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Textbook of Biochemistry

for Allied and Healthcare Students



P Ramamoorthy

3rd Edition

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CHAPTER

3

Chemistry of Lipids

CHAPTER OUTLINE

- Lipids
- Biomedical Importance/Functions
- Classification of Lipids
- Related Terms in Lipid Chemistry

LIPIDS

Lipids are a heterogeneous group of organic compounds. They are oily or greasy substances. They are relatively insoluble in water but considerably soluble in organic solvents, such as chloroform, benzene and ether, etc.

Alternative Name
Fat.

Occurrence
They are widely distributed throughout the plant and animal kingdoms.

Composition
They contain fatty acid(s), alcohol and/or related substances.

BIOMEDICAL IMPORTANCE/FUNCTIONS

1. *Energy:* The lipids are important constituents of the diet because of their high calorific value (9C/g) and due to fat soluble vitamins and essential fatty acids present in them. They provide about 25% of energy to the body.
2. *Storage:* They are stored mainly in adipose tissue (stored fat is called as fat depots).
3. *Structural components:* Lipoproteins and phospholipids present in cell membrane are essential for maintaining cell integrity.
4. *Insulation:* They serve as thermal insulator in the subcutaneous tissues and as electrical insulators in neurons. They act as padding material around certain internal organs.
5. *Biochemical compounds:* Vitamin D, steroid hormones and bile acids are all synthesized from cholesterol. Prostaglandins are fatty acid derivatives.
6. *Transport:*
   - They help in the absorption and transport of fat soluble vitamins.
   - Lipoproteins are used as transport forms of certain metabolic fuel in the blood.
7. *Miscellaneous:* They act as:
   - Lung surfactant (dipalmitoyl lecithin)
   - Lipotropic factor to prevent formation of fatty liver (inositol)
   - Emulsifying agent in digestion and absorption (bile salts).
   - Metabolic regulation (prostaglandins)

Clinical Importance

- Lipids are the causative agents in obesity, atherosclerosis, etc.
- Defective metabolism of lipids due to enzyme deficiency may lead to inborn errors of metabolism, e.g., Gaucher's disease, Tay-Sachs disease.

CLASSIFICATION OF LIPIDS (FIG. 3.1)

According to Bloor's modified classification, lipids are divided into four major groups based on their composition:

1. Simple lipids
2. Compound lipids
3. Derived lipids
4. Miscellaneous lipids

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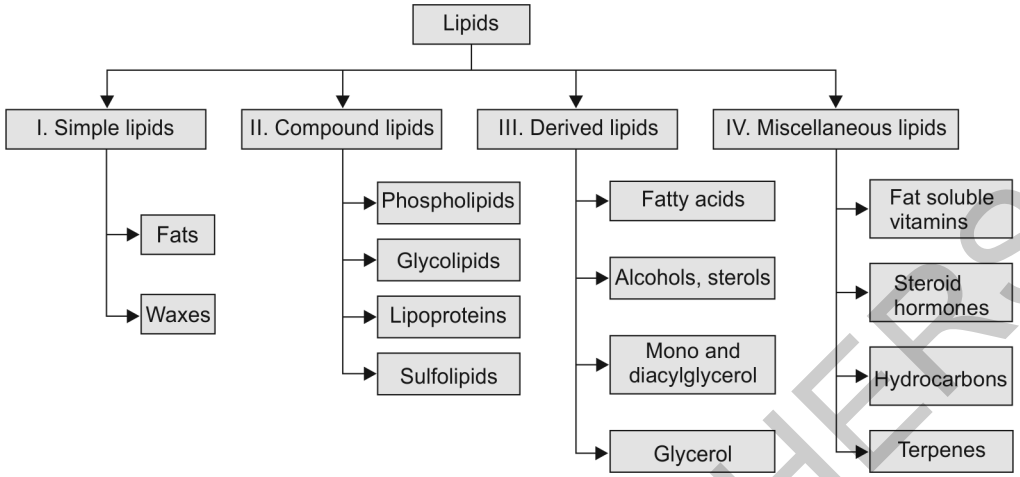


Fig. 3.1: Classification of lipids.

I. Simple Lipids

Definition

Simple lipids are esters of fatty acids with various alcohols.

Composition

Simple lipid = Fatty acids + Alcohol

Subclasses

They are divided into two subclasses:
1. Fats
2. Waxes

I. Fats

Alternative names:
- Triacylglycerols
- Triglycerides
- Neutral fats

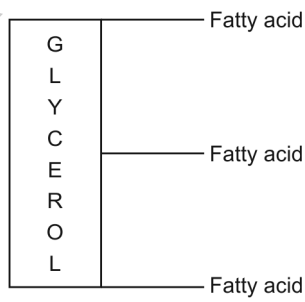
Definition

Fats are the esters of fatty acids with glycerol.

Composition

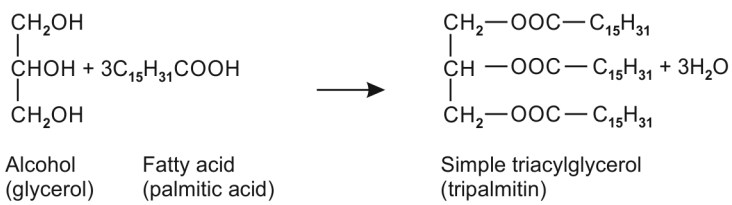
Fat = Fatty acids + Glycerol

Structure



Examples

- *Simple triacylglycerol:* If three molecules of same fatty acid combine with one molecule of glycerol, the resulting fat is a simple *triacylglycerol*, e.g., tripalmitin.
- *Mixed triacylglycerol:* If fatty acids are different, the resulting fat is a mixed *triacylglycerol*.



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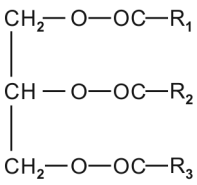


Mixed triacylglycerol

R_1, R_2, R_3—Different fatty acids

Functions

The fats serve several physiological functions in the body.

- They are storage lipids for energy in adipose tissue.
- They provide insulation against the loss of body heat.
- They act as padding material of support and protect internal organs.

Clinical Importance

Increased in cardiovascular diseases.

Sources

Fats represent the most common and widespread class of lipids in nature.

Plant fats

Coconut oil, olive oil, gingelly oil, cotton seed oil, groundnut oil, and soya bean oil.

They contain mostly unsaturated fatty acids such as oleic acid, linoleic acid and linolenic acid.

Animal fats

Butter, fish oil, lard, milk, eggs and tallo (ox/sheep fat)

They mostly contain saturated fatty acids such as palmitic acid and stearic acid.

