PITHAPUR RAJAH'S GOVERNMENT COLLEGE

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Affiliated to Adikavi Nannaya University

Opp. Mc Laurin School, Raja Ram Mohan Roy Road, Kakinada 533001, Andhra Pradesh, India

E-mail: kakinada.jkc@gmail.com, Tel: 0884-2379480

DR. SUDHAKAR cheedi Msc.MPhil PHD

LECTURER IN MICROBIOLOGY

DEPARTMENT OF MICROBIOLOGY

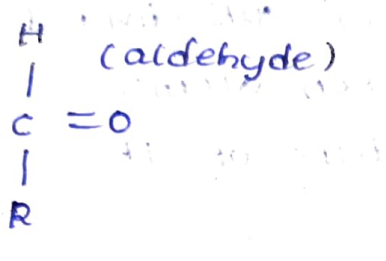
P.R.G.C (A),KAKINADA

biomolecules and enzymology

Unit-I - Carbohydrates

Carbohydrates

Carbohydrates are defined chemically as aldehyde or ketone derivatives of the polyhydric alcohols or compounds which yield these derivatives on hydrolysis. Each carbohydrate therefore contains an aldehyde or a ketone group.



Carbohydrates occur abundantly in nature. Cellulose of wood and paper, starches present in cereals roots and tubers, cane sugar and milk sugar are some of the examples of carbohydrates in plant kingdom. Further, plants can build up carbohydrate from carbon dioxide by photosynthesis. In animal kingdom, tissues contain glycogen and body fluids contain glucose both of which are carbohydrates. Many plants and animals contain large quantities of carbohydrates as reverse food material. These are also important structural components.

The general formula of carbohydrates is $C_n(H_2O)_n$ chemically they contain the elements carbon, hydrogen and oxygen, the later two are in the same ratio as in H_2O. Hence, they are so called carbohydrates. They are also called saccharides (sakcharon means sugar).

Classification: carbohydrates are divided into 4 major groups

(I) Monosaccharides
(II) Disaccharides
(III) Oligosaccharides

(IV) Polysaccharides

I. MONOSACCHARIDES:

These are also called 'simple' sugars. monosaccharides are those which cannot be hydrolysed further into simple forms. The general formula of monosaccharides is $C_nH_{2n}O_n$.

Monosaccharides contain two to ten carbons per molecules. these are further sub divided depending upon the number of carbon atoms.

I. Depending on the nature of the carbonyl group they possess,

(a) Aldoses: They possess an aldehyde group (-CHO).

(b) Ketones: They possess a ketone group (C=O).

II. Depending upon the number of carbon atoms they possess,

(1) Bioses: The formula of bioses is $C_2H_4O_2$. They contain two carbon atoms in chain.

Eg: Glycolaldehyde

(2) Trioses: The formula of trioses is $C_3H_6O_3$. They contain three carbon atoms in chain.

Eg: Glyceraldehyde and Dihydroxyacetone

(3) Tetroses: The formula of tetroses in $C_{14}H_8O_4$. They contain 4 carbon atoms in chain

Eg: Erythrose, Erythrulose

(4) Pentoses: The formula of pentoses is $C_5H_{10}O_5$. they contain 5 carbon atoms in chain.

Eg: D-Ribose, D-Xylose

(5) Hexoses: The formula of hexoses is $C_6H_{12}O_6$. They contain 6 carbon atoms in chain.

Eg: D-Glucose, D-galactose, D-fructose

(6) Heptoses: These contain seven carbon atoms in chain. Molecular formula is $C_7H_{14}O_7$.

Eg: Sidoheptulose, Glucoheptose

II. DISACCHARIDES:

These are formed by the union of two monosaccharides. They are united by linkage between the first carbon of one monosaccharide with the second or fourth carbon of another monosaccharide by glycosidic linkage. On hydrolysis, they yield two molecules of monosaccharides of same or different type.

Eg: Maltose, Lactose, Sucrose.

(a) Maltose: This is made up of two alpha-glucose molecules united by the 1,4-glycosidic linkage. On hydrolysis, maltose yields 2 molecules of glucose.

(b) Lactose: This is made up of a molecule of alpha D-glucose united by 1,4-glycosidic linkage to a molecule of beta D-galactose. it gives on molecule of glucose and one molecule of galactose on hydrolysis.

(c) Sucrose: It is made up of one molecule of alpha D-glucose and one of beta D-fructose united by a glycosidic linkage between the aldehyde and keto groups. On hydrolysis, sucrose gives one molecule of glucose and one molecule of fructose.

III. OLIGOSACCHARIDES:

These are formed by the union of 3-10 monosaccharides units per molecule. On hydrolysis oligosaccharides yield 3-10 monosaccharides.

Depending upon the number of monosaccharide unit they possess, they are divided into trisaccharides, tetraasaccharides, pentasaccharides etc.

IV. POLYSACCHARIDES :

They are formed by the union of more monosaccharide molecules and on hydrolysis they yield more monosaccharides molecules. Polysaccharides are further divided into two groups homopolysaccharides (or) homoglycans and heteropolysaccharides (or) heteroglycans.

A. Homopolysaccharides (homoglycans):

They contain only one type of monosaccharides units. they include Glucans, Galactans, Mannans, Xylans, Fructans.

B. Heteropolysaccharides (heteroglycans):

They contain at least two types of monosaccharides and on hydrolysis these yield at least two types of monosaccharides molecules.

Eg: Neutral sugars, mucopolysaccharides

(a) Neutral sugars: Eg: Hemicellulose, some gums, mucilages, pectic substances.

(b) Mucopolysaccharides : These contain amino sugars + Uronic acid and some of their derivatives.

Eg: Hyaluronic acid, Chondroitin sulphates, Heparin.

Biomedical importance of functions of carbohydrates:

(1) The most important function of carbohydrate is to provide energy to the body. carbohydrates are stored in the animal body in the form of glycogen About 60% of the total energy requirement of man is provided by the breakdown of carbohydrates.

Glucose supplies the immediate energy needed by tissues and it is the sole form of energy for the brain and other nervous tissue.

(2) Carbohydrates are constituents of conjugated proteins and compound lipids.

(3) Carbohydrates are important components of some structural materials of living organisms. Monosaccharides are important constituents of nucleic acids, coenzymes, flavoproteins and blood group substances.

(4) Immunopolysaccharides play a part in the resistance of infections.

(5) The cell wall of plants and the polysaccharides in the capsule of bacteria are made up of carbohydrates.

(6) Some carbohydrates are essential for normal oxidation of fats. When carbohydrates are restricted in the diet, it leads to ketosis. This is common in uncontrolled diabetes mellitus.

(7) Some carbohydrates play a role in gastrointestinal function. Lactose promotes the growth of desirable bacteria in the small intestine. These bacteria synthesize certain B complex vitamins. Lactose also increases calcium absorption.

(8) Certain carbohydrate derivatives are used as drugs like cardiac glycosides / antibiotics.

(9) Degradation products are utilized for synthesis of other substances such as fatty acid, cholesterol, amino acid etc.

Unit-2 Lipids and fatty acids

Lipids

Fats and their derivatives are collectively known as lipids the term 'lipid' was proposed by the biochemist Bloor. Bloor has defined lipids as "a group of naturally occuring substances which are relatively insoluble in water and soluble in organic solvent like chloroform, ether and benzene". They occur widely in the plant and animal kingdom.

Eg: oils and fats.

"Bloor" divided lipids into 3 major classes.

(1) Simple lipids
(2) Compound lipids
(3) Derived lipids

I SIMPLE LIPIDS:

Simple lipids includes the most abundant of all lipids the fats or triglycerides and the less abundant waxes. Simple lipids are esters of fatty acids with various alcohol such as trihydric alcohol and glycerol.

(A) **Fats**: the true fats are most abundant of all lipids. if they are liquid at ordinary temperatures, they are reffered to as oils. these are also known as glycerides. chemically these are triglycerides. when 3 molecules of fatty acids condense with 1 molecule of glycerol, fat is formed. Hence these are triglycerides.

