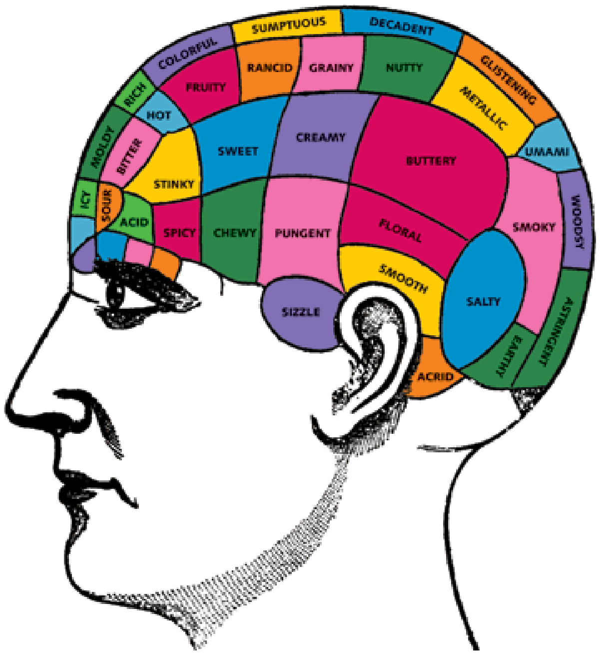

LECTURE 13: IMPACT OF RAW MATERIALS AND PROCESSING ON FLAVOR OF DRIED AND OTHER FOOD PRODUCTS

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Outline

1. Introduction

   1.1 Definition of Flavor

   1.2 The Chemical Senses

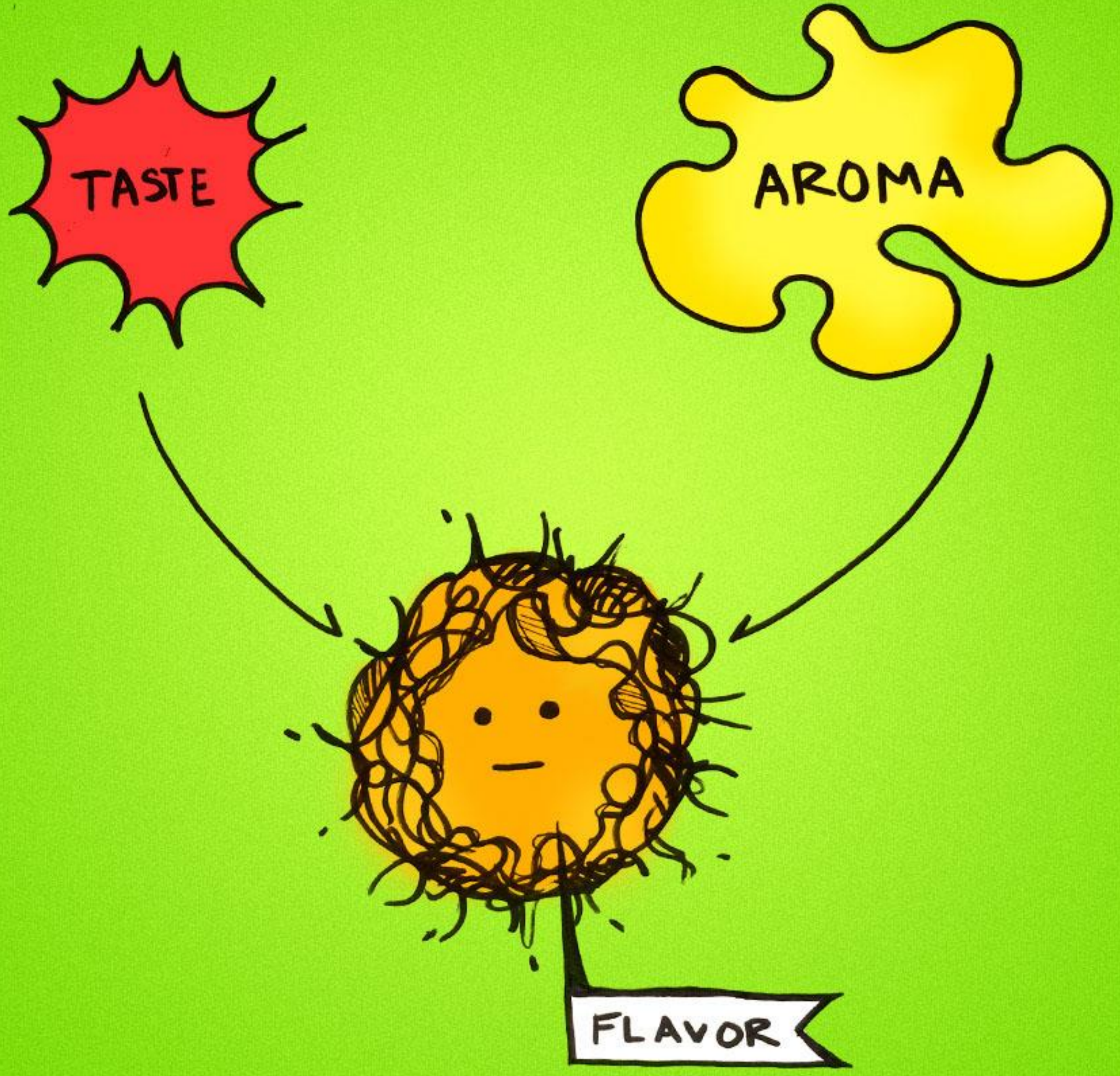
2. Factor s effect on flavor of dried and other food products

3. **Flavor compounds in Fruit and Vegetable Flavor**

4. **Flavor Analysis**
   - **4.1 Objective : Instrumental analysis**
   - **4.2 Subjective : Sensory Evaluation**

5. **Case Study**

   How to use flavor to determine quality and acceptability of products?


TASTE
AROMA
FLAVOR

1. INTRODUCTION

WHAT IS FLAVOR?

- Definition has changed recently
- Past - aroma, taste and chemesthetic (used to be called “trigeminal” responses
- Now – complex interaction of taste, smell, appearance, mouth feel, exposure, etc.

INTEREST?

- Health and well being - people eat what they like - not what is good for them.

  - Low fat, low calorie, calcium fortified, etc.

INTEREST?

- Illness - cancer

  - changes in perception
  - starve to death

INTEREST?

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

ISSUES

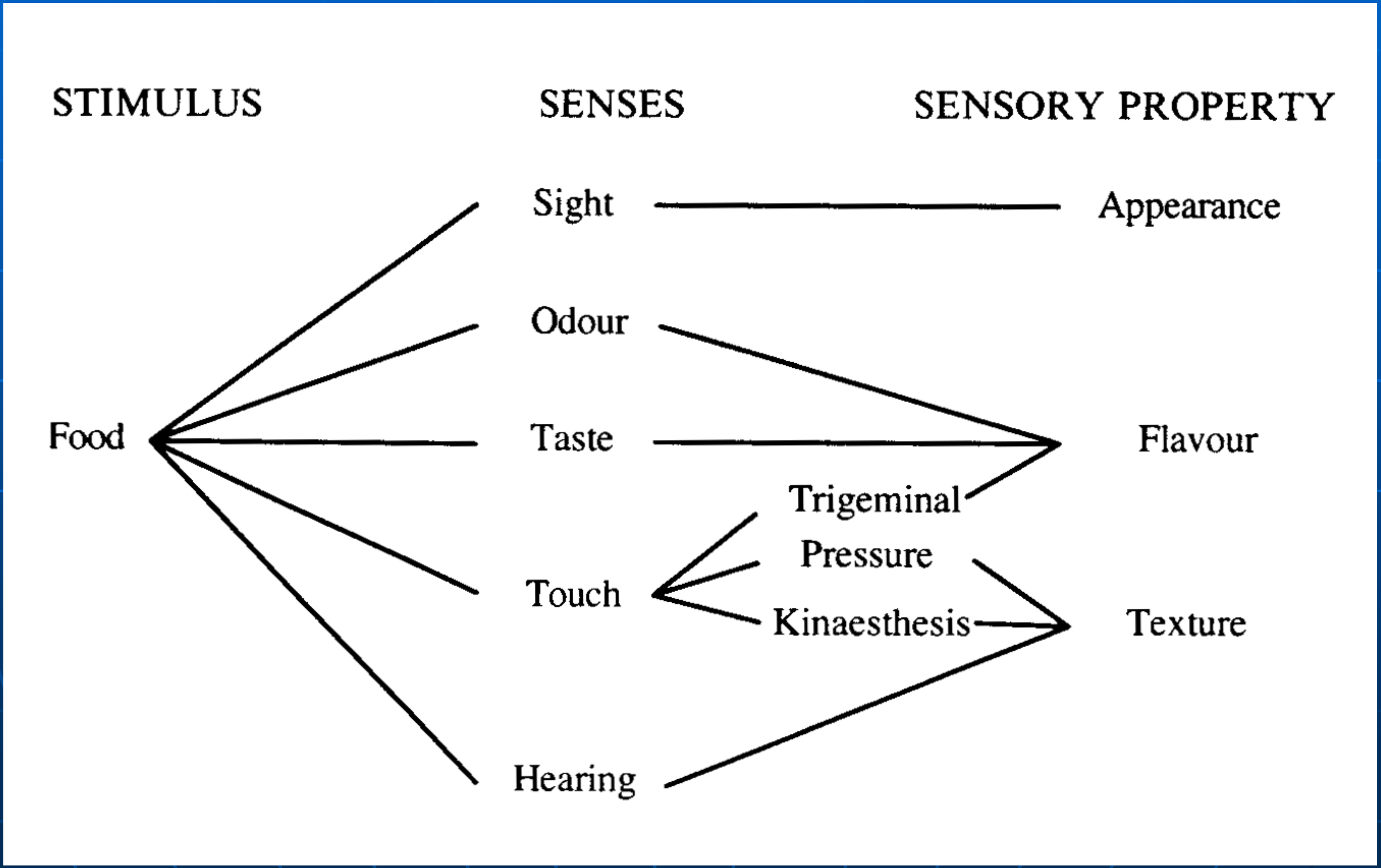
- Desirable flavor - What physical/chemical stimuli are responsible for desirable flavor?
  - Flavor uniformity across processing locations
  - Enhancing the flavor of a food
  - How to deliver flavor
- Flavor problems – What stimuli are responsible for off flavors?
  - Extending shelf-life
  - Stopping undesirable flavor

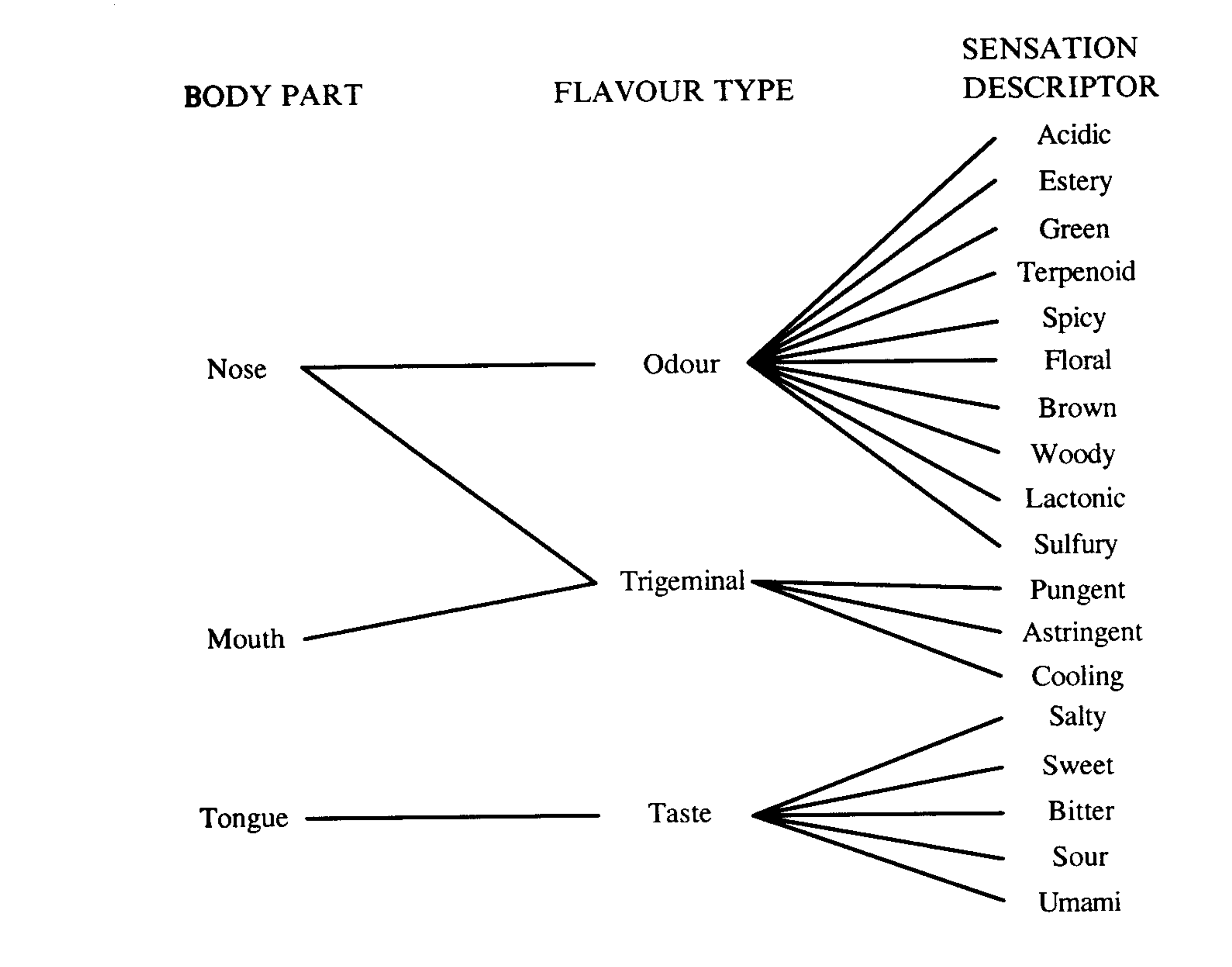
Flavor of Foods

1) Desirable flavor
   - orange juice
   - potato chip
   - roast beef

2) Undesirable flavor (off-flavor)
   - oxidized
   - stale
   - rancid
   - warmed-over

Classification of Food Flavor




BODY PART
FLAVOUR TYPE
SENSATION DESCRIPTOR
Acidic
Estery
Green
Terpenoid
Spicy
Floral
Brown
Woody
Lactonic
Sulfury
Nose
Odour
Trigeminal
Pungent
Astringent
Cooling
Mouth
Salty
Sweet
Tongue
Taste
Bitter
Sour
Umami

The Chemical Senses

- Taste and smell only separated when animals moved to land. Since in sea, all chemicals are dissolved in the same medium (water) there is no need for two separate senses. Fish and other sea creatures have one general chemical sense.

What is a chemical sense?

- Both smell and taste constitute a chemical sense
- Molecules from the environment enter the nose/mouth and stimulate the receptors
- Smell and taste interact
  - Can’t taste many foods with the loss of the ability to smell (anosmia)

- Taste and smell are chemical senses. They give us information about the chemical composition of our surroundings.

- Taste is an immediate sense – a final checkpoint for the acceptability of food before it enters the body.

- Smell is a more distant sense allowing us to detect small concentrations of airborne substances.

The Gatekeeper

- Function to identify things that the body needs for survival
- Detect things that would be bad for the body and that should be rejected
- Emotional component
  - Things taste/smell good and bad
  - Triggers memories

The Nervous System

1. Communication is vital to the survival of living organisms.
2. To interact with their environment, multicellular organisms have developed a communication system at the Cellular Level.
3. Specialized Cells (Neurons) allow Messages to be carried from one cell to another so that communication among all body parts is smooth and efficient.
4. In HUMANS, these Cells called **NEURONS** make up the Nervous System.

The Nervous System has **FOUR FUNCTIONS**

that enable the body to respond quickly. The Nervous System:

A. **Gathers information** both from the outside world and from inside the body. **SENSORY FUNCTION**

B. **Transmits the information** to the processing area of the brain and spinal cord.

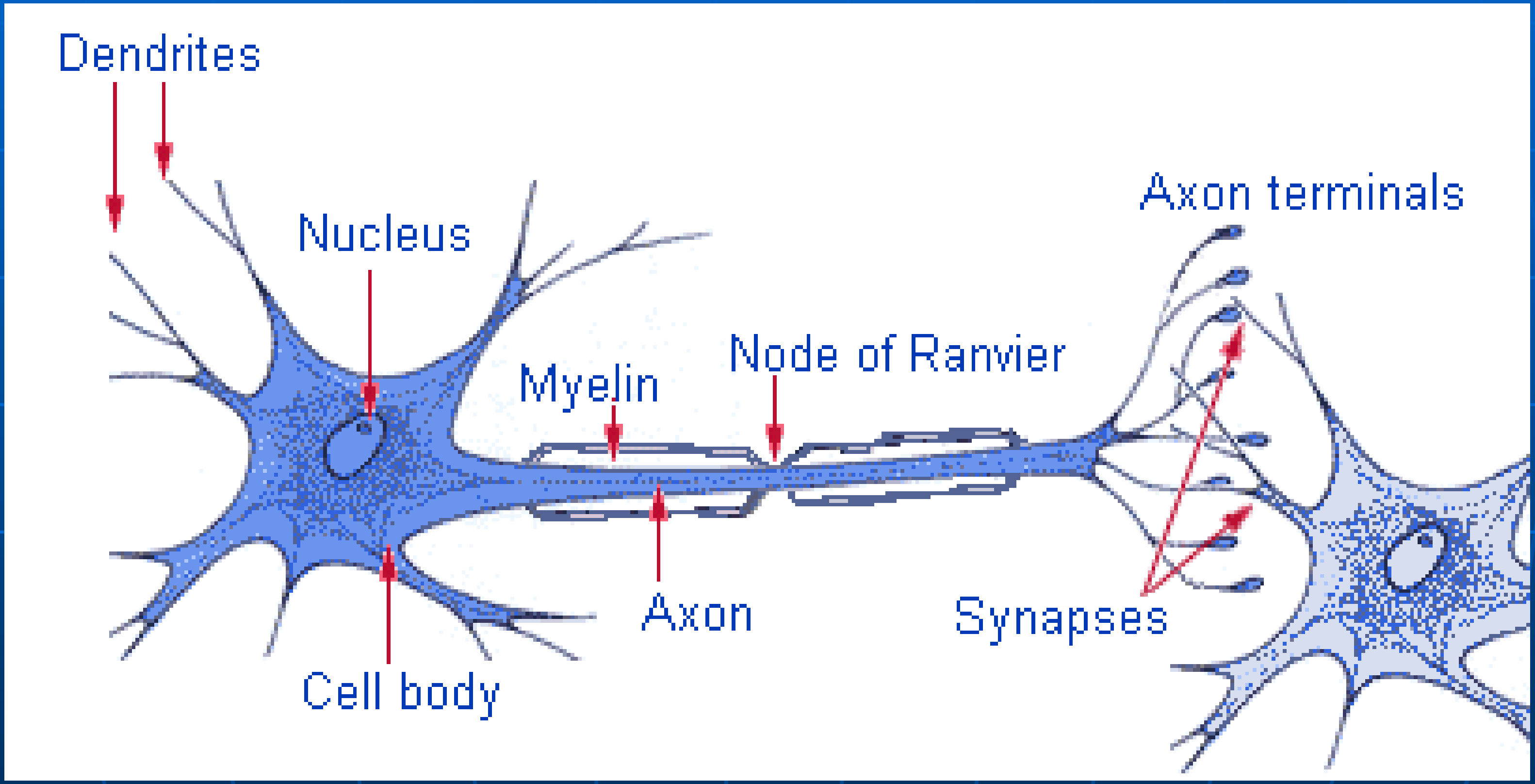
C. **Processes the information** to determine the best response. **INTEGRATIVE FUNCTION**

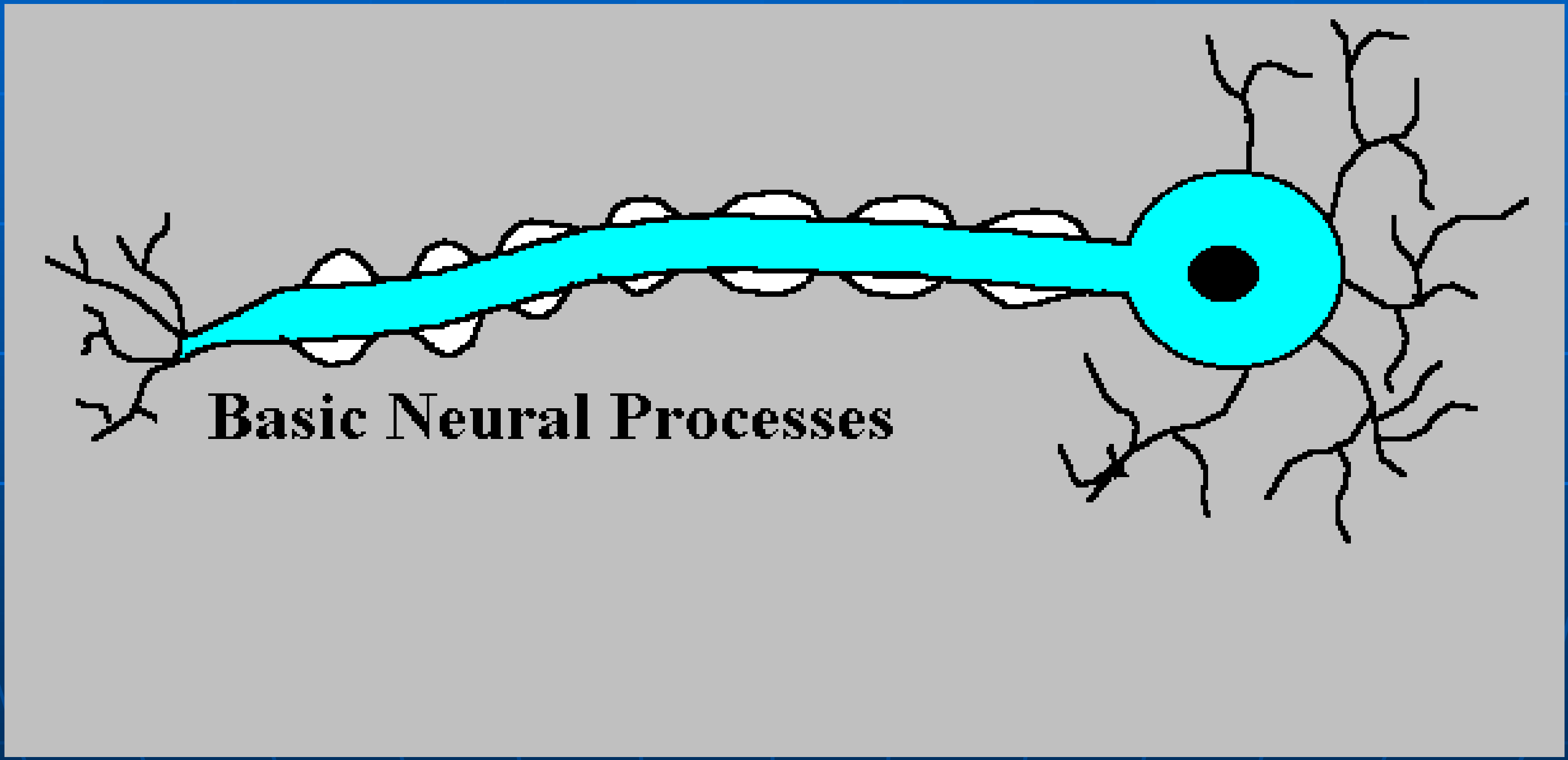
D. **Sends information to muscles, glands, and organs (effectors) so they can respond correctly**. Muscular contraction or glandular secretions. **MOTOR FUNCTION**

THE NEURON

1. The CELLS that Carry Messages Throughout the Nervous System are called **NEURONS**.

2. The Neuron is the Basic Functional Unit of the Nervous System.
3. Whatever their specific function, all neurons have the same physical parts: The Cell Body, Dendrites and One Axon.
4. Messages take the form of **ELECTRICAL SIGNALS**, and are known as **IMPULSES**. A Neuron carries impulses in only ONE direction.


Dendrites
Nucleus
Axon terminals
Node of Ranvier
Myelin
Axon
Synapses
Cell body



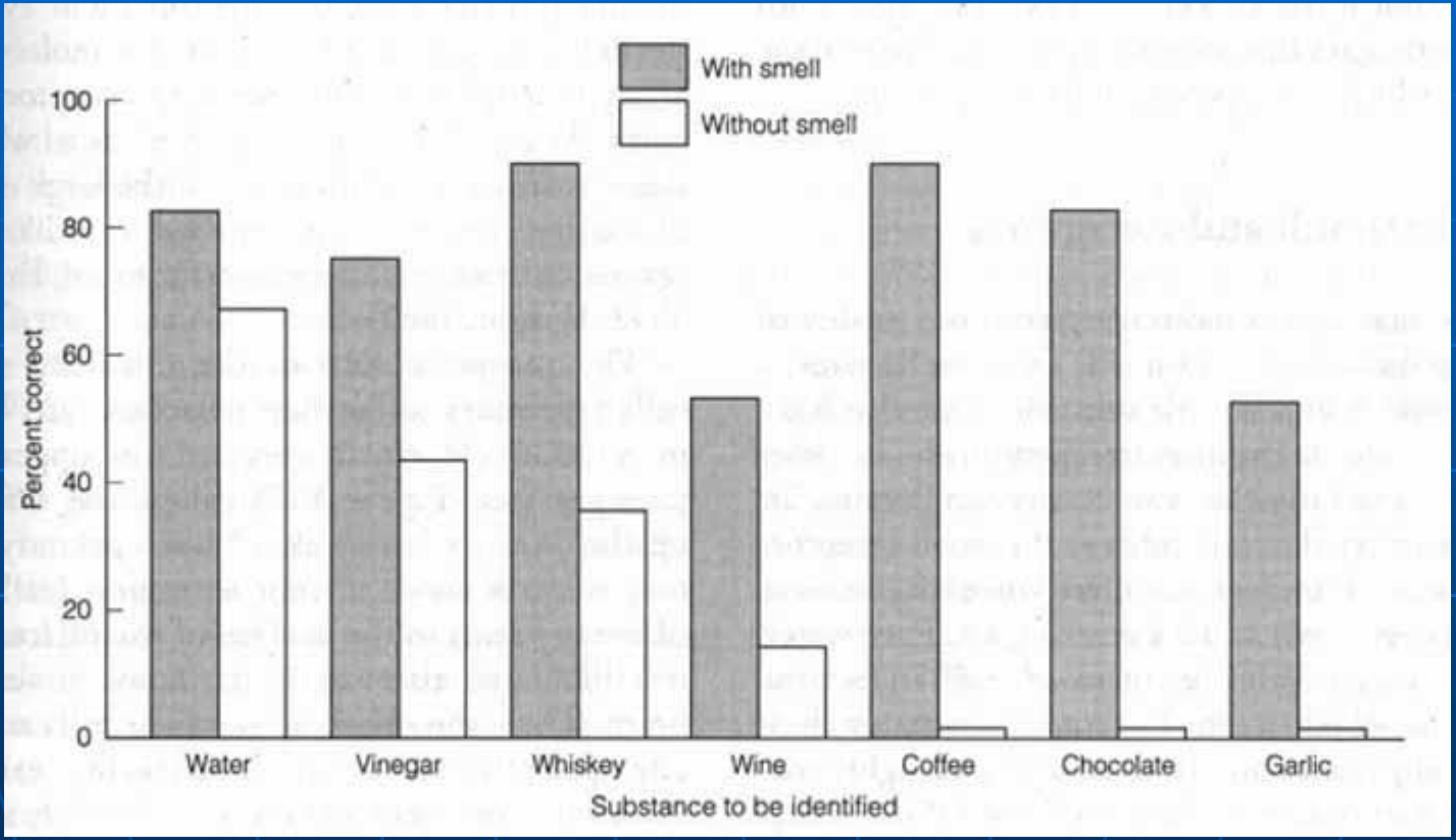
Basic Neural Processes

II. Smell

Why do we need smell?

Smell is our distant chemical sense. We can discern information about the chemical composition of substances before coming into more direct contact with them.

For many animals, smell is the most important sense.
Although for humans smell is not as important as say vision or hearing, we do use smell more than we think to guide behavior.
Smell is an important part of taste. Many qualities of foods that we think we taste, are actually a function of smell.


With smell
Without smell
100
80
60
40
20
0
Percent correct
Water
Vinegar
Whiskey
Wine
Coffee
Chocolate
Garlic
Substance to be identified

AROMA

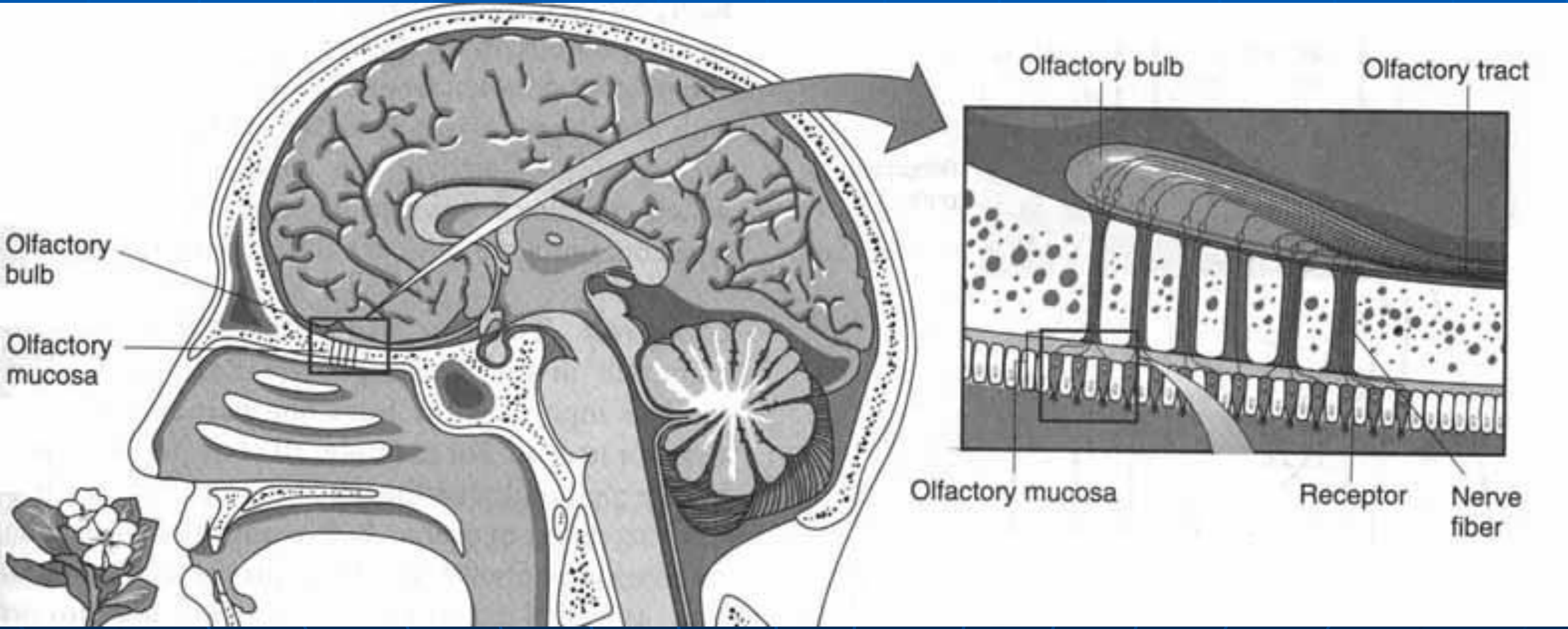
- Exceedingly complex

  a given food aroma may consist of several 100 volatiles

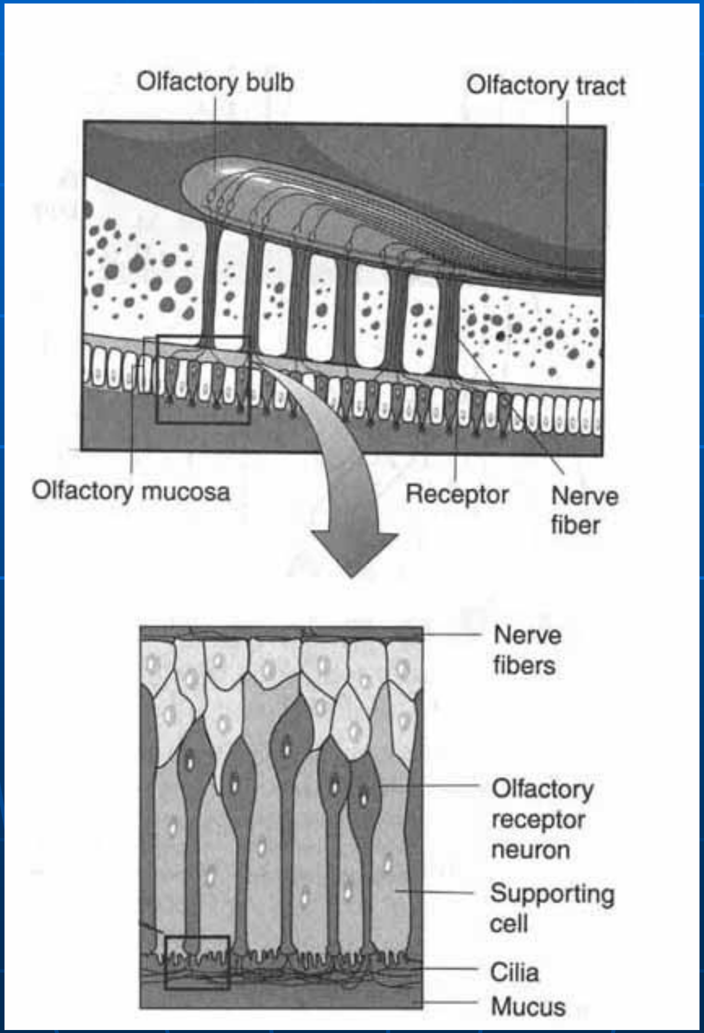
- Exceedingly sensitive - nose 10^{-17} g of some odorants

Anatomy of Smell

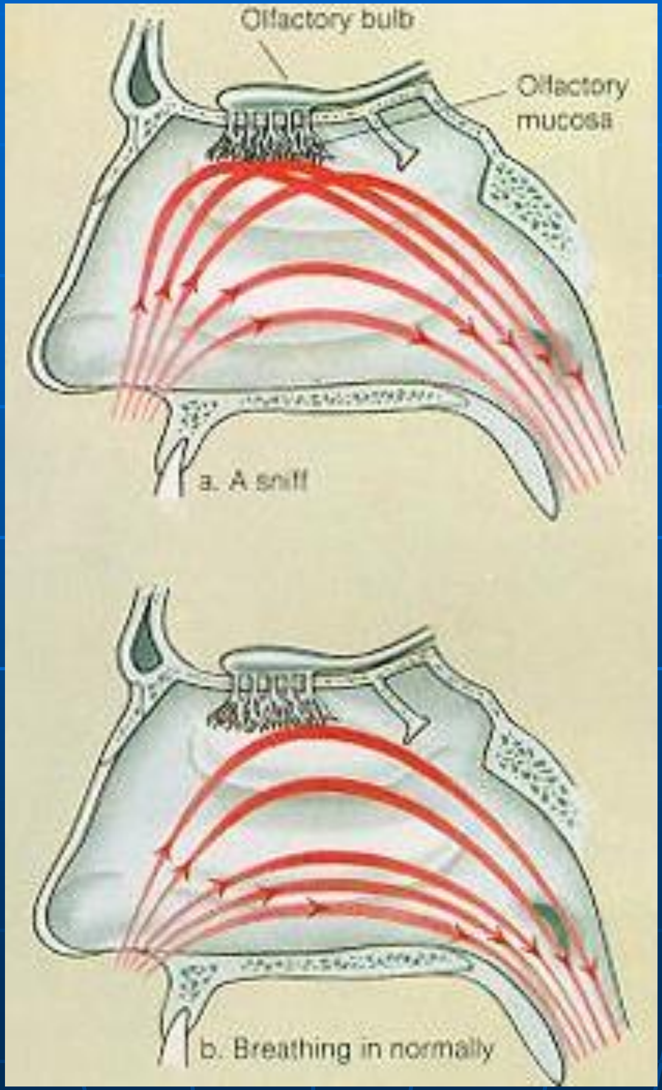
The **Olfactory Mucosa** is a dime-sized region located high inside the nasal cavity and is the site of olfactory transduction.



Olfactory receptor neurons have **cilia** (little hair-like projections) which contain the **olfactory receptor proteins**



The Nasal Cavity



The Smell Pathway

Olfactory transduction occurs when odorant molecules reach the olfactory mucosa and bind to the olfactory receptor proteins on the cilia of the olfactory receptor neurons.

When odorants bind to the receptor site, the receptor protein changes shape which in turn triggers the flow of ions across the receptor-cell membrane and an electrical response is triggered in the cilium.

Electrical responses in the cilia spread to the rest of the receptor cell, and from there are passed onto the **olfactory bulb** of the brain in the olfactory nerve.

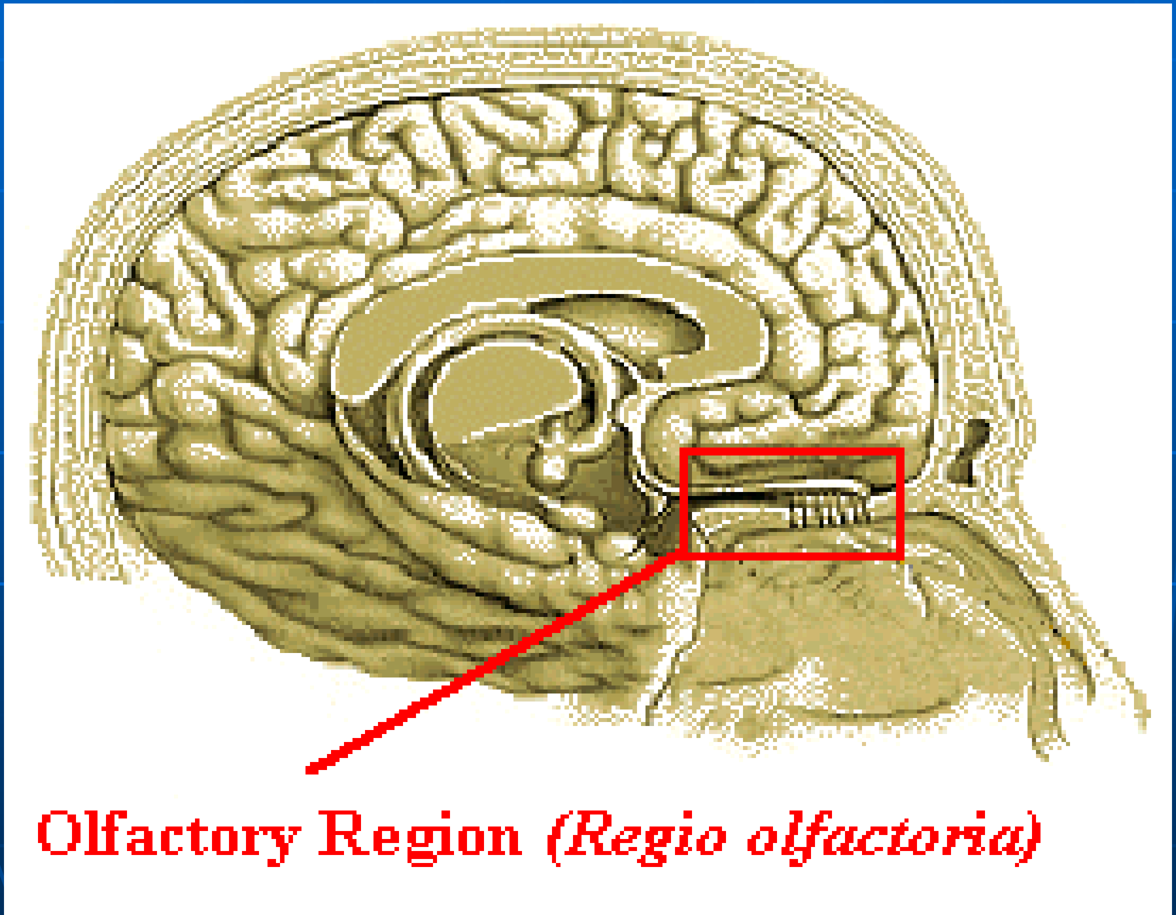
There are about 1,000 different types of receptor proteins each sensitive to different odorants.

We have a total of about 10 million receptor neurons. Each receptor neuron has about 1,000 similar receptor proteins. Because there are 1,000 different receptor proteins, there are also 1,000 different receptor neurons.

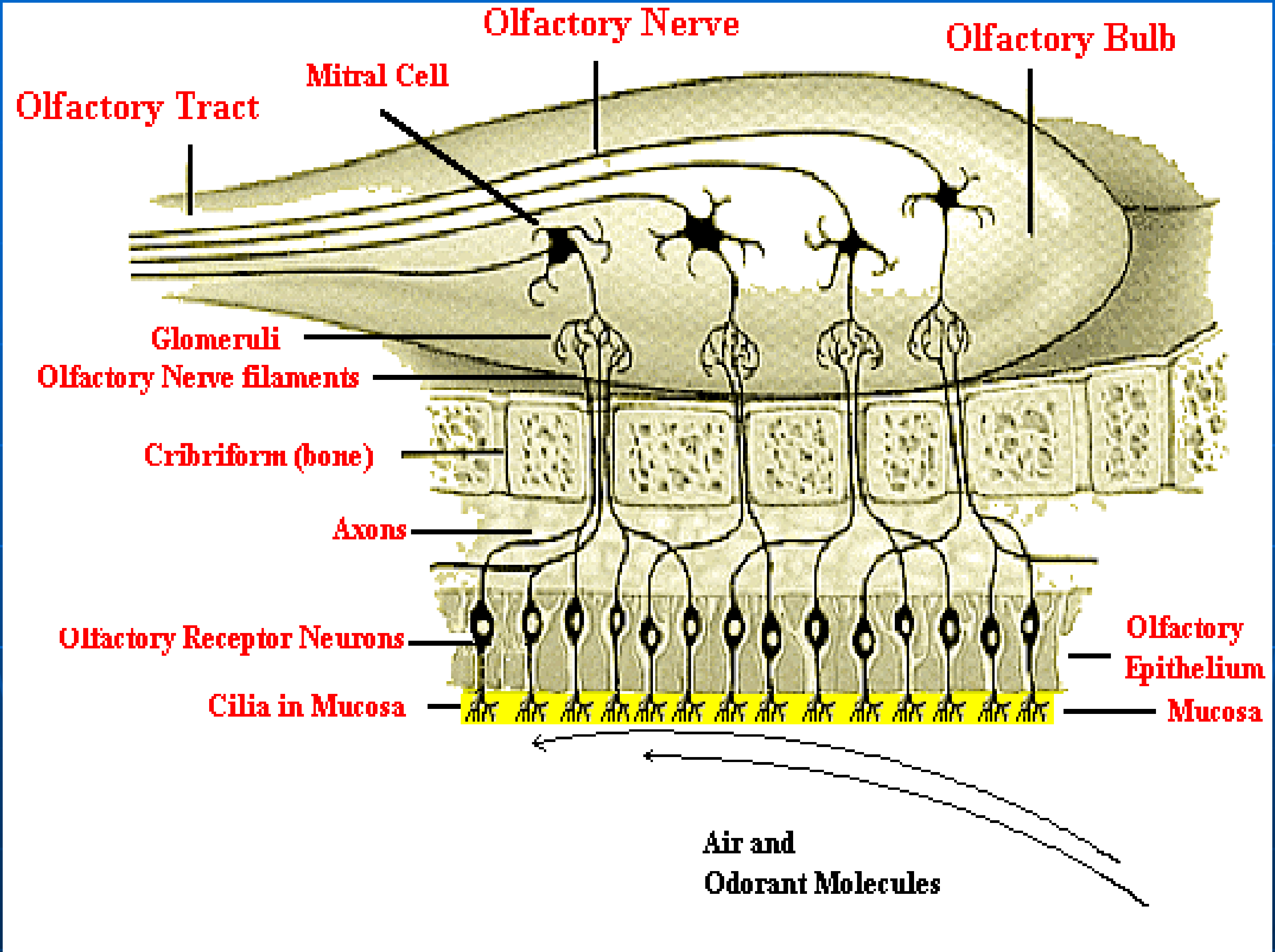
Inputs from similar receptor neurons go to similar **glomeruli** (collections of cells within the olfactory bulb). Because there are 1,000 different types of receptor neurons, there are 1,000 different types of glomeruli.

From the olfactory bulb, mitral cells and tufted cells carry olfactory information to the olfactory cortex, and to the orbitofrontal cortex.

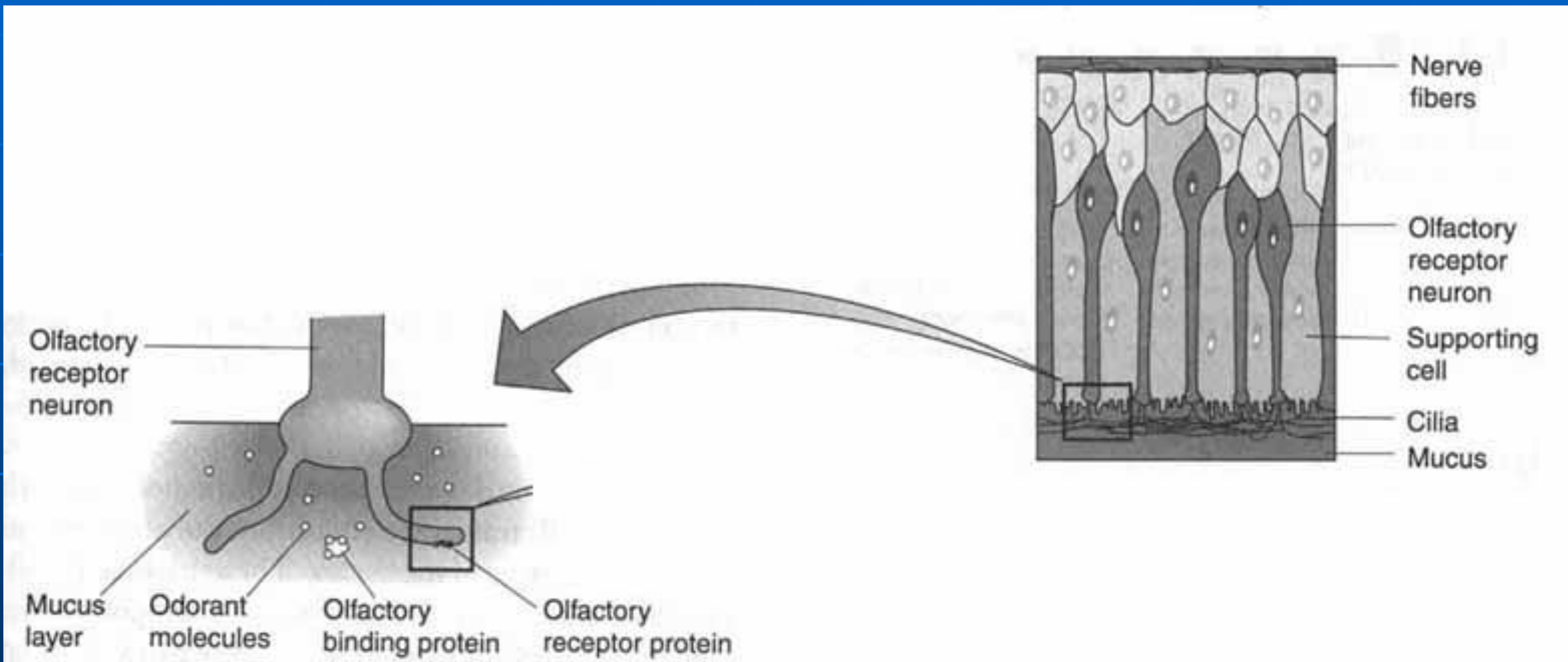
Small region - area of a postage stamp. 50,000,000 receptors!



http://www.leffingwell.com/olfaction.htm



http://www.leffingwell.com/olfaction.htm



Nerve fibers
Olfactory receptor neuron
Supporting cell
Cilia
Mucus
Olfactory receptor neuron
Mucus layer
Odorant molecules
Olfactory binding protein
Olfactory receptor protein

The Neural Code for Smell

because odorants are such complicated stimuli, we don't yet have a complete picture of how smell is encoded by the brain

different areas of the mucosa are sensitive to different types of odorants

smells appear to be organized spatially in the olfactory bulb (similar smells are grouped together)

an **odotope** is a group of odorants that share some chemical feature and cause similar patters of neural firing. Neurons that fire to the same odotope are usually located near each other.

