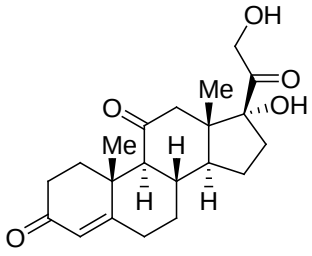
Module 10 Lipids

Lecture 27 Lipids I

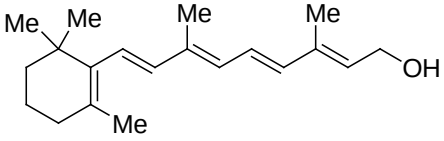
10.1 Introduction

Lipids are organic compounds that are found in living organisms. They have variety of structures and functions, and soluble in organic solvents due to their hydrocarbon component. Scheme 1 illustrates some examples:

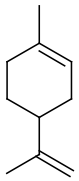


Cortisone

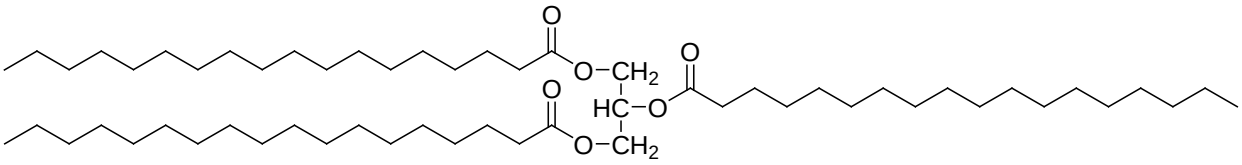
Hormone



Vitamin A



Limonene
in orange and lemon oils



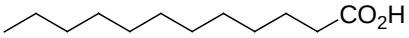
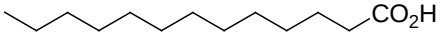
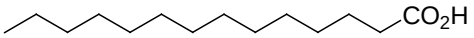
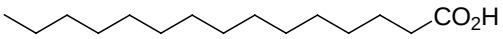
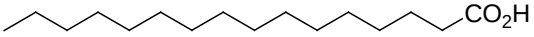
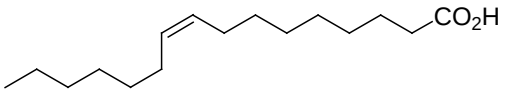
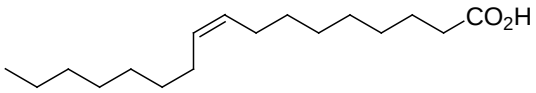
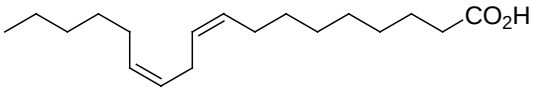
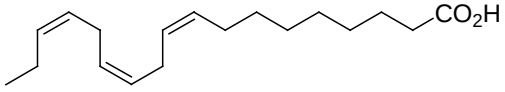
Tristearin

Fat

Scheme 1

10.2 Fatty Acids

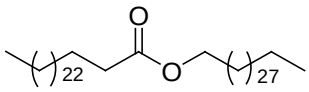
Fatty acids are unbranched carboxylic acids having long hydrocarbon chains (Scheme 2). Most of the naturally available fatty acids bears an even number of carbon atoms due to their synthesis from acetate. Both saturated and unsaturated fatty acids are available. In unsaturated fatty acids, the double bonds have cis-configuration and are separated by one CH_2 group. Thus, unsaturated fatty acids have less intermolecular interactions compared to saturated fatty acids. As a result, the unsaturated fatty acids have lower melting points in comparison to saturated fatty acids. The melting point decreases as the number of double bonds increases.

Number of Carbons	Common Name	Structure	Melting Point (^oC)
Saturated			
12	Lauric acid		44
14	Lauric acid		58
16	Palmitic acid		63
18	Stearic acid		69
20	Arachidic acid		77
Unsaturated			
16	Palmitoleic acid		0
18	Oleic acid		13
18	Linoleic acid		-5
18	Linolenic acid		-11

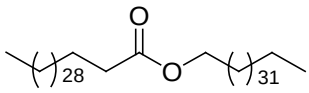
Scheme 2

10.3 Waxes

Waxes are esters of long chain carboxylic acids with long chain alcohols. For example, beeswax contains a 26 carbon carboxylic acid and a 30 carbon alcohol component, while carnauba wax has a 32 carbon carboxylic acid component and a 34 carbon alcohol component. The latter is an example for a hard wax, and is widely used as a car wax and in floor polishes (Figure 1).



a major component of beeswax



a major component of carnauba wax

Figure 1

Waxes are also common in living organisms (Figure 2). For example, wax is found on the surfaces of some leaves, where it serves as protectant against parasites and minimizes the

evaporation of water. Similarly, the feathers of birds are coated with wax to make them water repellent.

