aminoketones may yield pyrazine derivatives that are also powerful aroma compounds.

Polymerization

- ✓ Formation of brown nitrogen-containing pigments (melanoidins) by aldol condenssation and carboyl-amine polymerization
- ✓ Production of N-, O-, S-heterocyclic compounds.


MAILLARD BROWNING PATHWAY
ALDOSE SUGAR
+
AMINO COMPOUND
N-SUBSTITUTED GLYCOSYLAMINE
+ H 2O
AMADORI REARRANGMENT
1-AMINO-1-DEOXY-2-KETOSE (1,2-ENOL FORM)
(acidic)
-2 H2O
(basic)
(High T)
+ a-AMINO ACID
SCHIFF BASE OF HMF OR FURFURAL
REDUCTONES
STRECKER DEGRADATION
-AMINO COMP' D + H2O
-2H
+2H
CO2
+
HMF OR FURFURAL
DEHYDRO REDUCTONES
FISSION PRODUCTS (ACETOL, PYRUVALDEHYDE DIACETYL, ETC)
ALDEHYDE
+ AMINO COMPOUND
WITH OR WITHOUT AMINO COMP'D
+ AMINO COMP'D
+ AMINO COMP'D
ALDOLS AND N-FREE POLYMERS
ALDIMINES
+ AMINO COMP'D
ALDIMINES OR KETIMINES
ALDIMINES
MELANOIDINS
(BROWN NITROGENOUS POLYMERS AND COPOLYMERS

Summary of Maillard Reaction

- The general types of products and consequences of this reaction include:
  - insoluble brown pigmented products, ‘melanoidins’, which have variable structures, molecular weights and nitrogen content.
  - volatile compounds that contribute to the aroma associated with many cooked foods.
  - flavored compounds, often bitter substances.
  - reducing compounds that may help prevent oxidative deterioration, increasing the stability (shelf life) of the food.
  - the formation of mutagenic compounds.
  - loss of (essential) amino acids.

Monitoring

- ✓ Initial stage
  - No UV absorption (Schiff base, Amadori/ Heyns products)
- ✓ Intermediate stage
  - Strong UV absorption (dicarbonyls, HMF, etc)
- ✓ Final stage:
  - Dark brown color (420 nm)

