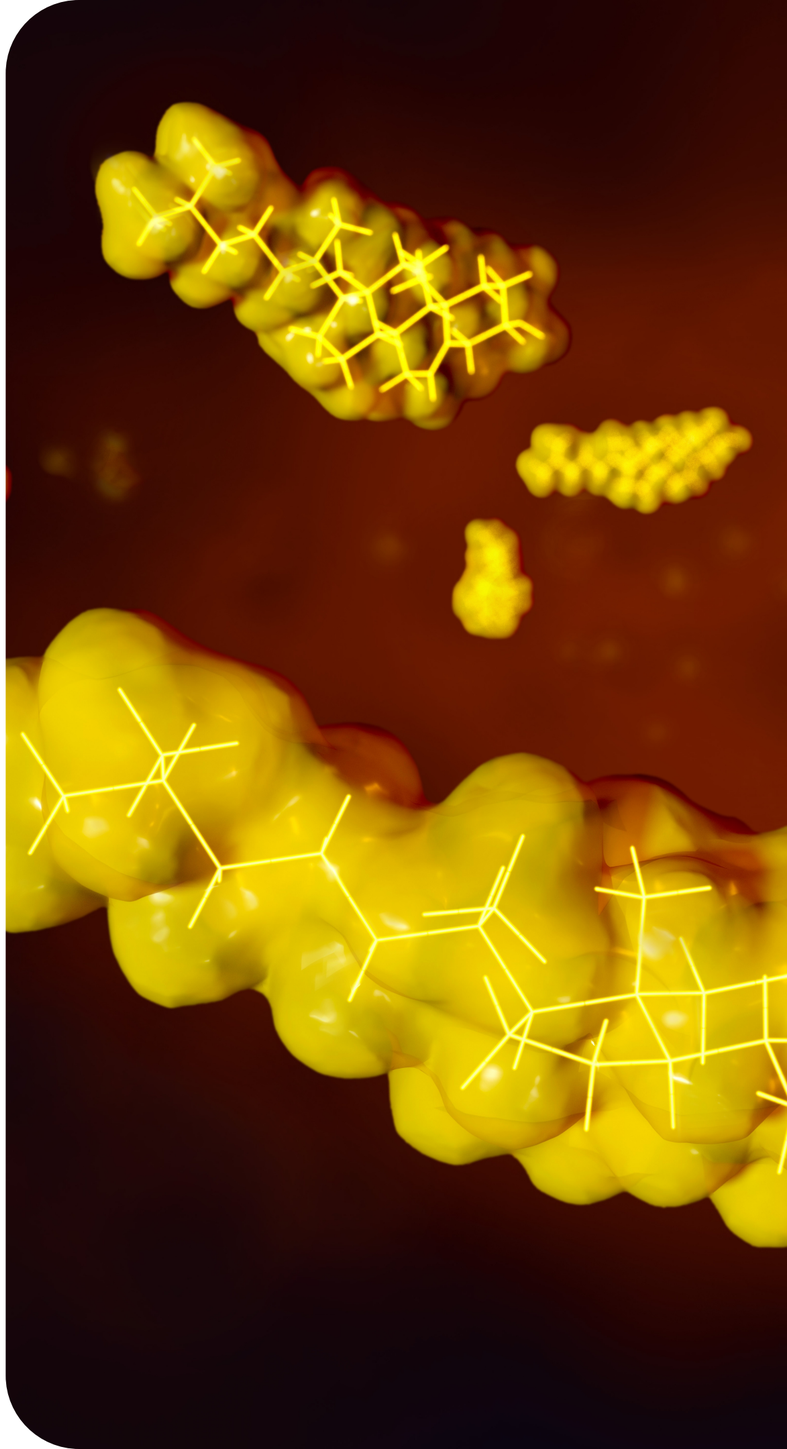
Chem 113

Lipids

Prepared by
Robert D. Unciano



Lipids

- A lipid is an organic compound found in living organisms that is insoluble (or only sparingly soluble) in water but soluble in non-polar organic solvents.
- Unlike other biomolecules, lipids do not have a common structural features that serves as the basis for defining such compounds.
- Classification: They are classified on the basis of solubility characteristics not on any functional groups.
- Insoluble or sparingly soluble in water
- Soluble in non-polar organic solvents

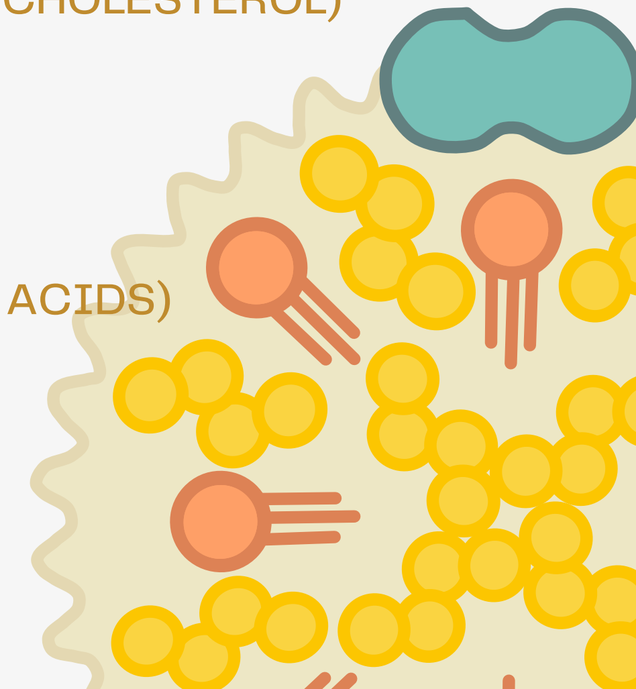
Lipids

- Lipids molecules (fat, biological wax, steroid, glycerophospholipid, sphingophospholipid and sphingoglycolipid, etc.) have structural diversity (acyclic, cyclic, or polycyclic).
- The common thread that ties all of these compounds together is solubility rather than structure.
- All lipids are insoluble in water.

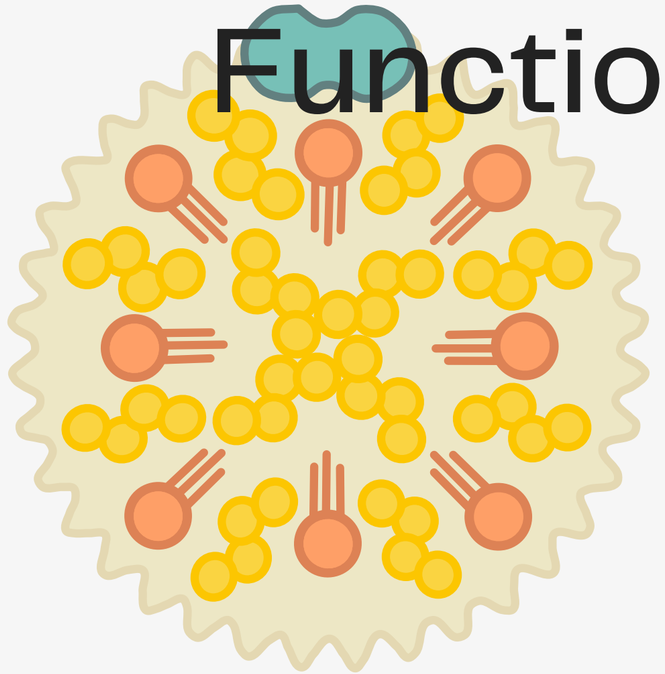
Two Common Methods for Subclassifying Lipids
1. Biochemical function
2. Saponification reaction

Biochemical Function

1. ENERGY-STORAGE LIPIDS (TRIACYLGLYCEROL)
2. MEMBRANE LIPIDS (PHOSPHOLIPIDS, SPHINGOGLYCOLIPIDS, CHOLESTEROL)
3. EMULSION LIPIDS (BILE ACIDS)

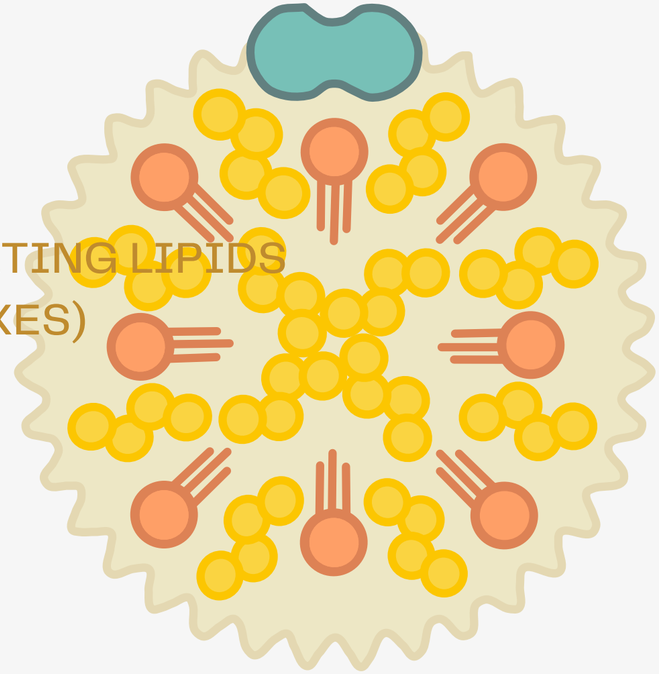


Biochemical Function



4 MESSENGER LIPIDS (STEROID HORMONES AND EICOSANOIDS)

5 PROTECTIVE-COATING LIPIDS (BIOLOGICAL WAXES)



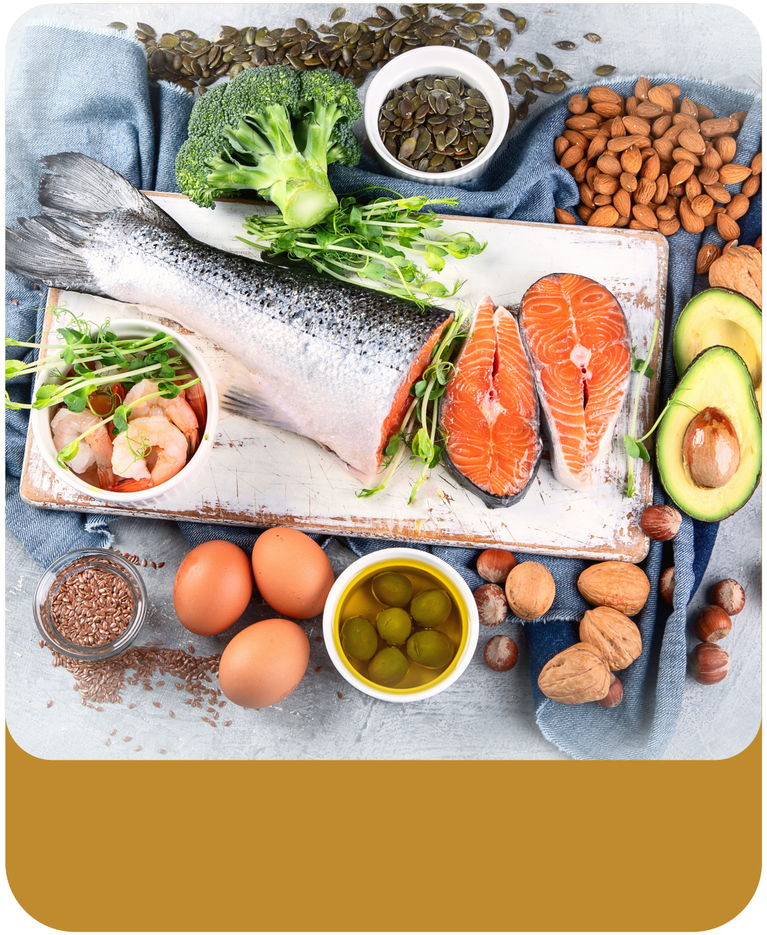
Saponification Reaction

Based on saponification reaction, lipids are divided into two categories:

1. Saponifiable lipids
(triacylglycerols, phospholipids, sphingoglycolipids and biological waxes)

2. Nonsaponifiable lipids
(cholesterol, steroid hormones, bile acids, eicosanoids)

Soap



Fatty Acid

- The most frequently encountered lipid building block is the structural unit called fatty acid.
- All energy-storage lipids, the most abundant type of lipid, contain fatty acid building blocks.
- Most membrane lipids, the second most abundant type of lipid, also contain fatty acid building blocks.
- Fatty acids are rarely found free in nature but rather occur as part of the structure of more complex lipid molecules.

Fatty Acid

- Fatty acid is a naturally occurring monocarboxylic acid.

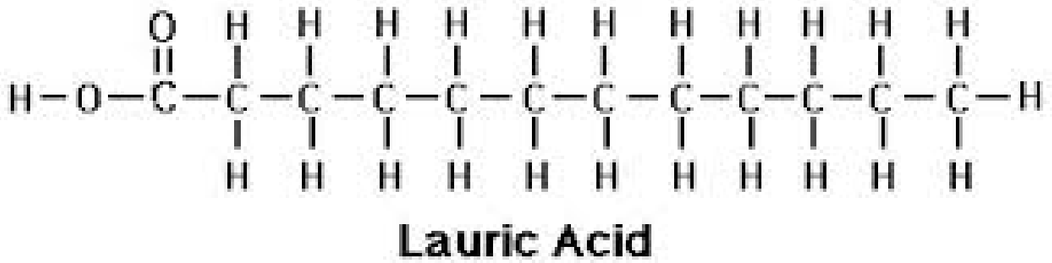
Ex. Lauric acid: CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-COOH or CH3-(CH2) 10-COOH

- Fatty acids nearly always contain an even number of carbon atom and have a carbon chain that is unbranched.

Ex. Lauric acid has 12 carbon atoms and unbranched.

In terms of carbon chain length, fatty acids are characterized as:

a. short-chain fatty acids (C4 – C6)
b. medium-chain fatty acids (C8 – C10)
c. long-chain fatty acids (C12 – C26)



Lauric Acid

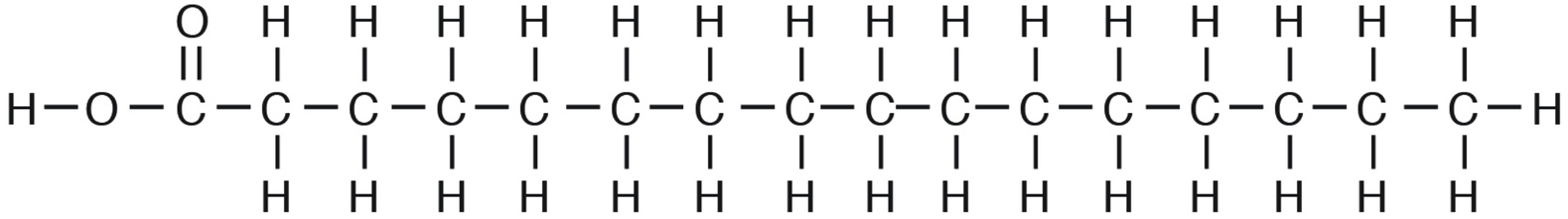
Two Types of Fatty Acids

Saturated Fatty Acid (SFA)

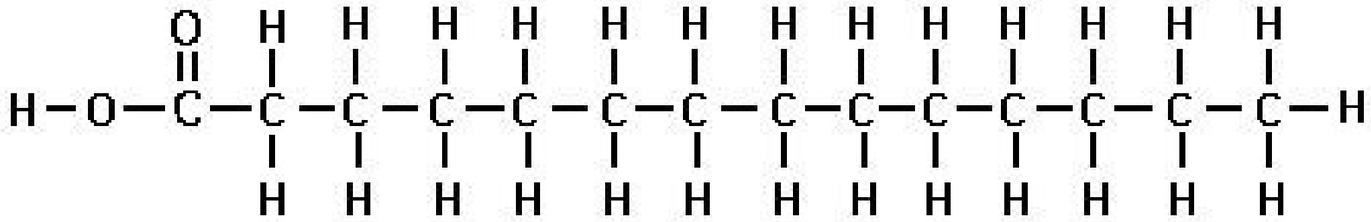
a fatty acid with a carbon chain in which all carbon–carbon bonds are single bond.

Ex. Lauric acid: CH3–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–CH2–COOH

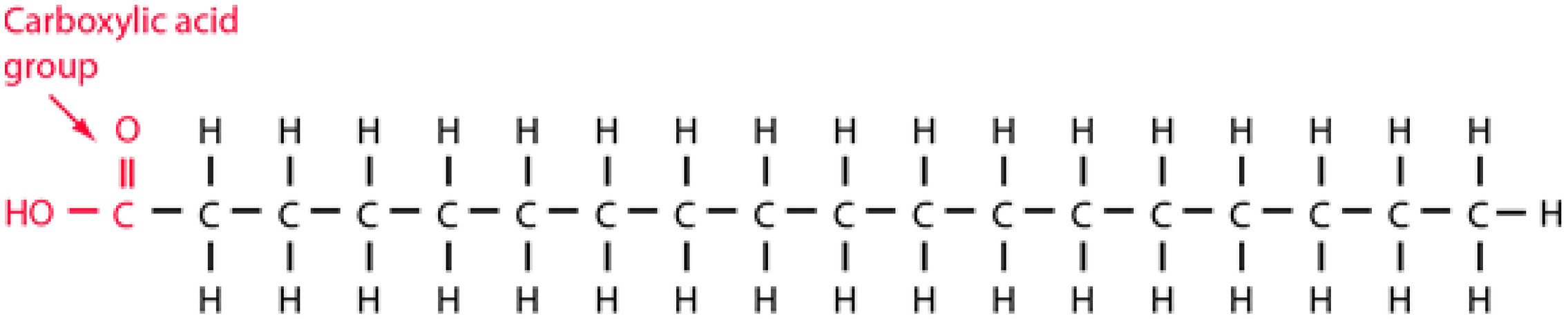
• Numbering starts from the end of –COOH group



Palmitic Acid



Myristic Acid



Stearic acid, an example of a saturated fatty acid

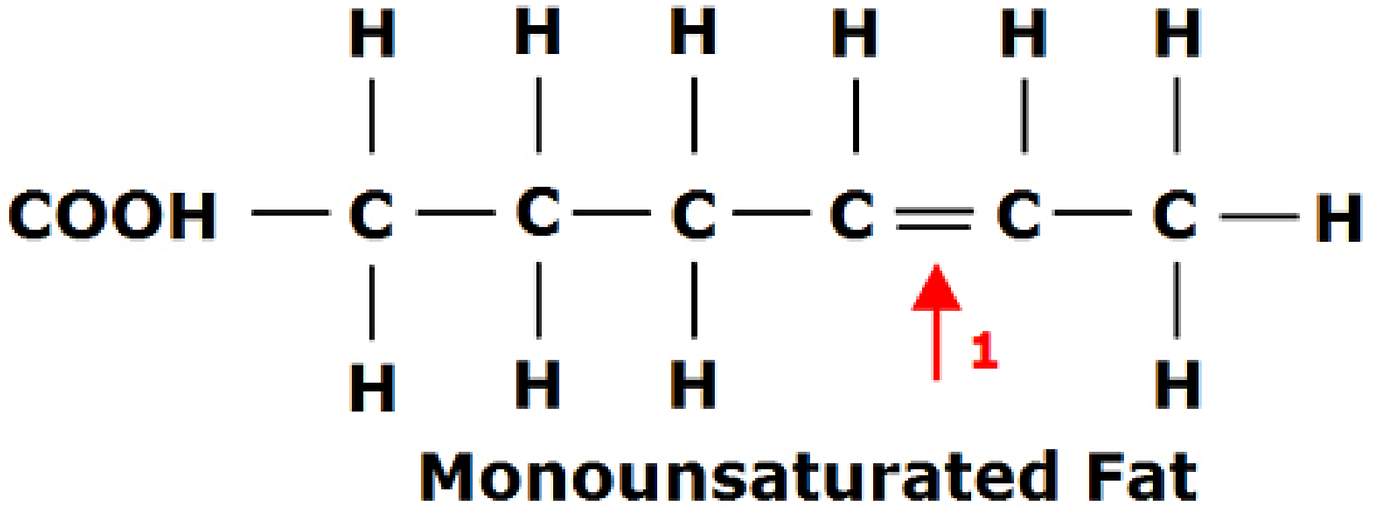
Table 11.1: Some common saturated fatty acids present in natural fats and oils

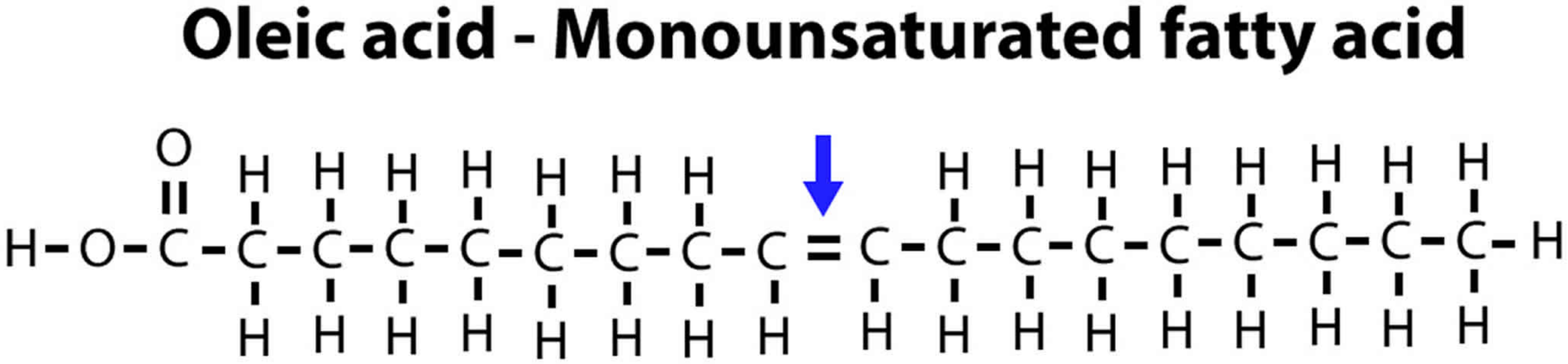
Common name	Systematic name	Chemical structure	Source
Butyric acid (C_4)	n-But**anoic** acid	$CH_3–(CH_2)_2–COOH$	Butter, milk
Caproic acid (C_6)	n-Hex**anoic** acid	$CH_3–(CH_2)_4–COOH$	Butter, milk, coconut oil
Lauric acid (C_{12})	n-Dodec**anoic** acid	$CH_3–(CH_2)_{10}–COOH$	Butter, coconut oil
Myristic acid (C_{14})	n-Tetradec**anoic** acid	$CH_3–(CH_2)_{12}–COOH$	Butter, coconut oil
Palmitic acid (C_{16})	n-Hexadec**anoic** acid	$CH_3–(CH_2)_{14}–COOH$	Animal and plant fats
Stearic acid (C_{18})	n-Octadec**anoic** acid	$CH_3–(CH_2)_{16}–COOH$	Animal and plant fats
Arachidic acid (C_{20})	n-Eicos**anoic** acid	$CH_3–(CH_2)_{18}–COOH$	Peanut oil
Lignoceric acid (C_{24})	n-Tetracos**anoic** acid	$CH_3–(CH_2)_{22}–COOH$	Peanut oil, cerebrosides

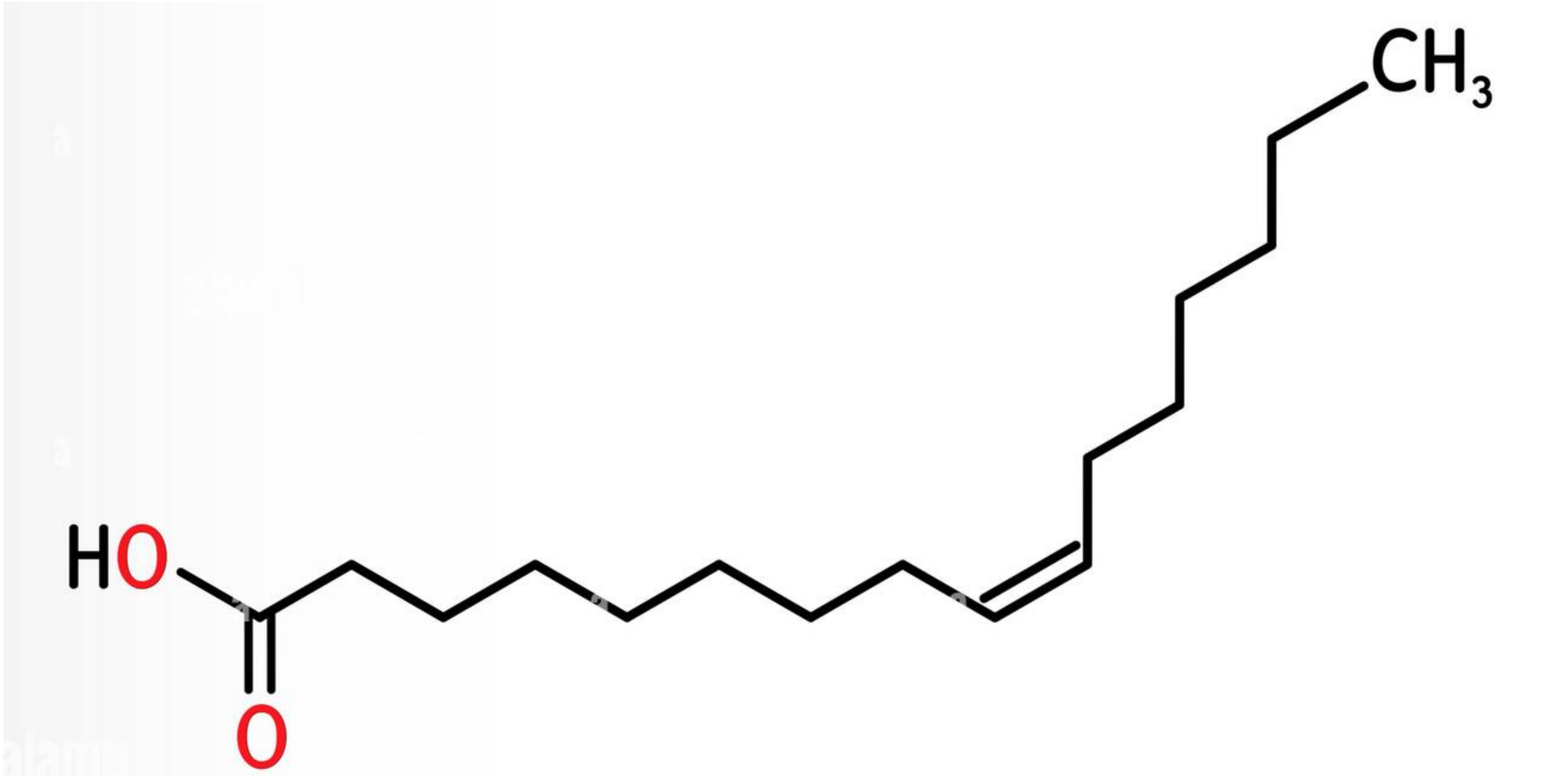
Two Types of Fatty Acids

Unsaturated Fatty Acids

Monounsaturated Fatty Acids (MUFA) –fatty acid with a carbon chain in which one carbon–carbon double bond is present.
Ex. Oleic acid: CH3–(CH2)7–CH=CH–(CH2)7–COOH



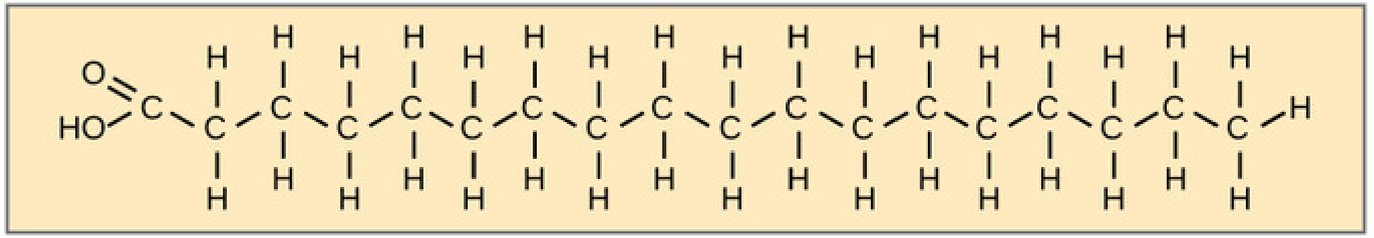




Palmitoleic acid

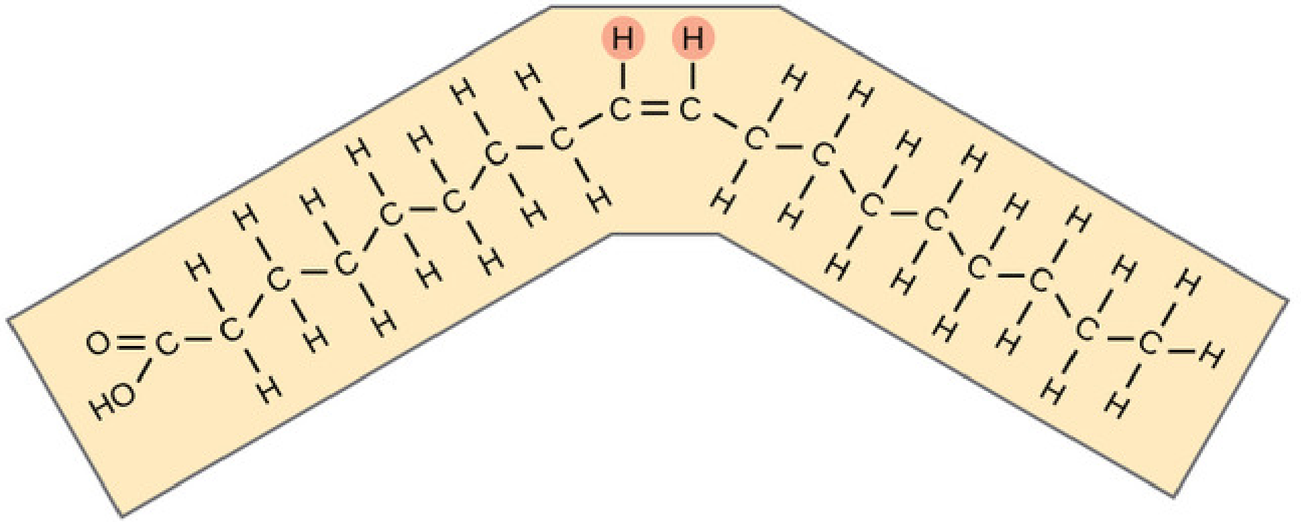
Saturated fatty acid

Stearic acid

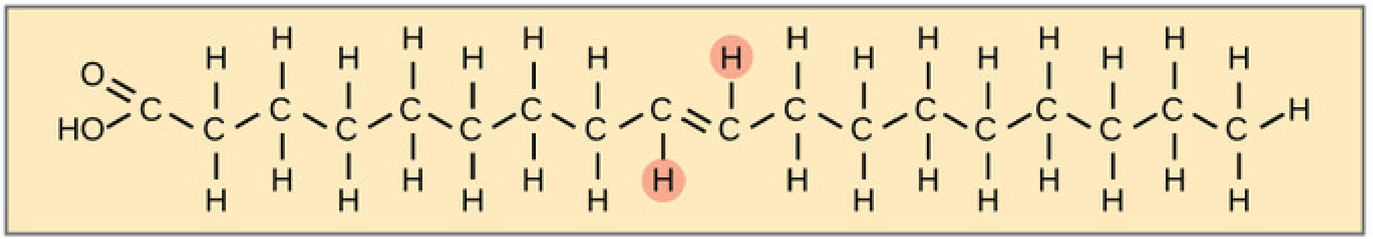


Unsaturated fatty acids

Cis oleic acid



Trans oleic acid



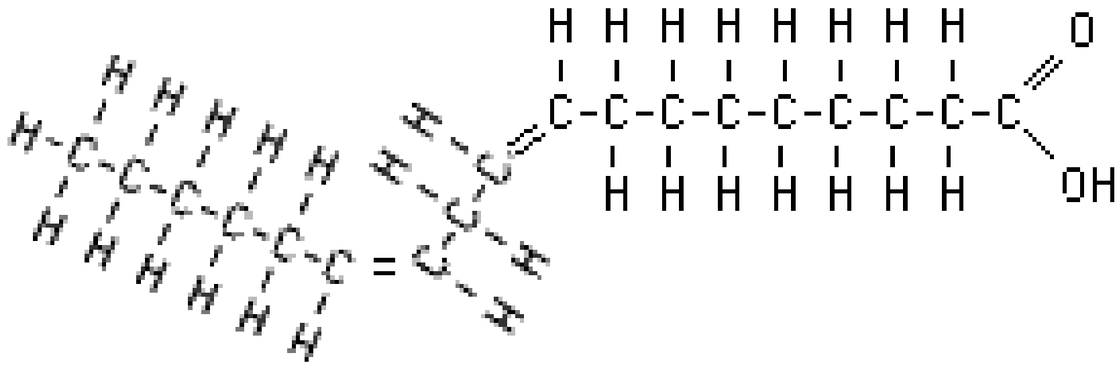
Two Types of Fatty Acids

Unsaturated Fatty Acids

Polyunsaturated Fatty Acids (PUFA)

–fatty acid with a carbon chain in which two or more carbon–carbon double bond is present. Up to six double bonds are found in biochemically important PUFAs.