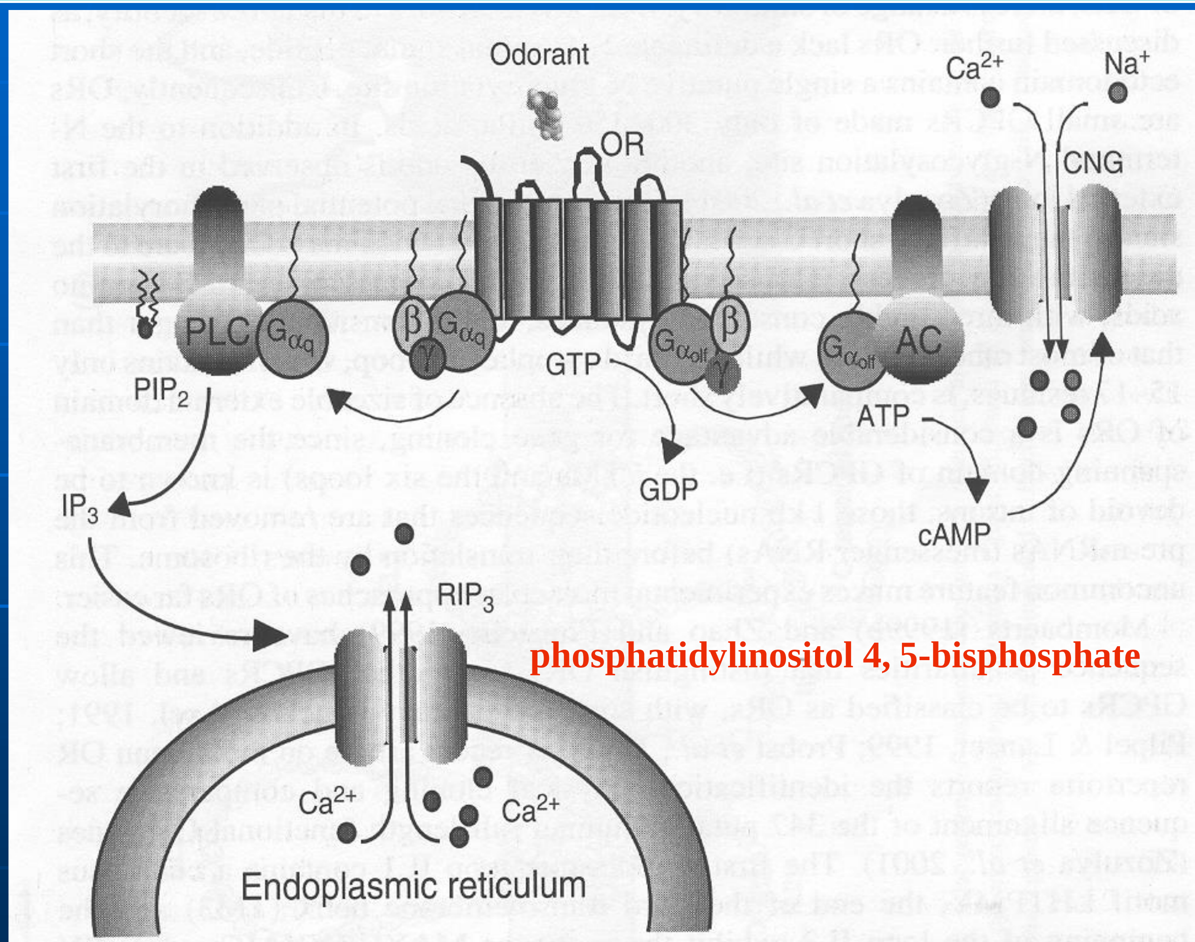
Experience of Smell

Humans can tell the difference between 10,000 different odors. But often it is difficult to name the odors. People who are trained to recognize odors (wine experts or perfume experts) are not necessarily any more sensitive with their nose - just better at retrieving names of smells from memory.

Dogs can be 10,000 times more sensitive to odors than humans. Yet, a individual human olfactory receptor is no less sensitive than a dog's. What makes dogs so sensitive? Although their receptors aren't any better, they have many many more of them (1 billion receptors in dogs compared to only 10 million in humans).

Pleasant smells (like fresh-baked bread or coffee) are used in supermarkets to encourage customers.

Two pathways – Odorant binding activates G protein, stimulates Adenylate Cyclase or Phospholipase C, AC generates cAMP – phosphorylates ion channel allowing cations in; or PLC activates PIP which opens an alternative channel.

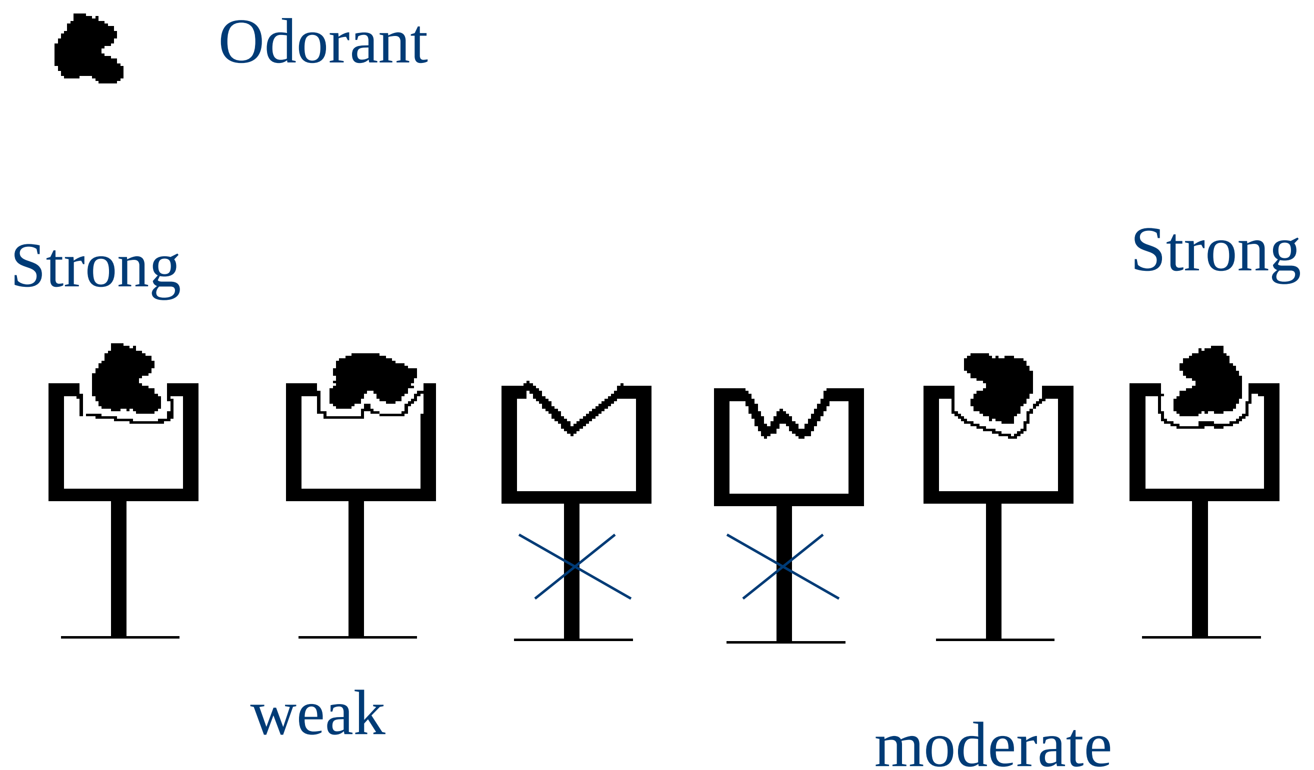


Pernollet, J.-C.,L. Briand, *Structural recognition between odorants, olfactory-binding proteins and olfactory receptors-first events in odour coding*, in *Flavor Perception*, A.J. Taylor, D.D. Roberts, Eds. 2004, Blackwell Publ.: Ames. p. 86

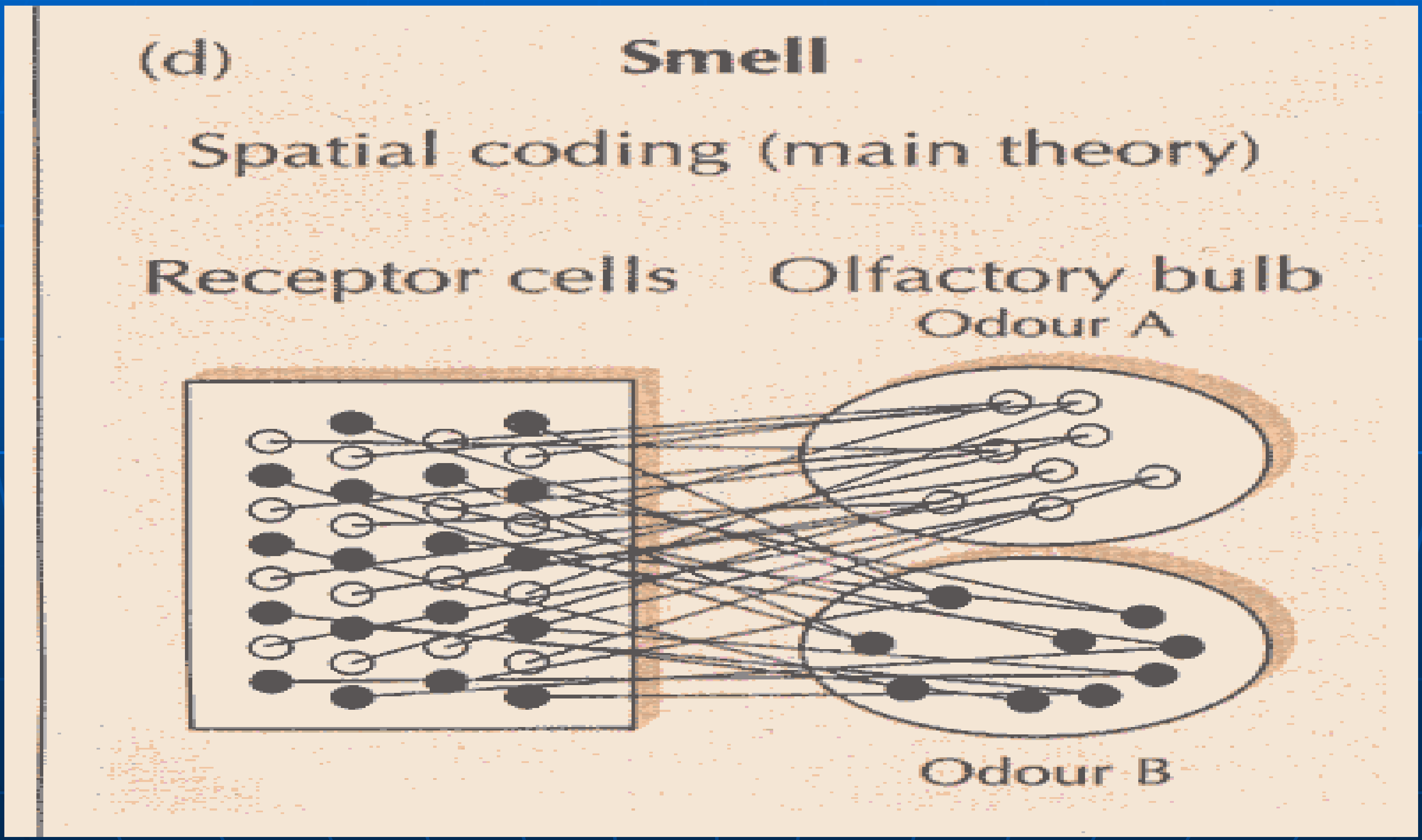
ODORANT CODING

- > 1,000 different receptors
- Each odorant will trigger several different receptors to varying levels (recognizes different parts of the odorant molecule)
- Get a pattern of receptor responses - position and strength of firing

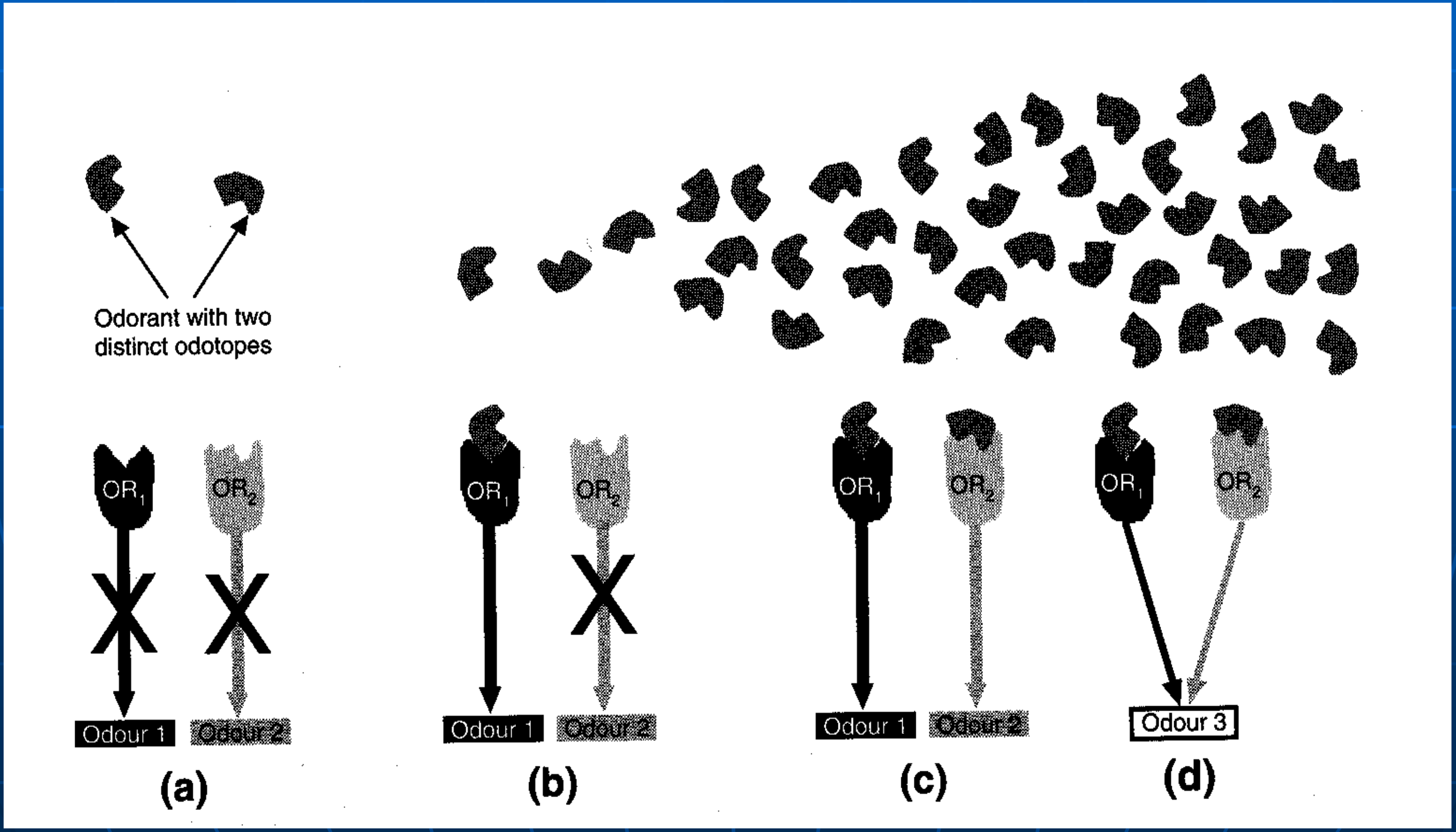
ODOR CHARACTER



PATTERN RECOGNITION



CHANGE IN ODOR CHARACTER WITH CONCENTRATION



GENETICS AND PERCEPTION? OR LIKING?

- Seems a distance away yet but … its it?
- Virtual nose

VIRTUAL NOSE

- Characterize all of the olfactory receptors
- Structurally characterize all odorants
- Molecular modeling to be able to predict interactions and strength of interactions of each odorant with each receptor (gives pattern)
- Correlations between odorant patterns and human perception – character and strength
- Link to genetic composition (to correct for inter human differences)

Taste

Why do we need taste?

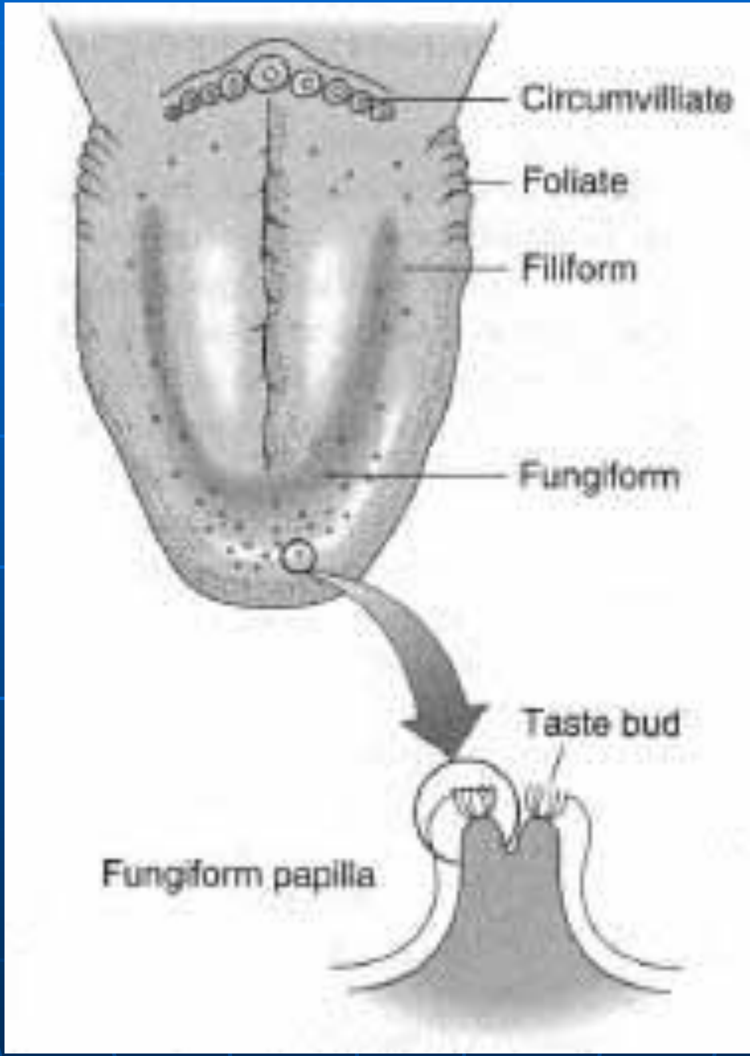
Taste is a gate-keeper sensory mechanism designed to test food and other substances before they enter the body.

Things that are potentially useful for the body tend to taste good, and things that are potentially harmful taste bad.

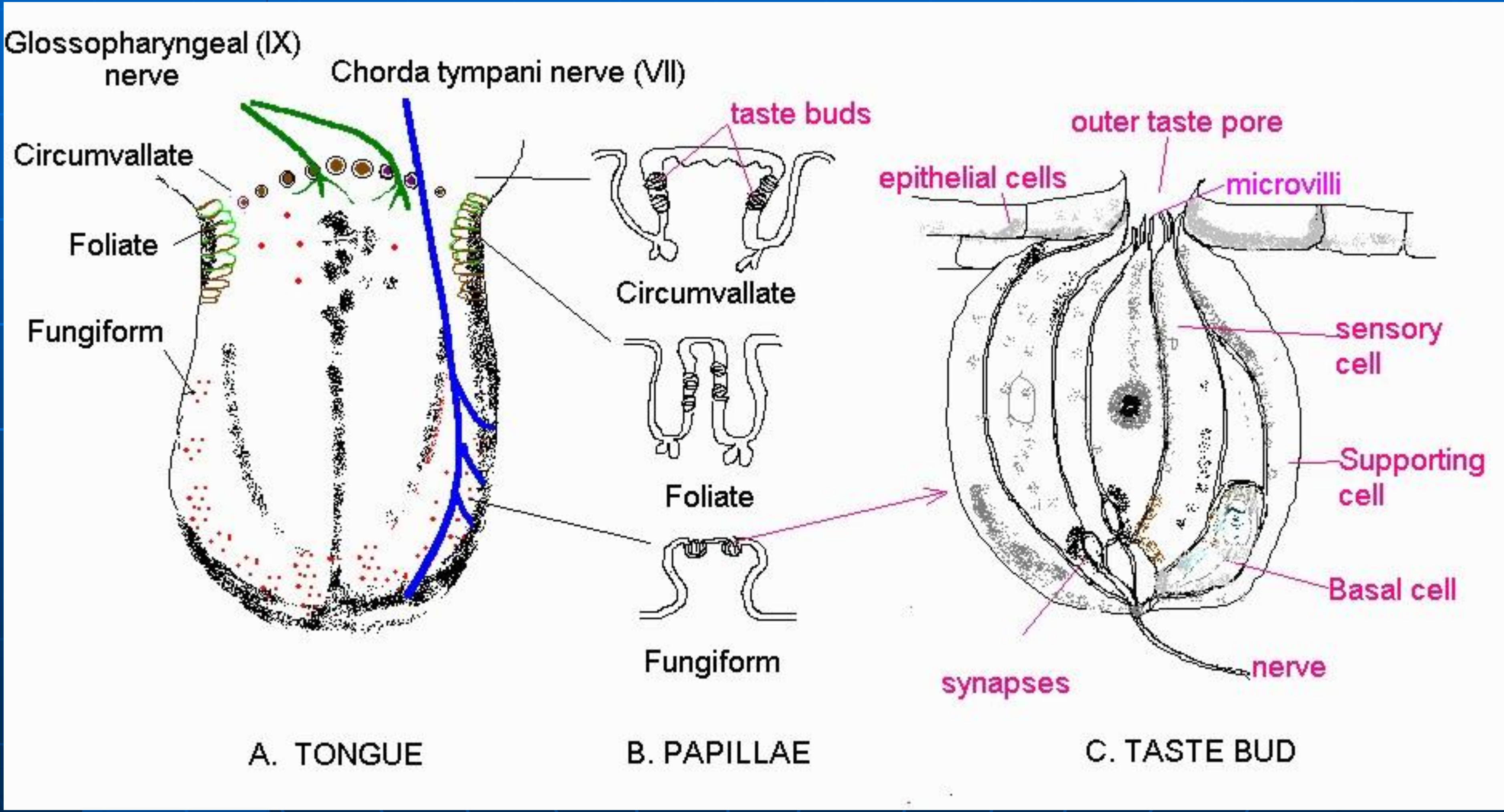
Anatomy of Taste

The tongue contains many ridges and valleys called **papillae**.
There are four types of papillae:

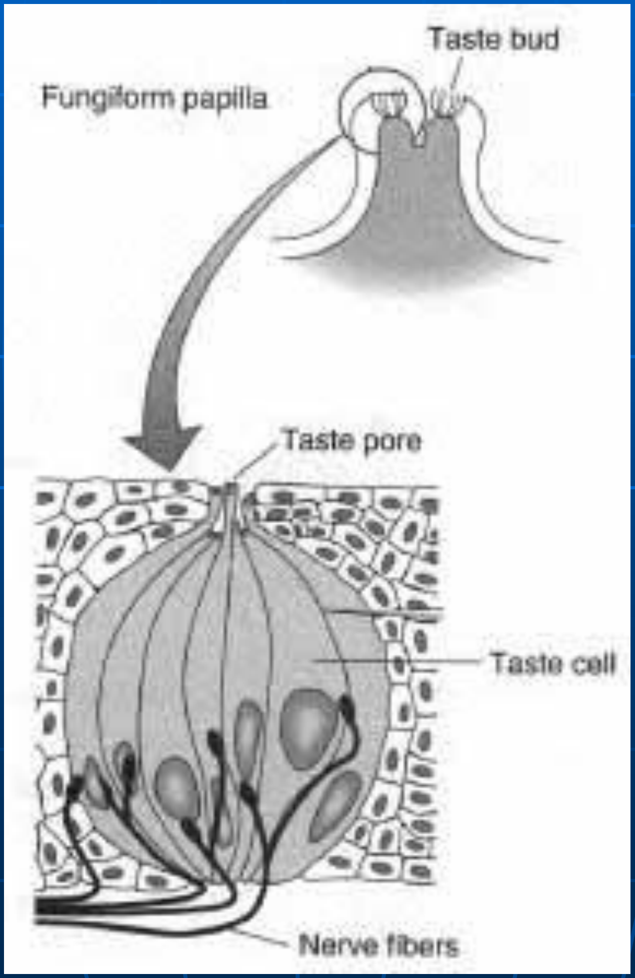
1. Filiform papillae: cone shaped & found all over the tongue (which is why tongues look rough)
2. Fungiform papillae: mushroom shaped & found at the tip and sides of the tongue
3. Foliate papillae: a series of folds along the sides of the tongue
4. Circumvallate papillae: shaped like flat mounds surrounded by a trench & found at the back of the tongue


Circumvilliate
Foliate
Filiform
Fungiform
Taste bud
Fungiform papilla

Papillae, Neural Pathways, and Taste Bud



All papillae except filiform contain taste buds (so the very center of your tongue which only has filiform papillae is "taste-blind") Each taste bud contains a number of taste cells which have tips that protrude into the taste pore.



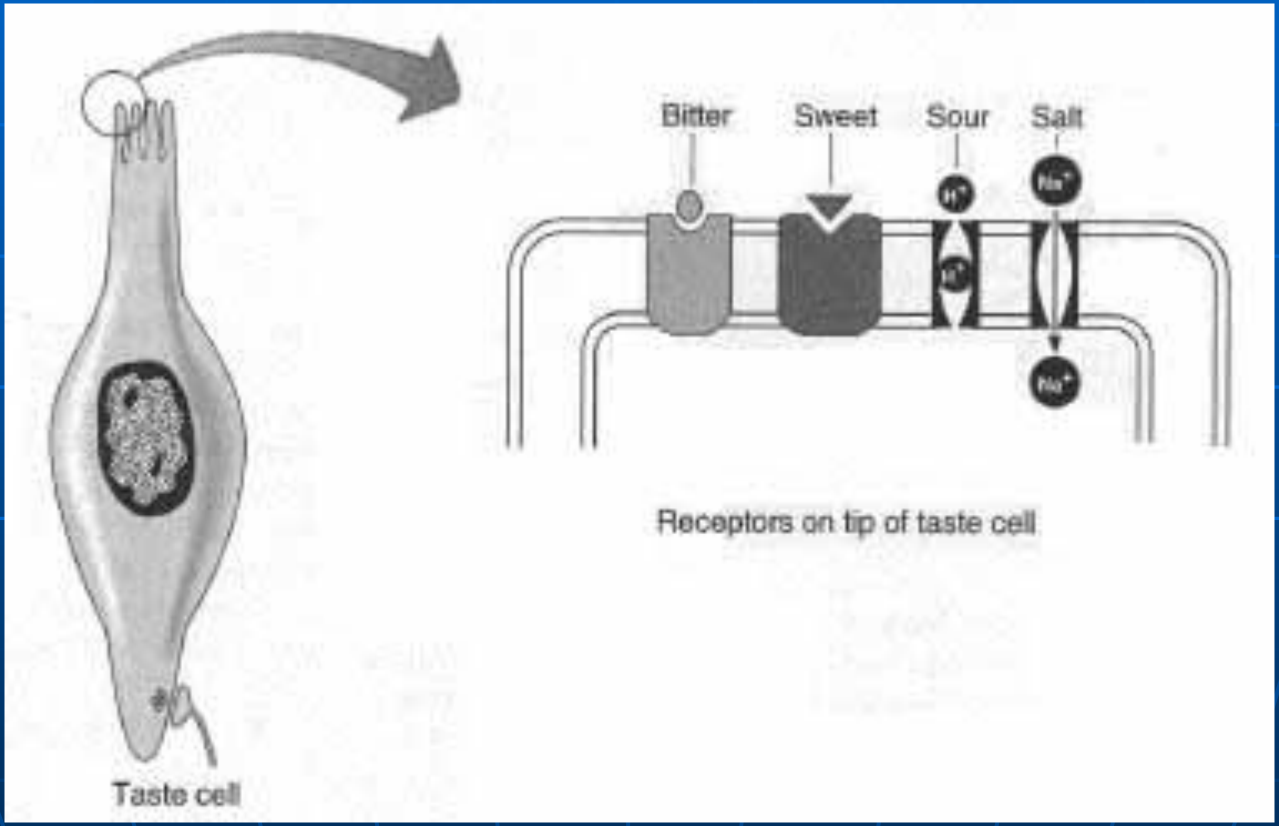
The Taste Pathway

Transduction occurs when different taste substances cause a change in the flow of ions across the membrane of a taste cell.

Different substances affect the membrane in different ways.

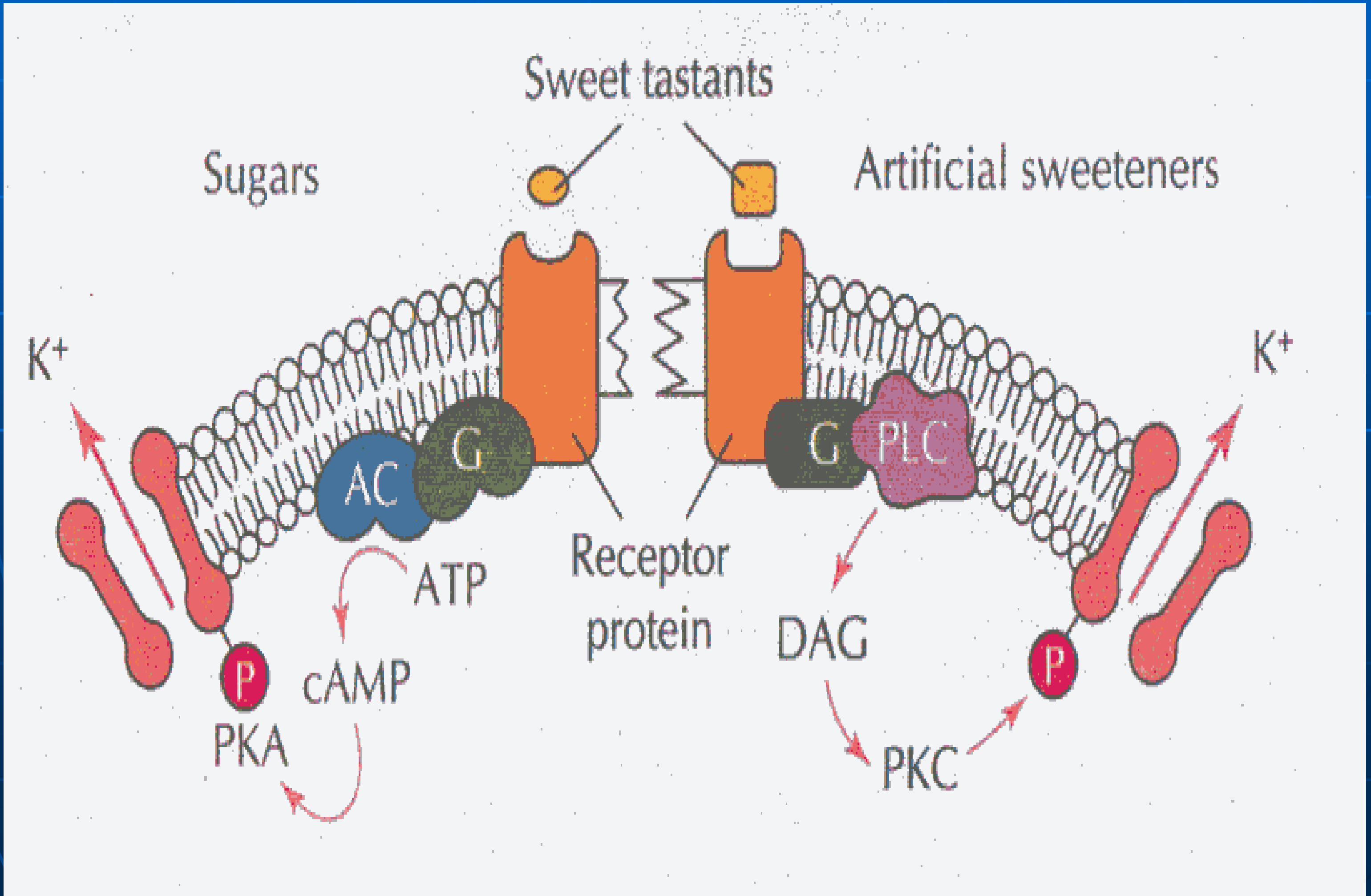
Bitter and sweet substances bind into receptor sites which release other substances into the cell.

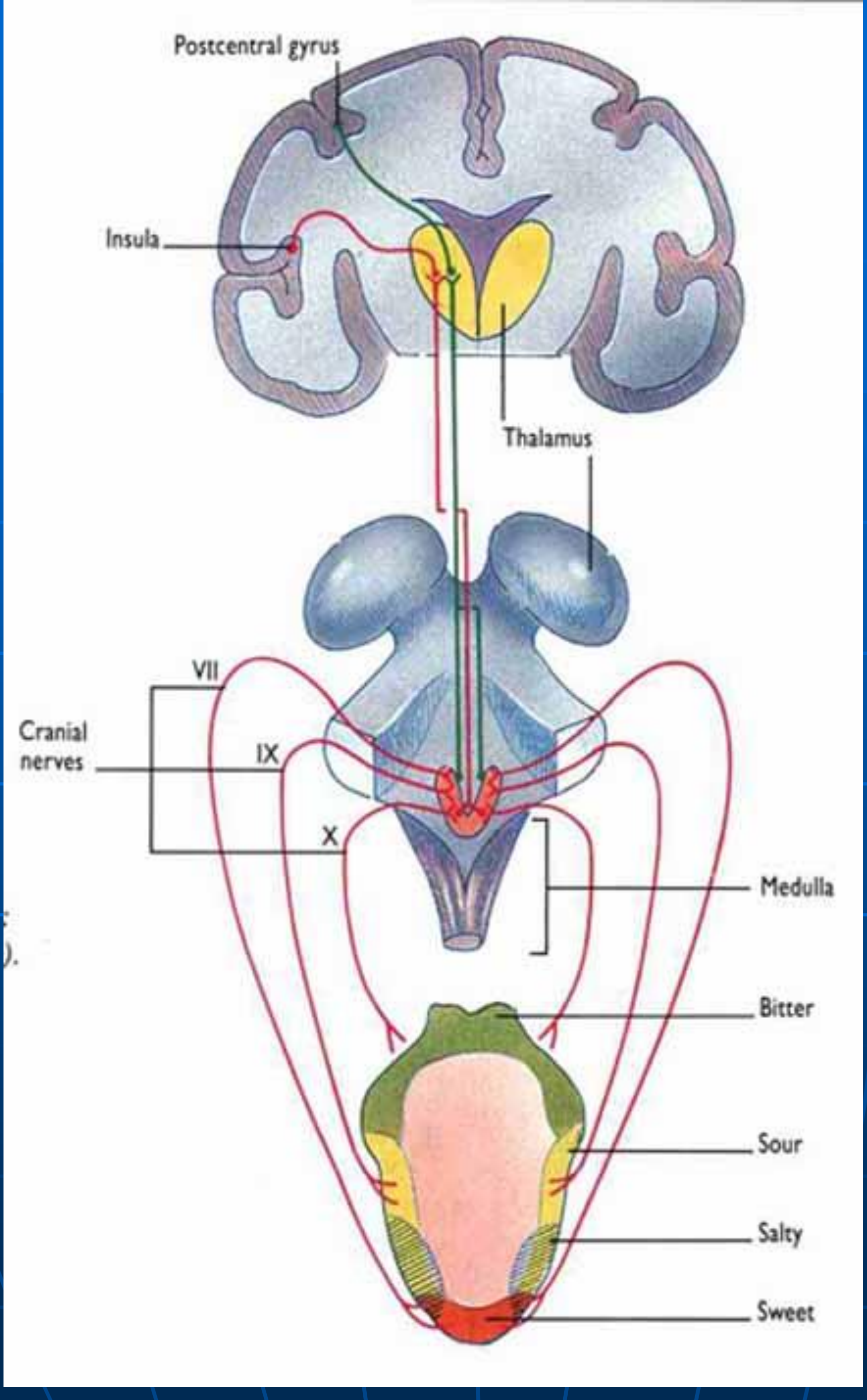
Sour substances contain H+ ions that block channels in the membrane. Salty substances break up into Na+ ions which flow through the membrane directly into the cell.



Bitter
Sweet
Sour
Salt
Receptors on tip of taste cell
Taste cell

Tastant binding activates the G protein to stimulate adenylate cyclase to syn. Cyc AMP. cAMP activates protein kinase to phosphorylate the K+ channel closes it causing a potential – nerve impulse



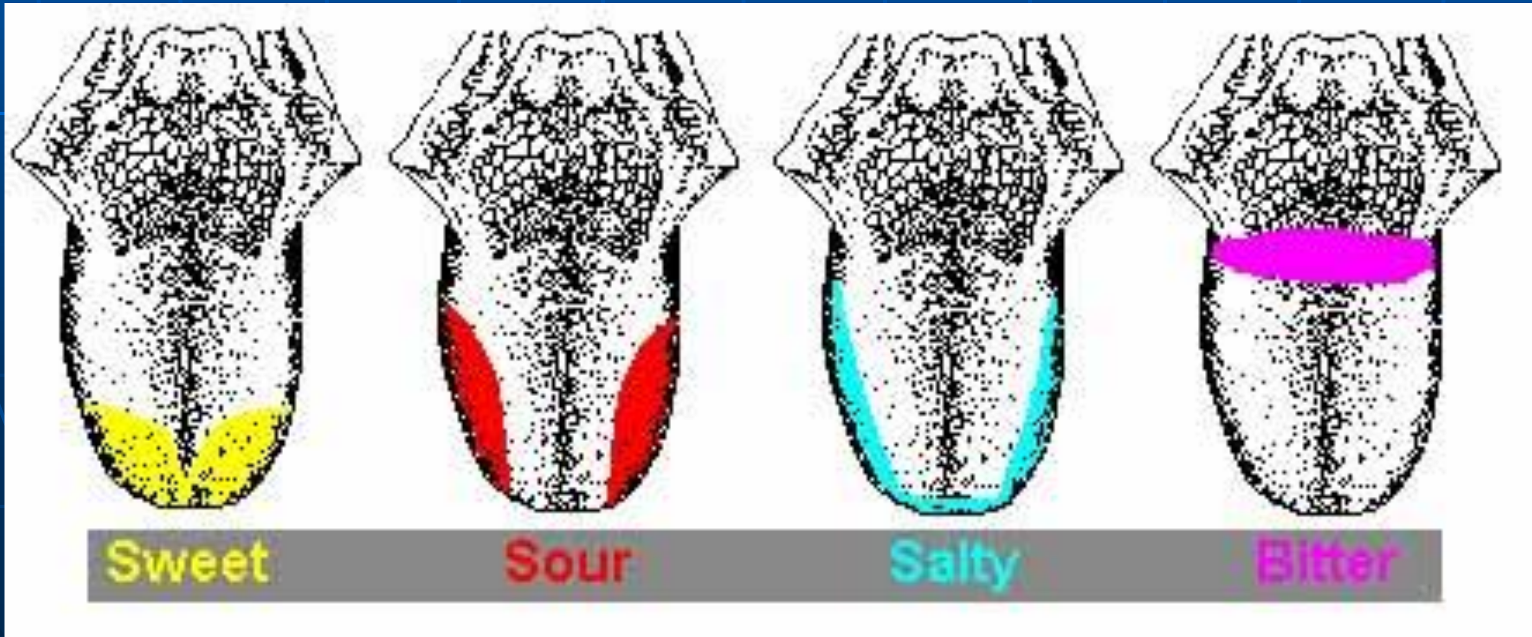


Postcentral gyrus
Insula
Thalamus
VII
Cranial nerves
IX
X
Medulla
Bitter
Sour
Salty
Sweet

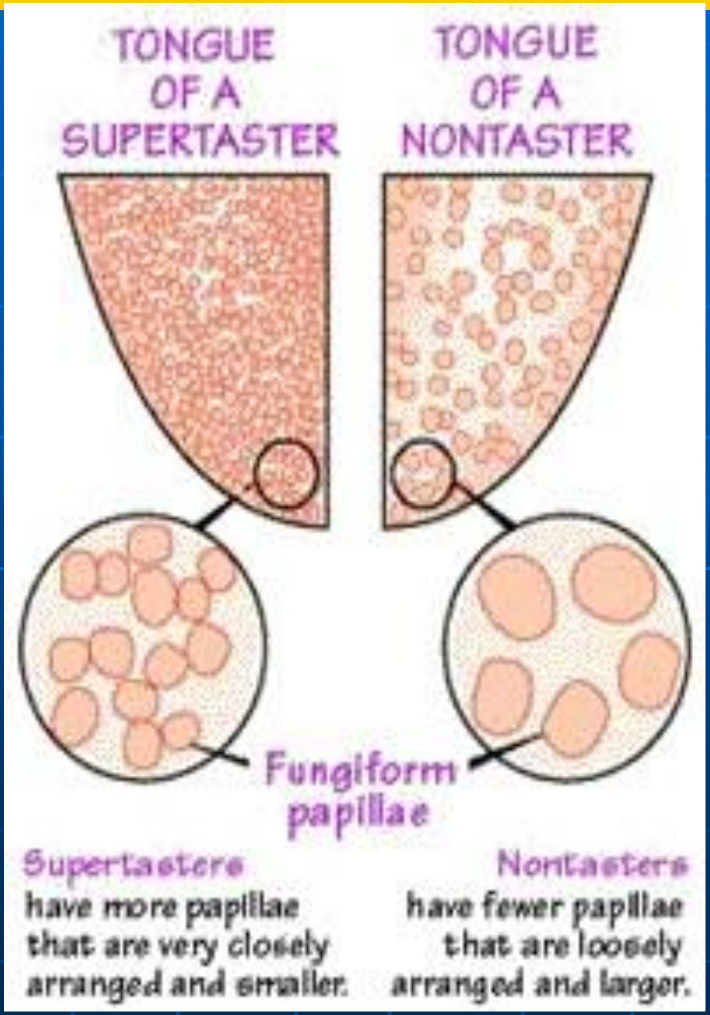
The Neural Code for Taste

What tastes do we taste? The four basic tastes are sour, sweet, salty, and bitter. All of our taste sensations can be described as a combinatio of these four basic tastes.

Different taste receptors (and therefore different parts of the tongue) are most sensitive to different tastes.



