Lipids

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Definition and Classification

Lipids are substances of biological origin that are soluble in organic solvents such as chloroform and methanol but are only slightly, if at all, soluble in water. Lipids may be extracted from biological material by organic solvents such as ether or chloroform and methanol. They may be fractionated by thin layer chromatography, adsorption chromatography and reverse-phase chromatography. They serve diverse functions in biological systems. Fats and oils, that are derivatives of fatty acids, are universally used for energy storage and thermal insulation in living organisms. Phospholipids and sterols serve as structural components of biological membranes. Other lipids, which are present in smaller amounts act as enzyme cofactors, electron carriers, light absorbing pigments, hydrophobic anchors for proteins, emulsifying agents, hormones and intracellular messengers. A broad classification of lipids is shown below in Fig. 1.

![Fig. 1: A broad classification of lipids]

Fatty Acids

Fatty acids are long-chain hydrocarbon molecules containing a carboxylic acid moiety at one end. They rarely occur in free form and are usually found in esterified form as the major components of various lipids. Fatty acids with less than 12 and more than 24 carbon atoms are uncommon in biological systems. The most abundant species are those with 16 and 18 carbon atoms. Most of the fatty acids have even number of carbon atoms as they are synthesized in biological systems by condensation of two-carbon acetate units. The numbering of carbons in fatty acids begins with the carbon of the carboxylate group. As their name suggests, all of them are acids with pK_a value in water of approximately 4.5. Hence at physiological pH, the carboxyl group is readily ionized, rendering a negative charge onto the fatty acids.

\[ pK_a = 4.5 \]

\[ RCOOH \leftrightarrow RCOO^- + H^+ \]
Classification

Fatty acids that do not contain carbon-carbon double bonds (-C=C-) are called saturated fatty acids since they cannot undergo further hydrogenation. Those that contain double bonds are known as unsaturated fatty acids, which may further be hydrogenated. If a fatty acid contains more than one carbon-carbon double bond, it is called polyunsaturated fatty acid. Over half of the fatty acid residues of plants and animal lipids are unsaturated or polyunsaturated. Bacterial fatty acids may be branched, hydroxylated or contain cyclopropane rings. Certain waxes and oils of plant origin also contain unusual fatty acids as their components.

Nomenclature

A simplified numeric nomenclature for fatty acids uses the number of carbon atoms (chain length) and the number of double bonds, separated by a colon. For example, the 18-carbon saturated fatty acid (stearic acid) is denoted by 18:0 and the 16-carbon monounsaturated fatty acid (palmitoleic acid) is denoted by 16:1. The positions of any double bonds are specified by superscript numbers following Δ (delta). For example, palmitoleic acid is denoted by 16:1 (Δ⁹). A 20-carbon fatty acid with one double bond between C₉ and C₁₀ and another between C₁₂ and C₁₃ is denoted by 20:2 (Δ⁹,Δ¹₂).

In another system of nomenclature, fatty acids are named after the hydrocarbons with the same number and arrangement of carbon atoms, by substituting the final –e with –oic. The saturated acids end in –anoic, e.g., octadecanoic acid for 18-carbon saturated fatty acid 18:0, and unsaturated acids end in –enoic acid, e.g., octadecenoic acid for 18:1(Δ⁹).

Carbon atoms adjacent to C₁, i.e. C₂, C₃, C₄ are also known as the α, β, γ carbons respectively, and the terminal methyl carbon is known as the ω or n-carbon. ω₉ indicates a double bond on the 9th carbon counting from the ω-carbon. If the fatty acid has additional double bond, it occurs between the first existing double bond and the carboxyl carbon generating three series of fatty acids known as ω₉, ω₆, and ω₃ families.

Structure and properties of saturated and unsaturated fatty acids

An examination of the structures of different unsaturated and polyunsaturated fatty acids indicates a common pattern in the location of double bond. In most monounsaturated fatty acids, the double bond is between C₉ and C₁₀ (i.e. Δ⁹). The other double bonds, if present, are generally Δ¹₂ and Δ¹₅ with an exception of arachidonic acid. The double bonds of polyunsaturated fatty acids are almost never conjugated (as in -CH=CH=CH=CH-) but are separated by a methylene group (as in -CH=CH-CH₂-CH=CH-). Triple bonds very rarely occur in fatty acids.

Because of the freedom of rotation about the C-C single bonds, saturated fatty acids are flexible molecules theoretically capable of assuming a wide range of conformations. However, they exclusively occur in the fully extended conformation since it has the least steric interference between neighboring methylene groups hence, has the minimum energy. In nearly all naturally occurring fatty acids, the double bonds are in cis configuration. This produces a sharp kink of approximately 30° in the hydrocarbon chain of unsaturated fatty acid that interferes with their efficient packing (Fig. 2).
### Table: Names of and symbols for fatty acids

