Lipids
Chapter 24

Structure and Classification of Lipids

Lipids are defined by their solubility in nonpolar solvents and contain large hydrocarbon portions and not many polar groups.

Lipids that are esters or amides of fatty acids:

- **Waxes** are carboxylic acid esters with long, straight hydrocarbon chains in both R groups. They perform mostly external protective functions.
- **Triacylglycerols** (triglycerides) are carboylic acid esters of glycerol. These make up the fat stores in our bodies and most dietary fats and oils.
- **Glycerophospholipids** are trimesters of glycerol. They are abundant in the cell membrane.
- **Sphingomyelins** are amides derived from an amino alcohol. They are essential to the structure of cell membranes and abundant in nerve cell membranes.
- **Glycolipids,** amids derived from sphingosine, contain polar CHO groups that sit on the cell surface and act as receptors for intracellular messengers.

Lipids that are not esters or amids:

- **Steroids** contribute to the structure of cell membranes.
- **Eicosanoids** are carboxylic acids that are a special kind of intracellular chemical messenger.

Fatty Acids and Their Esters

Most fatty acids have an even number of carbon atoms.

Naturally occurring fats and oils are trimesters formed between glycerol and fatty acids. FA are long, unbranched hydrocarbon chains with a CA group at one end. Some contain double bonds, but not all of them do. If it has one or more double bonds, then it is unsaturated. If it has only single bonds, then it is saturated…meaning it is saturated with as many H atoms as it can hold. Think about the way that a fully saturated chain can stack together tightly and it's easy to remember that saturated fats are solids at room temp (butter). Note also that unsaturated fats have lower melting points…they are liquids at room temperature, more or less.

The most common saturated fatty acids:

- Palmitic acid (16 carbons)
- Stearic acid (18 carbons)

Most common unsaturated fatty acids:

- Oleic acid (18 carbons and monounsaturated)
- Linoleic acid (18 carbons and polyunsaturated)

Essential fatty acids (must get from diet):

- Linoleic acid
- Linolenic acid (also polyunsaturated)

Waxes
Waxes are the simplest fatty acids…they are a mixture of fatty acid—long-chain alcohol esters. Waxes are found on leaves of plants, feathers of aquatic birds, and most fruits.

The acids have an even number from 16 to 36 carbons.

The alcohols have an even number from 24 to 36 carbons.

Triacylglycerols
Animal fats and vegetable oils are the most plentiful lipids in nature. All fats and oils are composed of trimesters of glycerol (1,2,3-propanediol) with three fatty acids. They are often called triglycerides!

Note that the three fatty acids of any specific triglyceride are not necessarily the same. For this reason, triacylglycerols can be a mixture of saturated and unsaturated fatty acids. For example, olive oil is made up of palmitic acid, stearic acid (both saturated) and oleic and linoleic (both unsaturated).

Properties of Fats and Oils

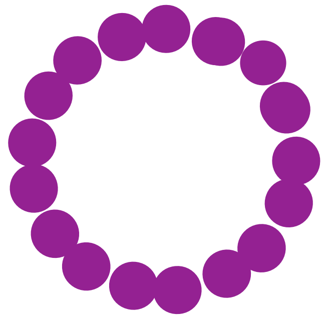
- The more double bonds a FA has, the lower the melting point
- The more highly unsaturated the acyl groups are in a triacylglycerol, the lower its melting point (vegetable oils are lower melting than animal fats)
- Saturated fats appears straight
- Unsaturated fats bend due to cis double bonds
- Triacylglycerols are uncharged, nonpolar molecules that are hydrophobic
- Pure oils are colorless and odorless
- Overheating causes rancidity

Chemical Reactions of Triacylglycerols
HYDROGENATION occurs in triacylglycerols in much the same way an alkene can react with hydrogen to yield an alkane. Essentially you eliminate the double bond of an unsaturated fat to yield a saturated fat. The diagram in the book shows the exact same reaction as alkene to alkane…including the metal catalyst.

The extent of the hydrogenation varies with the number of double bonds, and the extent of the saturation varies also, depending on how much H is added. This enables the consistency of the final product to be controlled so that you end up with a margarine will remain soft when refrigerated but melt on toast.

