بسم الله الرحمن الرحيم

BIOCHEMISTRY

Lecture 9

Lipids (pt. 2)

وتعظم في عين الصغير صغارها
وتصغر في عين العظيم العظـائم

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Omega fatty acids

Omega-3 is present in fish → Japanese and people in polar regions have a healthy diet.

Linoleic (ω-6 precursor) and **Linolenic** (ω-3 precursor) acids are essential fatty acids.

Essential means that our body cannot make them, and we should get them from our diet.

- Omega-3 fatty acids
  - α-linolenic acid (essential) → Eicosapentaenoic acid (EPA) → Docosahexaenoic acid (DHA)
    - They reduce inflammatory reactions (by different mechanisms); they are beneficial to our body overall.
    - Good for **brain** and **memory** because they are involved in the structure of neuronal plasma membrane.
- Omega-6 fatty acids
  - Arachidonic acid

  Linoleic acid (essential) → Arachidonic acid → Eicosanoids
- Omega-9 fatty acids
  - Oleic acid → olive oil is beneficial
    - It reduces cholesterol in the circulation.

Healthy mediterranean food

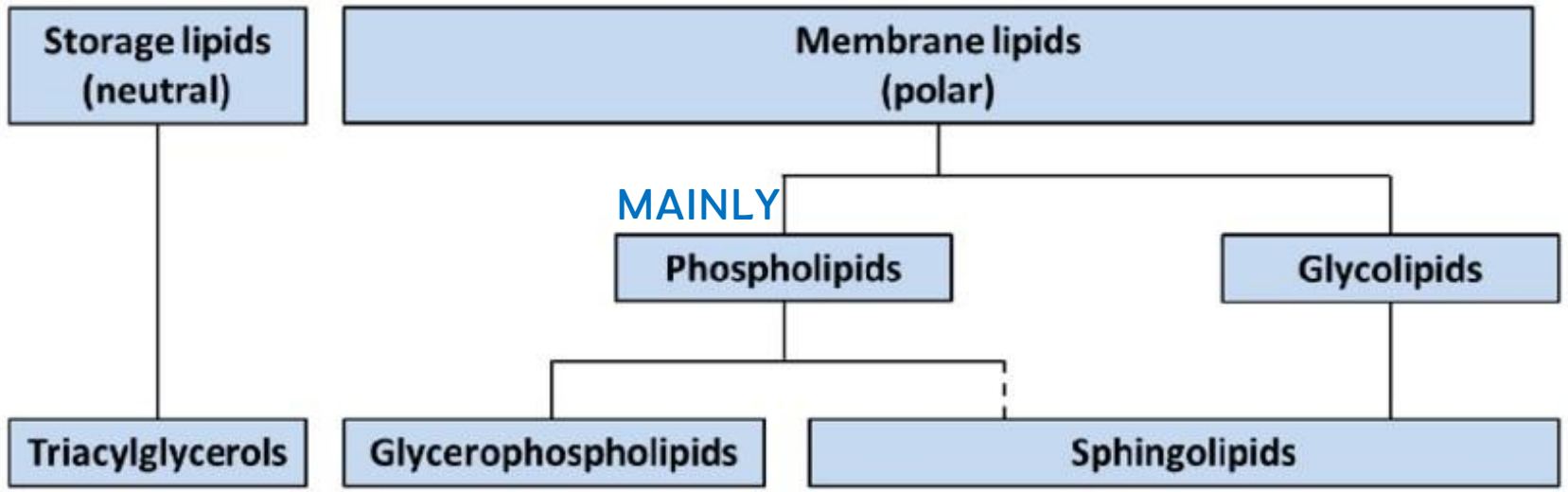
Omega-3 (like any other thing) can be harmful if taken in excess amounts.
Omega-6 is not good to take **daily** because arachidonic acid → eicosanoids can lead to induction of inflammation.

Complex lipids

each made from [backbone + attached molecules]

Energy source

Constituents of plasma membranes and other membrane types

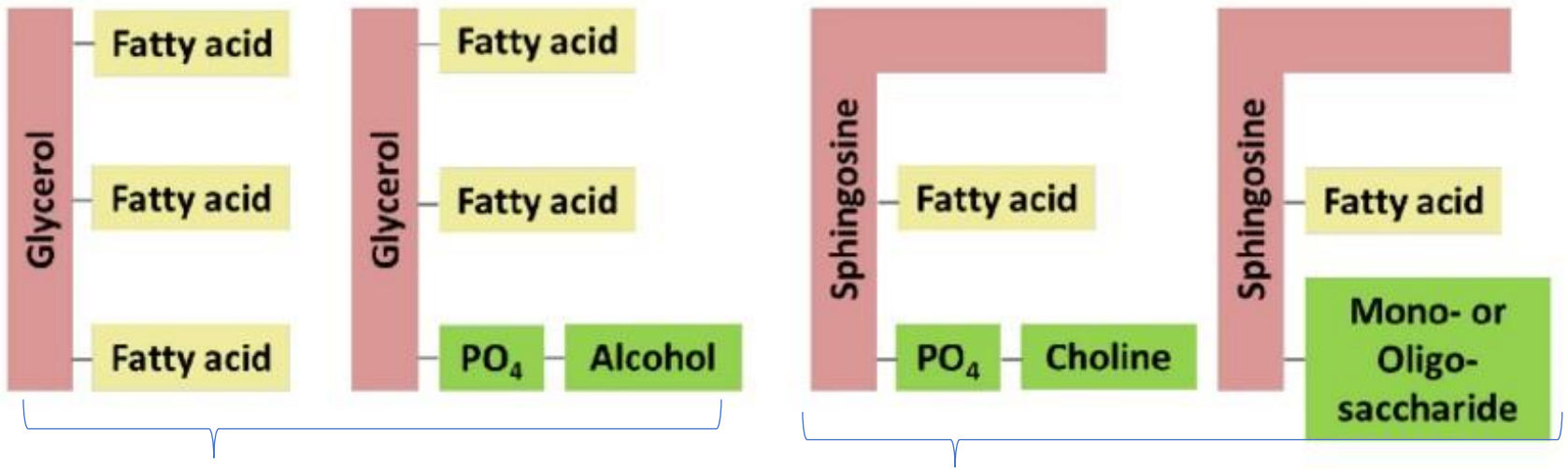


Only one molecule in this category !

