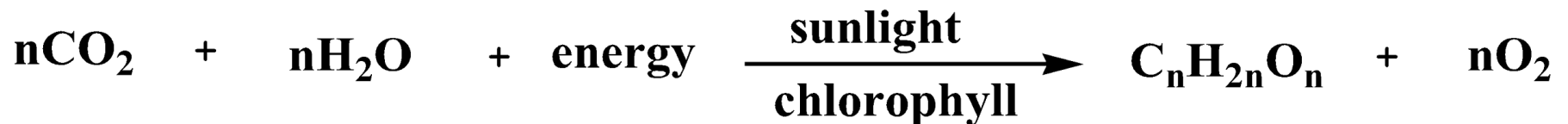


# Carbohydrates

Carbohydrates are the most abundant organic compounds in the plant world.

They act as storehouses of chemical energy (glucose, starch, glycogen); are components of supportive structures in plants (cellulose), shells (chitin), and connective tissues in animals (acidic polysaccharides); and are essential components of nucleic acids

Carbohydrates are the most abundant class of organic compounds found in living organisms. They originate as products of photosynthesis.



The name carbohydrate means hydrate of carbon and derives from the formula  $C_n (H_2O)_m$ . eg.

Glucose (blood sugar):  $C_6H_{12}O_6$ , or alternatively  $C_6 (H_2O)_6$

Sucrose (table sugar):  $C_{12}H_{22}O_{11}$ , or alternatively  $C_{12} (H_2O)_{11}$

Most carbohydrates are polyhydroxyaldehydes, polyhydroxyketones, or compounds that yield either of these after hydrolysis.

The fact that carbohydrates have only two types of functional groups. All the simplest carbohydrates contain multiple chiral centers. For example, glucose, contains one aldehyde group, one primary and four secondary hydroxyl groups, such as four chiral centers.

The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Carbohydrates are called saccharides or if they are relatively small, sugars. Several classifications of carbohydrates have proven useful and are outlined in the following table 1.

**Table 1**

Complexity	Simple Carbohydrates Monosaccharides			Complex Carbohydrates Disaccharides, oligosaccharides & polysaccharides		
	Triose $C_3H_6O_3$	Tetrose $C_4H_8O_4$	Pentose $C_5H_{10}O_5$	Hexose $C_6H_{12}O_6$	Heptose $C_7H_{14}O_7$	Octose $C_8H_{16}O_8$
C=O Function	<b>Aldose</b> Sugars having an aldehyde function or an acetal equivalent. <b>Ketose</b> Sugars having a ketone function or an acetal equivalent.					
Reactivity	<b>Reducing</b> Sugars oxidized by Tollen's reagent (or Benedict's or Fehling's reagents). <b>Non-reducing</b> Sugars not oxidized by Tollen's or other reagents.					



# Monosaccharides

## A. Structure and Nomenclature

Monosaccharides have the general formula  $C_nH_{2n}O_n$  with one of the carbons being the carbonyl group of either an aldehyde or a ketone.

The most common monosaccharides have 3-8 carbon atoms. The suffix-ose indicates that a molecule is a carbohydrate, and the prefixes *tri-*, *tetr-*, *pent-*, and so forth indicate the number of carbon atoms in the chain.

Monosaccharides containing an aldehyde group are classified as aldoses; those containing a ketone group are classified as ketoses.

## Monosaccharides

Another type of classification scheme is based on the hydrolysis of certain carbohydrates to simpler carbohydrates i.e. classifications based on number of sugar units in total chain.

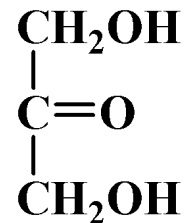
Monosaccharides:	single sugar unit
Disaccharides:	two sugar units
Oligosaccharides:	3 to 10 sugar units
Polysaccharides:	more than 10 units

Monosaccharides cannot be converted into simpler carbohydrates by hydrolysis. Glucose and fructose are examples of monosacchides. Sucrose, however, is a disaccharide-a compound that can be converted by hydrolysis into two monosaccharides glucose and fructose/.

There are only two trioses: the aldotriose glyceraldehyde and the ketotriose dihydroxyacetone.



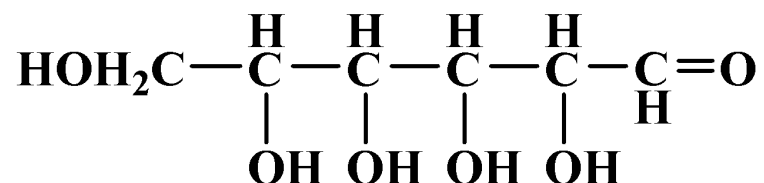
**Glyceraldehyde**  
(an aldotriose)



**Didroxyacetone**  
(a ketotriose)

## B. Stereochemistry and Configuration:

We'll consider the stereochemistry of carbohydrates by focusing largely on the aldoses with six or fewer carbons. The aldohexoses have four asymmetric carbons and therefore exist as 24 or sixteen possible stereoisomers. These can be divided into two enantiomeric sets of eight diastereomers.



**Aldohexoses**

**four asymmetric carbons**

**$2^4 = 16$  stereoisomers**

The three most abundant hexoses in the biological world are D-glucose, D-galactose, and D-fructose.

The first two are D-aldohexoses; the third is a D-2-ketohexose.

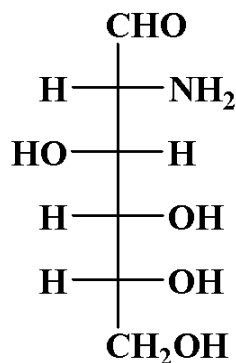
Glucose, by far the most common hexose, is also known as dextrose because it is dextrorotatory.

Other names for this monosaccharide are grape sugar and blood sugar. Human blood normally contains 65-100 mg of glucose/100 mL of blood.

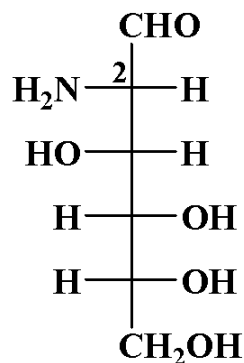
D-Fructose is found combined with glucose in the disaccharide sucrose (table sugar). D-Galactose is obtained with glucose in the disaccharide lactose (milk sugar).

## C. Amino Sugars:

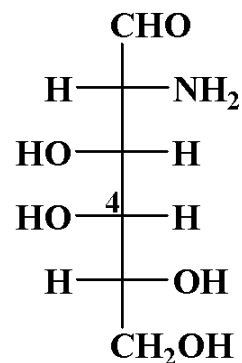
Amino sugars contain an  $\text{-NH}_2$  group in place of an  $\text{-OH}$  group. Only three amino sugars are common in nature: D-glucosamine, D-mannosamine, and D-galactosamine.



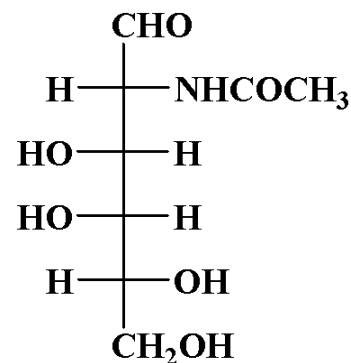
D-Glucosamine



D-Mannosamine  
(C-2 stereoisomer  
of D-Glucosamine)



D-Galactosamine  
(C-4 stereoisomer  
of D-Glucosamine)

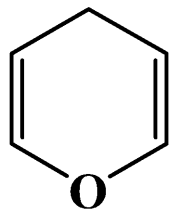


N-Acetyl-D-Glucosamine

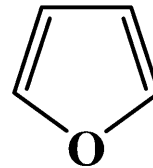
N-Acetyl-D-glucosamine, a derivative of D-glucosamine, is a component of many polysaccharides, including chitin, the hard shell-like exoskeleton of lobsters, crabs, shrimp, and other shellfish. Many other amino sugars are components of naturally occurring antibiotics.

The  $\alpha$ - and  $\beta$ -forms which differ in configuration at C1 only are known as anomers (ano, upper). That the hydroxyl group on C1 is cis to the hydroxyl on C2 in the  $\alpha$ -form and trans in the  $\beta$ -form.

The ring structure of glucose (1,5) is a six-membered ring and is described as a pyranose ring by similarity to pyran while the five-membered ring is described as a furanose ring.



**pyran**



**furan**

## **Disaccharides and Oligosaccharides:**

Most carbohydrates in nature contain more than one monosaccharide unit. Those that contain two units are called disaccharides, those that contain three units are called trisaccharides, and so forth. The general term oligosaccharide is often used for carbohydrates that contain from four to ten monosaccharide units. Carbohydrates containing larger numbers of monosaccharide units are called polysaccharides.

Disaccharides may differ in the constituent of monosaccharides they yield on hydrolysis. For example, sucrose yields D-glucose and D-fructose on hydrolysis; lactose yields D-glucose and D-galactose; and maltose yields two molecules of D-glucose.



Sucrose (table sugar) is the most abundant disaccharide in nature. It is obtained principally from the juice of sugar cane and sugar beets. In sucrose, carbon 1 of  $\alpha$ -D-glucopyranose is joined to carbon 2 of  $\beta$ -D-fructofuranose by an  $\alpha$ -1,2-glycosidic bond.

Note that glucose is a six-membered (pyranose) ring, whereas fructose is a five-membered (furanose) ring. Because the anomeric carbons of both the glucopyranose and fructofuranose units are involved in formation of the glycosidic bond, sucrose is a nonreducing sugar.

## **Polysaccharides;**

Polysaccharides consist of large numbers of monosaccharide units bonded together by glycosidic bonds. Four important polysaccharides are starch, glycogen, cellulose and chitin.

### **A. Starch: Amylose and Amylopectin:**

Starch is used for energy storage in plants. It is found in all plant seeds and tubers and is the form in which glucose is stored for later use. Starch can be separated into two principal polysaccharides: amylose and amylopectin. Although the starch from each plant is unique, most starches contain 20-25% amylose and 75-80% amylopectin.

Complete hydrolysis of both amylose and amylopectin yields only D-glucose. Amylose is composed of unbranched chains of up to 4000 D-glucose units joined by  $\alpha$ -1,4-glycosidic bonds. Amylopectin contains chains up to 10,000 D-glucose units also joined by  $\alpha$ -1,4-glycosidic bonds. In addition, there is considerable branching from this linear network. At branch points, new chains of 24 to 30 units are started by 1,6-glycosidic bonds.

## **B. Glycogen:**

Glycogen is the energy-reserve carbohydrate for animals. Like amylopectin, glycogen is a branched polysaccharide of approximately  $10^6$  glucose units joined by  $\alpha$ -1,4- and  $\beta$ -1,6-glycosidic bonds. The total amount of glycogen in the body of a well-nourished adult human is about 350 g, divided almost equally between liver and muscle.

## **C. Cellulose:**

Cellulose, the most widely distributed plant skeletal polysaccharide, constitutes almost half of the cell material of wood. Cotton is almost pure cellulose, Cellulose is a linear polysaccharide of glucose units joined by  $\beta$ -1, 4-glycosidic bonds. It has an average molecular weight of 400,000 g/mol, corresponding

To approximately 2200 glucose units per molecule. Cellulose molecules act very much like stiff rods, a feature that enables them to align themselves side by side into well-organized water-insoluble fibers in which the OH groups form numerous intermolecular hydrogen bonds. This arrangement of parallel chains in bundles gives cellulose fibers their high mechanical strength. It is also the reason cellulose is insoluble in water. When a piece of cellulose-containing material is placed in water, there are not enough water molecules on the surface of the fiber to pull individual cellulose molecules away from the strongly hydrogen-bonded fiber.

Humans and other animals cannot use cellulose as food because our digestive systems do not contain  $\beta$ -glucosidases, enzymes that catalyze hydrolysis of  $\beta$ -glucosidic bonds. Instead, we have only  $\alpha$ -glucosidases; hence, the polysaccharides we use as sources of glucose are starch and glycogen. On the other hand, many bacteria and microorganisms do contain  $\beta$ -glucosidases and so can digest cellulose. Ruminants and horses can also digest grasses and hay because  $\beta$ -glucosidase-containing microorganisms are present in their alimentary systems.

## **D-Chitin:**

Chitin is a polysaccharide that also occurs widely in nature-notably, in the shells of arthropods (for example, lobsters and crabs). Crab shell is an excellent source of nearly pure chitin

Chitin is a polymer of *N*-acetyl-D-glucosamine (or, as it is known systematically, 2-acetamido-2-deoxy-D-glucose). Residues of this carbohydrate are connected by  $\beta$ -1,4-glucosidic linkages within the chitin polymer. *N*-Acetyl-D-glucosamine is liberated when chitin is hydrolyzed in aqueous acid. Stronger acid brings about hydrolysis of the amide bond to give D-glucosamine hydrochloride and acetic acid.

Glucosamine and *N*-acetylglucosamine are the best-known examples of the **amino sugars**. A number of amino sugars occur widely in nature. Amino sugars linked to proteins(glycoproteins) are found at the outer surfaces of cell membranes, and some of these are responsible for blood-group specificity.



## *E. Heparin*

Heparin is a heterogeneous mixture of variably sulfonated polysaccharide chains, ranging in molecular weight from 6000 to 30,000 g/mol. This acidic polysaccharide is synthesized and stored in mast cells of various tissues, particularly the liver, lungs, and gut. Heparin has many biological functions, the best known and understood of which is its anticoagulant activity. It binds strongly to antithrombin III, a plasma protein involved in terminating the clotting process.

The repeating monosaccharide units of heparin are N-acetyl-D-glucosamine, D-glucuronic acid, D-glucosamine, and L-iduronic acid bonded by a combination of  $\alpha$ -1,4- and  $\beta$ -1,4-glycosidic bonds.

# Heteroglycans



## **Heteroglycans**

- Are natural plants hydrocolloids containing more than one kind of monosaccharide units.

# I. Gums

- Natural products that yield with hydrolysis **more than one type of** monosaccharide units or their salts or their acids.
- Salts: Mg, Ca, K salts.
- Acids: called uronic acids.

## **Uronic acids:**

- Glucose       $\longrightarrow$     glucuronic acid
- Galactose    $\longrightarrow$     galacturonic acid
- Arabinose    $\longrightarrow$     Arabic acid

- **Definition of Gums:**

Translucent, amorphous substances which formed on the stems or branches ( higher plants parts ) after injury.

- **Gums forms:**

1. exudates gums: formed in barks of the stems and branches-
  - to prevent dehydration
  - to heal the cavities
2. seeds gum: formed in seeds embryo- to reserve food
3. marine gum: component of the cell wall or intracellular region
  - to reserve food

## **A. Tragacanth gum:**

- The dried gummy exudations obtained by incision from the stems and branches of the Tragacanth trees.
- **Physicochemical properties:**
  1. Translucent.
  2. Amorphous.
  3. Solid substance.
  4. White or pale yellow colour.
  5. Odourless.
  6. Mucilaginous taste.
  7. Partly soluble in water: 30% water soluble.
  8. Insoluble in organic solvents.
  9. Has resistance to the hydrolysis by acids

# Constituents

1. Bassorin 70%: water insoluble portion.

Bassorin ---Hydrolysis--- galactose+ Arabinose

2. Tragacanthin 30%: water soluble portion.

Tragacanthin yields with hydrolysis demethoxylated bassorin.

3. Starch.

4. Proteins

# Uses

1. Demulcent.
2. Emollient.
3. Laxative ( bulk laxative ).
4. Pharmaceutical uses:
  1. Suspending agent.
  2. Emulsifying agent.
  3. Stabilizer.
  4. Thickener.
5. Cosmetics: hand creams and body lotions ( emollient and emulsifying agent )



## B. Arabic gum : Acacia gum:



# Arabic gum

The dried gummy exudations obtained by incision from the stems and branches of Arabic gum trees (Acacia trees)

## Physicochemical properties

1. Translucent.
2. Amorphous.
3. White or pale yellow colour.
4. Odourless.
5. Mucilaginous taste.
6. Soluble in water.
7. Insoluble in organic solvents.

# Constituents

1. Arabin: a mixture of Ca, Mg, K salts for

1. Arabic acid.
2. Glucuronic acid.
3. Galacturonic acid.
4. Rhamnurnic acid.

Arabin (hydrolysis)————→Arabinose +Rhamnose  
+ Glucose+ Galactose

2. Enzymes:

- Oxidase enzyme.
- Peroxidase enzyme.
- Pectinase enzyme.

# Uses:

1. Demulcent: ( more than the other gums ) : required in the following preparations:
  - Anti-tussives.
  - Anti-diarrheal preparations ( suspending, demulcent ).
  - Throat problems.
2. Emollient.
3. Laxative ( bulk laxative ).
4. Pharmaceutical uses:
  1. Suspending agent.
  2. Emulsifying agent.
  3. Tablet binder.

## II. Mucilages

- Natural plants product, heteroglycan complex polysaccharide.
- Mucilage give with hydrolysis :
  - a. monosaccharide units.
  - b. Ca, Mg, K, Na salts of monosaccharides.
  - c. Monosaccharide acids.
  - d. Ca, Mg, K, Na salts of monosaccharide acids.

They founded in some plants part as food reservoir or and as water reservoir ( hydrophilic substances).

- **Examples for plants parts containing mucilage :**
  1. Leaves: Buchu.
  2. Roots and rhizomes: Cinnamon and Marshmallow.
  3. Seeds: Lin (flax), Mustard, Fenugreek.
  4. Weeds: Marine plants ( Red Algae ).

**Examples on mucilage**

# 1. Agar

Is: Natural product, Dry powder, Hydrophilic substance.  
Obtained from:

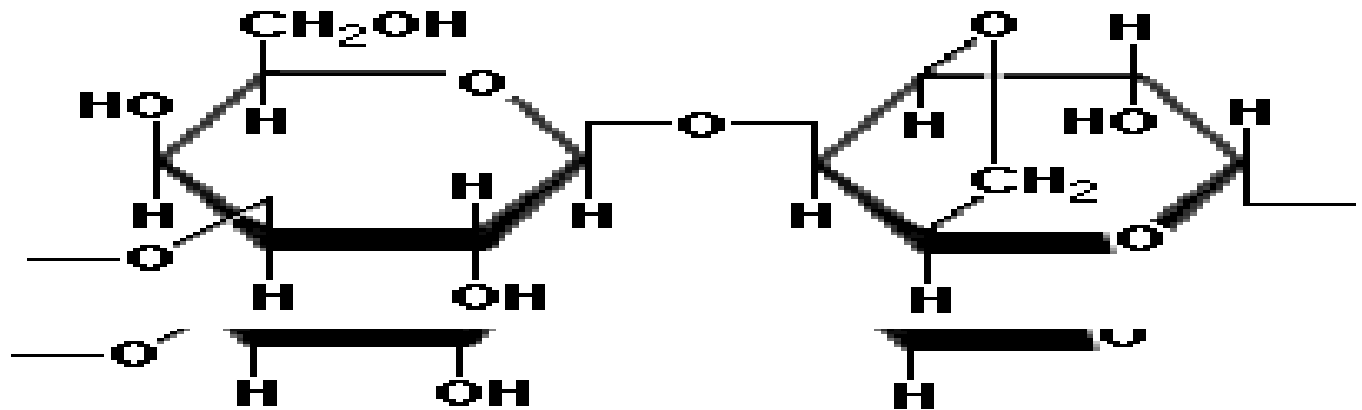
1. Red Algae.
2. Gracilaria.
3. Gelidium.

## **Physicochemical properties:**

1. Yellowish white powder.
2. Odourless or with slight odour.
3. Mucilaginous taste.
4. Slowly soluble in water —————→viscous mass
5. insoluble in the organic solvents.

# Agar contains

1. Proteins.
2. Mixture of :
  - a) L-galactose.
  - b) D-galactose.
  - c) Galacturonic acid.
  - d) Sulphate ions .



**Agarobiose is the repeating disaccharide unit in agar**  
Agar is a polymer of agarobiose, a disaccharide composed of D-galactose and 3,6-anhydro-L-galactose



# **1. Agar main uses:**

**pharmaceutical uses:** Suspending, Emulsifying, Gelating agent for suppositories.

2. Laxative ( bulk laxative ).

3. Food industry.

4. Highly refined agar is used as a medium for culturing bacteria, cellular tissues, and for DNA fingerprinting.

### III. Pectin

- Heteroglycan complex polysaccharide, present in the cell wall of plants tissues which function as intercellular cementing agent, obtained from:
  - **Citrus fruits.**
  - **Apple pomace.**
- Protopectin  $\xrightarrow{90^{\circ} \text{ C} + \text{HCl (pH=3.4-4), organic solvent}}$  pectin

Note:

- Protopectin: water insoluble.
- Pectin: water soluble.
- Organic solvent used to precipitate pectin.

- **Pectin**
- Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. The white portion of the rind of lemons and oranges contains approximately 30% pectin. Pectin is an important ingredient of fruit preserves, jellies, and jams.

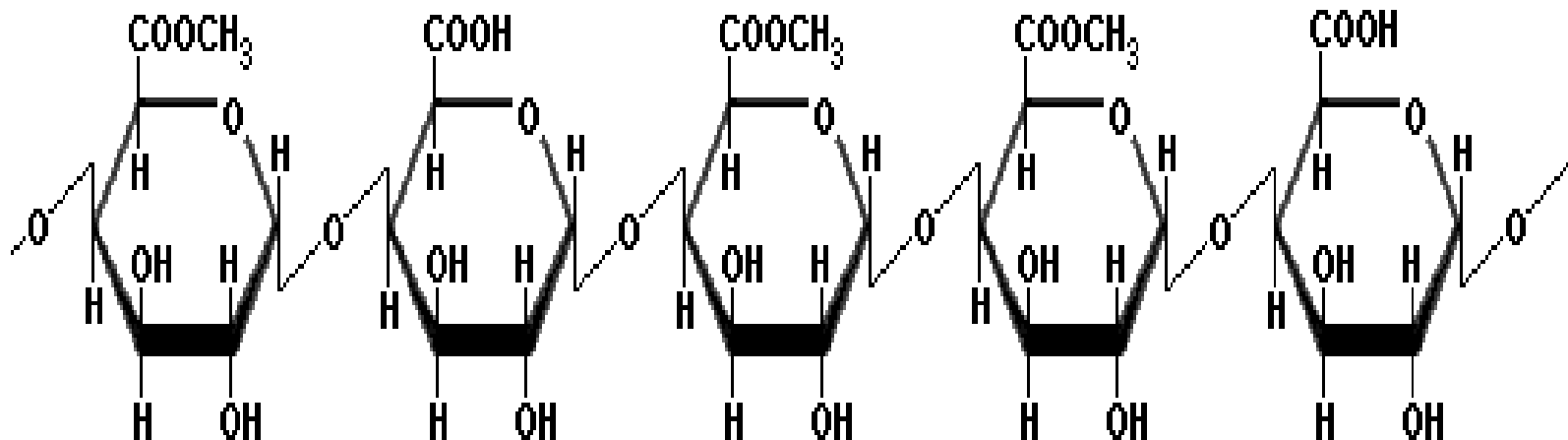
### **Physicochemical properties:**

1. Yellowish white powder.
2. Odourless.
3. Mucilaginous taste.
4. Soluble in water ( 1:20 ).
5. Insoluble in the organic solvents

- **Constituents of Pectin:** is a mixture of : 1. Galactose. (alpha-D-galacturonic acid- methoxylated)alpha1,4-bond galacturonan. 2. Fructose. (traces), 3. Arabinose and Xylose. Traces

### **Pectin is $\alpha$ -1, 4 –linkage**

1. Pectin is a polymer of  $\alpha$ -Galacturonic acid with a variable number of methyl ester groups
2. The structure shown here has three methyl ester forms (-**COOCH<sub>3</sub>**) for every two carboxyl groups (-**COOH**)



## Uses:

1. Treatment of diarrhoea: absorbent anti-diarrheal agent.

Absorption of : Fluids, Bacteria, Toxins and Gases.

2. Emulsifying and gelling agent in the pharmaceuticals and cosmetics.

3. Thickening agent in food industry.

Pectin usually comes with kaolin.

- **Kaolin:**

- Absorbent anti-diarrheal agent obtained from:

- Sand stones.

- Rocks.

- Clay.

All contain  $\text{Al}_2\text{O}_3 + \text{SiO}_2$

- **Uses:**

- Treatment of diarrhoea (the same way as pectin).

- Coat for irritated intestinal mucosa caused by diarrhoea.



# RESINS AND RESIN COMBINATIONS

# Resin and Resin Combination

Resin is a hydrocarbon secreted by many plants, particularly coniferous trees, valued for its chemical constituents and uses such as in varnishes and adhesives. Plants produce resins for various reasons whose relative importance is debated. It is known that resins seal plant's wounds, kill insects and fungi, and also allow the plant to eliminate excess metabolites. It is distinct from other liquid compounds found inside plants or exuded by plants, such as sap, latex, or mucilage. More broadly, the term "resin" is also used for many thick liquids, some of them artificial polymer bases (synthetic resins), that during normal use, harden into transparent or opaque solids.

Resins are complex mixtures of resin acids, resin alcohols, resin phenols, and their esters. Resins associated with volatile oils are oleoresins, with gums are gum-resins or with oil and gum are oleo-gum-resins. These products are usually contained in schizogenous or schizolysigenous ducts or cavities. The formation of **resins** in the plant is by virtue of its normal physiological functions. However, its yield may be enhanced in certain exceptional instances by inflicting injury to the living plant.