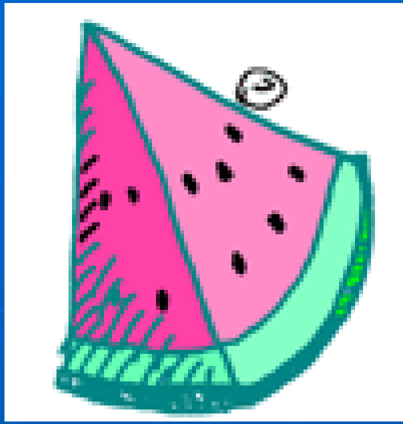
Genetic Differences

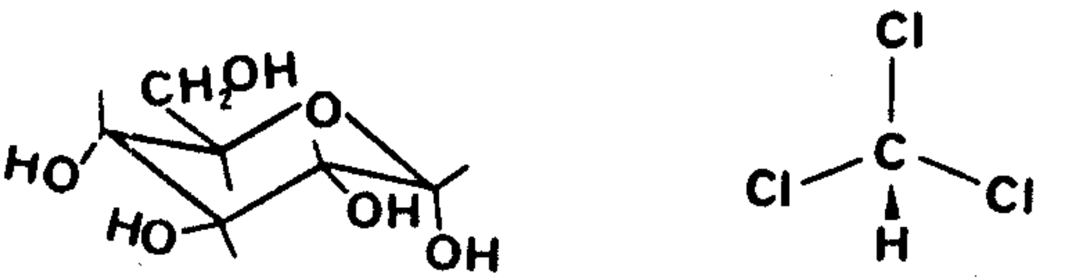


A. Taste Substance

1. Sweetness

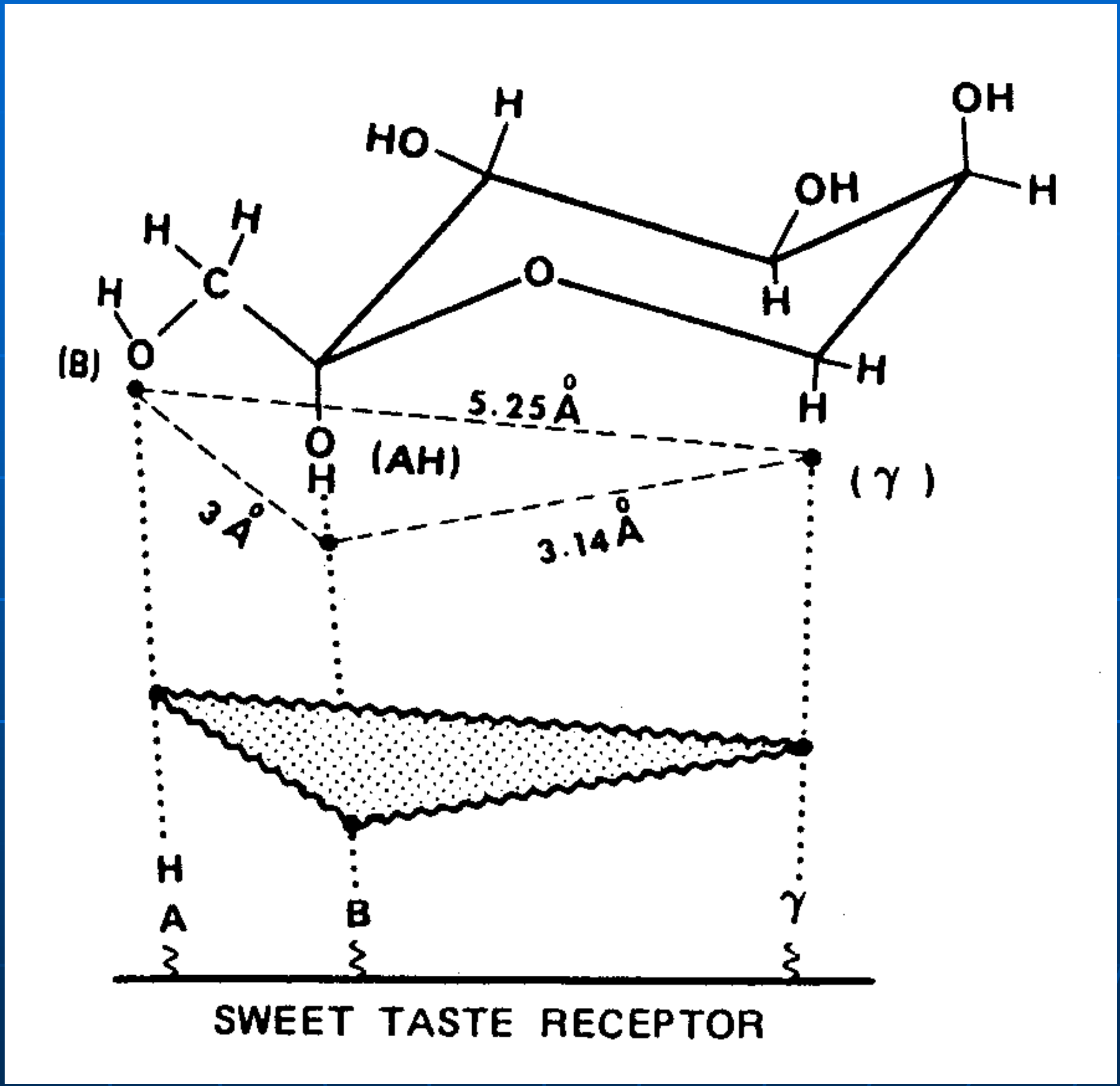
-OH $CHCl_3$

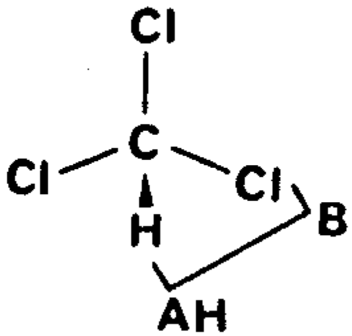




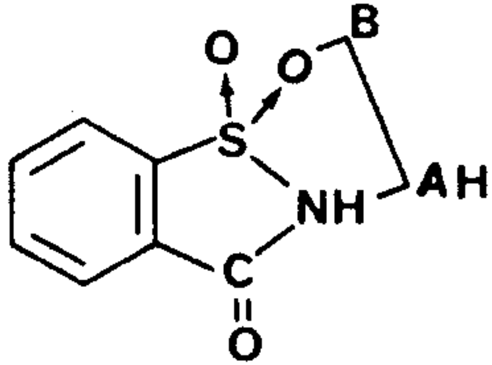
D-GLUCOSE   CHLOROFORM

AH/B theory

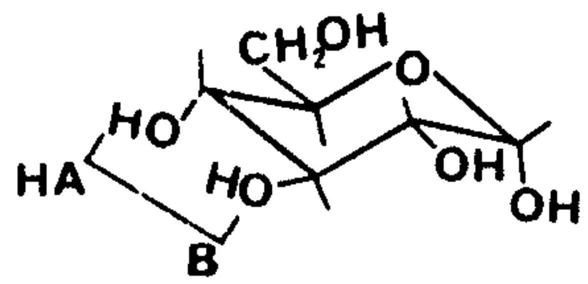

HO
H
OH
OH
H
H
H
C
H
O
H
(B) O
H
H
H
5.25 Å
O
H
(AH)
(γ)
3 Å
3.14 Å
H
A
B
γ
SWEET TASTE RECEPTOR



CHLOROFORM

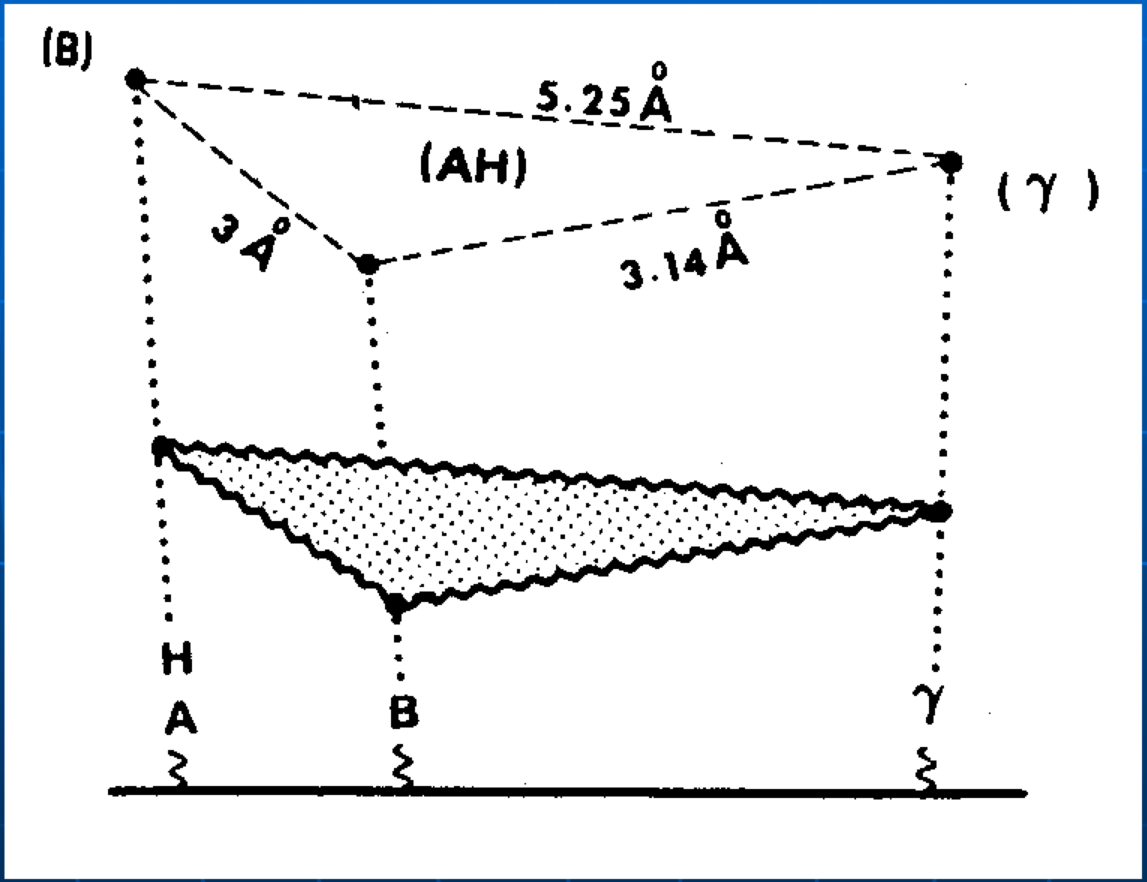


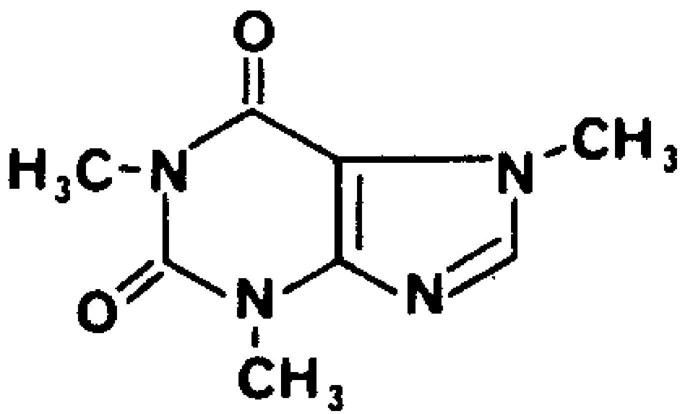
SACCHARIN



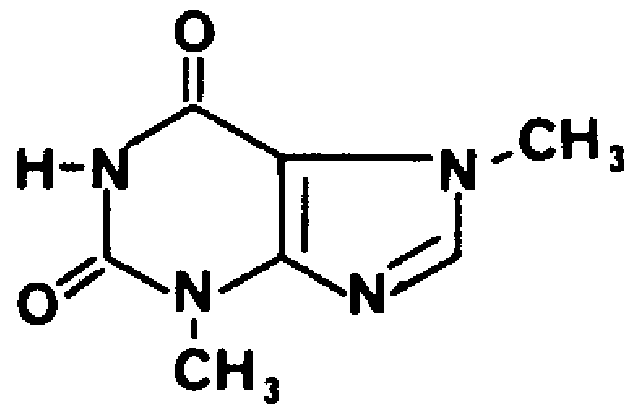
D-GLUCOSE

2. การรับรสขม

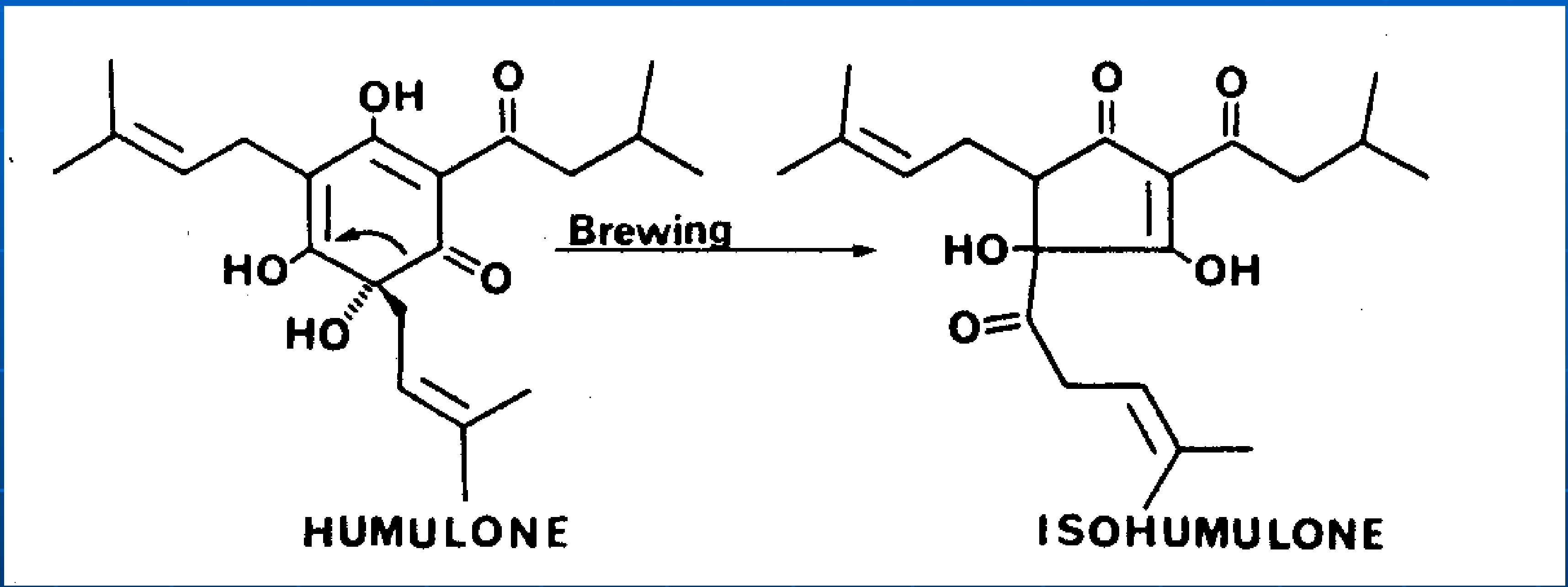


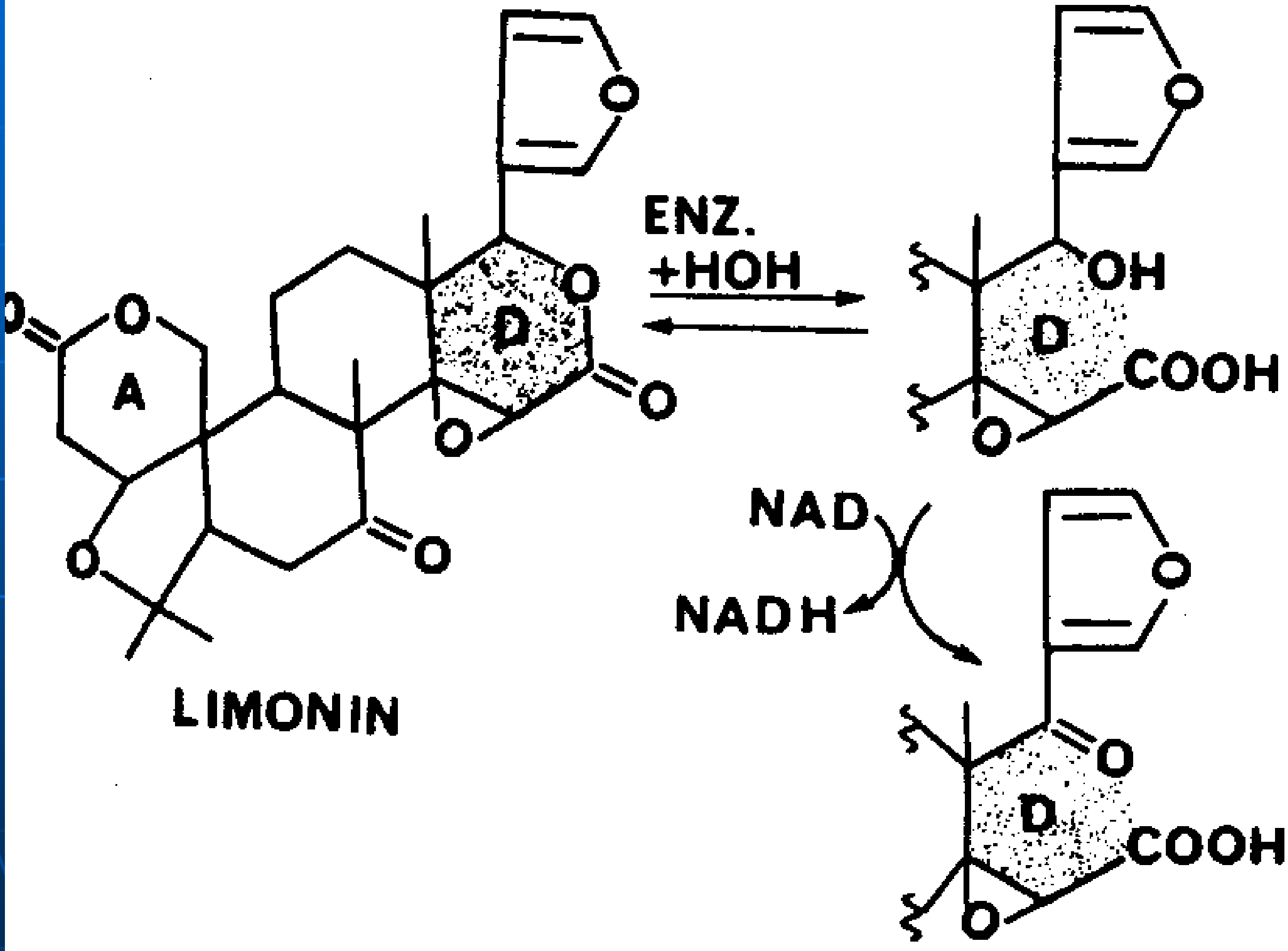


CAFFEINE



THEOBROMINE


OH
O
HO
HO
O
Brewing
HUMULONE
O
O
HO
OH
O
ISOHUMULONE



O
O
A
O
O
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D
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LIMONIN
ENZ.
+HOH
OH
D
COOH
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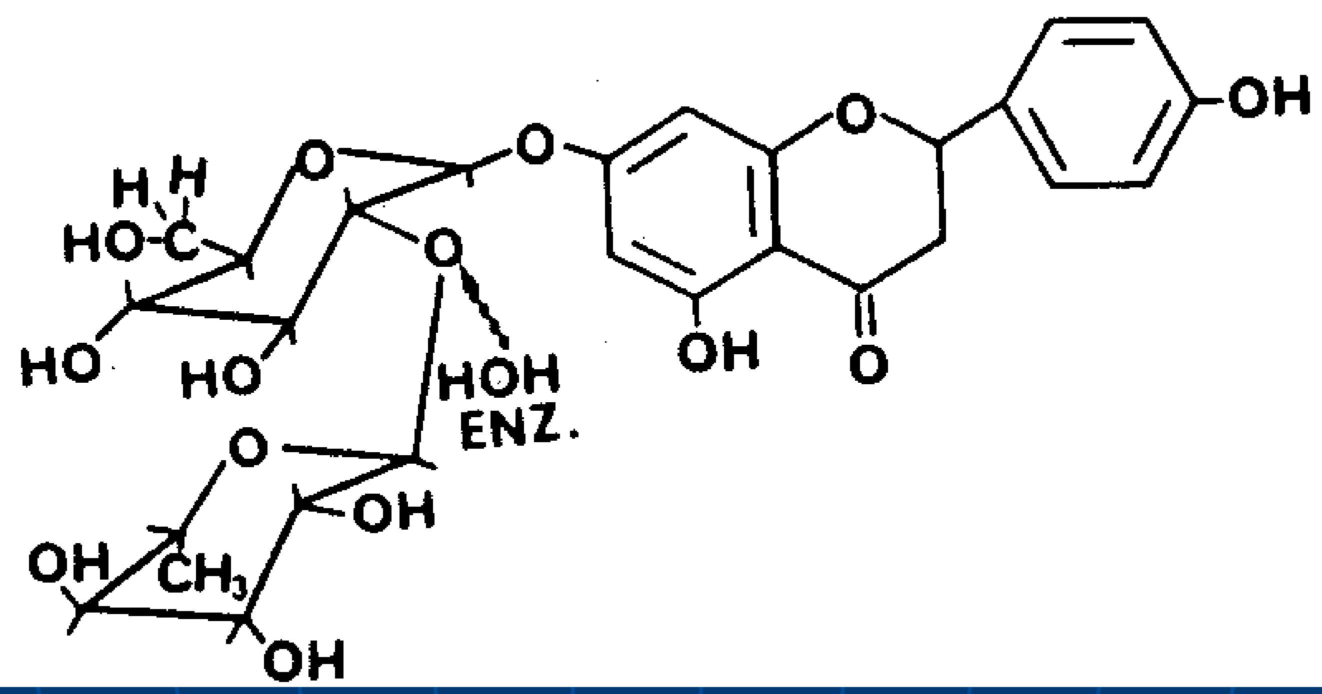
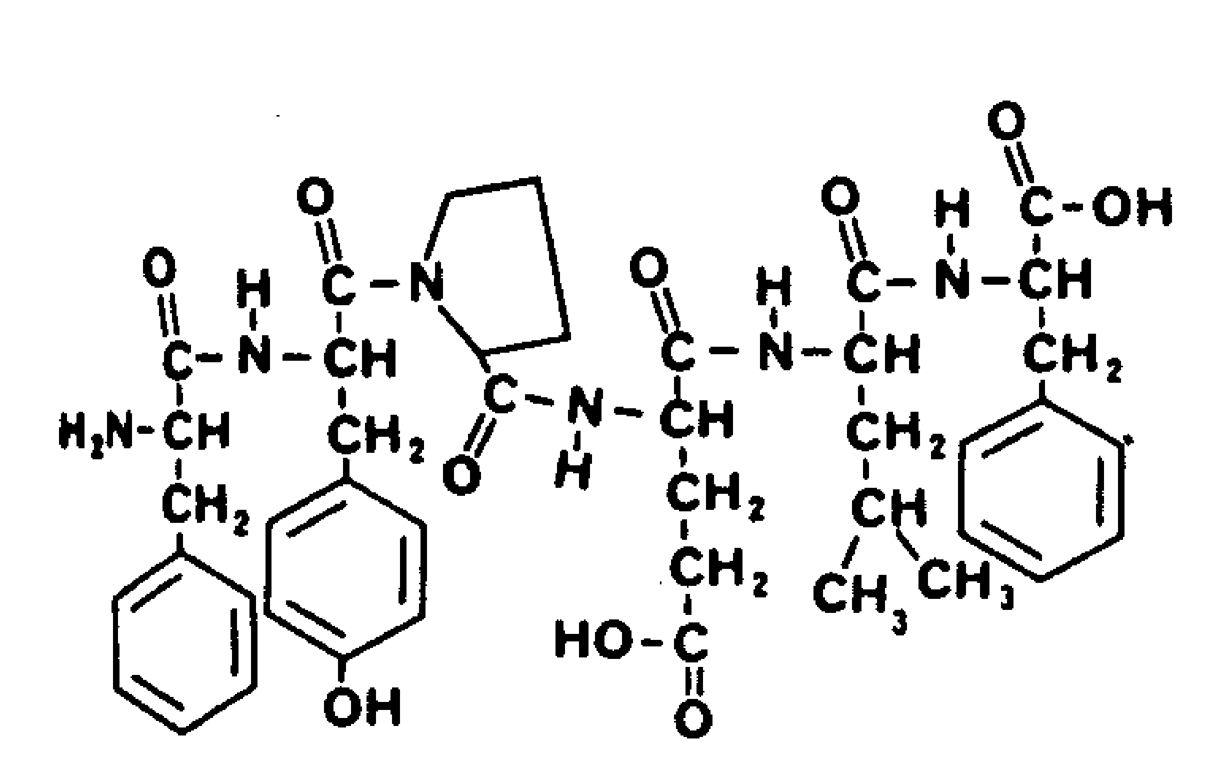
NAD
NADH
O
O
D
COOH
O



Naringin

- **Bitter peptide**



(phe-tyr-pro-glu-leu-phe)

- Protein bitterness

$$Q = \frac{\Sigma \Delta g}{n}$$

contribution of a.a. side chain

Mean hydrophobicity of protein

Calculated Δg Values for Individual Amino Acids

Amino acids	Δg Value (cal/mol)
Glycine	0
Serine	40
Threonine	440
Histidine	500
Aspartic acid	540
Glutamic acid	550
Arginine	730
Alanine	730
Methionine	1300
Lysine	1500
Valine	1690
Leucine	2420
Proline	2620
Phenylalanine	2650
Tyrosine	2870
Isoleucine	2970
Tryptophan	3000

Source: From Ney (68).

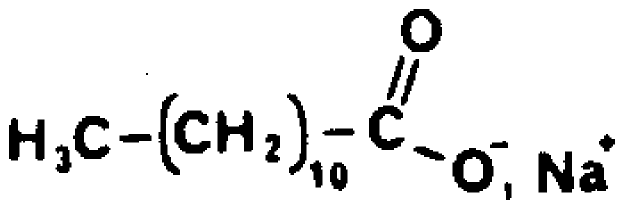
3. Salty and Sour

Salty

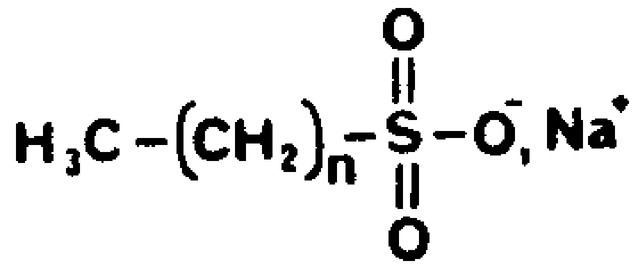
- Classic salty taste – Sodium chloride
- Complex taste   overall perception of sweetness, bitter, sour, salty
- Potassium and other cation salty and bitter taste

Sour

- Concentration of hydrogen ion



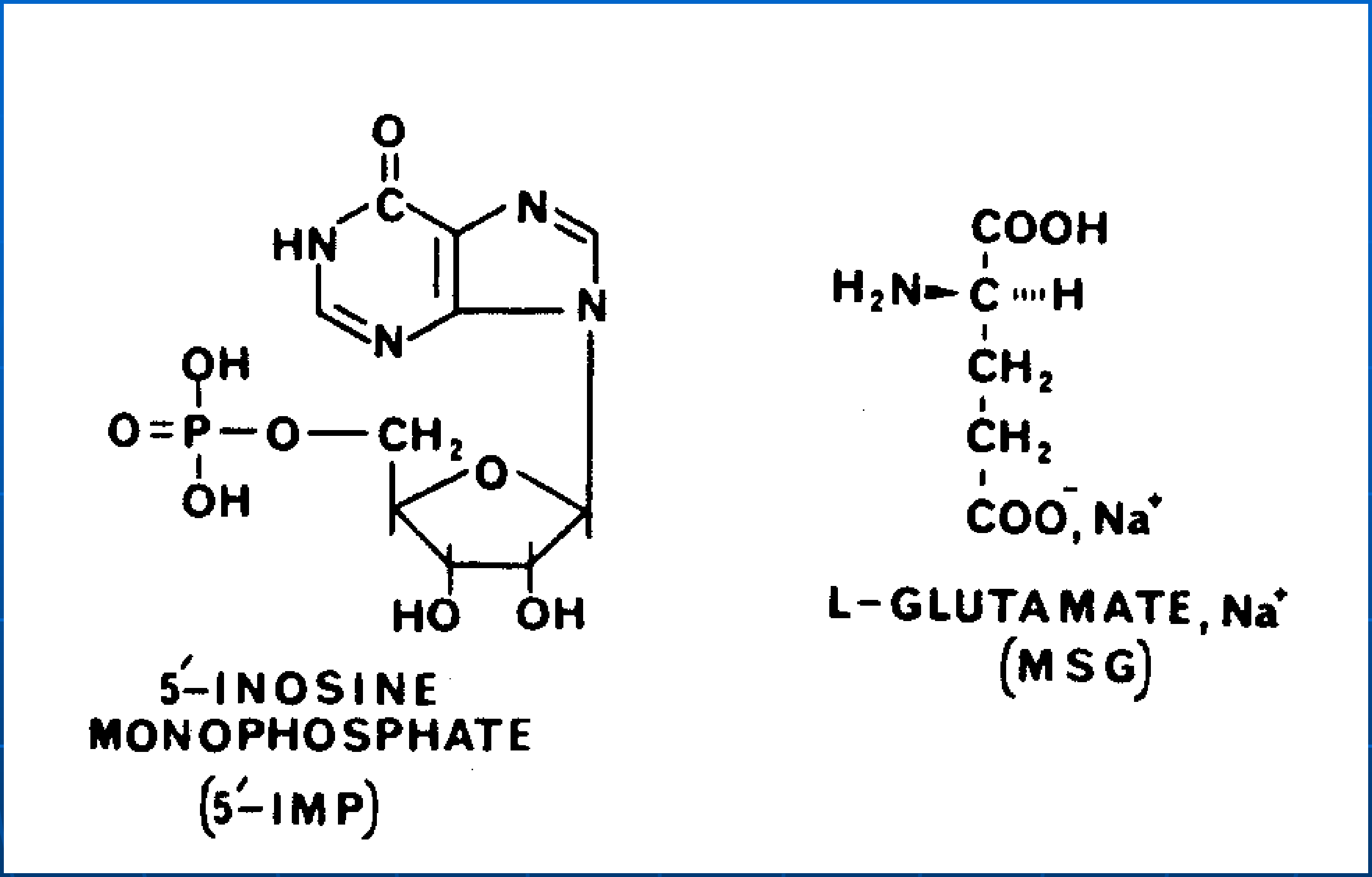
SODIUM LAURATE



SODIUM LAURYL SULFATE

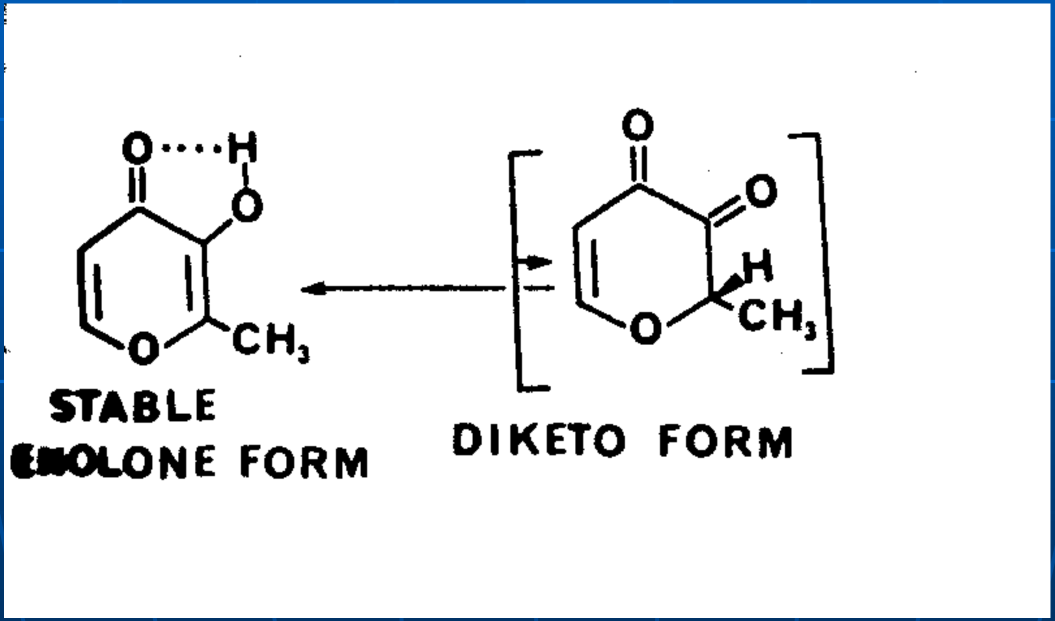
B. Flavor Enhancers

- ให้รสอร่อย หรือ umami taste เมื่อใช้ > threshold
  และจะเพิ่มรสชาติเมื่อใช้ < threshold
- ผลที่เด่นชัด และทำให้เกิดความพึงพอใจ ในกลิ่นรส ของ
  ผัก ผลิตภัณฑ์นม เนื้อสัตว์



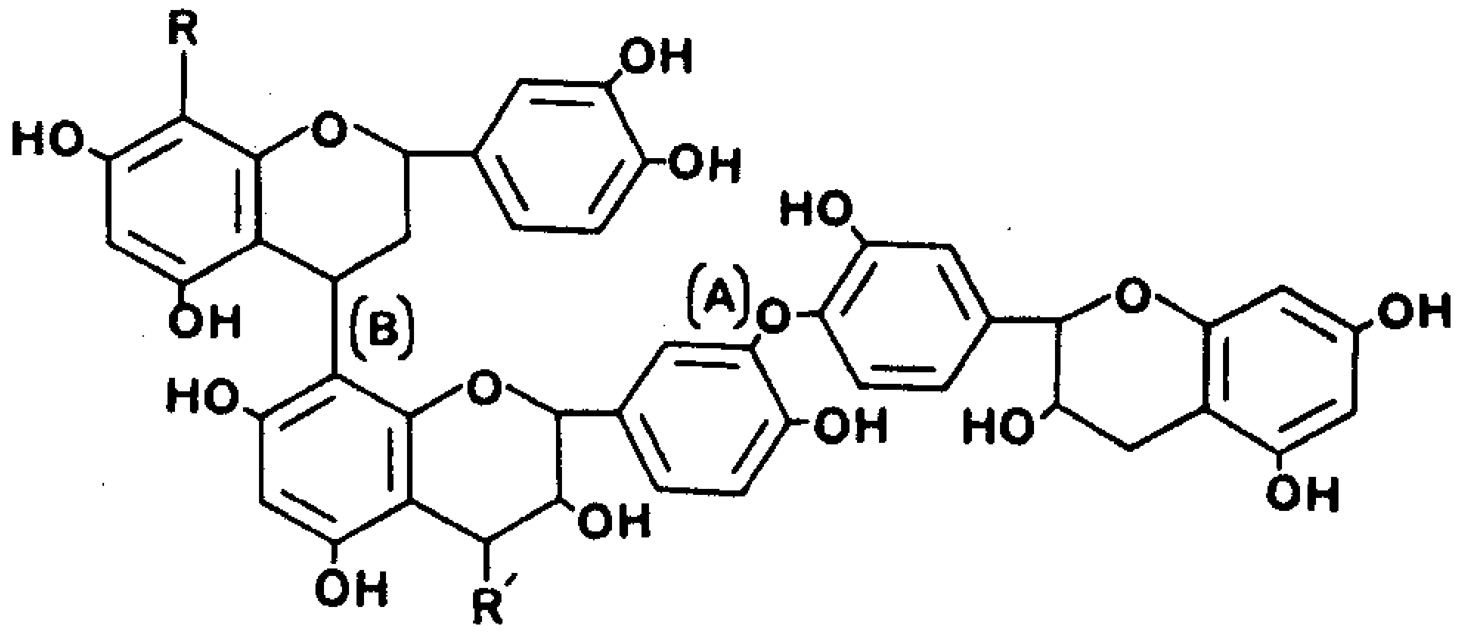
- โดยมากมาจากจุลินทรีย์

- synergistic interaction of MSG and 5'- ribonucleotide
- maltol or ethyl maltol are using in confectionery, beverages



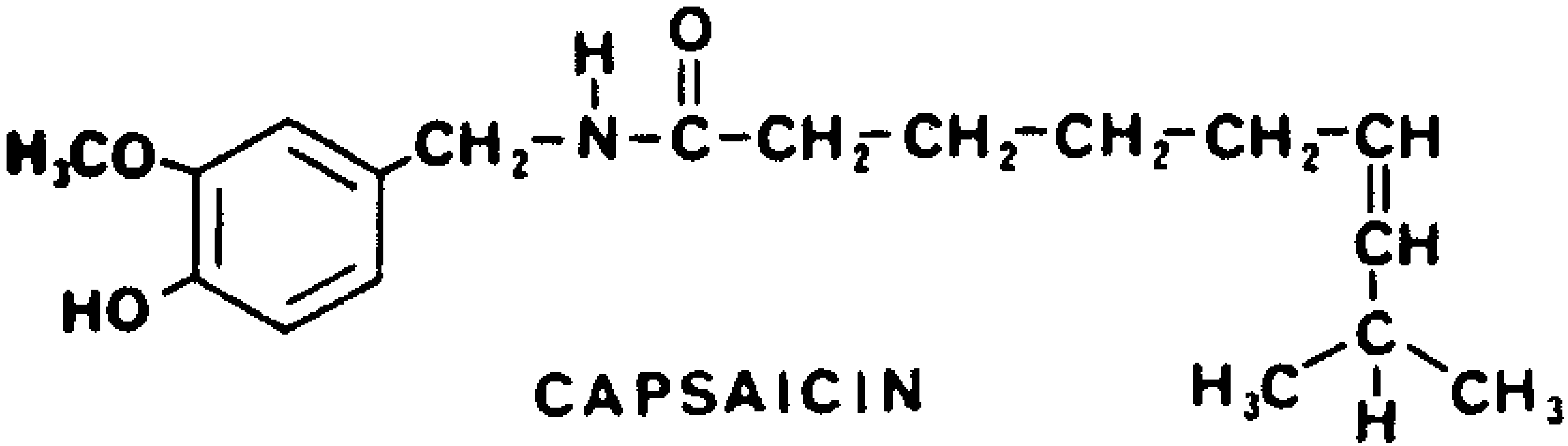
- burnt caramel aroma
- Sweet taste at low conceentration

C. Astringency



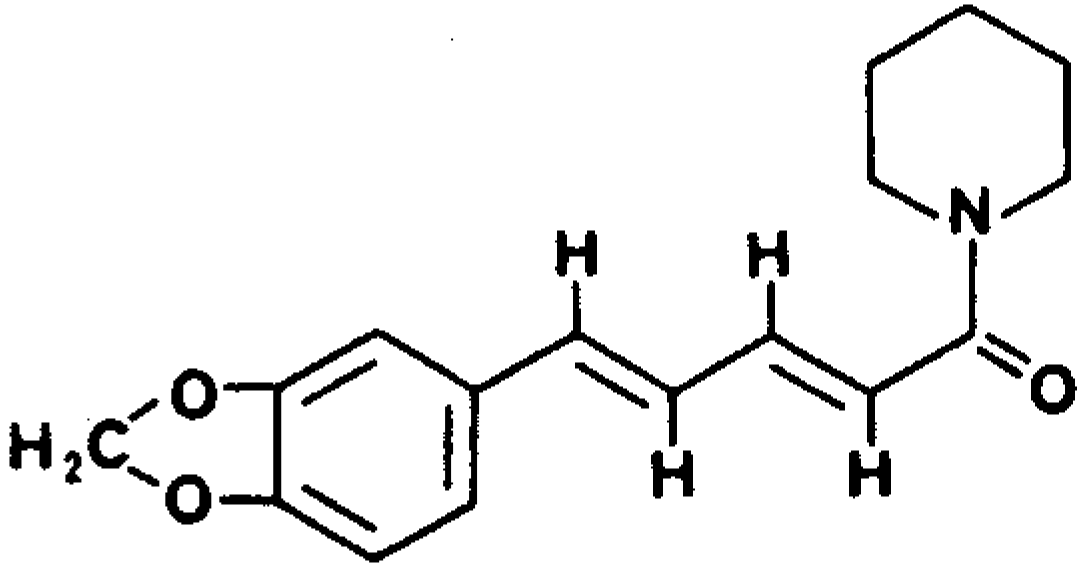
Tannin

D. Pungency



CAPSAICIN

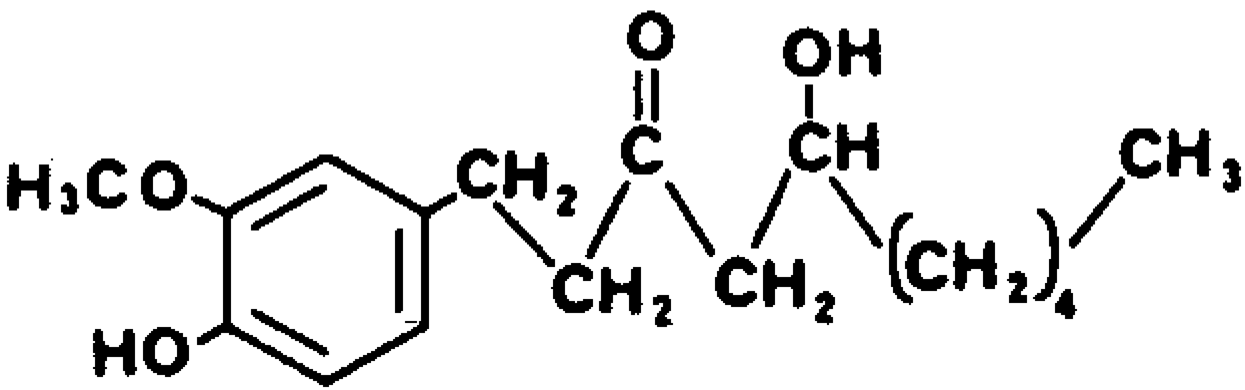
vanillylamides of monocarboxylic acids



PIPERINE

- black and white pepper

phenylakyl ketones



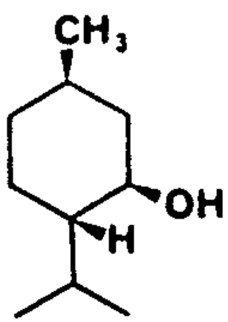
[6]-GINGEROL

- shogaols

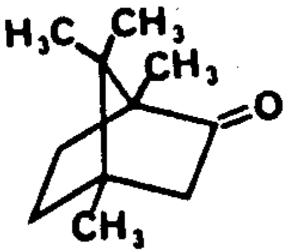
E. Cooling

- react at receptor
- cooling effect related with mint like flavour

  (spearmint peppermint wintergreen)