Controling Maillard Reactions

Nature of the Reactants

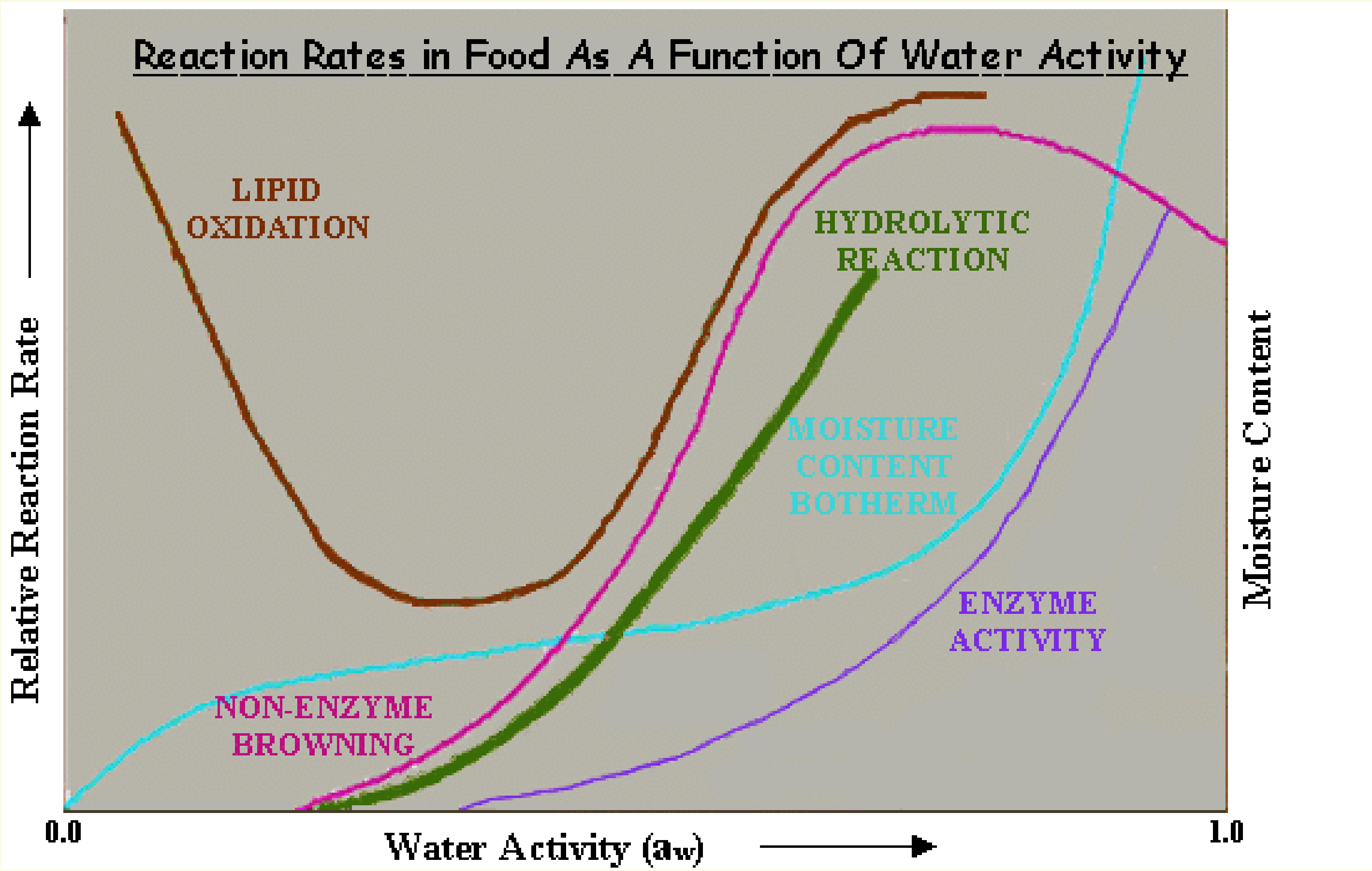
- ✓ Sugars (acyclic forms and mutarotation rate)
  - Reducing sugars
  - Sucrose
  - Pentoses > hexoses > disaccharides
  - Fructose increased rates of reaction due to greater extent in the open chain form as compared to aldoses
  - Among hexoses:
    - Reactivity decreased in order of:

      D-galactose > D-mannose > D-glucose
  - The % open chain form and rate of mutarotation increases with Temperature and pH

Nature of the Reactants

- ✓ Amino Compounds
  - Act as nucleophiles
  - Basic and hydroxy aminoacids react strongly with reducing compounds
  - Important in aroma compounds ⇒ Strecker
- ✓ L-ascorbic acid ⇒ Oxidation
- ✓ Phenolic Compounds ⇒ O_2, Alkaline conditions, metals
- ✓ Others
  - Lipid oxidation products
  - Organic acids