Ex. Linoleic acid: CH3–(CH2)7–CH=CH–CH2–CH=CH–(CH2)4–COOH



Linoleic acid, a polyunsaturated fatty acid. Both double bonds are *cis*.

Fatty Acid

Two types of unsaturated fatty acids.

An omega-3 (ω-3) fatty acid is an unsaturated fatty acid with its endmost double bond three carbon atoms away from its methyl (CH_3-) end.

Linolenic acid:

Fatty Acid

Two types of unsaturated fatty acids.

An omega-6 (ω-6) fatty acid is an unsaturated fatty acid with its endmost double bond six carbon atoms away from its methyl end

Linoleic acid: 

n-3 polyunsaturated fatty acids

α-Linoleic acid (ALA; 18:3n-3)

Eicosapentaenoic acid (EPA; 20:5n-3)

Docosahexaenoic acid (DHA; 22:6n-3)

n-6 polyunsaturated fatty acids

Linoleic acid (18:2n-6)

Arachidonic acid (20:4n-6)

Physical Properties of Fatty Acids

1

WATER SOLUBILITY

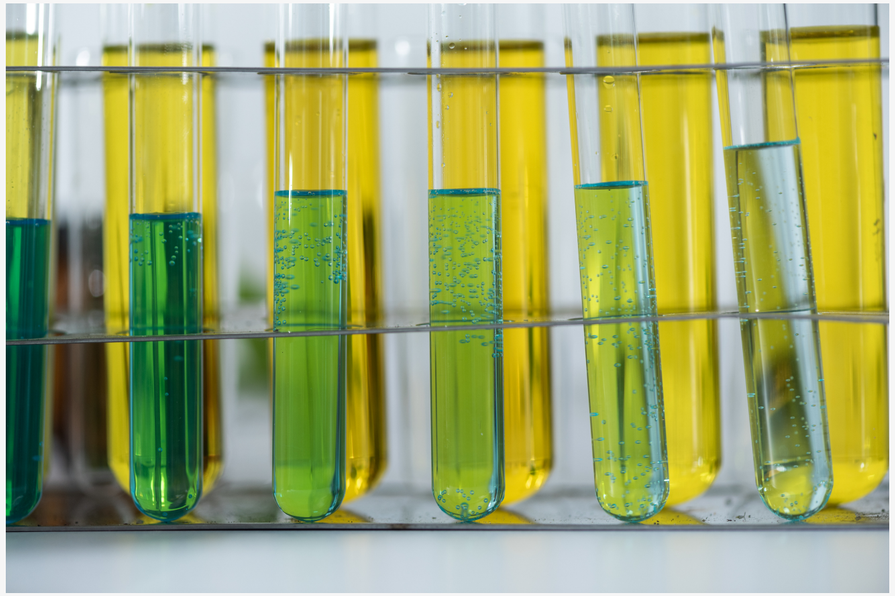
a. solubility decreases as carbon chain length increases
b. short-chain fatty acids have a slight solubility in water
c. long-chain fatty acid are essentially insoluble in water

2

MELTING POINT

a. carbon chain length increases, melting point increases
b. saturated fatty acids have higher melting point than unsaturated fatty acids with same number of carbon atom
c. greater the degree of unsaturation, the greater the reduction in melting point

Physical Properties of Fatty Acids



3

PHYSICAL STATE

a. long-chain saturated fatty acids tend to be solids at room temperature
b. long-chain unsaturated fatty acids tend to be liquid at room temperature

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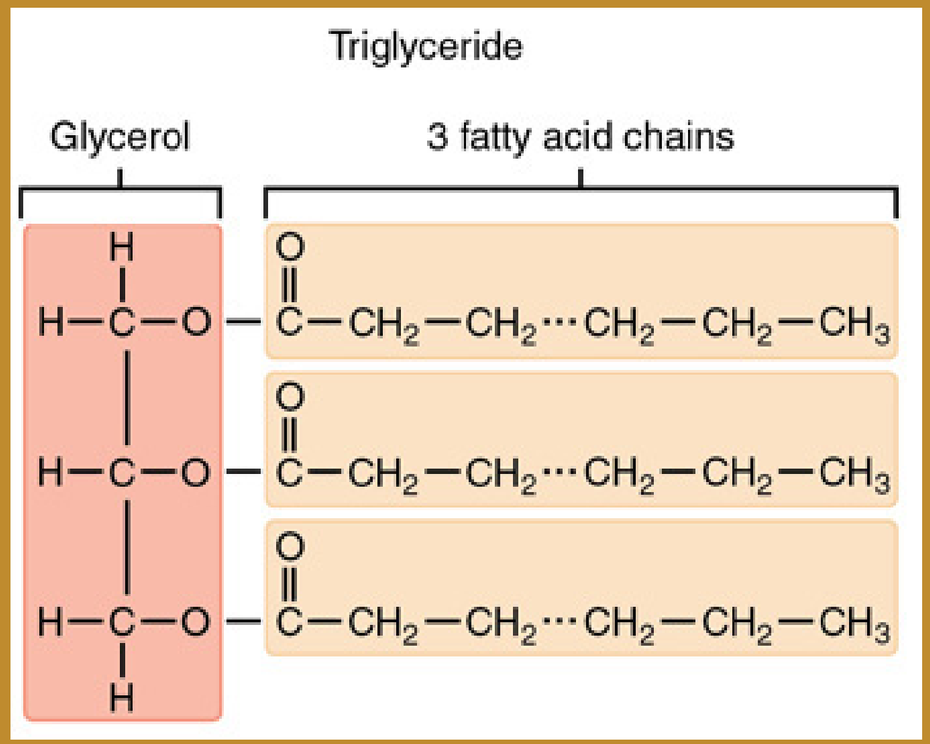
BENDS

a. the double bonds in unsaturated fatty acids generally have a cis-trans configuration forming “bends” in the carbon chains of these molecules.
b. the greater the number of double bonds, the less efficient the packing.



1. Energy-Storage Lipids: Triacylglycerols

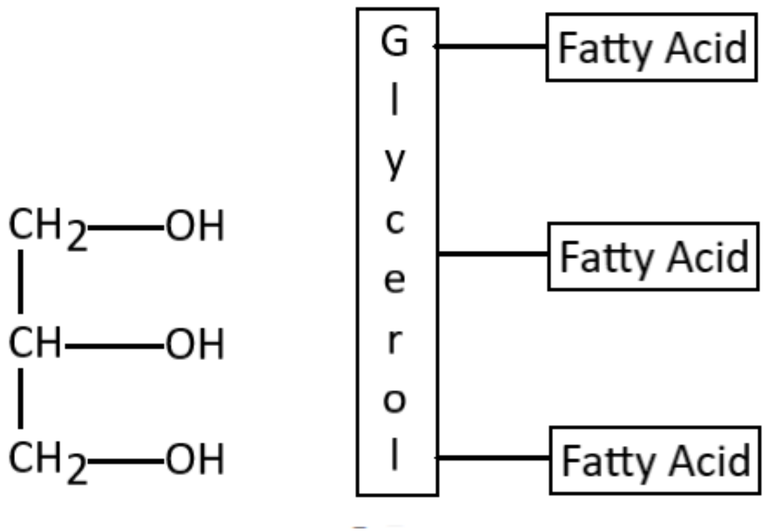
- Aside from carbohydrate glycogen, the most widespread energy storage material within cells, lipids known as triacylglycerol also function within the body as energy-storage materials.
- Triacylglycerols are concentrated primarily in special cells (adipocytes) that are nearly filled with the material.

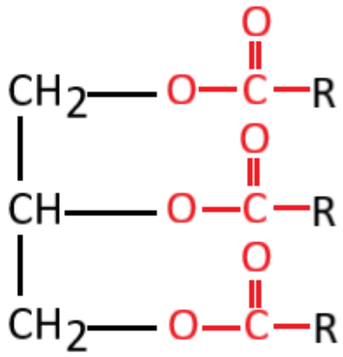
1. Adipose tissue containing these cells is found in various parts of the body: under the skin, abdominal cavity, mammary glands and around various organs.
2. These energy-storage lipids are the most abundant type of lipid present in the human body.

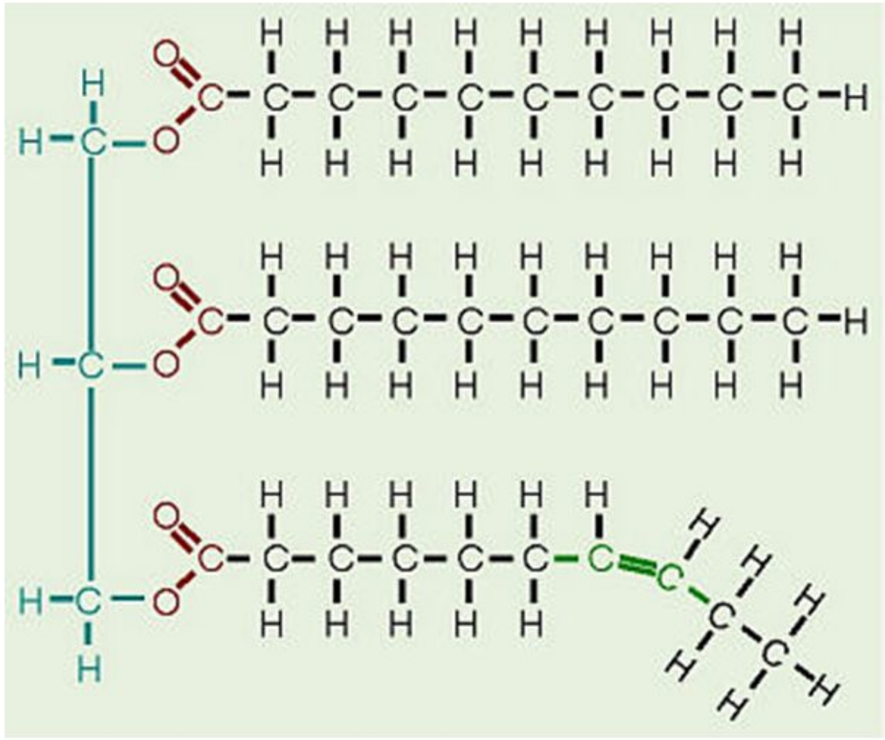
Triacylglycerols

Triacylglycerol molecules contain three fatty acid residue (three acyl groups) attached to a glycerol residue.

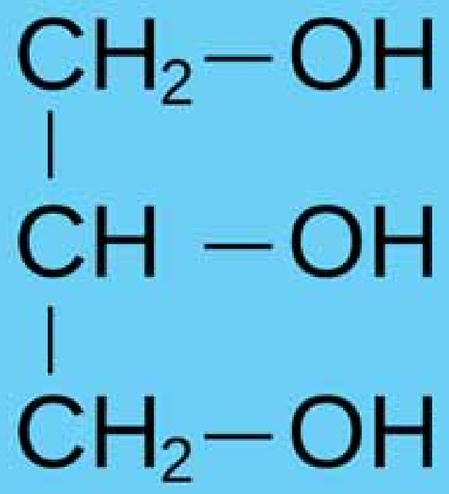
- Triacylglycerol is a lipid formed by esterification of three fatty acids to a glycerol molecule.
- An older name that is still frequently used for triacylglycerol is triglyceride.



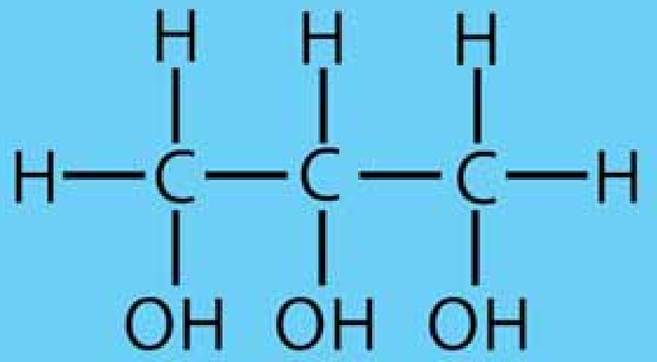




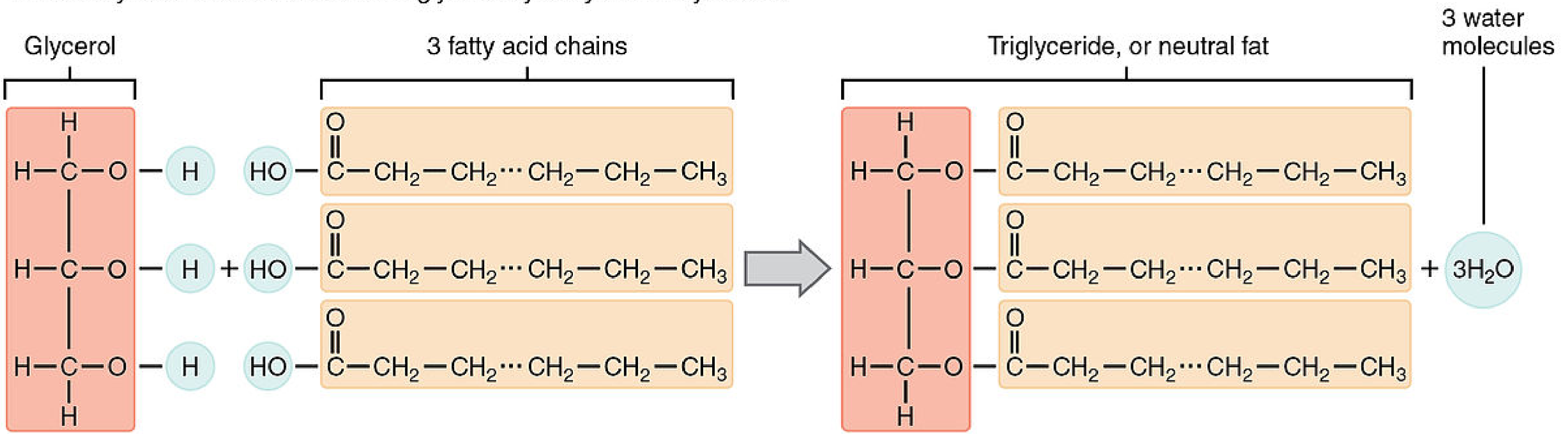
Glycerol structure formula



Or



Three fatty acid chains are bound to glycerol by dehydration synthesis.



Two Types of Triacylglycerols

1

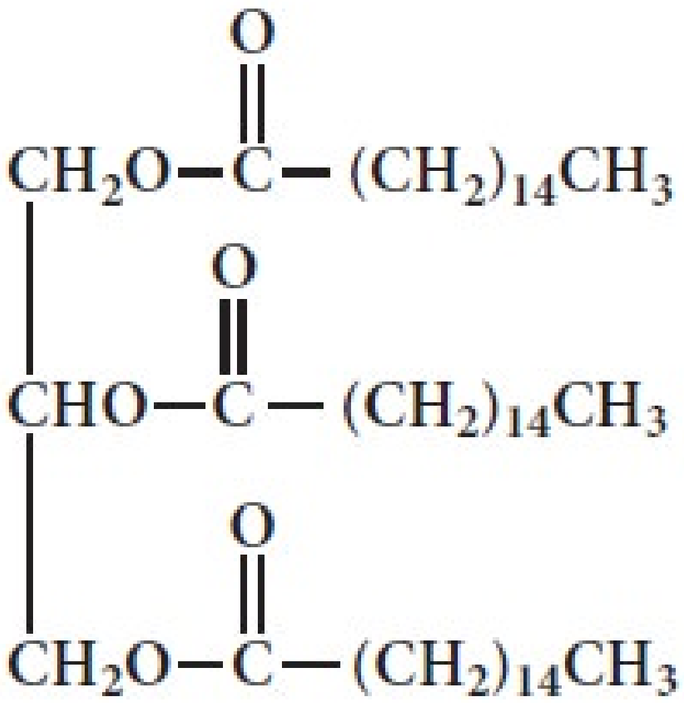
SIMPLE TRIACYLGLYCEROL

A triester formed from the esterification of glycerol with three identical fatty acid molecules.

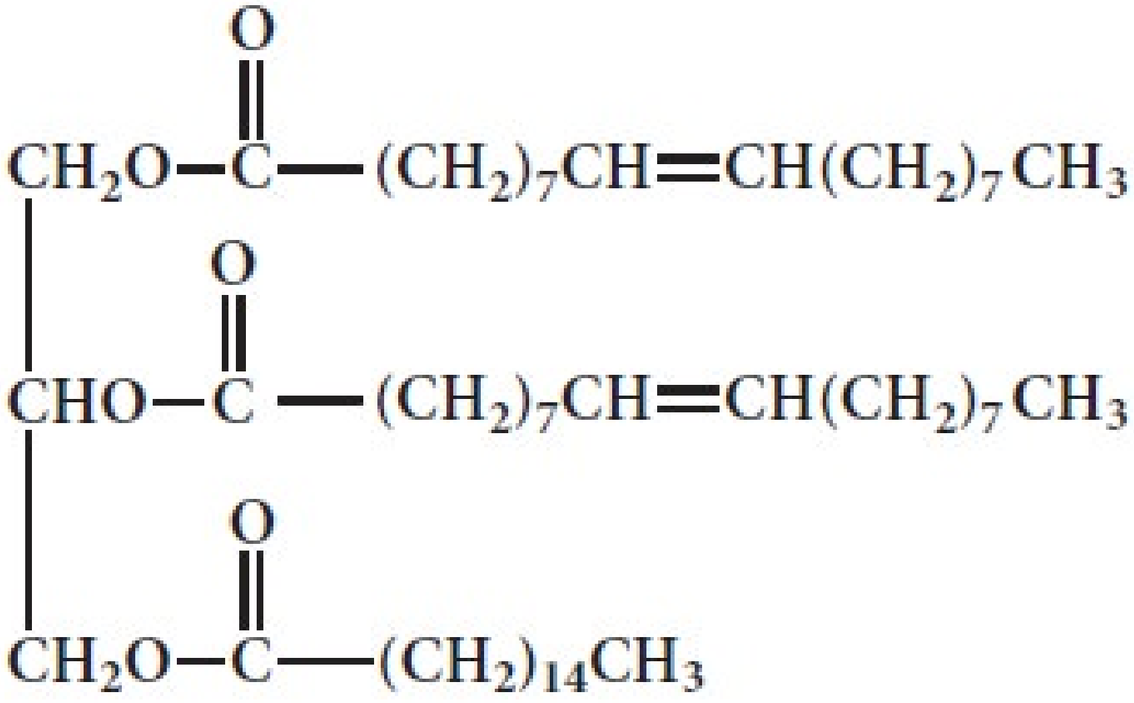
2

MIXED TRIACYLGLYCEROL

A triester formed from the esterification of glycerol with more than one kind of fatty acid molecules.



Tripalmitin (Simple)



Dioleopalmitin (Mixed)

Fats and Oils

1

FAT

A triacylglycerol mixture that is solid or a semi-solid at room temperature (25oC). Generally, fats are obtained from animal sources. Examples: beef fat, pork fat, butterfat

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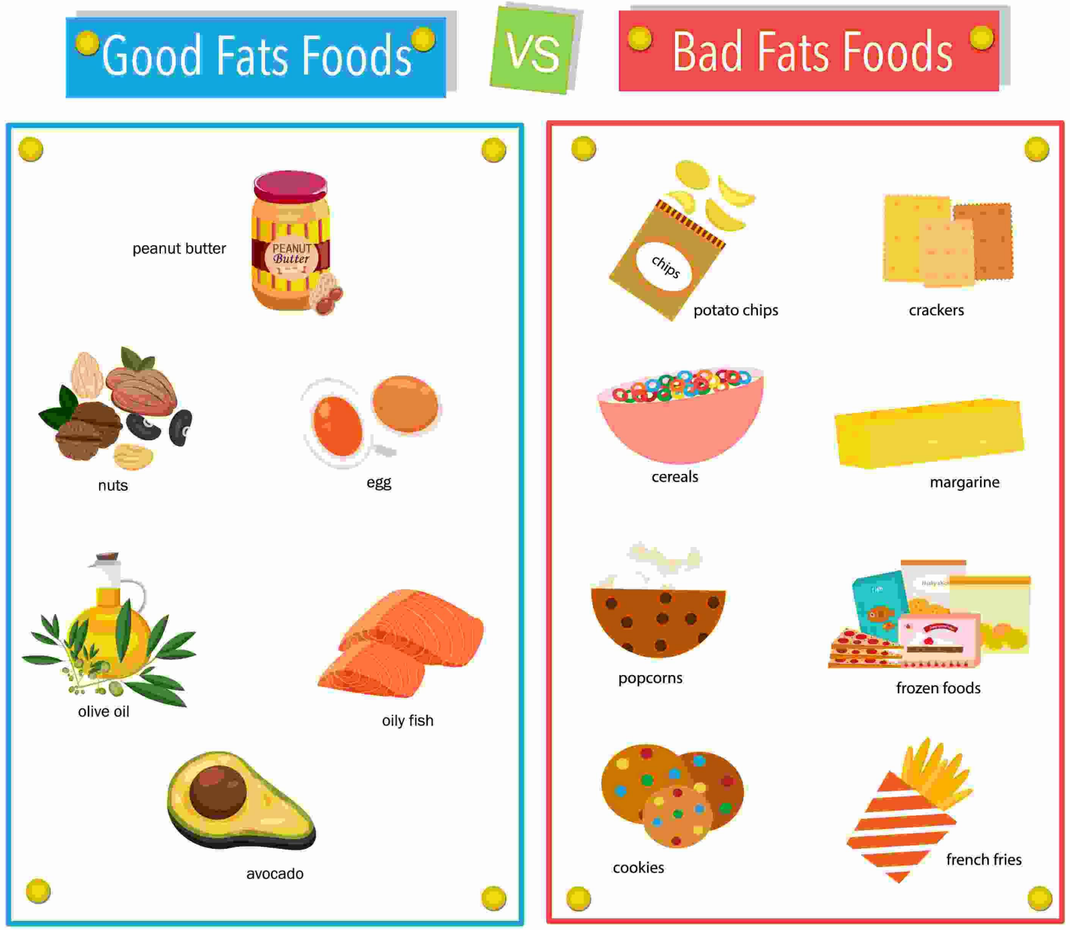
2

OIL

a triacylglycerol mixture that is liquid at room temperature (25oC). Generally, oils are obtained from plant sources. Examples: Corn oil, olive oil, coconut oil

Dietary Considerations and Triacylglycerols

- Considerable researches been carried out concerning the role of dietary factors as a cause of diseases (obesity, diabetes, cancer, hypertension and atherosclerosis).
- Numerous studies have shown that, in general, nations whose citizens have high dietary intakes of triacylglycerols (fats and oils) tend to have higher incidences of heart disease and certain types of cancers.



Dietary Considerations and Triacylglycerols

- In dietary discussion, the term fat is used as a substitute for the term triacylglycerol. Thus a dietary fat can be either a “fat” or an “oil”.
- In simplified terms, research studies indicate that saturated fats (SFAs) are “bad fat”, monosaturated fats (MUFAs) are “good fat”, and polyunsaturated fats (PUFAs) can be both “good fat” and “bad fat”.

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Dietary Considerations and Triacylglycerols

Studies indicate:

- that SFAs can increase heart disease risk.
- othat MUFAs (olive oil, avocado oil, canola oil, tree nuts and peanuts) can decrease both heart disease and breast cancer risk.
- that PUFAs can reduced heart disease risk but promote the risk of certain types of cancers.
- MUFAs help reduce the stickiness of blood platelets. This helps prevent the formation of blood clots and may also dissolve clots once they form.

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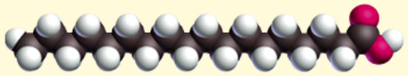
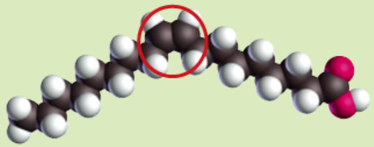
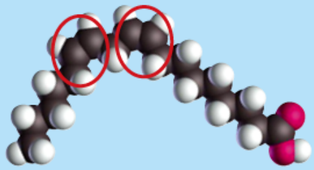
Types of Fatty Acids	Examples of Sources	Health Impacts and Intake Recommendations
Saturated  • No double bond • Straight structure • Solid at room temperature	 Beef  Butter  Coconut oil	• Increase risk of heart disease • Less than 20g of saturated fats per day (for a 2000 kcal diet)
Trans  • One or more double bonds in trans configuration • Straight structure • Semi-solid/Solid at room temperature	 Margarine  Cream soup with puff pastry  Chicken pie	• Increase risk of heart disease • Less than 2.2g of trans fats per day (for a 2000 kcal diet)
Monounsaturated  • One double bond in cis configuration • Bent structure • Liquid at room temperature	 Olive oil  Canola oil  Peanut oil	• May reduce risk of heart disease • Moderate intake of monounsaturated fats
Polyunsaturated  • Multiple double bonds in cis configuration • Even more “bent” in structure • Liquid at room temperature	 Soybean oil  Corn oil  Fatty fish	• May reduce risk of heart disease • Moderate intake of polyunsaturated fats

Omega-3 and Omega-6 Fatty Acids

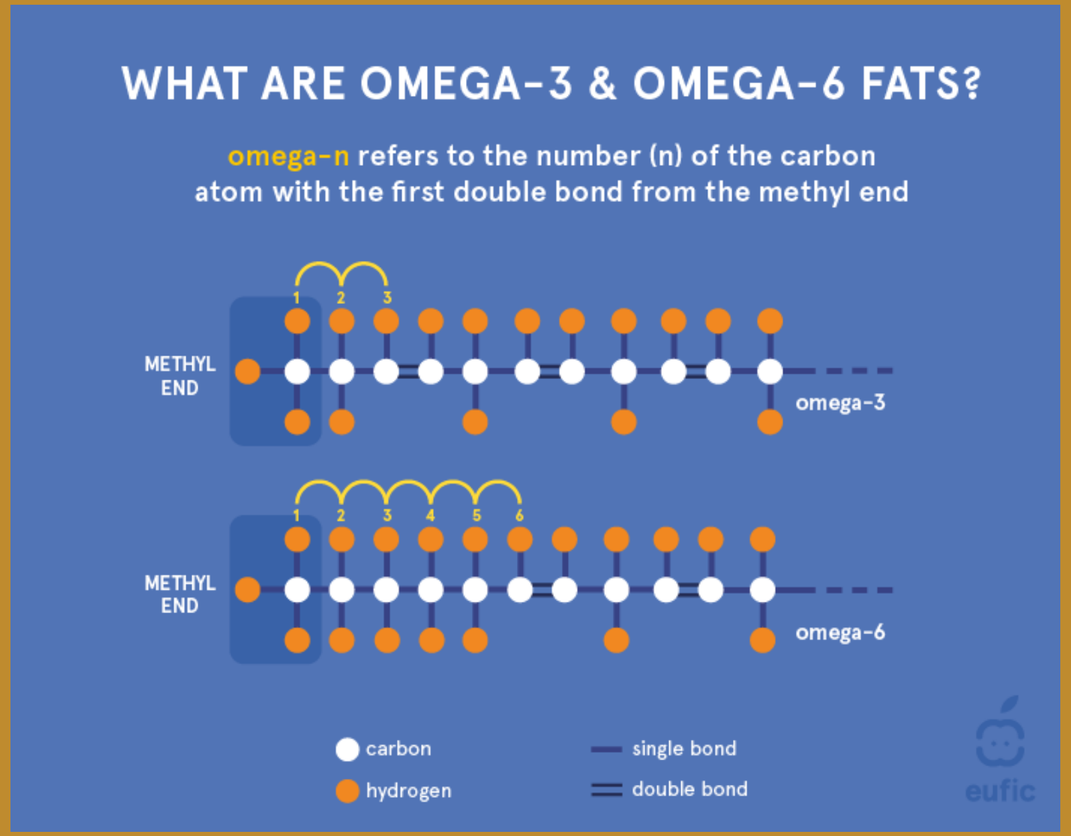
- Several large studies now confirm that benefits can be derived from eating several servings of fish each week. However, the choice of fish is important.
- Deep sea cold-water fish, also called fatty fish (tuna, salmon, and mackerel) contain more omerga-3 acids than leaner, warm water fish (cod, catfish).
- Leaner, warm-water fish do not appear to offer as great a positive effect on heart health as do their “fatter” counterparts.
- Omega-6 fatty acids (from plant oils) high-fat diet exhibits high incidence of heart disease.

