FOOD CHEMISTRY

FLAVORS

Introduction

What's so interesting about flavors in food?

- **Health & well being**

  People eat what they like, not what's good for them

  i.e. low fat, low calorie, Ca fortified food

- **Illness**

  Causing changes in perceptions until starve to death

  i.e. influenza, coughing, cancer

- **Commercial value**
  - **People buy foods that taste good**
  - **Number one complaint from customers is flavor (off-flavors)**

What is flavor?

- **In the past**

  Aroma, taste & chemesthetic responses (tongue, mouth, lips, throat, olfactory region)

- **Now**

  Complex interaction of taste, smell. Appearance, feeling, exposure, etc.

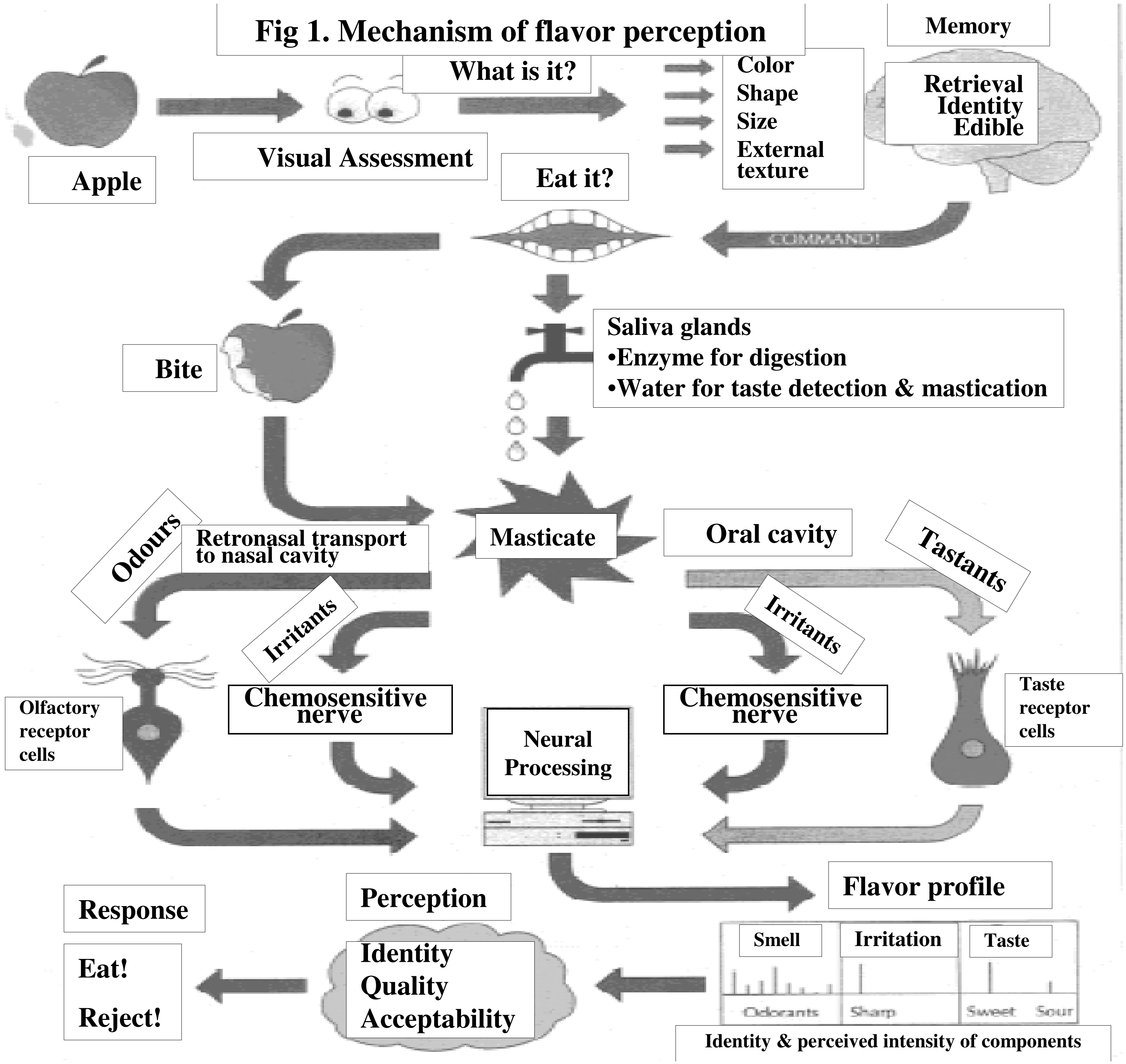
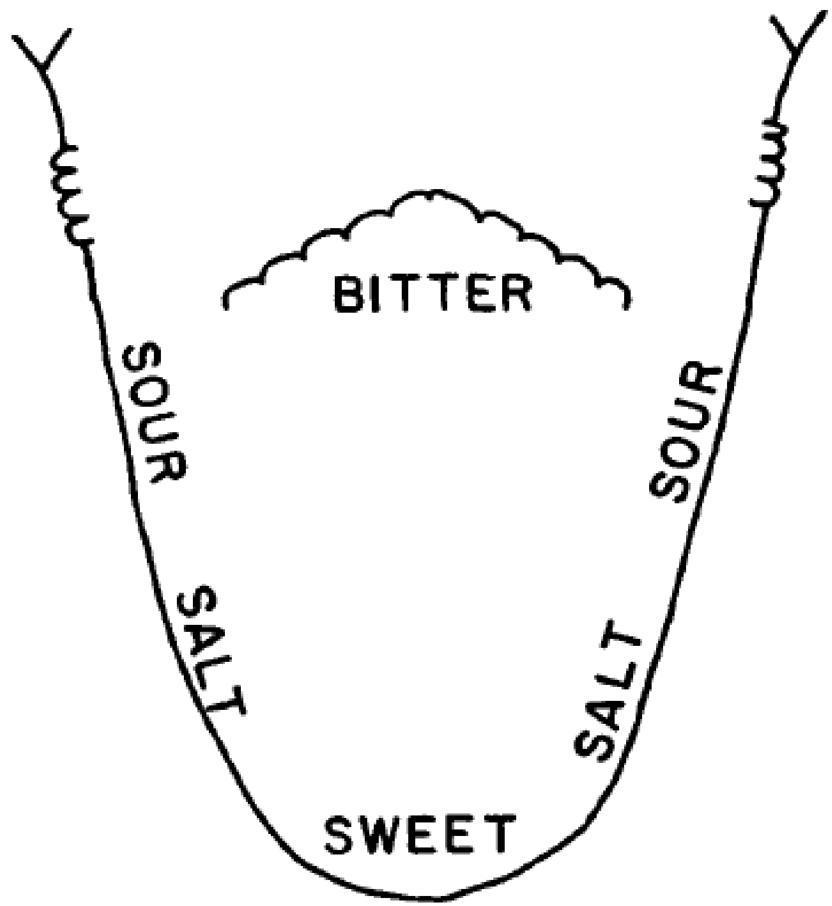


