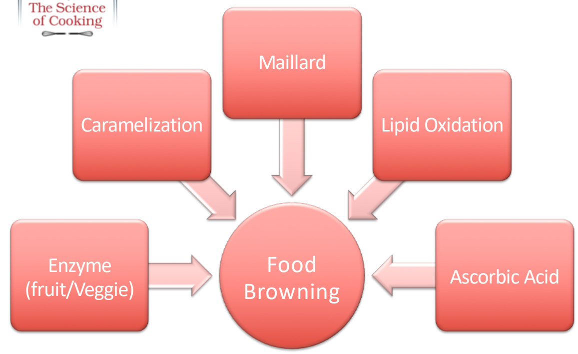
Chapter 6 Browning

The impact of browning reactions make food more attractive and better tasting!

- Both chicken were cooked to a safe temp, chicken on the left was pan fried, the chicken on the right was boiled.

Browning Reactions



The Maillard Reaction

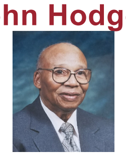
Also known as "Browning"

- Reaction between sugars and amino acids in the presence of high heat
- NOT the same as burning – that just turns food to charcoal

Louis Maillard

French MD - Studied the physiology of kidney disease and reactions between amino acids and simple sugars - 1912

John Hodge



US Oil Chemist – Defined the complicated and still fully undetermined reaction mechanism - 1953

What can be browned?

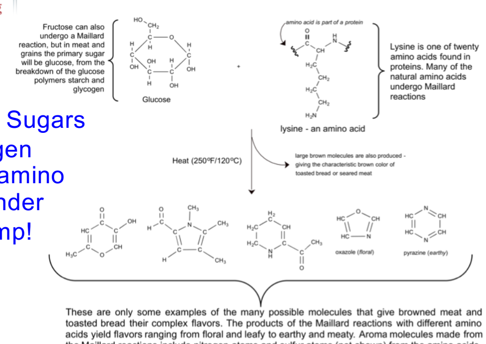
Anything with sugars and amino acids

- Crusty bread, seared meat, vegetables and beer

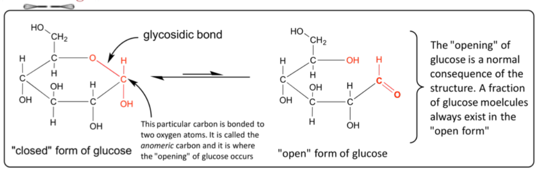
Amino Acid	Volatile Compound	Aroma
Alanine	Acetaldehyde	Roasted barley
Cysteine	Thiol, H_2S	Meaty
Valine	2-Methylpropanal	
Leucine	3-Methylbutanal	Cheesy
Lysine		Bread-like
Methionine	Methional	

Maillard – sugar and protein

Reducing Sugars and nitrogen atoms of amino acids – under higher temp!



Reducing Sugars…????



Simple monosaccharides and many disaccharides can "open" and "close"

- The carbon involved in opening and closing is an anomeric carbon. When in the "open" form, the C=O (carbonyl group) can react with nitrogen atoms from proteins
- *If the oxygen atom bound to anomeric carbon is involved in a bond with another atom besides H, the sugar can no longer "open"*

Where do these reactants come from?

Sugar – Simple sugars (carbohydrates) found in many foods. Some sugars brown better than others – complex carbohydrates do not brown as well (reducing sugar…)

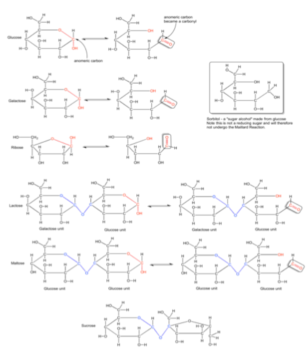
- Ribose – important for vitamins and making DNA; meat and mushrooms are rich in this sugar
- Glucose: found in pasta cereals and rice
- Lactose – milk sugar

Ribose the most reactive sugar

Sugars that "open" aka reducing sugars

Monosaccharides are more reactive than disaccharides

Pentoses>hexoses> disaccharides



Amino acids and sugars – provide diverse products!