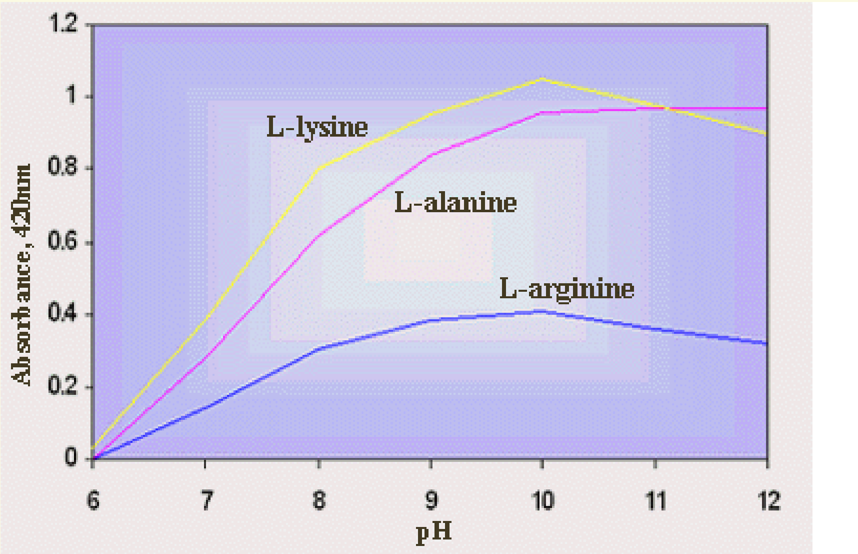
Water Activity



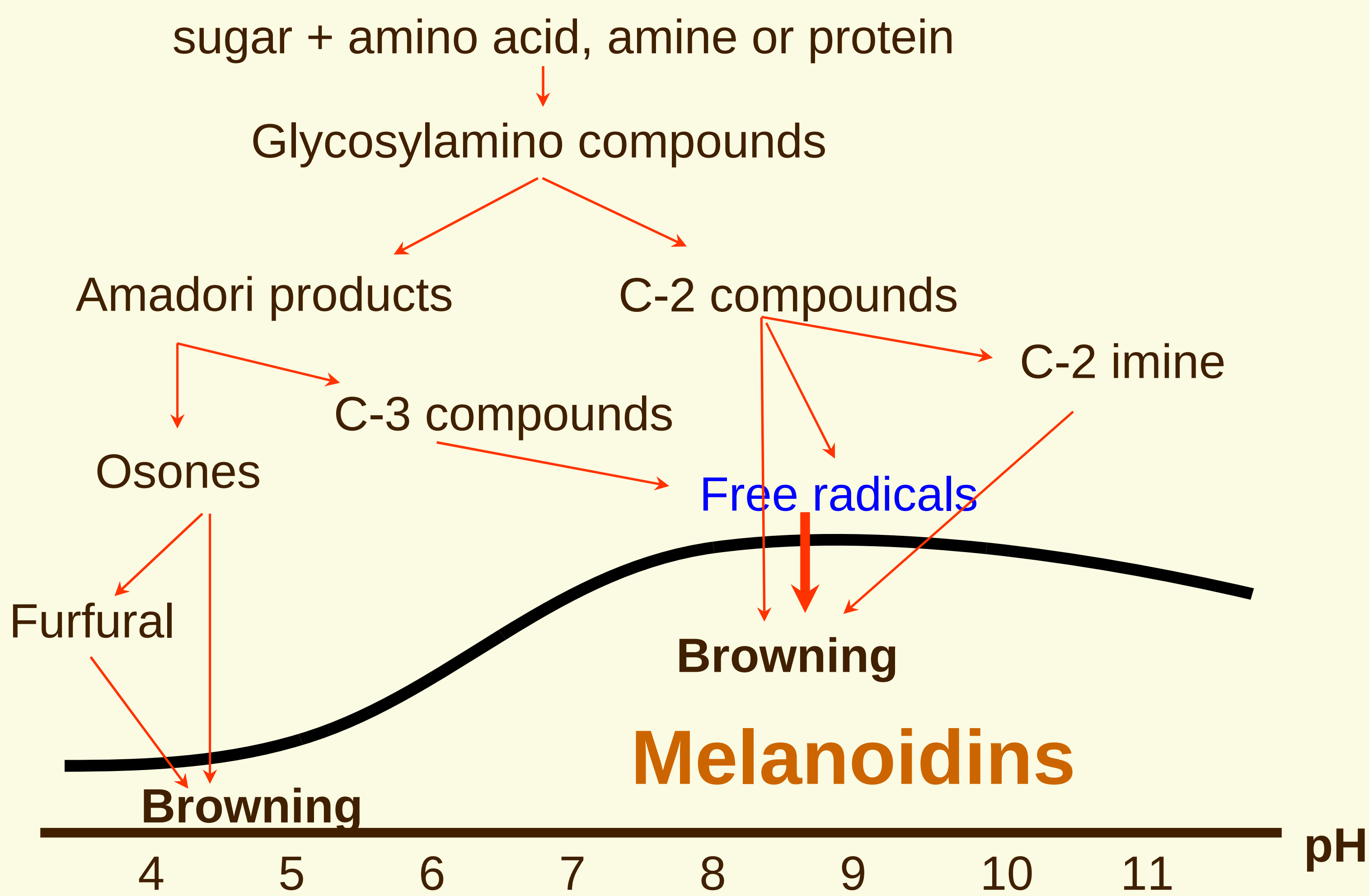
pH

- pH influences the ratio of products formed
- the rate of color formation can be reduced by decreasing the pH
- Under alkaline conditions, the 2,3-enolization pathway is favored

D-glucose at
121°C for 10 min"