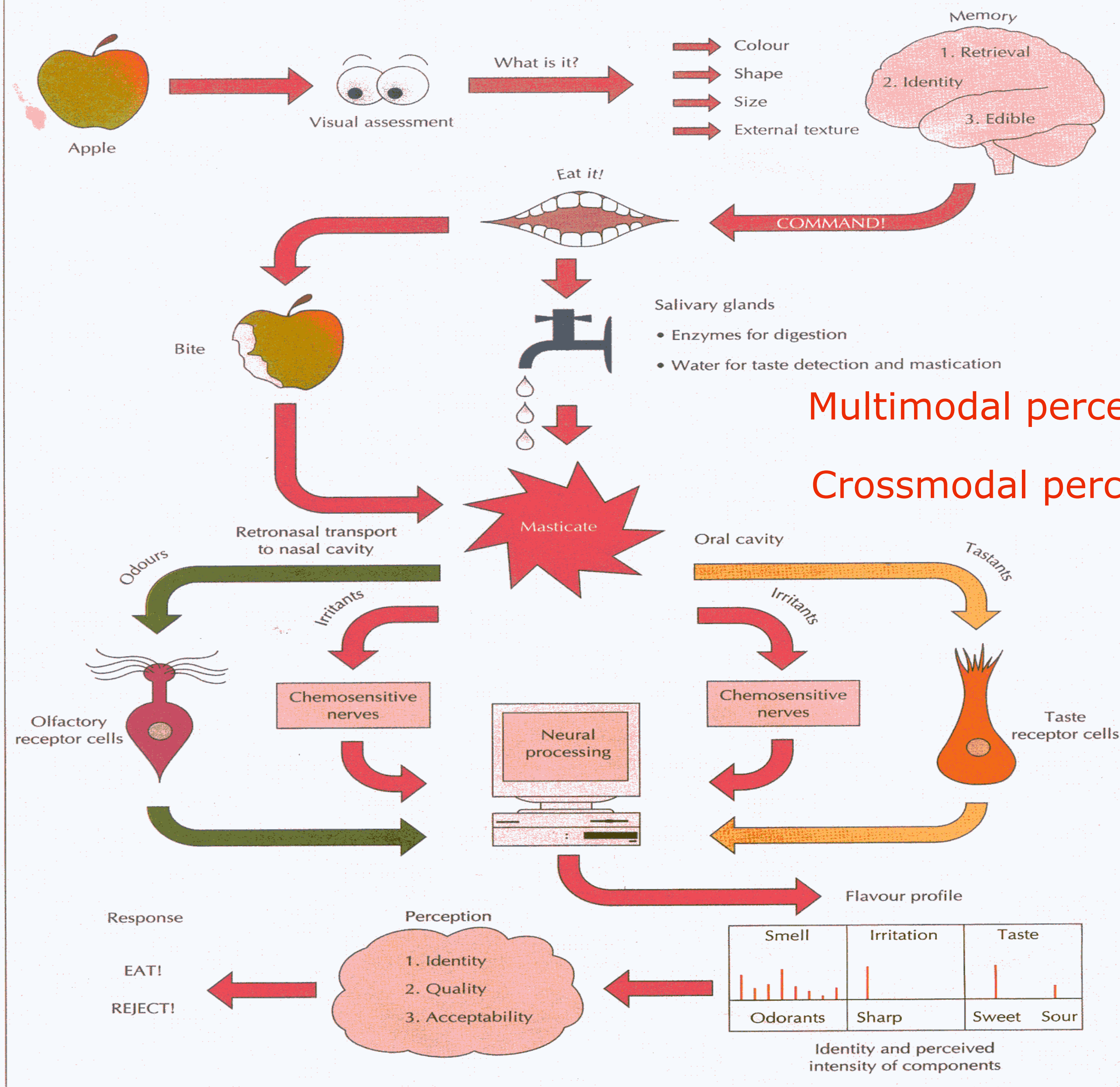
(–)-MENTHOL



d-CAMPHOR

Flavour Perception

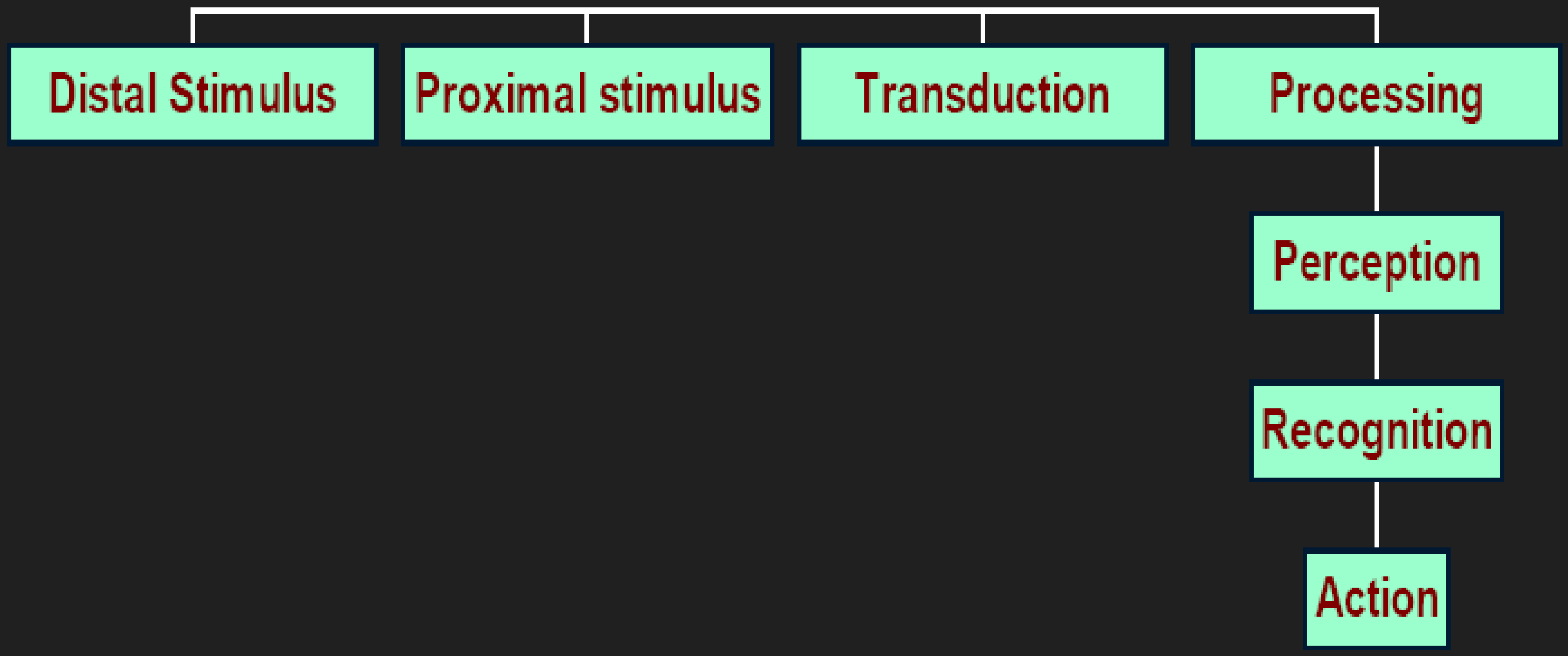
Fig. 1 Mechanisms of flavour perception

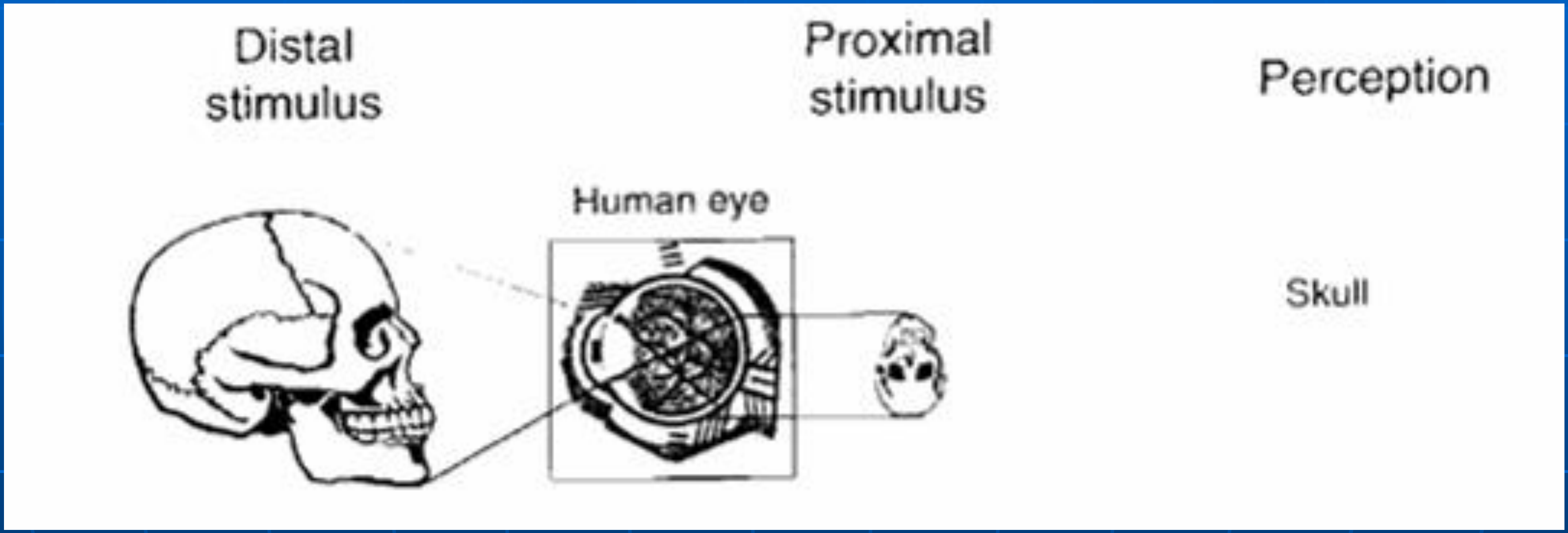


Multimodal perception

Crossmodal perception

Steps in perception process




Distal stimulus
Proximal stimulus
Perception
Human eye
Skull

Flavour Perception

Psychological view of perception applied to flavour

Distal Stimulus

Proximal stimulus

Perception

Flavour composition in food

Static headspace

Orthonasal signal

Aroma and taste profile at receptors

Ortho, retro nasal signal

Combination of taste, aroma and mouthfeel signals in brain

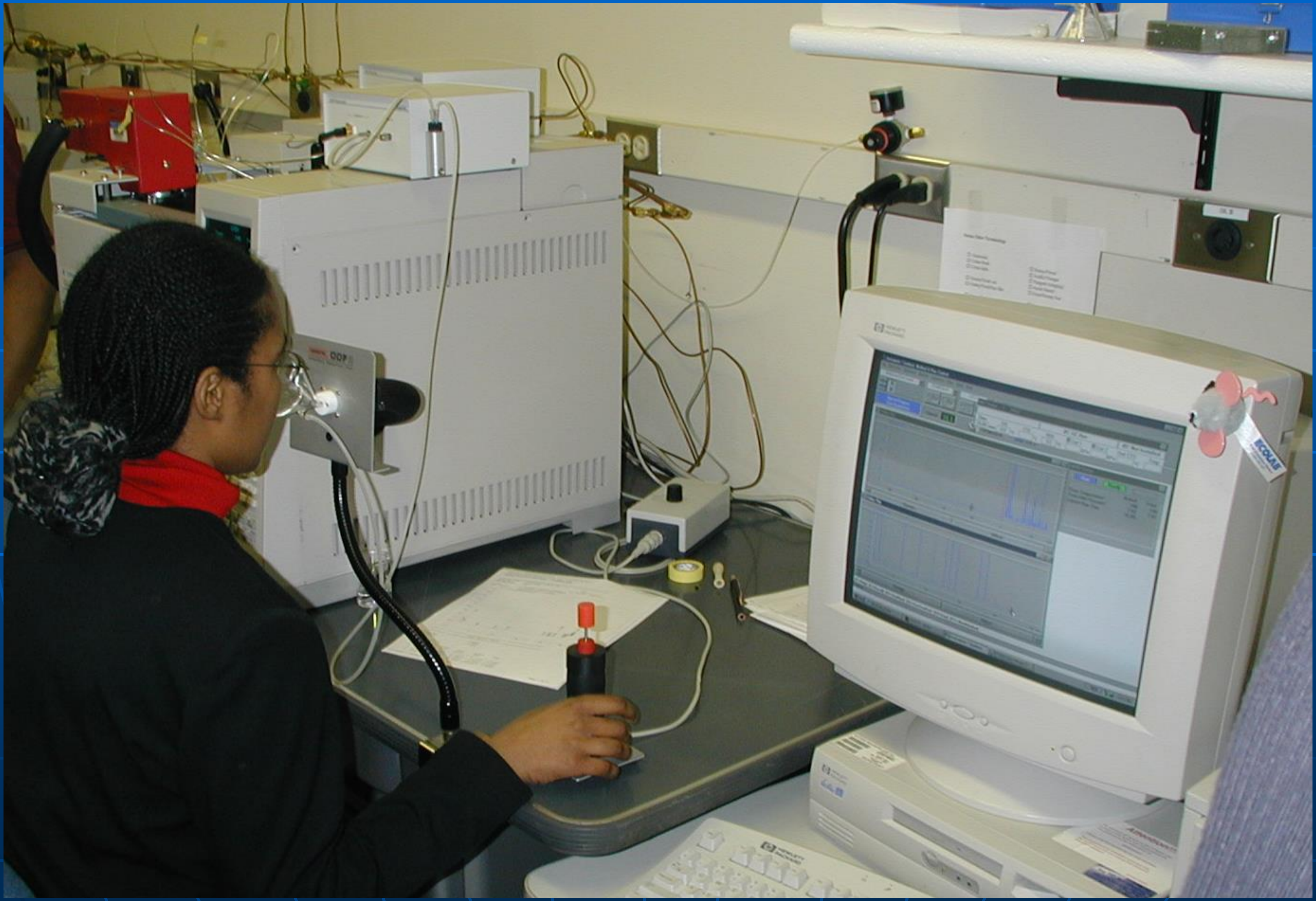
Measured by extraction & GC-MS

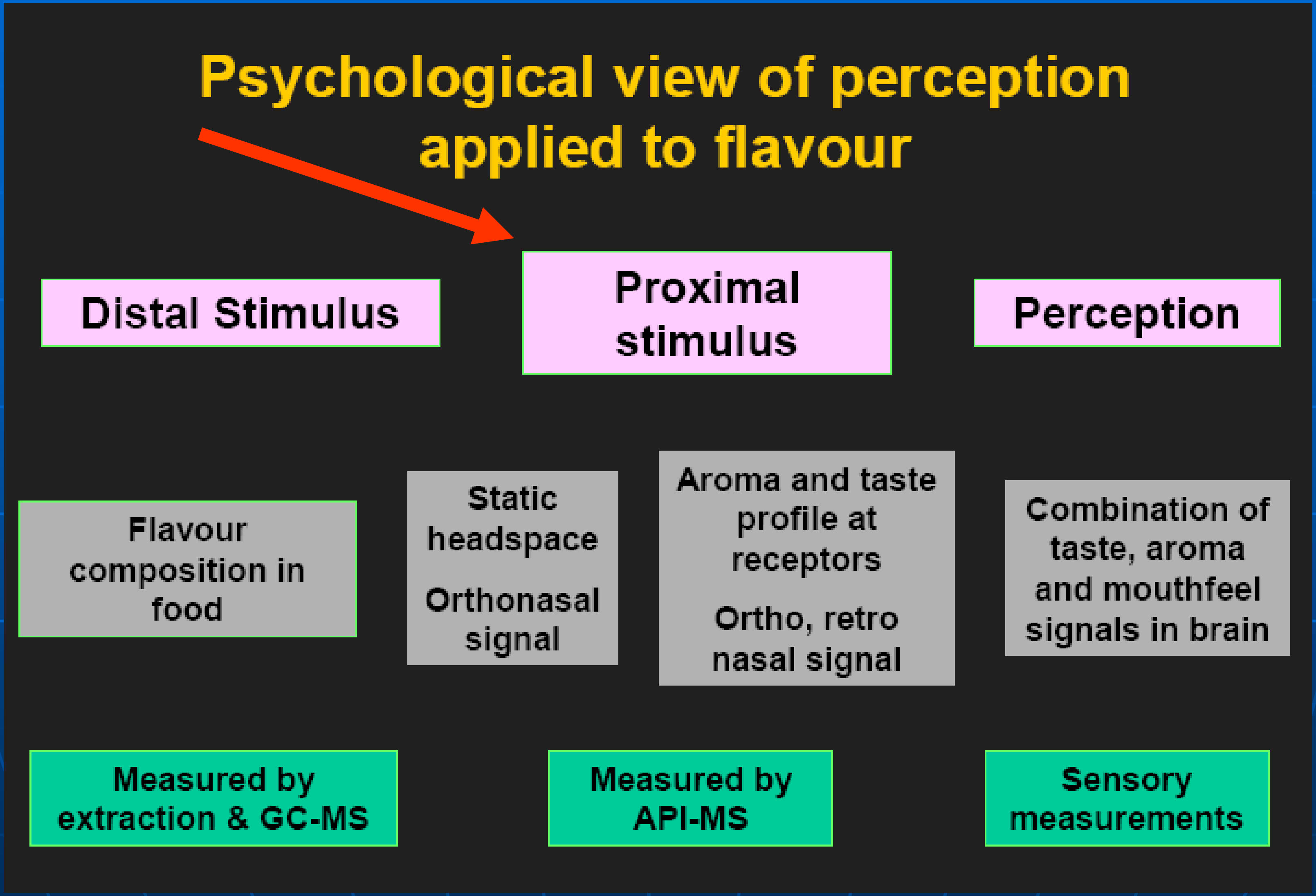
Measured by API-MS

Sensory measurements

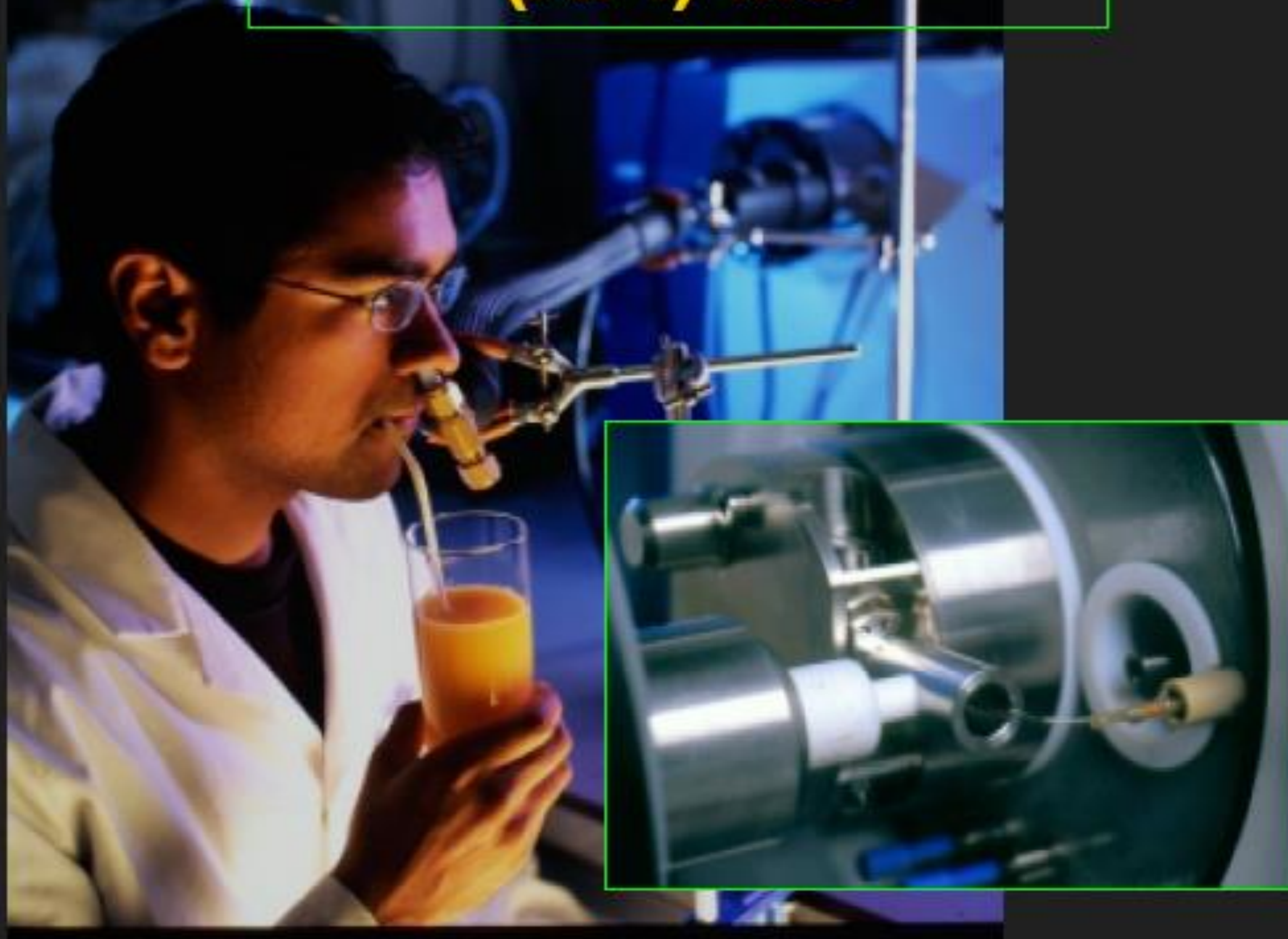
Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Olfactometry (GC-O)




Psychological view of perception applied to flavour
Distal Stimulus
Proximal stimulus
Perception
Flavour composition in food
Static headspace
Orthonasal signal
Aroma and taste profile at receptors
Ortho, retro nasal signal
Combination of taste, aroma and mouthfeel signals in brain
Measured by extraction & GC-MS
Measured by API-MS
Sensory measurements

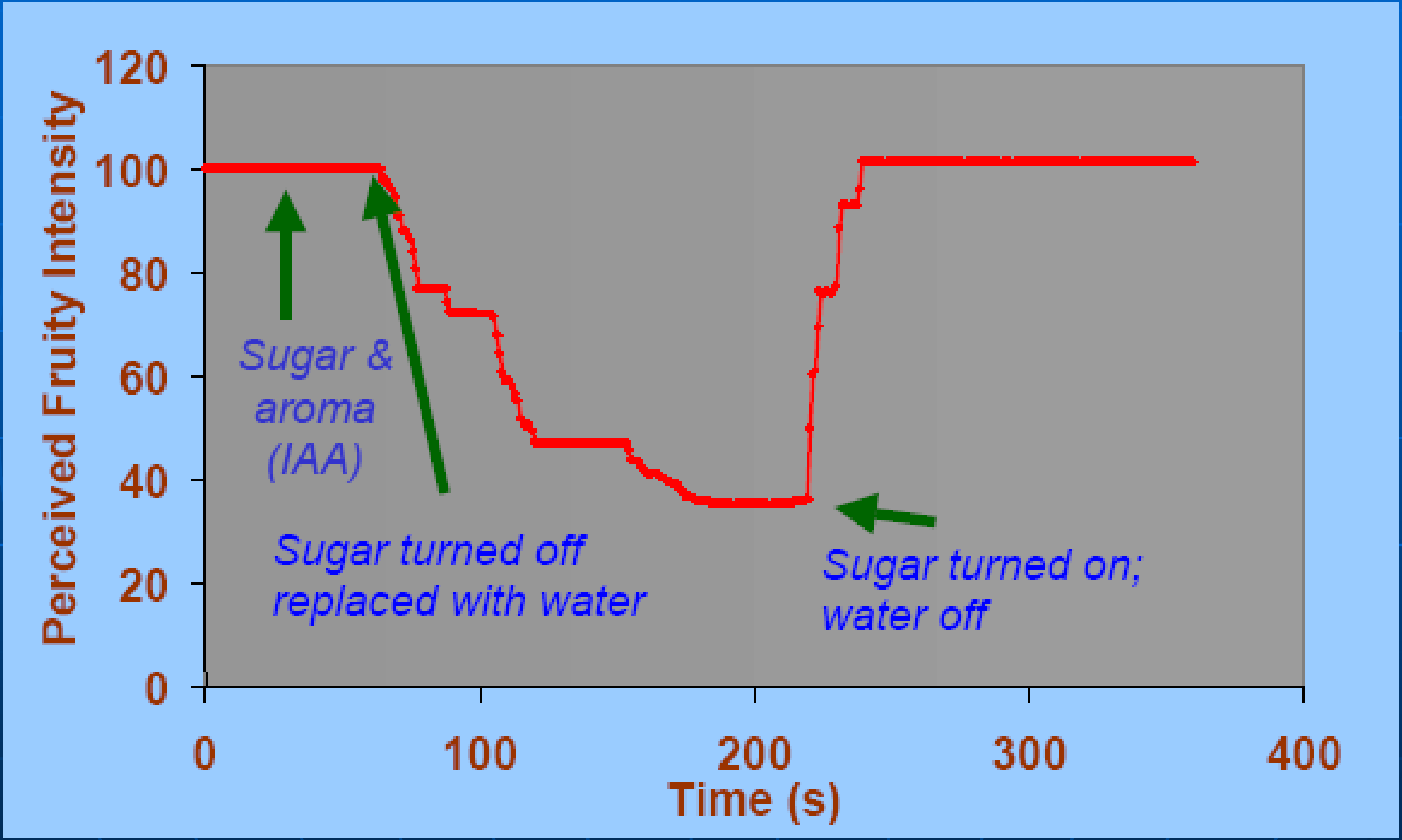
Atmospheric Pressure Ionisation (API)-MS



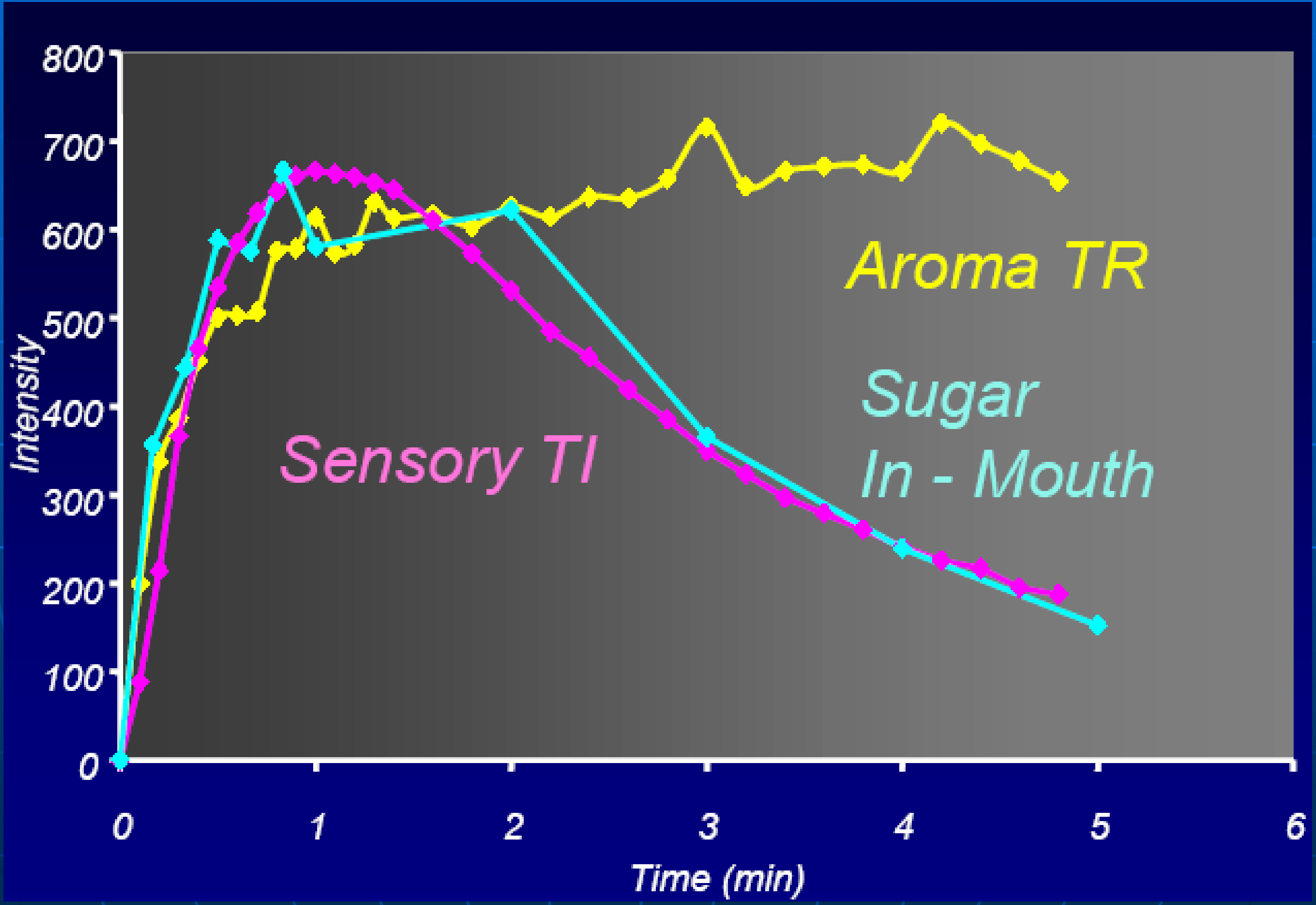
Psychological view of perception applied to flavour

Distal Stimulus	Proximal stimulus	Perception
Flavour composition in food	Static headspace Orthonasal signal | Aroma and taste profile at receptors Ortho, retro nasal signal	Combination of taste, aroma and mouthfeel signals in brain
Measured by extraction & GC-MS	Measured by API-MS	Sensory measurements

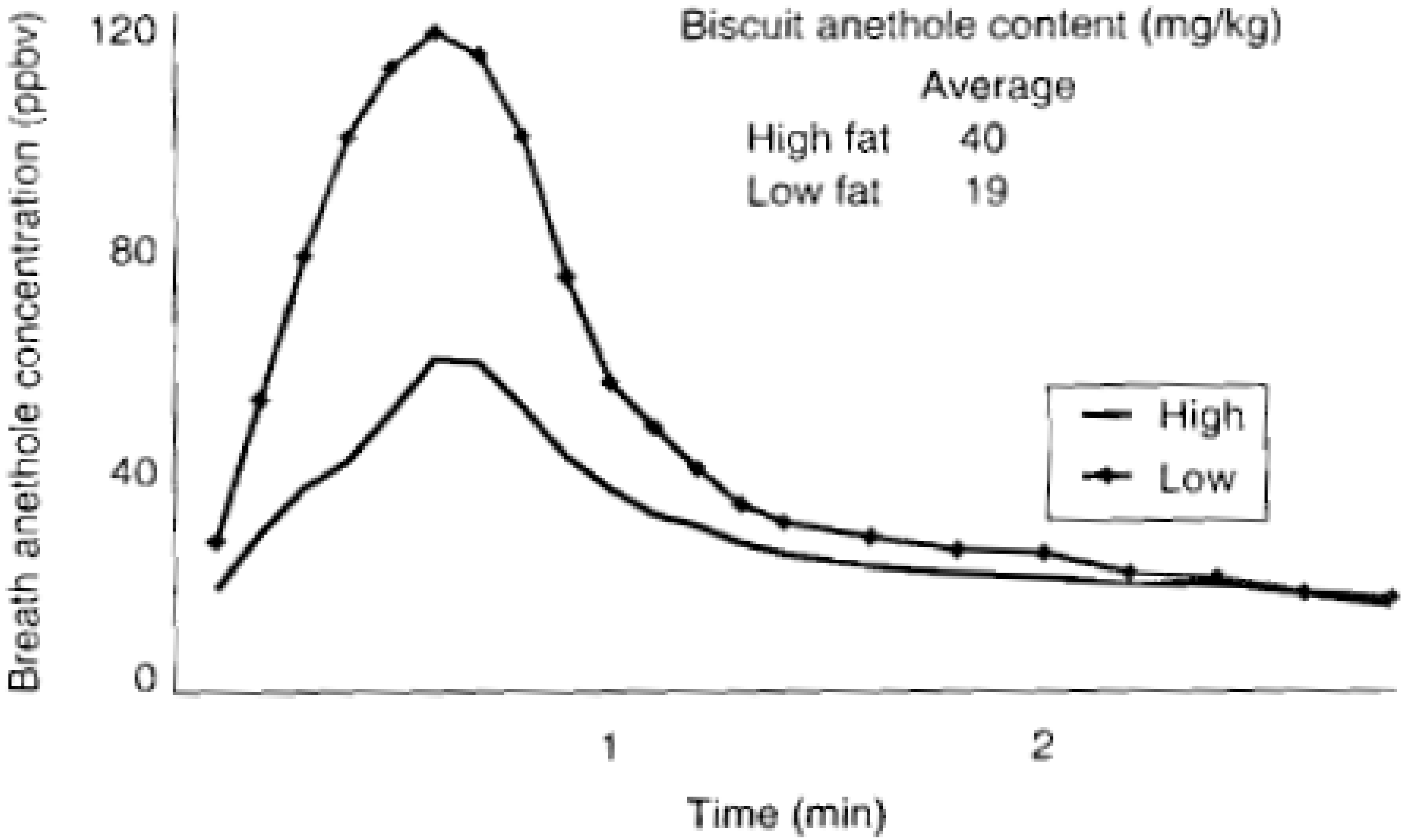
Evidence of a sugar –aroma interaction



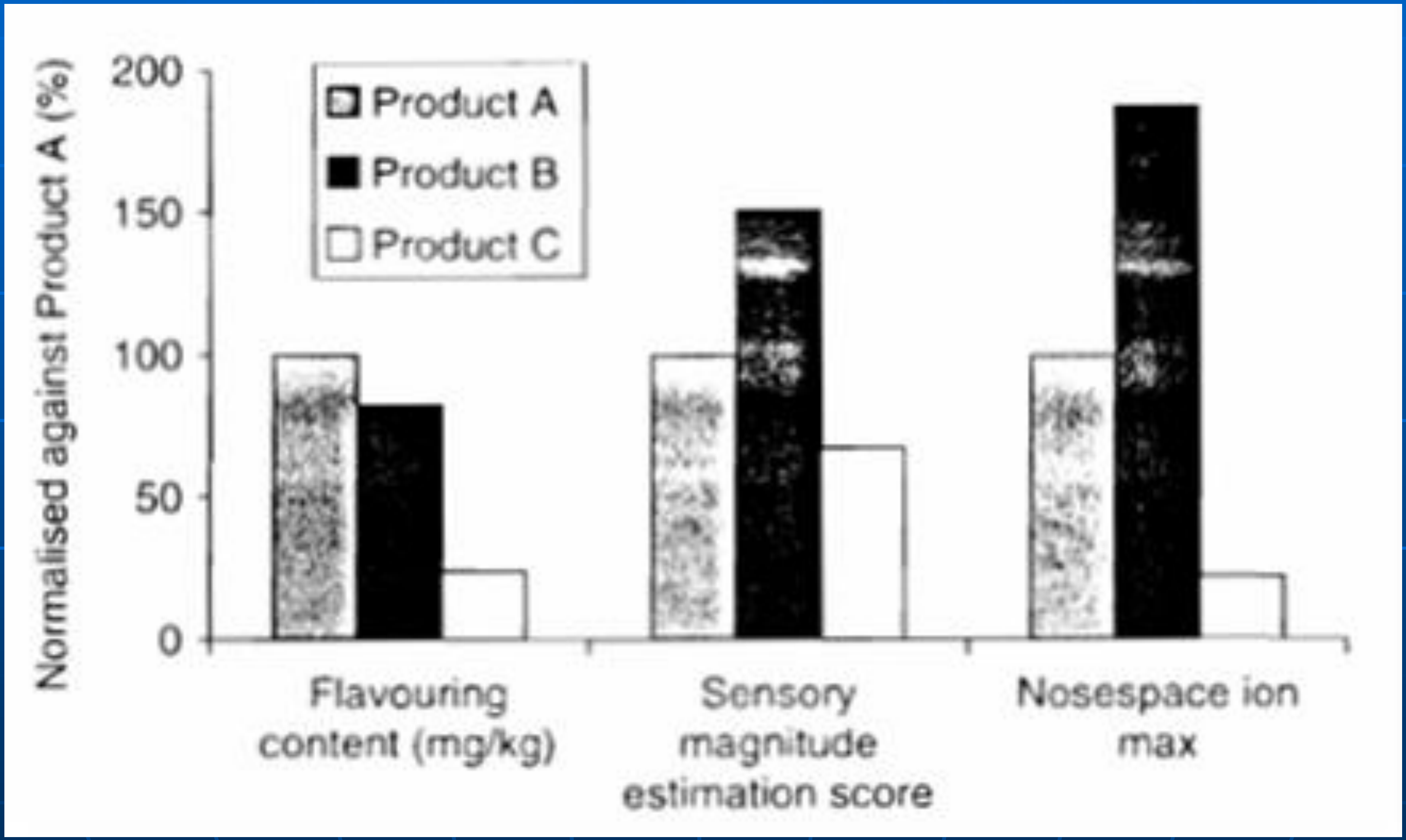
Stick Gum: Aroma, Sensory and Sugar



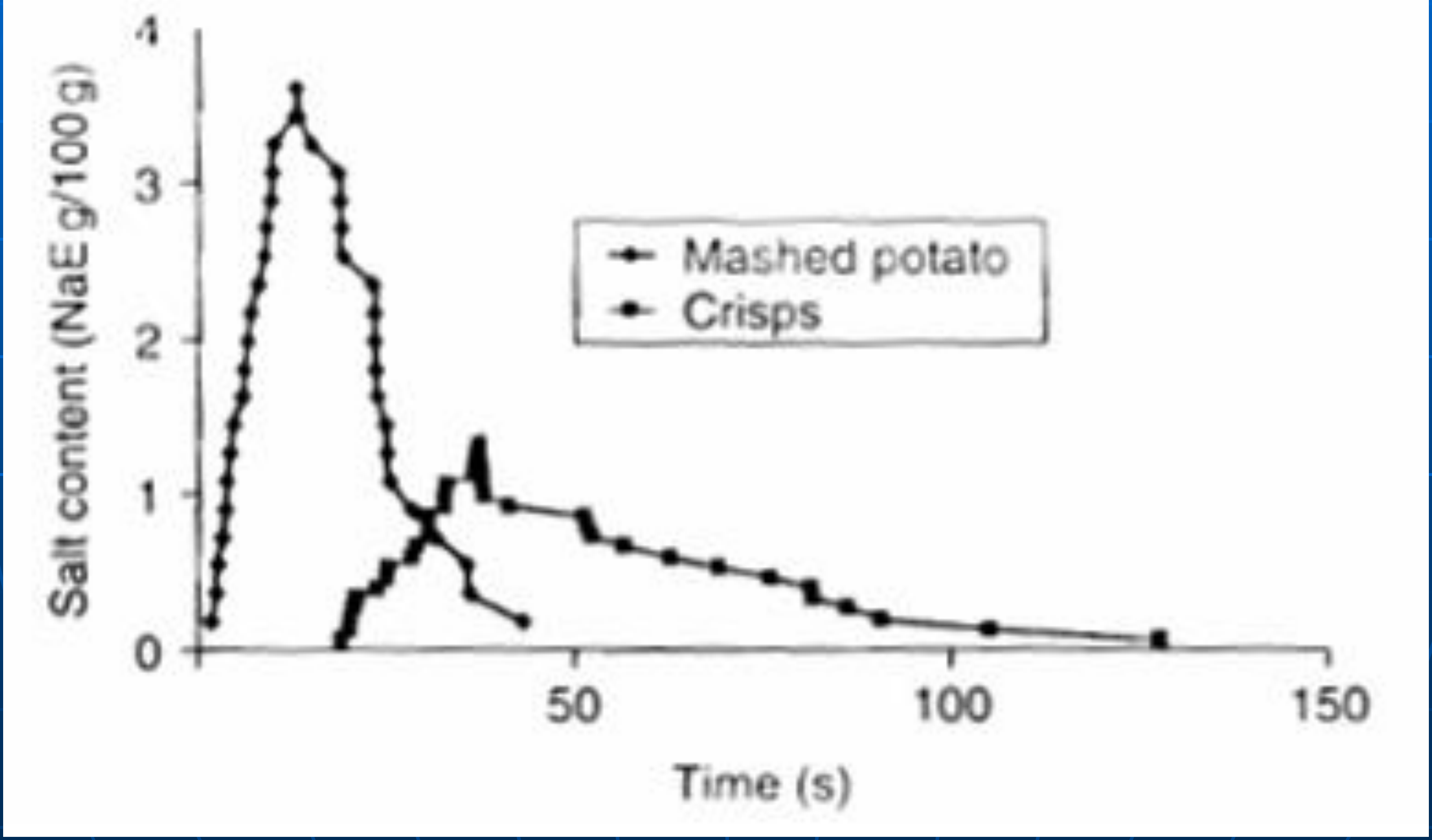
Examples of differences in distal and proximal aroma stimuli



Relating proximal aroma stimuli to flavour perception



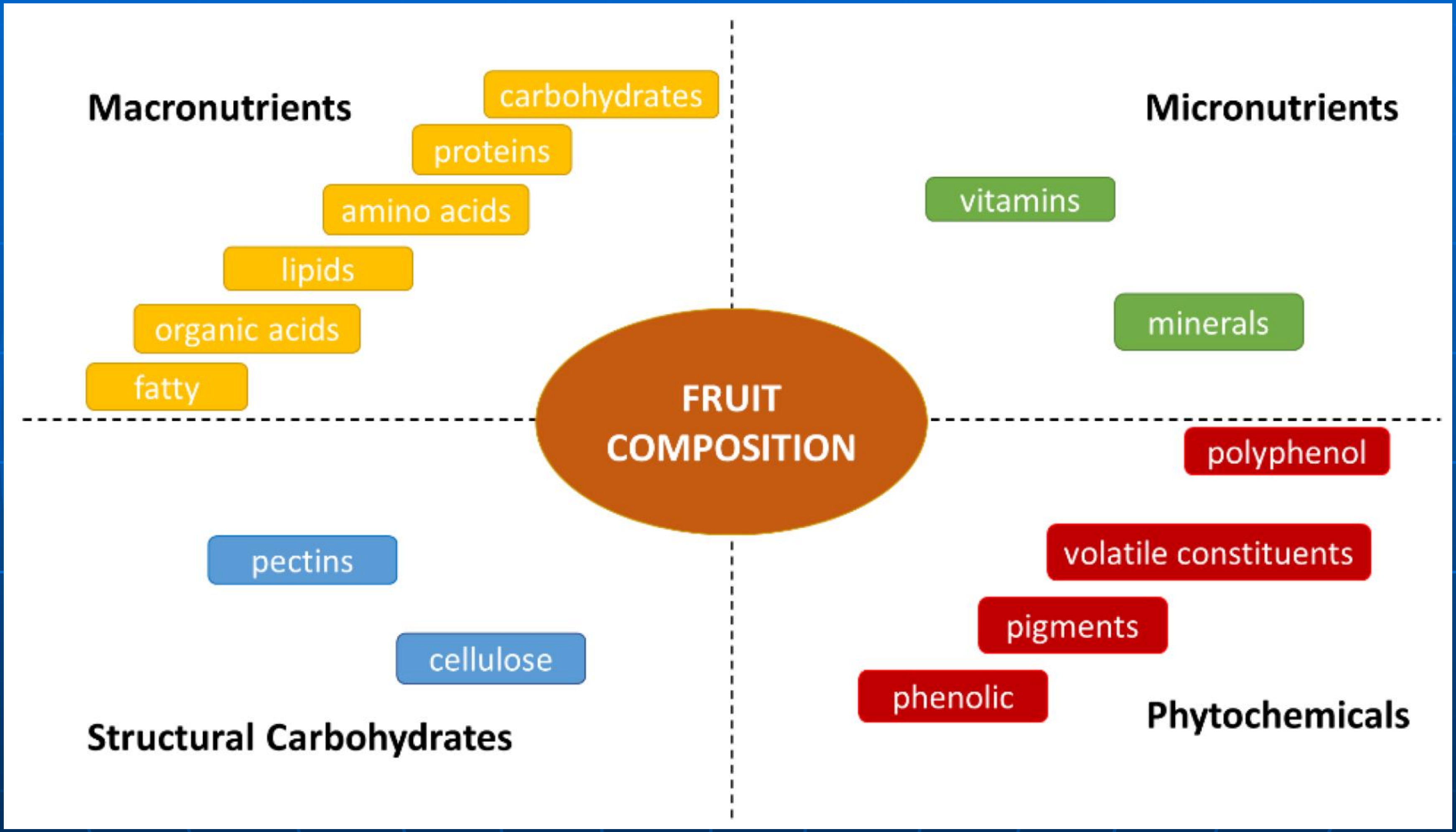
Taste


Salt content (NaE g/100 g)
4
3
2
1
0
50
100
150
Time (s)
Mashed potato
Crisps

2. Factor s effect on flavor of dried and other food products

Fruits and vegetables are important sources of vitamins, minerals, dietary fiber, and antioxidants.

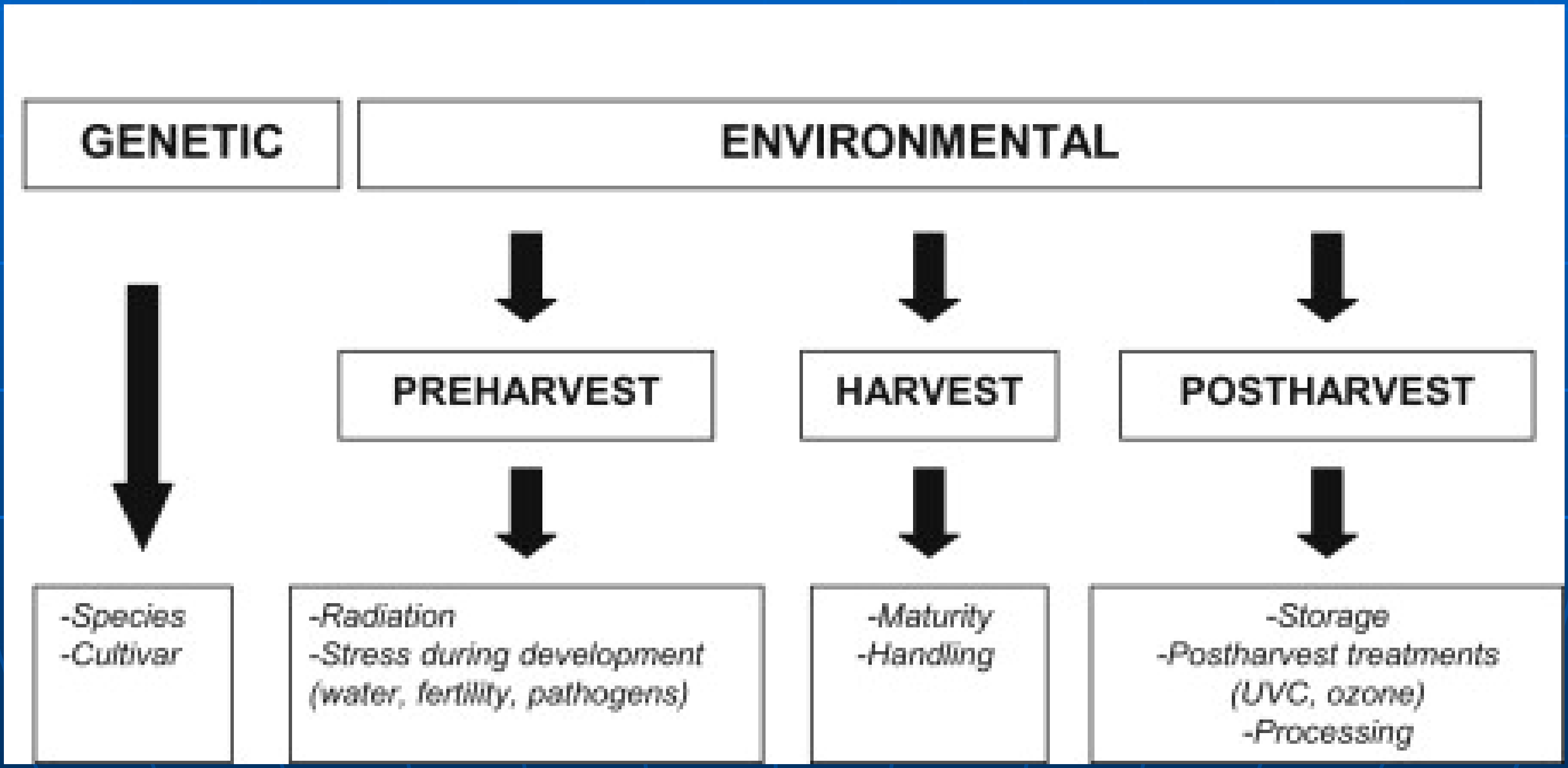
The relative contribution of each commodity to human health and wellness depends upon its nutritive value and percapita consumption.



Macronutrients
carbohydrates
proteins
amino acids
lipids
organic acids
fatty
Micronutrients
vitamins
minerals
FRUIT COMPOSITION
polyphenol
volatile constituents
pigments
phenolic
Phytochemicals
pectins
cellulose
Structural Carbohydrates

Quality change is greatly influenced consumer preferences and degree of satisfaction from eating the fruit or vegetable.

Factor s effect on flavor of dried and other food products



1. Genetic

Thus, it is essential that good flavor quality be emphasized in the future by selecting the best-tasting genotypes to produce.

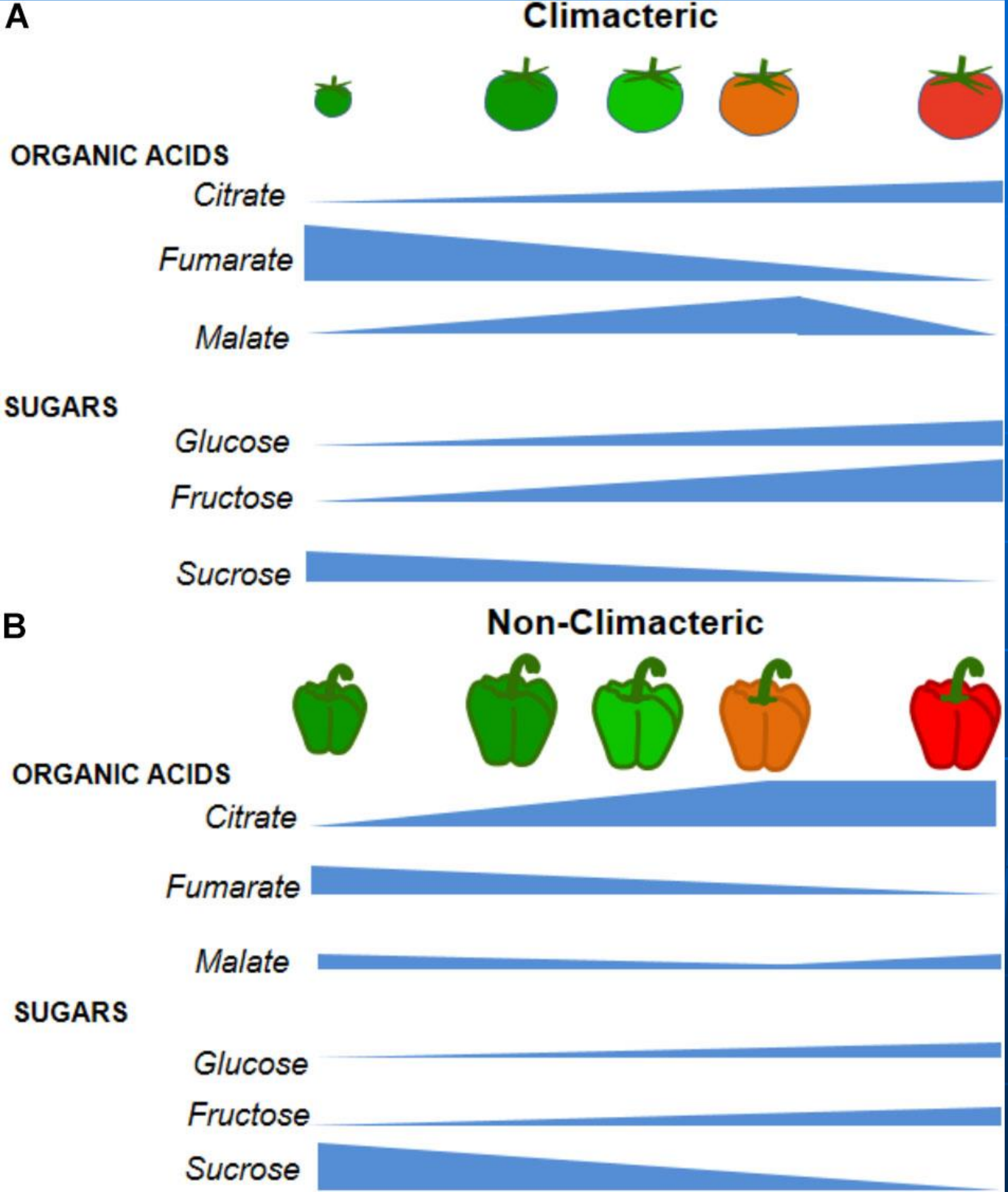
2. Preharvest, harvesting

Using an integrated crop management system and harvesting at the maturity or ripeness stage that will optimize eating quality at the time of consumption.

3. Postharvest factors.

The longer the time between harvest and eating, the greater the losses of characteristic flavor (taste and aroma) and the development of off-flavors in most fruits and vegetables.

Postharvest life based on flavor and nutritional quality is shorter than that based on appearance and textural quality and by using the postharvest handling procedures that will maintain optimal flavor and nutritional quality of fruits and vegetables between harvest and consumption.