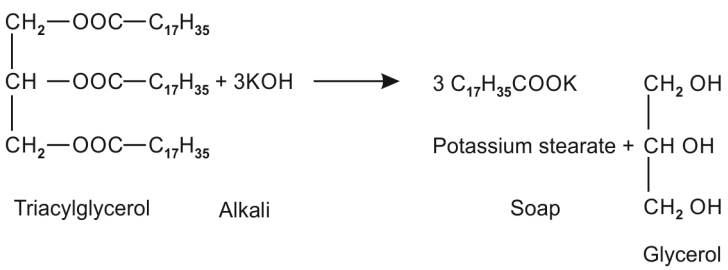
Properties

A. Physical properties

- *State:* They are greasy in nature. Animal fats are solid at room temperature. Plant fats are liquids at room temperature and are known as plant oils.
- *Solubility:* They are insoluble in water, but are readily soluble in organic solvents, such as chloroform, ether, etc.
- *Color, odor, and taste:* Pure fats are colorless, odorless and tasteless. But they develop flavor and color due to presence of certain foreign substances or bacterial flora.
- *Reaction:* Neutral. But after exposure to air, they become acidic.
- *Specific gravity:* They have less specific gravity than water and therefore they float on water.
- *Melting point:* Fats containing saturated fatty acids have higher melting point. Those containing unsaturated fatty acids have lower melting point.
- *Spreading:* Liquid fats spread uniformly over the surface of water when it is placed on it. This property called spreading is to reduce surface tension of water and help transport of fat.
- *Emulsification*
  - *Definition:* It is the process by which lipid mass is converted into a number of small lipid droplets.
  - *Process:* Fats may be emulsified by shaking either with water or with emulsifying agents, such as soaps, gums, proteins, etc.
  - *Importance:* The process of emulsification has great metabolic significance. Emulsification greatly increases the surface area of fats. Fats are emulsified by bile salts before they are absorbed by the intestinal wall.

B. Chemical properties

- **Hydrolysis**
  - Alkali hydrolysis (*Saponification*)
    - *Definition:* The hydrolysis of a fat by an alkali is called as saponification. The resulting products are glycerol and alkali salts of fatty acids.



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- *Importance:* Soaps consist largely of sodium or potassium salts of palmitic or stearic acids.

- *Enzymatic hydrolysis:* The fats are hydrolyzed by the enzyme lipase of pancreatic juice to yield first diacylglycerol, then monoacylglycerol and finally fatty acids and glycerol *(refer below)*.

❖ *Auto-oxidation:* Some of the natural oils containing unsaturated fatty acids when exposed to atmosphere and light absorb oxygen and undergo auto-oxidation. This process is used in the manufacture of paints and varnishes.

❖ *Rancidity:*

- *Definition:* Auto-oxidation occurring in natural edible fats is called rancidity. The rancidity develops disagreeable odor and taste and becomes unfit for consumption.
- *Causes/types:* Rancidity may be caused by the following:
  - *Hydrolytic rancidity:* It involves partial hydrolysis of triacylglycerol to mono or diacylglycerol, glycerol and fatty acids, by the influence of moisture, warmth and enzymes-like lipases. Butter becomes rancid in summer due to liberation of volatile fatty acids, (e.g., Butyric acid).
  - *Oxidative rancidity:* (Lipid peroxidation) (*refer* Chapter 32).

    The unsaturated fatty acids may be oxidized to form peroxides which then decompose to form aldehydes and ketones giving objectionable odor and taste. This type of rancidity is known as lipid peroxidation. It occurs more frequently in animal fats.

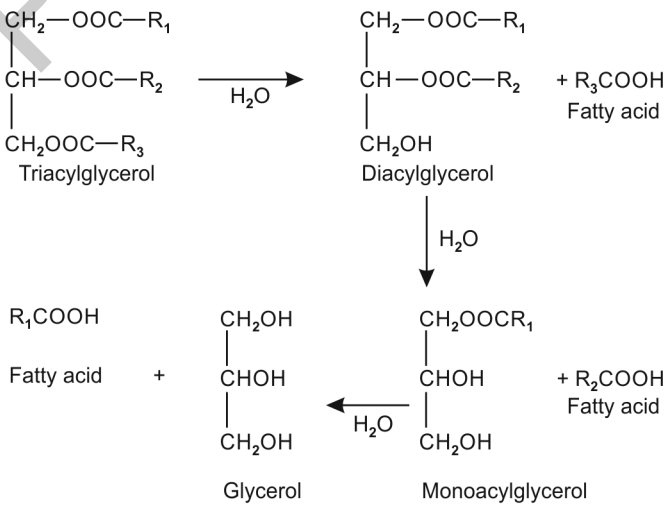
    Causes: It may be initiated by *free radicals* (ROO.) formed in the body. It will affect integrity of biomembranes leading to cell death, aging, cancer, atherosclerosis, inflammatory diseases, etc.
- *Prevention (antioxidants)*
  - Addition of antioxidants, such as vitamin C, A and E, phenols, gallic acid, etc.
  - Storing fats in air-tight nonmetallic vessels and keeping away from light, moisture and warmth.
  - Refrigeration

❖ *Addition reactions:* The unsaturated fatty acids present in fat undergo all the addition reactions, e.g., hydrogenation, halogenation, etc.

Hydrogenated oils and refined oils: The unsaturated fatty acids of fats may be hydrogenated in the presence of nickel catalyst.

$$\underset{\text{(unsaturated fat)}}{\text{Olein}} \xrightarrow{H} \underset{\text{(saturated fat)}}{\text{Stearin}}$$

This process is used to prepare cooking fat and margarine in food industry. Oils which are liquids at ordinary temperature become solids on hydrogenation. This is the basis of manufacture of vanaspathi.



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Tests for purity of fats (Characterization of fats)

Fats and oils form essential constituents of diet. So, it is necessary to detect the impurities and adulterations in food fat and also to determine the proportions of different types of fat in a mixture. Following tests are employed:

Physical methods

- Specific gravity
- Refractive index
- Melting point
- Solidification point

Chemical methods

- *Saponification number (SN):* It is the number of mg of KOH required to saponify (hydrolyze) 1 g of fat or oil. It gives a measure of their molecular weight and size of the fatty acid chain in the fat.
  SN of butter = 233–240
  SN of coconut oil = 250–264
- *Iodine number (IN):* It is the number of grams of iodine absorbed by 100 g fat or oil. Thus, it is a measure of degree of unsaturation of fat.
  - Oils have higher iodine number because they contain more unsaturated fatty acids. Fats have lower iodine number because they contain more saturated fatty acids.
    IN of butter = 26–28
    IN of sunflower oil = 125–135
  - Certain iodized oils (e.g., iodized poppy seed oil) are used in medicine for injection into body cavities to be X-rayed.
- *Acid number (AN):* It is the number of mg of KOH required to neutralize the free fatty acids present in 1 g fat or oil.
  - It is of value in determining rancidity due to free fatty acids. The edibility of fat is inversely proportional to the acid number.
    AN of butter = 0.35–0.45

Note

Other chemical methods are also used, e.g., acetyl number.

