Physiology and biochemistry of aroma and off-odors in fresh-cut produce

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Importance of flavor
• Flavor is a human perception
• Good flavor is needed to achieve consumer satisfaction
• Acceptable flavor is often lost prior to decline in visual appearance
• Maintaining flavor in fresh-cut produce can be challenging

Role of aroma volatiles
• Provide unique flavor characteristics
  – 70-80% of flavor attributed to volatiles
• Most dynamic component
  – Can change dramatically during storage and marketing
  – Product maturity /ripening
  – Altered by storage environment
• Indicator of quality
  – Sign of spoilage

Olfaction (Smell)
• Interaction of volatile compounds with olfactory receptors in the nasal cavity
  – Orthonasal – odor/aroma
  – Retronasal – flavor
• Over 8,000 volatile compounds in food
• Fewer than 1,000 contribute to odor
  – ppb to ppt or less

Aroma of fresh-cut produce
• Chemistry
• Biochemistry
• Mechanisms controlling aroma
• Factors affecting aroma
  – Initial Quality
  – Cutting
  – Packaging

Fresh fruits and vegetables
• Diverse
  – Morphology
  – Physiology
  – Chemistry

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Fresh fruits and vegetables
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  – Chemistry
Volatile chemistry

- Analyzed using gas chromatography (GC)
  - Mass spectroscopy
  - Olfactory detection
- Volatile profiles
  - Hundreds of compounds
  - Wide range of concentrations

### GC volatile profiles

![Graph showing volatile profiles for Strawberry, Raspberry, and Blueberry]

### Olfactory thresholds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Olfactory Threshold (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>10,000 - 100,000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>100 - 1,000&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methyl butanoate</td>
<td>1.0 - 10&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Linalool</td>
<td>0.1 - 1.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethyl hexanoate</td>
<td>0.01 - 0.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethyl butanoate</td>
<td>0.001 - 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
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<sup>a</sup>Devo et al. (1990)  
<sup>b</sup>Larson and Pool (1992)

### Aroma impact compounds

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<tr>
<th>Compound Structure</th>
<th>Crop</th>
<th>Aroma*</th>
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<tr>
<td>Terpenoids</td>
<td></td>
<td></td>
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<tr>
<td>α-Terpineol</td>
<td>Lime</td>
<td>Pine, tangerine, lilac, citrus</td>
</tr>
<tr>
<td>α-Ionone</td>
<td>Raspberry</td>
<td>Sweet, woody, floral, violet, tropical fruity</td>
</tr>
<tr>
<td>Geosmin</td>
<td>Red beet</td>
<td>Freshly plowed soil, earthy</td>
</tr>
</tbody>
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<tr>
<th>Esters</th>
<th></th>
<th></th>
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<tr>
<td>Ethyl 2-methylbutyrate</td>
<td>Apple</td>
<td>Fruity, estery</td>
</tr>
<tr>
<td>Allyl caproate</td>
<td>Pineapple</td>
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### Aldehydes

- Benzaldehyde
- (1)-2-Nonenal
- (2)-3-Hexenal

### Ketones

- 1-Octen-3-one
- Allylpropanone

### Alcohols

- (2,2,6,6-Tetramethylheptanol

- www.thegoodscentscompany.com

### Lactones

- γ-Octalactone

### Acids

- γ-Octalactone

### Furanoids

- γ-Octalactone

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<td>γ-Octalactone</td>
<td>Peach</td>
<td>Creamy, fruity, coconut, peach</td>
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<td>Celery</td>
<td>Herbal, colery</td>
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<td>Strawberry</td>
<td>Sweet, cotton candy, caramel, strawberry</td>
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<tr>
<td>Sulfur compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td><img src="image" alt="Structure" /></td>
<td>Asparagus, cabbage, corn</td>
<td>Sulfury, onion, sweet corn, cabbage</td>
</tr>
<tr>
<td>2-Isobutyl thiazole</td>
<td><img src="image" alt="Structure" /></td>
<td>Tomato</td>
<td>Green, wasabi, privet, tomato leaf</td>
</tr>
<tr>
<td>4-methylthiobutyl isothiocyanate</td>
<td><img src="image" alt="Structure" /></td>
<td>Broccoli</td>
<td>Cabbage, radish</td>
</tr>
<tr>
<td>Propyl propenethiosulfonate</td>
<td><img src="image" alt="Structure" /></td>
<td>Onion</td>
<td>Roasted alliaceous</td>
</tr>
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*www.thegoodscentscompany.com

