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SUBJECT NAME: BIOCHEMISTRY

CHAPTER 2: BIOMOLECULES

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BIOMOLECULES

•They are composed of the elements carbon, hydrogen and oxygen. The name carbohydrate means ‘hydrates of carbon’ because C, H, and O being present in a same ratio as in water and thus corresponded to the formula Cn(H2O)n.

•But later on it was found that certain carbohydrates do not correspond to this formula.eg. Rhamnose – C6H12O5.

•While several compounds although not carbohydrates correspond to this formula

eg. Formaldehyde – CH2O.

•So nowadays carbohydrates are defined as following.

•Carbohydrates may be defined as polyhydroxy aldehydes or ketones or compounds which produce them on hydrolysis.

•The term ‘sugar’ is applied to carbohydrates soluble in water and sweet to taste.

Functions of carbohydrates

•Carbohydrates participate in a wide range of functions.

1.They are the most abundant dietary source of energy (4 Cal/g) for all organisms.

2.Carbohydrates (as glycoproteins and glycolipids) participate in the structure of ceIl membrane and cellular functions such as cell growth, adhesion and fertilization.

3.They are structural components of many organisms. These include the fiber (cellulose) of plants, exoskeleton of some insects and the cell wall of microorganisms.

4.Carbohydrates also serve as the storage form of energy (glycogen) to meet the immediate energy demands of the body.

CLASSIFICATION OF CARBOHYDRATES

•Carbohydrates are often referred to as saccharides (Greek: sakcharon-sugar). They are broadly classified into three major groups-

•Monosaccharides, oligosaccharides and polysaccharides.

•Monosaccharides and oligosaccharides are

•sweet to taste,

•crystalline in character and

•soluble in water,

•hence they are commonly known as sugars.

•Monosaccharides

•(Greek: mono-one) are the simplest group of carbohydrates and are often referred to as simple sugars. They have the general formula Cn(H2O)n, and they cannot be further hydrolysed.

•The monosaccharides are divided into different categories, based on the functional group and the number of carbon atoms.

•Aldoses :

•When the functional group in monosaccharides is an aldehyde (-CHO), they are known as aldoses eg. Glyceraldehyde, glucose.

•Ketoses :

•When the functional group is a keto (-C=O) group, they are referred to as ketoses.

eg. Dihydroxy acetone, fructose.

•Based on the number of carbon atoms,

•the monosaccharides are regarded as

Trioses (3C),

Tetroses (4C),

Pentoses (5C),

Hexoses (6C)

Heptoses (7C).

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| Sr. No. | Questions | Answer |
| 1 | The general formula of monosaccharides  is | CnH2nOn |
| 2 | Two sugars which differ from one another only in configuration around a single carbon atom are termed | Epimers |
| 3 | The most important epimer of glucose is | Galactose |
| 4 | ααα-D-glucose and β -D-glucose are | Anomers |
| 5 | The most important epimer of glucose is | Galactose |
| 6 | A triose sugar is | Glycerose |
| 7 | The aldose sugar is | Glycerose |
| 8 | The pentose sugar present mainly in the heart muscle is | Lyxose |
| 9 | The number of isomers of glucose is | 16 |

Oligosaccharides

•Oligosaccharides (Greek : oligo – few) contain 2-10 monosaccharide molecules which are liberated on hydrolysis.

•Based on the number of monosaccharide units present, the oligosaccharides are further subdivided to disaccharides, trisaccharides etc.

Polysaccharides

•Polysaccharides (Greek : poly-many) are polymers of monosaccharide units with high molecular weight (up to million).

•tasteless (non-sugars) and

• form colloids with water.

•The polysaccharides are of two types- homopolysaccharides and heteropolysaccharides.

Monosaccharides – structural aspects

•A carbon is said to asymmetric when it is attached to four different atoms or groups.

•Glyceraldehyde (triose) is the simplest monosaccharide with one asymmetric carbon atom.

D and L isomers

•The D and L isomers are mirror images of each other. The spatial orientation of –H and –OH groups on the carbon atom (C5 for glucose) that is adjacent to the terminal primary alcohol carbon determines whether sugar is D- or L-isomer.

•If the -OH group is on the right side, the sugar is of D-series, and if on the left 'side, it belongs to L-series.

•It may be noted that the naturally occurring monosaccharides in the mammalian tissues are mostly of D-configuration. The enzyme machinery of cells is specific to metabolise D-series of monosaccharides.

•In the medical practice, the term dextrose is used for glucose in solution. This is because of the dextrorotatory nature of glucose.

Optical activity of sugars

•Optical activity is a characteristic feature of compounds with asymmetric carbon atom. When a beam of polarized light is passed through a solution of an optical isomer, it will be rotated either to the right or left.

•The term dextrorotatory (+) and levorotatory (-) are used to compounds that respectively rotate the plane of polarized light to the right or to the left.

•Recemic mixture : If D- and L- isomers are present in equal concentration, it is known as racemic mixture or DL mixture.

•Recemic mixture does not exhibit any optical activity.

Epimers

•If two monosaccharides differ from each other in their configuration around a single specific carbon atom, they are referred to as epimers to each other.

•For instance, glucose and galactose are epimers with regard to carbon 4. That is they differ in the arrangement of -OH group at C4.Glucose and mannose are epimers with regard to carbon 2.

•The interconversion of epimers is known as epimerisation, and a group of enzymes – namely – epimerases catalyse this reaction.

**Structure of glucose**

•For a better understanding of glucose structure, let us consider the formation of hemiacetals and hemiketals, respectively produced when an aldehyde or a ketone reacts with alcohol.

•The hydroxyl group of monosaccharides can react with its own aldehyde or keto functional group to form hemiacetal and hemiketal.

•Thus, the aldehyde group of glucose at C1 reacts with alcohol group at C5 to form two types of cyclic hemiacetals namely α and β.

**Pyranose and furanose structures**

•Haworth porjection folmula are depicted by a six-membered ring pyranose (based on pyran) or a five-membered ring furanose (based on furan). The cyclic forms of glucose are known as α-D-glucopyranose and α-D-glucofuranose.

Anomers – mutarotation

•The α and β cyclic forms of D-glucose are known as anomers. They differ from each other in the configuration only around C1 known as anomeric carbon (hemiacetal carbon).

•In case of α anomer, the –OH group held by anomeric carbon is on the

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| Sr.No. | Questions | Answer |
| 1 | ααα-D-glucose + 1120→ + 52.50 ← + 190 βββ-D-glucose for glucose above represents | Mutarotation |
| 2 | Isomers differing as a result of variations  in configuration of the —OH and —H on  carbon atoms 2, 3 and 4 of glucose are  known as | Epimers |
| 3 | Polysaccharides are | Polymers |
| 4 | In glucose the orientation of the —H and  —OH groups around the carbon atom 5  adjacent to the terminal primary alcohol  carbon determines | D or L series |
| 5 | The carbohydrate of the blood group  substances is | Fucose |
| 6 | Erythromycin contains | Erythromycin contains |
| 7 | A sugar alcohol is | Mannitol |
| 8 | The major sugar of insect hemolymph is | Trehalose |
| 9 | The sugar found in DNA is | Ribulose |
| 10 | The sugar found in milk is | Galactose |

opposite side of the group – CH2OH of sugar ring. The reverse is true for β-anomers.

•The anomers differ in certain physical and chemical properties.

**•Mutarotation**

The α and β anomers of glucose have different optical rotations.The specific optical rotation of a freshly prepared glucose (α anomer) solution in water is +112.2 whichgradually changes and attains an euilibrium with a constant value of+52.7 . In the presence of alkali, the decrease in optical rotation is rapid.The optical rotation of β- glucose is +18.7.

