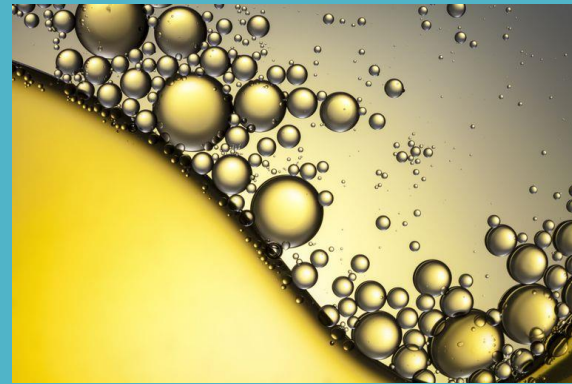


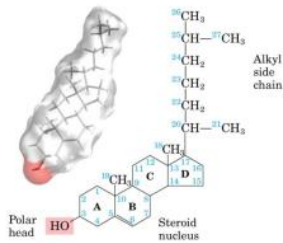
LIPIDS

Asst. Prof. Cansu Ekin GUMUS



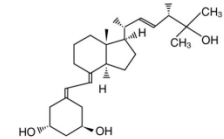
Lipids: What are They?

Definition – Lipids are components that are soluble in organic solvents, but insoluble in water

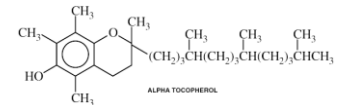


Cholesterol

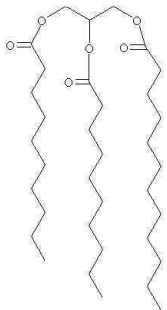
Carotenes



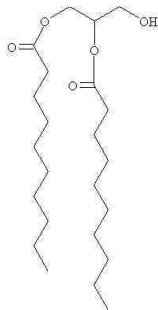
Vitamin D



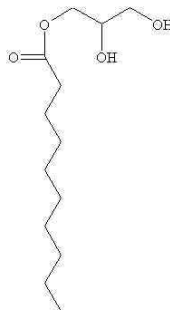
Vitamin E



Triacylglycerol



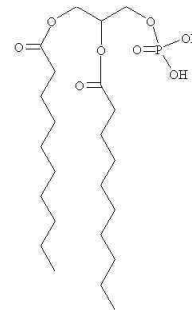
Diacylglycerol



Monoacylglycerol



Fatty acids



Phospholipids

LIPIDS

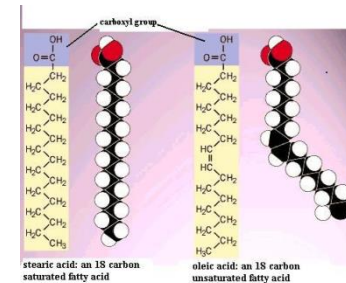
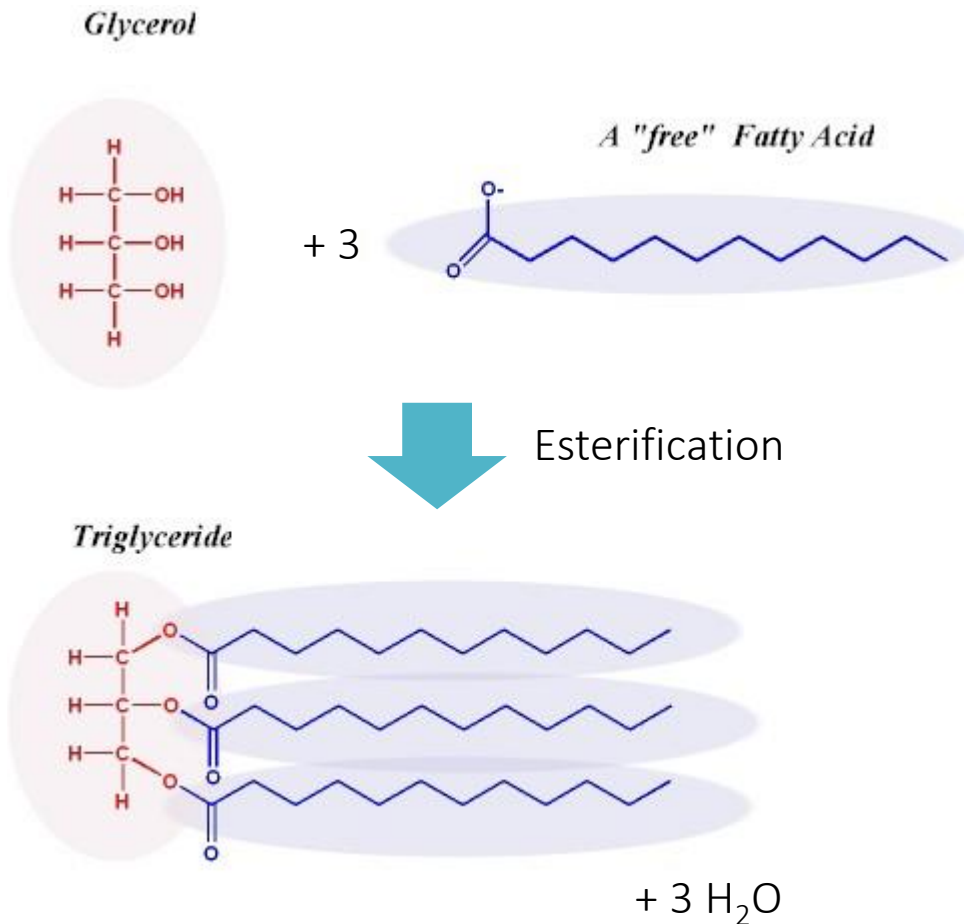
- Together with proteins and carbohydrates, they form *adipose tissue* and are among the main structural components of all living cells.
- Glycerol esters of fatty acids constitute 99% of the fat content of vegetable and animal tissues. These are called **fats** (solid at room temperature) and **oils** (liquid at room temperature)



- The most important feature that separates lipids from proteins and carbohydrates is that they are not soluble in water.
- Some lipids are surface active compounds and have both a hydrophilic and hydrophobic end.
- Some lipids are constituents of biological membranes. It surrounds cells or intracellular organelles. These types of lipids are found in almost all foods, but their level is generally less than 2%.
- Triglycerides can be deposited in some animal tissues and some plant organelles.

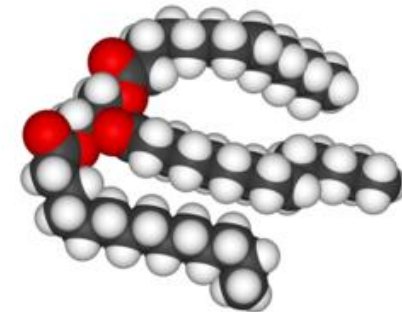
Lipids: Triacylglycerols (TAG)

Usually more than 95% of the lipids in foods are triacylglycerols (also known as triglycerides). In summary, fats are esters of different chain length fatty acids (R-COOH) and glycerine [C₃H₅(OH)₃].



Fatty Acids in TAG Vary:

- Position on Glycerol
- Chain Length
- Unsaturation



TAG

- In a triglyceride, $[C_3H_5(OH)_3]$ glycerol (92g) forms a very small fraction of its molecular weight, while fatty acid related radicals (R-COO) – weigh between 650-970g. Therefore, the character of the lipid is mainly determined by the fatty acid in the structure (approximately 94-96% of the molecule).

Example

tripalmitin: Glycerol (92g) + 3 x Palmitic a. (768g) = 860g - 3 H₂O (54g) = 806 g

Tripalmitin molecular weight = 806 g

$(768/806) \times 100 = \%95$



Lipids



Biological tissue lipids

Importance of Studying Lipids in Foods

- **Nutrition**
 - *Important source of energy*
 - *Important source of nutraceuticals*
 - *Some lipids can be harmful to health*
- **Food Quality**
 - *Appearance, Texture, Flavor*
 - *Processing, Stability*
- **Food Cost**



Bulk lipids



Emulsified lipids

FAT CONTENTS OF SOME FOODS

Product	Fat (%)
Asparagus	0.25
Oats	4.4
Barley	1.9
Rice	1.4
Walnut	58
Coconut	34
Peanut	49
Soybean	17
Sunflower	28
Milk	3.5
Butter	80
Cheese	34
Hamburger	30
Beef cuts	10-30
Chicken	7
Ham	31
Cod	0.4
Haddock	0.1
Herring	12.5

- ✓ Nutritional / physiological importance of lipids: **ENERGY** source (9 kcal / g) , source of **ESSENTIAL FATTY ACID** and **OIL SOLUBLE VITAMINS**.
- ✓ Also, fats in foods creates the creamy perception of the food that is desired in the mouth,
- ✓ It provides the solubility of many flavor and aroma compounds and thus contributes to the desired texture, taste and aroma of the food,



- ✓ It creates an environment in frying processes,
- ✓ Some lipid compounds can be used as emulsifiers in foods,
- ✓ It functions as a solvent for oil-soluble pigments – and food coloring.

Sources of Edible Fats & Oils

Plants

▪ Seeds

- Soybean, corn, sunflower, rapeseed, cottonseed

▪ Fruit

- Avocado, olive, palm, coconut

Animals

▪ Body fat

- Lard, tallow (beef fat)

▪ Products

- Milk, butter

Marine

▪ Fish

Conversion to Food Ingredients

- Identification
- Extraction
- Purification



Menhaden



Mackerel



Salmon



Tuna



Sardine



Oil Extraction and Purification

Lipids are extracted from many biological sources to create food ingredients

- **Identification:** Characterization of oil source
- **Extraction:** Optimization of isolation method
- **Purification:** Optimization of methods to remove impurities from oil (*e.g.*, cell tissue, metals, pro-oxidants)
- **Processing:** Winterization, hydrogenation...