Essential Fatty Acids

Essential fatty acids is a fatty acid needed in the human body that must be obtained from dietary sources because it cannot be synthesized within the body in adequate amounts from other substances.

There are two essential fatty acids:

1. Linoleic acid (ω-6)
2. Linolenic acid (ω-3)



Essential Fatty Acids

Essential Fatty Acids

- Linoleic acid and Linolenic acid are:

a. needed for proper membrane structure.
b. serve as the starting materials for the production of several nutritionally important longer-chain omega-6 and omega-3 acids.

- When these two acids are missing from the diet:

a. the skin reddens and become irritated.
b. infection and dehydration are likely to occur
c. the liver may develop abnormalities.

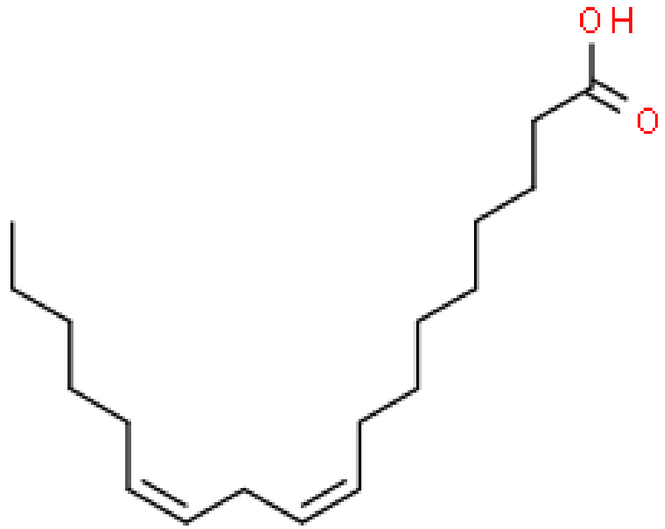
- Infants are especially in need of these acids for their growth.
- Human breast milk has a much higher percentage of essential fatty acids than cow's milk

American Diet

Sufficient in omega 6 fatty acids

- Deficient in omega 3 fatty acids
- Fish – good source for omega 3 fatty acids
- High rate of heart disease may be due to imbalance in omega 3 and 6 fatty acids
- Ideal ratio: Omega 6 : Omega 3 (4 – 10 g: 1g)

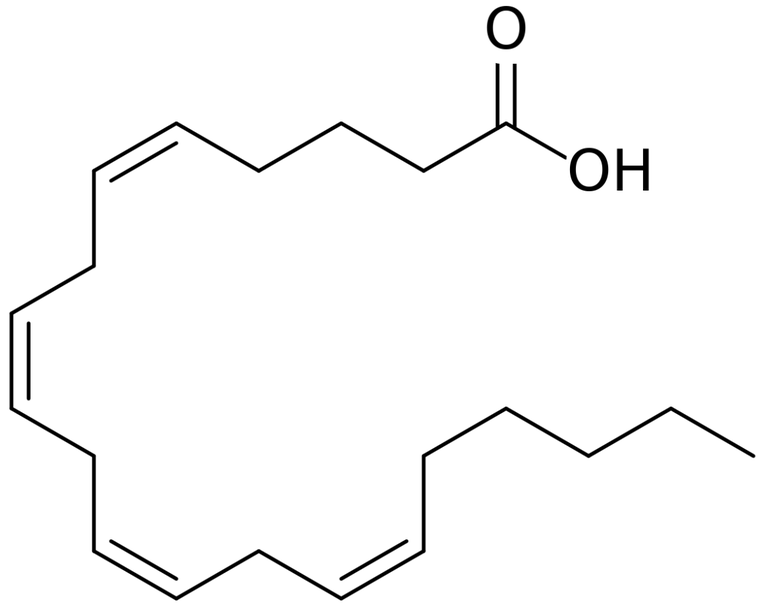
Linoleic acid (18:2)



- **Linoleic acid is the primary member of the omega-6 acid family.**
- **It is the starting material for the biosynthesis of arachidonic acid**

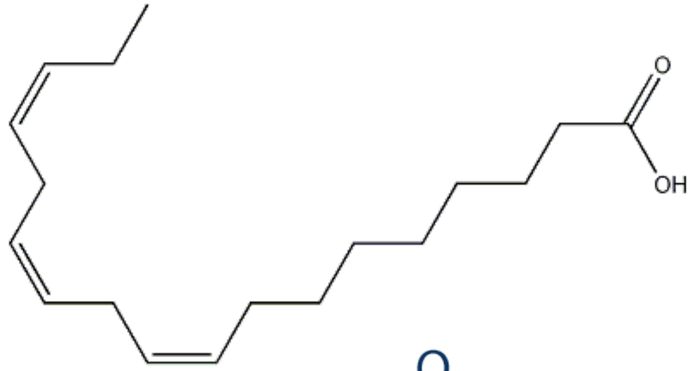
Linoleic acid (18:2)
(omega-6)

Arachidonic acid (20:4)
(omega-6)

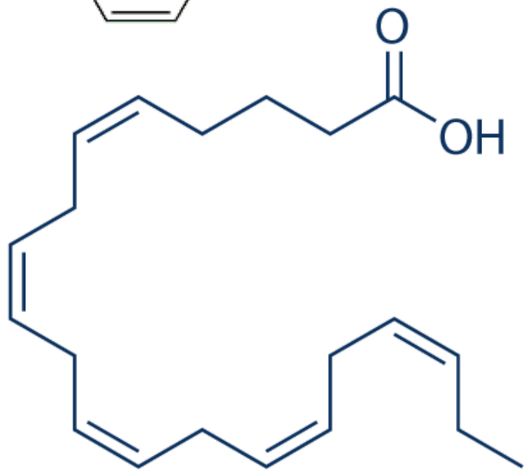


Arachidonic acid is the major starting point for eicosanoids substances that help regulate blood pressure, clotting, and other several other important body functions

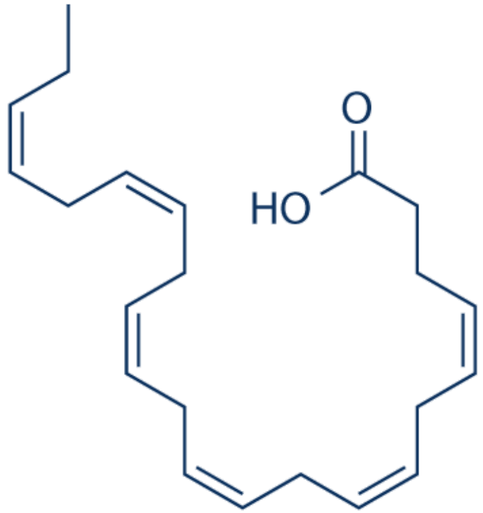
Linolenic acid (18:3)



- **Linolenic acid is the primary member of the omega-3 acid family.**
- **It is starting material for the biosynthesis of two additional omega-3 fatty acids.**



Linolenic acid (18:3)
(omega-3)
→
EPA (20:5)
(omega-3)
→
DHA (22:6)
(omega-3)

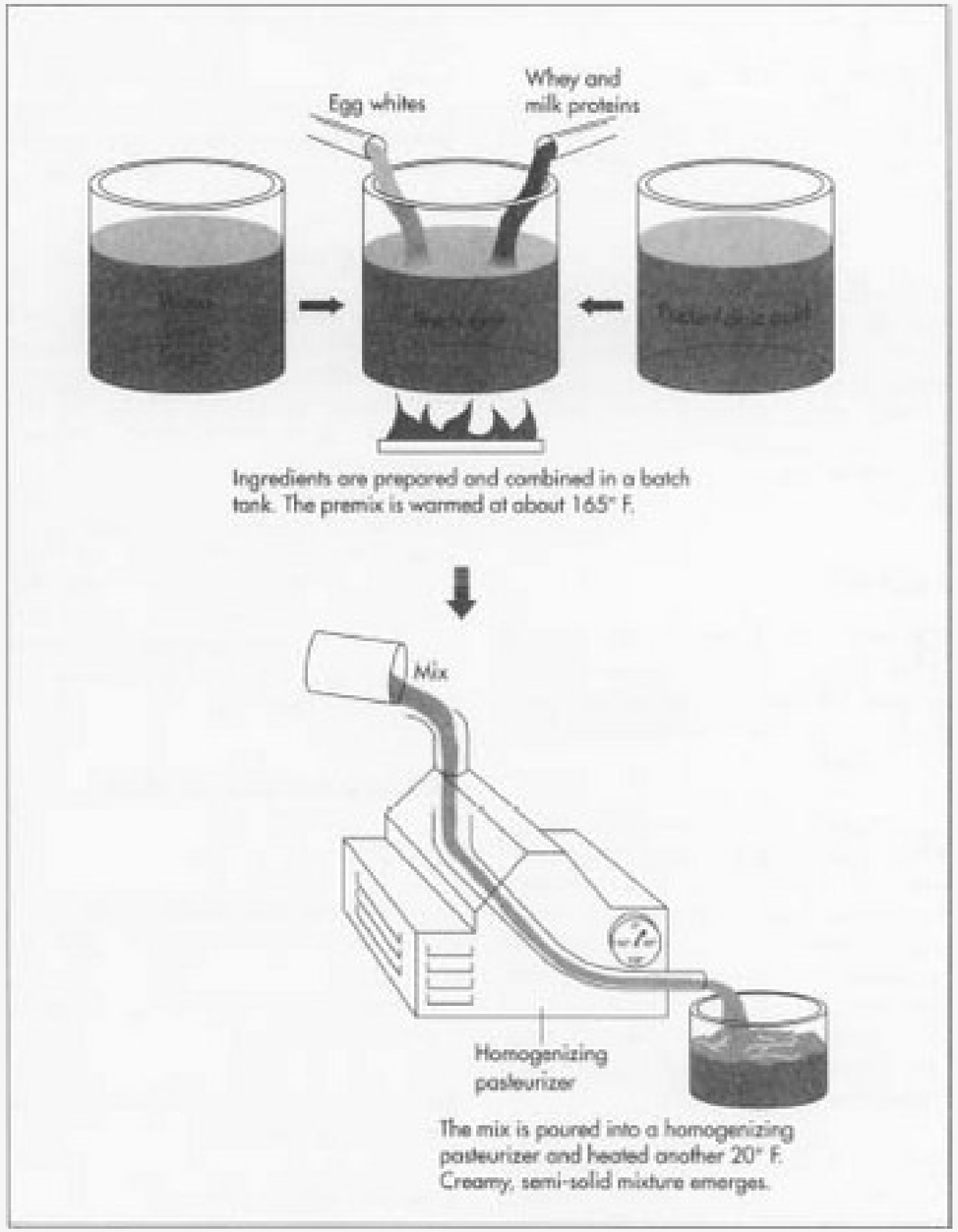


- EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid) are important constituents of the communication membrane of the brain and are necessary for normal brain development.
- EPA and DHA are also active in the retina of the eye.

Fat Substitutes (Artificial Fats)

- In respond to consumer demand for low-fat, low-calorie foods,
- food scientists have developed several types of “artificial fats”.
- Such substances replicate the taste, texture, and cooking properties of fats but are themselves not lipids.

There are two types of fat substitutes:
1. Calorie-reduced fat substitutes
2. Calorie-free fat substitutes



Calorie-reduced Fat Substitutes

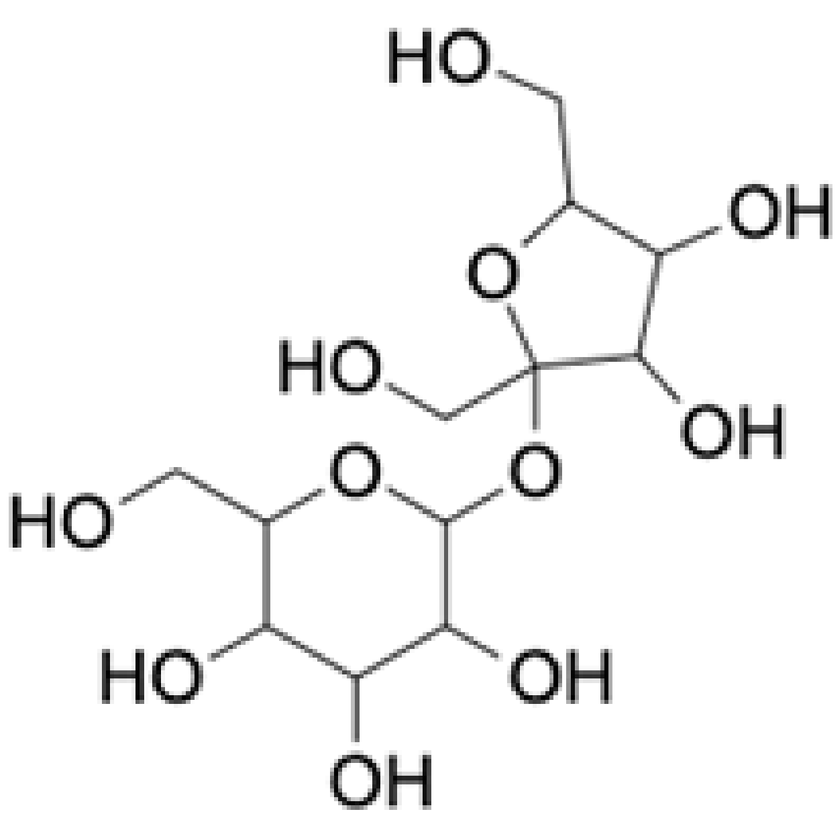
Simplesse, the best known calorie-reduced fat substitute (FDA approval 1990), is made from the protein of fresh egg whites and milk by procedure called **microparticulation.**

- This procedure produces tiny, round protein particle so fine that the tongue perceives them as a fluid rather than as the solid they are.
- Their fineness creates a sensation of smoothness, richness, and creaminess on the tongue.

Calorie-reduced Fat Substitutes

In the body, Simplesse is digested and absorbed contributing to energy intake. But 1 gram of Simplesse provides 1.3 cal compared with 9 cal provided by 1g of fat.

- It is used only to replace fats in formulated foods such as salad dressings, cheeses, sour creams, and other dietary products.
- It is unsuitable for baking and frying because it turns rubbery or rigid (gels) when heated.
- Subsequently, it is not available for home use



Olestra

Calorie-free Fat Substitutes

Olestra, the best known calorie-free fat substitute (FDA approval 1996), is produced by heating cottonseed and/or soybean oil with sucrose in the presence of methyl alcohol.

- It passes through the digestive tract undigested.
- It looks, feels, and tastes like dietary fat and can substitute for fats and oils in foods such as shortening, oils, margarines, snacks, ice cream, and other desserts.
- It has the same cooking properties as fats and oils.

Calorie-free Fat Substitutes

In digestive tract, Olestra interferes with the absorption of both dietary and body-produced cholesterol, thus it may lower total cholesterol levels.

- But, olestra inhibits the absorption of the fat-soluble vitamins (A, D, E and K) and other nutrients.
- In some individuals, it can cause gastrointestinal irritation and/or diarrhea

Fat Substitutes Terminology

The terminology used to describe products that contain fat substitutes can be confusing:

- Fat-free means less than 0.5 g of fat per serving.
- Low-fat means 3 g or less fat per 50 g serving.
- Reduced-fat or less-fat means at least 25% less fat per serving than the “regular” food.
- Calorie-free means less than 0.5 kcal per serving
- Human breast milk has a much higher percentage of essential fatty acids than cow’s milk

Chemical Reactions of Triacylglycerols

1

HYDROLYSIS

- The reaction of organic chemical (triacylglycerol) with water to form glycerol and fatty acid. Triacylglycerol hydrolysis, when carried out in a laboratory setting, requires the presence of an acid or base.

2

SAPONIFICATION

- A reaction carried out in an alkaline (basic) solution. For fats and oils, the products of saponification are glycerol and fatty acid salts.

Chemical Reactions of Triacylglycerols

3

HYDROGENATION

- A chemical reaction that involves hydrogen addition across carbon–carbon multiple bonds, which increases the degree of saturation as some double bonds are converted to single bonds.

4

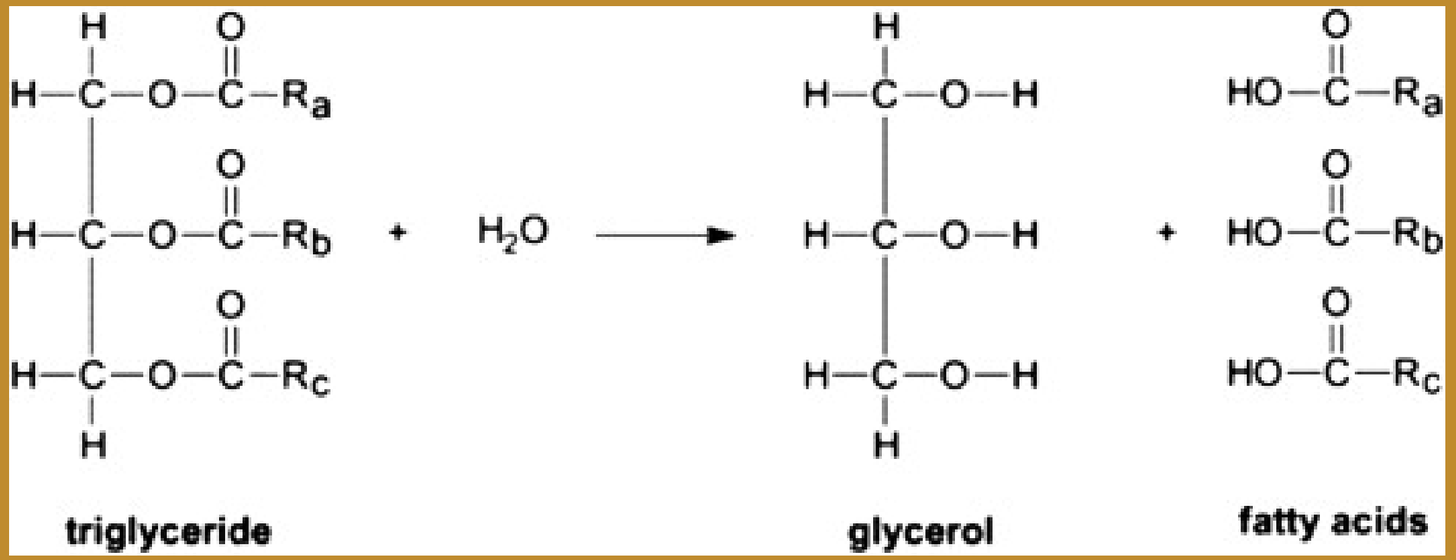
OXIDATION

- A chemical reaction that breaks the carbon–carbon double bonds in triacylglycerol producing both aldehyde and carboxylic acid products.

Hydrolysis Reaction

Hydrolysis of triacylglycerols is the reverse of esterification reaction by which it was formed. Triacylglycerol hydrolysis, when carried out in laboratory setting, requires the presence of an acid or base.

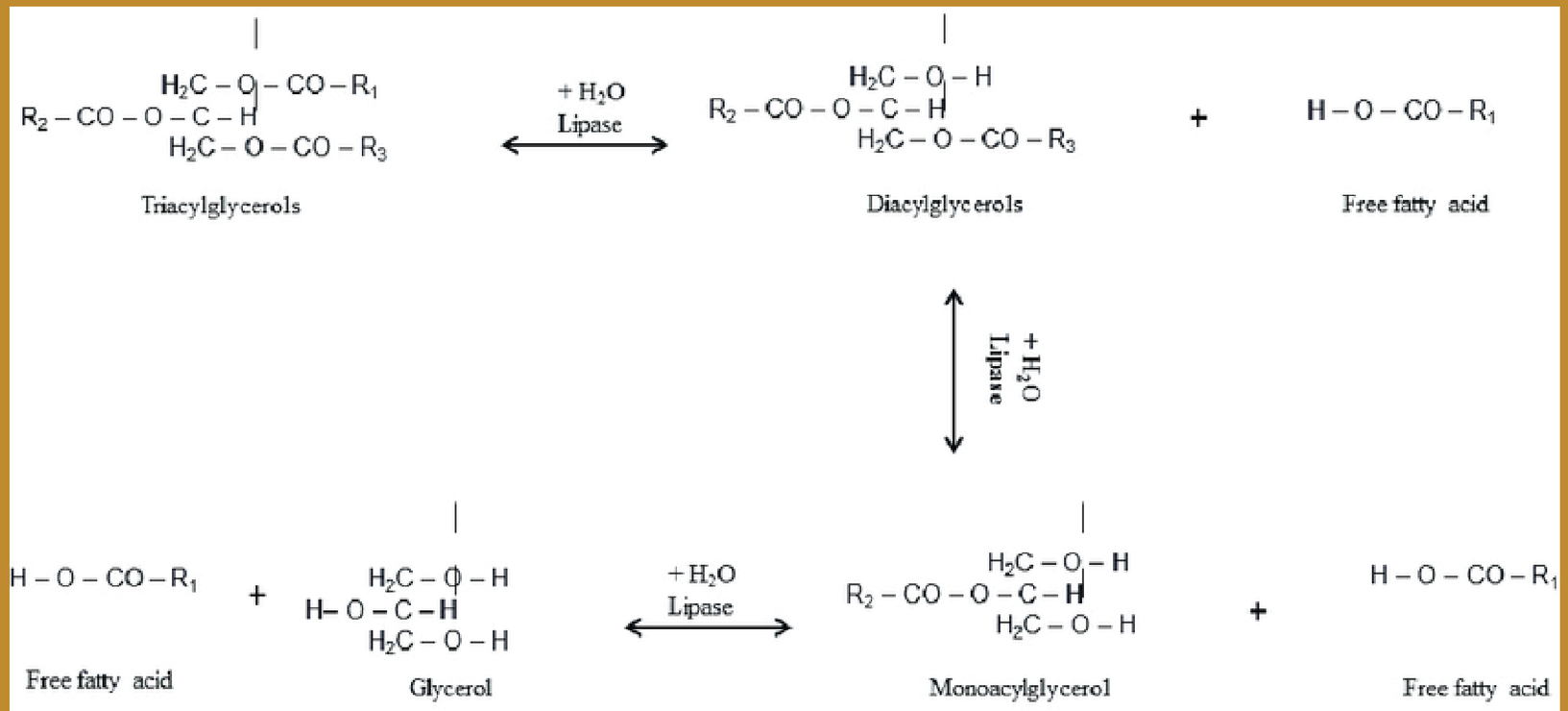
a. Under acidic conditions, the hydrolysis products are glycerol and fatty acids.
b. Under the basic conditions, the hydrolysis products are glycerols and fatty acid salts.



Hydrolysis Reaction

Within the human body, triacyglycerol hydrolysis occurs during the process of digestion. Such hydrolysis requires the help of enzymes (protein catalysts) produced by pancreas. The end product of the digestion (hydrolysis) removed one, two, or all of the three fatty acids leaving a free molecule of glycerol.

- Complete hydrolysis occurs when all three fatty acids are removed.
- Partial hydrolysis occurs when one or more fatty acids residues remain attached to the glycerol.



Saponification Reaction

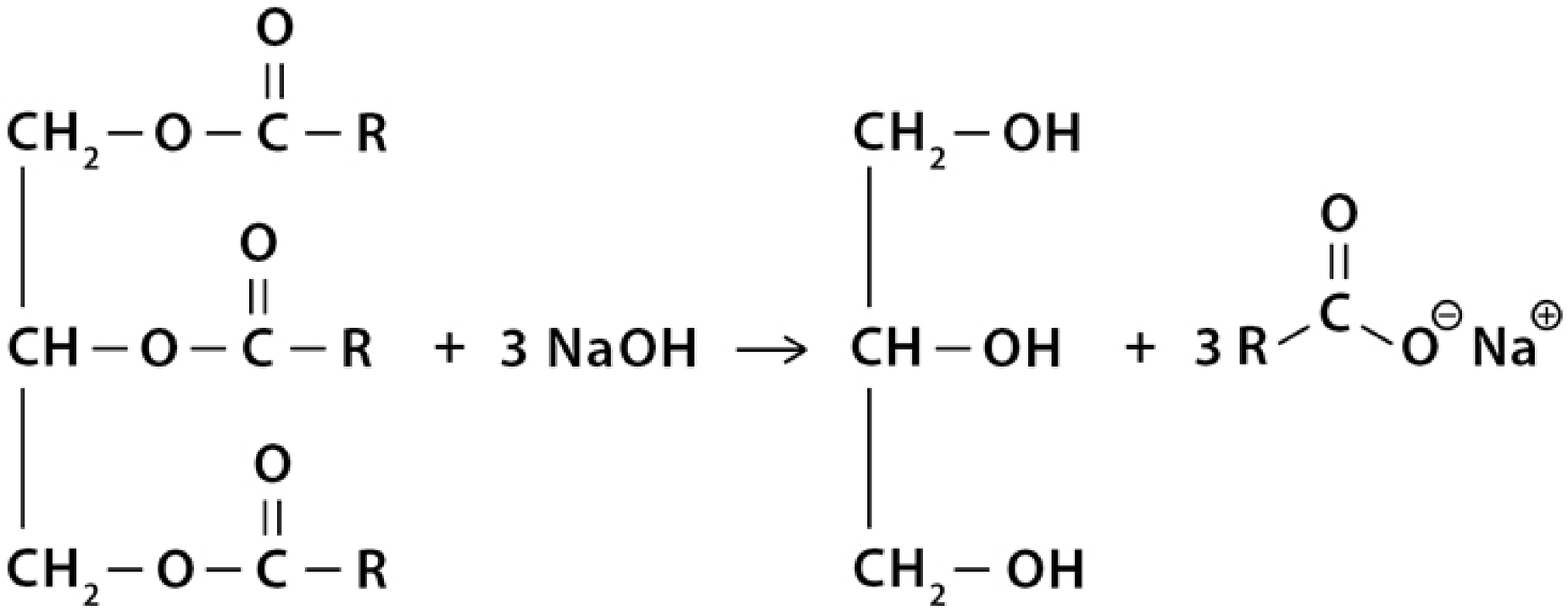
Saponification is a reaction carried out in an alkaline (basic) solution. For fats and oils, the products of saponification are glycerol and fatty acid salts.

1 st Step: fat or oil + 3 H_2O → 3 fatty acids + glycerol

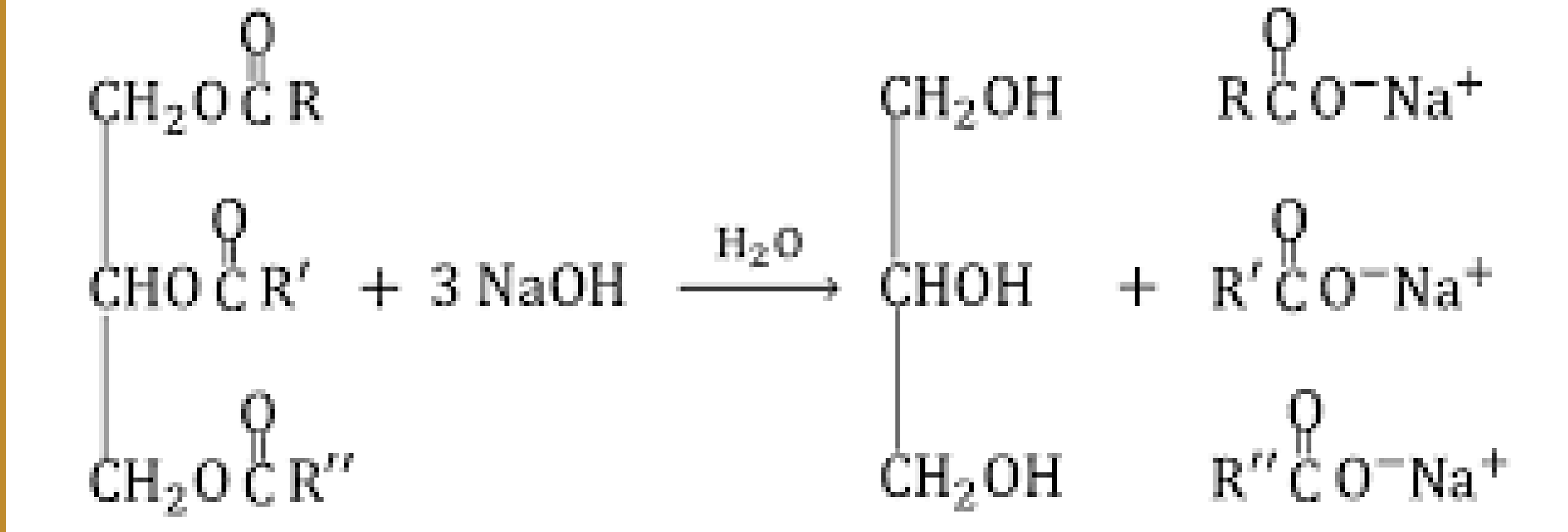
2 nd Step: 3 fatty acids + 3 NaOH → 3 fatty acid salts + 3 H_2O

Saponification of animal fat is the process by which soap was made in pioneer times. Soap making involves heating lard (fat) with lye (ashes of wood, an impure form of KOH). Today most soap is prepared by hydrolyzing fats and oils (animal fat and coconut oil) under high pressure and high temperature. Sodium carbonate is used as the base.