Effect of pH on Melanoidin Formation



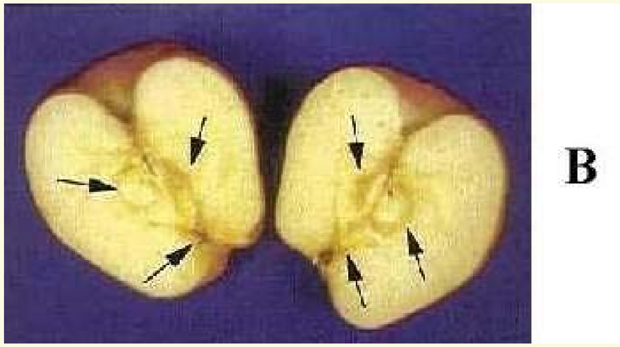
Additives

- Sulfur dioxide

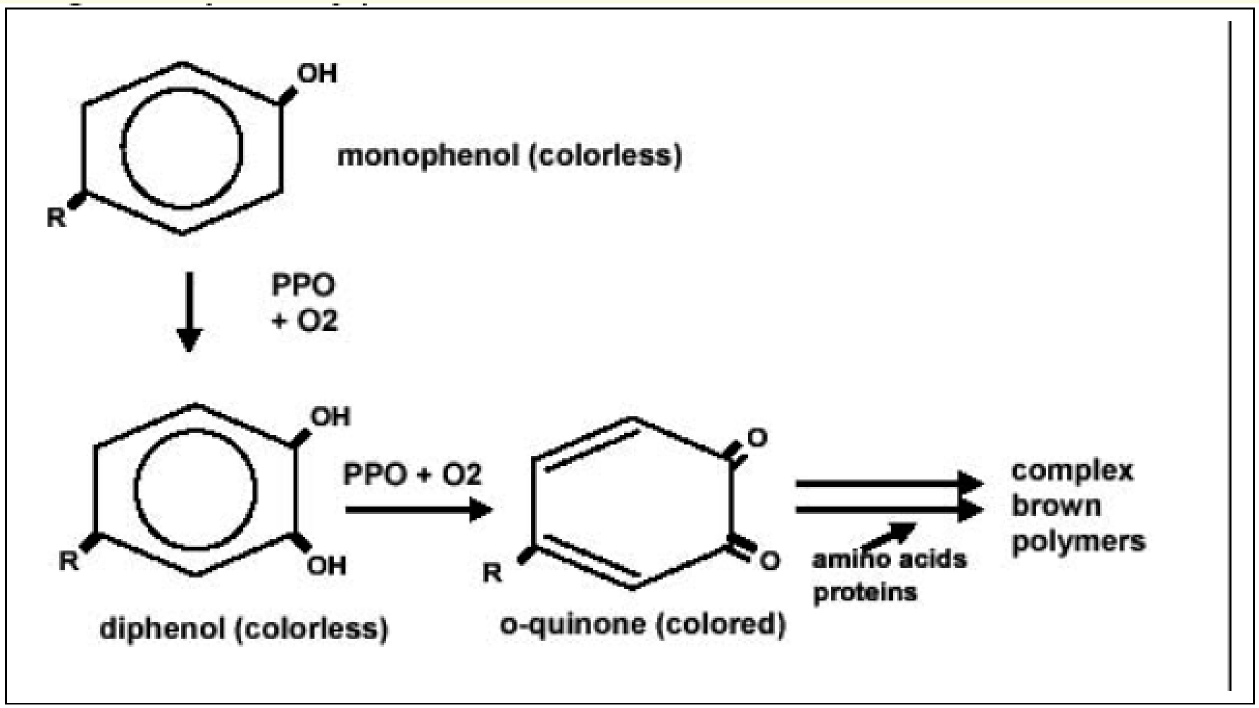
Enzymatic Browning

Overview of enzymatic browning

- ✓ Occurs 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 melanoidins
- ✓ Catalyze 2 types of reactions
- ✓ Active between pH 5-7
- ✓ Cu cofactor



PPO Catalyzed Reaction

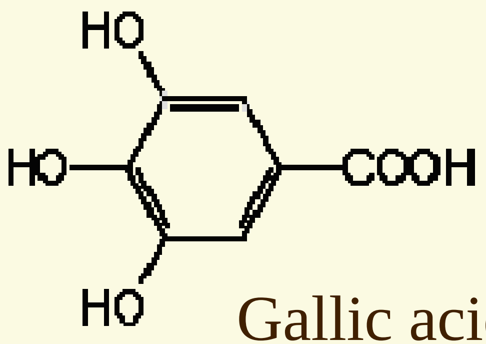


- ✓ Quinone formation is both dependant of enzyme and oxygen
- ✓ Once the reaction starts, the subsequent reactions occur spontaneously and no longer depend of oxygen or enzyme