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Numeric Symbol</th>
<th>Structure of R in [CH$_3$-(R)-COOH]</th>
<th>Systematic Name$^a$</th>
<th>Trivial Name$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10:0</td>
<td>-[CH$_3$]$_8$</td>
<td>Decano-</td>
<td>Capr$^c$</td>
</tr>
<tr>
<td>2</td>
<td>12:0</td>
<td>-[CH$<em>2$]$</em>{10}$</td>
<td>Dodecano-</td>
<td>Laur-</td>
</tr>
<tr>
<td>3</td>
<td>14:0</td>
<td>-[CH$<em>2$]$</em>{12}$</td>
<td>Tetradecano-</td>
<td>Myrist-</td>
</tr>
<tr>
<td>4</td>
<td>16:0</td>
<td>-[CH$<em>2$]$</em>{14}$</td>
<td>Hexadecano-</td>
<td>Palmit-</td>
</tr>
<tr>
<td>5</td>
<td>16:1</td>
<td>-[CH$_2$]$_2$CH=CH[CH$_2$]$_7$</td>
<td>9-Hexadeceno-</td>
<td>Palmitole-</td>
</tr>
<tr>
<td>6</td>
<td>18:0</td>
<td>-[CH$<em>2$]$</em>{16}$</td>
<td>Octadecano-</td>
<td>Stear-</td>
</tr>
<tr>
<td>7</td>
<td>18:1(Δ$^9$)</td>
<td>-[CH$_2$]$_2$CH=CH[CH$_2$]$_7$</td>
<td>cis-9-Octadeceno-</td>
<td>Ole-</td>
</tr>
<tr>
<td>8</td>
<td>18:1(Δ$^{11}$)</td>
<td>-[CH$_2$]$_2$CH=CH[CH$_2$]$_9$</td>
<td>11-Octadeceno-</td>
<td>Vaccen-</td>
</tr>
<tr>
<td>9</td>
<td>18:2(Δ$^{9,12}$)</td>
<td>-[CH$_2$]$_3$(CH$_2$CH=CH)$_2$[CH$_2$]$_7$</td>
<td>cis,cis-9,12-Octadecadieno-</td>
<td>Linole</td>
</tr>
<tr>
<td>10</td>
<td>18:3(Δ$^{9,12,15}$)</td>
<td>-[CH$_2$CH=CH][CH$_3$][CH$_2$]$_7$</td>
<td>9,12,15-Octadecatrieno-</td>
<td>(9,12,15)-Linolen-</td>
</tr>
<tr>
<td>11</td>
<td>18:3(Δ$^{6,9,12}$)</td>
<td>-[CH$_3$]$_3$(CH$_2$CH=CH)$_3$[CH$_2$]$_7$</td>
<td>6,9,12-Octadecatrieno-</td>
<td>(6,9,12)-Linolen-</td>
</tr>
<tr>
<td>12</td>
<td>18:3(Δ$^{9,11,13}$)</td>
<td>-[CH$_2$]$_3$(CH$_2$CH=CH)$_3$[CH$_2$]$_7$</td>
<td>9,11,13-Octadecatrieno-</td>
<td>Eleostear-</td>
</tr>
<tr>
<td>13</td>
<td>20:0</td>
<td>-[CH$<em>2$]$</em>{18}$</td>
<td>Icosano$^d$</td>
<td>Arachid-</td>
</tr>
<tr>
<td>14</td>
<td>20:2(Δ$^{8,11}$)</td>
<td>-[CH$_2$]$_4$(CH$_2$CH=CH)$_2$[CH$<em>2$]$</em>{10}$</td>
<td>8,11-Icosadieno$^d$</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>20:3(Δ$^{5,8,11}$)</td>
<td>-[CH$_2$]$_5$(CH$_2$CH=CH)$_3$[CH$<em>2$]$</em>{10}$</td>
<td>5,8,11-Icosatrieno$^d$</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>20:4(Δ$^{5,8,11,14}$)</td>
<td>-[CH$_2$]$_6$(CH$_2$CH=CH)$_4$[CH$<em>2$]$</em>{13}$</td>
<td>5,8,11,14-Icosatetraeno$^d$</td>
<td>Arachidon-</td>
</tr>
<tr>
<td>17</td>
<td>22:0</td>
<td>-[CH$<em>2$]$</em>{20}$</td>
<td>Docosano-</td>
<td>Behen-</td>
</tr>
<tr>
<td>18</td>
<td>24:0</td>
<td>-[CH$<em>2$]$</em>{22}$</td>
<td>Tetracosano-</td>
<td>Lignocer-</td>
</tr>
<tr>
<td>19</td>
<td>24:1(Δ$^{15}$)</td>
<td>-[CH$_2$]$_2$CH=CH[CH$<em>2$]$</em>{13}$</td>
<td>cis-15-Tetracoseno-</td>
<td>Nervon-</td>
</tr>
</tbody>
</table>

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$^a$ Ending in '-ic', '-ate', '-yl', for acid, salt or ester, acyl radical, respectively.

$^b$ Ending in '-ic', '-ate', '-oyl' for acid, salt or ester, or acyl radical, respectively.

$^c$ Not recommended because of confusion with caproic (hexanoic) and caprylic (octanoic) acids. Decanoic is preferred.


The physical properties of fatty acids, and of the lipids that contain them, are largely determined by the length and degree of unsaturation of the hydrocarbon chains. Their poor solubility in water is because of the presence of nonpolar hydrocarbon chain. For example, lauric acid (12:0) has a solubility in water of 0.063 mg/g that is much less than that of glucose (1100 mg/g) which is of similar molecular weight. The rule appears to be, the longer the fatty acyl chain and the fewer the double bonds, the lower the solubility in water. The carboxylic acid group, that is polar and ionized at neutral pH, accounts for the slight solubility of short-chain fatty acids in water.
Fig. 2: Structure of saturated (a) and unsaturated (b) fatty acids. The lower part shows the packing of saturated (c) and unsaturated (d) fatty acids within membranes

The melting points of fatty acids and lipids containing them are also determined by the length and degree of unsaturation of the hydrocarbon chain. At room temperature, saturated fatty acids from 12:0 to 24:0 are physically like wax, whereas unsaturated fatty acids of corresponding lengths are liquids like oils. This difference in melting point is because of lower compaction, or inefficient packing, of the hydrocarbon chains which have a sharp kink at every C=C double bond in cis configuration. This leads to a reduction in van der Waals interaction that accounts for lower melting point. The melting point decreases with increase in the degree of unsaturation. Similarly, the fluidity of membranes containing high proportions of lipids with unsaturated fatty acyl residues is higher than their counterparts containing saturated fatty acyl residues. This phenomenon has significant bearing on the activity and functions of biological membranes and the proteins embedded in them.

**Essential fatty acids**

The fatty acids that can not be biosynthesized in adequate amounts by the organisms are considered as nutritionally essential fatty acids. Palmitoleic and oleic acids are not essential in the diet because the tissues can introduce a double bond at Δ⁹ position of saturated fatty acids. The first double bond introduced into a saturated fatty acid is nearly always in the Δ⁹ position by an enzyme system Δ⁹ desaturase in the endoplasmic reticulum. Out of the polyunsaturated fatty acids, only linoleic and linolenic acids are known to be essential for complete nutrition of many species of animals, including humans. They are known as nutritionally essential fatty acids. Other polyenoic acids such as C₂₀, C₂₂ and C₂₄, are derived from oleic, linoleic and linolenic acids by chain elongation by elongase and desaturase enzyme systems. In most mammals,
arachidonic acid, 20:4 ($\Delta^{5,8,11,14}$), can be formed from linoleic acid. Double bonds can be introduced at $\Delta^4$, $\Delta^5$, $\Delta^6$ and $\Delta^9$ positions in most animals, but never beyond the $\Delta^9$ position. Plants, however, are able to synthesize the nutritionally essential fatty acids by introducing double bonds at the $\Delta^{12}$ and $\Delta^{15}$ positions. Humans can acquire them by consuming a variety of plants or else by eating the meat of animals that have consumed these plant fats.

