Bio-organic chemistry

Lecture #13

Phospholipids. Their classification, structure, chemical properties. Physiological role. Unsaponifiable lipids (terpenes, steroids). Their classification, structure, chemical properties. Physiological role.

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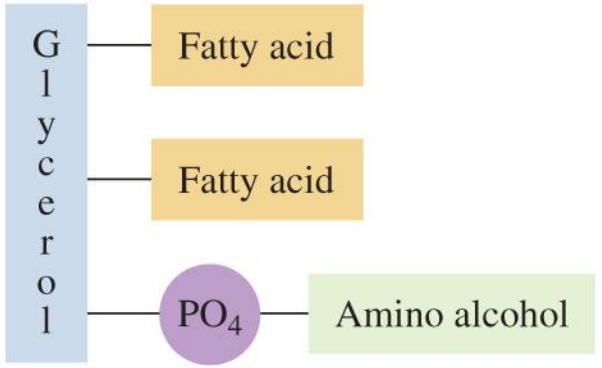
Glycerophospholipids

Glycerophospholipids, the most abundant lipids in cell membranes, contain

- two fatty acids, which form ester bonds with the first and second hydroxyl group of glycerol.
- a third hydroxyl group, which forms an ester with phosphoric acid, which then forms another phosphoester bond with an amino alcohol.



Glycerophospholipid

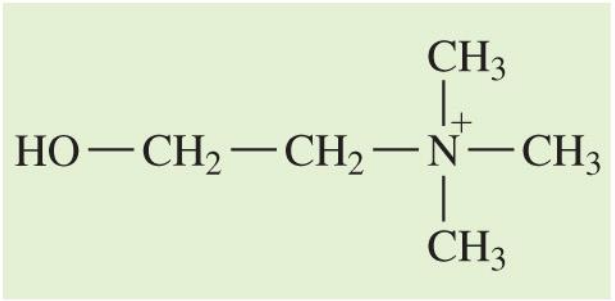
Lecithin and Cephalin

Lecithin and **cephalin** are glycerophospholipids that
are abundant in brain and nerve tissues.
are found in egg yolk, wheat germ, and yeast.
contain choline (in lecithins) or either ethanolamine or serine (in cephalins).

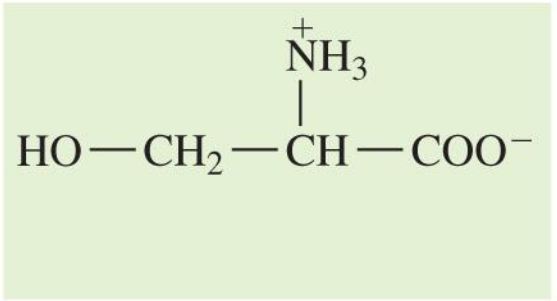
Glycerophospholipids Contain Amino Alcohols.

Three amino alcohols found in glycerophospholipids are choline, serine, and ethanolamine.
In the body, at a physiological pH of 7.4, these amino alcohols are ionized.

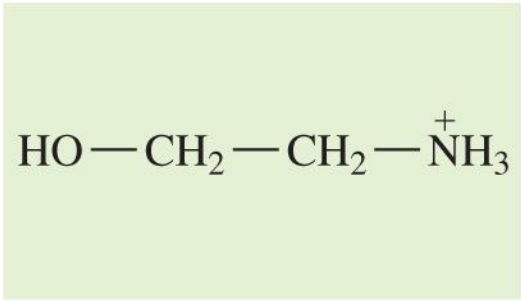
Insert structures of amino alcohols pg 618 bottom



