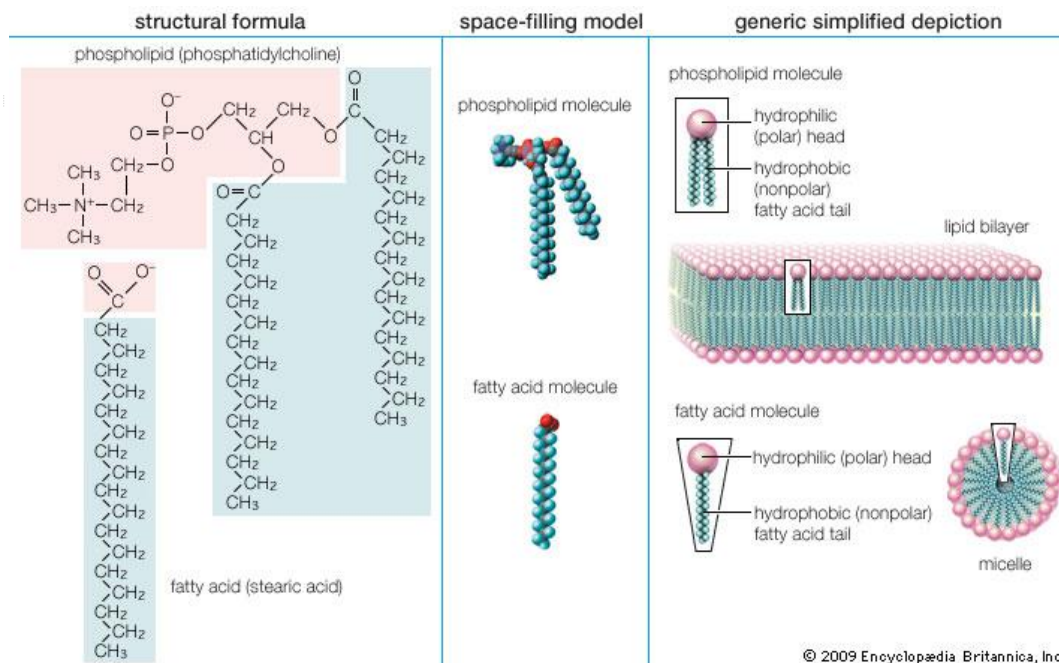


Biological lipids are not large macromolecular [polymers](#) (e.g., proteins, nucleic acids, and polysaccharides), many are formed by the chemical linking of several small constituent molecules. Many of these molecular building blocks are similar, or homologous, in structure. The homologies allow lipids to be classified into a few major groups: fatty acids, [fatty acid](#) derivatives, [cholesterol](#) and its derivatives, and lipoproteins. This article covers the major groups and explains how these molecules function as energy-storage molecules, chemical messengers, and structural components of cells.



Biological fatty acids, members of the class of compounds known as [carboxylic acids](#), are composed of a [hydrocarbon](#) chain with one terminal carboxyl group (COOH). The fragment of a [carboxylic acid](#) not including the hydroxyl (OH) group is called an acyl group. Under physiological conditions in water, this acidic group usually has lost a hydrogen ion (H⁺) to form a negatively charged carboxylate group (COO⁻). Most biological fatty acids contain an even number of carbon atoms because the biosynthetic pathway common to all organisms involves chemically linking two-carbon units together (although relatively small amounts of odd-number fatty acids do occur in some organisms). Although the [molecule](#) as a whole is water-insoluble by virtue of its hydrophobic hydrocarbon chain, the negatively charged carboxylate is hydrophilic. This common form for biological lipids—one that contains well-separated hydrophobic and hydrophilic parts—is called amphipathic.

In addition to straight-chain hydrocarbons, fatty acids may also contain pairs of carbons linked by one or more double bonds, methyl branches, or a three-carbon cyclopropane ring near the centre of the carbon chain.