II. Waxes

Definition

Waxes are the esters of higher fatty acids with long chain alcohol.

Composition

Waxes = Higher fatty acids + Long-chain alcohol
C_{24} to C_{31} (myricyl alcohol)

Examples

- *Common wax:* This is cholesterol ester (cholesterol palmitate) found in human blood plasma and sebaceous glands.
- *Lanolin (or) woolwax:* It is used for making ointments and cosmetics.
- *Carnauba wax:* It is plant wax used for manufacture of polishes.
- *Bees wax:* This is secreted by honey bee to form honey comb. Its chief ingredient is myricyl palmitate.

Properties

They are not easily hydrolyzed and hence no nutritional value.

Biomedical importance/functions

- Used as protective coatings of the skins and furs of animals.
- Presence of wax on feathers and hairs of birds helps to keep them soft and flyable.
- Highly resistant to atmosphere oxidation. Hence used in polishing furniture and automobiles and in manufacture of wax coat paper to preserve perishable food products.

II. Compound Lipids (Complex Lipids)

Definition

Compound lipids are esters of fatty acids with alcohol containing additional groups.

Composition

Compound lipid = Fatty acid + Alcohol + Other group(s).

Subclasses

They are subdivided into:

- Phospholipids
- Glycolipids
- Lipoproteins
- Sulfolipids

Phospholipids

Definition

They are esters of fatty acids with glycerol or other alcohols containing phosphoric acid, nitrogenous base and other constituents.

Composition

Phospholipid = Fatty acid + Glycerol/Other alcohol + Phosphoric acid + Nitrogenous base + Other constituent

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Biomedical importance/functions

- *Structure:* They are components of lipoprotein complexes, which constitute the matrix of cell walls and membranes, microsomes, mitochondria and myelin sheath.
- *Absorption:* Lecithin aids in emulsification of lipid-water mixture for digestion and absorption of lipids from GI tract.
- *Transport:*
  - They take an active part in the transport of triacylglycerol as chylomicrons.
  - They are required for the formation of very low-density lipoprotein (VLDL) which carries endogenous triacylglycerol from liver to various tissues.
- *Blood coagulation:* They play an essential role in blood coagulation.
  - In conversion of prothrombin to thrombin
  - In the activation of factor VIII
- *Insulation:* Phospholipids present in myelin sheaths provide insulation around nerve fibers.
- *Lipotropic action:* Lecithin provides choline which acts as a lipotropic factor to prevent the formation of fatty liver.
- *Hormone action:* Phosphatidylinositol acts as second messenger in hormone action.

Clinical Importance

- Deficiency of dipalmitoyl lecithin in premature babies may produce respiratory distress syndrome.
- Lecithin/sphingomyelin ratio can be used as an indicator for evaluation of fetal lung maturity.

Sources

They are present in large amounts in nerve tissue, brain (white matter), liver, kidney, pancreas, heart, egg yolk and soya bean oils.

Subclasses

They are divided into three subgroups based on the type of alcohol present:

1. Phosphoglycerides
2. Phosphoinositides
3. Phosphosphingosides

Phosphoglycerides

Definition

These are triesters of glycerol 3-phosphate and a nitrogenous base. They are derivatives of phosphatidic acid.

Composition

Fatty acids + Glycerol + Phosphoric acid → Phosphatidic acid; Phosphatidic acid + Nitrogenous base

Examples

1. Lecithin
2. Cephalin
3. Plasmalogens
4. Cardiolipin

Lecithin:

Alternative name: Phosphatidyl choline.

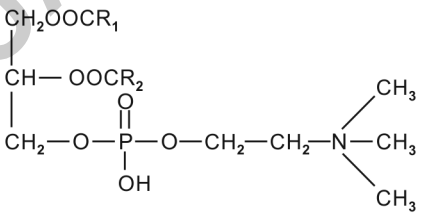
Composition:

Lecithin = Fatty acids + Glycerol + Phosphoric acid + Choline

Sources:

- *Animal:* Nerve tissue, glandular tissue, egg yolk
- *Plant:* Soyabean oil, yeast.

Structure



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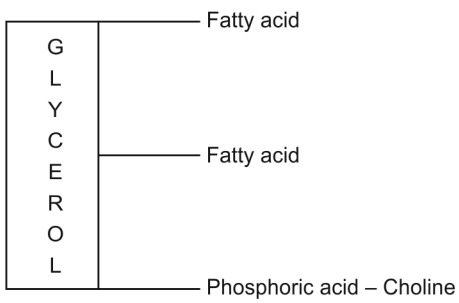

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Properties

- It is a waxy white substance when pure but turns brown on exposure to air and light due to auto-oxidation and decomposition.
- Soluble in all fat solvents except acetone.
- Exists as zwitterions
- *Hydrolysis:* Lecithins can be hydrolyzed by dilute acids, alkalis or enzymes called *lecithinases (phospholipases)*. Complete hydrolysis of lecithin yields glycerol, phosphoric acid, choline and fatty acids. But partial hydrolysis of lecithins by lecithinases yields various products, such as lysolecithins which are potent *hemolytic poisons.*

There are mainly four types of lecithinases (phospholipases) **(Table 3.1)**.

Action of Lecithinases on Lecithins (*refer* Chapter 12): They hydrolyze lecithin in a characteristic way.

Lecithin $\xrightarrow{A_2}$ Fatty acid + Lysolecithin

Lecithin $\xrightarrow{A_1}$ Fatty acid + Glyceryl phosphoryl choline

Lecithin $\xrightarrow{C}$ Diacylglycerol + Phosphoryl choline

Lecithin $\xrightarrow{D}$ Choline + Phosphatidic acid

Biomedical importance:

- Lecithins are necessary for normal transport and utilization of other lipids especially in liver. In their absence, accumulation of lipids occurs in liver leading to a disorder called fatty liver. Choline is a lipotropic factor which prevents fatty liver formation.
- Maintain cell integrity
- They act:
  - As a store of labile methyl groups, e.g., choline
  - As emulsifying agent in digestion and absorption of fats.
- Involved in transmission of nerve impulses, e.g., acetylcholine

Table 3.1: Types of phospholipases.

Types	*Present in*
Phospholipase A2	Cobra, spider venom and poisonous stings
Phospholipase A1	Penicillium notatum, pancreas
Phospholipase C	Snake venom, human brain, plants
Phospholipase D	Carrots, cabbages, cotton seed

Clinical Importance

Respiratory distress syndrome: Dipalmitoyl lecithin acts as lung surfactant and lowers surface tension in lung alveoli. Its absence in premature babies may result in collapse of lung alveoli producing respiratory distress syndrome (RDS). Its symptoms are rapid and shallow breathing, and blue skin. Patient should be given breathing support and oxygen therapy.