Choline



Serine



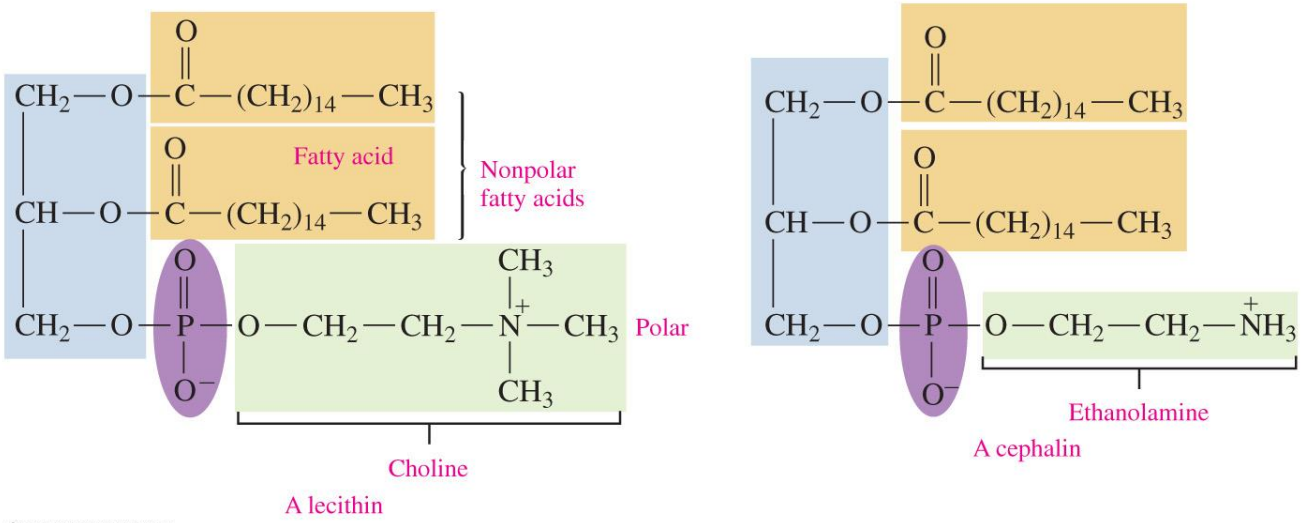
Ethanolamine

Glycerophospholipids are Polar and Nonpolar.

Glycerophospholipids have
both polar and nonpolar regions that allow them to interact with polar and nonpolar substances.
an ionized amino alcohol and phosphate portion, called “the head,” which is polar and strongly attracted to water.
a hydrocarbon chain known as “the tail,” which is soluble in nonpolar substances.

Formation of Glycerophospholipids

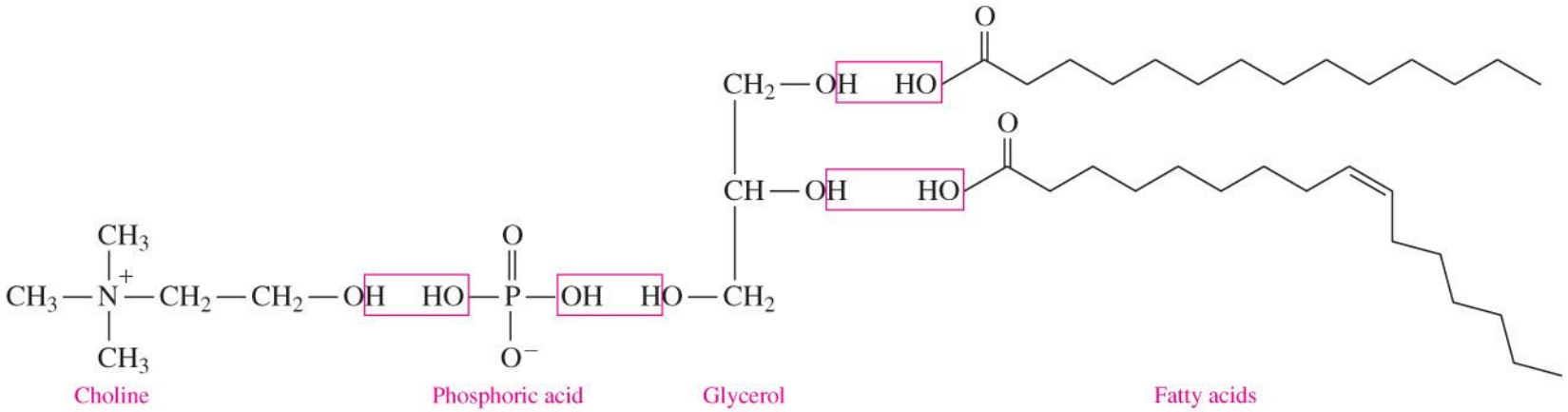
The formation of a glycerophospholipid occurs when ester bonds form between glycerol and two fatty acids, and two phosphoester bonds form between phosphoric acid and an ionized amino alcohol and glycerol, such as palmitic acid.



Components of Glycerophospholipids

The components of a glycerophospholipid are choline, phosphoric acid, glycerol, and two fatty acids.