20 common amino acids

- 18 have one nitrogen
- 2 have two nitrogen atoms

8 commonly found reducing sugars

There are several reaction paths after amadori product

>576 different possible Maillard reaction products.

Think about which foods are rich in various sugars or amino acids/peptides/proteins

– the kinds of flavors are nearly unending!

Not each reaction pair is the same

Sugars and amino acids were heated for 10 min

Brown product was measured at 420nm

Note: some combinations are more "reactive" than others…

Five-carbon sugars (e.g. ribose) brown faster than glucose
Lactose (milk sugar) also browns very well
Sucrose and glucose brown less efficiently than some sugars

Free amino acids react faster than proteins

Lysine and ribose are the most reactive pairing

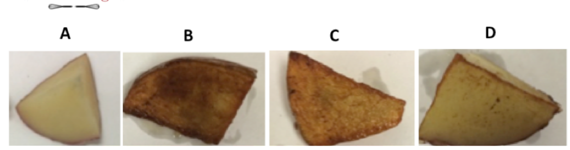
Egg washes provide proteins to carbo-rich foods like bread

Whey is rich in lysine and used for browning enhancer

Ribose is produced in aged meat from the breakdown of ATP and DNA/RNA (nucleotides)

Cysteine and ribose produces brown meaty flavors

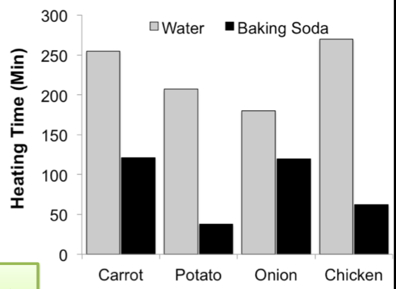
pH and temp alter Maillard



Potatoes dipped in a dilute solution of sugar (ribose) and an amino acid was lightly fried for 3 min and 45 second. A. Water control - no sugar or amino acid. B. Ribose-Leucine, C. Ribose-Lysine, and D Ribose-Glycine

Speed up browning with pH!

Baking soda (alkali) increased pH and reduced cooking time to brown food!



Pretzels and some noodles are dipped in lye (strong base; NaOH) to speed browning

Browning doesn't lock in flavor

It makes the flavor!

- searing heat on raw meat creates a savory flavored crust to provide the taste as this is undergoing the Maillard reaction

-Bread in the toaster, causes the sugars in the bread to react with the proteins from the flour – brown toast

-Heat is needed >140°C for reasonable speeds

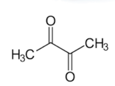
-Water (liquid) slows the process – energy is used to boil/evaporate the water rather than provide energy to reaction

Products of the reaction…

Amino acid drives the ultimate end product – glycine bearlike odors, valine rye-bread smalls, cysteine is responsible for meat and cracker aromas

The Maillard reaction is responsible for many colors and flavors in foodstuffs:

•the browning of bread into toast
•the color of beer, chocolate, coffee, and maple syrup
•the flavor of roast meat
•the color of dried or condensed milk
•6-acetyl-1,2,3,4-tetrahydropyridine is responsible for the biscuit or cracker-like odor present in baked goods like bread, popcorn, tortilla products.
•2-acetyl-1-pyrroline flavors aromatic varieties of cooked rice. Both compounds have odor thresholds below 0.06 ng/l.

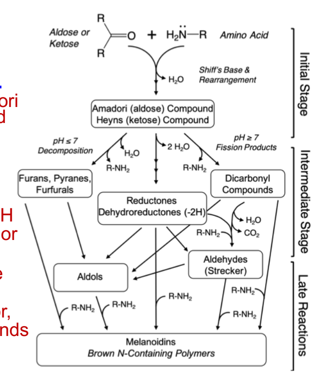


2,3-butanedione
aka diacetyl

Maillard – Detailed Reaction

Three phases (Hodge defn)