Figure 2

10.4 Fats and Oils

The solid or semisolid triglycerides at room temperature are called fats, while the liquid is called oil (Figure 3). Fats are generally obtained from animals, while oils come from plant products. In fats, saturated fatty acid is usually involved in the formation of ester with glycerol, whereas in oils, unsaturated fatty acid is involved. In case of fats, the saturated fatty acid chain can pack closely together causing them to be solids at room temperature. In case of oil, the unsaturated fatty acid chain can not pack tightly together, and therefore, that leads to usually have low melting points.

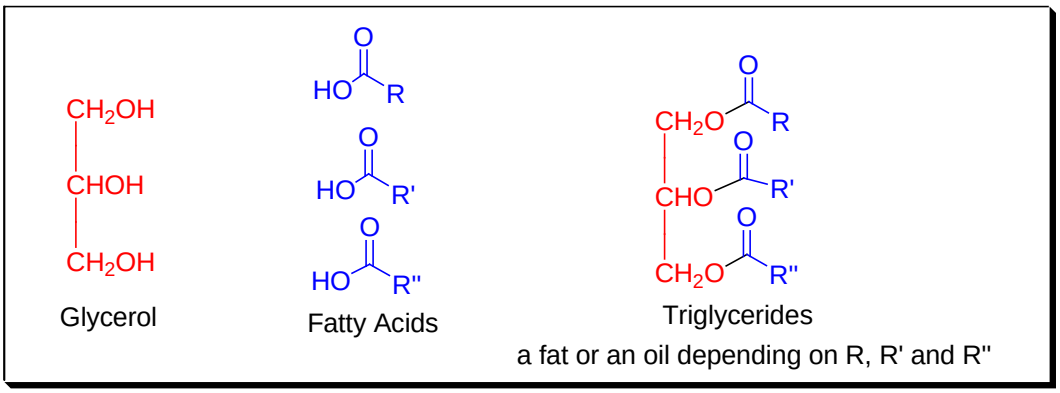
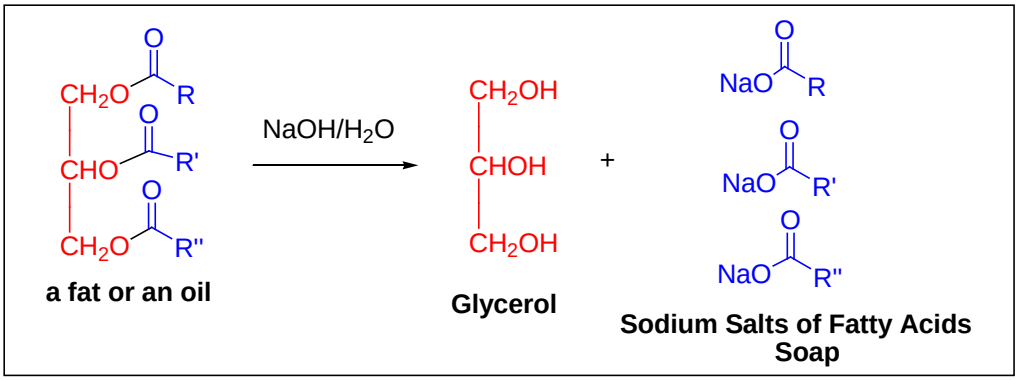


Figure 3

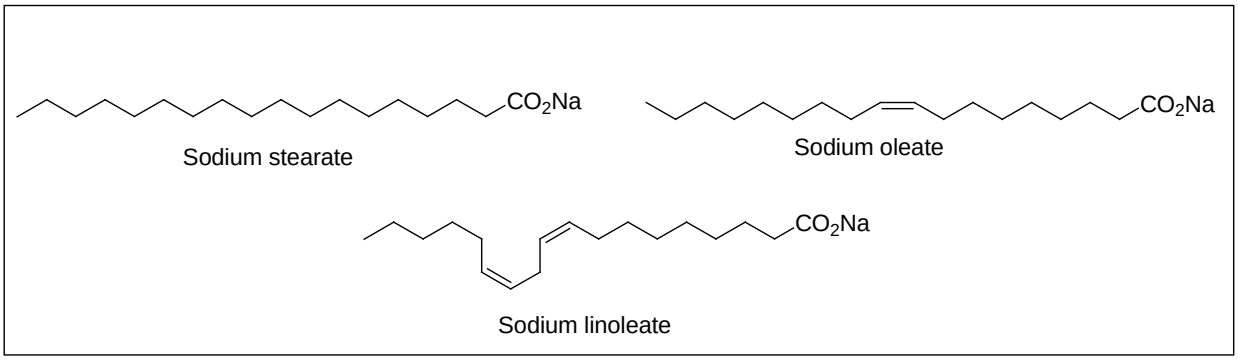
Polyunsaturated fats and oils are prone to undergo oxidation by O_2 via radical reaction. The allylic H is the one that is easily removed because the resulting radical is resonance stabilized by the [illegible] oxidation reaction and smell associated with sour milk and rancid butter.