Front. Plant Sci., 20 November 2018
Sec. Plant Physiology
Volume 9 - 2018

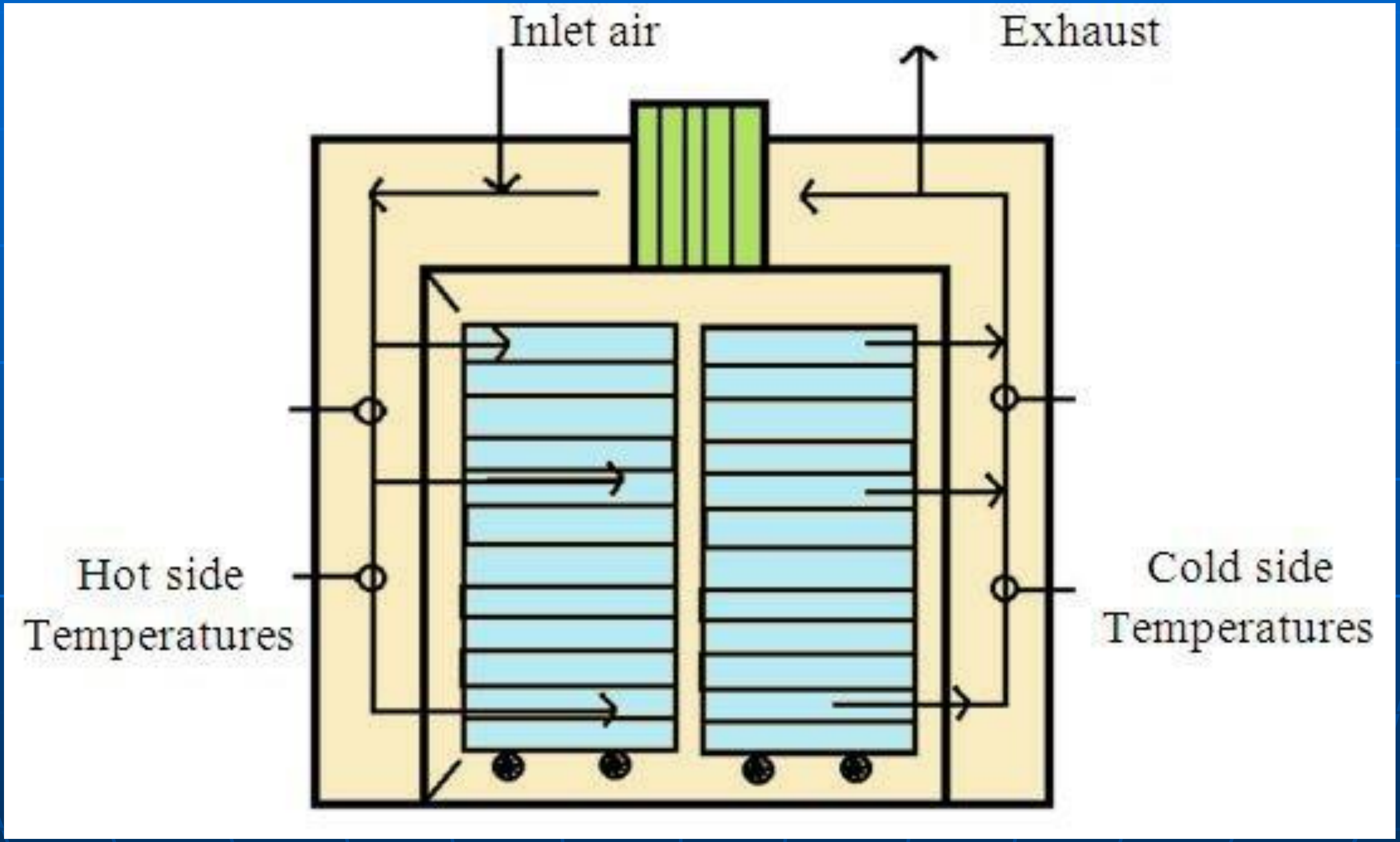
Effect of Drying Process effect the quality change of product

1. Raw material preparation : Washing, Trimming, Slice, Soaking

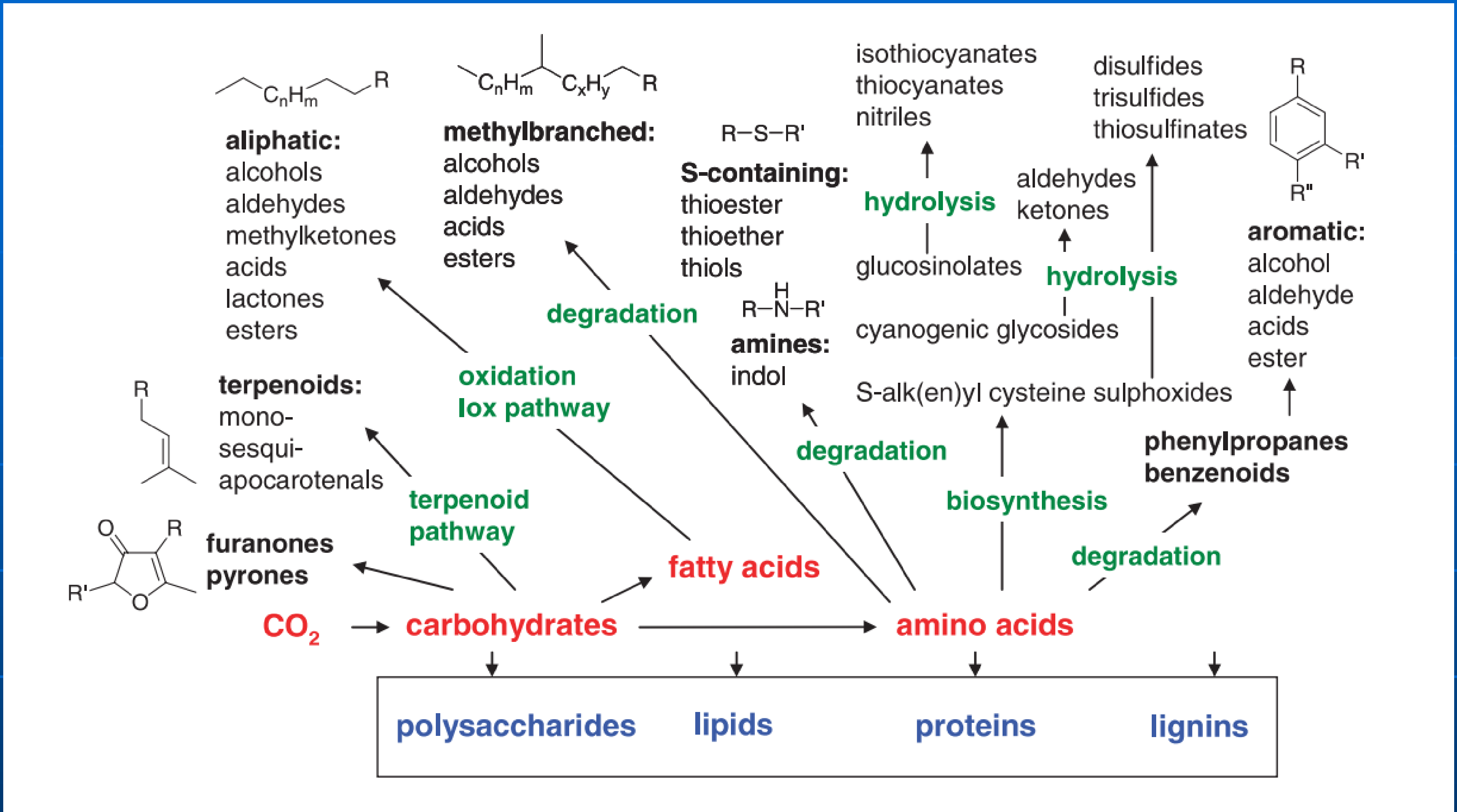
   enzyme reaction effect on flavor of products

2. Drying process.

   Oxidation (lipid, carotenoids) and Mallard reaction
   (non enzymatic reaction)


Inlet air
Exhaust
Hot side
Temperatures
Cold side
Temperatures

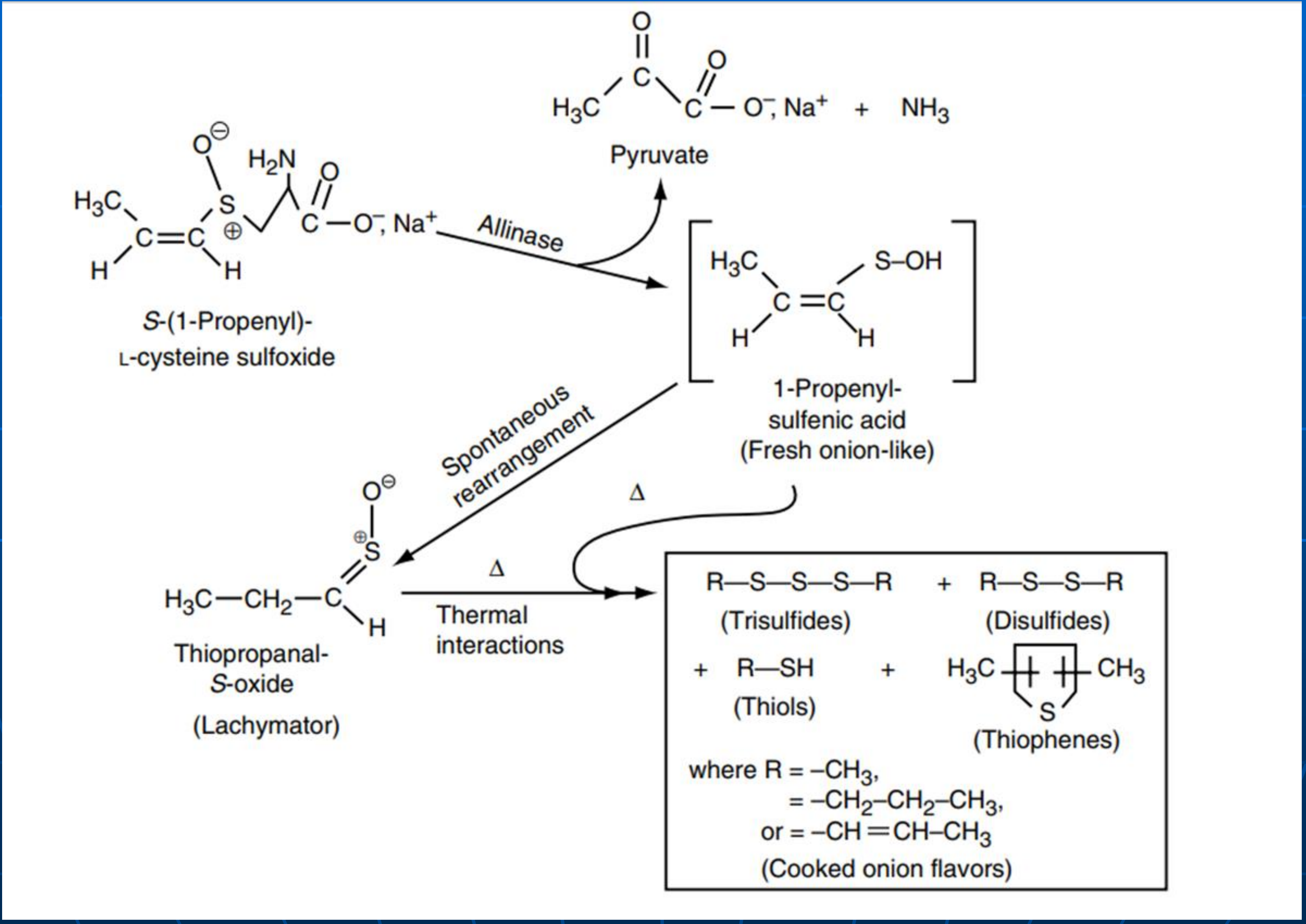
3. Flavor compounds in Fruit and Vegetable Flavor

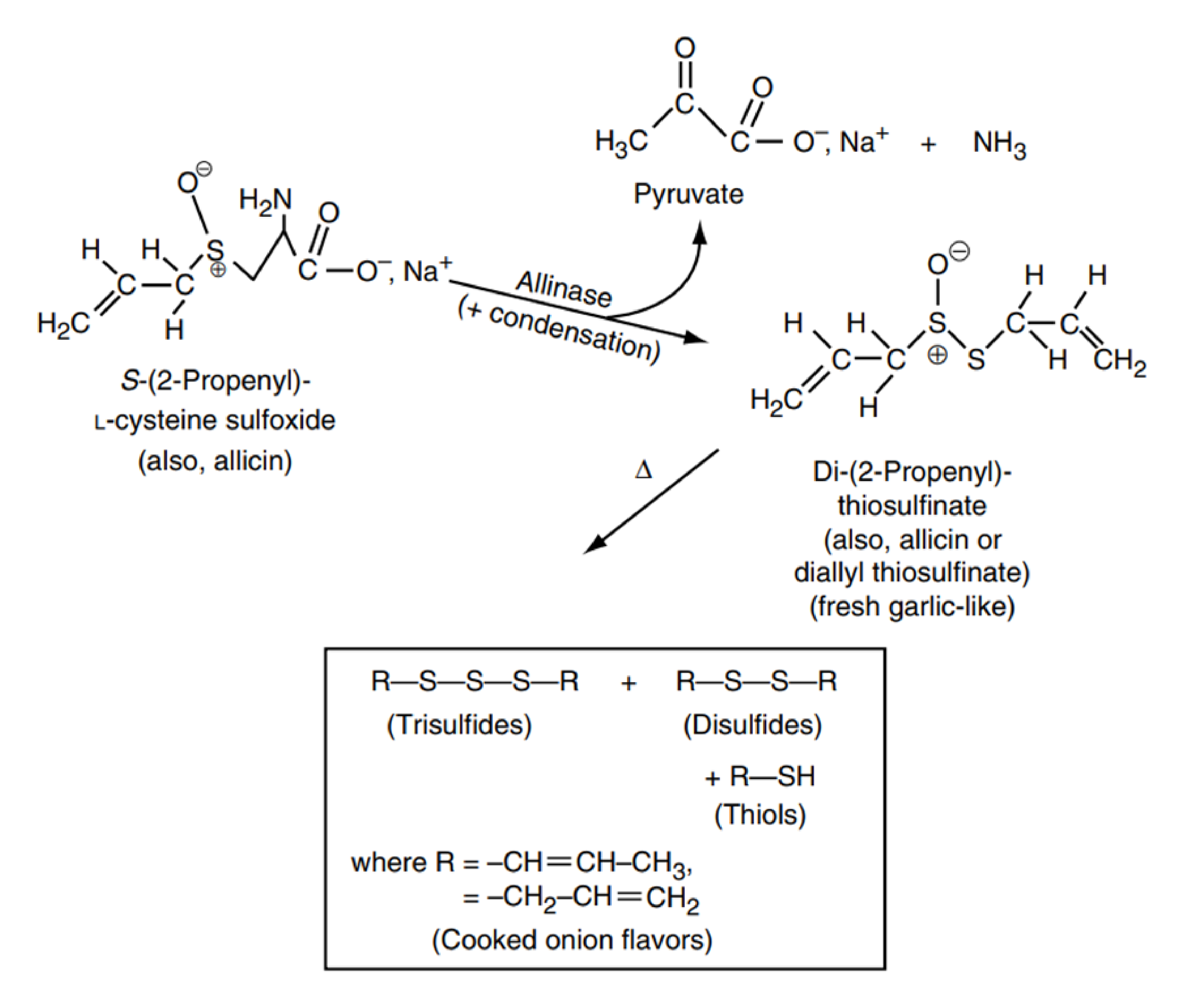


Natural carbon pools for the production of flavor compounds, and the pathway

The Plant Journal, (2008), 54, 712–732

Flavor from Vegetable, Fruit, and Spice Flavors

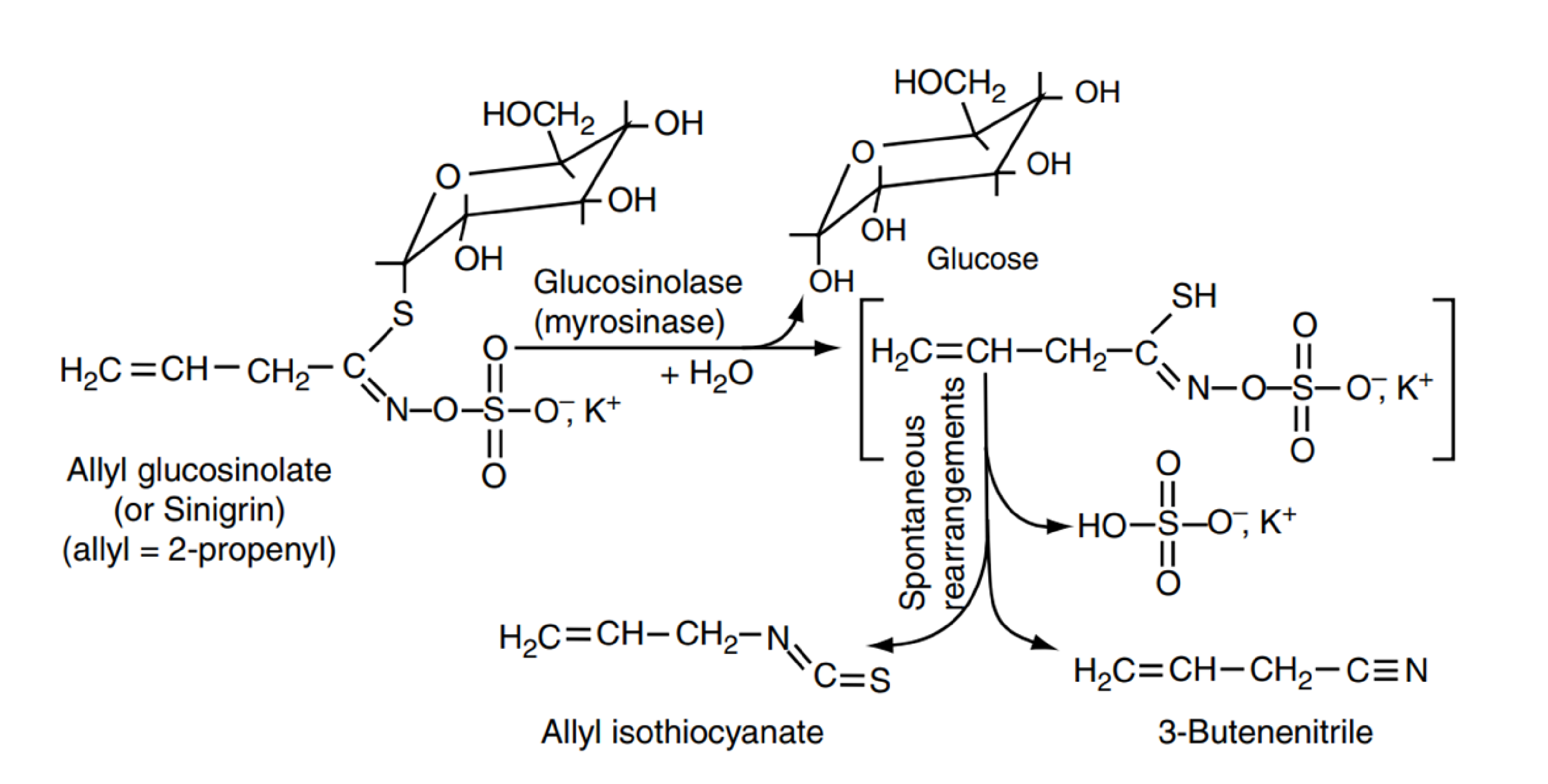




Formation of the principle flavor compound in fresh garlic

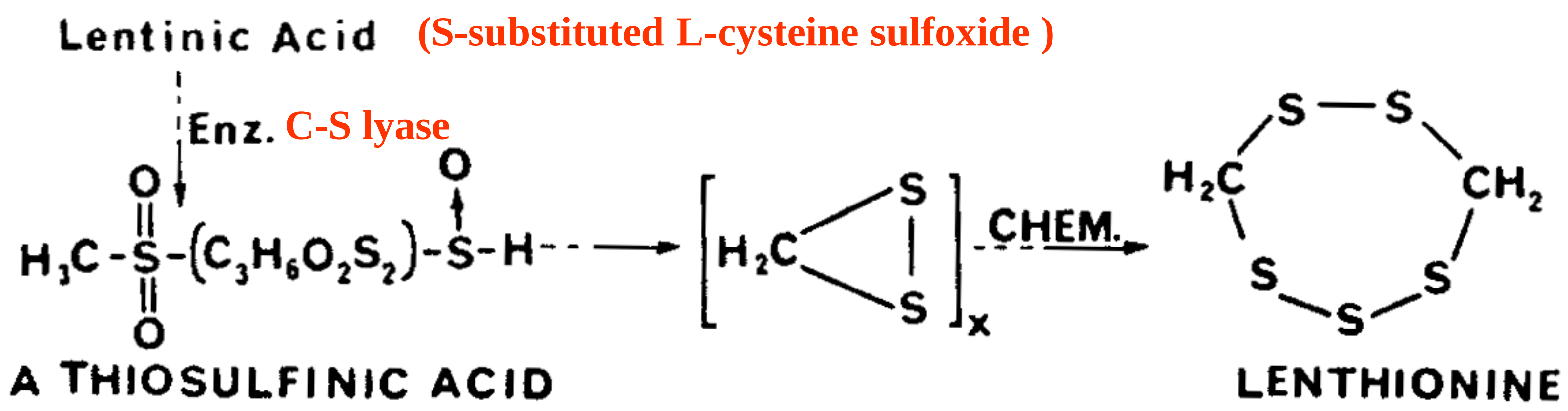
B. Sulfur-Containing Volatiles in the Cruciferae.

Cabbage, brussels sprouts, turnips, mustard, watercress and Horseradishes.



Reactions involved in the formation of Cruciferae flavors

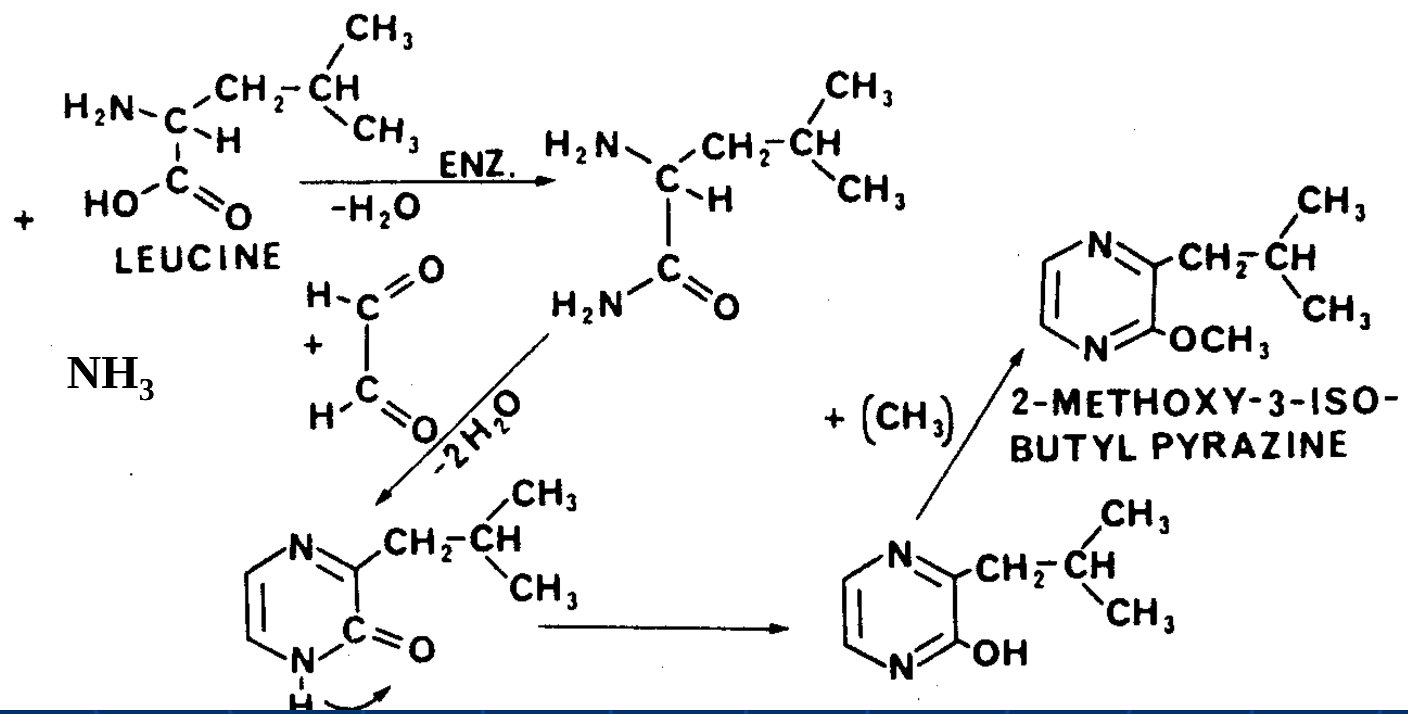
C. Unique Sulfur Compound in Shiitake Mushrooms



Formation of lenthionine in Shiitake mushrooms

D. Methoxy Alkyl Pyrazine Volatiles in Vegetables.

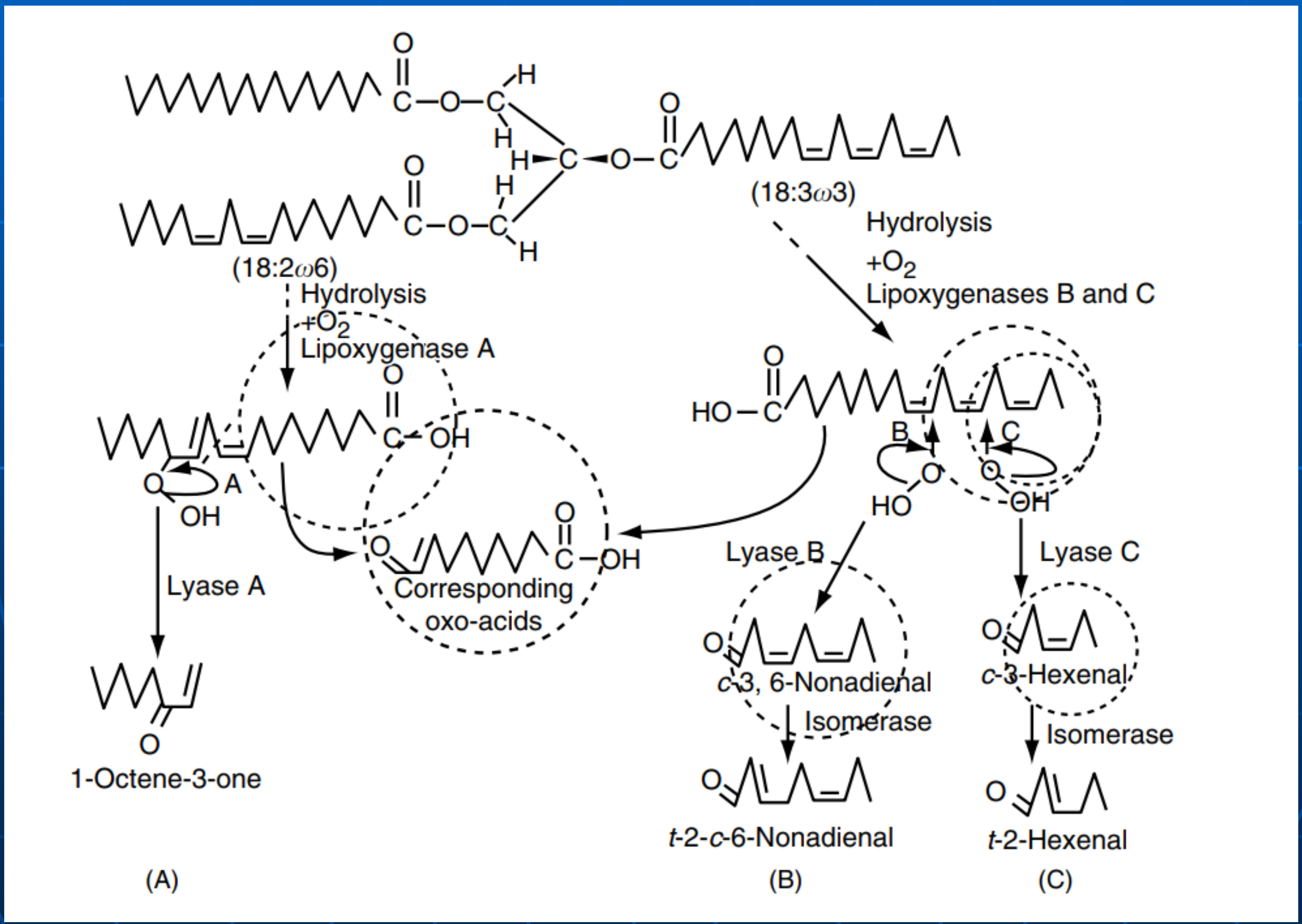
Green-earthy aroma ใน Bell pepper Potato Green pea

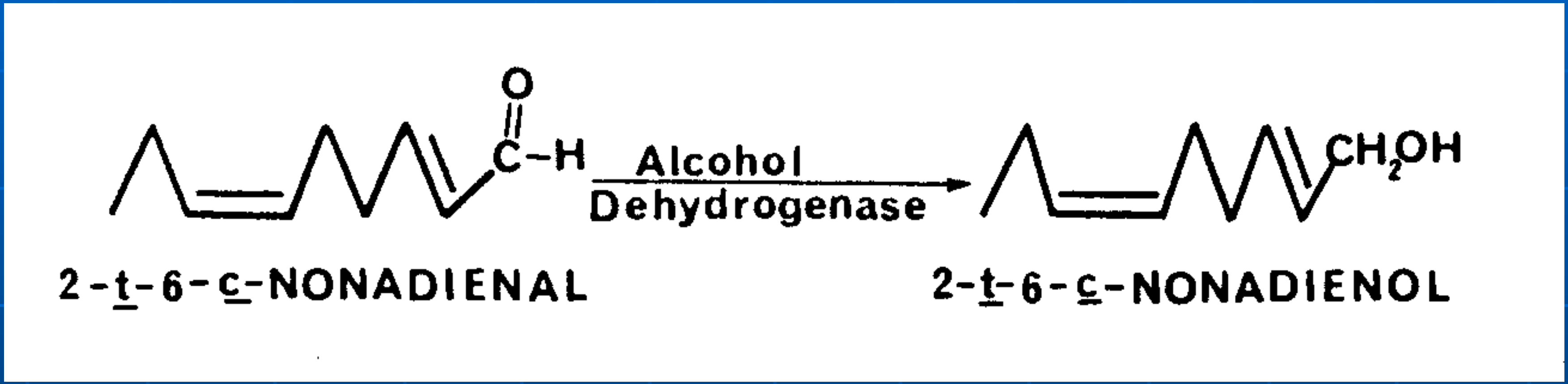


Proposed enzymic scheme for the formation of methoxy alkyl pyrazines

E. Enzymically Derived Volatiles from Fatty Acids.

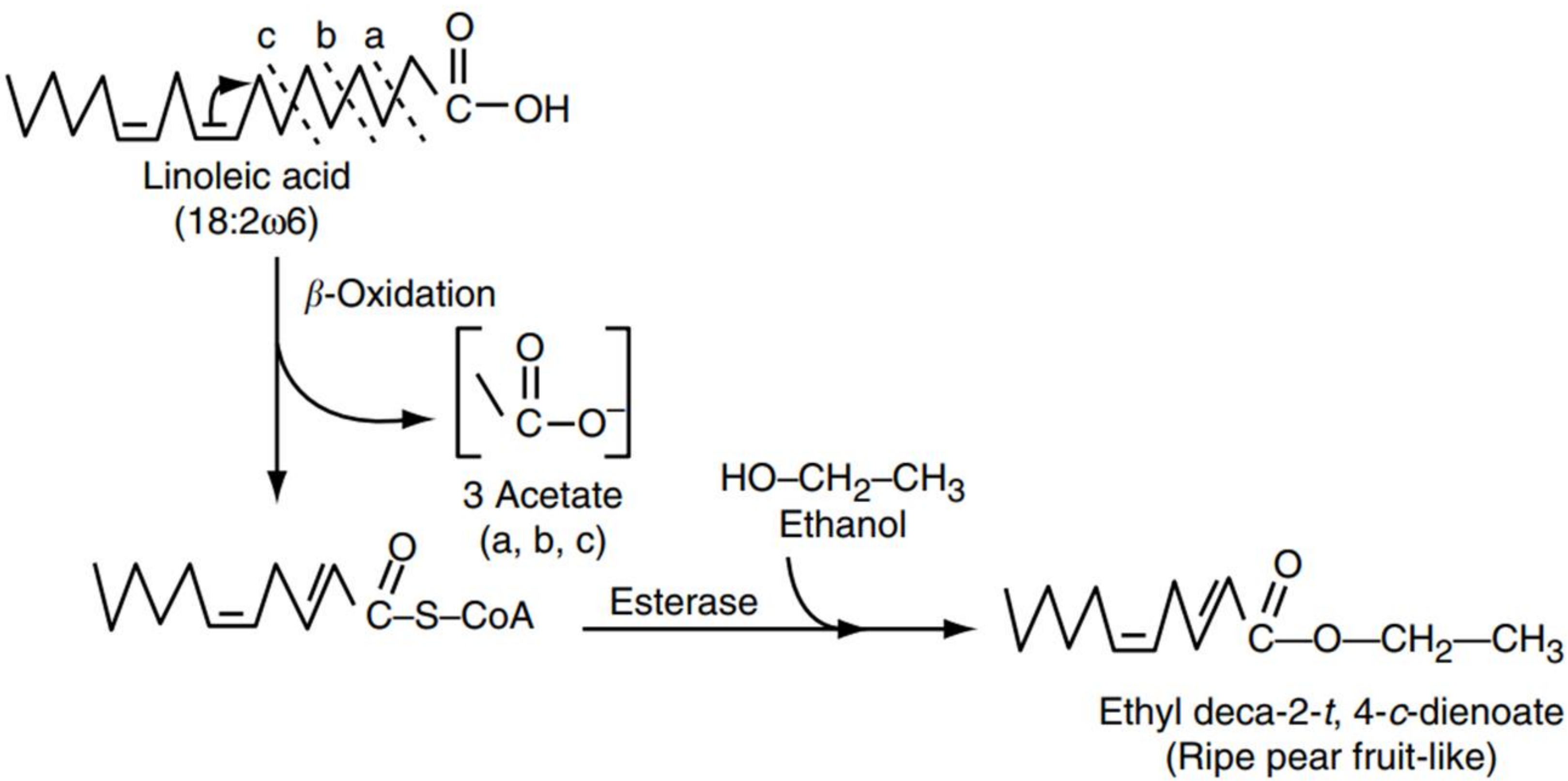
1. Lipoxygenase-Derived Flavors in Plants.



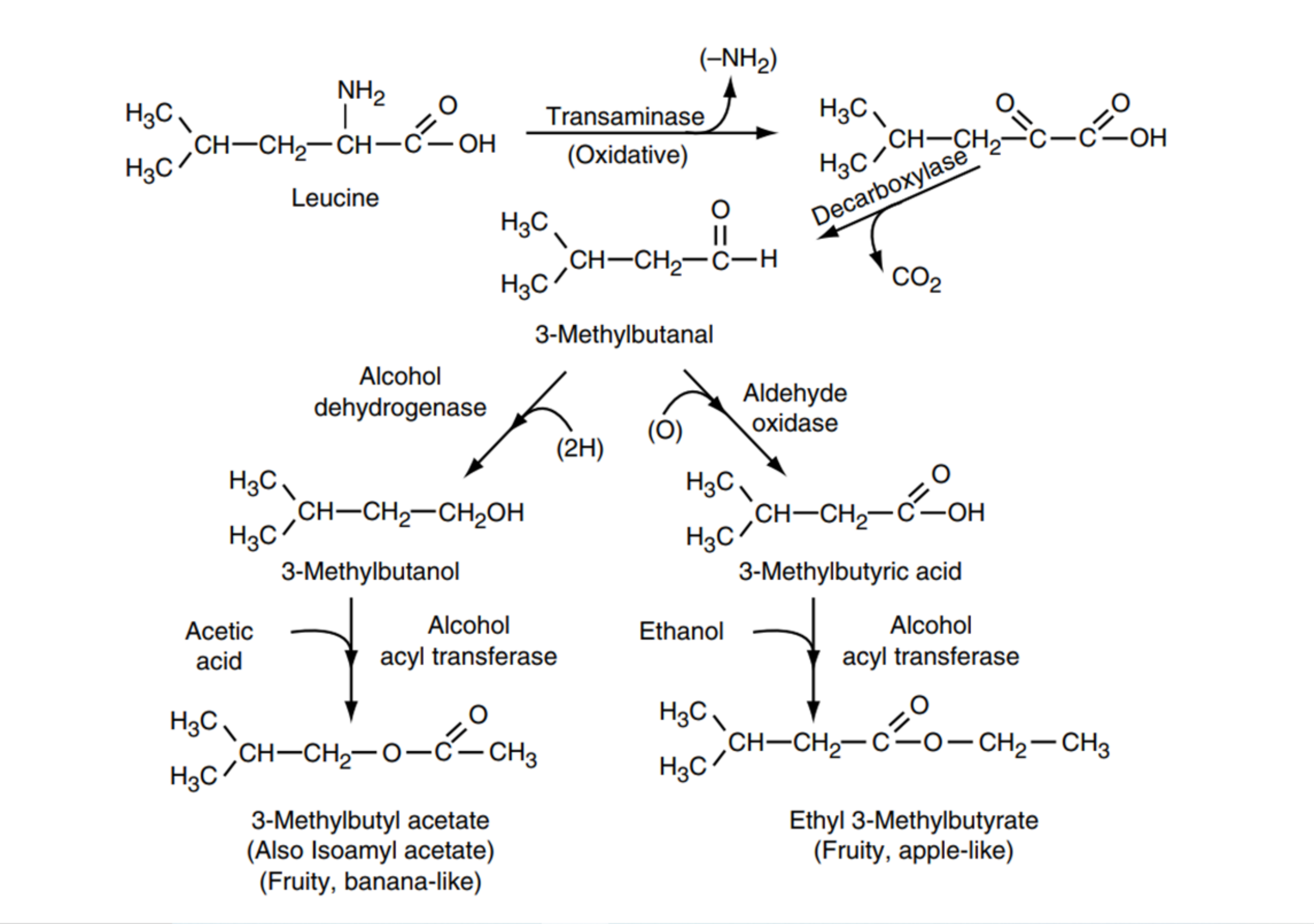


Conversion of aldehyde to alcohol resulting in subtle flavor modifications in cucumbers and melons

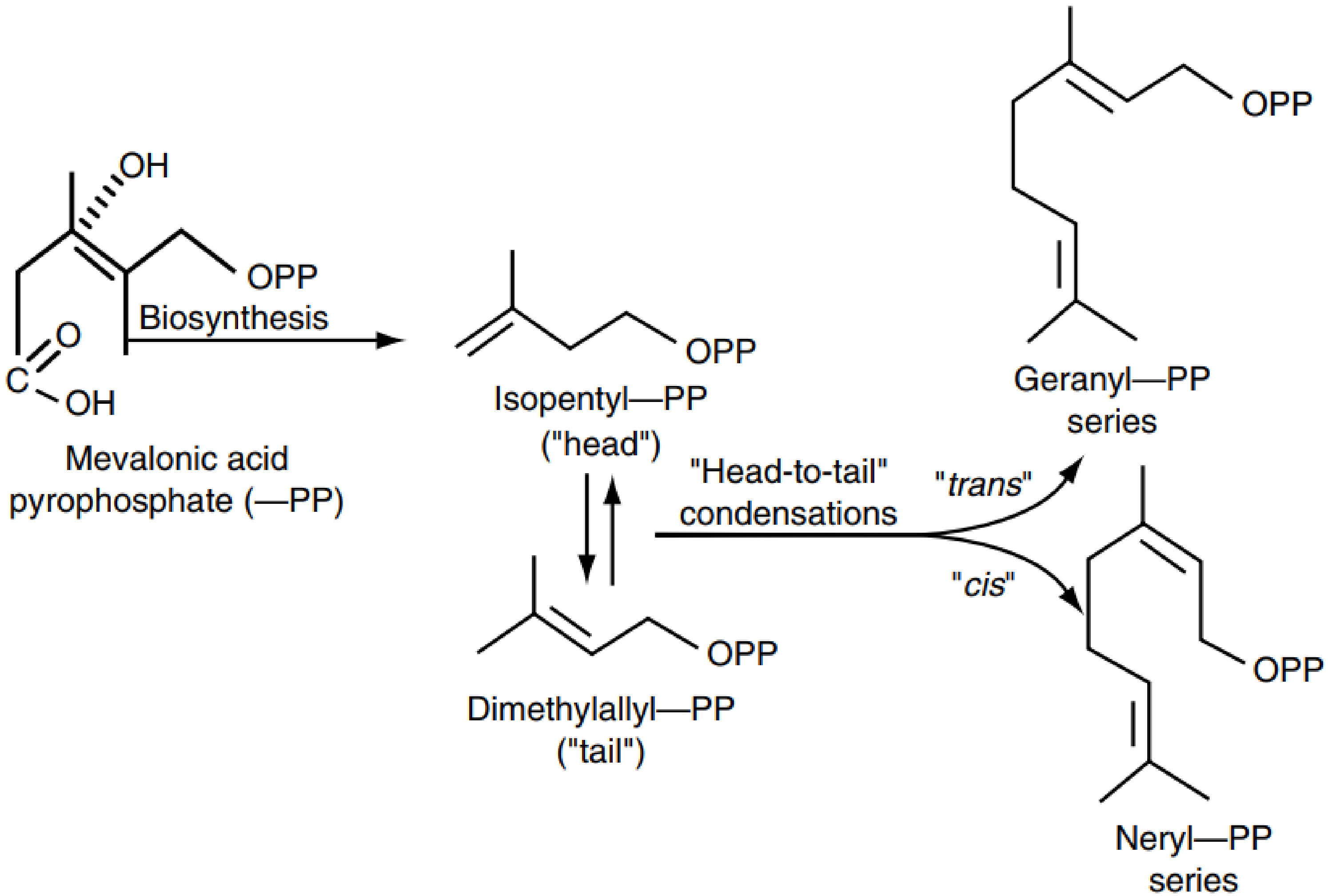
2. Volatiles from Beta-Oxidation of Long-Chain Fatty Acids

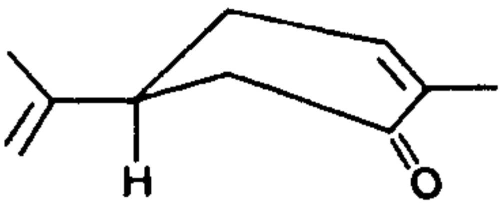


F. Volatiles from Branched-Chain Amino Acids

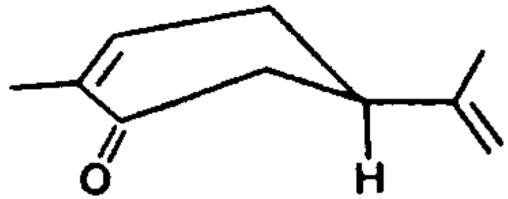


G. Volatiles Terpenoids in Flavors

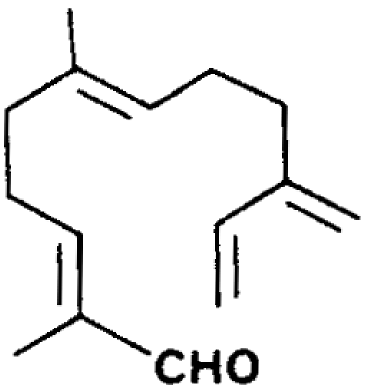




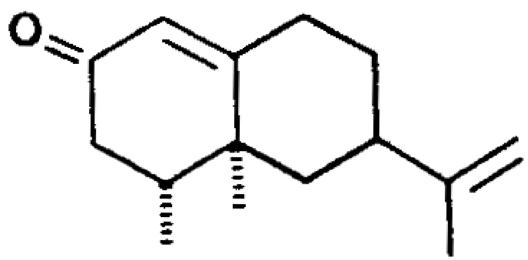
(4S)-(+)-CARVONE
(caraway)



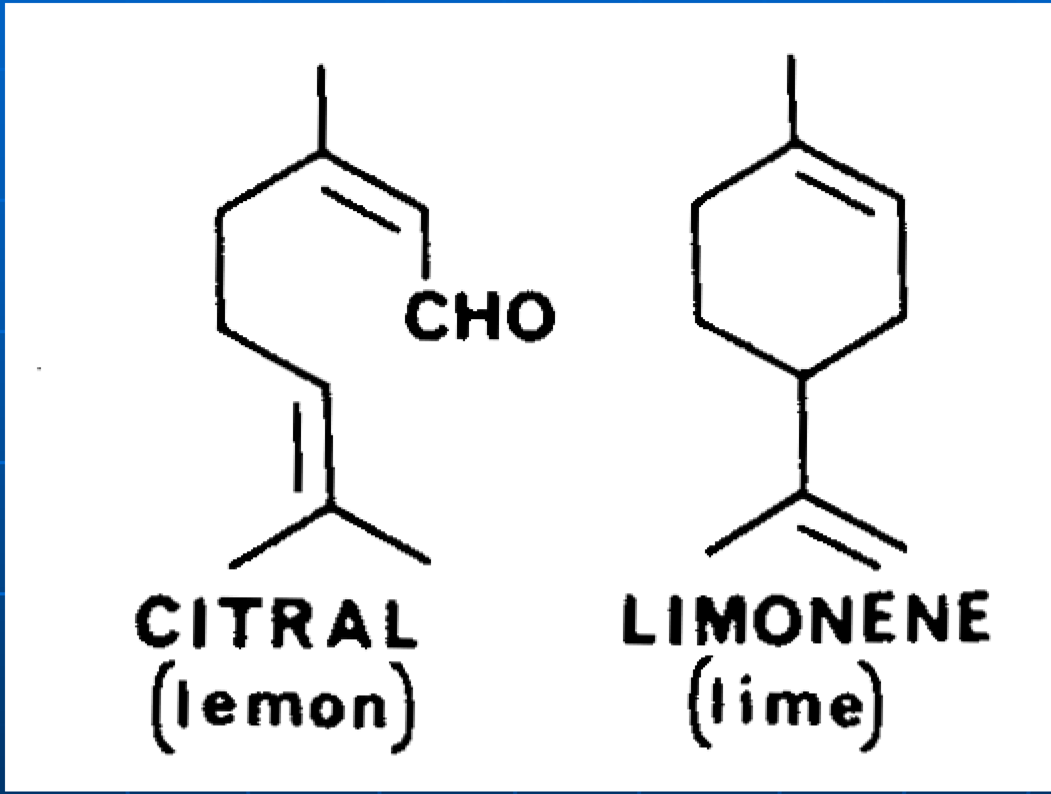
(4R)-(–)-CARVONE
(spearmint)



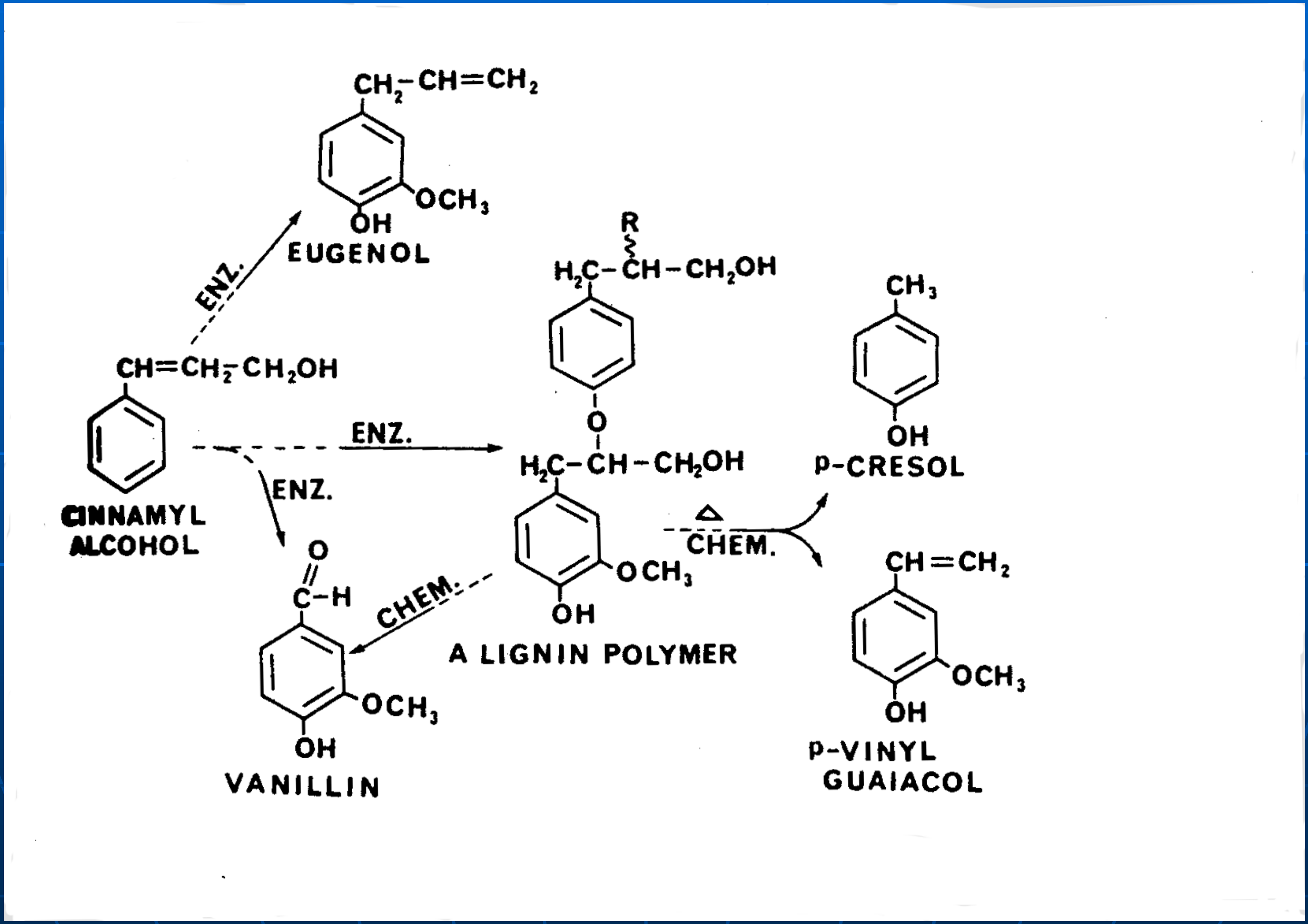
β–SINENSAL
(orange)



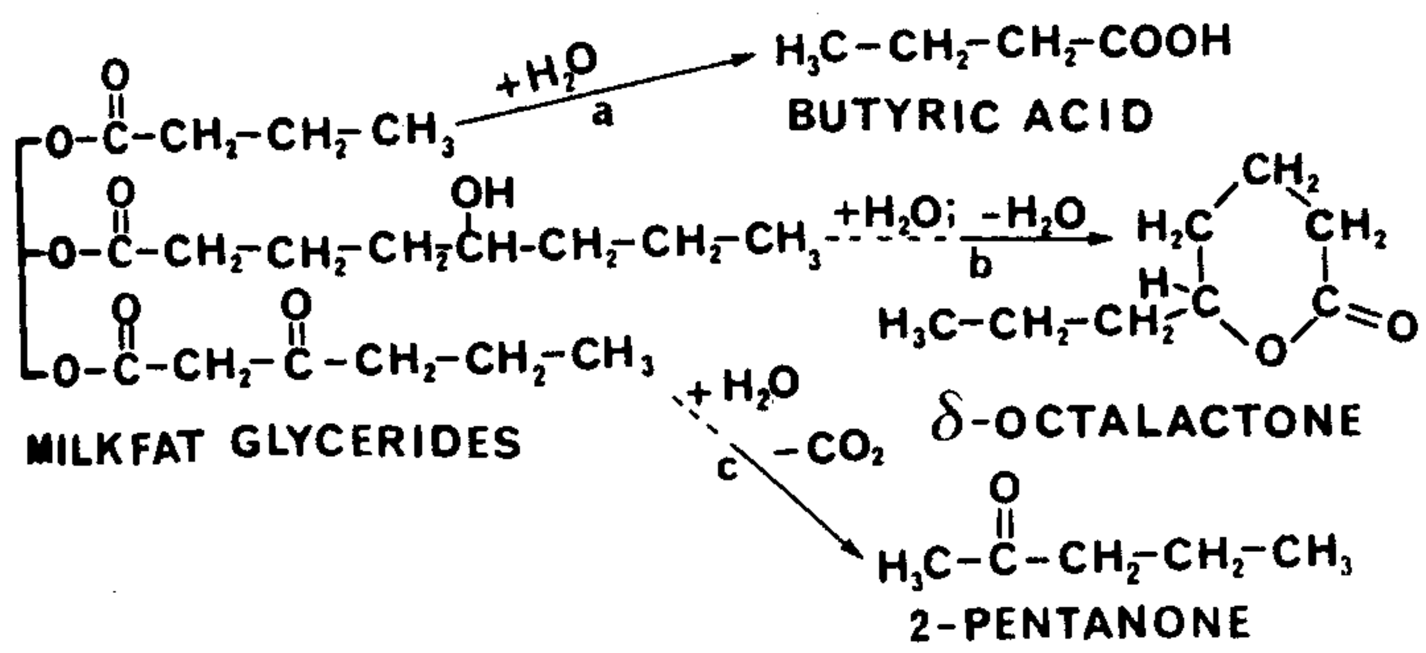
NOOTKATONE
(grapefruit)


CHO
CITRAL
(lemon)
LIMONENE
(lime)