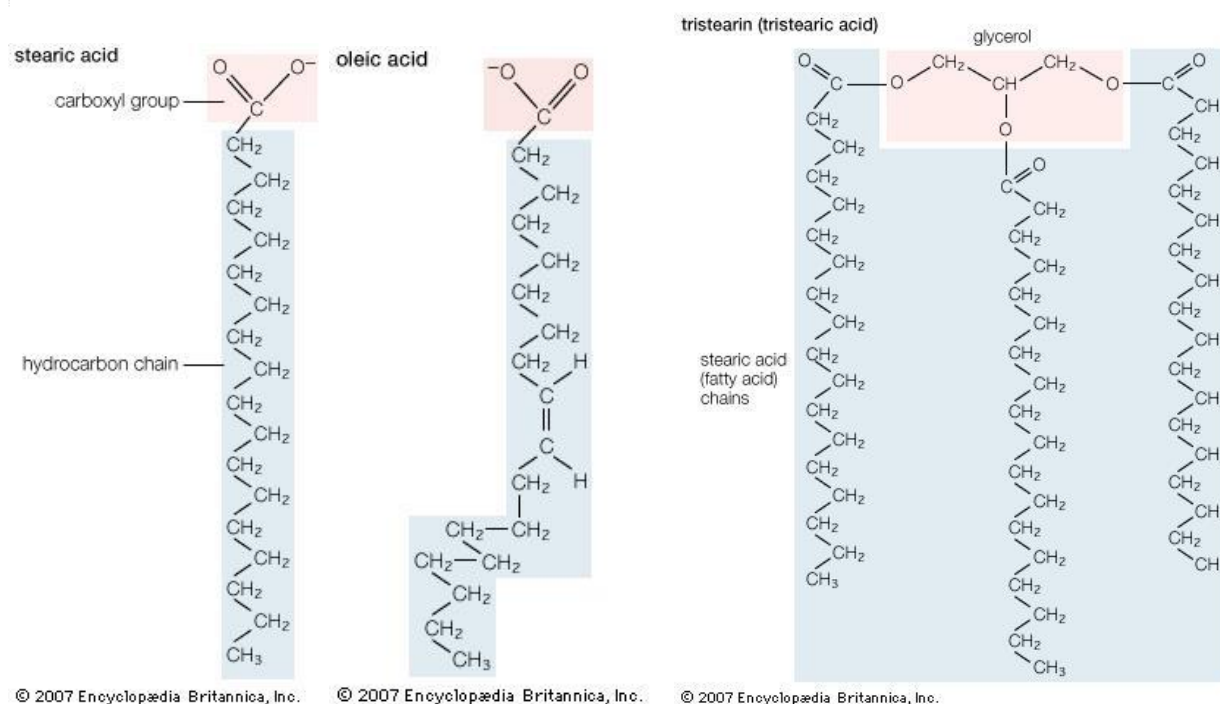
SATURATED FATTY ACIDS

The simplest fatty acids are unbranched, linear chains of CH₂ groups linked by carbon-carbon single bonds with one terminal carboxylic acid group. The term *saturated* indicates that the maximum possible number of hydrogen atoms are bonded to each carbon in the molecule. Many saturated fatty acids have a trivial or common name as well as a chemically descriptive systematic name. The systematic names are based on numbering the carbon atoms, beginning with the acidic carbon. Although the chains are usually between 12 and 24 carbons long, several shorter-chain fatty acids are biochemically important. For instance, butyric acid (C₄) and caproic acid (C₆) are lipids found in milk. Palm kernel oil, an important dietary source of fat in certain areas of the world, is rich in fatty acids that contain 8 and 10 carbons (C₈ and C₁₀).

Common saturated fatty acids

trivial name	systematic name	number of carbons in chain	typical sources
lauric acid	<i>n</i> -dodecanoic acid	12	palm kernel oil, nutmeg
myristic acid	<i>n</i> -tetradecanoic acid	14	palm kernel oil, nutmeg

palmitic acid	<i>n</i> -hexadecanoic acid	16	olive oil, animal lipids
stearic acid	<i>n</i> -octadecanoic acid	18	cocoa butter, animal lipids
behenic acid	<i>n</i> -docosanoic acid	22	brain tissue, radish oil
lignoceric acid	<i>n</i> -tetracosanoic acid	24	brain tissue, carnauba wax



UNSATURATED FATTY ACIDS

Unsaturated fatty acids have one or more carbon-carbon double bonds. The term *unsaturated* indicates that fewer than the maximum possible number of hydrogen atoms are bonded to each carbon in the molecule. The number of double bonds is indicated by the generic name—*monounsaturated* for molecules with one double bond or *polyunsaturated* for molecules with two or more double bonds. Oleic acid is an example of a monounsaturated fatty acid. The prefix *cis-9* in the systematic name of palmitoleic acid denotes that the position of the double bond is between carbons 9 and 10. Two possible conformations, *cis* and *trans*, can be taken by the two CH₂ groups immediately adjacent to the double-bonded carbons. In the *cis* configuration, the one occurring in all biological unsaturated fatty acids, the two adjacent carbons lie on the same side of the double-bonded carbons. In the *trans* configuration, the two adjacent carbons lie on opposite sides of the double-bonded carbons.