10.5 Soaps, Detergents and Micelles

Sodium or potassium salts of fatty acids are called soaps. They are obtained by basic hydrolysis of triglycerides which is called saponification (Scheme 3). Scheme 4 shows the three most common soaps used. In aqueous solution, the long chain carboxylic acids arrange themselves in spherical clusters called micelles as shown in Figure 4. Each micelle contains 50-100 long-chain carboxylates.



Scheme 3



Scheme 4

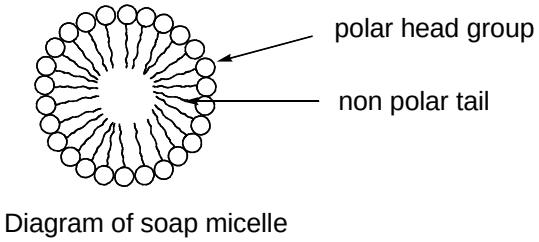
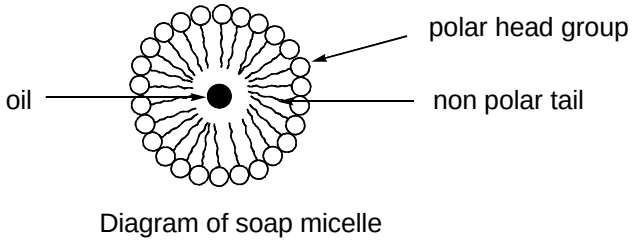


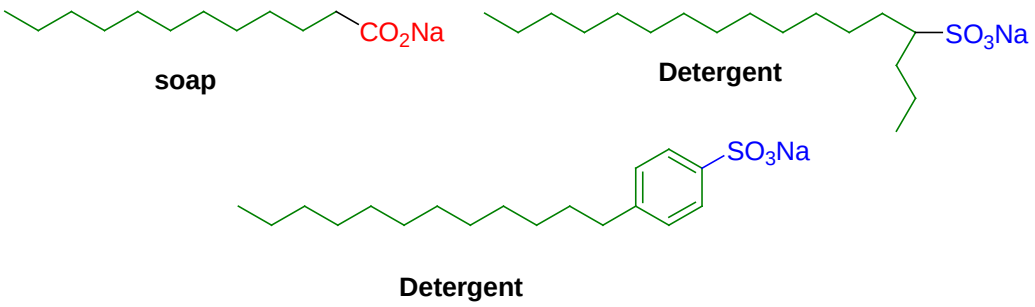
Figure 4

Soap contains the cleaning property because nonpolar oil that carry dirt dissolve in the nonpolar interior of the micelle and are carried out away with the soap during rinsing.



Scheme 5

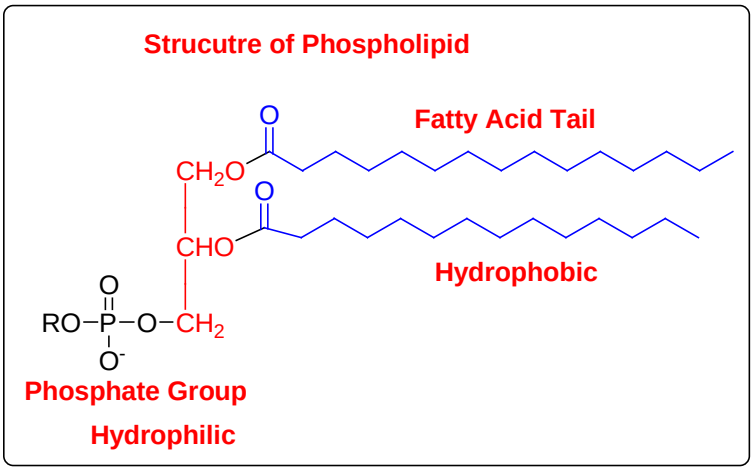
Since soap can undergo precipitation (soap scum) in hard water due to reaction with calcium and magnesium ions, synthetic soaps (salt of benzenesulphonic acid) called detergents have been developed that don't form soap scum in hard water.