Lipids: Important Properties

Health & Nutrition

Energy (Calories)

Beneficial: Essential Nutrients & Nutraceuticals

Harmful: Saturated fat, trans-fat, cholesterol

Chemical Stability

Oxidation, hydrolysis

Physical Properties

Melting behavior

Texture

Appearance

Cooking medium

Flavor Profile

Desirable or undesirable flavor compounds

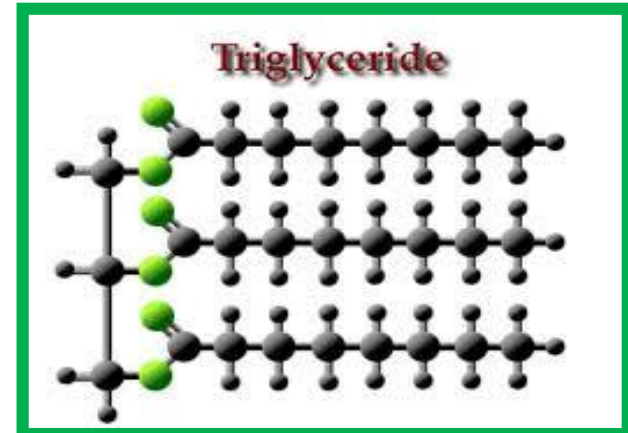
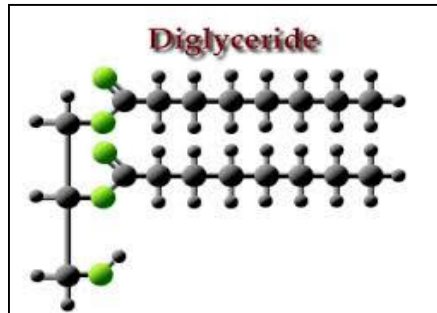
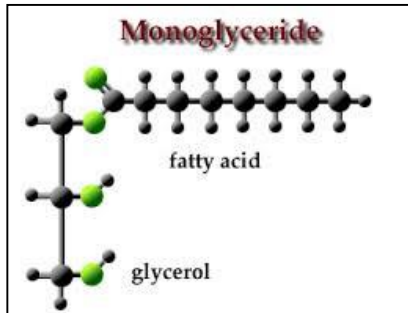
Solvent for non-polar flavors

Pleasant mouthfeel

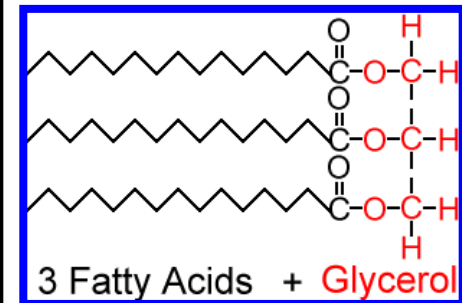


Glycerides

The esterification of 1, 2 or 3 of the OH group in the glycerine structure with fatty acid, is named mono-, di-, and tri-glyceride, respectively.

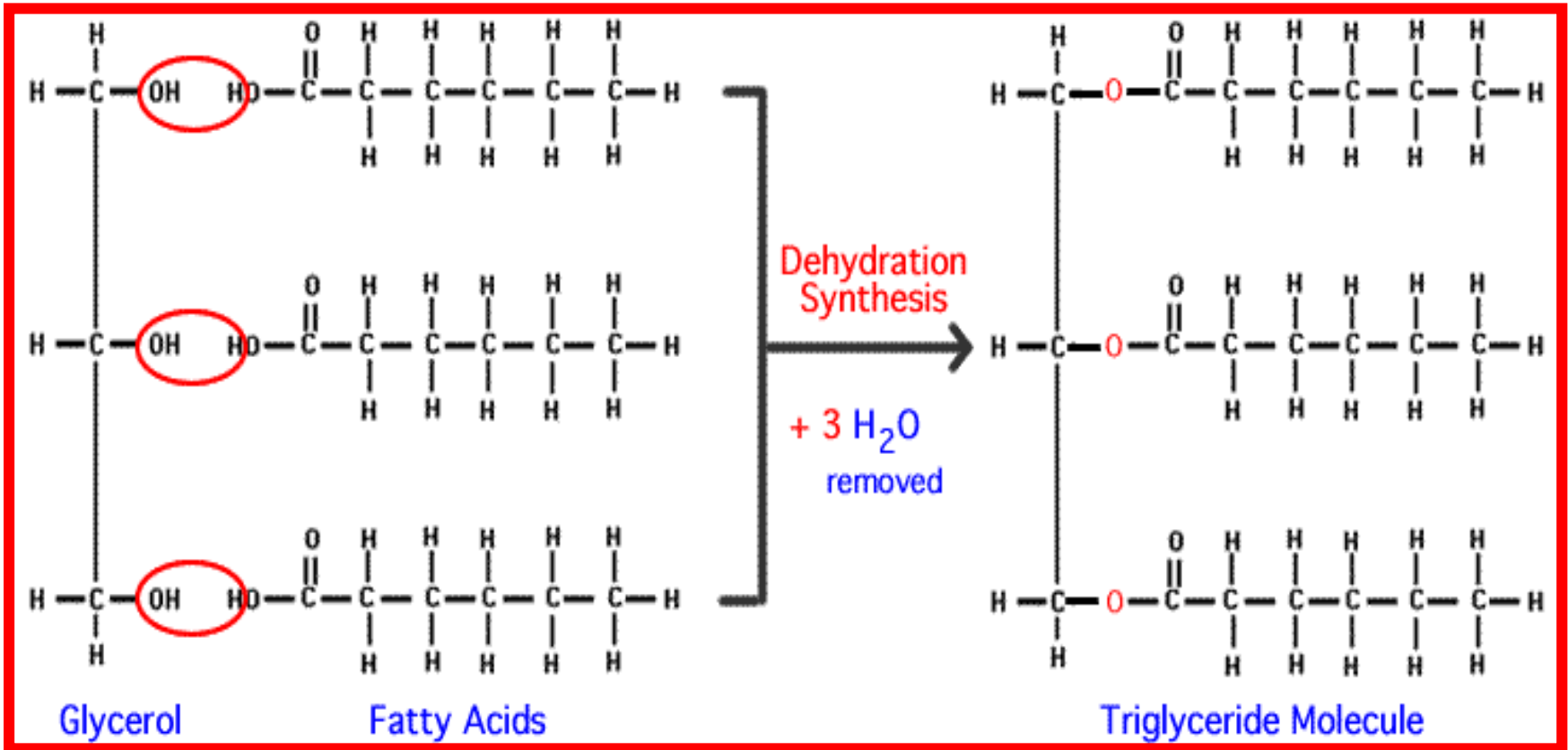


Monoglyceride	Diglyceride	Triglyceride
$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-O-C(=O)(CH}_2\text{)}_{14}\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{-O-C(=O)(CH}_2\text{)}_7\text{CH=CH(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-O-C(=O)(CH}_2\text{)}_{14}\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{-O-C(=O)(CH}_2\text{)}_{14}\text{CH}_3 \\ \\ \text{CH-O-C(=O)(CH}_2\text{)}_{14}\text{CH}_3 \\ \\ \text{CH}_2\text{-O-C(=O)(CH}_2\text{)}_{14}\text{CH}_3 \end{array}$



In Di- and triglyceride; If the fatty acids in the structure are the same, these are called simple glycerides (ex. Tripalmitin), if different it is called mixed glyceride (ex. Stearodipalmitin).

Glyceride formation



Lipids: Nomenclature




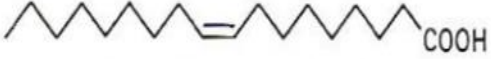


❖ The abbreviated system is generally used for naming fatty acids.

For example; **18:2** (9, 12):

The fatty acid has 18 carbons, it has 2 double bonds, these bonds are between the carbons 9-10 and 12-13 (This compound is LINOLEIC ACID).

❖ Numbering is done from the COOH group and if there is no additional statement, that oil is in the form of CIS. In trans form, the phrase «t» is added next to the abbreviation.

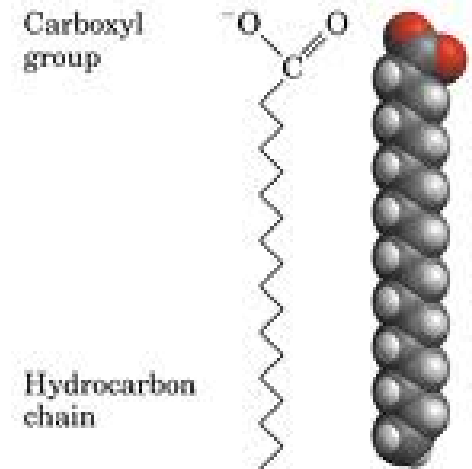
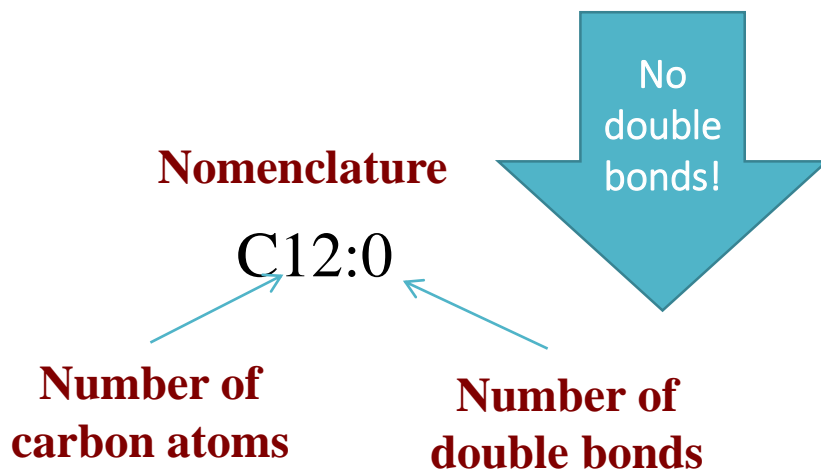
❖ The carbon skeleton structure is generally shown in a zigzag pattern.

Abbreviated designation	Structure ^a	Common name
14:0		Myristic acid
16:0		Palmitic acid
18:0		Stearic acid
18:1 (9)		Oleic acid
18:2 (9, 12)		Linoleic acid
18:3 (9, 12, 15)		Linolenic acid

^a Numbering of carbon atoms starts with carboxyl group-C as number 1.
^b A percentage estimate based on world production of edible oils.