Tri: 3 Fatty acids

Acyl: acyl group in fatty acids

Glycerol: Dihydroxyacetone derivative sugar alcohol; acts as a backbone.



Backbone = Glycerol

Backbone = Sphingosine

Each of the 4 types will be discussed in detail in the coming slides and in the next lecture

Triglycerides (or Triacylglycerols)

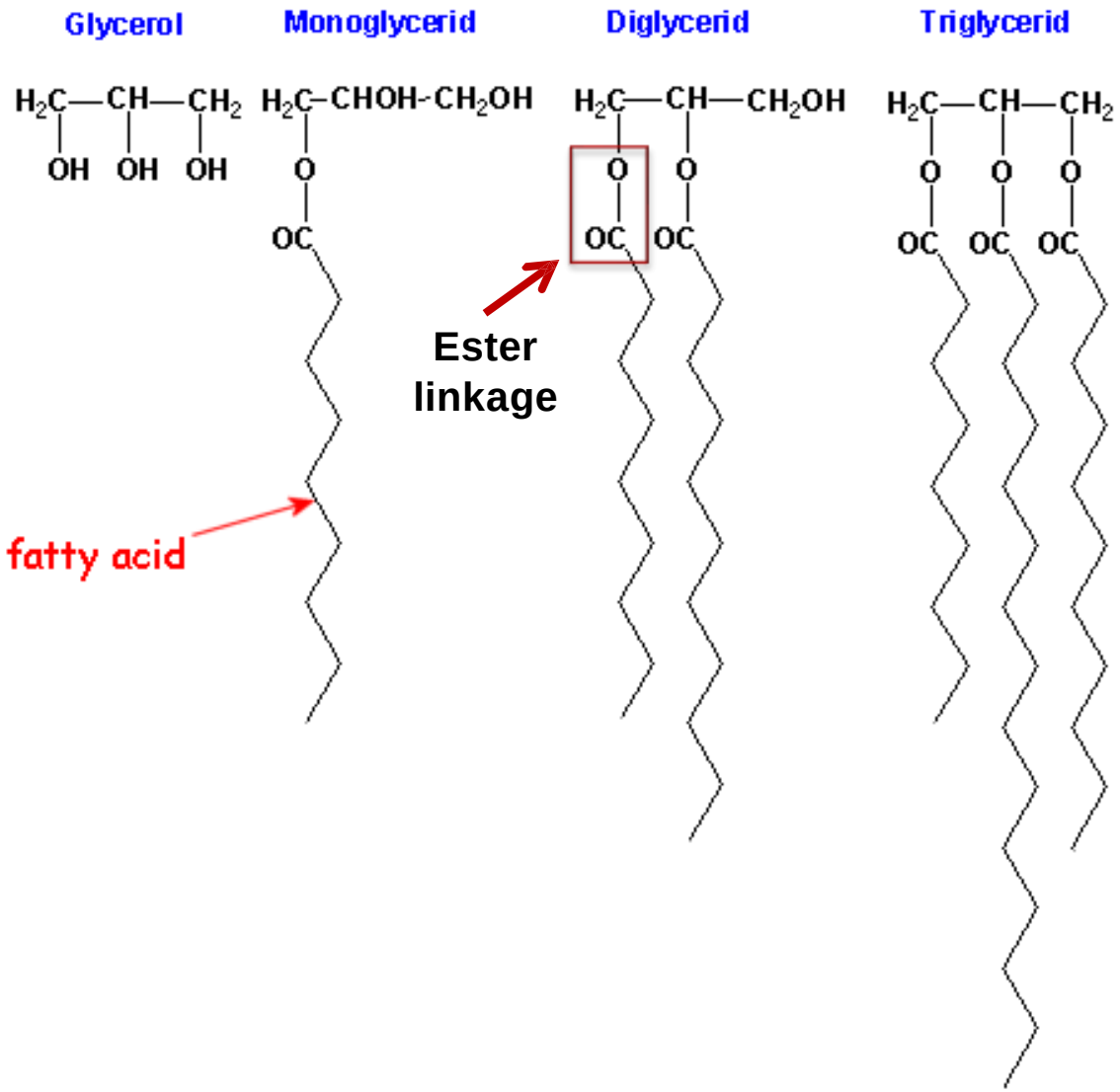
Each glycerol molecule has 3 OH groups (which are reactive groups).

Each OH group can react with one fatty acid forming an **ester bond in a dehydration reaction** where a water molecule is formed as well.

If one fatty acid reacts with the glycerol molecule, a monoacylglycerol forms.

If two fatty acids react with a glycerol molecule, a diacylglycerol forms.

If three fatty acids react with a glycerol molecule, a triacylglycerol forms.

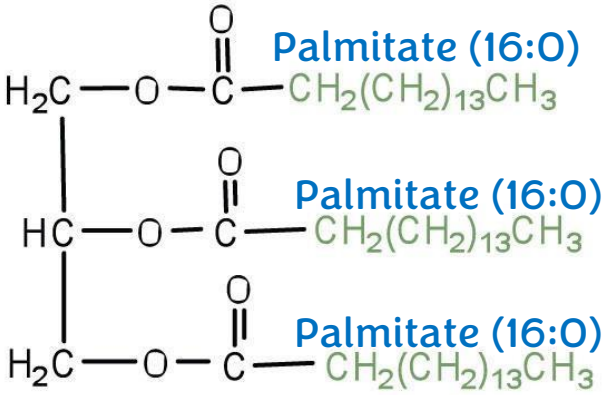


Energy is stored in fatty tissue as **triacylglycerols**, a glycerol molecule covalently bonded to 3 fatty acids by ester linkages (ester bonds).