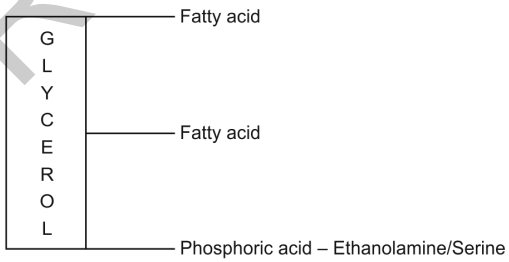
Cephalin

Alternative name: Phosphatidylethanolamine/ phosphatidylserine.

Composition: Cephalin resembles lecithin except that choline is replaced by ethanolamine or serine.

Cephalin = Glycerol + Fatty acids + Phosphoric acid + Ethanolamine/serine.

Structure



Occurrence: Cephalins are present in brain, spinal cord, soya bean oil.

Properties: They have characteristic properties similar to lecithins. They are more acidic and less soluble in alcohol than lecithins.

Biomedical importance/functions: It is a part of enzyme thromboplastin and so it has thromboplastic activity.

Plasmalogens

They resemble lecithin or cephalin, but one fatty acid molecule is replaced by an unsaturated ether. The nitrogenous base is usually ethanolamine or choline.

Composition:

Plasmalogen = Fatty acid + Unsaturated ether + Glycerol + Phosphoric acid + Ethanolamine/Choline

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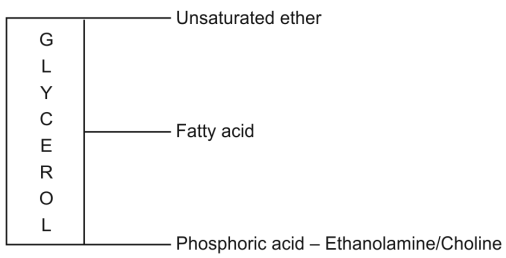
Structure



e.g., 1. Phosphatidylcholine
2. Phosphatidylethanolamine

Occurrence: Present in brain and muscle.

Importance: Platelet activating factor is a plasmalogen.

Cardiolipin

Composition:
Cardiolipin = Glycerol + Fatty acid + Phosphoric acid,
e.g., Diphosphatidylglycerol

Structure:
Phosphatidic acid — Glycerol — Phosphatidic acid

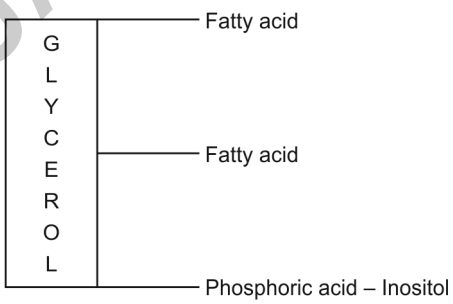
Occurrence: Present in mitochondria and mainly in myocardium.

Biomedical importance:
- Used as an antigen in serological test (VDRL) for syphilis.
- Essential for mitochondrial function. Its deficiency produces cardiomyopathy.

Phosphoinositides
These are phospholipids where a cyclic hexahydroxy alcohol called inositol (as myoinositol) replaces base, e.g., phosphatidylinositol.

Composition:
Fatty acids + Glycerol + Phosphoric acid + Inositol

Structure



Occurrence: Brain and nerve tissues, tubercle bacilli, soya beans.

Importance: Involved in transport process in cell; Acts as a precursor of second messenger in hormone action.

Phosphosphingosides
These are phospholipids which do not contain glycerol but an amino alcohol called sphingosine along with fatty acid, phosphoric acid and choline, e.g., *sphingomyelins*.

Composition

$$\underbrace{\text{Fatty acids} + \text{Sphingosine}}_{\text{Ceramide}} + \text{Phophoric acid} + \text{Choline}$$

Structure
Sphingosine - Fatty acid
|
Phosphoric acid - Choline

Sources
Brain and nerve tissue especially in the myelin sheath.

Function: Cell signaling

Clinical Importance

Niemann–Pick disease: It is an inherited disorder of sphingomyelin metabolism (inborn error of lipid metabolism). It is a lipid storage disease. In this disease, sphingomyelin is not degraded due to absence of enzyme sphingomyelinase. Hence large quantity of sphingomyelin accumulates in brain and also in liver and spleen especially in children. The clinical symptoms are enlargement of abdomen, liver, spleen and mental retardation.

Glycolipids

Definition
Lipids containing carbohydrate moiety are called glycolipids.

Composition
Similar to sphingolipids but base is replaced by a sugar. Also they do not contain phosphoric acid.
Fatty acid + Sphingosine + Sugar.

Functions:
- Maintains stability of cell membrane
- Cell-cell interaction
- Insulator of nerves.

Classification
They are classified into two types:
1. Cerebrosides
2. Gangliosides.

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Cerebrosides

Occurrence:

- *High:* Brain (white matter and myelin sheath)
- *Low:* Gray matter and other tissues

Composition: They contain galactose (instead of choline) and sphingosine and a higher molecular weight fatty acid. They do not contain phosphoric acid.

Structure:

Sphingosine–Fatty acid
|
Galactose

Properties: They mostly resemble sphingomyelins in properties.

Types: Four types of cerebrosides have been identified **(Table 3.2)**.

Clinical Importance

Gaucher's disease: It is a lipid storage disease. It is an inborn error of lipid metabolism due to deficiency of enzyme β *Glucosidase*. Galactose in cerebrosides is replaced by glucose. Glucose cerebrosides accumulate in liver and spleen. Cerebronic acid is the major fatty acid increased in this condition. The clinical symptoms are enlarged liver and spleen, osteoporosis and mental retardation.

Gangliosides

Occurrence: Present in ganglions and hence the name gangliolipids. High in grey matter of brain.

Composition: They are similar to cerebrosides in structure but also contain N-acetyl galactosamine and neuraminic acid. e.g., GM_1, GM_2, GM_3.

Structure

Fatty acid – Sphingosine – Glucose – Galactose
– N-acetylgalactosamine
N-acetylneuraminic acid (NANA)

Clinical Importance

Tay–Sachs disease: It is an inborn error of lipid metabolism due to deficiency of the enzyme hexosaminidase A. It is also a lipid storage disease. Concentration of gangliosides increases in brain and nervous tissue in this disorder. The clinical symptoms are muscular weakness, blindness and mental retardation.

Table 3.2: Types of cerebrosides and their fatty acid components.

Sl. No.	Examples	Fatty acid component
1.	Nervon	Nervonic acid
2.	Oxynervon	Oxynervonic acid
3.	Kerosin	Lignoceric acid
4.	Cerebron	Cerebronic acid

Lipoproteins

Definition

They are macromolecular complexes of lipids and proteins (also called as conjugated proteins).

Lipid + Protein = Lipoprotein

Classification (types)

They are classified into many subclasses depending on ultracentrifugation and electrophoresis **(Table 3.3)**.

