Chapter 6 Browning

The Science of Cooking

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 – cooking reaction

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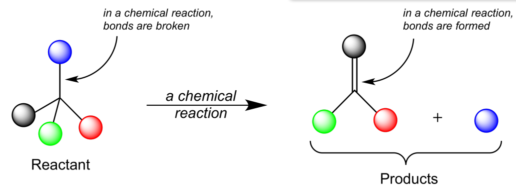
Browning food

- Browning / Maillard
- Fruit and Vegetable Browning
- Caramelization

These are all examples of chemical change – chemical reactions

Kinetics – For a reaction to occur, atoms must collide with enough force and at the right geometry to break and make bonds. *Increasing energy makes this happen!*



Energy Diagram for a Chemical Reaction.

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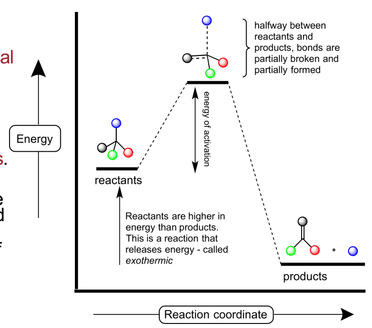
The progress of a chemical reaction is shown on the horizontal axis (reaction coordinate) and the free energy of the substances involved in the reaction is shown on the vertical axis.

- The energy required for the reaction to reach the intermediate (also called a transition state) of the reaction is the energy of activation.
- A spontaneous reaction will end with less free energy than the starting compounds possessed.



Chemical Change

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Adding heat from the flame provides the energy needed for the reaction of oxidation of sugar

- without addition of energy, this reaction will take place very slowly or not at all

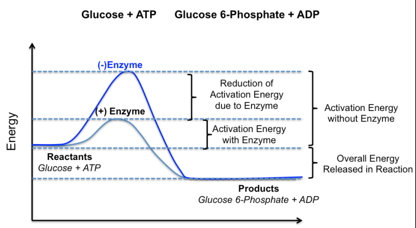
$C_{12}H_{22}O_{11}$ + 12 O_2 -> 11 H_2O + 12 CO_2

Sucrose + Oxygen react to form water and carbon dioxide

Catalysts reduce the activation energy requirement of a reaction.

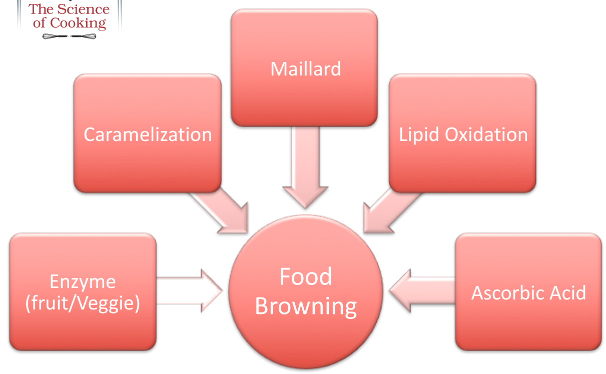
Enzymes (a class of proteins) catalyze reactions – reduce the energy needed to overcome a reaction

– enzymes speed up a reaction at a given temp



Enzymes have limits! – heating protein (food) above 45oC-65oC (113oF-149oF) will denature most enzymes leaving them unable to catalyze a reaction (inactive).

Browning Reactions



The Maillard Reaction

Also known as "Browning"

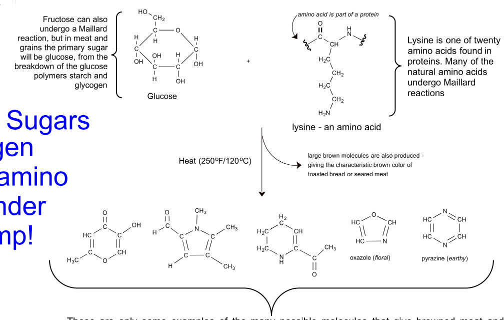
- Reaction between sugars and amino acids in the presence of high heat
- NOT the same as burning – that just turns food to charcoal

What can be browned?

