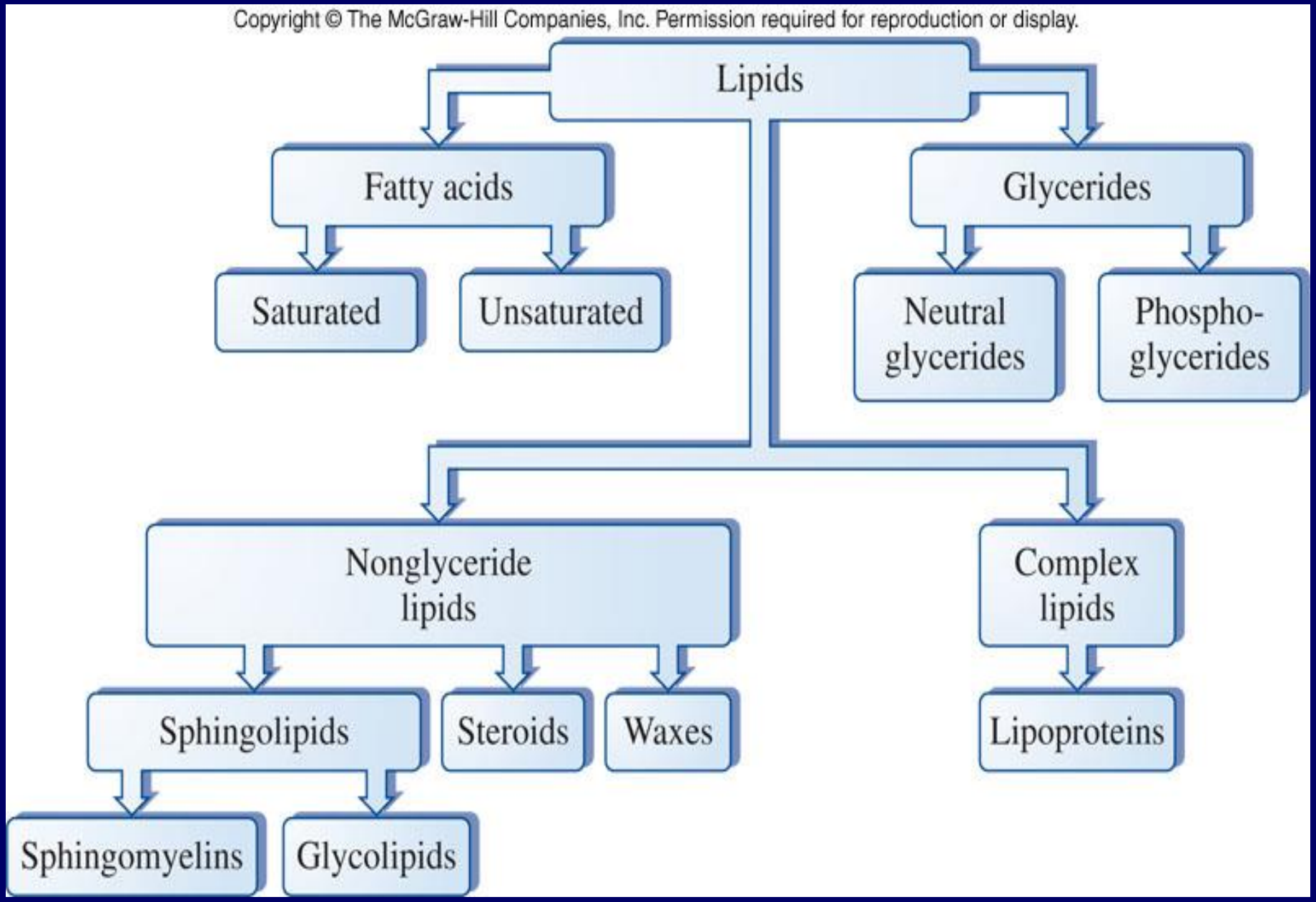
Lipids

9th lect. of medical chemistry

Dr. Salih Mahdi Salman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Lipids
Fatty acids
Glycerides
Saturated
Unsaturated
Neutral glycerides
Phospho-glycerides
Nonglyceride lipids
Complex lipids
Sphingolipids
Steroids
Waxes
Lipoproteins
Sphingomyelins
Glycolipids

Glycerides

Chemical Structure

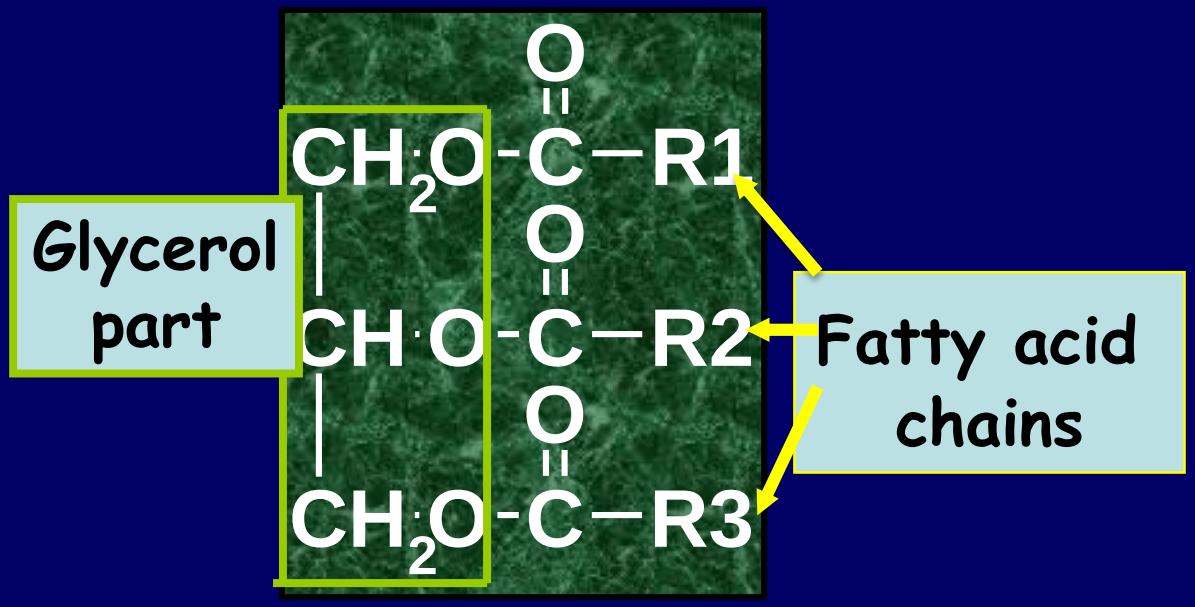
Glycerides are lipid esters

Alcohol group of glycerol form an ester with a fatty acid

Esterification may occur at one, two, or all three alcohol positions producing:

- Monoglyceride
- Diglyceride
- Triglyceride

Triglycerides



- ✓A triglyceride places fatty acid chains at each alcohol group of the glycerol
- ✓A neutral triacylglycerol or a triglyceride
- ✓Triglycerides are nonionic and nonpolar
- ✓Triglycerides serve as energy storage in adipose cells

