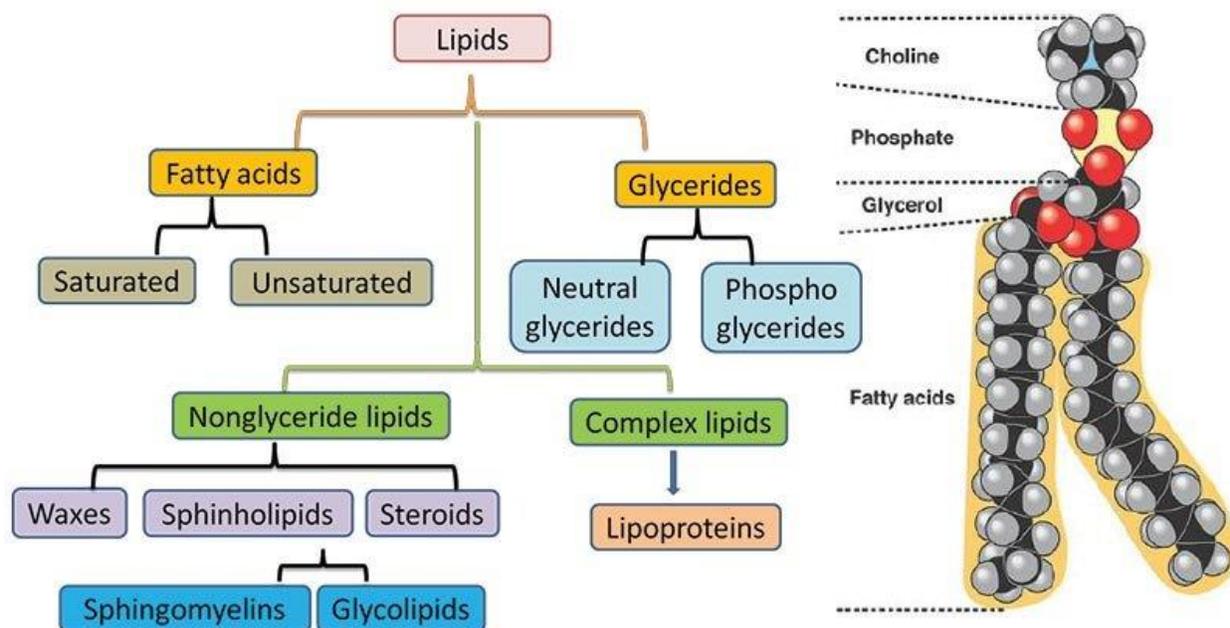


# Lipids- definition, properties, structure, types, examples, functions

## Lipids definition

- Lipids are a heterogeneous group of organic compounds that are insoluble in water and soluble in non-polar organic solvents.
- They naturally occur in most plants, animals, microorganisms and are used as cell membrane components, energy storage molecules, insulation, and hormones.



## Properties of Lipids

- Lipids may be either liquids or non-crystalline solids at room temperature.
- Pure fats and oils are colorless, odorless, and tasteless.
- They are energy-rich organic molecules
- Insoluble in water
- Soluble in organic solvents like alcohol, chloroform, acetone, benzene, etc.
- No ionic charges
- Solid triglycerols (Fats) have high proportions of saturated fatty acids.

- Liquid triglycerols (Oils) have high proportions of unsaturated fatty acids.

### **1. Hydrolysis of triglycerols**

Triglycerols like any other esters react with water to form their carboxylic acid and alcohol— a process known as hydrolysis.

### **2. Saponification:**

Triacylglycerols may be hydrolyzed by several procedures, the most common of which utilizes alkali or enzymes called lipases. Alkaline hydrolysis is termed saponification because one of the products of the hydrolysis is a soap, generally sodium or potassium salts of fatty acids.

### **3. Hydrogenation**

The carbon-carbon double bonds in unsaturated fatty acids can be hydrogenated by reacting with hydrogen to produce saturated fatty acids.

### **4. Halogenation**

Unsaturated fatty acids, whether they are free or combined as esters in fats and oils, react with halogens by addition at the double bond(s). The reaction results in the decolorization of the halogen solution.

### **5. Rancidity:**

The term rancid is applied to any fat or oil that develops a disagreeable odor. Hydrolysis and oxidation reactions are responsible for causing rancidity. Oxidative rancidity occurs in triacylglycerols containing unsaturated fatty acids.

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## **Structure of Lipids**

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- Lipids are made of the elements Carbon, Hydrogen and Oxygen, but have a much lower proportion of water than other molecules such as [carbohydrates](#).
- Unlike polysaccharides and proteins, lipids are not polymers—they lack a repeating monomeric unit.
- They are made from two molecules: **Glycerol and Fatty Acids**.
- A glycerol molecule is made up of three carbon atoms with a hydroxyl group attached to it and hydrogen atoms occupying the remaining positions.
- Fatty acids consist of an acid group at one end of the molecule and a hydrocarbon chain, which is usually denoted by the letter 'R'.
- They may be **saturated or unsaturated**.
- A fatty acid is saturated if every possible bond is made with a Hydrogen atom, such that there exist no C=C bonds.

- Unsaturated fatty acids, on the other hand, do contain C=C bonds. Monounsaturated fatty acids have one C=C bond, and polyunsaturated have more than one C=C bond.

## Structure of Triglycerides

- Triglycerides are lipids consisting of one glycerol molecule bonded with three fatty acid molecules.
- The bonds between the molecules are covalent and are called Ester bonds.
- They are formed during a condensation reaction.
- The charges are evenly distributed around the molecule so hydrogen bonds do not form with water molecules making them insoluble in water.