Types of glycerides

(diverse regarding type of fatty acids attached to the glycerol backbone)

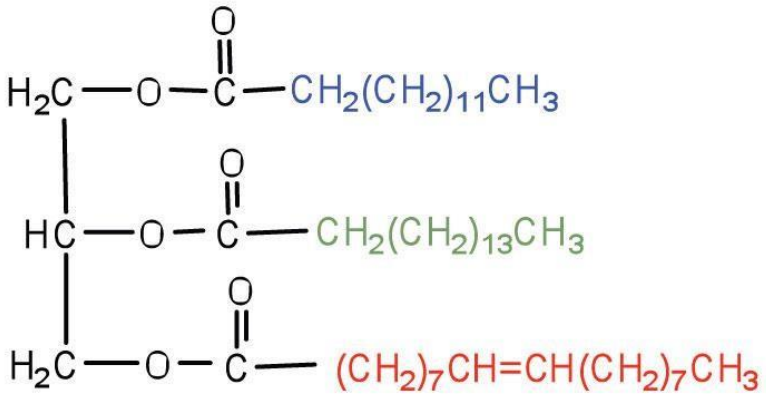
3 identical fatty acids



Tripalmitin

a simple triglyceride

3 different fatty acids



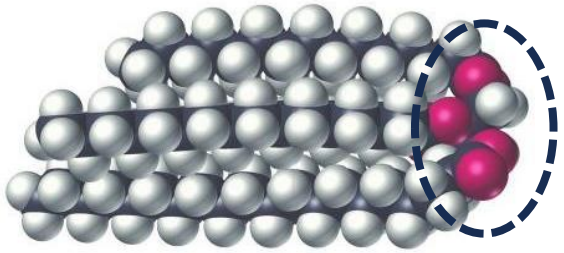
a mixed triglyceride

How soluble will a triglyceride be if fatty acids are unsaturated?

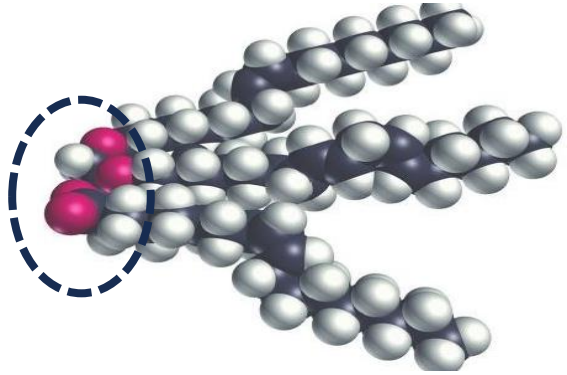
Solid vs. liquid fats

- Vegetable oils consist almost entirely of unsaturated fatty acids, whereas animal fats contain a much larger percentage of saturated fatty acids.
  - This is the primary reason for the different melting points of fats and oils.

Fatty acids chains in fat (solid)



→ Glycerol backbone ←



Fatty acids chains in oil (liquid)

A fat is a **triacylglycerol** where <u>all 3 fatty acids are saturated.</u>

They are condensed because they have straight hydrocarbon chains with <u>no kinks.</u>

Fat molecules are tightly packed together by hydrophobic interactions.

Oil forms of triacylglycerols where **at least one** of the 3 fatty acids is <u>unsaturated</u>.

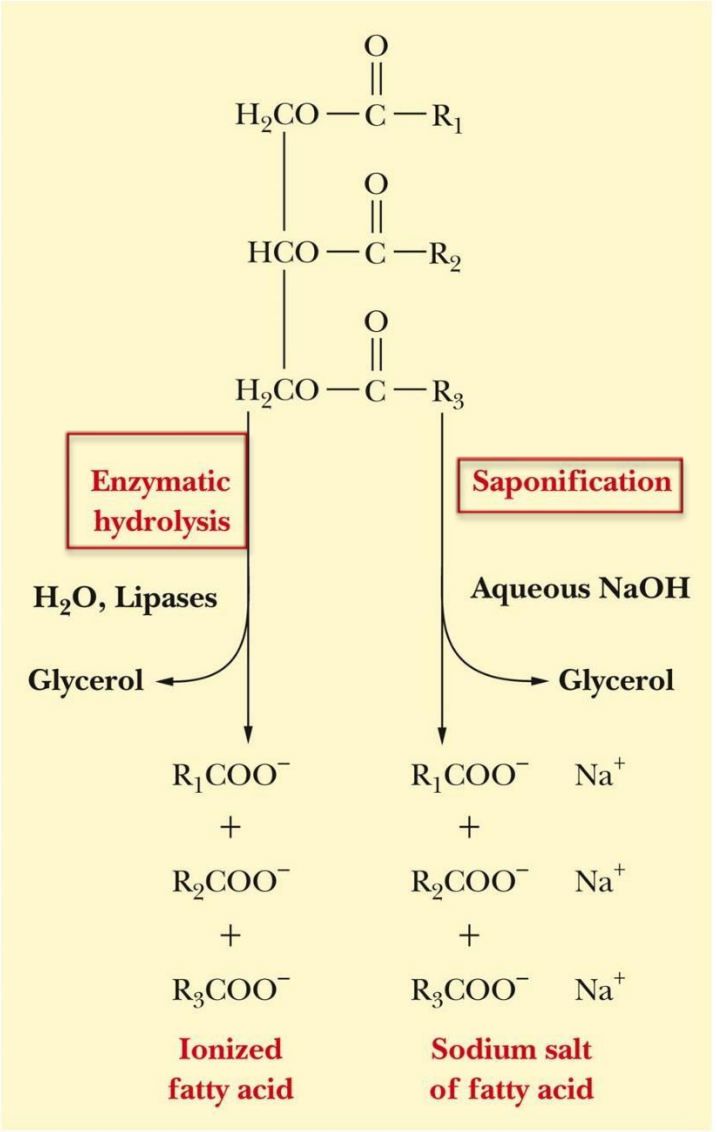
Such molecules are <u>not tightly packed</u> and have spaces between them due to the presence of **cis** double bonds ,which kinks the fatty acid .

