Chapter 1

BASICS ON LIPID CHEMISTRY

This chapter deals with the basics of lipid chemistry. Chemical structures, biosynthetic pathway and some properties of important lipids are explained.

1-1 Saturated fatty acid

Saturated fatty acids have no double bond in the carbon chains. Naturally occurring fatty acids usually have carbons of even numbers, but the ones with odd number of carbons also exist. Acids from C_2 to C_{30} (or longer) are known, but the most common and most important fall in the range of C_{12} to C_{22}. Table 1-1-1 shows some major saturated fatty acids.

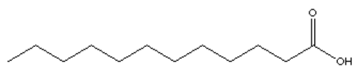
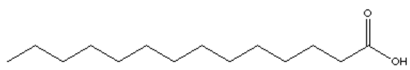
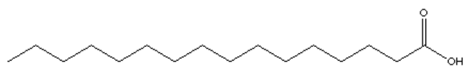
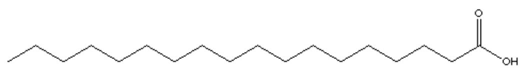
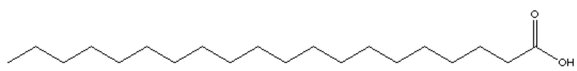
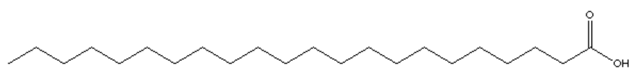
Systematic Name	Trivial name	Chemical structure
dodecanoic acid	lauric acid	
tetradecanoic acid	myristic acid	
hexadecanoic acid	palmitic acid	
octadecanoic acid	stearic acid	
eicosanoic acid	arachidic acid	
docosanoic acid	behenic acid	

Table 1-1-1: Saturated fatty acid.

1-2 Unsaturated fatty acid

Unsaturated fatty acids are the ones with one or more double bonds. Table 1-2-2 summarizes some major unsaturated fatty acids. Usually, the double bonds are in *cis* or *Z* configuration, and double bonds in di- or polyunsaturated fatty acids are interrupted by a methylene (-CH_2-) group (Figure 1-2-1). Thus, generally, unsaturated fatty acids can be expressed by (i) number of carbons, (ii) number of double bonds and (iii) the position at which the first double bond from the ω-position (= methyl group) appears. For example, an expression "18:2 ω-6 for linoleic acid" indicates "a fatty acid with 18 carbons, with 2 double bonds starting at the 6th carbon from the methyl end".

Figure 1-2-1: Structure of methylene-interrupted diene.

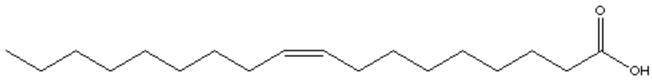
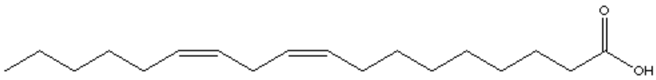
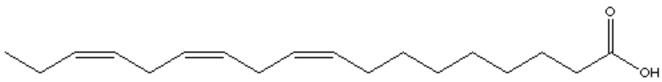
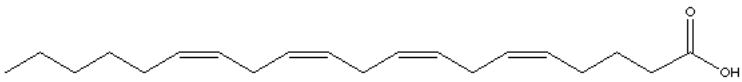
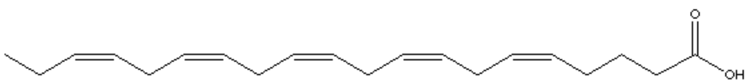
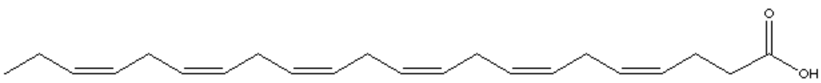
Trivial name	Symbolic expression	Chemical structure
oleic acid	18:1 ω-9	
linoleic acid	18:2 ω-6	
α-linolenic acid	18:3 ω-3	
arachidonic acid	20:4 ω-6	
eicosapentaenoic acid *(not trivial name)*	20:5 ω-3	
docosahexaenoic acid *(not trivial name)*	22:6 ω-3	

Table 1-2-1: Unsaturated fatty acid.

