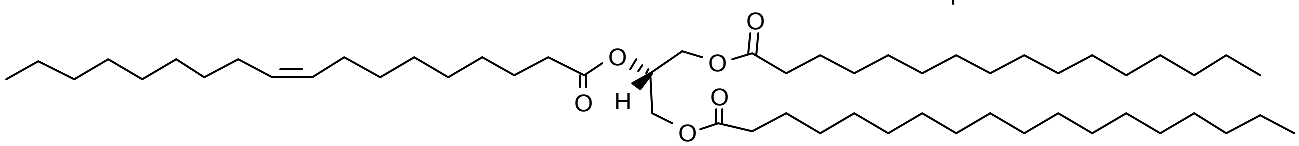
LIPIDS

TRIGLYCERIDES

Natural fats and oils are triglycerides **-** triesters of glycerol with fatty acids, the natural carboxylic acids with an even number of carbons an unbranched chain, some with **(Z)** double bonds. Their biosynthesis from acetate accounts for the even number of carbons. Many fatty acids are available to higher organisms **only** through their diet, and are thus "essential"; for humans this is especially true of some of the unsaturated ones. These glycerol esters have specific structures for specific purposes in each organism, and are often chiral. Their most important role is the construction of cell membranes, with energy storage a secondary role. You are familiar with them as the fat in foods. Liquid fats tend to be more unsaturated than solid fats **-** the **(Z)** double bonds force an bend in the chain which keeps the chains from packing into a solid. The unsaturated fats in foods often come from dehydrogenated saturated fats; their unnatural **(E)** double bonds provide structure and activity more like saturated fats (including obstruction of the arteries) than the natural **(Z)** compounds. Often fatty acid structures are reported by the number of carbons and the number of double bonds, e.g. 18:1 is oleic and 20:4 arachidonic, without specifying their position (natural stereochemistry is ***Z***).

Cocoa butter contains: palmitic

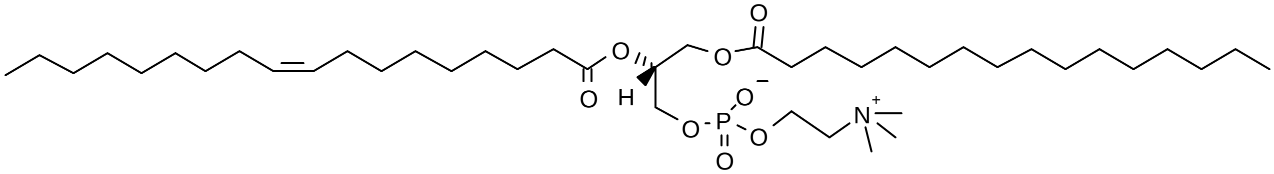


oleic stearic

Hydrolysis of these esters in base - saponification - was one of the earliest chemical reactions discovered, and is still used today to make soaps, the salts of fatty acids. The salts have long greasy water-insoluble tails and charged water-soluble heads. They aggregate in stable micelles with the hydrocarbon tails tucked inside and the charged (hydrophilic) heads exposed to the water. They also form double-layered vesicles with the hydrocarbon tails next to each other (a bilayer) and water inside and out. They clean by dissolving oils in the non-polar interior of the micelles, suspending the oil in water in the micelles, a process called emulsification. Detergents copy these properties, using sulfates and ammonium salts to provide the hydrophilic ends and both alkyl and aromatic groups to provide the non-polar, hydrophobic, ends.

PHOSPHOLIPIDS

Replacement of one of the fatty acids in a triglyceride with a phosphoric acid to create an **(R)** glycerol triester generates a phopholipid. It has two more reactive OH's on the phosphorus. In nature, one OH is ionized and the other esterified, usually with a group that can hold a positive charge, like choline or ethanolamine, giving families of structures like the lecithins. These phospholipids also self-assemble into micelles and vesicles; the vesicle bilayer structure forms the membranes of most cells. As with triglycerides, the **(Z)** shape of the unsaturated fatty acids, makes the phospholipid more liquid-like and the membrane more flexible. Membrane flexibility and permeability is also modified by the incorporation of proteins and of other lipids such as cholesterol and its esters. Phospholipids are effective emulsifiers and are often added to processed foods to prevent separation of the oil and water phases.