H. Flavors Derived from the Shikimic Acid Pathway

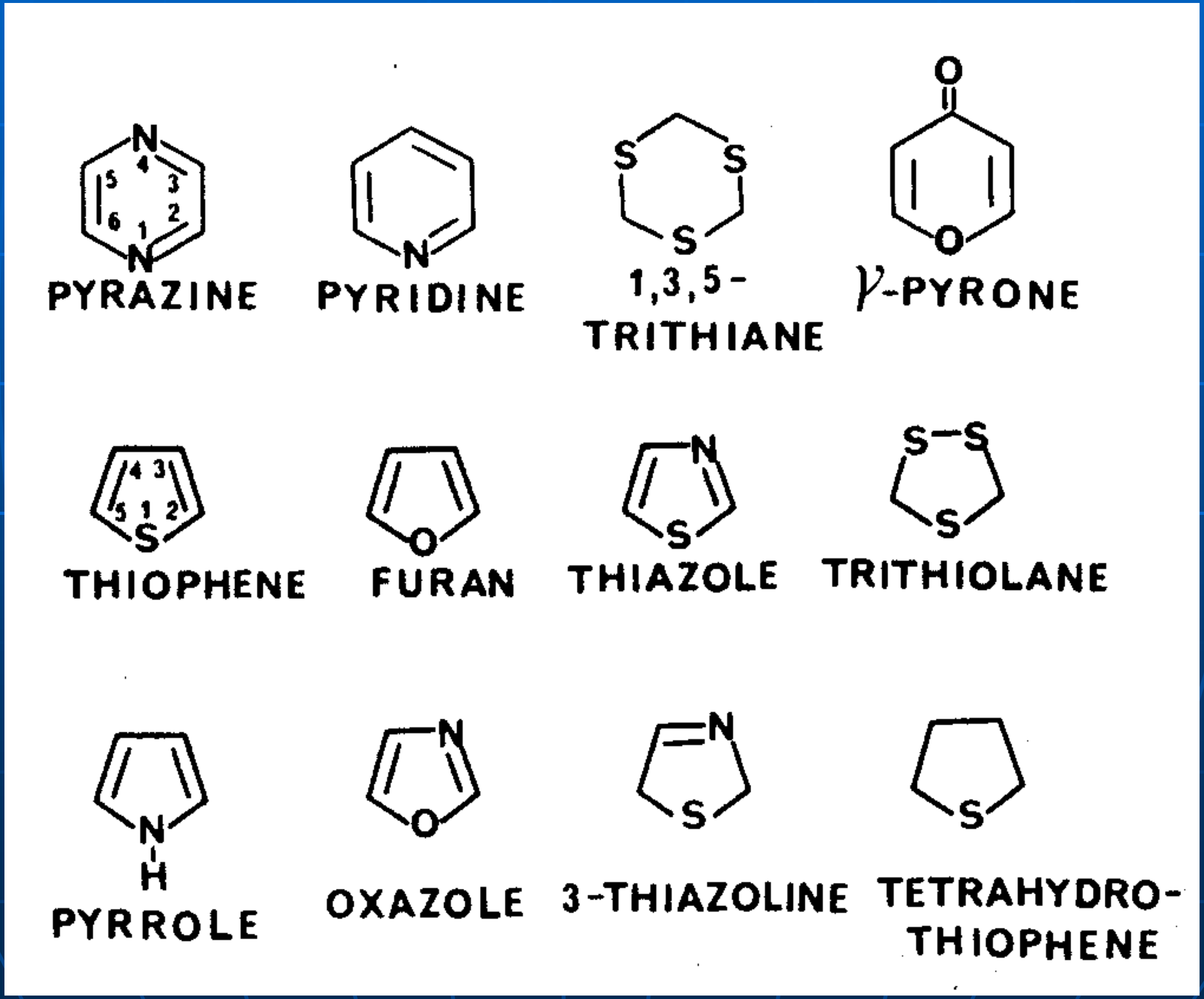


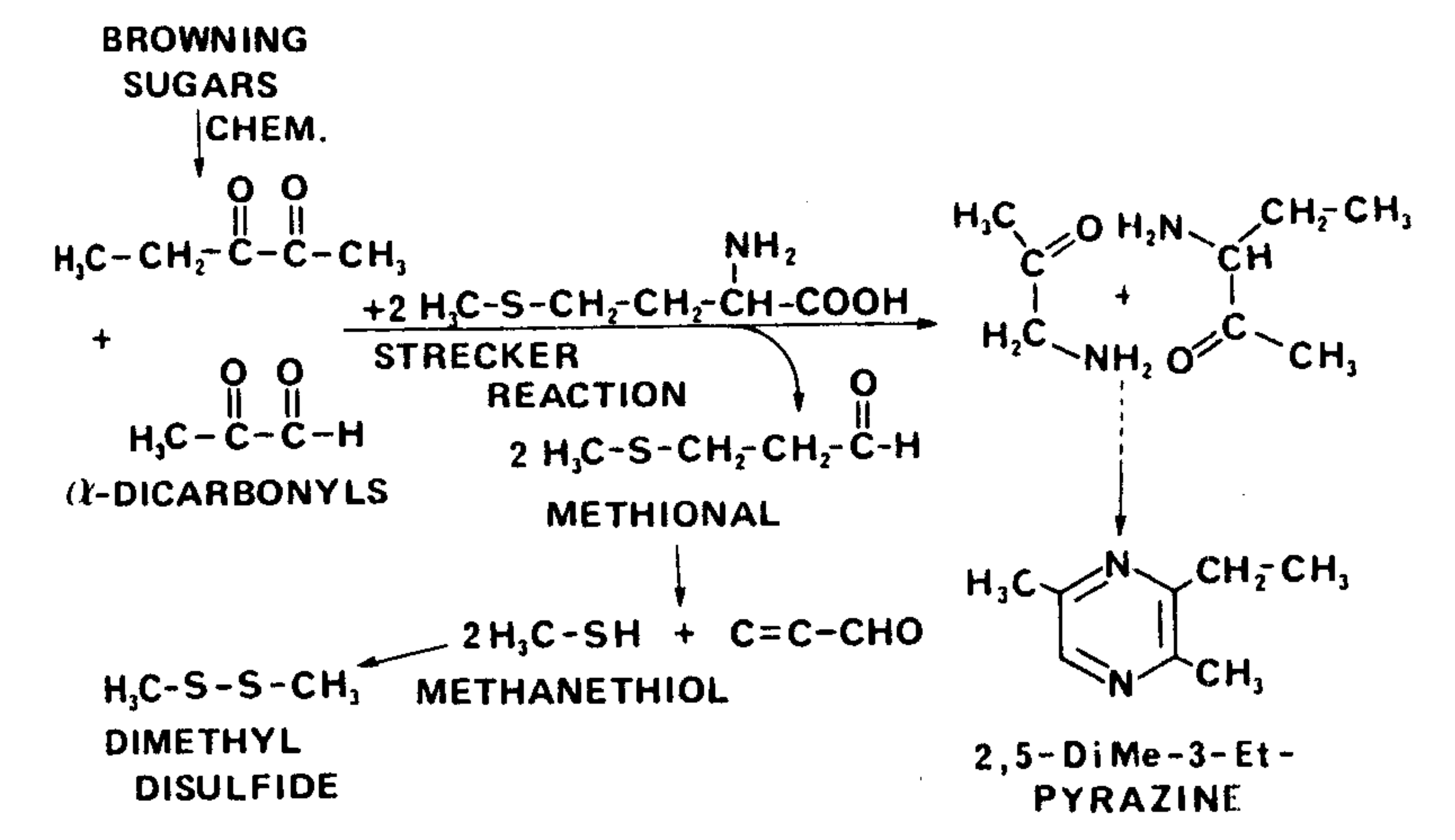
Flavors Volatiles from Fats and Oils

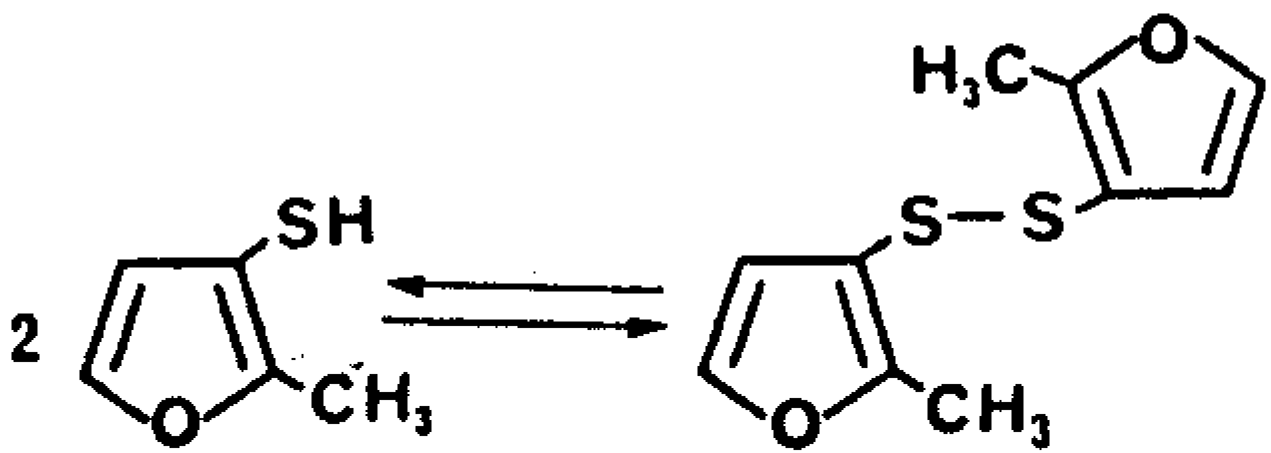


Development of “Process” or “Reaction” Flavor Volatiles

A. Thermally Induced Process Flavors

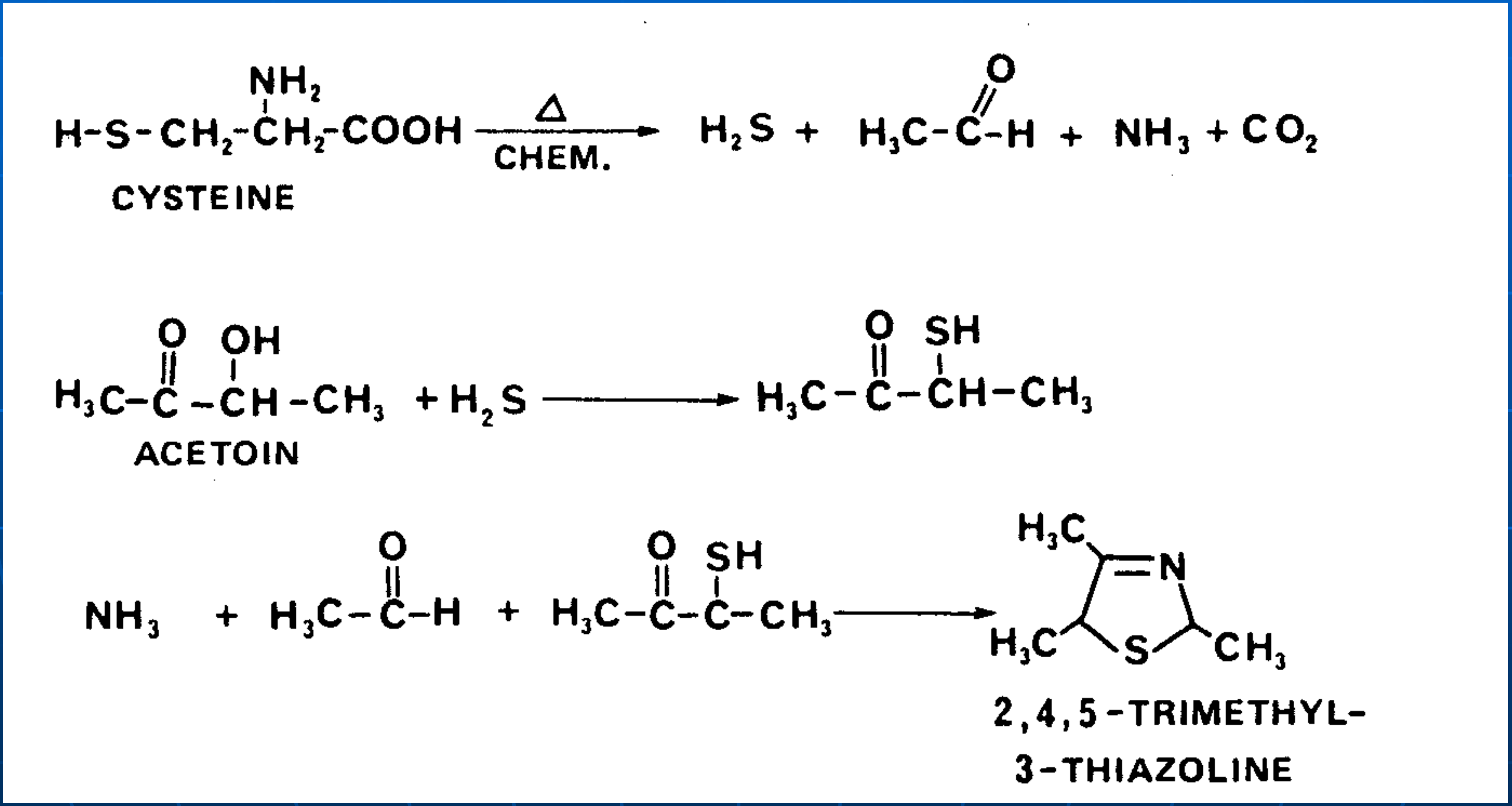



BROWNING
SUGARS
CHEM.
STRECKER
REACTION
α-DICARBONYLS
METHIONAL
METHANETHIOL
DIMETHYL
DISULFIDE
2,5-DiMe-3-Et-
PYRAZINE

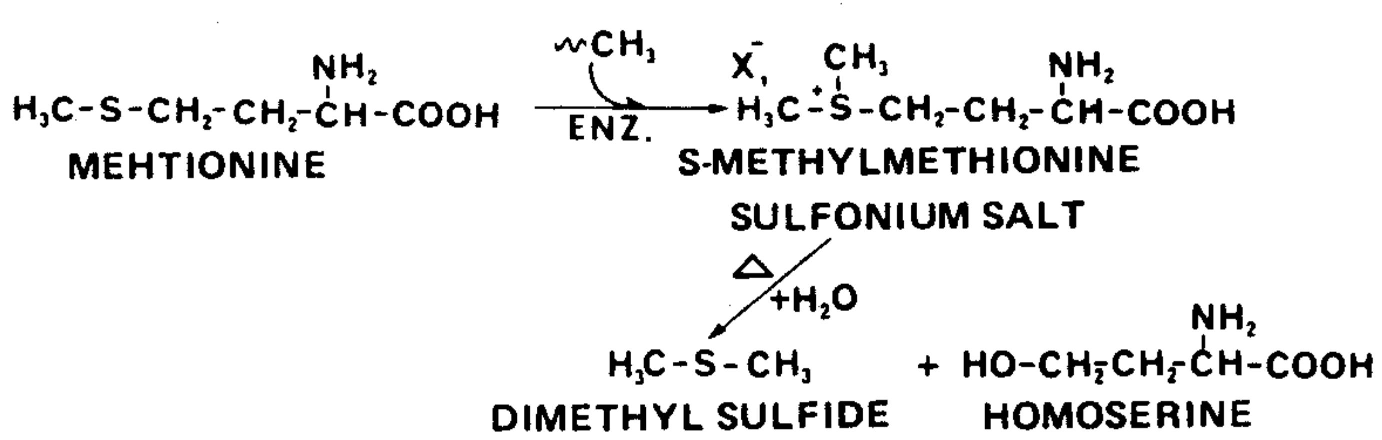


2-Me-3-FURAN-THIOL

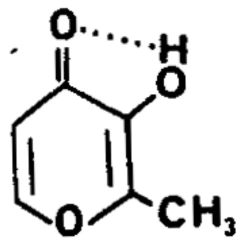
(2-Me-3-FURYL)-bis-DISULFIDE



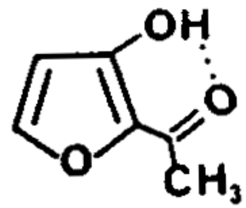
CYSTEINE
CHEM.
ACETOIN
2,4,5-TRIMETHYL-
3-THIAZOLINE



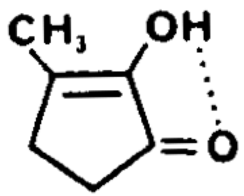
~CH3
ENZ.
MEHTIONINE
S-METHYLMETHIONINE
SULFONIUM SALT
+H2O
DIMETHYL SULFIDE
HOMOSERINE



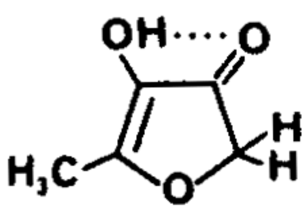
MALTOL



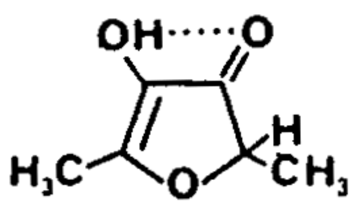
ISOMALTOL



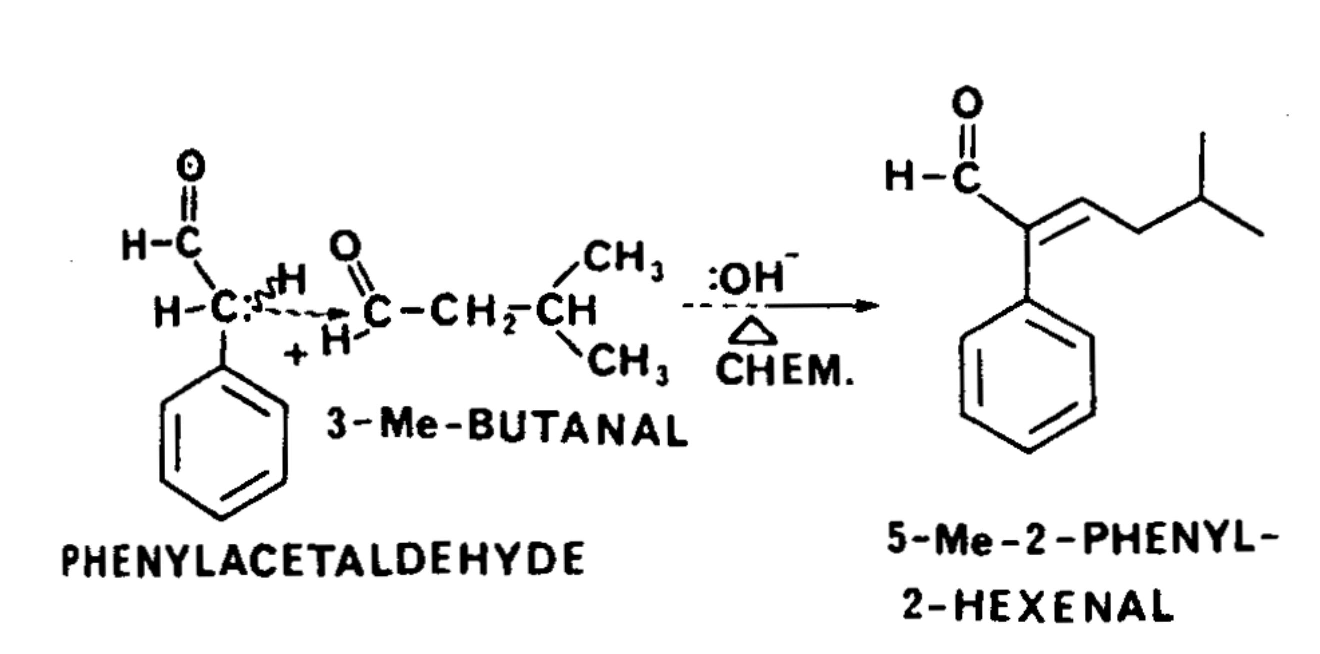
CYCLOTENE[R]



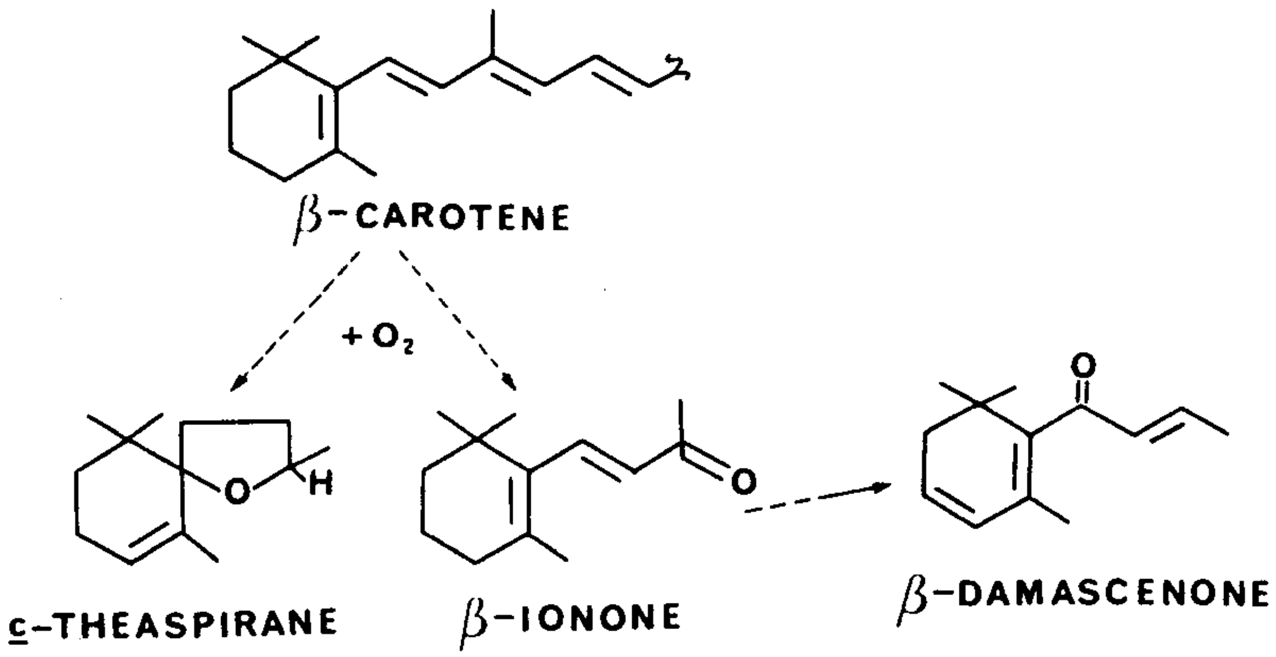
4-OH-5-Me-3(2H)-FURANONE



4-OH-3,5-DiMe-3(2H)-FURANONE


:OH⁻
CHEM.
3-Me-BUTANAL
PHENYLACETALDEHYDE
5-Me-2-PHENYL-
2-HEXENAL

B. Volatiles Derived from Oxidative Clevage of Carotenoids



4. Flavor Analysis

4.1 Objective : Instrumental analysis

4.2 Subjective : Sensory Evaluation

Flavor Analysis

1. Objective analysis: Instrumental analysis

    1.1 Isolation and Separation of Flavor Compounds

    1.2 Flavor Identification by Spectrometric Methods

2. Subjective analysis :Sensory Evaluation

ISOLATION AND SEPARATION OF FLAVOR COMPOUNDS

I. Objectives

Isolation of volatile flavor compounds of the original good flavor with minimum artifact.

1. Selection of good flavor sample
2. Isolation of volatile flavor compounds
3. Extraction and concentration
4. Fractionation
5. Preparation of pure compound
6. Identification of flavor compounds
7. Synthesis of compounds
8. Reconstitution of the flavor

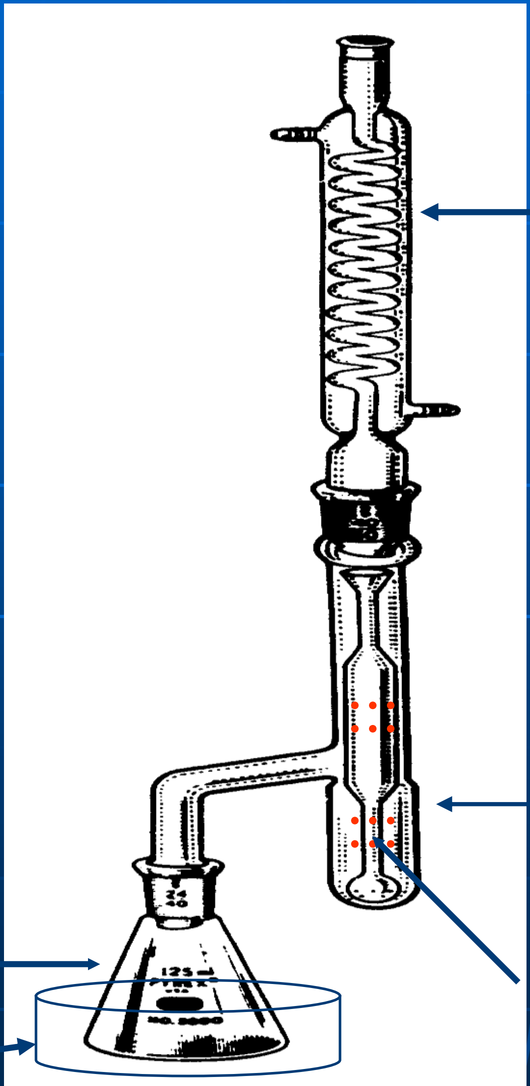
II. Prerequisites

1. Selection of sample
2. No alternation of the original flavor
3. No artifacts

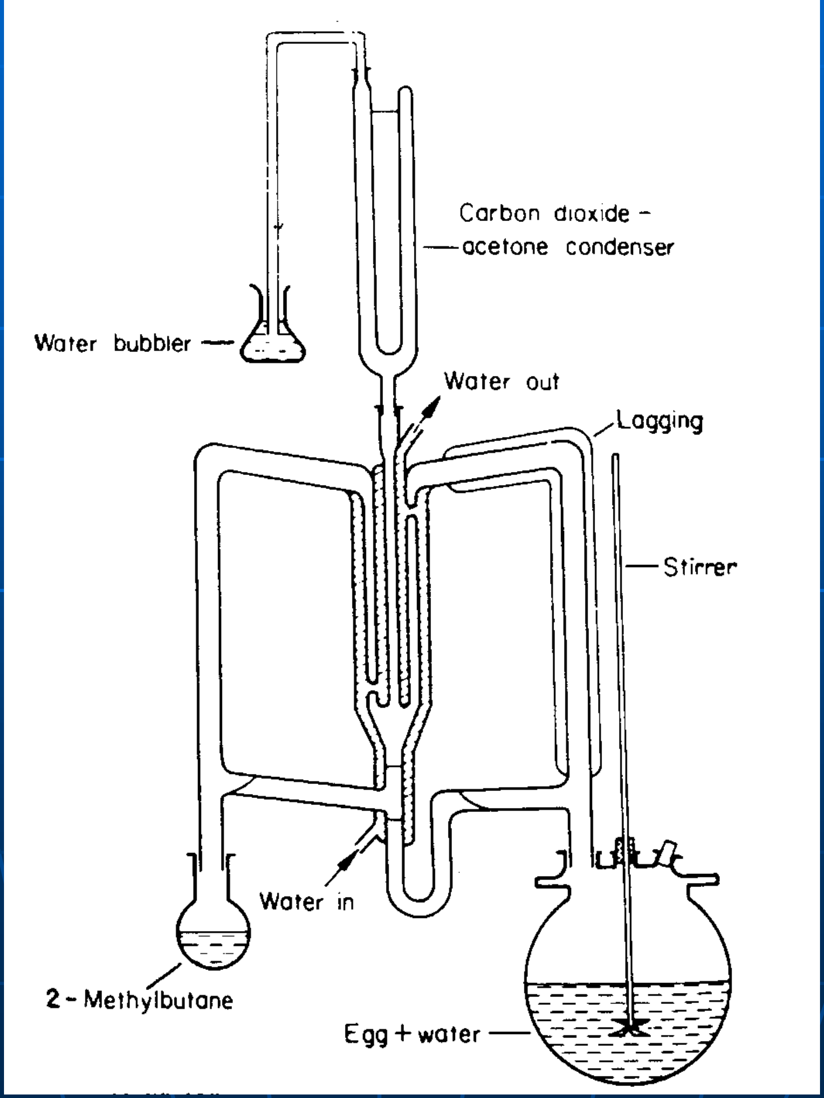
   due to : decomposition

   autooxidation

Continuous Solvent Extraction



Steam distillation and continuous solvent extraction



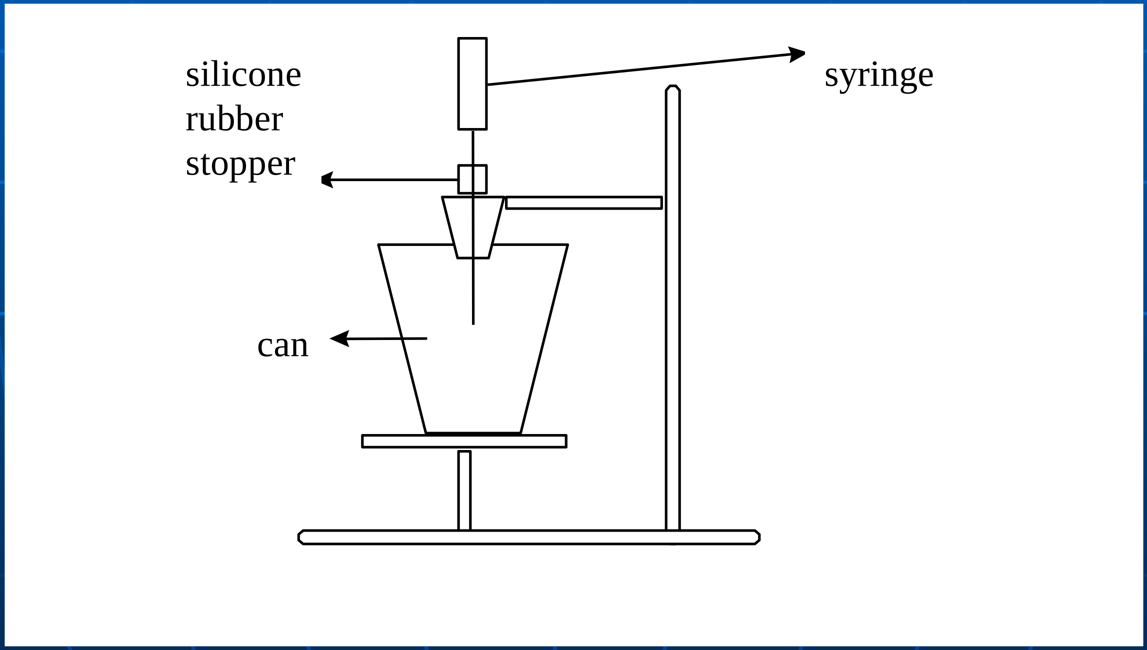
Instrumental Analysis of Volatile Compounds

- Static headspace analysis
- Dynamic headspace analysis
- Solid phase microextraction

III. Apparatus for Isolation

1. Headspace analysis

1) Without enrichment



VI. Dynamic Headspace Analyzer

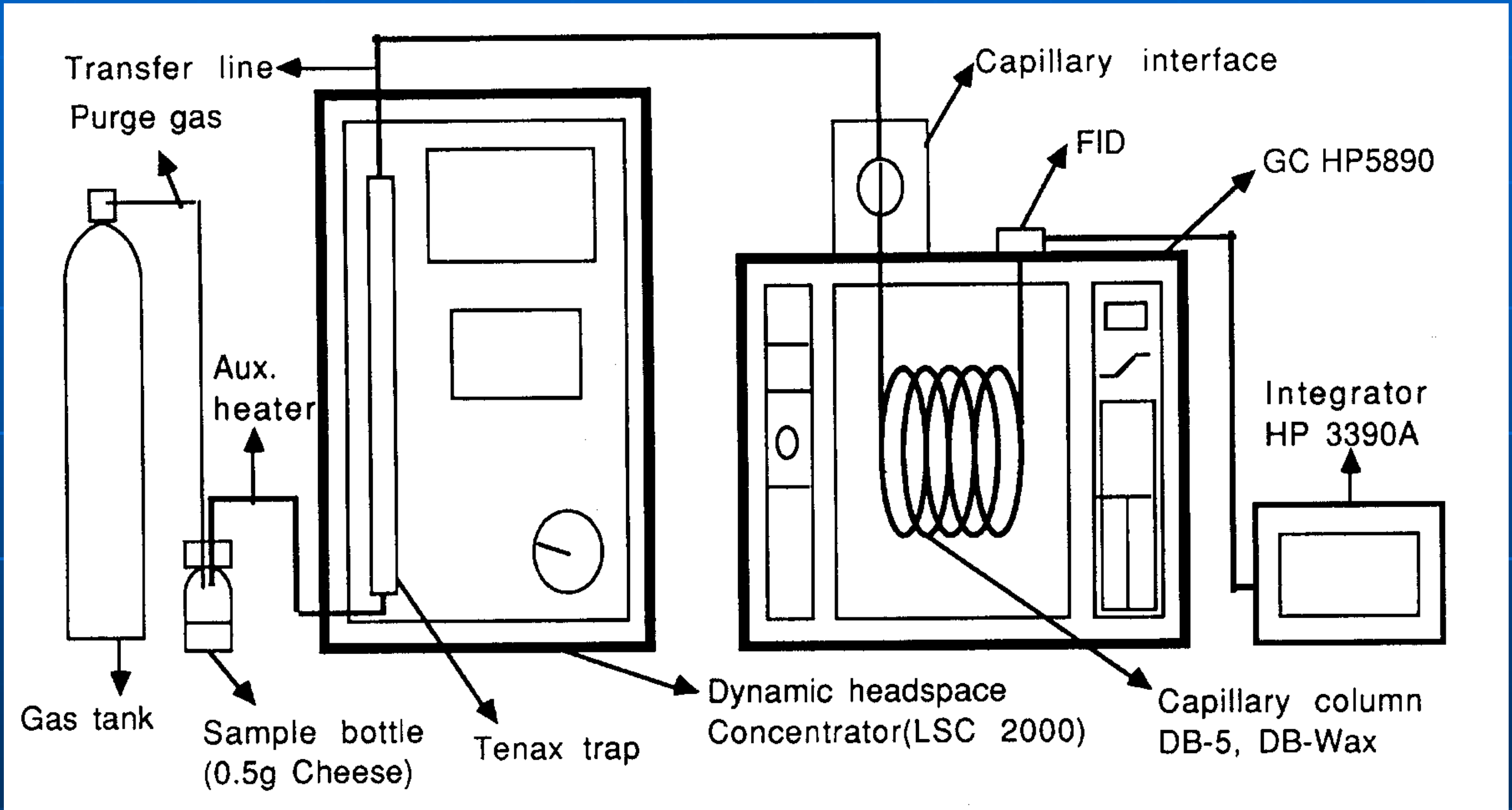


Diagram of dynamic headspace sampler and gas chromatographer

Solid-phase Microextraction Analyses of Flavor Compounds in Foods

Objectives of Solid Phase Microextraction

Conventional Sample Preparation

- Time and Labor Intensive
- Multiple Steps
- Loss of Sample
- Errors in each steps
- Contamination

To produce sample with highest compound concentration, lowest level contamination and shortest sample preparation time

Solid Phase Microextraction

Solid Phase Microextraction has been commercially available for 15 years and developed for flavor and food analyses rapidly

A technique that uses a short, thin, solid rod of fused silica, coated with absorbent polymer for extraction of volatile compounds

Theory of Solid Phase Microextraction

It is essential to understand the theory to develop and optimize SPME method for maximizing sensitivity and minimizing isolation and desorption times

- Compound partition between fiber and sample for absorption of compound to the fiber
- Like "dissolves" like
- The isolated and concentrated compound desorbs from the fiber into an analytical instrument

Detection Limits and Precision of Organic Volatiles[a] in Water

Technique	Detection Limit with FID (ppb)	Precision (% rsd)
SPME	0.05-0.3	1-3
Static Headspace	1-2	1-3
Dynamic Headspace	0.003-0.005	1-8
Direct Injection	17-240	2-13

a; Methyl chloride, chloroform, dioxane, TCE, benzene, toluene, xylene, and 1,2,4-trimethylbenzene

SPME Fiber with Holder

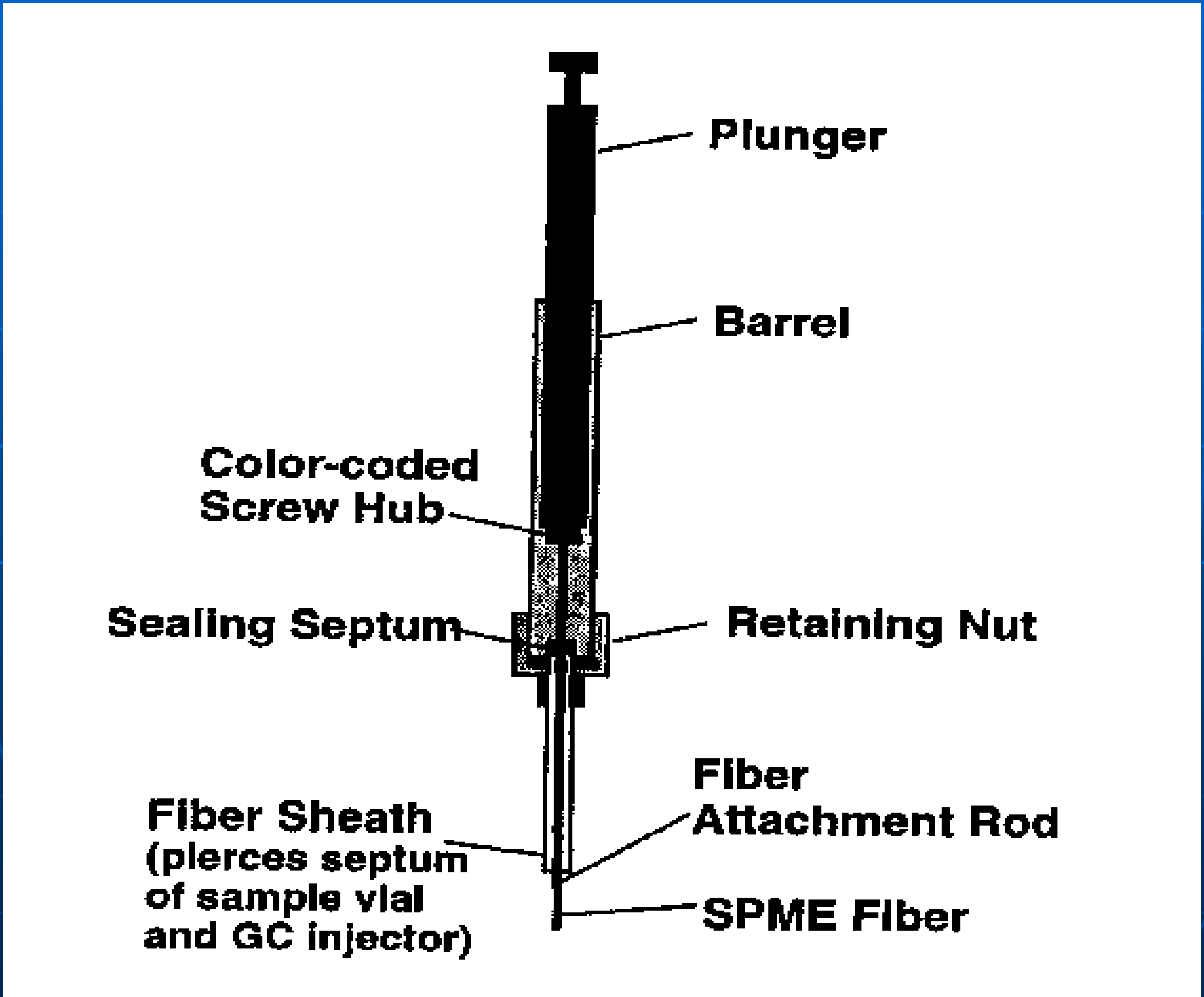
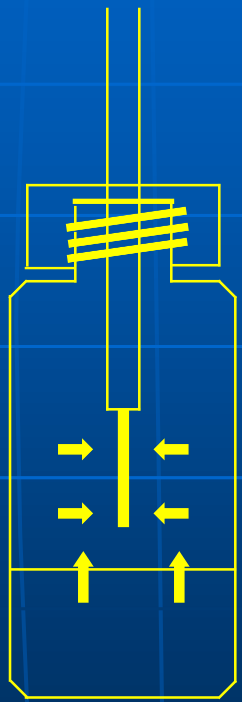
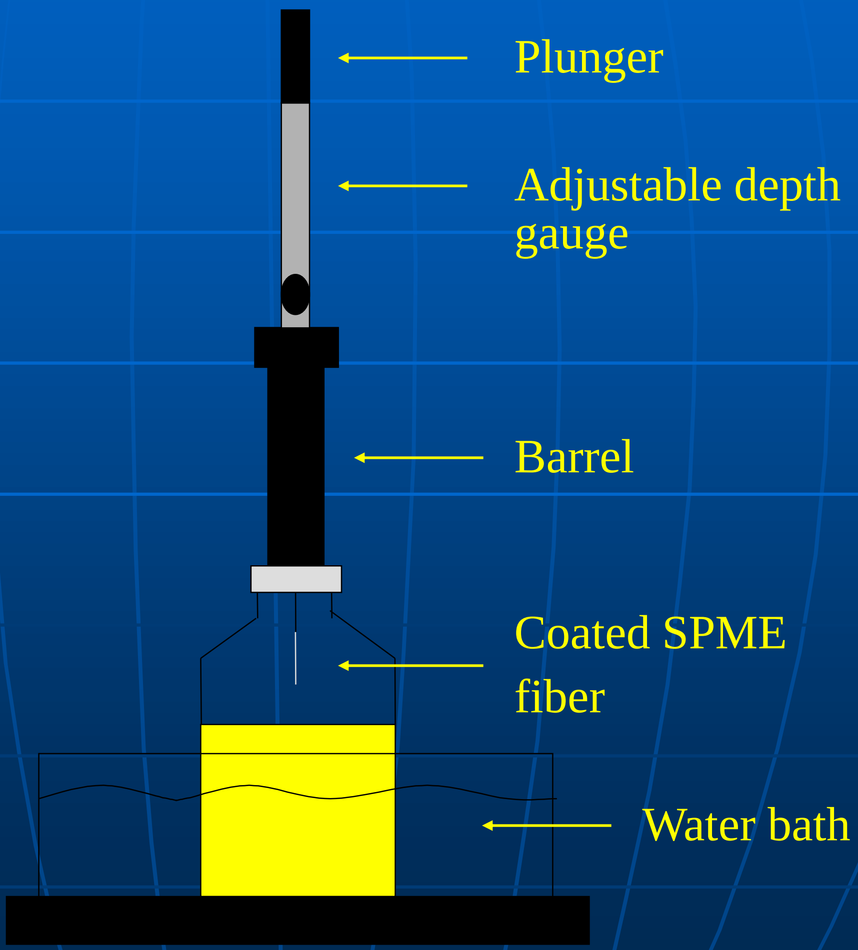


Diagram of SPME Extraction



Headspace SPME

SPME Analysis of Volatile Compounds



Principles of Headspace SPME

$$n_f = \frac{K_{fh} V_f V_s C_o}{K_{fh} V_f + K_{hs} V_h + V_s}$$

n_f: The # of moles in fiber coating

K : Partition coefficient

$$K_{fh} = \frac{\text{Concentration of coating}}{\text{Concentration of headspace}}$$

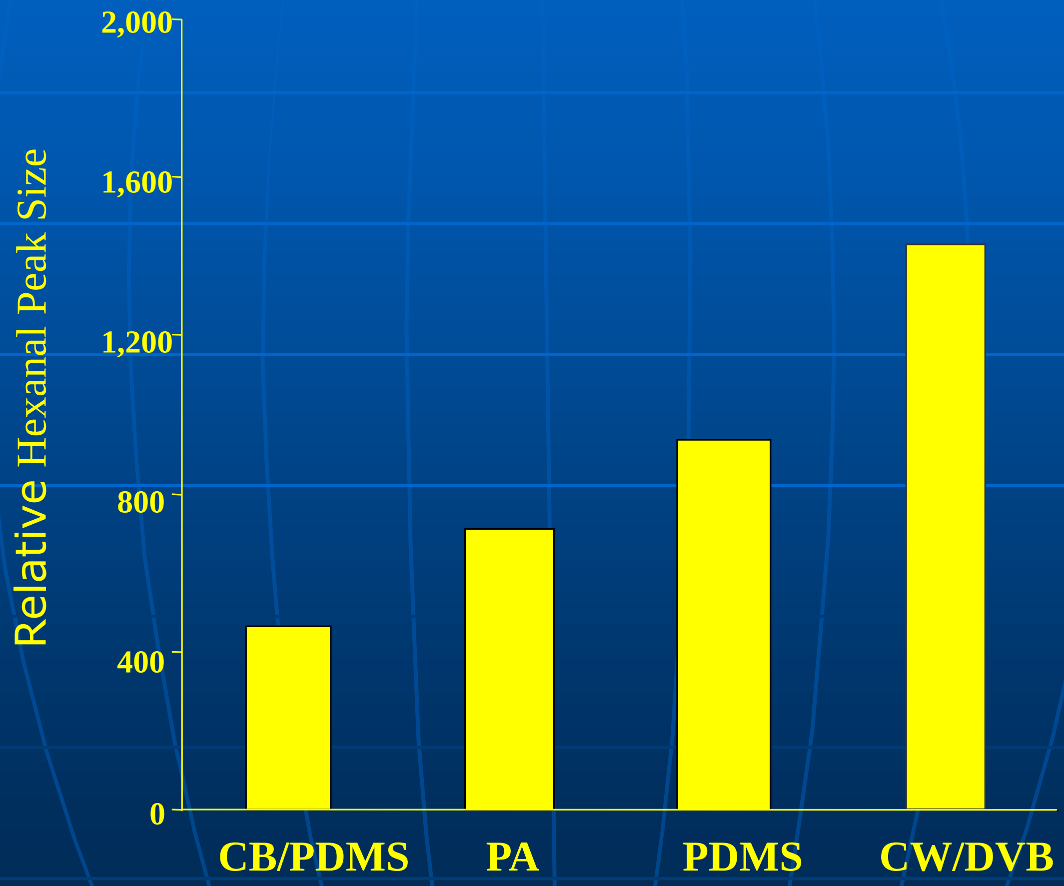
V_f, V_s, V_h: Volume of fiber coating, solution, and headspace, respectively

C_o: Initial concentration of analyte in the solution

Effects of Different Fibers on the Volatile Compound Extraction of Soybean Oil

- CB/PDMS:Carboxen/Polydimethylsiloxane
- PDMS: Polydimethylsiloxane
- CW/DVB: Carbowax/Divinylbenzene
- PA: Polyacrylate.