HYDROLYSIS OF TRIACYLGLYCEROLS…SAPONIFICATION
In the body, hydrolysis is catalyzed by hydrolases and is the first reaction in the digestion of dietary fats and oils. When you make soap, you take a triacylglycerol (either animal or vegetable) and react it with a base (NaOH or KOH). The initial products of saponification are one molecule of glycerol and three molecules of fatty acid carboxylate salts (the soap).

HOW DOES SOAP WORK? The two ends of the soap molecule are different…the sodium salt end is ionic and hydrophilic, so it dissolves in water. The hydrocarbon chain is nonpolar and hydrophobic. These opposing forces make soap attracted to both grease and water. When soap is dispersed in water, the anions cluster together to form micelles (hydrophobic on the inside.) Grease and dirt are trapped in the center of the molecule and washed away.

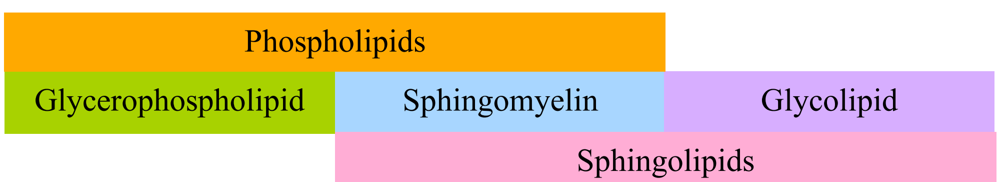


<u>Cell Membrane Lipids: Phospholipids and Glycolipids</u>

Cell membranes establish a hydrophobic barrier between the watery environments outside and inside the cell.

Three major cell membrane lipids:

1. Phospholipids.
    a. Contain a phosphate ester link and are built up from either glycerol (glycerophospholipids) or from the alcohol sphingosine (to produce sphongomyelins)
2. Glycolipids
    a. Also derived from sphingosine.
    b. Contain no phosphate group
    c. Have an attached CHO that is a monosaccharide or short chain of monosaccharides.
3. Cholesterol
    a. A steroid (4 fused ring structure)

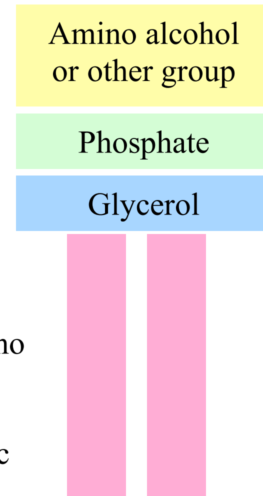


Phospholipids

How are phospholipids similar to soap?

They have ionized phosphate groups at one end so they have hydrophilic heads and hydrophobic tails. They DIFFER, in that they have two tails instead of one.

Glycerophospholipids (aka phosphoglycerides) are trimesters of glycerol 3-phosphate and are the most abundant membrane lipids.



The basic structure from the head down is:

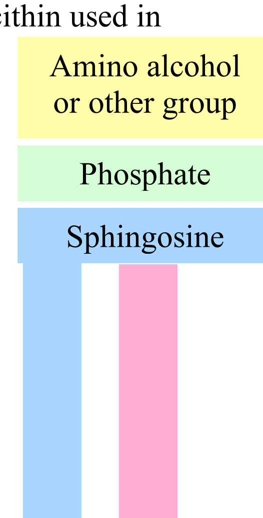
- Amino alcohol or other group
- Phosphate
- Glycerol
- Two fatty acids

The basic definition of a glycerophospholipid is: A lipid in which glycerol is linked by ester bonds to two fatty acids and one phosphate, which is in turn linked by another ester bond to an amino alcohol (or other alcohol).