Common monounsaturated fatty acids

trivial name	systematic name	number of carbons in chain	typical sources
palmitoleic acid	<i>cis</i> -9-hexadecenoic acid	16	marine algae, pine oil
oleic acid	<i>cis</i> -9-octadecenoic acid	18	animal tissues, olive oil
gadoleic acid	<i>cis</i> -9-eicosenoic acid	20	fish oils (cod, sardine)
erucic acid	<i>cis</i> -13-docosenoic acid	22	rapeseed oil
nervonic acid	<i>cis</i> -15-tetracosenoic acid	24	sharks, brain tissue

Fatty acids containing more than one carbon-carbon double bond ([polyunsaturated fatty acids](#)) are found in relatively minor amounts. The multiple double bonds are almost always separated by a CH₂ group (–CH₂–CH=CH–CH₂–CH=CH–CH₂–), a regular spacing motif that is the result of the biosynthetic mechanism by which the double bonds are introduced into the hydrocarbon chain. [Arachidonic acid](#) (C₂₀) is of particular interest as the precursor of a family of molecules, known as eicosanoids (from Greek *eikosi*, “twenty”), that includes [prostaglandins](#), thromboxanes, and leukotrienes. These compounds, produced by cells under certain conditions, have potent physiological properties, as explained in the section [Intracellular and extracellular messengers](#). Animals cannot synthesize two important fatty acids, linoleic acid (an omega-6 fatty acid) and alpha-linolenic acid (an omega-3 fatty acid), that are the precursors of the eicosanoids and so must obtain them in the diet from plant sources. For this reason, these precursors are called essential fatty acids.

Common polyunsaturated fatty acids

trivial name	systematic name	number of carbons in chain	typical sources
linoleic acid	<i>cis</i> -9-, <i>cis</i> -12-octadecadienoic acid	18	corn oil, animal tissues, bacteria
linolenic acid	<i>cis</i> -9-, <i>cis</i> -12-, <i>cis</i> -15-octadecatrienoic acid	18	animal tissues
	5,8,11-eicosatrienoic acid	20	brain tissue
	8,11,14-eicosatrienoic acid	22	phospholipids
	7,10,13-docosatrienoic acid	22	
	8,11,14-docosatrienoic acid		
arachidonic acid	5,8,11,14-eicosatetraenoic acid	20	liver, brain tissue
	4,7,10,13-docosatetraenoic acid	22	brain tissue
	4,7,10,13,16,19-docosahexaenoic acid	22	brain tissue

[Trans](#) polyunsaturated fatty acids, although not produced biosynthetically by mammals, are produced by microorganisms in the gut of ruminant animals such as cows and goats, and they are also produced synthetically by partial hydrogenation of fats and oils in the manufacture of margarine (the so-called [trans fats](#)). There is evidence that ingestion of *trans* fats can have deleterious metabolic effects.

SUBSTITUENT GROUPS

In addition to the very common fatty acids with straight saturated or unsaturated acyl chains, many fatty acids are chemically modified by substituents on the hydrocarbon chain. For example, the preening gland of ducks secretes a fatty acid 10 carbons long with methyl (CH₃) groups substituted for one of the hydrogens on carbons 2, 4, 6, and 8. Some bacteria produce fatty acids that have a methyl group on the carbon atom farthest from the acidic group or on the penultimate carbon. Other bacteria incorporate a cyclopropane ring near the centre of the acyl chain. The

bacterium that causes [tuberculosis](#) (*Mycobacterium tuberculosis*) synthesizes a whole family of cyclopropane-containing fatty acids called α -mycolic acids. Similar fatty acids are found in related bacteria. A third common constituent is a hydroxyl group (OH). Monohydroxyl acids are found in both plants and animals in relatively small amounts, but they are more prevalent in bacteria.

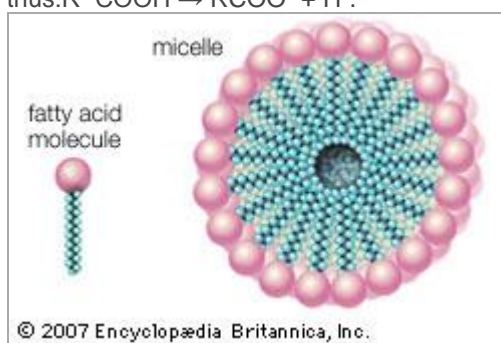
Physical properties

Pure fatty acids form crystals that consist of stacked layers of molecules, with each layer the thickness of two extended molecules. The molecules in a layer are arranged so that the hydrophobic (water-fearing) hydrocarbon chains form the interior of the layer and the hydrophilic (water-loving) carboxylic acid groups form the two faces. For a specific fatty acid the details of the molecular packing may vary, giving rise to different crystal forms known as polymorphs.