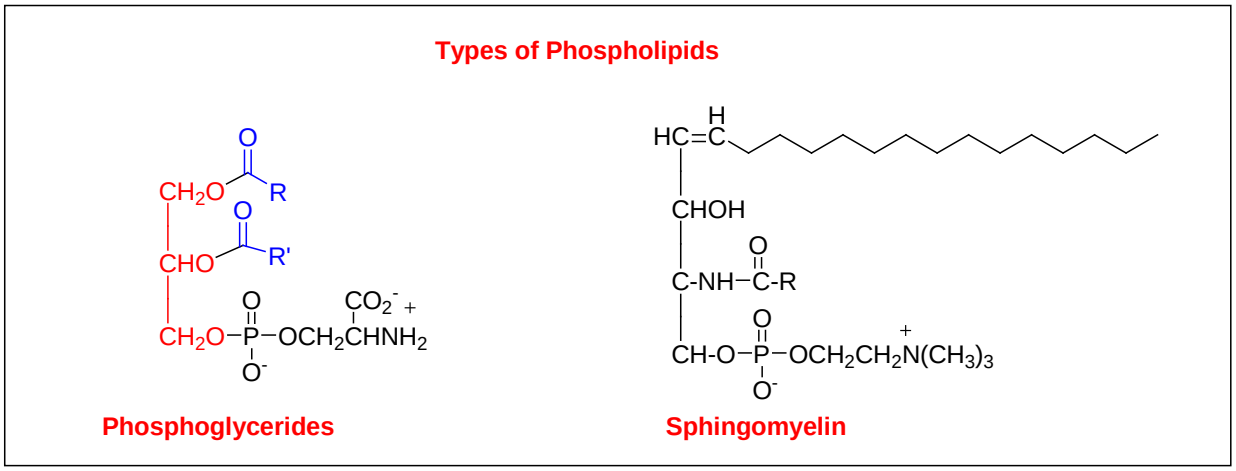


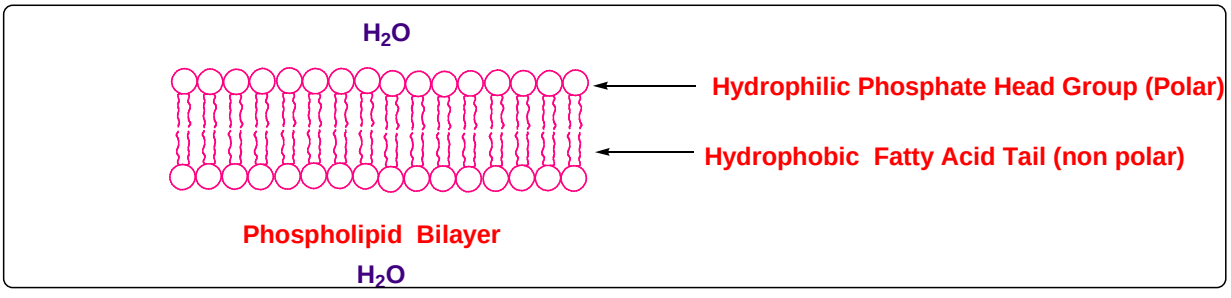
Scheme 6

10.6 Phospholipids

Lipids that contain a phosphate group are called phospholipids. There are two kinds of phospholipids: phosphoglycerides and sphingolipids (Scheme7). These lipids form membranes by arranging themseleves in a lipid bilayer. The polar hydrophilic groups of the phospholipids are on the outside of the bilayar, while non-polar fatty acid tail form interior of the bilayer.