Composition (Table 3.4)

- They have characteristic density, mol.wt and size.
- They differ in their composition.

Lipids present in lipoproteins

Triacylglycerol, phospholipids, cholesterol, cholesterol esters.

Proteins present in lipoproteins

Apoproteins (A, B, C, E with subclasses)
(*refer* Chapter 4)

Biomedical importance/functions

- Maintain structural integrity of cellular membranes, mitochondria, microsomes.
- Involved in transport and metabolism of lipids (*refer* Chapter 12).

Clinical Importance

Lipoproteins present in plasma are of *clinical importance*. They may alter in:

- Atherosclerosis
- Hyperlipoproteinemia
- Hypolipoproteinemia

(*refer* Chapter 12)

Table 3.3: Types of lipoproteins based on ultracentrifugation and electrophoresis.

Sl. No.	Ultracentrifugation	Electrophoresis
1.	Chylomicrons	Chylomicrons
2.	Very low-density lipoproteins (VLDL)	Pre β-lipoproteins
3.	Intermediate density lipoproteins (IDL)	–
4.	Low-density lipoproteins (LDL)	β-lipoproteins
5.	High-density lipoproteins (HDL)	α-lipoproteins

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Table 3.4: Composition of lipoproteins.

Sl. No.	Fraction	Protein %	Total lipid %	Triglycerides %	Phospholipids %	Cholesterol %	Cholesterol esters %	Free fatty acids %
1.	Chylomicrons	1–2	98–99	88	8	3	1	-
2.	VLDL	7–10	90–93	56	20	15	8	1
3.	IDL	11	89	29	26	34	9	1
4.	LDL	21	79	13	28	48	10	1
5.	HDL	33	67	16	43	31	10	–

Note: LDL contains more cholesterol.

Sulfolipids

Composition

They resemble cerebrosides but galactose is sulfated.

Structure

Sphingosine-Fatty acid
|
Galactose-Sulfate

Occurrence

Present in high concentration in white matter of brain and also in liver, kidney, testes and tumors. Widely distributed in plants (chloroplast).

Clinical Importance

Accumulates in metachromatic leukodystrophy due to deficiency of enzyme aryl sulfatase A.

III. Derived Lipids

Definition

They are derivatives obtained by the hydrolysis of simple or compound lipids.

Examples

1. Fatty acids
2. Alcohols (glycerol, sterols)
3. Monoacylglycerol and diacylglycerols

Fatty acids

Definition

Fatty acids are characteristic building block components of the most of the lipids. Most of the fatty acids are monocarboxylic acids. They have a single ionizable carboxyl group and a long nonpolar hydrocarbon chain.

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - COOH$$

Biomedical importance/functions

- They act as fuel molecules. They are stored as triacylglycerols and catabolized to generate energy.
- They are components of cell membranes
- Derivatives of fatty acids serve as:
  - Local hormones (prostaglandins)
  - Second messenger (diacylglycerol).

Numbering of carbon atoms (Table 3.5)

It is by two ways:

1. *Delta system:* The position of carbon atoms in the fatty acids chain is indicated by numbering. In this case, carboxyl carbon is numbered as C_1. The carbon adjacent to C_1 is C_2 and so on.
2. ω *system:* Position of carbon atoms in the fatty acid chain may be indicated by Greek letters. The carbon atom adjacent to carboxyl group is α carbon. Next to α carbon is β carbon. ω carbon is farthest from the carboxyl group.

Indicating position of double bonds

Various conventions are in use for indicating the number and position of double bonds.

- A widely used convention is to indicate the number of carbon atoms, the number of double bond(s) and the position of the double bond(s). Position of a double bond is indicated

Table 3.5: Numbering of carbon atoms in fatty acids.

Methyl terminus/ω terminus							*Carboxyl terminus*			
	CH_3–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	CH_2–	COOH
Numbering	10	9	8	7	6	5	4	3	2	1
Letter										
Designation ω	ω						γ	β	α	

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by the lower number of two carbon atoms included in double bond, e.g., oleic acid : 18 : 1 : 9 (or) 18 : 1 : Δ9

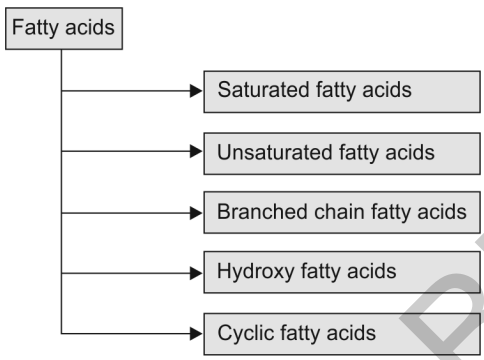
$CH_3 (CH_2)_7 CH = CH (CH_2)_7 COOH$

(It has 18 carbon atoms and one double bond between 9 and 10 carbon atoms).

- Alternative method to name the unsaturated fatty acid is to write first the position of double bonds in numerals and then the total number of carbon atoms in Roman followed by the suffice 'enoic acid'.
  For example: Oleic Acid: 9 Octadecenoic acid.

Classification/types

They are classified as:



Saturated fatty acids

They do not contain double bond(s). Their general molecular formula is C_nH_{2n+1} COOH. They are built from acetic acid which is the first member of the series, e.g.,

- Palmitic acid $C_{15}H_{31}COOH$
- Stearic acid $C_{17}H_{35}COOH$

They contain generally even number of carbon atoms, but few odd carbon fatty acids are also present. Animal fats contain saturated fatty acids. Presence of saturated fatty acid makes the fat solid, but there are some exceptions, e.g., coconut oil is a liquid fat containing saturated fatty acids.

Unsaturated fatty acids

They are characterized by having one or more double bonds. Their general molecular formula is $C_nH_{2n-1}COOH$. They are usually liquids (plant oils).

They are subdivided based on the degree of unsaturation, (i.e., according to number of double bonds).

- *Monounsaturated fatty acids-MUFA* (only one double bond), e.g., oleic acid

  (9 octadecenoic acid) $C_{17}H_{33}COOH$

  $CH_3(CH_2)_7CH = CH(CH_2)_7COOH$

- *Polyunsaturated fatty acids* (more than one double bond)—PUFA
  - Fatty acid with two double bonds, e.g., linoleic acid (9, 12, octadecadienoic acid) $C_{17}H_{31}COOH$

    $CH_3–(CH_2)_4–CH = CH–CH_2–CH= CH–(CH_2)_7 COOH$
  - Fatty acid with three double bonds, e.g., α-linolenic acid

    (9, 12, 15 Octadecatrienoic acid) $C_{17}H_{29}$ COOH

    $CH_3–CH_2–CH = CH–CH_2 – CH = CH – CH_2 CH = CH (CH_2)_7 – COOH$
  - Fatty acid with four double bonds, e.g., arachidonic acid

    (5, 8, 11, 14 eicosatetraenoic acid) $C_{19}H_{31}$ COOH

    $CH_3 (CH_2)_4 CH = CH CH_2 CH = CH – CH_2CH = CH CH_2 CH = CH (CH_2)_3 COOH$

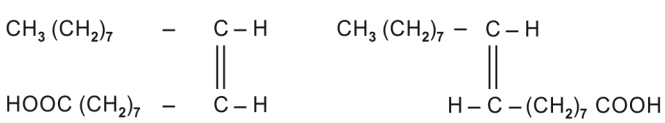
All three polyunsaturated fatty acids are essential fatty acids *(refer Page 43)*.