The melting temperatures of saturated fatty acids of biological interest are above 27 °C (81 °F) and rise with increasing length of the hydrocarbon chain. Monounsaturated and polyunsaturated molecules melt at substantially lower temperatures than do their saturated analogs, with the lowest melting temperatures occurring when the carbon-carbon double bonds are located near the centre of the hydrocarbon chain, as they are in most biological molecules. As a result, these molecules form viscous liquids at room temperature.

The hydrophobic character of the hydrocarbon chain of most biological fatty acids exceeds the hydrophilic nature of the carboxylic acid group, making the water [solubility](#) of these molecules very low. For example, at 25 °C (77 °F) the solubility in grams of fatty acid per gram of solution is 3×10^{-6} . Water solubility decreases exponentially with the addition of each carbon atom to the hydrocarbon chain. This relationship reflects the energy required to transfer the molecule from a pure hydrocarbon solvent to water. With each CH₂ group, for instance, more energy is required to order water molecules around the hydrocarbon chain of the fatty acid, which results in the hydrophobic effect.

In pure water the carboxylate group can dissociate a positively charged hydrogen ion to only a very small degree thus: $R-COOH \rightarrow RCOO^- + H^+$.



Here R represents the hydrocarbon chain. The carboxylate ion, bearing a negative charge, is more polar than the undissociated acid. RCOOH can be converted completely to the ion RCOO⁻ by adding an equal number of molecules of a base such as sodium hydroxide (NaOH). This effectively replaces the H⁺ with Na⁺ to give the salt of the fatty acid, which is a [soap](#). The very useful detergent property of soaps stems from the fact that the RCOO⁻ anions in water spontaneously form stable, spherical aggregates called micelles. The interior of these structures, formed by the hydrocarbon chains, is an excellent solvent in which grease and hydrophobic dirt of all sorts can be sequestered. The diameter of each [micelle](#) is roughly twice the length of the extended fatty acid.

Dispersions of micelles in water can be made quite concentrated and exhibit great cleansing power. These dispersions are stable and generally look very much like pure water. Bubbles and foams on the surface of soap dispersions are the result of the spontaneous adsorption of RCOO^- ions at the interface between the aqueous dispersion and air, with the result that the air-water interfaces are energetically stabilized and can therefore be mechanically expanded.

Chemical properties

The most chemically reactive portion of fatty acids is the acidic [carboxyl group](#) (COOH). It reacts with alcohols ($\text{R}'\text{OH}$) to form products known as [esters](#) (RCOOR') and releases water in the process. This [ester](#) bond is the principal covalent bond linking fatty acid moieties to other groups in the more-complex lipids discussed in other sections of this article. A second chemical bond, occurring much less frequently in biological lipids involving fatty acids, is the [ether](#) bond ($\text{R}'\text{-O-R}$). Ether bonds are chemically more stable than ester bonds.

The hydrocarbon part of a fatty acid molecule is quite resistant to chemical attack unless carbon-carbon double bonds are present. A number of different kinds of molecules react with such a double bond. For example, when a catalyst such as platinum is present, hydrogen gas adds to the double bond to give a saturated fatty acid. [Halogens](#) (chlorine, bromine, and iodine) and their derivatives such as hydroiodic acid (HI) also react with the double bond to form saturated fatty acids, but in these cases one or two atoms of the halogen replace one or two of the hydrogens normally found in the saturated acyl chain. Carbon-carbon double bonds can also react with oxygen in either nonenzymatic processes or enzymatically catalyzed oxidation reactions. This process generates a variety of products, some of which contribute to the rancid smell in spoiled meat and vegetable products. In general, the more highly unsaturated the fatty acid, the more easily it is oxidized.

Waxes

A second group of neutral lipids that are of physiological importance, though they are a minor component of biological systems, are waxes. Essentially, waxes consist of a long-chain fatty acid linked through an ester oxygen to a long-chain [alcohol](#). These molecules are completely water-insoluble and generally solid at biological temperatures. Their strongly hydrophobic nature allows them to function as water repellents on the leaves of some plants, on feathers, and on the cuticles of certain insects. Waxes also serve as energy-storage substances in [plankton](#) (microscopic aquatic plants and animals) and in higher members of the aquatic food chain. Plankton apparently use the biosynthesis of waxes to adjust their buoyant density and thus their depth in the ocean. It has been suggested that a major source of [petroleum](#) found in deep-sea sediments originates from the deposition of wax-rich dead plankton over vast periods of time. Whales and many fishes also store large quantities of waxes.