# Physical Properties of Resin

The various physical properties of **resins** can be generalized as detailed below:

- **Resins**, as a class, are hard, transparent or translucent brittle materials.
- They are invariably heavier than water having the specific gravity ranging from 0.9-1.25.
- **Resins** are more or less amorphous materials but rarely crystallisable in nature.
- On being heated at a relatively low temperature **resins** first get softened and ultimately melt down thereby forming either an adhesive or a sticky massive fluid, without undergoing any sort of decomposition or volatilization.
- On being heated in the air *i.e.*, in the presence of oxygen, resins usually burn readily with a smoky flame by virtue of the presence of a large number of C-atoms in their structure.
- On being heated in a closed container *i.e.*, in the absence of oxygen, they undergo decomposition and very often give rise to **empyreumatic products** *i.e.*, products chiefly comprising of hydrocarbons.
- Resins are bad conductors of electricity, but when rubbed usually become negatively charged.
- They are practically insoluble in water, but frequently soluble in ethanol, volatile oils, fixed oils, chloral hydrate and non-polar organic solvents *e.g.*, benzene, n-hexane and petroleum ether.
- Resins are often associated with volatile oils (*oleoresins*), with gums (*gum-resins*) or with oil and gum (*oleo-gum-resins*).



# Chemical Properties of Resin

The various chemical properties of **resins** may be summarized as stated below:

- Resins, in general, are enriched with carbon, deprived of nitrogen and contain a few oxygen in their respective molecules.
- Majority of them undergo slow atmospheric oxidation whereby their colour get darkened with impaired solubility.
- Resins are found to be a mixture of numerous compounds rather than a single pure chemical entity.
- Their chemical properties are exclusively based upon the functional groups present in these substances.
- Consequently, the resins are broadly divided into resin alcohols, resin acids, resin esters, glycosidal resins and resenes (*i.e.*, inert neutral compounds).
- Resins are regarded as complex mixtures of a variety of substances, such as: resinotannols, resin acids, resin esters, resin alcohols and resenes.
- One school of thought believes that resins are nothing but oxidative products of terpenes.
- They may also be regarded as the end-products of *destructive metabolism*.
- The acidic resins when treated with alkaline solutions they yield soaps (or resin-soaps).

# Classification of Resins:

The Resins are broadly classified under three major categories:

1. **Taxonomical Classification:** The resins are grouped together according to their botanical origin such as:

**Corniferous Resins:** Colophony

**Berberidaceae Resins:** Podophyllum

2. **Chemical Classification:** The resins may also be classified as per the presence of the predominating chemical constituents for instance:

**Acid Resins:** Colophony, Myrrh, Copaiba

**Ester Resins:** Benzoin

**Resin Alcohol:** Balsam of Peru, Gurjun Balsam

**Resene Resins:** Dragon's Blood

3. **Constituents of Resin:** Resins may also be classified according to the major constituents present either in the resin or resin combinations:

**Resins:** Colophony, Cannabis.

**Oleoresins:** copaiba, ginger.

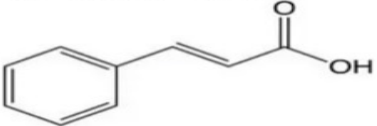
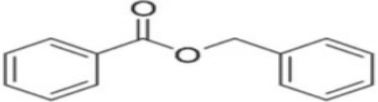
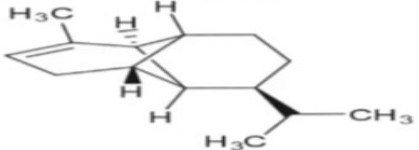
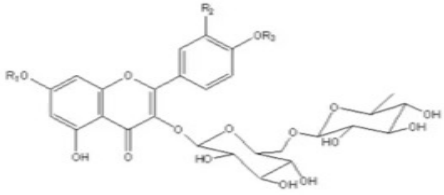
**Oleo-gum-resins:** Myrrh.

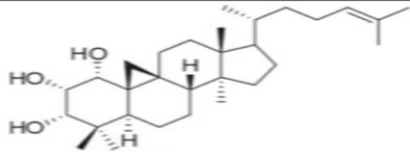
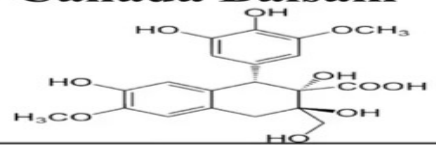
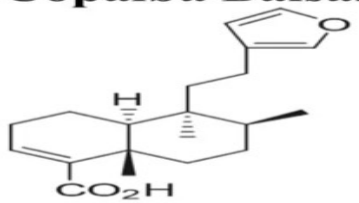
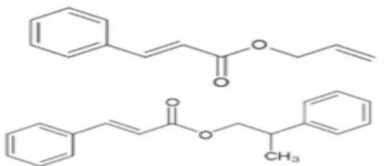
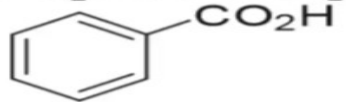
**Balsams:** Balsam of Tolu, Balsam of Peru.

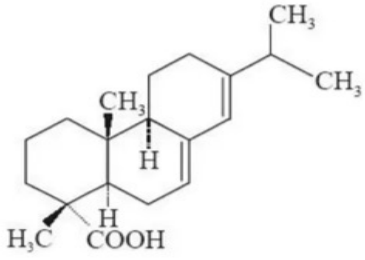
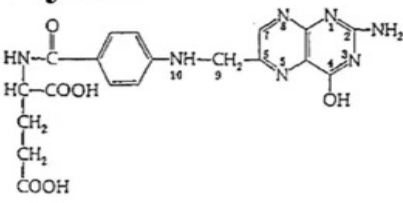
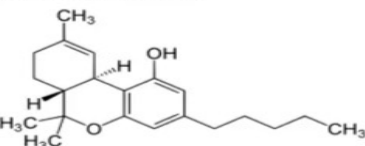
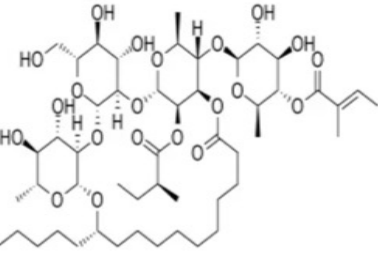
**Glycoresins:** Jalap

**Resenes:** Asafoetida

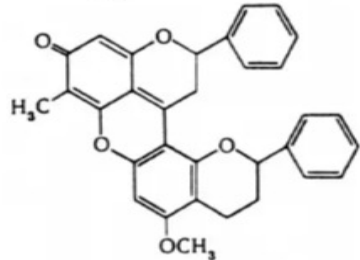
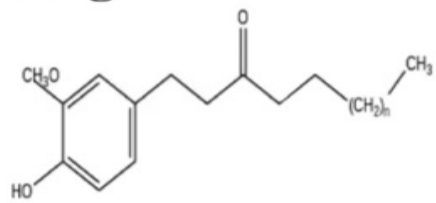
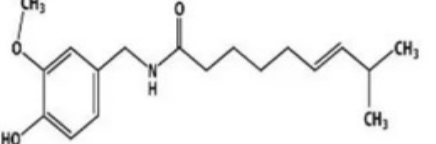
## **Table of Examples:**

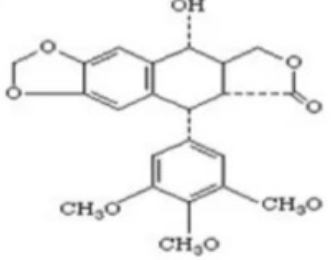
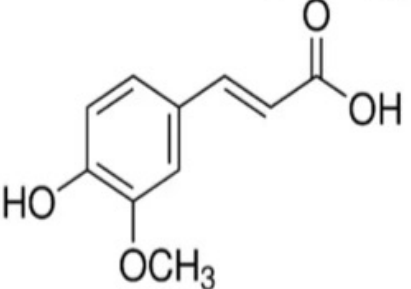
Sl	Name and Structure	Source (Family)	Type and Inhabitant	Therapeutic Uses
1	<b>Tolu Balsam</b> 	<i>Myroxylon balsamum</i> , <i>Myroxylon toluiferum</i> (Fabaceae)	<b>Tree</b> , Colombia and Venezuela	Treatment of bronchitis, laryngitis, diarrhea and leucorrhoea, treat wounds, ulcers, and scabies, sun block agent
2	<b>Cabreuva Balsam</b> 	<i>Myroxylon peruiferum</i> , <i>Toluifera peruifera</i> (Fabaceae)	<b>Tree</b> , Brazil & other countries of South America	Treat asthma, rheumatism, cold and external wounds, tuberculosis, headaches and abscess
3	<b>Peru Balsam</b> 	<i>Myroxylon pereirae</i> , <i>Myrospermum sonsonatense</i> , (Fabaceae)	<b>Tree</b> , Peru & Central America	Treat asthma, catarrh, rheumatism, external wounds, stimulant, expectorant, parasiticide
4	<b>Egyptian or Judea Balsam</b>  <p>1 R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = OH, R<sub>3</sub> = CH<sub>3</sub>, 2 R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H, 3 R<sub>1</sub> = H, R<sub>2</sub> = OH, R<sub>3</sub> = H</p>	<i>Commiphora opobalsamum</i> , (Burseraceae)	<b>Small tree</b> , Saudi Arabia, Yemen, Oman, and southeast Egypt	Anti-tumor, anti-cancer, antifungal, local anesthetic, anti-inflammatory, antioxidant, stimulant, hepatoprotective
5	<b>Gurjun Balsam</b>	<i>Dipterocarpus dyeri</i> , (Dipterocarpaceae)	<b>Semideciduous tree</b> ,	Anti-AIDS, anti-inflammatory, anti-bacterial, anti-fungal,

			Forest regions of Southeast Asia	anti-oxidant activities.
6	<b>Canada Balsam</b> 	<i>Abies balsamea</i> , (Pinaceae)	<b>Tree</b> , Eastern Canada	Treat common cold , Anti-cancer
7	<b>Copaiba Balsam</b> 	<i>Copaifera reticulate</i> , <i>C. guianensis</i> , <i>C. multijuga</i> and <i>C. officinalis</i> (Fabaceae)	<b>Tree</b> , Tropical regions of Latin America and West Africa	Healing capacity, remedy for gonorrhea, chronic bronchitis, chronic diarrhea, treat asthma, headaches, snakebites, dermatitis, eczemas, anti-inflammatory , analgesic , antitumor
8	<b>Benzoin (i. Siam Benzoin &amp; ii. Sumatra Benzoin)</b> 	i. <i>Styrax tokinensis</i> , <i>Styrax benzoides</i> (Styracaceae)	<b>Tree</b> , Indochina and Thailand	Antiseptic, expectorant , antioxidant, organoleptic, antidepressant, anti-inflammatory, anti-rheumatic
		ii. <i>Styrax benzoin</i> and <i>Styrax paralleloneurum</i> (Styracaceae)	<b>Tree</b> , Java, Sumatra and Borneo	
9	<b>Liquid Storaque</b> 	<i>Liquidambar orientalis</i> , (Altingiaceae)	<b>Tree</b> , Forest of the Middle East, Turkey and northeastern Syria.	Antimicrobial, antimutagenic and antioxidant effects

10	<b>Rosins/ Colophony</b> 	<i>Picea abies</i> , <i>Pinus</i> (Pinaceae)	<b>Evergreen tree</b> , Southern Norway, Sweden and Central Europe	Antibacterial combat gastric troubles, treat rheumatism, burns, sores, abscesses, influenza, tuberculosis, cold, cough, ulcers, smallpox, syphilis, anti-cancer
11	<b>Myrrh</b> 	<i>Commiphora myrrha</i> (Burseraceae)	<b>Tree</b> , Kingdom of Saudi Arabia and Jizan area on Red Sea coast	Antimicrobial, anticancer, antioxidant, antitumor, anti-inflammatory, antimalarial, analgesic, improve cardiac function
12	<b>Cannabis</b> 	<i>Cannabis sativa</i> , <i>Cannabis indica</i> , <i>Cannabis ruderalis</i> (Cannabaceae)	<b>Annual, dioecious, flowering herb</b> , Central Asia and Indian subcontinent	Psychotropic, antibacterial, anti-inflammatory, anti-cancer, muscle relaxant, neuro-antioxidative, sedative, analgesic, treat nausea/vomiting
13	<b>Jalap</b> 	<i>Ipomoea purga</i> (Convolvulaceae)	<b>Stout, perennial herb</b> , Mexico	Constipation from deficient secretion of intestinal glands; pain and griping in lower bowel; colic, with stercoraceous vomiting; general gastro-intestinal torpor. Emptying and cleansing the bowels.



14	<b>Dragon's Blood</b> 	<i>Daemonorops draco</i> , (Palmaceae) <i>Dracaena cinnabari</i> (Dracaenaceae)	<b>Evergreen tree</b> , East India, Thailand, Indonesia	Astringent, antidiarrhetic, wound healing, Lowering fevers, dysentery, internal ulcers of mouth, throat, intestines and stomach, treat gonorrhea, stoppage of urine, watery eyes and minor burns, Anticancer, anti inflammatory and antirheumatic.
15	<b>Ginger</b> 	<i>Zingiber officinale</i> , (Zingiberaceae)	<b>Perennial herb</b> , India, China, South East Asia, West Indies, Mexico and other parts of the world	Treat cold-induced disease, nausea, asthma, cough, colic, heart palpitation, swellings, dyspepsia, loss of appetite, rheumatism; carminative, antipyrexia, analgesic, anti-cancer, hepatoprotective
16	<b>Capsicum</b> 	<i>Capsicum annuum</i> , <i>Capsicum frutescens</i> , <i>Capsicum chinense</i> (Solanaceae)	<b>Perennial shrub</b> , America	Used in cleansing products, food flavoring, antimicrobial, nervine stimulant, appetizer
17	<b>Podophyllum</b>	<i>Podophyllum hexandrum</i>	<b>Perennial herb</b> ,	Anti-cancer, anti-viral, anti-mitotic, anti-rheumatic, treatment

		(Berberidaceae)	East Asia extends from Afghanistan to China & through the Himalayas	of colds, constipation, septic wounds, burning sensation, erysipelas, plague, cancer of the brain, bladder, lung, Hodgkin's disease
18	<b>Asafoetida (Hing)</b> 	<i>Ferula foetida</i> , <i>Ferula asafetida</i> , (Umbelliferae)	<b>Perennial herb</b> , Deserts of Iran and mountains of Afghanistan and is mainly cultivated in nearby India	Used as a digestive aid, treatment of hysteria, bronchitis, asthma and whooping cough, Antispasmodic, carminative, expectorant, laxative, and sedative , anti-cancer , epatoprotective , effect on CNS , used in hypertension

# Tannins

Historically, the importance of tannin-containing drugs •  
is linked to their tanning properties, in other words their  
ability to transform fresh hides into an imputrescible  
.material: leather

**Tannins** are "phenolic natural products that precipitate •  
."proteins from their aqueous solutions



The consequence of tanning is the formation of bonds •  
between the collagen fibers in the hide, which imparts  
resistance to water, heat, and abrasion. This  
capability of tannins to combine with  
macromolecules explains why they precipitate  
cellulose, pectins, and proteins; it also explains their  
characteristic astringency and tartness: by  
precipitating the glycoproteins contained in saliva,  
.tannins make the latter lose its lubricating power  
Most *true tannins* have molecular weights from •  
.about 1000 – 5000

# Pseudotannins

They are compounds of lower molecular weight than true •  
tannins and they do not respond to the *goldbeater's skin*  
*.test*

:Examples of drugs containing Pseudotannins are •

***Gallic acid:* Rhubarb**

***Catechins:* Guarana, Cocoa**

***Chlorogenic acid:* Mate, Coffee**

***Ipecacuanhic acid:* ipecacuanha**

# Function of tannins in plants

- 1. Tannins are considered the source of energy through their oxygen content
- 2. They serve as a protective to the plant (plant antiseptics)
- 3. They may have function in respiratory activity, i.e. in the mechanisms of hydrogen transfer in plant cells
- 4. Tannins play an important part in the acceptance of many foods and beverages by consumers e.g. tea, cocoa

# Classification of tannins

In higher plants, two groups of tannins are generally • distinguished, which differ by their structure, as well as their biosynthetic origin: hydrolysable tannins and condensed tannins

## Hydrolysable tannins •

Hydrolysable tannins are esters of a sugar (or related polyol) and of a variable number of phenolic acid • molecules

.The sugar is most generally glucose •

The phenolic acid is either **gallic acid**, in the case of •  
*gallitannins*, or **Ellagic acid**, in the case of the tannins •  
.conventionally referred to as *ellagitannins*

Ellagic acid can arise by lactonization of •  
*hexahydroxydiphenic acid* (= HHDP) during chemical •  
.hydrolysis of the tannin

**Hydrolysable tannins** *were formerly known as* •  
*pyrogallol tannins*, because on dry distillation gallic •  
*acid and similar components are converted into* •  
*pyrogallol*

## ,Biosynthetically •

gallic acid (= 3,4,5-trihydroxybenzoic acid) arises •

.from the metabolism of shikimic acid

:Examples of drugs containing Hydrolysable tannins •

Gallitannins: rhubarb, cloves, Chinese galls, Turkish galls, hamamelis, chestnut and maple. Ellagitannins: pomegranate rind, pomegranate bark, eucalyptus .leaves, and oak bark

## Condensed tannins (proanthocyanidins) •

Condensed tannins or *proanthocyanidins* are polymeric flavans. They consist of **flavan-3-ol** units linked together by carbon-carbon bonds, most often 4→8 or 4→6, which result from coupling between the electrophilic C-4 of a flavanyl unit from a flavan-4-ol or flavan-3,4-diol and a nucleophilic position (C-8, less commonly C-6) of another unit, generally a flavan-3-ol

Unlike hydrolysable tannins, these are not readily •  
hydrolyzed to simpler molecules and they do not contain  
.a sugar moiety

**Biosynthetically**, flavonoids are derived from acetate •  
.and shikimate pathways

Condensed tannins occur due to polymerization •

.(condensation) reactions between flavonoids

.The polymers may include up to 50 monomer units •

*On treatment with acids or enzymes condensed tannins •*  
*are converted into red insoluble compounds known as*  
***phlobaphenes***. Phlobaphenes give the characteristic red  
.colour to many drugs such as red cinnamon bark



.The following are rich in condensed tannins •

***Barks:*** cinnamon, wild cherry, cinchona, willow, (1)  
acacia, oak and hamamelis

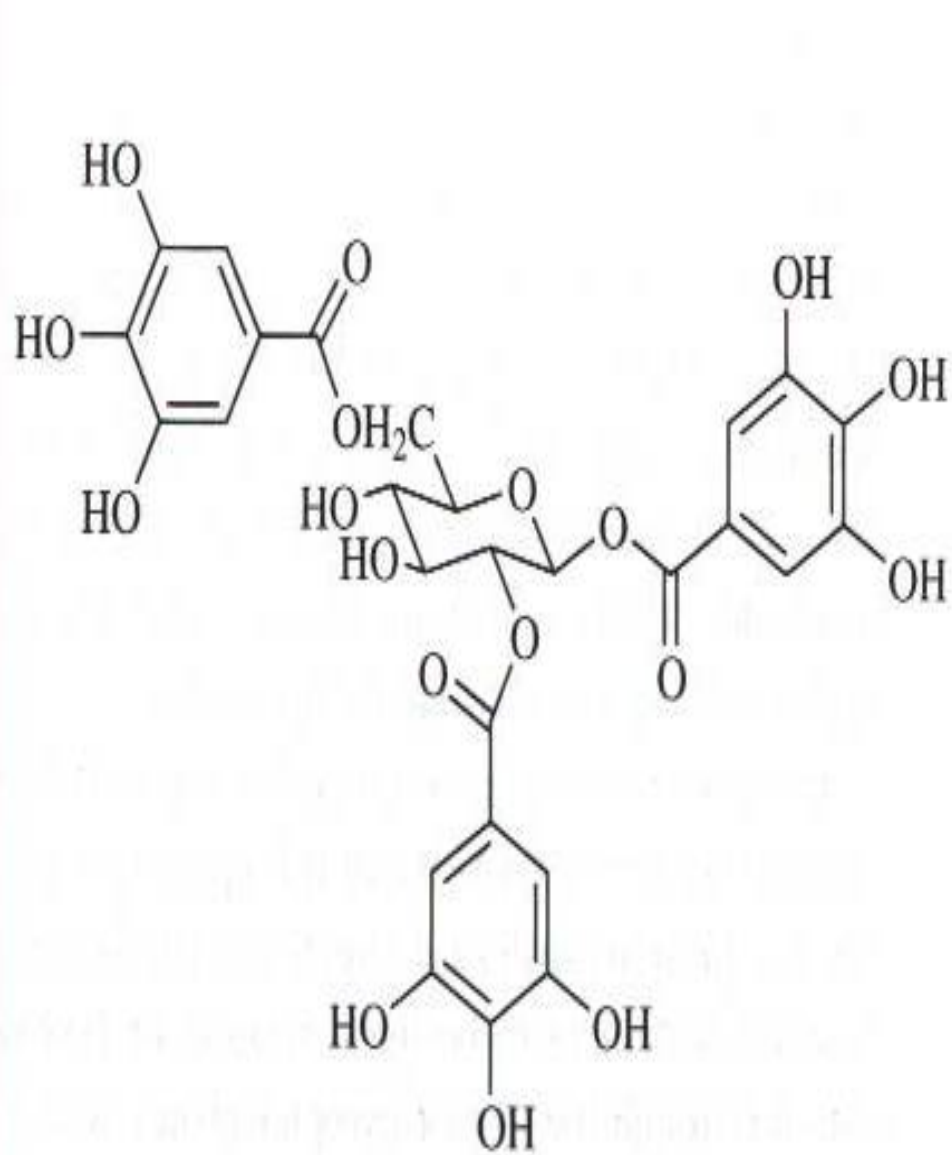
***Roots and rhizomes:*** krameria (rhatany) and male (2)  
fern

***Flowers:*** lime and hawthorn (3)

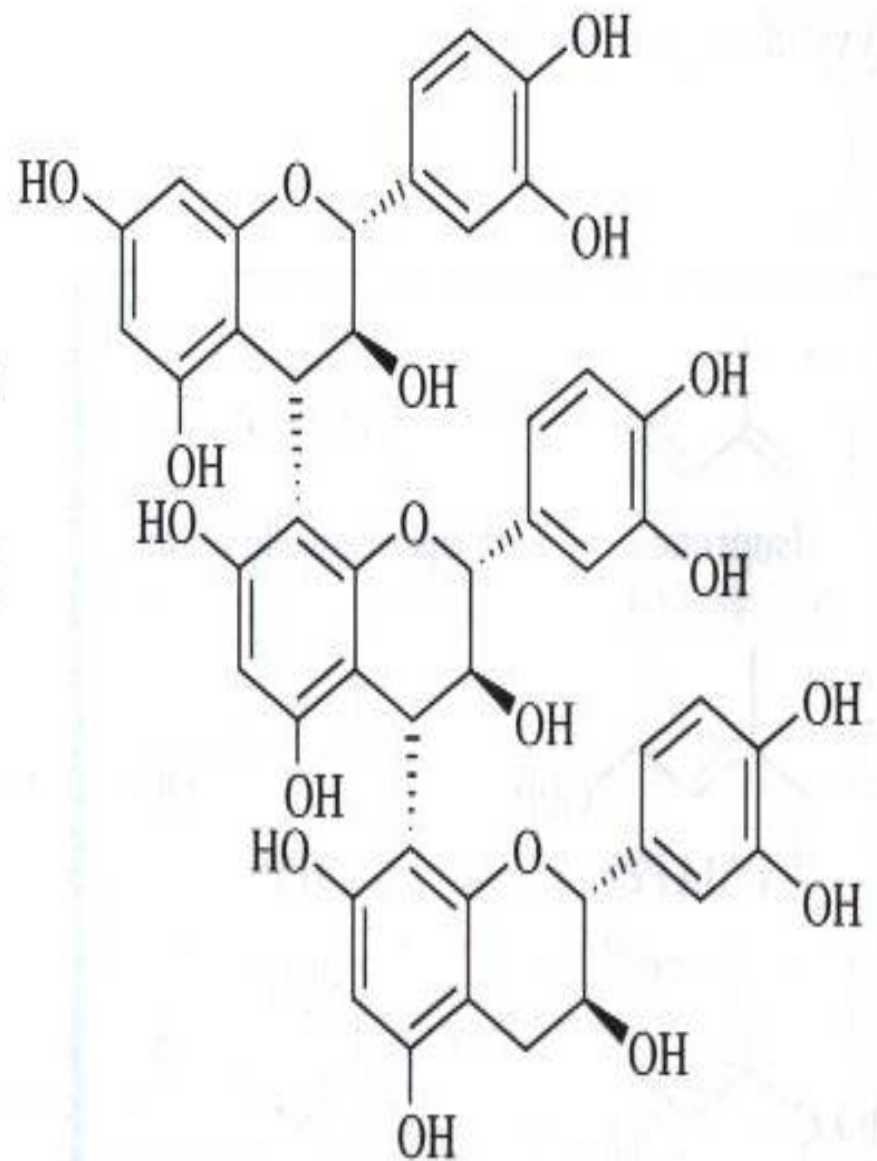
***Seeds:*** cocoa and kola (4)

***Leaves:*** hamamelis and tea, especially green tea (5)

***Extracts and dried juices:*** acacia (6)



**Hydrolysable tannin (trigalloyl glucose)**



**Non-hydrolysable tannin (flavonoid trimer)**

## Properties and tests of tannins

Tannins are soluble in water, dilute alkalis, alcohol, •  
glycerol and acetone, but generally only sparingly  
.soluble in other organic solvents

Solutions precipitate heavy metals, alkaloids, glycosides •  
.and gelatin

With ferric salts, gallitannins and ellagitannins give •  
blue-black precipitates and condensed tannins  
brownish-green ones. If a very dilute ferric chloride  
solution is gradually added to an aqueous extract of  
hamamelis leaves (which contains both types of tannin),  
a blue colour is produced which changes to olive-green  
.as more ferric chloride is added