Saponification



Triglyceride | Sodium hydroxide | Glycerol | Soap



Triacylglycerols

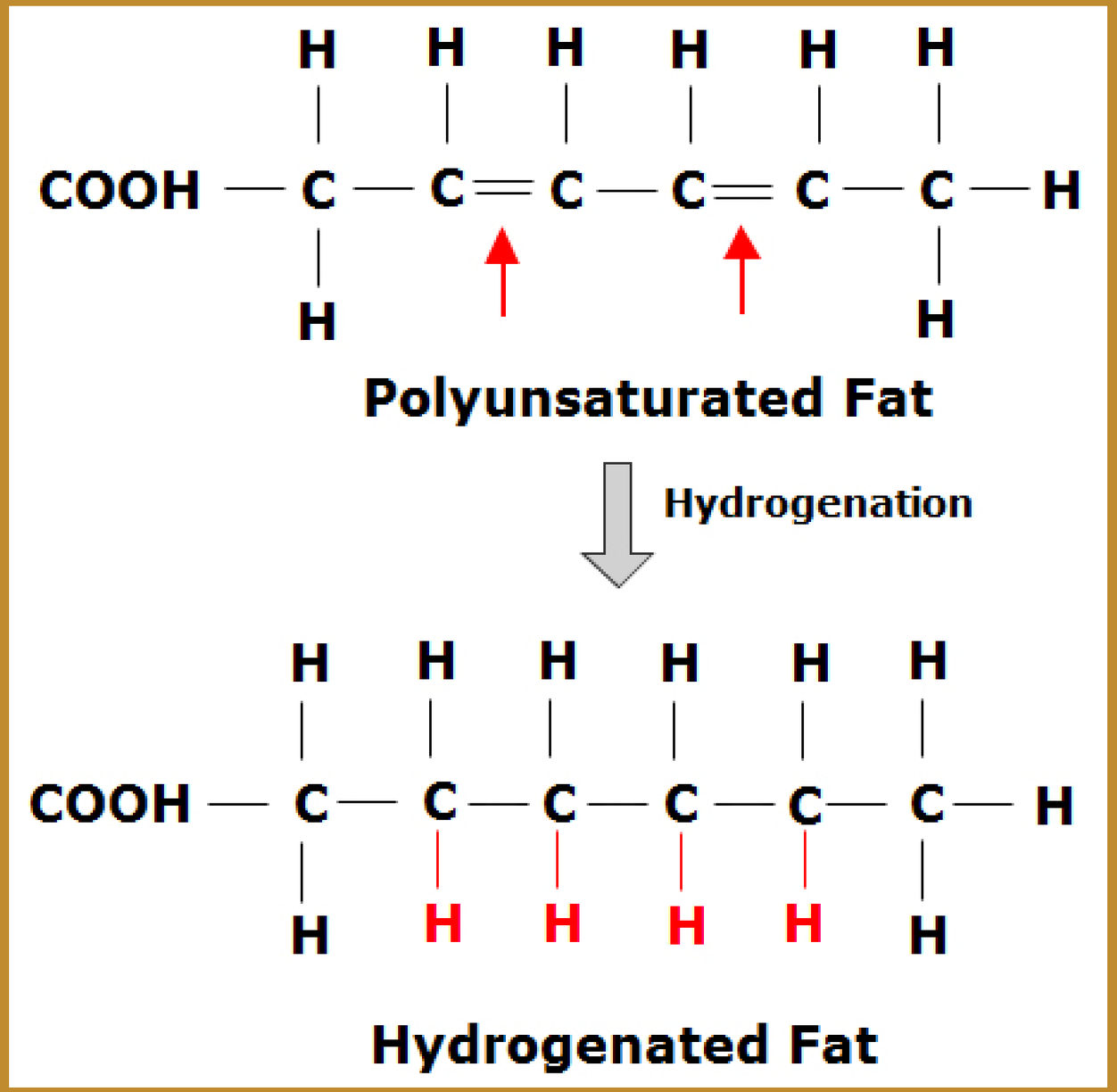
Glycerol

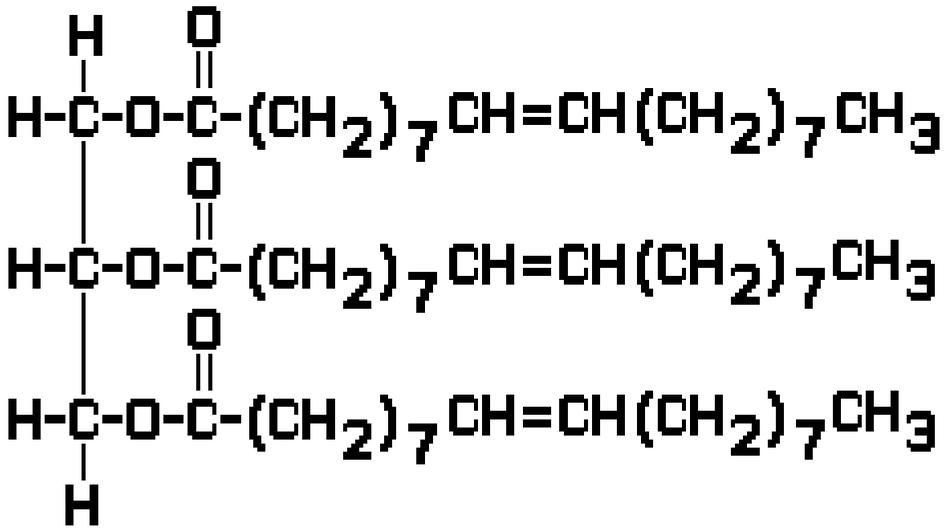
Salts of the carboxylic acids

Hydrogenation Reaction

Hydrogenation is a chemical reaction that involves hydrogen addition across carbon–carbon multiple bonds, which increases the degree of saturation as some double bonds are converted to single bonds. With this change, there is a corresponding increase in the melting point of the substance.

- Many food products are produced via partial hydrogenation. In partial hydrogenation, some, but not all, of the double bonds present are converted into single bonds. In this manner, liquids (usually plant oils) are converted into semi-solid materials.

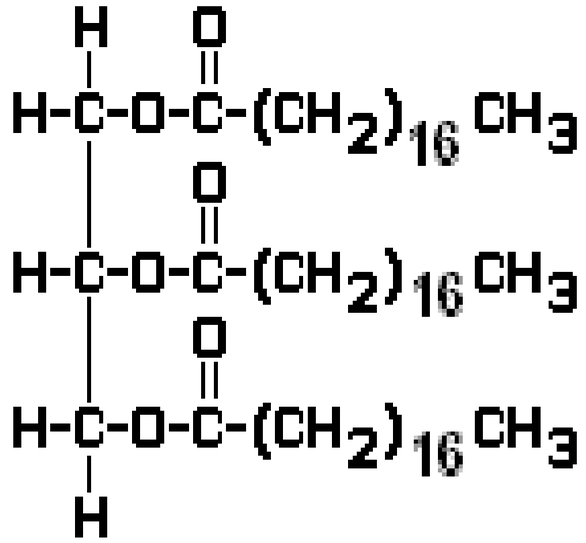

COOH
H
C
C
C
C
C
C
H
Polyunsaturated Fat
Hydrogenation
COOH
H
C
C
C
C
C
C
H
Hydrogenated Fat



triglyceride or triester unsaturated fat

Unsaturated fat some double bonds

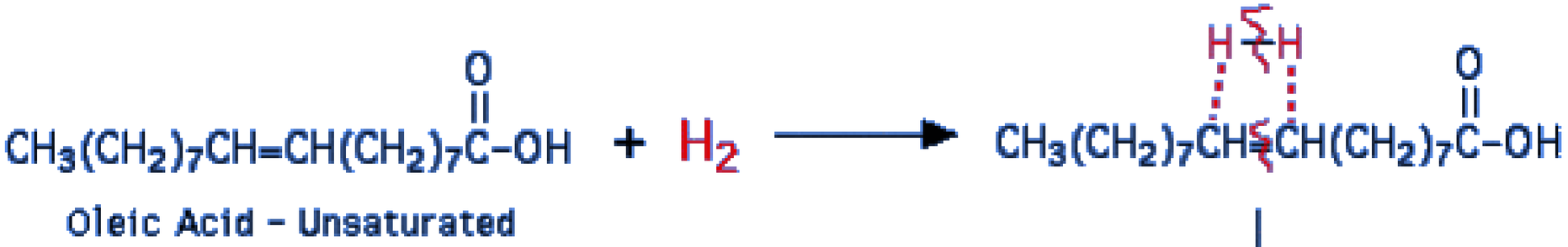
+ 3 H_2

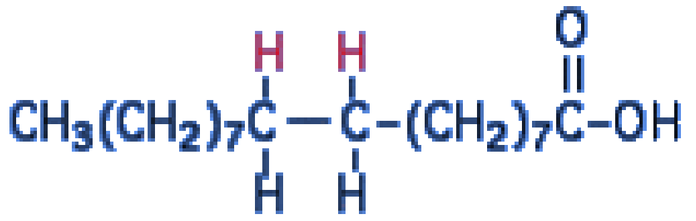


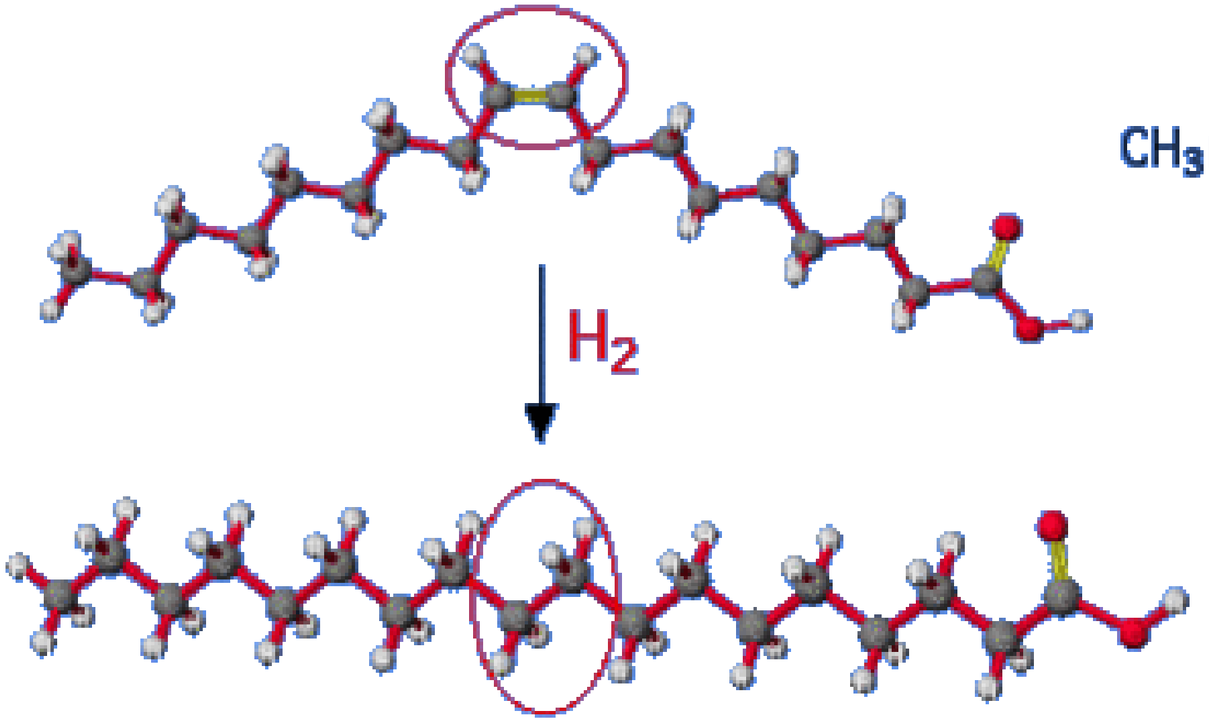
triglyceride or triester saturated fat

saturated fat no double bonds

Hydrogenation of Oleic Acid







Hydrogenation Reaction

Peanut butter (from peanut oil), solid cooking shortening, stick margarine (from plant oils), and soft-spread margarines are produced from partial hydrogenation.

- Concern has arisen about food products obtained from hydrogenation process because the hydrogenation process itself converts some cis double bonds within fatty acid residues into trans double bonds, producing trans unsaturated fatty acids.
- Trans fatty acids (TFAs) are found naturally in meat and dairy products. Studies shows that fatty acids with trans double bonds affect blood cholesterol levels in a manner similar to saturated fatty acids.

Oxidation Reaction

The carbon–carbon double bonds present in the fatty acid residues of triacylglycerol are subject to oxidation with molecular oxygen (from air) as the oxidizing agent.

- Such oxidation breaks these bonds, producing both aldehyde and carboxylic acid products

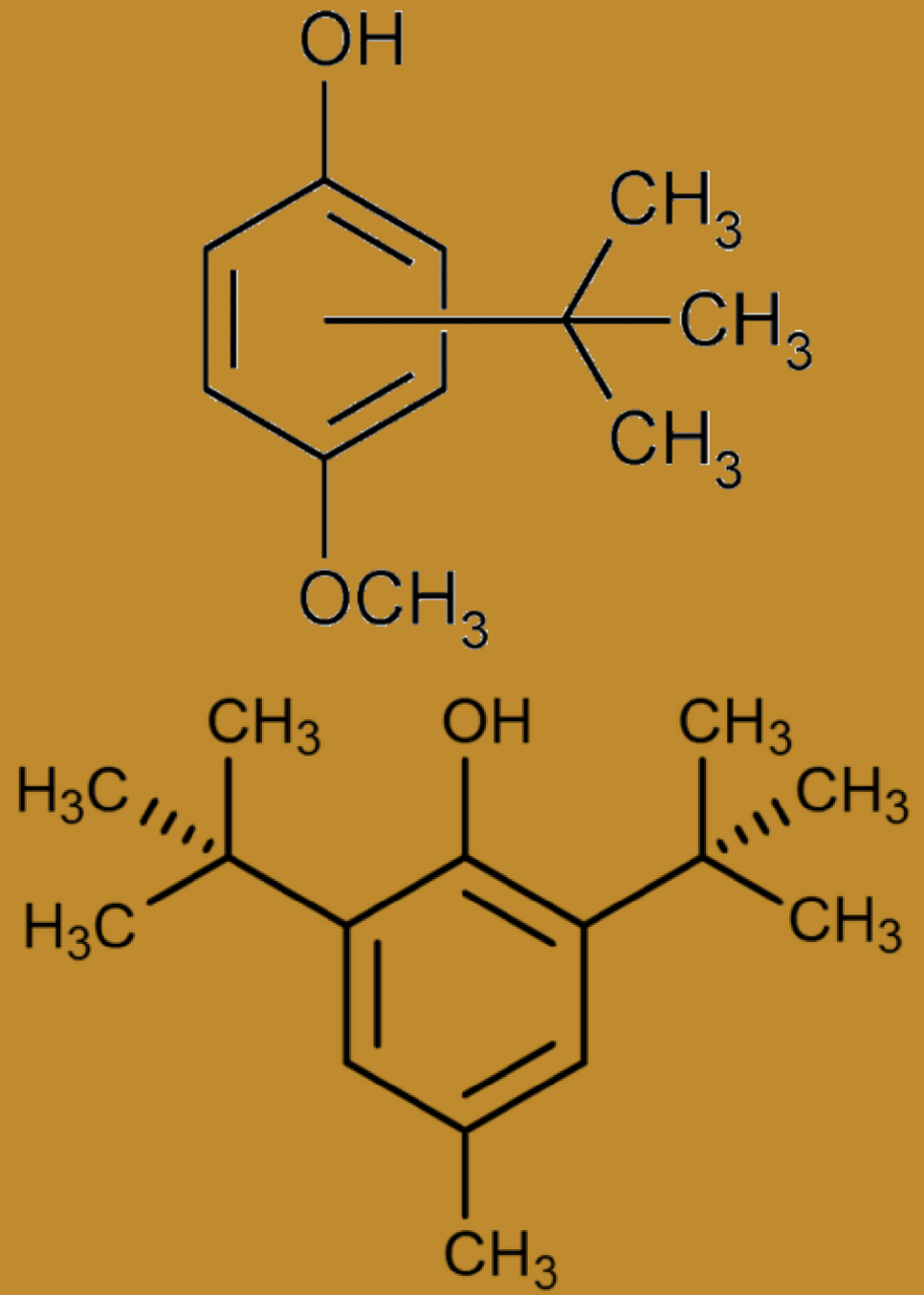
Oxidation Reaction

The short-chain aldehydes and carboxylic acids so produced often have objectionable odors, and fats and oils containing them are said to have become rancid.

- To avoid this unwanted oxidation process, commercially prepared foods containing fats and oils nearly always contain antioxidants. In the presence of air, antioxidants, rather than food, are oxidized.
- Two naturally occurring antioxidants are vitamin C and vitamin E.

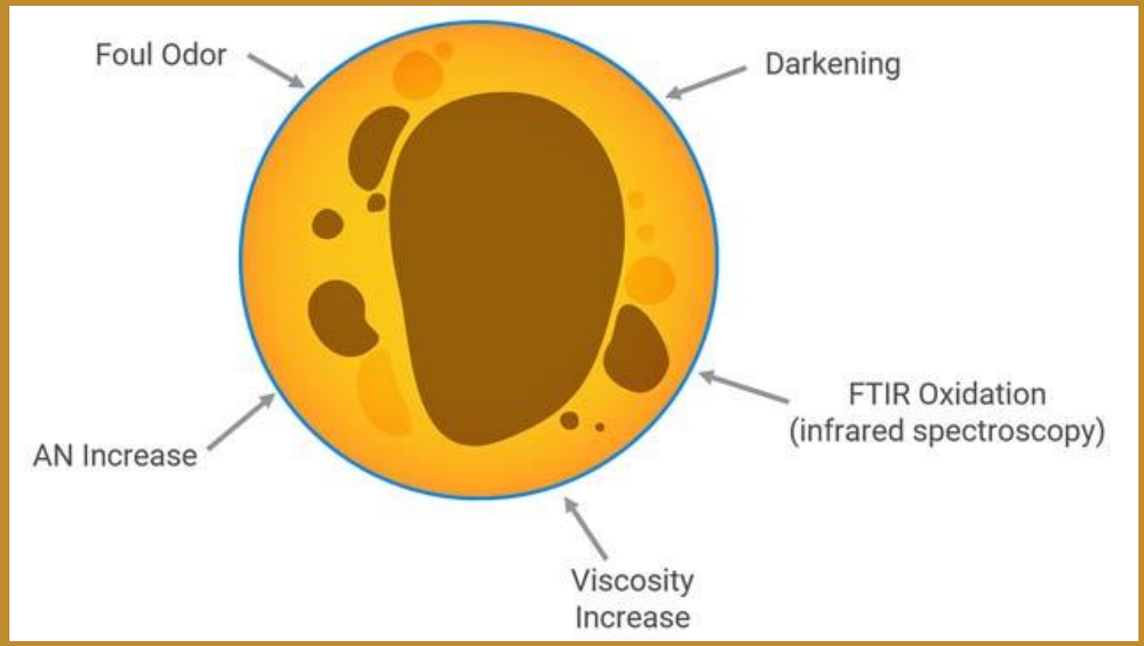
Two synthetic oxidation inhibitors are:

1. BHA (butylated hydroxyanisole)
2. BHT (butylated hydroxytoluene)

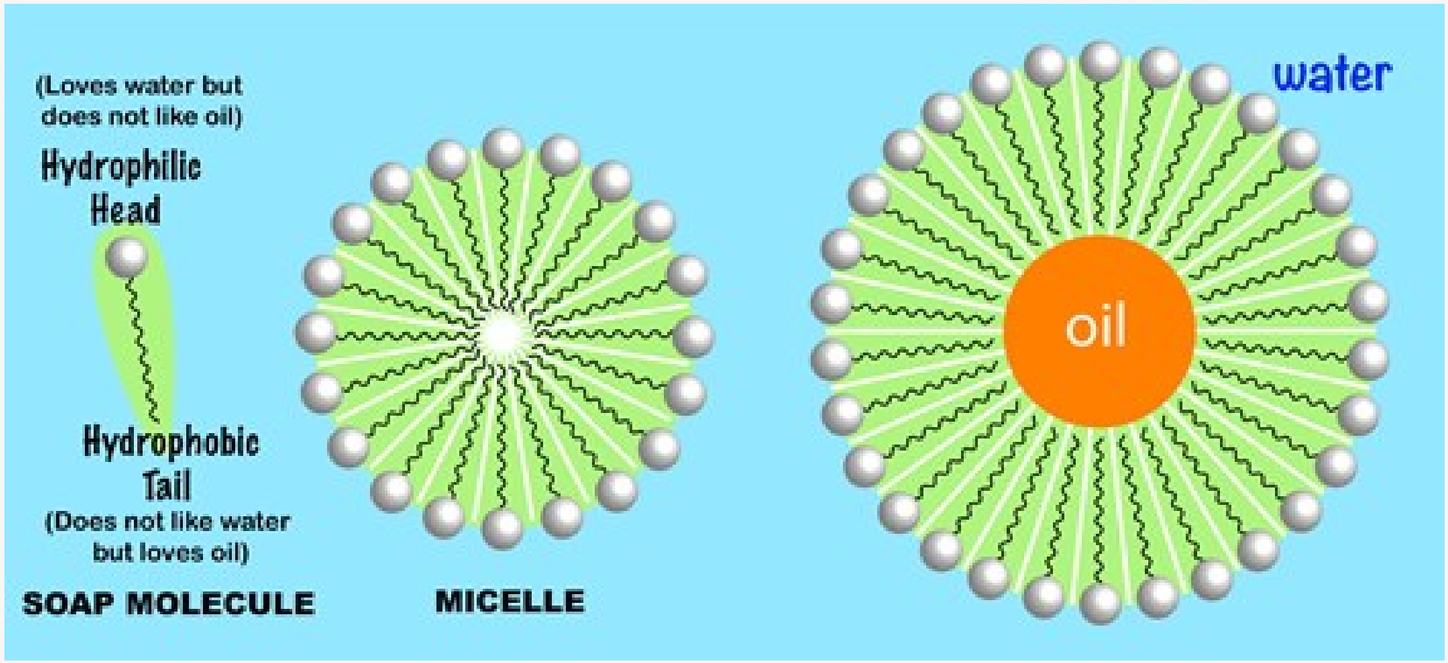


Oxidation Reaction

- Perspiration generated by strenuous exercise or by “hot and muggy” climatic conditions contains numerous triacylglycerols (oils).
- Rapid oxidation of these oils, promoted by microorganisms on the skin, generates the body odor that accompanies most “sweaty” people



The Cleansing Action of Soap and Detergents

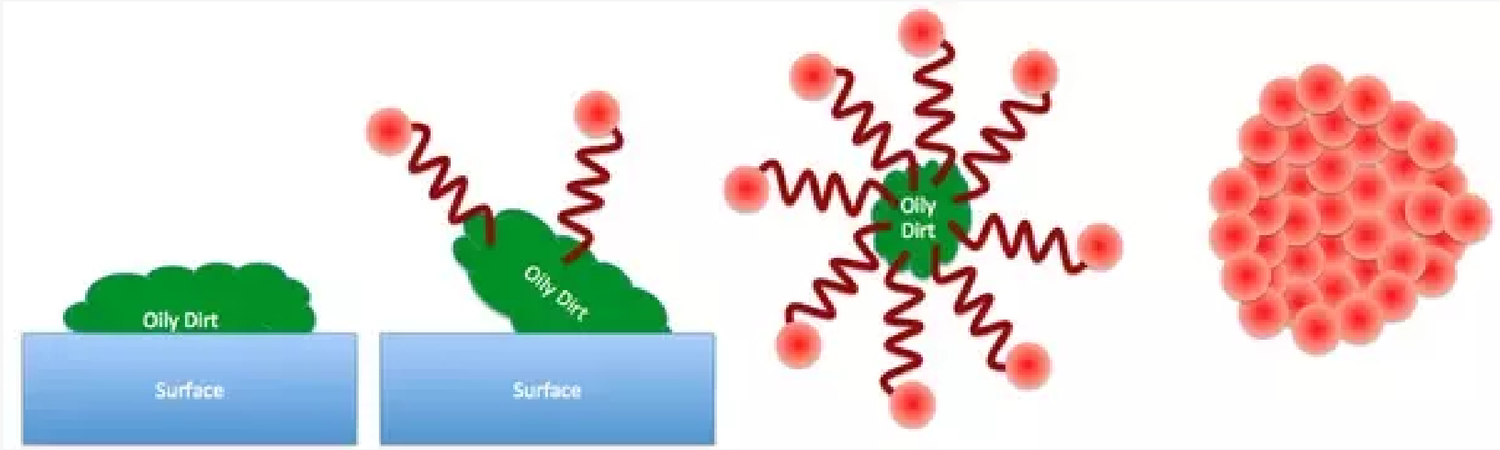


The cleansing action of soap is related to the structure of the carboxylate ions present in the fatty acid salts of soap and the fact that these ions readily participate in micelle formation.

- A micelle is a spherical cluster of molecules in which the polar portions of the molecules are on the surface, and the nonpolar portions are located in the interior

The Cleansing Action of Soap and Detergents

- The nonpolar portion dissolves in the nonpolar oil or grease, and the polar portion maintains its solubility in polar water.
- Soaps and detergents solubilize oily and greasy materials.
- The penetration of the oil or grease by the nonpolar end of the carboxylate is followed by the formation of micelles.
- The micelles do not combine into larger drops because their surfaces are all negatively charged, and like charges repel each other. The micelle exterior and water molecules are attracted to each other, causing the solubilizing of the micelle. The water soluble micelles are subsequently rinsed away, leaving a material devoid of oil and grease

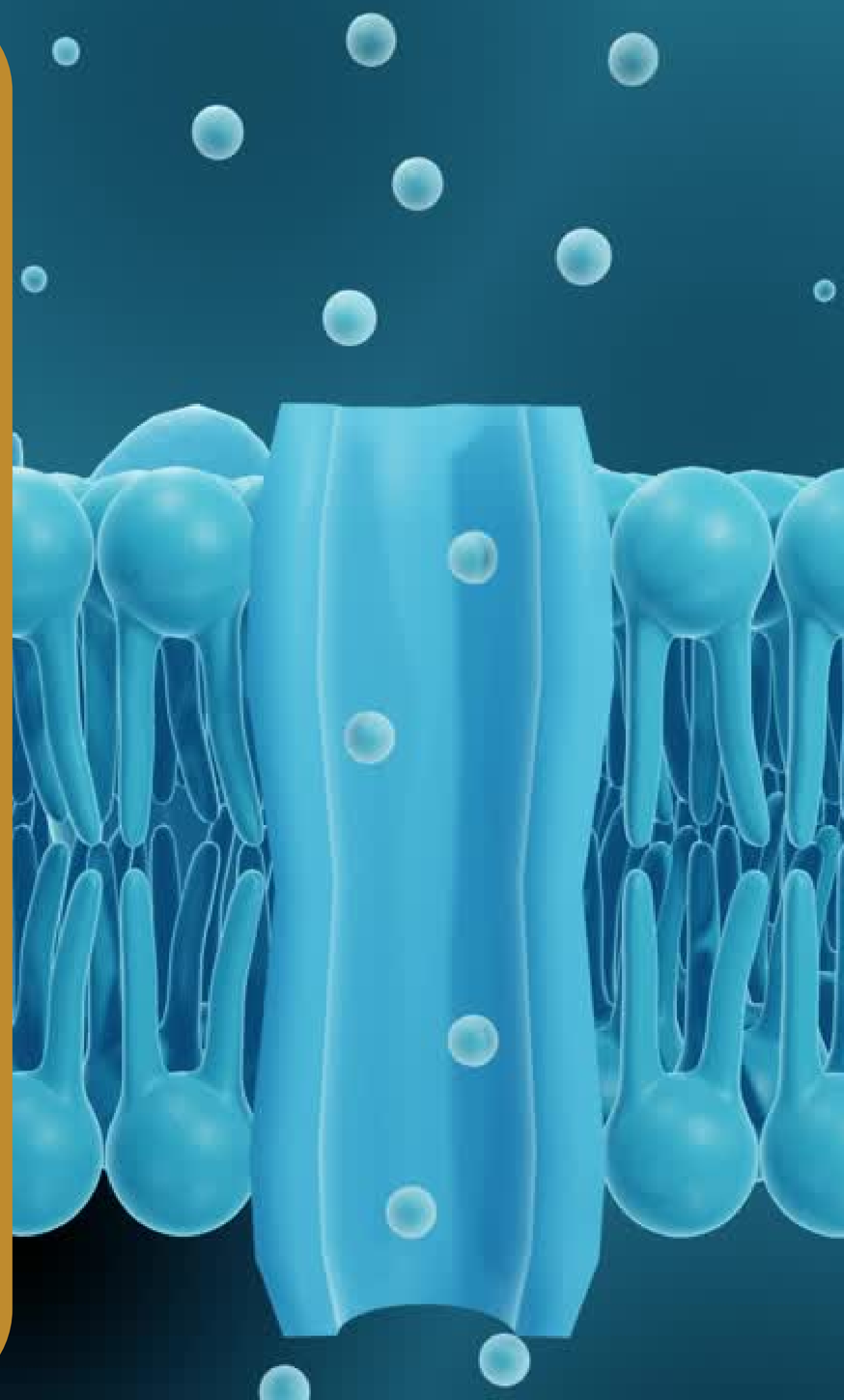


2. Membrane Lipids

All cells are surrounded by a membrane that confines their contents. Up to 80% of the mass of a cell membrane can be lipid materials and the rest is primarily protein. It is membranes that give cells their individuality by separating them from their environment.