Primary pathways/precursors

- Terpenoids pathway
  - Isoprene (C_5)
- Fatty acids
  - β-oxidation
  - Lipoxygenase (LOX) pathway
- Amino acids
- Carotenoids
  - norisoprenoids

Terpenoid synthesis

Mevalonic Acid Pathway (MVA) - Cytosol

- C_5
  - Isopentenyl diphosphate (IPP)

Methylenerythritol Pathway (MEP) - Plastid

- C_10 Monoterpenes
- C_15 Sesquiterpenes
- C_30 Triterpenes
- C_40 Tetraterpenes

Norisoprenoids → Carotenoids

β-Oxidation

- Straight-chain alcohols
- Aldehydes
- Straight-chain esters
- Acids
- Esters
- Lactones

Fatty acids

- C_{14}
- C_{12}
- C_{10}
- C_9
- C_8
- C_6
- C_4

Amino acids

- Provide an array of backbones for volatile synthesis
  - Aliphatic
  - Branched
  - Aromatic
- Source of N and S
- Precursors
  - Alcohols
  - Acids
  - Esters
  - Glucosinolates/isothiocyanates
  - Sulphoxides
Fermentation

Other Volatiles → CHO → Glycolysis → PDC → Acetaldehyde → ADH → Acetate esters → Ethanol → AAT → Ethyl esters

Krebs Cycle + Oxidative Phosphorylation → Mitochondria

Induction of fermentation

• Ripening
• Senescence
• Stress
  – Low O₂ / high CO₂
  – Heat
  – Chilling
  – Freezing
  – Water stress
  – Ozone

Mechanisms of aroma change

• Metabolism
  – Synthesis
  – Catabolism
• Diffusion
  – Gain
  – Loss

Initial Quality

• Cultivar selection
• Production practices
  – Fertilization
  – Spacing
  – Pruning
• Environmental stress
  – Water
  – Temperature

Postharvest treatments

• Treatments prior to processing affect aroma
  – Manipulation of ripening
  – Temperature management
  – Postharvest treatments
  – Controlled atmosphere (CA) storage

Postharvest ripening – ‘Kensington Pride’ mango

• Fruit ripened at 21 °C to 1.5 kg cm⁻² firmness
• Total volatiles highest in mature green fruit
  – Monoterpenes
• Ripe fruit had more esters

Lalel et al., 2003
**Heat treatments - Broccoli**

- Hot water dips extends shelf-life
  - Delays yellowing
  - Reduces decay
- Off-odour produced by 52°C – 2 or 3 min treatment

**CA Storage**

- Prolonged storage in CA may reduce fruit aroma
- Low O₂ concentrations can increase aroma loss
- May partially recover aroma by holding in air

**Package atmospheres**

- ‘Ambrosia’ Slices packaged in PE zip-loc bags
  - OTR – 3500 mL m⁻² d⁻¹
- O₂ decreased to:
  - 2.0 kPa

**Cutting**

- Alters physiology
  - Respiration
  - Volatile synthesis
- Induces production of secondary volatiles
- Removes diffusional barriers
  - Increases aroma loss
Product respiration

- Shredding cabbage
- Increased respiration 5-fold
- After 9 days remained 3.5-fold greater

Product respiration – ‘Gala’ apples

- Doubles CO₂ production
- Sustained over 48 hours

Ester release from cut apples

- Headspace ester increases with maturity
- Cutting stimulates ester production/release
  - Greatest in early harvest fruit
  - Lower MW esters