# Medicinal and biological properties

The applications of tannin-containing drugs are limited, and result from their affinity for proteins

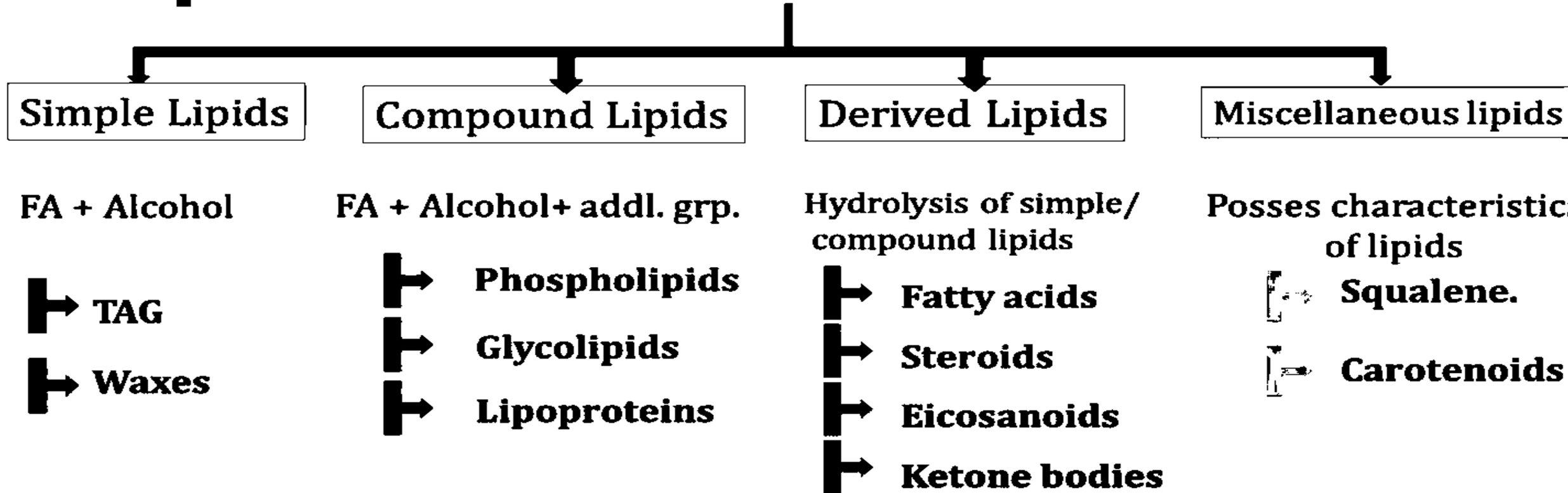
Tannin-containing drugs will precipitate protein and have •  
been used traditionally as styptics and internally for the  
.protection of inflamed surfaces of mouth and throat

They act as antidiarrhoeals and have been employed as •  
antidotes in poisoning by heavy metals, alkaloids and  
.glycosides

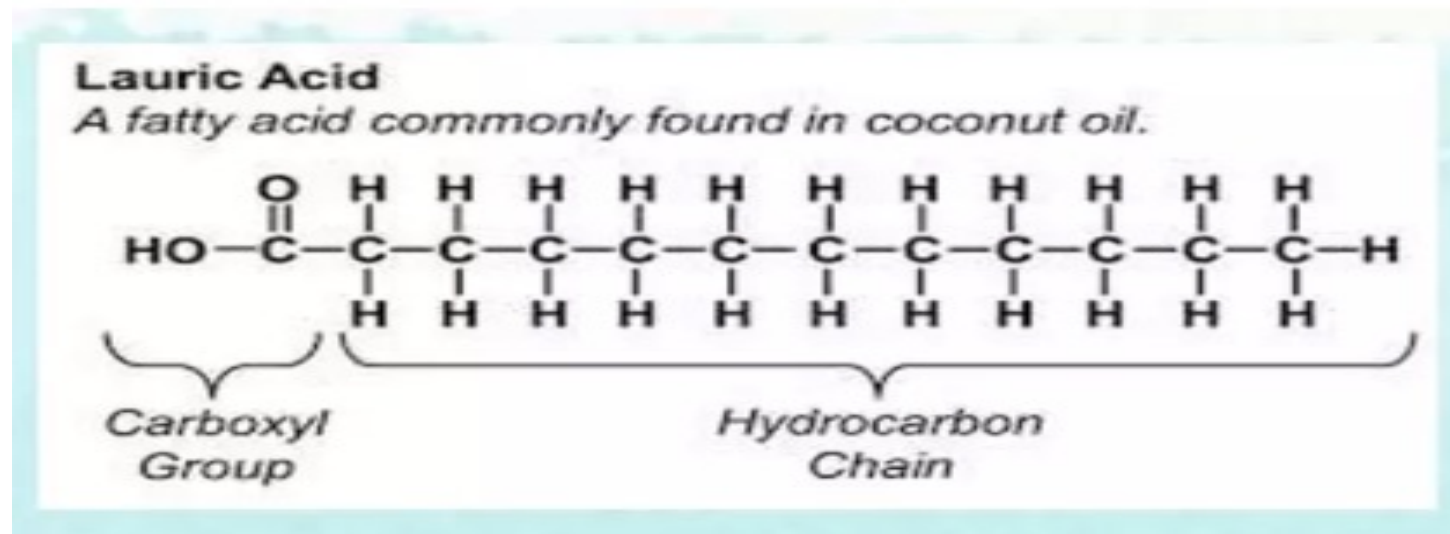
# Types

Lipid Chemistry-1

## Lipids: Definition & Classification



**Lipids** (fixed oils, fats, and waxes) are esters of long-chain *fatty acids* and alcohols, or of closely related derivatives.



# Classification

## By structure:

1. Simple: fats, oils, waxes, steroids.
2. Complex: phospholipids, spingolipids, glycolipids.
3. They derivatives: hormones, fat-solubility vitamins

On the basis of whether they undergo hydrolysis reactions in alkaline solution:

1. Saponifiable **lipids** can be hydrolyzed under alkaline conditions to yield salts of fatty acids.
2. Nonsaponifiable **lipids** do not undergo hydrolysis reactions in alkaline solution.

## LIPIDS

**Lipids are a class of biological molecules defined by low solubility in water and high solubility in nonpolar solvents.**

As molecules that are largely hydrocarbon in nature, lipids represent highly reduced forms of carbon and, upon oxidation in metabolism, yield large amounts of energy. Lipids are thus the molecules of choice for metabolic energy storage.

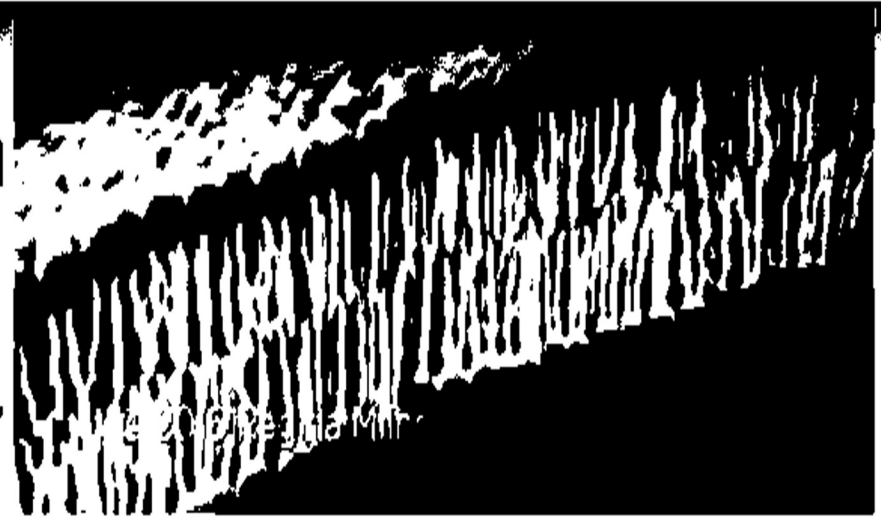
# Lipids

- **Lipids** (fixed oils, fats, and waxes) are esters of long-chain fatty acids and alcohols, or of closely related derivatives. The chief difference between these substances is the type of alcohol; in fixed oils and fats, glycerol combines with the fatty acids; in waxes, the alcohol has a higher molecular weight, e.g., acetyl alcohol[CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>OH].
- Fats and oils are made from two kinds of molecules: glycerol (*a type of alcohol with a hydroxyl group on each of its three carbons*) and three fatty acids joined by dehydration synthesis. Since there are three fatty acids attached, these are known as triglycerides.



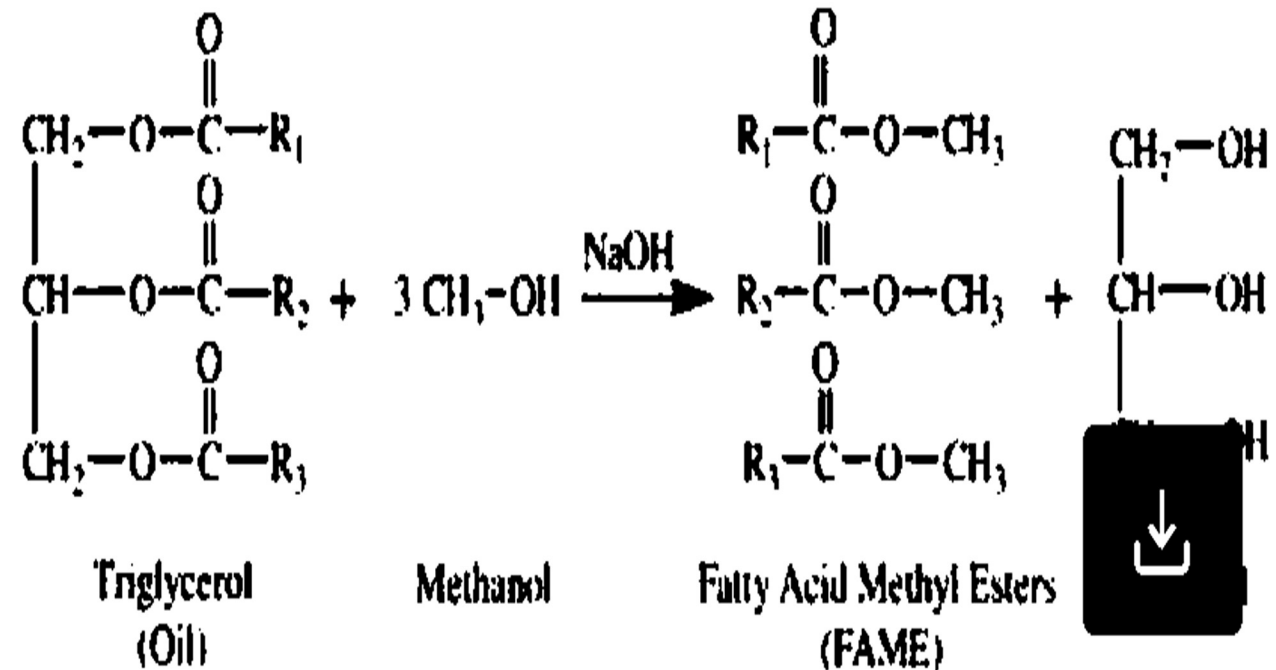
## type of alcohol.

- In **fixed oils and fats**, glycerol combines with the **fatty acids**.
- In **waxes**, the alcohol has a higher molecular weight.  
For example: Cetyl alcohol,  $[\text{CH}_3(\text{CH}_2)_{15}\text{OH}]$ .

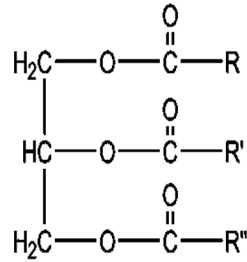


Fats and fixed oils are obtained from either plants (olive oil, peanut oil) or animals (lard).

Their primary function is food (energy) storage.

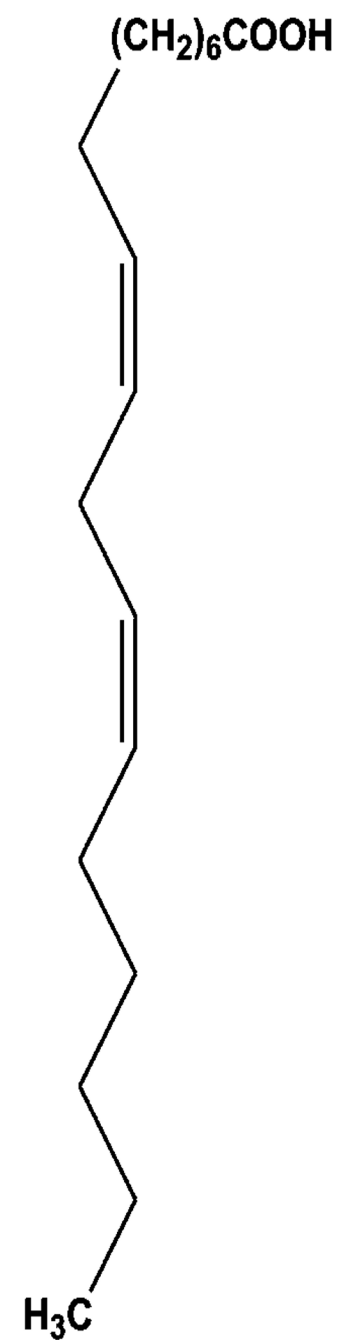


triglyceride



## Structure of Fatty Acids

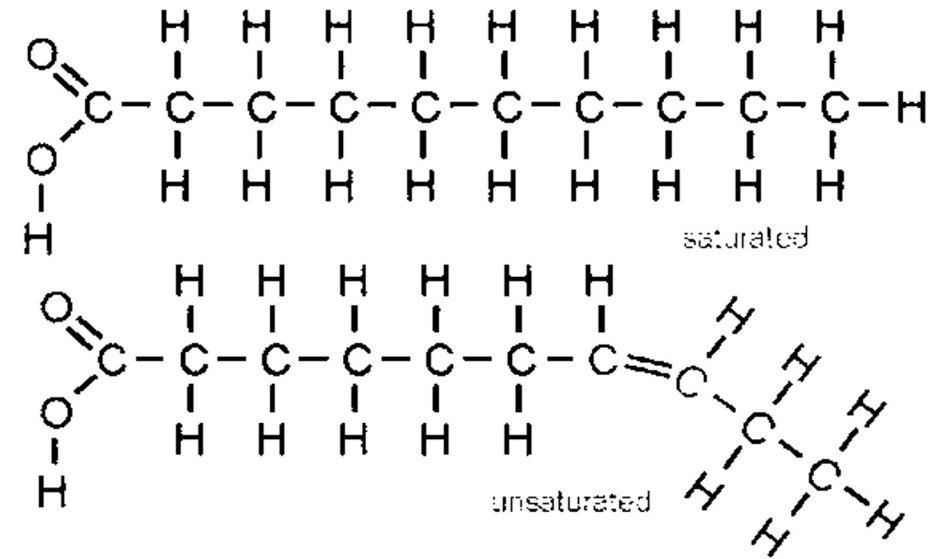
- The “tail” of a fatty acid is a long hydrocarbon chain, making it hydrophobic. The “head” of the molecule is a carboxyl group which is hydrophilic. Fatty acids are the main component of *soap*, where their tails are soluble in oily dirt and their heads are soluble in water to *emulsify* and wash away the oily dirt. However, **when the head end is attached to glycerol to form a fat, that whole molecule is hydrophobic.**



- where R, R', and R'' are long alkyl chains; the three fatty acids RCOOH, R'COOH and R''COOH can be all different, all the same, or only two the same.

- The terms saturated, mono-unsaturated, and poly-unsaturated refer to the number of hydrogens attached to the hydrocarbon tails of the fatty acids as compared to the number of double bonds between carbon atoms in the tail.

- Fats, which are mostly from animal sources, have all single bonds between the carbons in their fatty acid tails, thus all the carbons are also bonded to the maximum number of hydrogens possible.



# Biosynthesis of lipids

- The biosynthesis of saturated and unsaturated fatty acids is from combinations of acetate units (acetate pathway).

## Applications of fixed oils and fats

1. Soap manufacture
2. Suppositories, tablet coating
3. Dietary supplements
4. Emulsifying agents
5. Manufacture of paints, varnishes and lubricants
6. Therapeutic uses (castor oil).

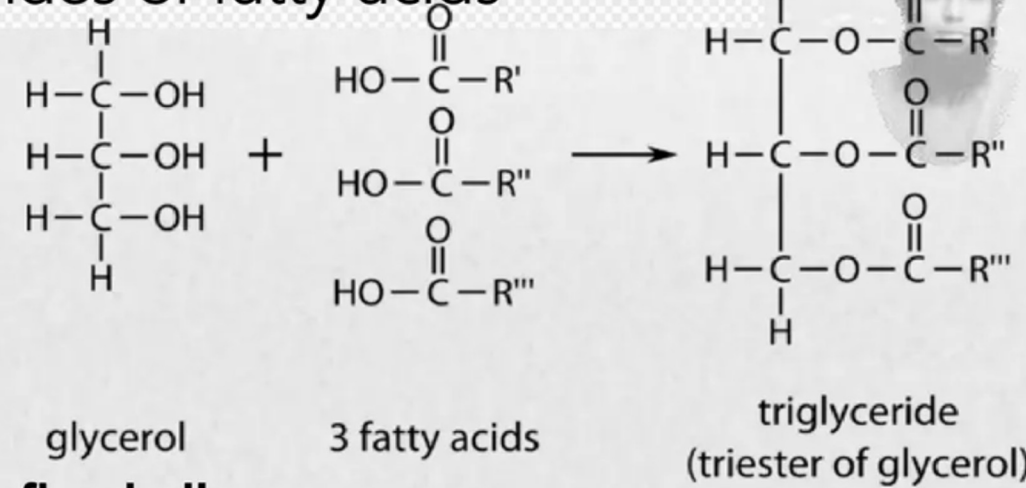
Chemically, the fixed oils and fats are glycerides of fatty acids

Fats and oils are made from two kinds of molecules **glycerol** (a type of alcohol with a hydroxyl group on each of its three carbons) and **three fatty acids** joined by dehydration synthesis. Since there are three fatty acids attached, these are known as **triglycerides**.

**Fixed oils** and **Fats** differ only as to **melting point**.

Those that are liquid at normal temperatures are known as **fatty or fixed oils**,

Whereas those that are semisolid or solid at ordinary temperatures are known as **fats**.

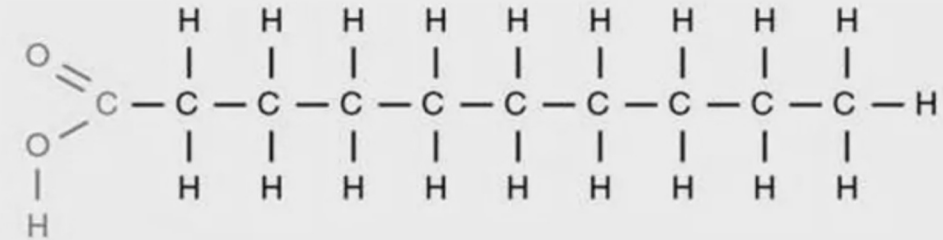


Usually, the glycerides of **unsaturated fatty acids** are **liquid**

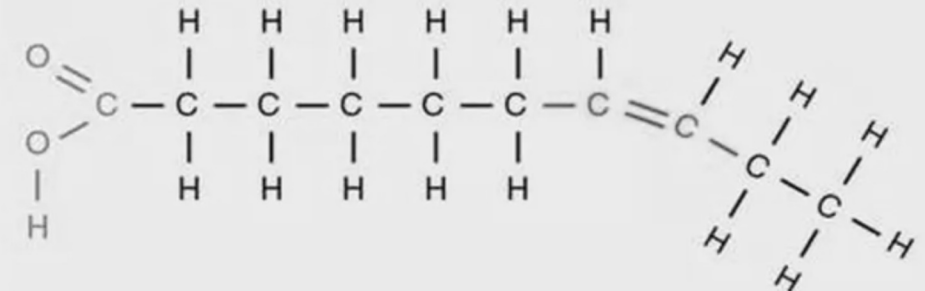
Whereas the glycerides of **saturated fatty acids** (**no C=C bonds**) of sufficient chain length are **solid**.

When a drop of fats or oils is placed on a paper, they form a permanent translucent stain on it. Due to this property they are called as **fixed oils**.

(a) Saturated



(b) Unsaturated



## Production of fixed oils and fats

### **Extraction by expression:**

Fixed oils and fats of vegetable origin are obtained by expression in hydraulic presses. If the expression is carried out in the cold, the oil is known as a "virgin oil" or a "cold-pressed oil". In contrast, if the expression is carried out in heat, the oil is known as a "hot-pressed oil."

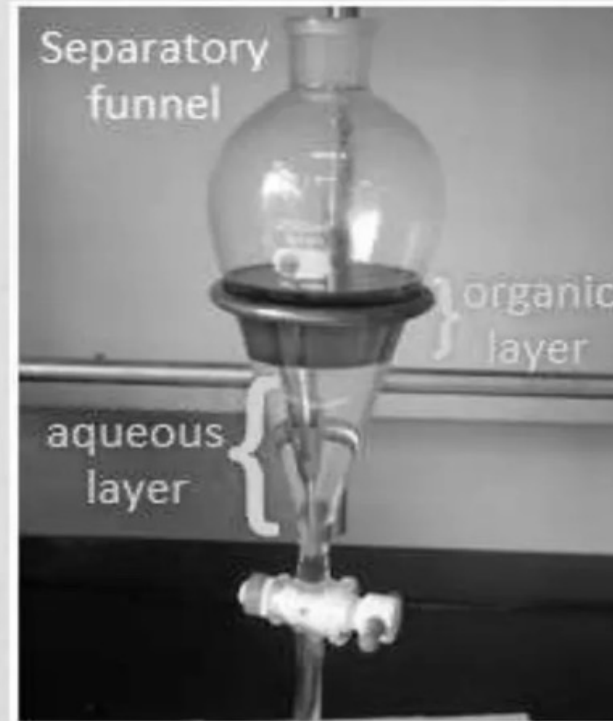
### **Extraction by solvents:**

Sometimes organic solvents are used for the extraction of oils.

Animal fats are separated from other tissues by rendering with steam, with or without pressure.

The heat melts the fat, which rises to the top and may be separated by decantation.

**Animal fats** are separated from other tissues by rendering with steam, with or without pressure. The heat melts the fat, which rises to the top and may be separated by decantation.





## Evaluation of fixed oils

According to United States Pharmacopeia, certain tests are used to determine the identity, quality, and purity of fixed oils. These tests are based on the chemical constitution of the fatty acids.

**1. The acid value or acid number:** It is the number of milligrams of potassium hydroxide (KOH) required to neutralize the free fatty acids in one gram of the substance. It indicates the amount of free fatty acids present in the oil.

**2. The saponification value:** It is the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acids and saponify the esters contained in one gram of the substance.

**3. Iodine number:** It is the number of grams of iodine absorbed, under prescribed conditions, by 100 g of the substance. It indicates the degree of unsaturation.



### Biodiesel Lab 3



Determination of the Acid Number of Vegetable Oils by Titration

### Iodine Value

AOAC 920.159

A COMPLETE PROCEDURE



Common fatty acids are:

Caproic .....  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$

Caprylic .....  $\text{CH}_3(\text{CH}_2)_6\text{COOH}$

Capric .....  $\text{CH}_3(\text{CH}_2)_8\text{COOH}$

Lauric ....  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$

Myristic .....  $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$

Palmitic .....  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$

Stearic .....  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

Arachidic .....  $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$



### Unsaturated Fatty Acids Detected in Oils and Fats

Palmitoleic	$\text{CH}_3 (\text{CH}_2)_5 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Oleic	$\text{CH}_3 (\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Ricinoleic	$\text{CH}_3 (\text{CH}_2)_5 \text{CHOH-CH}_2 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Linoleic	$\text{CH}_3 (\text{CH}_2)_4 \text{CH}=\text{CHCH}_2 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Linolenic	$\text{CH}_3 \text{CH}_2 \text{CH}=\text{CHCH}_2 \text{CH}=\text{CHCH}_2 \text{CH}=\text{CH-} (\text{CH}_2)_7 \text{COOH}$
Eleostearic	$\text{CH}_3 (\text{CH}_2)_3 (\text{CH}=\text{CH})_3 (\text{CH}_2)_7 \text{COOH}$
Licanic	$\text{CH}_3 (\text{CH}_2)_3 (\text{CH}=\text{CH})_3 (\text{CH}_2)_4 \text{CO}(\text{CH}_2)_2 \text{COOH}$
Parinaric	$\text{CH}_3 \text{CH}_2 (\text{CH}=\text{CH})_4 (\text{CH}_2)_7 \text{COOH}$
Tariric	$\text{CH}_3 (\text{CH}_2)_7 \text{C}\equiv\text{C} (\text{CH}_2)_7 \text{COOH}$
Gadoleic	$\text{CH}_3 (\text{CH}_2)_9 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$
Arachidonic	$\text{CH}_3 (\text{CH}_2)_4 (\text{CH}=\text{CHCH}_2)_4 (\text{CH}_2)_2 \text{COOH}$
Cetoleic	$\text{CH}_3 (\text{CH}_2)_9 \text{CH}=\text{CH} (\text{CH}_2)_9 \text{COOH}$
Erucic	$\text{CH}_3 (\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_{11} \text{COOH}$
Selacholeic or nervonic	$\text{CH}_3 (\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_{13} \text{COOH}$

### Saturated Fatty Acids Detected in Oils and Fats

Butyric	$\text{CH}_3 (\text{CH}_2)_2 \text{COOH}$
Isovaleric	$(\text{CH}_3)_2 \text{CHCH}_2 \text{COOH}$
Caproic	$\text{CH}_3 (\text{CH}_2)_4 \text{COOH}$
Caprylic	$\text{CH}_3 (\text{CH}_2)_6 \text{COOH}$
Capric	$\text{CH}_3 (\text{CH}_2)_8 \text{COOH}$
Lauric	$\text{CH}_3 (\text{CH}_2)_{10} \text{COOH}$
Myristic	$\text{CH}_3 (\text{CH}_2)_{12} \text{COOH}$
Palmitic	$\text{CH}_3 (\text{CH}_2)_{14} \text{COOH}$
Stearic	$\text{CH}_3 (\text{CH}_2)_{16} \text{COOH}$
Arachidic	$\text{CH}_3 (\text{CH}_2)_{18} \text{COOH}$

# FIXED OILS

## Castor Oil

**Biological Source :** Castor oil is a fixed oil obtained by cold expression from the ripen seeds (**Castor bean or castor oil seed**) of *Ricinus communis* (Family: Euphorbiaceae).