- Each starts with an Amadori or Heyns intermediate and unstable glycoslamine
- Amadori rearrangement produces ketose/aldose compounds
- Next phase depends on pH resulting in a dehydration or fission
- Late reactions can involve long polymers or intermediates of dark color, aroma and flavor compounds

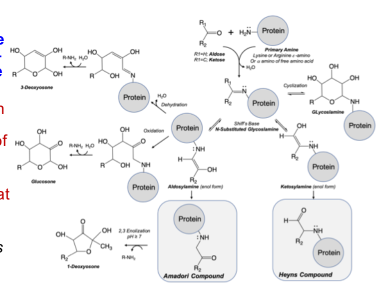


Ketone or Aldehyde

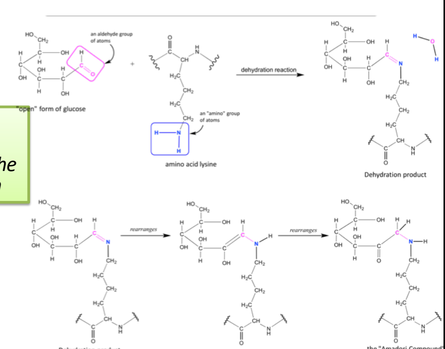
First step – results in one of two products both N—substituted glycoslamine

- Condensation forming Shiff base – can happen with N termini and free amino acids. R-group of Lysine especially reactive
- Peptides can react but at lower rate than free amino acids or Lysines

Free amino acids, peptides or protein intermediates provide wide diversity in final product

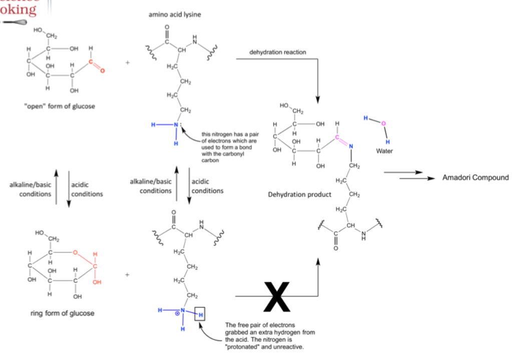


Initial reaction rearranges



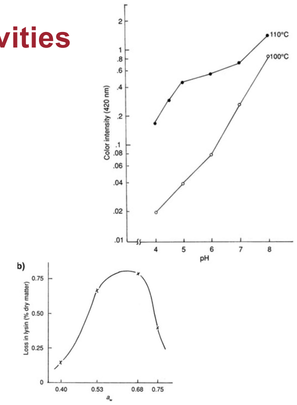
Amadori Compound is an intermediate in the Maillard reaction

Acids slow Maillard – why?



Reactivities

Foods with free amino acids or protein hydrosolyates including coffee, soy, wheat gluten all brown readily due to amino groups.

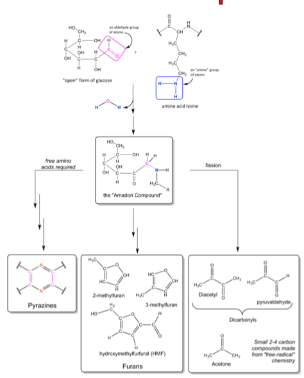


pH and heat influence reactions as does water activity

After the Amadori Compound

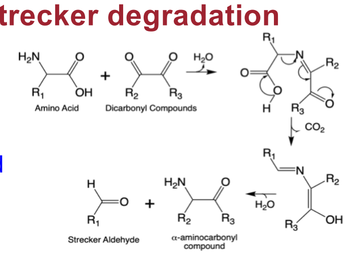
Three possible pathways for final Maillard reaction:

- Fission small compounds for butter and fruity smell
- Dehydration – Furan rings roasted coffee and meat smell
- Free amino acid – aromatic and dark colored products



Strecker degradation

Products impart a key flavor on roasted food profiles like meats, cocoa and coffee beans



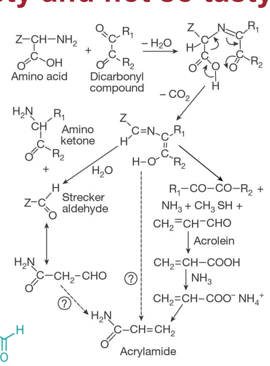
Part of Maillard reaction sequence or a separate additional reaction involving amino acids and their conversion into aldehydes.