Saponification (formation of soap)

- Hydrolysis: steam, acid, enzyme (e.g., lipase of pancreas)

- Saponification: Alkaline hydrolysis produces **salts of fatty acids (soaps).** This reaction targets the ester bonds between glycerol and fatty acids, removing fatty acids from the glycerol backbone.

  Soaps cause emulsification of oily material.



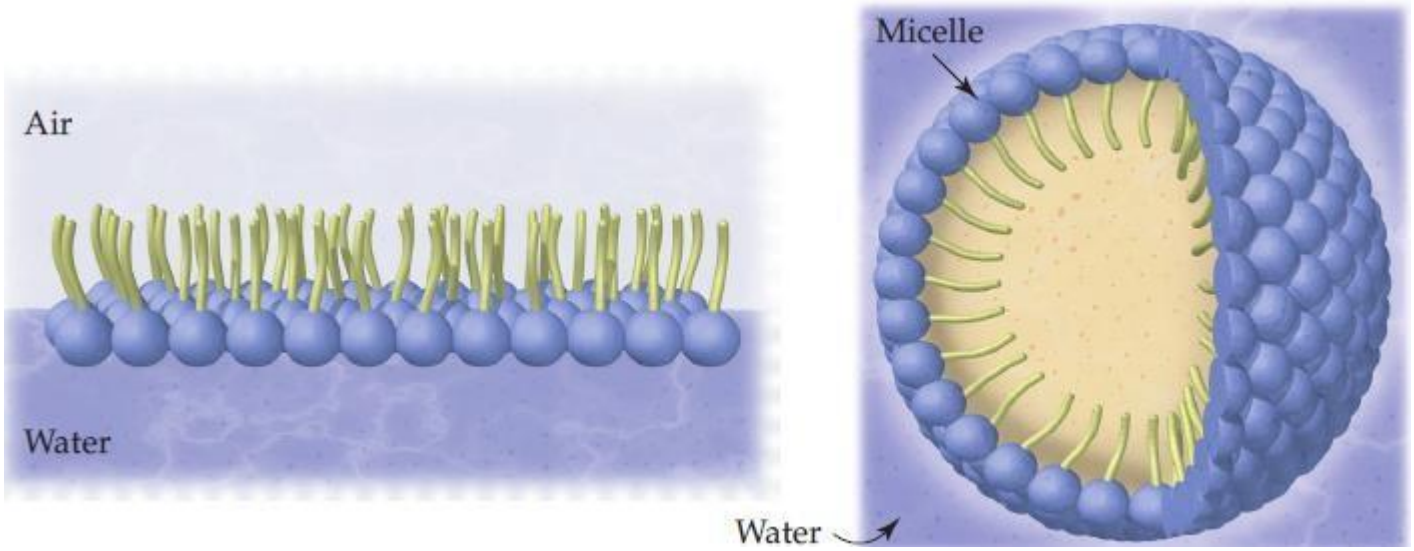
R group is hydrophobic while **COO⁻** is hydrophilic.

So, soap molecules are amphipathic.

How does soap work?

Nonpolar parts (hydrophobic tails) are directed towards air because air is made of nonpolar molecules (such as O_2 and CO_2)
Polar parts are directed towards the aqueous solution.

- When mixed with water, the hydrophobic hydrocarbon tails cluster together to create a nonpolar microenvironment and the hydrophilic ionic heads interact with water.
- The resulting spherical clusters are called micelles.
- Grease and dirt are trapped inside micelles and the complex can be rinsed away.



A micelle is a structure formed by soap molecules such that carboxylic groups are all directed towards the outside (facing water) and hydrophobic tails directed towards the inside (facing the grease trapped in the micelle).

When you wash your greasy hands, grease (nonpolar fat) is trapped inside the region enclosed by soap molecules.

When water is washed away, micelles trapping the grease are washed away too, and this is how soap functions !

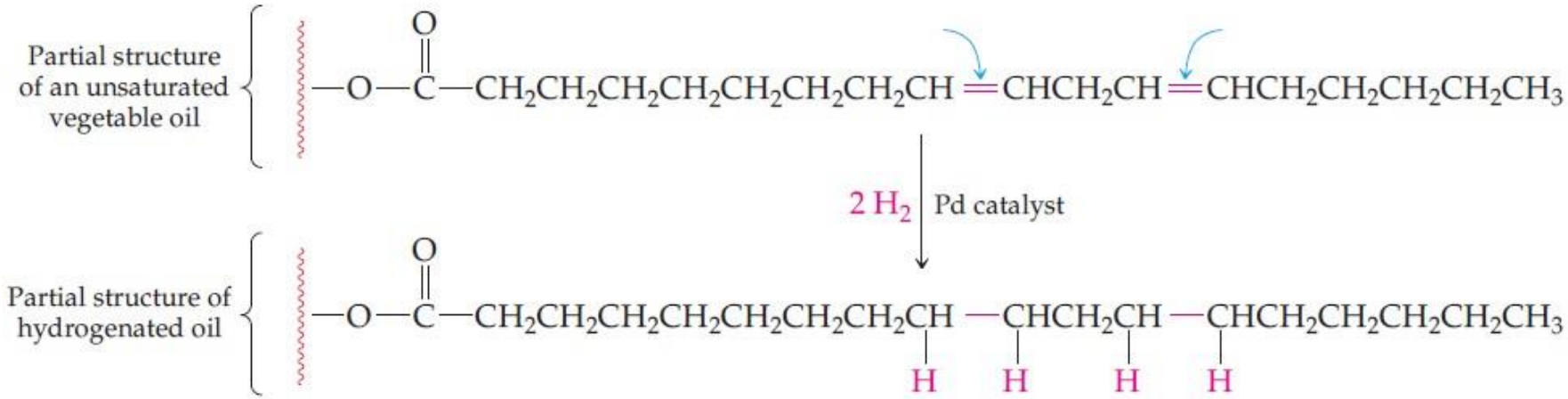
Hydrogenation

Hydrogenation is the process of adding hydrogens (reduction) to an unsaturated fatty acid making it fully saturated with hydrogens (no presence of double bonds).