Fig 1. Mechanism of flavor perception
Apple
Visual Assessment
What is it?
Color
Shape
Size
External texture
Memory
Retrieval
Identity
Edible
Eat it?
COMMAND!
Bite
Saliva glands
•Enzyme for digestion
•Water for taste detection & mastication
Masticate
Oral cavity
Odours
Retronasal transport to nasal cavity
Tastants
Irritants
Irritants
Chemosensitive nerve
Chemosensitive nerve
Olfactory receptor cells
Taste receptor cells
Neural Processing
Flavor profile
Smell
Irritation
Taste
Odorants
Sharp
Sweet
Sour
Identity & perceived intensity of components
Perception
Identity
Quality
Acceptability
Response
Eat!
Reject!

Areas of Taste Sensitivity of the Tongue



Taste

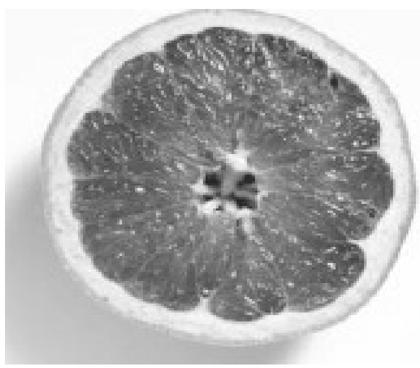
- **Sweet**

i.e. polyhidroxy compound,
saccharin

- **Salty**

i.e. NaCl (Sodium chloride)
LiCl (Lithium chloride)

- **Sour**



i.e. acetic acid, lactic acid

- **Bitter**

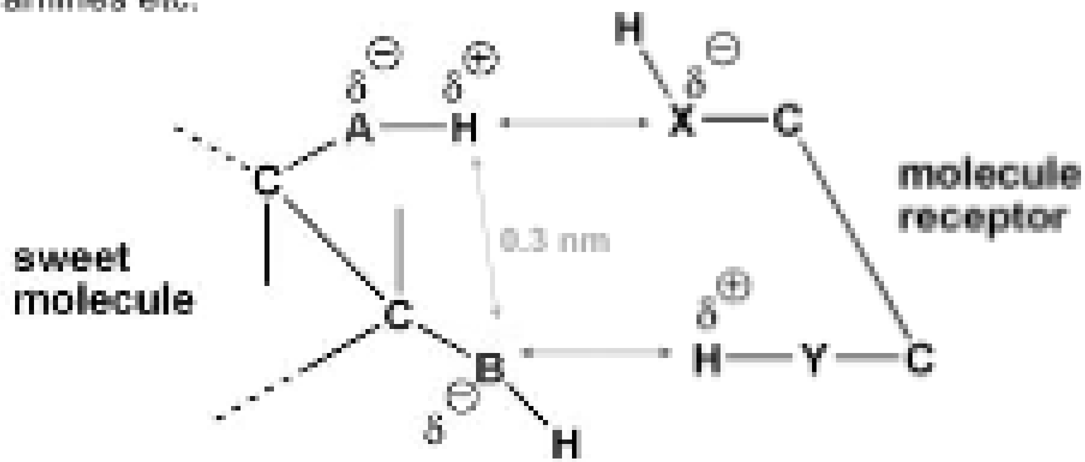
i.e. Lean meat → creatine
Coffee, cocoa → caffeine

Sweetness

- Sweetness is found in many types of molecules (not just sugars), and relative sweetness is normally compared to sucrose
- Natural sugars –sucrose (1.0); glucose (0.76); fructose (1.52)
- Also artificial sweeteners –sodium cyclamate (30); acesulpham-K (140); aspartame (200); saccharin (350); 1-*n-propoxy-2-amino-4-nitrobenzene (4000)*

Schallenberg's "saporous unit" theory

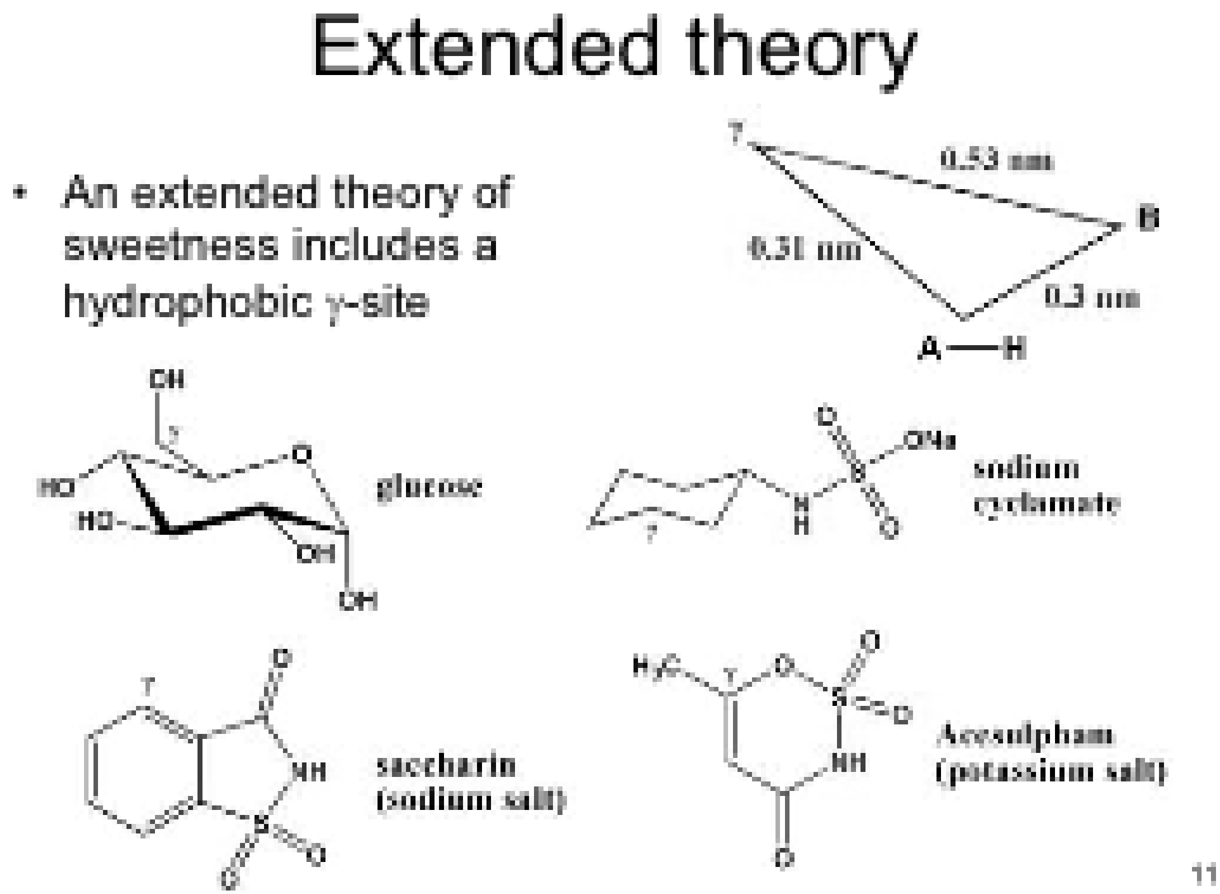
- Sweet molecules contain H-bonding groups such as hydroxyls, amines etc.