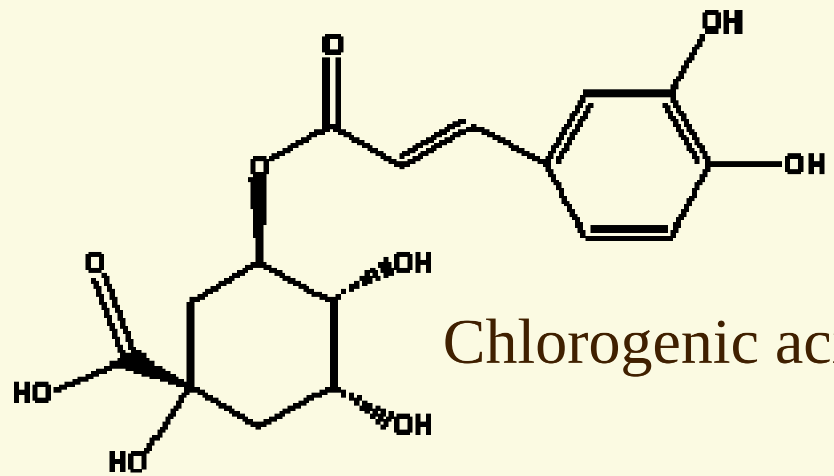
Phenolic substrates

- ✓ Phenolic compounds are widely distributed in the plant kingdom and are considered to be secondary metabolites.
- ✓ Structurally they contain an aromatic ring bearing one or more hydroxyl groups, together with a number of other substituents
  - – Simple phenolics
  - – Cinnamic acid derivatives
  - – Flavonoids

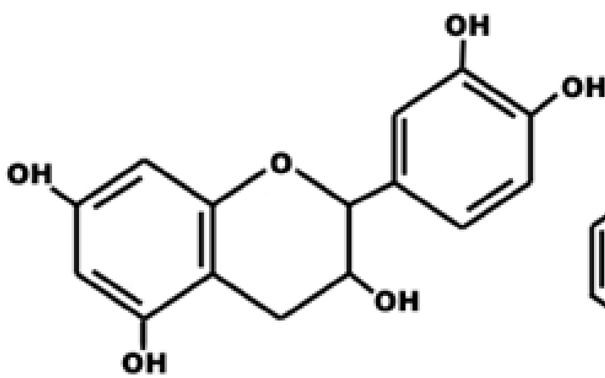
Phenolic acids



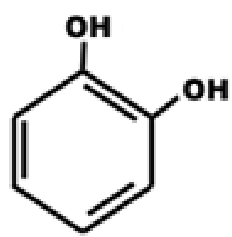
Gallic acid



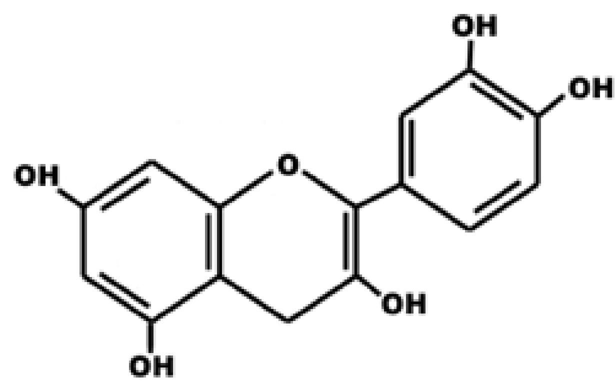
Chlorogenic acid



catechin ($C_{15}H_{14}O_6$)



catechol ($C_6H_6O_2$)



anthocyanin ($C_{15}H_{12}O_6$)