Mutarotation is defined as the change in the specific optical rotation representing the interconversion of α and β forms of D-glucose to an equilibrium mixture.

α -D-Glucose -------- Equilibrium mixture -------- β-D-Glucose

+ 112.2° <---------- +52.7 <---------- +18.7

•The equilibrium mixture contains 63% β-anomer and 36% α-anomer of glucose with 1% open chain form. In aqueous solution, the β form is more predominant due to its stable conformation.

**Reactions of monosaccharides**

**1.Tautomerization or enolization**

•The process of shifting a hydrogen atom from one carbon atom to another to produce enediols is known as tautomerization. Sugars possessing anomeric carbon atom undergo tautomerization in alkaline solutions.When glucose is kept in alkaline solution for several hours, it undergoes isomerization to form D-fructose and D-mannose resulting in the formation of a common intermediate- namely enediol.The enediols are highly reactive, hence sugars in alkaline solution are powerful reducing agents.

**2.Reducing properties**

•The sugars are classified as reducing or non reducing. The reducing property is attributed to the free aldehyde or keto group of anomeric carbon.In the laboratory, many tests are employed to identify the reducing action of sugars. These include Benedict’s test, Fehling’s, Barfoed’s test etc.The enediol forms or sugars reduce cupric ions (Cu+2) of copper sulphate to cuprous ions(Cu+) , which form a yellow precipitate of cuprous hydroxide or a red precipitate of cuprous oxide.

•Barfoed’s reagent is a solution of copper acetate in acetic acid and is used for distinguishing monosaccharides from reducing disaccharides. The acidic reaction of the reagent is not optimal for reduction, but the monosaccharides, being powerful reducing substances, will bring about a light reduction and produce a slight reddish precipitate.Disaccharides like lactose and maltose are less potent as reducing substances and fail to cause any reduction at all in the acid medium.

**3.Oxidation**

•Depending on the oxidizing agent used, the terminal aldehyde (or keto) or their terminal alcohol or both the groups may be oxidised. Oxidation of aldehyde group (CHO------COOH) results in the formation of gluconic acid. Oxidation of terminal alcohol group (CH2OH----COOH) leads to the production of glucuronic acid.

**4. Reduction**

•When treated with reducing agents such as sodium amalgum, the aldehyde of keto group of monosaccharide is reduced to corresponding alcohol.

•D-Glucose D-Sorbitol

•D-Galactose D-Dulcitol

•D-Mannose D-mannitol

•D-fructose D-mannitol dsorbitol

•Sorbitol and dulcitol when accumulate in tissues in large amounts cause strong osmotic effects leading to swelling of cells, and certain pathological conditions.

•Eg. Cataract, peripheral neuropathy, nephropathy.

**5.Dehydration**

•When treated with concentrated sulfuric acid, monosaccharides undergo dehydration with an elimination of 3 water molecules. Thus hexoses give hydroxymethyl furfural while pentoses give furfural of dehydration. These furfurals can condense with phenolic compounds (α-naphthol) to form coloured products. This is the chemical basis of the popular Molisch test.

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| Sr. No. | Question | Answer |
| 1 | The homopo lysacchar ide used for  intravenous infusion as plasma substitute  is | Agar |
| 2 | The polysaccharide used in assessing the  glomerular fittration rate (GFR) is | Inulin |
| 3 | Mutarotation refers to change in | Optical rotation |
| 4 | The constituent unit of inulin is | Fructose |
| 5 | The po lysacchar ide found in the  exoskeleton of invertebrates is | Chitin |

**6.Formation of esters**

•The alcoholic groups of monosaccharides may be esterified. Esterification of carbohydrate with phosphoric acid is a common reaction In metabolism.Glucose-6-phosphate and glucose-1-phosphate are good examples. ATP donates the phosphate moiety in ester formation.

**8.Glycosides**

•Glycosides are formed when the hemiacetal or hemiketal hydroxyl group (of anomeric carbon) of a carbohydrate reacts with a hydroxyl group of another carbohydrate or a non carbohydrate (eg. Methyl alcohol, phenol, glycerol).

•The bond so formed is known as glycosidic bond and the non-carbohydrate moiety is referred to as aglycon.

**DERIVATIVES OF MONOSACCHARIDES**

•There are several derivatives of monosaccharides, some of which are physiologically important.

**1 . Sugar acids :** Oxidation of aldehyde or primary alcohol group in monosaccharide results in sugar acids. Gluconic acid is produced from glucose by oxidation of aldehyde (C1 group) whereas glucuronic acid is formed when primary alcohol group (C6) is oxidized.

2. Sugar alcohols (polyols) : They are produced by reduction of aldoses or ketoses. For instance, sorbitol is formed from glucose and mannitol from mannose.

3. Amino sugars : When one or more hydroxyl groups of the monosaccharides are replaced by amino groups, the products formed are amino sugars.

eg. D-glucosamine, D-galactosamine.

•They are present as constituents of heteropolysaccharides.The amion groups of amino sugars are sometimes acetylated.

e.g. N-acetyl D-glucosamine.

4. Deoxysugars : These are the sugars that contain one oxygen less than that present in the parent molecule.

•The groups -CHOH and - CH20H become -CH2 and -CH3 due to the absence of oxygen. D-2 –deoxyribose is the most important deoxysugar since it is a structural constituent of DNA.

Disaccharides

•Among the oligosaccarides, disaccharides are the most common.

•As is evident from the name, a disaccharide consists of two monosaccharide units (similar or dissimilar) held together by a glycosidic bond.

•They are crystalline,

•water soluble and

•sweet to taste.

•The disaccharides are of two types.

1. Reducing disaccharides with free aldehyde or keto group.

eg. Maltose, lactose.

2. Non reducing disaccharides with no free aldehyde or keto group

eg. Sucrose.

Maltose

•Maltose is composed of two α-D-glucose units held together by α(1---4) glycosidic bond.

Sucrose

•Sucrose (cane sugar) is the sugar of commerce, mostly produced by sugar cane and sugar beets. Sucrose is made up of α-D-glucose and β-D-fructose.

•The two monosaccharides are held together by a glycosidic bond (α1---β2), between C1 of α-glucose and C2 of β-fructose.

•The reducing groups of glucose and fructose are involved in glycosidic bond, hence sucrose is a non-reducing sugar, and it cannot form osazones.

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| Disaccharides | | occurrence | |
| Sucrose | | As a constituent of cane sugar and beet sugar, pineapple | |
| Lactose | | Mil k sugar | |
| Maltose | | Product of starch hydrolysis, occurs in germinating seeds | |
| Sr. No. | Question | | Answer | |
| 1 | The constituent unit of inulin is | | Fructose | |
| 2 | The po lysacchar ide found in the  exoskeleton of invertebrates is | | Chitin | |
| 3 | Which of the following is a heteroglycan? | | Agar | |
| 4 | The glycosaminoglycan which does notcontain uronic acid is | | Keratan sulphate | |
| 5 | The glycosaminoglycan which does not contain uronic acid is | | Heparin | |
| 6 |  | |  | |

Lactose

•Lactose is more commonly known as milk sugar since it is the disaccharide found in milk. Lactose is composed of β-D-galactose and β-D-glucose held together by β (1---4) glycosidic bond.

•Lactose of milk is the most important carbohydrate in the nutrition of young mammals. It is hydrolysed by the intestinal enzyme lactase to glucose and galactose.