These acryl groups (R1, R2, R3) may be same or different fatty acids. if all the fatty acids acryl groups are same, then it is a simple

glyceride when 2 or more of these groups are different then it is mixed glyceride. These glycerides have not free acid or basic group Hence, these are called neutral fats. The fatty acids commonly in natural fats and oils contain even number of carbon atoms.

Eg: Butyric acid, Lauric acid, Palmitic acid

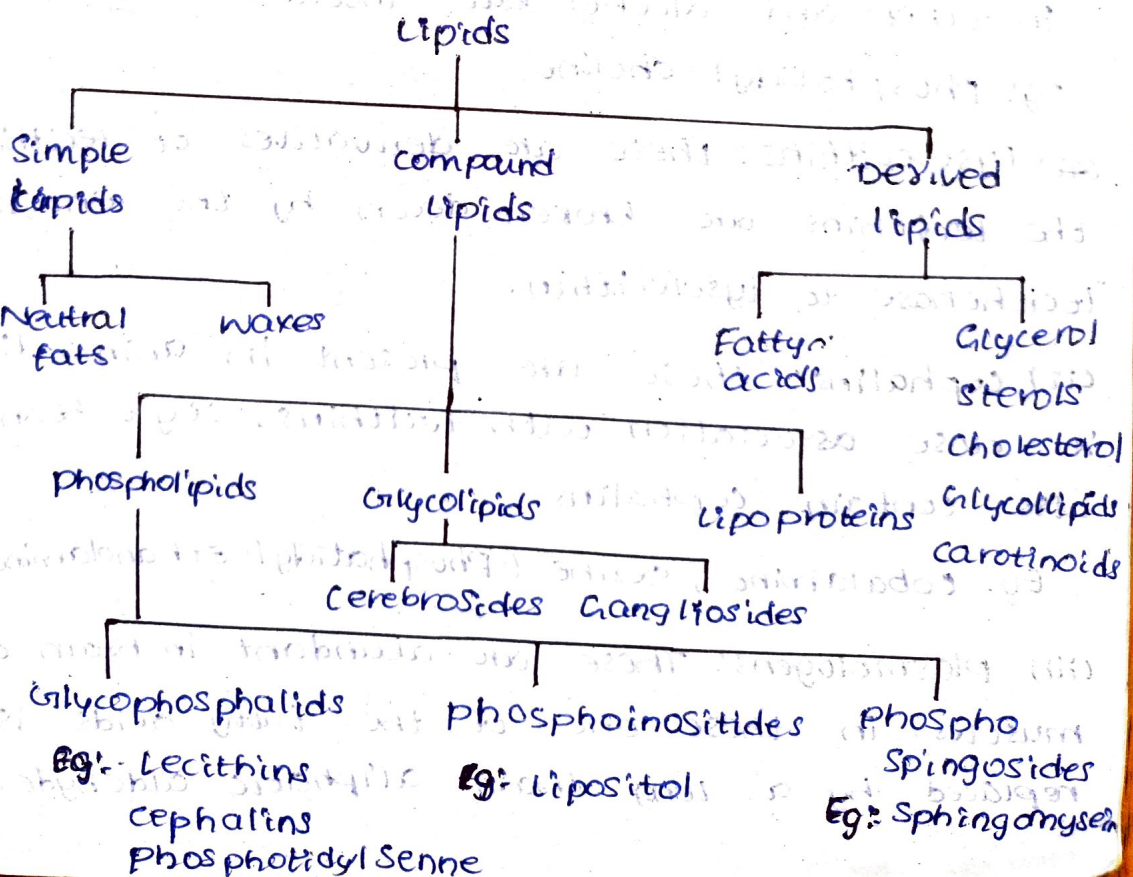
Fatty acids are divided into two main groups

(1) Unsaturated fatty acids

(2) saturated fatty acids

(B) Waxes: The waxes consists of fatty acids esterfied to alcohols other than glycerol. The alcohol present in waxes is having high molecular weight is long chain alcohol. they are insoluble in water. the contain 24-36 carbon atoms. waxes are generally observed in insect secretions, protective covering of animal fur and leaves.

Eg: Bees wax, spermatin, lanoline or wool fat.



II. COMPOUND LIPIDS:

Compound lipids contain some additional groups of elements besides fatty acids and glycerol. the additional group may be phosphorous, nitrogen, galactose or protein. these are phospholipids, galactolipids and lipoproteins.

(i) **phospholipids (or) phosphatides:** These contain phosphoric acid and nitrogen base in addition to glycerol and fatty acids. the phospholipids are abundantly present in brain and nervous tissue. Basing on the alcohol moiety of the phospholipid, they are further classified into (a) Glycophosphatids, (b) Phosphoinositides and (c) Phospho sphingosides.

(a) **Glycophosphatids:**

In these the alcohol group is glycerol.

Eg: Lecithins, cephalins, plasmalogens.

(i) **Lecithins:** these are yellowish grey solids. Soluble in ether and alcohol but insoluble in acetone.

Eg: Phosphotidyl choline

(ii) **Lysolecithins:** these are derivatives of lecithins. the lecithins are broken down by the enzyme lecitherase to lysolecithin.

(iii) **cephalins:** these are present in animal tissue in close association with lecithins. soya bean oil also contain cephalins.

Eg: cobalamine, serine (Phosphatidyl ethandamine)

(iii) **plasmologens:** These are abundant in brain and muscles. in these one of the fatty acids is replaced by a long chain aliphatic aldehyde.

(b) Phosphoinositides: In these the alcohol base is replaced by cyclic hexahydric alcohol inositol hence, these are also called lipoinositols. these are further divided into mono, di- and complex phosphoinositides. Monophosphoinositides are present in animals and plants. Diphosphoinositides are reported in brain.

(c) Phosphosphinogosides: these are also called sphinogolipids or sphinogomyelins. In these lipids, the glycerol is replaced by a complex amino alcohol sphinsine. these are found more in nervous tissue, but apparently lacking in plant and microorganisms.

(2) Galactolipids or glycolipids: these structure of galactolipids is some what similar to that of phosphosphingosides. in addition they contain galactose, sphingosine and one of the four different fatty acids cerebronic, lignoceric, nervonic. and oxynervonic acids. the galactolipids are abundantly found in animal organs.

Eg: cerebrosides, gangliosides.

(3) Lipoproteins: lipid-protein associations are present in certain cell systems particularly membranes which constitute lipoproteins. In this type of association, the hybrid molecule lipoprotein possess physical and chemical properties of both proteins and lipids. these 2 molecules are attracted and hold together by hydrophobic interactions rather than covalent bonding.

these lipoproteins help in transport of lipid which are insoluble in water to various organs

through blood circulation.

Eg: Milk, blood serum, egg yolk etc.

III: DERIVED LIPIDS:

This class includes the hydrolysis products of the first two classes and in addition, other compounds such as sterols, fatty acids, ketones, alcohols, essential oils etc. are present which are produced by the living organisms. the most important and abundant derived lipid is sterol.

Fatty acids: All the fatty acids have one carboxylic group. there are 2 types of fatty acids unsaturated and saturated.

Sterols: the term sterol means 'solid alcohol'. they are solid wax like substances. they occur in alcoholic forms or esters of fatty acids.

Eg: Cholesterol, Ergosterol, sex harmones, D-vitamins.

* Cholesterol: It was first isolated from gall stones. Cholesterol means solid alcohol from Bile. It was mainly present in brain, nervous tissue, adrenal glands and egg yolk.

* Ergosterol: It is present in small amount in fungi, yeast and vegetable matter. it was isolated from parasitic fungus claviceps purpurea (ergot) growing on rye plants. When ergosterol D (calciferol)

* Carotenoids: they are soluble in Fat solvents. carotenoids consists of carotene and xanthophyll. In carotens carbon and hydrogen are present. In xanthophylls, in addition to carbon and hydrogen oxygen is also present. Vitamin A

is derived from carotene. Other derived lipids are essential oils, bile acids, terpenes, ketones etc.

(1) Saturated fatty acids:

They have the general formula $C_nH_{2n+1}COOH$ they occur in two series ie. the ever numbered and the add numbered series the odd numbered series were found recently. Even numbered fatty acids from $C_2 \cdots C_{26}$ occur in both plants & Animal fats, and while acids as large as C_{3n} have been found in waxes. Odd numbered fatty acids $C_3 \rightarrow C_{25}$ have also been isolated fatty acids do not contain double bonds. the saturated fatty acids are built upon acetic acid which is the first number of the series.