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## Classification (Types) of Lipids

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Lipids can be classified according to their hydrolysis products and according to similarities in their molecular structures. Three major subclasses are recognized:

### 1. Simple lipids

- (a) **Fats and oils** which yield fatty acids and glycerol upon hydrolysis.
- (b) **Waxes**, which yield fatty acids and long-chain alcohols upon hydrolysis.

#### Fats and Oils

- Both types of compounds are called triacylglycerols because they are esters composed of three fatty acids joined to glycerol, trihydroxy alcohol.
- The difference is on the basis of their physical states at room temperature. It is customary to call a lipid a fat if it is solid at 25°C, and oil if it is a liquid at the same temperature.
- These differences in melting points reflect differences in the degree of unsaturation of the constituent fatty acids.

#### Waxes

- Wax is an ester of long-chain alcohol (usually mono-hydroxy) and a fatty acid.
- The acids and alcohols normally found in waxes have chains of the order of 12-34 carbon atoms in length.

### 2. Compound lipids

- (a) **Phospholipids**, which yield fatty acids, glycerol, amino alcohol sphingosine, phosphoric acid and nitrogen-containing alcohol upon hydrolysis.

They may be **glycerophospholipids** or **sphingophospholipid** depending upon the alcohol group present (glycerol or sphingosine).

- (b) **Glycolipids**, which yield fatty acids, sphingosine or glycerol, and a carbohydrate upon hydrolysis.

They may also be **glyceroglycolipids** or **sphingoglycolipid** depending upon the alcohol group present (glycerol or sphingosine).

### **3. Derived lipids:**

Hydrolysis product of simple and compound lipids is called derived lipids. They include fatty acid, glycerol, sphingosine and steroid derivatives.

Steroid derivatives are phenanthrene structures that are quite different from lipids made up of fatty acids.

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## **Functions**

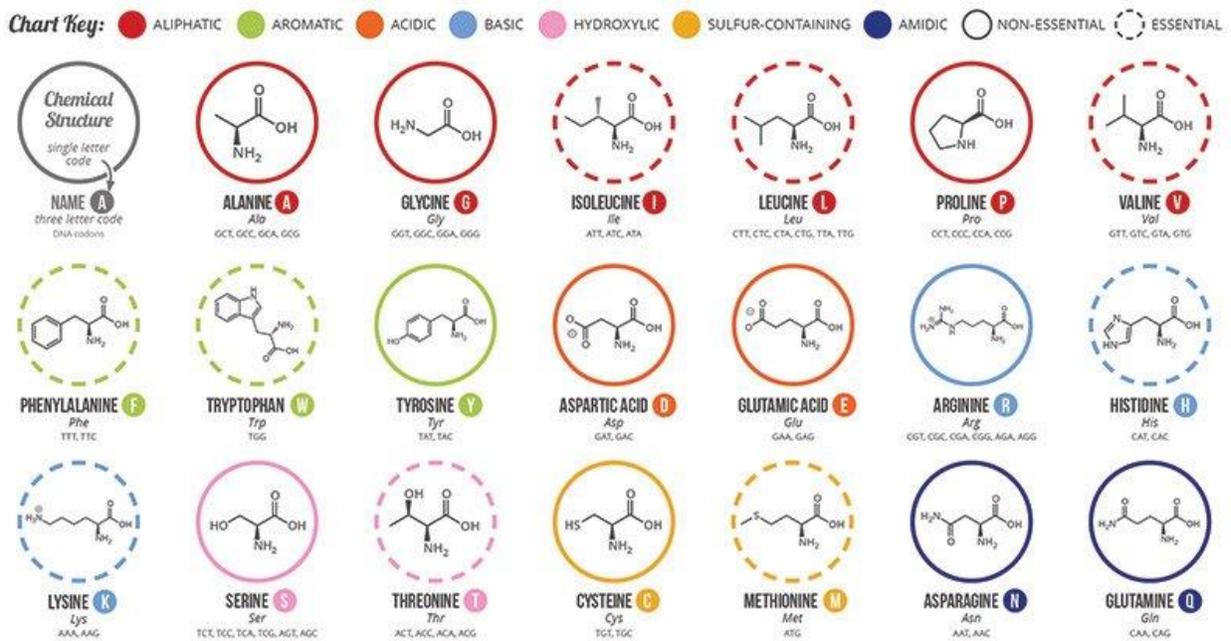
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It is established that lipids play extremely important roles in the normal functions of a cell. Not only do lipids serve as highly reduced storage forms of energy, but they also play an intimate role in the structure of cell membrane and organellar membranes. Lipids perform many functions, such as:

1. Energy Storage
2. Making Biological Membranes
3. Insulation
4. Protection – e.g. protecting plant leaves from drying up
5. Buoyancy
6. Acting as hormones
7. Act as the structural component of the body and provide the hydrophobic barrier that permits partitioning of the aqueous contents of the cell and subcellular structures.
8. Lipids are major sources of energy in animals and high lipid-containing seeds.
9. Activators of enzymes eg. glucose-6-phosphatase, stearyl CoA desaturase and  $\omega$ -monooxygenase, and  $\beta$ -hydroxybutyric dehydrogenase (a mitochondrial enzyme) require phosphatidylcholine micelles for activation.

# Amino Acids- Properties, Structure, Classification and Functions

- Amino acids constitute a group of neutral products clearly distinguished from other natural compounds chemically, mainly because of their ampholytic properties, and biochemically, mainly because of their role as protein constituents.
- An amino acid is a carboxylic acid-containing an aliphatic primary amino group in the  $\alpha$  position to the carboxyl group and with a characteristic stereochemistry.
- **Proteins** are biosynthesized from 20 amino acids in a system involving strict genetic control. Thus, amino acids are the basic unit of proteins.
- More than 300 amino acids are found in nature but only 20 amino acids are standard and present in protein because they are coded by genes. Other amino acids are modified amino acids and called non-protein amino acids.
- Some are residues modified after a protein has been synthesized by posttranslational modifications; others are amino acids present in living organisms but not as constituents of proteins.