A and B = N, O etc

- Geometry of so-called "saporous" units crucial for interaction with a "sweetness" receptor

AH can represent a hydroxyl group, an imine or amine group, or a methine group. Within a distance of about 0.3 nm from the AH proton, there must be a second electronegative atom B, which again can be oxygen or nitrogen.



This theory support Shallenberger's theory and indicate that the fourth hydroxyl group of glucopyranosides is of unique importance in determining sweetness, possibly by donating the proton as the AH group. As the molecular weight of saccharides increases, their sweetness decreases. Apparently, only one sugar residue in each oligosaccharide is involved in the interaction at the taste bud receptor site.

Relative sweetness of sugars & other sweeteners

Compound	*Relative Sweetness*
Sucrose	1
Lactose	0.27
Maltose	0.5
Sorbitol	0.5
Galactose	0.6
Glucose	0.5–0.7
Mannitol	0.7
Glycerol	0.8
Fructose	1.1–1.5
Cyclamate	30–80
Glycyrrhizin	50
Aspartyl-phenylalanine methylester	100–200
Stevioside	300
Naringin dihydrochalcone	300
Saccharin	500–700
Neohesperidin dihydrochalcone	1000–1500

Sourness

- Sourness assumed to be linked with acidic solutions
- However the presence of unionized organic acids (i.e. RCO_2H) is more important for the taste of sourness
  – citric, malic, tartaric (grape), isocitric, oxalic, acetic, lactic acid

- Citric acid was judged the most sour, fumaric and tartaric about equal, and adipic least sour.
- The tastes of citric and tartaric acids were preferred over those of fumaric and adipic acids.

In foods:

- Sourness of vinegar due to acetic acid, but also adds importantly to aroma, such as with fish and chips
- Lactic acid in pickled foods such as sauerkraut comes from bacterial fermentation of the sugars in the vegetables
- Sodium lactate is used in salt and vinegar flavored crisps

Saltiness

- The salty taste is best exhibited by NaCl.
- The taste of salts depends on the nature of both cation and anion.
- As the molecular weight of either cation or anion—or both—increases, salts are likely to taste bitter.
- NaCl enhances mouthfeel, sweetness, balance, and saltiness, and also masks or decreases off-notes.
- Salt substitutes based on potassium chloride do not enhance mouthfeel or balance and increase bitter or metallic off-notes.

Taste sensation of salts

Taste	*Salts*
Salty	LiCl, LiBr, LiI, $NaNO_3$, NaCl, NaBr, NaI, KNO_3, KCl
Salty and bitter	KBr, NH_4I
Bitter	CsCl, CsBr, KI, $MgSO_4$
Sweet	Lead acetate,[1] beryllium acetate[1]

[1]Extremely toxic

Bitterness

- **Several classes of compounds exhibit bitterness**
- **Taste buds at back of tongue responsive to:**
  – *group 1 and 2 halide salts*
  – *certain phenolics*
- **KBr is both salty and bitter**
  – *Halide salts with the sum of their ionic diameters > KBr are bitter, if the sum is less then they are salty*

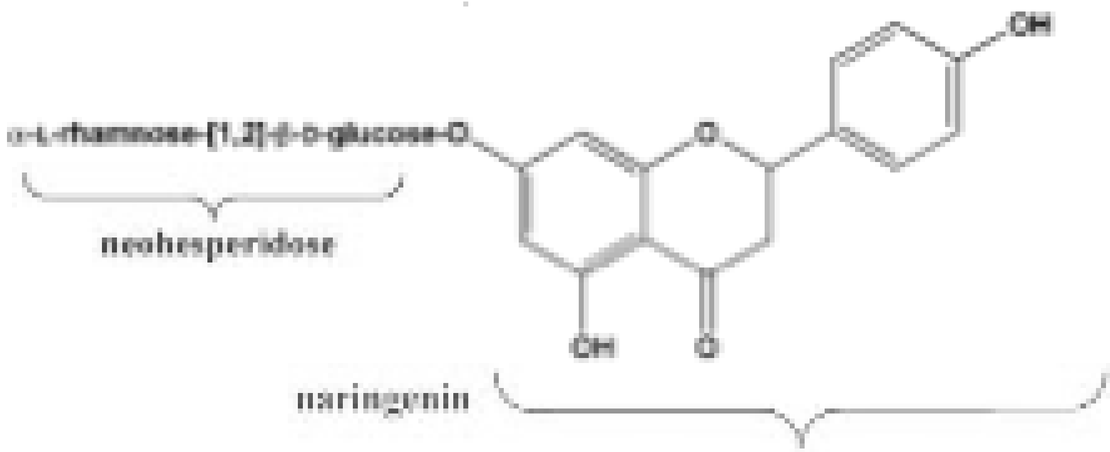
NaCl (0.556) < KBr (0.658 nm) < KI (0.706) < $MgCl_2$ (0.850)

Bitterness

- **Many plants contain molecules which we perceive as very bitter**
  – Nicotine, atropine, emetine
  - **Quinine**.- a flavor component of tonic water and bitter lemon
- **Role in plants unknown,** but many have undesired pharmacological properties
- Quinine antiplasmodial agent used to prevent and cure malaria by consumption of tonic waters

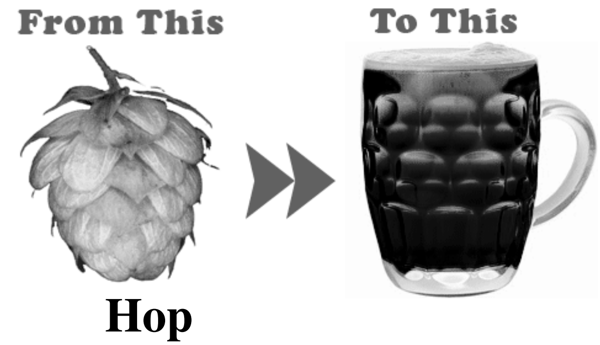
Phenolics: *Seville oranges*

- Phenolics in the form of flavanoids are source of bitterness in citrus fruits.
  - – **Naringin** is a bitter sugar-flavanone conjugate found in Seville oranges. Its bitterness is detected at 1:50,000 dilution.