- The carbon-carbon double bonds in vegetable oils can be hydrogenated to yield saturated fats in the same way that any alkene can react with hydrogen to yield an alkane.

Dehydrogenation is the process of removing hydrogens (oxidation) leading to the formation of a new double bond between two carbons in the fatty acid, this process will produce unsaturated fatty acids.

In our bodies, hydrogenation and dehydrogenation of fatty acids happen enzymatically.



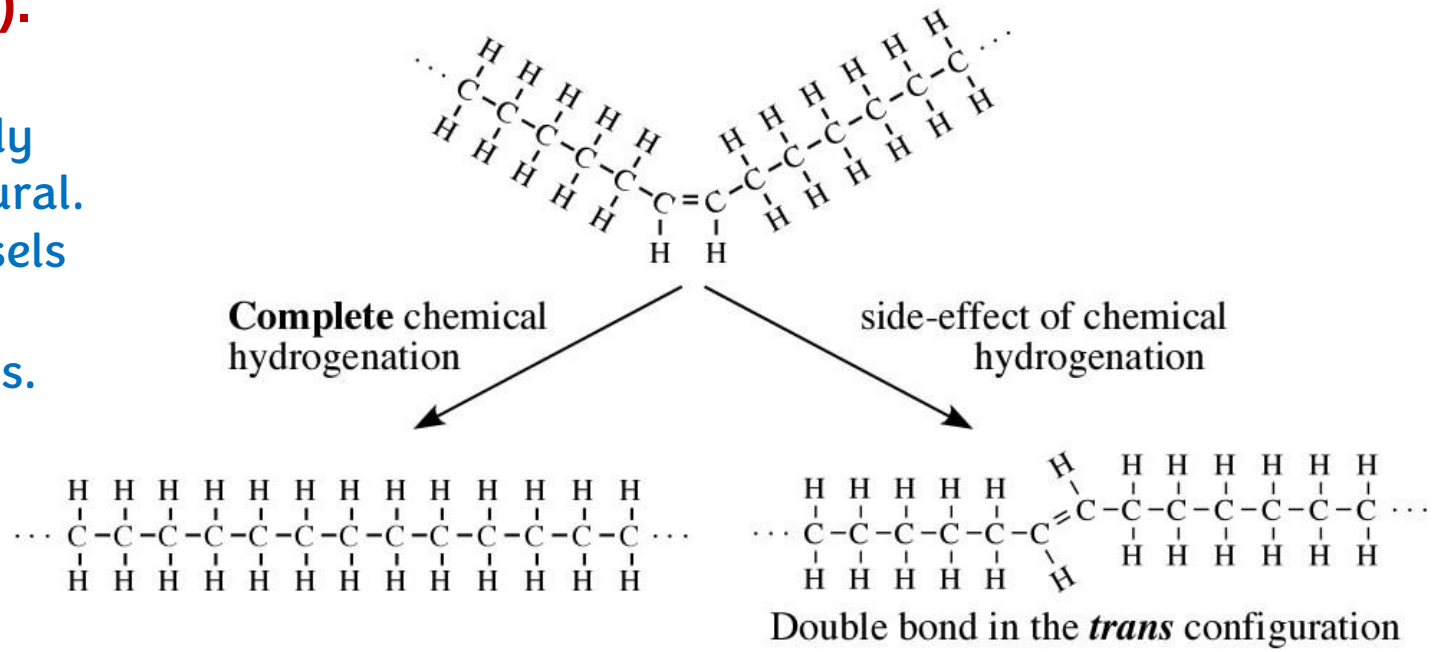
Trans fat

Hydrogenation of unsaturated fatty acids could be faulty thus producing unsaturated fatty acids with the double bonds in a **trans** configuration.

- Although the animal fat is unhealthy, it has better cooking properties and better taste.
- Therefore, chemists invented a method of converting unsaturated oil into solid form by partially hydrogenating it.
- Partial hydrogenation converts some, but not all, double bonds into single bonds generating (trans fats).

The primary health risk identified for trans fat consumption is an elevated risk of coronary heart disease (CHD).

Trans fats has a good taste but, unfortunately our body can't digest it because it is not natural. Accumulation of these fats in our blood vessels will lead to serious medical conditions such as **atherosclerosis**, heart disease and strokes.



Example: margarine

Butter is processed with dehydrogenation to make it soft and melty at room temperature, this process also gives trans fats which are unhealthy such in margarine.

- In margarine, only about two-thirds of the double bonds present in the starting vegetable oil are hydrogenated, so that the margarine remains soft in the refrigerator and melts on warm toast.

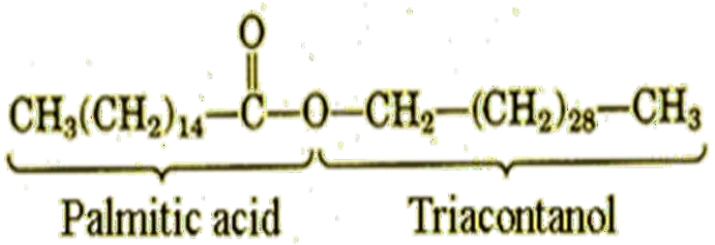
Nutrition Facts

Serving Size 1 Tbsp (14g)
Servings Per Container 32

Amount Per Serving	
Calories 100	Calories from Fat 100
	% Daily Value*
Total Fat 11g	17%
Saturated Fat 2g	10%
Trans Fat 3g	
Cholesterol 0mg	0%

Waxes

Waxes are formed by the reaction of a fatty acid with an alcohol forming an ester group. Waxes are hydrophobic because the ester group (which is hydrophilic) is considered small relative to the 2 hydrocarbon chains.