Eg: Acetic acid - CH_3COOH

Butyric acid - $CH_3(CH_2)_2COOH$ - present in butter fat

Palmitic acid - $CH_3(CH_2)_{14}COOH$ - coconut oil + animal fats.

Stearic acid - $CH_3(CH_2)_{16}COOH$ - present in animal + plant fats.

(2) Unsaturated fatty acids:

these are fatty acids which contain double bonds they are generally liquids at room temperature. they have a general formula $C_nH_{2n-1}COOH$. with a double bond. they are sub divided into fatty acids containing

(1) One double bond - oleic acid - $C_{12}H_{33}COOH$

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH \rightarrow$ Palm oil + animal fats

(2) Two double bonds - Lenolelc acid - $C_{17}H_{31}COOH$
(essential fatty acids)

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH \rightarrow$
plant + animal fat

(3) Three double bond: Lenolenic acid - $C_{17}H_{29}COOH$

$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
- linseed oil

(4) Four and more double bonds - Arochidonic acid

$CH_3(CH_2)_4(CH=CH-CH_2)_4-(CH_2)_2COOH$ -
phospholipids + liver fats ($C_{19}H_{31}COOH$)

(1) Hydroxy fatty acids:

They have hydroxy group in them

Eg: β-hydroxy butyric acid $C_3H_6(OH)COOH$

It is saturated hydroxy acid which is formed as an intermediate in fatty acid metabolism.

(2) Ricinolelc acid: $C_{17}H_{32}(OH)COOH$

It is unsaturated hydroxy acid found in castor oil.

Unit-3 - Amino acids and Proteins

Classification of aminoacids:

Aminoacids are building blocks of proteins. aminoacids are classified in different ways. Among these, the classification referring to the number of carboxyl groups present in the amino acids and nature of structure, (whether aliphatic, aromatic and heterocyclic) appears simple and conveneant.

Aminoacids are classified has Six groups:
Another group of aminoacid which are formed as intermediates during metabolic reactions.

(1) Mono amino mono carboxylic acids
(2) Mono amino dicarboxylic acids
(3) Diamino monocarboxylic acids
(4) Sulphur containing amino acid
(5) Aromatic amino acids
(6) Heterocyclic amino acids
(7) Amino acids formed as metabolic intermediates

(1) Mono amino mono carboxylic acid: these aminoacids have one amino group and one carboxylic group in the structure. they are neutral amino acids.

Ex: Glycine (α-amino acetic acid)
Alanine (α-amino propionic acid)
Serine (α-amino β-hydroxy propionic acid)
Threonine (α-amino β-hydroxyn = butryic acid)
Valine (α-amino isovaleric acid)
Leucine (α-amino isocaproic acid)
Isoleucine (α-amino β-methyl-n-valeric acid)

(2) Mono amino - dicarboxylic acids: these amino acids contain one amino group and two car-

boxylic groups. they are acidic amino acids.

Ex: Aspartic acid (α-amino succinic acid)
Glutamin acid (α-amino glutasic acid)

(3) Diamino mono carboxylic acid: these amino acids are α-amino acids containing two amino groups and one carboxyl group. they are also called basic amino acids.

Ex: Arginine (α-amino β-guanidino-n-valeric acid)
Lysine (αediamino-n-caproic acid)

(4) Sulphur containing amino acids: these amino acids are α amino acids containing aliphatic side chain with sulphur atoms.

Ex: Cystine (α-amino-β-thiopropionic acid)
cystine (dicysteine)
Methionine

(5) Aromatic aminoacids: the aromatic amino acids contain aromatic rings.

Ex: Phenylalanine
Tyrosine
Tryptophan

(6) Heterocyclic amino acids: these aminoacids contain either imidazole or indole ring.

Ex: Proline
Hydroxy proline
Histidine

(7) amino acids formed as metabolic intermediates: the following aminoacids are formed during metabolic reactions. they are physiologically important. Ex: Di iodotyrosine
Thyroxine
Ornithine

Essential	Non-essential
Arginine (Arg)	Alamine (Ala)
Histidine (His)	Asparagine (Ans)
Isoleucine (Ile)	Aspartic acid (ASP)
Leucine (Leu)	cysteine (Cys)
Lysine (Lys)	Glutamic acid (Glu)
Methionine (Met)	Glutamine (Glx)
Phenylalanine (Phe)	Glycine (Gly)
Threonine (Thr)	Proline (Pro)
Tryptophan (Trp)	Sevine (Ser)
valine (Val)	Tyrosine (Tyr)

Properties of Aminoacids:

Physical properties:

(1) Amino acids are white crystalline substances.

(2) They are generally soluble in water and insoluble organic solvents.

(3) They have characteristically high melting points, varying from 200°c to 300°c or even more.

(4) Amino acids may be tasteless, sweet or bitter. sodium glutamate is a valuable flavouring agent and used in the preparation of certain dishes and sauces.

(5) All aminoacids except glycine are optically active because they contain asymmetric cation atoms.

(6) In crystalline form of amino acids its structure is stabilized by electrostatic forces between the two oppositely charged ions which held them together.

Classification of Proteins

Proteins occur widely in nature and are numerous. Proteins may be devided into three major groups - I simple, II conjugated and III derived proteins.

I. Simple Proteins
- (1) Albumins
- (2) Globulins
- (3) Glutelin
- (4) Prolamines
- (5) Sclero protein or Albuminoids
- (6) Histones
- (7) Protamines

II. Conjugated Proteins
- (1) Nucleoproteins
- (2) Phosphoprotein
- (3) Mucoprotein and Glycoprotein
- (4) Chromoprotein
- (5) Lipoprotein
- (6) Metalloprotein

III. Derived proteins :
- (1) primary derivatives
  - Denatured Protein (Metaprotein)
- (2) Secondary derivatives
  - (a) Proteoses
  - (b) Peptones
  - (c) peptides
  - (d) Diketopiperazines

I. Simple proteins:

These proteins yield on hydrolysis, only alpha amino acids.

Albumin and Globulins: These are typical example of simple protein. they contain most of the aminoacids. Their characteristic property is coagulation on heating they differ from one another in their solubility. Albumin and is soluble in water. whereas globulin is insoluble in water. whereas globulin is insoluble in water. Both albumin and globulin are soluble in dilute neutral solution of salts and alkalies.

Source: Animal source of Albumin are, egg albumin myoalbumin of muscles, serum albumin.

Animal source of globulin are the same as for albumin namely, globulin of egg, myglobulin of muscles, serum globulin and lactoglobulin of milk

Plant sources for both albumin and globulin are the legumes of peas and beans and cereals.

Glutelin and Gliadin (Prolamines): Both glutelin and gliadin are present in cereals; especially wheat.

Glutelins are insoluble in water and absolute alcohol but soluble in dilute alkalies and acids.

Scleroproteins or Albuminoids: These are characterised by great stability and insolubility in water and salt solutions. They are called albuminoid because they are essentially similar to albumin and globulins.

collagen in cartilage and white fibrous connective tissues, ossein in bones and dentine in teeth.

keratin in hair, nails, hoofs and horns. keratins are readily soluble in alkaline sulphides and the aldehyde and keto groups. on hydrolysis, sucrose gives one molecule of glucose and one molecule of fructose.

Histones: Histones are more complex than protamines they are basic proteins and contain fiarly large amount of amino acid histidine they are soluble in water, but insoluble in ammonium hydroxide they are not readily coagulated by heat. they occur in the globin of hemoglobin, nucleoproteins and in spermatozoa of fish.

Protamines: these are simplest of the proteins and contain about 8 amino acids. Protamines are found in association with nucleic acid in the sperm cells of certain fish.

II. Conjugated proteins:

These are proteins composed of simple proteins combined with some non-protein substances known as prosthetic groups. they are classified according to the nature of the non-protein groups or the prothetic groups.

(1) Nucleo proteins: these are compounds of protein with nucleic acid. the protein moiety is usually a simple protein like protamines and histones. Nucleoproteins are important compounds found in the protoplasm and nuclei. they are also constituents of chromatin.