Three Common Types of Membrane Lipids

1. Phospholipids
2. Sphingoglycolipids
3. Cholesterol

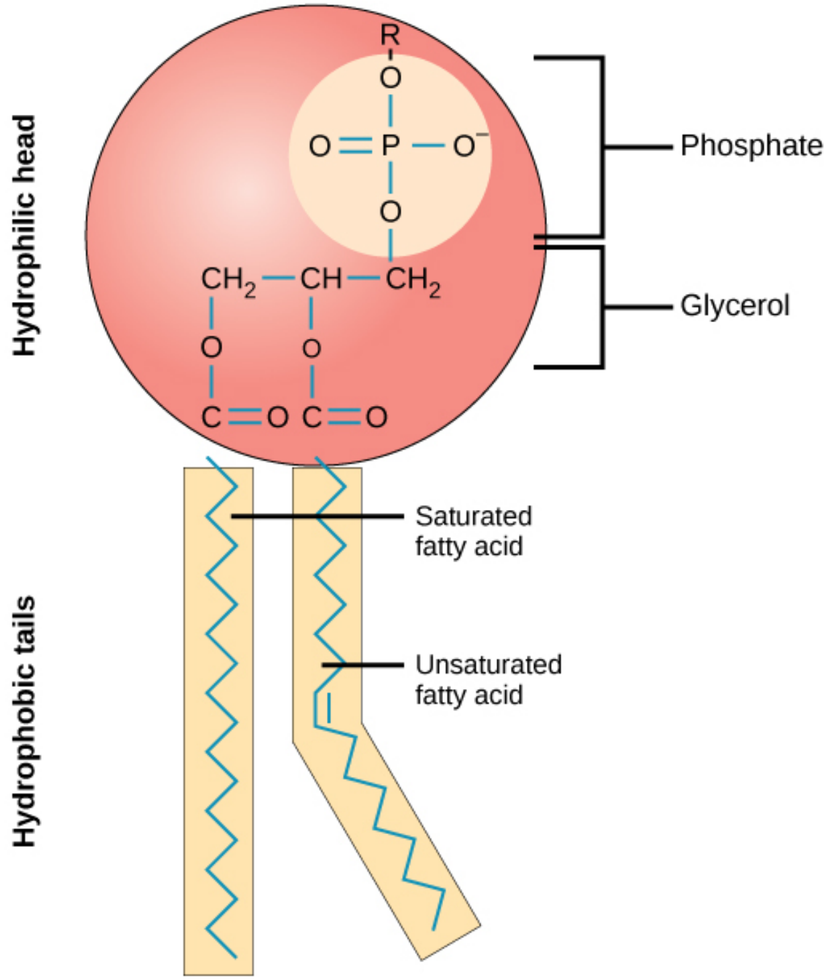


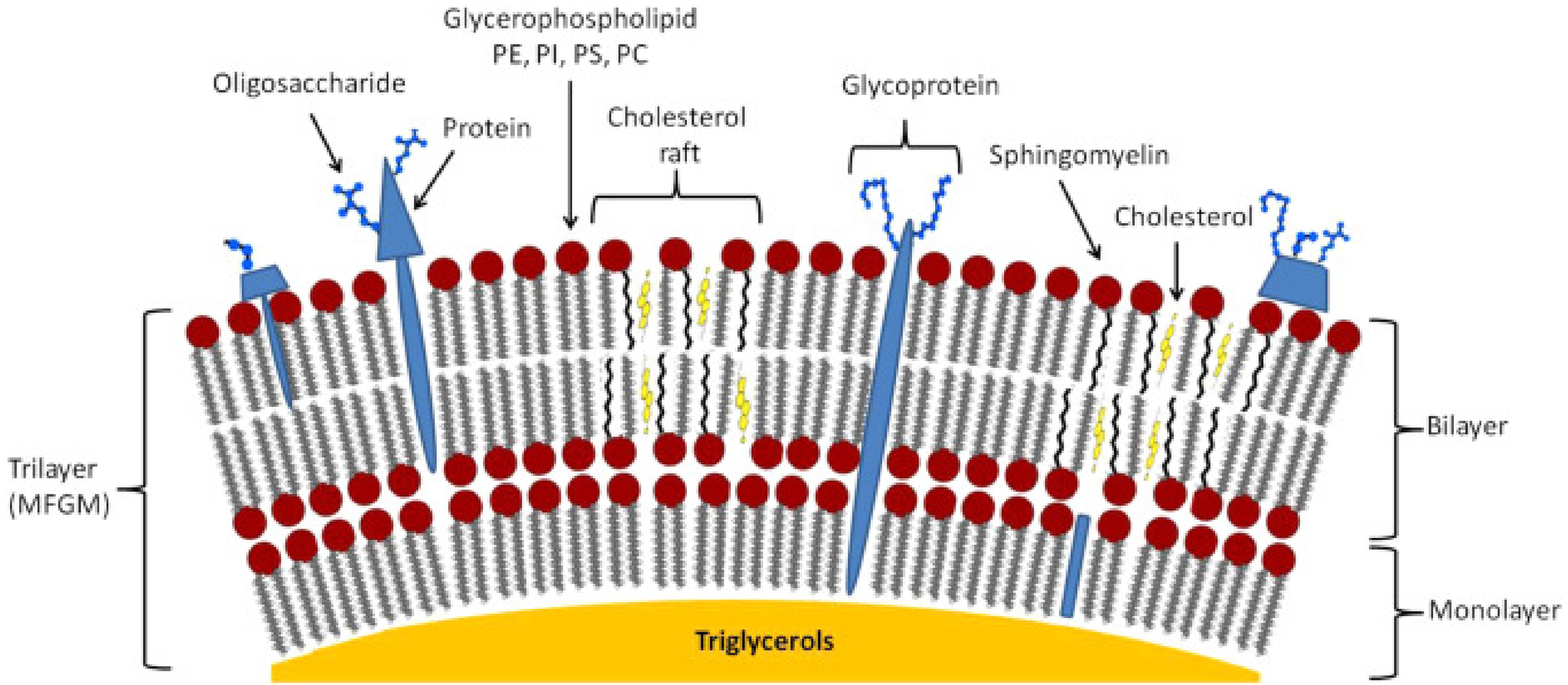
A. Membrane Lipids: Phospholipids

Phospholipids are the most abundant type of membrane lipids.

Phospholipids is a lipid that contains:
a. one or more fatty acids
b. a phosphate group
c. a platform molecule [Glycerol or Sphingosine, which the fatty acid(s) and the phosphate group are attached]
d. an alcohol that is attached to the phosphate group

The platform molecule on which a phospholipid is built may be the 3-carbon alcohol glycerol or more complex C18 aminodialcohol called sphingosine.




Glycerophospholipid
PE, PI, PS, PC
Oligosaccharide
Protein
Cholesterol
raft
Glycoprotein
Sphingomyelin
Cholesterol
Trilayer
(MFGM)
Bilayer
Monolayer
Triglycerols

Two Types of Phospholipids

A. Glycerophospholipids –are glycerol–based phospholipids.

B. Sphingophospholipids –are sphingosine–based phospholipids.

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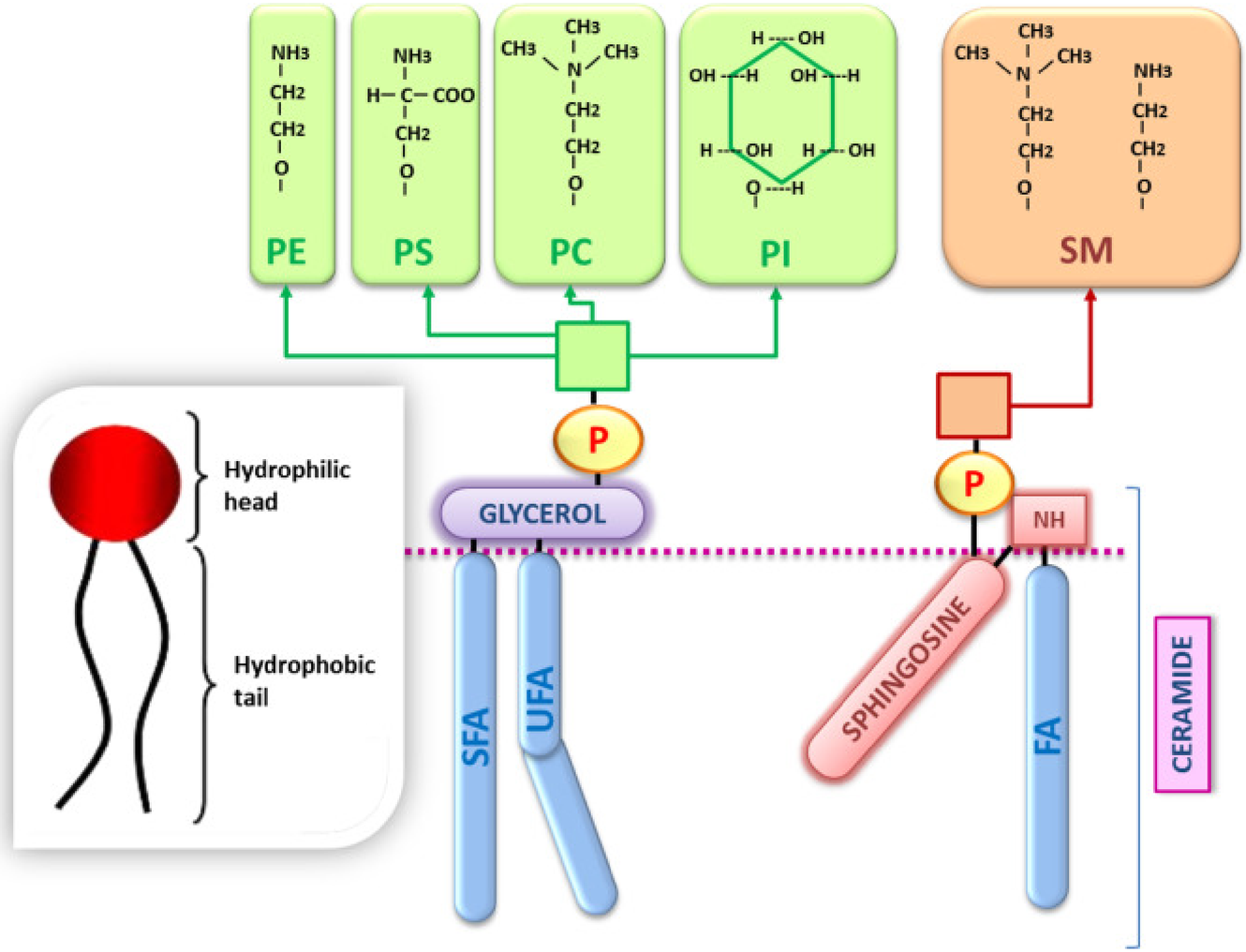
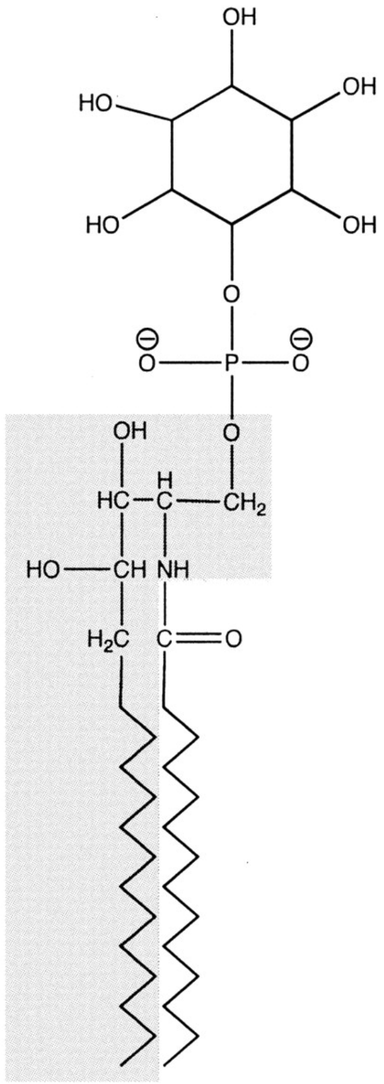
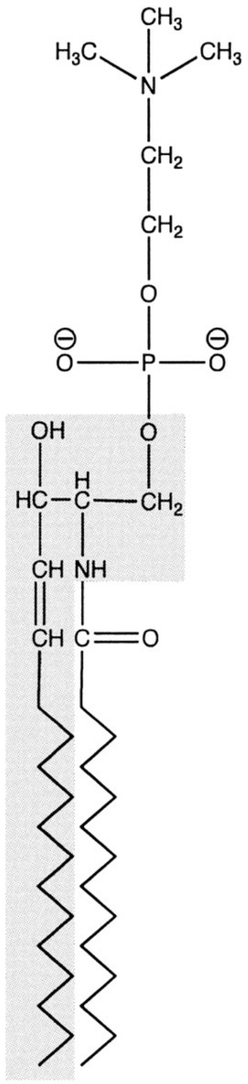


Sphingolipids

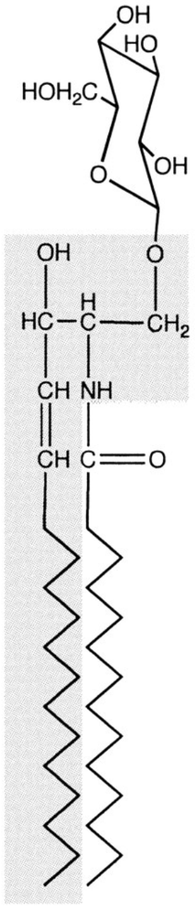
Glycerolipids



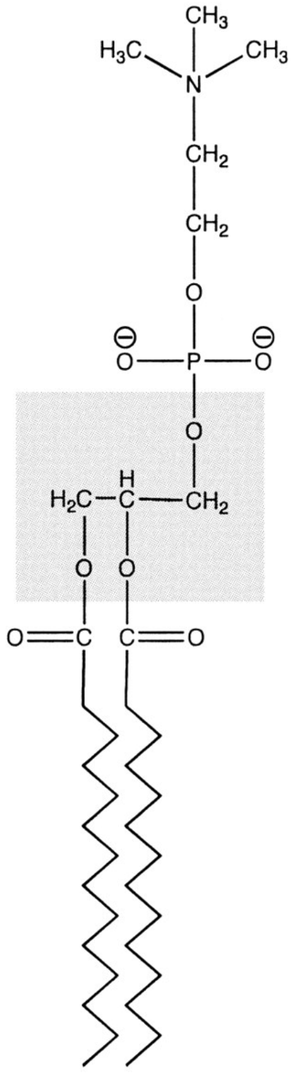
IPC



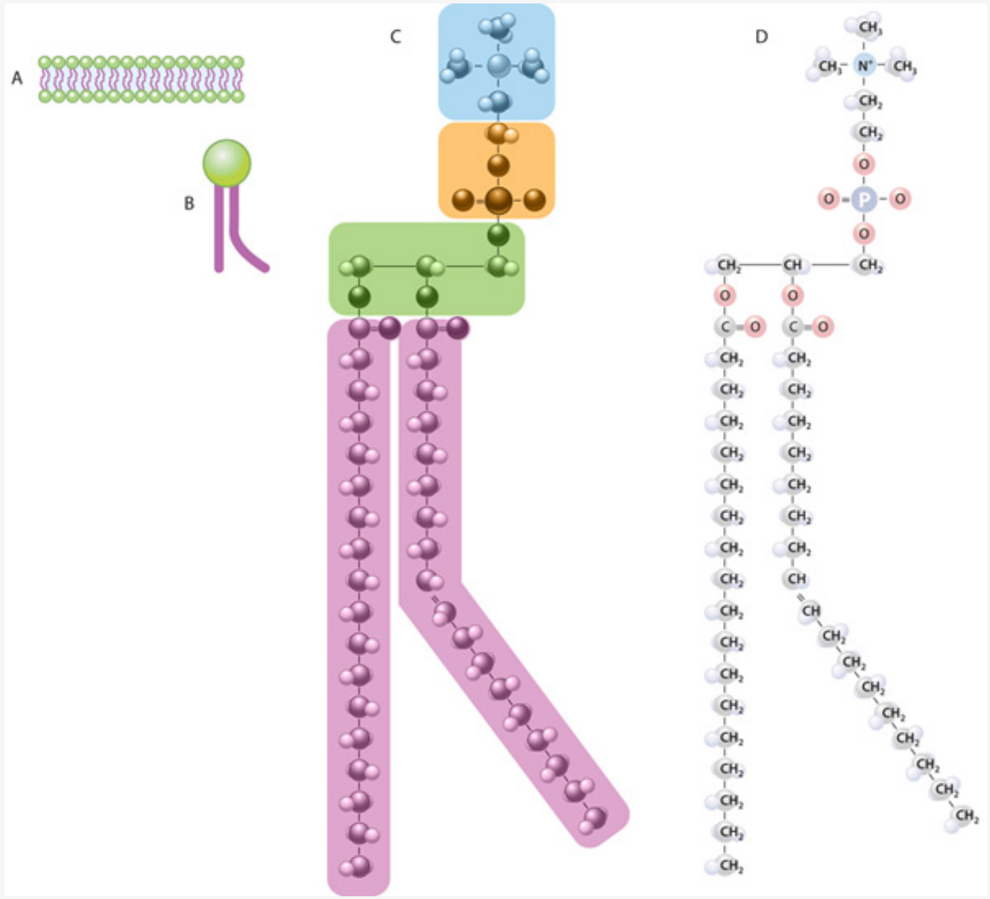
Sphingomyelin



Glucosylceramide



Phosphatidylcholine

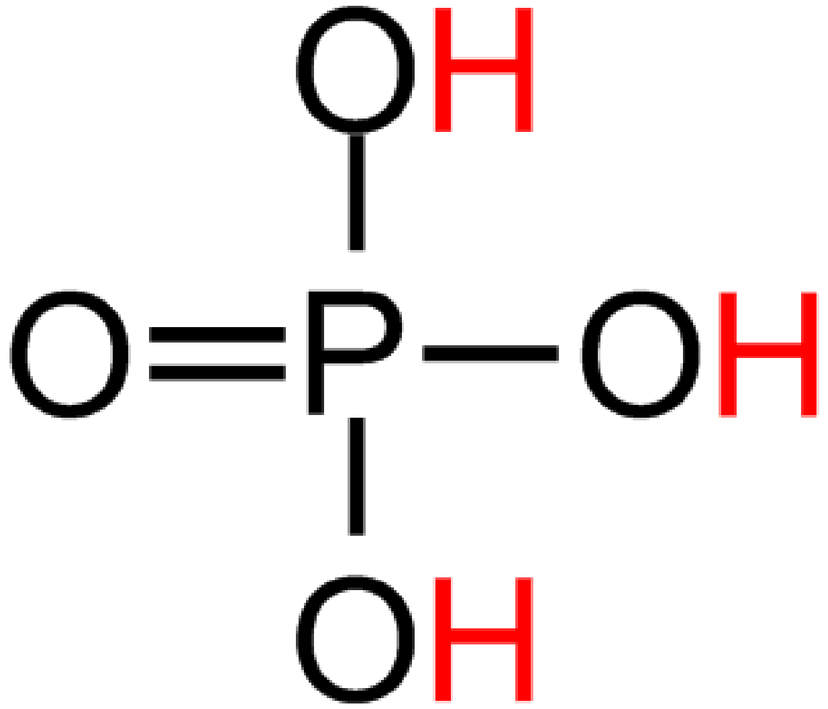


A. Glycerophospholipids

The nonpolar portion dissolves in the nonpolar oil or grease, and the Glycerophospholipid is a lipid that contains two fatty acids and a phosphate group esterified to a glycerol molecule and an alcohol esterified to the phosphate group.

- All attachments between groups are ester linkages and there are four ester linkages.
- Glycerophospholipids undergo hydrolysis and saponification reactions

The Phosphate



H_3PO_4

Phosphoric acid is the parent source for the minus charged phosphate group used in the formation of glycerophospholipids.

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The Alcohol

The alcohol attached to the phosphate group is usually one of the three amino alcohols: choline, ethanolamine or serine.

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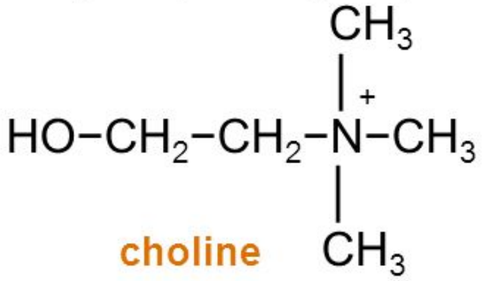
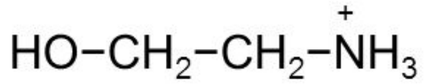
Polarity of Glycerophospholipids

A **glycerophospholipid** has

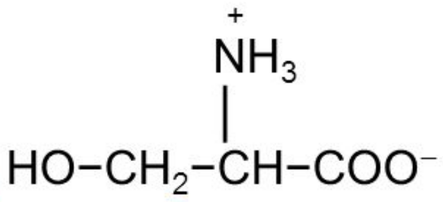
- two nonpolar fatty acid chains.
- A phosphate group and a polar amino alcohol.



choline



ethanolamine



serine

Amino alcohols

The Alcohol

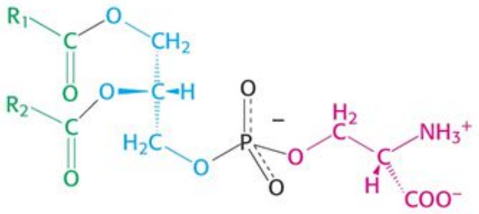
Gycerophospholipids containing these three amino alcohols are respectively known as:

a. Phosphatidylcholines

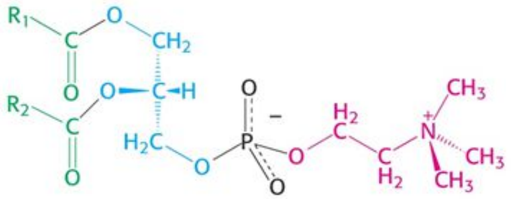
b. Phosphatidylethanolamines

c. Phosphatidylserines

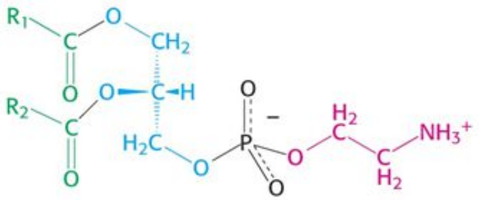
The glycerol, fatty acid, and phosphate portions of a glycerophospholipid structure constitute a phosphatidyl group.



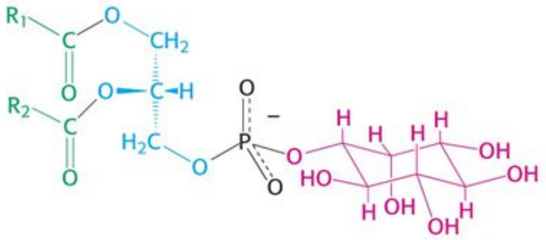
Phosphatidyl serine



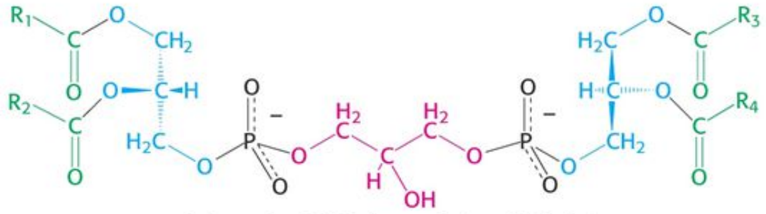
Phosphatidyl choline (lecithin)



Phosphatidyl ethanolamine



Phosphatidyl inositol



Diphosphatidyl glycerol (cardiolipin)

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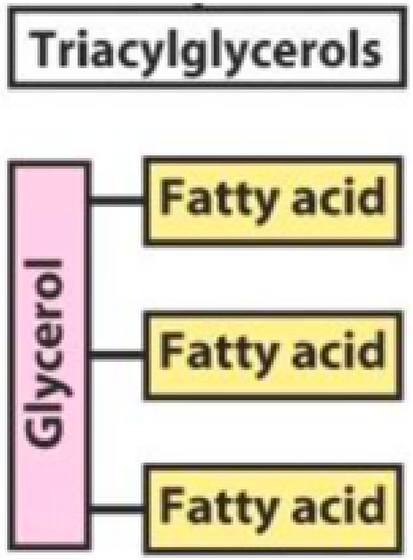
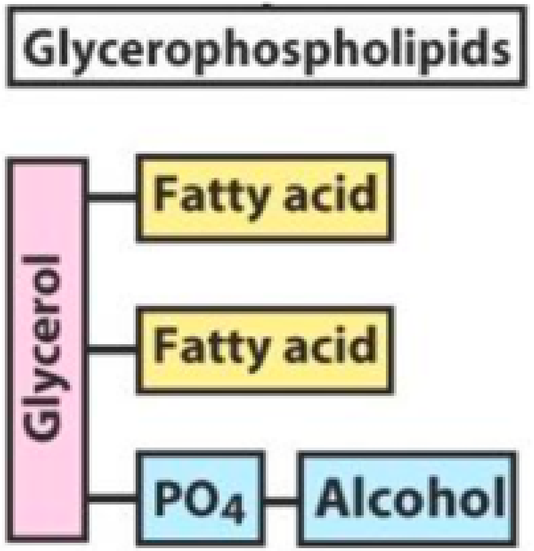
Differences

Triacylglycerol
1. Storage for metabolic fuel
2. Nonpolar lipids

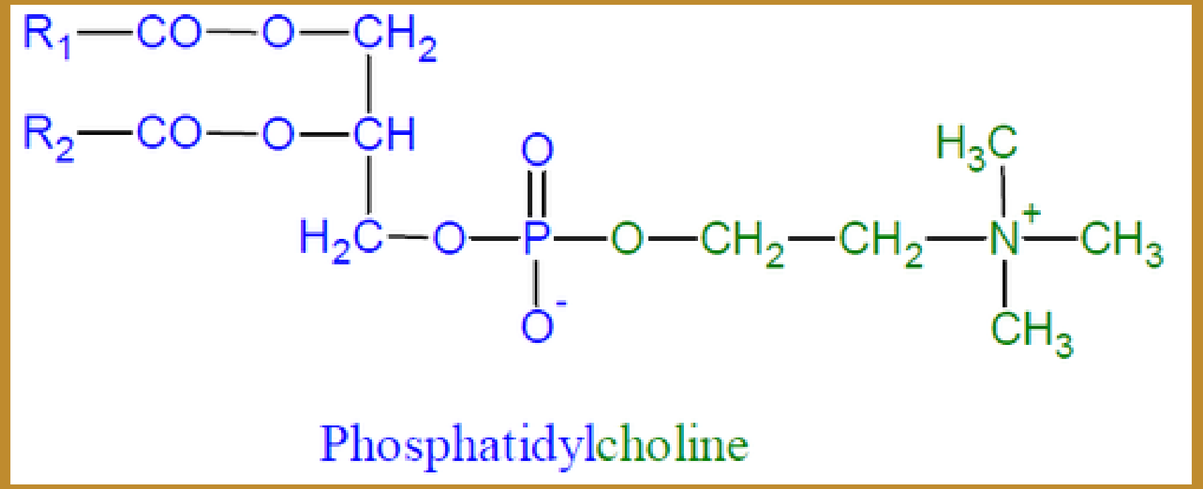




Glycerophospholipids
1. Function exclusively as component of cell membrane.
2. Polar lipids
3. There is a “head” part (alcohol and phosphate, polar)
There are two “tails” (two fatty acids, nonpolar)

Phosphatidylcholines

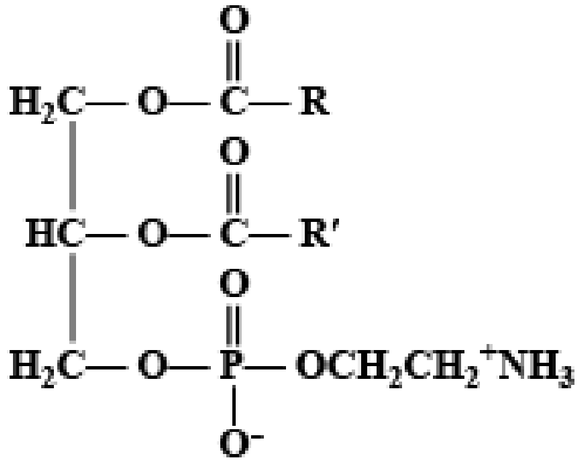
1. Also known as lecithins, are waxy solids that form colloidal suspensions in water.
2. Egg yolks and soy beans are good dietary sources of these lipids.
3. It is taken as nutritive supplement that will improve memory.
4. Within the body, they are prevalent in cell membranes.
5. Enzyme lecithinase in the intestine hydrolyzes most phosphatidylcholine taken orally before it passes into body fluids,
so it does not reach body tissues.
6. Food industry used it as emulsifiers to promote the mixing of otherwise immiscible materials (mayonnaise, ice cream, and custards are some of the products it formed).



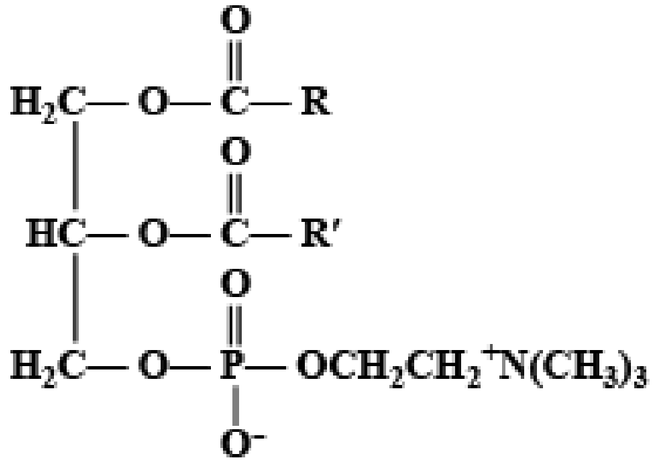
Phosphatidylcholine

Phosphatidylethanolamines and Phosphatidylserines

1. Also known as cephalins.
2. They are important in blood clotting.
3. These compounds are found in heart and liver tissue and in high concentrations in the brain.



Phosphatidylethanolamine
(cephalin)

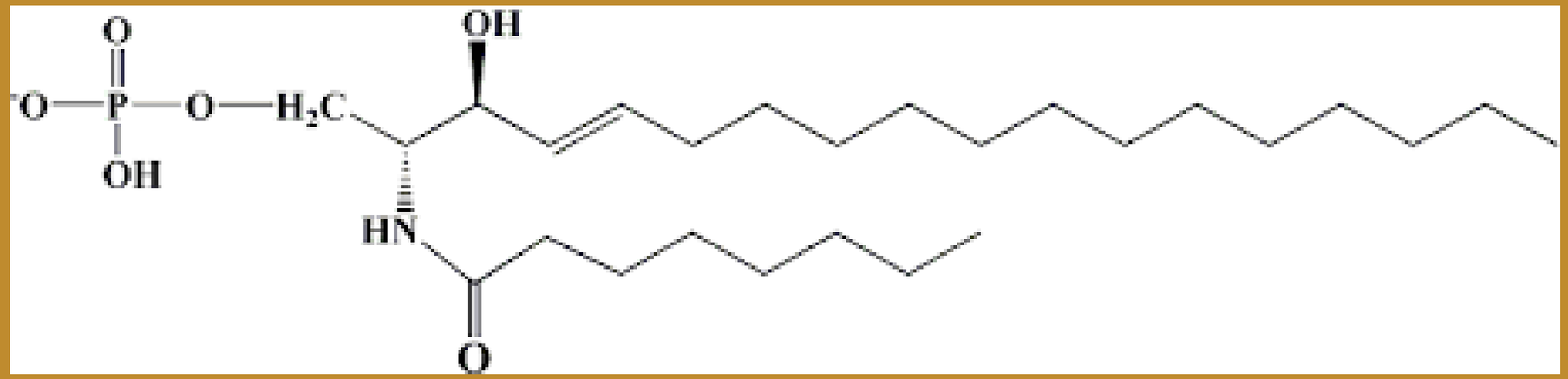


Phosphatidycholine
(lecithin)

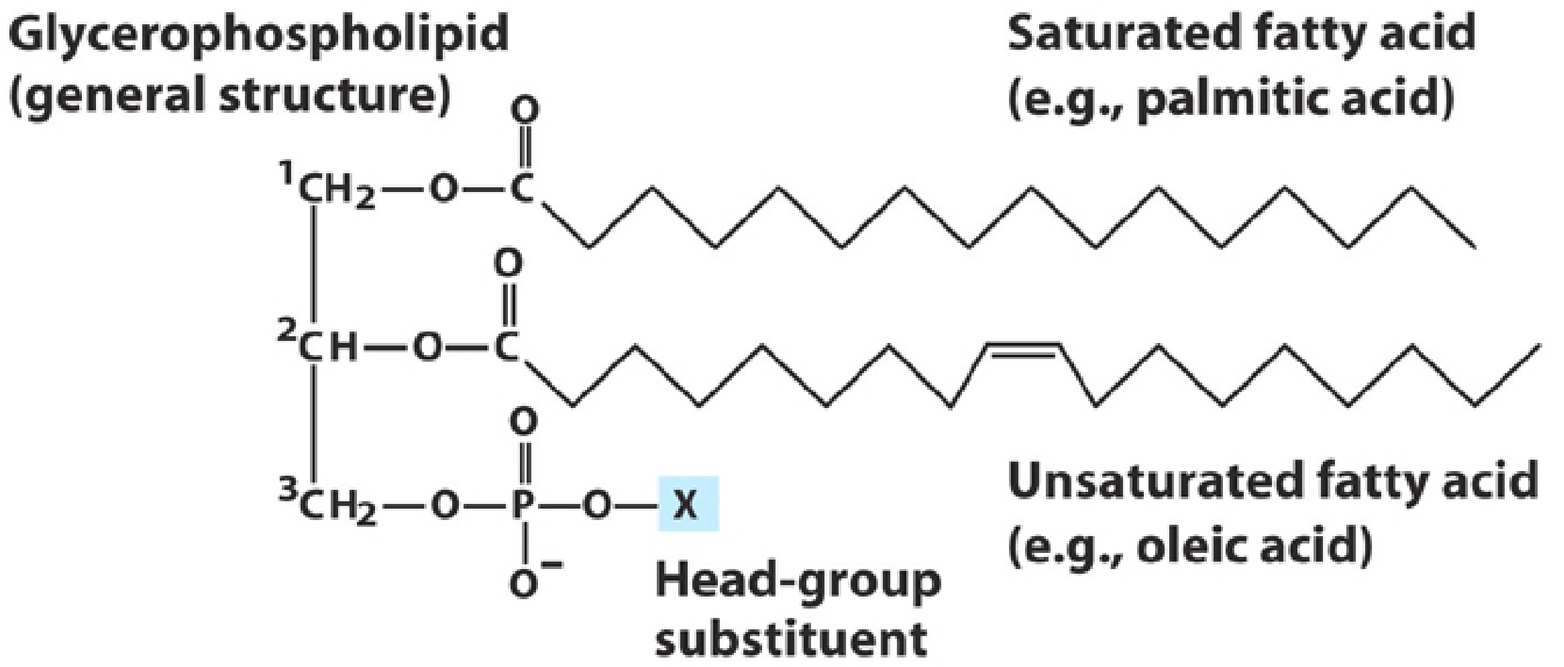
B. Sphingophospholipids

Sphingophospholipid is a lipid that contains one fatty acid, and one phosphate group attached to a sphingosine molecule and an alcohol attached to the phosphate group.