Lipids: Nomenclature – Saturated Fatty Acids

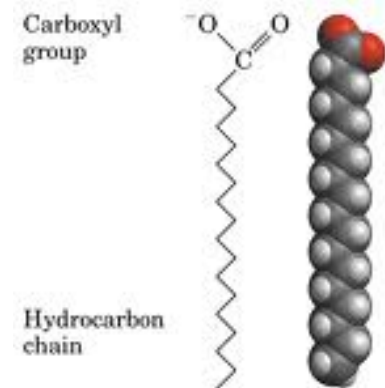
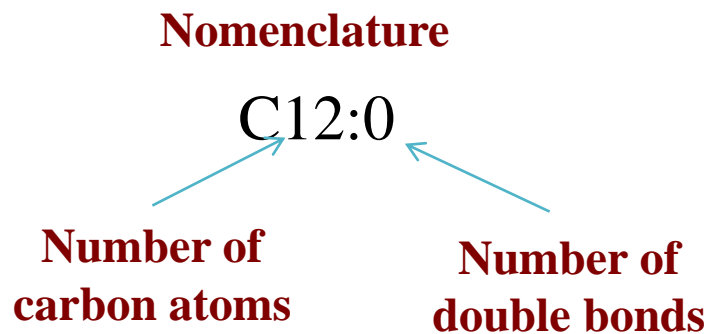
- Saturated fatty acids are described according to the number of carbon atoms they have per molecule.
- Saturated fatty acids have a carboxyl head group (which may be ionized in the free fatty acid) and a hydrocarbon chain
- Saturated fatty acids tend to be straight chained, which enables easy packing into crystal structures. They therefore have a relatively high melting point when compared to unsaturated fatty acids with similar chain lengths.



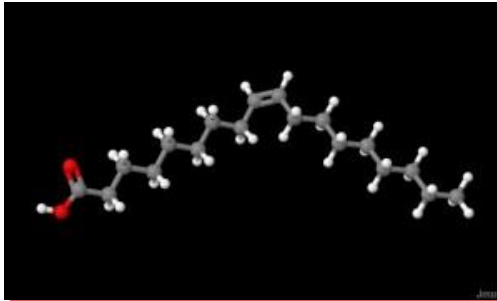
Lipids: Nomenclature – Saturated Fatty Acids

Saturated Fatty Acids: Structure, name and melting behavior

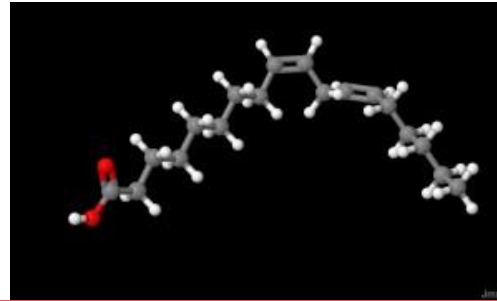
Formula	Common Name	Melting Point	Nomenclature
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	lauric acid	45 °C	C12:0
$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	myristic acid	55 °C	C14:0
$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	palmitic acid	63 °C	C16:0
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	stearic acid	69 °C	C18:0
$\text{CH}_3(\text{CH}_2)_{18}\text{CO}_2\text{H}$	arachidic acid	76 °C	C20:0



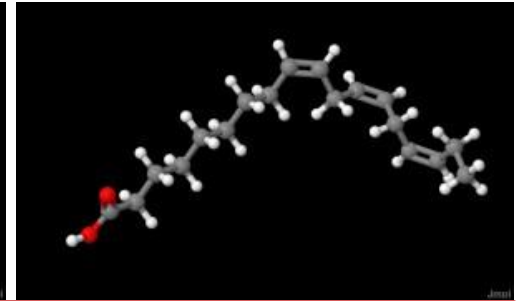
Lipid Structure: Nomenclature – Unsaturated Fatty Acids



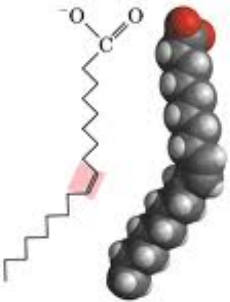
OLEIC A.



LINOLEIC A.



LINOLENIC A.

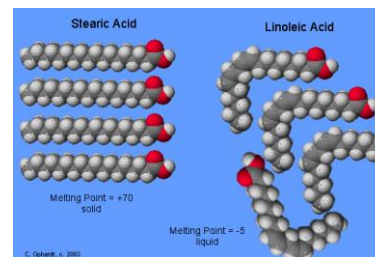


- Unsaturated fatty acids are described according to the number of carbon atoms and number of double bonds they have per molecule.
- Unsaturated fatty acids have a carboxyl head group (which may be ionized in the free fatty acid) and a hydrocarbon chain
- Unsaturated fatty acids tend to be bent chained, which makes their packing into crystal structures more difficult. They therefore have a relatively low melting point when compared to saturated fatty acids with similar chain lengths.

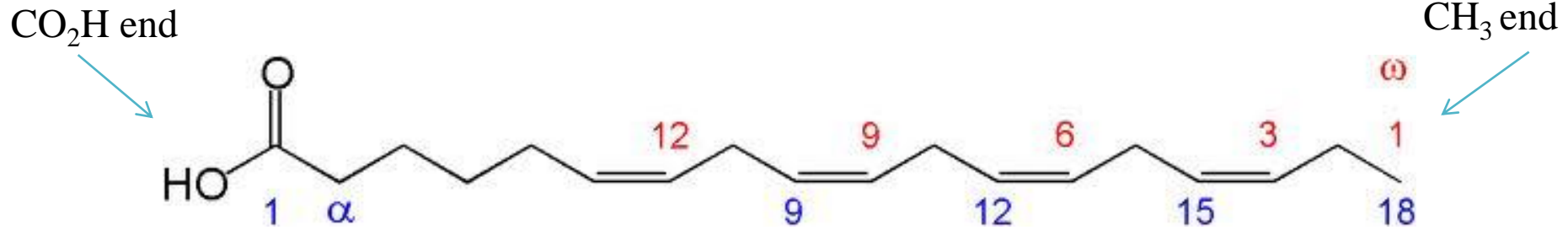
Lipid Structure: Unsaturated Fatty Acids

Unsaturated Fatty Acids: Structure, name and melting behavior

Formula	Common Name	Melting Point	Nomenclature
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	palmitoleic acid	0 °C	C16:1
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	oleic acid	13 °C	C18:1
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	linoleic acid	-5 °C	C18:2
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	linolenic acid	-11 °C	C18:3
$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{CO}_2\text{H}$	arachidonic acid	-49 °C	C20:4



Lipid Structure: Nomenclature – Unsaturated Fatty Acids



Need method of indicating position of double bonds along chain

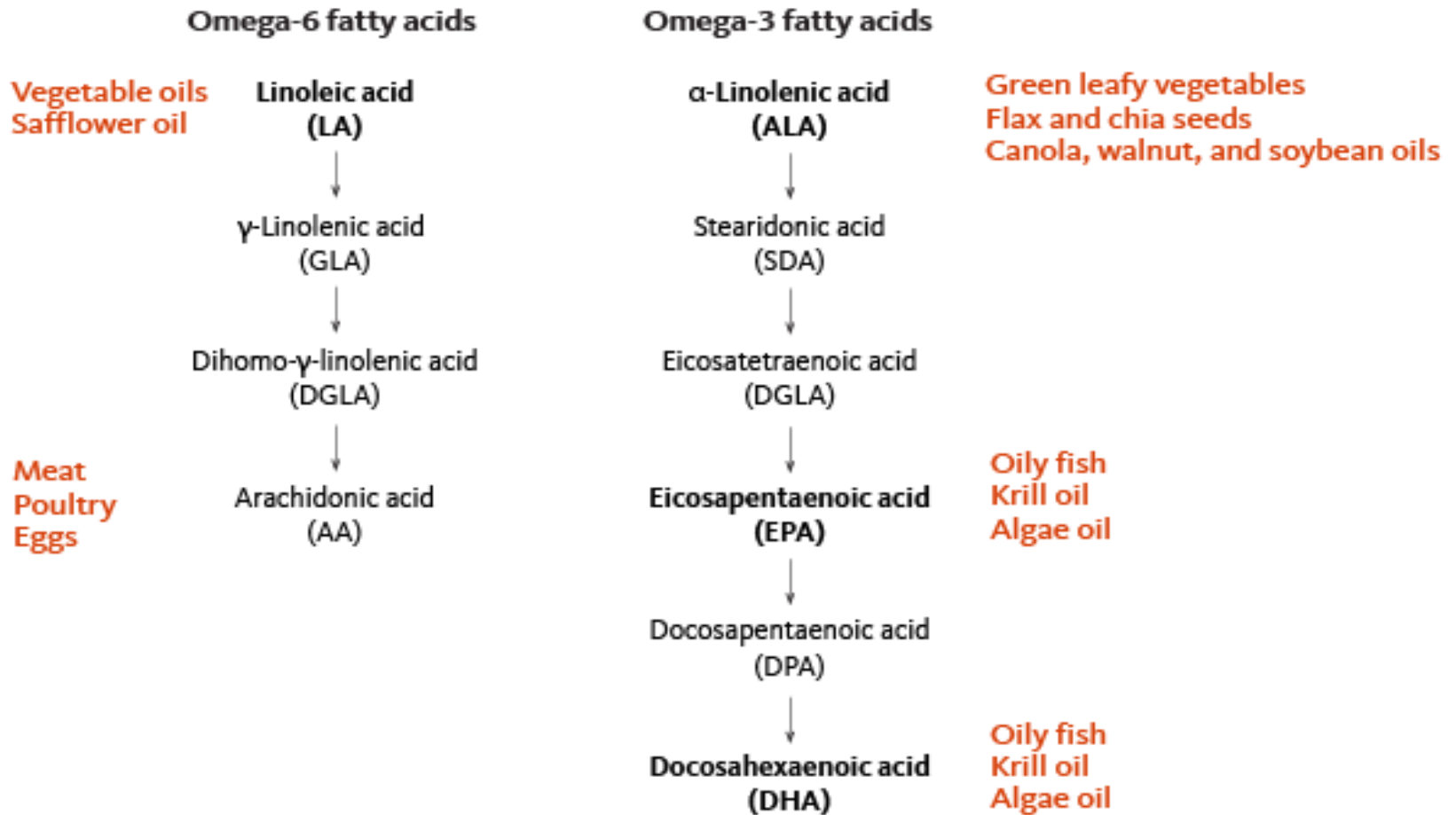
Stearidonic acid: 18:4 (n-3)

Number of carbon atoms

Number of double bonds

Nomenclature (ω-method): The carbon next to the carboxylate is known as α, the next carbon β, and so forth. Since biological fatty acids can be of different lengths, the last position is labeled as a "ω", the last letter in the Greek alphabet. Since the physiological properties of unsaturated fatty acids largely depend on the position of the first unsaturation relative to the end position and not the carboxylate, the position is signified by (ω - n). For example, the term ω-3 signifies that the first double bond exists as the third carbon-carbon bond from the terminal -CH₃ end (ω) of the carbon chain. The number of carbons and the number of double bonds is also listed. ω-3 18:4 (stearidonic acid) or 18:4 ω-3 or 18:4 n-3 indicates an 18-carbon chain with 4 double bonds, and with the first double bond in the third position from the CH₃ end

Essential fatty acids, are fatty acids that humans must ingest because the body requires them for good health but cannot synthesize them.