(2) Phosphoproteins: these are proteins containing phosphoric acid, in organic combination i.e. phosp

phoric acid is linked to the hydroxyl group of certain amino acids like serine in the protein

Ex: (i) Casein of milk

(ii) Vitelin of egg

they contain about 1% of phosphorus. phosphoproteins are sparingly soluble in water and dilute acids, but readily soluble even in dilute alkalies.

(3) Glycoproteins and Mucoproteins: these proteins are composed of simple proteins and are combined with carbohydrates like mucopolysaccharides which include hyaluronic acid and chondrotin sulphates.

They are important constituents of the ground substance of the connective tissues and are present in tendons, bones, cartilage, synovial fluid and mucous membrane.

(4) Chromoproteins: these proteins contain certain heterocyclic compounds like porphyrins as the prosthetic group. the porphyrins combine with metal giving rise to coloured proteins or chromoproteins.

Ex: Haemoglobin, flavoprotein, cytochrome, chlorophyll

(5) Lipoproteins: these are proteins conjugated with lipids such as neutral fat, phospholipids and cholesterol.

(6) Metallo proteins: these proteins contain metals as their prosthetic group.

Ferretin contains iron, ceruloplasmin contains cu and carbonic anhydrase an enzyme protein contains zn.

III. Derived proteins:

These are proteins derived from the simple proteins or conjugated proteins by the action of acids, alkalies or enzymes. They are product resulting from partial to complete hydrolysis of proteins. They include two types of derivatives

(1) Primary derivatives: Primary derivatives like meta proteins which are denaturation products of proteins of proteins resulting from the action of heat, acids & alkalies on proteins. They are heat coagulable.

(2) Secondary derivatives: These are obtained at a later stage of hydrolysis.

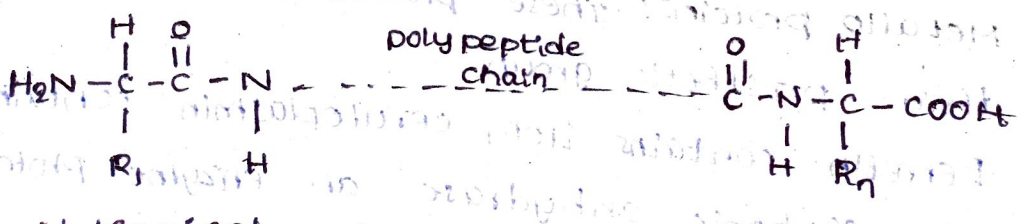
Ex: (1) Proteoses

(2) Peptones

(3) Peptides

(4) Diketopleperazines

N-terminal and C-terminal of a protein: the end of the protein or polypeptide where the amino-group is free in known as N-terminal end and that amino acid whose amino group is free is known as N-terminal amino acid. Sangier's Edmann's and Dansyl chloride are the reagent used to determine the N-terminal amino acids.



the end of the protein or polypeptide whose carboxylic group is free is known as C-terminal aminoacid. Hydrazine is used to detect the C-terminal aminoacid. while representing a protein on paper, the N-terminal aminoacid is written first (on the left) and the C-terminal aminoacid is the last one.

peptides of physiological importance

(a) Glutathione: It is a tripeptide made up of Glu, Cys and Gly. It is found in RBC and other tissues and functions to prevent oxidation of -SH groups of many enzymes.

(b) Bradykinin and kallidin: these are small polypeptides containing 9 and 10 amino acids respectively. they are formed by partial hydrolysis of plasma protein due to snake poisoning (venom). they are powerful vasodepressors and inhibitors of heart function. Others are tyrocidin, gramicidin, glucagon, insulin, oxytocin etc.

Structure of protein:

The structure of protein can be studied under four different levels of organization. Primary, secondary, tertiary and quaternary.

Primary structure of protein

Primary structure of proteins refers to the total number of amino acids and their sequence in that particular protein.

N-terminal | Met | Arg | Leu | Ala | Val | Phe | C-terminal

A fixed number of amino acids are arranged in a particular sequence. the sequence of amino acids in the protein determines its biological role.

Primary structure differentiates normal protein from abnormal one. Normal adult haemoglobin (HbA) is made up of 2 α chains and 2 β-chains. Each α chain has 141 amino acids and each β-chain has 146 aminoacids arranged in a specific sequence. Like in sickle cell haemoglobin (HbS).

Secondary structure of protein:

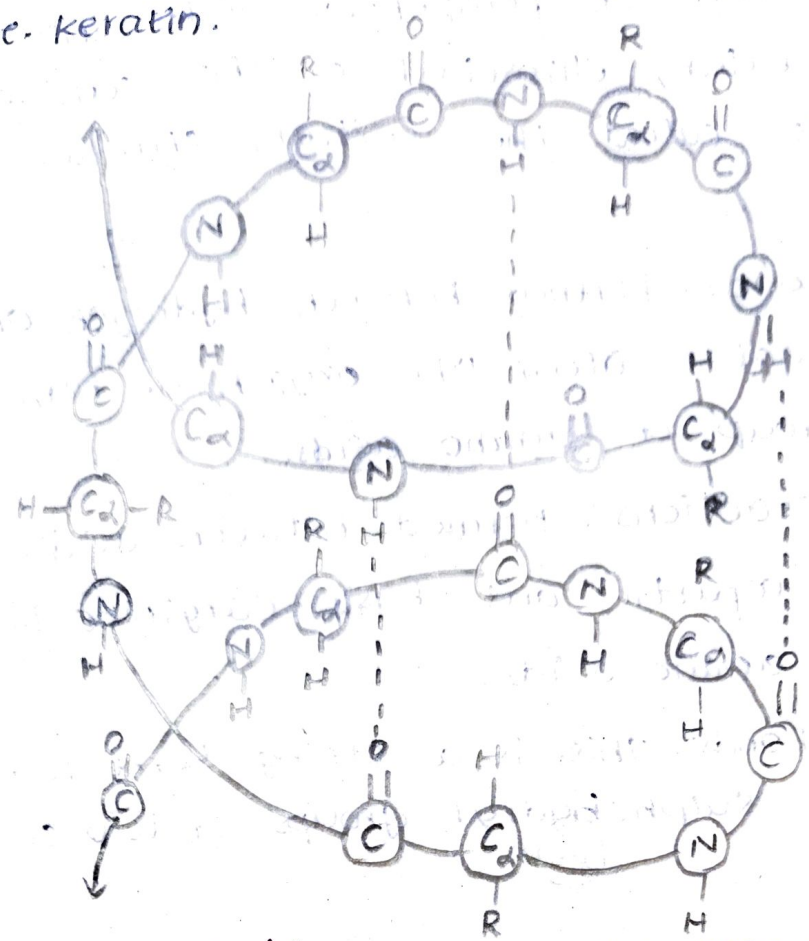
It refers to the twisting of the polypeptide chain into a helical form. three types of helical structures are found

(a) Alpha helix
(b) Beta pleated
(c) Reverse turn.

(1) **Alpha helix:** α means the first and the structure described below was the first among the helical structures to be discovered, hence known as alpha (α) helix. the salient features of this structure are as under.

* Here the polypeptide is twisted or coiled to form a right handed helical structure
* The distance between each turn of the coil is 5.4 A.
* There are 36 aminoacids per turn.
* The 'R' group are seen protruding out of the helix.
* The are intra chain hydrogen bonding, wherein the hydrogen of -NH group combines with oxygen of -CO group of the 4th amino acid behind it.
* Pure α-helix structure is seen in hair protein

ie. keratin.



2. Beta pleated: β means the second and the structure described below was the second discovery after α helix. the salient features of this structure are.

* Here the chain is not helical but zig-zag
* The distance between each turn is 7 A°.
* Polypeptide chains are arranged side by side in the form of pleats.
* There is inter-chain hydrogen bonding between the chains and each peptide group participates in hydrogen bonding.
* The chains are anti-parallel to each other.