**Composition:** Castor oil is a pale yellowish or almost colorless, transparent, viscid liquid. It has a faint, mild odor and a bland, characteristic taste.

Castor oil is composed of a mixture of triglycerides, about 75% of which is tri-ricinolein. The fixed oil consists of the glycerides of ricinoleic (87%), isorlinoleic, stearic (1%), dihydroxystearic (traces), linoleic (3%), oleic (7%), and palmitic (2%) acids.

### Uses

1. Castor oil is a stimulant cathartic
  2. Castor oil is used as a stiffening agent in some pharmaceutical formulations
- It is used as ointment base, for the preparation of flexible collodion



# Linseed Oil

**Biological Source :** Linseed is the dried, ripe seed of *Linum usitatissimum* Linn. Linseed oil is obtained by expression of linseeds.

**Composition:** Linseed oil is a yellowish liquid, with a peculiar odour and bland taste.

On hydrolysis Linseed oil produces unsaturated acids like linolenic acid (30-50%), linoleic acid (23-24%), oleic acid (10-18%) together with saturated acids-myristic, stearic and palmitic (5-11%).

## Uses

1. Linseed is used as demulcent and in form of poultices for gouty and rheumatic swellings.
2. Internally it is used for gonorrhea and irritation of the genitourinary system.
3. Linseed oil has emollient, expectorant, diuretic, demulcent and laxative properties and is utilized externally in lotions and liniments.





# Coconut Oil

## Biological Source :

Coconut oil is the fixed oil obtained by expression or extraction from the seed of the coconut palm, *Cocos nucifera* (Family: Palmae).

## Composition:

The oil consists of a mixture of glycerides in which 80 to 85% of the acids are saturated; it is a semisolid at 20C. It consists of the triglycerides of mainly lauric and myristic acids, together with smaller quantities of caproic, caprylic, oleic, palmitic and stearic acids

## Uses

1. Coconut oil and medium-chain triglycerides are used in the balanced dietary supplements.
2. It is a useful nonaqueous medium for the oral administration of some medicaments



# Olive Oil

## Biological Source :

**Olive** oil is the fixed oil obtained from the ripe fruit of *Olea europaea* (Family: Oleaceae). Olive oil is sometimes called **sweet oil**.

## Composition:

Olive oil is a pale yellow or light greenish-yellow due to presence of chlorophyll or carotenes, non-drying oily liquid with a pleasant delicate flavor. Taste is bland becoming faintly acid.

Olive oil contains mixed glycerides of oleic acid (83.5%), palmitic acid (9.4%), linoleic acid (7%), stearic acid (2.00/6), and arachidic acid (0.9%).

## Uses

1. It is used as a setting retardant for dental cements.
2. In the preparation of soaps, plasters, and liniments.
3. It is also a demulcent, an emollient, and a laxative.
4. Olive oil is a nutrient and is widely used as a salad oil



# Peanut oil

## Biological Source :

Peanut oil is the refined fixed oil obtained from the seed kernels of one or more of the cultivated varieties of *Arachis hypogaea* (Family: Leguminosae). Peanut oil is sometimes referred to as **arachis oil**.

## Composition:

It is a colorless or a yellowish liquid with a slightly nutlike odor and a bland taste. Peanut oil consists of a mixture of glycerides with component acids of the following approximate composition: oleic (50 to 65%); linoleic (18 to 30%); palmitic (8 to 10%); stearic, arachidic, behenic, and lignoceric acids (together, 10 to 12%).

## Uses

1. Peanut oil is a solvent for intramuscular injections.
2. It is used for the manufacture of margarine, soap, paints, liniments, plasters and ointments.
3. Groundnut oil is used as an edible oil, as a substitute for Olive oil



# WAXES

Waxes are the esters of higher straight-chain fatty acids with long-chain or high molecular weight monohydric alcohols, some containing more than 30 carbons in the chain.

## Source

**Plant origin:** Carnauba wax , Bayberry wax

**Animal origin:** Beeswax, Wool-fat, Spermaceti, etc.

## Function

In plants, waxes protect the loss of water  
It also protects the penetration of water to the inner part.

Waxes are employed in pharmaceuticals to 'harden" ointments and cosmetic creams.



# Beeswax

## Biological Source :

**Yellow beeswax** or **White beeswax** is the purified wax from the honeycomb of the bee, *Apis mellifera* or *Apis mellifica* Linn (Fam. Apidae).

## Composition:

The beeswax is yellowish to brownish-yellow, or white, pieces or plates, translucent when thin, soft to brittle, honey-like odour, slight balsamic taste. Beeswax consists mainly of myricyl palmitate (myricin) (~80%) myricyl stearate, free cerotic acid (15%) , aromatic substance cerolein, hydrocarbons, (~12%), lactones, moisture, cholesteryl ester, pollen pigments, and propolis (bee glue).

## Uses

A beeswax and vegetable oil mixture is used as a vehicle for the administration of respiratory forms of certain medicaments such. as penicillin and curare.

It is used in the formulation of medicinal preparations for treating skin cracks.

A combination containing of tallow, olive oil, camphor, beeswax and common salt is used for ulcer and external tumour treatment.





# LIPIDS

Soluble in non-polar solvents and insoluble in polar solvents. Lipid is not polymers.

Lipids:

1. Fatty acids
2. Neutral fats and oils
3. Waxes
4. Phospholipid
5. Sterols
6. Fat soluble vitamins



# Properties of Lipids

- Not readily dissolve in water
- Fats are solid at room temperature
- Oils are liquid at room temperature
- Triglycerides are the main form of lipids in food and body (storage)
- Energy dense (9 kcal /gm)
- **Functions of Lipids:**
- Provide energy
- Efficient storage of energy
- Insulation
- Protection
- Transport fat-soluble vitamins
- Flavor and mouth feel

Lipids are more commonly known as "fats", and are one of the three major families of nutrients along with proteins and carbohydrates.

They are made up of **fatty acids** which **are essential for the human body to function properly**:

1- they play a vital **structural role** and are the main constituents of cell membranes;

2- they **bring essential nutrients** to our body such as the liposoluble [vitamins A, D, E and K](#), and facilitate their absorption.

3- some fatty acids play a central role in the development and function of the nervous system (the brain) and the retina.

4- Lipids can also play a role in the prevention of certain diseases. In adults, for example, some fatty acids of the [omega-3](#) family help keep the cardiovascular system functioning properly.

Vegetable fats and oils are [lipid](#) Vegetable fats and oils are lipid materials derived from [plants](#) Vegetable fats and oils are lipid materials derived from plants. Physically, [oils](#) Vegetable fats and oils are lipid materials derived from plants. Physically, oils are liquid at [room temperature](#) Vegetable fats and oils are lipid materials derived from plants. Physically, oils are liquid at room temperature, and [fats](#) Vegetable fats and oils are lipid materials derived from plants.

The melting temperature distinction between oils and fats is rough, and typically natural oils have a melting range instead of a single melting point since natural oils are not chemically homogeneous.

Although thought of as [esters](#) of glycerin and a varying mix of fatty acids, fats and oils also typically contain free fatty acids, monoglycerides and diglycerides, and unsaponifiable lipids.

Vegetable fats and oils may or may not be edible.

Examples of inedible vegetable fats and oils include processed linseed oil, and castor oil used in lubricants, paints, cosmetics, pharmaceuticals, and other industrial applications.

# Types of Lipids:

- **Lipids with fatty acids**
- **Fats, oils, lipids, fatty acids, triglycerides, cholesterol.**

**Waxes**

**Fats and oils (triglycerides)**

**Phospholipids**

**Sphingolipids**

- **Lipids without fatty acids**

**Steroids**

# Fatty Acids

- Long-chain carboxylic acids
- Insoluble in water
- Typically 12-18 carbon atoms (even number)
- Some contain double bonds

corn oil contains 86%  
unsaturated fatty acids and  
saturated fatty acids

14%



# Saturated and Unsaturated Fatty Acids

**Saturated = C–C bonds**

**Unsaturated = one or more C=C bonds**



# Structures

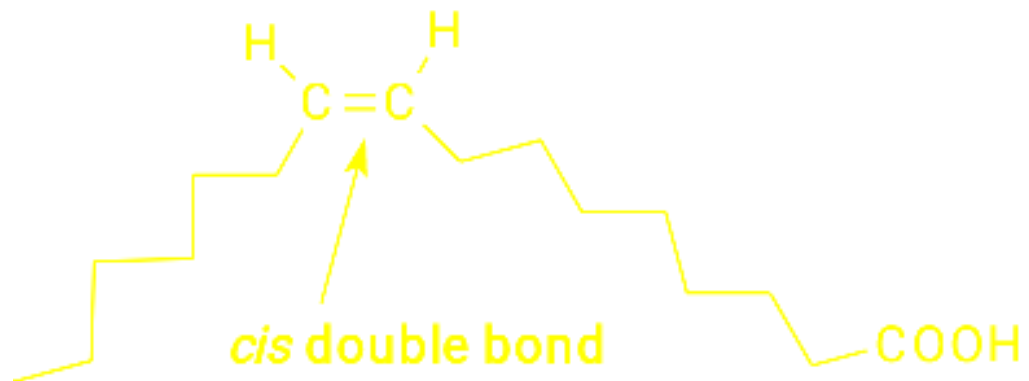
## Saturated fatty acids

- Fit closely in regular pattern



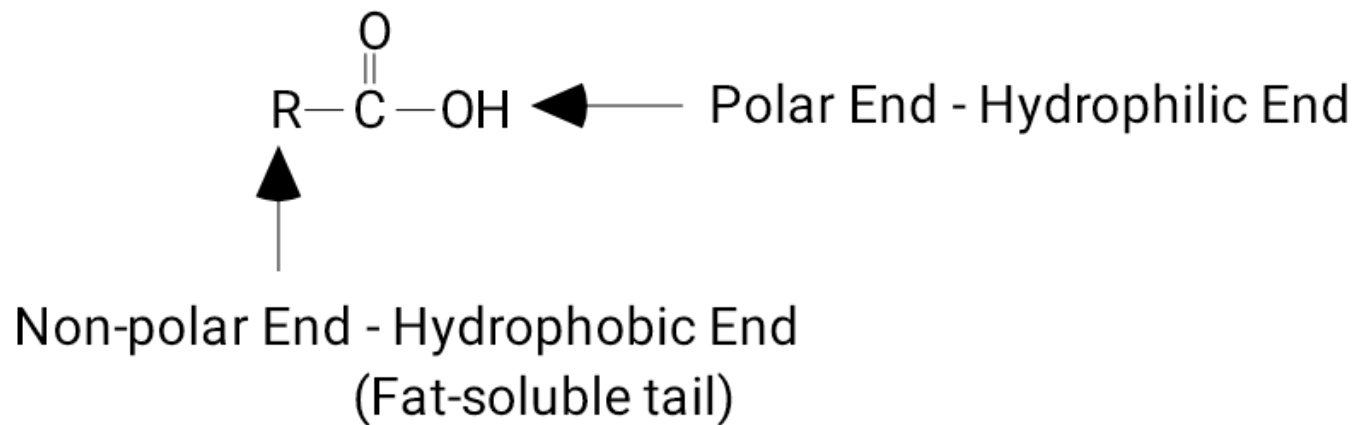
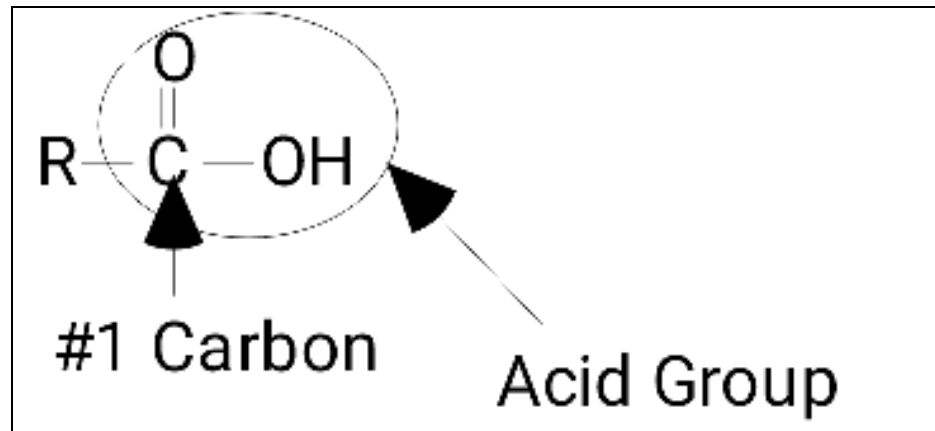
## Unsaturated fatty acids

- Cis double bonds

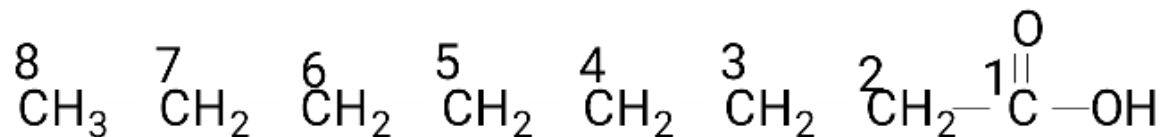




# Fatty Acids

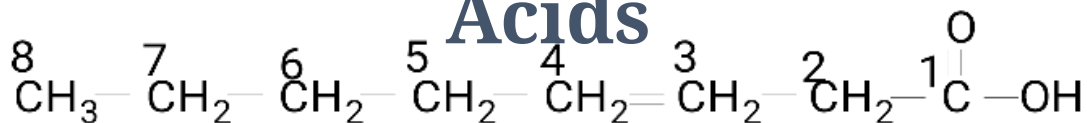


## Saturated Fatty Acids

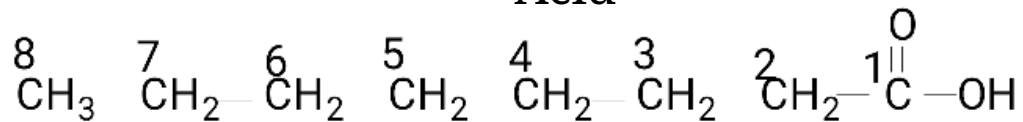


Octanoic Acid

## Unsaturated Fatty Acids

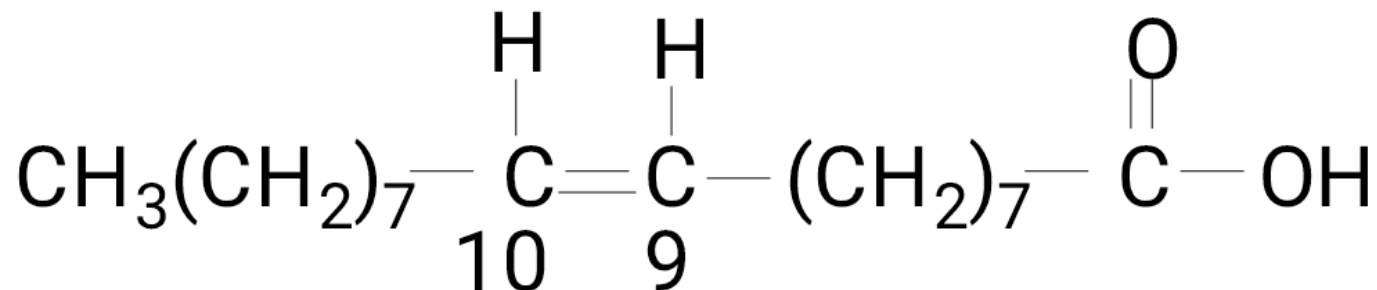


3 - Octenoic  
Acid

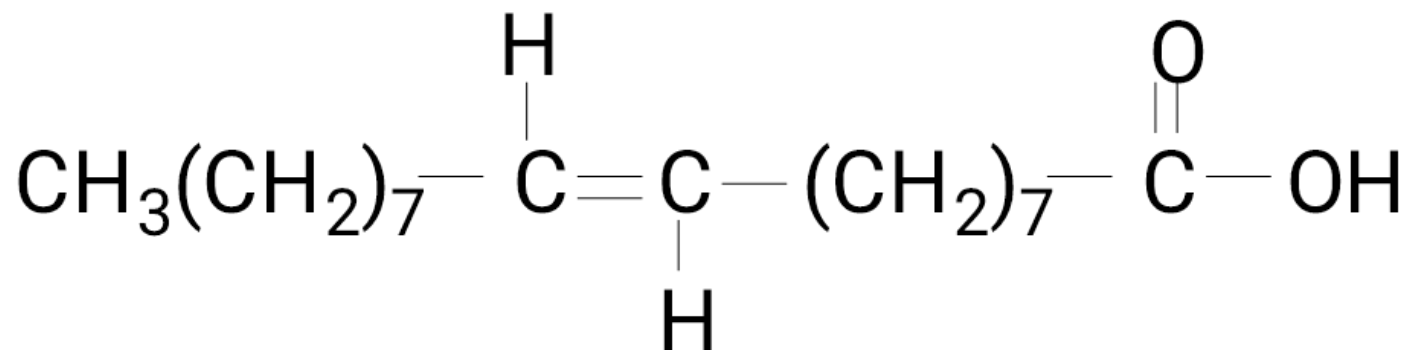


3, 6 - Octadienoic  
Acid

# Cis And Trans Fatty Acids



Cis 9 - Octadecenoic Acid (oleic)



Trans 9 - Octadecenoic Acid (elaidic acid)

## Polyunsaturated Fatty Acids

Linoleic acid: Cis, cis, 9, 12 - Octadecadienoic acid

Linolenic acid: Cis, cis, cis 9, 12, 15 - Octadecatrienoic acid

Arachidonic acid: Cis, cis, cis, cis 5, 8, 11, 14 -  
Eicosatetraenoic acid

Linoleic Acid



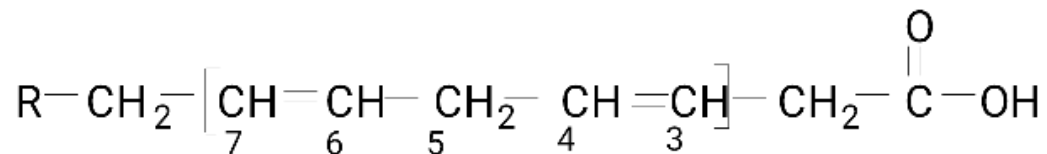
Linolenic Acid



Arachidonic

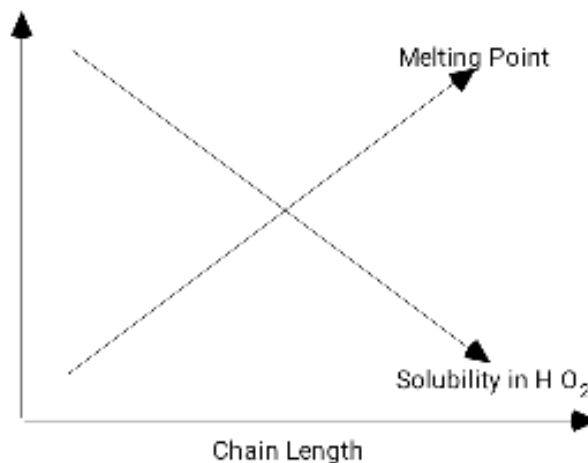
Acid

# Naturally-occurring fatty acids



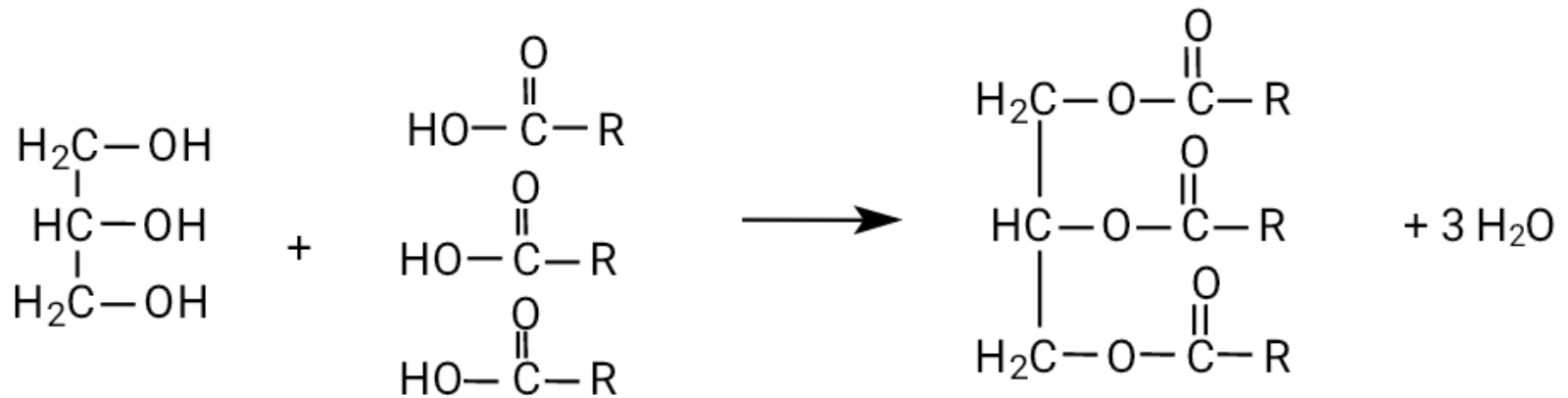
1. Cis form
2. Not conjugated --- isolated double bond.
3. Even numbered fatty acids.

## Relation between Melting Points and Solubility in Water of Fatty Acids



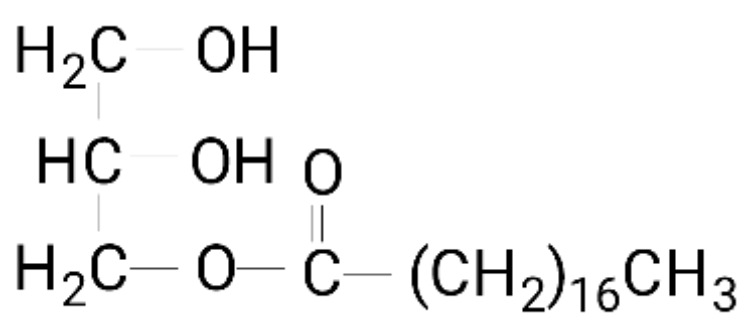
# FAT AND OILS

Mostly Triglycerides:

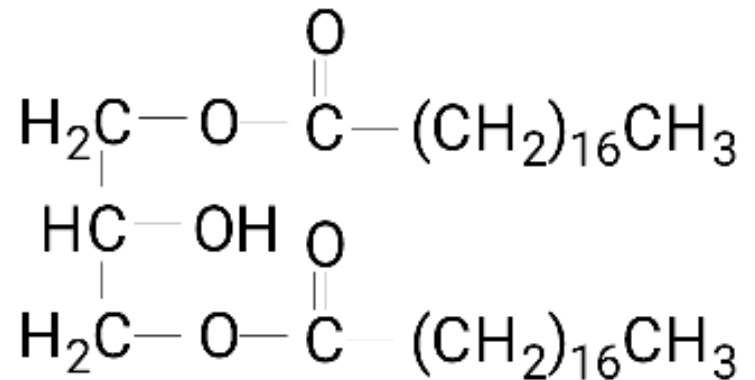


Glycerol      3 Fatty Acids

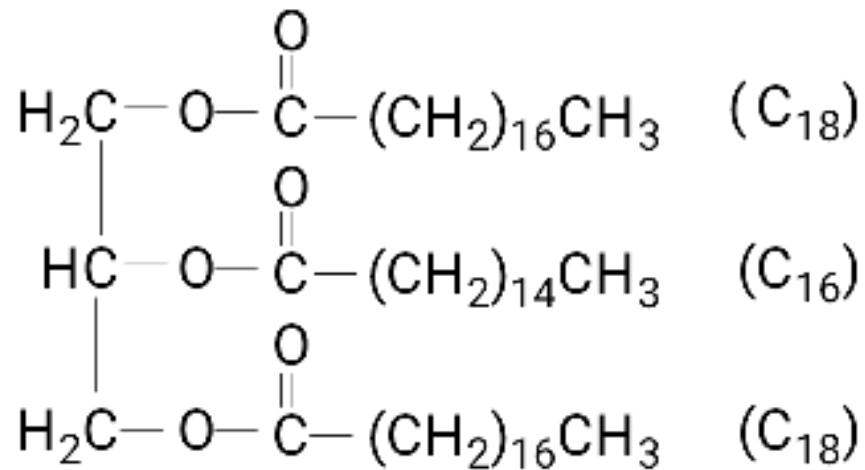
# GLYCERIDES



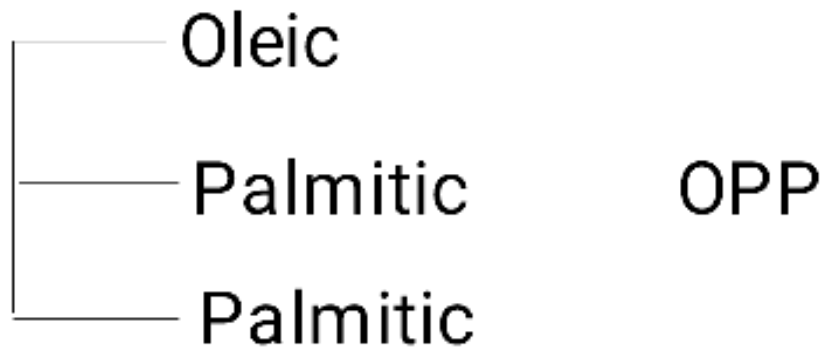
Monoglyceride ( $\alpha$  - monostearin)



Diglyceride ( $\alpha, \alpha'$  - distearin)

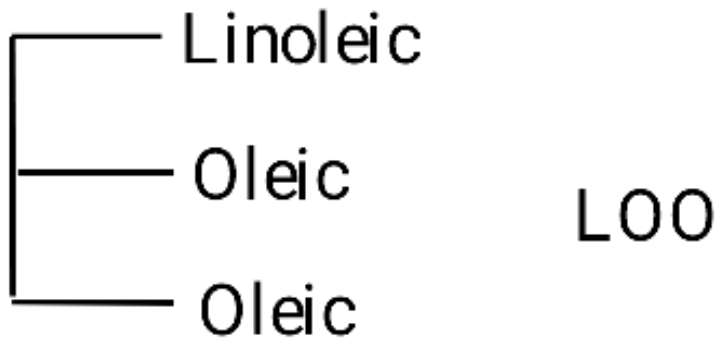


Triglyceride ( $\beta$  - palmityl distearin)



$\alpha$  - oleodipalmitin

1 - oleodipalmitin



$\alpha$  - Linoleyldiolein

1 - Linoleyldiolein



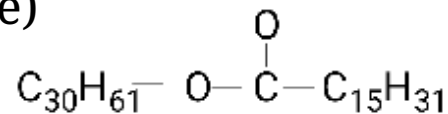
# WAXES

Fatty acids + Long chain alcohol

Important in fruits:

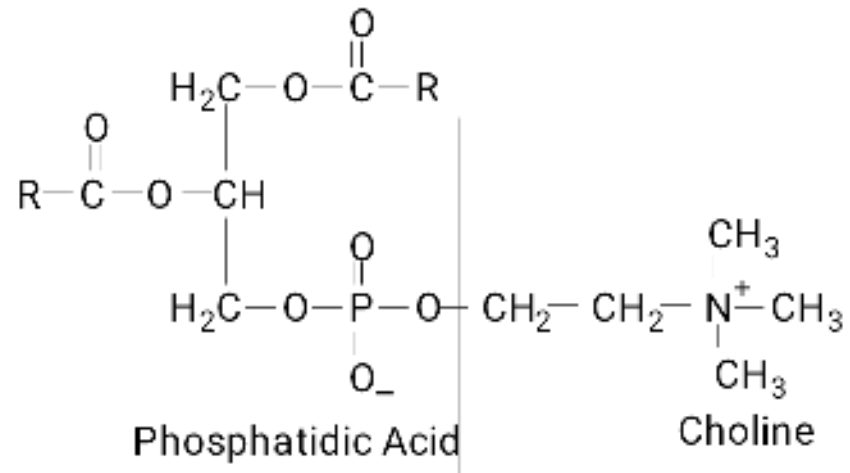
1. Natural protective layer in fruits, vegetables, etc.
2. Added in some cases for appearance and protection.