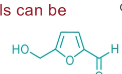
- First step is an oxidation dehydration condensation between aa and carbonyls
- Carbon dioxide is lost with addition of water moving amino group to the dicarbonyl reactant.

Maillard – tasty and not so tasty

Some Maillard products have bitter flavors – often the longer polymer compounds.

- Danger-HMF and acrylamide are produced have toxic principles.
- Asparagineasе reduces starting component in processed food
- HMF found in honey and other foods may both be partially responsible for anti-microbial effects and can relieve sickle cell problems
- BUT HMF at higher levels can be metabolized to potential carcinogens





Hydroxymethylfurfural

How to increase the reaction

Dry food – water inhibits the reaction.

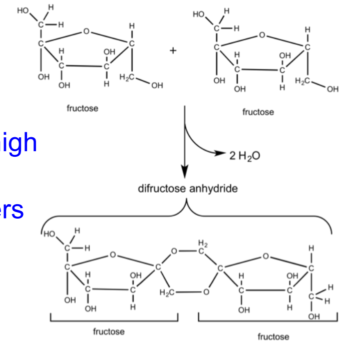
- Pat down the meat with a towel
- Otherwise the food has to heat longer and evaporate the moisture before browning will take place

High Heat – get up to about 300ºF in the oven

Let it sit! – when you move food from a hot grill, the reaction loses it's heat and slows down the browning

Browning - Caramelization

Degradation of mono- & di-saccharides in high heat to form complex polymers by dehydration



Caramelization…

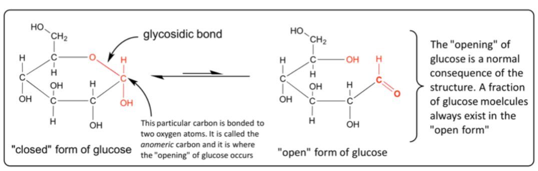
The term "browning" is used for all browning reactions by most food scientists, however popular culture, cookbooks and many web sources get caramelization and Maillard "browning" mixed up – beware!

- Browning (Mallaird) is a result of sugars and amino acids
- Caramelization – provides brown color but is a reaction without enzymes using ONLY sugar and heat – *no amino acids were used in the making of this reaction!*

Requirements – heat and reducing sugars

Table 6-3 Temperature required for caramelization of sugars:

Fructose	110°C
Glucose	160°C
Sucrose	160-180°C
Maltose	180°C.

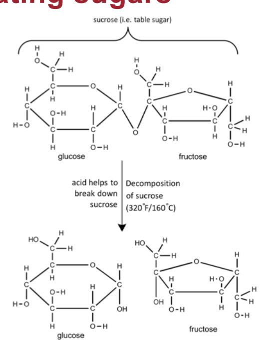


Heating sugars

The C=O needed to start the reaction comes from reducing sugars –

Sucrose – not a reducing sugar, can be converted into its monomers by heat and acid – or enzymatic reaction (invertase).

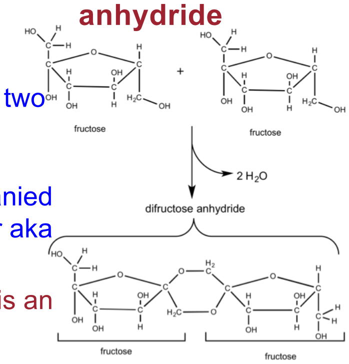
- "inverted" sugar is using heat and acid or invertase to break glycosidic bond
- Honey has mixture of sucrose and fructose and already has a reducing sugar for browning



Start with formation of an anhydride

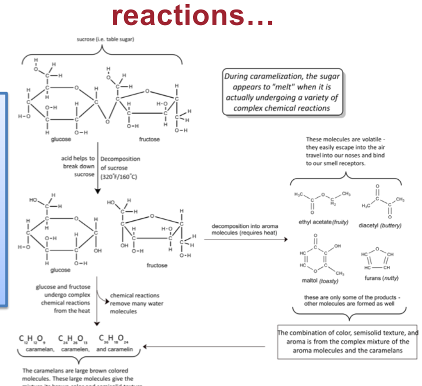
Combination of two molecules is a condensation. When accompanied by loss of water aka dehydration.