- Solid simple lipids containing a monohydric alcohol (C16 ~ C30, higher molecular weight than glycerol) esterified to long-chain fatty acids (C14 ~ C36).
  - Example: palmitoyl alcohol
- Insoluble in water
- Not easily hydrolyzed (fats) & indigestible
- Very resistant to rancidity That means it does not become rotten.
- No nutritional value

External coating of plant leaves that prevent loss of water

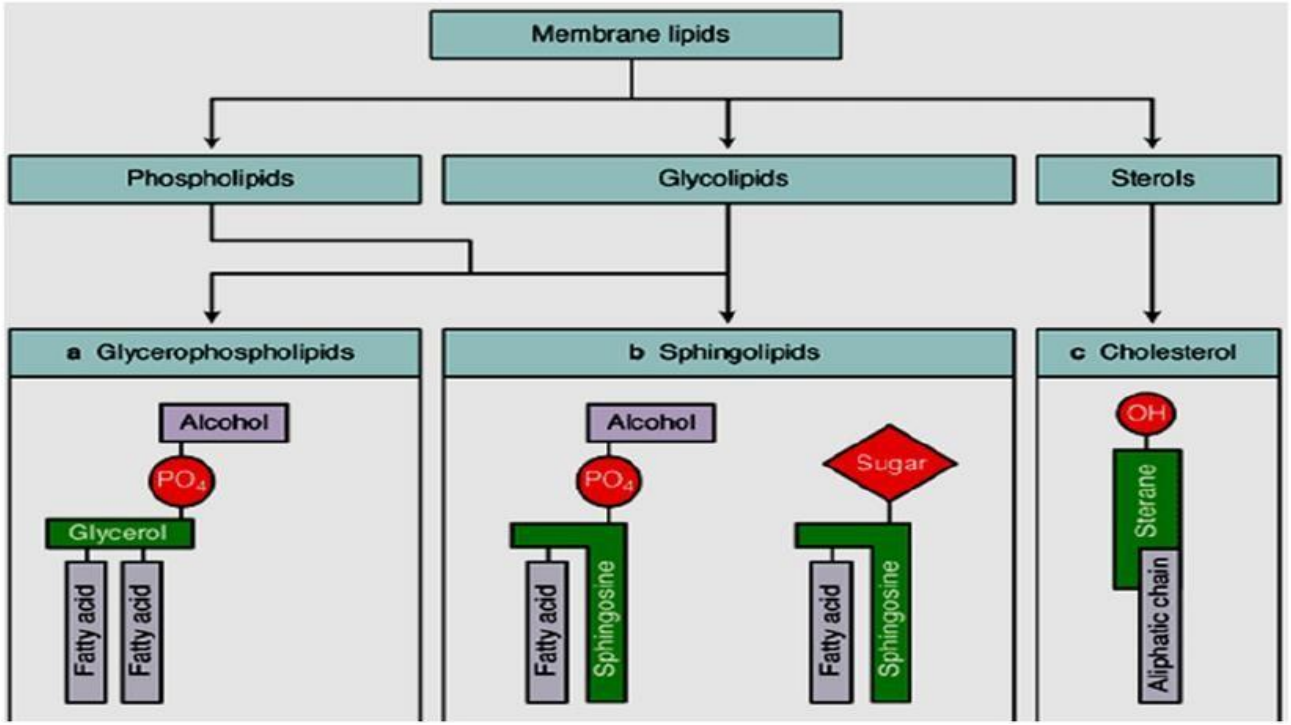
Do not memorize the structures but study them

Type	Structural Formula	Source	Uses
Beeswax	$CH_3(CH_2)_{14}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{29}CH_3$	Honeycomb	Candles, shoe polish, wax paper
Carnauba wax	$CH_3(CH_2)_{24}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{29}CH_3$	Brazilian palm tree	Waxes for furniture, cars, floors, shoes
Jojoba wax	$CH_3(CH_2)_{18}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{19}CH_3$	Jojoba	Candles, soaps, cosmetics

Membrane lipids

- Phospholipids are membrane lipids which have a phosphate group attached to the backbone.
- Depending on the backbone, phospholipids can be glycerophospholipids or sphingophospholipids, which have glycerol or sphingosine as their backbones, respectively.
- Glycolipids are lipids which have a sugar group attached to their backbone.
- The backbone of glycolipids is sphingosine.
- Another type of membrane lipids are sterols, such as cholesterol, which will be discussed later.

The most prevalent class of lipids in membranes is the <u>glycerophospholipids</u>



Phospholipids (phosphoacylglycerols)

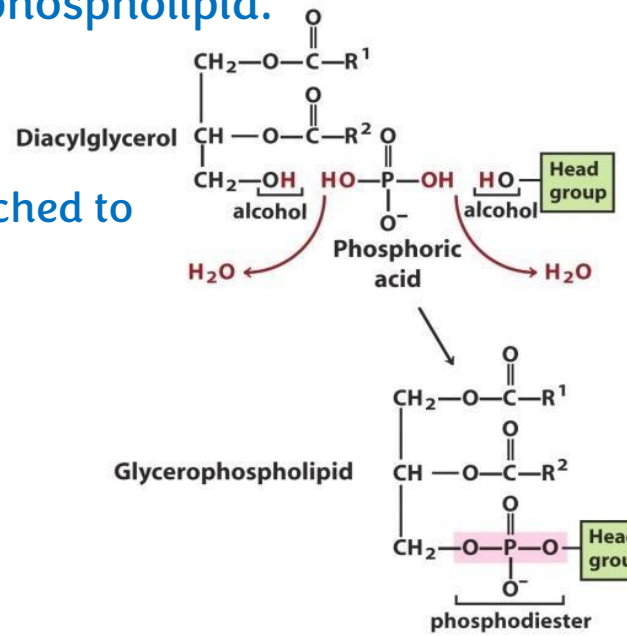
Looking at the figure on the right, you see the structure of diacylglycerol molecule which is composed of two fatty acid attached to a glycerol molecule with an ester linkage, if the 3rd hydroxyl group is attached to a phosphate group with a phosphoester linkage, the molecule becomes a glycerophospholipid.