Inversion of sucrose

•Sucrose, as such is dextrorotatory (+66.5). But, when hydrolysed, sucrose becomes levorotatory (-28.2).

•The process of change in optical rotation from dextrorotatory (+) to levorotatory (-) is referred to as inversion.

•The hydrolysed mixture of sucrose, containing glucose and fructose, is known as invert sugar.

Polysaccharides

•Polysaccharides (or simply glycans) consist of repeat units of monosaccharides, held together by glycosidic bonds.

•They are primarily concerned with two important functions- structural , and storage of energy.

•Polysaccharides are linear as well as branched polymers.

•Polysaccharides are of two types

•Homopolysaccharides which on hydrolysis yield only a single type of monosaccharide.

•Heteropolysaccharides on hydrolysis yield a mixture of a few monosaccharides.

Homopolysaccharides

•Starch

Starch is the carbohydrate reserve of plants which is the most important dietary source for higher animals, including man.

High content of starch is found in cereals, roots, tubers, vegetables etc. Starch is composed of D-glucose units held by α-glycosidic bonds. Starch consists of two polysaccharide components – water soluble amylose (15-20%) and a water insoluble amylopectin (80-85%). Chemically, amylose is a long unbranched chain with 200 – 1000 D-glucose units held by α(1---4) glycosidic linkages.Amylopectin, on the other hand, is a branched chain with α(1--6) glycosidic bonds at the branching points and α(1---4) linkages everywhere else.(20-30 glucose units per branch). Starches are hydrolysed by amylase (pancreatic or salivary) to liberate dextrins, and finally maltose and glucose units. Amylase acts specifically on α(1--4) glycosidic bonds.

•Dextrins

Dextrins are the breakdown products of starch by the enzyme amylase or dilute acids. The various intermediates (identified by iodine colouration) are soluble starch (blue), amylodextrin (violet), erythrodextrin (red) and achrodextrin (no colour).

•Inulin

Inulin is a polymer of fructose i.e. fructosan. It occurs in dahlia bulbs, onion etc. It is easily soluble in water. Inulin is not utilised by the body. It is used for assessing kidney function through measurement of glomerular filtration rate (GFR).

•Glycogen

Glycogen is the carbohydrate reserve in animals, hence often referred to as animal starch. It is present in high concentration in liver, followed by muscle, brain etc. The structure of glycogen is similar to that of amylopectin with more number of branches. In glycogen, branches occur at every 8 – 12 glucose units, while in amylopectin, branches occur at every 20 – 30 glucose units. Thus glycogen is extensively branched and compact molecule. Glucose is the repeating unit in glycogen joined together by α(1----4) glycosidic bonds, and α (1----6) glycosidic bonds at branching points.

•Cellulose

Cellulose occurs exclusively in plants and it is a predominant constituent of plant cell wall. Cellulose is comp osed of β-D-glucose units linked by β (1 4) glycosidic bonds. Cellulose cannot be digested by mammals-including man-due to lack of the enzyme that cleaves β - glycosidic bonds ( amylase breaks α bonds only). Certain ruminants and herbivorous animals contain microorganisms In the gut which produce enzymes that can cleave β-glycosidic bonds. Hydrolysis of cellulose yields a disaccharide cellobiose, followed by β-D-glucose. Cellulose, though not digested, has great importance in human nutrition. It is a major constituent of fiber, the non-digestable carbohydrate. The functions of dietary fiber include decreasing the absorption of glucose and cholesterol fron the intestine, besides increasing the buld of feces.

Chitin

•Chitin is composed of N-acetyl D-glucosamine units held together by β(1 4) glycosidic bonds. It is a structural polysaccharide found in the exoskeleton of some invertebrates eg. Insects, crustaceans.

Heteropolysaccharides

•When the polysaccharides are composed of different types of sugars, they are referred to as heteropolysaccharides or heteroglycans.

Mucopolysaccharides

•Mucopolysaccharides are made up of repeating units of sugar derivatives, namely amino sugars and uronic acids. These are more commonly known as glycosaminoglycans (GAG).

•Some of the mucopolysaccharides are found in combination with proteins to form mucoproteins or mucoids or proteoglycans.

•Mucopolysaccharides are essential components of tissue structure. The extracellular spaces of tissue (particularly connective tissue-cartilage,skin, blood vessels,tendons) consist of collagen and elastin fibers embeded in a matrix or ground substance. The ground substance is predominantly composed of GAG.

•The important mucopolysaccharides include hyaluronic acid, chondroitin 4-sulfate, heparin, dermatan sulfate and keratan sulfate.

•Hyaluronic acid

•Hyaluronic acid is an - important GAG found in the ground substance of synovial fluid of joints and vitreous humor of eyes. It is also present as a ground substance in connective tissues.

•Hyaluronic acid is composed of alternate units of D-glucuronic acid and n-acetyl D-glucosamine. Hyaluronic acid contains about 250-25,000 disaccharide uints (held by β 1----4 bonds).

•Hyaluronidase is an enzyme that breaks (β1-----4 linkages) hyaluronic acid and other GAG. Hyaluronidase of semen is assigned an important role in fertilization as this enzyme clears the gel better penetration of sperm into the ovum. Hyaluronidase of bacteria helps their invasion into the animal tissues

Chondroitin sulfates

•Chondroitin 4-sulfate (Greek : chondros-cartilage) is a major constituent of various mammalian tissues (bone, cartilage, tendons). Chondroitin 4-sulfate consists of repeating disaccharide units composed of D-glucuronic acid N-acetyl D-galactosamine 4-sulfate.

•Heparin

Heparin is an anticoagulant (prevents blood clotting). Heparin is composed of alternating units of N-sulfo D-glucosamine 6-sulfate and glucuronate 2-sulfate.

•Dermatan sulfate

The name dermatan sulfate is derived from the fact that this compound mostly occurs in the skin.

•Keratan sulfate

Keratan sulfate essentially consists of alternating units of D-galactosamine and N-acetylglucosamine 6-sulfate.

Glycoproteins

•Several proteins are covalently bound to carbohydrates which are referred to as glycoproteins.

•Glycoproteins are very widely distributed in the cells and perform variety of functions.

•These include their role as enzymes, hormones, transport proteins, structural proteins and receptors.

•Antifreeze glycoproteins : The Antarctic fish live below -2 C, a temperature at which the blood would freeeze. It is now known that these fish contain antifreeze glycoprotein which lower the freezing point of water and interfere with the crystal formation of ice.

•Blood group substances:

The blood group antigens (of erythrocyte membrane) contain carbohydrates as glycoproteins or glycolipids.

Introduction to proteins

•Proteins are the most abundant organic molecules of the living system. They occur in every part of the cell.

Origin of the word 'protein’

•The term protein is derived from a Greek word proteios, meaning holding the first place, they are organic compounds that are utmost important to life.

Functions of proteins

•Proteins perform a great variety of specialized and essential functions in the living cells. These functions may be broadly grouped as static (structural) and dynamic.

•Structural functions : Certain proteins are responsible for structure and strength of body. These include collagen and elastin found in bone matrix, vascular system and other organs and α-ketatin present in epidermal tissues.

•Dynamic functions ; These include proteins acting as enzymes, hormones, blood clotting factors, immunoglobulins, membrane receptors, storage proteins, besides their function in genetic control, muscle contraction, respiration etc.

Elemental composition of protein

•Proteins are predominantly constituted by five major elements. They are carbon, hydrogen, oxygen, nitrogen, sulfur.

•Proteins are polymers of amino acids.Proteins on complete hydrolysis yield L- α-amino acids. This is a common property of all the proteins. Therefore, proteins are the polymers of L- α-amino acids.