The essential fatty acids are found in structural lipids of the cell membranes, often in the C$_2$-position of glycerophospholipids. Arachidonic acid, that is enzymatically released from membrane lipids, is required for synthesis of a group of compounds called eicosanoids. Linoleic acid is especially important in that it is required for the synthesis of arachidonic acid. It is this role of fatty acids in eicosanoid synthesis that leads to poor growth, wound healing and dermatitis in persons on fat free diets. Also, linoleic acid is a constituent of epidermal cell sphingolipids that function as the skin-water permeability barrier. Essential fatty acids have several other functions also which are not very well understood.

**Triacylglycerols**

Triacylglycerols, also called triglycerides, are the simplest of lipids composed of three fatty acids each in ester linkage with a single glycerol molecule (Fig. 3). Those containing the same kind of fatty acid in all three positions are called simple triacylglycerols and are named after the fatty acid present (e.g. tripalmitin, tristearin and triolein that contain three palmitic, stearic and oleic acids respectively). However, majority of the naturally occurring triacylglycerides contain more than one type of fatty acids and are hence called mixed triacylglycerides. These compounds are unambiguously named by specifying the name and position of each fatty acid. This is done by numbering the carbon atoms of glycerol unambiguously by the stereochemical numbering (-sn) system.

![Diagram of triacylglycerol synthesis](image)

**Fig. 3: General structures of fatty acid, glycerol and triacylglycerol and their synthesis**

It may also be noted that C$_1$ and C$_3$ are not identical when viewed in three dimensions. Enzymes readily distinguish between them and are nearly always specific for one or the other carbon. For example, glycerol is always phosphorylated on sn-3 by glycerol kinase to produce glycerol-3-phosphate and not glycerol-1-phosphate.
**Physical Properties**

Triacylglycerols are non-polar, hydrophobic and essentially insoluble in water since the polar hydroxyls of glycerol and the polar carboxylates of fatty acids are bound in ester linkage. They also have densities lower than that of water and do not mix with water but form a separate phase and float on water. In most eukaryotic cells, triacylglycerols form a separate phase like oily droplets in the cytosol serving as depots of metabolic fuel. Vertebrate animals have specialized cells called adipocytes that store large amounts of triacylglycerols as fat droplets, which nearly fill the cell.

**Chemical Properties and Characterization of Fat**

The chemical properties of fats are the properties of their component glycerides, which in turn, depend upon the characters of the fatty acids present. All the glycerides are esters, so they give the reactions of esters. Those containing double bonds in fatty acyl chains, show the characteristic properties of unsaturation. The properties of fats are also used for their characterization, which are discussed below.

**Hydrolysis**

Triglycerides are very slowly hydrolyzed to glycerol and fatty acids when boiled at atmospheric pressure. Hydrolysis may, however, be readily accomplished by heating with water at high temperature and pressure in an autoclave preferably in the presence of catalysts such as acids. They may also be hydrolyzed by the action of the enzymes known as lipases that are widespread in both plants and animals.

\[
\begin{align*}
\text{Triacylglycerol} & \quad \text{Glycerol} \quad \text{Fatty acids} \\
\end{align*}
\]

**Saponification**

The triglycerides may be readily decomposed into glycerol and salts of constituent fatty acids (soaps) by boiling with strong bases such as NaOH or KOH. This process is called saponification that is further facilitated by addition of alcohol which dissolves the otherwise water-insoluble fat. Both soap and glycerol are soluble in water, but the soap may be separated by the addition of salt. The glycerol may be recovered by evaporation of water and vacuum distillation. In addition to commercial production of soap, saponification of fats is also used for making salts of fatty acids of fat for subsequent chemical analysis of the fatty acids present in a given fat.
Saponification Number

The number of milligrams of potassium hydroxide required to completely saponify one gram of oil or fat is called saponification number, saponification value or saponification equivalent. The material is saponified by refluxing with a known excess of alcoholic 0.5 N KOH solution. The alkali solution consumed for saponification is determined by titrating the excess alkali with standard hydrochloric acid. Since fats are mixtures of glycerides that, in turn, contain fatty acids of various chain lengths, the saponification number remains an index of the average molecular size of the fatty acids present.

Rancidity of Fats

The unpleasant odor and taste developed by most natural fats upon ageing is referred to as rancidity. Rancidity may be due to hydrolysis of component glycerides of a fat into free fatty acids and glycerol. If the hydrolysis is incomplete, a mixture of glycerol, monoglycerides and diglycerides with free fatty acids may be produced. This process is accelerated by the presence of lipases, which in the presence of moisture and at warm temperatures, bring about hydrolysis. Rancidity may also be caused by various oxidative processes. For example, oxidation at the double bonds of unsaturated fatty acyl residues may form peroxides, which then decompose to form aldehydes of bad odor and taste. This process is greatly increased by exposure to light. Addition of minute amounts of antioxidants can prevent the oxidation and significantly delay the oxidative rancidity.

Acid Number

The number of milligrams of potassium hydroxide required for neutralizing the free fatty acids present in one gram of fat or oil is called the acid number of that fat or oil. Acid number is used for determination of rancidity due to free fatty acids. There are several spectrophotometric and FT-IR spectroscopic methods currently available for detection of rancidity in edible oils.

Reichert-Meissel Number

It is also called volatile fatty acid number. It is the number of milliliters of 0.1N potassium hydroxide required to neutralize the soluble volatile fatty acids derived from five grams of fat that has been saponified. Reichert-Meissel number measures the quantity of short chain fatty acids in the fat molecule. Butter, which has high proportion of glycerides with short-chain fatty acids, has a high Reichert-Meissel number.
acids, has a Reichert-Meissel value of 26-33, whereas it is between 5 and 8 for coconut and palm oils.

**Iodine Number**

The relative unsaturation of fat is determined by measuring the quantity of halogen absorbed by the glycerides. The iodine number of a given fat is defined as the percent of iodine absorbed by the fat, or the grams of iodine absorbed by 100 grams of fat. Several methods are available for experimental determination of iodine number of fats that use a range of halogenating solutions in preference to the iodine solution. But regardless of the halogenating solution used, the results are always calculated in terms of iodine and expressed as iodine numbers.