Omega-6 (n-6) and omega-3 (n-3) fatty acids comprise the two classes of essential fatty acids (EFA). The parent compounds of each class, linoleic acid (LA) and α -linolenic acid (ALA) (bold font), give rise to longer chain derivatives inside the body. Due to low efficiency of conversion of ALA to the long-chain omega-3 PUFA, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), it is recommended to obtain EPA and DHA from additional sources. Dietary sources

Alpha linolenic (ALA) has preventive effects on heart diseases, and cancer.

ALA; is found in vegetable oils, especially soy, flax and walnut oil, and many green leafy vegetables, especially broccoli, spinach, lettuce, and cabbage.

The source of **EPA** (eicosapentanoic a.) and **DHA** (docosahexanoic a.) is fatty fish. The body can partially convert ALA to EPA and DHA.

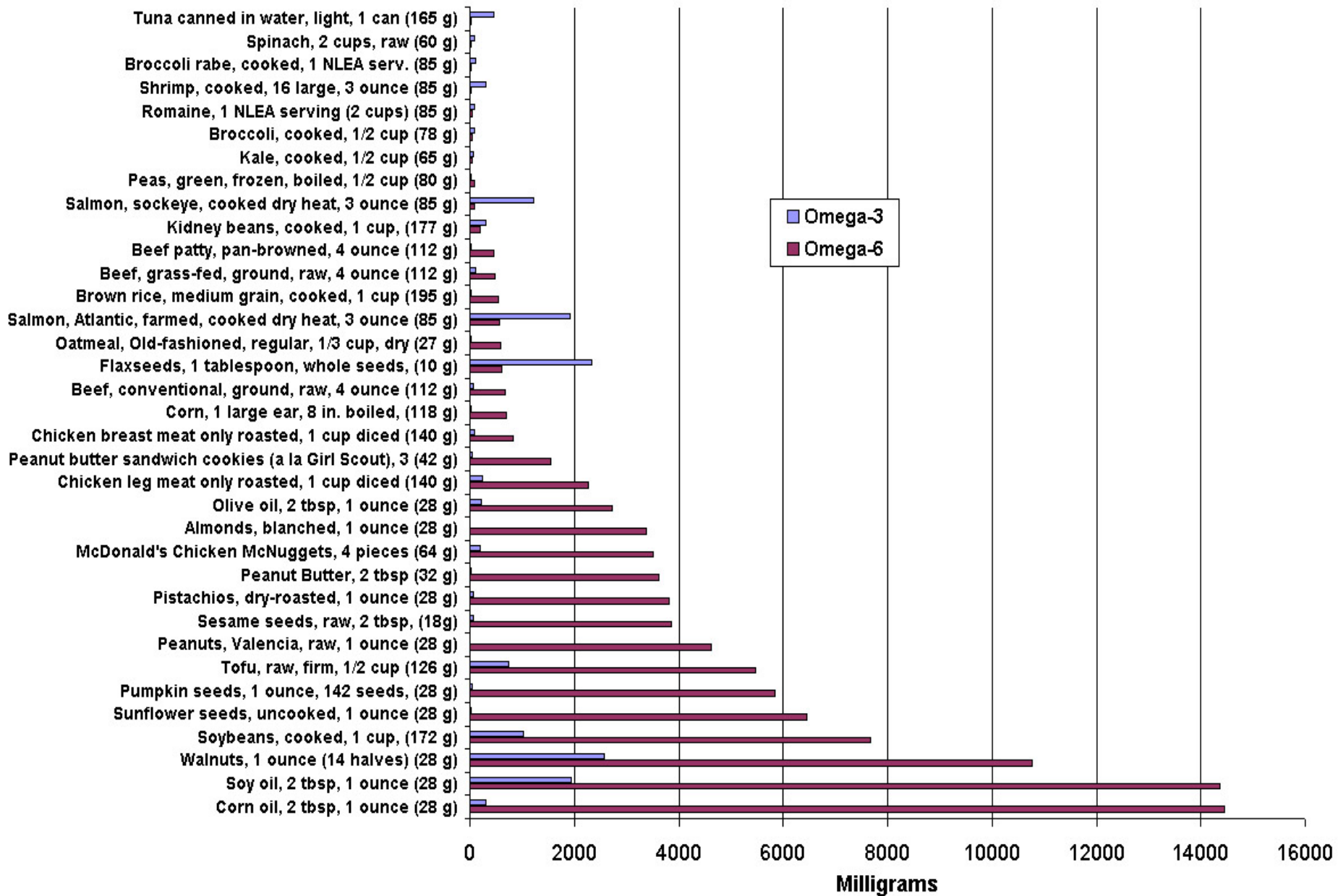
Omega 6 affects the cholesterol level in blood. The main sources are vegetable oils, oil seeds and nuts. (Linoleic and arachidonic acids)

It is recommended that the **linoleic acid (w6): ALA (w3)** ratio in the diet should be in the range of 5:1 to 10:1.

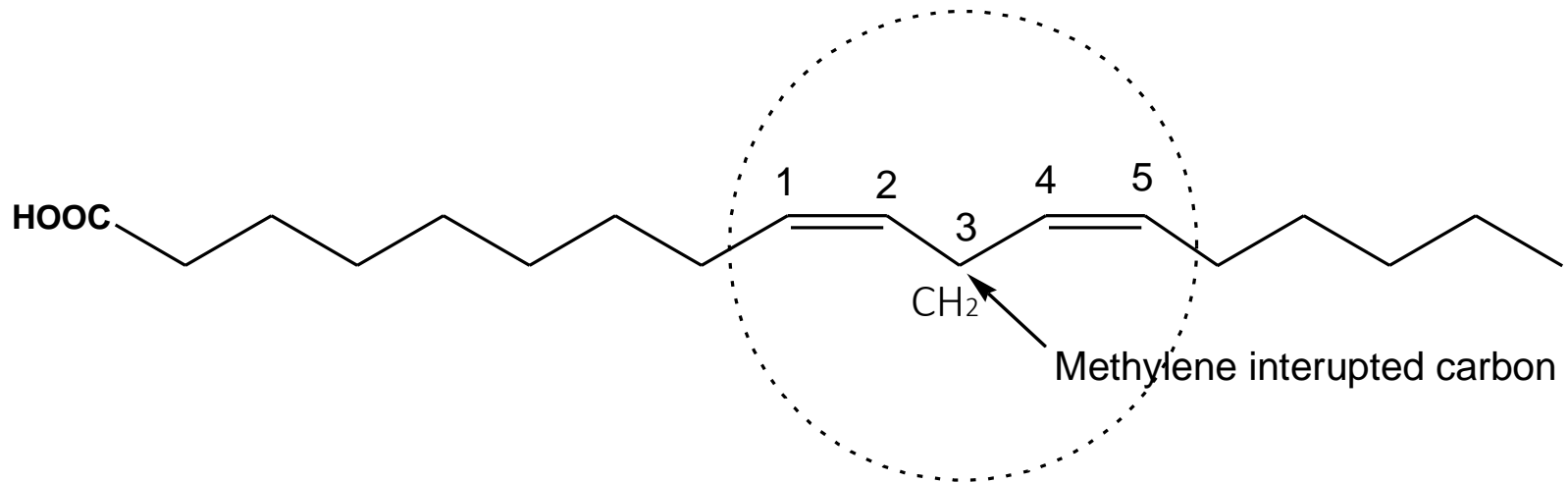
Omega 3 and 6 have positive effects especially on Type 2 diabetes.

A sample table is given for the omega 3 and omega 6 content of some foods.

Omega-6 and Omega-3 in Common Foods



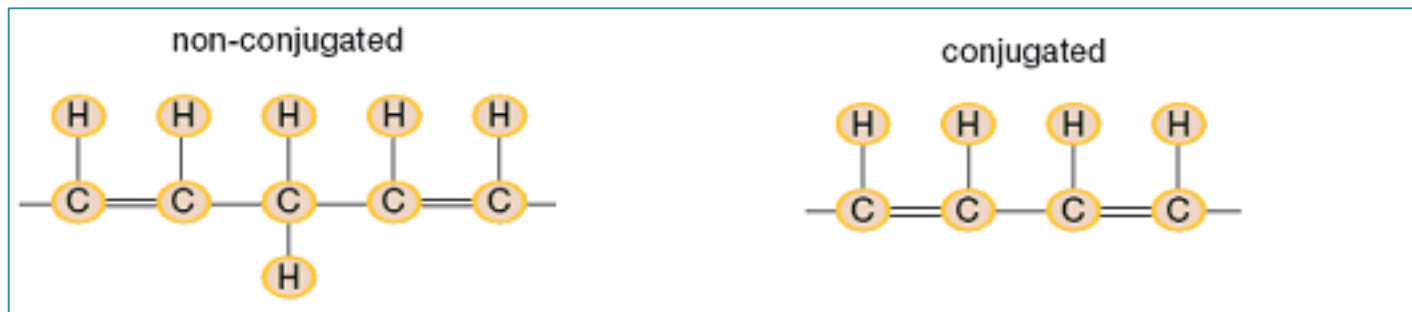
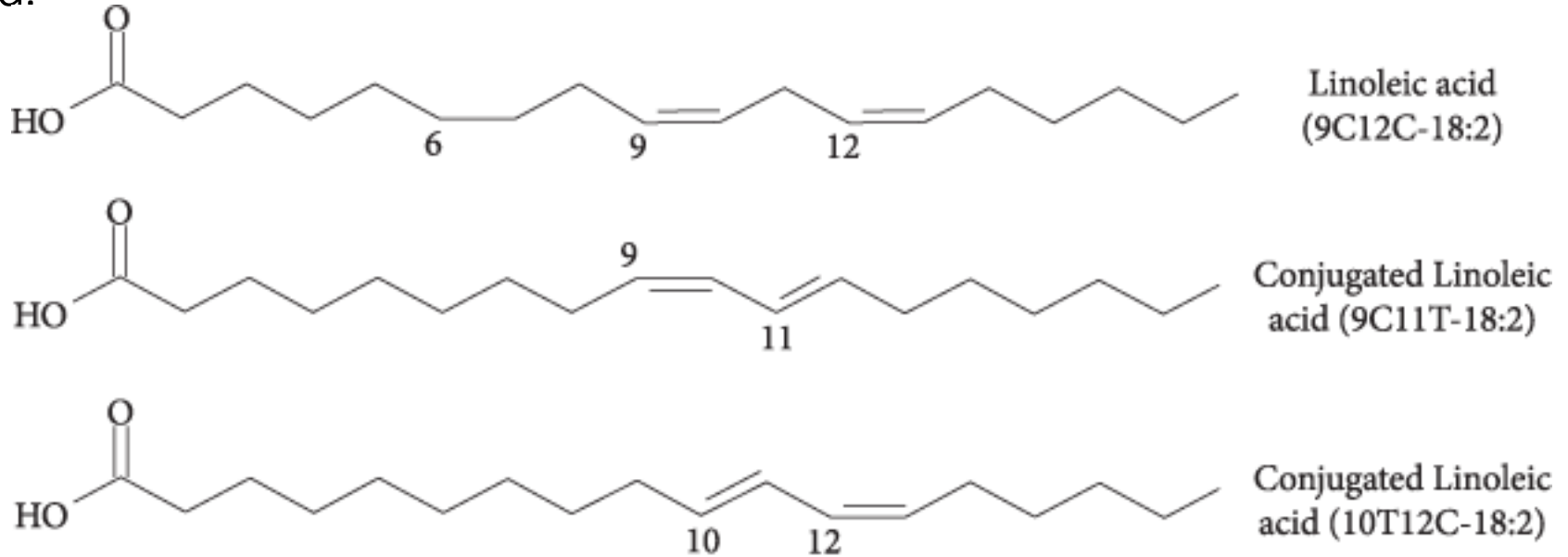
Lipid Structure: Polyunsaturated Fats