Isomerism in unsaturated fatty acids: Unsaturated fatty acids exhibit cis-trans isomerism (geometrical isomerism) depending on the orientation of atoms or groups around double bond.

In cis-isomer, acyl chains are on the same side of the bond, e.g., oleic acid.

All the naturally occurring unsaturated fatty acids are cis isomers.

In trans-isomer, acyl chains are on the opposite sides of the bond, e.g., elaidic acid.



Oleic acid (cis) Elaidic acid (trans)

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Transfatty acids

They are a type of unsaturated fatty acids which occur in small amount in meat, milkfat, and fastfoods. Artificial trans fats are also formed during hydrogenation of oils. They raise LDL (bad cholesterol) which may lead to heart disease.

Branched chain fatty acids

- They are present in certain foods, e.g., phytanic acid in butter.
- Sebum contains branched chain fatty acids.
- Tuberculostearic acid (C_{19}). It is found in Bacillus tuberculosis.

Hydroxy fatty acids

For example,

- *Ricinoleic acid:* It occurs in castor oil.
- *Cerebronic acid:* It is present in glycolipids.

Cyclic fatty acids

For example,

- Chaulmoogric acid
- Hydnocarpic acid

Both are present in chaulmoogra oil which is used to treat leprosy.

Properties

A. Physical properties

- *State:* Lower fatty acids from butyric acid (C_4) to capric acid (C_{10}) are liquids at ordinary temp. Higher fatty acids above C_{10} are solids.
- *Solubility:* Lower fatty acids are soluble in water. Higher fatty acids are insoluble in water.
- *Specific gravity:* Except acetic acid, all other fatty acids are lighter than water.
- *Melting point:* Increases with increase in chain length. Decreases with increase in unsaturation.
- *Boiling point:* Increases with increase in chain length.
- *Volatility:* The short chain fatty acids are steam volatile. Volatility decreases with increase in chain length.
- *Spreading: Refer* properties of "Fats".

B. Chemical properties

Due to carboxyl group

- *Alcohol or aldehyde formation:* A fatty acid can be reduced to alcohol or aldehyde at high temperature in the presence of hydrogen. The sodium salts of these derivatives are used as detergents.

  $RCOOH \rightarrow RCHO$ or RCH_2OH

- *Salt formation:* Fatty acids form salts with alkalis. The alkali salts of fatty acids are called as soaps.

  $RCOOH + NaOH \rightarrow RCOONa + H_2O$

- *Ester formation:* Fatty acid condenses with alcohol to form esters.

  $RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$

  For example, triacylglycerols, cholesterol esters.

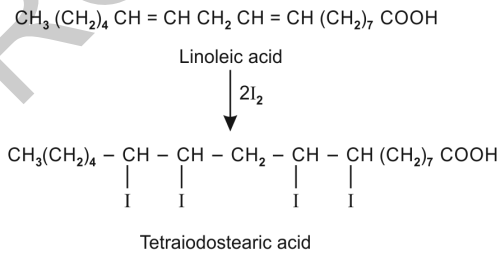
Due to hydrocarbon chain

- *Addition reaction:* Hydrogenation of unsaturated fatty acids using nickel as catalyst yields saturated fatty acids.

  $CH_3(CH_2)_7CH = CH-(CH_2)_7COOH$ (Oleic acid)

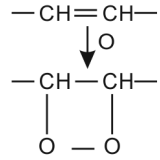
  $\xrightarrow{+2H} CH_3(CH_2)_{16}COOH$ (Stearic acid)

- *Halogenation:* Iodine and bromine are taken up by unsaturated fatty acids to give halogenated derivatives.



  This reaction is the basis of calculating iodine number.

- *Oxidation:*
  - *With atmospheric oxygen:* Unsaturated fatty acids are oxidized to form unstable peroxides which are later decomposed into a mixture of short-chain fatty acids and aldehydes. These give rancid taste and odor to the fats. This process is called as auto-oxidation or rancidity.



- *Biological oxidation:* In living systems, the fatty acids are enzymatically oxidized mainly by β oxidation (*refer* chapter 12).

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Essential fatty acids (EFA)

Definition

They are long chain polyunsaturated fatty acids which cannot be synthesized by the body. They have to be obtained from diet. They are essential constituents of diet (ω-group).

Examples

- Linoleic acid
- α-linolenic acid
- Arachidonic acid

Sources

Animal fats contain more saturated fatty acids, Vegetable fats contain more unsaturated fatty acids which are rich in EFA.

Vegetable oils: Sunflower oil—75%, Corn oil—50%, Cotton seed oil—45%, Peanut oil—25%.

Animal fats: Egg—9%, Lard—9%.

Biomedical importance/functions

- Required for growth and reproduction
- Prolong clotting time
- Diet containing animal fat (saturated fatty acid) tends to increase serum cholesterol.
- Diet containing vegetable oil (unsaturated fatty acids + EFA) tends to lower serum cholesterol. This property of EFA is important in the management of hypercholesterolemia, which is accompanied by atherosclerosis.
- Arachidonic acid and some related C20 fatty acids with double bonds give rise to a group of physiologically and pharmacologically active compounds:

  For example, prostaglandins, thromboxanes and leukotrienes.

Deficiency symptoms

Animals

Poor growth, dermatitis, decreased capacity to reproduce, impaired transport of lipids.

Human

Phrynoderma (toad skin): Characterized by scaly dermatitis on limbs, loss of hair, poor wound healing, and growth impairment, defective transport of lipids, fatty liver, degeneration changes in arterial wall.

Treatment

By EFA intake of 1–2% of total caloric requirement.

Note

- Arachidonic acid is essential if its precursor linoleic acid is not provided in the diet.

ω-Fatty Acids (Omega Fatty Acids)

Definition

Fatty acids may also be numbered starting from ω end (methyl end). According to this classification, unsaturated fatty acids are divided into 3 groups.

1. *ω-3 Fatty Acids*

It is unsaturated fatty acid with double bond between C_3 and C_4 from omega end of hydrocarbon chain. It is found in fish oils especially salmon and other cold water fish, flax seeds. It lowers LDL cholesterol and BP, e.g., α-linolenic acid.