Effects of Different Fibers on the Hexanal Analysis in Oil



Effects of Different Fibers on the Hexanal Analysis

Hexanal Peak in Electronic Count

	Mean	CV (%)
CB/PDMS	499	4.2
PA	739	7.2
PDMS	966	3.2
CW/DVB	1,520	10.7

CV: Coefficient Variation (%) for n =5

Significant difference ($P<0.05$)

Improving Sensitivity of Solid Phase Microextraction

- Fiber Thickness
- Extraction Temperature and Time
- Sample Agitation and Concentration
- Direct sampling versus Headspace Sampling
- Selection of Proper Fiber
- Saturation of Sample with Proper Salts
- Maximum Ratio of Sample to Headspace Volume
- Large Sampling Vial

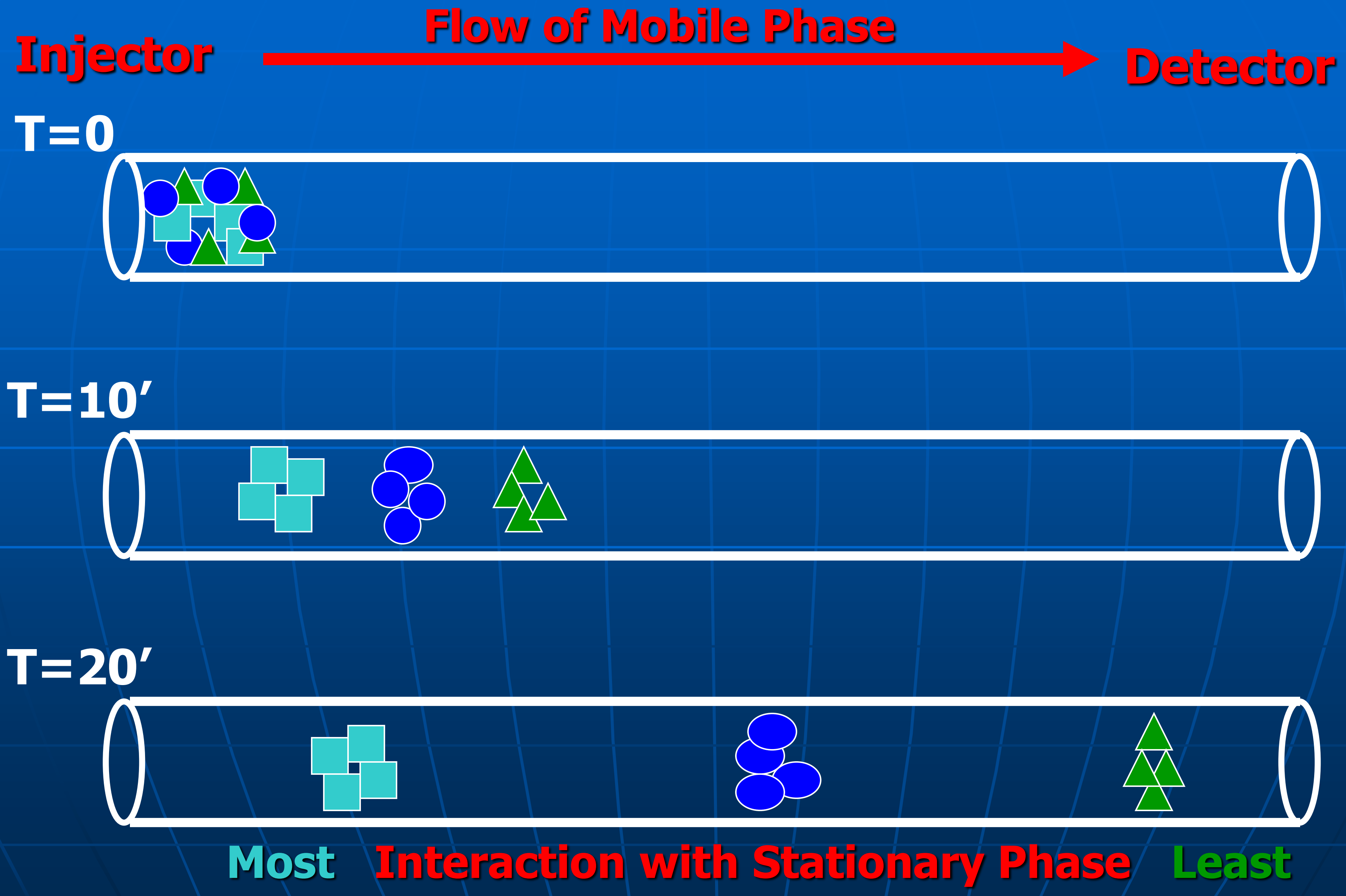
2. Final fractionation

Sample: as concentrate as possible

GC-Mass:
Use capillary column
Identification of the important peaks by mass spectrometry

Introduction

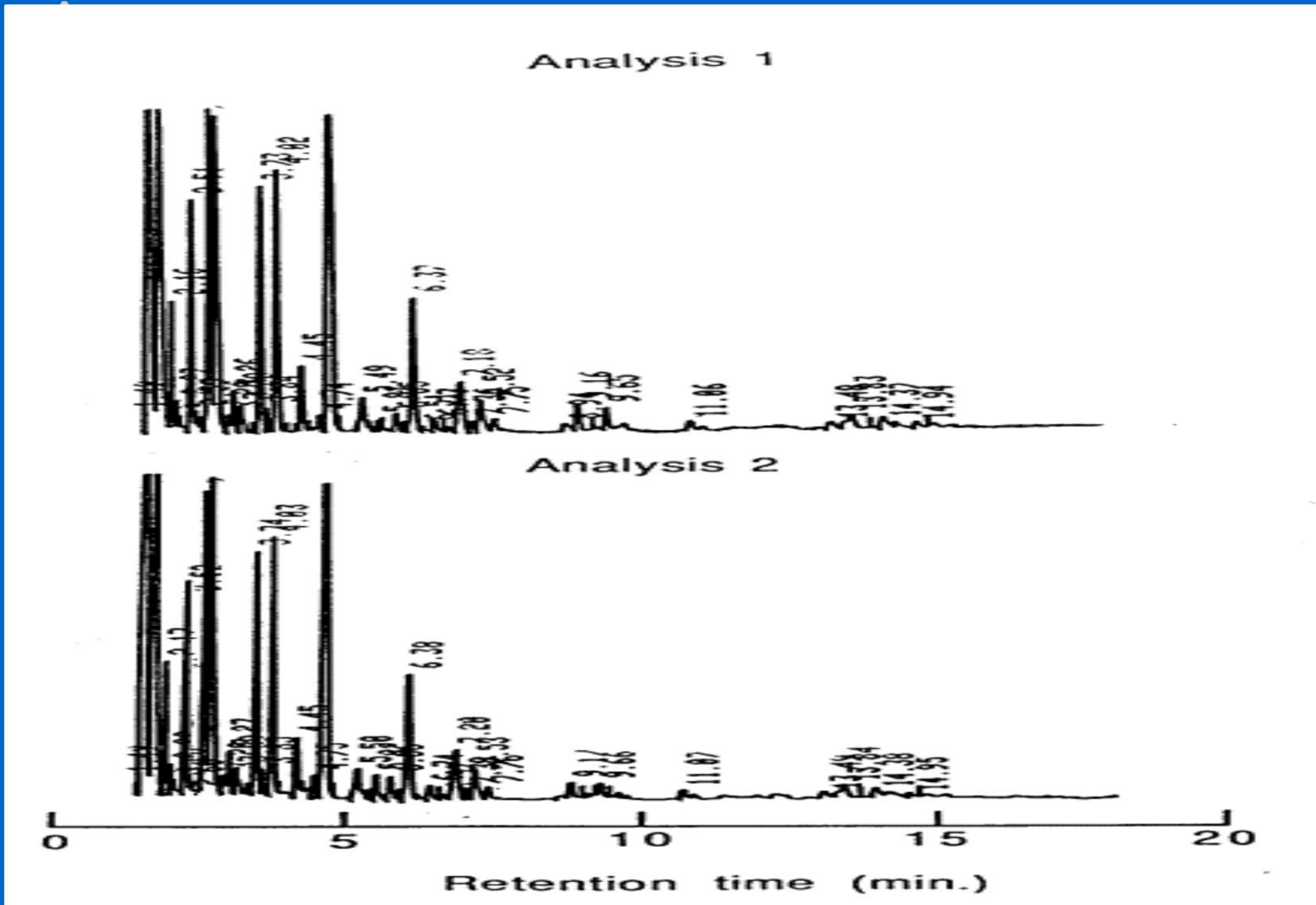
- Gas chromatography is an instrumental method for the separation and identification of chemical compounds.


Flow of Mobile Phase
Injector
Detector
T=0
T=10′
T=20′
Most
Interaction with Stationary Phase
Least

In gas chromatography

- the mobile phase is an inert carrier gas and
- the stationary phase is a solid or a liquid coated on a solid contained in a coiled column.

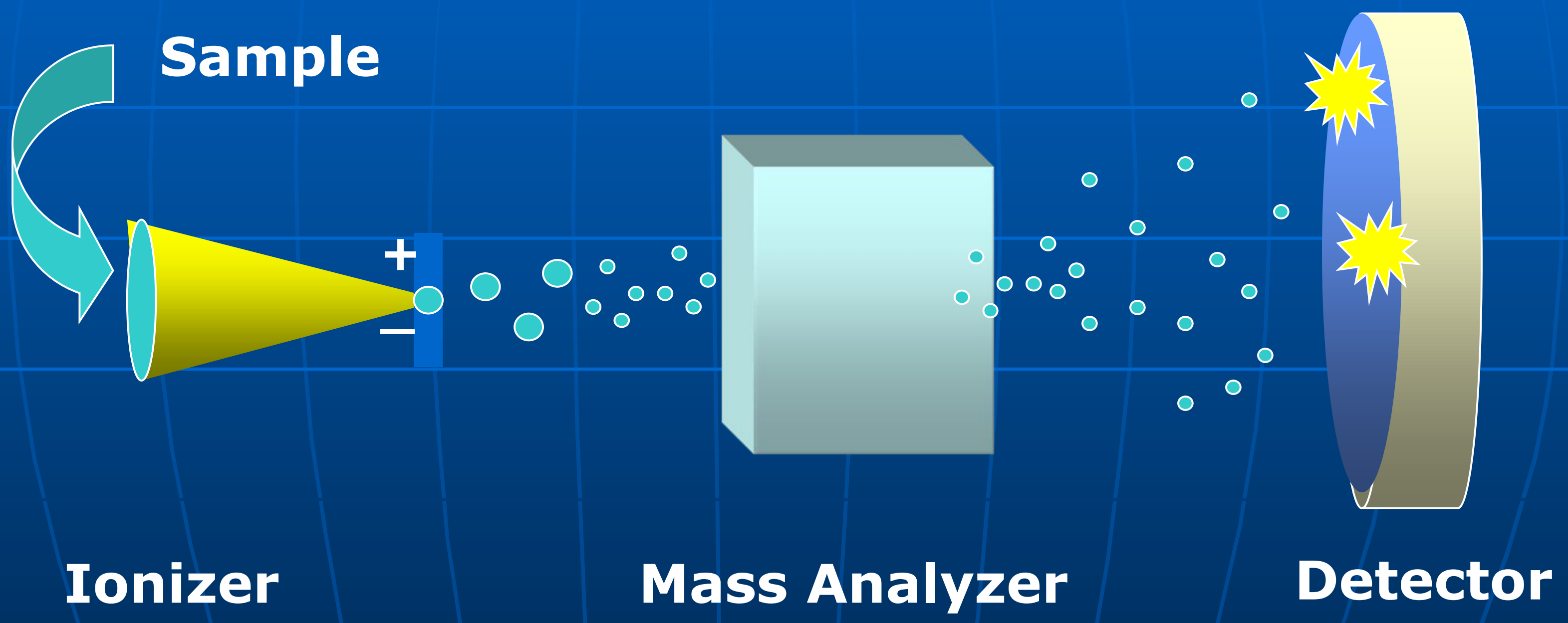
IDENTIFICATION of FLAVOR COMPOUND by SPECTROMETRIC METHODS


Analysis 1
Analysis 2
0
5
10
15
20
Retention time (min.)

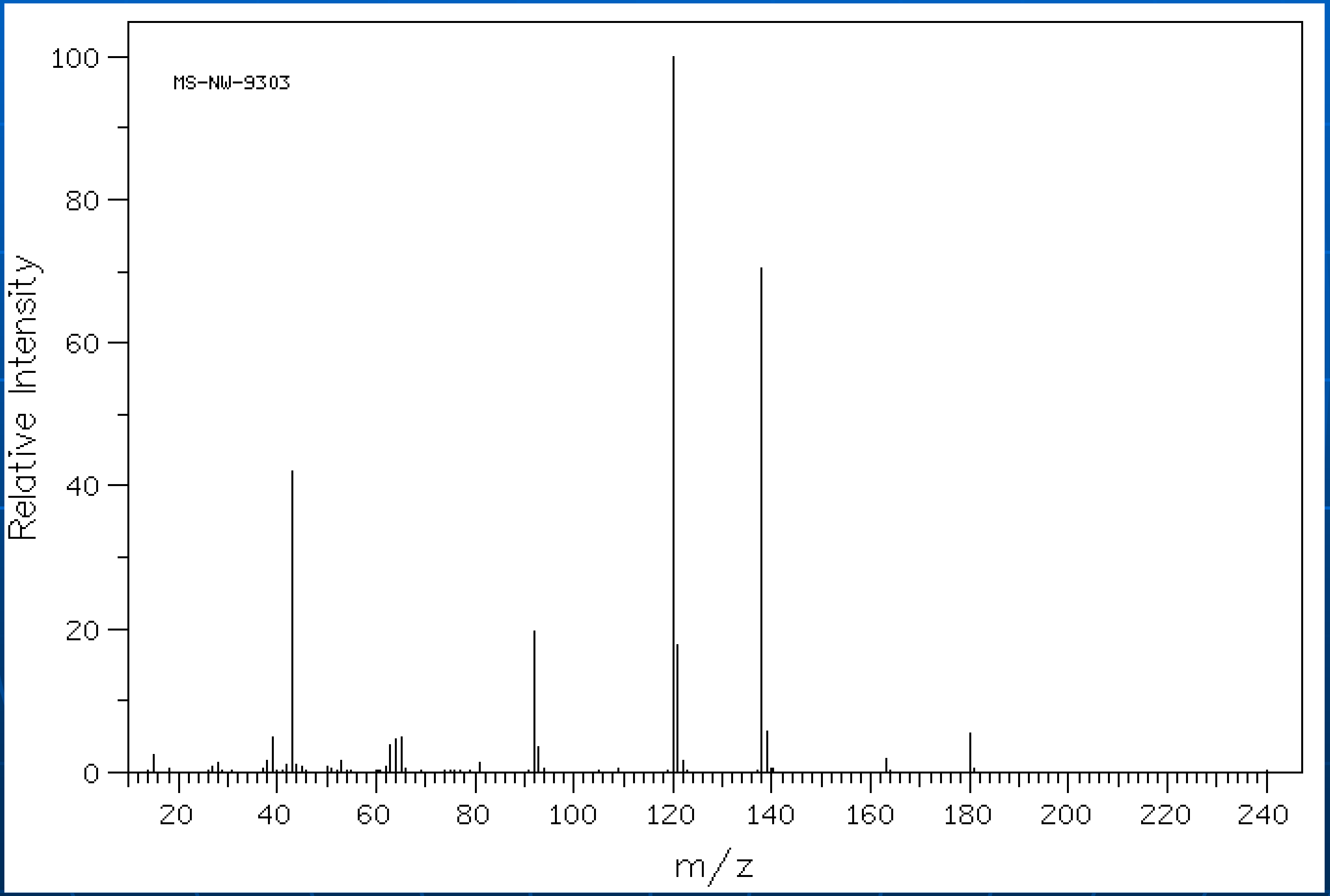
Mass Spectrometry

- Uses the interaction of electric and/or magnetic fields (i.e. electromagnetic radiation) with matter to determine weight or mass
- Measures mass, not absorption or emission of electromagnetic radiation

Mass Spec Principles

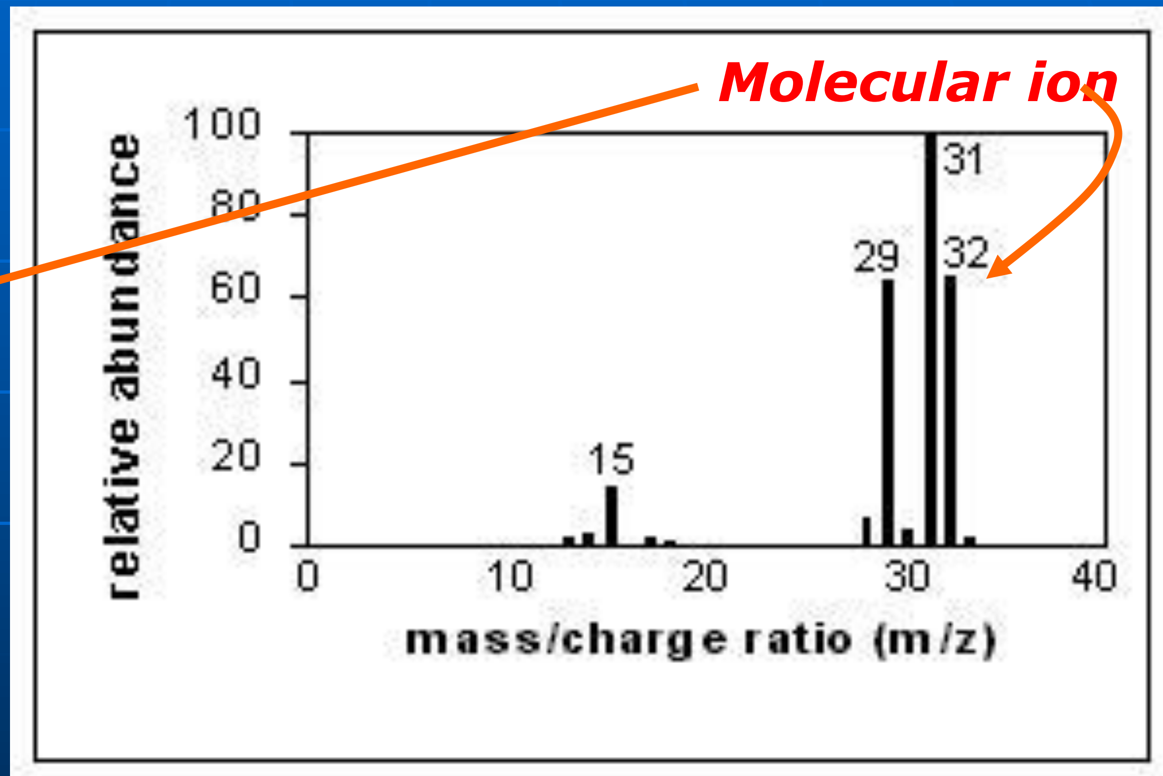


Typical Mass Spectrum



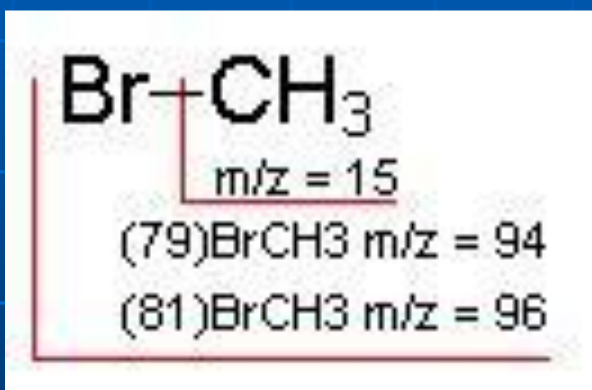
Electron Impact MS of CH_3OH

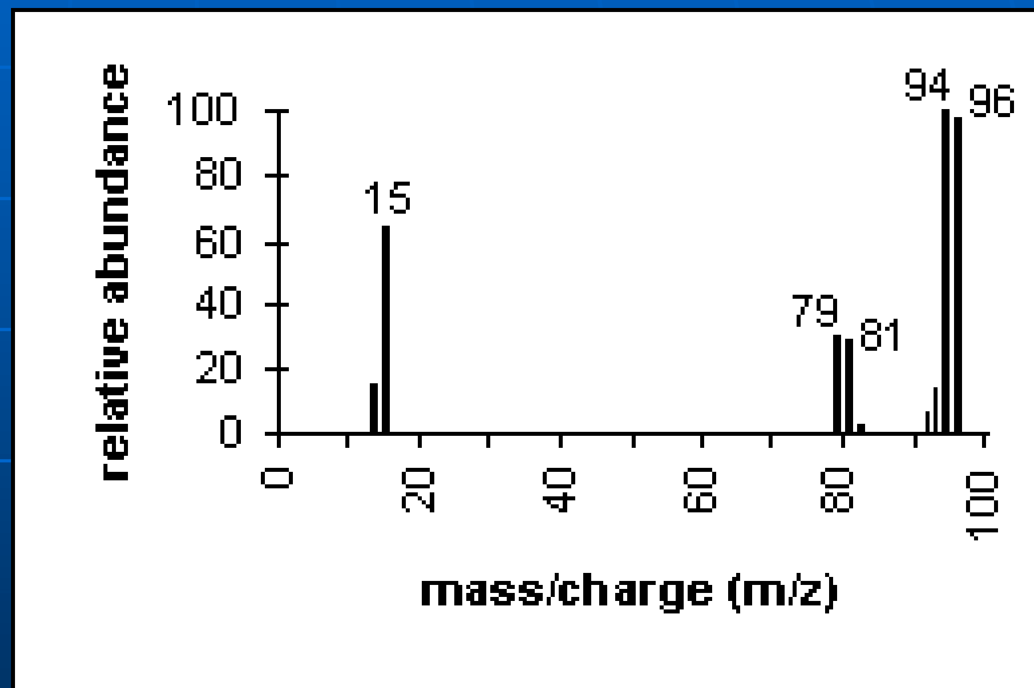
ions	m/z
$CH_3OH^{+\bullet}$	32
$H_2C{=}OH^+$	31
$HC{\equiv}O^+$	29
H_3C^+	15



EI Breaks up Molecules in Predictable Ways

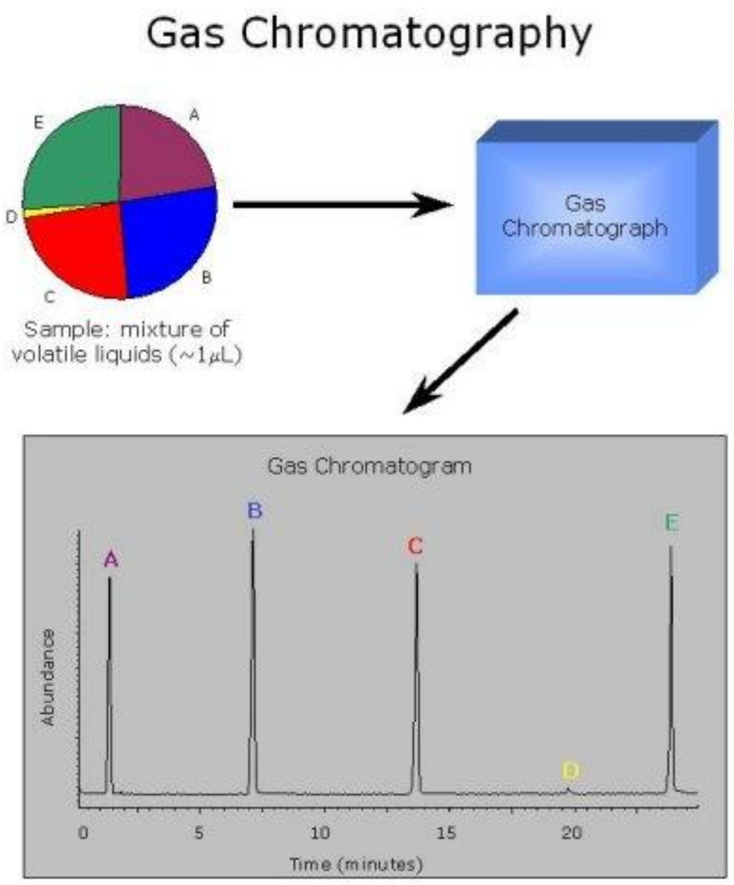
Electron Impact MS of CH_3Br

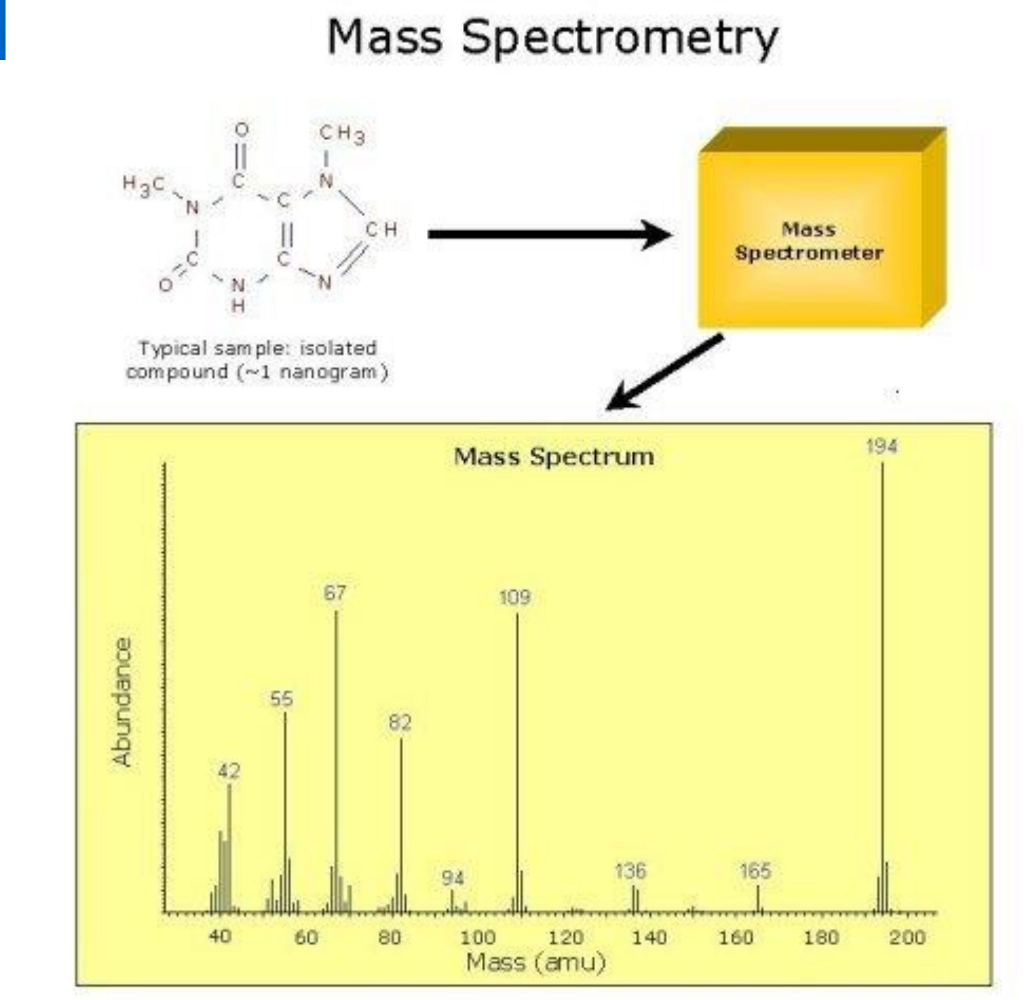




Isotopes can help in identifying compounds

GC-MS


Gas Chromatography
A
B
C
D
E
Sample: mixture of volatile liquids (~1μL)
Gas Chromatograph
Gas Chromatogram
Abundance
Time (minutes)
0
5
10
15
20

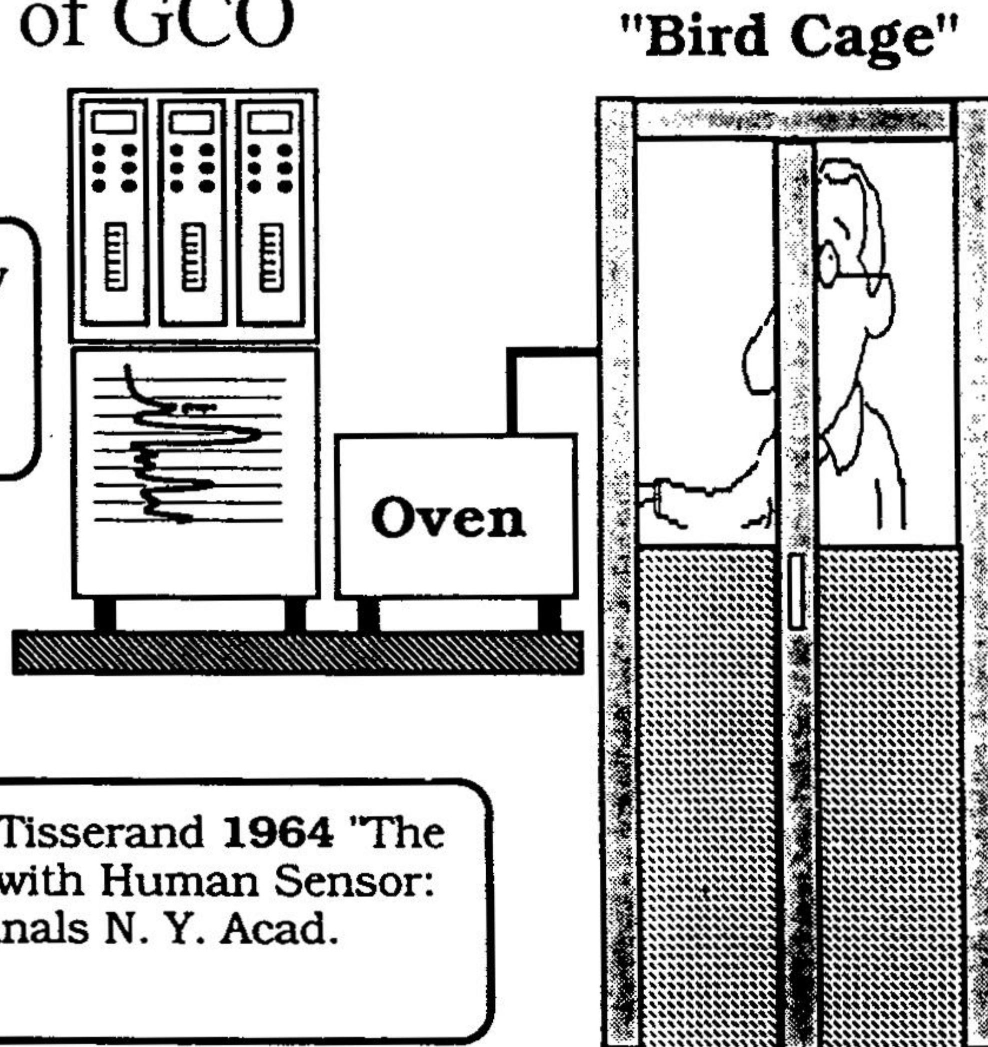

Mass Spectrometry
Typical sample: isolated compound (~1 nanogram)
Mass Spectrometer
Mass Spectrum
Abundance
Mass (amu)
42
55
67
82
94
109
136
165
194
40
60
80
100
120
140
160
180
200

Gas Chromatography - Olfactometry

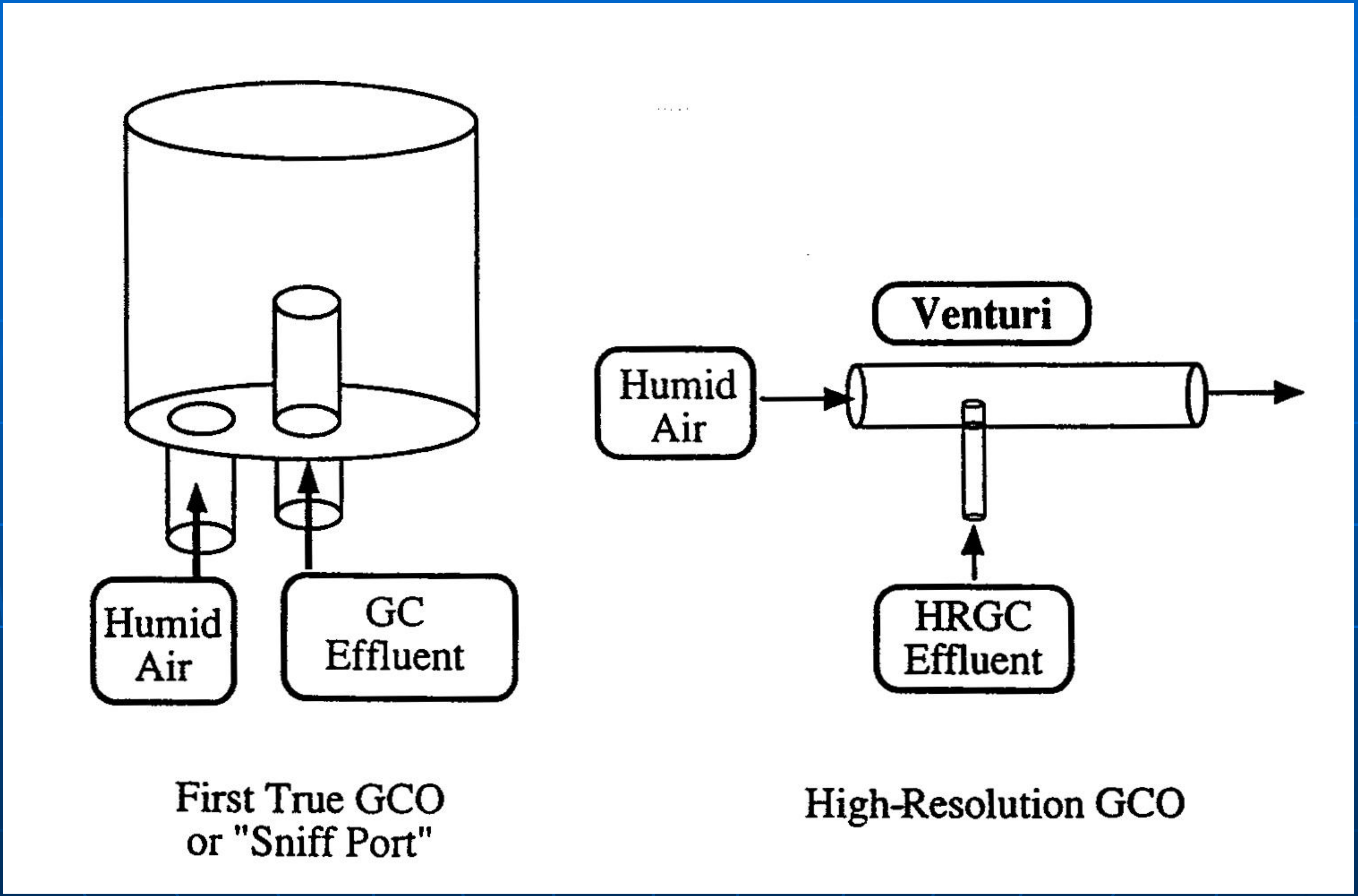
GC - O

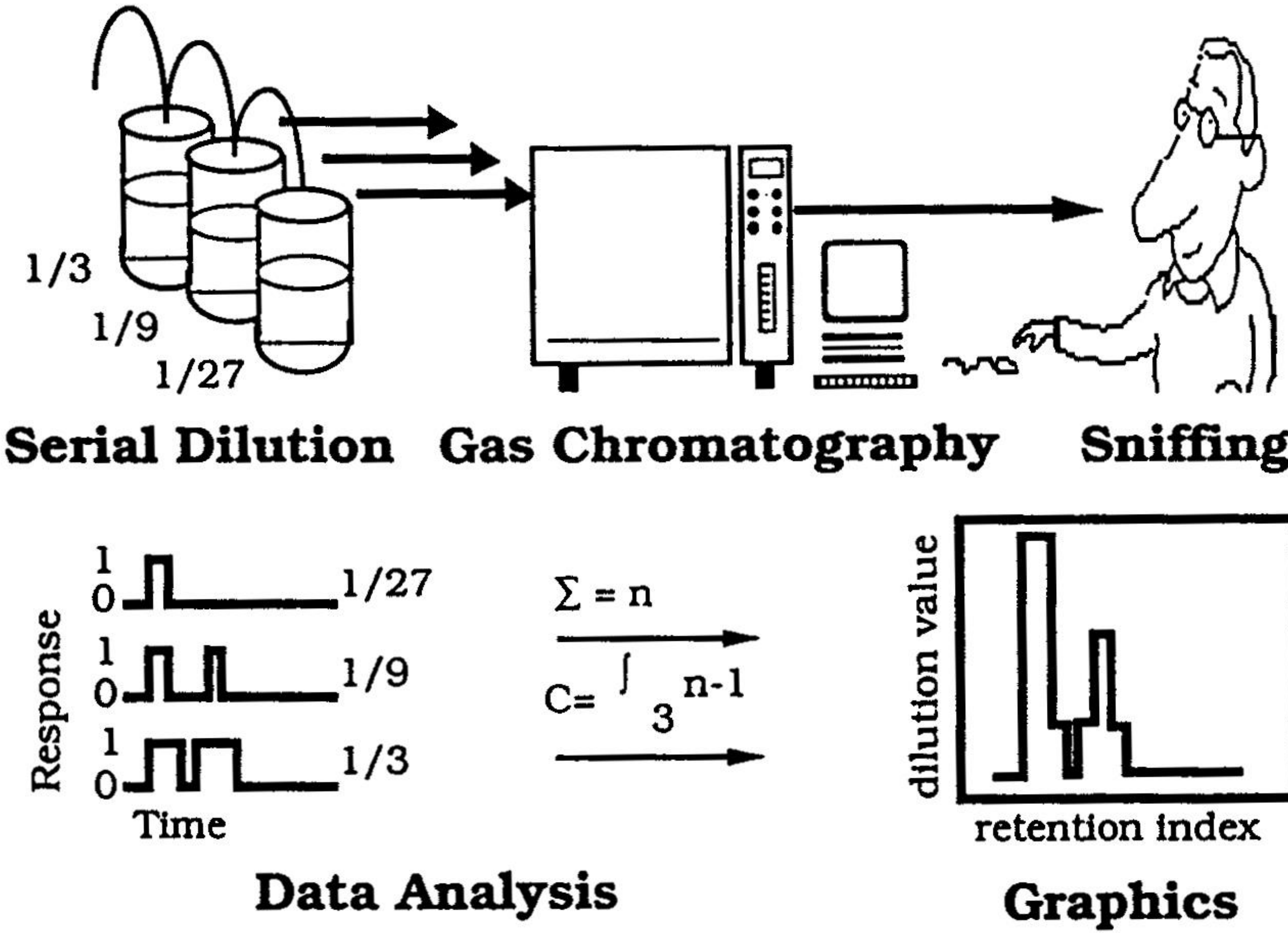
The Beginnings of GCO

Gas Chromatography invented by James & Martin **1952**

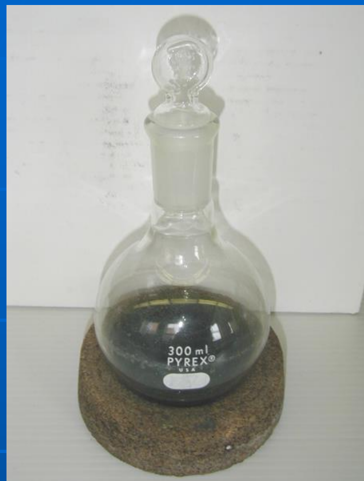


Fuller, Steltenkamp, Tisserand **1964** "The Gas Chromatograph with Human Sensor: Perfumer Model" , Annals N. Y. Acad. Sci.,116, 711-724.


Humid Air
GC Effluent
First True GCO or "Sniff Port"
Venturi
Humid Air
HRGC Effluent
High-Resolution GCO

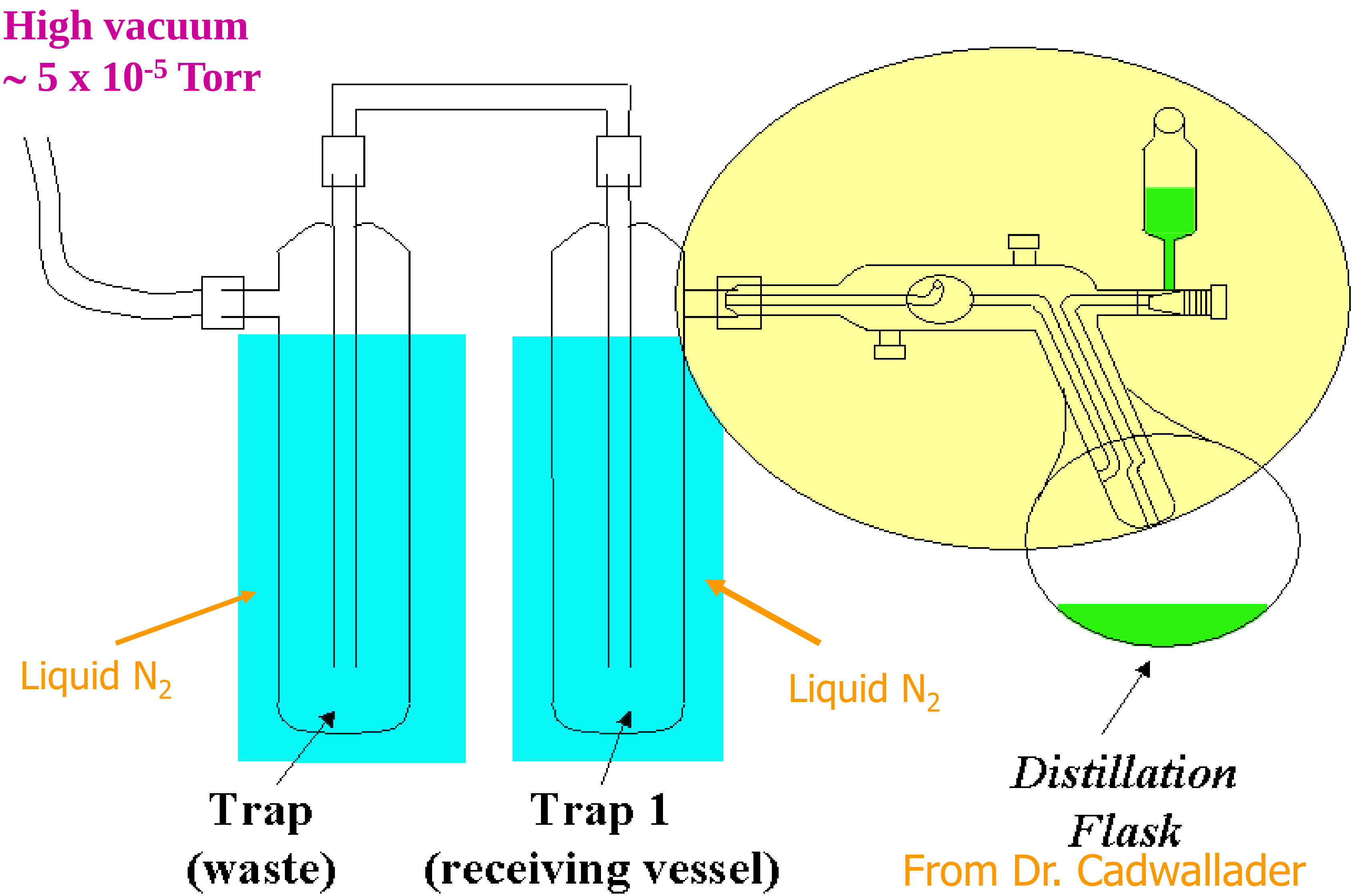


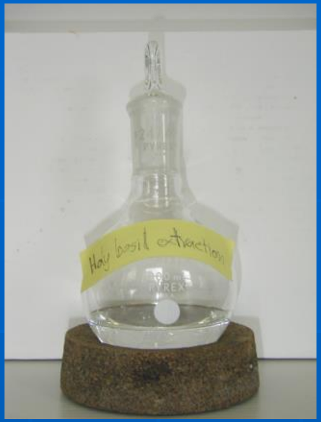
1/3
1/9
1/27
Serial Dilution
Gas Chromatography
Sniffing
Response
1
0
1/27
1
0
1/9
1
0
1/3
Time
Σ = n
C= ∫ 3 n-1
Data Analysis
dilution value
retention index
Graphics



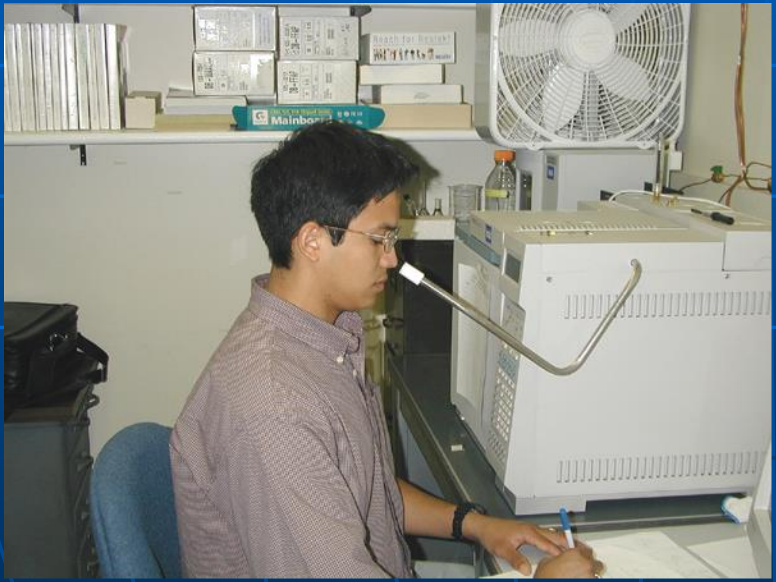
solvent assisted flavor evaporation = SAFE

SAFE – UIUC derivative





concentrated to 200 μl under a gentle stream of nitrogen gas



Gas Chromatography-Olfactometry (GCO)

Gas Chromatography-Mass Spectrometry (GC-MS)

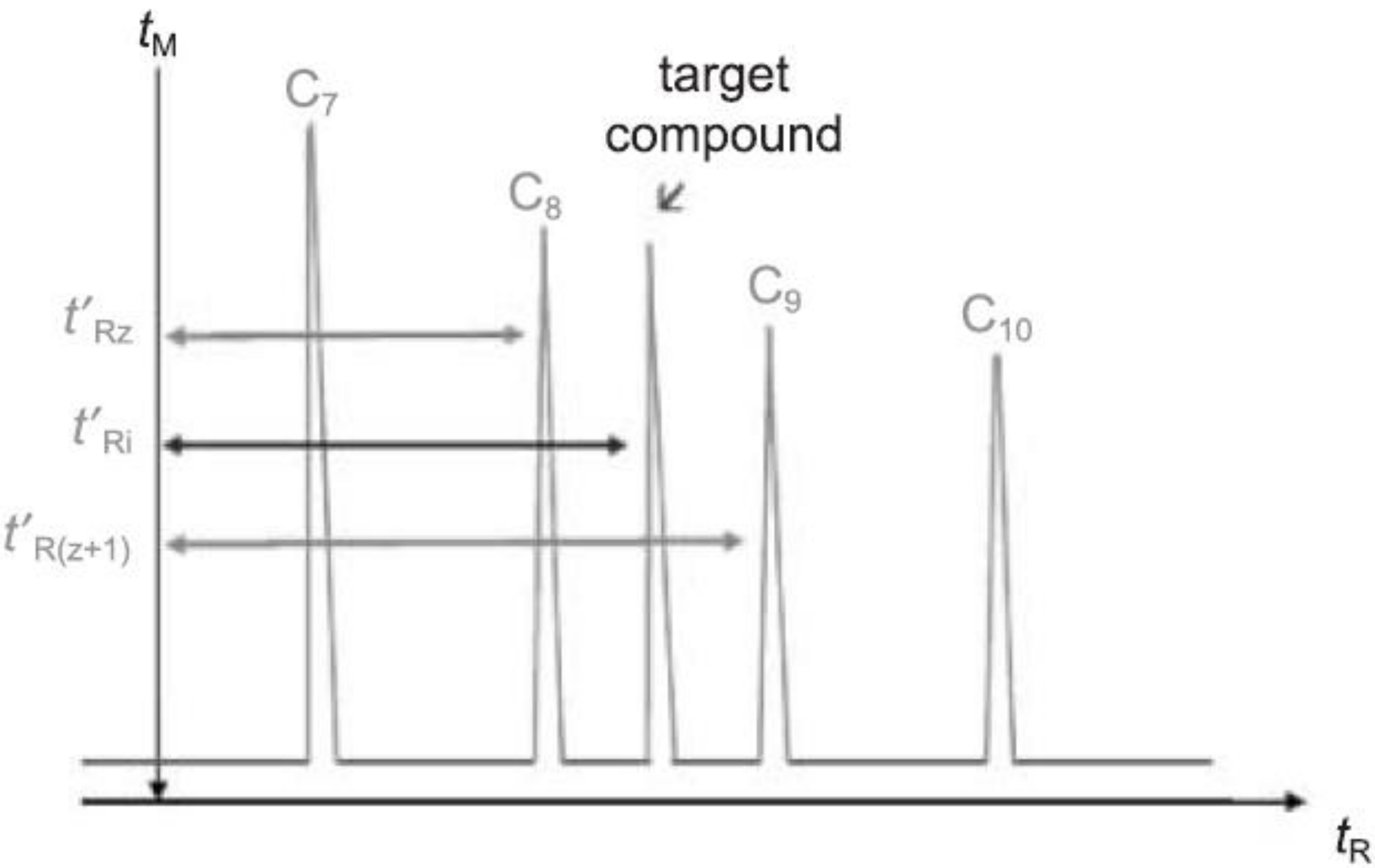


Figure 2. Scheme of the calculation of isothermal retention indices

$$LRI_x = \left[\left(\frac{t_x - t_n}{t_{n+1} - t_n}\right) + n\right] \times 100$$

LRI_x = Linear Retention Index ของ component X

t_x = Retention time ของ component X (min)

t_n = Retention time of standard alkane, eluting before component X (min) และ possessing n carbon atoms

t_{n+1} = Retention time of standard alkane, eluting after component x *(min)* and possessing n+1 carbon atoms

Table 2. Retention index values of limonene and their frequency of citation in *Flavour and Fragrance Journal* published throughout the year 2006

	Polar stationary phase		Non-polar stationary phase	
	LRI[a]	Frequency of citation	LRI[b]	Frequency of citation
Limonene	1183	3	1010	1
	1190	2	1013	1
	1195	1	1022	5
	1199	2	1023	1
	1201	1	1025	3
	1202	3	1026	2
	1203	10	1029	3
	1204	4	1030	10
	1205	5	1031	17
			1032	8
			1033	1
			1035	1
			1038	2

Table 1 Outline of aroma analysis

Step	Procedure
I	Separation of the extract containing the volatile fraction of a food by high-resolution gas chromatography and localization of potent odorants by charm analysis or aroma extract dilution analysis (AEDA)
II	Detection of highly volatile potent odorants by gas chromatography–olfactometry of static headspace samples (GCOH)
III	Enrichment and identification of potent odorants
IV	Quantification of potent odorants and calculation of their odour activity values (OAVs)
V	Preparation of a synthetic blend of the potent odorants on the basis of the quantitative data obtained in step IV. Critical comparison of the aroma profile of the synthetic blend, denoted aroma model, with that of the original
VI	Comparison of the overall odour of the aroma model with that of models in which one or more components are omitted (omission experiments)

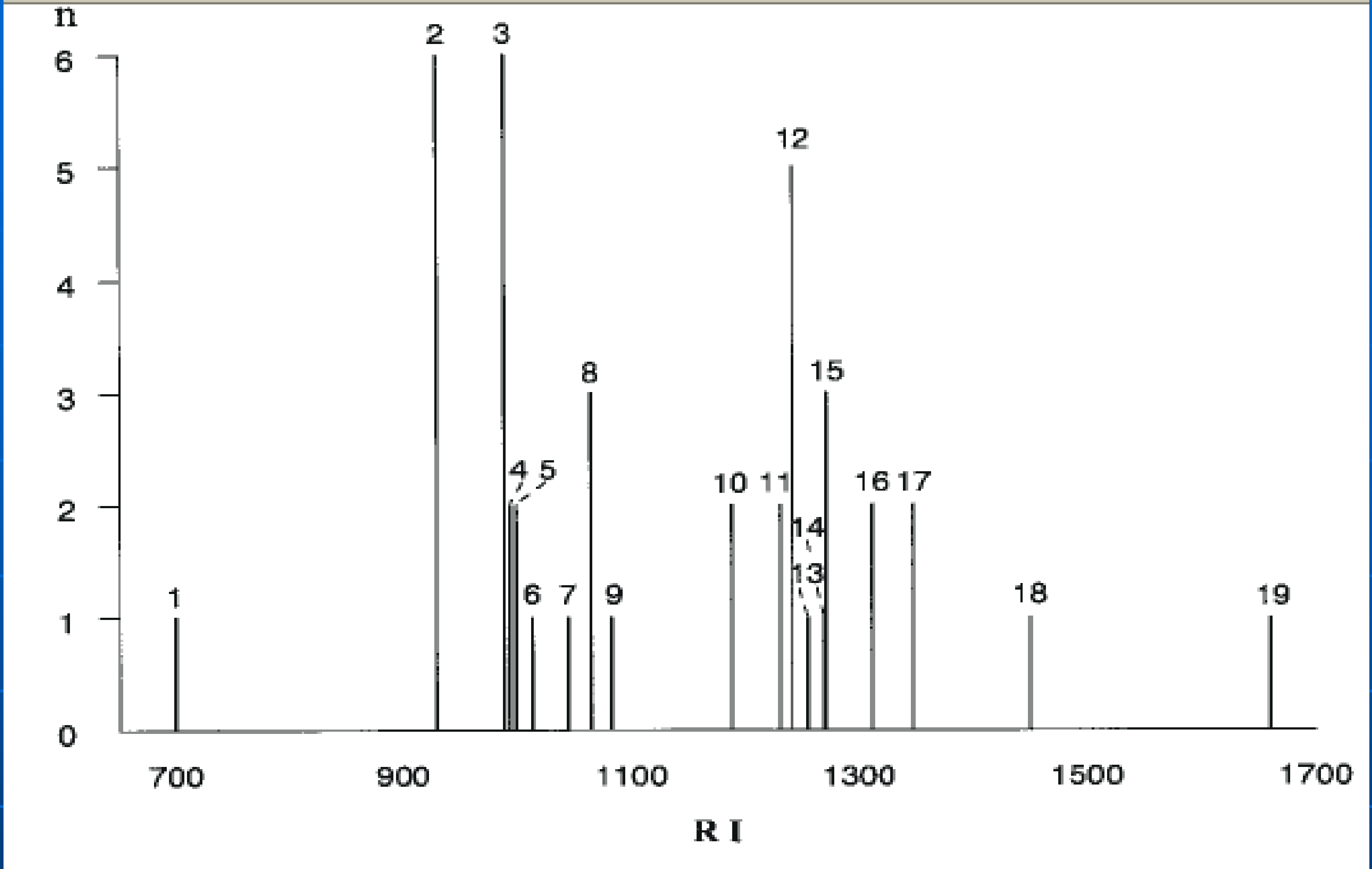


Figure 1 FD chromatogram of the volatile fraction isolated from boiled beef (Kerscher and Grosch, 1997). Ordinate: *n*, exponent of FD factor 2^n. Abscissa: retention index (RI) on the capillary OV-1701. The odorants were identified as: **(1)** 2,3-butanedione; **(2)** 2-methyl-3-furanthiol; **(3)** 2-furfurylthiol; **(4)** butyric acid; **(5)** 3-mercapto-2-pentanone; **(6)** 2-acetyl-1-pyrroline; **(7)** methional; **(8)** 1-octen-3-one; **(9)** octanal; **(10)** nonanal; **(11)** guaiacol; **(12)** 4-hydroxy-2,5-dimethyl-3(2H)-furanone; **(13)** (*Z*)-2-nonenal; **(14)** (*E*,*Z*)-2,6-nonadienal; **(15)** (*E*)-2-nonenal; **(16)** *p*-cresol; **(17)** 3-hydroxy-4,5-dimethyl-2(5H)-furanone; **(18)** (*E*,*E*)-2,4-decadienal; **(19)** 12-methyltridecanal.