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## Properties of Amino acids

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### Physical Properties

1. Amino acids are colorless, crystalline solid.
2. All amino acids have a high melting point greater than 200°
3. Solubility: They are soluble in water, slightly soluble in alcohol and dissolve with difficulty in methanol, ethanol, and propanol. R-group of amino acids and pH of the solvent play important role in solubility.
4. On heating to high temperatures, they decompose.
5. All amino acids (except glycine) are optically active.
6. Peptide bond formation: Amino acids can connect with a peptide bond involving their amino and carboxylate groups. A covalent bond formed between the alpha-amino group of one amino acid and an alpha-carboxyl group of other forming -CO-NH-linkage. Peptide bonds are planar and partially ionic.

### Chemical Properties

#### 1. Zwitterionic property

A zwitterion is a molecule with functional groups, of which at least one has a positive and one has a negative electrical charge. The net charge of the entire molecule is zero. Amino acids are the best-known examples of zwitterions. They contain an amine group (basic) and a carboxylic group (acidic). The -NH<sub>2</sub> group is the stronger base, and so it picks up H<sup>+</sup> from the -COOH group to leave a zwitterion. The (neutral) zwitterion is the usual form amino acids exist in solution.

#### 2. Amphoteric property

Amino acids are amphoteric in nature that is they act as both acids and base since due to the two amine and carboxylic group present.

#### 3. Ninhydrin test

When 1 ml of Ninhydrin solution is added to a 1 ml protein solution and heated, the formation of a violet color indicates the presence of α-amino acids.

#### 4. Xanthoproteic test

The xanthoproteic test is performed for the detection of aromatic amino acids (tyrosine, tryptophan, and phenylalanine) in a protein solution. The nitration of benzoid radicals present in the amino acid chain occurs due to reaction with nitric acid, giving the solution yellow coloration.

#### 5. Reaction with Sanger's reagent

Sanger's reagent (1-fluoro-2, 4-dinitrobenzene) reacts with a free amino group in the peptide chain in a mild alkaline medium under cold conditions.

#### 6. Reaction with nitrous acid

Nitrous acid reacts with the amino group to liberate nitrogen and form the corresponding hydroxyl.

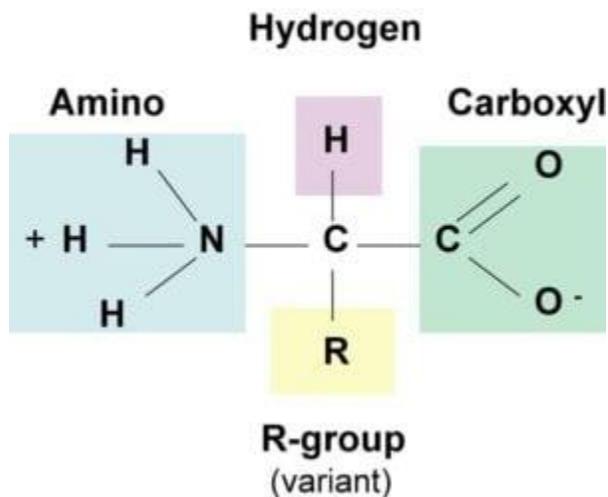
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## Structure of Amino acids

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- All 20 of the common amino acids are alpha-amino acids. They contain a carboxyl group, an amino group, and a side chain (R group), all attached to the  $\alpha$ -carbon.