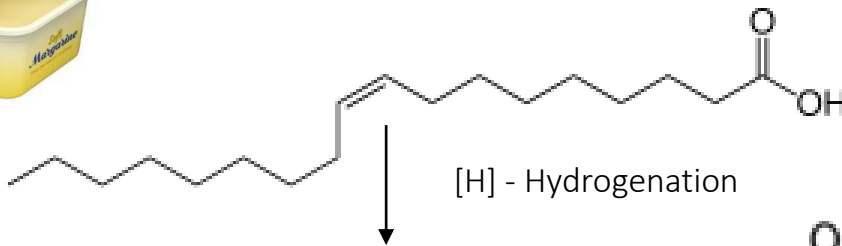
Pentadiene system of linoleic acid

Pentadiene system: In nature, polyunsaturated fatty acids have a *pentadiene system* consisting of non-conjugated double bonds, *i.e.*, they have a “methylene interrupted” carbon between the double bonds.

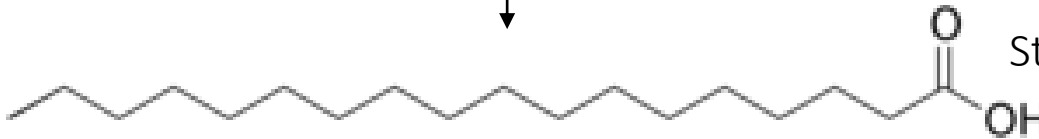
Conjugated Fatty Acid: Conjugated fatty acids are polyunsaturated fatty acids in which at least one pair of double bonds is separated by only one single bond.



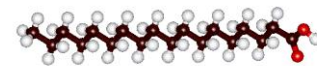
Lipid Structure: Hydrogenation



Oleic acid (C18:1)



Stearic acid (C18:0)

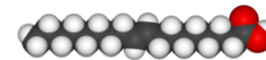


Higher melting point : more solid, less prone to oxidation

And, as side products...



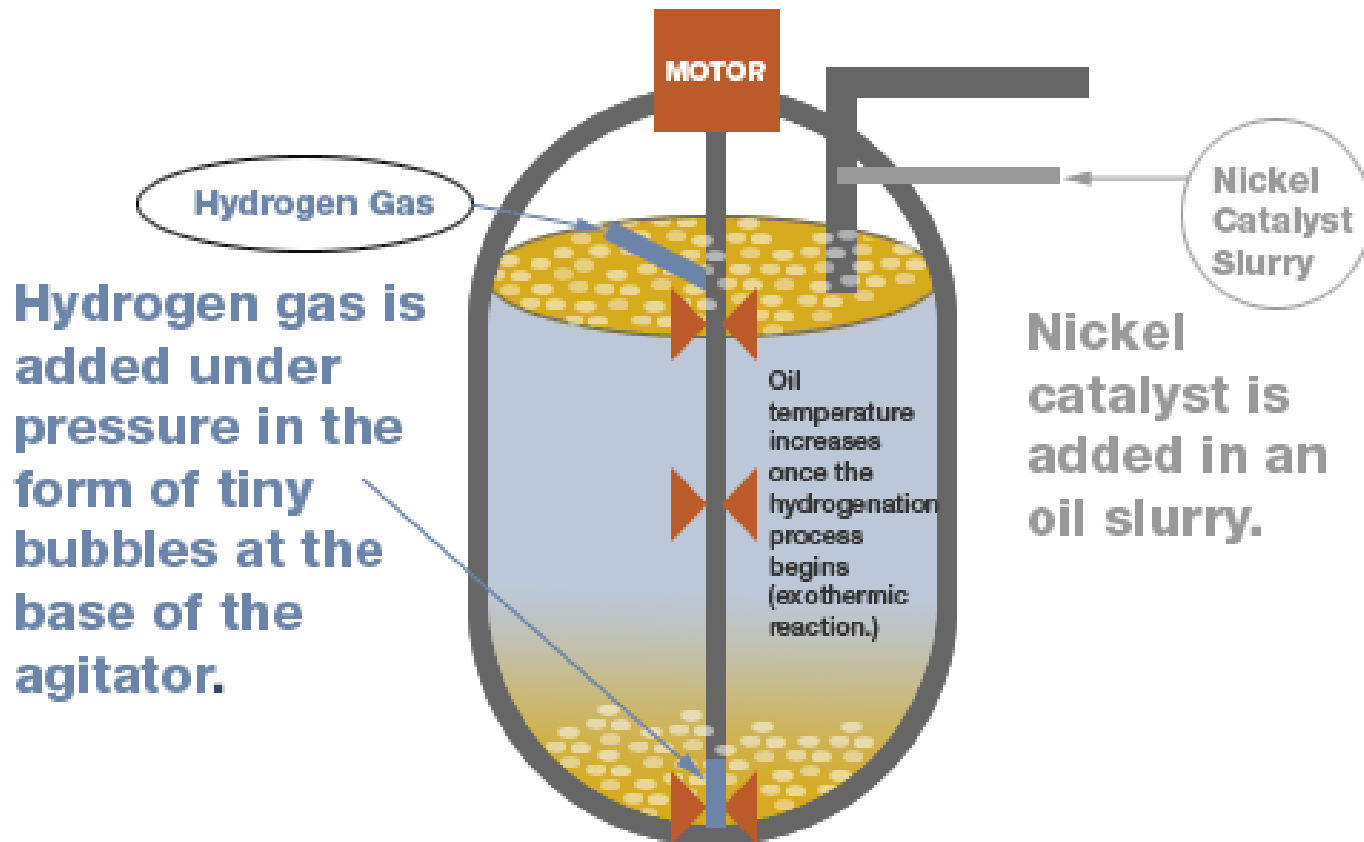
Eladic acid



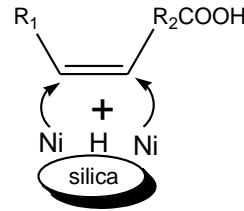
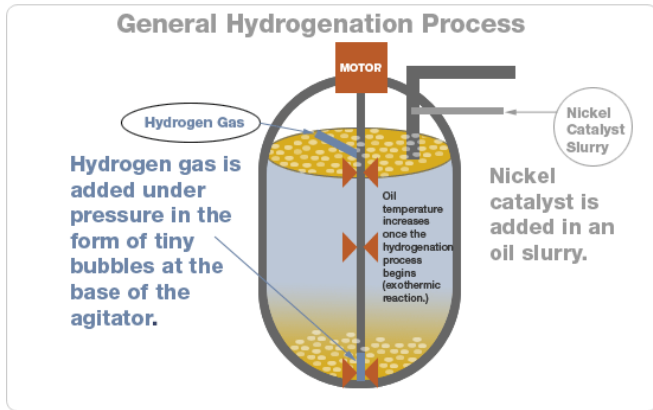
A trans-fatty acid

Lipid Structure: Hydrogenation Mechanism

General Hydrogenation Process

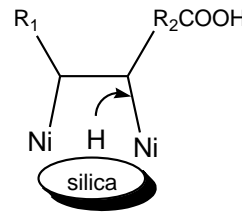


Lipid Structure: Hydrogenation Mechanism



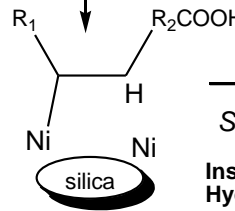
(1) An unsaturated lipid approaches the surface of a catalyst in the presence of hydrogen

Step 1

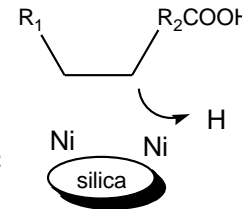


(2) A hydrogen atom binds to one of the carbon atoms originally involved in the double bond.