Standard amino acids

•As many as 300 amino acids occur in nature – Of these, only 20 – known as standard amino acids are repeatedly found in the structure of proteins.

Amino acids

•Amino acids are a group of organic compounds containing two functional groups- amino and carboxyl. The amino group (-NH2) is basic while the carboxyl group (-COOH) is acidic in nature.

Introduction to proteins

General structure of amino acids

•The amino acids are termed as α-amino acids, if both the carboxyl and amino group are attached to the same carbon atom,

•The a-carbon atom binds to a side chain represented by R which is different for each of the 20 amino acids found in proteins.

•The amino acids mostly exist in the ionized form in the biological system (shown above).

Optical isomers of amino acids

•If a carbon atom is attached to four different groups, it is asymmetric and therefore exhibits optical isomerism.The amino acids (except glycine) possess four distinct groups (R, H, COO-, NH;) held by a-carbon. Thus all the amino acids (except glycine where R = H) have optical isomers.

Classification of amino acids

•There are different ways of classifying the amino acids based on the structure and chemical nature, nutritional requirement, metabolic fate etc.

A. Amino acid classification based on the structure :

1.Amino acids with aliphatic side chains :

•This group consists of the most simple amino acids- glycine, alanine,valine, leucine and isoleuci ne. The last three amino acids (Leu, lle, Val) contain branched aliphatic side chains, hence they are referred to as branched chain amino acids.

2.Hydroxyl group containing amino acids:

•Serine, threonine and tyrosine are hydroxyl group containing amino acids..Tyrosine- being aromatic in nature- is usually considered under aromatic amino acids.

3.Sulfur containing amino acids : Cysteine and methionine are the two amino acids. Cystine, another important sulfur containing amino acid, is formed by condensation of two molecules of cysteine.

4.Acidic amino acids and their amides :

•Aspartic acid and glutamic acids are dicarboxylic monoamino acids while asparagine and glutamine are their respective amide derivatives.

5.Basic amino acids : The three amino acids lysine, arginine and histidine are dibasic monocarboxylic acids. They are highly basic in character.

6.Aromatic amino acids : Phenylalanine, tyrosine and tryptophan are aromatic amino acids.

7.Imino acids : Proline containing pyrrolidine ring is a unique amino acid. It has an imino group (=NH), instead of an amino group (-NH2). Therefore, proline is an α-imino acid.

B. Classification of amino acids based on polarity :

1.Non-polar amino acids : These amino acids are also referred to as hydrophobic (water hating). The amino acids included in this group are- alanine, leucine, isoleucine, valine, methionine, phenyl-alanine, tryptophan and proline.

2.Polar amino acids : They however possess groups such as hydroxyl, sulfhydryl and amide and participate in hydrogen bonding of protein structure. The amino acids in this group are- glycine, serine, threonine, cysteine, glutamine, asparagines and tyrosine.

C. Nutritional classification of amino acids :

•Based on the nutritional requirements, amino acids are grouped into two classes – essential and non essential.

1.Essential or indispensable amino acids :

•The amino acids which cannot be synthesized by the body and, therefore,need to be supplied through the diet are called essential amino acids. They are required for proper growth and maintenance of the individual. The ten amino acids listed below are essential for humans (and also rats) :

•Arginine, Valine, Histidine, Isoleucine, Leucine, Lysine, Methionine, Phenylalanine,Threonine, Tryptophan.

•[The code A. V. HILL, MP., T. T. (first letter of each amino acid) may be memorized to recall essential amino acids.

2.Non-essential or dispensable amino acids: The body can synthesize about 10 amino acids to meet the biological needs, hence they need not be consumed in the diet. These are- glycine, alanine, serine, cysteine, aspartate, asparagine, glutamate,glutamine, tyrosine and proline.

D. Amino acid classification based on their metabolic fate:

• The carbon skeleton of amino acids can serve as a precursor for the synthesis of glucose (glycogenic) or fat ketogenic) or both. From metabolic view point, amino acids are divided into three groups.

1.Glycogenic amino acids : These amino acids can serve as precursors for the formation of glucose or glycogen. e.g. alanine, aspartate, glycine, methionine etc.

2.Ketogenic amino acids : Fat can be synthesized from these amino acids. Two amino acids leucine and lysine are exclusively ketogenic.

3.Glycogenic and ketogenic amino acids:The four amino acids isoleucine, phenylalanine, tryptophan, tyrosine are precursors for synthesis of glucose as well as fat.

•The amino acids differ in their physicochemical properties :

A. Physical properties

1. Solubility: Most of the amino acids are usually soluble in water and insoluble in organic solvents.

2. Melting points: Amino acids generally melt at higher temperatures, often above 200 C.

3. Taste: Amino acids may be sweet (Gly, Ala, Val), tasteless (Leu) or bitter (Arg, lie).

4. Optical properties: All the amino acids except glycine possess optical isomers due to the presence of asymmetric carbon atom.

5. Amino acids as ampholytes : Amino acids contain both acidic (-COOH) and basic (-NH2) groups. They can donate a proton or accept a proton, hence amino acids are regarded as ampholytes.

Zwitterion or dipolar ion: The name zwitter is derived from the German word which means hybrid. Zwitter ion (or dipolar ion) is a hybrid molecule containing positive and negative ionic groups In strongly acidic pH (low pH), the amino acid is positively charged (cation) while in strongly alkaline pH (high pH), it is negatively charged (anion). Each amino acid has a characteristic pH (e.g. leucine, pH 6.0) at which it carries both positive and negative charges and exists as zwitterion. Isoelectric pH (symbol pl) is defined as the pH at which a molecule exists as a zwitterion or dipolar ion and carries no net charge. Thus, the molecule is electrically neutral.

B. Chemical properties

•The general reactions of amino acids are mostly due to the presence of two functional groups namely carboxyl (-COOH) group and amino (-NH2) group.

Reactions due to - COOH group

1. Amino acids form salts (- COONa) with bases and esters (- COOR') with alcohols.

2. Decarboxylation: Amino acids undergo decarboxylation to produce corresponding amines. This reaction assumes significance in the living cells due to the formation of many biologically important amines. These include histamine, tyramine and y-amino butyric acid (GABA) from the amino acids histidine, tyrosine and glutamate, respectively.

3. Reaction with ammonia: The carboxyl group of dicarboxylic amino acids reacts with NH3 to form amide Reactions due to -NH2 group

4. The amino groups behave as bases and combine with acids (e.g. HCI) to form salts.

5. Reaction with ninhydrin: The a-amino acids react with ninhydrin to form a purple, blue or pink colour complex (Ruhemann's purple).

Amino acid + Ninhydrin ---- Keto acid + NH3 + C02 + Hydrindantin

Hydrindantin + NH3 + Ninhydrin----Ruhemann's purple Ninhydrin reaction is effectively used for the quantitative determination of amino acids and proteins.

6. Colour reactions of amino acids: Amino acids can be identified by specific colour reactions .

7. Transamination: Transfer of an amino group from an amino acid to a keto acid to form a new amino acid is a very important reaction in amino acid metabolism..

8. Oxidative deamination : The amino acids undergo oxidative deamination to liberate free ammonia.

NON STANDARD AMINO ACIDS

•Besides the 20 standard amino acids (described above) present in the protein structure, there are several other amino acids which are biologically important.

A.Amino acid derivatives in proteins :

•These derivatives of amino acids are very important for protein structure and functions.

•eg. Collagen - contains 4-hydroxyproline and 5-hydroxylysine.

•Histones- the proteins found in association with DNA- contain many methylated, phosphorylated or acetylated amino acids.