### Amino Acid Structure



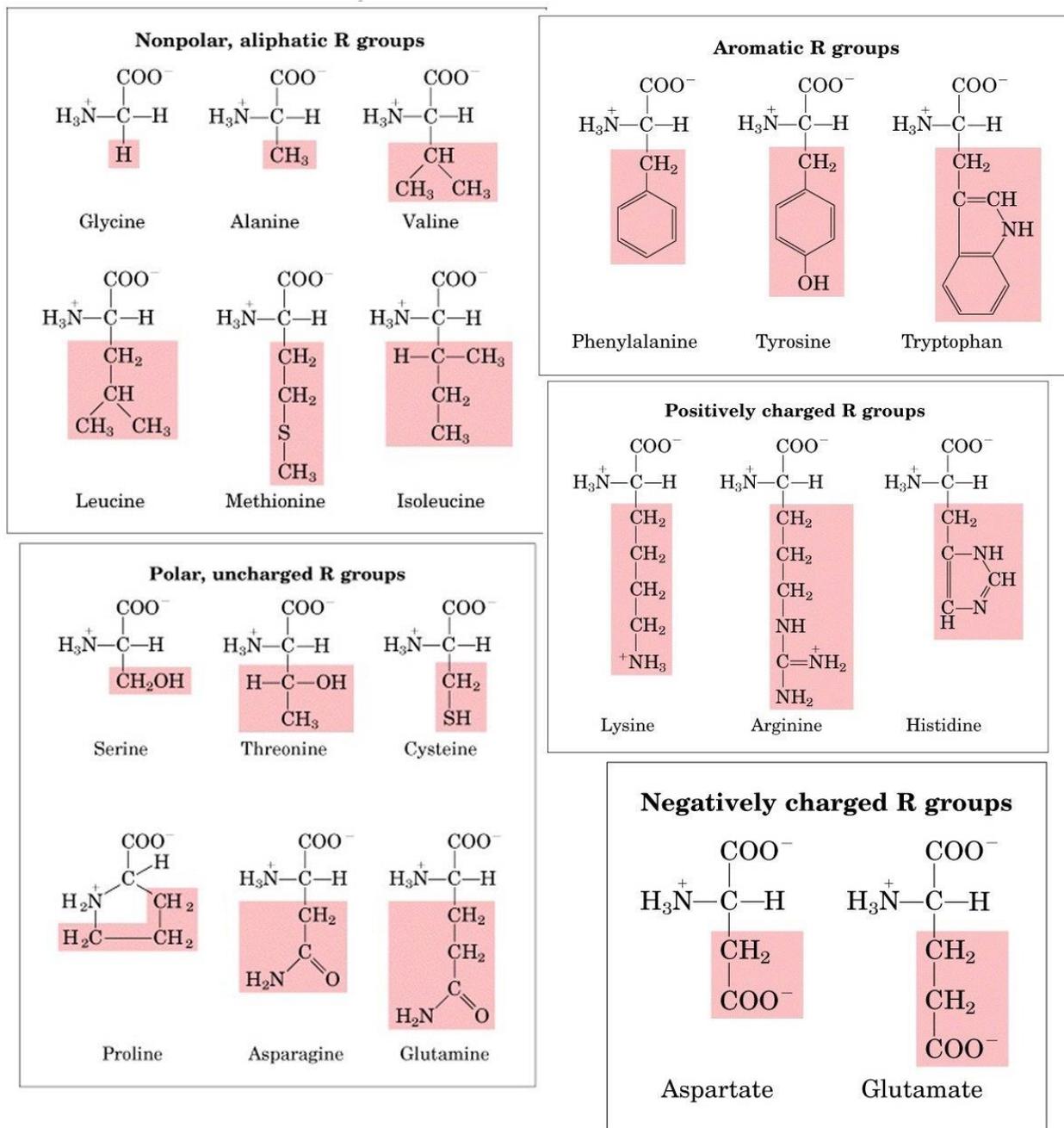
#### Exceptions are:

- Glycine, which does not have a side chain. Its  $\alpha$ -carbon contains two hydrogens.
- Proline, in which the nitrogen is part of a ring.
- Thus, each amino acid has an amine group at one end and an acid group at the other and a distinctive side chain. The backbone is the same for all amino acids while the side chain differs from one amino acid to the next.
- All of the 20 amino acids except glycine are of the L-configuration, as for all but one amino acid the  $\alpha$ -carbon is an asymmetric carbon. Because glycine does not contain an asymmetric carbon atom, it is not optically active and, thus, it is neither D nor L.

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## Classification of amino acids on the basis of R-group

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- Nonpolar, Aliphatic amino acids:** The R groups in this class of amino acids are nonpolar and hydrophobic. Glycine, Alanine, Valine, leucine, Isoleucine, Methionine, Proline.
- Aromatic amino acids:** Phenylalanine, tyrosine, and tryptophan, with their aromatic side chains, are relatively nonpolar (hydrophobic). All can participate in hydrophobic interactions.

3. **Polar, Uncharged amino acids:** The R groups of these amino acids are more soluble in water, or more hydrophilic, than those of the nonpolar amino acids, because they contain functional groups that form hydrogen bonds with water. This class of amino acids includes serine, threonine, cysteine, asparagine, and glutamine.
4. **Acidic amino acids:** Amino acids in which R-group is acidic or negatively charged. Glutamic acid and Aspartic acid
5. **Basic amino acids:** Amino acids in which R-group is basic or positively charged. Lysine, Arginine, Histidine

## Classification of amino acids on the basis of nutrition

Essential	Conditionally Non-Essential	Non-Essential
Histidine	Arginine	Alanine
Isoleucine	Cystine	Asparagine
Leucine	Glutamine	Aspartate
Lysine	Glycine	Glutamate
Methionine	Proline	Serine
Phenylalanine	Tyrosine	
Threonine		
Tryptophan		
Valine		

### 1. Essential amino acids (Nine)

Nine amino acids cannot be synthesized in the body and, therefore, must be present in the diet in order for protein synthesis to occur.

These essential amino acids are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine.

### 2. Non-essential amino acids (Eleven)

These amino acids can be synthesized in the body itself and hence not necessarily need to be acquired through diet.

Arginine, glutamine, tyrosine, cysteine, glycine, proline, serine, ornithine, alanine, asparagine, and aspartate.

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## Classification of amino acids on the basis of the metabolic fate

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Glucogenic amino acids	Glucogenic and ketogenic	Ketogenic amino acids
Alanine, Arginine, Asparagine, Aspartate, Asparagine, Cysteine, Methionine, Glutamate, Glutamine, Glycine, Histidine, Proline, Serine, Threonine, Valine	Tyrosine, Isoleucine, Phenylalanine, Tryptophan	Leucine, Lysine

1. **Glucogenic amino acids:** These amino acids serve as precursors gluconeogenesis for glucose formation. Glycine, alanine, serine, aspartic acid, asparagine, glutamic acid, glutamine, proline, valine, methionine, cysteine, histidine, and arginine.
2. **Ketogenic amino acids:** These amino acids breakdown to form ketone bodies. Leucine and Lysine.
3. **Both glucogenic and ketogenic amino acids:** These amino acids breakdown to form precursors for both ketone bodies and glucose. Isoleucine, Phenylalanine, Tryptophan, and tyrosine.