The unsaturated fatty acids are divided into families according to the position of the first double bond appears, (like ω-3 family, ω-6 family and ω-9 family). The acids within the same family are biosynthetically related, being interconverted by enzymatic processes of desaturation and chain elongation. Figure 1-2-2 illustrates biosynthetic pathway of unsaturated fatty acids. Animals can neither convert oleic acid (ω-9 family) to linoleic acid (ω-6 family) nor linoleic acid to α-linolenic acid (ω-3 family). In other words, animals can not self-synthesize linoleic acid and α-linolenic acid. Therefore, animals should take these fatty acids from their diet. This is why these fatty acids are called "essential fatty acids".

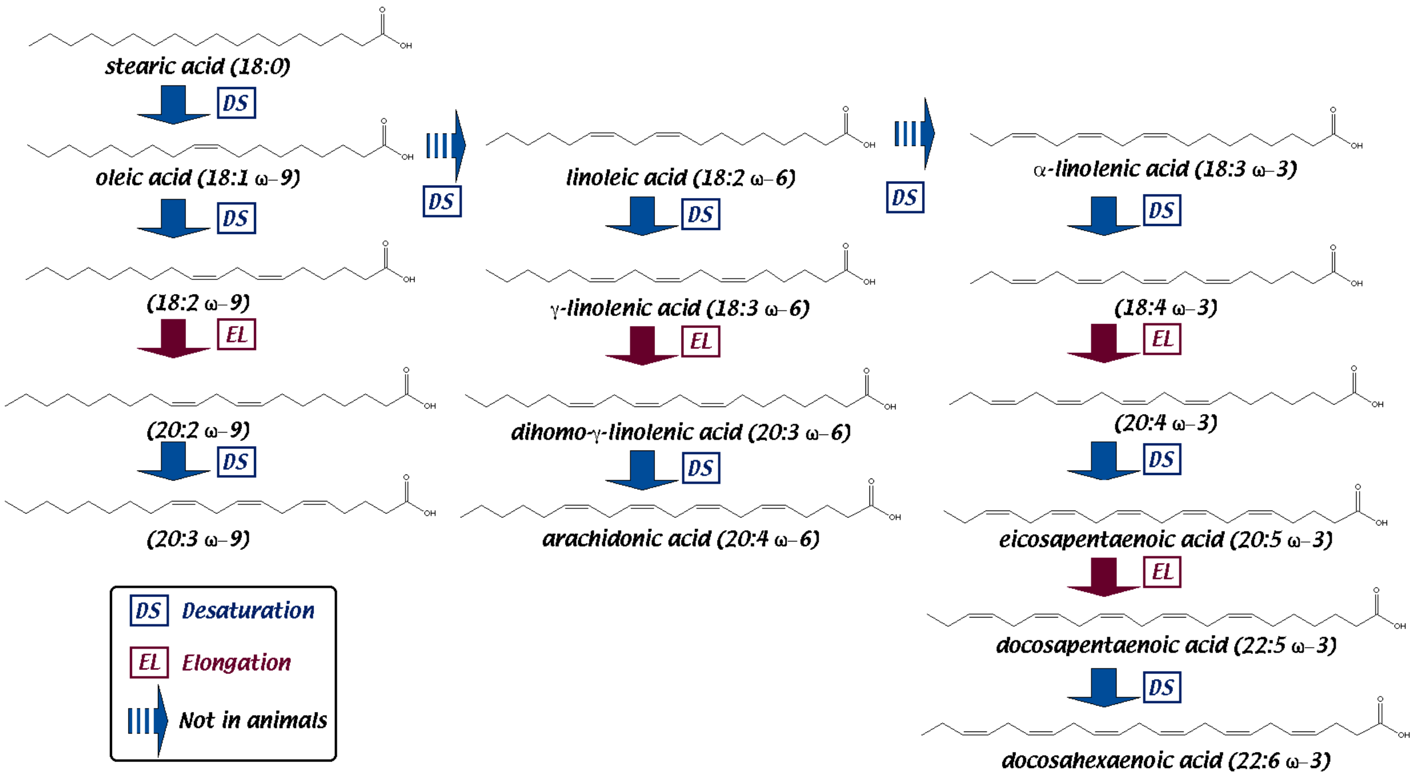


Figure 1-2-2: Biosynthetic pathway of unsaturated fatty acids.

