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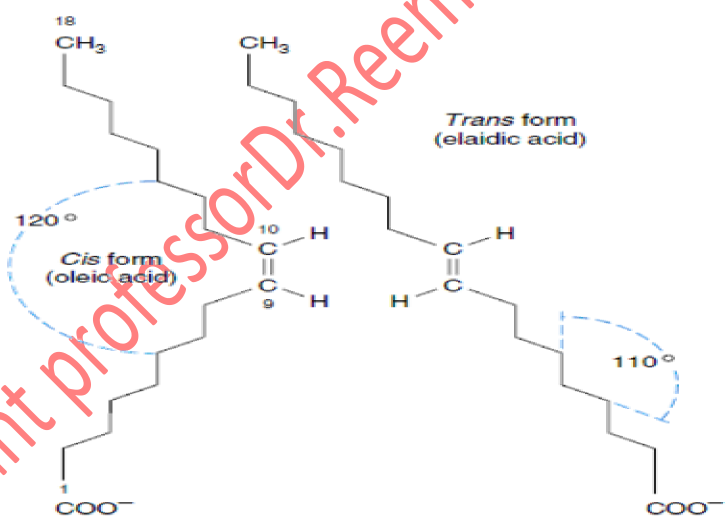
1-1 Isomerism in unsaturated fatty acids.

Due to the presence of double bond, fatty acids exhibit geometrical isomerism, which depends on the orientation of groups around the double bond.

The designation —cis‖ means that the acyl chains are on the same side.

Trans‖ means the acyl chains are on the opposite side of the —double bond.



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The double bonds in most naturally occurring fatty acids are in the cis configuration.

Cis and Trans isomers have different melting points and other physical constants. Trans fatty acids are stable but are injurious to health. Such as The trans form of oleic acid (cis) is called elaidic acid.

Trans fatty acids are formed when the vegetable oils are hydrogenated.

For example in the manufacturing of margarine.

Ruminant fat contains more trans long chain fatty acids than non-ruminants because rumen microbes isomerizes some plant cis long chain fatty acids to trans isomer.

Trans fatty acids compete with essential fatty acids so there is reduction in the absorption of essential fatty acids, which may increase the symptoms of essential fatty acid deficiency.

They have structures similar to saturated fatty acids.

Hence, they increase cholesterol level and the formation of atherosclerosis.

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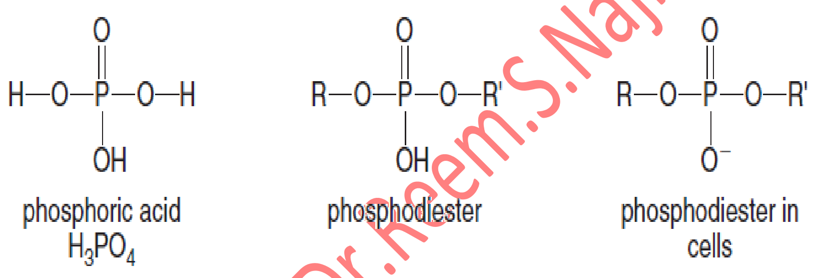
Phospholipids

Phospholipids: are lipids that contain a phosphorus atom. Phospholipids can be considered organic derivatives of phosphoric acid (H3PO4), formed by replacing two of the H atoms by R groups.

This type of functional group is called a phosphodiester. In cells, the remaining OH group on phosphorus loses its proton, giving the phosphodiester a net negative charge.



Phosphoacylglycerols (or phosphoglycerides) are the most common type of phospholipid.

They form the principal lipid component of most cell membranes.

Their structure resembles the triacylglycerols of the preceding section with one important difference.

Only two of the hydroxyl groups of glycerol are esterified with fatty acids.

The third OH group is part of a phosphodiester, which is also bonded to an alkyl group (R") derived from a low molecular weight alcohol.