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## Functions of Amino acids

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1. In particular, 20 very important amino acids are crucial for life as they contain peptides and proteins and are known to be the building blocks for all living things.
2. The linear sequence of amino acid residues in a polypeptide chain determines the three-dimensional configuration of a protein, and the structure of a protein determines its function.
3. Amino acids are imperative for sustaining the health of the human body. They largely promote the:  
Production of hormones
  - Structure of muscles

- Human nervous system's healthy functioning
  - The health of vital organs
  - Normal cellular structure
4. The amino acids are used by various tissues to synthesize proteins and to produce nitrogen-containing compounds (e.g., purines, heme, creatine, epinephrine), or they are oxidized to produce energy.
  5. The breakdown of both dietary and tissue proteins yields nitrogen-containing substrates and carbon skeletons.
  6. The nitrogen-containing substrates are used in the biosynthesis of purines, pyrimidines, neurotransmitters, hormones, porphyrins, and nonessential amino acids.
  7. The carbon skeletons are used as a fuel source in the citric acid cycle, used for gluconeogenesis, or used in fatty acid synthesis.

## Proteins- Properties, Structure, Classification and Functions

- Proteins are the most abundant biological macromolecules, occurring in all cells.
- It is also the most versatile organic molecule of the living systems and occur in great variety; thousands of different kinds, ranging in size from relatively small peptides to large polymers.
- Proteins are the polymers of amino acids covalently linked by the peptide bonds.
- The building blocks of proteins are the twenty naturally occurring amino acids.
- Thus, proteins are the polymers of amino acids.

Proteins  $\xrightarrow{\text{hydrolysis}}$  Peptides  $\xrightarrow{\text{hydrolysis}}$  Amino acids

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### Properties of Proteins

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#### Solubility in Water

- The relationship of proteins with water is complex.
- The secondary structure of proteins depends largely on the interaction of peptide bonds with water through hydrogen bonds.
- Hydrogen bonds are also formed between protein (alpha and beta structures) and water. The protein-rich static ball is more soluble than the helical structures.

- At the tertiary structure, water causes the orientation of the chains and hydrophilic radicals to the outside of the molecule, while the hydrophobic chains and radicals tend to react with each other within the molecule (hydrophobic effect).

### **Denaturation and Renaturation**

- Proteins can be denatured by agents such as heat and urea that cause unfolding of polypeptide chains without causing hydrolysis of peptide bonds.
- The denaturing agents destroy secondary and tertiary structures, without affecting the primary structure.
- If a denatured protein returns to its native state after the denaturing agent is removed, the process is called renaturation.

Some of the denaturing agents include

**Physical agents:** Heat, radiation, pH

**Chemical agents:** Urea solution which forms new hydrogen bonds in the protein, organic solvents, detergents.

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### **Coagulation**

When proteins are denatured by heat, they form insoluble aggregates known as coagulum. All the proteins are not heat coagulable, only a few like the albumins, globulins are heat coagulable.

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### **Isoelectric point**

- The isoelectric point (pI) is the pH at which the number of positive charges equals the number of negative charges, and the overall charge on the amino acid is zero.
- At this point, when subjected to an electric field the proteins do not move either towards anode or cathode, hence this property is used to isolate proteins.

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### **Molecular Weights of Proteins**

- The average molecular weight of an amino acid is taken to be 110.
- The total number of amino acids in a protein multiplied by 110 gives the approximate molecular weight of that protein.

- Different proteins have different amino acid composition and hence their molecular weights differ.
- The molecular weights of proteins range from 5000 to  $10^9$  Daltons.

## Posttranslational modifications

- It occurs after the protein has been synthesized on the ribosome.
- Phosphorylation, glycosylation, ADP ribosylation, methylation, hydroxylation, and acetylation affect the charge and the interactions between amino acid residues, altering the three-dimensional configuration and, thus, the function of the protein.

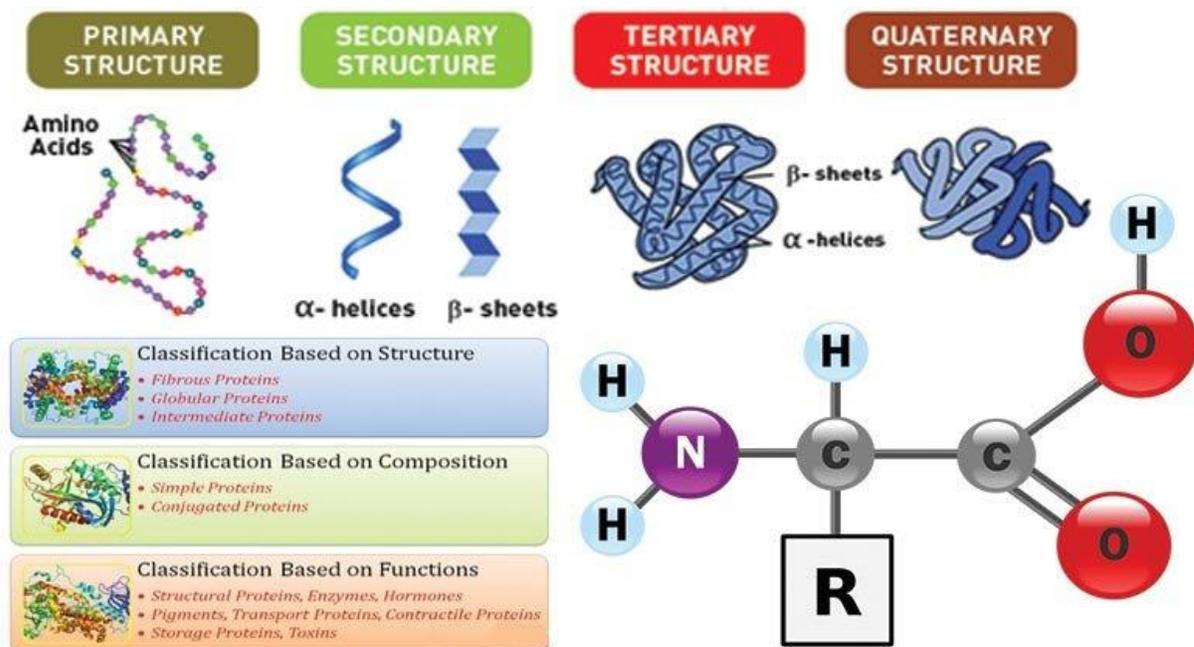
## Chemical Properties

### 1. Biuret test:

When 2 ml of test solution is added to an equal volume of 10% NaOH and one drop of 10% CuSO<sub>4</sub> solution, a violet colour formation indicates the presence of peptide linkage.