- Phosphatidic acids — Is the simplest glycerophospholipid (with H as a head group also it may be considered "without head group")
- Phosphatidylcholine (lecithin)
  - Most abundant membrane lipid
- Cephalins
  - Phosphatidylethanolamine
  - Phosphatidylserine
    - abundant in brain
- Phosphatidylinositol → The head group is inositol (sugar alcohol)
  - sends messages across cell membranes
- Cardiolipin
- Plasmalogens

Under physiological pH, phosphatidic acid is ionized and is called phosphatidate.

Notice that the phosphate is attached to a head group.

Different head groups gives different phospholipids.



Phosphatidic acid	—	— H
Phosphatidylethanolamine	Ethanolamine (3 hydrogens attached to N)	— CH_2—CH_2—NH_3^+
Phosphatidylcholine	Choline (3 methyls attached to N)	— CH_2—CH_2—$N^+(CH_3)_3$
Phosphatidylserine	Serine (Amino acid)	— CH_2—CH(NH_3^+)—COO^-

Glycerophospholipids - Lecithins

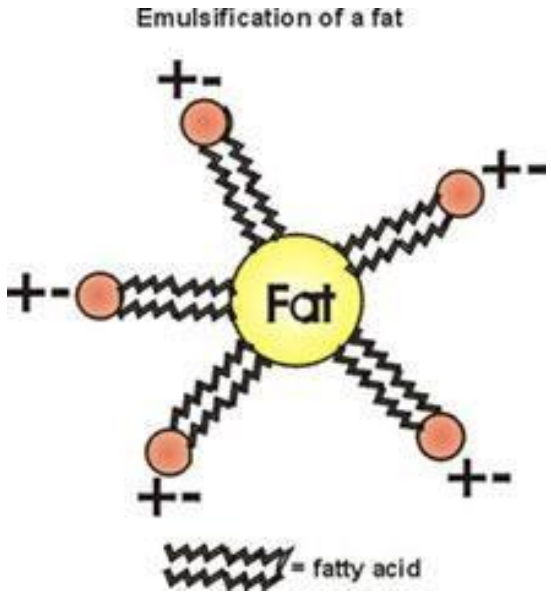
- Snake venom contain lecithinase, which hydrolyzes polyunsaturated fatty acids and converting lecithin into lysolecithin
  - Hemolysis of RBCs

Phosphatidylcholine **Choline** $-CH_2-CH_2-\overset{+}{N}(CH_3)_3$

Phosphatidylcholine is also called lecithin, snake venom contains lecithinase, an enzyme which targets lecithin, rupturing the plasma membrane of RBCs causing hemolysis (hemo: blood, lysis: break) which is fatal.

Emulsification

- Because of their **amphipathic** nature, they act as emulsifying agents, which are substances that can surround nonpolar molecules and keep them in suspension in water.



Emulsification is the process of having a fat surrounded by fatty acyl chains of phospholipids. As the phosphate head groups are charged, they will dissolve the surrounded fat in water.

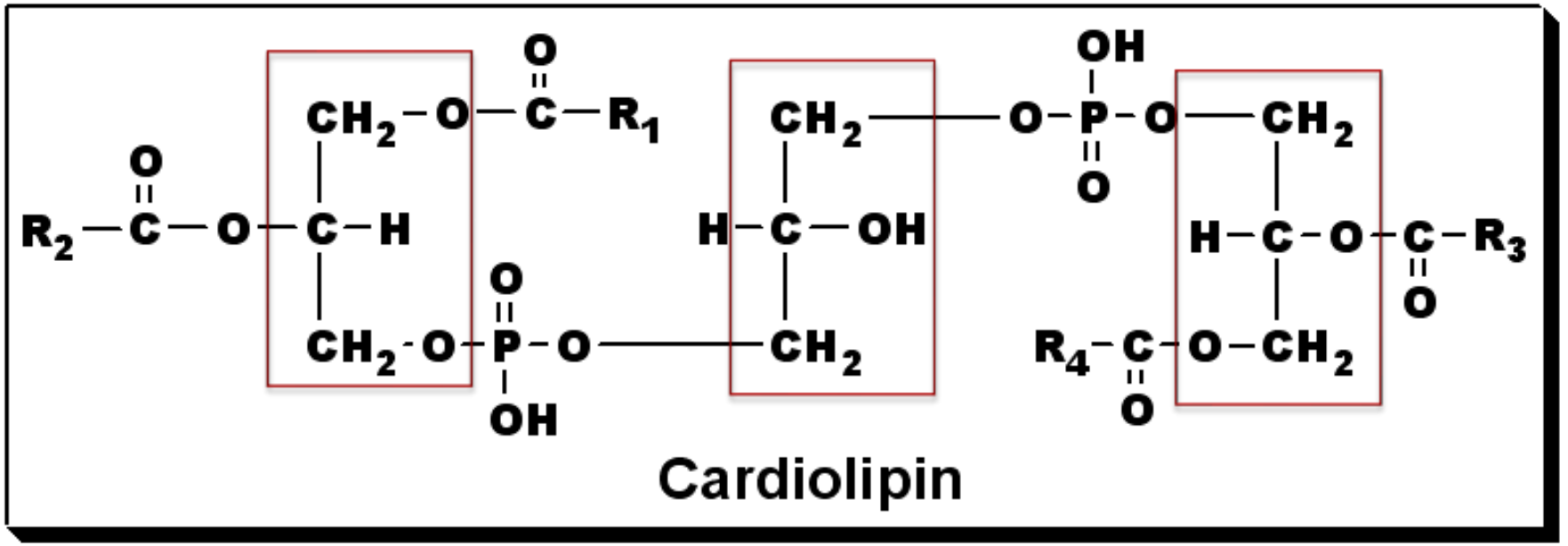
Phosphatidylcholine (lecithin) is an emulsifier; they add it to fatty food to dissolve fats in hydrophilic environment.