•y-Carboxyglutamic acid is found in certain plasma proteins involved in blood clotting.

•Cystine is formed by combination of two cysteines.

B.Non-protein amino acids :

•These amino acids, although never found in proteins, perform several biologically important functions. They may be either a-or non-a-amino acids.

C. D-Amino acids :

The vast majority of amino acids isolated from animals and plants are of L-category. Certain D-amino acids are also found in theantibiotics (actinomycin-D, valinomycin, gramicidin-S). D-serine and D-aspartate are found in brain tissue. D-Glutamic acid and D-alanine are present in bacterial cell walls.

1. α-Amino acids

|  |  |
| --- | --- |
| Amino acids | Functions |
| Ornithine | Intermediates in the biosynthesis of urea. |
| Citrulline |
| Arginosuccinic acid |
| Thyroxine | Thyroid hormones derived from tyrosine |
| Triiodothyronine |
| S-Adenosylmethionine | Methyl donor in biological system. |
| Homocysteine | Intermediate in methionine metabolisms. |
| Homoserine | Intermediate in threonine, aspartate and methionine metabolisms. |
| 3, 4-Dihydroxy phenylalanine (DOPA) | neurotransmitter, serves as a precursor for melanin pigment. |

• Creatinine

• Azaserine

2.. Non- α -amino acids

• S-Alanine

• S-Aminoisobutyric acid

• y-Aminobutyric acid (GABA)

• 8-Aminolevulinic acid (ALA)

• Taurine

Derived from muscle and excreted in urine. An antibiotic Component of vitamin pantothenin acid and coenzyme A. End product of pyrimidine metabolism.A neurotransmitter produced from glutamic acid. Intermediate in the synthesis of porphyrin (finally heme) Found in association with bile acids.

Structure of proteins

•Proteins are the polymers of L-α-amino acids.

•The structure of proteins is rather complex which can be divided into 4 levels of organization

1.Primary structure: The linear sequence of amino acids forming the backbone of proteins (polypeptides) .

2.Secondary structure: The spatial arrangement of protein by twisting of the polypeptide chain.

3.Tertiary structure: The three dimensional structure of a functional protein.

4.Quaternary structure: Some of the proteins are composed of two or more polypeptide chains referred to as subunits. The spatial arrangement of these subunits is known as quaternary structure.

•The protein is generally used for a polypeptide containing more than 50 amino acids.

Primary structure of protein :

•Each protein has a unique sequence of amino acids.

Peptide bond The amino acids are held together in a protein by covalent peptide bonds.

Formation of a peptide bond:

•When the amino group of an amino acid combines with the carboxyl group of another amino acid, a peptide bond is formed. Note that a dipeptide will have two amino acids and one peptide bond. Peptides containing more than 10 amino acids (decapeptide) are referred to as polypeptides.

Writing of peptide structures:

Conventionally, the peptide chains are written with the free amino end (N-terminal residue) at the left, and the free carboxyl end (C-terminal residue) at the right. The amino acid sequence is read from N-terminal end to C-terminal end. Incidentally, the protein biosynthesis also starts from the N-terminal amino acid.

SECONDARY STRUCTURE OF PROTEIN

•The conformation of polypeptide chain by twisting or folding is referred to as secondary structure. The amino acids are located close to each other in their sequence. Two types of secondary structures, α-helix and β-sheet, are mainly identified.

α -Helix

• α -Helix is the most common spiral structure of protein.

•The α-helix is a tightly packed coiled structure with amino acid side chains extending outward from the central axis. The a-helix is stabilized by extensive hydrogen bonding.

•All the peptide bonds, except the first and last in a polypeptide chain, participate in hydrogen bonding.

•Each turn of a-helix contains 3.6 amino acids and travels a distance of 0.54 nm. The spacing of each amino acid is 0.15 nm.

β-pleated sheet

•This is the second type of structure (hence β after α) . β-Pleated sheets (or simply β -sheets) are composed of two or more segments of fully extended peptide chains.

Parallel and antiparallel β-sheets

•The polypeptide chains in the β-sheets may be arranged either in parallel (the same direction) or anti-parallel (opposite direction).

•β-Pleated sheet may be formed either by separate polypeptide chains (H-bonds are interchain) or a single polypeptide chain folding back on to itself.

PROPERTIES OF PROTEINS

•1. Solubility: Proteins form colloidal solutions instead of true solutions in water. This is due to huge size of protein molecules.

•2. Molecular weight: The proteins vary in their molecular weights, which, in turn, is dependent on the number of amino acid residues. Each amino acid on an average contributes to a molecular weight of about110. Majority of proteins/polypeptides may be composed of 40 to 4,000 amino acids with a molecular weight ranging from 4,000 to 440,000.

•3. Shape: There is a wide variation in –the protein shape. It may be globular (insulin), oval (albumin) fibrous or elongated (fibrinogen).

•4. Isoelectric pH: Isoelectric pH (pI) as a property of amino acids has been described. At isoelectric pH, the proteins exist as zwitterions or dipolar ions. They are electrically neutral (do not migrate in the electric field) with minimum solubility, maximum precipitability.

•5. Precipitation of proteins : Proteins can be precipitated by dehydration or neutralization of polar groups.

Precipitation at pl : The proteins in general are least soluble at isoelectric pH. Certain proteins (e.g. casein) get easily precipitated when the pH is adjusted to pi (4.6 for casein). Formation of curd from milk is a marvellous example of slow precipitation of milk protein, casein at pI. This occurs due to the lactic acid produced by fermentation of bacteria which lowers the pH to the pl of casein.

•Precipitation by salting out: The process of protein precipitation by the additional of neutral salts such as ammonium sulfate or sodium sulfate is known as salting out. The higher is the protein molecular weight, the lower is the salt required for precipitation. Thus, serum globulins are precipitated by half saturation with ammonium sulfate while albumin is precipitated by full saturation.

•Precipitation by salts of heavy metals: Heavy metal ions like Pb2+, Hg2+, Fe2+, Zn2+, Cd2+ cause precipitation of proteins.

•Precipitation by anionic or alkaloid reagents: Proteins can be precipitated by trichloroacetic acid, sulphosalicylic acid, phosphotungstic acid, picric acid, tannic acid, phosphomolybdic acid etc.

•Precipitation by organic solvents: Organic solvents such as alcohol are good protein precipitating agents.

6. Colour reactions of proteins:

The proteins give several colour reactions which are often useful to identify the nature of the amino acids present in them.

Reaction Specific group or amino acid

• Biuret reaction Two peptide linkages

• Ninhydrin reaction α-amino acids

• Xanthoproteic reaction Benzene ring of aromatic amino acids (Phe, Tyr, Trp)

• Millons reaction Phenolic group (Tyr)

• Hopkins-Cole reaction Indole ring (Trp)

• Sakaguchi reaction Guanidino group (Arg)

• Nitroprusside reaction Sulfhydryl groups (Cys)

• Sulfur test Sulfhydryl groups (Cys)

• Pauly’s test Imidazole ring (His)

• Folin-Coicalteau’s test Phenolic groups (Tyr)

DENATURATION

•The phenomenon of disorganization of native protein structure is known as denaturation. Denaturation results in the loss of secondary, tertiary and quaternary structure of proteins. This involves a change in physical, chemical and biological properties of protein molecules.

Agents of denaturation

•Physical agents: Heat, violent shaking, X-rays, UV radiation .

•Chemical agents : Acids, alkalies, organic solvents (ether, alcohol), salts of heavy metals (Pb, Hg), urea, salicylate.:

Characteristics of denaturation

1.The native helical structure of protein is lost.

