Barrett 98

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SPECIAL TREATMENTS TO MAINTAIN PRODUCT QUALITY

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A number of special treatments may be utilized to maintain the quality and shelf life of fresh-cut products. In this presentation, prevention of oxidative browning and use of calcium as a firming agent will be highlighted.

Prevention of Oxidative Browning

Oxidative browning, which is catalyzed by the action of the enzyme polyphenol oxidase (PPO) on phenolics (tannins), is an ever-present problem in both fruit and vegetable postharvest handling. In cut, bruised or senescent horticultural products this oxidative reaction occurs more readily. Therefore, fresh-cut products are particularly susceptible to oxidative browning reactions.

There are several means of controlling browning in fruits and vegetables. In theory, PPO catalyzed browning may be prevented by:

1. heat inactivation of the enzyme
2. exclusion or removal of one or both substrates (oxygen and phenols)
3. lowering pH to 2 or more units below pH optimum
4. reaction-inactivation of the enzyme
5. addition of inhibitors of PPO

Inhibitors of PPO may be grouped according to their mode of action although some compounds may belong to more than one group. Inhibition may result from chelation of the prosthetic group (copper) of the enzyme, competition for the substrate, or by interaction with the products of the reaction.

The most common methods for controlling oxidative (enzymic) browning, both in industry and the laboratory, is by addition of reducing agents such as SO_2, metabisulfite and/or ascorbic acid. These compounds prevent browning by reducing the enzymatically formed quinones back to their parent o-diphenols, however they are consumed in the process.

Sulfurous acid, sulfur dioxide and metabisulfite have been utilized for many years and are extremely satisfactory agents for both the prevention of browning and the prevention of microbial growth. A sulfurous acid dip for 2-5 minutes in a solution of 2000-4000 ppm SO_2 effectively prevents peeled peaches, nectarines, apples, apricots and cherries from browning (Woodroof and Luh, 1986). However, residual concentration of SO_2 impart an objectional taste in some products and exposure to SO_2 may cause health problems in persons with respiratory illnesses.

Use of acid also prevents browning. The enzyme, polyphenol oxidase, has a pH optimum for activity which is close to neutrality, e.g. pH 6-7. Therefore, in lower pH products or products to which acid has been added, oxidative browning will proceed at a much slower rate. Acids typically used to raise acidity include citric, fumaric, malic, tartaric, acetic, phosphoric, lactic, tartaric and ascorbic.

Ascorbic acid is one of the primary agents used to prevent oxidative browning, not only because it lowers the pH of the product, but because it plays the unique role of a reducing agent. Ascorbic acid reduces oxidized phenolic compounds back to their reduced form, thereby preventing browning. The European community uses ascorbic acid to a large degree in fruit and beverage processing. Ascorbic acid is commonly added as a 1% solution to prevent browning at the cut surface of numerous horticultural products. In addition, ascorbic acid is often used in conjuction with citric acid or salt on horticultural commodities.

The addition of sugar, either dry or syrup, is another means of preventing browning in peeled and cut fruits or vegetables. Oxygen is required for the browning reaction to occur and the use of sugars lowers the amount of oxygen available. Sugar also helps in maintaining flavor and texture, in addition to color. To be the most effective in preserving fruit color, flavor and texture, sugar may be used in conjunction with citric and ascorbic acid.

Vacuum packaging or addition of antioxidants are another means of reducing oxidative browning. As mentioned, oxygen is an absolute requirement for browning to occur, therefore elimination of as much oxygen as possible from the package will assist in preventing browning. Both oil and water soluble antioxidants are utilized by the food processing industry. It should be noted that, depending on film or package permeability, oxygen from the environment will find its way back in to the product vicinity eventually.

Use of Calcium as a Firming Agent

The textural properties of plant tissues are determined by the turgor pressure within individual cells, the structural integrity of the cell walls, the rigidity of the middle lamella "cement" that holds plant cells together and the activity of softening enzymes. As horticultural products mature, their textural integrity weakens due to both loss of turgor pressure and breakdown of cell wall and middle lamella structure. In addition, thermal treatments such as blanching also result in a breakdown of the middle lamella. Calcium functions as a bridge to tighten the network of cell walls and middle lamella and to impart great firmness to plant tissue.

It is a common commercial practice to add low concentrations of calcium salts to horticultural products prior to processing in order to improve textural properties. Dips of between 0.5-1.0% calcium chloride may impart significant improvement in the firmness of the final product and have been utilized for fresh-cut apple, pear and other products.

Textural breakdown is often affected by the enzymes polygalacturonase and pectin esterase. Polygalacturonase (PG) hydrolyzes glycosidic bonds in the pectin polymer, which results in middle lamella and cell wall degradation and hence, loss of texture. Pectin esterase (PE) may have positive and negative effects on texture in that it hydrolzyes methyl esters on the galacturonic acid residues which constitute pectin. This both allows calcium to bind the free carboxyl groups, forming tighter bridges between adjacent pectin polymers, and also allows for easy PG access to glycosidic bonds. Judicious activation of PE in a calcium-rich environment may result in firmer textured products.

References:

Lee, C.Y. and JR. Whitaker. 1995. Enzymatic Browning and Its Prevention. ACS Symposium Series 600, Washington D.C. X

Luh, B.S. and J.G. Woodroof. 1975. Commercial Vegetable Processing. AVI Publishing Company, Westport, CN.