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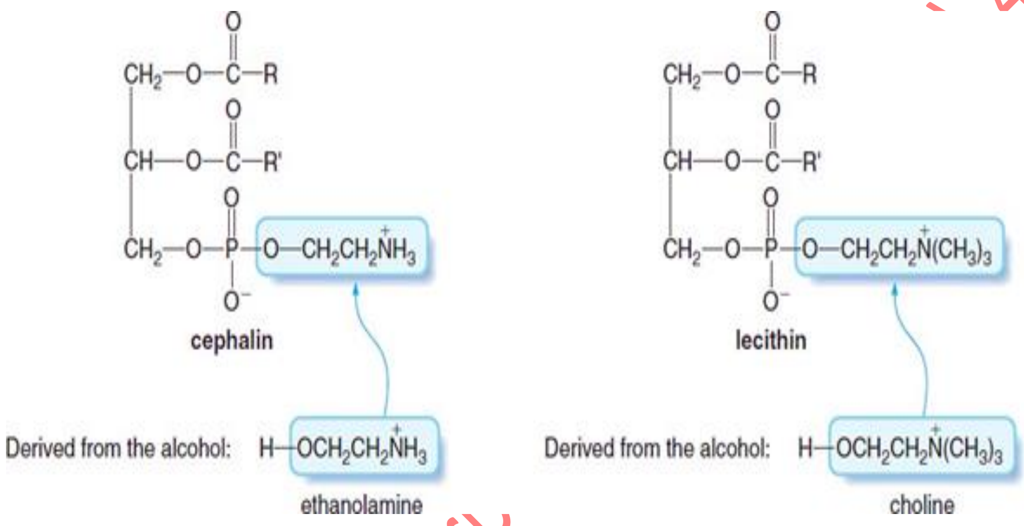
There are two prominent types of phosphoacylglycerols. They differ in the identity of the R" group in the phosphodiester.

- When R" = $CH_2CH_2NH_3^+$, the compound is called a *cephalin.*
- When R" = $CH_2CH_2N(CH_3)_3^+$, the compound is called a *lecithin.*



The phosphorus side chain of a phosphoacylglycerol makes it different from a triacylglycerol.

The two fatty acid side chains form two nonpolar —tails‖ that lie parallel to each other, while the phosphodiester end of the molecule is a charged or polar —head.‖

A three-dimensional structure of a phosphoacylglycerol is shown in Figure below:

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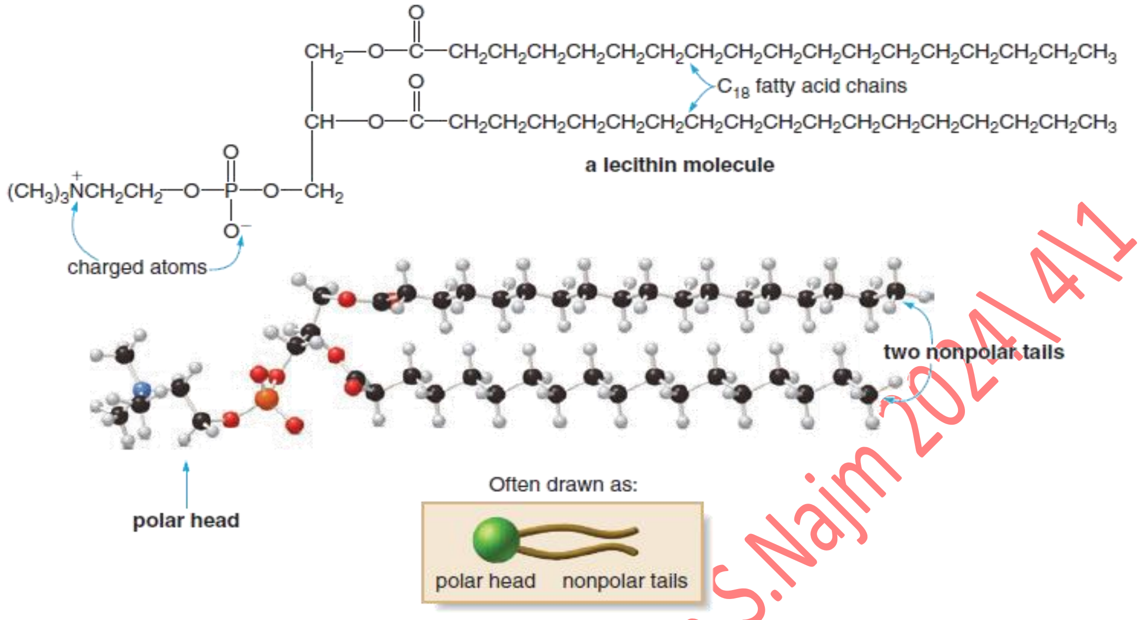

A phosphoacylglycerol has two distinct regions: two nonpolar tails due to the long- chain fatty acids, and a very polar head from the charged phosphodiester.