### 2. Ninhydrin test:

When 1 ml of Ninhydrin solution is added to 1 ml protein solution and heated, formation of a violet colour indicates the presence of  $\alpha$ -amino acids.



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## Protein Structure

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- The linear sequence of amino acid residues in a polypeptide chain determines the three-dimensional configuration of a protein, and the structure of a protein determines its function.
- All proteins contain the elements carbon, hydrogen, oxygen, nitrogen and sulfur some of these may also contain phosphorus, iodine, and traces of metals like iron, copper, zinc and manganese.
- A protein may contain 20 different kinds of amino acids. Each amino acid has an amine group at one end and an acid group at the other and a distinctive side chain.
- The backbone is the same for all amino acids while the side chain differs from one amino acid to the next.

The structure of proteins can be divided into four levels of organization:

### 1. Primary Structure

- The primary structure of a protein consists of the amino acid sequence along the polypeptide chain.
- Amino acids are joined by peptide bonds.
- Because there are no dissociable protons in peptide bonds, the charges on a polypeptide chain are due only to the N-terminal amino group, the C-terminal carboxyl group, and the side chains on amino acid residues.
- The primary structure determines the further levels of organization of protein molecules.

### 2. Secondary Structure

- The secondary structure includes various types of local conformations in which the atoms of the side chains are not involved.
- Secondary structures are formed by a regular repeating pattern of hydrogen bond formation between backbone atoms.
- The secondary structure involves  $\alpha$ -helices,  $\beta$ -sheets, and other types of folding patterns that occur due to a regular repeating pattern of hydrogen bond formation.
- The secondary structure of protein could be :
  1. **Alpha-helix**
  2. **Beta-helix**
- The  $\alpha$ -helix is a right-handed coiled strand.
- The side-chain substituents of the amino acid groups in an  $\alpha$ -helix extend to the outside.

- Hydrogen bonds form between the oxygen of the C=O of each peptide bond in the strand and the hydrogen of the N-H group of the peptide bond four amino acids below it in the helix.
- The side-chain substituents of the amino acids fit in beside the N-H groups.
- The hydrogen bonding in a  $\beta$ -sheet is between strands (inter-strand) rather than within strands (intra-strand).
- The sheet conformation consists of pairs of strands lying side-by-side.
- The carbonyl oxygens in one strand hydrogen bond with the amino hydrogens of the adjacent strand.
- The two strands can be either parallel or anti-parallel depending on whether the strand directions (N-terminus to C-terminus) are the same or opposite.
- The anti-parallel  $\beta$ -sheet is more stable due to the more well-aligned hydrogen bonds.

### **3. Tertiary Structure**

- Tertiary structure of a protein refers to its overall three-dimensional conformation.
- The types of interactions between amino acid residues that produce the three-dimensional shape of a protein include hydrophobic interactions, electrostatic interactions, and hydrogen bonds, all of which are non-covalent.
- Covalent disulfide bonds also occur.
- It is produced by interactions between amino acid residues that may be located at a considerable distance from each other in the primary sequence of the polypeptide chain.
- Hydrophobic amino acid residues tend to collect in the interior of globular proteins, where they exclude water, whereas hydrophilic residues are usually found on the surface, where they interact with water.

### **4. Quaternary Structure**

- Quaternary structure refers to the interaction of one or more subunits to form a functional protein, using the same forces that stabilize the tertiary structure.
- It is the spatial arrangement of subunits in a protein that consists of more than one polypeptide chain.

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## **Classification of Proteins**

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Based on the chemical nature, structure, shape and solubility, proteins are classified as:

1. **Simple proteins:** They are composed of only amino acid residue. On hydrolysis these proteins yield only constituent amino acids. It is further divided into:
  - Fibrous protein: Keratin, Elastin, Collagen
  - Globular protein: Albumin, Globulin, Glutelin, Histones
2. **Conjugated proteins:** They are combined with non-protein moiety. Eg. Nucleoprotein, Phosphoprotein, Lipoprotein, Metalloprotein etc.
3. **Derived proteins:** They are derivatives or degraded products of simple and conjugated proteins. They may be :
  - Primary derived protein: Proteans, Metaproteins, Coagulated proteins
  - Secondary derived proteins: Proteosesn or albumoses, peptones, peptides.

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## Functions of Proteins

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Proteins are vital for the growth and repair, and their functions are endless. They also have enormous diversity of biological function and are the most important final products of the information pathways.

- Proteins, which are composed of amino acids, serve in many roles in the body (e.g., as enzymes, structural components, hormones, and antibodies).
- They act as structural components such as keratin of hair and nail, collagen of bone etc.
- Proteins are the molecular instruments through which genetic information is expressed.
- They execute their activities in the transport of oxygen and carbon dioxide by hemoglobin and special enzymes in the red cells.
- They function in the homostatic control of the volume of the circulating blood and that of the interstitial fluids through the plasma proteins.
- They are involved in blood clotting through thrombin, fibrinogen and other protein factors.
- They act as the defence against infections by means of protein antibodies.
- They perform hereditary transmission by nucleoproteins of the cell nucleus.
- Ovalbumine, glutelin etc. are storage proteins.
- Actin, myosin act as contractile protein important for muscle contraction.