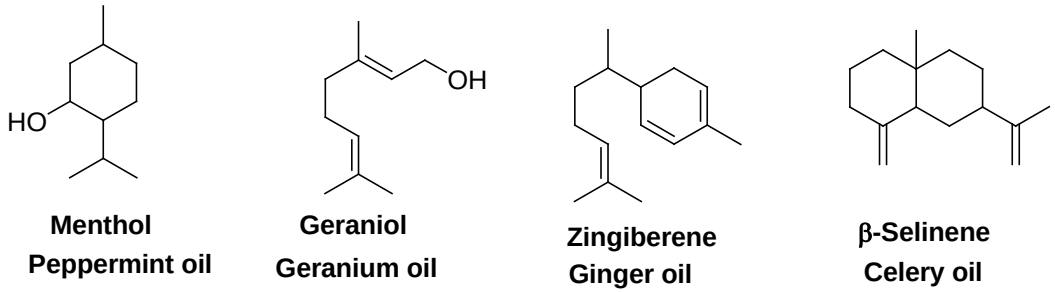
Scheme 7

Module 10 Lipids

Lecture 28 Lipids II

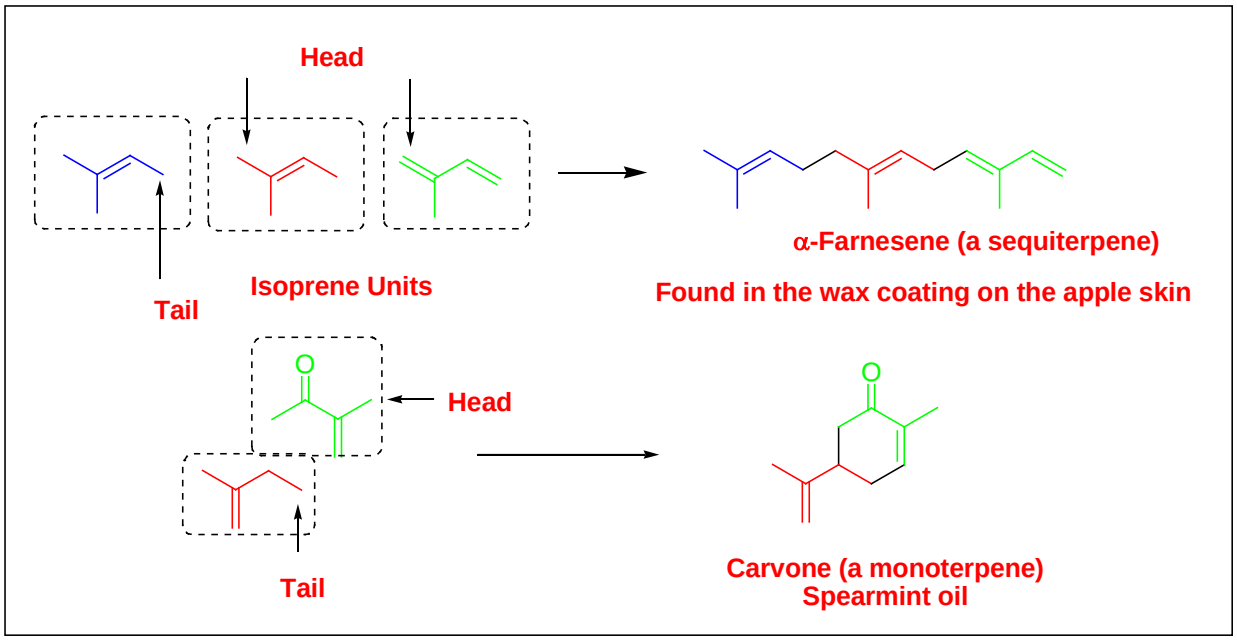
10.7 Terpenes

Terpenes are available in nature as a diverse class of lipids. Some of them are used as spices, perfumes and medicines for thousands of years (Scheme 1). The terpenes having functional groups such as OH and carbonyl group are called terpenoids.



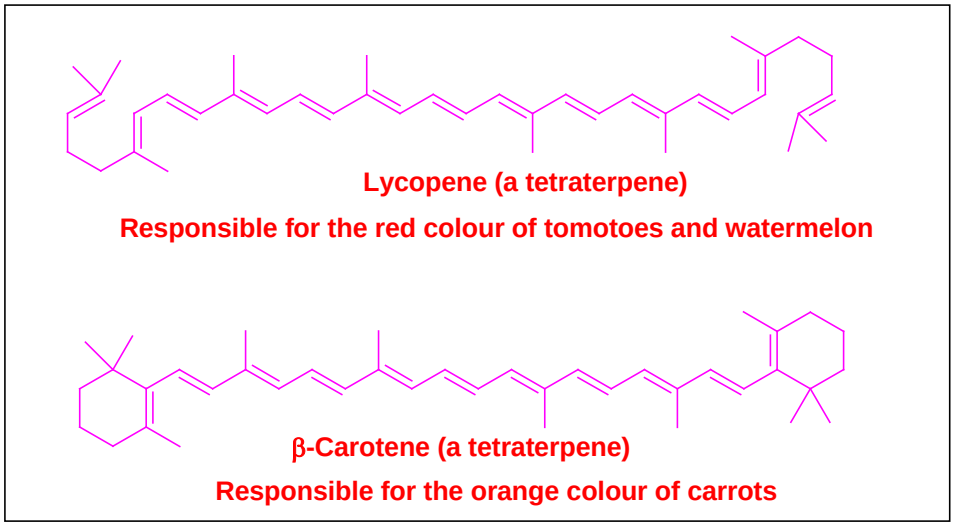
Scheme 1

The naturally available terpenes are usually made by joining together the isoprene units, usually in head-to-tail fashion. For examples, Scheme 2 shows the head-to-tail joining of the isoprene units.