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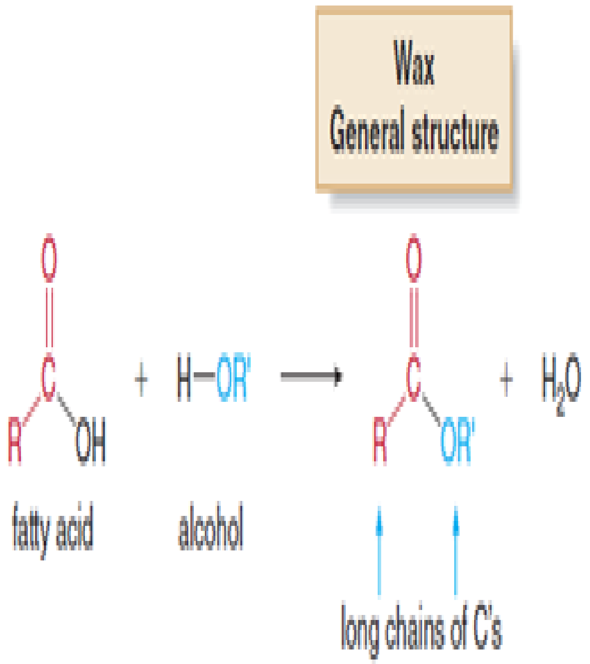
Waxes

Waxes are the simplest hydrolyzable lipids.

Waxes are esters (RCOOR') formed from a fatty acid (RCOOH) and a high molecular weight alcohol (R'OH).



Waxes form a protective coating on the feathers of birds to make them water repellent, and on leaves to prevent water evaporation.

Beeswax, a complex mixture of over 200 different compounds, contains the wax myricyl palmitate as its major component.

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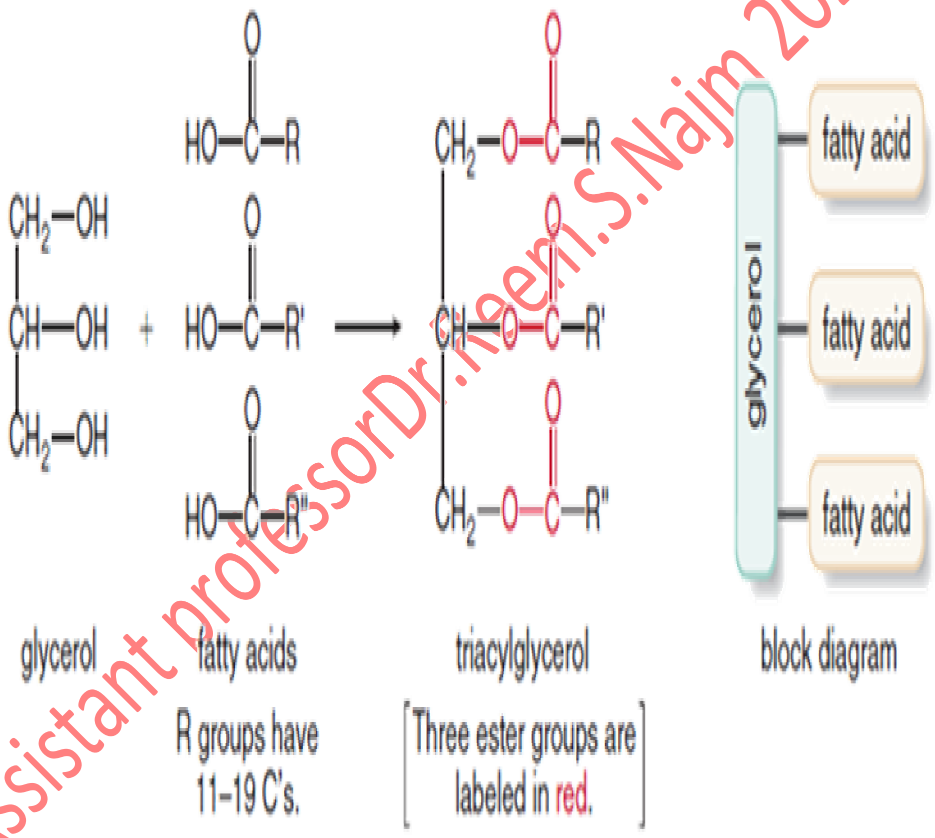
Triacylglycerols—Fats and Oils

Animal fats and vegetable oils, the most abundant lipids, are composed of Triacylglycerols.

Triacylglycerols, or triglycerides, are tri-esters formed from glycerol and three molecules of fatty acids.



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General Features

Triacylglycerols may be composed of three identical fatty acid side chains, or they may be derived from two or three different fatty acids. The fatty acids may be saturated or unsaturated.

Fats and oils are triacylglycerols with different physical properties.