Anything with sugars and amino acids

- Crusty bread, seared meat, vegetables and beer

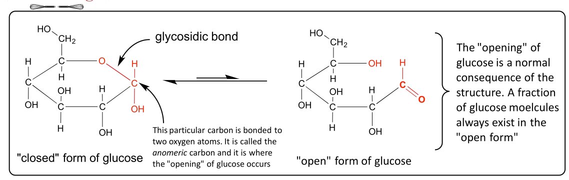
Maillard – sugar and protein



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

These are only some examples of the many possible molecules that give browned meat and toasted bread their complex flavors. The products of the Maillard reactions with different amino acids yield flavors ranging from floral and leafy to earthy and meaty. Aroma molecules made from the Maillard reactions include nitrogen atoms and sulfur atoms (not shown) from the amino acids.

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?

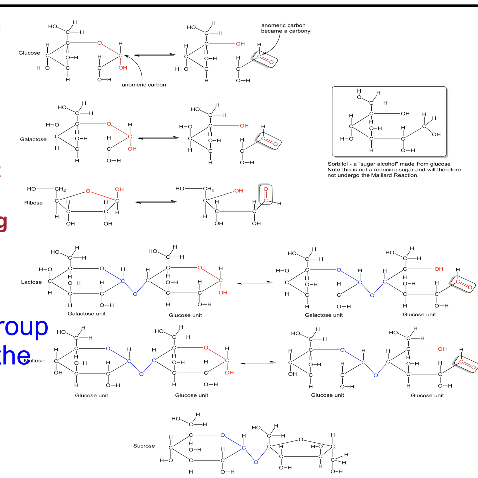
Sugar – Simple sugars (carbohydrates) found in many foods. Some sugars brown better than others – complex carbohydrates do not brown as well (reducing sugar…)

- 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

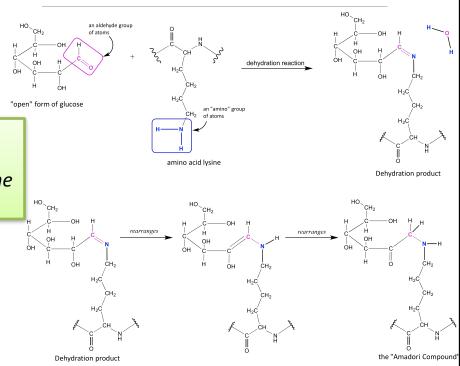
Sugars that "open" aka reducing sugars

Find the carbonyl group to identify the anomeric carbon



Initial reaction rearranges

Amadori Compound is an intermediate in the Maillard reaction



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

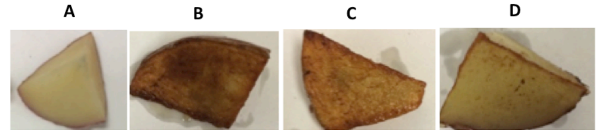
Whey is rich in lysine and used for browning enhancer

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

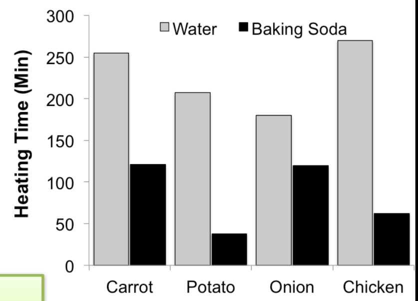
A B C D



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

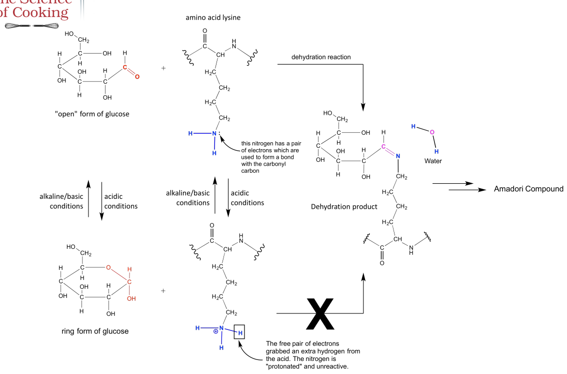
Speed up browning with pH!

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

Acids slow Maillard – why?



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

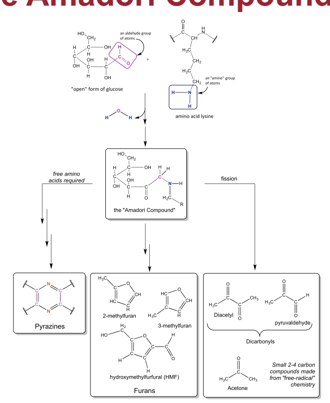
-Heat is needed >140ºC for reasonable speeds

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

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



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Products of the reaction…

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.