3. Reverse turn: folds back on itself in reverse direction of the chain.

Tertiary structure of proteins

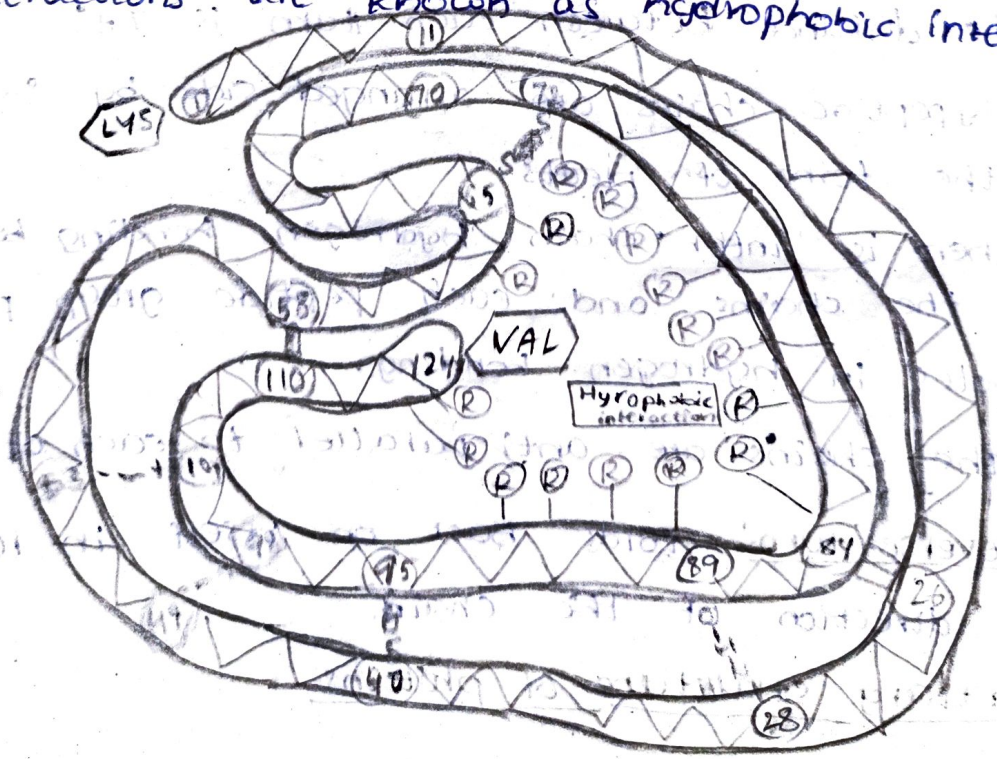
The helical form of polypeptide folds into spherical, globular, ellipsoidal or other conformation, which is called the tertiary structure of proteins.

(1) Hydrogen bonds: Formed between hydrogen and an electronegative atom like oxygen or nitrogen in the 'R' group of amino acids.

(2) Ionic interactions: Formed between acidic (glutamic and aspartic) and basic carginine, lysine or histidine) amino acids.

(3) Disulphide bonds: This is a strong bond formed between the sulphahydryl groups of two cysteine aminoacids.

(4) Hydrophobic interactions: The 'R' groups of the hydrophobic aminoacids aggregate together in the centre away from water, thereby developing a force of attraction between each 'R' group and a force of repulsion from the water and these interactions are known as hydrophobic interactions

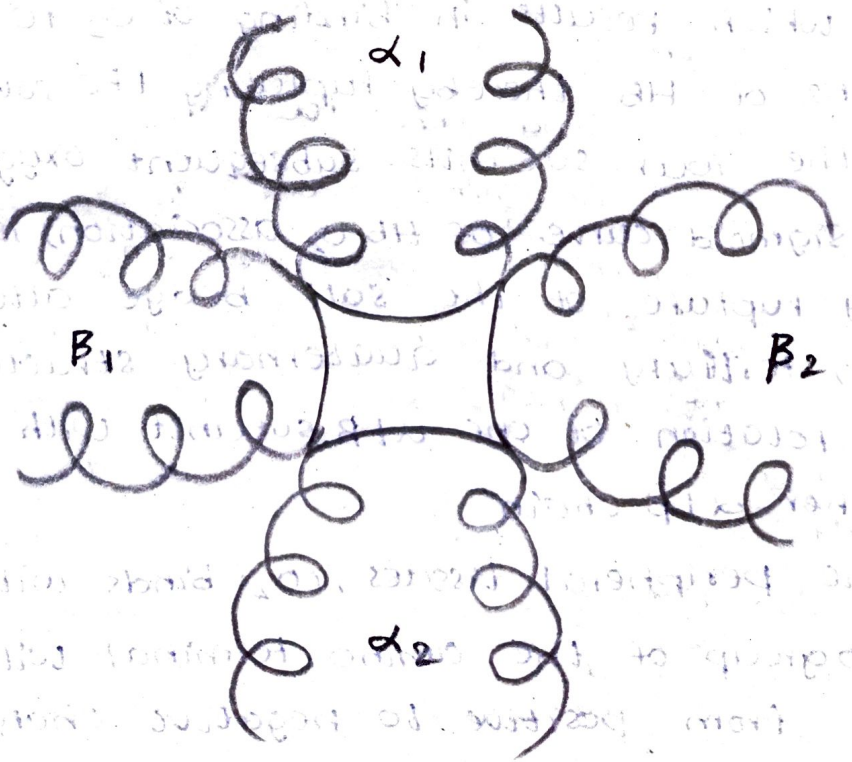


Quaternary structure of proteins:

Quaternary structure is exhibited by oligomeric proteins.

Oligomeric proteins: Are those which have two or more polypeptide chains.

Quaternary structure refers to the type of arrangement of the polypeptides is an oligomeric protein. these polypeptides are held together by either hydrogen bonds, ionic bonds or vander waal's forces eg. Heamoglobin has four polypeptide chains which are arranged in a particalar fashion that is referred to the quaternary structure of hemoglobin. these are made up of four polypeptide chains, two of which are α (α_1 & α_2) and the other two are β (β_1 & β_2). the two alpha chains are opposite to each other and adjacent to each β-chain. the α chains and the β chains are linked together by salt bridges.



Structure - Function relationship in Proteins:

Hemoglobin plays a vital role in transport of oxygen from the lungs to the peripheral tissues and transport of carbon dioxide from the tissues to the lungs. There are three types of normal hemoglobin.

(1) Adult hemoglobin (HbA) has $2\alpha 2\beta$ chains.

(2) Foetal ~~de~~hemoglobin (HbF) has $2\alpha 2\gamma$ chains.

(3) Minor adult hemoglobin (HbA$_1$) has $2\alpha 2\delta$ chains.

The number of amino acids in α chains is 141 amino acids and the other chains β, γ & δ chains have 146 aminoacids. the quaternary structure of hemoglobin creates a cavity in between the tetramer in which 2, 3, diphosphoglycerate (DPG or BPG) is present forming a salt bridge with the amino terminal of β-chain that stabilizes the hemoglobin, lowering the affinity to oxygen.

In the lungs, the partial pressure of oxygen is high which results in binding of O_2 to one of the chains of Hb thereby rupturing the salt bridges between the four subunits. subsequent oxygen binding (Sigmoid curve of Hb-O_2 association) is facilitated by rupture of the salt bridge altering secondary, tertiary and quaternary structures thus allowing rotation of one $\alpha\beta$ subunit with respect to another $\alpha\beta$ chain

In the peripheral tissues, CO_2 binds with a α-amino group of the amino terminal with its conversion from positive to negative charge which facours salt bridge formation between the polyp

eptide chains with return to the deoxy state (T-state), release of oxygen from Hb.

When a person take off on a flight, the aeroplane slowly rises in altitude resulting in lowering of the O_2 tension due to which oxygenation of Hb is not possible. Thus the person feels hypoxic, but the physiological mechanism of the body starts decreasing the production of DPG, due to which Hb can bind the oxygen even at lower pressure of oxygen.

Non protein aminoacids:

Gramicidin:

Gramicidin is a type of antibiotic that is derived from the soil bacterium Bacillus brevis.

Gramicidin works by:

(1) Forming channels in bacterial cell membranes, leading to changes in ion permeability and disruption of cellular processes.

(2) Inhibiting cell wall synthesis in bacteria.