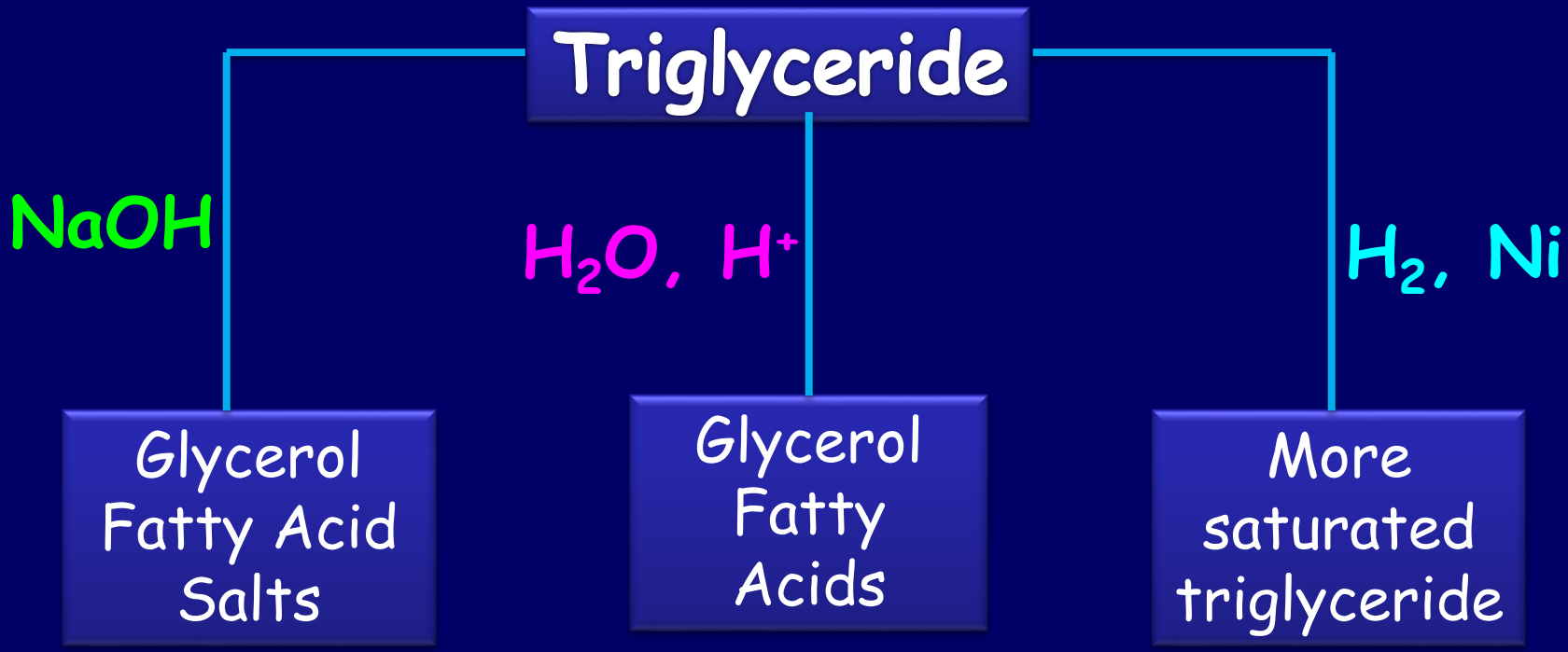
Chemical Properties

Triglyceride have typical ester and alkane or alkene chemical properties as they are composed of these two groups:

1. Saponification: replace H with salt from a strong base.
2. Hydrolysis: produces the fatty acids and glycerol, a reverse of formation.
3. Hydrogenation: saturates the double bonds.

Triglyceride Reactions

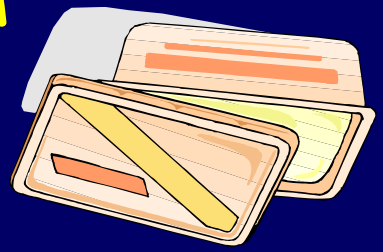
Triglycerides undergo three basic reactions. These reactions are identical to those studied in carboxylic acids.



Fats and Oils

Triglycerides or triacylglycerols fats are a combination of glycerol and the fatty acids.

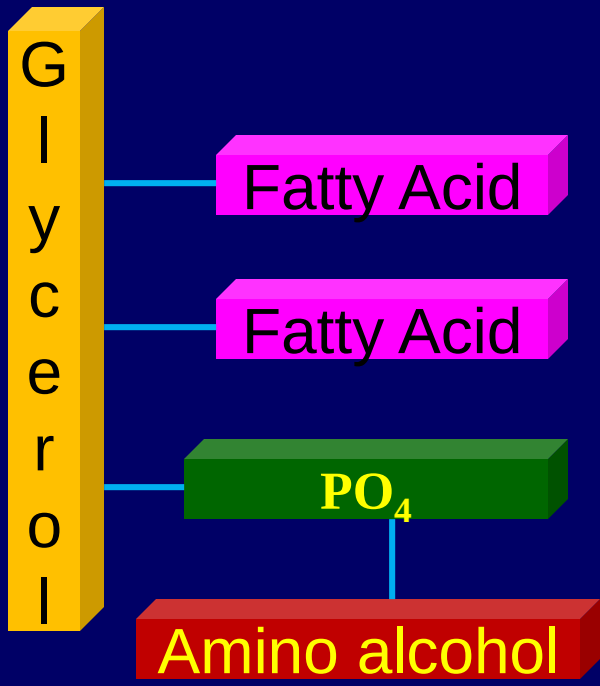
Fats mainly come from animals, unless from fish, and are solid at room temperature



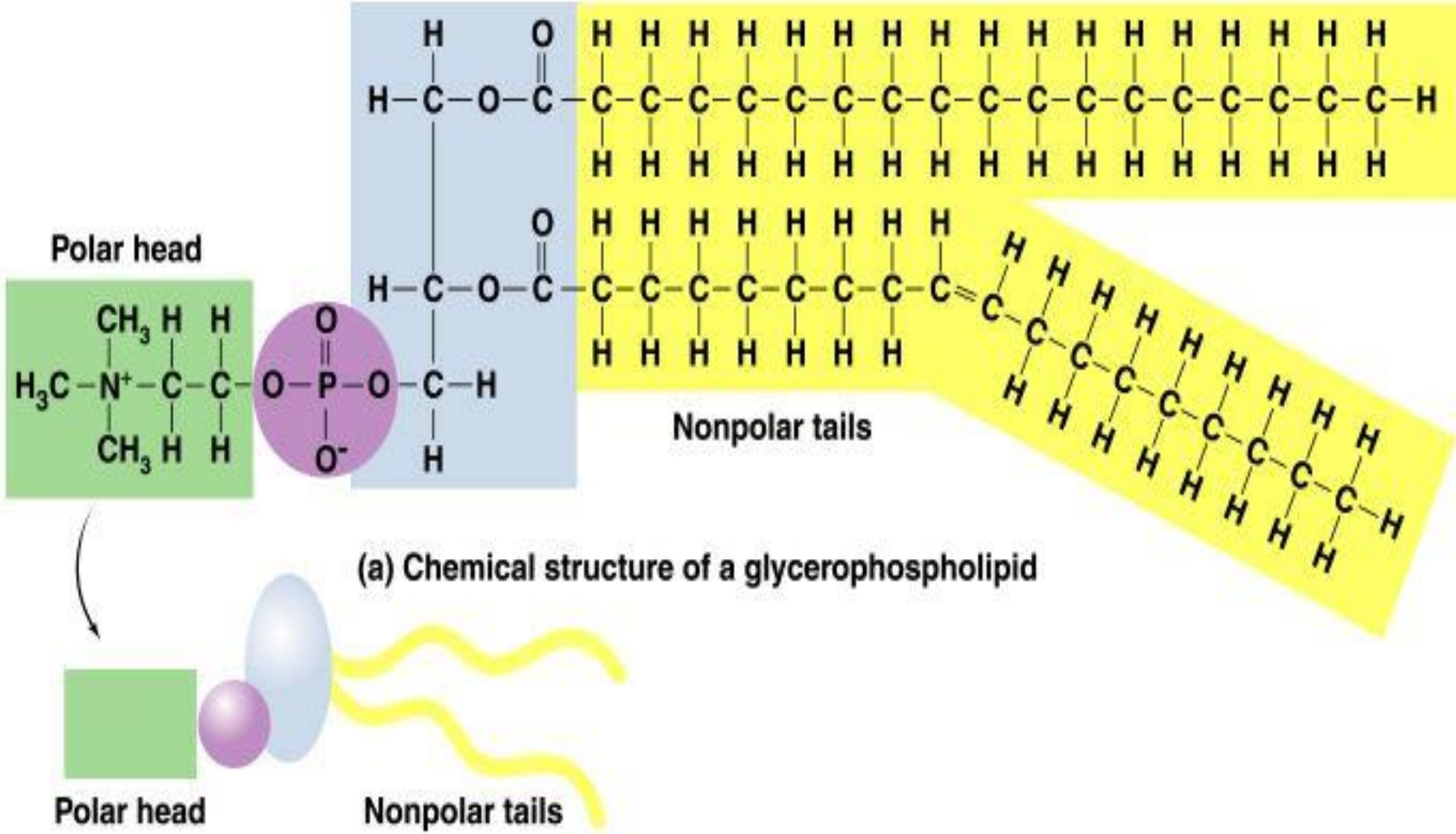
Oils mainly come from plants, and are liquid at room temperature