Fats have higher melting points—they are solids at room temperature.

Oils have lower melting points—they are liquids at room temperature.

The identity of the three fatty acids in the triacylglycerol determines whether it is a fat or an oil.

Increasing the number of double bonds in the fatty acid side chains decreases the melting point of the triacylglycerol.

Fats are derived from fatty acids having few double bonds.

Oils are derived from fatty acids having a larger number of double bonds.

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Solid fats have a relatively high percentage of saturated fatty acids and are generally animal in origin.

Thus, lard (hog fat), butter, and whale blubber contain a high percentage of saturated fats. With no double bonds, the three side chains of the saturated lipid lie parallel with each other, leading to a high melting point. Liquid oils have a higher percentage of unsaturated fatty acids and are generally vegetable in origin.

Thus, oils derived from corn, soybeans, and olives contain more unsaturated lipids. In the unsaturated lipid, a cis double bond places a kink in the side chain, making it more difficult to pack efficiently in the solid state, thus leading to a lower melting point.

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Cell Membranes

The cell membrane is a beautifully complex example of how chemistry comes into play in a biological system.

Structure of the Cell Membrane

The basic unit of living organisms is the cell. The cytoplasm is the aqueous medium inside the cell, separated from water outside the cell by the cell membrane.

The cell membrane serves two apparently contradictory functions. It acts as a barrier to the passage of ions and molecules into and out of the cell, but it is also selectively permeable, allowing nutrients in and waste out. Phospholipids are the major component of the cell membrane. Phospholipids contain a hydrophilic polar head and two nonpolar tails composed of C-C and C-H bonds.

When phospholipids are mixed with water, they assemble in an arrangement called a lipid bilayer, with the ionic heads oriented on the outside and the nonpolar tails on the inside.

The polar heads electrostatically interact with the polar solvent H_2O, while the nonpolar tails are held in close proximity by numerous London (dispersion forces Van der Waals forces).

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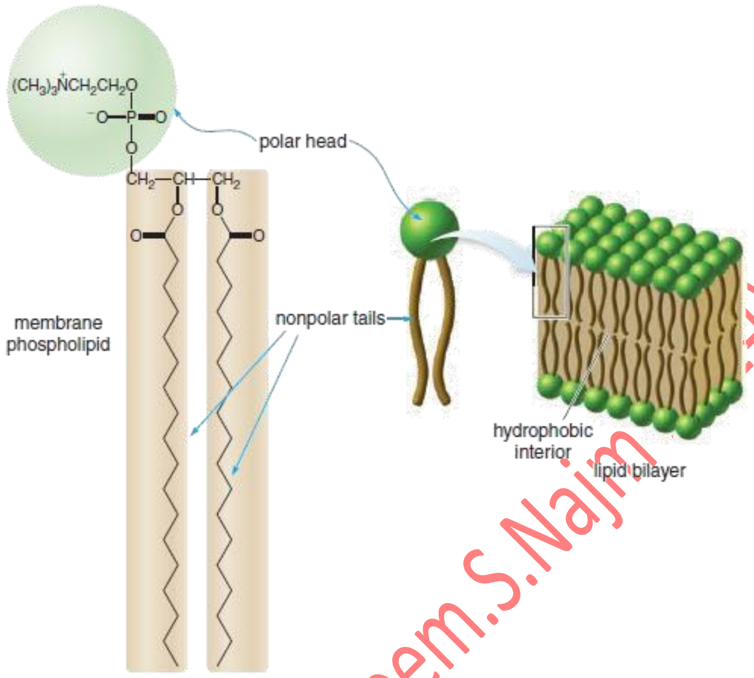

Cell membranes are composed of a lipid bilayer having the hydrophilic polar heads of phospholipids arranged on the exterior of the bilayer, where they can interact with the polar aqueous environment inside and outside the cell. The hydrophobic tails of the phospholipid are arranged in the interior of the bilayer, forming a ―greasy‖ layer that is only selectively permeable to the passage of species from one side to the other.