Woodroof, J.G. and B.S. Luh. 1986. Commercial Fruit Processing. AVI Publishing Company, Westport, CN.

Prevention of oxidative browning

- Refrigeration (slows enzymatic reactions)
- Inhibition of phenylalanine ammonia-lyase (in vegetables)
- Inhibition of polyphenol oxidases
- Exclusion of oxygen (CA, MAP, edible films)
- Use of reducing agents (ascorbic acid, etc.)
- Other chemical agents

Enzymatic Browning

Phenylalanine $\xrightarrow{PAL}$ cinnaminc acid → → other phenolics

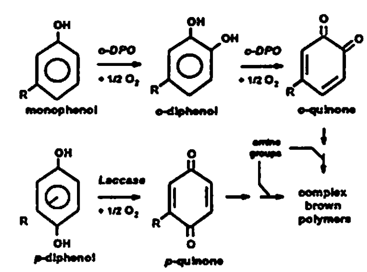
$\downarrow + O_2$ (PPO) o-Diphenol oxidase, Laccase

complex brown polymers ← ← quinones

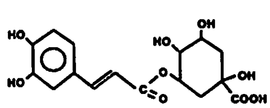
PAL = phenylalanine ammonia-lyase
PPO = polyphenol oxidase

Properties of Polyphenol oxidase (PPO)

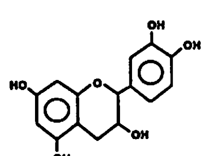
- Generic term for enzymes catalyzing the oxidation of mono- or diphenolic compounds to form complex brown compounds.
- 2 enzyme groups: o-diphenol oxidases and laccases
- Enzymes found in plants, microorganisms and animals
- Requires oxygen for reaction
- In plants, active pH range from about 6 to 7
- Contains copper as prosthetic group
- Somewhat heat unstable
- Enzyme localized in plastids
- Genes have been cloned



Simple phenolic compounds (colorless)



Chlorogenic acid



Catechin

Enzymatic Browning

Phenylalanine $\xrightarrow{PAL}$ cinnaminc acid → → other phenolics

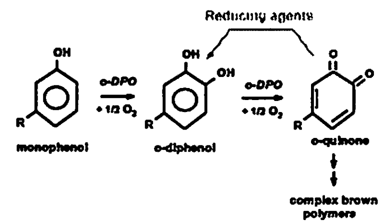
$\downarrow + O_2$ (PPO) o-Diphenol oxidase, Laccase

complex brown polymers ← ← quinones

PAL = phenylalanine ammonia-lyase
PPO = polyphenol oxidase

Prevention of browning in vegetables

- CA and MAP (very low O_2 required to inhibit browning in lettuce)
- Heat shock treatment (inhibits PAL)
- Chemical treatments



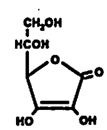
Sulfites

Na_2SO_3
$NaHSO_3$
SO_2

Inhibit polyphenol oxidase
React with PPO intermediates to form colorless products

- no longer GRAS for fruits and vegetables served raw, sold raw or presented to customer as raw
- foods containing detectable level of sulfiting agent (10 ppm) must label contents

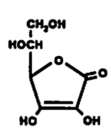
Ascorbic acid



Reduces quinones to phenolic compounds

- acid and salt forms used
- salt (neutral pH) form may be more active
- water soluble
- often used in combination with citric acid

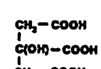
Erythorbic Acid



Reduces quinones to phenolic compounds

- Isomer of ascorbic acid
- Acid and sodium salt used
- Sodium salt may be more effective
- Cheaper (1/5 cost) than ascorbic acid

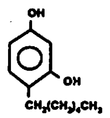
Citric acid



Inhibits PPO by reducing pH and chelating copper prosthetic group. Also inhibits oxidation by chelating other metal ions

- synergistic with ascorbic acid

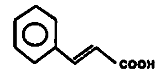
4-Hexylresorcinol



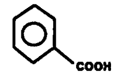
Inhibits polyphenol oxidase

- approved for use on shrimp to control browning

Cinnamic and benzoic acids



t-cinnamic acid

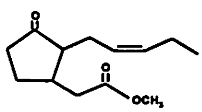


benzoic acid

Inhibit o-diphenol oxidase by acting as substrate analogues

- approved for food use

Methyl jasmonate



Inhibits browning

- natural product of all plants
- very slightly soluble in water (soluble in alcohol)
- can be applied as a gas

Other anti-browning agents

1. Ethylene diamine tetraacetic acid (EDTA)
   Inhibits PPO by chelating copper in prosthetic group. Approved
2. Polyvinylpolypyrollidone (PVPP)
   Binds phenolic compounds. Is insoluble. Approved for apple juice fining agent.
3. Carbon monoxide
   Inhibits PPO by binding to copper in prosthetic group. Approved although is dangerous to handle during treatment.
4. Pineapple juice

Effect of calcium upon texture

- Calcium makes cell walls more rigid by forming ionic bonds between pectin molecules with negative charge.
- Pectinesterase can cleave methylesters to form more free carboxylic acid groups allowing more Ca2+ to bind creating stronger walls.

$\vdash COO^- \; Ca^{2+} \; {}^-OOC \dashv$

$\vdash COOCH_3 \; CH_3OOC \dashv$