Beeswax (myricyl palmitate)



# PHOSPHOLIPID

Lecithin (phosphatidyl choline)



# STEROLS

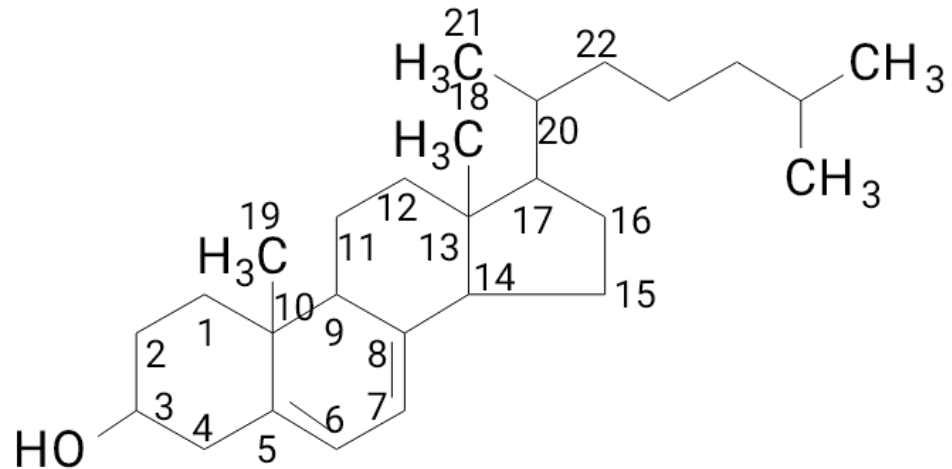
Male & female sex hormones

Bile acids

Vitamin D

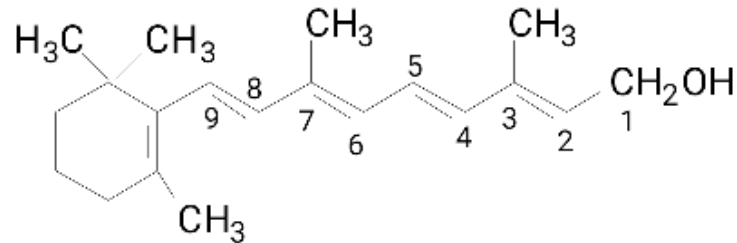
Adrenal corticosteroids

Cholesterol

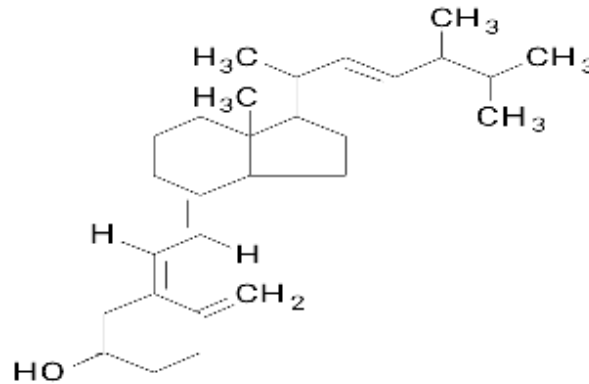


# FAT SOLUBLE VITAMINS

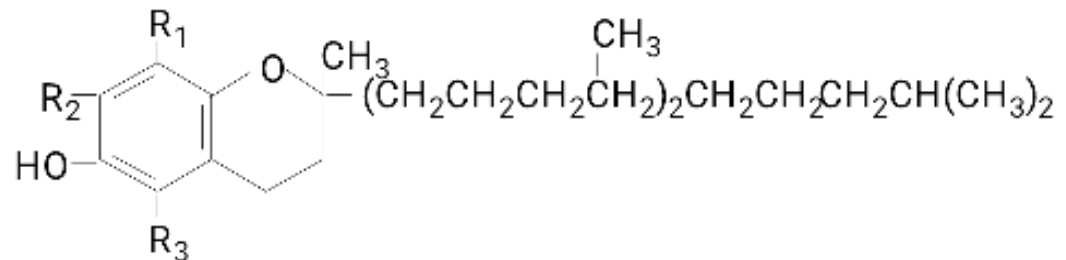
Vitamin A:



Vitamin D2



Vitamin E



# **ANALYTICAL METHODS TO MEASURE THE CONSTANTS OF FATS AND OILS**

1. Acid Value
2. Saponification Value
3. Iodine Value
4. Gas Chromatographic Analysis for Fatty Acids
5. Liquid Chromatography
6. Cholesterol Determination

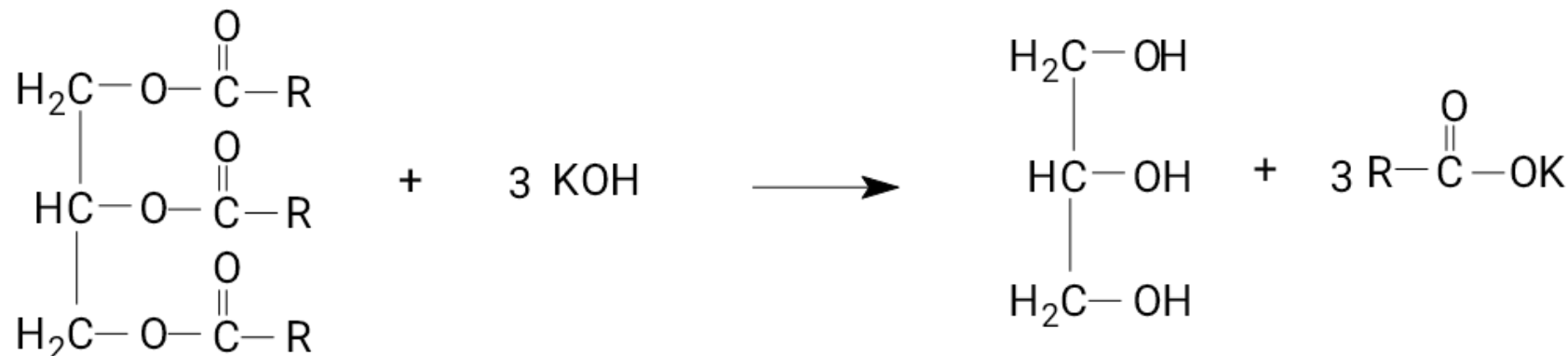
# 1. Acid Value

Number of mgs of KOH required to neutralize the Free Fatty Acids in 1 g of fat.

# 2. Saponification Value

Number of mgs of KOH required to neutralize and saponification the Free Fatty Acids in 1 g of fat.

Saponification - hydrolysis of ester under alkaline condition.



**3. Iodine Number:** is number of iodine (g) absorbed by 100 g of oil. Molecular weight and iodine number can calculate the number of double bonds. 1 g of fat adsorbed 1.5 g of iodine value = 150.

### **Iodine Numbers of Triglycerides examples**

<b>Fatty Acids</b>	<b># of Double-bonds</b>	<b>Iodine #</b>
Palmitoleic Acid	1	95
Oleic Acid	1	86
Linoleic Acid	2	173
Linolenic Acid	3	261
Arachidonic Acid	4	320

- **Properties of Saturated Fatty Acids**

- Contain only single C–C bonds
- Closely packed
- Strong attractions between chains
- High melting points
- Solids at room temperature.

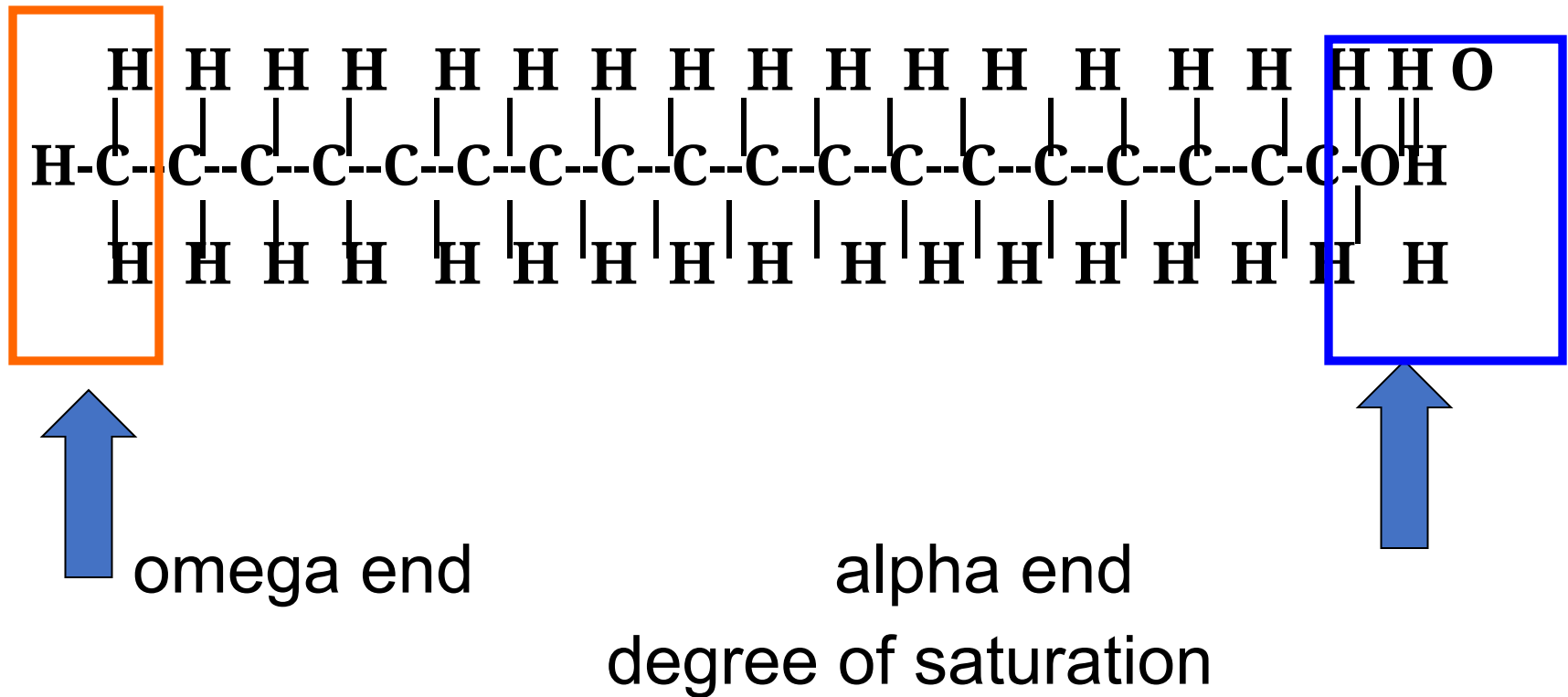


## **Properties of Unsaturated Fatty Acids**

- Contain one or more double C=C bonds
- Nonlinear chains do not allow molecules to pack closely
- Few interactions between chains
- Low melting points
- Liquids at room temperature

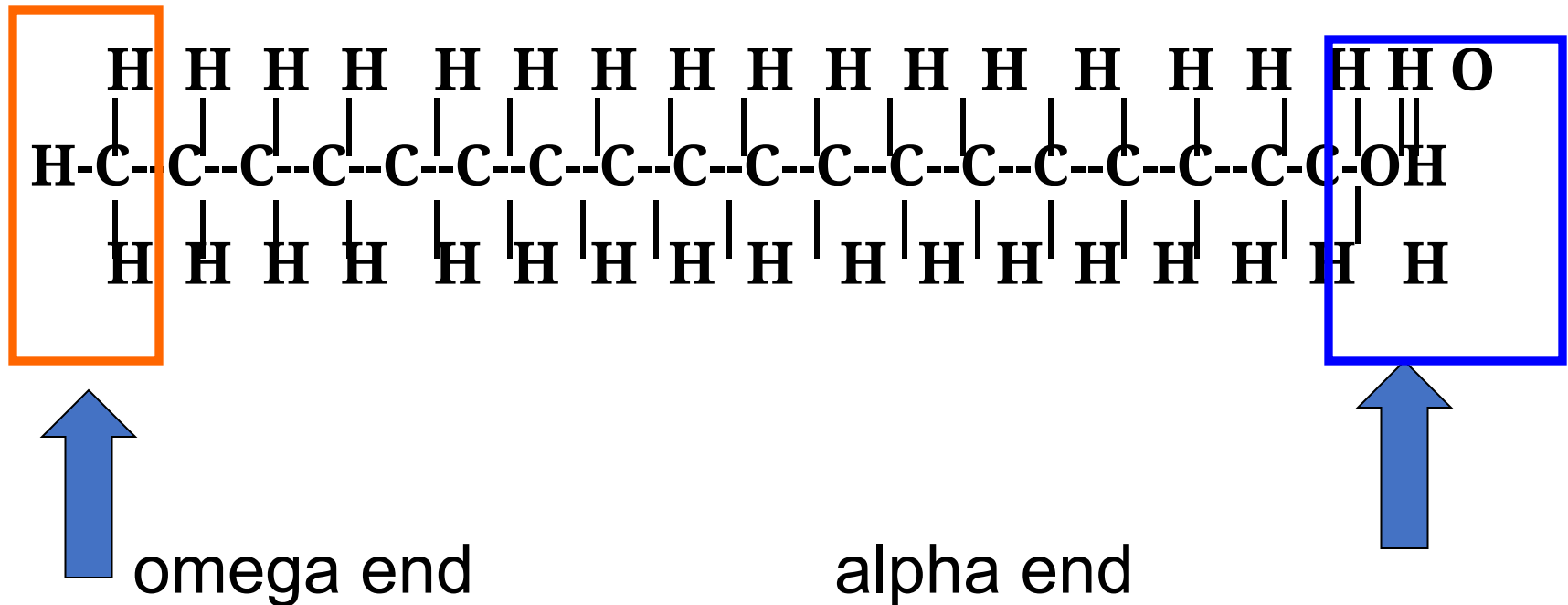


# Fatty Acid Structure



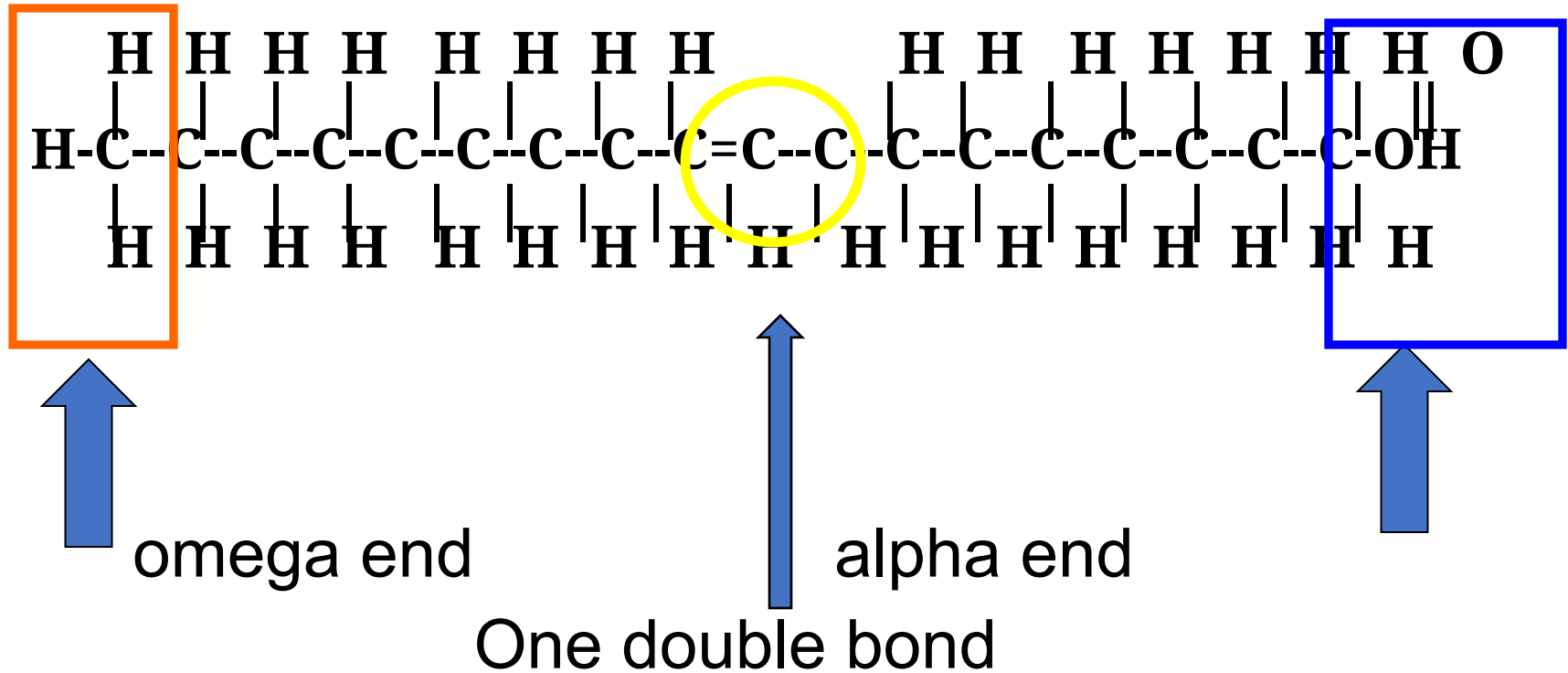


# Saturated Fatty Acid Structure

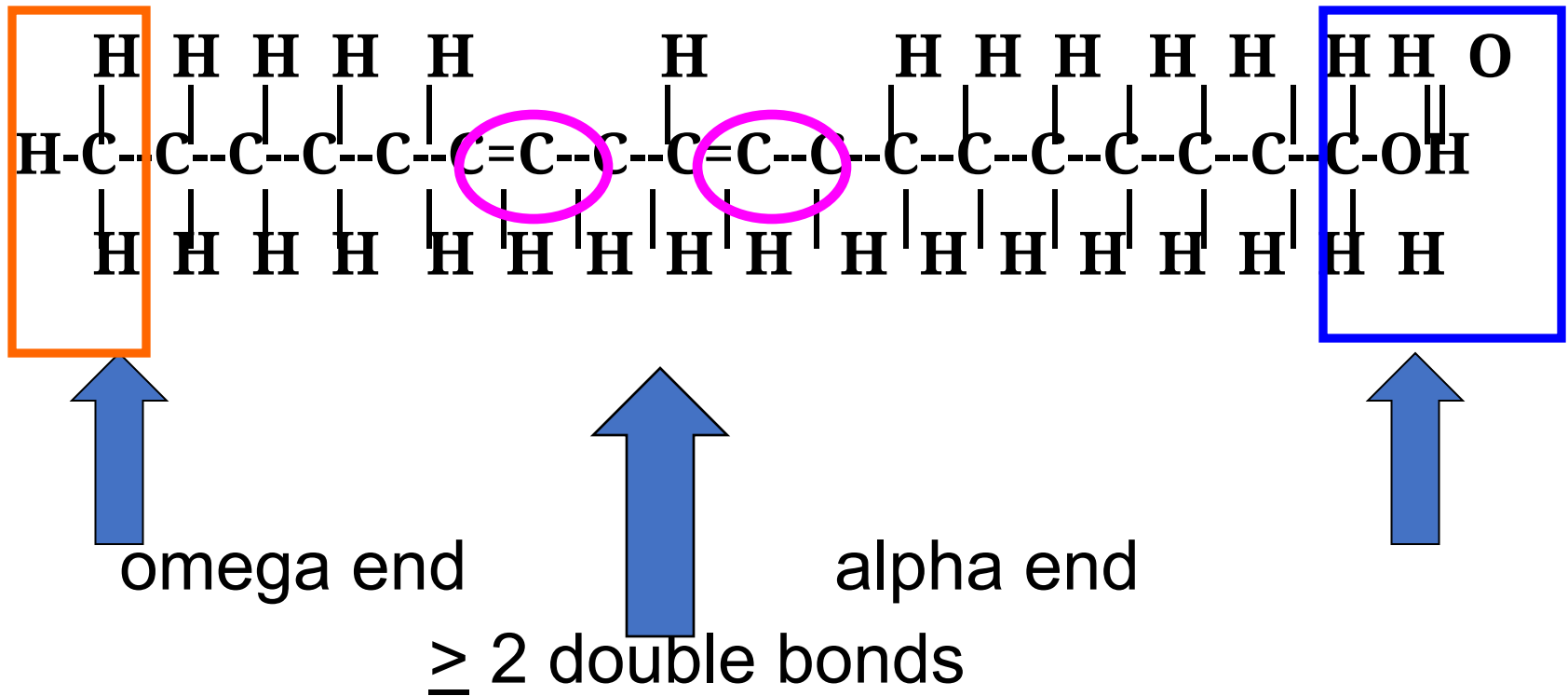


degree of saturation: single carbon bond

# Monounsaturated Fatty Acid Structure



# Polyunsaturated Fatty Acid Structure



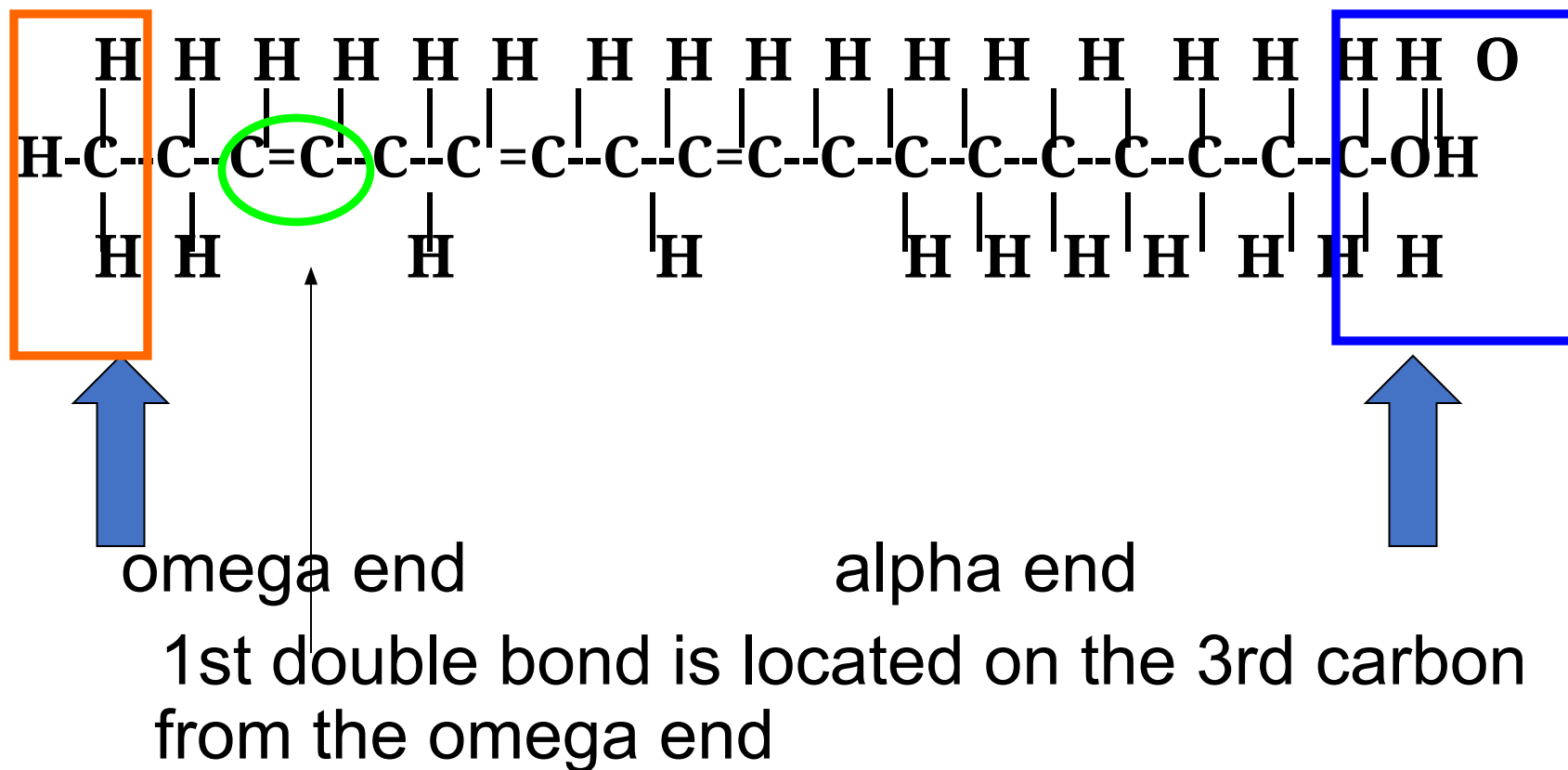
## Chain Length of Fatty Acids

- Long chain FA  $\geq 12$  Carbons
- Medium chain FA 6 - 10 Carbons
- Short chain FA  $< 6$  Carbons