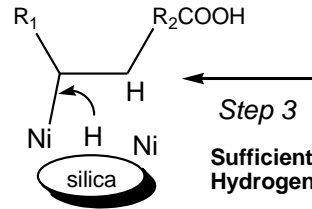
Step 2



Step 4
Insufficient Hydrogen

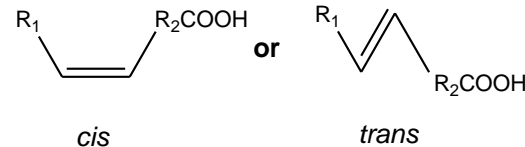
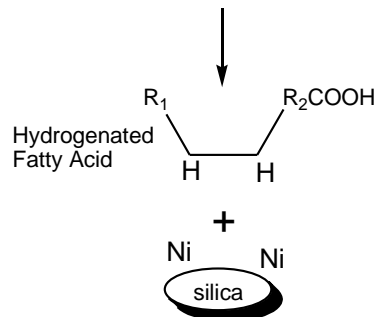


(4) In the presence of insufficient hydrogen, the first hydrogen atom is lost, and a mixture of cis- and trans- unsaturated fatty acids are formed (partial hydrogenation)




Step 3
Sufficient Hydrogen


(3) In the presence of sufficient hydrogen, another hydrogen atom binds to the original fatty acid and forms a saturated fatty acid (fully hydrogenation)



Lipid Structure: Hydrogenation

	Soybean Oil (Liquid)	Hydrogenated Soybean/Cottonseed Oil Shortening (Solid)
Saturated Fatty Acids	15.7%	↑ 27.6%
Monounsaturated Fatty Acids	22.8%	↑ 39.4%
Polyunsaturated Fatty Acids	57.7%	↓ 25.8%
<i>Trans</i> fatty acids	0.7%	↑ 14.0%
Cholesterol	0	0



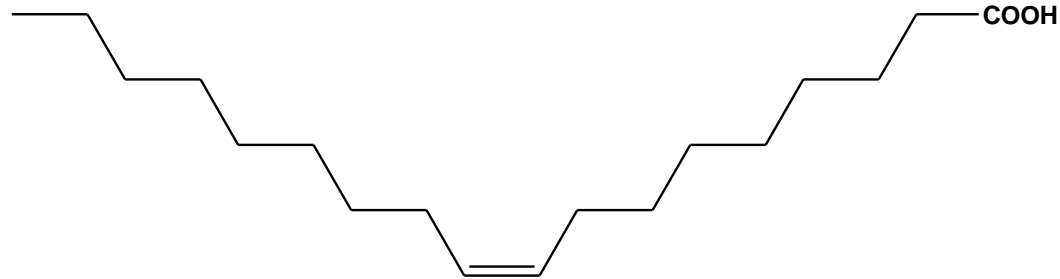


Used to be up to 40%
But is now limited to 2%

Example of increase in *Trans* fatty acids in a commercial soybean oil after hydrogenation

Lipid Structure: Trans versus Cis Forms

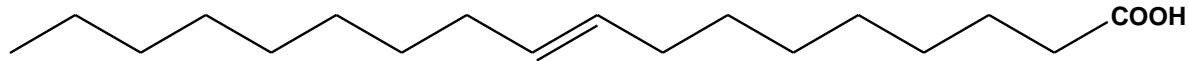
Cis-form



Most common in nature

cis-9-octadecenoic acid (oleic acid)

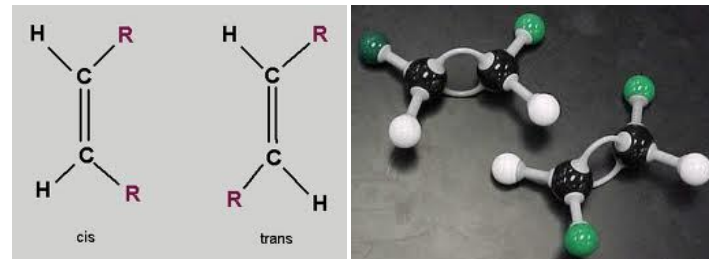
Trans-form



Occurs during processing

trans-9-octadecenoic acid (elaidic acid)

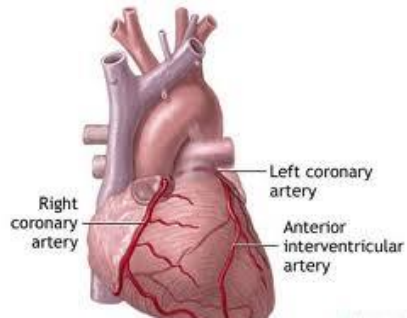
Practical Importance: Trans-fatty acids have a higher melting point than cis-fatty acids, have greater solidity, and are less prone to lipid oxidation



Health Problems: Trans-Fats

Increased Health Risks

- Coronary Heart Disease
- Cancer
- Obesity
- Diabetes



increases LDL and
decreases HDL

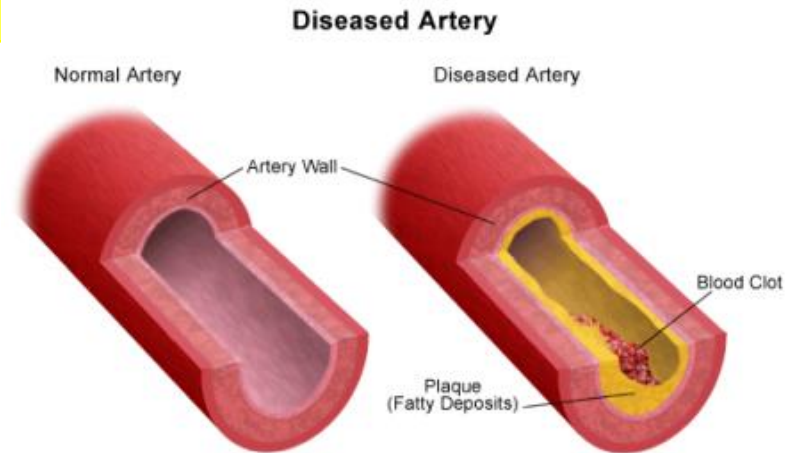
Saturated fatty acids:
increases LDL and HDL

2019 April: European Commission limited the amount of *industrial* trans fatty acids in food products to 2 grams per 100 grams of fat.

Trans-fats ban is full effective starting April 1st 2021

Many food companies removing trans-fats from their products – problems associated with reformulation

- *Increased tendency for oxidation*
- *Not solid enough*



In Turkey, TFAs in foods have also been banned as in EU. It will be effective on 1st of January 2021.

TYPES OF FATTY ACIDS

(according to the number of double bonds)



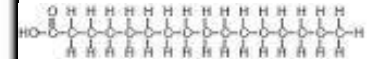
Saturated (No bond)



Monounsaturated (1 bond)



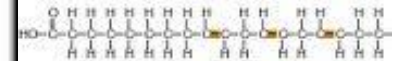
Polyunsaturated (>1 bond)



(a) Palmitic acid (saturated)



Saturated triglyceride



(b) Linoleic acid (polyunsaturated)



Unsaturated triglyceride



arachidic



stearic



palmitic



erucic



oleic



arachidonic



linoleic



linolenic

Health Benefits: Polyunsaturated fats (PUFAs)

Decreased Health Risks

- Coronary Heart Disease
- Cancer
- Obesity
- Diabetes

increases HDL
Lowers LDL

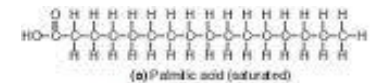


ω -3 fatty acids

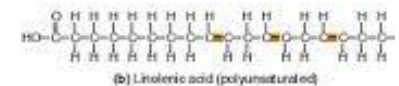


Saturated Fatty acids:

- Straight chains
- Efficient molecular packing
- High m.p.; More solid
- Potential health problems



Saturated triglyceride



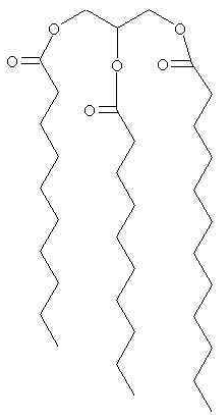
Unsaturated triglyceride

Unsaturated Fatty acids:

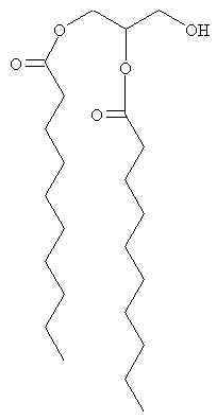
- Bent chains
- Inefficient molecular packing
- Low m.p.; More liquid
- Potential health benefits

Lipid Structure: Other Acylglycerols

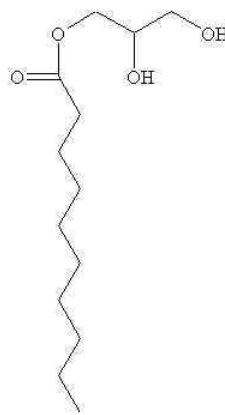
Other acylglycerols are also used in foods as functional ingredients



**Triacylglycerol
(TAG)**



**Diacylglycerol
(DAG)**



**Monoacylglycerol
(MAG)**

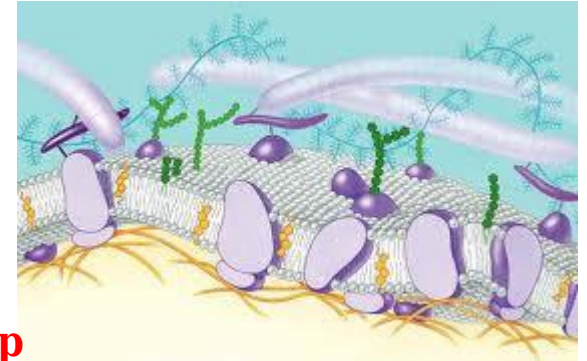
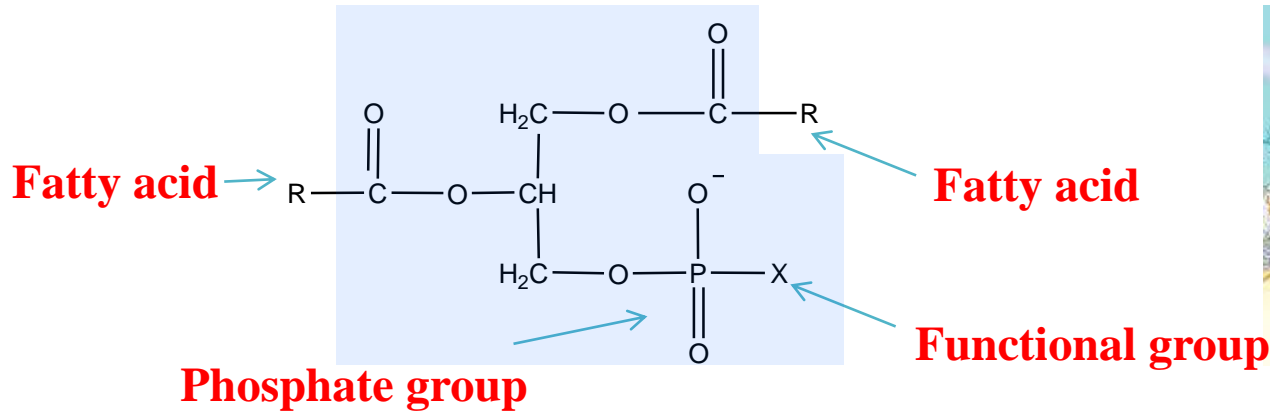