GLYCEROPHOSPHOLIPIDS

Lipids of this class are the most abundant in biological membranes. In glycerophospholipids, fatty acids are linked through an ester oxygen to carbons 1 and 2 of glycerol, the backbone of the molecule. Phosphate is ester-linked to carbon 3, while any one of several possible substituents is also linked to the **phosphate** moiety. Glycerophospholipids are amphipathic—glycerol and phosphate form the polar end of the molecule, while hydrocarbon chains form the nonpolar end. Although the fatty acids can be any of those common in biological systems, usually those attached to carbon 1 are saturated and those attached to carbon 2 are unsaturated. The various combinations of two fatty acids give rise to many different molecules bearing the same substituent group. Since this is true for each head group, there are altogether about a thousand possible types of glycerophospholipids. The great majority are found in biological membranes.

From the standpoint of physical properties, the greatest difference among various molecules lies in the particular substituent. This is due in part to the different sizes of the various types and in part to differences in their electric charges. The phosphatidylcholines and phosphatidylethanolamines are zwitterionic, meaning they have one

negative and one positive charge on the substituent group. Phosphatidic acid, **phosphatidylserine**, and **phosphatidylinositol** have a net negative charge. Differences in fatty acid composition also contribute to differences in physical properties of a series of molecules with the same substituent. In the presence of an excess of water, the molecules form aggregates with a variety of geometries, the most common of which is the **bilayer**.

In bilayers many glycerophospholipids as well as **sphingomyelin** (discussed below) can be in either one of two states, gel or liquid-crystalline. In the solidlike gel state, the lipid molecules in each half of the bilayer are arranged in a two-dimensional lattice, with their two acyl chains in the extended form. With the application of heat, the gel converts into the liquid-crystalline state at some temperature characteristic of the lipid mixture. In this state the molecules in each half of the bilayer remain in a fairly regular two-dimensional lattice but are free to rotate about their long axes and slide laterally through the layer. Their acyl chains now undergo considerable motion, leading to transiently kinked conformations. These motions give the bilayer a quasi-liquid behaviour that is characteristic of the bilayers in all biological membranes.

SPHINGOLIPIDS

A second major class of lipids usually associated with the membranes surrounding cells is sphingolipids.

Sphingolipids are based on an 18-carbon amine alcohol, sphingosine, and to a much lesser extent on a 20-carbon analog, phytosphingosine. All but one generic member of this class have a simple or complex sugar linked to the alcohol on carbon 1. The single deviant member is sphingomyelin, a molecule with a phosphorylcholine group (the same polar head group as in phosphatidylcholine) instead of the sugar moiety, making it an analog of phosphatidylcholine. All sphingolipids have, in addition to the sugar, a fatty acid attached to the amino group of sphingosine. Among the sphingolipids, only sphingomyelin, a **phospholipid**, is a major component of biological membranes.

The principal factor determining the physical properties of sphingolipids is the substituent group attached to carbon 1 of sphingosine. Minor variations in properties depend upon the particular fatty acid component.

The **glycosphingolipids**, all containing a sugar attached to carbon 1 of sphingosine, have physical properties that depend primarily on the complexity and composition of this substituent. Two generic types of glycosphingolipids are recognized: neutral glycosphingolipids, which contain only neutral sugars, and gangliosides, which contain one or more sialic acid residues linked to the sugar. Many hundreds of different glycosphingolipids have been isolated, and many more unidentified types probably exist. Glycosphingolipids are found exclusively on the external surface of the cell membrane, where their sugar moieties often act as antigens and as receptors for hormones and other signaling molecules.

Cholesterol and its derivatives

Cholesterol may be the most intensely studied small molecule of biological origin. Not only are its complex biosynthetic pathway and the physiologically important products derived from it of scientific interest, but also the strong correlation in humans between high blood cholesterol levels and the incidence of [heart attack](#) and [stroke](#) (diseases that are leading causes of death worldwide) is of paramount medical importance. The study of this molecule and its biological origin have resulted in more than a dozen Nobel Prizes.