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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 300°F 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

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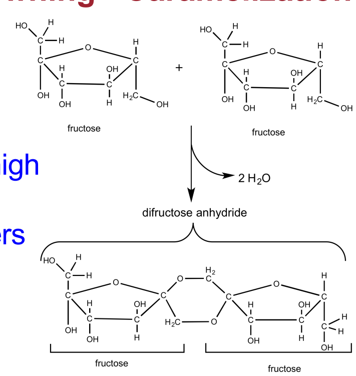
Browning - Caramelization

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



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Caramelization…

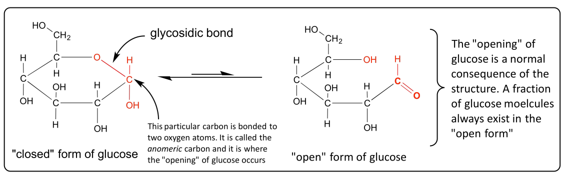
The term "browning" is used for all browning reactions by most food scientists, however popular culture, cookbooks and many web sources get caramelization and Maillard "browning" mixed up – beware!

- 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.

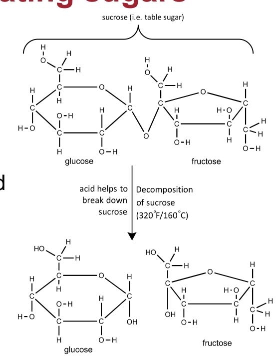


Heating sugars

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).

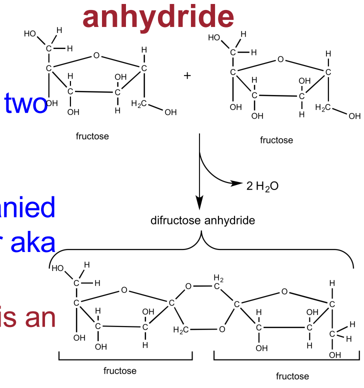
- "inverted" sugar is using heat and acid or invertase to break glycosidic bond
- Honey has mixture of sucrose and fructose and already has a reducing sugar for browning



Start with formation of an anhydride

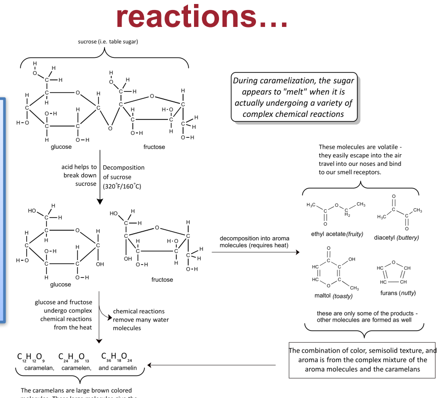
Combination of two molecules is a condensation. When accompanied by loss of water aka dehydration.

- 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

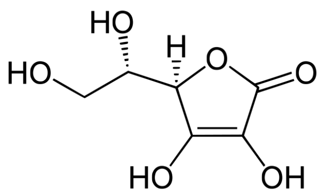
Light caramel (caramelan and little Maillard) – 120°C/250°F

180°C/350°F gives darker more flavored candy – adding Maillard and caramelen and caramelin to the finished product

Ascorbic Acid Browning

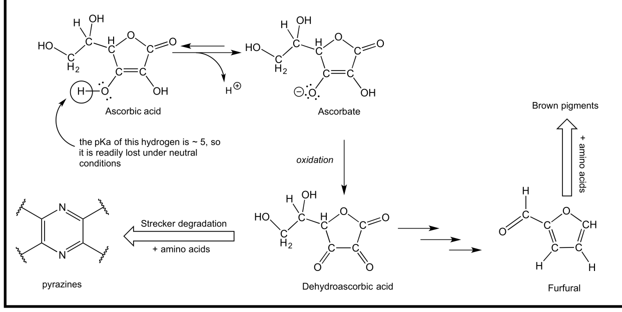
Derived from glucose, ascorbic acid is an acid, an antioxidant, and a vitamin (C).

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

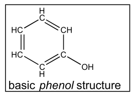
Fruit Browning – TOTALLY DIFFERENT

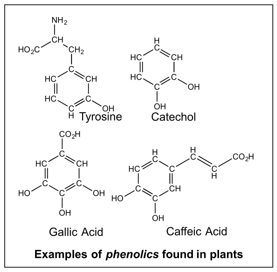
Fruits, vegetables (potatoes, salads…) and even some shellfish, turn brown soon after cutting or just sitting on shelf/counter.