(3) Interacting with bacterial membrane, causing leakage of cellular contents and ultimately leading to cell death.

Gramicidin is effective against a range of gram-positive bacteria, including:

(1) Staphylococcus aureus

(2) Bacillus anthracis

(3) Clostridium perfringens

However, it is not effective against Gram-negative bacteria, such as E-coli, due to their outer membrane structure.

Gramicidin has been used in various applications

Unit-IV: Nucleic acids and vitamins

Structure and properties of Nucleic acids:

Like proteins, the nucleic acids are also biopolymers of high molecular weight with as their repeating units. just as amino acids are the repeating units of proteins. the nucleic acids contain carbon, hydrogen, oxygen, nitrogen and phosphorous.

There are two kinds of ~~medi~~ Nucleic acids

(1) Deoxyribo nucleic acid (DNA)

(2) Ribonucleic acid (RNA)

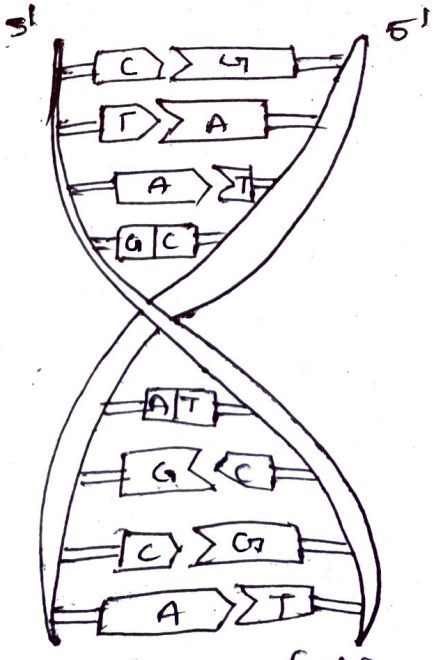
~~(3)~~ DNA found mainly in the chromatin of the cell nucleus whereas most of the RNA (90%) is present in the cell cytoplasm and a little (10%) in the nucleolus.

Upon hydrolysis, the two nucleic acids yield 3 components:

(1) Phosphoric acid

(2) a pentose sugar

(3) nitrogenous bases.



Structure of Nucleic acid

Nucleic acids are high molecular weight polymers which occur in every living cell. they were discovered by "Miescher" in 1969 in fish sperm cells. their main function is storage and transmission of genetic information

(1) Deoxyribo nucleic acid (DNA):

J. watson and F. Crick proposed a model for explaining the structure of DNA molecule.

Structure of DNA

(1) DNA is the chemical basis of heredity.

(2) DNA is composed of four deoxyribonucleotides; deoxyadenylate, deoxyguanylate, deoxycytidylate and deaxy thymidylate.

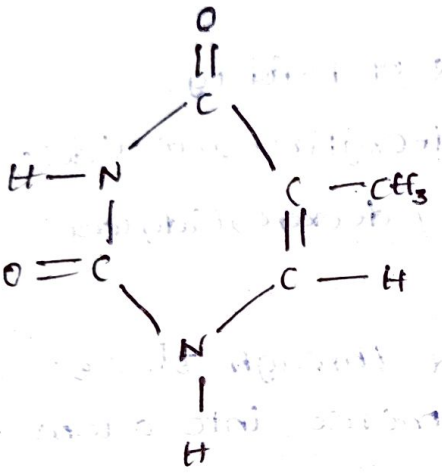
(3) these units are combined through 3'—>5' phosphodiester bonds to polymerise into a long chain.

(4) the nucleotide is formed by a combination of base + sugar + phosphoric acid. the 3'-hydroxyl of one sugar is combined to the 5'-hydroxyl of another sugar through a phosphate group.

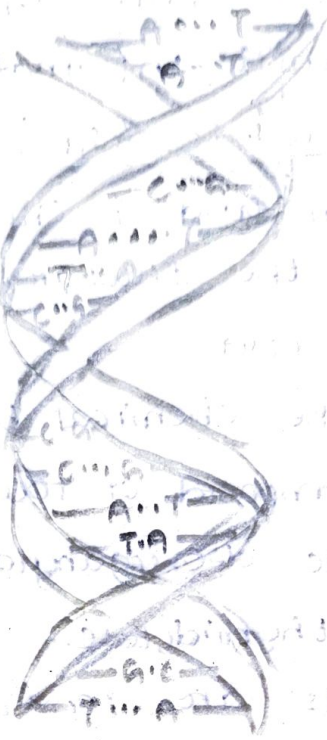
(5) the polymer posses a polarity one end has a 5'-hydroxyl or phosphate terminus while the other has 3'-phosphate or hydroxyl moiety.

(6) In DNA molecules the concentration of adenosine (A) nucleotides equals that of Thymidine (T) nucleotides (A = T). the concentration of guanosine (G) nucleotides equals that of cytidine (C) nucleotides (G = C). the ratio of purine to pyrimidine bases in the DNA molecule is always around 1. this is known as chargaff's rule

(7) DNA consists of two poly deoxyribonucleotide chains twisted around one another in a right handed double helix similar to a spiral staircase.



D. Thymine



Double helix structure of DNA

(8) the base pairing rule is maintained. the two strands are complementary to each other. In other words, the Adenine of one strand will pair with thymine of the opposite strand. while guanine will pair with cytosine. the base pairing (A with T and G with C) is through hydrogen bond.

(9) The DNA strands are held together by hydrogen bonds between the purine and pyrimidine bases. there are two hydrogen bonds between A and T while there are three hydrogen bonds between C and G. the GC bond is G≡C therefore

stronger than the AT bond A=T. so regions rich in the GC bond pair are more resistant to denaturation.

(10) The two strands in a DNA molecules run anti-parallel, which means that one strand runs in the 5' to 3' direction, while the other is in the 3' to 5' direction.

(11) In the DNA molecule, the genetic information resides on one strand called the template strand or sense strand. the opposite strand is called antisense strand.

(12) DNA can exist in several conformations depending upon the base composition and under different physical conditions. in all the these conformations the same base pairing rules apply changes do not affect the information content of the DNA. the most common conformation is B-DNA other types are A-DNA, C-DNA and Z-DNA.

Functions of DNA:

(1) DNA is the genetic material.

(2) DNA controls every function of the cell through protein synthesis.

(3) DNA has two important functions - heterocatalytic and autocatalytic. in heterocatalytic function DNA directs the synthesis of chemical molecules e.g:- synthesis of RNA, proteins etc.

DNA, the Master copy - DNA does not directly control the formation of a polypeptide, instead it forms an intermediate template, for mRNA molecule, which in turn directs the synthesis of the polypeptide.

(4) In autocatalytic function DNA directs the synthesis of DNA itself.

(2) Ribonucleic acids (RNA):

Ribonucleic acid is a polymer of ribonucleotides of Adenine, Uracil, Guanine and cytosine, joined together by 3'-5' phosphodiester bonds. thymine is absent in RNA. RNA is found in the nucleolus, Nissl granules, Ribosomes. mitochondria and cytoplasm. the pentose sugar of the nucleotide is D-ribose.

Structure of RNA:

(1) RNA is single strand and having Ribose sugar, Nitrogenous bases and phosphoric acid.

(2) there are three forms of RNA in the cell

(i) m-RNA
(ii) t-RNA
(iii) r-RNA.

Each of them having different role in protein synthesis.

Primary structure of RNA:

(1) the primary structure of RNA is defined as the number and sequence of ribonucleotides in the chain.

(2) Each linear strand is held together by the ribonucleotides bound to each other by 3',5' phosphodiester bonds joining 3'-OH of the next

Secondary structure of RNA

(1) The secondary structure of RNA involves various coil formation.

(2) These coil structures are stabilized by hydrophobic interactions between the purine and pyrim

idine bases.

(3) There are intra-chain hydrogen bonds between G-C and A-U. the hydrogen bonds are the same as in DNA.

Tertiary structure of RNA:

(1) the tertiary structure of RNA involves the folding of the molecule into three dimensional structure.

(2) The cross-linking also occurs at various sites stabilized by hydrophobic and hydrogen bonds producing a compactly coiled globular structure.