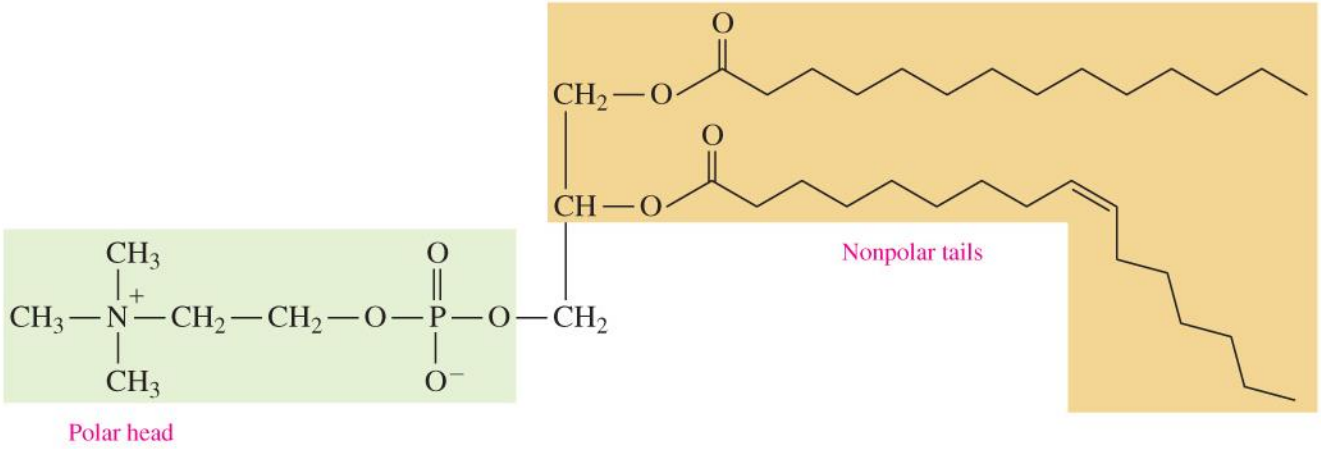
Insert structure from figure 17.6a



Components of Glycerophospholipids

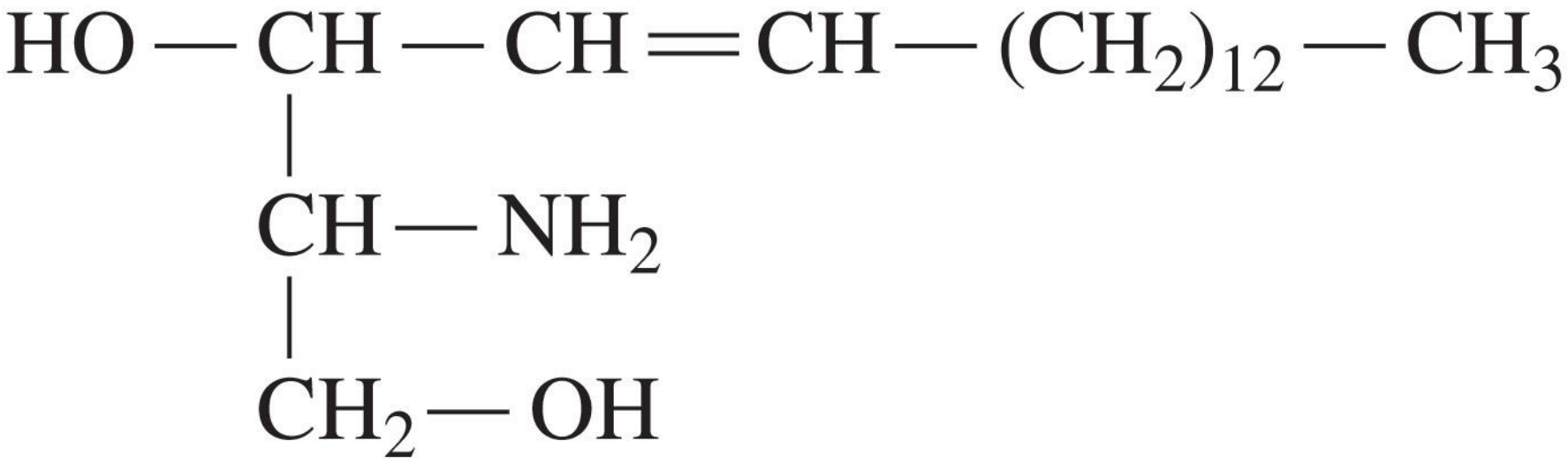
In a glycerophospholipid, a polar “head” contains the ionized amino alcohol and phosphate, while the hydrocarbon chains of two fatty acids make up the nonpolar “tails.”