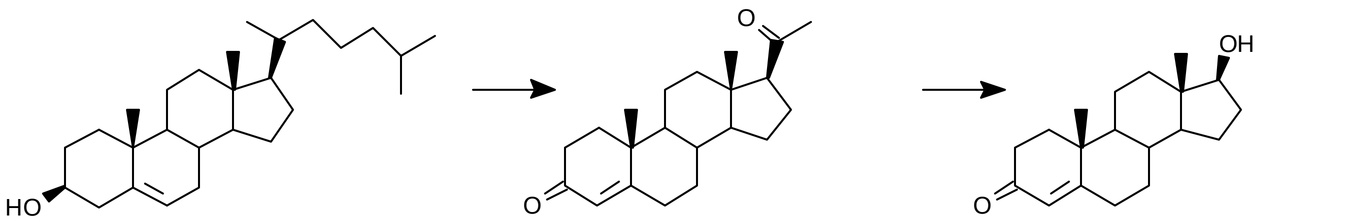
a phosphatidyl choline (lecithin)

SPHINGOLIPIDS

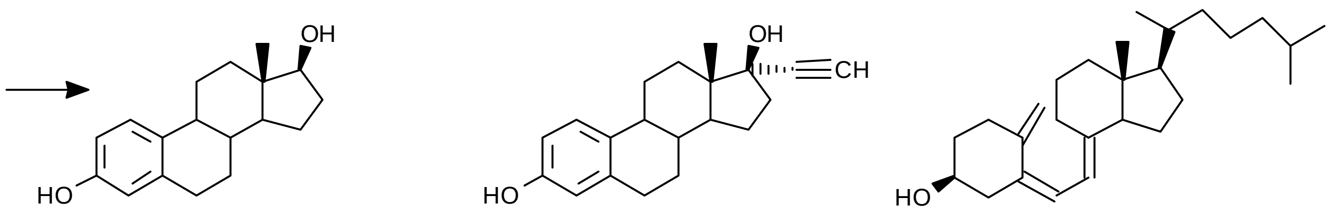
Sphingolipids form specialized membranes of nerve cells in the brain; they are phosphatidylcholine esters like lecithin, but have a long carbon chain as part of the backbone, instead of glycerol, and an amide linkage instead of one of the esters.

STEROIDS

The structure of steroids bears no resemblance to glycerides. They are called lipids primarily because of the fat-solubility conferred by their high hydrocarbon content; the alcohols are often found in the body as fatty acid esters, e.g. cholesterol. Steroid biosynthesis is begun in plants by the production of terpenes; the cyclization of squalene to lanosterol produces the steroid ring system, which is then modified by organs and organisms to produce needed hormones. By far the most important steroid is cholesterol, used to modify the flexibility of cell membranes and as a starting material for most of the other steroids: the sex hormones estrogen, progesterone and testosterone, the adrenal hormone cortisone, the D vitamins and the bile acids. Steroids modified to prevent their destruction in the stomach, such as ethynylestradiol, are used as hormone supplements and in birth control pills.



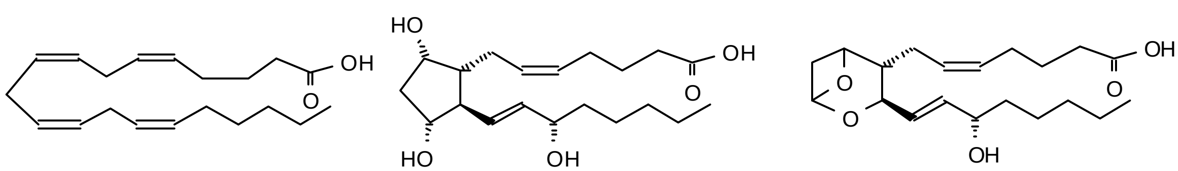
cholesterol progesterone testosterone



estradiol ethynylestradiol Vitamin D_3

PROSTAGLANDINS

These interesting acids are synthesized from the essential arachidonic acid (20:4). Like the steroids, prostaglandins (PG=s) serve as hormones, messenger molecules which regulate metabolic activity, particularly smooth muscle activity, inflammation, gastric secretions. Natural and modified prostaglandins have been used to induce labor (early or at term) and to treat cardiovascular disorders.



arachidonic acid $PGF_{2\alpha}$ thromboxane

FURTHER READING

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