2.Peptide bonds are not hydrolysed.

3.The protein loses its biological activity.

4.Denatured protein becomes insoluble in the solvent in which it was originally soluble.

5.Loss of hydrogen and disulfide bonds.

6.Denatured protein is more easily digested. This is due to increased exposure of peptide bonds to enzymes. Cooking causes protein denaturation and, therefore, cooked food (protein) is more easily digested.

8. Denaturation is usually irreversible.

Coagulation :

•The term ‘coagulum’ refers to a semi-solid viscous precipitate of protein. Heat coagulation test is commonly used to detect the presence of albumin in urine.

CLASSIFICATION OF PROTEINS

•Based on their function, chemical nature and solubility properties and nutritional importance are discussed here.

A. Functional classification of proteins

•Based on the functions they perform, proteins are classified into the following groups (with examples)

1.Structural proteins: Keratin of hair and nails, collagen of bone.

2.Enzymes or catalytic proteins: Hexokinase,pepsin .

3.Transport proteins: Hemoglobin, serum albumin.

4.Hormonal proteins: Insulin, growth hormone.

5.Contractile proteins: Actin, myosin .

6.Storage proteins: Ovalbumin, glutelin.

7.Genetic proteins: Nucleoproteins.

8.Defense proteins: Snake venoms, Immunoglobulins.

9.Receptor proteins for hormones, viruses.

B. Protein classification based on chemical nature and solubility

•It is based on the amino acid composition, structure, shape and solubility properties. Proteins are broadly classified into 3 major groups

1.Simple proteins: They are composed of only amino acid residues.

2.Conjugated proteins: Besides the amino acids, these proteins contain a non-protein moiety known as prosthetic group or conjugating group.

3.Derived proteins: These are the denatured or degraded products of simple and conjugated proteins.

1. Simple proteins

(a) Globular proteins:

•These are spherical or oval in shape, soluble in water or other solvents and digestible.

(i)Albumins: Soluble in water and dilute salt solutions and coagulated by heat. e.g. serum albumin, ovalbumin (egg), lactalbumin (milk).

(ii)Globulins: Soluble in neutral and dilute salt solutions e.g. serum globulins, vitelline (egg yolk).

(iii)Glutelins: Soluble in dilute acids and alkalies and mostly found in plants e.g. glutelin (wheat), oryzenin (rice).

(iv) Prolamines: Soluble in 70% alcohol e.g. gliadin (wheat), zein (maize).

(v) Histones: Strongly basic proteins, soluble in water and dilute acids but insoluble in dilute ammonium hydroxide e.g. thymus histones, histones of codfish sperm.

(vi) Globins: These are generally considered along with histones. However,globins are not basic proteins and are not precipitated by NH40H.

(vii) Protamines: They are strongly basic and resemble histones but smaller in size and soluble in NH40H. Protamines are also found in association with nucleic acids e.g. sperm proteins.

(b) Fibrous proteins:

•These are fiber like in shape, insoluble in water and resistant to digestion. Albuminoids or scleroproteins constitute the most predominant group of fibrous proteins.

(i)Collagens are connective tissue proteins lacking tryptophan. Collagens, on boiling with water or dilute acids, yield gelatin which is soluble and digestible.

(ii)Elastins: These proteins are found in elastic tissues such as tendons and arteries.

(iii) Keratins: These are present in exoskeletal structures e.g. hair, nails,horns. Human hair keratin contains as much as 14% cysteine.

2.Conjugated proteins

(a)Nucleoproteins: Nucleic acid (DNA or RNA) is the prosthetic group e.g. nucleohistones, nucleoprotamines.

(b)Glycoproteins: The prosthetic group is carbohydrate, which is less than 4% of protein. The term mucoprotein is used if the carbohydrate content is more than 4%. e.g. mucin (saliva), ovomucoid (egg white).

(c)Lipoproteins: Protein found in combination with lipids as the prosthetic group e.g. serum lipoproteins, membrane lipoproteins.

(d)Phosphoproteins: Phosphoric acid is the prosthetic group e.g. casein (milk), vitelline (egg yolk).

(e)Chromoproteins : The prosthetic group is coloured in nature e.g. hemoglobins, cytoc hromes.

(f)Metalloproteins: These proteins contain metal ions such as Fe, Co, Zn, Cu, Mg etc., e.g. ceruloplasmin (Cu), carbonic anhydrase (Zn).

3. Derived proteins :

The derived proteins are of two types. The primary derived are the denatured or coagu lated or first hydrolysed products of proteins. The secondary derived are the degraded (due to breakdown of peptide bonds) products of proteins.

•(a) Primary derived proteins

(i)Coagulated proteins: These are the denatured proteins produced by agents such as heat, acids, alkalies etc. e.g. cooked proteins, coagulated albumin (egg white).

(ii)Proteans: These are the earliest products of protein hydrolysis by enzymes, dilute acids, alkalies etc. which are insoluble in water. e.g. fibrin formed from fibrinogen.

(iii)Metaproteins: These are the second stage products of protein hydrolysis obtained by treatment with slightly stronger acids and alkalies e.g. acid and alkali metaproteins.

•(b) Secondary derived proteins: These are the progressive hydrolytic products of protein hydrolysis. These include proteoses, peptones, polypeptides and peptides.

C. Nutritional classification of proteins

•The nutritive value of proteins is determined by the composition of essential amino acids (described already). From the nutritional point of view, proteins are classified into 3 categories.

1.Complete proteins:

•These proteins have all the ten essential amino acids in the required proportion by the human body to promote good growth. e.g. egg albumin, milk casein.

2.Partially incomplete proteins:

•These proteins are partially lacking one or more essential amino acids and hence can promote moderate growth. e.g. wheat and rice proteins (limiting Lys, Thr).

3.Incomplete proteins:

•These proteins completely lack one or more essential amino acids. Hence they do not promote growth at all e.g. gelatin (lacks Trp), zein (lacks Trp, Lys).

Introduction to Lipids

•Lipids (Greek: Lipos-fat) are of great importance to the body as the chief concentrated storage form of energy, besides their role in cellular structure and various other biochemical functions.

•Lipids may be regarded as organic substances relatively insoluble in water, soluble in organic solvents (alcohol, ether etc.), actually or potentially related to fatty acids and utilized by the living cells.

•Unlike the polysaccharides, proteins and nucleic acids, lipids are not polymers. Further, lipids are mostly small molecules.

Classification of Lipids

•Lipids are broadly classified into simple, complex, derived and miscellaneous lipids.

1.Simple Lipids: Esters of fatty acids with alcohols. These are mainly of two types

a.Fats and oils (Triacylglycerols): These are esters of fatty acids with glycerol. The difference between fat and oils is only physical. Thus, oil is liquid while fat is a solid at room temperature.

b.Waxes: Esters of fatty acids (usually long chain) with alcohols other than glycerol. Cetyl alcohol is most commonly found in waxes.

2.Complex Lipids: These are esters of fatty acids with alcohols containing additional groups such as phosphate, nitrogenous base, carbohydrates, protein etc. They are further divided as follows

a. Phospholipids

b. Glycolipids

c. Lipoproteins

3.Derived Lipids: These are the derivatives obtained on the hydrolysis of group 1 and group 2 lipids which possess the characteristics of lipids. These include glycerol and other alcohols, fatty acids, mono- and diacylglycerols, lipid (fat) soluble vitamins, steroid hormones, hydrocarbons and ketone bodies.