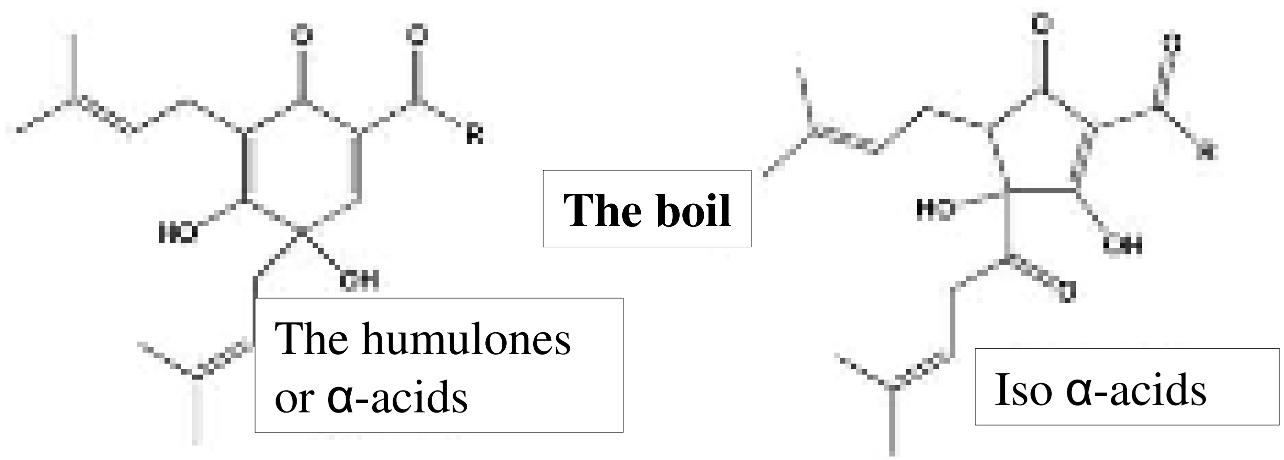


- The non-sugar unit attached to sugar known generally as the aglycone
- Here the sugar is neohesperidose, and the aglycone is naringenin

Phenolics: *beer*



- Before the fermentation stage of the brewing process, the flowers of the hop plant, *Humulus lupulus,* are added to the wort
- Hops are added to add both flavor & bitterness



- The humulones are converted to the more soluble and more bitter iso α-acids in the boil

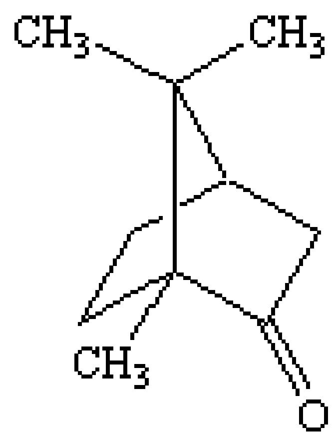
Nonspecific Sensations

- Umami
- Pungency
- Astringency

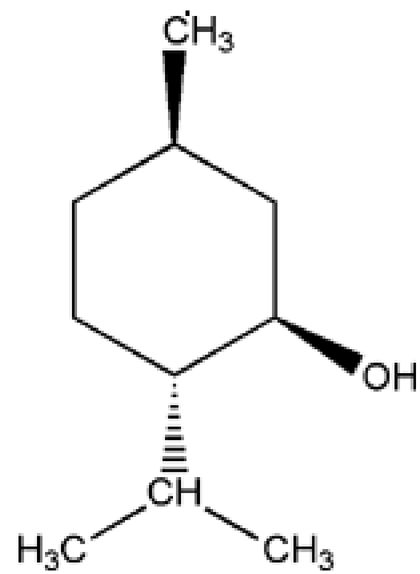
i.e. Tea leaves & red wines →polyphenols tannin; unripe bananas

- Cooling

i.e. Peppermint, Spearmint, wintergreen → l-isomer of menthol; camphor



Camphor



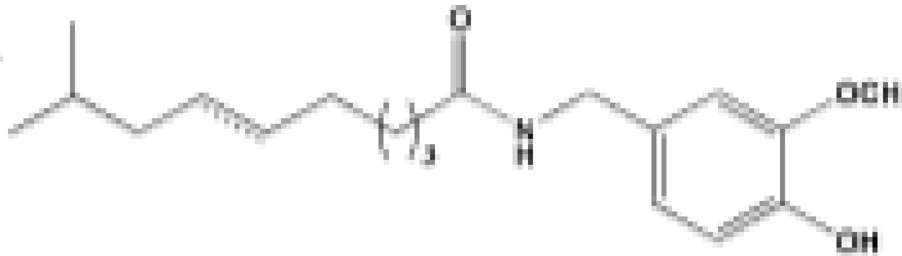
L- menthol

Astringency

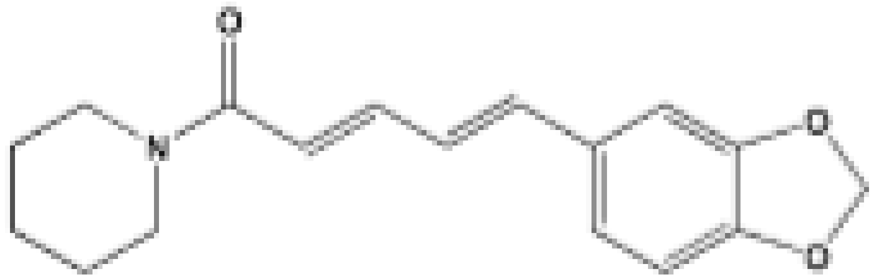
- This sensation causes drying & puckering over the whole surface of the mouth & tongue, due to the interaction of astringent compounds with protein & glycoprotein in the mouth → the reaction has been found to be occur between salivary proteins that are rich in proline (PRPs).
- PRPs have a high affinity for polyphenols.
- Astringent compounds are present in fruits & beverages derived from fruit (juice, wine & cider), in tea & cocoa → higher molecular weight of TANNIN.
- Some anthocyanins are both bitter & astringent.