Insert structure from figure 17.6b



Sphingosine

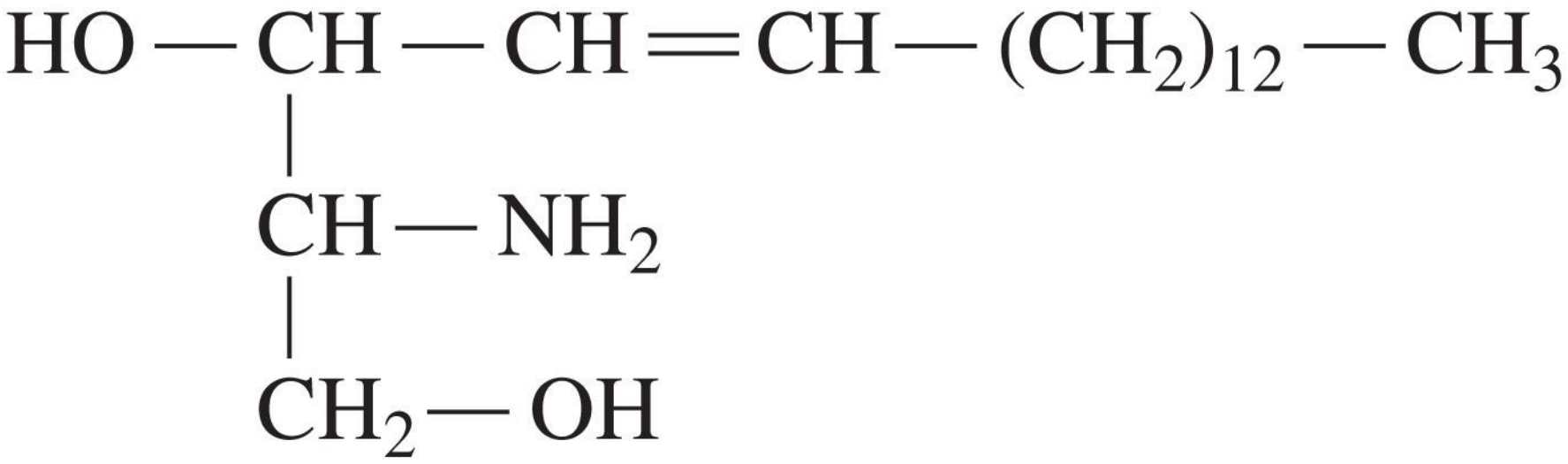
Sphingosine is an 18-carbon unsaturated amino alcohol.



Sphingosine

Sphingolipids

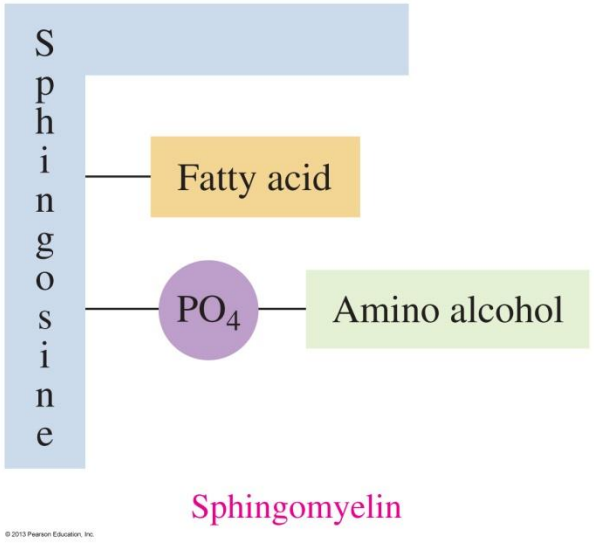
Sphingolipids are phospholipids that contain a long-chain amino alcohol called ***sphingosine,*** rather than glycerol.



Sphingosine

Sphingomyelins

Sphingomyelins, are a group of sphingolipids in which the amine group forms an amide bond to a fatty acid, and the hydroxyl group of sphingosine forms an ester bond with phosphate forming another phosphoester bond to an amino alcohol, such as choline.



Sphingomyelins, are abundant in the white matter of the myelin sheath, a coating surrounding the nerve.
cells that increase the speed of nerve impulses and insulate and protect the nerve cells.