Cholesterol is a prominent member of a large class of lipids called [isoprenoids](#) that are widely distributed in nature. The class name derives from the fact that these molecules are formed by chemical condensation of a simple five-carbon molecule, [isoprene](#). Isoprenoids encompass diverse biological molecules such as [steroid hormones](#), sterols (cholesterol, [ergosterol](#), and sitosterol), bile acids, the lipid-soluble vitamins (A, D, E, and K), phytol (a lipid component of the photosynthetic pigment chlorophyll), the insect juvenile hormones, plant hormones (gibberellins), and polyisoprene (the major component of natural rubber). Many other biologically important isoprenoids play more-subtle roles in biology.

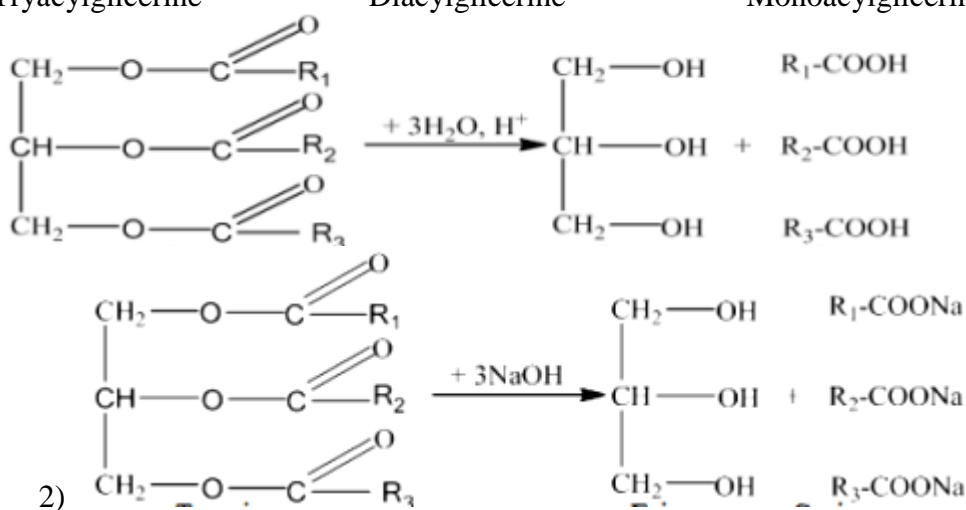
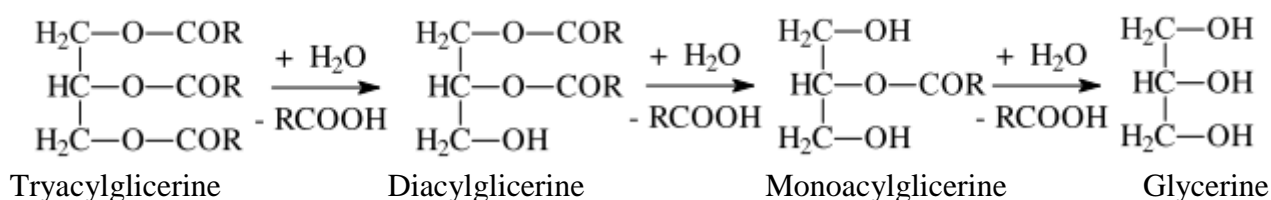
Structure and properties

The sterols are major components of biological membranes in eukaryotes (organisms whose cells have a nucleus) but are rare in prokaryotes (cells without a nucleus, such as bacteria). Cholesterol is the principal sterol of animals, whereas the major sterol in fungi is **ergosterol** and that in plants is sitosterol. The characteristic feature of each of these three important molecules is four rigidly fused carbon rings forming the **steroid nucleus** and a hydroxyl (OH) group attached to the first ring. One molecule is distinguished from another by the positions of the carbon-carbon double bonds and by the structure of the hydrocarbon side chain on the fourth ring.