- 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

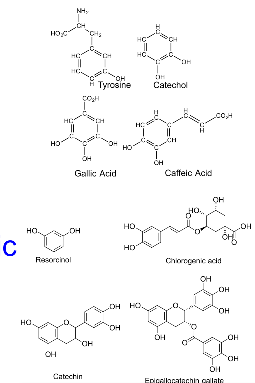
Starts with oxidation of cell wall phenols and phenolic acids





Many Kinds of Plant Phenolics

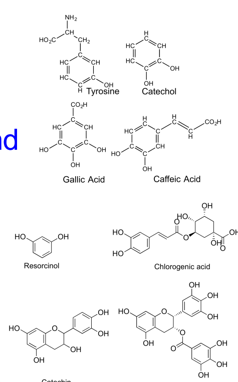
- Simple Phenols: Tyrosine based – catechol & resourcinol
- Acids – gallic & chlorogenic acid
- Flavonoids – two or more benzene rings
- Lignins – long complex ring structures



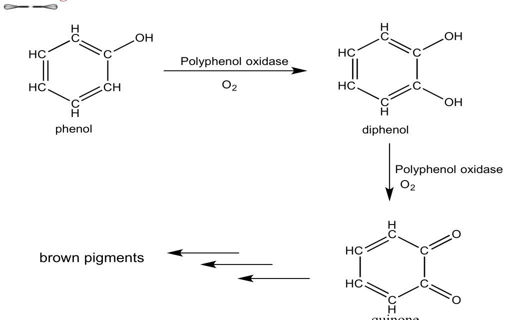
Can you identify the phenol in each class? What are the other functional groups?

Examples of Plant Phenolics

- Gallic acid – tea, grapes and apples
- Chlorogenic acid – coffee beans
- Resorcinol – grape skins
- Others in tea leaves and other plant and herbs.



Polyphenol Oxidase PPO



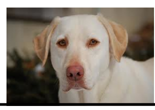
AKA Tyrosinase, catechol oxidase or lactase

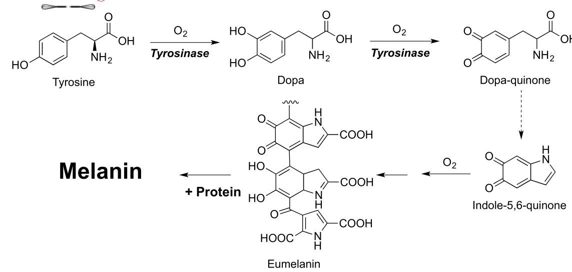
Tyrosinase / Phenoloxidase

Enzyme found in plant cells but also in some other interesting places

•Noses of dogs, Siamese cats, Himalayan rabbits

- These animals have a variant gene (mutated) with two glycine amino acid in place of arginine and tryptophan
- Mutant enzyme in animals is cold sensitive – the enzyme does not work when it is cool
- When cold, the enzyme can work. Normal gene continues to function and converts tyrosine (non-colored) to melanin (black pigment).
- The mutant gene is "expressed or active" in some body parts.
- Thus animals left outside or their cold noses over a longer period of time turn light colored due to lack of continued malanin production





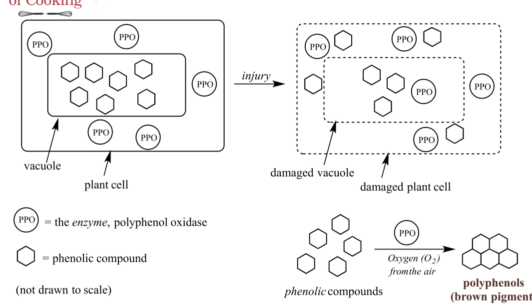
Tyrosinase Starts the Conversion of Tyrosine to the Pigment Melanin. One of the metabolic fates of the amino acid tyrosine is to be converted to the dark pigment melanin. The activity of tyrosinease can be influence by temperature.

Tyrosinase / Phenoloxidase

What does this have to do with food?

- Plants are helpless and can not run away or defend themselves
  - When the skin of fruit or vegetables are punctured, bugs and microbes can and will take over and kill the plant
  - Plant chemical warfare to the rescue again!
  - Polyphenols (wide variety of them naturally exist) are found on surface of many plant cells or packages away from the rest of the plant cell in vacuoles
    - These molecules give color and flavor to apples, teas and other fruit and veggie characteristics
  - Browning enzymes (phenoloxidase and tyrosinase) are stored away from phenols – until plant is damaged where the two can mix!

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 $CaCl_2$