**Reactions of Glycerol**

Glycerol is a component of triglycerides and glycerophospholipids. It is a liquid, sweet in taste, with a specific gravity of 1.26 at 20ºC. It is miscible with water and alcohol in all proportions but insoluble in ether, chloroform and benzene. Glycerol is an excellent solvent, it can take up and hold water and is widely used in medicines and cosmetics as a moisturizing agent. It is nontoxic to animals and humans.

Glycerol can be oxidized with hydrogen peroxide (H₂O₂) in slightly alkaline solutions in the presence of an iron salt to give a mixture of glyceric aldehyde and dihydroxyacetone. Either a primary or the secondary alcohol group of glycerol may be oxidized to give an aldehyde or ketone respectively.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CHO} & \quad \text{CH}_2\text{OH} \\
\text{CHOH} + \text{O}_2 & \quad \text{CHOH} \quad \text{and} \quad \text{CHOH} + \text{H}_2\text{O} \\
\text{CH}_3\text{OH} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

**Glycerol** \quad **Glyceric aldehyde** \quad **Dihydroxyacetone**

Both Glyceric aldehyde and dihydroxyacetone are triose sugars and the mixture produced in this reaction reduces alkaline copper reagents forming the basis of Fehling and Benedict tests.

Another important property of glycerol is production of the unsaturated aldehyde, acrolein, when glycerol is heated with a dehydrating agent such as KHSO₄ or P₂O₅.

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{Heat} & \quad \text{Heat} & \quad \text{React} \\
\text{KHSO}_4 & \quad \text{KHSO}_4 & \quad \text{KHSO}_4 \\
\text{+ 2 H}_2\text{O} & \quad \text{+ 2 H}_2\text{O} & \quad \text{+ 2 H}_2\text{O} \\
\end{align*}
\]

**Glycerol** \quad **Acrolein**
Glycerol can also dissolve metallic hydroxides such as Cu(OH)$_2$. It combines with positive metal ions through coordination of the ions with free electron pairs of the hydroxyl oxygen atoms to form slightly dissociated soluble complexes. The reaction proceeds in alkaline solution, and the complexes are broken up by acidification.

Because of the presence of double bonds in their fatty acyl residues, the unsaturated glycerides may be hydrogenated by treatment with hydrogen preferably in the presence of a nickel catalyst.

\[
\begin{align*}
\text{Unsaturated triglyceride} & \\
\text{Saturated triglyceride}
\end{align*}
\]

The hydrogenation of vegetable oils is commercially used for production of cooking media such as ‘Dalda’ (‘vanaspati ghee’) and margarines. However, the glycerides are only partially hydrogenated to keep the fat optimally soft. Complete hydrogenation would make it too hard to be conveniently used and difficult for efficient digestion and absorption.

**Biological Significance of Fats**

Triacylglycerols are ideal molecules for efficient storage of metabolic energy. This is because they are more highly reduced than the other molecules such as carbohydrates or proteins and hence yield significantly more energy upon oxidation. Another advantage is that, fats, being nonpolar substances, can be stored in anhydrous form without carrying an extra load of water and occupying less space during storage. Glycogen, on the other hand, binds about twice its weight of water. Triacylglycerols, therefore, provide about six times more energy than an equal weight of hydrated glycogen. Hence, fat appears to be an efficient storage form, but being hydrophobic it does not allow quick mobilization to meet physiological energy requirements. This is the reason that fats are molecules ideally suited for long-term storage of metabolic energy. Glycogen present in human body can meet the metabolic energy requirement only for less than a day, whereas the fat stored in adipocytes can fuel the mammals for days and even months. The adipose tissue is most abundant in subcutaneous layer and in the abdominal cavity and mammary glands. The fat content of normal men and women is about 20% and 26% respectively, which allows them to survive more than a month of starvation. The subcutaneous layer of triacylglycerols also functions to provide thermal insulation, which is very important particularly for warm-blooded inhabitants of the colder regions of biosphere. In hibernating animals, huge fat reserves accumulated before hibernation serves dual purpose of energy storage and insulation. Because of its low specific gravity, a store of triacylglycerols in sperm whale, additionally helps the organism to match the buoyancy of their bodies to that of their surroundings during deep dives in cold waters.
Fat is also stored in the form of oil in seeds of many plants providing energy and biosynthetic precursors during seed germination. Both adipocytes and germinating seeds contain lipases that catalyze the hydrolysis of stored triacylglycerols, releasing fatty acids for export to sites where they are required as fuel.

**Waxes**

Waxes are esters of long chain (14 to 36 carbon) saturated and unsaturated fatty acids with long chain (16 to 30 carbon) alcohols (Fig. 4). Waxes are the chief storage form of metabolic fuel in phytoplanktons. They have higher melting point than triglycerides and have water-repellent properties. Skin glands of certain vertebrates secrete waxes to protect their hair and skin and keep them lubricated and waterproof. Certain birds also have wax secreting glands to prevent their feather from being wet. The leaves of certain tropical plants are also coated with wax to prevent excessive evaporation of water and for protection against parasites. Waxes of biological origin are commercially important too. They are widely used in pharmaceutical, cosmetic and other industries for the manufacture of ointments and polish.

![Wax molecule](image)

**Fig. 4:** The honeybee wax, triacontanol-palmitate, is an ester of palmitic acid and the alcohol triacontanol

**Glycerophospholipids**

Glycerophospholipids, also called phosphoglycerides, are the major components of biological membranes. The common glycerophospholipids are diacylglycerols linked to the head group alcohols through a phosphodiester linkage. They consist of sn-glycerol-3-phosphate esterified to fatty acids at C₁ and C₂ positions. The phosphoryl group at C₁ is covalently attached to a variable group X (Fig. 5). Glycerophospholipids are amphipathic molecules with nonpolar tails and a polar phosphoryl-X head. They differ from triacylglycerols in possessing a highly polar head group in addition to their hydrocarbon tails. All the glycerophospholipids have a negative charge on the phosphate group at pH 7.0. The head group alcohol may also contribute one or more charges at pH near 7.0. The simplest glycerophospholipid is phosphatidic acid, which has a hydrogen atom as the variable group X. The head groups of common glycerophospholipids found in biological membranes are derived from polar alcohols as shown in the table (Fig. 5).