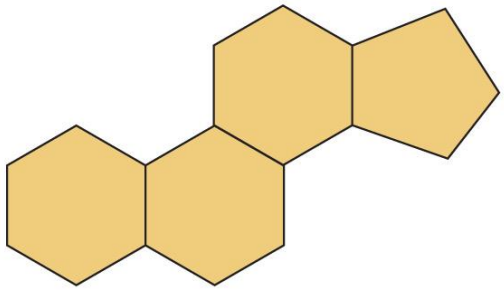
Multiple Sclerosis

In multiple sclerosis,

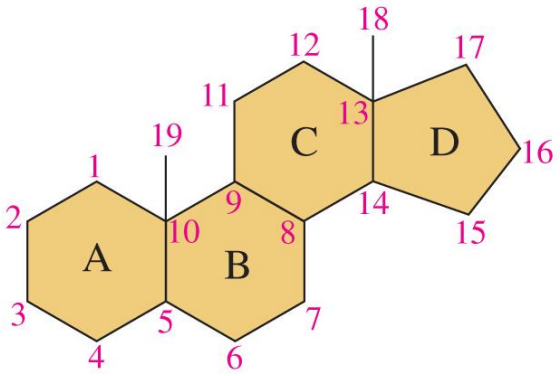
- sphingomyelin is lost from the myelin sheath, which protects the neurons in the brain and spinal cord.
- scars form on the neurons and impair the transmission of nerve signals.

Steroid Nucleus

Steroid molecules contain a **steroid nucleus** with
3 cyclohexane rings,
1 cyclopentane ring,
no fatty acids, and
a total of four rings A, B, C, D.
The steroid nucleus is numbered from the carbon atoms in ring A to two methyl groups at 18 and 19.



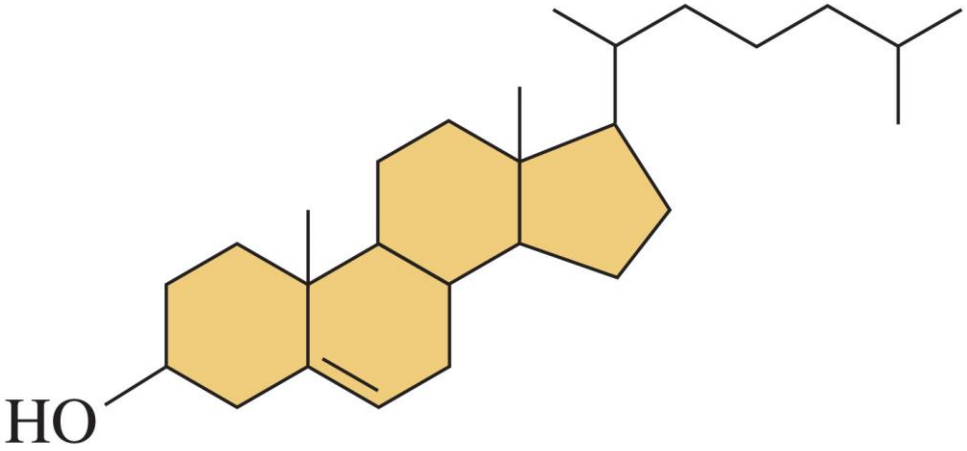
Steroid nucleus



Steroid numbering system

Cholesterol

Cholesterol
is the most important and abundant steroid in the body.
is a *sterol* because it contains an oxygen atom as a hydroxyl group, –OH on carbon 3.
has a double bond between carbon 5 and carbon 6.
has methyl $–CH_3$ groups, at carbon 10 and 13.
has a carbon chain at carbon 17.



Cholesterol

Cholesterol is a component of cellular membranes, myelin sheaths, and brain and nerve tissues.

Cholesterol in the Body

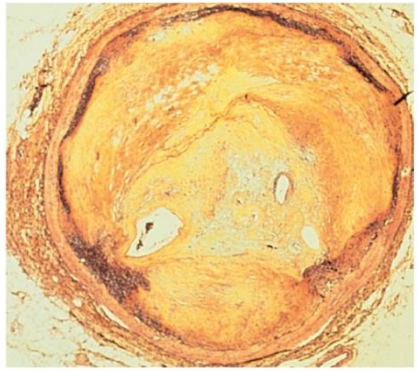
Cholesterol in the body

is obtained from meats, milk, and eggs and synthesized in the liver.

clogs arteries when high levels form plaque.

A normal, open artery.