# Biological Oxidation

This article gives the answer to the question as to “**How do the food we take in and the oxygen we respire, produce energy to continue the process of life**”. The simplest answer is that the food we take in is oxidized by the enzymes present in the body.

During this process some reducing equivalents viz. NADH and  $\text{FADH}_2$  are produced which are electron rich in nature. These reducing equivalents donate their electrons to the oxygen we respire in, during which energy is released to produce adenosine triphosphate (ATP). ATP is known as the energy currency of the cell and it brings about the biological process of life. In order to understand the above process, we need to understand some basic terminologies.

**Oxidation and reduction can be defined in three different ways as under:**

- i. Oxidation is ‘Addition of oxygen’ or ‘removal of hydrogen’ or ‘removal of electrons’.
- ii. Reduction is ‘Removal of oxygen’ or ‘addition of hydrogen’ or ‘addition of electrons’.

**Oxidizing agent or oxidant:**

An electron acceptor is an oxidizing agent or oxidant.

**Reducing agent or reductant:**

An electron donor is a reducing agent or reductant.

**Redox potential ( $E_o$ ):**

The relative tendency of reductant to donate electrons as compared to hydrogen is termed as oxidation-reduction potential or ‘redox potential’ ( $E_o$ ).

The redox potential of hydrogen is taken as zero at pH 0 (-0.417),  $25^\circ\text{C}$ , in a solution of 1 molar concentration (1.0 atom of hydrogen).

- i. A compound having a negative value of  $E_o$  is a better electron donor than hydrogen.
- ii. A compound having a positive value of  $E_o$  is a poor electron donor than hydrogen.

The electrons flow from compounds with negative value of redox potential to those with positive values of redox potential, because there will be loss of energy and thus, the compound becomes stable.

### **Free energy ( $F_o$ ):**

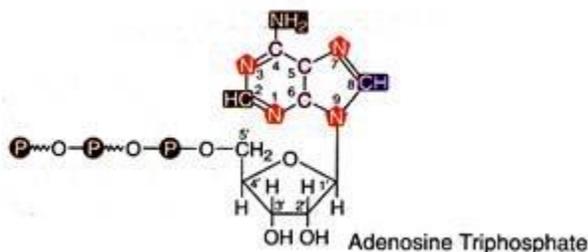
Every chemical substance has a certain amount of energy built into it, which is the energy of the chemical bonds holding the atoms together. This is the free energy.

### **High energy compounds and energy rich bond (~):**

Any bond, which on hydrolysis gives a minimum free energy of 7.4 Kcal/mol, is known as energy rich bond and the compound which has an energy rich bond is known as high energy compound. Ex. ATP, pyrophosphate, 1, 3-diphosphoglyceric acid, phosphoenol pyruvate, creatine phosphate and acetyl-CoA.

### **Adenosine triphosphate (ATP):**

ATP is also known as the 'energy currency' of the living cell, because it transfers energy from energy yielding sources to the energy requiring cell processes. ATP has two pyrophosphate bonds. On hydrolysis of each of the terminal two phosphate groups there is release of more than 7.4 Kcal/mol of energy but the third bond yields only 3 Kcal/mol of energy, hence it is not a high energy bond. On hydrolysis ATP is converted to ADP and to AMP.



### **Biological oxidation:**

Biological oxidation is catalysed by enzymes which function in combination with coenzymes and/or electron carrier proteins.

**Different enzymes associated with biological oxidation are:**

**1. Oxidoreductases:**

These enzymes catalyse the removal of hydrogen from the substrate and add it to another substance, thus bringing about oxidation reduction reaction. Ex. Glyceraldehyde—3—Phosphate dehydrogenase.

**2. Oxidases:**

These enzymes catalyse the removal of hydrogen from the substrate and add directly to the molecular oxygen. Ex. Cytochrome oxidases, tyrosinase, uricase.

**3. Oxygenases:**

These enzymes incorporate oxygen into the substrates.

**(a) Mono-oxygenases:**

Adds only one atom of oxygen to the substrate. These are also known as mixed function oxidases.

**(b) Di-oxygenases:**

Adds both the atoms of oxygen to the substrate. Ex. Homogentisic acid di-oxygenase.

**4. Aerobic dehydrogenases:**

These enzymes remove hydrogen from the substrate and add it either directly to oxygen or any other artificial acceptors like methylene blue. The product formed is hydrogen peroxide.

**5. Anaerobic dehydrogenases:**

These enzymes use other substrates or substances to donate the hydrogen. They transfer hydrogen's to some other hydrogen acceptor,

but not directly to oxygen. Thus the hydrogen acceptors are NAD, FAD and FMN. Heme proteins like cytochromes also receive hydrogen's. The cytochromes are 'b', 'c<sub>1</sub>', 'c', 'a' and 'a<sub>3</sub>'.

### **6. Hydro peroxidases:**

These enzymes have either hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or organic peroxide as their substrate.

**There are two types of hydro peroxidases:**

(1) Peroxidase and

(2) Catalase.

Their prime function is destruction of H<sub>2</sub>O<sub>2</sub>.

### **Electron Transport Chain:**

When electrons are transferred from the most electronegative system [(NADH or FADH<sub>2</sub>) (-0.32V)] to the most electropositive system (+0.82V) (Oxygen), there will be liberation of all the energy at one time in an explosive manner. But, if they are transferred in a step wise manner through some intermediate systems then there will be slow release of energy and it can be captured by the cell to synthesize energy rich compounds. During biological oxidation, electrons are transferred through electron transport proteins which are arranged in a specific chain to form the electron transport chain (ETC), which is situated in the inner mitochondrial membrane.