Phosphoglycerides
Chemical Structure

✓Phospholipid is a more general term.
✓Any lipid containing phosphorus.
✓Phosphoglycerides contain:
Glycerol
Fatty acid
phosphate ester with an amino alcohol



✓They are similar to triacylglycerols, but have one ester bond replaced with an amino alcohol phosphate ester



Properties & Functions

Glycerophospholipids are the main lipid component of cell membranes, and are important in the cell's semipermeability.

They also interact with triacylglycerols and cholesterol to increase their solubility in the blood.

These abilities of glycerophospholipids are due to their *amphipathic* nature, with a polar head group and nonpolar tails.

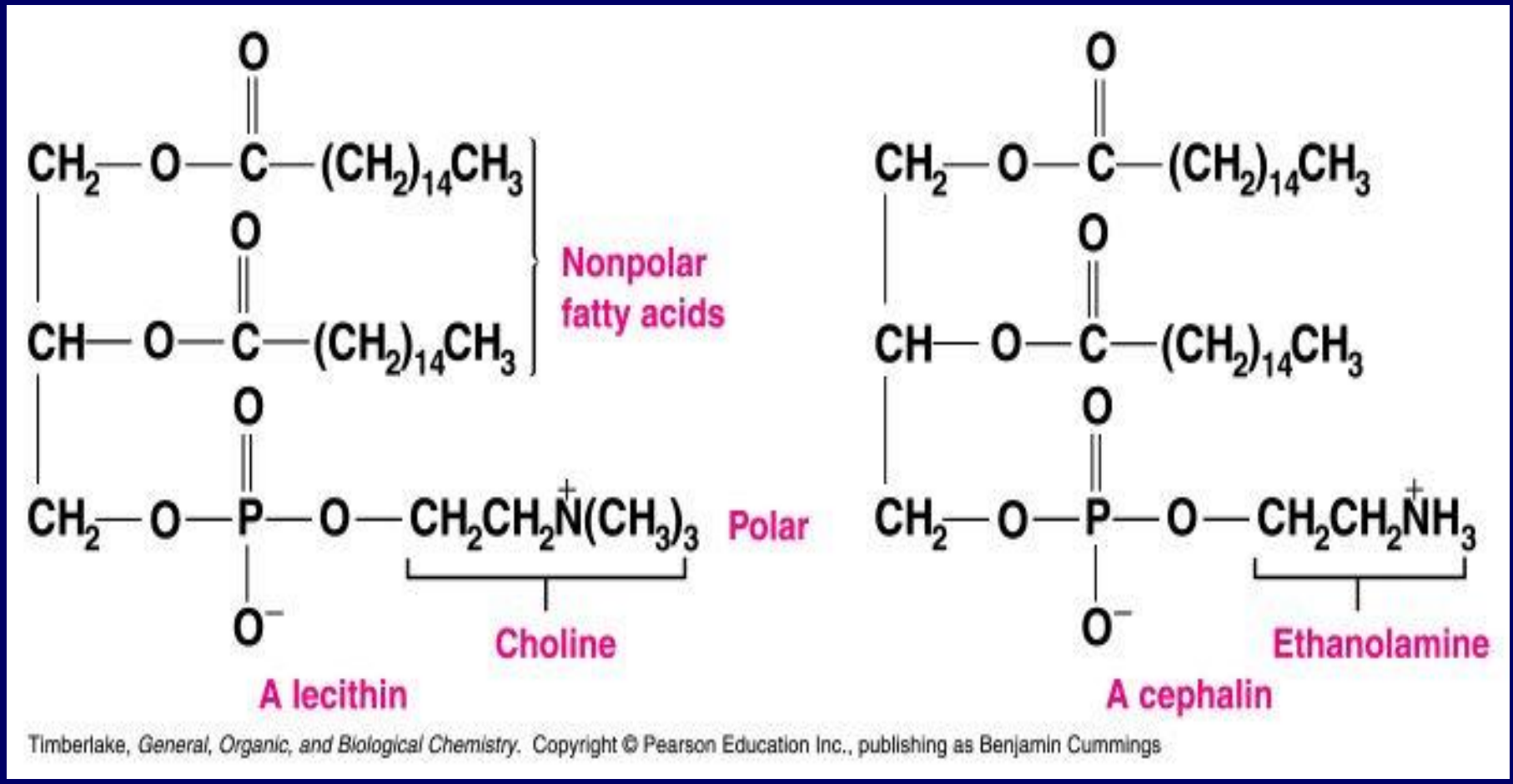
They are used in:

1. Cell membranes
2. Emulsifying
3. Micelle-forming agents in the blood

Types of Phosphoglycerides

Glycerophospholipids can be classified based on the amino alcohol group

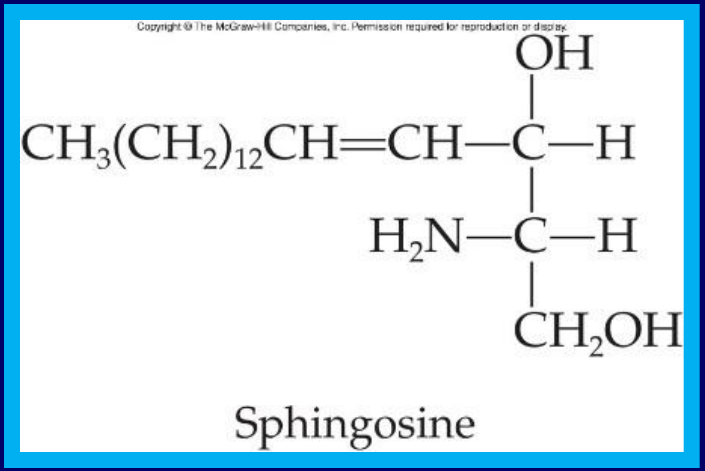
1. Ones made with *choline* are called *lecithin*
2. Those made with either ethanolamine or serine are called *cephalins*



Lecithins and cephalins are highly abundant in brain and nerve tissues, and are also found in egg yolks, wheat and yeast.