Pungency:
chillies, peppers, ginger

- Chillies
  (*Capsicum frutescens*)
  - Capsaicin and dihydrocapsaicin



- Black pepper
  (*Piper nigrum*)
  - Piperine



- Ginger
  (*Zingiber officinale*)
  - Gingerols and shogaols – ketones similar to capsaicin with hydroxy or alkene groups in a variable length aliphatic side chain

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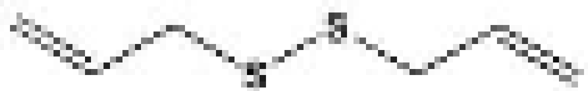
Pungency = hotness, which is usually associated with spices. There are three groups of natural pungent compounds—the capsaicinoids, piperine, and the gingerols.

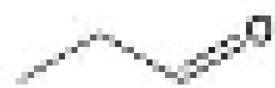
Pungency: *onion and garlic*

- Garlic and onions – belong to *Allium* species
- Early (19th century) studies using steam distillation isolated non-odorous species
  - Gave rise to trivial name of 'allyl' for the prop-1-enyl unit



garlic oil

allyl disulfide



onion oil

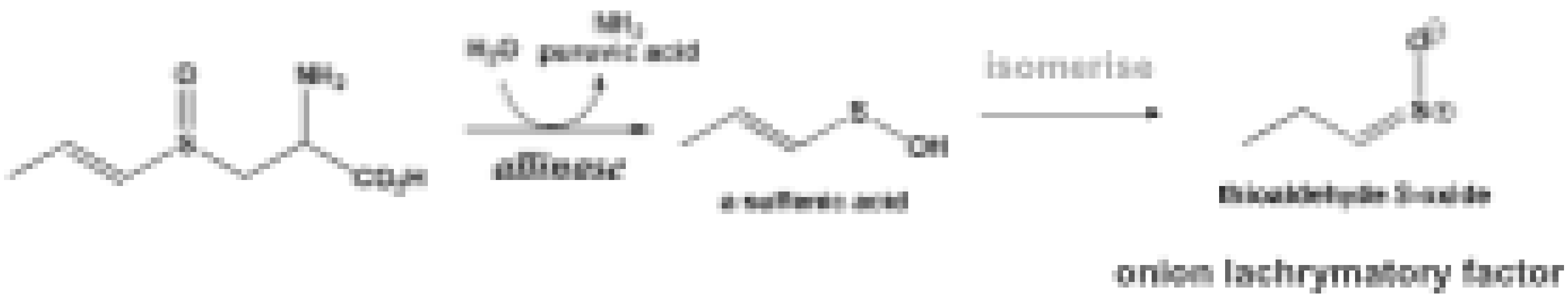
propionaldehyde

- Gentler extraction processes (lower temp, ethanol as solvent) isolated more interesting molecules!

Pungency: *onion and garlic*

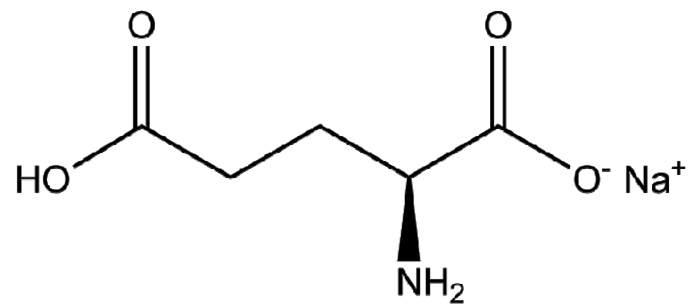
- Garlic: on cell rupture *allinase* reacts with alliin, a derivative of the amino acid cysteine

- Onion: *allinase* reacts with an isomer of alliin

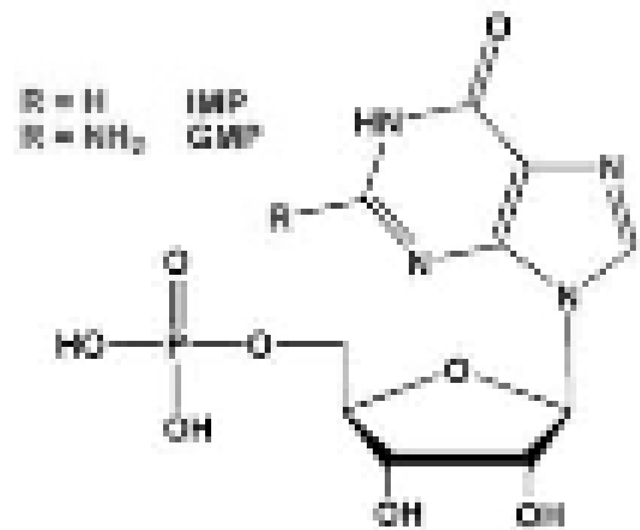


■ Umami

- Water soluble, non-volatile taste components
- Monosodium glutamate, MSG, umami$_1$
  – Levels of 10-35 mg/100 g meat



- Inosine monophosphate (IMP) umami$_2$
  – Levels of 1-200 mg/100 g
  – Also, but less important, guanosine monophosphate, GMP (0-10 mg/100 g)