(a)



(b)

An artery clogged by cholesterol plaque

Cholesterol in Foods

A typical American diet includes 400–500 mg of cholesterol per day. The American Heart Association has recommended no more than 300 mg of cholesterol per day. Saturated fats in the diet may stimulate the production of cholesterol by the liver.

TABLE 17.4 Cholesterol Content of Some Foods

Food	Serving Size	Cholesterol (mg)
Liver (beef)	3 oz	370
Large egg	1	200
Lobster	3 oz	175
Fried chicken	$3\frac{1}{2}$ oz	130
Hamburger	3 oz	85
Chicken (no skin)	3 oz	75
Fish (salmon)	3 oz	40
Butter	1 tablespoon	30
Whole milk	1 cup	35
Skim milk	1 cup	5
Margarine	1 tablespoon	0

Bile salts

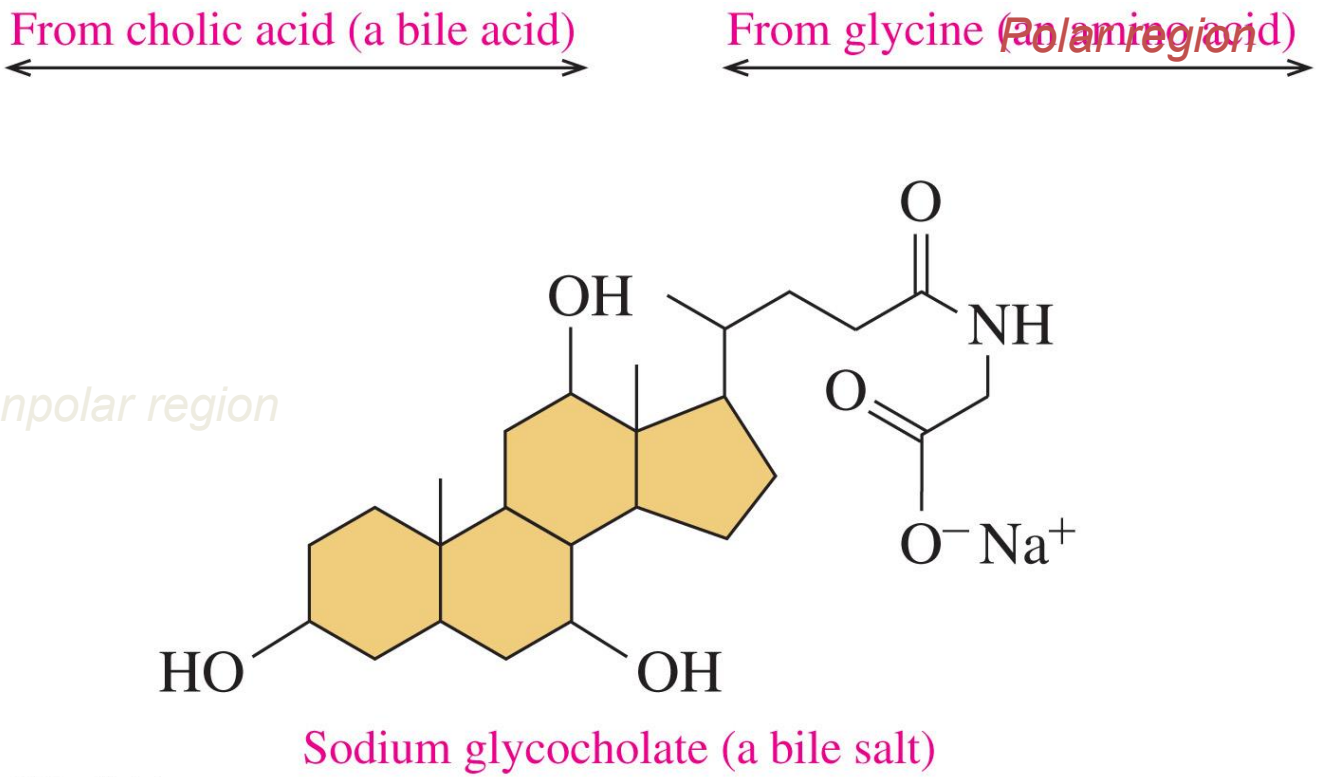
are synthesized from cholesterol in the liver.

are stored in the gallbladder and secreted into the small intestine.

have a polar and a nonpolar region.

help in the absorption of cholesterol into the intestinal mucosa.