Nonglyceride Lipids (Sphingolipids) Chemical Structure

Sphingolipids are phospholipids that are based on the 18-carbon amino alcohol **sphingosine**, instead of on glycerol.



A fatty acid is linked to the amine group by an amide bond, and an amino alcohol phosphate ester or sugar is linked to the bottom hydroxyl group (the top hydroxyl group remains free).

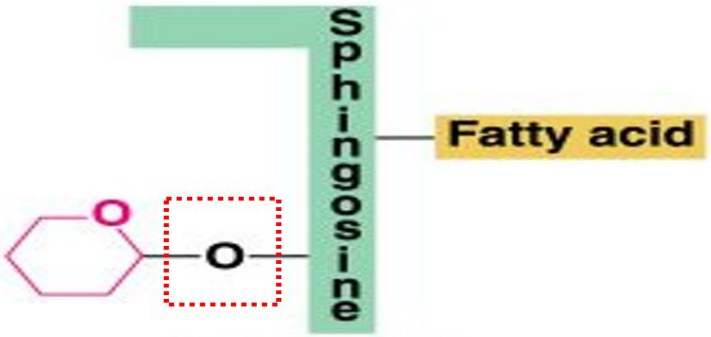
Types of Sphingolipids

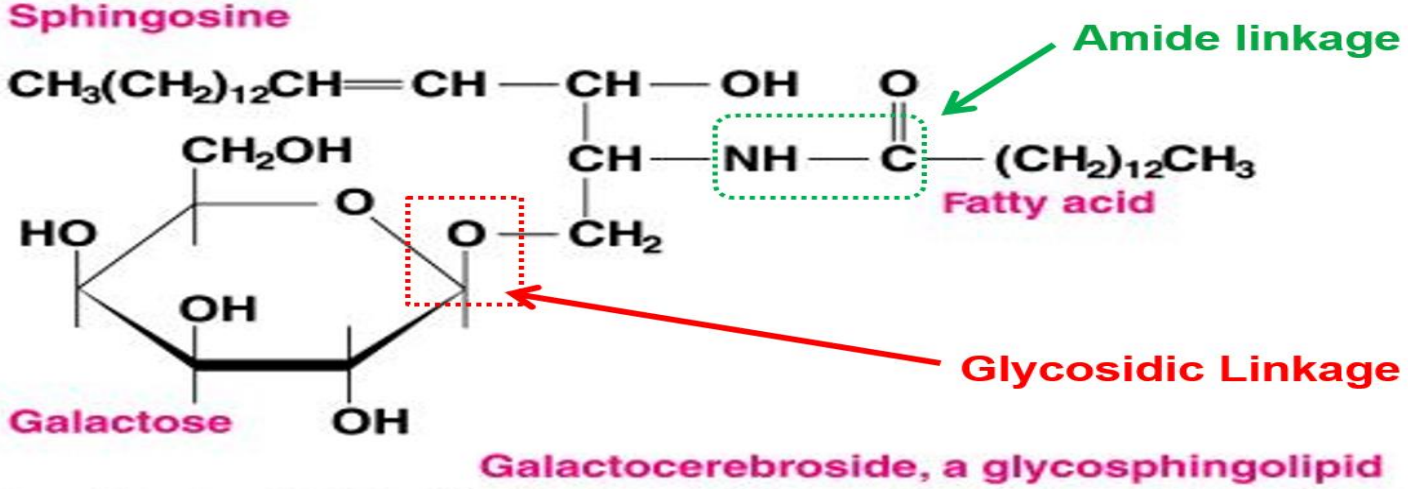
Major categories
- 1. Glycosphingolipids
- 2. Sphingomyelins

1. Glycosphingolipids

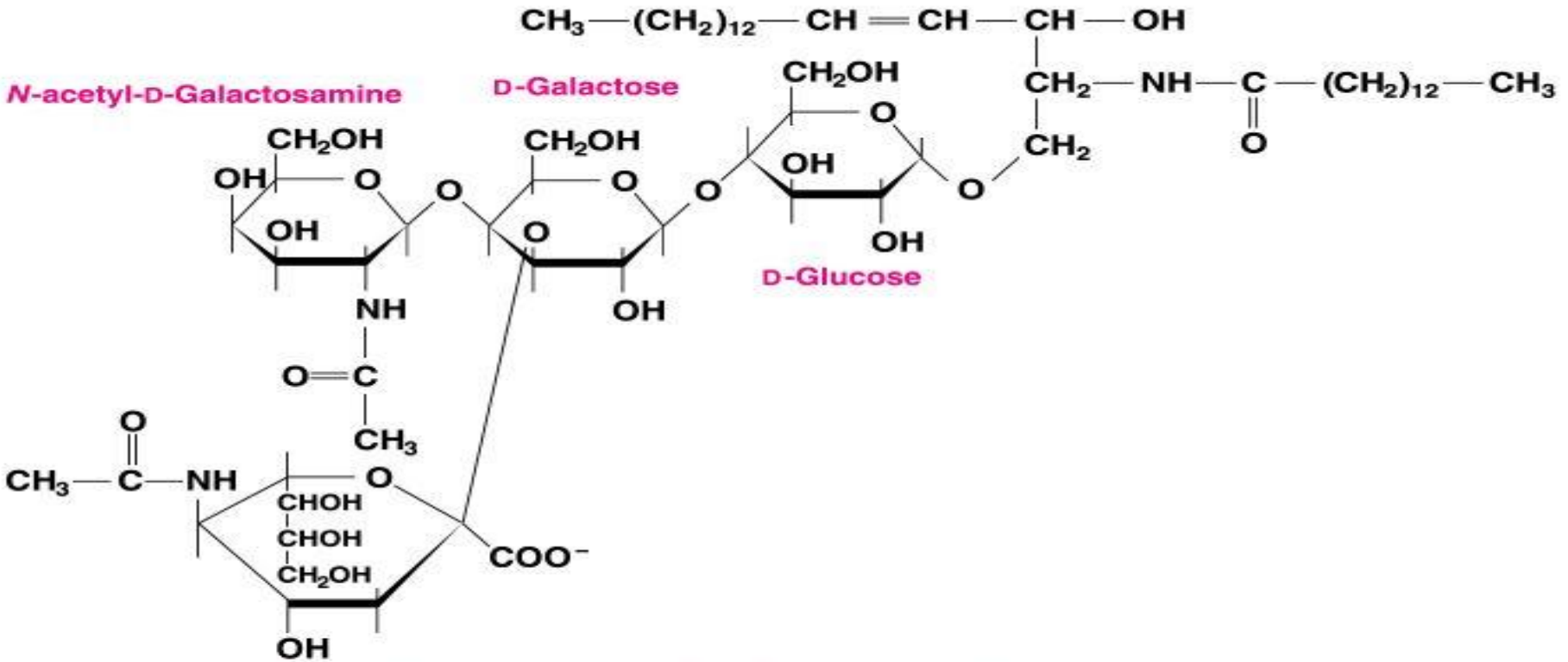
are sphingolipids that have one or more monosaccharides linked by glycosidic bonds to the bottom hydroxyl of the sphingosine.

1-1. Cerebrosides have a single monosaccharide (usually galactose). they are usually present at the cell surface, and are involved in cellular recognition and immunity.