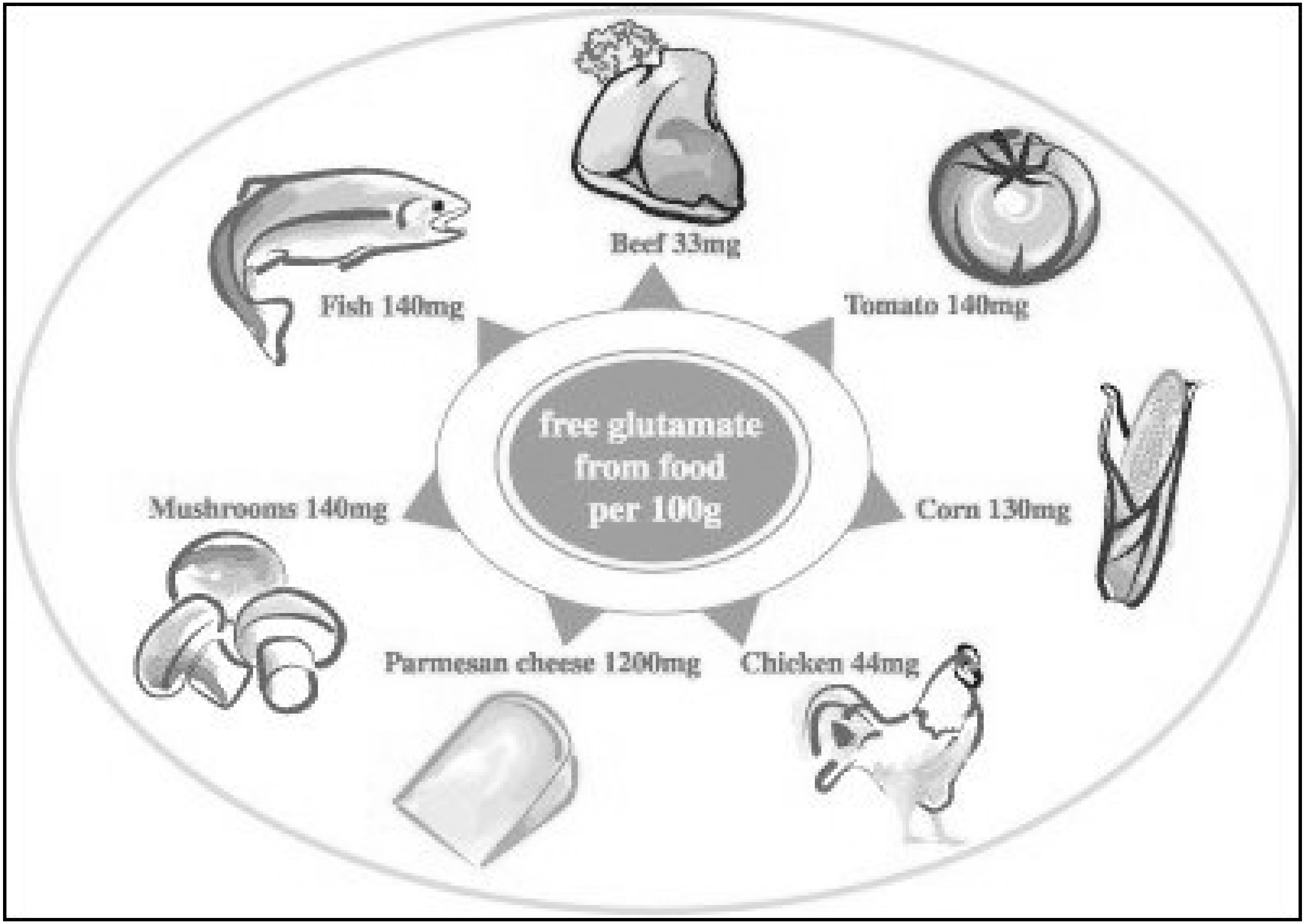


Figure. Glutamate containing food

- Metallic taste
  - It is observable over a wide area of the surface of the tongue and mouth and, like irritation and pain.
  - The metallic taste can be generated by salts of metals such as mercury and silver (which are most potent) but normally by salts of iron, copper, and tin.
  - In canned foods, the possibility of metallic ion exchange between the food and the container.
  - The threshold concentration of copper is increased by salt, sugar, citric acid, and alcohol.
  - Tannin, on the other hand, lowers the threshold value and makes the copper taste more noticeable.
  - The metallic taste is frequently observed as an aftertaste.

FRUIT FLAVOR

- Aliphatic amino acids → alcohols + acids → Esters (fruity)
- Aromatic amino acids → aromatic aldehydes (spicy)
- Fat → free fatty acids → acids + alcohols →Esters
- Terpenes (glycosidically bound)

FACTORS INFLUENCING FLAVOR

- **Genetics**

A. Different precursors

B. Different enzyme systems

Example:

Onions - 5 fold variation in flavor intensity

Orange (var. Mandarine ≠ Florida ≠ California)

■ Environments

A. Soil

i.e. Carrots

- *California* - most flavor, most sweet, least harsh
- *Florida* - low in sweetness, low in flavor
- *Texas* - most harsh/rough, otherwise moderate

B. Rainfall

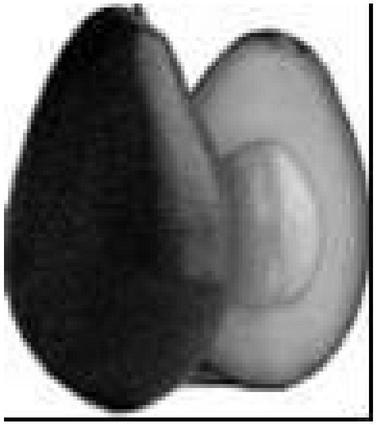
- High rainfall - large, abundant produce, little flavor

  e.g. Onions → 4 x difference in aroma on low water vs high water

C. Temperature

Generally large temperature extremes (stress)→ ↑ flavor

▪ Maturity



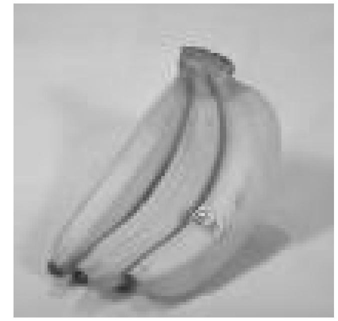
- Pick fruit early and allow to ripen away from plant → **Climacteric Fruits**

  i.e. Avocado, banana, mango – ok

- Otherwise → **Non Climacteric Fruits** - no!

  i.e. Peaches, tomato - total flavor imbalance

▪ Post harvest storage



A. Temperature - banana

- Temp. < 5 C - no banana flavor
- Temp. 10 - 12 C - 60% reduction in flavor
- Temp. > 27 C - high levels of ethanol & ethyl acetate

B. Controlled Atmosphere Storage

Storage equipped with specific air composition of CO_2 & O_2

5% CO_2 + 2% O_2 ---> No flavor

C. Humidity

Apples - low humidity flavor imbalance

FLAVOR ANIMAL PRODUCTS

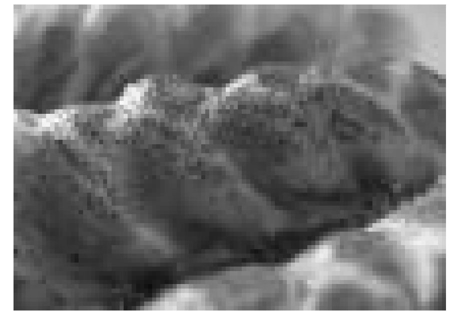
- **Diets**
  → can get major flavor influence