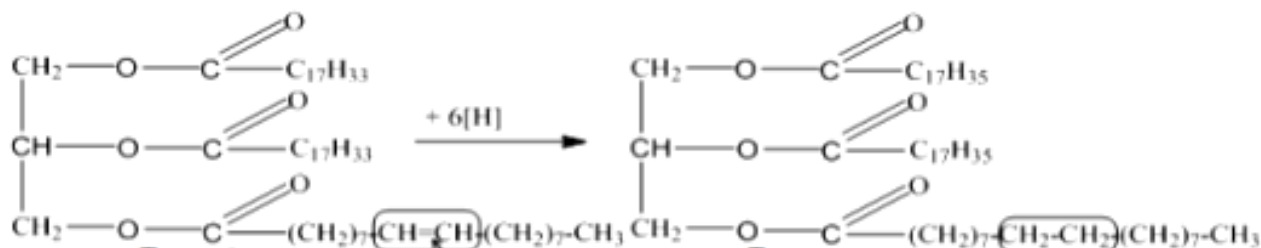
Cholesterol and its relatives are hydrophobic molecules with exceedingly low water solubility. The overall hydrophobicity is negligibly affected by the hydrophilic OH group. The structure of cholesterol is such that it does not form aggregates in water, although it does shoehorn between the molecules of biological membranes, with its OH group located at the water-membrane interface. The stiff fused ring structure of cholesterol adds rigidity to liquid-crystalline phospholipid bilayers and strengthens them against mechanical rupture. Cholesterol is thus an important component of the membrane surrounding a cell, where its concentration may rise as high as 50 percent by weight.

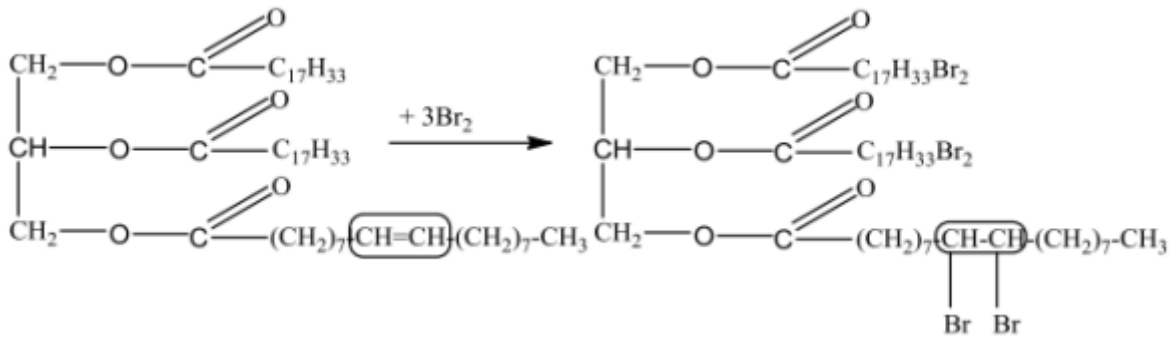
Chemical properties

1) Acid hydrolyses

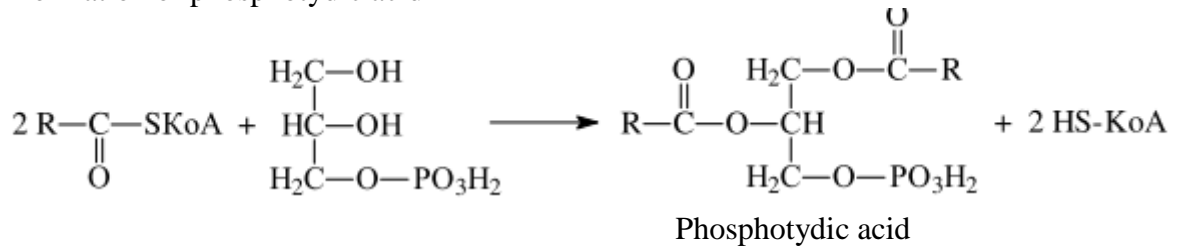


3) If lipids contain unsaturated bonds in fatty acid radicals addition reaction is observed.