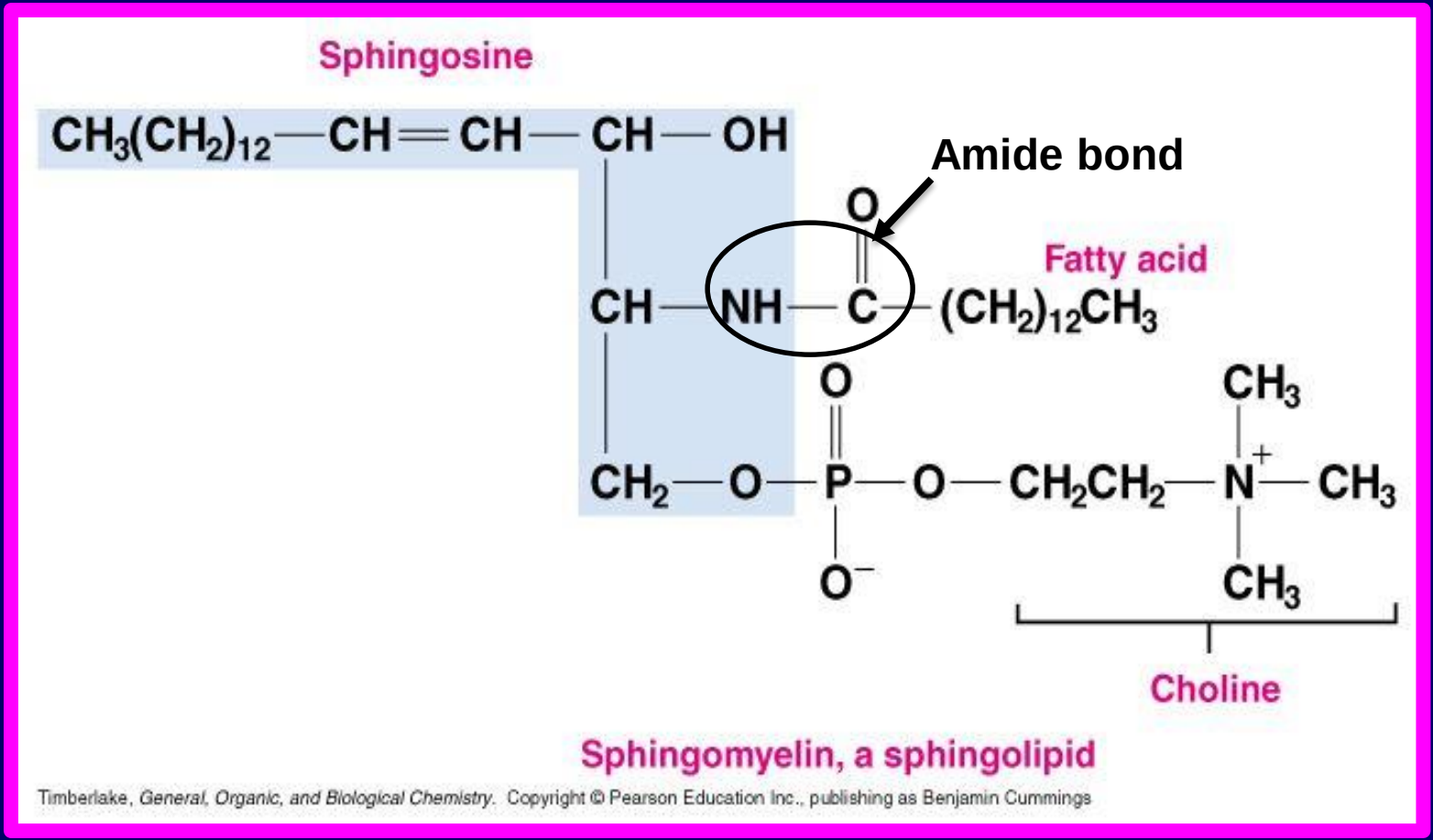


1-2.Gangliosides have two or more sugar unit, usually glucose and galactose they are abundant in the cell membranes of neurons they act at the cell surface as receptors for hormones. Accumulation of the ganglioside GM_2 causes Tay-Sachs.



2. Sphingomyelins

the sphingosine is linked to amino alcohol phosphate ester (ethanol amine). Sphingomyelin is the main component of the myelin sheath of nerve cells.



Lipid Diseases

There are many diseases involving lipids:-

- Usually, lack of an enzyme leads to accumulation of a particular lipid, causing symptoms such as enlarged spleen and liver, seizures, blindness, mental retardation and death

- Lipid deficiencies are rare, but also cause serious problems, such as in multiple sclerosis, where sphingomyelins are lost from the myelin sheath, impairing nerve signal transmission and causing symptoms such as muscle weakness and loss of coordination and vision

Sphingolipid Storage Diseases

Disease	Symptom	Sph. Lip	Enzyme
Tay-Sachs	Blindness, muscles weak	Ganglioside GM_2	β-hexose-aminidase A
Gaucher's	Liver & spleen enlarge, MR	Gluco-cerebroside	β-glucosidase
Krabbe's	demyelation, MR	Galacto-cerebroside	β-galactosidase
Nieman-Pick	MR	Sphingomyelin	Sphingomyelinase

MR=Mitral regurgitation

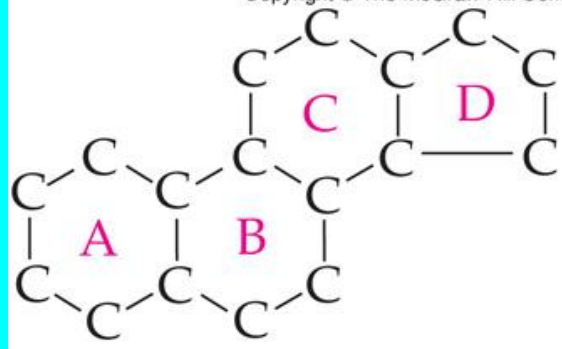
Steroids

✓**Steroids** are lipids containing a steroid nucleus (core structure)

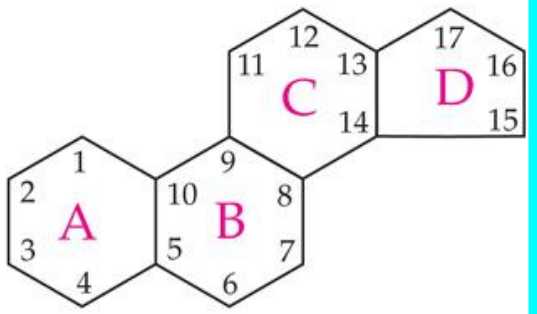
✓The **steroid nucleus** is a fused ring system consisting of three cyclohexane rings and one cyclopentane ring

✓The rings are designated A, B, C and D

✓Attachment of different groups to the core steroid structure leads to a wide variety of steroid compounds, including cholesterol, bile salts and steroid hormones