2. *ω-6 Fatty Acids*

It is unsaturated fatty acid, e.g., linoleic acid. It has double bond between C_6 and C_7 from ω end of hydrocarbon chain. It is present in, sunflower oil, corn, soyabean. They have anti-inflammatory effects and are mainly used for energy.

3. *ω-9 Fatty Acids*

For example, oleic acid: Present in olive oil. It has double bond between *9–10* position from methyl end of hydrocarbon chain. It increases HDL cholesterol (good cholesterol) and decreases. LDL cholesterol (bad cholesterol). They help eliminate plaque buildup in the arteries which causes heart attack and stroke.

Derivatives of fatty acids

Eicosanoids (*refer* Chapter 31)

Definition

Eicosanoids are the derivatives of eicosanoic fatty acids (C_{20}), namely—arachidonic acid.

- *Discovered by:* Von Euler
- *Sources:* All tissues especially seminal fluid.

Classification/types ***(Fig. 3.2)***

Eicosanoids are divided into two major classes which are further subdivided.

Biomedical importance/functions

Prostaglandins:

- Induce labor, abortion
- Act as contraceptives
- Prevent aggregation of platelets
- Lower blood pressure
- Affect membrane permeability
- Used to treat gastric ulcer, asthma
- Induce inflammation

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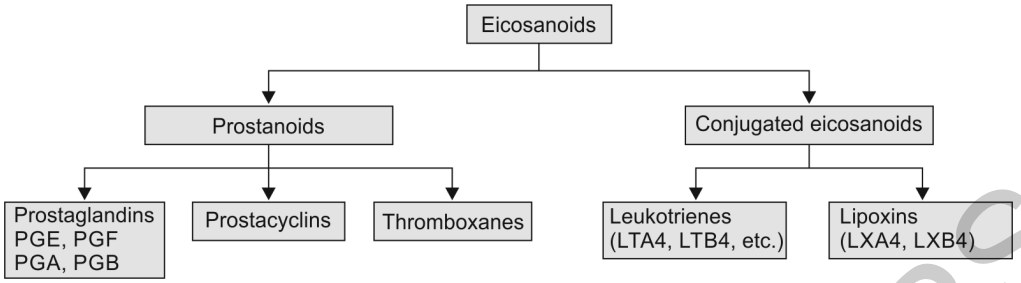

Fig. 3.2: Types of eicosanoids.

Thromboxanes:
Increase—
- Vasoconstriction
- Platelet aggregation
- Lymphocyte proliferation
- Bronchoconstriction.

Leukotrienes: Involved in chemotaxis, inflammation and allergic reactions.

Alcohols

Glycerol

Structure: It is a trihydroxy saturated alcohol.

CH_2OH
|
CHOH
|
CH_2OH

Properties: It is a colorless heavy fluid. It is a byproduct of soap manufacture. It is a component of triacylglycerol, lecithin, etc. It is obtained from lipolysis of fat in adipose tissue. It can be converted to glucose by gluconeogenesis in the body and thus possesses nutritional value.

Importance: Glycerol therapy is used in cerebrovascular disease. Nitroglycerin is a vasodilator. Glycerol is used in the preparation of culture medium and in manufacture of cosmetics.

Test: It can be detected by *Acrolein test.*

Sterols

They are a class of steroids characterized by: Cyclopentanoperhydrophenanthrene ring **(Fig. 3.3).**

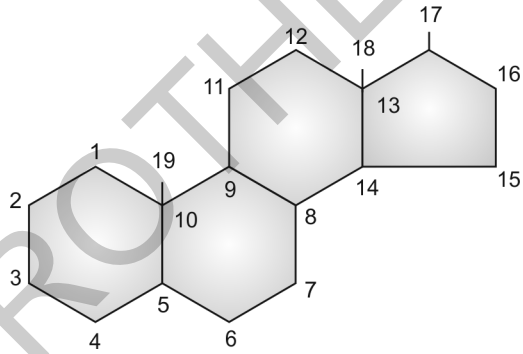

Fig. 3.3: Steroid nucleus (cyclopentanoperhydrophenanthrene ring).

Types:
- Animal sterols
- Plant sterols

Animal sterols
- *Cholesterol:* It is the most important sterol present in mammalian body. It is absent in plants, but widely distributed in all animal tissues.
  Alternative name: Solid bile alcohol (first isolated from bile).

Sources

High	*Moderate*
Brain and nervous tissues	Liver
Adrenal cortex	Kidney
Corpus luteum	Spleen
Testes	Skin
Egg yolk	Plasma

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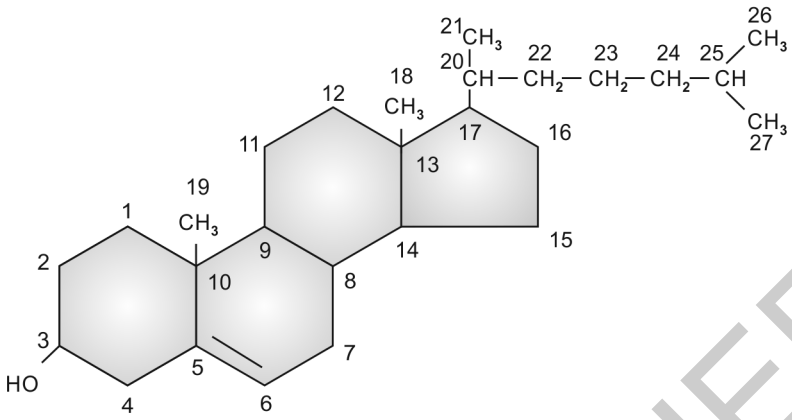

Fig. 3.4: Structure of cholesterol.

Structure ***(Fig. 3.4)***

- Its molecular formula is $C_{27}H_{45}OH$.
- It has cyclopentanoperhydrophenanthrene ring.
- An aliphatic side chain attached to C-17.
- A secondary alcoholic hydroxyl group attached to C_3.
- A double bond between C_5 and C_6.
- Two methyl groups (one at C_{10} and another at C_{13}).

Properties

Physical properties:

- *Shape:* It is a white shinning crystal. It looks like rhombic plates with characteristics notches at its corner **(Fig. 3.5)**.
- *Taste and odor:* Tasteless, odorless
- *Solubility:* It is insoluble in water but soluble in fat solvents, soap solution and bile salt solution.

Chemical properties:

- *Addition and hydrogenation:* It is an unsaturated alcohol and hence its chemical properties are mostly based on these characteristics.
- *Oxidation:* On oxidation, it gives various ketones, hydroxy compounds and acids, depending on oxidizing agents used and experimental conditions involved.
- *Esterification:* It forms esters with acids, e.g., cholesterol acetate, cholesteryl palmitate.
- *Hydroxylation:* OH group in cholesterol reacts with digitonin to form an insoluble digitonide. This property is used to separate cholesterol from its esters.
- *Color reactions/tests:*
  - Liebermann Burchard reaction
  - Salkowski reaction

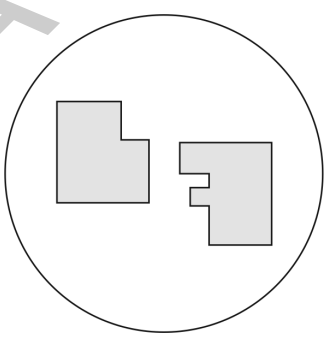

Fig. 3.5: Cholesterol crystals.