**Phosphatidylcholine**

They are also called the lecithins. At physiological pH, phosphatidylcholines are neutral zwitterions. They contain primarily palmitic or stearic acid at carbon 1 and primarily oleic, linoleic or linolenic acid at carbon 2. Dipalmitoylphosphatidylcholine is a component of lung or pulmonary surfactant. It contains palmitate at both C₁ and C₂ of glycerol and is the major phospholipid found in the extracellular lipid layer lining the pulmonary alveoli.
Fig. 5: Structure of sn-glycerol-3-phosphate, general structure and common classes of glycerophospholipids

**Phosphatidylethanolamine**
These molecules are also neutral zwitterions at physiological pH and usually contain palmitic or stearic acid on C₁ and a long chain unsaturated fatty acid (e.g. 18:2, 20:4 and 22:6) on C₂.

**Phosphatidylserine**
Phosphatidylserines carry a net negative charge at physiological pH and are composed of fatty acids similar to the phosphatidylethanolamines.

**Phosphatidylinositol**
These molecules almost exclusively contain stearic acid at C₁ and arachidonic acid at C₂. Phosphatidylinositols composed exclusively of non-phosphorylated inositol exhibit a net negative charge at physiological pH. They exist in membranes with various levels of phosphate esterified to the hydroxyls of the inositol. Molecules with phosphorylated inositol are termed
polyphosphoinositides. The polyphosphoinositides are important intracellular transducers of signals emanating from the plasma membrane.

**Phosphatidylglycerol**

Phosphatidylglycerols exhibit a net negative charge at physiological pH. They are abundant in mitochondrial membranes and as components of pulmonary surfactant. An important role of phosphatidylglycerol is that it acts as a precursor for the synthesis of cardiolipin.

**Diphosphatidylglycerols**

These molecules are very acidic, exhibiting a net charge of -2 at physiological pH. They are found primarily in the inner mitochondrial membrane and also as components of pulmonary surfactant. An important class of diphosphatidylglycerols is the cardiolipin the structure of which is shown below.

Glycerophospholipids, in general, contain a saturated fatty acid at C₁ and an unsaturated fatty acid at C₂. The fatty acyl groups are commonly 16 or 18 carbon long but there are wide variations. The membrane phospholipids of most cells are continuously degraded and replaced. The hydrolytic enzymes responsible for degradation of membrane phospholipids are called phospholipases. There are four different type of phospholipases A₁, A₂, C and D which are specific for specific bonds in the glycerophospholipids (Fig. 6). Phospholipases of the A type remove one of the two fatty acids producing a lysophospholipid. These are esterases that do not attack the ether link in plasmalogens. The remaining fatty acid of the lysophospholipid can be removed by lysophospholipases.

**Ether Lipids**

In some of the glycerophospholipids, one of the two fatty acyl chains is attached to glycerol in ether, rather than, ester linkage (Fig. 7). These lipids are called ether lipids and plasmalogen (Fig. 7A) is one of its examples. Three major classes of plasmalogens have been identified that contain ethanolamine, choline and serine as the head group. Ethanolamine plasmalogen is prevalent in myelin. Choline plasmalogen is abundant in cardiac tissue. Ether lipids are also abundant in membranes of halophilic bacteria, ciliated protists and certain invertebrates. Functional significance of ether lipids in membranes is not clearly understood but they confer resistance to phospholipases that can cleave ester-linked fatty acids in membranes.
One of the choline plasmalogens, 1-alkyl, 2-acetyl phosphatidylcholine (Fig. 7B), has been identified as an extremely potent biological mediator, capable of inducing cellular responses at subnanomolar concentrations. This molecule is called platelet activating factor (PAF). It functions as a mediator of hypersensitivity, acute inflammatory reactions and anaphylactic shock. It is released from WBC called basophils and stimulates platelet aggregation and the release of serotonin from platelets. It exerts a variety of effects on liver, smooth muscle, heart, uterine and lung tissue and plays important role in inflammation and allergic response.

**Galactolipids and Sulfolipids**

Galactolipids and sulfolipids form another class of membrane lipids that predominantly occur in plants, particularly thylakoid membranes. Galactolipids have one or two galactose residues joined by a glycosidic bond to C₃ of a 1,2-diacylglycerol. They may constitute up to 75 percent of the total membrane lipids in higher plants. There is no phosphate present in galactolipids. Structures of the most commonly found galactolipids, monogalactosyldiacylglycerol (MGDG) and digalactosyldiacylglycerol (DGDG) are shown in Fig. 8. In sulfolipids, a sulfonated glucose
residue is joined to diacylglycerol in glycosidic linkage (Fig. 8). The sulfonate in the head group bears a negative charge similar to the phosphate group in phospholipids.

Fig. 8: Structures of monogalactosyldiacylglycerol (MGDG), digalactosyldiacylglycerol (DGDG) and sulfoquinovosyldiacylglycerol (SQDG)

**Sphingolipids**

Sphingolipids make the second largest class of membrane lipids. They have a polar head and two nonpolar tails but contain no glycerol. Sphingolipids are composed of:

(i) A molecule of long-chain (C_{18}) amino alcohol, sphingosine, or one of its derivative (e.g. dihydrosphingosine or their C_{16}, C_{17}, C_{19} and C_{20} homologs)

(ii) A molecule of long-chain fatty acid,

(iii) A polar head alcohol, and

(iv) Sometimes phosphoric acid in diester linkage at the polar head group

Fig. 9: Structures of sphingosine and ceramide, that acts as precursor for the synthesis of cerebroside, sphingomyelin and gangliosides
A sphingosine molecule has -OH, -NH₂ and -OH at C₁, C₂ and C₃ positions respectively, which are structurally homologous to the three -OH groups of glycerol in glycerophospholipids.

In the early days following their discovery, the biological functions of sphingolipids seemed as enigmatic as the ‘Sphinx’ for which they were named. Now they are known to be involved in various recognition events at the cell surface. They are involved in receptor function of some pituitary glycoprotein hormones and toxicity of some bacterial toxins such as cholera toxin. They are also important components of specific receptor sites on the surface of cell membranes. For example, they are found in the specific sites on nerve endings to which neurotransmitter molecules become bound during the chemical transmission of an impulse from one nerve cell to the next.