Induced fermentation

- Both ethanol and ethyl acetate increased in response to cutting
- Rise in ethanol transient
- Fermentation alters ester composition

Secondary volatile formation - Cut onion

- Volatile sulfur compounds are formed after cutting
  - Reaction of alliinase and cysteine sulfoxides
- Products are unstable and continue to react

Packaging

- Integral part of the fresh-cut product
- Physical protection
- Atmosphere modification (MAP)
- Impact aroma
Modified Atmosphere Packaging (MAP)

Package atmosphere effects

• 'Gala' apples - 12 slices/apple
• Sealed in polymer bags
  – Solid film (S) - multi-layered polyolefin
    • OTR – 660 mL m⁻² d⁻¹
    • CO₂ TR – 3430 mL m⁻² d⁻¹
  – Micro-perforated film (P) - 2-100 µm holes/package
    • OTR – 3740 mL m⁻² d⁻¹
    • CO₂ TR – 3230 mL m⁻² d⁻¹
• Stored at 5°C for 21 d

Package atmosphere composition

• Equilibrium package atmospheres
  – Solid film
    • 3 kPa O₂
    • 6 kPa CO₂
  – Micro-perforated film
    • 16 kPa O₂
    • 6 kPa CO₂

Sensory analysis

PCA of volatile composition

Raspberry volatiles
Volatiles

- Total variation, 58%

- Score 1, 35%

- Score 2, 23%

Monoterpenes
Sesquiterpenes
C13 norisoprenoids
Esters
Ketones
Aldehydes
Alkenes
Alcohol
Total volatiles

Anaerobic volatiles

- Induced by anaerobic conditions/stress

  - Ethanol
    - Air-stored doubled
    - 2% O2/12.5% CO2, 15-fold increase
    - 12.5% CO2, 10-fold increase
    - 2% O2 cultivar dependent
  
  - Acetaldehyde
    - 2% O2/12.5% CO2, 3-fold increase
    - 12.5% CO2, 2.5-fold increase
    - 2% O2 increase similar to air-stored

Avoid injurious atmospheres in MAP

- Low O2 and/or high CO2 atmospheres may induce off-odors
  
  - Ethanol and acetaldehyde universally produced under stress
    - Not directly responsible for off-odor
  
  - Off-odor development variable among commodities

Broccoli anaerobic off-odor

- Strong off-odor induced by low O2
  - Rotten cabbage
  
  - Identified methanethiol as primary mal-odorant
    - 1 - Hydrogen sulfide
    - 2 - Methanethiol
    - 3 - Dimethyl sulfide
    - 4 - Dimethyl disulfide

Forney et al., 1991
Variable response of fresh-cut *Brassicas* to low O₂

![Graph showing concentration of various compounds in headspace](image)

**Interaction of packaging materials**

- Permeation of aroma compounds
- Adsorption (scalping) of volatiles
- Determines diffusional loss
- Dependent on polymer chemistry
  - Polyolefins – high affinity for volatiles
  - Polyethylene, polypropylene
  - Polyesters – weak affinity for volatiles
  - Polylactic acid (PLA)

**Packaging effects on aroma retention - Onions**

- Sealed PLA maintained headspace volatiles
  - 9/10 S-volatiles significantly greater in sealed PLA
  - Fresh onion aroma maintained for 12 days in sealed PLA

**Diced yellow onions – Loss of volatiles**

- Sealed PLA maintained headspace volatiles
  - 8 S-volatiles significantly greater in Sealed PLA-stored onions

**Conclusions**

- Fresh-cut produce aroma is complex and dynamic
  - Chemistry, biochemistry and human perception
- Cutting induces metabolic changes that affect aroma volatiles and enhances diffusional losses
- Stress can induce fermentation and production of off-odors
- Packaging can alter aroma by atmosphere modification or affecting diffusional loss
Conclusions

• To optimize the aroma of fresh-cut produce:
  – Start with high quality product
  – Minimize stress during processing and marketing
  – Maintain an environment conducive to aroma maintenance