- All sphingophospholipids have structures based on the 18-carbon monosaturated aminodialcohol sphingosine.
- Sphingophospholipids participate in hydrolysis and saponification reactions.



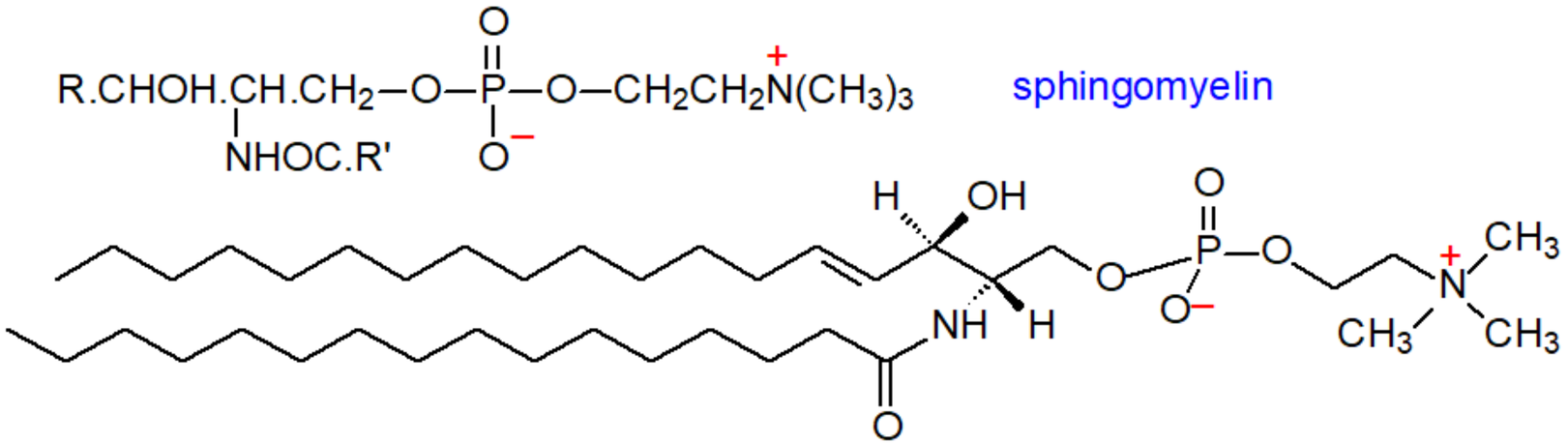

Sphingosine
HO—3CH—CH=CH—(CH2)12—CH3
Fatty acid
2CH—N—C
H
1CH2—O—X
Sphingolipid
(general
structure)


Glycerophospholipid
(general structure)
Saturated fatty acid
(e.g., palmitic acid)
1CH2—O—C
2CH—O—C
3CH2—O—P—O—X
O−
Unsaturated fatty acid
(e.g., oleic acid)
Head-group
substituent

Sphingomyelins

Sphingophospholipids in which the alcohol esterified to the phosphate group is choline are called sphingomyelins.

Sphingomyelins are found in all cell membranes and are important structural components of myelin sheath (the protective and insulating coating that surrounds nerves).



N-(hexadecanoyl)-sphing-4-enine-1-phosphocholine

Sphingomyelin

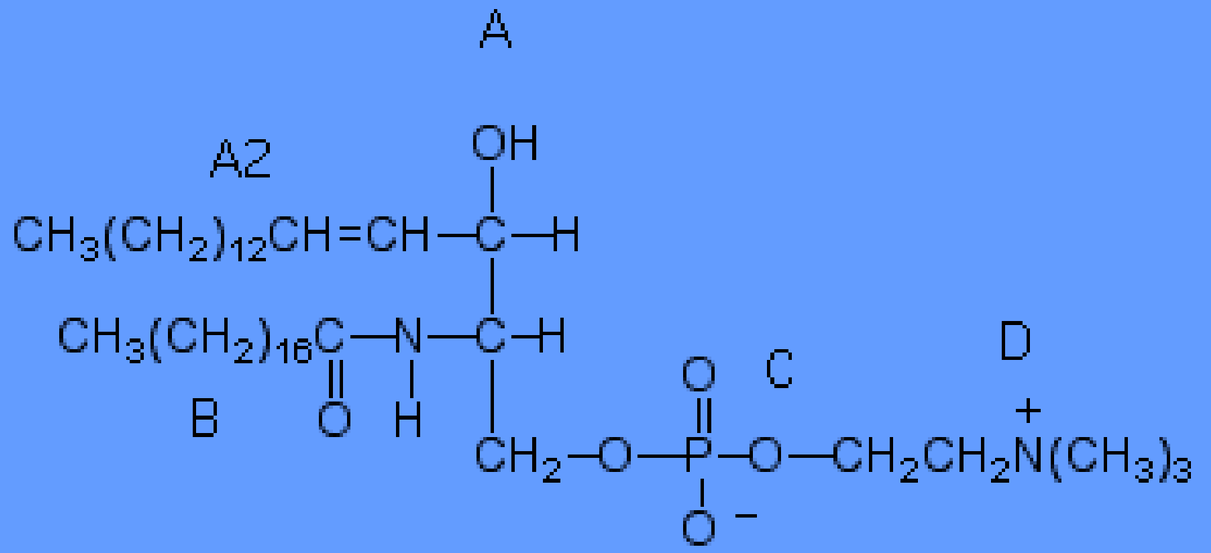
Sphingosine

Hydrocarbon chain

Fatty Acid

Phospate

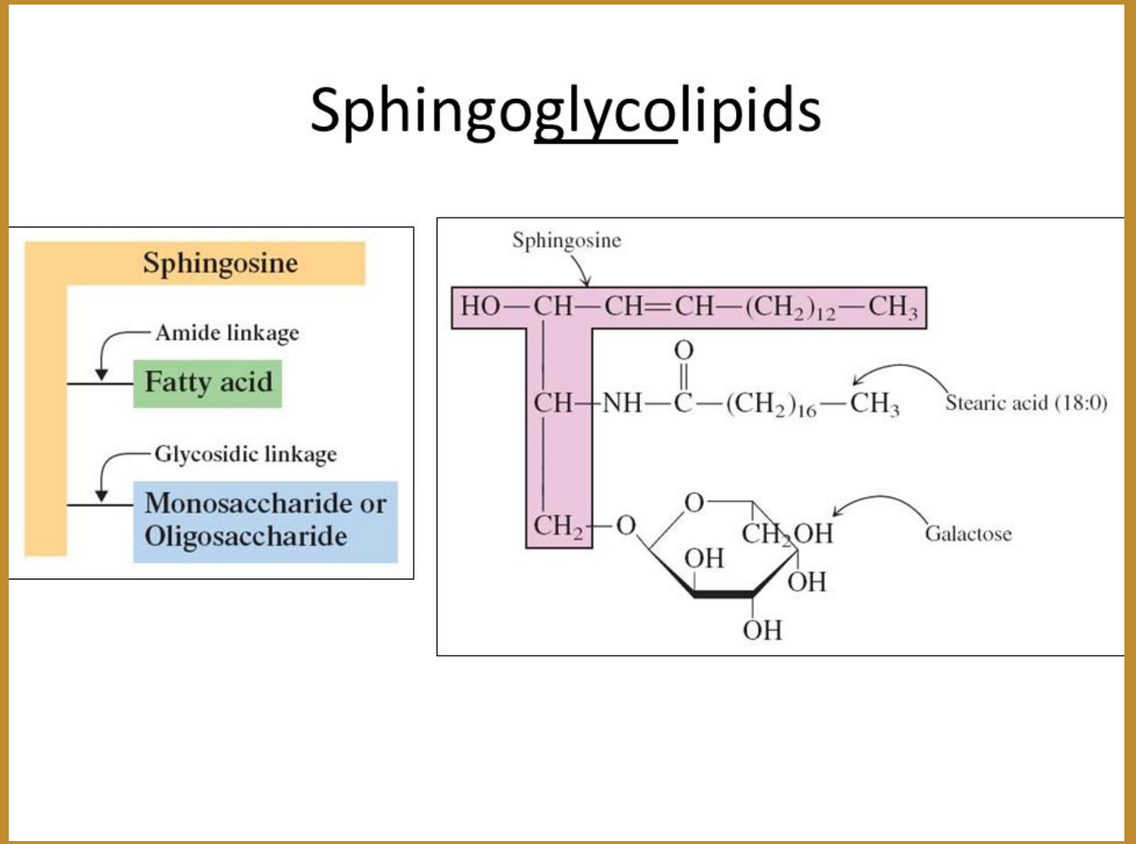
Choline



Membrane Lipids: Sphingoglycolipids

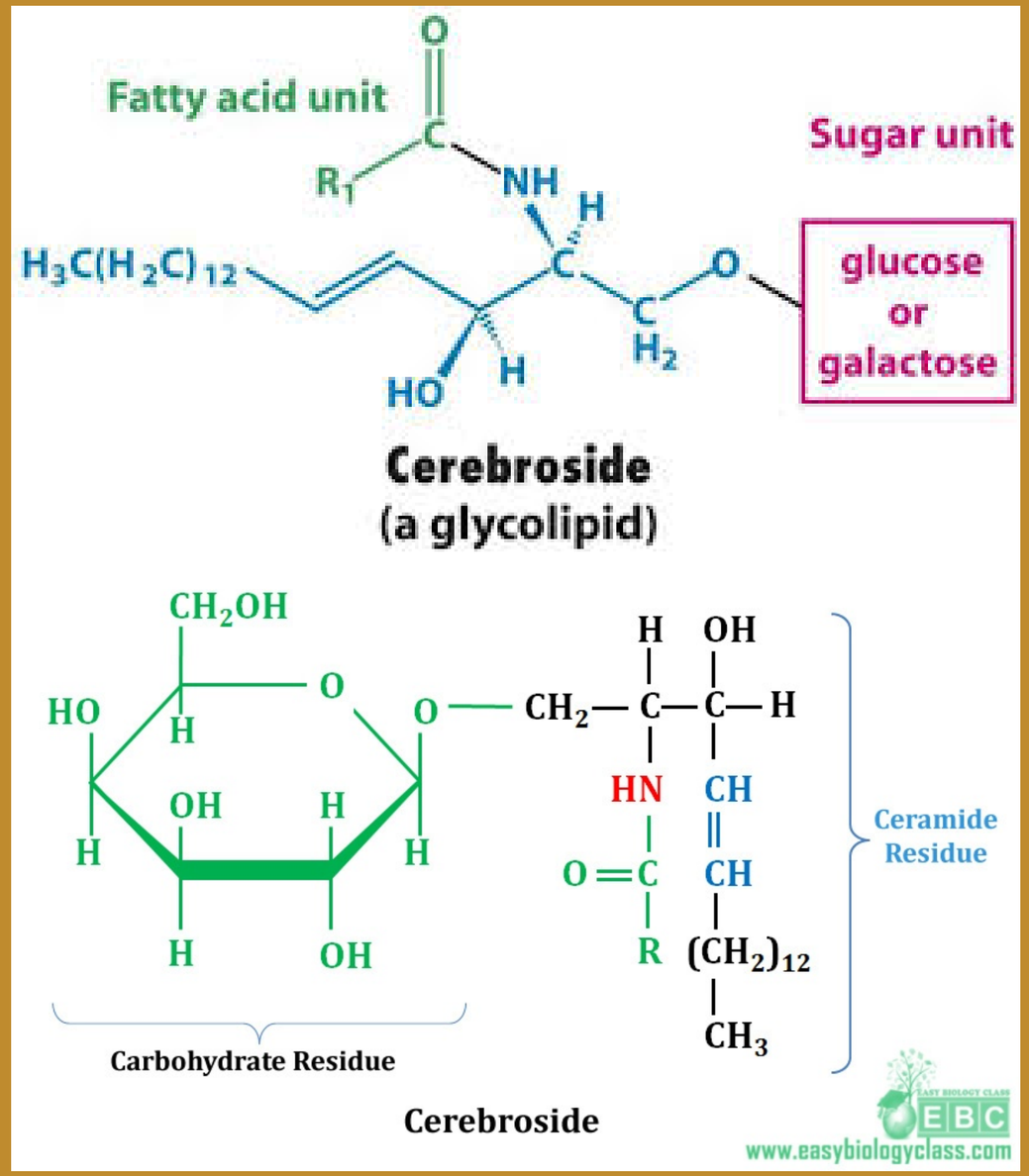
Sphingoglycolipid is a lipid that contains both a fatty acid and a carbohydrate component attached to a sphingosine molecule.

- A fatty acid is attached to the sphingosine through an amide linkage, and a monosaccharide or oligosaccharide is attached to the sphingosine at the terminal –OH carbon atom through a glycosidic linkage.



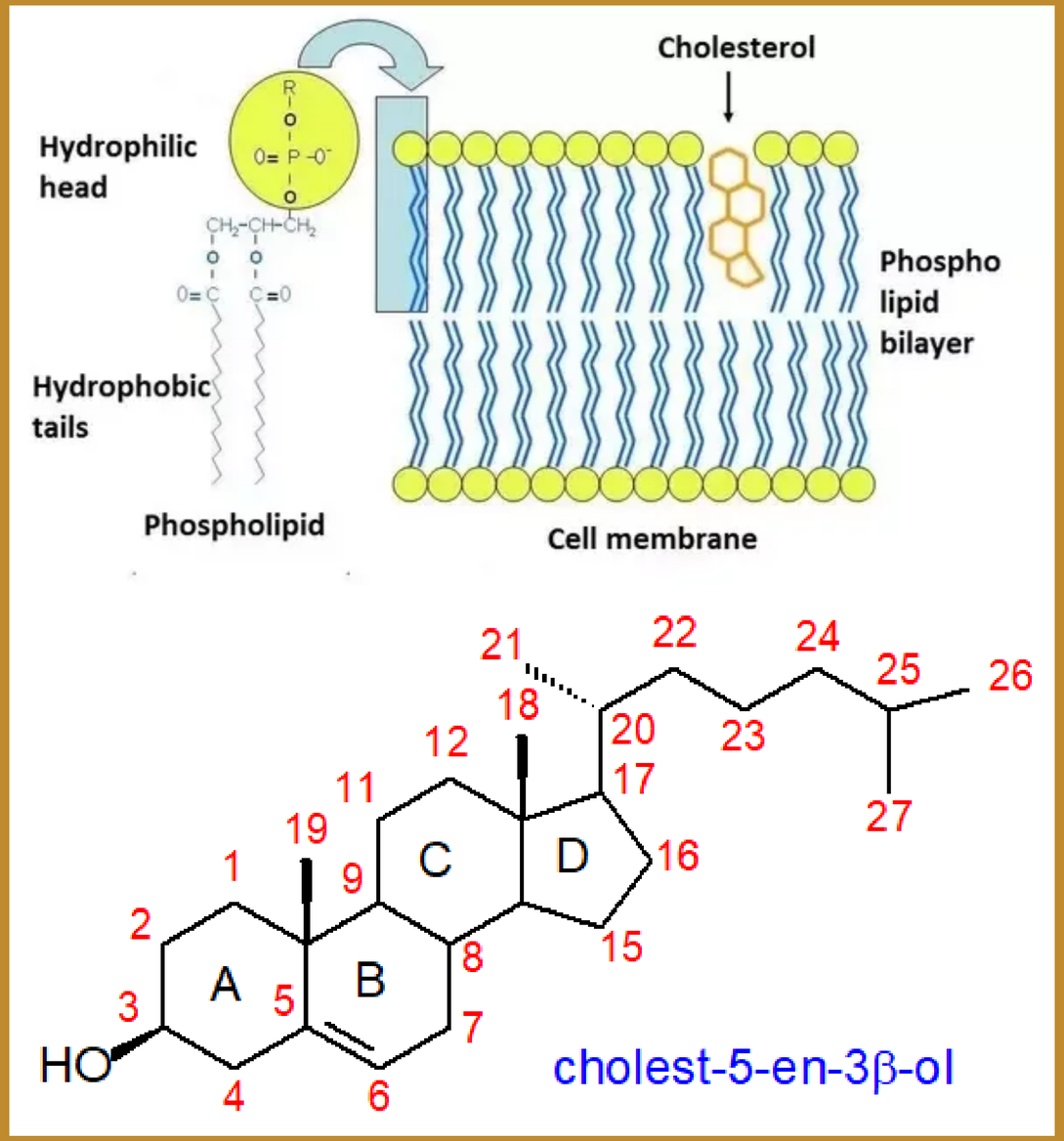
Sphingoglycolipids

- Cerebrosides, the simplest sphingoglycolipids, contain a single monosaccharide unit –either glucose or galactose.
- Cerebrosides occur primarily in brain. Also, they are present in myelin sheath of nerves.
- More complex sphingoglycolipids, called gangliosides, contain a branched chain of up to seven monosaccharide residues. These substances occur in the gray matter (contain most of the brain's neuronal cell bodies) of the brain as well as in the myelin sheath

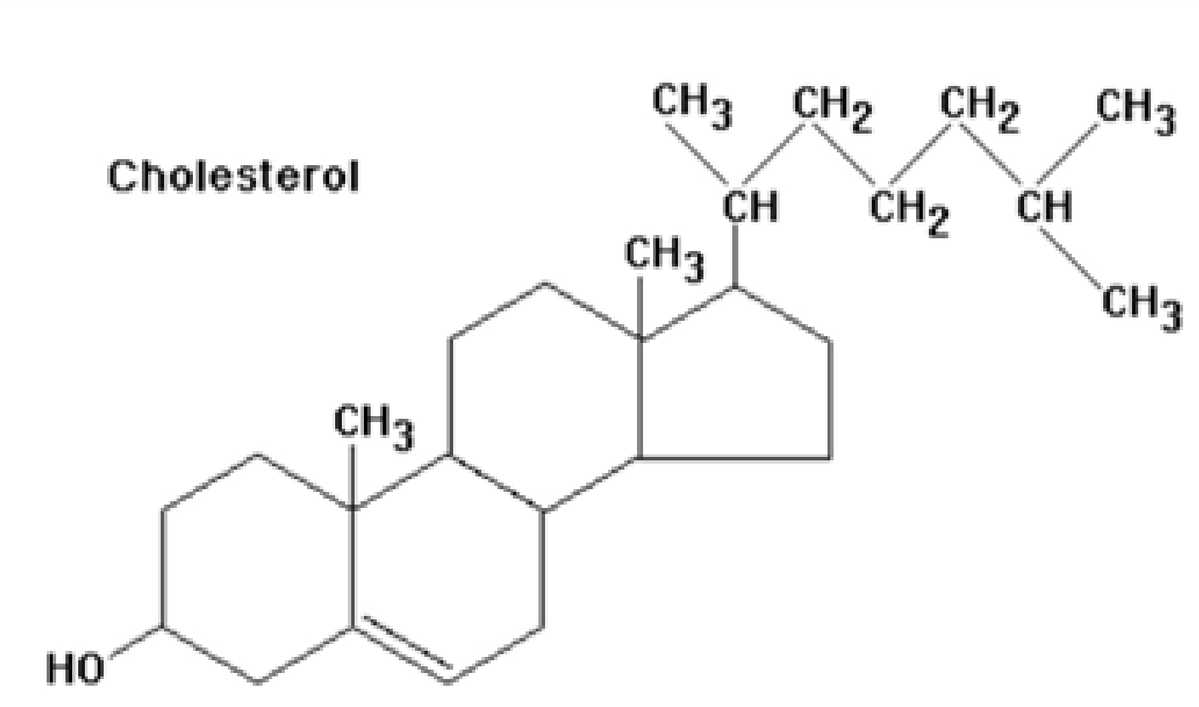


Membrane Lipids: Cholesterol

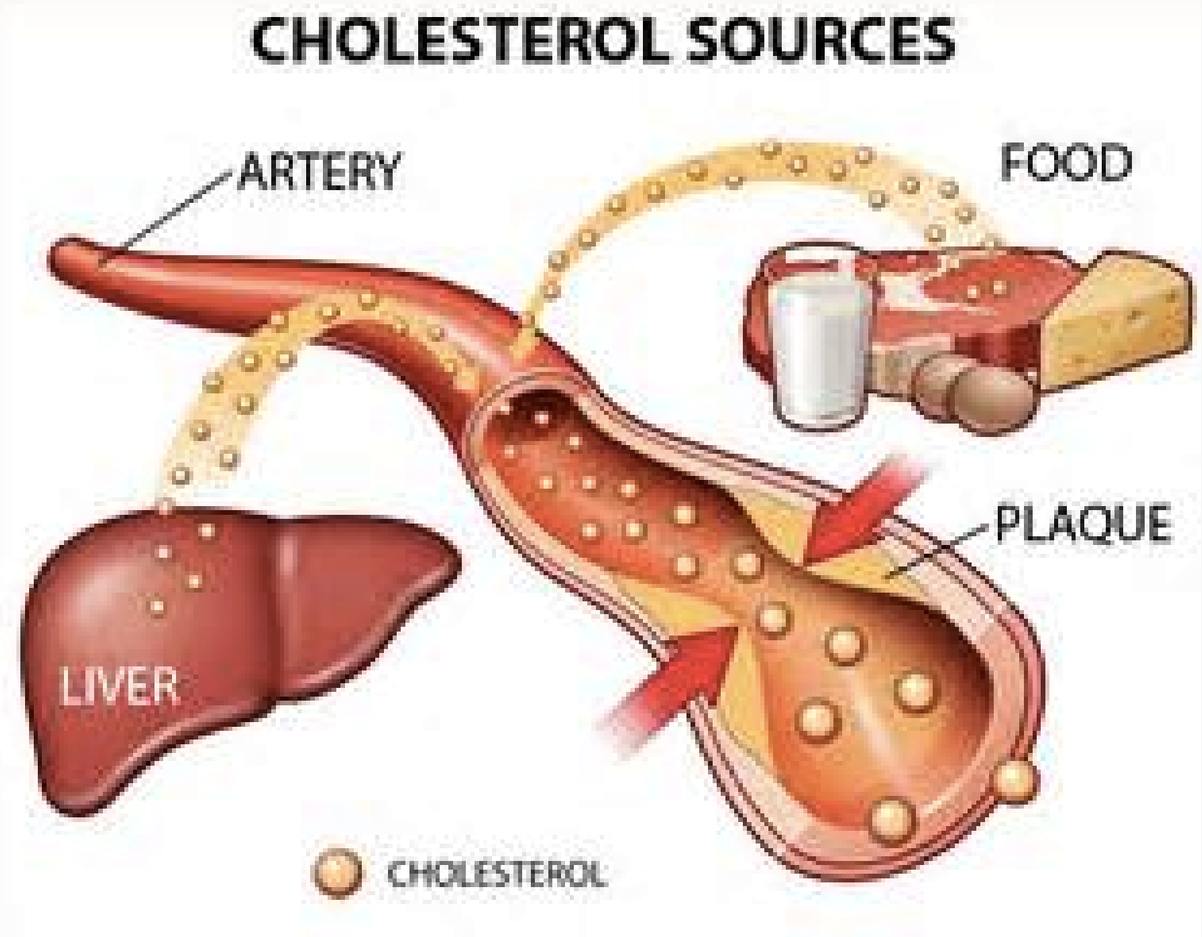
- Cholesterol is specific compound in that (1.) there is no fatty acid residues present and (2.) neither glycerol nor sphingosine is present as the platform molecule.
- Cholesterol is a steroid.
- A steroid is a lipid whose structure is based on a fused-ring system that involves three six-membered rings and one five membered ring. Most steroids have an oxygen functional group (=O or –OH) at carbon 3 and some kind of side chain at carbon 17. Many also have a double bond from carbon 5 to either carbon 4 or carbon 6



Cholesterol



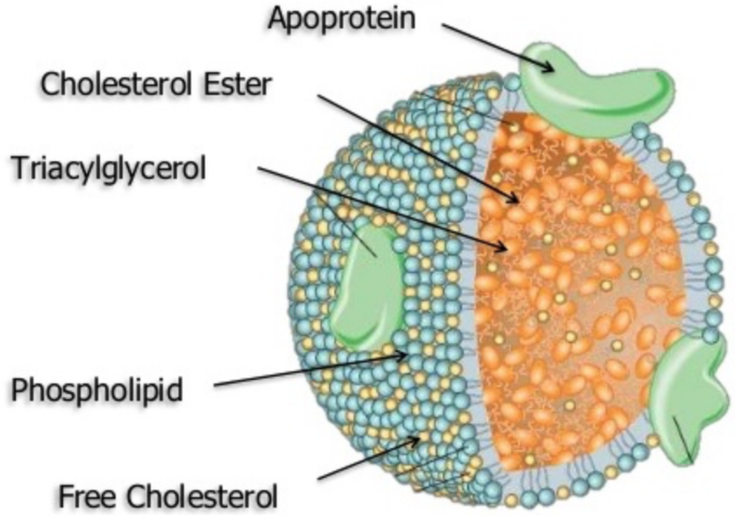
- Cholesterol is a C27 steroid molecule that is a component of cell membranes and a precursor for other steroid-based lipids. It is the most abundant steroid in the human body.
- The –ol ending in the name cholesterol conveys the information that an alcohol functional group is present in this molecule; it is located on carbon 3 of the steroid nucleus.
- In addition, cholesterol has a methyl group attachment at carbon 10 and 13.
- Carbon-carbon double bond between carbon 5 and 6.
- An eight-carbon branched side chain at carbon 17.



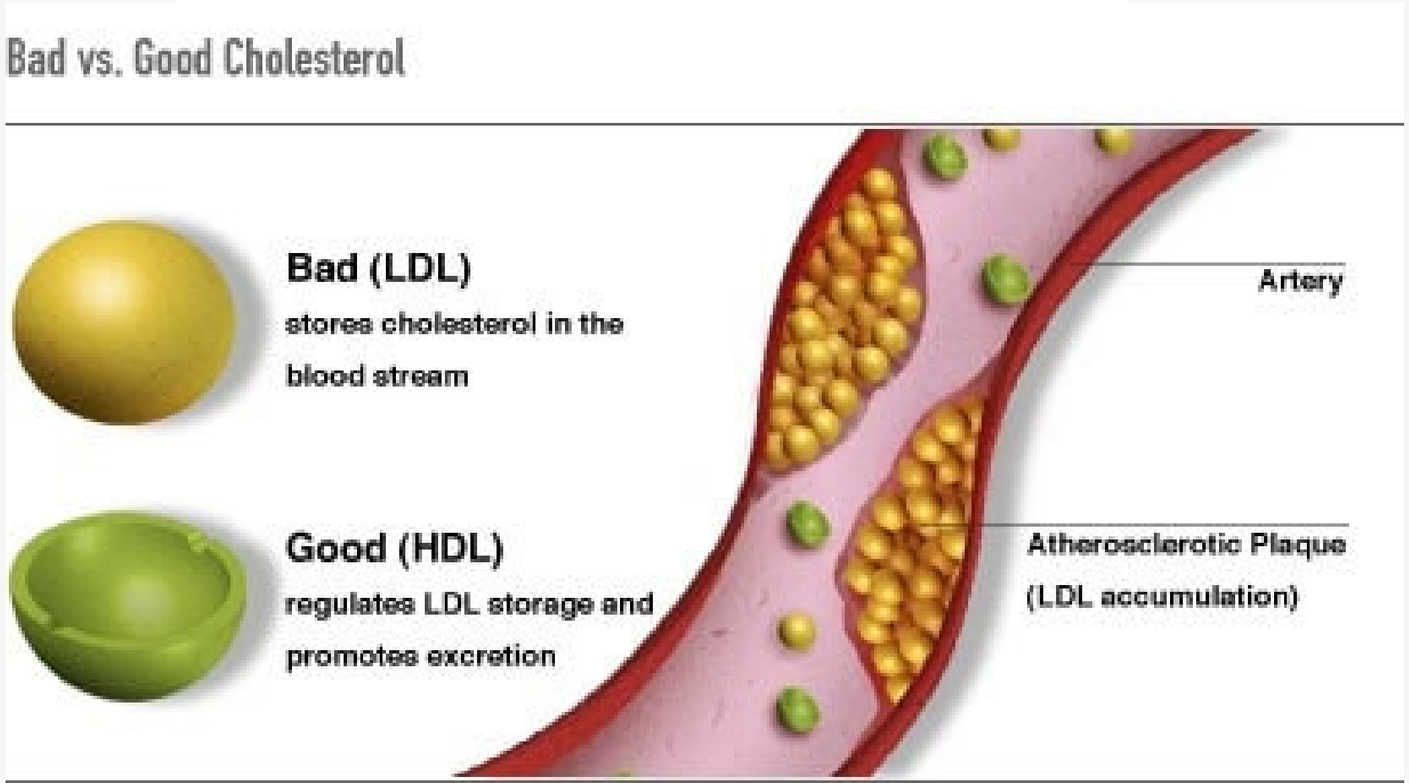
Cholesterol

- Within the human body, cholesterol is found in cell membranes (up to 25% by mass), in nerve tissue, in brain tissue (about 10% by dry mass), and in virtually all fluids. Although a portion of the body's cholesterol is obtained from dietary intake, most of it is biosynthesized by the liver and (to a lesser extent) the intestine.
- Biosynthetic cholesterol is distributed to cells throughout the body for various uses via the bloodstream. Because cholesterol is only sparingly soluble in water (blood), protein carrier system is used for its distribution. These cholesterol–protein combinations are called lipoproteins.