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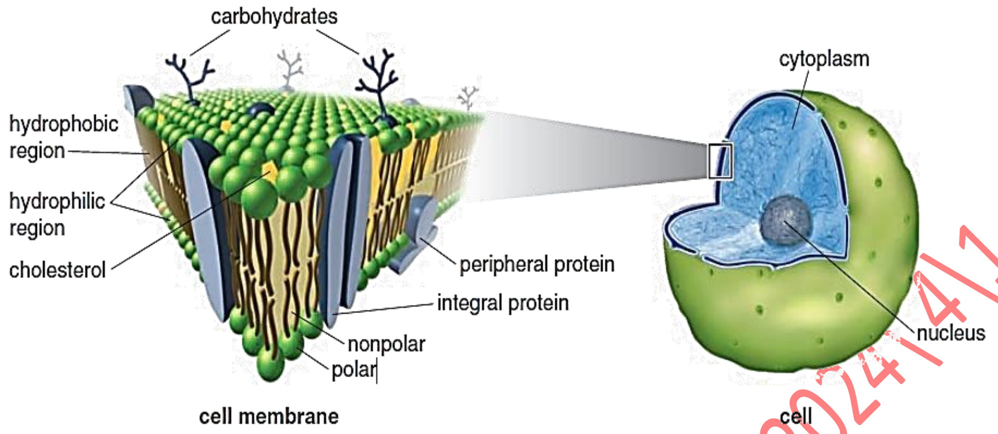

Cell membranes are composed of these lipid bilayers (above Figure). The charged heads of the phospholipids are oriented towards the aqueous interior and exterior of the cell.

The nonpolar tails form the hydrophobic interior of the membrane, thus serving as an insoluble barrier that protects the cell from the outside. While the phospholipid bilayer forms the main fabric of the cell membrane, proteins and cholesterol (will be discussion in section) are embedded in the membrane as well.

Peripheral proteins are embedded within the membrane and extend outward on one side only. Integral proteins extend through the entire bilayer.

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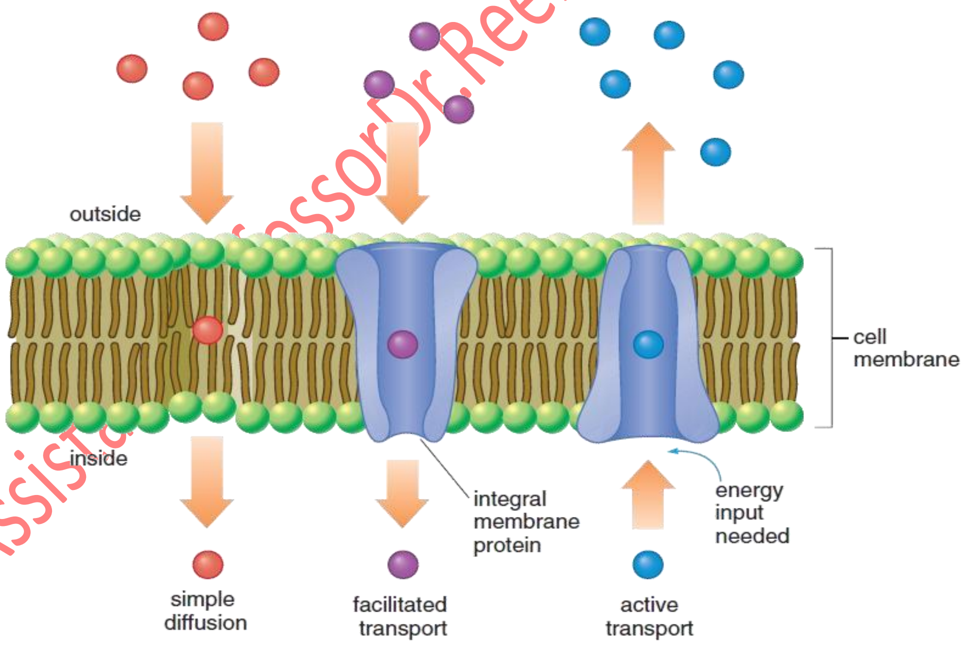
Transport across a cell membran

How does a molecule or ion in the water on one side of a cell membrane pass through the nonpolar interior of the cell membrane to the other side? A variety of transport mechanisms occur.

Small molecules like O_2 and CO_2 can simply diffuse through the cell membrane, traveling from the side of higher concentration to the side of lower concentration. With larger polar molecules and some ions, simple diffusion is too slow or not possible, so a process of facilitated transport occurs. Ions such as Cl^- or HCO_3^- and glucose molecules travel through the channels created by integral proteins.



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Some ions, notably Na^{+}, K^{+}, and Ca^{2+}, must move across the cell membrane against the concentration gradient—that is, from a region of lower concentration to a region of higher concentration.

To move an ion across the membrane in this fashion requires energy input, and the process is called active transport.

Active transport occurs whenever a nerve impulse causes a muscle to contract. In this process, energy is supplied to move K+ ions from outside to inside a cell, against a concentration gradient