Scheme 2

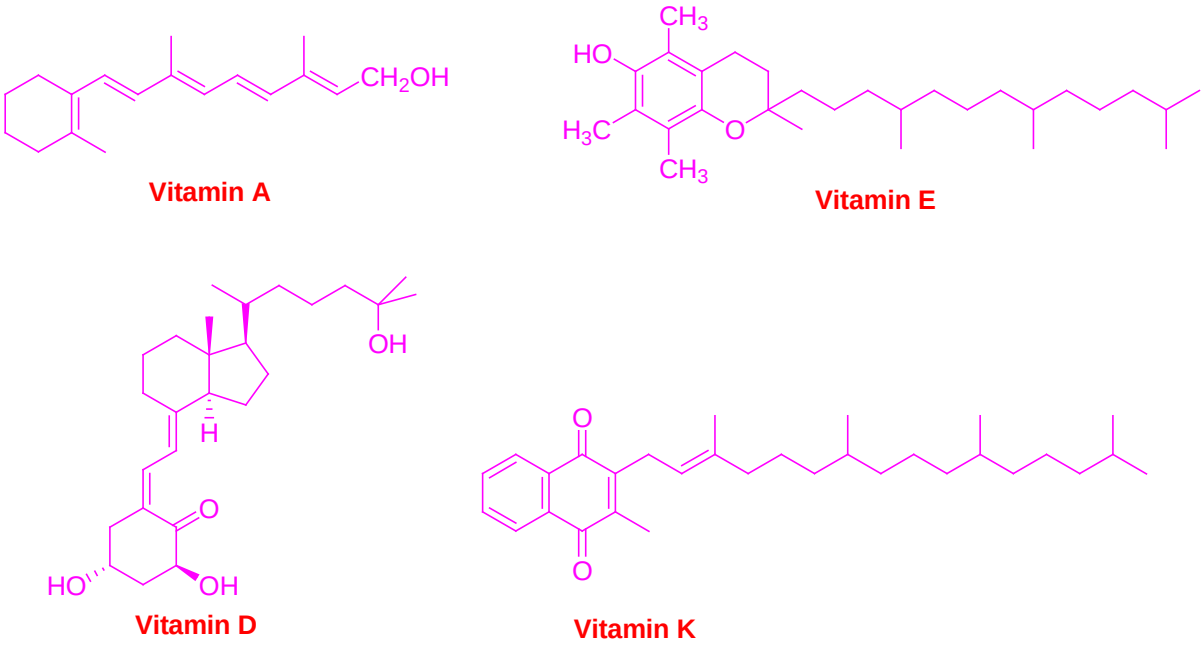
Scheme 3 shows examples for tetraterpenes having eight isoprene units which are responsible for colours of tomatoes and carrots.



Scheme 3

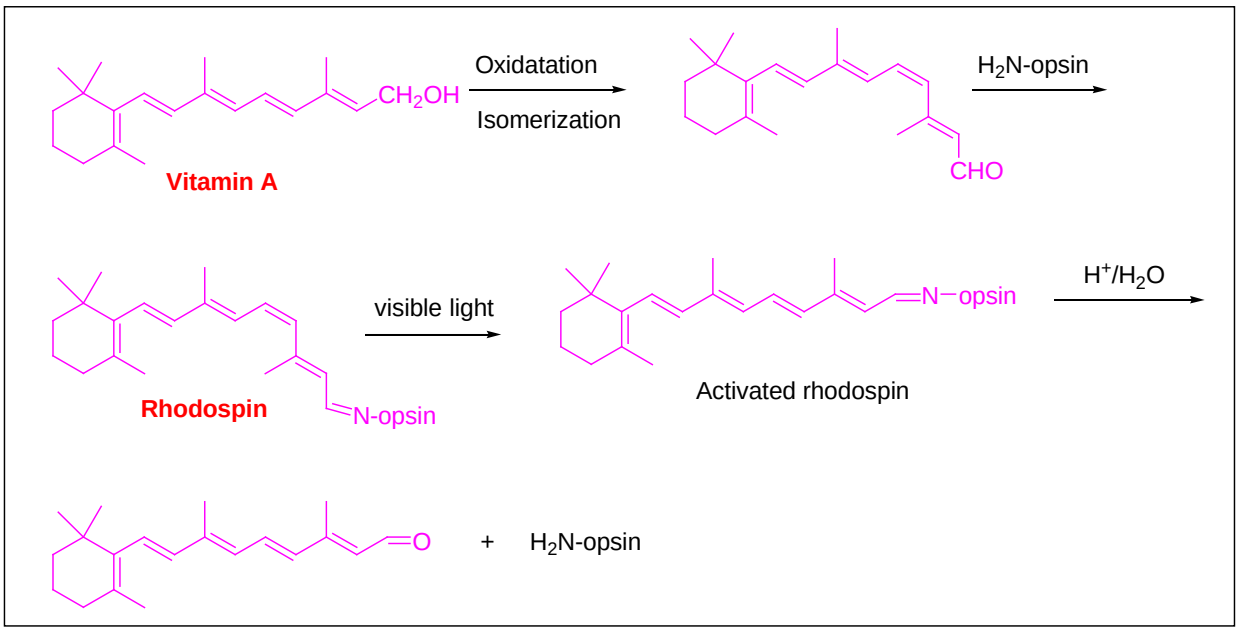
10.8 Vitamins

- Vitamins A, D, E and F are lipids (Scheme 4). Cleaving of -carotene generates two molecules of vitamin A that plays important role in vision. Vitamin A is also called as retinol.