Various types of RNA:

There are two kinds of nucleic acids

(1) deoxyribonucleic acid (DNA)

(2) Ribonucleic acid (RNA).

DNA is found mainly in the chromatin of the cell nucleus whereas most of the RNA (90%) is present in the cell cytoplasm and a little (10%) in the nucleolus.

RNA is single stranded and having Ribose sugar, nitrogenous bases and phosphoric acid. there forms of RNA in the cell

(i) m-RNA

(ii) t-RNA

(iii) r-RNA

Functions of RNA:

(1) The RNA's are synthesized from DNA and play important role on the process of protein synthesis.

(a) m RNA transfers genetic information from genes (DNA) to ribosomes for proteins synthesis.

influencing DNA structure, gene
evolutionary relationships.

Vitamins and their Role in Body metabolism:

Introduction:

Definition of vitamins:

- Organic compounds essential in small quantities for various bodily functions.
- cannot be synthesized by the body in sufficient amounts, hence must be obtained from the diet.

Classification of vitamins:

(1) Fat-soluble vitamins : A, D, E, K

(2) Water-soluble vitamins B-complex (B1, B2, B3, B5, B6, B7, B9, B12) and C

Importance in Metabolism:

* Act as coenzymes or precursors for coenzymes.
* crucial in biochemical reactions including energy production, DNA synthesis, and repair.

(I) Fat soluble vitamins:

(i) Vitamin A (Retinoids and carotenoids)

Functions: Vision, immune function, reproduction and cellular communication.

Metabolism: Retinol, retinal and retinoic acid are active forms; stored in the liver.

Sources: Liver, fish oils, milk, eggs and colorful vegetables (carrots, spinach).

Deficiency: Night blindness, xerophthalmia and immune deficiencies.

(ii) Vitamin D (calciferol)

Functions: calcium and phosphorus homeostasis, bone health.

Metabolism: Synthesized in skin upon UV exposure, converted to active form (calcitriol) in liver and kidneys.

Sources: Sunlight, fatty fish, fortified dairy products

Deficiency: Rickets in children, osteomalacia in adults.

(iii) Vitamin E (Tocopherols and Tocotrienols)

Function: Antioxidant, protects cell membranes from oxidative damage.

Metabolism: Absorbed in intestine, transported in blood by lipoproteins.

Sources: Vegetable oils, nuts, seeds, green leafy vegetables.

Deficiency: Rare, but can cause hemolytic anemia and neurological issues.

(iv) Vitamin K (Phylloquinone and Menoquinones)

Functions: Blood clotting (cofactor for clotting factors) bone metabolism.

Metabolism: Synthesized by gut bacteria, involve
in carboxylation reactions.
Sources: Green leafy vegetables, fermented foods.
Deficiency: Bleeding disorders, osteoporosis.

(2) Water-soluble Vitamins:

(i) Vitamin B1 (Thiamine)

Functions: Energy metabolism (coenzyme in carb
ydrates metabolism), nerve function.
Metabolism: converted to thiamine pyrophospha
(TPP), active in the krebs cycle.
Sources: Whole grains, pork, legumes.
Deficiency: Beriberi, Wernicke-korsakoff syndrome.

(ii) Vitamin B2 (Riboflavin)

Functions: Energy production, cellular function and
metabolism of fats, drugs and steroids.
Metabolism: converted to FAD and FMN, crucial for
electron transfort chain.
Sources: Dairy, eggs, green leafy vegetables
Deficiency: Ariboflavinosis, Characterized by sore throa
redness and swelling of the mouth.

(iii) Vitamin B3 (Niacin)

Functions: DNA Repair, production of steroid hormo
nes and oxidative metabolism.
Metabolism: converted to NAD+ and NADP+, essential
in redox reactions.
Sources: Meat, fish, poultry, whole grains.
Deficiency: pellagra (dermatitis, diarrhea, dementia).

(iv) Vitamin B5 (Pantothenic Acid):

Functions: Synthesis of coenzyme A, fatty acid metabolism.

Metabolism: Integral part of CoA, involved in the synthesis and oxidation of fatty acids.

Sources: Chicken, beef, potatoes, oats.

Deficiency: Rare, symptoms include fatigue, depression and irritability.

(v) Vitamin B6 (Pyridoxine)

Functions: Amino acid metabolism, neurotransmitter synthesis, hemoglobin production.

Metabolism: converted to pyridoxal phosphate (PLP) coenzyme in many reactions.

Sources: Fish, beef liver, potatoes (non-citrus fruits.

Deficiency: Anemia, peripheral neuropathy.

(vi) Vitamin B7 (Biotin)

Functions: Carbohydrate, fat and protein metabolism.

Metabolism: Coenzyme for carboxylase enzymes.

Sources: Egg yolk, liver, yeast

Deficiency: Dermatitis, hair loss, neurological symptoms.

(vii) Vitamin B9 (Folate):

Functions: DNA synthesis, repair and methylation

Metabolism: converted to tetrahydrofolate (THF) crucial for nucleotide synthesis.

Sources: leafy greens, legumes, nuts.

Deficiency: megaloblastic anemia, neural tube defects in pregnancy.

(viii) Vitamin B12 (Cobalamin).

Functions: Red blood cell formation, neurological function, DNA Synthesis.

Metabolism: Requires Intrinsic factor for absorption stored in the liver.

Sources: Meat, fish, dairy products.

Deficiency: pernicious anemia, neurological disorders.

(ix) Vitamin C (Ascorbic acid)

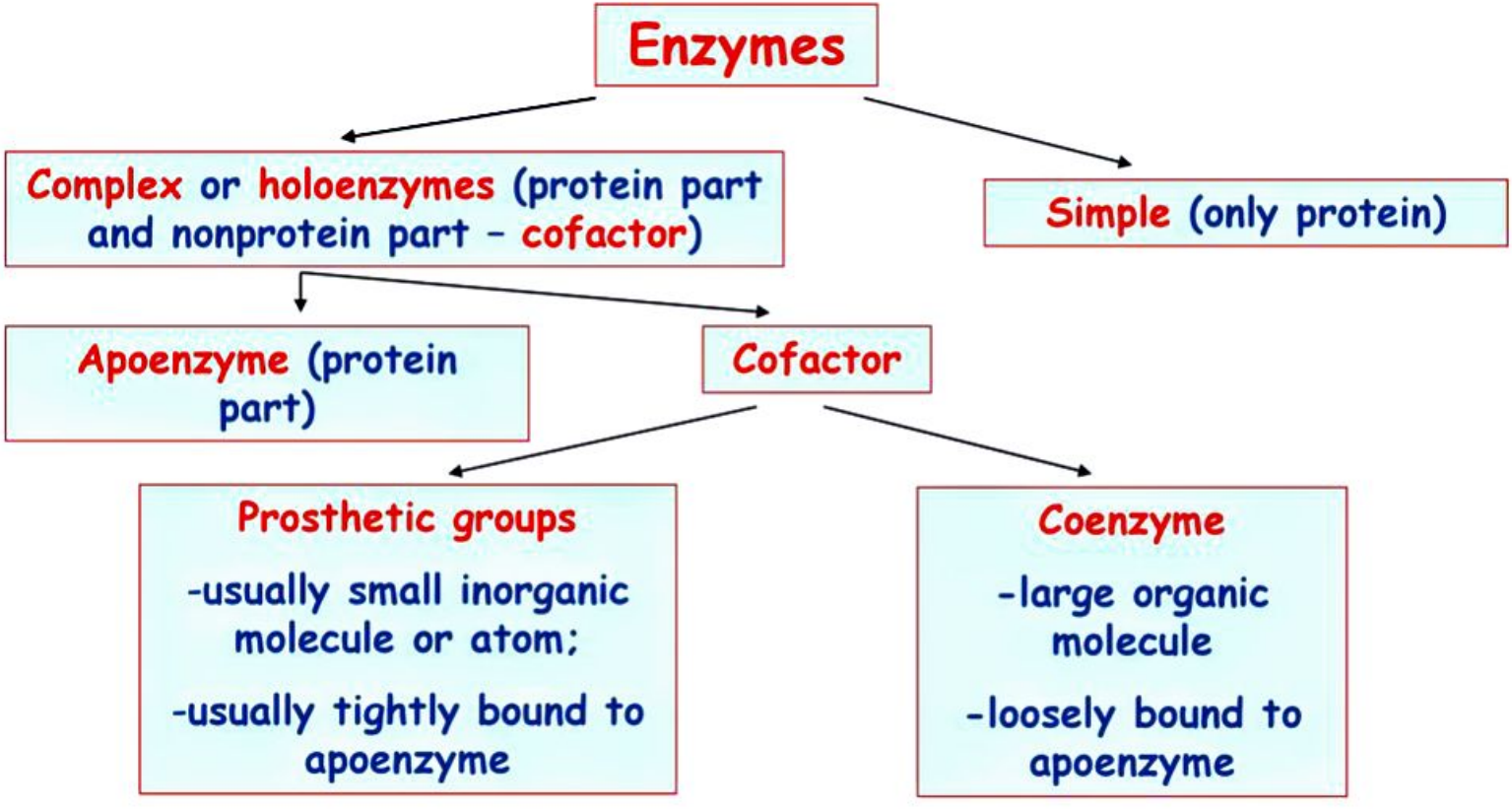
Functions: collagen synthesis, antioxidant, enhances iron absorption, immune function.