1-3 Conjugated polyene fatty acids

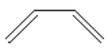


Figure 1-3-1: Conjugated double bonds. Two double bonds are not interrupted by methylene. Compare Figure 1-2-1.

Conjugated polyene fatty acids have conjugated double bonds (Figure 1-3-1). Although these fatty acids occur as "minor" components of some natural oils, but recently have attracted researchers' attention because of their biological activities.

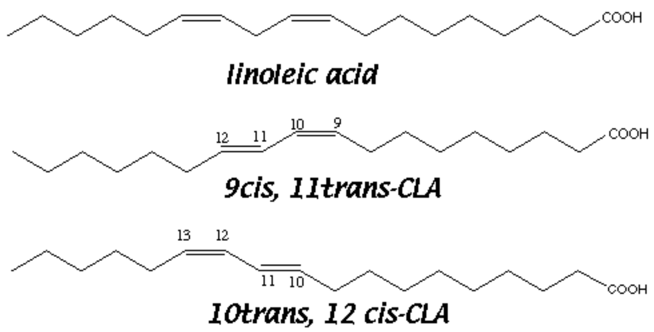


Figure 1-3-2: Conjugated linoleic acid.

One of the most well-studied conjugated fatty acids is conjugated linoleic acid (CLA) (Figure 1-3-2). CLA was first isolated as an anti-cancer agent from cooked meat. Afterwards, discovery of its body-fat-reducing-effect made CLA be used for diet food.

There can be many isomers of CLA with respect to the position and the configuration (i.e. *cis* or *trans*) of the double bonds. Industrial method of CLA production by alkaline isomerization of linoleic acid generates a mixture consisting of mainly 9*cis*, 11*trans*-form and 10*trans*, 12*cis* form, among which the 10-*trans*, 12-*cis* form is thought to be biologically important.

1-4 Hydroxy fatty acids

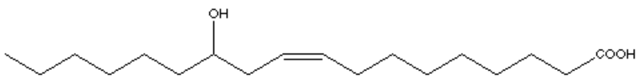


Figure 1-4-1: Ricinoleic acid.

Natural fatty acids with a functional group other than the carboxyl group and one or more unsaturation are relatively unusual, but among such acids hydroxy compounds are the most common. Ricinoleic acid (12-hydroxyoleic acid) is the best known hydroxy fatty acid (Figure 1-4-1). Ricinoleic acid is the major fatty acid (80-90 %) in castor oil. Because of such an unusual fatty acid composition, castor oil is not suitable for food. However, ricinoleic acid is a very important compound, from which various chemical product including plasticizers, detergents, cosmetics, paints etc., can be obtained.

1-5 Eicosanoids

Eicosanoids are given to a group of compounds with remarkable pharmacological properties. As the name "eicosanoids" indicates, these compounds are derived from C20 polyunsaturated fatty acids such as dihomo-γ-linoleic acid, arachidonic acid and eicosapentaenoic acid. Eicosanoid includes three different classes, prostaglandin (PG), thromboxane (TX) and leukotriene (LT).

These eicosanoids are not stored in mammalian tissue, but elaborated in response to various stimuli.

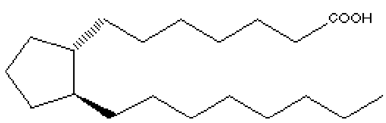


Figure 1-5-1: Structure of prostanoic acid, the basic structure of prostaglandins.

PGs are a group of eicosanoids having prostanoic acid as the basic structure (Figure 1-5-1). PGs are classified into three types, type1, 2 and 3, which are generated from eicosatrienoic acid (dihomo-γ-linoleic acid) (20:3 ω-6), arachidonic acid (20:4 ω-6) and eicosapentenoic acid (20:5 ω-3), repectively. Figure 1-5-2 illustrates biosynthetic pathway of major PGs.