- The product is an "anhydryde"



Another complicated set of reactions…

Continued polymerization and many other reactions will form long complicated polymers and some smaller breakdown aromatic products



Caramelization products are classified into three groups

1) Caramelans (12 Carbons) – formed by loss of water after shorter cook timies, smaller molecules with bitter taste and nutty/light-brown color
2) Caramelens (24-36 Carbons) -are larger polymers produced after longer cooking times, loss of 8 H_2O
3) Caramelin (36-125 Carbons) – dark intense flavored large polymers poorly dissolved in water

Classification of Caramelization Products

Table 6-4 Classification of Caramel used in Food and Beverage

Class	Classification	Preparation	Uses
I	Plain or spirit caramel	No ammonium or sulfur compounds can be used	Distilled high alcohol spirits such as whisky
II	Caustic sulfite caramel	High pH (NaOH) and sulfite (SO_3^{2-}) used	Beer, malt bread, sherry, malt vinegars
III	Ammonia caramel	No sulfites but ammonium compounds can be used	Beer, sugar candies, soy sauce,
IV	Sulfite ammonia caramel	Both sulfite and ammonium can be used	Widely used for soft drink and in acidic solutions

50 metric tons of caramelized products produced per year
- Some have concerns about using caramelized food as an additive
- 4-methylimidazole (4-MEI) in very high doses for long periods of time increase risk of cancer in mice… to reach this dose humans would have to consume thousands of products on a regular basis to approach the increased cancer risk found in mice.

Maillard and Caramelization?

Intermediates of both browning reactions will form new complexes with each other – chocolate, coffee and beer all have combination products

Grandma's Caramel

- The choice of staring sugar impacts the ability to start caramelization – sucrose, corn syrup, honey, lemon juice.
- Heat before or after cream starts inverting or caramelization before Maillard
- Added whipped cream brings proteins/amino acids to the party for Maillard reaction

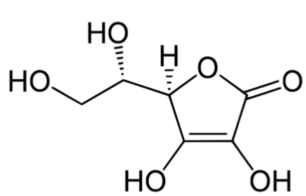
Light caramel (caramelan and little Maillard) – 120ºC/250ºF

180ºC/350ºF gives darker more flavored candy – adding Maillard and caramelen and caramelin to the finished product

Ascorbic Acid Browning

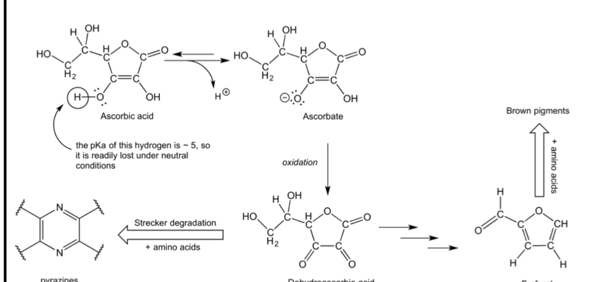
Derived from glucose, ascorbic acid is an acid, an antioxidant, and a vitamin (C).

Found as an acid at high concentrations in fruit juice is responsible for browning color.



Reaction with oxygen produces dehydroascoric acid and amino acids - many possible brown colored outcomes.

- Strecker pathway involves Maillard
- Acid low O2 and acid, produce furfural



How to limit Ascorbic acid browning?

- Remove amino acids via chemical processing
- Limit oxygen (head space and packaging)
- Sulfites (metabisulfite) additives compete with ascorbic acid to limit first reaction

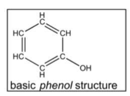
Fruit Browning – TOTALLY DIFFERENT

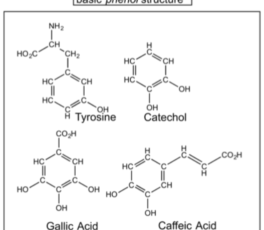
Fruits, vegetables (potatoes, salads…) and even some shellfish, turn brown soon after cutting or just sitting on shelf/counter.