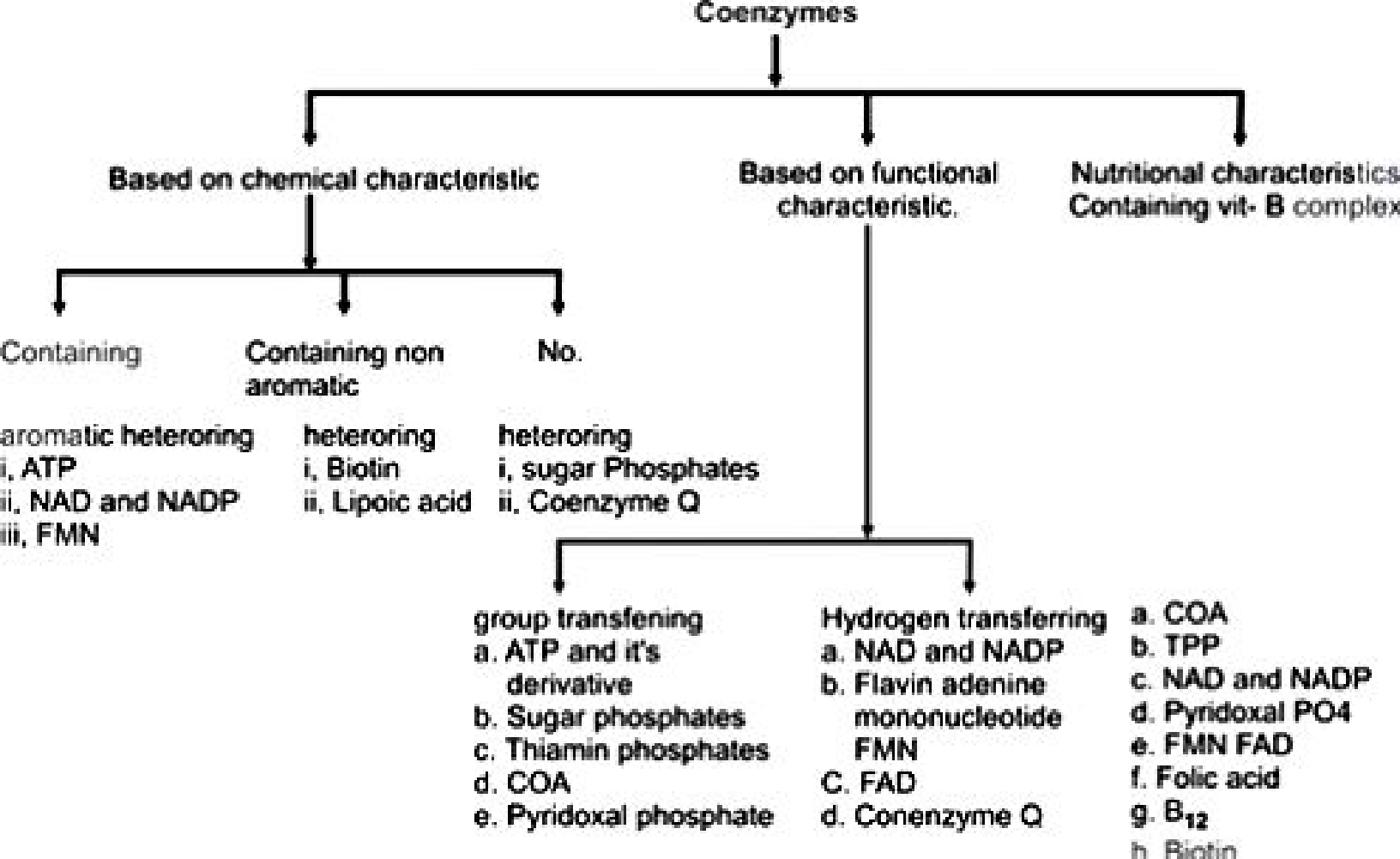
Metabolism: participates in redox reactions, cofactor for enzymes.

Sources: citrus fruits, strawberries, bell peppers.

Deficiency: scurvy (bleeding gums, weakness, anemia

Structure of enzymes




Coenzymes
Based on chemical characteristic
Based on functional characteristic.
Nutritional characteristics
Containing vit- B complex
Containing
Containing non aromatic
No.
aromatic heteroring
i, ATP
ii, NAD and NADP
iii, FMN
heteroring
i, Biotin
ii, Lipoic acid
heteroring
i, sugar Phosphates
ii, Coenzyme Q
group transfening
a. ATP and it's derivative
b. Sugar phosphates
c. Thiamin phosphates
d. COA
e. Pyridoxal phosphate
Hydrogen transferring
a. NAD and NADP
b. Flavin adenine mononucleotide FMN
C. FAD
d. Conenzyme Q
a. COA
b. TPP
c. NAD and NADP
d. Pyridoxal PO4
e. FMN FAD
f. Folic acid
g. B_{12}
h. Biotin

Enzyme Inhibition

Definition:

Any substance that decreases the velocity of an enzyme catalysed reaction.

Types of Inhibition:

1. Competitive inhibition
2. Non competitive inhibition
3. Allosteric inhibition
4. Suicide inhibition

Non Competitive Inhibition (Irreversible Inhibition)

1.Heavy metals (mercury, lead, silver etc) bind covalently to – SH groups in the active site of the enzyme. They bind irreversibly they are highly toxic

$E - SH + Hg^{2+} \longrightarrow ES --- Hg^{2+} + H^{+}$

Eg: delta ALA $\xrightarrow[\text{ALA dehydratase – Lead}]{}$ Porphobilinogen

Proto porphyrin IX $\xrightarrow[\text{Ferrochelatase – Lead}]{Fe^{2+}}$ Heme

2. Cyto chrome C oxidase inhibited by cyanide poisoning

Types of inhibition

In **competitive inhibition** a molecule very close in shape to the true substrate competes for the active site of the enzyme. This means less enzyme is available to act on the actual substrate and the reaction is slowed down.

Competitive inhibition is reversible

Tip - You can tell if an enzyme is competitive by changing the concentration of the **substrate** .

Explanation - Rate of reaction can be increased by adding more of the substrate so that the enzyme is more likely to collide with correct substrate molecule.

A common mechanism for controlling the rate of enzyme reactions in cells uses end products which compete with the substrate for active sites. This is called 'End Product Inhibition' and is a special example of competitive inhibition

B. Non-competitive Inhibition (Irreversible) (cont.)

- types of inhibitions is shown in Table 5.6. Examples are:

iia. Cyanide inhibits cytochrome oxidase.

iib. Fluoride will remove magnesium and manganese ions and so will inhibit the enzyme, enolase, and consequently the glycolysis.

iic. Iodoacetate would inhibit enzymes having-SH group in their active centers.

iid. BAL (British Anti Lewisite; dimercaprol) is used as an antidote for heavy metal poisoning.

The heavy metals act as enzyme poisons by reacting with the SH group.

BAL has several SH groups with which the heavy metal ions can react and thereby their poisonous effects are reduced