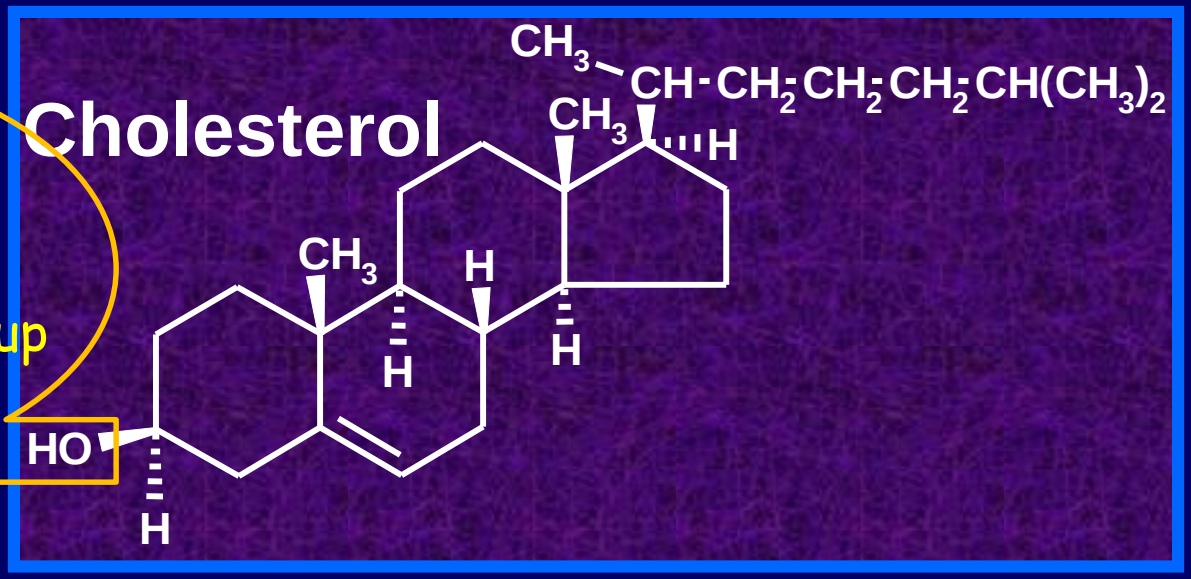
Carbon skeleton of the steroid nucleus



Steroid nucleus

Cholesterol

Cholesterol is called a *sterol* because it contains an alcohol group

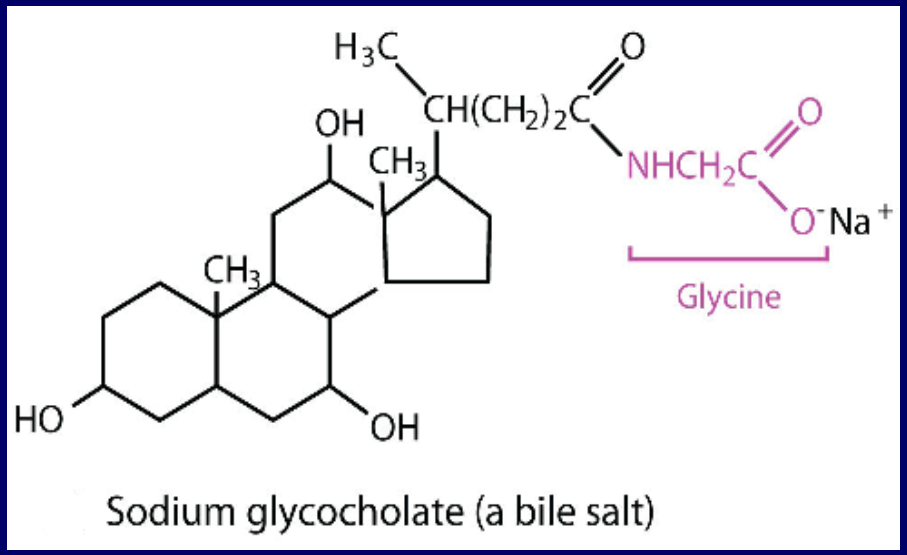


- A major component of cell membranes, and affects the fluidity of the membrane due to its bulky structure
- We can obtain cholesterol from our diet (animal products), but our liver can also synthesize all the cholesterol that we need.

- The liver synthesizes more cholesterol when dietary intake is low.
- Excessive blood cholesterol is associated with atherosclerosis and formation of gallstones
- A precursor for biosynthesis of many other steroids such as bile salts, male and female sex hormones, vitamin D, and the adrenocortical hormones.

Bile Salts

- Bile salts are synthesized from cholesterol in the liver.
- they are stored in the gall bladder and released into the upper small intestine to help break down fats and oils (like soaps)
- too much accumulated cholesterol in the gall bladder can lead to gallstones; if a gallstone passes into the bile duct, severe pain results and the gallbladder often has to be removed



Sodium glycocholate (a bile salt)

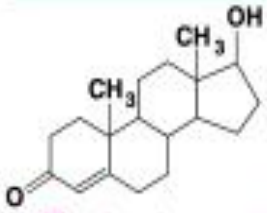
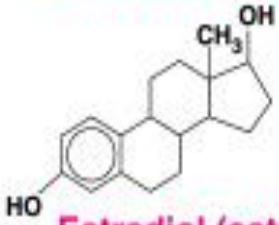
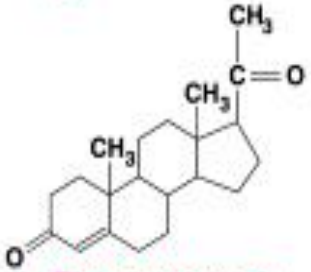
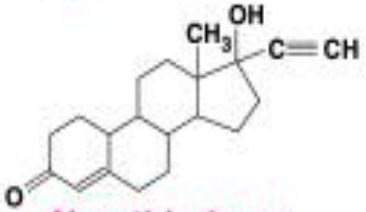
Steroid Hormones

Hormones act as chemical messengers.

They are secreted from endocrine glands (and placenta).

Usually control metabolism at the gene level.

Steroid hormones are biosynthesized from cholesterol.

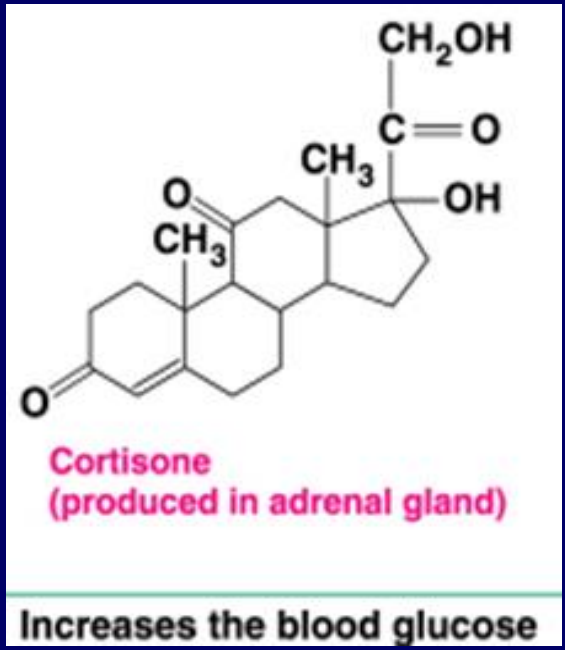
Hormone	Biological Effects
 Testosterone (androgen) (produced in testes)	Development of male organs; male sexual characteristics including muscles and facial hair; sperm formation
 Estradiol (estrogen) (produced in ovaries)	Development of female sexual characteristics; ovulation
 Progesterone (produced in ovaries)	Prepares uterus for fertilized egg
 Norethindrone (synthetic progestin)	Contraceptive (birth control) pill

Adrenal Corticosteroids

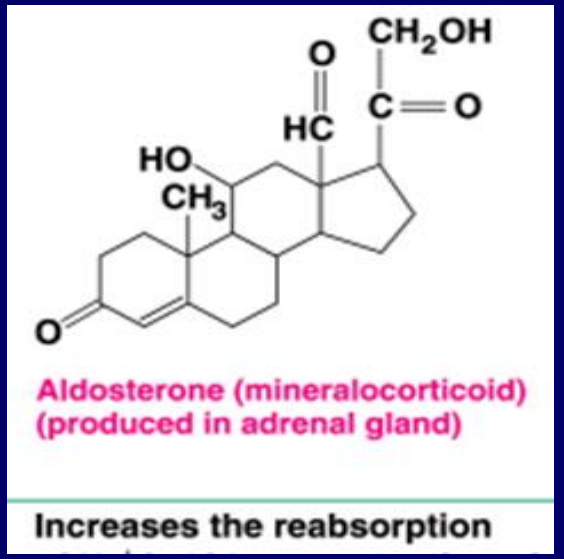
Adrenal corticosteroids are hormones produced in the adrenal glands.