When a fatty acid is attached to C₂ in amide linkage to the NH₂, it is called a ceramide; that is, ceramides are N-acetyl fatty acyl derivatives of sphingosine. Ceramides occur in small amounts in plants and animals but are the parent compound for more abundant sphingolipids such as sphingomyelins, cerebrosides and gangliosides (Fig. 9). Ceramide is structurally similar to diacylglycerol and is the fundamental structural unit common to all sphingolipids. There are three subclasses of sphingolipids, (i) Sphingomyelins, (ii) Neutral glycolipids or Glycosphingolipids, and (iii) Gangliosides. All of these are derivatives of ceramide but differ in their head groups.

**Sphingomyelins (also called Sphingophospholipids)**

Sphingomyelins are the simplest and most abundant sphingolipids. As they contain phosphorous, they along with glycerophospholipids, can be categorized as phospholipids. They characteristically contain phosphocholine (Fig. 10) or phosphoethanolamine as their polar head groups. Sphingomyelins closely resemble phosphatidylcholine in their general properties, three-dimensional structure and in having no net charge on their head groups. Sphingomyelins are present in plasma membrane of animal cells. The myelin sheath, present around the axons of myelinated neurons, is characteristically rich in sphingomyelins.

![Fig. 10: Structure of sphingomyelin with phosphocholine head group](image)

**Neutral Glycolipids**

Neutral glycolipids are also classified as glycosphingolipids and occur largely in the outer face of plasma membrane. They contain one to six, sometimes more, sugar units in their head group connected directly to the -OH at C₁ of the ceramide moiety. They do not contain phosphorous. The most commonly found sugars are D-glucose, D-galactose and N-acetyl-galactosamine.
Cerebrosides are the simplest neutral glycolipids and have a single sugar linked to ceramide. Cerebrosides with \( \beta \)-D-galactose, galactocerebrosides (Fig. 11a), are characteristically found in plasma membranes of cells in neuronal tissue. In some cases, \( \beta \)-D-galactose of galactocerebrosides is sulfated at \( C_3 \) position to form ionic compounds called sulfatides (Fig. 11b). Cerebrosides with \( \beta \)-D-glucose are called glucocerebrosides which are present in plasma membrane of the cells in non-neuronal tissue. More complex cerebrosides occur largely in the outer layer of cell membranes and constitute important components of cell surface.

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**Fig. 11a: Galactocerebroside**

**Fig. 11b: Sulfatide**

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**Gangliosides**

Gangliosides are the most complex sphingolipids. They are given identifying symbols that indicate the structure of the head group. More than 60 members have been found in cell membranes. They are specifically abundant at nerve endings and at specific hormone receptor sites on cell surfaces. They contain very large polar heads made up of several sugar units. Characteristically, one or more terminal sugar units of gangliosides is N-acetyl neuraminic acid (also called sialic acid) that is ionized at pH 7.0 and bears a negative charge. Gangliosides make up to 6 percent of the membrane lipids in the gray matter of the brain but are found in lesser amounts in the membranes of most non-neuronal tissues. The ganglioside \( G_{M1} \) (Fig. 12) is the point of attachment of cholera toxin as it attacks an animal cell. They are also the determinants of cell-cell recognition and play important roles in growth and differentiation as well as in carcinogenesis. Glycosphingolipids are also the determinants of the ABO human blood groups (Fig. 13).

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**Fig. 12: Structure of ganglioside \( G_{M1} \)**

The membranes of human nervous system have at least 15 different gangliosides without a known function. The metabolism of membrane sphingolipids is prone to genetic defects of
enzymes involved in their degradation. If their biosynthesis remains normal and degradation is impaired then sphingolipids and their partial degradation products accumulate in the tissue. Derangement in the metabolism of gangliosides and cerebrosides underlie several human genetic diseases. Neumann-Pick diseases is caused by a genetic defect in sphingomyelinase that cleaves phosphocholine from sphingomyelin. This leads to accumulation of sphingomyelin in brain, spleen and liver leading to mental retardation and an early death of the individual. In Tay-Sachs disease, a specific ganglioside and its partially degraded products accumulate in brain and spleen due to a lack of a lysosomal enzyme hexosaminidase A that is responsible for cleavage of bond between N-acetyl-galactosamine and D-glucose in the polar head of the ganglioside. This leads to degeneration of the nervous system, progressive retardation in development, paralysis, blindness and death by the age of 3 to 4 years. One in 28 jews of the eastern Europe carry a defective gene coding for hexosaminidase A in recessive form.

Fig. 13: Structure of the ABO blood group carbohydrates, with sialylated antigen. R= the linkage to protein in the secreted forms, sphingolipid in the cell-surface bound form, open square = N-acetyl glucosamine (GlcNAc), open diamond = galactose, filled square = fucose, filled diamond = N-acetyl galactosamine (GalNAc), filled diamond = N-acetyl neuraminic acid (sialic acid)

Properties and Functions of Phospholipids

Owing to their polar heads and nonpolar tails (Fig. 14), the phospholipids tend to associate in an orderly manner in the aqueous medium to avoid exposure of their hydrophobic tails to water. They can form monolayer at the air-water interface, micelles, unilamellar vesicles (also called liposomes, formed by rolling of a sheet of lipid bilayer that enclose aqueous compartment) or multilamellar vesicles.
Phospholipids are Structural Components of Biological Membrane

Polar lipids are major components of biological membranes. Among the lipids of the membranes, glycerophospholipids are the most abundant. The lipids that constitute the plasma membrane are also termed as the structural lipids. The membrane may additionally have other polar lipids such as sphingolipids, glycolipids, sulfolipids, cholesterol and ether lipids. Membrane lipids make up 5 to 10 percent of the dry mass of most cells. With some important exceptions, these lipids play a passive role in the cell forming impermeable or semipermeable barriers around cells and cellular compartments.

![Structure of a glycerophospholipid molecule (phosphatidylcholine)](image)

**Fig. 14: Structure of a glycerophospholipid molecule (phosphatidylcholine) showing the polar (hydrophilic) head and nonpolar (hydrophobic) tail. The right part shows the orderly aggregation of amphipathic glycerophospholipids in aqueous medium to form micelles, bilayer membrane and liposomes**

**Phospholipids are involved in Membrane Fusion and Exocytosis**

Phosphatidylinositol and its phosphorylated derivatives act at several levels to regulate cell structure and metabolism. Phosphatidylinositol-4,5-bisphosphate in the inner face of the plasma membrane serves as a specific binding site for certain cytoskeletal proteins and for some soluble proteins involved in membrane fusion during exocytosis.