Cholesterol: Lipoproteins

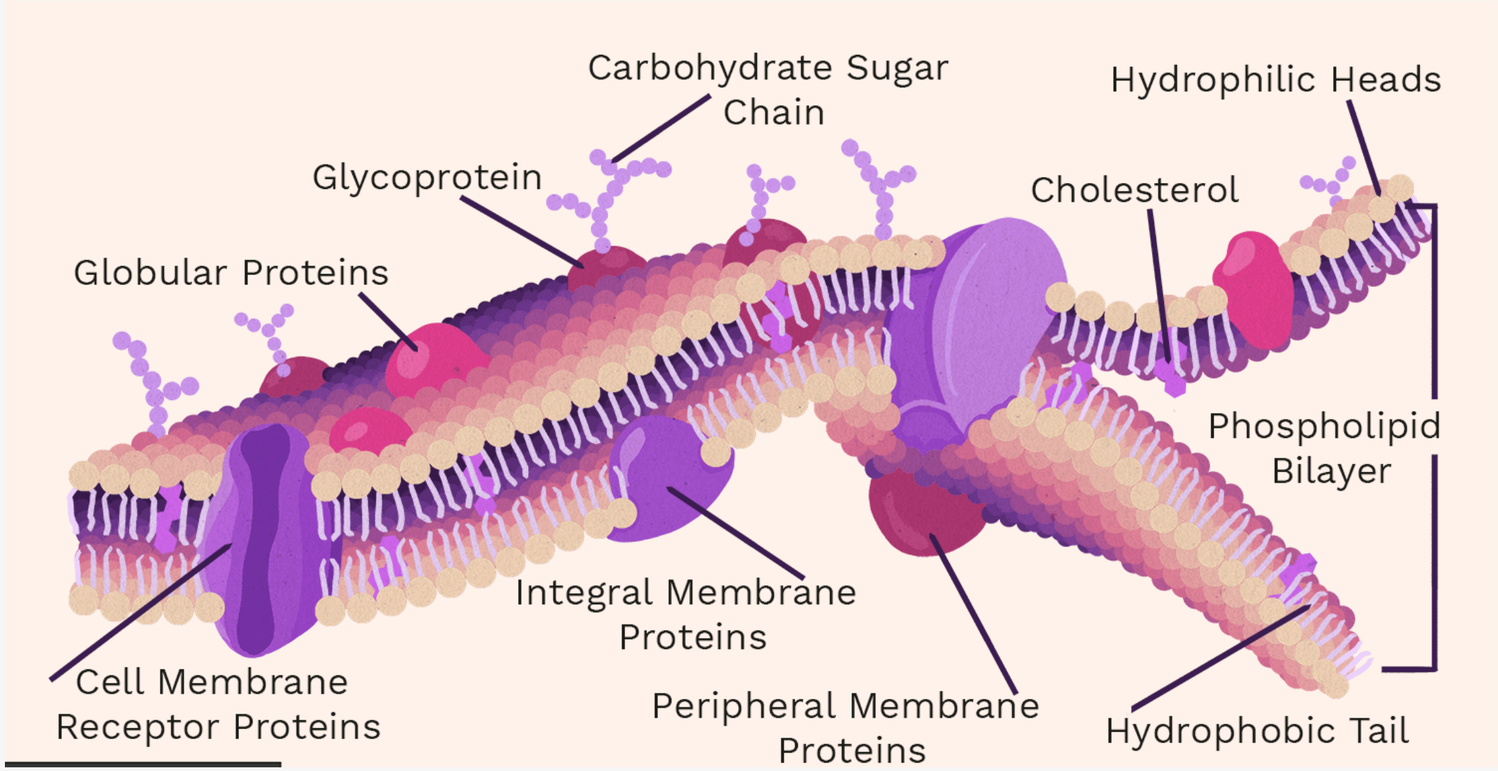


Structure of a Lipoprotein



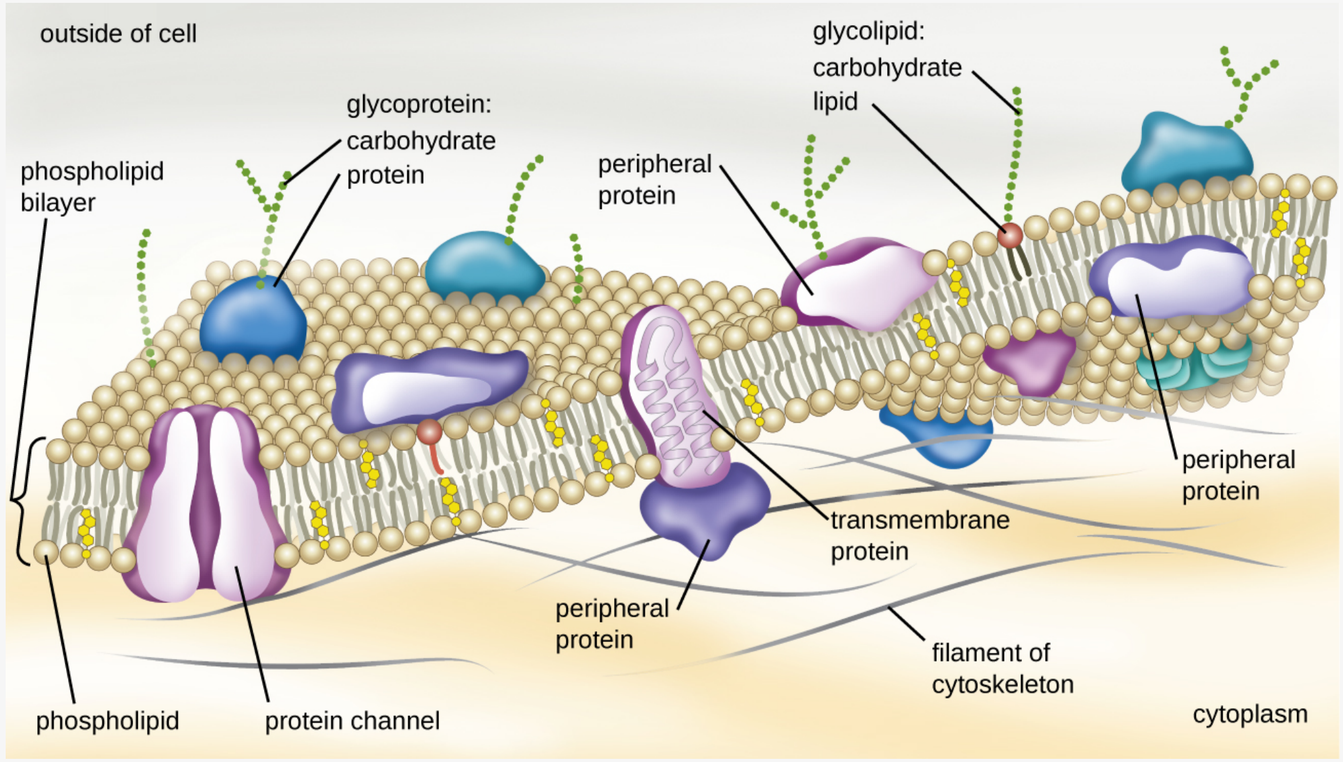
- LDL (low-density lipoproteins) – the lipoproteins that carry cholesterol from liver to the various tissues. LDL is often called bad cholesterol.
- HDL (high-density lipoproteins) – the lipoproteins that carry excess cholesterol from tissues back to the liver. HDL is often called good cholesterol.
- High blood cholesterol levels contribute to atherosclerosis, a form of cardiovascular disease characterized by the build-up of plaque along the inner walls of arteries. Plaque is a mound of lipid material mixed with smooth muscle cells and calcium. Much of the lipid in plaque is cholesterol. Plaque deposits in the arteries that serve the heart reduce blood flow to the heart muscle and can lead to a heart attack.

Cell Membranes



- Cell membrane is a lipid-based structure that separates a cell's aqueous-based interior from the aqueous environment surrounding the cell. Also, cell membrane controls the movement of substances. into and out of the cell. Up to 80% of the mass of a cell membrane is lipid material consisting primarily of the three types of membrane lipids: phospholipids, glycolipids, and cholesterol.
- Lipid bilayer is a two-layer-thick structure of phospholipids and glycolipids in which the nonpolar tails (hydrophobic, water-hating) of the lipids are in the middle structure and the polar heads (hydrophilic, water-loving) are on the outside surfaces of the structure. There are distinct parts to the bilayer: the exterior polar "heads", the interior polar "heads", and the central nonpolar "tails".

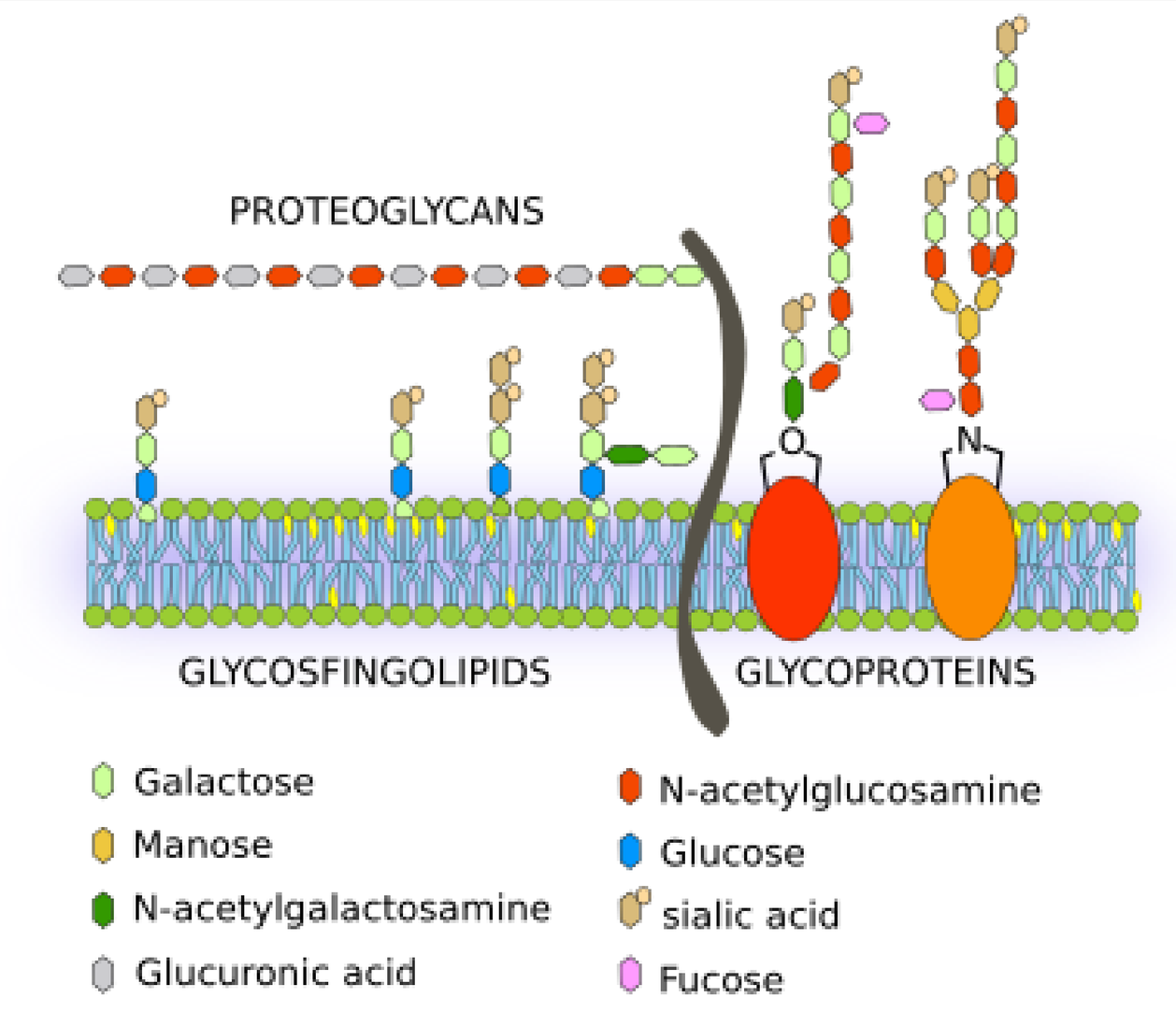
Cell Membranes



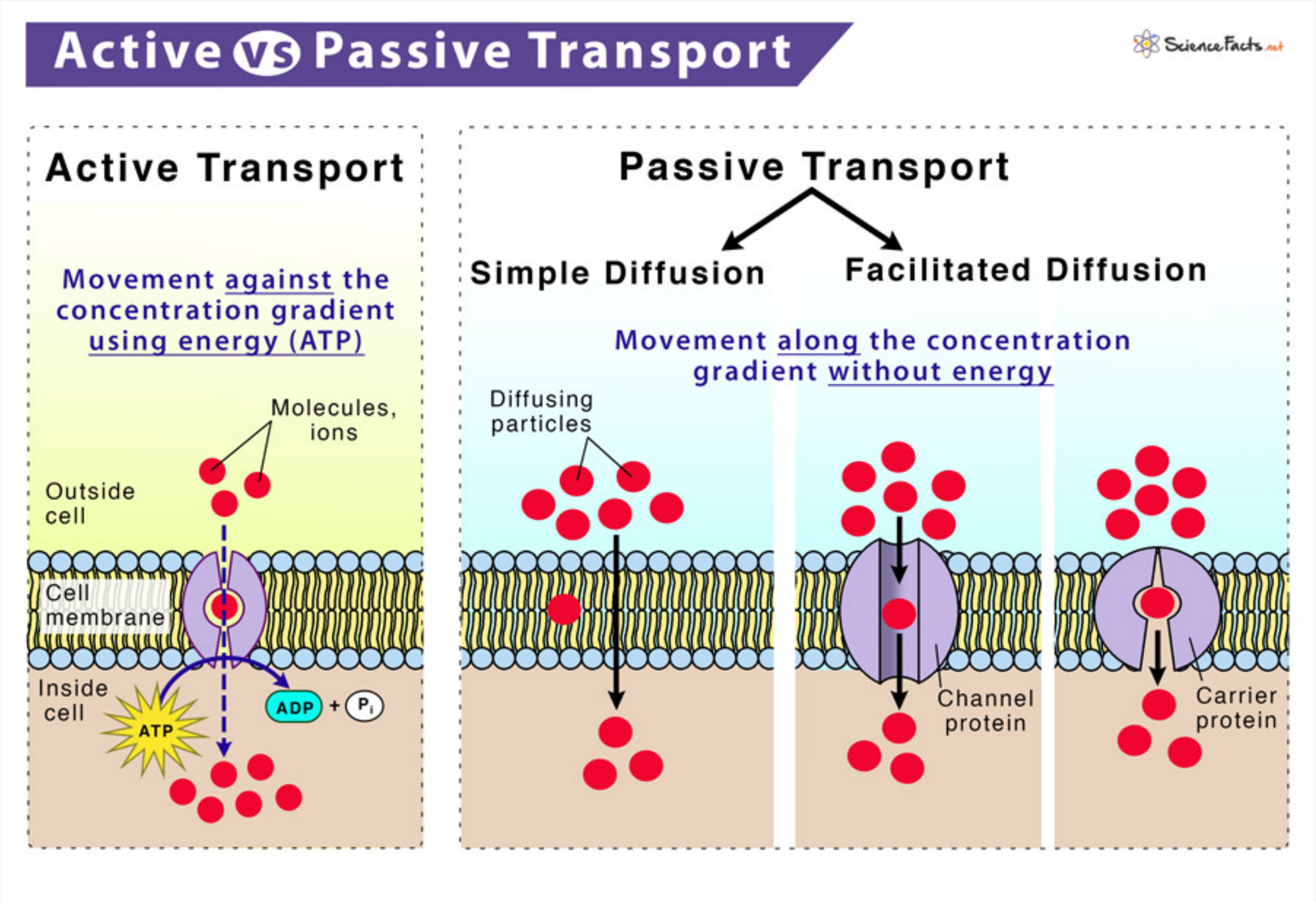
- Cholesterol molecules are also components of cell membranes. They regulate membrane rigidity. Because of their compact shape, cholesterol molecules fit between the fatty acid chains of the lipid bilayer restricting movement of fatty acid chains.
- Proteins are also components of lipid bilayers. The proteins are responsible for moving substances such as nutrients and electrolytes across the membrane, and they also act as receptors that bind hormones and neurotransmitters. There are two general types of membrane proteins:

a. Integral membrane protein is a membrane protein that penetrates the cell membrane.
b. Peripheral membrane protein is a non-repeating membrane protein located on the surface of the cell membrane. Intermolecular forces govern the interaction between membrane proteins and the lipid bilayers.

Cell Membranes



- Small carbohydrate molecules, usually oligosaccharides, are also components of cell membranes. They are found on the outer membrane and are covalently bonded to protein molecules or lipid molecules. The carbohydrate chains extend outward from the membrane into the surrounding aqueous environment.
- Such carbohydrate–protein and carbohydrate–lipid combinations are called glycoproteins and glycolipids, respectively. Functionally, the carbohydrate portions of these glycoproteins and glycolipids are markers, substances that play key roles in the process by which different cells recognize each other.



3 Common Transport Mechanisms

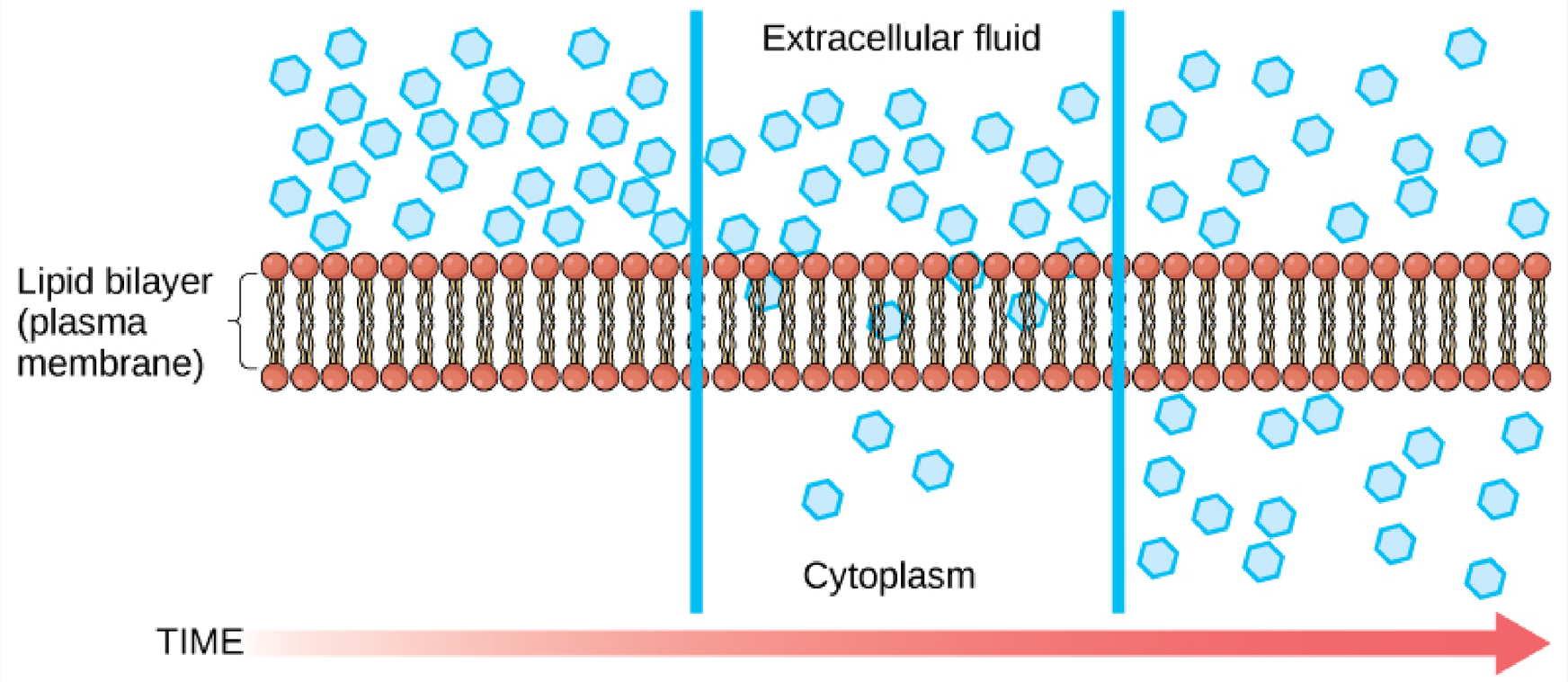
- In order for the cellular processes to be maintained, molecules of various types must be able to cross cell membranes.

Three common transport mechanisms exist by which molecules can enter and leaves cells.

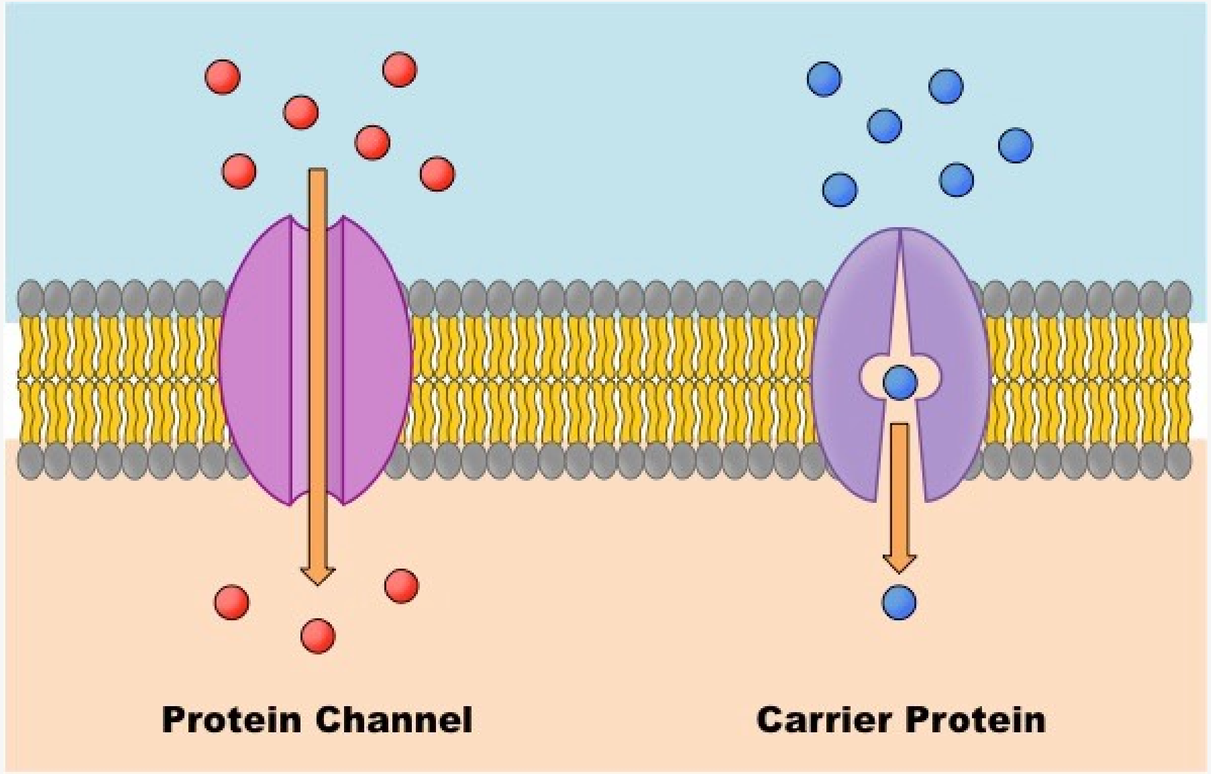
1. Passive transport
2. Facilitated transport
3. Active transport

Passive Transport

- Passive transport is the transport process in which a substance moves across a cell membrane by diffusion from a region of higher concentration to a region of lower concentration without the expenditure of any cellular energy.
- Only a few types of molecules, including O2 , N2 H2O, urea, and ethanol, can cross membranes in this manner.
- Passive transport is closely related to the process of osmosis.



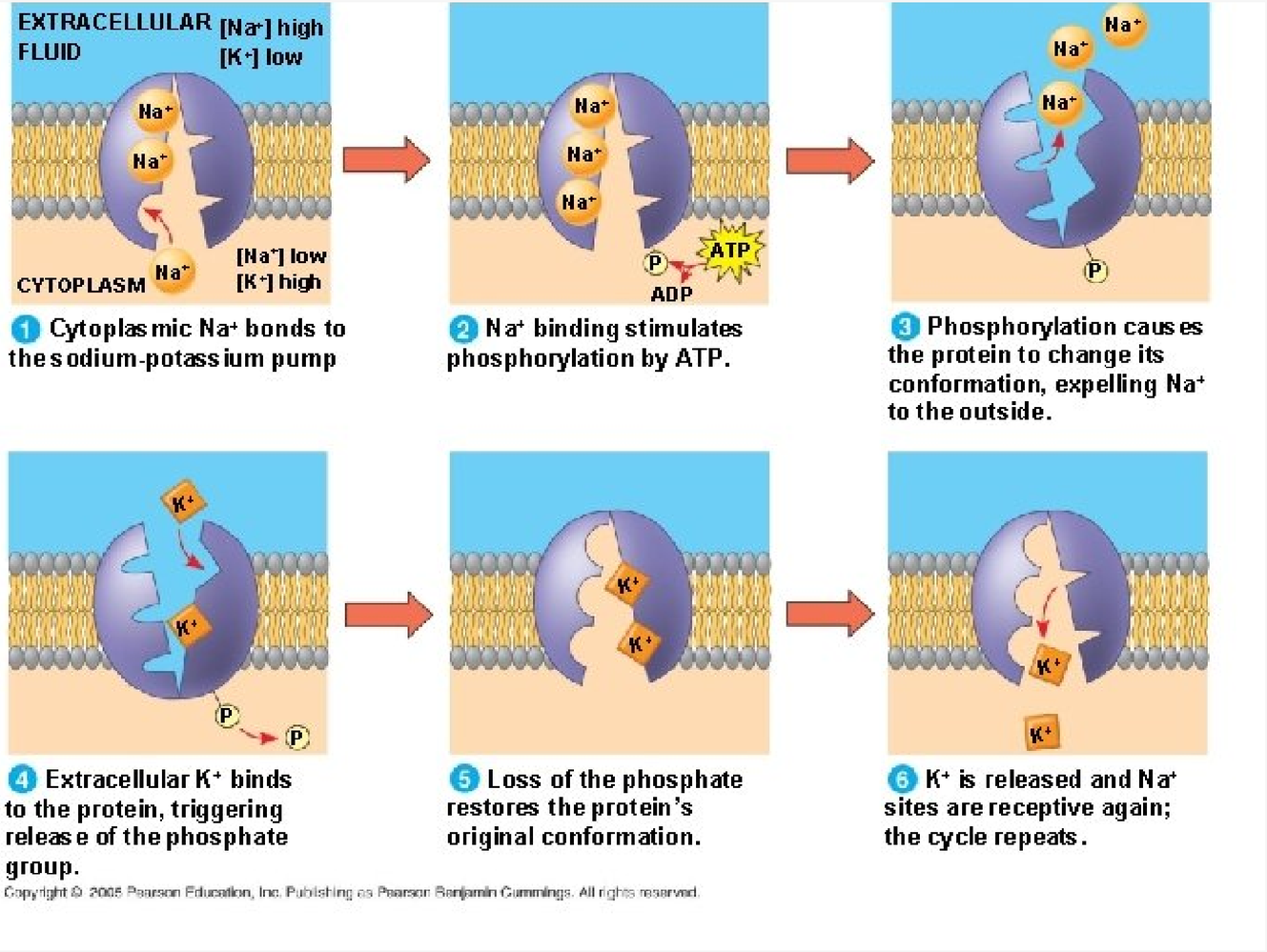
Facilitated Transport



- Facilitated transport is the transport process in which a substance moves across a cell membrane, with the aid of membrane proteins, from a region of higher concentration to a region of lower concentration without the expenditure of cellular energy.
- The specific protein molecules involved in the process are called carriers or transporters.

A carrier protein forms a complex with a specific molecule at one surface of the membrane.

- Formation of the complex induces a conformational change in the protein that allows the molecule to move through a “gate” to the other side of the membrane. Once the molecule is released, the protein returns to its original conformation.
- Glucose, chloride ion, and bicarbonate ion cross membranes in this manner.