Functions of Lipids

1. They are the concentrated fuel reserve of the body(triacylglycerols).

2.Lipids are the constituents of membrane structure and regulate the membrane permeability (Phospholipids and cholesterol)

3.They serve as a source of fat soluble vitamins (A, D, E and K).

4.Lipids are important as cellular metabolic regulators (Steroid hormones and prostaglandins)

5.Lipids protect the internal organs, serve as insulating materials and give shape.

FTTY ACIDS

Fatty acids are carboxylic acids with hydrocarbon side chain. They are simplest form of lipids.

•Even and odd carbon fatty acids

Most of the fatty acids that occur in natural lipids are of even carbons (usually 14C-20C). Plamitic acid (16C) and stearic acid (18C) are most common. Among the odd chain fatty acids, propionic acid (3C) and Valeric acid (5C) are well known.

•Saturated and unsaturated fatty acids Saturated fatty acids do not contain double bonds, while unsaturated fatty acids contain one or more double bonds. Fatty acids with one double bond are monounsaturated, and those with 2 or more double bonds are collectively known as polyunsaturated fatty acids (PUFA).

Examples of fatty acids

Common name Structure Number of carbon atoms

Saturated fatty acids

• Acetic acid CH3COOH 2

• Propionic acid CH3CH2COOH 3

• Butyric acid CH3(CH2)2COOH 4

• Valeric acid CH3(CH2)3COOH 5

• Caproic acid CH3(CH2)4COOH 6

• Caprylic acid CH3(CH2)6COOH 8

• Capric acid CH3(CH2)8COOH 10

• Lauric acid CH3(CH2)10COOH 12

• Myristic acid CH3(CH2)12COOH 14

• Palmitic acid CH3(CH2)14COOH 16

• Stearic acid CH3(CH2)16COOH 18

• Arachidic acid CH3(CH2)18COOH 20

• Behenic acid CH3(CH2)20COOH 22

• Lignoceric acid CH3(CH2)22COOH 24

Unsaturated fatty acids

• Palmitoleic acid 16:1:9 16

• Oleic acid 18:1:9 18

• Linoleic acid 18:2:9,12 18

• Linolenic acid 18:3:9,12,15 18

• Arachidonic acid 20:4:5,8,11,14 20

Nomenclature of fatty acids

•The saturated fatty acids end with as suffix –anoic (eg. Octanoic acid) while the unsaturated fatty acids end with a suffix –enoic (eg.

Octadecanoic acid)

Numbering of carbon atoms:

It starts from the carboxyl carbon which is taken as number 1. The carbons adjacent to this (carboxyl C) are 2, 3, 4 and so on or alternately α, β, γ and so on. The terminal carbon containing methyl group is known as omega (ω) carbon. The numbering of carbon atoms in two different ways is given below.

Length of hydrocarbon chain of fatty acids Depending on the length of carbon chains, fatty acids are categorized into 3 groups – Short chain with less than 6 carbons; medium chain with 8 to 14 carbons; long chain with 16 to 24 carbons.

Shorthhand representation of fatty acids

•The general rule is that the total number of carbon atoms are written first, followed by the number of double bonds and finally the (first carbon) position of double bonds, starting from the carboxyl end. Thus, saturated fatty acid, palmitic acid is written as 16:0, oleic acid as 18:1;9, arachidonic acid as 20:4;5,8,11,14.

•There are other conventions of representing the double bonds. 9 indicates that the double bond is between 9 and 10 of the fatty acid. ω9 represents the double bond position (9 and 10) from the ω end.

ESSENTIAL FATTY ACIDS

•The fatty acids that cannot be synthesized by the body and, therefore, should be supplied in the diet are known as essential fatty acids (EFA). Chemically, they are polyunsaturated fatty acids, namely linoleic acid and linolenic acid. Arachidonic acid becomes essential, if its precursor linoleic acid is not provided in the diet in sufficient amounts.

Hydroxyl fatty acids:

•Some of the fatty acids are hydroxylated. Beta-hydroxybutyric acid, one of the ketone bodies produced in metabolism, is a simple example of hydroxyl fatty acids. Cerebronic acid is long chain fatty acid.

Cyclic fatty acids:

Fatty acids with cyclic structures are rather rare eg chaulmoogric acid found in chaulmoogra oil (used in leprosy) contains cyclopentenyl ring.

Eisosanoids:

These compounds are related to eicosapolyenoic fatty acids and include prostaglandins, prostacyclins, leukotrienes and thromboxanes.

TRIACYLGLYCEROLS

•Triacylglycerols (formerly triglycerides) are the esters of glycerol with fatty acids. They are insoluble in water and non-polar in character and commonly known as neutral fats.

•Fats as stored fuel: Triacylglycerols are the most abundant group of lipids that primarily function as fuel reserves of animals.

•Fats primarily occur in adipose tissue: Adipocytes of adipose tissue predominantly found in the subcutaneous layer and in the abdominal cavity are specialized for storage of triacylglycerols. The fat is stored in the form of globules dispersed in the entire cytoplasm.

•Simple triacylglycerols contain the same type of fatty acid residue at all the three carbons eg tristearin.

•Mixed triacylglycerols are more common. They contain 2 or 3 different types of fatty acid residues.

•Triacylglycerols of plants, in general, have higher content of unsaturated fatty acids compared to that of animal.

PROPERTIES OF TRIACYLGLYCEROLS

•A few important properties of triacyglycerols which have biochemical relevance are

1. Hydrolysis :

Heating with superheated steam or boiling with acids or alkalies will produce hydrolysis of the neutral fat into glycerol and fatty acids. In case alkali has been used for the hydrolysis, the fatty acids liberated will combine with the base to form soaps. The process of hydrolysis, catalysed by lipases is important for digestion of fat in the gastro intestinal tract.

2. Saponification :

The hydrolysis of triacylglycerols by alkali to produce glycerol and soaps is known as saponification.

3. Rancidity:

Rancidity is the term used to represent the deterioration of fats and oils resulting in an unpleasant taste. It occurs when fats and oils are exposed to air, moisture, light, bacteria etc.

•Hydrolytic rancidity occurs due to partial hydrolysis of triacylglycerols. Oxidative rancidity occurs due to oxidation of unsaturated fatty acids. This results in the formation of unpleasant products such as dicarboxylic acids, aldehydes, ketones etc. Rancid fats and oils are unsuitable for human consumption.

•Antioxidants: The substances which can prevent the occurrence of oxidative rancidity are known as antioxidants. Trace amounts of antioxidants such as tocopherols, hydroquinone, gallic acid and alpha-napthol are added to the commercial preparations of fats and oils to prevent rancidity. Propyl gallate, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) are the antioxidants used in food preservation.

4. Lipid peroxidation in vivo:

In the living cells, lipids undergo oxidation to produce peroxides and free radicals which can damage tissue. The free radicals are believed to cause inflammatory diseases, ageing, cancer, atherosclerosis etc.

Tests to check purity of fats and oils

•Several tests are employed in the laboratory to check the purity of fats and oils.

•Iodine number:

It is defined as the number of grams of iodine absorbed by 100 gm of fat or oil. It is useful to know the relative unsaturation of fats, and is directly proportional to the content of unsaturated fatty acids.

•Saponification number:

It is defined as the number of mg of KOH required to hydrolyse (saponify) one gram of fat or oil. It is a measure of the average molecular size of the fatty acids presents.

•Reichert-Meissl (RM) number:

It is defined as the number of ml of 0.1 N KOH required to completely neutralize the soluble volatile fatty acids distilled from 5 g fat.