- **Aging**
  → Beef, lamb, mutton

FLAVOR FORMED DURING PROCESSING

- **NONENZYMATIC BROWNING/NEB (The Maillard Reaction)**

  - Characteristic flavor of many baked, fried, or otherwise thermally processed foods



Flavor formation of NEB reaction

Amino acids + reducing sugars

↓

Complex

↓

Fragmentation of complex

↓

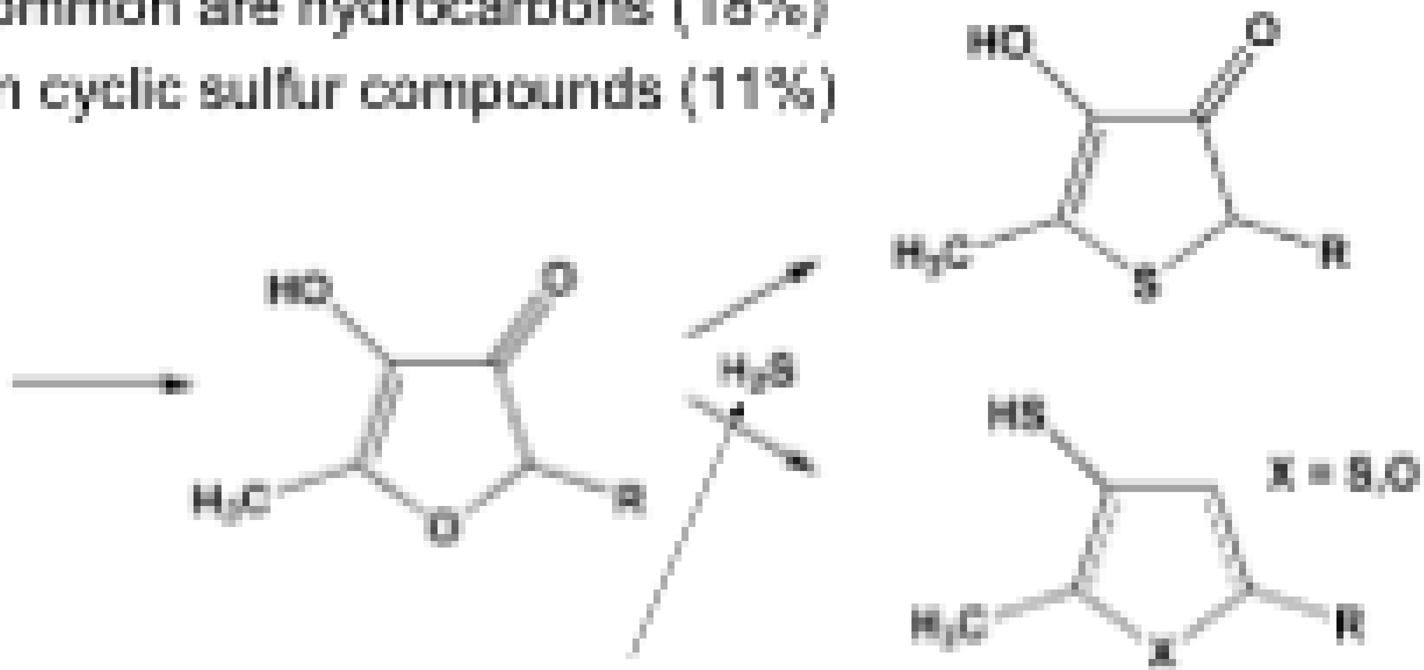
Recombination to form flavor

Factors : pH, Water activity, Oxidation/reduction state, Temperature, Time

Meatiness

- Many volatile aromas present in meats
  - Over 650 identified in beef
  - Most common are hydrocarbons (18%) and non cyclic sulfur compounds (11%)