## Essential Fatty Acids

- Must be eaten
- Body can only make double bonds after the 9th carbon from the omega end
- Needed for immune function, vision, cell membrane, and production of hormone-like compounds

# Essential Fatty Acid- Omega-3 (alpha-linolenic acid)



## **Omega-3 Fatty Acid**

Primarily from fish oil

Also found in canola or soybean oil

Eicosapentaenoic acid (EPA) and  
docosahexaenoic acid (DHA) are related  
Metabolized to form eicosanoids

## **Omega-6 Fatty Acid**

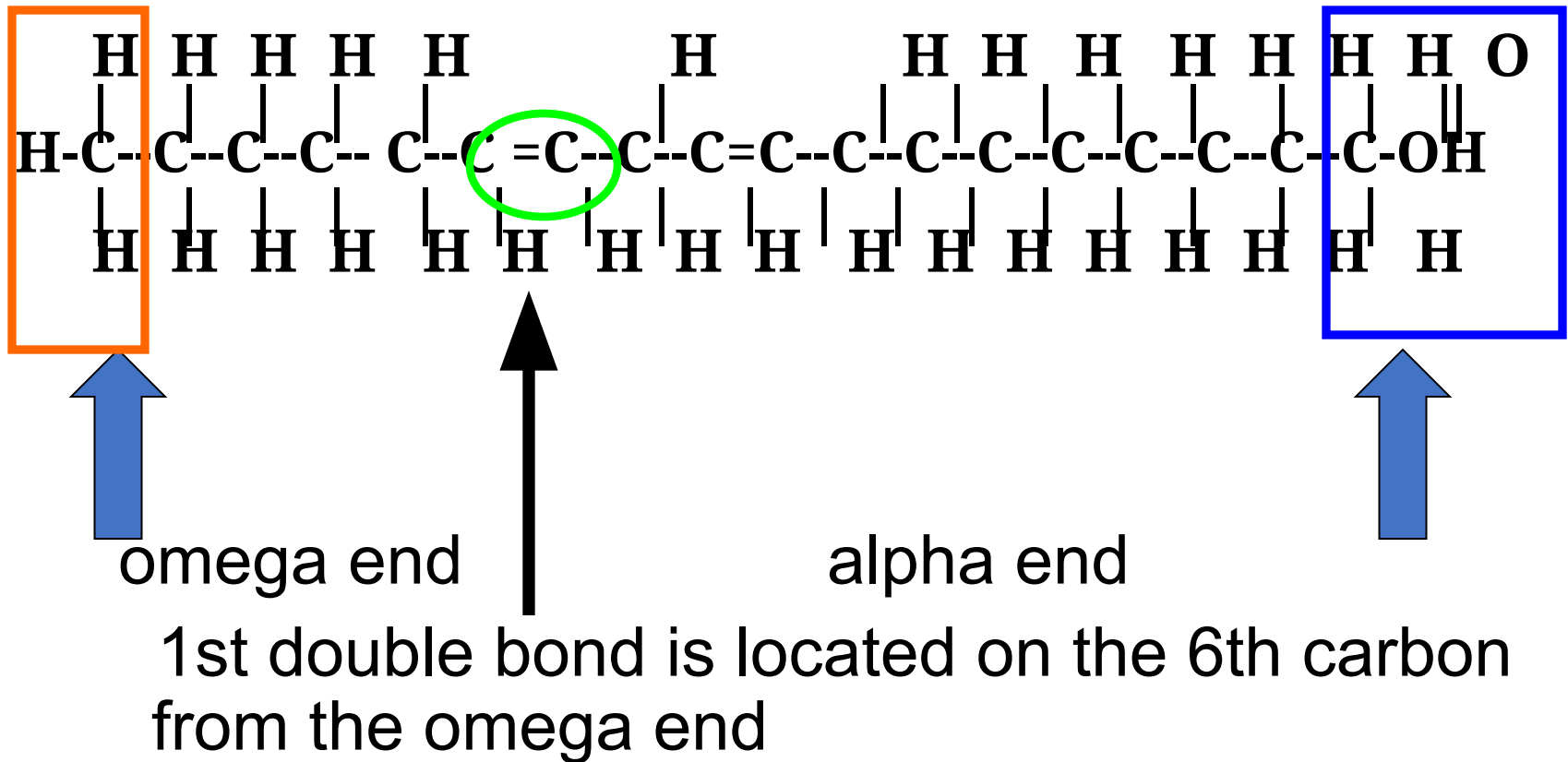
Found in vegetable oils

Only need ~ 1 tablespoon a day

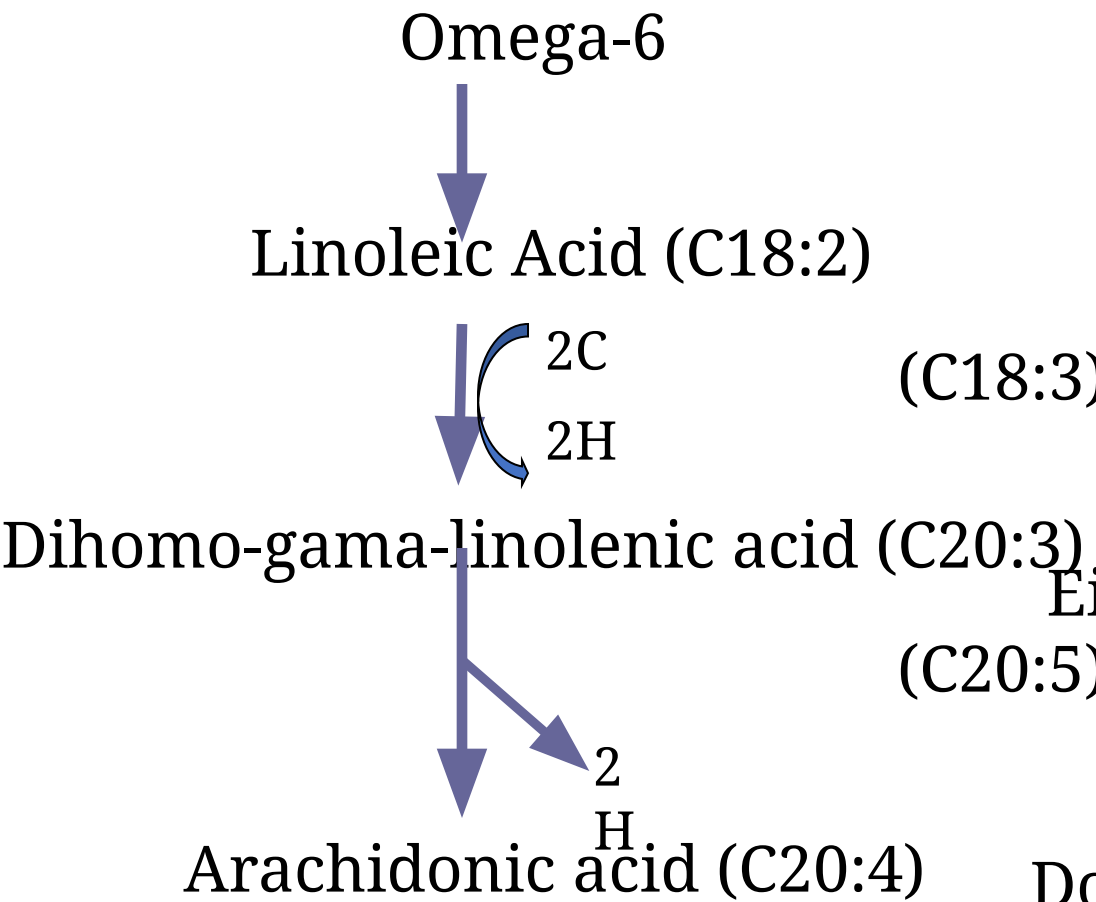
Arachidonic acid can be made from omega-6

Metabolized to form eicosanoids

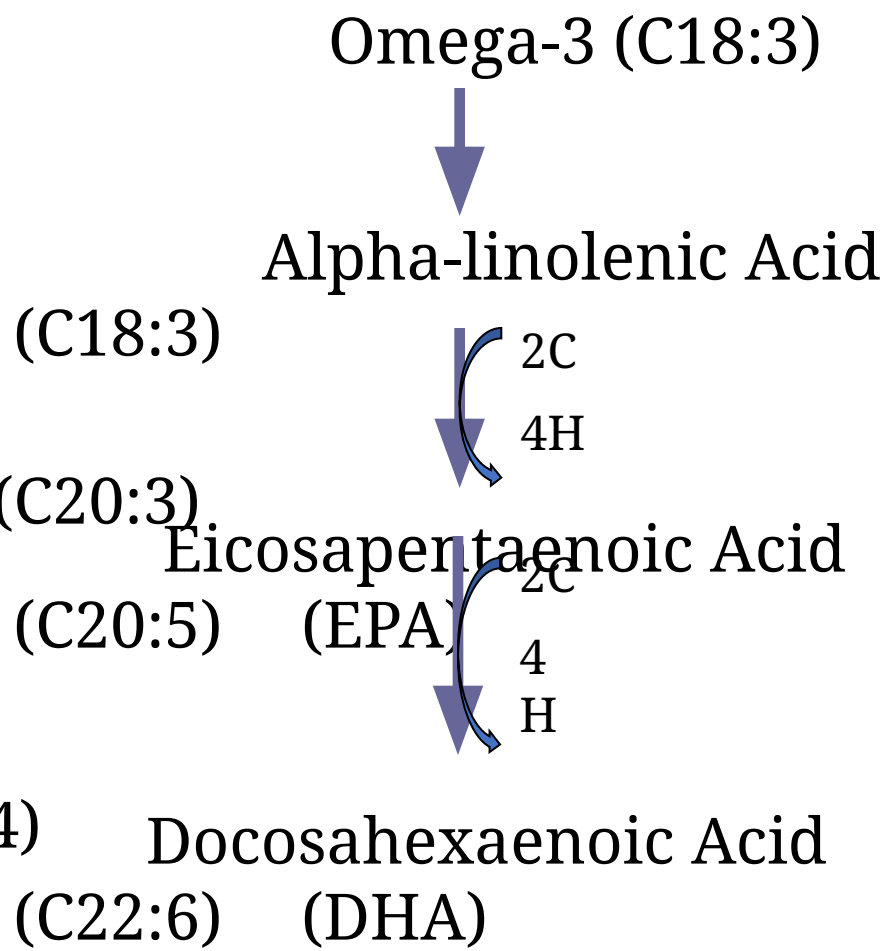
# Essential Fatty Acid- Omega-6 (linoleic acid)



# Omega-6 Fatty Acid



# Omega-3 Fatty Acids





# Eicosanoids

- A group of hormone-like compounds
- Regulates blood pressure, childbirth, clotting, immune responses, inflammatory responses, & stomach secretions
- By-pass the blood stream and work in the area of origin.
- **Eicosanoids Have Different Effects:**
- Omega-6 eicosanoids; Arachidonic acid
  - increase blood clotting
  - increase inflammatory responses
- Omega-3 eicosanoids, DHA, EPA
  - decrease blood clotting
  - reduce heart attack
  - excess may cause hemorrhagic stroke
- Eicosanoid has different effect on different tissues

# **Signs and Symptoms of Essential Fatty Acids Deficiency**

- peeling, itchy skin
- Diarrhea
- Infections
- Retarded growth and wound healing
- Anemia

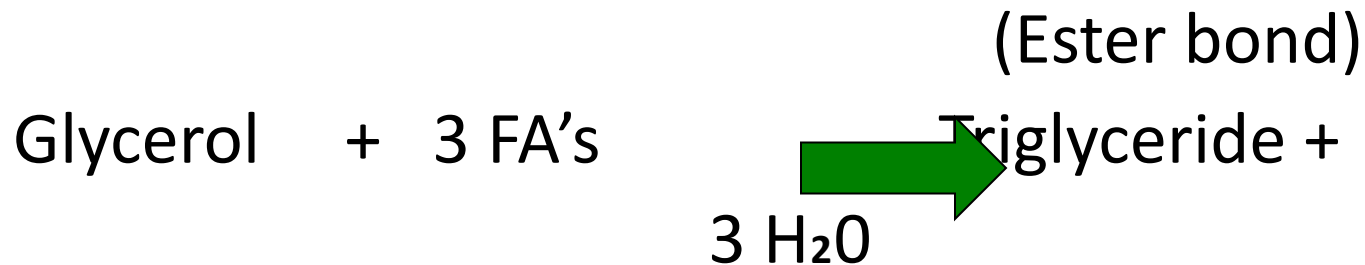
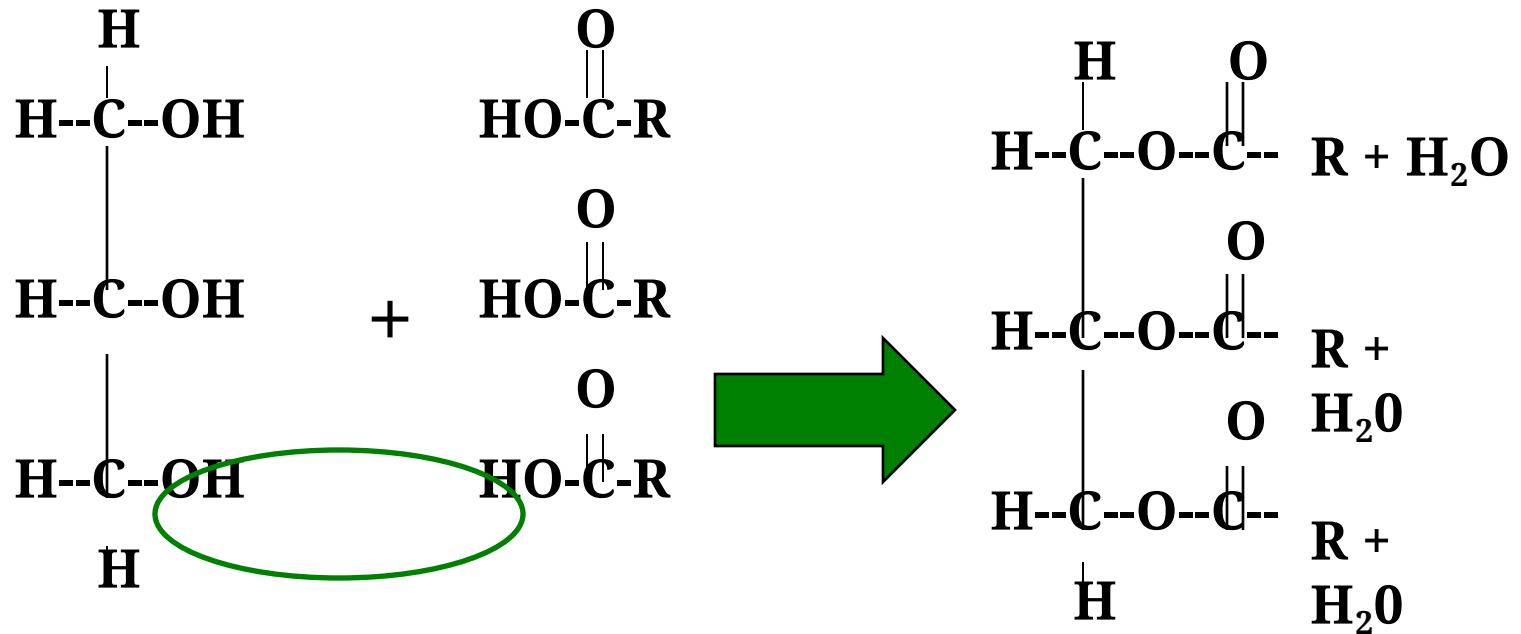
# Sources of Dietary Lipids

Dietary fat	Cholesterol (mg/tbsp)	Breakdown of fatty-acid content (normalized to 100%)			
Canola oil	0	6%	22%	10%	62%
Safflower oil	0	10%	77%	Trace	13%
Sunflower oil	0	11%	69%		20%
Corn oil	0	13%	61%		25%
Olive oil	0	14%	8%	- 1%	77%
Soybean oil	0	15%	54%	7%	24%
Margarine	0	17%	32%	- 2%	49%
Peanut oil	0	18%	33%		49%
Vegetable shortening	0	28%	26%	- 2%	44%
Palm oil	0	45%	12%	- 1%	37%
Palm kernel oil	0	52%	10%	- 1%	11%
Coconut oil	0	92%	2%		6%
Lard	12	41%	11%	- 1%	47%
Beef fat	14	52%	3%	- 1%	44%
Butter fat	33	66%	2%	- 2%	30%

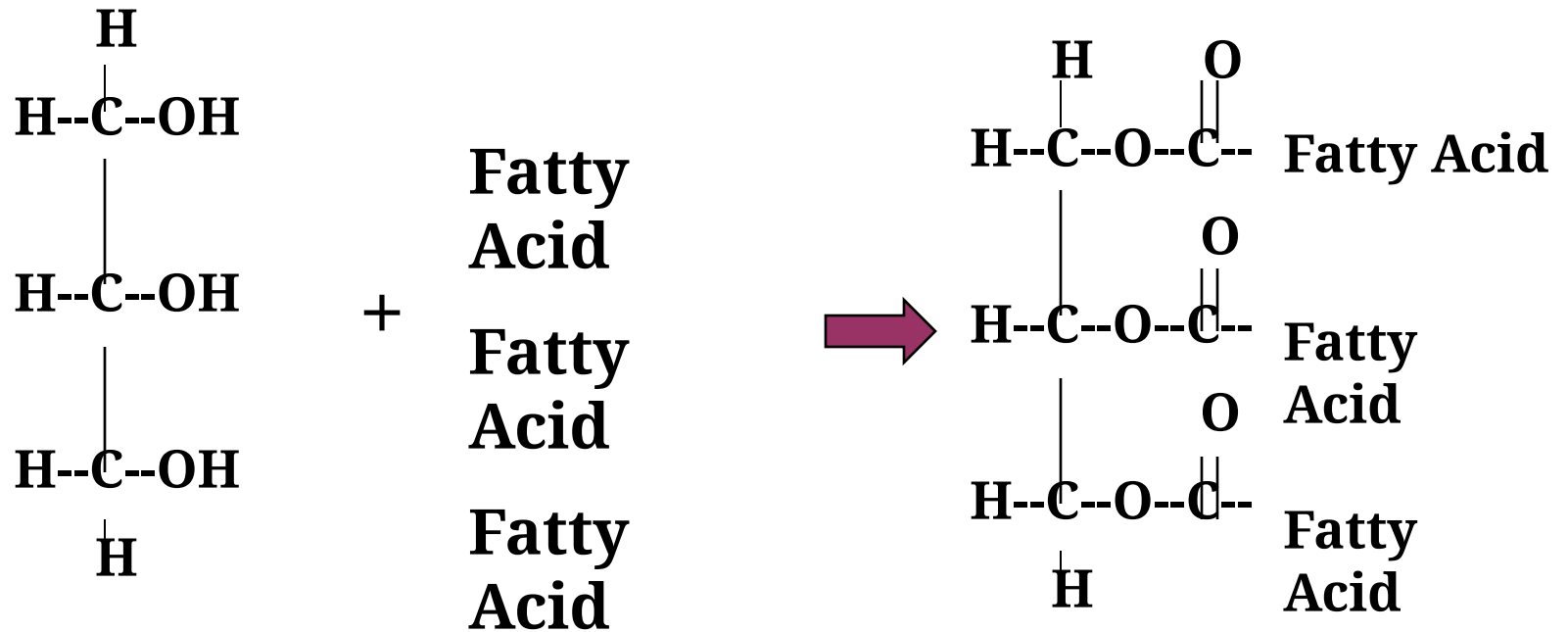
Polyunsaturated fat

Saturated fatty acid 
  Linoleic acid 
  Alpha-linolenic acid 
  Monounsaturated fatty acid 
 

# Triglycerides



# Triglycerides



esterification/reesterification



desterification



# Waxes

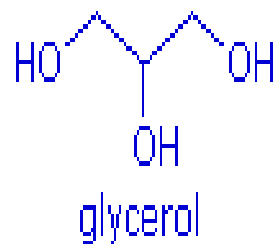
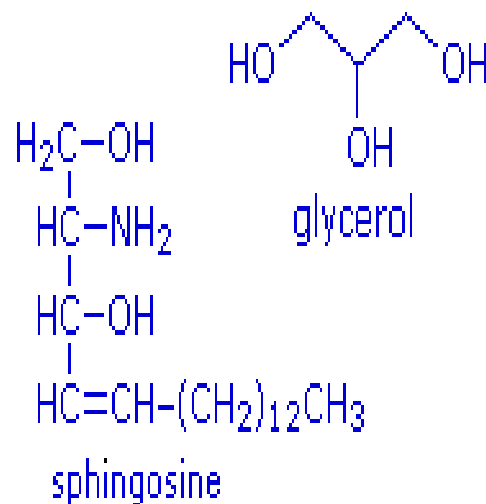
- Waxes are esters of fatty acids with long chain monohydric alcohols (one hydroxyl group). Natural waxes are often mixtures of such esters, and may also contain hydrocarbons. The formulas for three well known waxes are given below:
- **Spermaceti**      $\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2-(\text{CH}_2)_{15}\text{CH}_3$
- **Beeswax**         $\text{CH}_3(\text{CH}_2)_{24}\text{CO}_2-(\text{CH}_2)_{29}\text{CH}_3$
- **carnuba wax**    $\text{CH}_3(\text{CH}_2)_{30}\text{CO}_2-(\text{CH}_2)_{33}\text{CH}_3$
- Waxes are widely distributed in nature.
- The leaves and fruits of many plants have waxy coatings, which may protect them from dehydration and small predators.
- The fine hair of birds and the fur of some animals have similar coatings which serve as a water repellent.

# Phospholipids

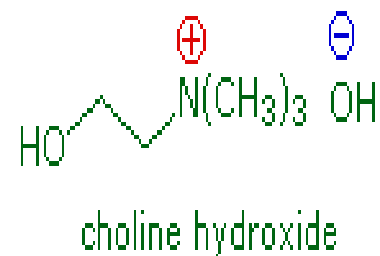
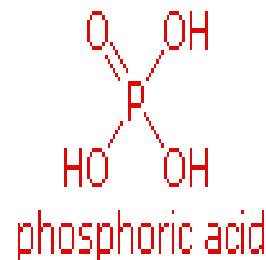
- Phospholipids are the main constituents of cell membranes. They resemble the triglycerides in being ester or amide derivatives of glycerol or sphingosine with fatty acids and phosphoric acid. The phosphate moiety of the resulting phosphatidic acid is further esterified with ethanolamine, choline or serine in the phospholipid itself.