Sodium Glycocholate, a Bile Salt



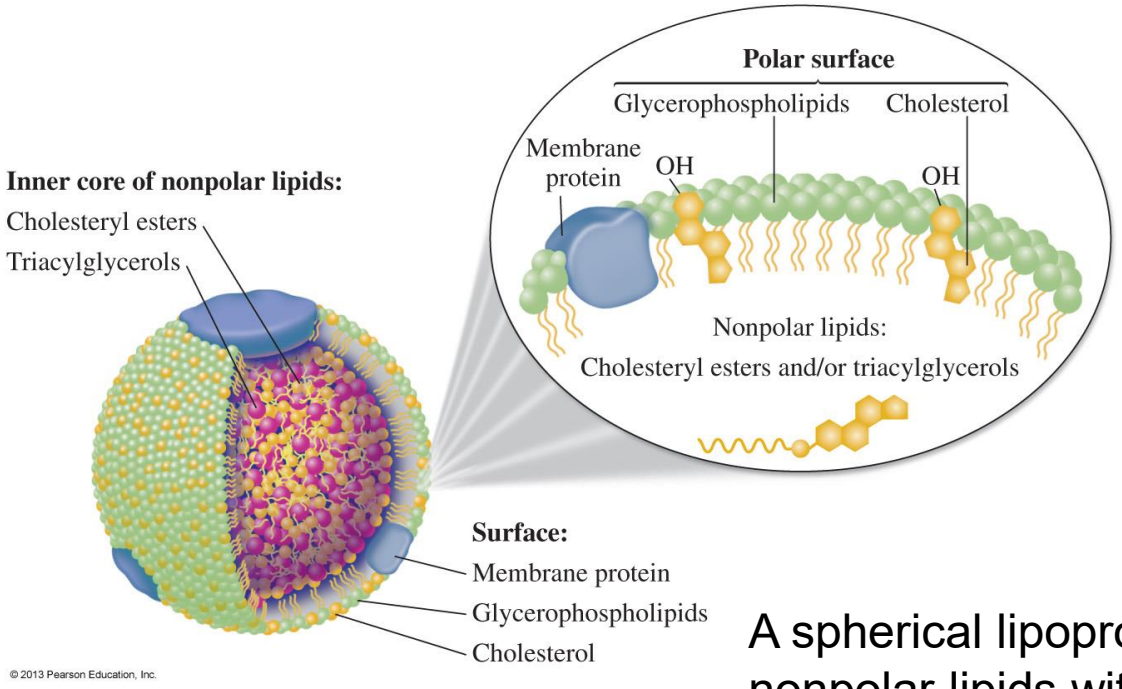
Gallstones

Gallstones are
formed when large amounts of cholesterol accumulate in the gallbladder.
composed of almost 100% cholesterol, with some calcium salts, fatty acids, and glycerophospholipids.

Lipoproteins

Lipoproteins

are spherical particles with an outer surface of polar proteins and glycerophospholipids that surround hundreds of nonpolar molecules of triacylglycerols and cholesteryl esters.
combine lipids with proteins and phospholipids.
are soluble in water because the surface consists of polar lipids.



A spherical lipoprotein particle surrounds nonpolar lipids with polar lipids and protein for transport to body cells.

Types of Lipoproteins

Lipoproteins differ in density, composition, and function
and include
chylomicrons, very low-density lipoprotein (VLDLs);
low-density lipoproteins (LDLs), which carry cholesterol to the tissues; and
high-density lipoproteins (HDLs) that pick up cholesterol from the tissues and carry it to the liver.