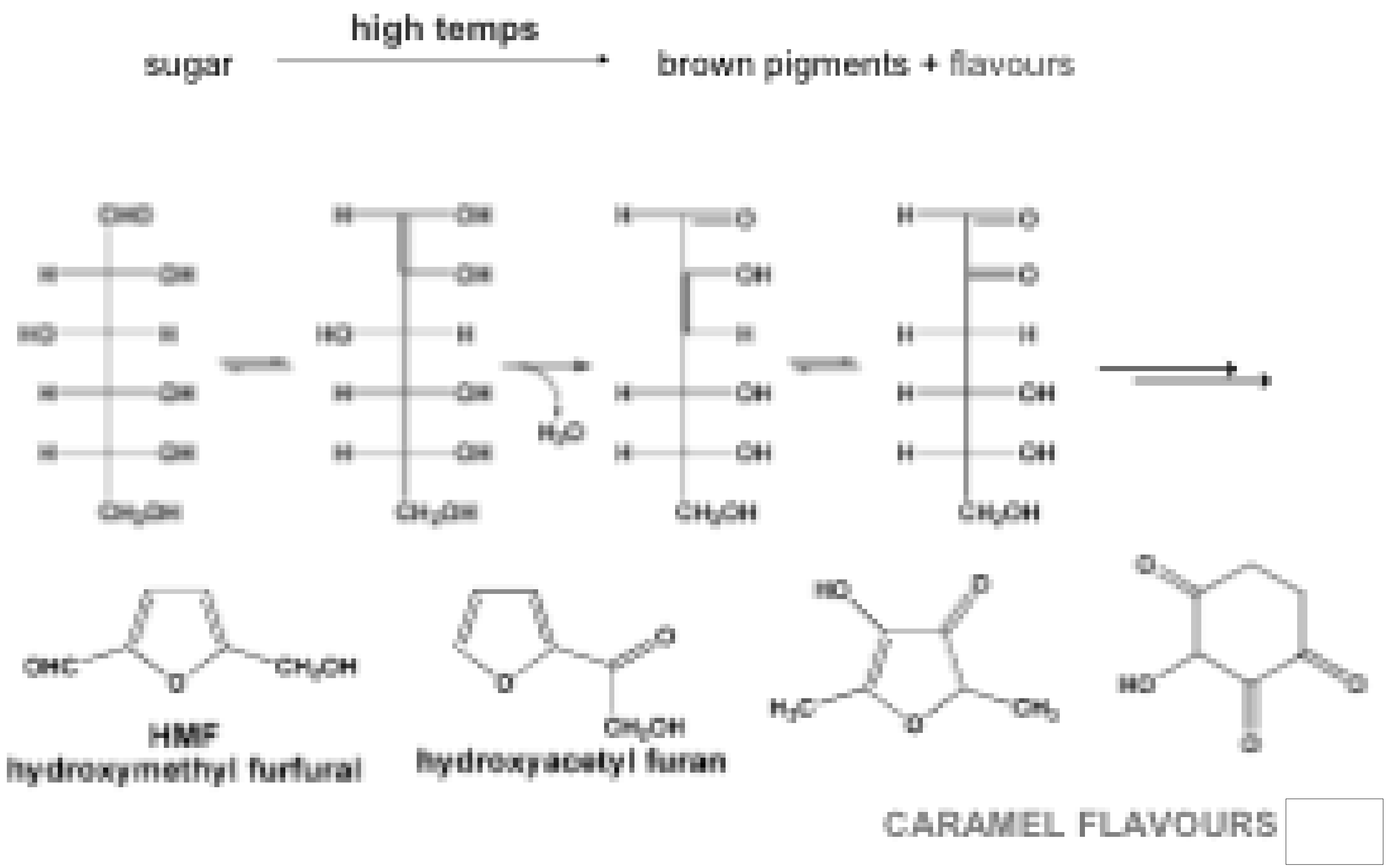
Maillard



breakdown of S-containing amino acids

ROASTED MEAT FLAVOURS

- **Caramelization**
  - acid / base catalysed (organic acids / water)
  - any sugar –here glucose



▪ LIPID OXIDATION

→ Potential in most foods containing fat or oil.

Factors influence lipid oxidation:

- **Unsaturated fatty acids**
- **Water activity**
- **Antioxidants**
- **Temperature**
- **Catalysts**

■ FERMENTATION

1. *Primary products* - acids, alcohols, aldehydes

   Examples: some cheeses, yoghurt, beer

2. *Secondary products* - ketones, esters, amino acids

   Examples: aged cheeses

Flavor & Off-Flavor

- Off-flavor defined as unpleasant odors or flavors imparted to food through internal deteriorative changes.
- Taints defined as unpleasant odors or flavors imparted to food through external sources.
- Off-flavor can be caused by heat, oxidation, light, or enzymic action.
- Even very low levels of a chemical that produces off-flavors may cause a significant number of people to complain.

Flavor & Off-Flavor

- Several examples of off-flavors:
  - Dairy products: non-2-enal; 2,4-dienal (carboard); lactones (stale off flavors)
  - Canned salmon: dimethylsulfide
  - Wine: acetaldehyde

Bread

- The flavor of white bread is formed mainly from the fermentation & baking processes.
- Freshly bread has a delightful aroma that is rapidly lost on cooling & storage → disappearance volatile flavor.
- During fermentation, a number of alcohols are formed, including ethanol, *n*-propanol, isoamyl & amyl alcohol, isobutyl alcohol, β-phenol alcohol.

  → much of the alcohols are lost during baking.

Bread

- A large number of organic acids are also formed, including formic, capric, lactic, succinic, pyruvic, hydrocinnamic, benzilic, itaconic, and levulinic acid.
- The large number of carbonyl compounds has been identified in bread, including 14 aldehydes and 6 ketones.
- The formation of crust and browning during baking contribute to bread flavor.
- Browning → from Maillard reaction, result in formation of furfural, hydroxymethyl furfural, & other aldehydes.

Bread

- In the Maillard reaction, the amino acids are transformed into aldehydes.
- The significant aroma of wheat bread includes:
  - ethanol
  - 2-methylpropanal
  - 3-methylbutanal
  - 2,3-butanedione
  - 3-methylbutanol

Meat

- Meat flavor can be developed by heating → Maillard reaction.
- The overall flavor impression is the result of the presence of a large number of nonvolatile compounds & the volatile compounds produced during heating.
- Meat extract contain a large number of amino acids, peptides, nucleotides, acids & sugars.
- Basic flavor component of meat : inosine 5’-monophosphate

Meat

living tissue → after slaughtering → deaminated

adenosine 5'triphosphate → adenosine 5'triphosphate → inosine 5' monophosphate

- Combination of inosine 5' monophosphate with other compounds will form meaty taste.
- Lean beef, pork, and lamb are similar in flavor.
- Volatile flavors contribute to meat aroma: hydrogen sulfide & methyl mercaptan.
- Other volatiles from carbonyls: acetaldehyde, propionaldehyde, 2-methylpropanal, 3-methylbutanal, acetone, 2-butanone, *n*-hexanal, & 3-methyl-2-butanone.

Fish

- Fish contains sugars & amino acids → Maillard reaction during heat procesessing (canning).
- Proline is amino acid in fish, which may contribute to sweetness.
- Flavor contributors: ribose, glucose, & glucose-6-phosphate.
- Meaty flavor: 5’-inosinic acid.
- Fish flavor (fish aroma): hydrogen sulfide, methylmercaptan, & dimethylsulfide.

Fish

- The presence of sugars, including glucose & fructose give a sweet impression → the flavor of cooked fish.
- Umami arises from the synergism between inosine monophosphate and free amino acids.
- In fresh fish, a small amount of free ammonia exists (pH level below 7). As spoilage increases, the pH rises and ammonia releases.
- The main source of ammonia is trymethylamine (TMA) → a degradation product of trymethylamineoxide (TMAO)

Fish

- 5'-inosinate accumulates in fish muscle as a postmortem degradation product of ATP.
- The inosinate slowly degrades into hypoxanthine, which has strong bitter taste, for example in tuna and mackerel.

Milk

- The flavor of normal fresh milk is probably produced by the cow's metabolism and is comprised of free fatty acids (FFAs), carbonyl compounds, alkanols, and sulphur compounds.
- Proteins and lactose may be precursors of flavor compounds in milk.
- FFAs → the action of milk lipase/ bacterial lipase.
- Sulphur compounds that can be formed by heat from β-lactoglobulin, include: dimethyl sulfide, hydrogen sulfide, dimethyl disulfide, and methanethiol.

Milk

- Some of those sulphur compounds are also produced from methionine when milk is exposed to light.
- Heterocyclic compounds are produced by nonenzymatic browning reactions.
- Bitter peptides can be formed by milk or bacterial lipases.
- The basic taste of milk is slightly sweet & salty.

Milk

- Low heat treatment produces traces of hydrogen sulfide.
- UHT treatment results in slightly fruity, ketone-like flavor.
- Sterilization results in strong ketone-like & caramelization flavors, 2-alkanones and heterocylic compounds due to Maillard reaction.


THANK
YOU!