The glycerophospholipids are named as derivatives of phosphatidic acids:

R group is connected to a H: Phosphatidate (basic structure of glycerophospholipids)
R group connected to choline: Phosphatidylcholine (basic structure of lecithin)
R group connected to ethanolamine: Phosphatidylethanolamine (membrane lipids)
R group connected to serine: Phosphatidylserine (present in most tissues, brain)
R group connected to myo-Inositol: Posphatidylinositol (relays chemical signals)

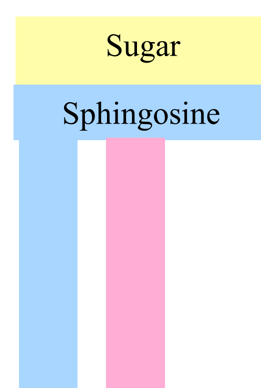
Glycerophospholipids are emulsifying agents because of their combination of hydrophobic tails and hydrophilic heads…a common emulsifying agent is lecithin used in chocolates.



In sphingolipids the amino alcohol sphingosine provides one of the two hydrophobic hydrocarbon tails…the other one is from a fatty acid connected by an amide link to the –NH_2 in sphingosine.

Sphingomyelins are sphingosine derivatives with a phosphate ester group at C1 of sphingosine. They are major components of the coating around nerve fibers (myelin sheath).

Glycolipids



Glycolipids are derived from sphingosine. They are different from sphingomyelins in that they have a CHO group at C1 instead of a phosphate group bonded to choline. They reside in the cell membrane with the CHO segment extending out as receptors.

Some glycolipids:

- Cerebrosides: abundant in nerve cell membranes in the brain.
- Gangliosides: the CHO is a small polysaccharide. Over 60 are known. The oligosaccharides responsible for blod types are part of ganglioside molecules

Cell Membrane Lipids: Cholesterol

Cholesterol is synthesized in the liver!

Cholesterol is the most abundant animal steroid and all steroids have in common their four-ring system. The steroids other than cholesterol have many roles throughout the body such as hormone functions and acting as bile acids essential for the digestion of fats and oils. Cholesterol has two important functions: cell membrane and as the starting material for the synthesis of all other steroids. Except for its –OH group, cholesterolis hydrophobic…within a cell membrane, cholesterol molecules are wedged among the hydrophobic tails of phospholipids. Because they are more rigid than the tails they help maintain the structure of the cell membrane.

Structure of Cell Membranes

Lipid bilayer is composed of two parallel sheets of membrane lipid molecules arranged tail to tail. When phospholipids are shaken with water they spontaneously form liposomes which have a water center. Water-soluble substances can be trapped in the center of liposomes and lipid-soluble substances can be incorporated into the bilayer. The fluid mosaic model is used to describe the overall structure of the cell membrane. Some miscellaneous facts about the cell membrane:

- Glycolipids, cholesterol and proteins are in the membrane
- Many of the proteins are glycoproteins
- 20% or more of the weight of a membrane consists of protein molecules
- Peripheral proteins on just one side
- Integral proteins extend completely through the membrane…some form channels
- Bilayer is not easily ruptured
- Small nonpolar molecules can easily enter
- Some lipid or protein molecules can diffuse rapidly from place to place within the membrane

Membrane Transport

Passive transport: Substances move across the membrane freely by diffusion from regions of higher concentration to regions of lower concentration. Can be simple diffusion or facilitated diffusion.

Simple diffusion: A form of passive transport…small molecules such as CO_2, NO, O_2 and lipid-soluble substances such as steroid hormones. Molecules passing through channel proteins is also simple (hydrophilic substances do this).

Facilitated diffusion: Solutes are helped across the membrane by proteins that basically change shape to get the molecule across…glucose is transported in this way.

Active transport: Substances can cross the membrane only when energy is supplied and molecules move against their concentration gradient.

Energy!

<u>Eicosanoids: Prostaglandins and Leukotrienes</u>

Eicosanoids are a group of compounds derived from 20-carbon unsaturated fatty acids (eicosanoid acids) and synthesized throughout the body. They function as local hormones.

Prostaglandins and leukotrienes are two classes of eicosanoids that differ a bit in their structure. They are synthesized in the body from arachidonic acid (which is syntethized from linolenic acid).

Prostaglandins:

- Can lower blood pressure
- Influence platelet aggregation during blood clotting
- Stimulate uterine contractions
- Lower the extent of gastric secretions
- Responsible for some pain and swelling that accompany inflammation

Leukotrienes

- Leukotriene release has been found to trigger the ashmatic response, severe allergic reactions and inflammation