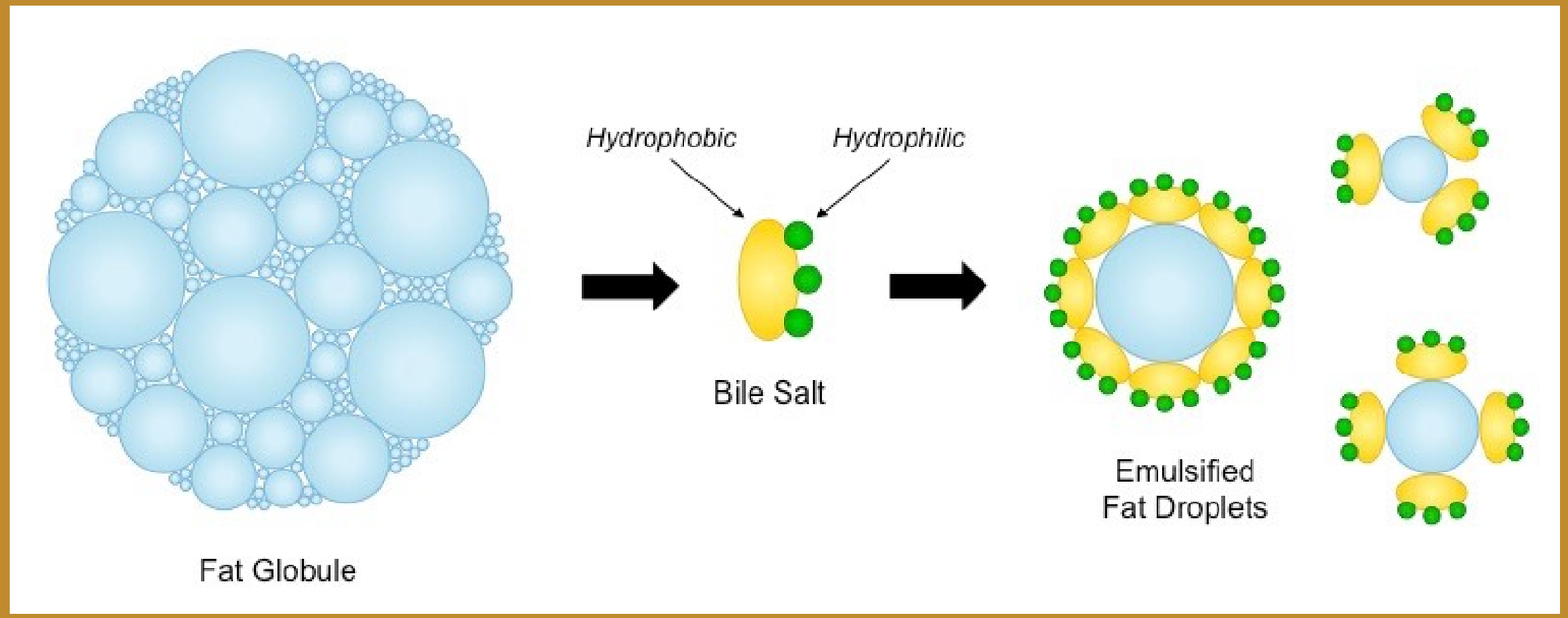


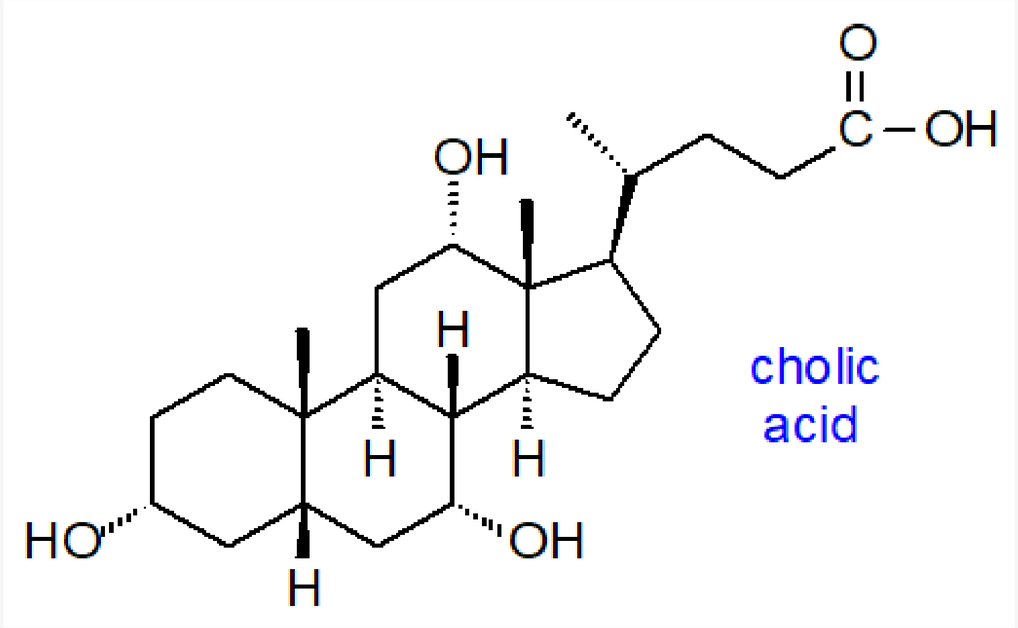
Active Transport

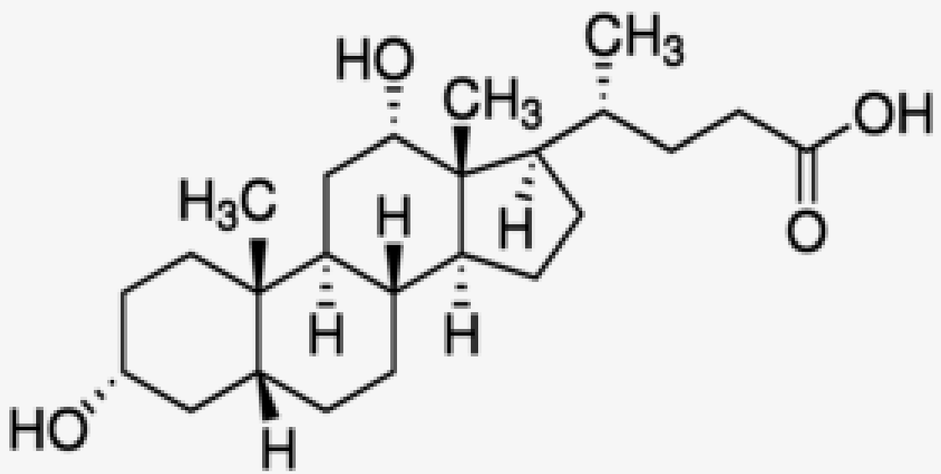
- Active transport is the transport process in which a substance moves across a cell membrane, with the aid of membrane proteins, against a concentration gradient with the expenditure of cellular energy.
- Proteins involved in active transport are called “pumps” because they require energy much as a water pump requires energy to function.
- The needed energy is supplied by molecules such as ATP. Sodium, potassium, and hydronium ions cross membranes through activetransport.

3. Emulsification Lipids: Bile Acids

- An emulsifier is a substance that can disperse and stabilize water insoluble substances as colloidal particles in an aqueous solution.
- Bile acids, a cholesterol derivative, function as emulsifying agents that facilitate the absorption of dietary lipids in the intestine. Their mode of action is much like that of soap during washing.
- Bile acid is a cholesterol derivative that that functions as a lipid emulsifying agent in the aqueous environment of the digestive tract. From one-third to one-half of the daily production of cholesterol by the liver is used to replenish bile acid stores.







Three Major Types of Bile Acids

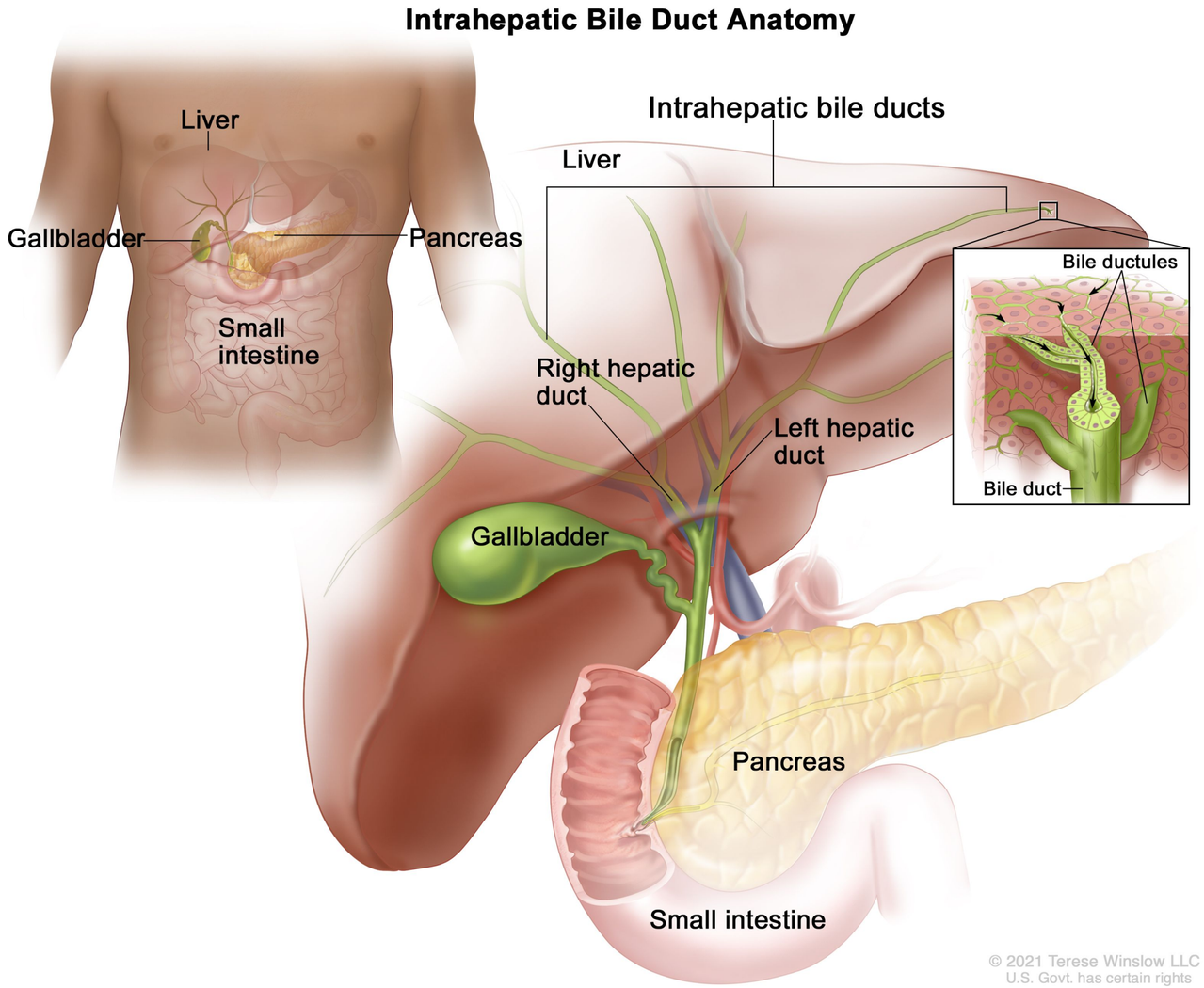
Bile acids, produced from cholesterol by biochemical function:

1. Cholic acid (C24)
2. 7-deoxycholic acid (C24)
3. 12-deoxycholic acid (C24)

- Bile acids always carry an amino acid (either glycine or taurine) attached to the side chain carboxyl group via an amide linkage.
- The presence of this amino acid attachment increases both the polarity of the bile acid and its water solubility.

Bile

- The medium through which bile acids are supplied to the small intestine is bile.
- Bile is a fluid containing emulsifying agent that is secreted by the liver, stored in the gall bladder, and released into the small intestine during digestion.
- Besides bile acids, bile also contains bile pigments (breakdown product of hemoglobin), cholesterol itself, and electrolytes such as bicarbonate ion.
- The bile acids that are present increase the solubility of cholesterol in the bile fluid



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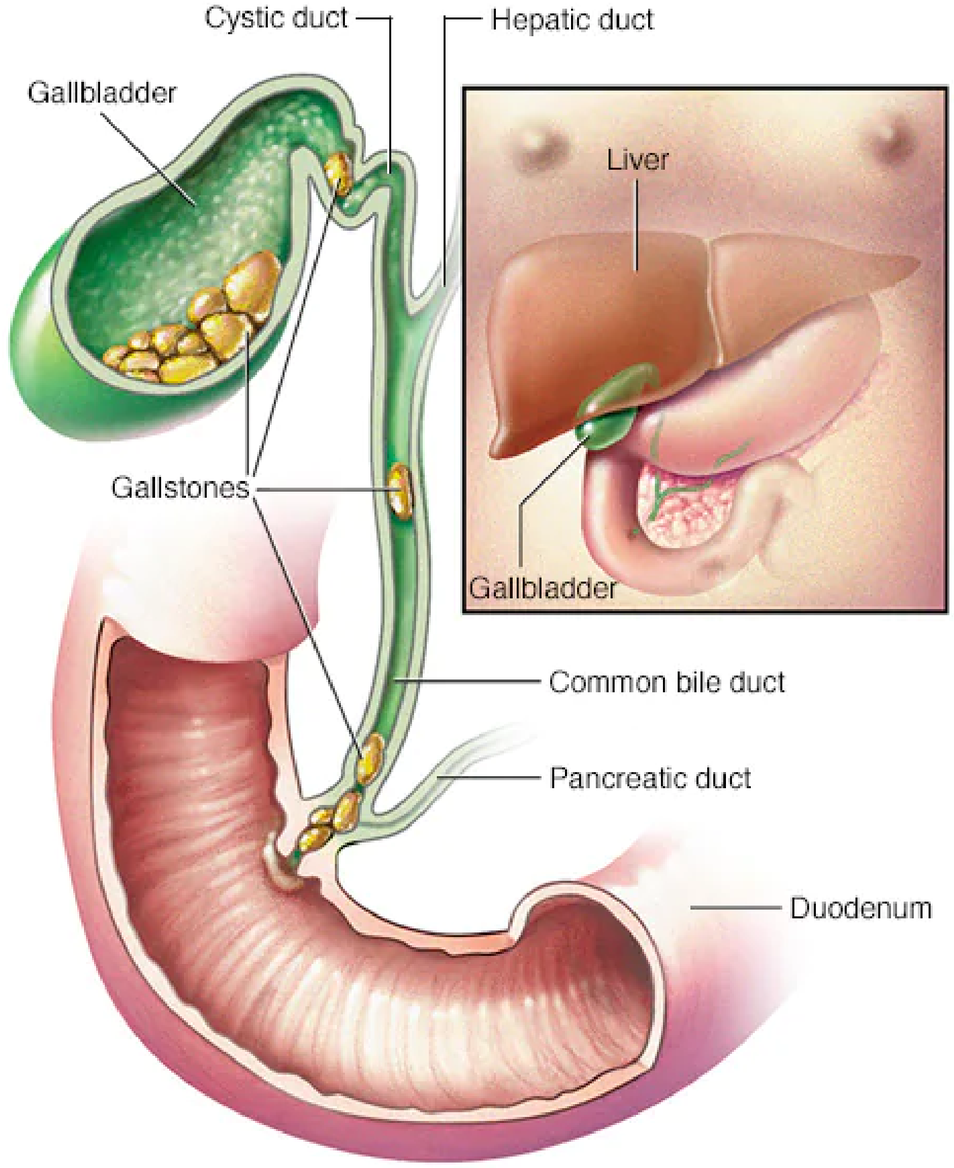
Bile

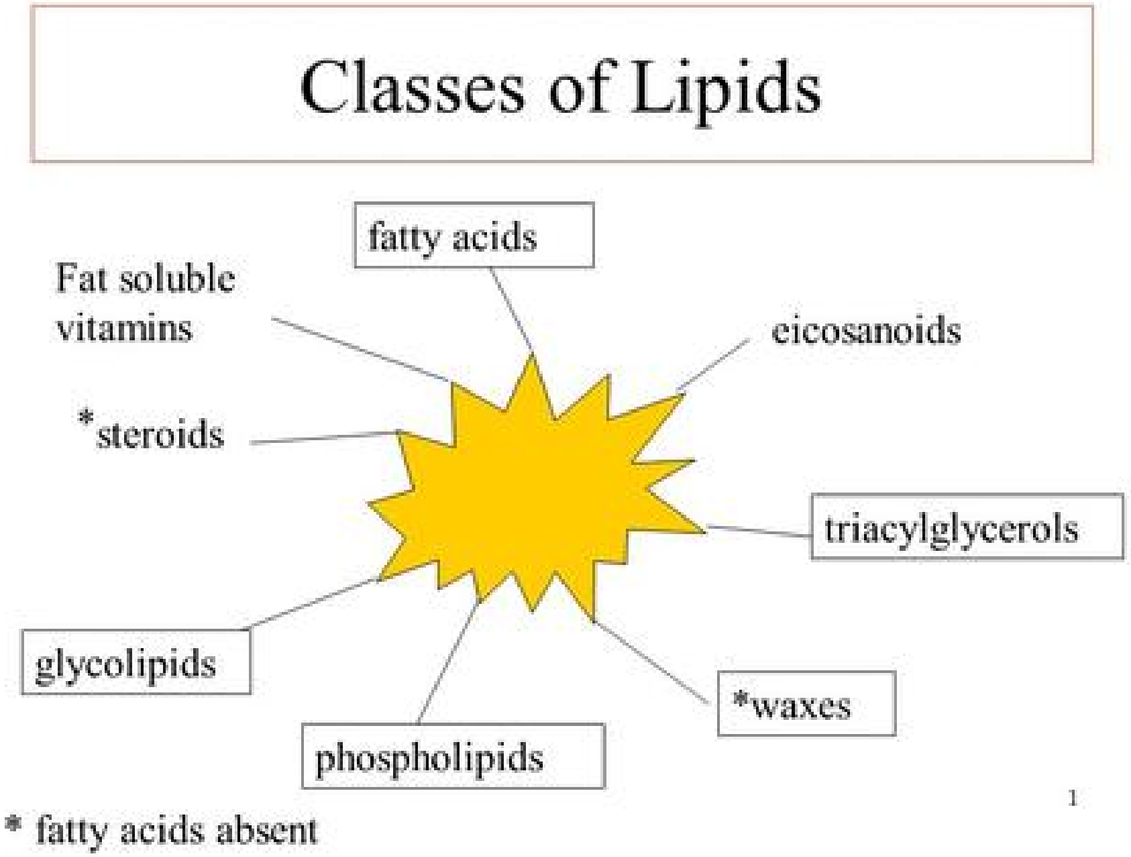
- A number of factors, including increased secretion of cholesterol and a decrease in the size of the bile pool, can upset the balance between the cholesterol present in the bile and the bile acid derivatives needed to maintain cholesterol's solubility in the bile.
- The result is the precipitation of crystallized cholesterol from the bile and the resulting formation of gallstone in the gallbladder.



Messenger Lipids

An additional role played by the lipids is that of chemical messenger.
1. Steroid hormones –are cholesterol derivatives.
2. Eicosanoids –are fatty acid derivatives.

- Hormone is a biological substance, produced by a ductless gland has a messenger function. Hormones serve as a means of communication between various tissues. Some hormones, though not all, are lipids



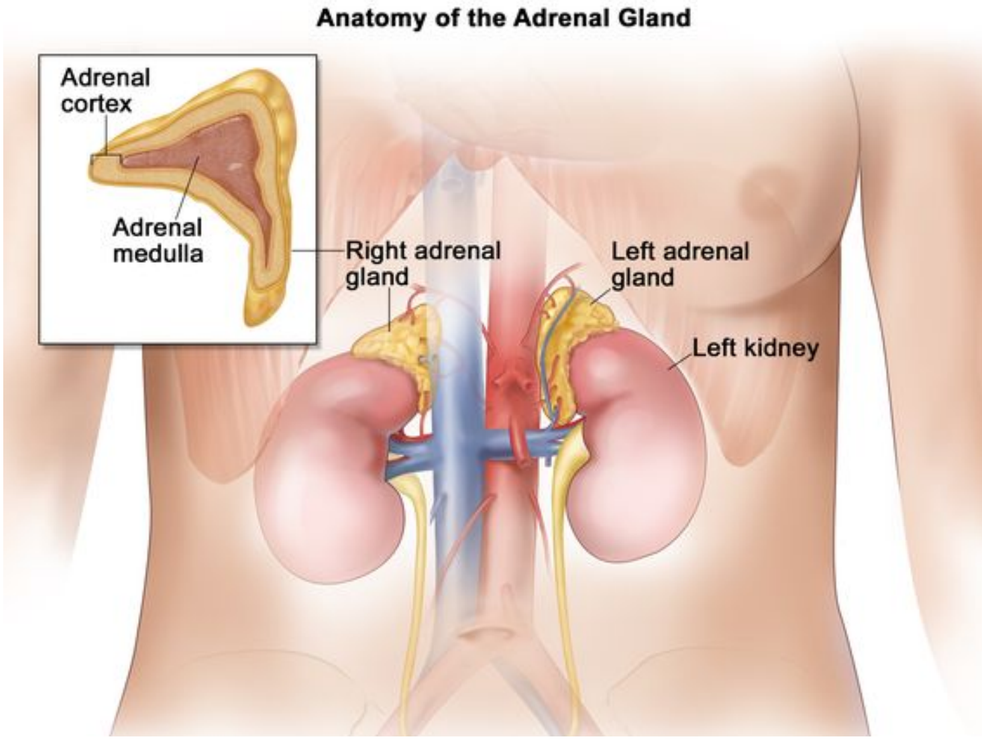
Messenger Lipids: Steroid Hormones

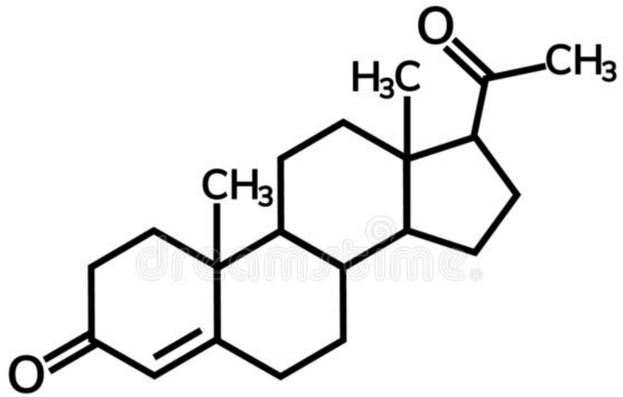
Sex Hormones

The sex hormones can be classified into three major groups:
1. Estrogens (the female sex hormones)
– synthesized in the ovaries and adrenal cortex, and are responsible for the development of female secondary sex characteristics at the onset of puberty and for the regulation of menstrual cycle. They also stimulate the development of mammary glands during pregnancy and induce estrus (heat) in animals.

2. Androgens (the male sex hormones)
–synthesized in the testes and adrenal cortex, and promote the development of male secondary sex characteristics. They also promote muscle growth.

3. Progestins (the pregnancy hormones)
–synthesized in the ovaries and the placenta, and prepare the lining of the uterus for implantation of the fertilized ovum. They also suppress ovulation.





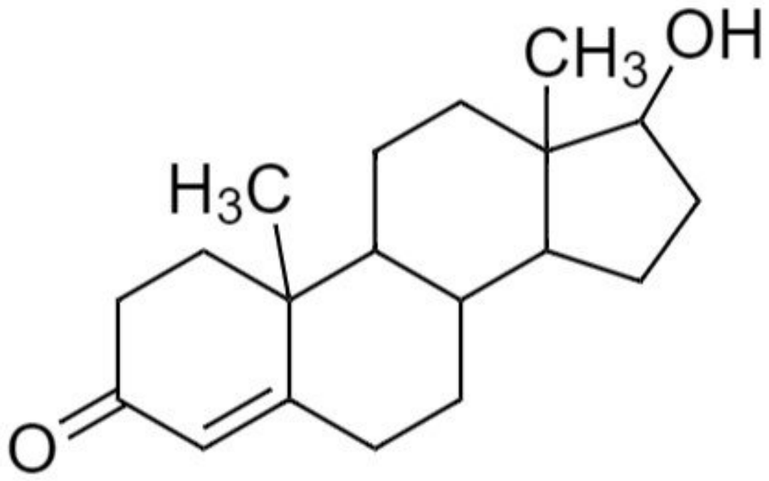
progesterone

Messenger Lipids: Steroid Hormones

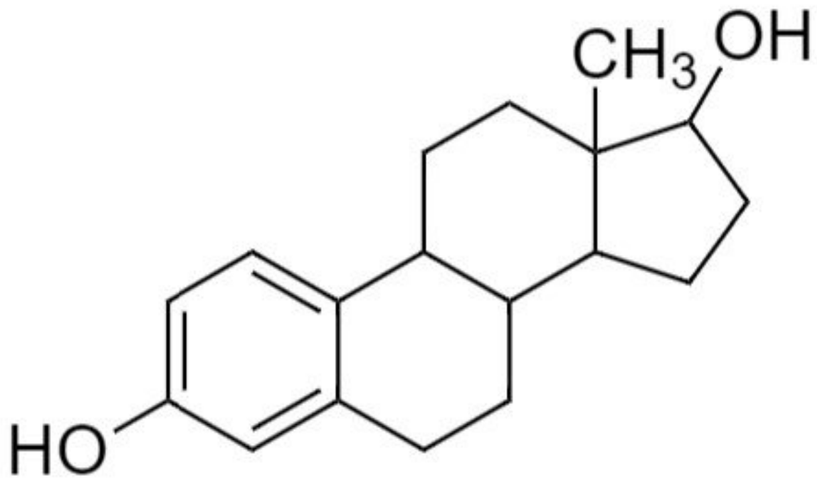
Natural Sex Hormones

Estradiol. The primary estrogen, responsible for secondary female characteristics.

a. Testosterone. The primary androgen, responsible for secondary male characteristics.
b. Progesterone. The primary progestin, prepares the uterus for pregnancy.



testosterone

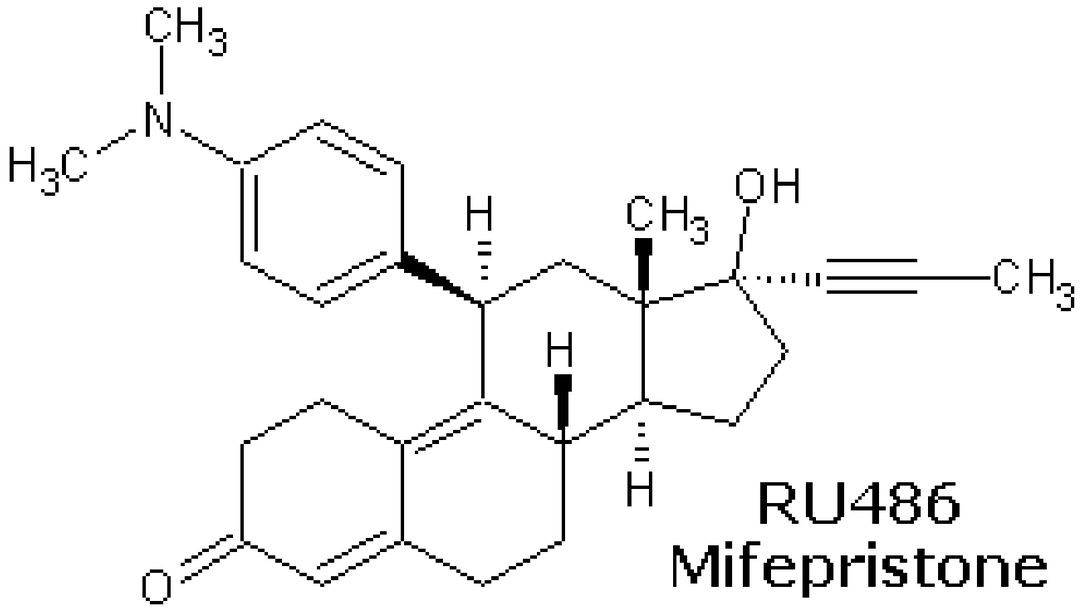


estrogen(estradiol)

Messenger Lipids: Steroid Hormones

Synthetic Hormones

- Oral contraceptives are used to suppress ovulation as a method of birth control. Generally, a mixture of a synthetic estrogen and a synthetic progestin is used. The synthetic estrogen regulates the menstrual cycle, and the synthetic progestin prevents ovulation.
- RU-486 interferes with gestation of a fertilized egg, and terminates pregnancy within the first nine weeks of gestation more effectively and safely than surgical methods.
- Anabolic steroids include the illegal steroid drugs used by some athletes to build up muscle strength and enhance endurance. Such steroids are now known to have serious side effects in the user

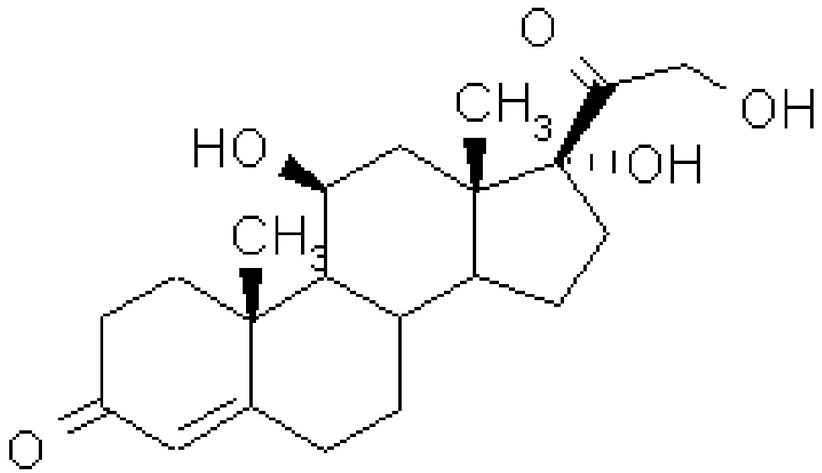


Adrenocorticoid Hormones

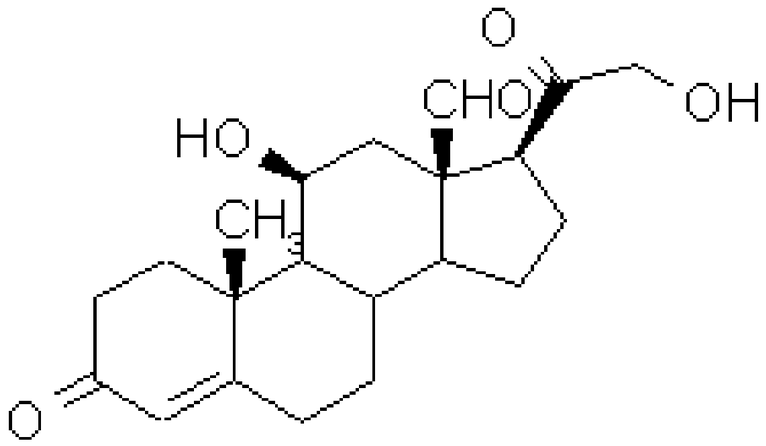
The adrenocorticoid hormones are produced by adrenal glands, a small organ located on top of each kidney. There are two types of adrenocorticoid hormones:

a. Mineralocorticoids control the balance of Na+, K+ ions in cells and body fluids. The major mineralocorticoid is aldosterone.
b. Glucocorticoids control glucose metabolism and counteract inflammation. The major glucocorticoid is cortisol (hydrocortisone).

- Cortisol and its synthetic ketone derivative cortisone exert powerful anti-inflammatory effects in the body. It is used as prescription drugs to control inflammatory diseases such as rheumatoid arthritis.



cortisol



aldosterone