Three types:-

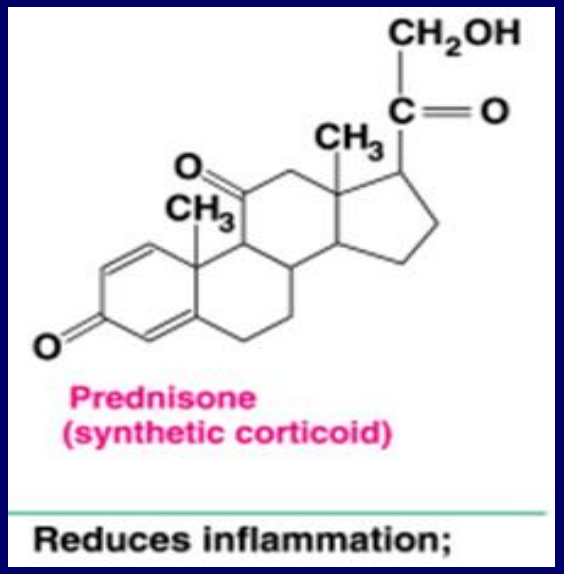
1. **Glucocorticoids** such as cortisol control carbohydrate, fat and protein metabolism, and are anti-inflammatory by preventing phospholipid release.



1. **Mineralocorticoids** such as aldosterone control electrolyte and water levels, mainly by promoting sodium retention in the kidney.



2. **Prednisone** synthetic corticoid used to treat various inflammatory conditions, such as asthma and rheumatoid arthritis.



Waxes

Waxes are esters that combine a long-chain fatty acid with a long-chain alcohol (14-30 carbons in each chain, (unbranched).

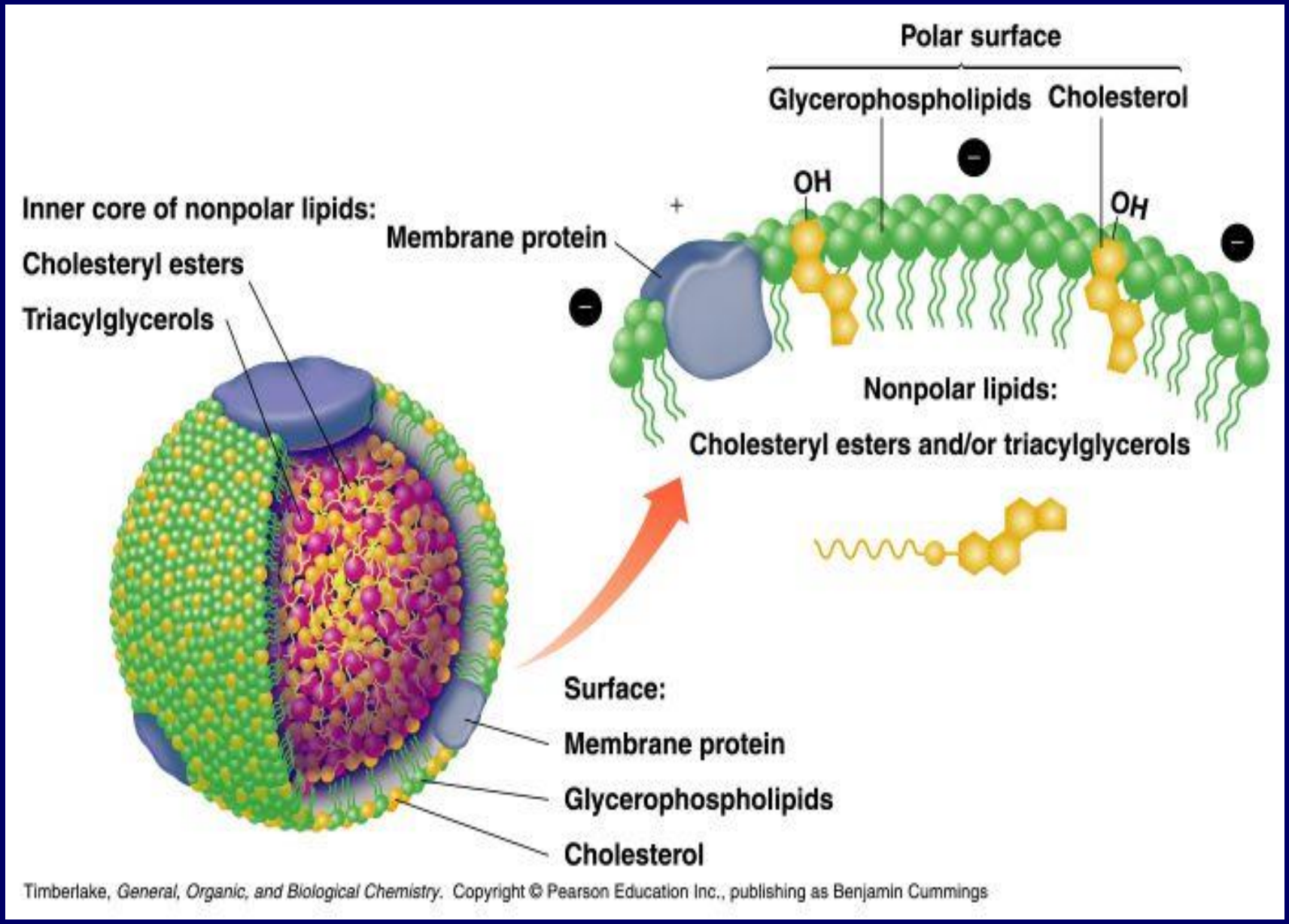
Some Typical Waxes

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

- Plants produce waxes on the surfaces of their leaves, stems and fruits to prevent water loss and protect against pests
- Animals produce waxes on their fur or feathers to provide a water-proof coating (ducks, polar bears, etc.)
- Waxes are used commercially to produce many products, such as car wax, candles and cosmetics.

Complex Lipids
Lipoproteins

- Are water-soluble complexes of lipids, phospholipids and proteins
- Used to transport lipids through the blood
- Soluble in water because their surface is polar.
- The polar head groups of phospholipids and the hydroxyl groups of cholesterol form a polar layer on the surface of the lipoprotein
- Nonpolar triacylglycerides and cholesterol esters (cholesterol in the blood is mostly fatty acid esters) are stored in the interior