•Acid number:

It is defined as the number of mg of KOH required to completely neutralize free fatty acids present in one gram fat or oil. Oils on decomposition due to chemical or bacterial contamination yield free fatty acids. Therefore oils with increased acid number are unsafe for human consumption.

COMPOUND LIPIDS

PHOSPHOLIPIDS

5.These are complex or compound lipids containing phosphoric acid, in addition to fatty acids, nitrogenous base and alcohol. There are two classes of phospholipids Glycerophospholipids that contain glycerol as the alcohol. Sphingophospholipids that contain sphingosine as the alcohol

Glycerophospholipids

These are the major lipids that occur in biological membranes

1.Phosphatidic acid: This is the simplest phospholipid. If the base, choline, is removed from glycerophospholipids, the resulting structure is called phosphatidic acid.

2.Lecithins : They are widely distributed in the body, but particularly rich in the liver. These are the most abundant group of phospholipids in the cell membranes. Chemically, lecithin is a phosphatidic acid with choline as the base. Phosphatidylcholins represents the storage from of body’s choline. In the plasma, they serve the very useful function of keeping cholesterol and its ester in the dissolved state.

3.Cephalins: Ethanolamine is the nitrogenous base present in cephalins. Thus, lecithin and cephalin differ with regard to base.

4.Phosphatidylinositol

6.Phosphatidylserine: the amino acid serine is the present in this group of glycerophospholipids.

7.Plasmalogens: When a fatty acid is attached by an ether linkage at C1 of glycerol in the glycerophospholipids, the resultant compound is plasmalogen. Choline, inositol and serine may substitute ethanolamine to give other plasmalogens.

8.Cardiolipin: It is so named as it was first isolated from heart muscle. Structurally a cardiolipin consist of two molecules of phosphatidic acid held by an additional glycerol through phosphate groups.

Sphingomyelins

•Sphingosine is an amino alcohol present in it. They do not contain glycerol at all.

Action of Phospholipases

•Phospholipases are a group of enzymes that hydrolyse phospholipids

Functions of Phospholipids

•Phospholipids constitute an important group of compound lipids that perform a wide variety of functions

1.In association with proteins, phospholipids form the structural components of membranes and regulate membrane permeability.

2.They are essential for the synthesis of different lipoproteins, and thus participate in the transport of lipids.

3.Accumulation of fat in liver (fatty liver) can be prevented by phospholipids, hence they are regarded as lipotropic factors.

4.Arachidonic acid, an unsaturated fatty acid liberated from phospholipids, serve as a precursor for the synthesis of eicosanoids

5.Phospholipids act as surfactants. Respiratory distress syndrome in infants is associated with insufficient production of this surfactant.

GLYCOLIPIDS

•They contain sphingol, a carbohydrate-galactose, and fatty acids.

•Glycolipids are important constituents of cell membrane and nervous tissue (Particularly in brain). Cerebrosides are the simplest form of glycolipids.

Gangliosides: They constitute 6% of total lipids in gray matter. These are predominantly found in ganglions and are the most complex form of glycoshingolipids. They are the derivatives of cerebrosides and contain one or more molecules of N-acetylneuraminic acid (NANA), the most important sialic acid. NANA is made up of a molecule of N-acetyl, D-mannosamine combined with a molecule of pyruvic acid.

LIPOPROTEINS

•The term lipoprotein is used for the complex formed by the combination of various lipids (such as tri acyl glycerol, phospholipids, and cholesterol) with proteins. Since the lipids are insoluble in water (hydrophobic), the problem arises how a large quantity of such material is transported in aqueous environment. The outer hydrophilic coat of the lipoproteins faces the water and gives these lipid rich structures water solubility and aid in the transport of lipids via blood from the small intestine to the fat depots and tissues. It is in this way that the neutral fats are transported from the intestine as chylomicrons and from the liver as VLDL to most tissues for oxidation and to adipose tissue for storage.

There are five types of lipoproteins, namely

1. Chylomicrons,

2. Very low density lipoproteins (VLDL),

3. Low density lipoproteins (LDL),

4. High density lipoproteins (HDL) and

5. Free fatty acid-albumin complexes.

•The protein components of plasma lipoproteins are called the apoproteins.

•The cholesterol in LDL, called LDL cholesterol, is known as ‘bad’ cholesterol, because LDL, if present in excess numbers, also deposit cholesterol in and around smooth muscle fibers in arteries, forming fatty atherosclerotic plaques that increase the risk of coronary artery disease.

•HDL cholesterol is known as ‘good’ cholesterol, because it helps to remove excess cholesterol from body cells and transport it to the liver for elimination and prevent accumulation of cholesterol in the blood. So, sigh HDL level is associated with decreased risk of coronary artery disease.

DERIVED LIPIDS

STEROIDS

•Steroids are the compounds containing a cyclic steroid nucleus namely cyclopentanoperhydrophenanthrene (CPPP). It consists of a phenanthrene nucleus (ring A, B, and C) to which a cyclopentane ring (D) is attached.

•There are several steroids in the biological system. These include cholesterol, bile acids, vitamin D, sex hormones, adrenocortical hormones, sitosterols, cardiac glycosides and alkaloids. If the steroid contain one or more hydroxyl groups it is commonly known as sterol.

Cholesterol

•Cholesterol, exclusively found in animals, is the most abundant animal sterol. It is widely distributed in all cells and is major component of cell membranes and lipoproteins.

•Several reactions given by cholesterol are useful for its qualitative identification and quantitative estimation. These include Salkowski’ test, Liebermann-Burchard reaction and Zak’s test.

Funtions of cholesterol:

•It is poor conductor of heat and electricity. It is present in abundance in nervous tissues. It appears that cholesterol functions as an insulating cover for the transmission of electrical impulses in the nervous tissue. It has a role in membrane structure and function, in the synthesis of bile acids, hormones and vitamin D.

Tertiary structure of protein

•The three dimentional arrangement of protein structure is referred to as tertiary structure.

•Bonds of tertiary structure: Besides the hydrogen bonds, disulfide bonds (-5-5), ionic interactions (electrostatic bonds) and hydrophobic interactions also contribute to the tertiary structure of proteins.

Quaternary structure of protein

•Some of the proteins, however, consist of two or more polypeptides which may be identical or unrelated. Such proteins are termed as oligomers and possess quaternary structure. The individual polypeptide chains are known as monomers, protomers or subunits. A dimer consists of two polypeptides while a tetramer has four.

•Bonds in quaternary structure: The monomeric subunits are held together by nonconvalent bonds namely hydrogen bonds, hydrophobic interactions and ionic bonds.

•Importance of oligomeric proteins: These proteins play a significant role in the regulation of metabolism and cellular function.

•Examples of oligomeric proteins : Hemoglobin, aspartate transcarbomylase, lactate dehydrogenase.

Bonds responsible for protein structure

•Protein structure is stabilized by two types of bonds-covalent and non-covalent.

•1. Covalent bonds: The peptide and disulfide bonds are the strong bonds in protein structure.

•Disulfide bonds: A disulfide bond (-5-5) isformed by the sulfhydryl groups (-SH) of two cysteine residues,

•2. Non-covalent bonds: There are, mainly, four types of non-covalent bonds.

•(a) Hydrogen bonds: The hydrogen bonds are formed by sharing of hydrogen atoms between the nitrogen and carbonyl oxygen of different peptide bonds.

•(b) Hydrophobic bonds: The non-polar side chains of neutral amino acids tend to be closely associated with each other in proteins.

•Electrostatic bonds: These bonds are formed by interactions between negatively charged groups (e.g. COO-) of acidic amino acids with positively charged groups (eg –NH3+) of basic amino acids.