**Phospholipids play a role in Intracellular Signaling**

Phosphatidylinositol serves as a reservoir of messenger molecules that are released inside the cell in response to extracellular signals interacting with specific receptors on the outer surface of plasma membrane. The signal acts through a series of steps that begin with enzymatic removal of phospholipid head group and ultimately leads to activation of an enzyme, protein kinase (Fig. 15). For example, when the hormone vasopressin binds to its receptor in plasma membrane of epithelial cells of the renal collecting duct, a specific phospholipase C is activated. Phospholipase C hydrolyzes the bond between glycerol and phosphate in phosphatidylinositol-4,5-bisphosphate releasing the water-soluble inositol 1,4,5-trisphosphate (IP$_3$) and diacylglycerol (DAG) that remains associated with plasma membrane. IP$_3$ triggers release of Ca$^{2+}$ from the endoplasmic reticulum, and the combination of diacylglycerol and elevated cytosolic Ca$^{2+}$ activates protein kinases. The protein kinases, utilizing ATP, phosphorylate specific amino acid
residues in more than one target proteins, thereby altering their activity and consequently the metabolism of the cell.

Inositol phospholipids also serve as points of nucleation for assembly of certain supramolecular complexes involved in signaling and exocytosis. Specific proteins are known to bind phosphatidylinositols in membranes with high specificity and affinity and initiate the formation of multienzyme complexes at the cytosolic surface. A number of proteins also specifically bind to phosphatidylinositol-3,4,5-trisphosphate, and the formation of this phospholipid in response to extracellular signals brings the proteins together at the surface of the plasma membrane.

Fig. 15: Role of membrane phosphatidylinositols in cellular regulation

Membrane sphingolipids also can serve as sources of intracellular messengers. Both ceramide and sphingomyelin are potent regulators of protein kinases. Ceramide and its derivatives are
known to be involved in the regulation of cell division, differentiation and migration, and programmed cell death called apoptosis.

**Role in the generation of Eicosanoids**

Activation of phospholipase A$_2$ may release arachidonic acid from the membrane phospholipids that contain them. This free arachidonic acid may serve as the precursor molecule for synthesis of different classes of eicosanoids such as prostaglandins, thromboxanes and leukotrienes. These molecules function as paracrine hormones and have diverse range of biological functions (see the section Eicosanoids).

**Role in Plants**

Vascular plants also contain phosphatidylinositol-4,5-bisphosphate, as well as the phospholipase that releases IP$_3$. They use IP$_3$ to regulate the intracellular concentration of Ca$^{2+}$. Brassinolide (Fig. 16) and the related group of brassinosteroids are potent growth regulators in plants that increase the rate of stem elongation and control the organization of cellulose microfibril arrangement in cell wall during growth.

![Fig. 16: Structure of brassinolide](image)

![Fig. 17: Structure of jasmonate](image)

Jasmonate (Fig. 17) is a derivative of membrane phospholipids containing linolenic acid [18:3($\Delta^{9,12,15}$)]. It is chemically similar to eicosanoids of animal tissue and acts as a powerful signal triggering the plant’s defenses in response to insect-inflicted damage. The methyl ester of jasmonate gives the characteristic fragrance of jasmine oil that is of commercial interest.

**Eicosanoids**

Eicosanoids are fatty acid derivatives with a variety of extremely potent hormone like actions on various tissues of vertebrate animals. They are all derived from arachidonic acid [20:4($\Delta^{5,8,11,14}$)] (Fig. 18). They are paracrine hormones and differ from endocrine hormones in that they are not transported between tissues in the blood, but act only on cells near the point of their synthesis. Various eicosanoids are produced in different cell types by different synthetic pathways and have different target cells and biological actions in vertebrate animals. Three different eicosanoic fatty
acids give rise to three different eicosanoids characterized by the number of double bonds in their side chains, eg. PG\textsubscript{1}, PG\textsubscript{2}, PG\textsubscript{3}. Eicosanoids are known to be involved in reproductive functions; inflammation, fever and pain associated with injury or disease; formation of blood clot; regulation of blood pressure; gastric acid secretion etc. There are three classes of eicosanoids, (i) Prostaglandins, (ii) Thromboxanes, and (iii) Leukotrienes and Lipoxins.

**Prostaglandins**

The prostaglandins are named so since they were first recognized in the prostate gland. They exist in virtually every mammalian tissue. All of them contain a cyclopentane ring of five carbon atoms originally part of the arachidonic acid chain (Fig. 19). They are further divided into two groups, ether-soluble prostaglandins (PGE), and phosphate buffer-soluble prostaglandins (PGF). The E-type of prostaglandins have a keto group in position 9, whereas the F-type prostaglandins have a hydroxyl group in this position. Each of these contains many subtypes eg. PGE\textsubscript{1}, PGE\textsubscript{2} etc. Prostaglandins act by regulating the synthesis of 3',5'-cAMP that is an intracellular messenger. Cyclic AMP, in turn, mediates the action of many hormones, hence prostaglandins also mediate a wide range of functions. The physiological roles of prostaglandins may be summarized as follows:

1. Stimulation of contraction of smooth muscles of uterus during labor and menstruation,
2. Regulation of blood flow in specific organs,
3. Regulation of wake-sleep cycle,
4. Regulation of responsiveness of certain tissues to hormones such as epinephrine and glucagon, and
5. Elevation of body temperature producing fever and cause inflammation.

![Diagram of eicosanoid synthesis](attachment:Fig_18.png)

**Fig. 18:** Synthesis of eicosanoids from arachidonic acid released from membrane lipids by the activation of phospholipase
**Thromboxanes**

The thromboxanes were first isolated from thrombocytes (blood platelets). They have a six-membered ring containing an ether (Fig. 19). They are produced by platelets and act in the formation of blood clot and in reduction of blood flow to the site of the clot.

**Leukotrienes and Lipoxins**

Leukotrienes constitute the third group of eicosanoids formed via the lipoxygenase pathway. They were first found in leukocytes. They characteristically contain three conjugated double bonds (Fig. 19). They induce contraction of muscle lining of the airways to the lungs. Leukotrienes are potent proinflammatory agents, cause bronchoconstriction and play a role in asthma. Lipoxins (Fig. 19) are also related compounds produced via the same pathway but have four conjugated double bonds.