# Structures of some of Phospholipids components

## Phospholipid Components



Fatty Acids  
saturated &  
unsaturated

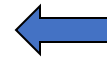
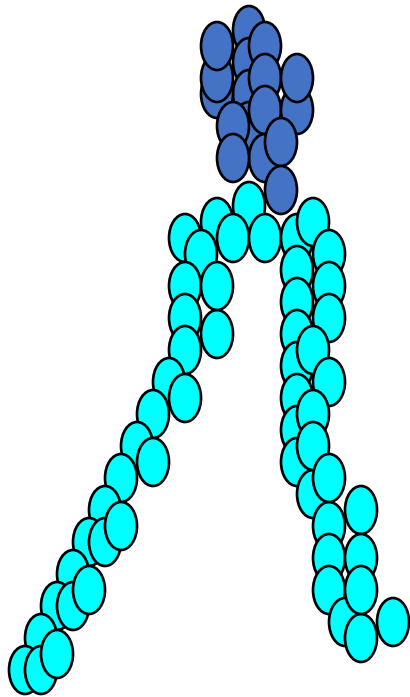




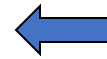
# Phospholipids

- Built on a glycerol backbone
- Has at least one fatty acid replaced with phosphorus containing compound
- Found in body
- Synthesized by the body as needed.
- **Functions of Phospholipids:**
- Makes up cell membrane
- Eicosanoid synthesis
- Emulsifier
- Bile acids
- Lecithins

# Emulsifier

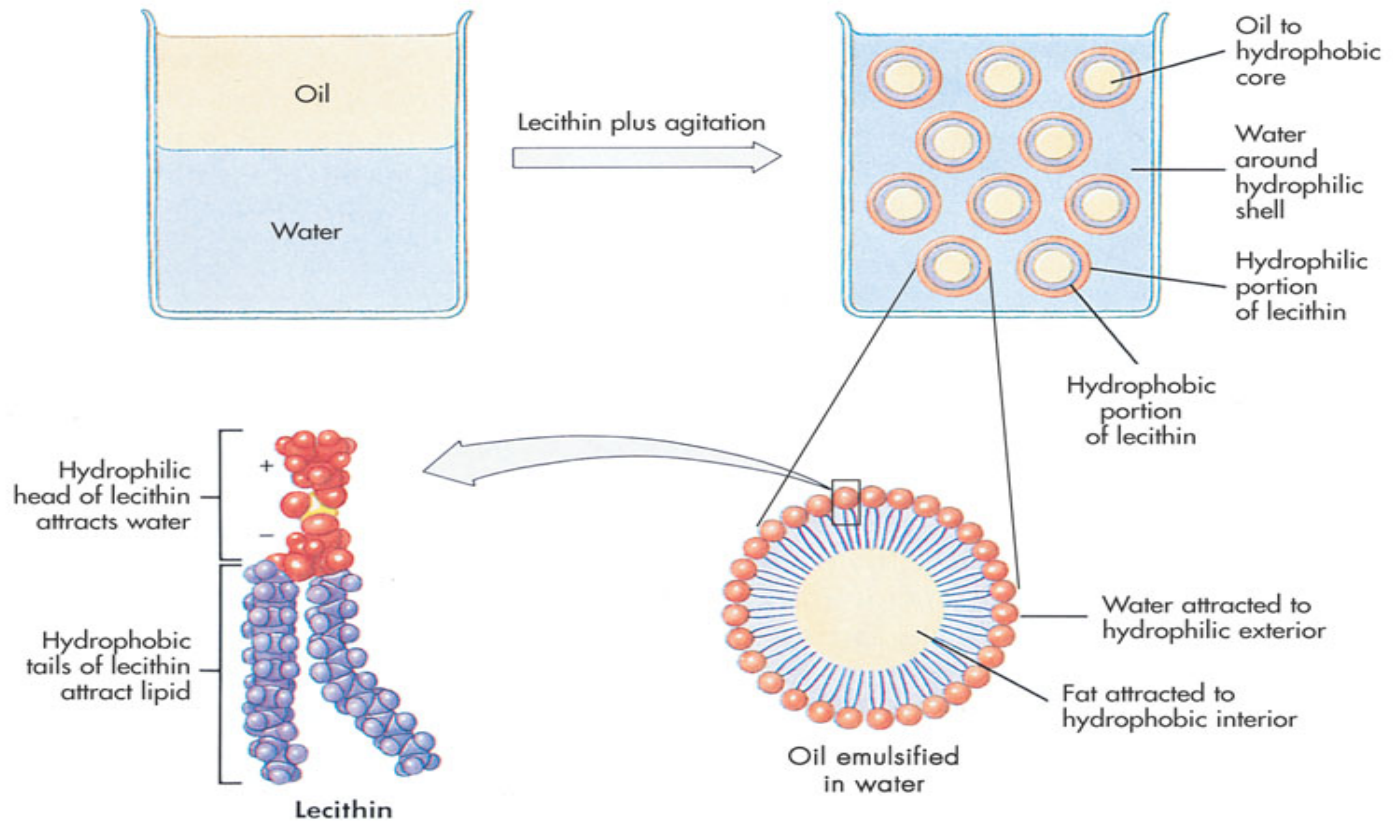


Hydrophilic end  
(attracts water)



Hydrophobic end  
(attracts lipid)

# Emulsification

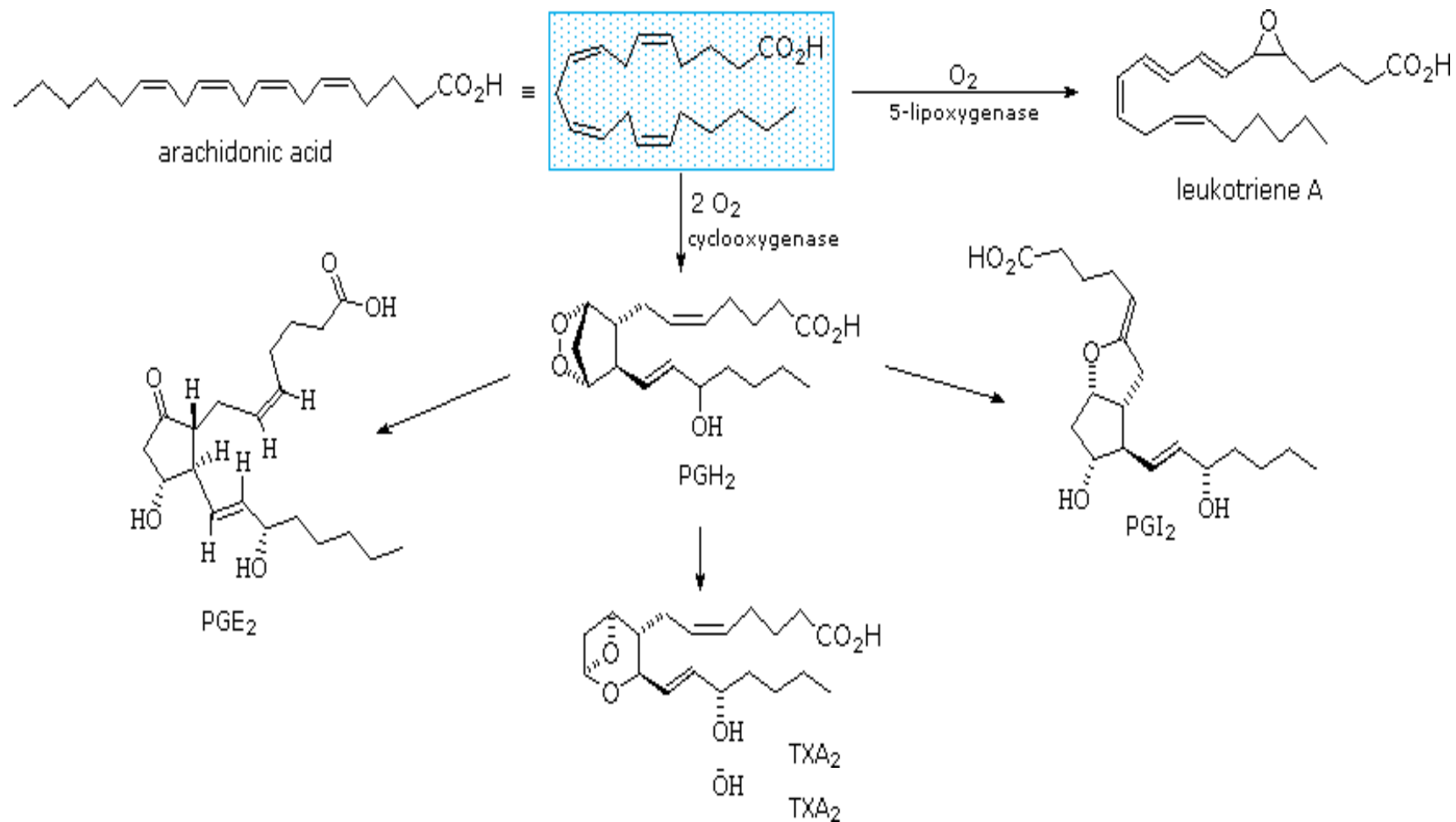


# Sterols

- A multi-ringed structure
- Do not have a glycerol backbone
- Waxy substance
- Do not readily dissolve in water
- Cholesterol is a sterol
- **Functions of Cholesterol**
- Essential component of cell membrane
- Produced by the liver
- Found only in animal products
- Forms important hormones
- Estrogen, testosterone, vitamin D
- Precursor to bile acids

# Prostaglandins, Thromboxanes & Leukotrienes

- The members of this group of structurally related natural hormones have an extraordinary range of biological effects.
- They can lower gastric secretions, stimulate uterine contractions, lower blood pressure, influence blood clotting and induce asthma-like allergic responses.
- Because their genesis in body tissues is tied to the metabolism of the essential fatty acid arachadonic acid (5,8,11,14-eicosatetraenoic acid) they are classified as **eicosanoids**.
- Many properties of the common drug aspirin result from its effect on the cascade of reactions associated with these hormones.



# VOLATILE OILS

- Volatile or essential oils are volatile in steam.
- They differ entirely in both chemical and physical properties from fixed oils.
- They are secreted in:
  - oil cells e.g. Cinnamon
  - Oil glands e.g. Clove
  - Secretion ducts (vittae) e.g. Anise
  - Glandular hairs e. g. Chamomile
- They are frequently associated with other substances such as gums (oleo gum) and resins (oleoresin) or both (oleo gum resin)
- They tend to resinify on exposure to air.

Natural essential oil constituents play an important role in cancer prevention and treatment. Essential oil constituents from aromatic herbs and dietary plants include monoterpenes, sesquiterpenes, oxygenated monoterpenes, oxygenated sesquiterpenes and phenolics among others. Various mechanisms such antioxidant, antimutagenic and antiproliferative, enhancement of immune function and surveillance, enzyme induction and enhancing detoxification, modulation of multidrug resistance and synergistic mechanism of volatile constituents are responsible for their chemopreventive properties.



Essential oils or volatile odoriferous oil, are aromatic oily liquids extracted from different parts of plants, as leaves, peels, barks, flowers, buds, seeds, and so on. They can be extracted from plant materials by several methods, steam distillation, expression ....etc. Among all methods, for example, steam distillation method has been widely used, especially for commercial scale production. Essential oils have been widely used as food flavors. Essential oils found in many different plants, especially the aromatic plants, vary in odor and flavor, which are governed by the types and amount of constituents present in oils.

Parts of plant material containing essential oils as shown in table:

Leaves	Basil, common sage, eucalyptus, mint, peppermint, pine, rosemary, tea tree, thyme.
Seeds	Almond, anise, cardamom, coriander, cumin, nutmeg, fennel
Wood	Sandalwood
Bark	Cassia, cinnamon, sassafras, katrafay
Berries	Allspice, juniper
Resin	Frankincense, myrrh
Flowers	Chamomile, Clove, cumin,
Peel	grapefruit, lemon, orange, mandarin
Root	Ginger, turmeric.
Fruits	nutmeg, black pepper

## **Extraction of Essential Oils**

Essential oils can be extracted from several plants with different parts by various extraction methods. The manufacturing of essential oils, and the method used for essential oil extraction are normally dependent on botanical material used.

Extraction method is one of prime factors that determine the quality of essential oil. Inappropriate extraction procedure can lead to the damage or alter action of chemical signature of essential oil. This results in the loss in bioactivity and natural characteristics. For severe case, discoloration, off-odor/flavor as well as physical change such as the increased viscosity can occur. Those changes in extracted essential oil must be avoided. Extraction of essential oils can be carried out by various means, as shown in Table:

Extraction methods	Plants
Solvent extraction – <i>Solvent</i>	sage ( <i>Salvia officinalis</i> ), lemon( <i>Citrus x limon</i> )
– <i>Supercritical CO<sub>2</sub></i>	rosemary ( <i>Rosmarinus officinalis</i> ), fennel( <i>Foeniculum vulgare</i> ), anise ( <i>Pimpinella anisum</i> ), cumin seed ( <i>Cuminum cyminum</i> )
– <i>Subcritical water</i>	Coriander seeds ( <i>Coriandrum sativum</i> L.)

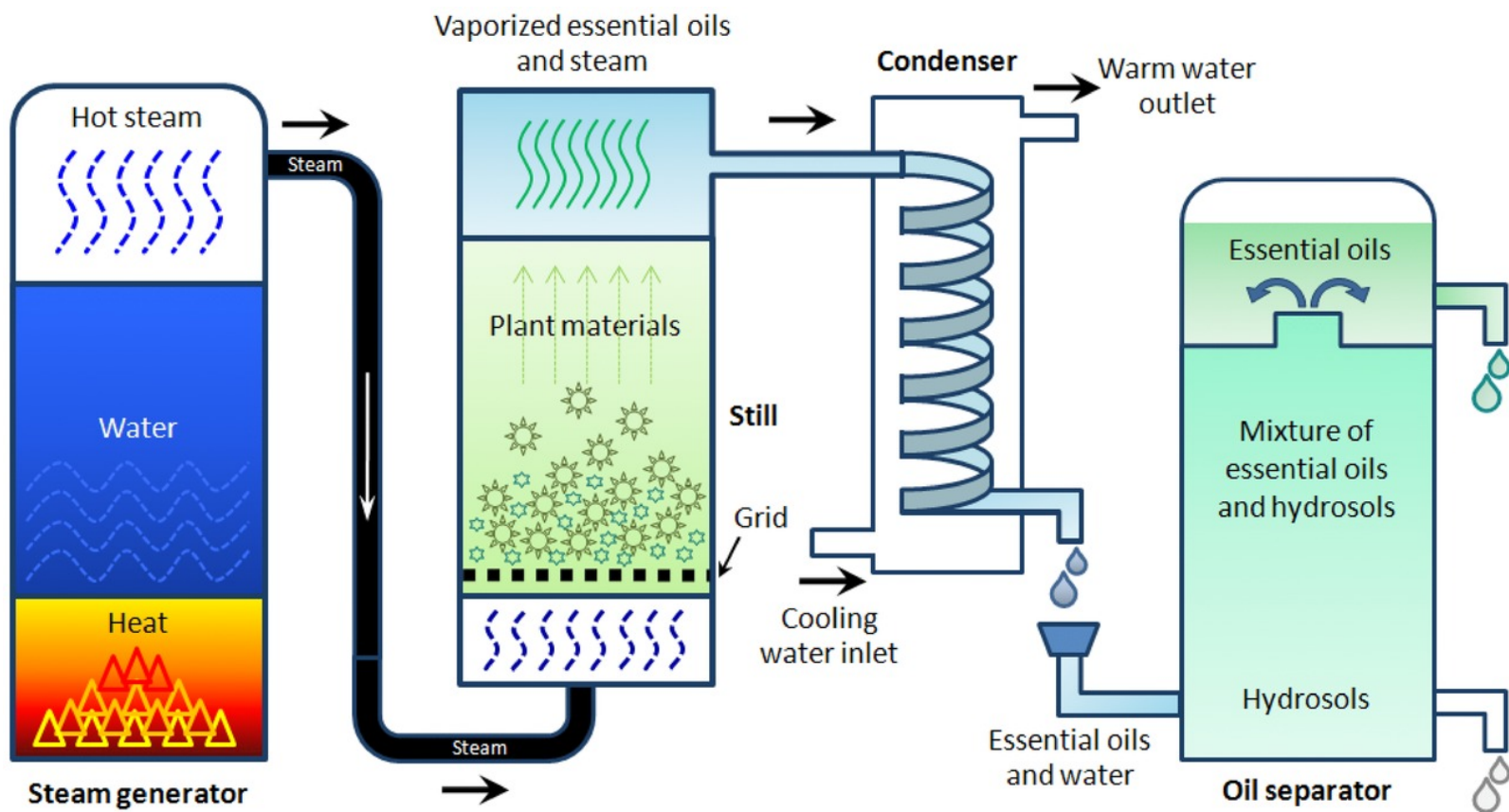
# **Distillation**

## **Steam distillation**

Steam distillation is the most widely used method for plant essential oil extraction, the proportion of essential oils extracted by steam distillation is 93% and the remaining 7% can be further extracted by other methods.

Basically, the plant sample is placed in boiling water or heated by steam.

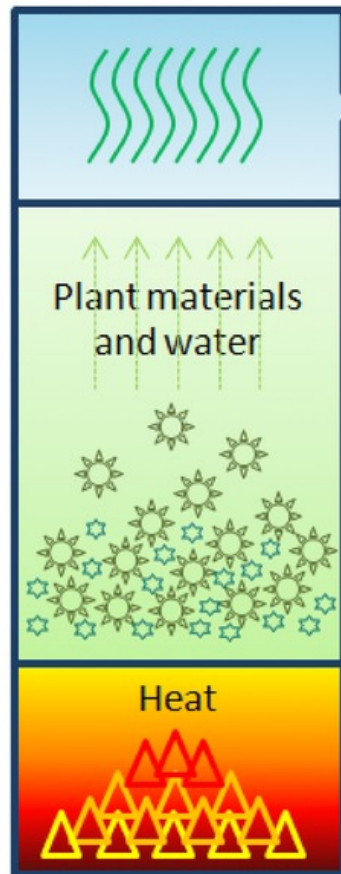
As a consequence, the aromatic compounds or essential oils from plant material are released. The temperature of heating must be enough to break down the plant material and release aromatic compound or essential oil. A new process design and operation for steam distillation of essential oils to increase oil yield and reduce the loss of polar compounds in wastewater was developed. The system consists of a packed bed of the plant materials, which sits above the steam source. Only steam passes through it and the boiling water is not mixed with plant material. Also, water-soluble compounds are dissolved into the aqueous fraction of the condensate at a lower extent.



- **Hydrodistillation**

- HD has become the standard method of essential oil extraction from plant material such as wood or flower, which is often used to isolate nonwater-soluble natural products with high boiling point. The process involves the complete immersion of plant materials in water, followed by boiling. This method protects the oils extracted to a certain degree since the surrounding water acts as a barrier to prevent it from overheating. The steam and essential oil vapor are condensed to an aqueous fraction. The advantage of this technique is that the required material can be distilled at a temperature below 100 °C. An advanced HD technique utilizing a microwave oven in the extraction process, MAHD was superior in terms of saving energy and extraction time (75 min, compared to 4 h in HD). No changes in the compounds of the essential oils obtained were found in comparison with HD.

Vaporized essential oils  
and steam



Steam generator

Still

Condenser



Warm water  
outlet



Cooling  
water inlet



Essential oils  
and water



Essential oils



Mixture of  
essential oils  
and hydrosols

Hydrosols

Oil separator





- **Hydrodiffusion**

- Hydrodiffusion extraction is a type of steam distillation, which is only different in the inlet way of steam into the container of still. This method is used when the plant material has been dried and is not damaged at boiling temperature. For hydrodiffusion, steam is applied from the top of plant material, whereas steam is entered from the bottom for steam distillation method. The process can also be operated under low pressure or vacuum and reduces the steam temperature to below 100 °C. Hydrodiffusion method is superior to steam distillation because of a shorter processing time and a higher oil yield with less steam used. In the isolation of essential oil from rosemary leaves (*R. officinalis*). The MHG (microwave HD) method exhibits the excellent advantages over traditional alternatives including shorter isolation times (15 min against 3 h for HD), environmental impact (energy cost is fairly higher to perform HD than that required for rapid MHG isolation), cleaner features (no residue generation and no water or solvent used), increased antimicrobial and antioxidant activities.

## Solvent extraction

Conventional solvent extraction has been implemented for fragile or delicate flower materials, which are not tolerant to the heat of steam distillation. Different solvents including acetone, hexane, petroleum ether, methanol, or ethanol can be used for extraction.

For general practice, the solvent is mixed with the plant material and then heated to extract the essential oil, followed by filtration. Subsequently, the filtrate is concentrated by evaporation. The concentrate is resin (resinoid), or concrete (a combination of wax, fragrance, and essential oil). From the concentrate, it is then mixed with pure alcohol to extract the oil and distilled at low temperatures. The alcohol absorbs the fragrance and when the alcohol is evaporated, the aromatic absolute oil is remained.

However, this method is a relatively time-consuming process, thus making the oils more expensive than other methods.

Other methods as:

Supercritical carbon dioxide

Subcritical water

Solvent-free microwave

# Production and Uses of Volatile Oils

There are about 100 commercially valuable volatile oils directly derived from plants.

- Volatile oils are used:

- 1- For their therapeutic action: antiseptic e.g. thyme and clove, carminative e.g. Mentha
- 2- Flavoring (e.g. oil of lemon),
- 3- in perfumery (e.g. oil of rose)
- 4- starting materials for the synthesis of other compounds (e.g. oil of turpentine).

- **Role of Essential Oils as Food Additives**

Essential oils from plants have been known to act as natural additives, for example, antimicrobial agents, antioxidant, and so on. Their activities vary with source of plants, chemical composition, extraction methods, and so on. Due to the unique smell associated with the volatiles, this may limit the use of essential oil in some foods since it may alter the typical smell/flavor of foods.

- **Antimicrobial activity**

The ability of plant essential oils to protect foods against pathogenic and spoilage microorganisms has been reported. Among chemical components in several essential oils, carvacrol has been shown to exert a distinct antimicrobial action, carvacrol is the major component of essential oil from oregano (60% - 74% carvacrol) and thyme (45% carvacrol). It has a broad spectrum of antimicrobial activity against most gram-positive and gram-negative bacteria, carvacrol disintegrates the outer membrane of gram-negative bacteria, releasing lipopolysaccharides and increasing the permeability of the cytoplasmic membrane. In general, the higher antimicrobial activity of essential oils is observed on gram-positive bacteria than gram-negative bacteria .

## Antioxidant activity

Several compounds in essential oils have the structure mimicking the well-known plant phenols with antioxidant activity. Among the major compounds available in the oil, thymol and carvacrol were reported to possess the highest antioxidant activity.

Essential oils have several modes of actions as antioxidant, such as prevention of chain initiation, free radical scavengers, reducing agents, termination of peroxides, prevention of continued hydrogen abstraction. With those functions, essential oils can serve as the potential natural antioxidants, which can be used to prevent lipid oxidation in food systems. Phenolics are organic compounds consisting of hydroxyl group (-OH) attached directly to a carbon atom that is a part of aromatic ring. The hydrogen atom of hydroxyl group can be donated to free radicals, thereby preventing other compounds to be oxidized

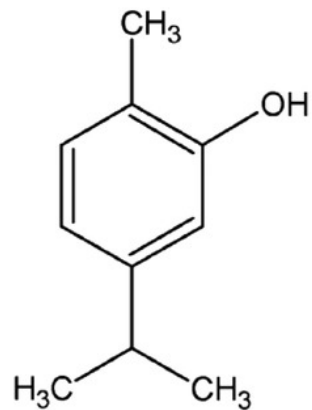
- For therapeutic purposes they are administered as inhalations (e.g. eucalyptus oil), orally (e.g. peppermint oil), as gargles and mouthwashes (e.g. thymol) and transdermally (many essential oils including those of lavender, rosemary and bergamot are employed in the practice of aromatherapy).
- Those oils with a high phenol content, e.g. clove and thyme have antiseptic properties, whereas others are used as carminatives. Oils showing antispasmodic activity, and much used in popular medicine. e.g. fennel, mentha, caraway, chamomile, anise, rosemary.

# Composition of Volatile Oils

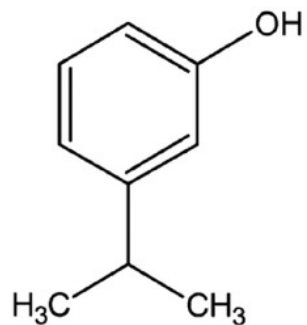
- Volatile oils are generally mixtures of hydrocarbons and oxygenated compounds derived from these hydrocarbons.
- The odour and taste of volatile oils is mainly determined by these oxygenated constituents, which are to some extent soluble in water but more soluble in alcohol.



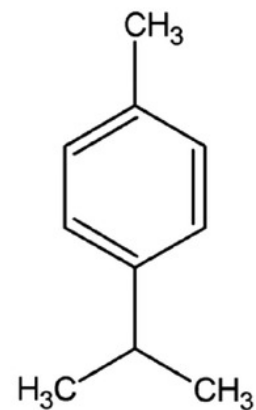
- Practically all volatile oils consist of chemical mixtures that are often quite complex; they vary widely in chemical composition.
- Almost any type of organic compound may be found in volatile oils (hydrocarbons, alcohols, ketones, aldehydes, ethers, oxides, esters, and others). “usually volatile oils are classified according to the type of organic compounds”.
- It is not uncommon for a volatile oil to contain over 200 components, and often the trace constituents are essential to the odor and flavor. The absence of even one component may change the aroma.