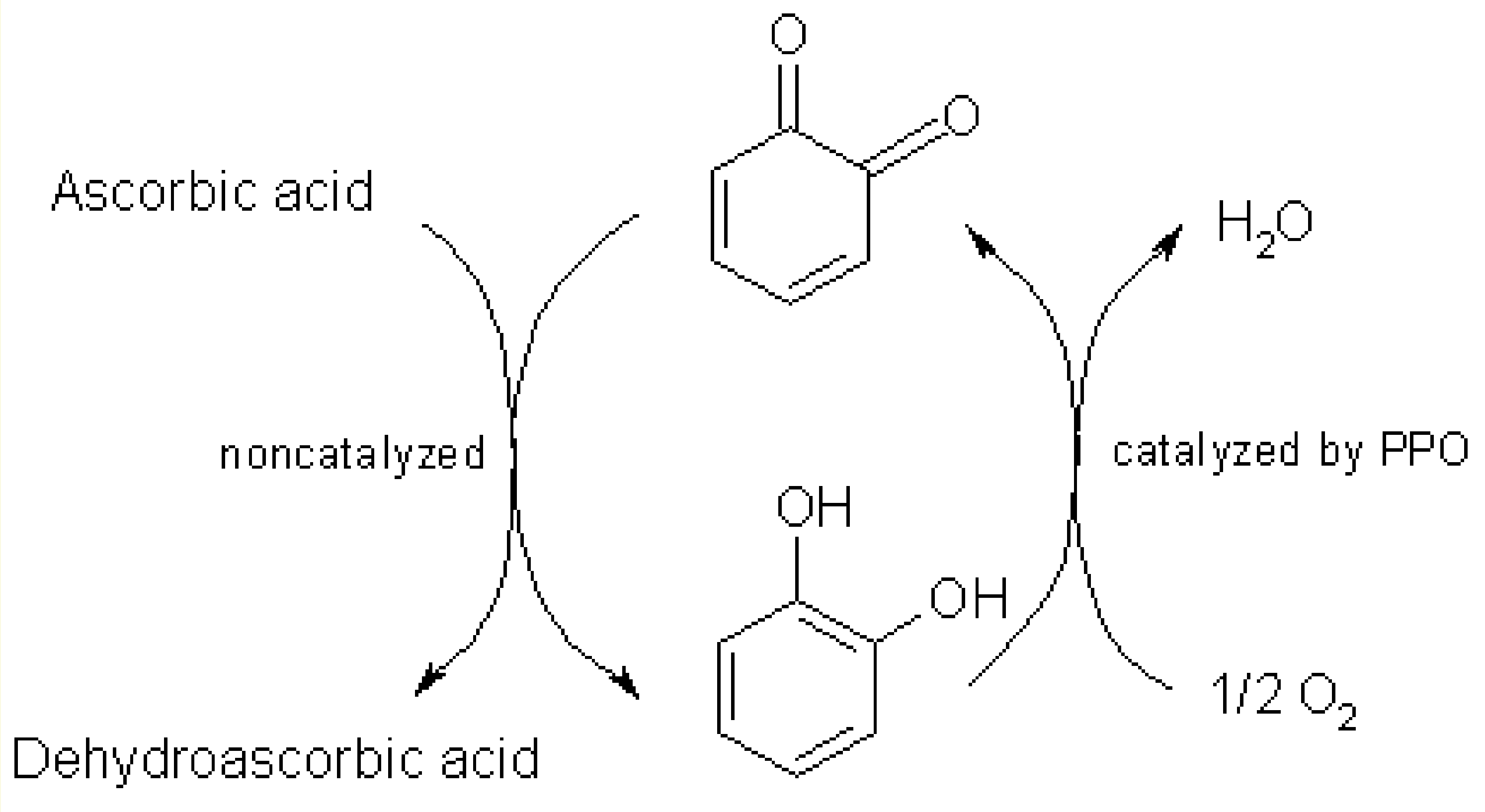
Control of Enzymatic Browning

- ✓ Exclusion of Oxygen
  - – Exclusion of oxygen is possible by immersion in water, syrup, brine, or by vacuum treatment.
- ✓ Application of heat
  - – Blanching
- ✓ pH treatment
  - – Lowering the pH
  - – Citric, malic, phosphoric and ascorbic acid

Control of Enzymatic Browning

- ✓ Chelators
  - – phosphates
  - – EDTA
  - – organic acids
- ✓ Reducing agents
  - – Sulfites
    - Formation of colorless addition products with quinones
    - Change in protein conformation
  - – ascorbic acid and analogs
  - – cysteine
  - – glutathione

Mechanism of prevention of colour formation by ascorbic acid



Control of Enzymatic Browning

- ✓ Enzyme inhibitors
- ✓ Enzyme treatments to modify substrate
  - oxygenases
  - *o*-methyl transferase
  - proteases
- ✓ Complexing agents
  - cyclodextrins