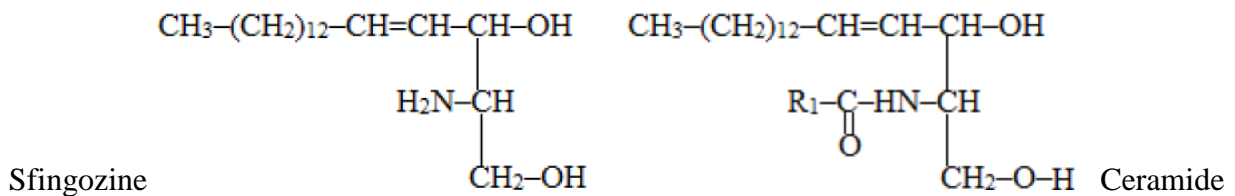




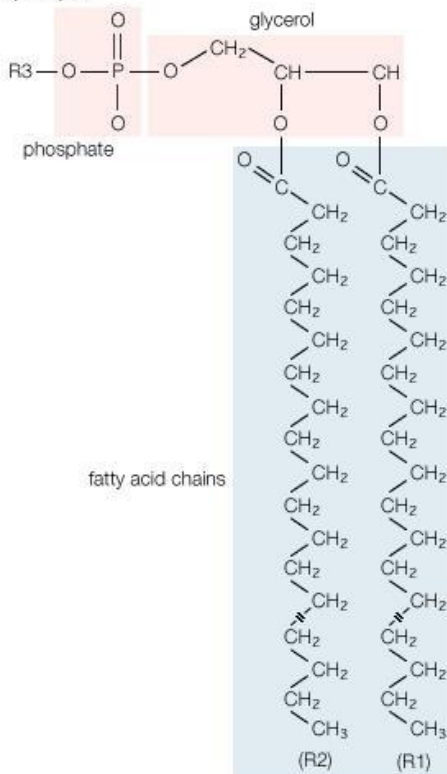
4) Formation of phosphotydic acid



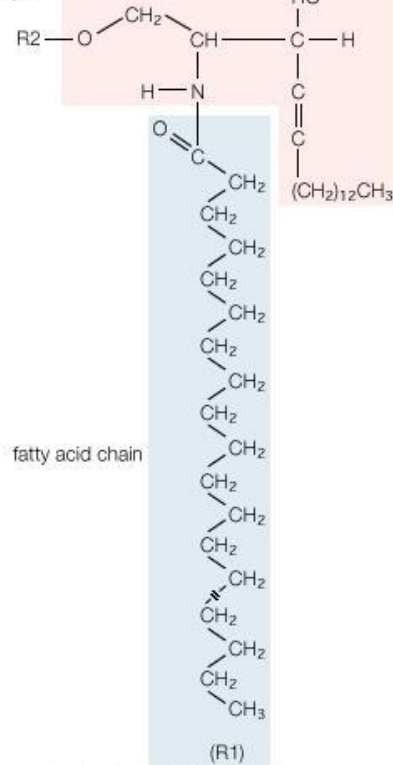
Compound saponifiable Lipids



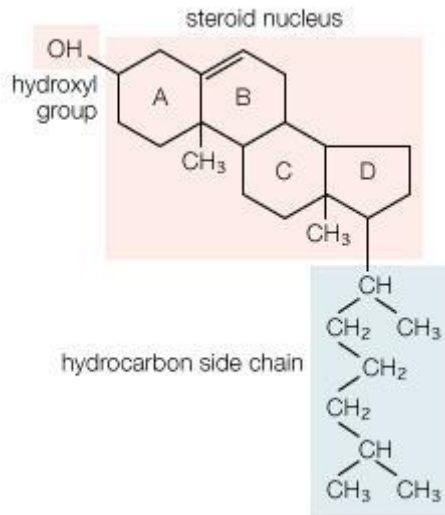
glycerophospholipid



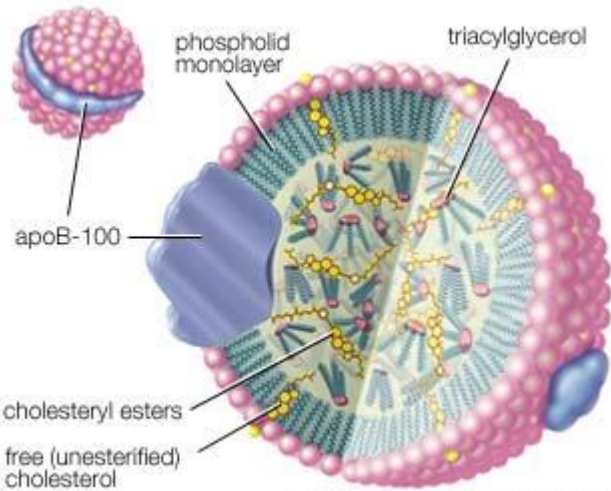
sphingolipid



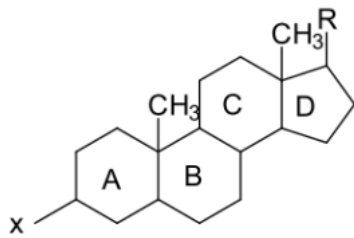
cholesterol



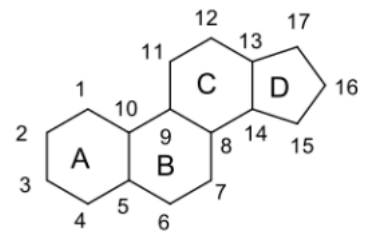
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Steroids, where (x – OH; –OR ; =O)



Sterane

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