**Free Fatty acid
(FFA)**



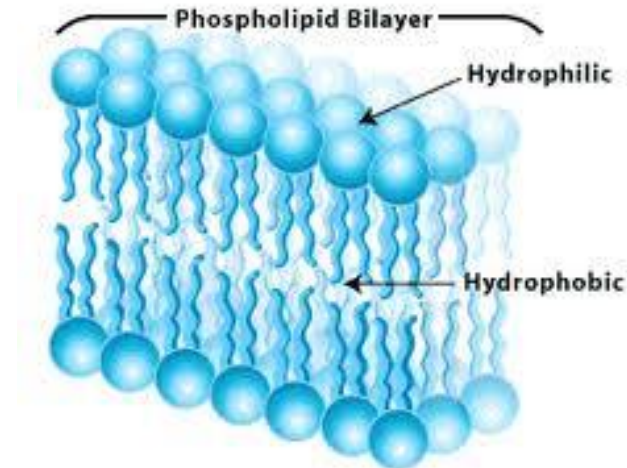
- DAG and MAG are often used as emulsifiers
- DAG, MAG and FFA are digestion products of TAG

Other Lipid Structures: Phospholipids

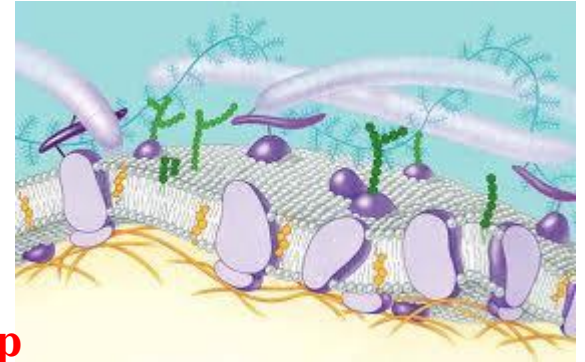
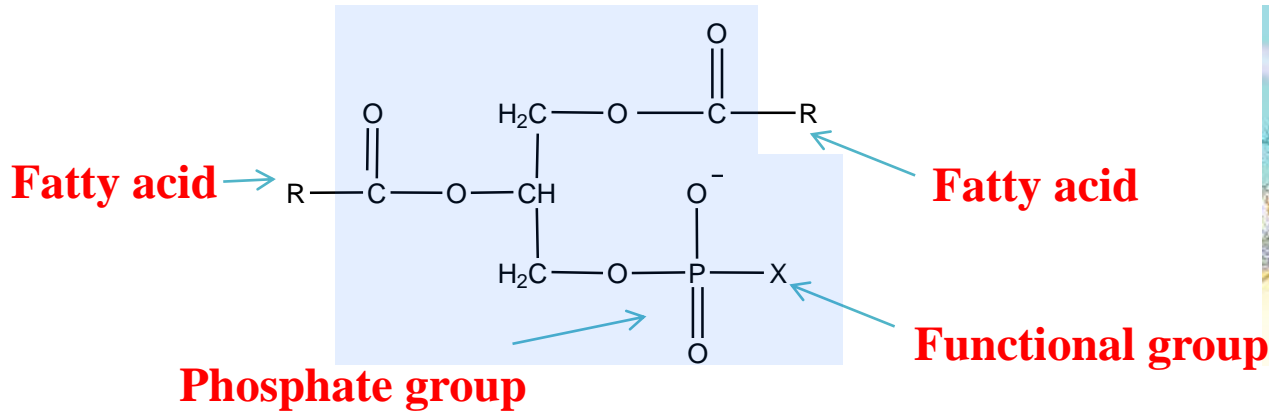


Phospholipids are important natural constituents of the cell walls of plants and animals.

- **They consist of a phosphate head group that is esterified to a glycerol that also contains two fatty acid chains**
- **There may be different functional groups (X) attached to the phosphate group**
- **Phospholipids can be used as functional ingredients in foods because of their surface-active properties.**



Other Lipid Structures: Phospholipids

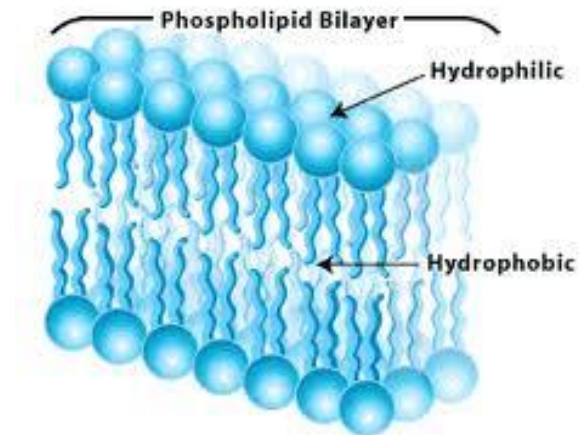
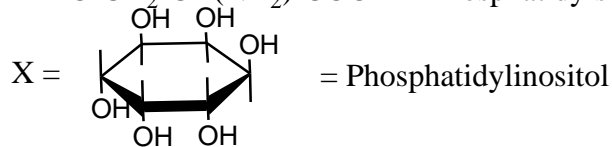


X = OH = Phosphatidic acid

X = O-CH₂-CH₂-NH₂ = Phosphatidylethanolamine

X = O-CH₂-CH₂-N⁺(CH₂)₃ = Phosphatidylcholine

X = O-CH₂-CH(NH₂)-COOH = Phosphatidylserine



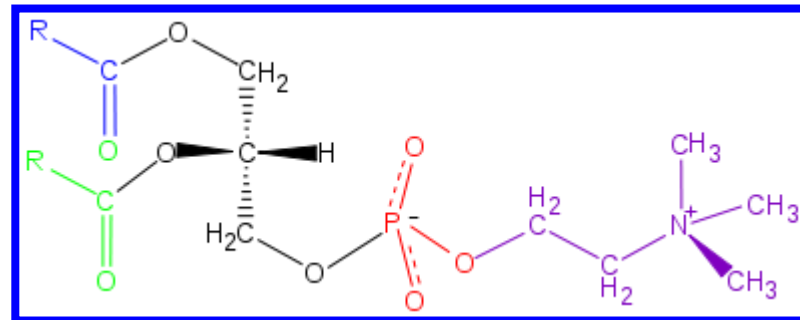
Phospholipids - or phosphoglycerides - are triglycerides containing phosphate group and sometimes nitrogen in their structure (typically at the 3rd carbon). Phospholipids differ according to the group attached.

PHOSPHOLIPIDS (PL)

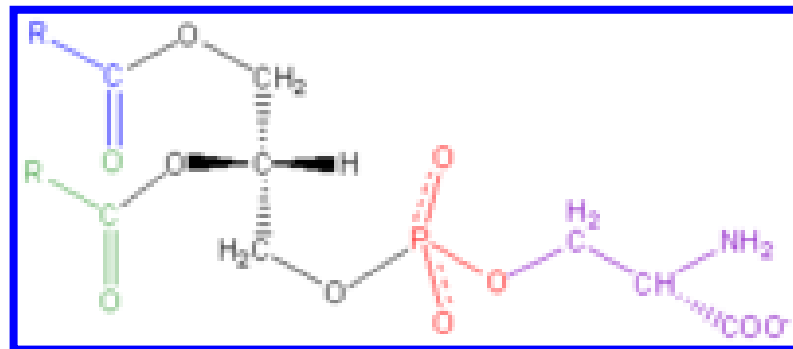
A fatty acid and a nitrogenous base (choline, ethanolamine, serine) are formed by their hydrolysis. The simplest PL is phosphatidic acid, which does not contain nitrogen in structure.

The most common PL in foods are phosphatidyl ethanolamine (Cephalin), phosphatidylcholine (Lecithin) and phosphatidylserine.

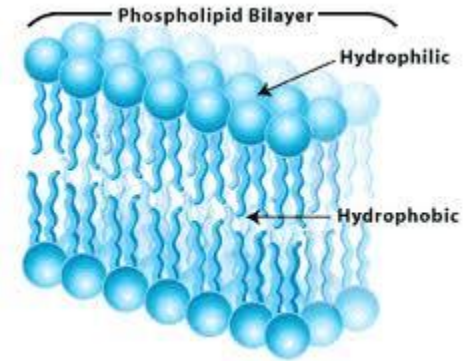
PHOSPHATIDYL CHOLIN (Lecithin)



PHOSPHATIDILSERINE



PLs

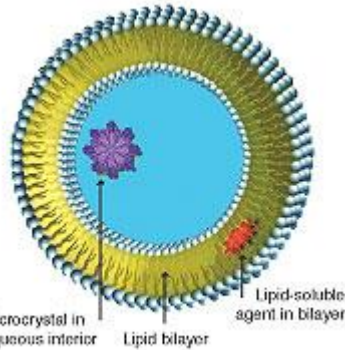
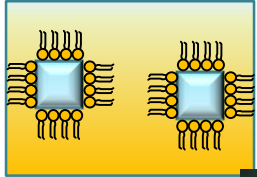


They are surface active compounds because they contain phosphate with high polarity in their structure. Therefore, they ensure that biological membranes have multiple layers and are the main components of the membrane. The tail part of the molecule is hydrophobic and the head part is hydrophilic.

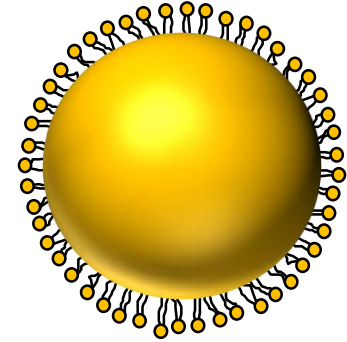
Due to their surface activity, they are used as emulsifiers in the food industry (especially soy lecithin) and they disperse the water-oil phase together. The foods they are most abundant in are soy, eggs, mustard, sunflower, milk and caviar.