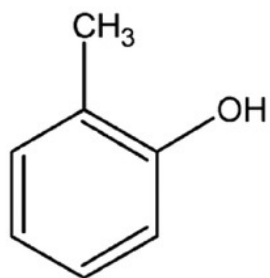
Carvacrol



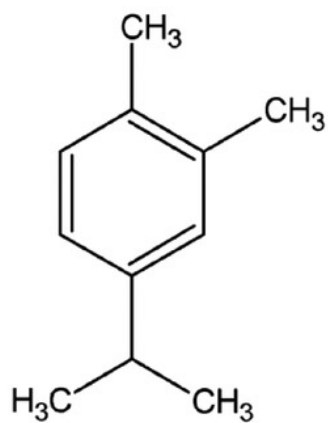
3-isopropylphenol



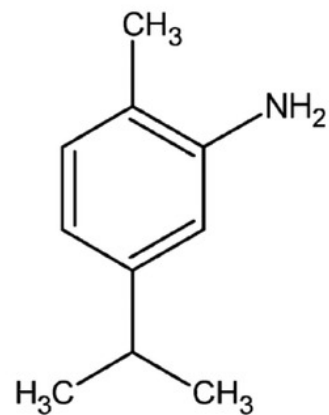
*p*-cymene



o-cresol



3,4-dimethylcumene



2-amino-*p*-cymene

## Terpene hydrocarbons:

The hydrocarbons are the molecule, constituting of H and C atoms arranged in chains. These hydrocarbons may be acyclic, alicyclic (monocyclic, bicyclic, or tricyclic), or aromatic. Terpenes are the most common class of chemical compounds found in essential oils. Terpenes are made from isoprene units (several 5 carbon base units,  $C_5$ ), which are the combinations of 2 isoprene units, called a “terpene unit.” Essential oils consist of mainly monoterpenes ( $C_{10}$ ) and sesquiterpenes ( $C_{15}$ ), which are hydrocarbons with the general formula  $(C_5H_8)_n$ . The diterpenes ( $C_{20}$ ), triterpenes ( $C_{30}$ ), and tetraterpenes ( $C_{40}$ ) exist in essential oils at low concentration.

## Oxygenated compounds (Terpenoids)

These compounds are the combination of C, H, and O. Oxygenated compounds can be derived from the terpenes, in which they are termed “terpenoids.” Some oxygenated compounds prevalent in plant essential oils, as

- Phenols*: thymol, eugenol, carvacrol, thymol.
- Alcohols: Monoterpene alcohol: borneol,  $\alpha$ -terpineol.  
Sesquiterpenes alcohol: santalol,  $\alpha$ -santalol.
- Aldehydes*: citral, citronellal, cinnamaldehyde, benzaldehyde.
- Ketones*: carvone, menthone, fenchone, camphor, thujone.
- *Esters*: linalyl acetate, citronellyl acetate, geranyl acetate.
- *Oxides*: 1,8-cineole, bisabolone oxide, linalool oxide.
- *Lactones*: bergaptene, psoralen, aesculatine.
- Ethers*: anethole, myristicin.
- Different constituents in essential oils exhibit varying smell or flavor.

# Physical Properties

Although volatile oils differ greatly in their chemical constitution, they have a number of physical properties in common:

1. They possess characteristic odors.
2. They are characterized by high refractive indices.
3. Most of them are optically active.
4. Their density is generally lower than that of water (the essential oils of sassafras, clove, or cinnamon are the exceptions).
5. As a rule, volatile oils are immiscible with water, but they are sufficiently soluble to impart their odor to water. The aromatic waters are dependent on this slight solubility.

# Difference between Volatile and Fixed Oils

- Several points of differentiation exist between volatile oils and fixed oils.
1. Volatile oils can be distilled from their natural sources.
  2. Volatile oils do not consist of glyceryl esters of fatty acids. Hence, they do not leave a permanent grease spot on paper and cannot be saponified with alkalies.
  3. Volatile oils do not become rancid as do the fixed oils, but instead, on exposure to light and air, they oxidize and resinify.

# Preparation of volatile oils

- The principal methods used in the preparation of volatile oils from plants depend on:
  1. Distillation in water or steam.
  2. Scarification and expression.
  3. Extraction with solvents.
  4. Enzymatic hydrolysis (for glycosidic volatile oils e.g. mustard oil).
  5. Enfleurage (extraction of oils used in perfumery).

# Uses of drugs containing essential oils

- Pharmacy
- Perfumery
- Food technology
- Miscellaneous industries (as starting materials for the synthesis of the active principles of medicines, vitamins, and fragrances).



# 1- Clove (Caryophylli)

the dried flower buds of *Syzygium aromaticum*,  
F. Myrtaceae

## Active constituents:

1. Volatile oil (15 -20%) contains eugenol (85%).
2. Pyrogallol tannin.

## Uses:

1. Local anesthetic for toothache.
2. Antispasmodic and carminative.
3. Spice.
4. In manufacture of vanillin.



## 2- German chamomile

The dried flower heads of  
*Matricaria chamomilla* F.  
Compositae (Asteraceae).

**Active constituents:** 1- volatile oil  
contains matricarin which  
converted to chamazulene by  
heating.

2- flavonoid glycosides.

**Uses:** 1- carminative,  
antispasmodic.

2- tranquilizer.

3- local anti-inflammatory for sun  
burns and diaper rashes.



# 3- Anise Fruit

(Fructus Anisi, Aniseed)

The dried ripe fruits of *Pimpinella Anisum*  
F. Umbelliferae

**Active constituents:** 1- volatile oil  
containing anethol  
2- fixed oil and protein.

**Uses:** stimulant, carminative and flavoring  
agent.



# 4- Cinnamon Bark

(Cortex Cinnamomi)

The dried bark of the branches of the coppiced trees of *Cinnamomum zylanicum* F. Lauraceae.

**Active constituents:** 0.5-1% volatile oil contains cinnamaldehyde and eugenol  
Mucilage and tannins.

**Uses:** 1- carminative and flavoring agents  
2- Antiseptic and mild astringent.  
3- Emmenagogue.



## 5- Cardamom Seed

حبهان- حب الهال- الهيل

The dried ripe or nearly ripe seeds of  
*Elettaria cardamomum* F. Zingiberaceae.

**Active constituents:** 1- volatile oil contains terpinyl acetate and cineole.

2- starch, fixed oil and calcium oxalate

**Uses:** 1- flavoring agent in pharmaceutical industry.

2- spice





## 6- Mentha Herb (Peppermint)

The dried leaves and flowering tops of *Mentha piperita* F. Labiatae.



**Active constituents:** 1- volatile oil contains menthol  
2- tannin.

### Uses:

1. carminative, flavoring agent and aromatic stimulant.
2. Menthol is used in pharmaceutical preparations as local antipruritic, counter irritant and antiseptic.
3. Used in tooth paste, mouth wash and similar oral preparations.
4. Recently the oil is used for treatment of colitis.

## 7- Ginger, Zingiber

The dried rhizome of *Zingiber officinale* F.  
Zingiberaceae.

### Active constituents:

1. volatile oil contains monoterpenes (phellandrene, camphene, cineole, citral and borneol) and sesquiterpenes (zingiberene and bisabolene).
2. Resin, starch and mucilage.

### Uses:

1. carminative and stimulant.
2. Antiemetic.
3. Antirheumatic.
4. Condiment.



**Al Noor University College****Department of Pharmacy****Pharmacognosy**3<sup>rd</sup> Class, 1<sup>st</sup> Semester

Reference text: ***Robbers JE, Speedie MK, Tyler VE (Eds.); Pharmacognosy and Pharmacobiotechnology; latest edition.***

**Objectives:** This course is intended to study chemistry of natural product namely glycosides, volatile oils, fixed oils, tannins and resins. The course includes chemistry, pharmacology, uses of these constituents and plants containing these constituents.

No	Lecture title	hours
1.	Introduction: General biosynthesis pathways of secondary metabolites.	2
2.	Carbohydrates.	2
3.	Glycosides: Biosynthesis, physical and chemical properties; cardiac glycosides; saponin glycosides; anthraquinone glycosides; flavonoid glycosides; cyanophore glycosides.	5
4.	Glycosides: Isothiocyanate glycosides; aldehyde glycosides; alcoholic glycosides; phenolic glycosides; lactone glycosides; coumarins and chromones.	5
5.	Resins and resin combination; tannins.	2
6.	Lipids: fixed oils and waxes.	3
7.	Volatile oils: Introduction; chemistry of volatile oils; biosynthesis of volatile oils; hydrocarbons as volatile oils; alcohols as volatile oils; aldehydes as volatile oils.	4
8.	Ketones as volatile oils; Phenols as volatile oils; Oxides as volatile oils; Ester as volatile oils; Phenolic ethers as volatile oils.	3
9.	Non- medicinal toxic plants.	2
10.	Vitamins and Amino acids.	2



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# **A Biosynthetic Approach of Medicinal Natural Products**



# Plant Secondary Metabolites

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Secondary metabolites or secondary compounds are compounds that are not required for normal growth and development, and are not made through metabolic pathways common to all plants

Most plants have not been examined for secondary compounds and new compounds are discovered almost daily

Secondary compounds are grouped into classes based on similar structures, biosynthetic pathways, or the kinds of plants that make them. The largest such classes are the alkaloids, terpenoids, and phenolics

Secondary compounds often occur in combination with one or more sugars. These combination molecules are known as glycosides. Usually the sugar is a glucose, galactose or rhamnose. But some plants have unique sugars

Plants make a variety of less widely distributed compounds such as morphine, caffeine, nicotine, menthol, and rubber. These compounds are the products of secondary metabolism, which is the metabolism of chemicals that occurs irregularly or rarely among plants, and that have no known general metabolic role in plants

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# Functions of Secondary Compounds

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The most common roles for secondary compounds in plants are ecological roles that govern interactions between plants and other organisms

Many secondary compounds are brightly colored pigments like anthocyanin that color flowers red and blue. These attract pollinators and fruit and seed dispersers

Nicotine and other toxic compounds may protect the plant from herbivores and microbes

Other secondary compounds like rubber and tetrahydrocannabinol (THC) from cannabis plants have no known function in plants

**Biosynthesis:** Formation of a chemical compound by a living organism.

**Biogenesis:** Production or generation of living organisms from other living organisms.



- Organisms vary widely in their capacity to synthesize and transform chemicals. For instance, plants are very efficient at synthesizing organic compounds via photosynthesis from inorganic materials found in the environment, whilst other organisms such as animals and microorganisms rely on obtaining their raw materials in their diet, e.g. by consuming plants.

The pathways for generally modifying and synthesizing carbohydrates, proteins, fats, and nucleic acids are found to be essentially the same in all organisms, apart from minor variations.

These processes are collectively described as **primary metabolism**, with the compounds involved in the pathways being termed **primary metabolites**.

- Primary metabolism ( $\equiv$  Biochemistry)



# Secondary Metabolism

---

- ❑ **Secondary metabolism**, metabolic pathways that are not essential for growth, development or reproduction, but that usually have environmental function.
- ❑ **Secondary metabolites** are those chemical compounds in organisms that are not directly involved in the normal growth, development or reproduction of an organism. In this sense they are "secondary".
- ❑ Secondary metabolites, are found in only specific organisms, or groups of organisms, and are an expression of the individuality of species.
- ❑ Secondary metabolites are not necessarily produced under all conditions, and in the vast majority of cases the function of these compounds and their benefit to the organism is not yet known.



- Some secondary metabolites are produced for easily appreciated reasons, e.g.
  1. ~~As toxic materials providing defense against predators.~~
  2. As volatile attractants towards the same or other species.
  3. As coloring agents to attract or warn other species.
  
- Secondary metabolism ( $\equiv$  Natural products chemistry).
  
- **The building blocks**
- The building blocks for secondary metabolites are derived from primary metabolism.
  
- The number of building blocks needed is surprisingly few.



- The most important building blocks employed in the biosynthesis of secondary metabolites are derived from:
- 

1. **Acetyl coenzyme A (acetyl-CoA)**
2. **Shikimic acid**
3. **Mevalonic acid**
4. **1-deoxyxylulose 5-phosphate**
5. **Amino acids**

- **1. Acetate pathway**

- The form in which acetate is used in most of its important biochemical reactions is acetyl coenzyme A (acetyl-CoA).
  - **Acetyl-CoA** is formed by oxidative decarboxylation of the glycolytic pathway product pyruvic acid.
  - Important secondary metabolites formed from the acetate pathway includes:
    1. Phenols
    2. Prostaglandins
    3. Macrolide antibiotics
-

**Coenzyme A:** present in all living cells that functions as an acyl group carrier.





## 2. Shikimate pathway

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- Shikimic acid is produced from a combination of phosphoenolpyruvate, a glycolytic pathway intermediate, and erythrose 4-phosphate from the pentose phosphate pathway.
- The shikimate pathway leads to a variety of:
  1. Phenols
  2. Cinnamic acid derivatives
  3. Lignans
  4. Alkaloids

## 3. Mevalonate pathway

Mevalonic acid is itself formed from **three molecules of acetyl-CoA**, but the mevalonate pathway change acetate into a different series of compounds than does the acetate pathway.



## 4. Deoxyxylulose phosphate pathway

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- Deoxyxylulose phosphate arises from a combination of two glycolytic pathway intermediates, namely pyruvic acid and glyceraldehyde 3-phosphate.
- The mevalonate and deoxyxylulose phosphate pathways are together responsible for the biosynthesis of a vast array of terpenoid and steroid metabolites.

## □ 5. Amino acids pathway

- Peptides, proteins, alkaloids and many antibiotics are derived from amino acids.
- Intermediates from the glycolytic pathway and the Krebs cycle are used in constructing many of them.
- The aromatic amino acids phenylalanine, tyrosine, and tryptophan are themselves products from the shikimate pathway.



- Secondary metabolites can be synthesized by combining several building blocks of the same type, or by using a mixture of different building blocks.
- Many of secondary metabolites also contain one or more sugar units in their structure.
- **To appreciate how a natural product is elaborated, it is of value to be able:**
  1. To divide its structure into the basic building blocks from which it is made up.
- To propose how these are mechanistically joined together.
- **Oxygen atoms** can be introduced and removed by a variety of processes, and so are not considered in the initial analysis, except as a pointer to an acetate or shikimate origin.
- Relatively few building blocks are routinely employed, and the following list includes those most frequently encountered in producing the carbon and nitrogen skeleton of a natural product.



- $C_1$ : the simplest of the building blocks is composed of a single carbon atom, usually in the form of a methyl group, and most frequently it is attached to oxygen or nitrogen, but occasionally to carbon. It is derived from the S-methyl of **L-methionine**.
- $C_2$ : A two-carbon unit may be supplied by **acetyl-CoA**. Acetyl-CoA is first converted into the more reactive **malonyl-CoA** before its incorporation.
- $C_5$ : the branched-chain  $C_5$  “isoprene” unit is a feature of compounds formed from **mevalonate** or **deoxyxylulose phosphate**.
- $C_6C_3$ : this refers to a phenylpropyl unit and is obtained from the carbon skeleton of either **L-phenylalanine** or **L-tyrosine**.
- $C_6C_2N$ : again, this building block is formed from either **L-phenylalanine** or **L-tyrosine**.



- **Indole.C<sub>2</sub>N**: the third of the aromatic amino acids is **L-tryptophan**.

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- **C<sub>4</sub>N**: the C<sub>4</sub>N unit is usually found as a heterocyclic pyrrolidine system and is produced from **L-ornithine** (non-protein amino acid).
- **C<sub>5</sub>N**: it is produced by using **L-lysine** and the unit tends to be found as a piperidine ring system.



# The construction mechanisms

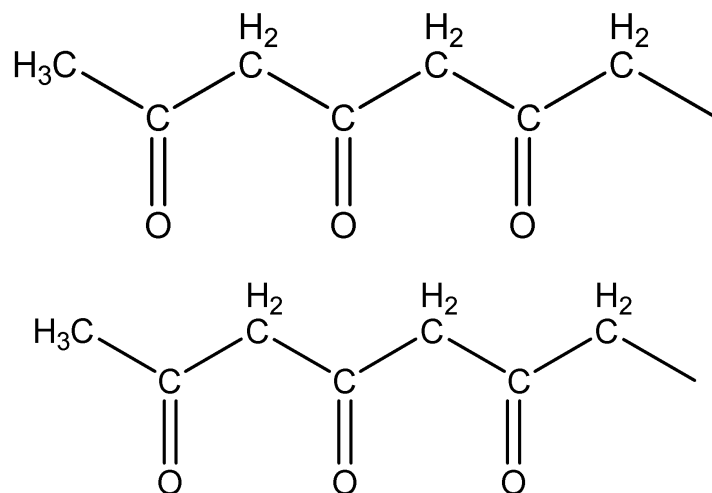
- Natural product molecules are biosynthesized by a sequence of reactions which are catalyzed by enzymes.
- Enzymes have the power to effect these transformations:
  1. More efficiently and more rapidly than the chemical analogy.
  2. Under very much milder conditions.
  3. Carry out reactions in a stereospecific manner.

1. Alkylation reactions
  2. Aldol and Claisen reactions
  3. Schiff base formation and the Mannich reaction
  4. Transamination
  5. Decarboxylation reactions
  6. Oxidation and reduction reactions
  7. Phenolic oxidative coupling
  8. Glycosylation reactions
- 

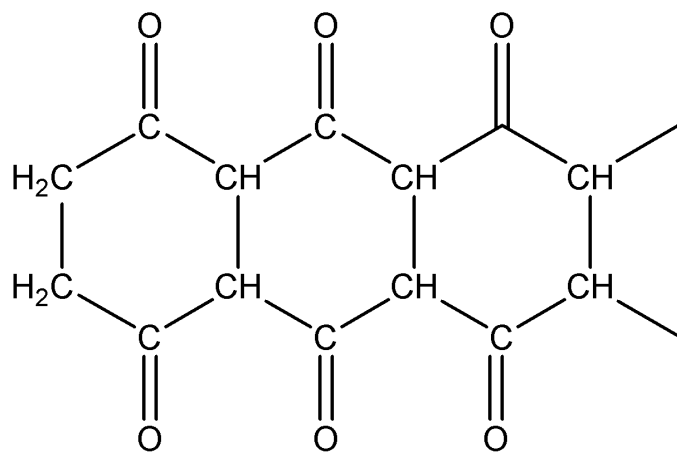


## □ Biosynthesis of Anthraquinone glycosides:

- Knowledge of the biosynthesis has been obtained from studies of microorganisms. Feeding of labeled acetate to *pencillium islandicum*, a species that produces several anthraquinone derivative revealed that the distribution of radio activity in these compound is reliable with formation via head to tail condensation of acetate units.



- A poly- $\beta$ -ketomethylene acid intermediate is probably first produced and then gives rise to the various oxygenated aromatic compounds after intramolecular condensation. Anthranols and anthrones are likely intermediates in the formation of anthraquinones.



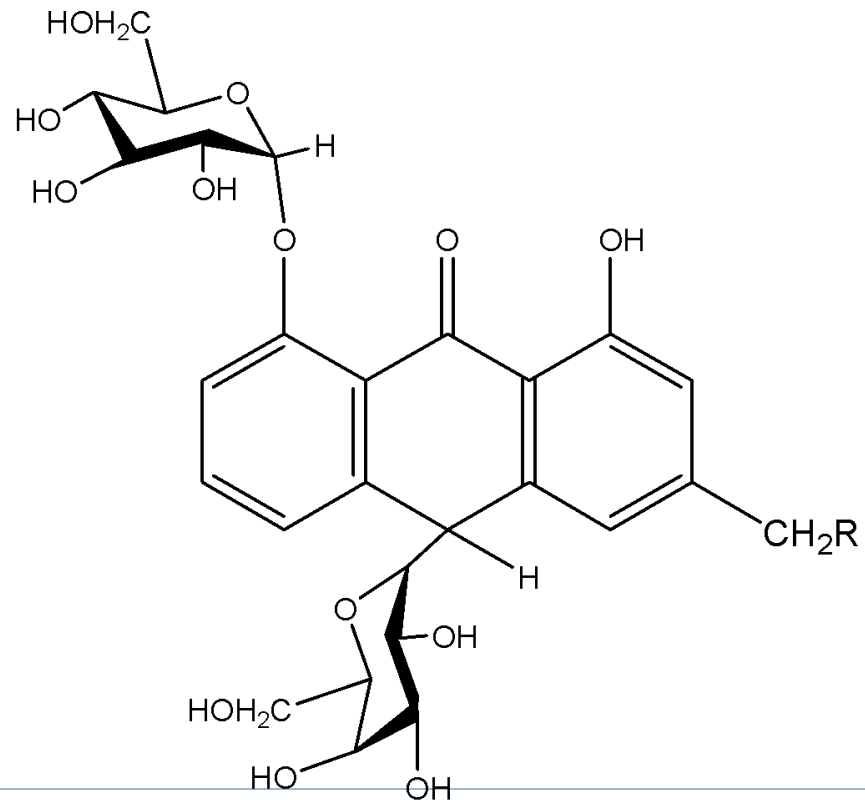
- The emodin like anthraquinones is formed in the higher plants by a similar pathway.
- The transglycosylation reaction, which creates a glycoside probably occur at a late stage in the pathway after the anthraquinone molecule has been formed.



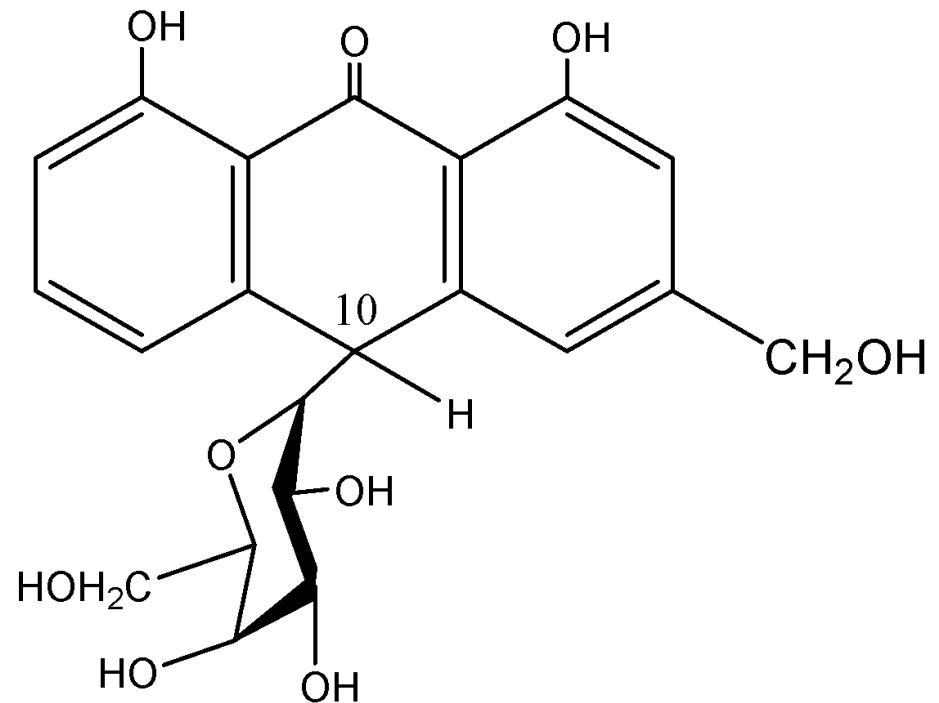
- Cascaroside A    R= OH ( 10 S )
- Cascaroside B    R= OH ( 10 R )
- Cascaroside C    R= H    ( 10 S )
- Cascaroside D    R=H    ( 10 R )

□ All 4 of cascarosides are actually both O – and C glycosides.

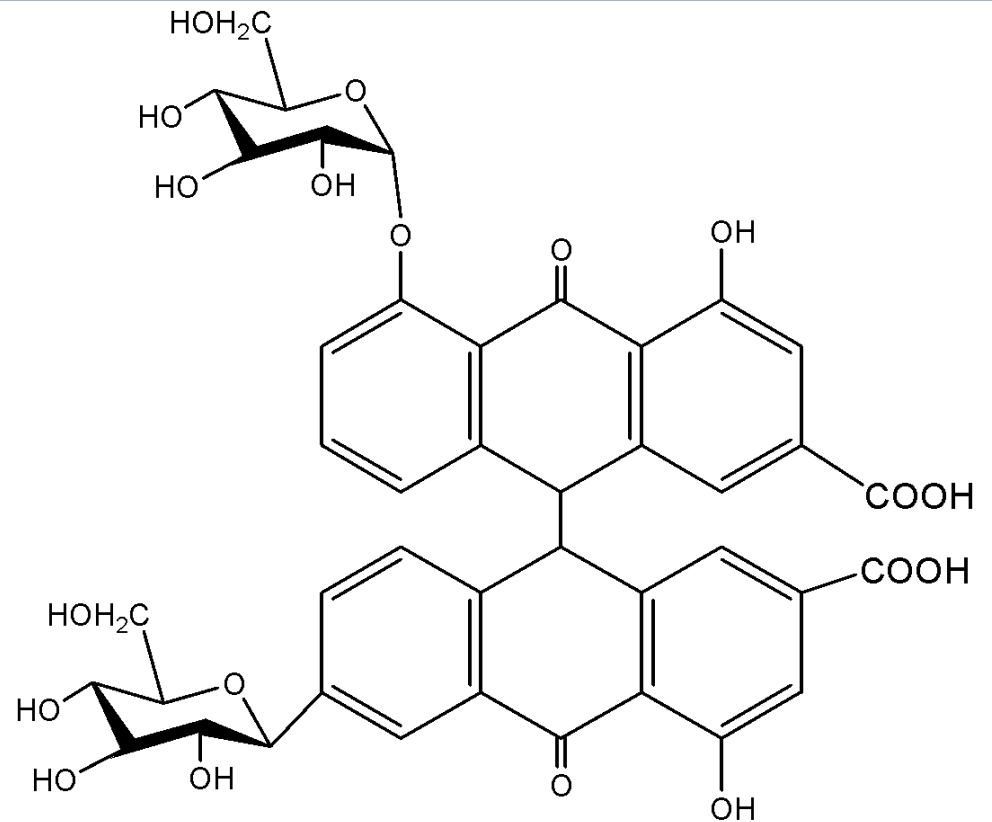
**Uses:** as cathartic □



Aloin A 10 R  
and Aloin B 10 S  
used as a cathartic



# Sennoside A



## □ **Biosynthesis of Saponin glycosides**

- The main pathway for both steroid and triterpenoid saponin glycosides are similar.
- Acetate → Acetyl CoA → Aceto acetate CoA →  
sequalene → cholesterol → Steroid → Steroidal  
saponins
- or from Sequalene → pentacyclclic compounds (triterpenord)