![Fig. 19: Structures of different types of eicosanoids](image)

**Isoprenoids**

Isoprenoids are synthesized from five-carbon precursors related to isoprene (Fig. 20). The isoprenoids include fat-soluble vitamins A, D, E and K and many biological pigments.
Fat-soluble vitamins

The structures of fat soluble vitamins are shown in Fig. 21. The vitamin A, called retinol, is an isoprenoid and functions as a pigment for vision in animals. It is also found in fish liver oil. Most animals are able to enzymatically convert carotenoids, acquired from plants, to vitamin A. Vitamin D is a derivative of cholesterol, e.g. cholecalciferol, that is known as the vitamin D$_3$. Vitamin E is a collective name of a group of closely related lipids called tocopherols, all of which contain a substituted aromatic ring and a long hydrocarbon side chain. Vitamin K is an isoprenoid cofactor required for blood clotting. Phylloquinone, vitamin K$_1$ is found in leaves while menaquinone, vitamin K$_2$, is found in bacteria present in animal intestine. The repeating unit, isoprene is marked for an understanding in Fig. 22.

Electron carriers

The lipid quinones, ubiquinone and plastoquinone are also isoprenoid derivatives that function as electron carriers in mitochondria and chloroplast respectively (Fig. 23). Ubiquinone is also called coenzyme Q and has ten isoprene units. Plastoquinone is the plant equivalent of ubiquinone. Both of these can accept either one or two electrons.
Dolichols

Dolichols form another group of isoprenoids which function as sugar carriers in biological systems (Fig. 24). During the assembly of complex carbohydrates of bacterial cell walls and during the addition of polysaccharide to certain proteins (glycoproteins) in eukaryotes, the sugar units to be added are chemically activated by attachment to dolichols. Animal dolichols have 17 to 21, bacterial dolichols have 11 and plant and fungal dolichols have 14 to 24 isoprene units. Dolichols are very hydrophobic compounds and participate in sugar transfer reactions.

Steroids

Steroids form a large class of compounds found in nature. All of them have the parent nucleus of 17-carbon perhydrocyclopentanophenanthrene, which consists of three six-membered rings and a five-membered ring fused together (Fig. 25). In most of the natural steroids a methyl group is present at C10. One or more alcoholic group(s) may also be present in the ring structure. These secondary alcohols are called sterols. Sterols are also synthesized from five-carbon isoprene units. In addition to the sterols, bile acids, male and female sex hormones, adrenocorticoids, and some alkaloids also have this parent ring structure.
Cholesterol

Cholesterol is the most abundant steroid of the animal kingdom and as many as 13 Nobel prizes have been awarded on cholesterol. It is found in all animal tissues but not in plants. Bacteria also lack cholesterol with rare exceptions. The concentration of cholesterol in different animal tissue varies 0.01 to 10.0 percent. Cholesterol is insoluble in water, acids and alkali, and soluble in organic solvents such as ether, benzene, chloroform and acetone. When it is mixed with fat or oil, it enables the latter to absorb large amounts of water by forming water-in-oil emulsions. Cholesterol is not saponifiable with alkali and prolonged exposure to alkali slowly decomposes it. It has a high dielectric constant, hence can act as a good electrical insulator for impulse generating and transmitting structures of the nervous system.

The structure of cholesterol is shown in Fig. 26. It is a steroid alcohol and its chemical properties are related to its secondary hydroxyl group and the double bonds. Majority of the animal sterols are of $\Delta^5$ type, having a double bond between C5 and C6, but $\Delta^7$ sterols, having a double bond between C7 and C8, are also found in nature. Oxidation of cholesterol yields the corresponding ketone, the cholestenone. The hydroxyl group of cholesterol readily forms esters with fatty acids that are widespread in different tissues. The presence of double bonds in cholesterol allows its hydrogenation to produce dihydrocholesterol that is found in animals along with cholesterol. It could also be halogenated like unsaturated fat and has an iodine number of 65.8. Oxidation of cholesterol may produce various ketones, hydroxy compounds and acids depending upon the
oxidizing agent and conditions used. Cholesterol is considered as an amphipathic molecule like the membrane glycerophospholipids. The hydroxyl group at C₃ functions as the small polar head while the rest of the structure is rigid and highly hydrophobic. The molecule can stably exist within the lipid bilayer of biological membranes, and its presence decreases the fluidity of the membrane in a concentration-dependent manner. For storage and transport, the hydroxyl group at C₃ condenses with a fatty acid to form a sterol ester.

**Ergosterol**

Ergosterol, the structure of which is shown in Fig. 27, is the principle sterol of fungi and yeast. It has been named after the ergot bodies, which form on rye plants infected with ergot fungi, from which it was first isolated. Its properties are similar to those of cholesterol. Ergosterol is also important since it serves as the precursor molecule for vitamin D biosynthesis.

**Stigmasterol**

Stigmasterol, the structure of which is also very similar to that of cholesterol, is found in the cell membranes of higher plants. It differs from cholesterol only in having a double bond between C₂₂ and C₂₃ (Fig. 28).

![Fig. 27: Ergosterol](image)

![Fig. 28: Stigmasterol](image)

**Biologically important cholesterol derivatives**

The sterols are also used in biological system as precursors for a large number of molecules with specific biological activity. Most important among them are the steroid hormones such as testosterone, estrogen, progesterone and corticosteroids (Fig. 29) which bring about specific biological effects by regulating the expression of a number of target genes. Bile acids (Fig. 30), that are polar derivatives of cholesterol, are known to act as detergents in the intestine to emulsify the dietary fat for allowing them to be digested easily by digestive lipases.

Cholesterol and its esters with long-chain fatty acids are important components of plasma lipoproteins. Four major classes of lipoproteins have been recognized. Chylomicrons transport lipids resulting from digestion and absorption. Very low density lipoproteins (VLDL) transport triglycerides from the liver. Low-density lipoproteins (LDL) deliver cholesterol to the tissues, and high-density lipoproteins (HDL) remove cholesterol from the tissues and return it to the liver for excretion.
Fig. 29: The steroid hormones

Fig. 30: The structure of bile acids

Suggested Reading