One of the most successful therapeutic applications of PGs is in the field of obstetrics and gynecology, where PGE_2 and $PGF_{2\alpha}$ are used for induction of labor.

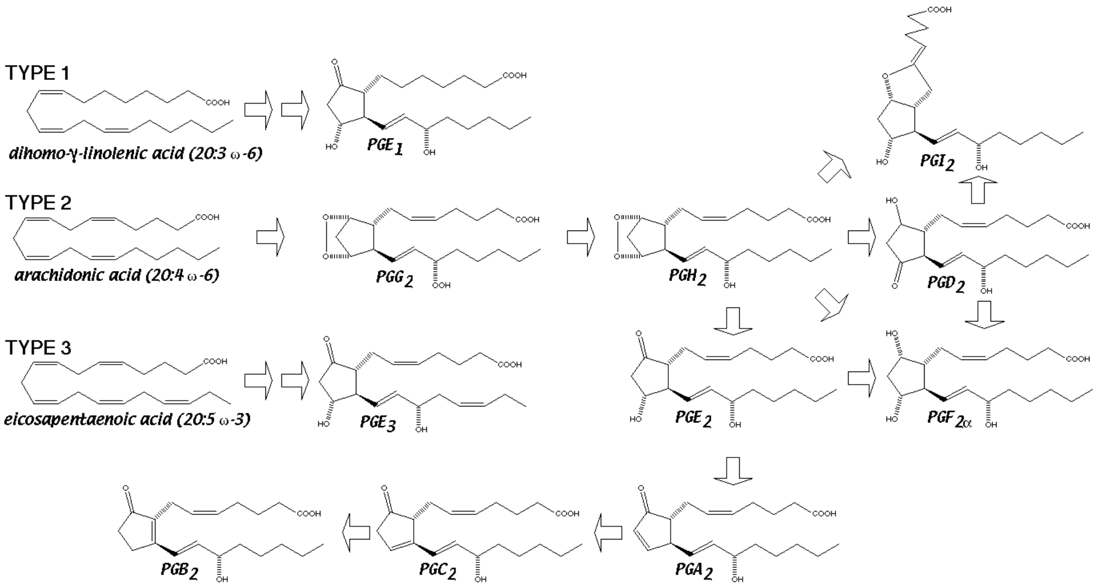


Figure 1-5-2: Biosynthetic pathway of prostaglandins.

Thrombanoic acid is the basic structure of TXs (Figure 1-5-3). Leukotriene is the third group of eicosanoid, with three conjugated double bonds and a oxygen atom at C5 position (Figure 1-5-4).

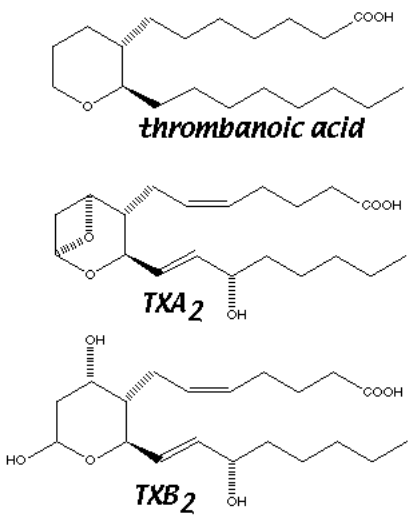


Figure 1-5-3: Structures of thromxanes.

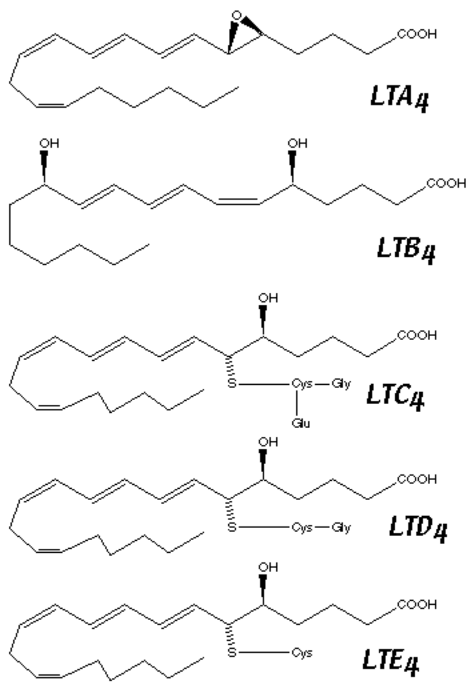


Figure 1-5-4: Structures of leukotrienes.