Glycerophospholipids - Cardiolipins

Focus on the slide's notes ↓

- Diphosphatidyl-glycerol
- Found in the inner membrane of mitochondria
- found in the heart tissue but , Initially isolated from heart muscle (cardio) ,
- Structure: 3 molecules of glycerol, 4 fatty acids & 2 phosphate groups

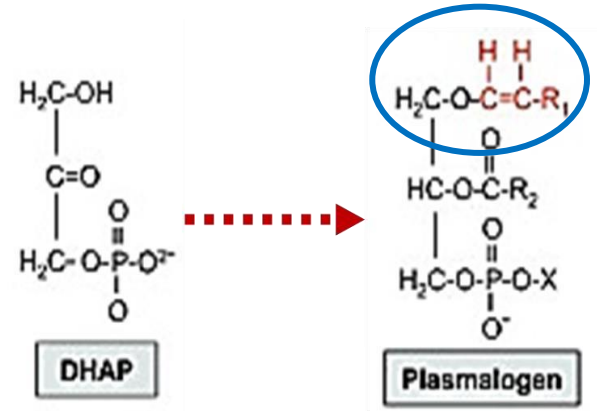
Do not memorize the structures but study them

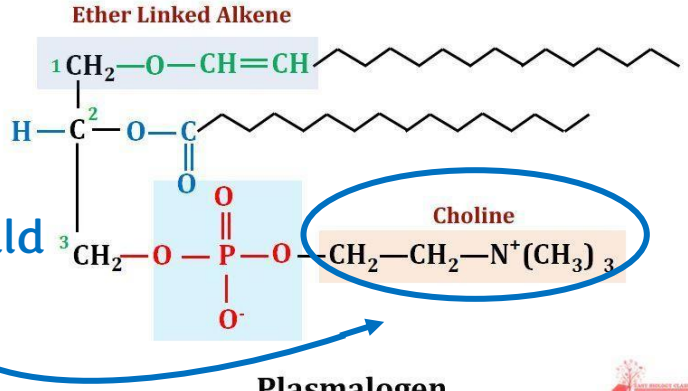


Plasmalogens

The difference between plasmalogens and glycerophospholipids is that instead of having an ester group at C#1 of glycerol we have an ether group, notice that there is a double bond between 2 carbons (ether linked alkene, shown in red).

- They are found in the cell membrane phospholipids fraction of brain & muscle, liver, and semen.
- They have a protective role against reactive oxygen species
- Structure:
  - Precursor: Dihydroxyacetone phosphate
  - Unsaturated fatty alcohol at C1 connected by ether bond
  - In mammals: at C3; phosphate + ethanolamine or choline
- Major classes of plasmalogens
  - Ethanolamine plasmalogen (myelin-nervous tissues)
  - Choline plasmalogen (cardiac tissue)
    - Platelet activating factor
  - Serine plasmalogens



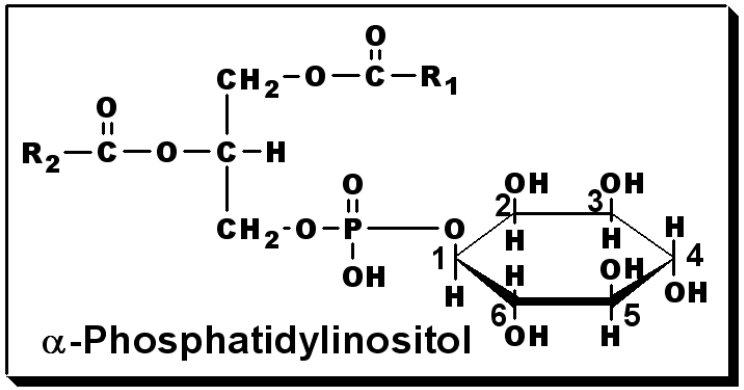


Different head groups could be here.

Glycerophospholipids - Inositides

What is special about inositides is that the head group attached to the phosphate is the sugar alcohol inositol which is important for signaling. Everything else is the same as any glycerophospholipid (fatty acids are connected to glycerol by ester bonds) .

- Phosphatidyl inositol
- Nitrogenous base: cyclic sugar alcohol (inositol)
- Structure: glycerol, saturated FA, unsaturated FA, phosphoric acid, & inositol
- Source: Brain tissues



- Functions:
  - Major component of cell membrane
  - Signaling molecules are produced upon hydrolysis

For any feedback, scan the code or click on it.

Corrections from previous versions:

Versions	Slide # and Place of Error	Before Correction	After Correction
V1 → V2	15; bottom left text	The ionized form of phosphatidic acid is phosphatide	The ionized form of phosphatidic acid is phosphatidate
V2 → V3			

Additional Resources Used:

1. Campbell Textbook:
   sec. 8.2:
   (The Chemical Natures of Lipid Types)
   sec. 8.3:
   (Biological Membranes)

رسالة من الفريق العلمي:

وإن كـــان خرقٌ فادَّرِكْه بفضـــلة
من الحلم وليصلحه مَن جاد مِقْوَلا

الإمام الشاطبي – رحمه الله.