- This is a very different reaction than Mallaird's reaction
- Due to cell walls in plant cells reacting with oxygen
- Reaction is called oxidation and catalyzed by an enzyme – tyrosinase aka phenyloxidase

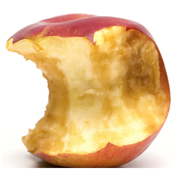
Fruit Browning

Starts with oxidation of cell wall phenols and phenolic acids

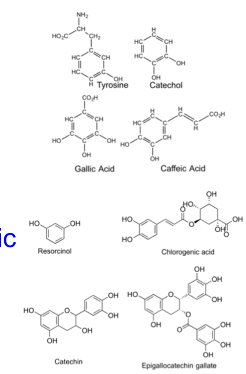




Examples of *phenolics* found in plants

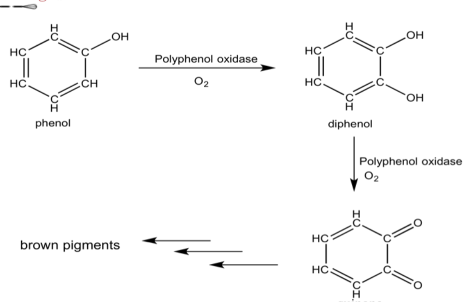


Many Kinds of Plant Phenolics

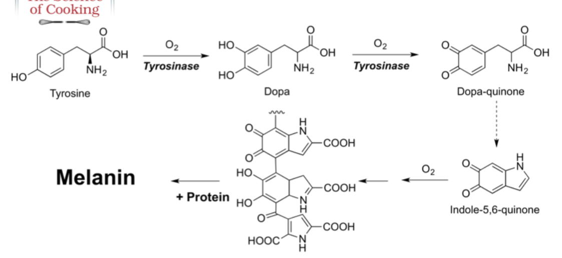


- Simple Phenols: Tyrosine based – catechol & resourcinol
- Acids – gallic & chlorogenic acid
- Flavonoids – two or more benzene rings
- Lignins – long complex ring structures

Polyphenol Oxidase PPO

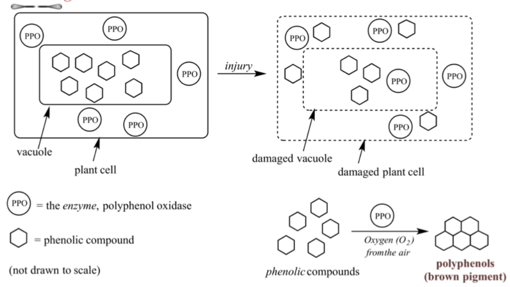


AKA Tyrosinase, catechol oxidase or lactase



Tyrosinase Starts the Conversion of Tyrosine to the Pigment Melanin. One of the metabolic fates of the amino acid tyrosine is to be converted to the dark pigment melanin. The activity of tyrosinease can be influence by temperature.

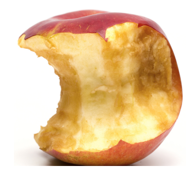
PPO



Damage to plant cells (fruits or vegetables) causes the release of the enzyme polyphenol oxidase (PPO) which can then interact and react with its substrate - the phenolic compounds found on the plant cell wall.

PPO Products

Brown products inhibit mold and plant pathogens and taste bitter to discourage further eating



Genetically Modified Organisms (GMO) apples – Artic Apple, have the 8 different PPO genes silenced to limit browning during shipping (bruising slight cuts).

Stop the browning…

- Organic competitive inhibitors (phenol mimic – guaiacol…)
- Heat denaturing of PPOs: blanching is moderately effective as PPOs are stable
- Food acids – decrease pH slowing reaction
- Ascorbic acid reverses initial reaction
- Calcium salts – NatureSeal uses ascorbic acid and $CaCl_2$