1-6 Acylglycerols

Acylglycerols are glycerol esters of fatty acids.They include tri- di- and mono-acylglycerols (Figure 1-6-1).

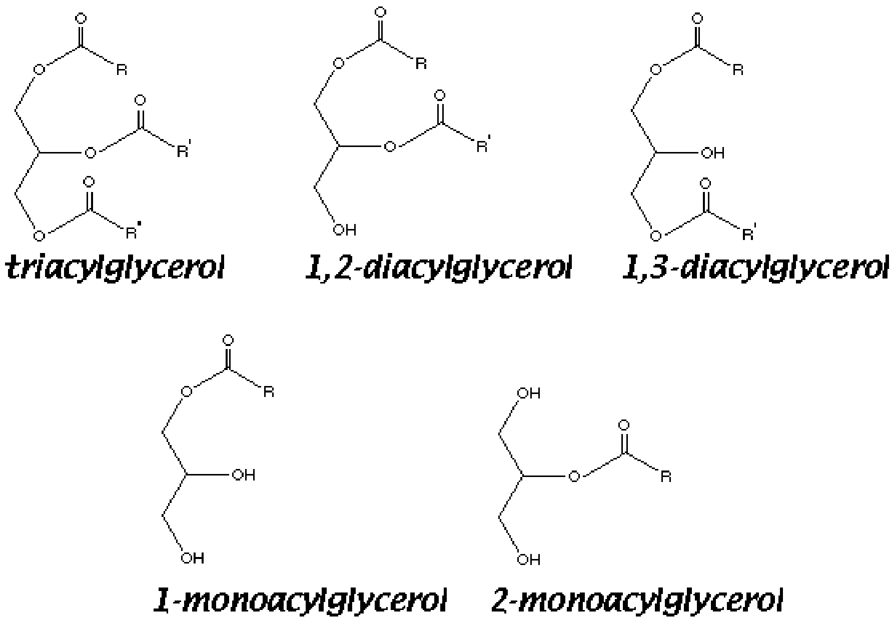


Figure 1-6-1: Acylglycerols.

Triacylglycerol may be the most common species. The main components of oils and fats, which we usually eat, are triacylglycerols. Depending on the sources, the fatty acid composition is different. This will be described in the next chapter.

Diacylglycerols are ones with two fatty acid moieties. There are two possible isomers of diacylglycerols, 1,2-diacylglycerol and 1,3-diacylglycerol. Diacyl forms occur in a small amount in edible oil, mainly due to hydrolysis of triacylglycerols during the industrial extraction process. Recently 1,3-diacylglycerols are used as a special cooking oil which prevents body-fat accumulation.

Monoacylglycerols have one fatty acid moiety attached either 1- or 2-position of the glycerol backbone. Monoacylglycerols are also minor components in natural oil, but they are formed as intermediates during the metabolism of acylglycerols. Due to the hydrophobic acyl groups and hydrophilic -OH groups, monoacylglycerol is industrially used as a food emulsifier.

1-7 Phospholipids

Phospholipids are lipids containing phosphorus. There are mainly two classes of phospholipids, glycerophospholipids and sphingophospholpids. They are main constituents of biomembranes.

Glycerophospholipids have two fatty acids and one phosphodiester attached to the glycerol backbone (Figure 1-7-1). The head group moiety attached to the phosphate includes nitrogenous bases (amino alcohols) or polyols. Glycerophospholipids are obtained from various natural sources as a mixture of various phospholipid species. Generally this mixture of glycerophospholipids is called lecithin, which is used as an emulsifier industrially.

Sphingophospholipid contains sphingosine (see the Sphingolipid section) structure as well as phosphorus. The commonest one in this class is the phosphorylcholine ester of N-acylsphingosine, which is called sphingomyelin (Figure 1-7-2).