LDLs

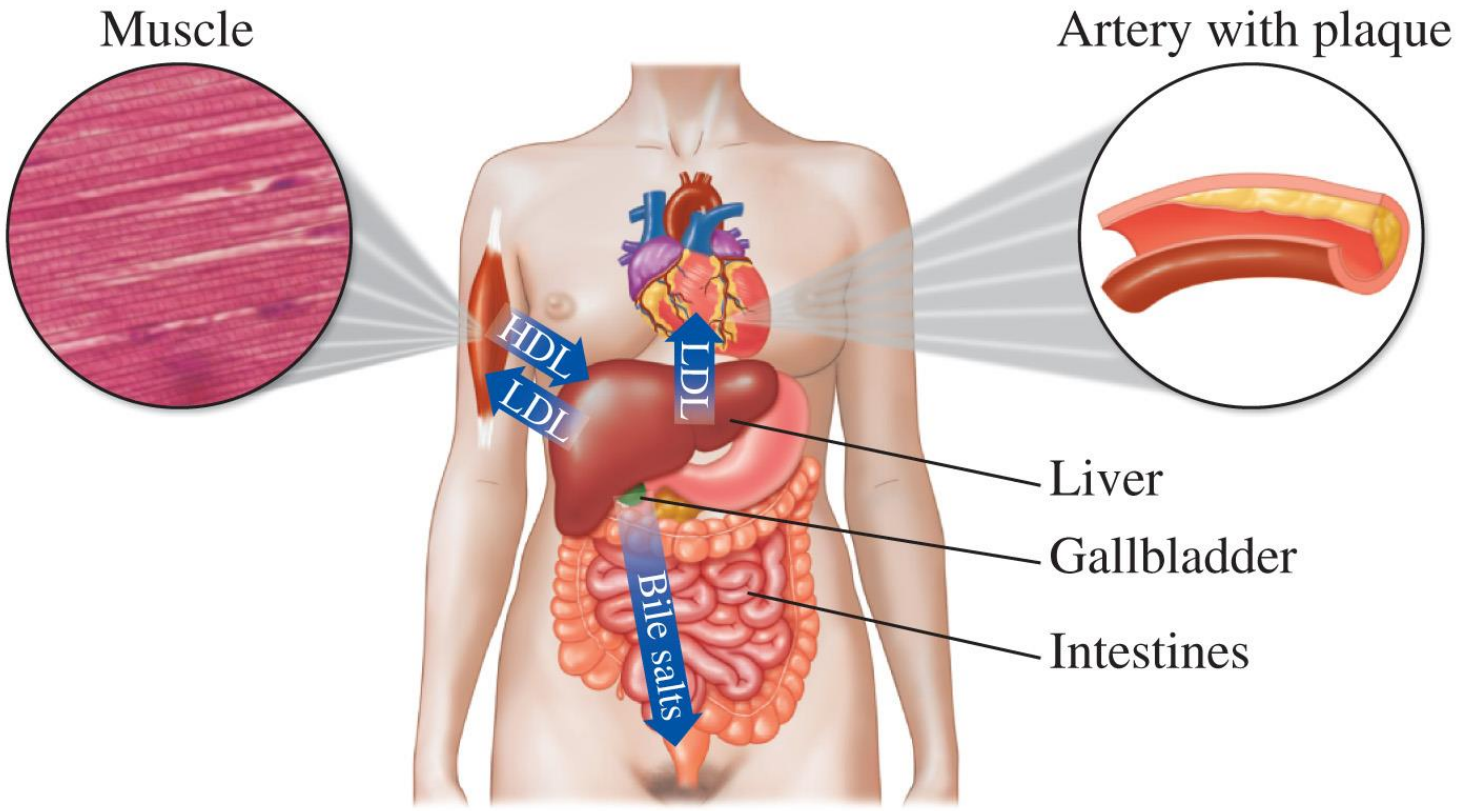
LDLs
transport cholesterol to tissues where it can be used for synthesis of cell membranes and steroid hormones.
deposit cholesterol in the arteries in the form of plaque when cholesterol levels exceed levels needed by tissues.
called “bad” cholesterol for their contribution to heart disease.

HDLs

HDLs
are more dense than LDLs due to the increased amount of protein present.
pick up cholesterol from the tissues and carry it to the liver, where it can be converted to bile salts, which are eliminated from the body,
are called “good” cholesterol.

VLDLs

VLDLs carry the triacylglycerols synthesized in the liver to the adipose tissues for storage.



Lipid Panel

A lipid panel is a blood test that measures serum lipid levels including
cholesterol
triglycerides
high-density lipoprotein (HDL)
low-density lipoprotein (LDL)
The results of a lipid panel are used to evaluate a patient's risk of heart disease.

Lipid Panel	Recommended Level	Greater Risk of Heart Disease
Total Cholesterol	Less than 200 mg/dL	Greater than 240 mg/dL
Triglycerides (triacylglycerols)	Less than 150 mg/dL	Greater than 200 mg/dL
HDL ("good" cholesterol)	Greater than 60 mg/dL	Less than 40 mg/dL
LDL ("bad" cholesterol)	Less than 100 mg/dL	Greater than 160 mg/dL
Cholesterol/HDL Ratio	Less than 4	Greater than 7

Transport Pathways Through Cell Membranes