Biomedical importance/functions

- *Membrane fluidity:* It helps in maintaining the structure of membrane by providing fluidity.
- *Insulation:* It functions as an electrical insulator in brain neurons and spinal cord, because it is a poor conductor of electricity.
- *Precursors of bile acids, steroid hormones and vitamin D:* It is the precursor of other biologically important sterols, such as bile acids and steroid hormones and vitamin D.
- It is an important constituent of lipoproteins.

Clinical Importance

- Normal level in blood 150–200 mg/100 mL.
- If it exceeds its normal level in blood, it will lead to hypercholesterolemia resulting in atherosclerosis (*refer* Chapter 12).

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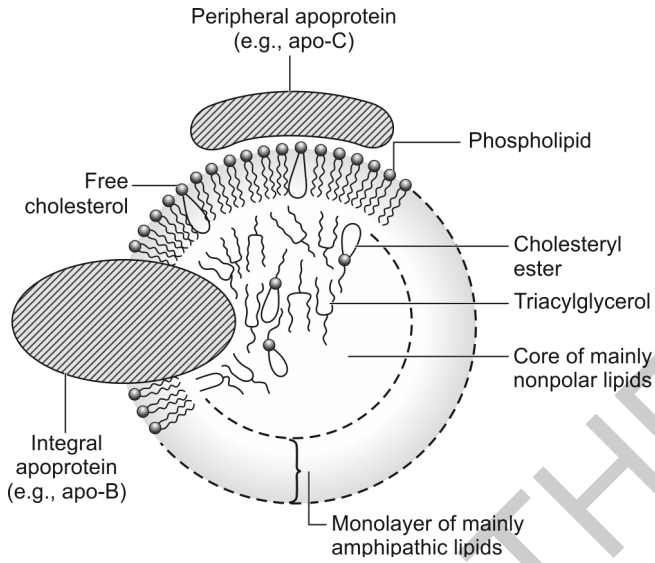

Fig. 3.6: Lipoprotein structure.

Coprosterol
It occurs in feces due to reduction of cholesterol by bacterial action.

7-dehydrocholesterol (provitamin D3)
It is present in skin.

Plant sterols

Examples	*Sources*
a. Stigmasterol	Soya bean oils
b. Sitosterol	Wheat germ oil
c. Ergosterol (provitamin D_2)	Ergot

IV. Miscellaneous Lipids

Definition

These compounds have characteristics of lipids.

Examples

- Fat soluble vitamins A, D, E and K (*refer* Chapter 8)
- Steroid hormones (*refer* Chapter 25)
- Hydrocarbons
- Terpenes

RELATED TERMS IN LIPID CHEMISTRY

- *Amphipathic lipids:* Lipids which contain both hydrophobic and hydrophilic groups are called as amphipathic lipids, e.g., fatty acids, phospholipids, sphingolipids, bile salts, cholesterol.
- *Micelles:* When amphipathic lipids are mixed in water in particular concentration, micelles are formed. They are small particles (lipids droplets). They aid in lipid digestion and absorption facilitated by bile salts.
- *Emulsions:* They are much larger particles formed by nonpolar lipids in aqueous medium. They are stabilized by emulsifying agents.
- *Neutral lipids:* The uncharged lipids are neutral lipids, e.g., cholesterol, cholesteryl esters, glycerides (acylglycerols).
- *Lipid bilayer:* It is basic structural feature of biological membranes. In this form, polar head orient towards outer aqueous phase on either side and the nonpolar tail into the interior.
- *Liposomes:* When amphipathic lipids in aqueous medium are subjected to sonification, liposomes are formed. They are used as carriers of drugs to target tissues.
- *Lipoprotein molecule (structure)* ***(Fig. 3.6)****:* Lipoprotein is a complex molecule consisting of both lipids and proteins. It is a compound/complex lipid. It is also called as conjugated protein. There are mainly four types of lipoproteins (chylomicrons, VLDL, LDL, HDL). The outer shell of all lipoprotein consists of apolipoproteins and amphiphilic lipids—unesterified cholesterol and phospholipids. The interior part contains triacylglycerols and cholesterol esters (neutral lipids).

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ADDITIONAL INFORMATION

- *Globosides:* A group of glycolipids
- *Lipofusion:* Age pigment (mixture of lipid and protein)
- *Non-phosphorylated lipids:* Glycolipids, sulpholipids
- *Lipos (Greek):* Fat
- *Sphingolipids:* Sphingosine (alcohol) containing lipids, e.g.,
  - Sphingomyelin (Phospholipid)
  - Gangliosides } Glycolipids
  - Cerebrosides
- *Detergents:* Amphipathic molecules
  - Naturally occurring detergents—bile salts
  - Synthetic detergents—sodium lauryl sulphate
- *Soaps: Refer* page 82
- Glycerin = Fatty acid triesters of glycerol, used in skin care.

SUMMARY

Lipids are a natural diverse (heterogenous) group of organic compounds. They are relatively insoluble in water but soluble in organic solvents. They are classified into simple lipids, compound lipids, derived lipids, and miscellaneous lipids. Fatty acids, are the components of the most of the lipids. Essential fatty acids should be supplied in the diet and they are precursors of prostaglandin synthesis. Triglycerides are stored in adipose tissue as energy reserve. Phospholipids are the membranous lipids. Cholesterol is one of the steroids containing a cyclo pentano perhydro phenanthrene ring. It produces several compounds like vitamin D, sterols, hormones, bile acids, etc. It is the important component of lipoproteins. Hypercholesterolemia may lead to atherosclerosis and obesity.

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P Ramamoorthy PhD (Biochemistry, Faculty of Medicine) was a Professor in the Department of Biochemistry at ACS Medical College and Hospital, Dr MGR University, Chennai, Tamil Nadu, India. He earned both his postgraduate and doctoral degrees in Biochemistry (Faculty of Medicine) from Madras Medical College, Chennai.

With over 30 years of teaching experience across prestigious institutions such as Madras Medical College, Sri Ramachandra Medical College and Research Institute, ACS Medical College, and Mahatma Gandhi Medical College and Research Institute, Puducherry, he has contributed extensively to medical, dental, and allied and healthcare education.

He also possesses international postdoctoral research experience in biochemistry and molecular biology, and has authored several books in the field, including viva voce guides, MCQ collections, question banks, and practical manuals for various health science disciplines. He has also served as an examiner in biochemistry for numerous medical and allied health science colleges across India.

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