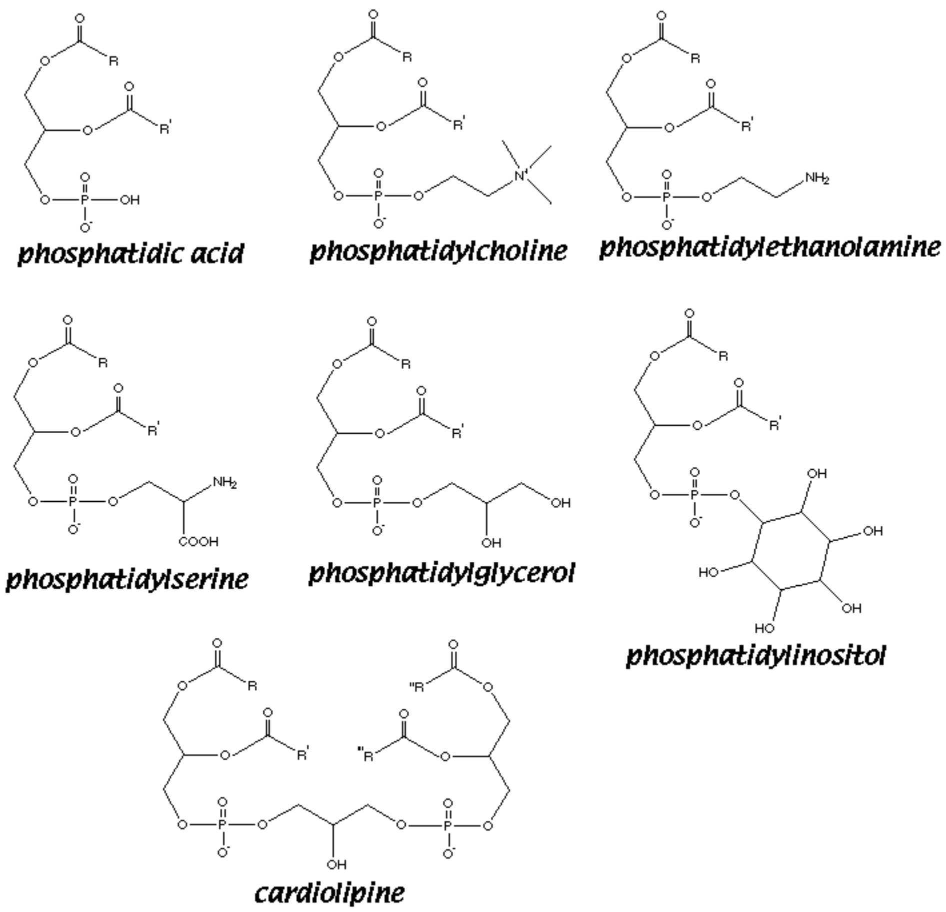


Figure 1-7-1: Glycerophospholipids.

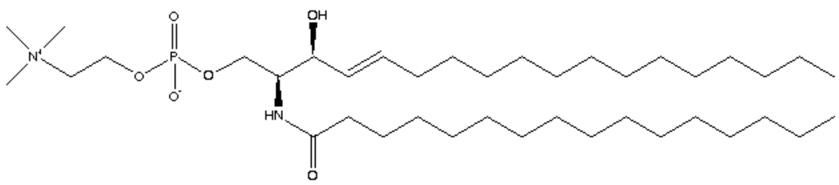


Figure 1-7-2: Sphingomyelin.

1-8 Sphingolipids

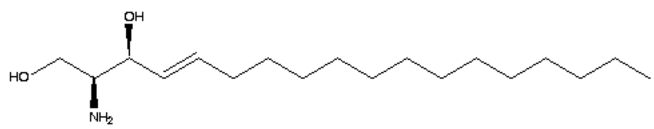


Figure 1-8-1: Sphingosine.

Sphingolipids are derivatives of sphingosine (Figure 1-8-1). Attachment of a fatty acid to the amino group (via an amide linkage) of sphingosine or other related amino alcohols gives rise to a ceramide.

An application of ceramide is its use for cosmetics. Ceramides are involved in moisturekeeping ability of skin. Featuring this property, some cosmetic products such as skin-care cream and lotions containing ceramides or synthetic analogues are marketed.