Table 2 GCOH of boiled beef[a]

No.	Odorant	Volume[b] (ml)	FD factor[c]
1	Methanethiol	0.5	40
2	Dimethyl sulphide	1.0	20
3	Dimethyl trisulphide	2.5	8
4	Octanal	2.5	8
5	Nonanal	2.5	8
6	Acetaldehyde	5.0	4
7	Methylpropanal	5.0	4
8	Hexanal	5.0	4
9	2-Methyl-3-furanthiol	5.0	4
10	Methional	5.0	4
11	2-Furfurylthiol	5.0	4
12	3-Methylbutanal	10.0	2
13	1-Octen-3-one	10.0	2
14	Dimethyl tetrasulphide	10.0	2
15	2-Methylbutanal	20.0	1
16	(E)-2-nonenal	20.0	1

Table 5 Odorants showing OAVs ≥10 in Gewürztraminer and/or Scheurebe wines[a]

Odorant	Gewürztraminer		Scheurebe	
	Conc. (μg/l)	OAV[b]	Conc. (μg/l)	OAV[b]
Ethyl octanoate	630	315	270	135
Ethyl hexanoate	490	98	280	56
3-Methylbutyl acetate	2900	97	1450	48
Ethyl isobutyrate	150	10	480	32
(E)-β-damascenone	0.84	17	0.98	20
Linalool	175	12	307	20
Wine lactone	0.10	10	0.10	10
Ethyl butyrate	210	11	184	9
cis-Rose oxide	21	105	3.0	15
4-Mercapto-4-methylpentan-2-one	<0.01	n.d.[c]	0.40	667

[a]Source: Guth (Guth, 1997a, 1998).

[b]The odour activity values (OAVs) were calculated as the ratio of concentration to odour threshold values of the compound in water/ethanol (9 + 1, w/w).

[c]Not determined.

Subjective analysis :Sensory Evaluation

B. Descriptive

1. **Single sample** (monodic) - present one sample at a time
2. **Ranking -**
3. **Quality rating** (scalar scoring) -
4. **Magnitude estimation** - based on assignment of a number for the first sample tested, after which all subsequent numbers for the subsequent samples are assigned in proportion.
5. **Texture profile** - the analysis of a product's perceived manifestation of the structure or inner make-up of foods in terms of: fell (tactile) and resistance to applied forces (kinesthetic).
6. **Quantitative descriptive analysis** - relies heavily on statistical analysis to determine the appropriate terms, procedures, and panelists to be used for analysis of a specific product.
   - Training requires the use of product and ingredient references to stimulate the generation of terminology.
   - Evaluated on computer. Reported in "spider web" with a branch or spoke for each attribute
7. **Flavor profile** - the analysis of a product's perceived aroma and flavor characteristics, their intensities, order of appearance, and aftertaste.
   - An amplitude rating is generally included as part of the profile

The flavor profile method (Arthur D. Little, Inc., 1940's)

1. Components

   a. Character notes

      (1) Cooked beef lean

      (2) Cooked beef fat

      (3) Browned

      (4) Serum/bloody

      (5) Grainy/cowy

      (6) Cardboard

      (7) Painty

      (8) Fishy

b. Intensity - category scale, 15 point

- 2= soda in saltines
- 5= apple in Mott's apple sauce
- 7 = orange in Minute Maid frozen
- 10= grape in Welch's grape juice
- 12 = cinnamon in Big Red gum

c. Order of appearance

d. Aftertaste

What is Descriptive Flavor Analysis?

TASTE A

- A tool used to describe a Flavor Profile
- Allows us to quantify & graphically represent the Flavor Profile
- Allows Flavorists & the Customers to use the same language
- Helps the Customers see the impact of our products on their products
- Allows the Customer to participate in the creative process

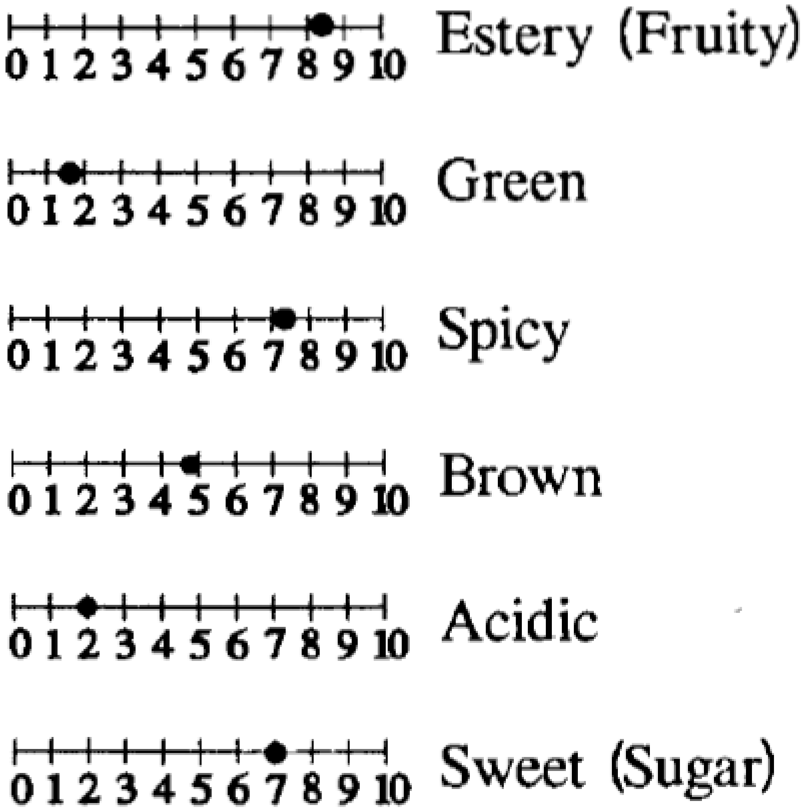
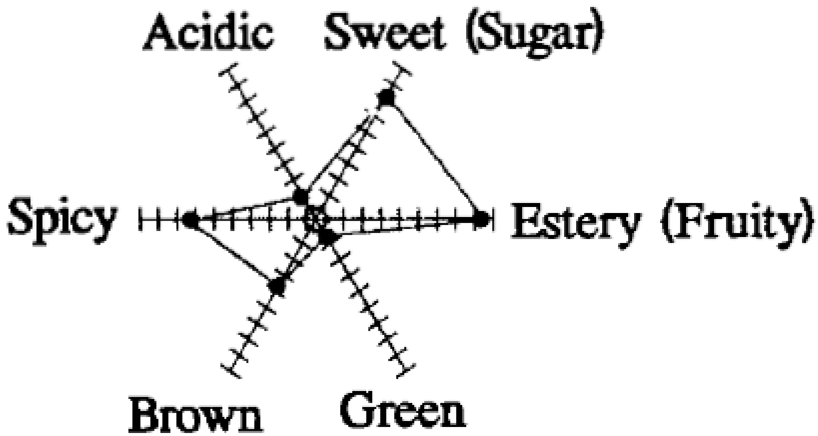


Fig. 1—**Impact vs Stimulus** *(left)*

Fig. 2—**Spider-Web Profile of Impact vs Stimulus** *(below)*



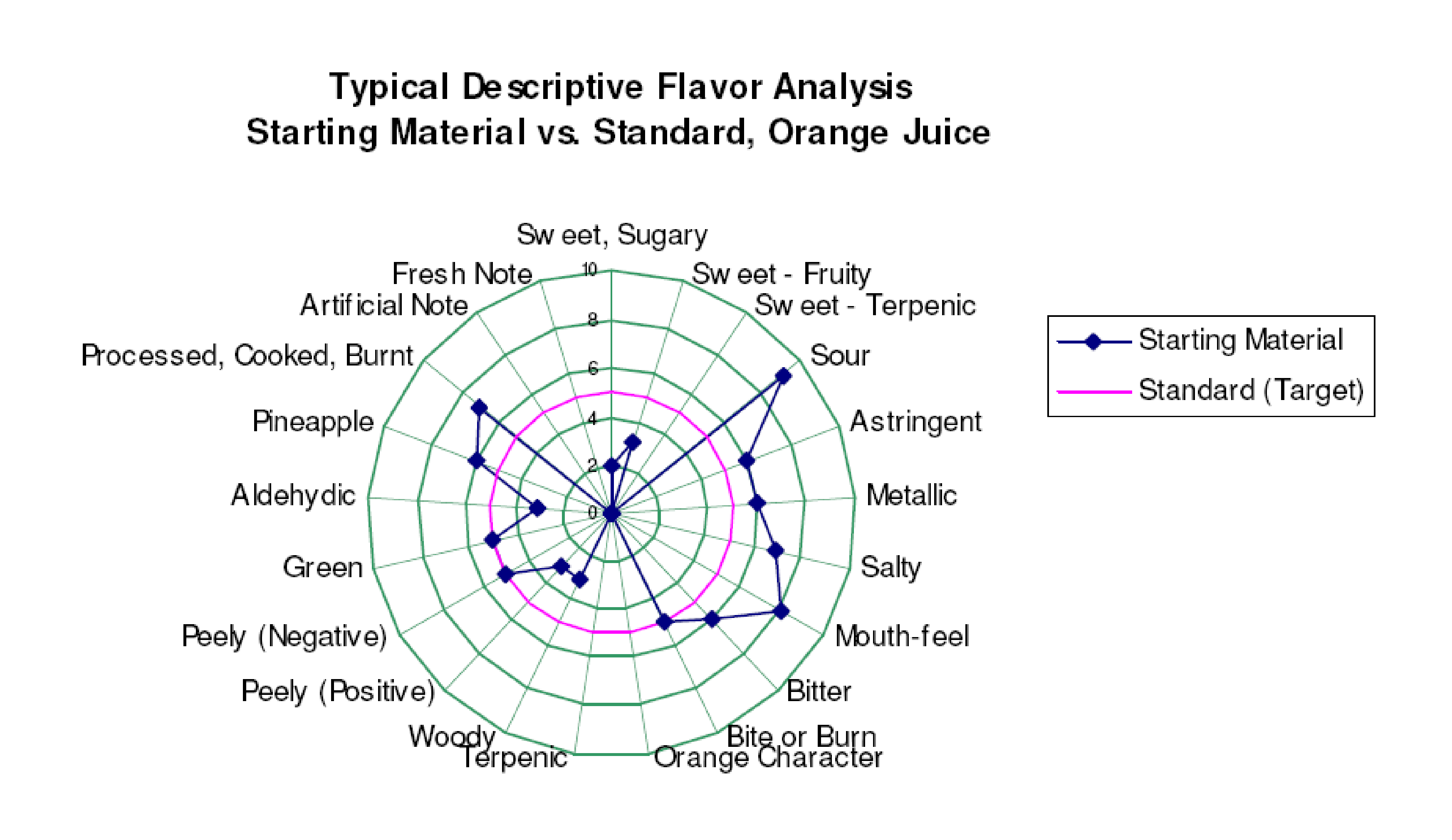

Typical Descriptive Flavor Analysis
Starting Material vs. Standard, Orange Juice
Sweet, Sugary
Sweet - Fruity
Sweet - Terpenic
Sour
Astringent
Metallic
Salty
Mouth-feel
Bitter
Bite or Burn
Orange Character
Terpenic
Woody
Peely (Positive)
Peely (Negative)
Green
Aldehydic
Pineapple
Processed, Cooked, Burnt
Artificial Note
Fresh Note
10
8
6
4
2
0
Starting Material
Standard (Target)

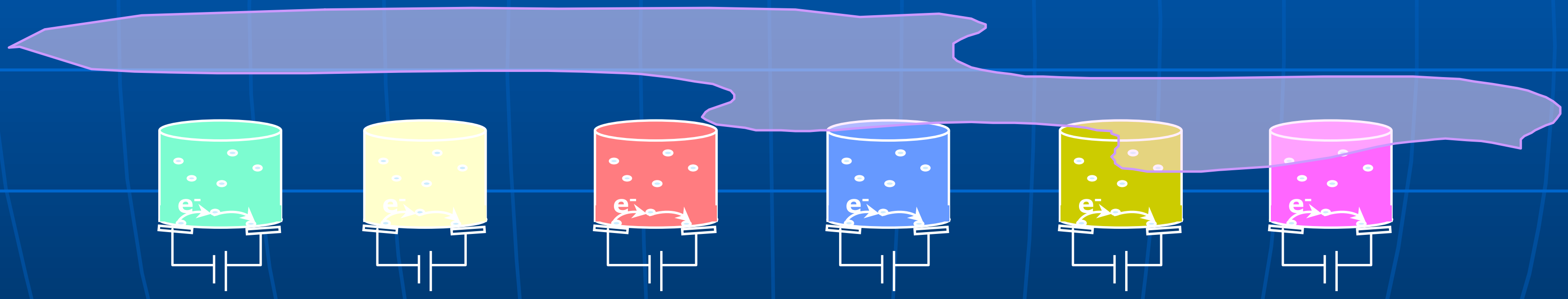
Table 1.Differences in the flavor attributes, intensity of flavor attributes and order of appearance for 2 bean and cheese burritos using a 15-point scale with 0.5 point increments.

Company's Current Product Flavor Attributes		Market Leader Flavor Attributes	
Amplitude	8.0	Amplitude	11.0
Oil-Heated	7.0	Overall Spice	5.0
Overall Spice	4.0	Oregano	3.0
Cumin	3.0	Tarragon	2.0
Meat Identity	5.0	Turmeric	2.0
Bean (Pinto)	10.0	Black Pepper	2.5
Wheat	4.0	Chicken Identity	5.0
Doughy	4.5	Beans (Pinto)	4.0
Onion-Fresh	4.0	Onion-Dried	3.0
Red Pepper	2.5	Wheat	5.0
Processed Cheese	2.5	Toasted	4.0
Chili Pepper (Green)	2.5	Processed Cheese	2.5
Oily Mouthfeel	3.0	Chili Pepper (Green)	2.0
Heat Burn	2.0	Heat Burn	5.5
Salty	7.0	Salty	8.0
Sour	2.5	Sour	2.5
Bitter	3.0	Bitter	2.5

E-Nose

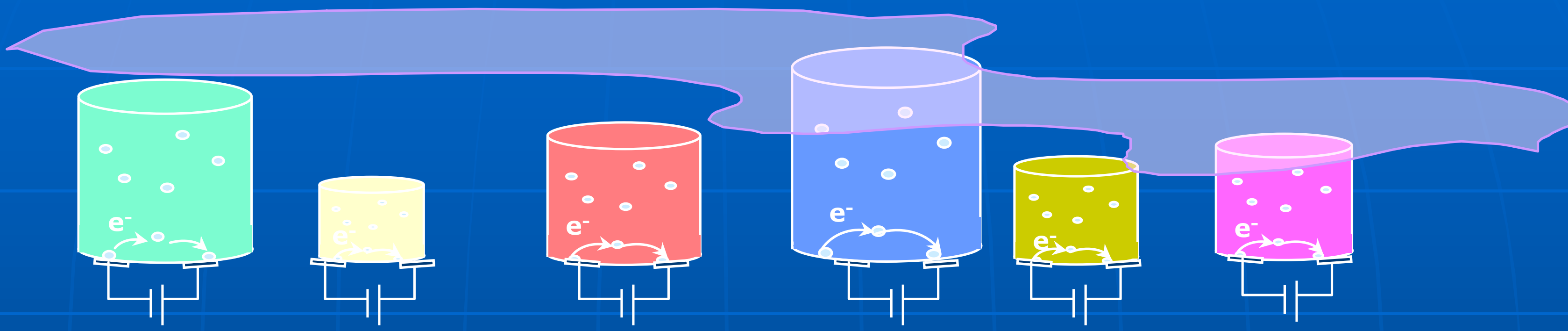
BASELINE RESISTANCE

All of the polymer films on a set of electrodes (sensors) start out at a measured resistance, their *baseline resistance*. If there has been no change in the composition of the air, the films stay at the baseline resistance and the percent change is zero

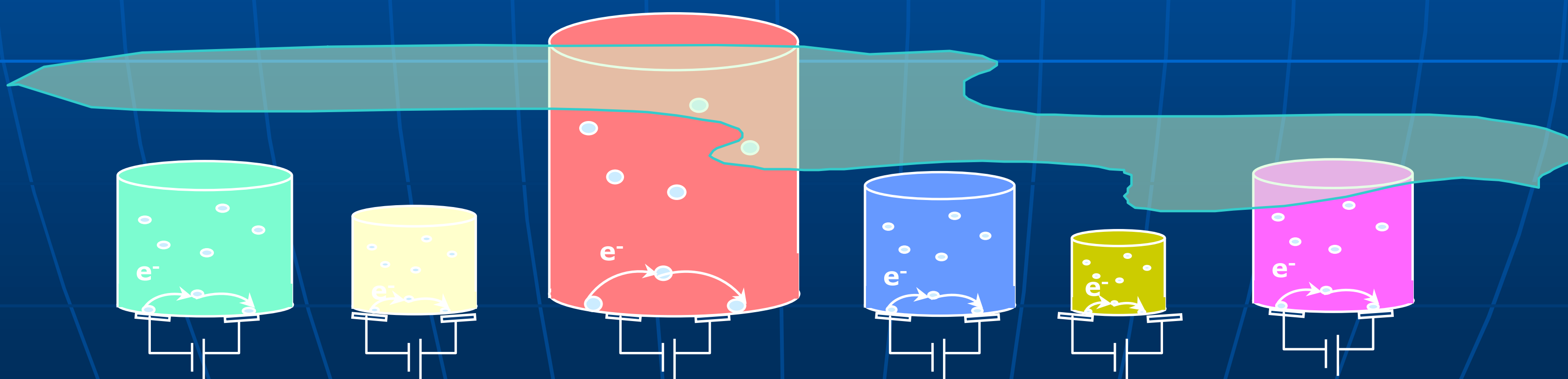


THE ELECTRONIC NOSE SMELLS SOMETHING

Each polymer changes its size, and therefore its resistance, by a different amount, making a pattern of the change



If a different compound had caused the air to change, the pattern of the polymer films' change would have been different:



5. Case Study

How to use flavor to determine quality and acceptability of products?

Tom Yum flavor

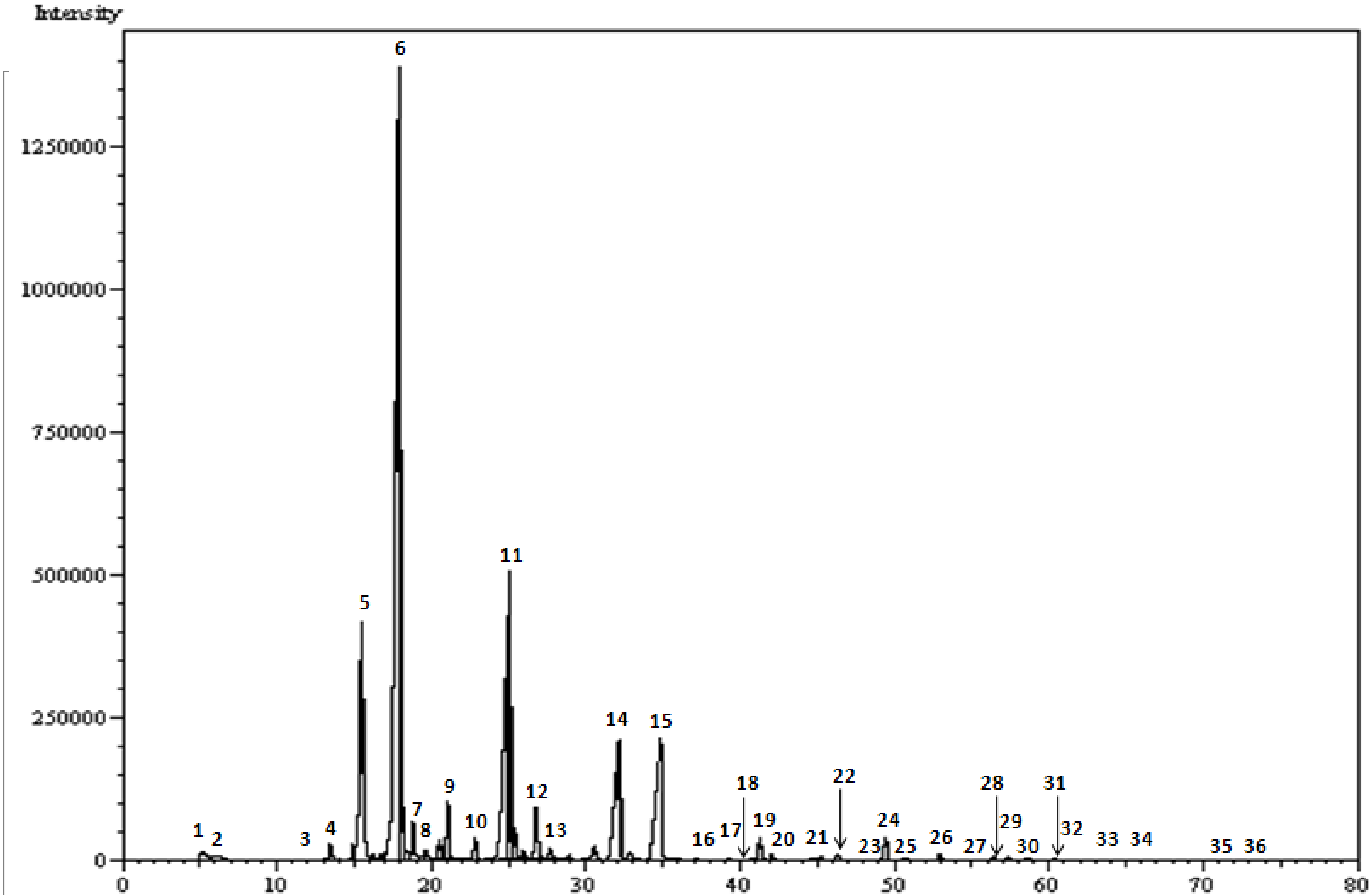
Soraya Oonjitti
Department of Food Technology
Silpakorn University



วิธีการทดลอง

2. Volatile compound analysis using GC-O And Detection frequency

Gas Chromatography Olfactometry-Flame Ionization Detector (GCO-FID)



GC-FID chromatogram of Tom Yum flavor

Volatile compound of Tum Yum Flavor

Peak	Compound	LRI[a]	NIF[b]	SNIF[c]	Descriptive
1	ethanol	537	9.1	0.22	sweet
2	methylbutenol	615	9.1	0.19	herb
3	alpha-pinene	932	36.4	2.64	fresh camphor earthy woody
4	camphene	947	54.5	4.55	camphor woody herbal fresh
5	beta-pinene	993	90.9	5.43	herb woody pine green
6	1,8-cineole	1034	100	9.16	citrus herb minty pepper spicy woody
7	beta-ocimene	1049	54.5	1.32	citrus herb flower green woody
8	gamma-terpinene	1059	27.3	1.18	lemon lime herbal
9	linalool	1102	81.8	6.60	flower citrus floral lemon orange
10	E,Z-alloocimene	1128	9.1	0.55	grassy
11	citronellal	1157	100	16.69	lemon fresh green-citrusy
12	4- terpineol	1178	100	4.14	lemon lime herb green
13	cis-carveol	1205	27.3	0.67	herb spicy green
14	(Z)-citral, (Z)- neral	1241	100	16.05	citrus lemon green-citrusy
15	(E)-citral, (E)- geranial	1273	100	19.61	citrus lemon green-citrusy
16	geranyl formate	1303	9.1	0.63	citrus
17	methyl geranate	1321	18.2	0.67	flower green
18	delta-elemene	1333	9.1	0.27	woody

Peak	Compound	LRI[a]	NIF[b]	SNIF[c]	Descriptive
19	alpha-cubebene	1341	9.1	0.29	herb
20	(-)-alpha- copaene	1369	72.7	4.62	spice herbal green-citrusy
21	neryl acetate	1383	45.5	1.63	fruity lemon lime sweet
22	(-)-beta-elemene	1388	63.6	2.16	herb fresh green green-citrusy
23	methyl eugenol	1404	27.3	0.90	clove, spice
24	caryophyllene	1413	63.6	2.17	green-citrusy spicy herb
25	alpha-caryophyllene	1443	54.5	2.53	fruity woody mint green
26	beta-farnesene	1454	63.6	2.67	fruity, citrus-like, woody
27	germacrene D	1471	9.1	0.21	spice
28	beta-selinene	1475	27.3	0.33	herb green-citrusy
29	alpha-selinene	1485	54.5	1.81	orange herb flower sweet green-citrusy
30	beta-bisabolene	1504	9.1	0.27	herb
31	delta-cadinene	1516	9.1	0.82	herb
32	valencene	1523	18.2	0.61	orange green
33	trans-nerolidol	1560	27.3	0.78	waxy, floral
34	hinesol	1602	18.2	0.29	spicy peppery woody
35	(R)-gamma-cadinene	1641	9.1	0.52	herb
36	10s,11s-himachala-3(12),4-diene	1678	9.1	0.31	herb

Key volatile compound of Tom Yum Flavor

Peak	Compound	LRI[a]	NIF[b]	SNIF[c]	Odour descriptions
5	β-pinene	993	90.90	5.43	herb woody pine green
6	1,8-cineole	1034	100.00	9.16	citrus herb minty pepper spicy woody
9	linalool	1102	81.80	6.60	flower citrus floral lemon orange
11	citronellal	1157	100.00	16.69	lemon fresh green-citrusy
12	4-terpineol	1178	100.00	4.14	lemon lime herb green
14	neral	1241	100.00	16.05	citrus lemon green-citrusy
15	geranial	1273	100.00	19.61	citrus lemon green-citrusy

Note

[a] Linear Retention Index using HP-5 capillary column

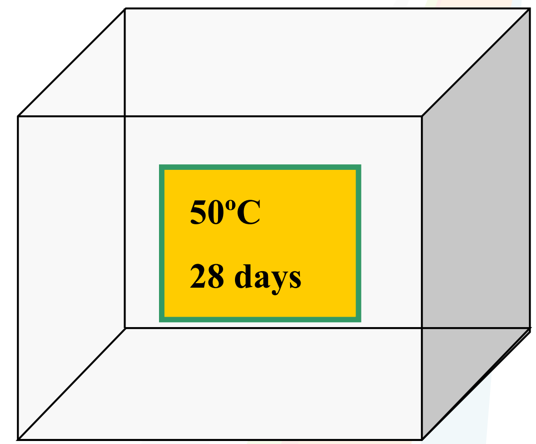
[b] % of panelist who recognized flavor

[c] duration od smell

Volatile compound during storage

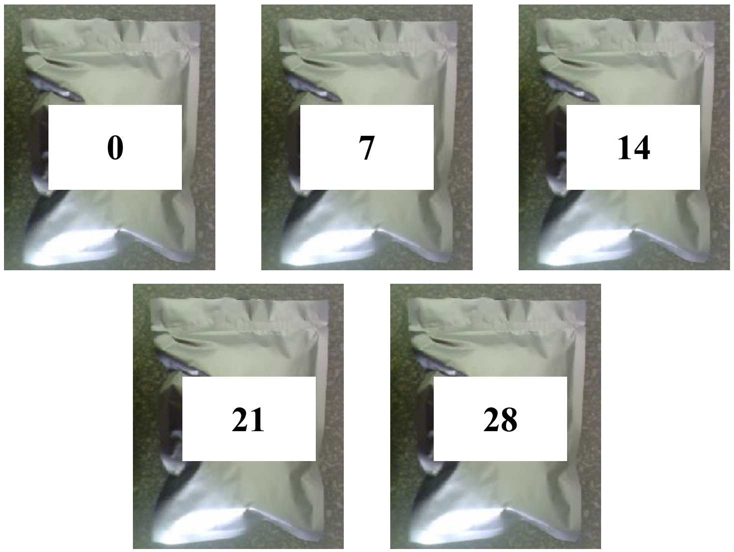
MAP

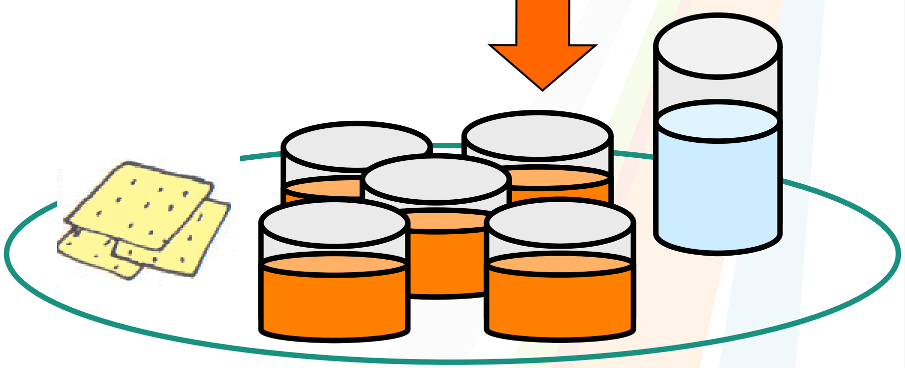
$N_2:O_2:CO_2$ 25:50:25



Volatile compound analysis at 0, 7, 14, 21 and 28

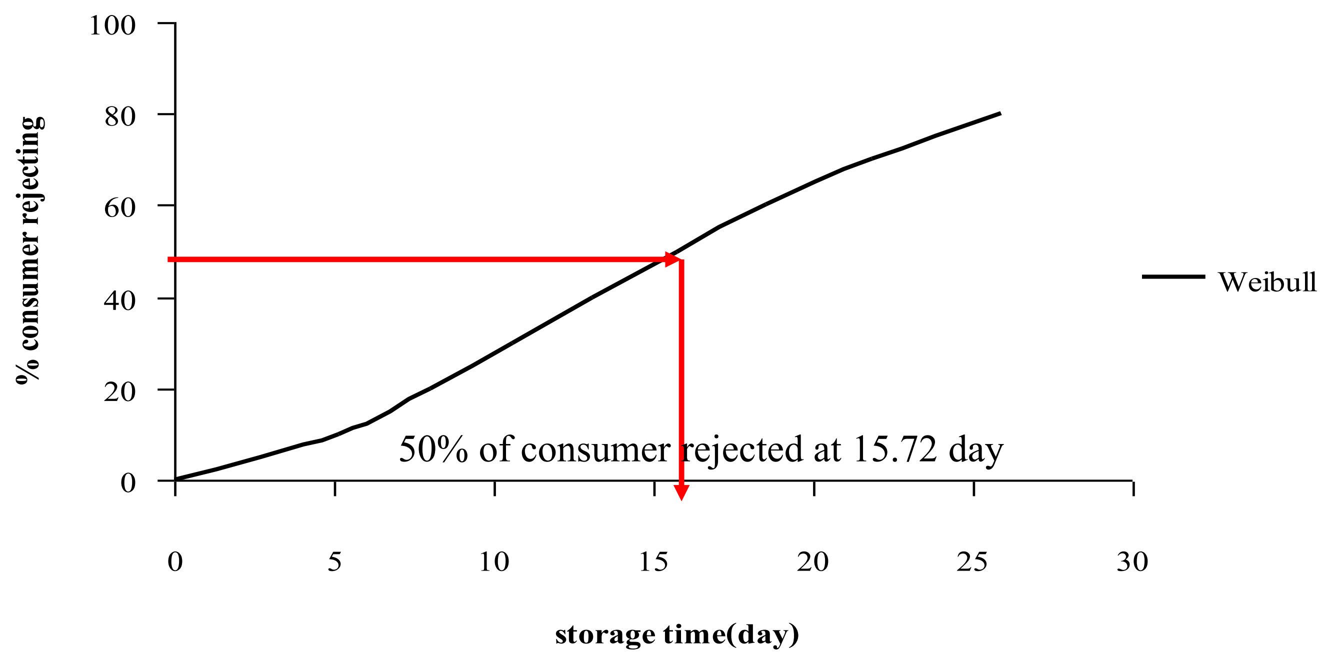
Sensory evaluation of volatile compounds





- **Survival analysis**

100 consumers 9 point hedonic scale and acceptability test


100
80
60
40
20
0
% consumer rejecting
Weibull
50% of consumer rejected at 15.72 day
0
5
10
15
20
25
30
storage time(day)

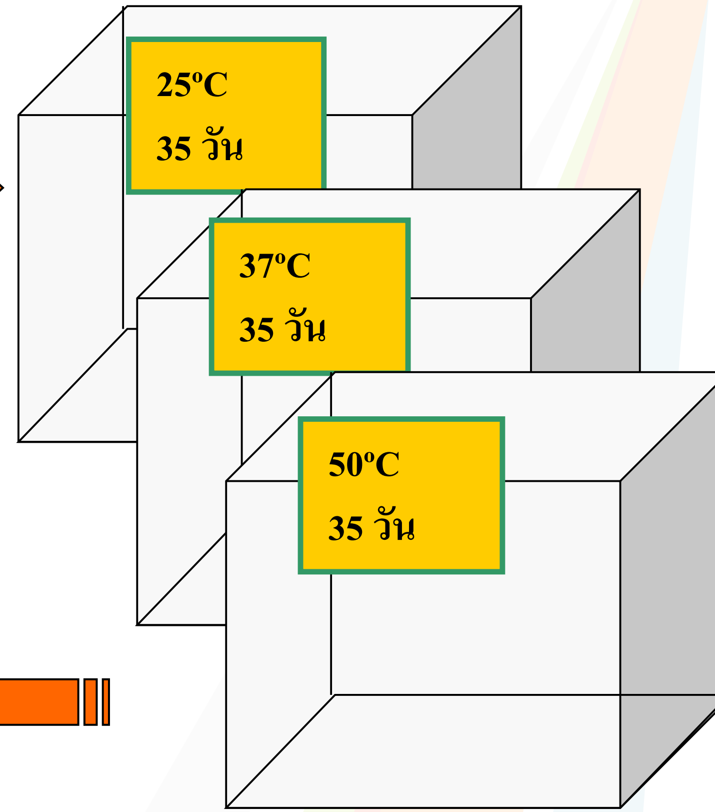
Equation and R square of each key volatile compounds

Compound	Equation	R^2	**(mg/g)**
beta-pinene	$y=0.0007x^2-0.0304x+0.6954$	0.9757	**2.54**
linalool	$y=0.0007x^2-0.031x+0.6802$	0.9521	**2.40**
citronellal	$y=0.0079x^2-0.3822x+9.2011$	0.9501	**34.36**
4-terpineol	$y=0.0002x^2-0.0107x+0.2528$	0.9649	**0.94**
neral	$y=0.0195x^2-0.9757x+23.805$	0.9933	**88.54**
geranial	$y=0.0149x^2-0.7407x+18.532$	0.9848	**69.68**

These value calculated from survival analysis that 50% of consumer rejected at 15.72 day

วิธีการทดลอง

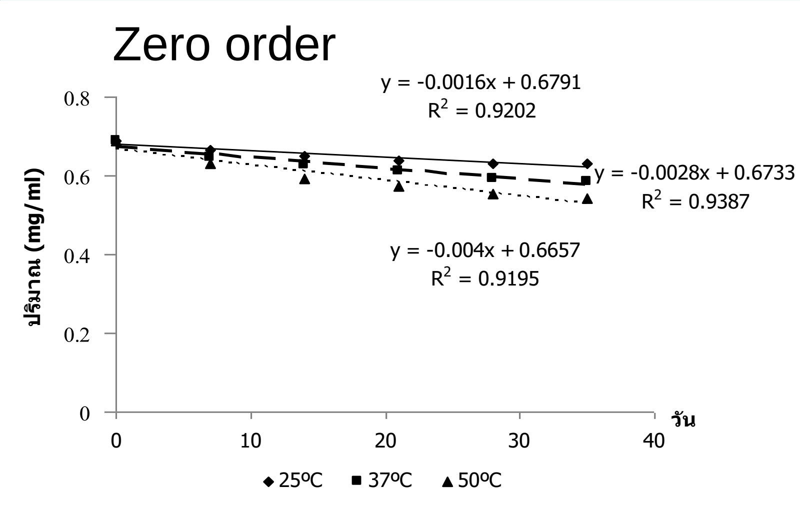
Shelf life under acceleration condition

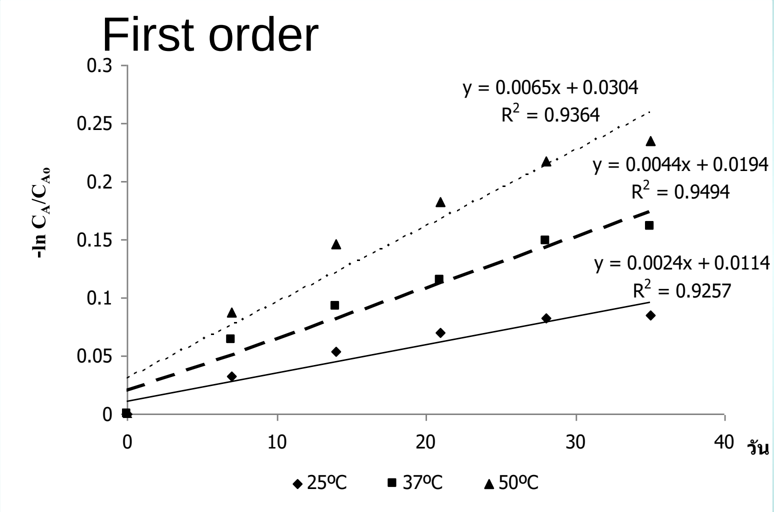


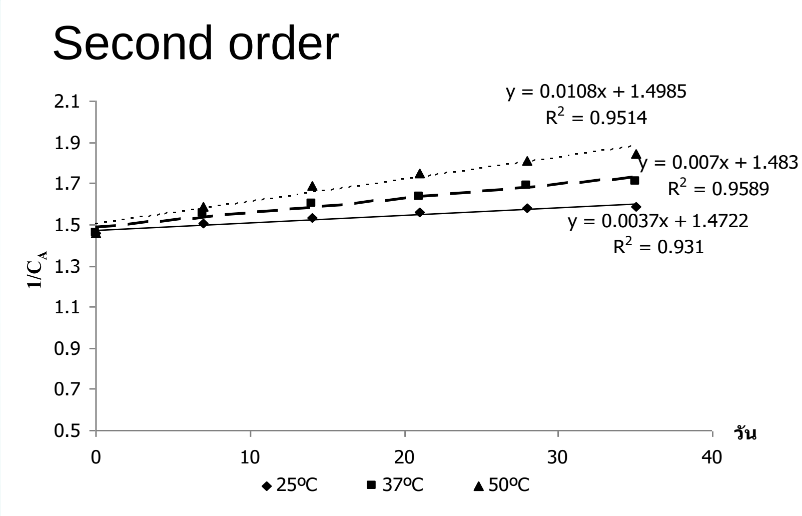
Volatile compound analysis every 7 days

Shelf life evaluation

From Rate's Law) , determine which order should be zero order (n=0) first order (n=1) or second order (n=2) of **beta-pinene**







R square of each compound and differcent temperature

zero order kinetic model	25ºC	37ºC	50ºC
beta-pinene	0.9202	0.9387	0.9195
linalool	0.9245	0.9319	0.9383
citronellal	0.9820	0.9412	0.9137
4-terpineol	0.9696	0.9537	0.9248
neral	0.9463	0.9901	0.9394
geranial	0.9798	0.9742	0.9937

first order kinetic model	25ºC	37ºC	50ºC
beta-pinene	0.9257	0.9494	0.9364
linalool	0.9316	0.9432	0.9561
citronellal	0.9853	0.9495	0.9292
4-terpineol	0.9473	0.9914	0.9486
neral	0.9721	0.9585	0.9379
geranial	0.9798	0.9747	0.9943

second order kinetic model	25ºC	37ºC	50ºC
beta-pinene	0.9310	0.9589	0.9514
linalool	0.9383	0.9534	0.9706
citronellal	0.9883	0.9570	0.9434
4-terpineol	0.9745	0.9629	0.9498
neral	0.9484	0.9925	0.9569
geranial	0.9798	0.9751	0.9943

K, rection constant of each volatile compound at different temperature

Key volatile compound	Reaction rate constant (k)		
	25ºC	37ºC	50ºC
beta-pinene	0.00060	0.00110	0.00160
linalool	0.00060	0.00140	0.00220
citronellal	0.00004	0.00006	0.00010
4-terpineol	0.00010	0.00021	0.00028
neral	0.000003	0.00001	0.00003
geranial	0.000005	0.00001	0.00003

•

$$1/C_A = 1/C_{A0} - kt$$

Where C_A volatile compound content at the time consumer rejected

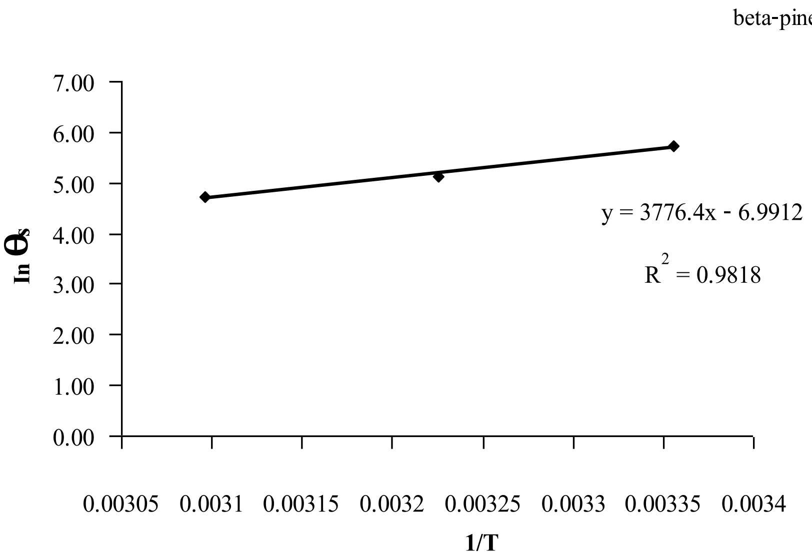
C_{A0} volatile compound content at beginning ($t = 0$)

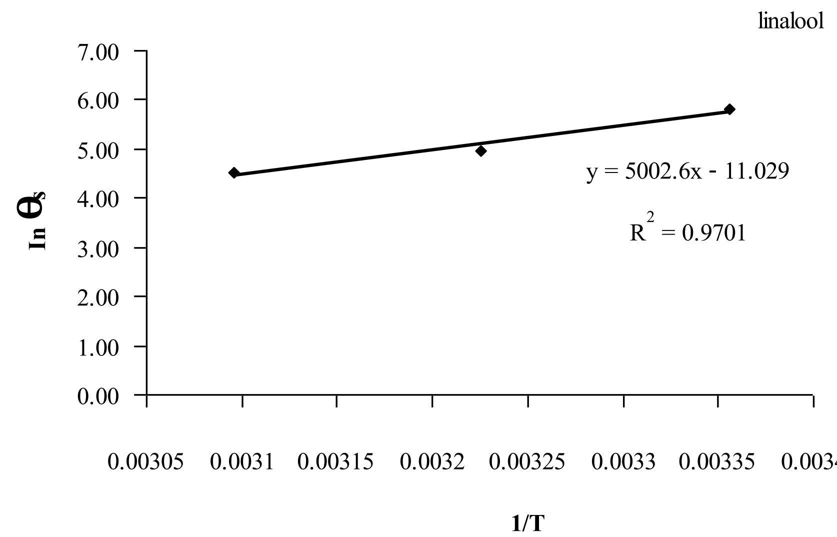
k reaction rate constant

t storage time

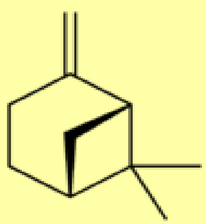
Shelf life evaluation of Tom Yum flavor

Key volatile compound	Shelf life (day)			R square
	25ºC	37ºC	50ºC	
beta-pinene	305	166	114	0.9818
linalool	338	144	92	0.9701
citronellal	332	222	133	0.9956
4-terpineol	492	234	175	0.9391
neral	1689	507	169	0.9993
geranial	1280	639	213	0.9832

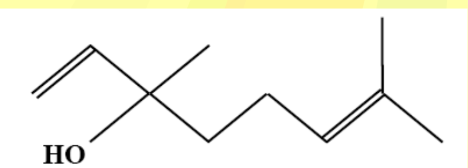




beta-pinene



linalool



Molecular Weight : 136.234 g /mol

Boiling point : 163 -166°C ที่ 760 mm Hg

Vapor pressure : 2.93 mm/Hg ที่ 25.00 °C

Molecular Weight: 154.24 g/mol

Boiling point : 194-197°C ที่ 760 mm Hg

Vapor pressure : 0.16 mm/Hg ที่ 25.00 °C


The End