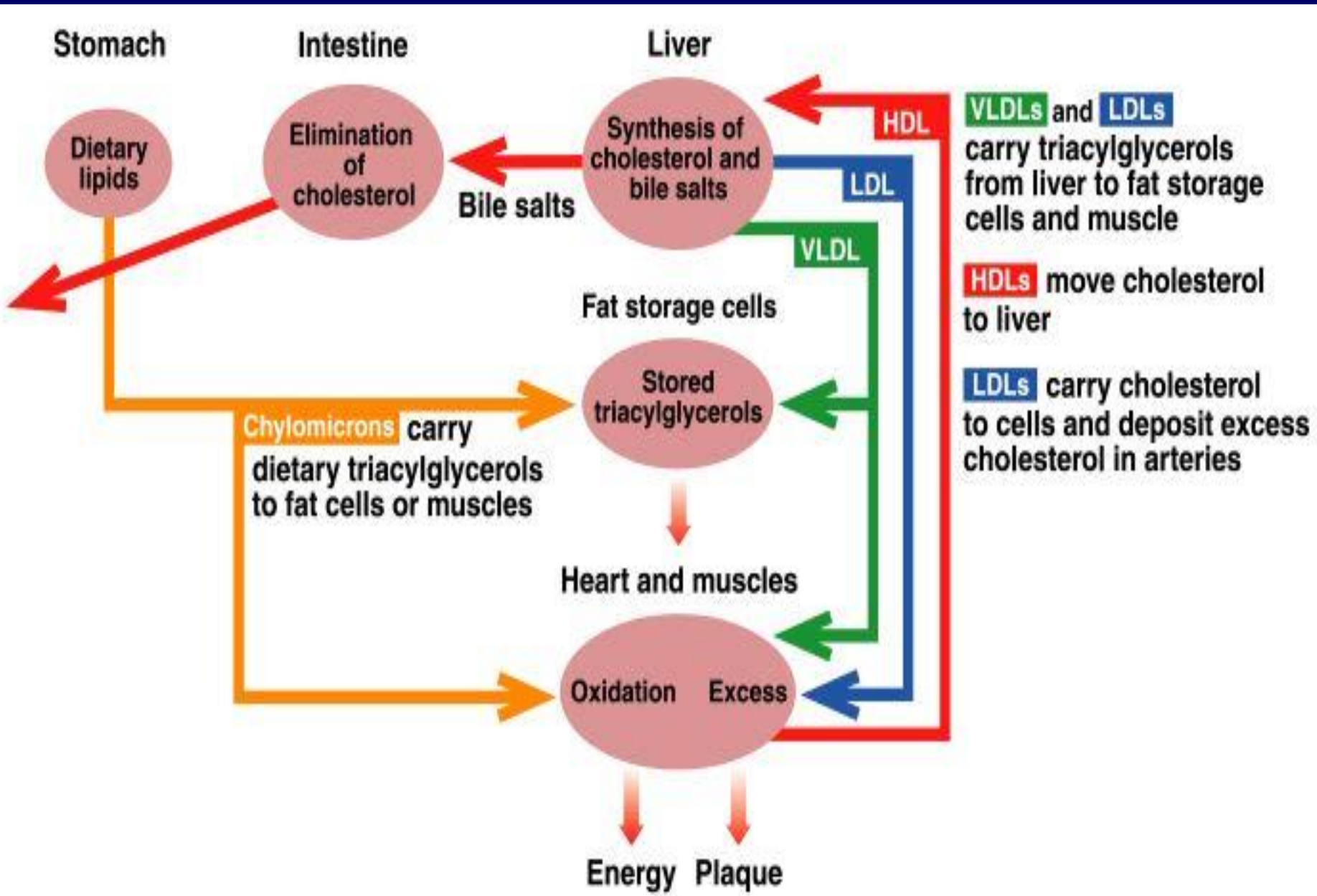


Types of Lipoproteins

Lipoproteins differ by density, composition and function.

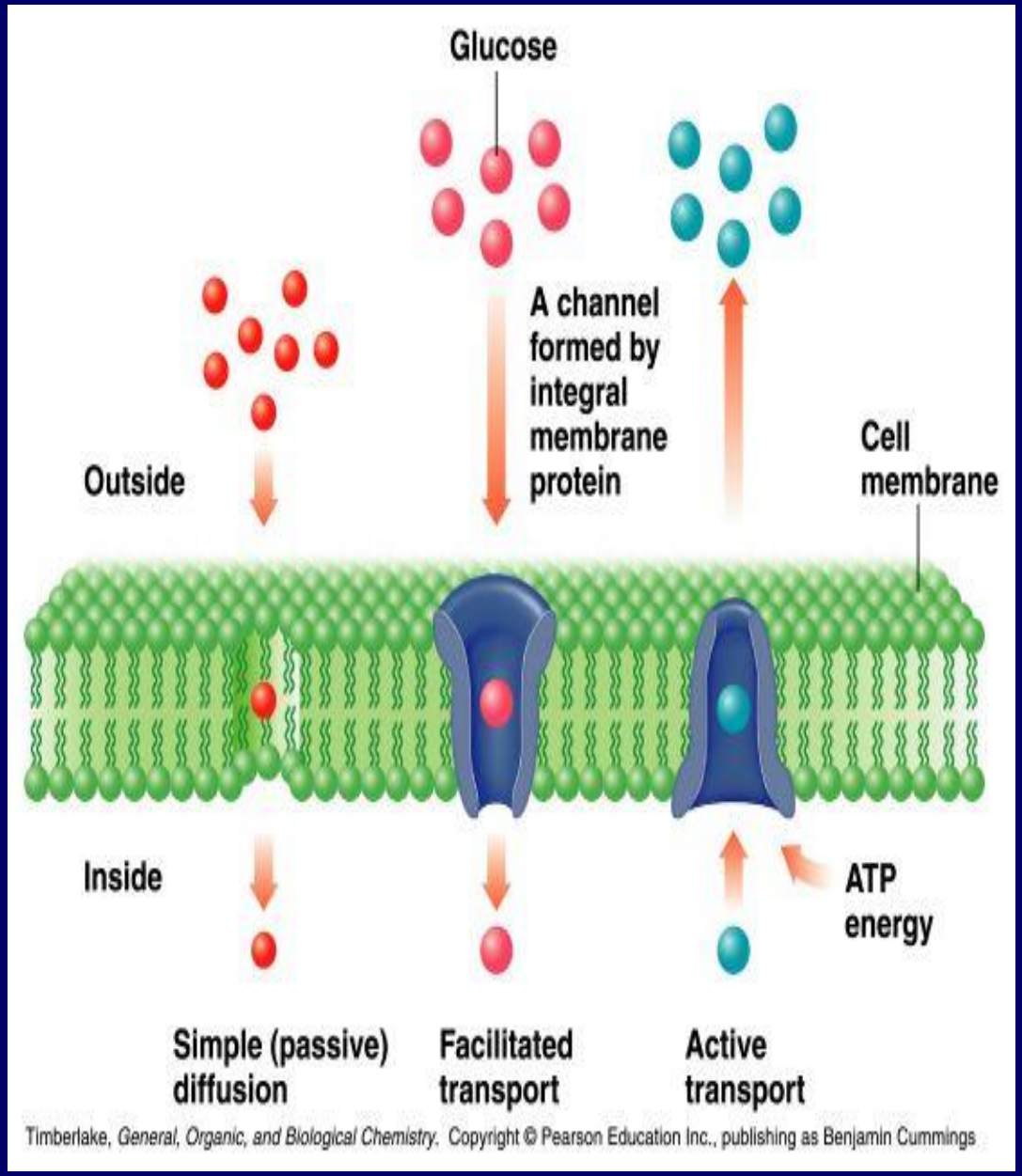
Types of lipoproteins include:-

1. Chylomicrons
2. Very-low-density lipoprotein (VLDL)
3. Low-density lipoprotein (LDL)
   transport cholesterol to cells for biosynthesis or storage, and when blood cholesterol in LDL's becomes excessive, the LDL's deposit the excess cholesterol on artery walls.
4. High-density lipoprotein (HDL)
   transport excess cholesterol from tissues to the liver , which converts cholesterol to bile salts, some of which are eliminated, but most are returned to the liver for re-use.



Transport Through Cell

1. **Membranes diffusion (passive transport)** moves particles from a higher to a lower concentration (requires no energy source)
2. **Facilitated transport** uses protein channels to increase the rate of diffusion (requires no energy source)
3. **Active transport** moves ions against a concentration gradient (requires ATP as an energy source)

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