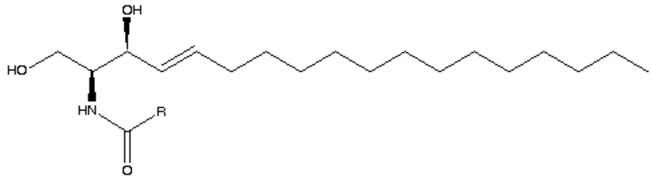


Figure 1-8-2: Basic structure of ceramide.

1-9 Terpenes

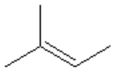


Figure 1-9-1: Isoprene structure

Terpenes include a large variety of compounds with isoprene (C5) structure as the basic unit (Figure 1-9-1). These are biosynthesized via mevaonic acid pathway to form various pyrophosphate esters, each of which is further converted to monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), sesterterpenes (C25), triterpenes (C30), and carotenoids (C40) (Figure 1-9-2). Steroids, such as cholesterol, are synthesized from C30 squalene.

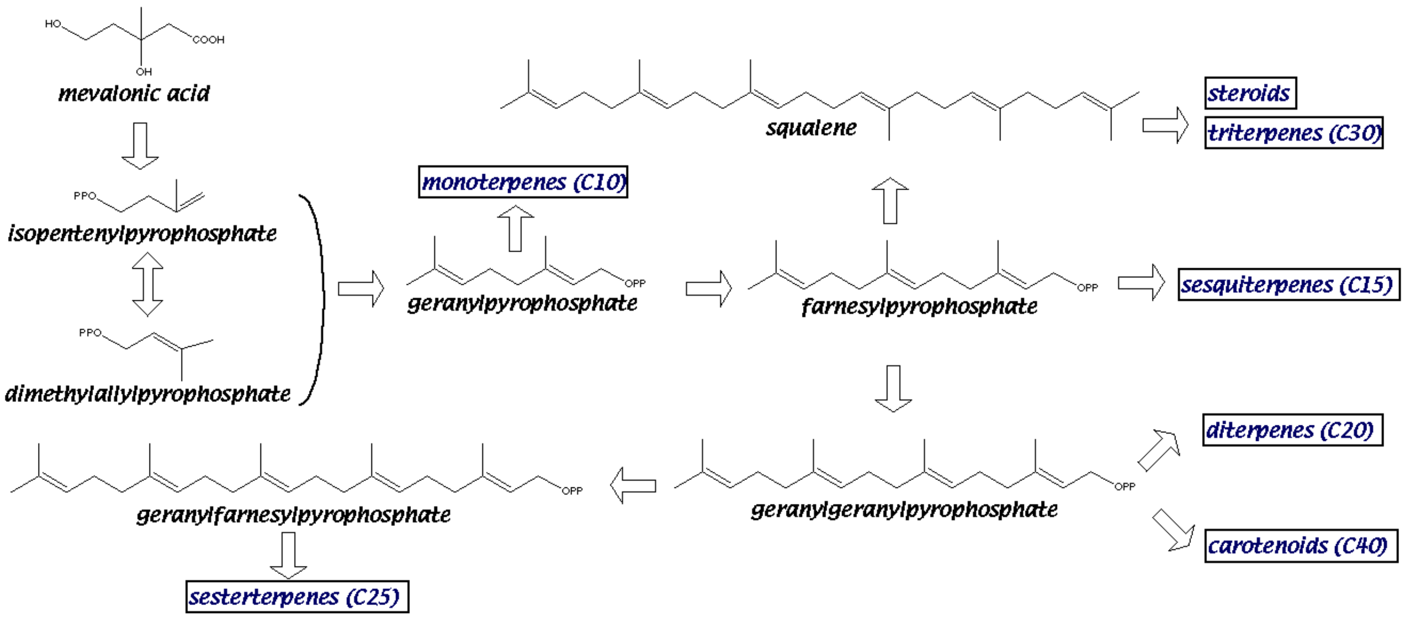


Figure 1-9-2: Mevalonic acid pathway for terpene biosynthesis