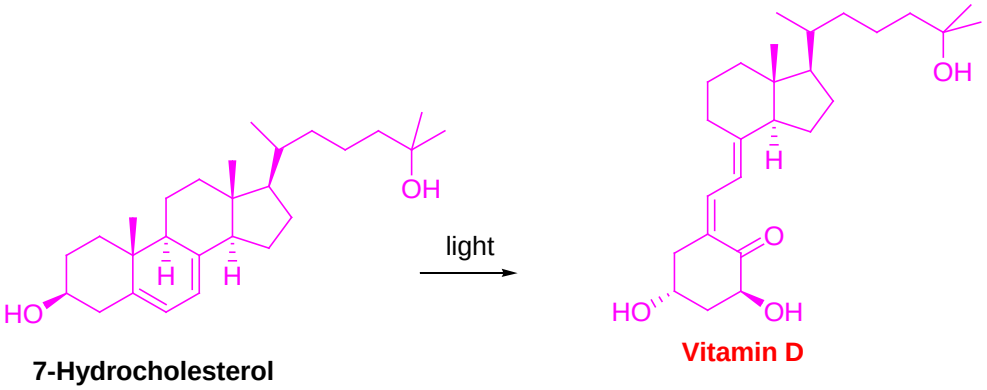


Scheme 4

Scheme 5 describes the chemistry of vision. In retinol, the cone cells are responsible for vision in bright light, while the rod cells are responsible for the vision in the dim light. In rod cells, the vitamin A is oxidized to aldehyde that undergoes isomerization of *trans* double to *cis* double bond at C-11 carbon. The latter reacts with protein opsin to form an imine with (C-11 Z)-retinal, giving rhodopsin. When rhodopin absorbs light, the *cis* double bond isomerizes to a *trans* double bond. This geometry change causes an electrical signal to be sent to the brain, where it is perceived as a visual image. The *trans* isomer of rhodospin is not stable, thus, it undergoes hydrolysis to give (11E)-retinal and opsin. (C-11 E)-Retinal is then transformed back to (C-11 Z)-retinal to complete the vision cycle.



Scheme 5. The Chemistry of Vision



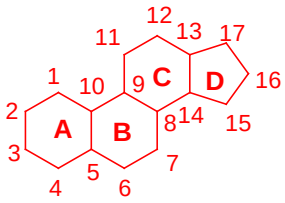
7-Hydrocholesterol **Vitamin D**

Scheme 5

- Vitamin K is required for proper clotting of blood. The deficiency of vitamin K is rare due its presence in the leaves of green plants as well as its synthesis by intestinal bacteria.
- Vitamin E is a radical inhibitor (anti-oxidant) found in biological system. It is water insoluble and traps radicals formed in non-polar membranes.
- The body synthesizes vitamin D from 7-hydrocholesterol, found in skin, in the presence of ultraviolet light.

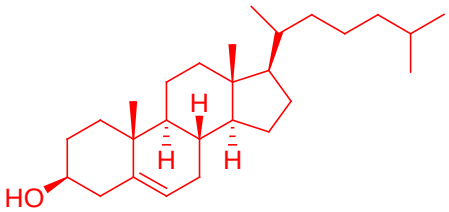
10.9 Steroids

Steroids are lipids having a tetracyclic system composed of three six membered rings and one five membered ring. Their non-polar character allows them to cross the cell membranes, so they can leave the cells in that they are produced and enter their target cells.