Phospholipids: Applications

- **Phospholipids can be used as functional ingredients in foods because of their surface-active properties.**

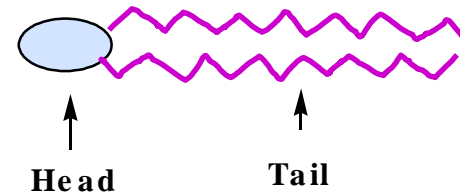


Encapsulants – To encapsulate, stabilize and release functional food ingredients



Emulsifiers – To form & stabilize emulsions

Head group (hydrophilic, polar)
Fatty acid chains (hydrophobic, nonpolar)



Dispersants – To stabilize sugar particles in chocolate

Phospholipids are used as functional ingredients in foods (e.g., as emulsifiers, dispersants, wetting agents, viscosity modifiers, encapsulants).

Other Lipid Structures: Waxes

Edible waxes are esters formed by long chain alcohols and acids that have solid-like (“plastic”) characteristics near ambient temperatures, but melt at higher temperatures. Like other lipids, waxes are insoluble in water but soluble in organic nonpolar solvents.

Waxes can be grouped as animal (lanolin), herbal (carnauba) or mineral (petroleum wax). They act as protectors on the outer surface of animals and plants. They have been used in the food industry for hundreds of years as a coating agent to slow respiration in stored fruits and eggs.

Applications:

- Coatings
- Encapsulants

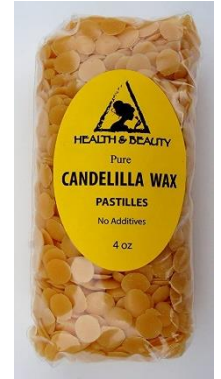


Waxes are found in a variety of plant and animal sources *e.g.*, bees wax (honeycombs), shellac wax (insects), Candelilla and Carnauba (plants), paraffin wax (hydrocarbon)

Other Lipid Structures: Waxes



Carnauba wax is a natural **wax**. It comes from the leaves of the *Copernicia prunifera* palm grown only in Brazil.



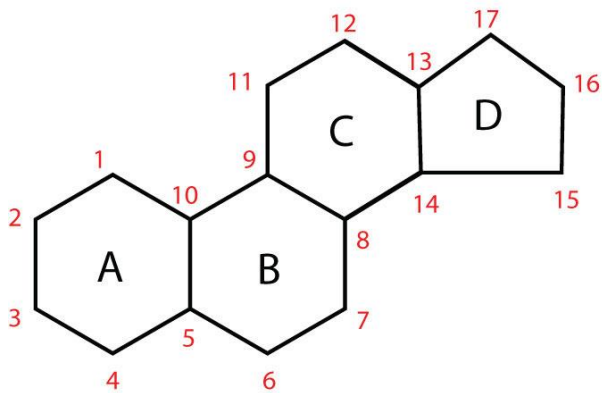
Candelilla wax is a **wax** derived from the leaves of the small Candelilla shrub native to northern Mexico and the southwestern United States,



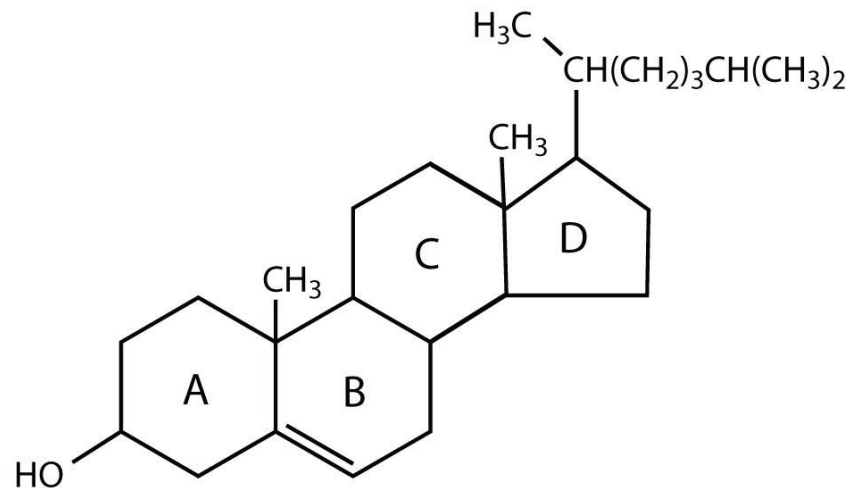
STEROLS

Basic structure of sterols

- Derivatives of steroids.
- A carbon skeleton with **four rings including three 6-carbon rings** and **one hydroxyl group (OH)** in the carbon 3-position of the A-ring.
- Various side chains are attached to the ring.



(a) Steroid skeleton

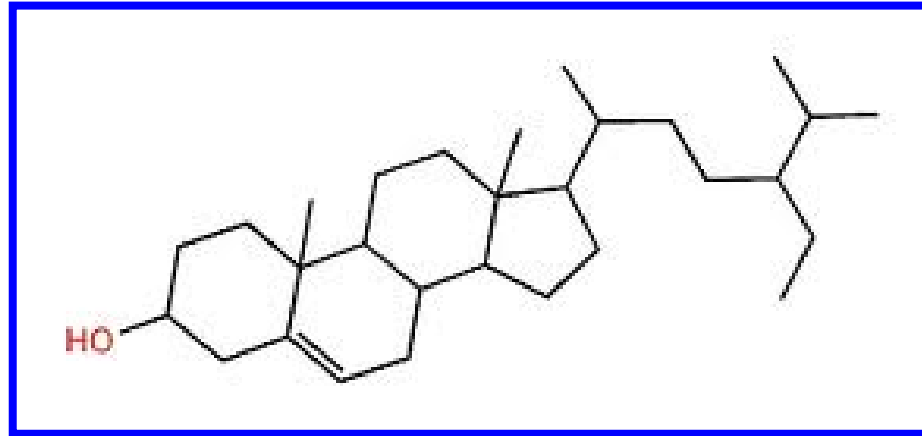


(b) Cholesterol

STEROLS

They are lipids found in plants (phytosterols) and animals (zoosterols). The most common sterol in animal tissues is **cholesterol**. In plants, **beta sitosterol** and **stigmasterol** are the most common.

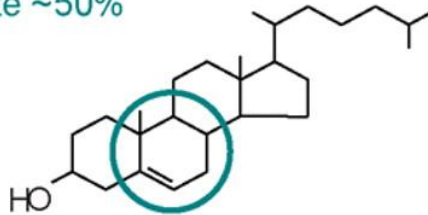
Beta sitosterol



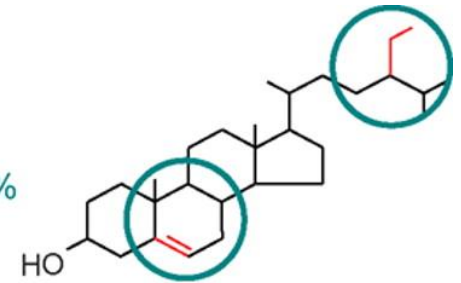
Phytosterols are molecules that can be extracted from plant sources that have a similar structure to cholesterol. They have been shown to be effective at reducing coronary heart disease, and are therefore be incorporated into functional foods. Its main sources are fatty nuts and unrefined oils.

Phytosterols

Cholesterol
Absorption rate ~50%

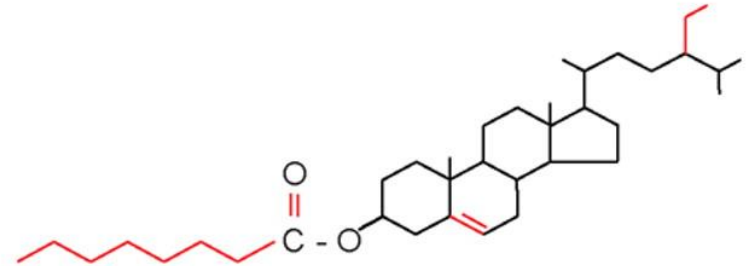


Plant sterol
Main component:
sitosterol
Absorption rate ~0.5%



Cholesterol is present in the cell membranes of human beings and plays a vital function in maintaining human health. However, too much cholesterol in the diet can lead to heart disease, which has been linked to cholesterol build up in the arteries.

Plant sterol ester

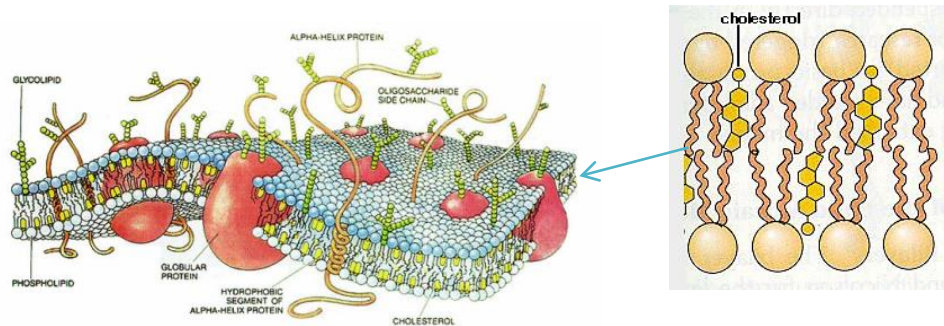
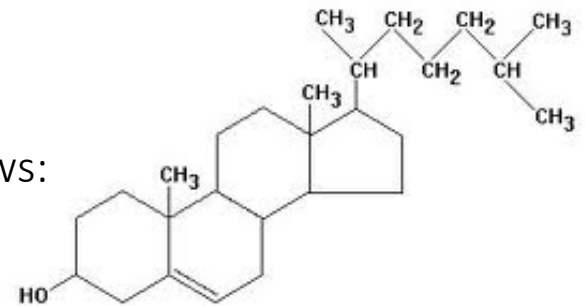


Phytosterols have similar structures to cholesterol – they can reduce cholesterol levels and improve human health

Cholesterol

Cholesterol concentrates in the cell membrane and stabilizes the structure. Cholesterol is also a precursor in the production of bile acids and in the synthesis of vitamin D with the help of sunlight. Since there is a link between high cholesterol levels and cardiovascular diseases, it is recommended to reduce its dietary intake.

The foods with the highest cholesterol (mg / 100g) are as follows:
Brain 3100, egg yolk 1085, caviar 588, egg 372, butter 250.



Some cholesterol is essential for normal cell functions



Too much cholesterol can cause health problems: such as clogged arteries and heart disease