The Steroid Ring System

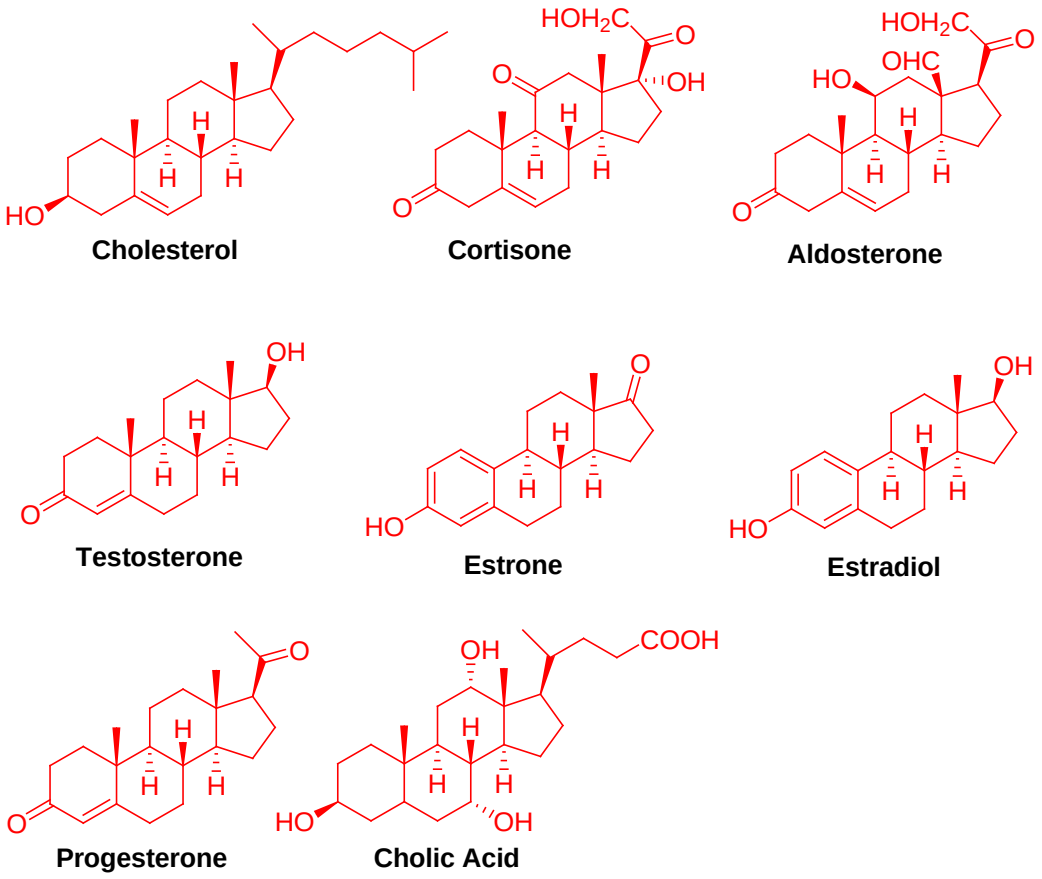
In animals, the most abundant member of steroid is cholesterol, which is the precursor of all other steroids. Cholesterol has 8 asymmetric centers, thus 256 stereoisomers are possible. However, in nature only one exists. Cholesterol is an important component of cell membranes and related to heart disease.



Cholesterol

Steroids can be broadly classified into five groups: glucocorticoids, mineralocorticoids, androgens, estrogents, and progestins.

- Glucocorticoids are involved in metabolism of glucose, proteins and fatty acids. Cortisone is an example for this type of steroid. Cortisone is used as anti-inflammatory agent to treat arthritis.
- Mineralocorticoids are responsible for the increased reabsorption of Na^+, Cl^- and HCO_3^- ions by the kidneys that can lead to an increase in the blood pressure. Aldosteron is an example of a mineralocorticoid.
- Antrogens are male sex hormones. They are responsible for the development of male secondary sex characteristics during puberty. Testosterone is an example of androgens.
- Estrone and estradiol are female sex hormones known as estrogens. They are responsible for the development of female secondary characteristics and secreted by the ovaries. Estrogens also regulate the menstrual cycle.
- Progesterone is the hormone that is essential for the maintenance of preganancy. It also prevents ovulation during pregnancy.

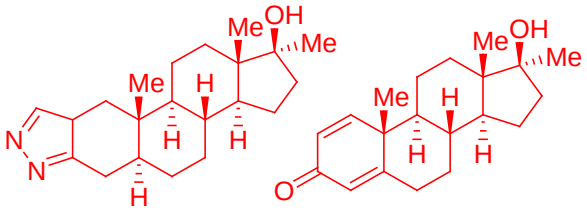


Scheme 6

In addition to the precursor of all the steroid hormones in animals, cholesterol is also precursor for the synthesis of the bile acids. For example, the bile acid, cholic acid synthesized in liver, stored in gallbladder and secreted into the small intestine, where it acts as an emulsifying agent so that fats and oils can be digested by water-soluble enzymes.

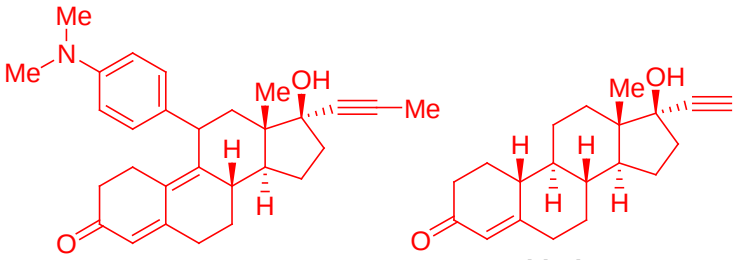
10.9 Synthetic Steroids

The potent physiological properties of naturally occurring steroids have led to the development of synthetic steroids. For examples, stanozolol and dianbol are drugs developed in this way exhibit the same muscle-building effect as testosterone.



Stanozolol **Dianabol**

Some of the synthetic steroids have been found to be more potent than natural steroids. For examples, norethindrone is better than progesterone in arresting ovulation, while RU 486 terminates preganancy within the first nine weeks of gestation. These oral contraceptives have structures similar to that of progesterone.



RU 486 **Northindrone**