### ***Respiratory Chain or ETC:***

Transfer of electrons from substrate to molecular oxygen through a chain of electron carriers is called electron transport chain or respiratory chain. Mitochondria contains a series of catalysts forming the respiratory chain which are involved in the transfer of electrons and hydrogen and their final reaction is with oxygen to form water. The components of respiratory chain are arranged sequentially in the order of increasing redox potential.

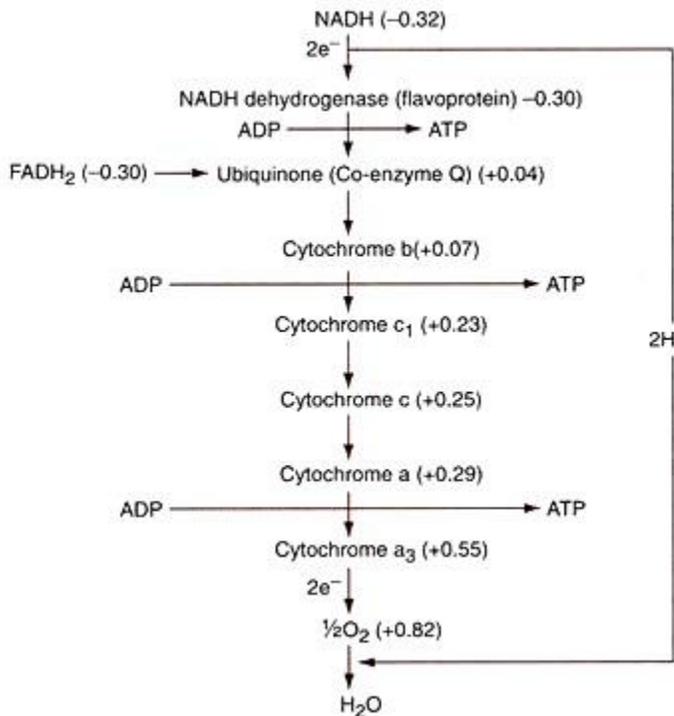
Electrons flow through the chain in a stepwise manner from lower redox potential to higher redox potential. Some amount of energy is liberated with transfer of electron from one component to another. Whenever there is a release of 7.4 Kcal of energy or a little more, then

ATP formation takes place there. NADH forms 3 ATPs whereas FADH<sub>2</sub> forms only 2 as it enters ETC at the site beyond the first site of ATP formation.

**The/three sites of ATP formation in the ETC or respiratory chain are:**

1. Between NADH dehydrogenase (flavoprotein) and ubiquinone (coenzyme Q).
2. Between cytochrome-b and cytochrome-c<sub>1</sub>.
3. Between cytochrome-a and cytochrome-a<sub>3</sub> (cytochromes oxidase).

**The components of ETC, their redox potential and their sequence is:**



**Phosphorylation:**

Esterification of a phosphate through a high energy bond (7.4 Kcal) is known as phosphorylation. Combination of inorganic phosphate (Pi) with any other compound through high energy bond is known as phosphorylation. Or formation of ATP from ADP and phosphate or NTP from NDP and P<sub>i</sub> is known as phosphorylation.

**There are two types of phosphorylation:**

### **1. Substrate level phosphorylation:**

Formation of high energy phosphate bond at the level of a substrate without the involvement of the respiratory chain is known as substrate level phosphorylation. Ex. Phosphoenolpyruvate is converted to pyruvate by pyruvate kinase where ATP is formed from ADP.

### **2. Oxidative phosphorylation:**

The enzymatic phosphorylation of ADP to ATP coupled with electron transport from a substrate to molecular oxygen is known as oxidative phosphorylation or respiratory chain phosphorylation.

### ***Mechanism of Oxidative Phosphorylation:***

There are three theories or hypothesis, explaining the formation of ATP through electron transport chain.

### **They are as follows:**

#### **1. Chemical coupling hypothesis:**

It states that a high energy compound is formed taking the energy liberated by electron transfer and this compound in turn phosphorylates ADP to ATP.

#### **2. Conformational coupling hypothesis:**

There are many proteins in the wall of inner mitochondrial membrane; one of them is  $F_0F_1$ , ATPase, which is responsible for the ATP production. According to this hypothesis the energy liberated from ETC brings a conformational change in the proteins of the membrane and is then transferred to  $F_0F_1$ ATPase which thereby also gets a conformation change and hence becomes unstable. In order to attain stability it provides energy for ATP synthesis.

#### **3. Chemiosmotic hypothesis:**

It states that electron transport pumps  $H^+$  from the mitochondrial matrix across the inner mitochondrial membrane to the outer aqueous phase, thereby the matrix becomes basic and the outer phase becomes acidic. Due to this osmotic difference (i.e. more acidic outside and more basic inside the mitochondrial matrix) the  $H^+$  influx (diffuse) into

the matrix through a pore in the  $F_0F_1$  ATPase which provides the energy for the ATP synthesis.

***P/O Ratio:***

The number of inorganic phosphates esterified per atom of oxygen consumed is known as P/O ratio. For NADH it is 3 and FADH, it is 2.

***Formation and Detoxification of  $H_2O_2$ :***

During ETC,  $O_2$  accepts four electrons forming two  $H_2O$ . If by chance  $O_2$  accepts only two electrons, the product formed is  $H_2O_2$  and if it accepts only one electron then superoxide radical ( $:O_2^-$ ) is formed. Both these damage the membrane structure by attacking the unsaturated fatty acids of the membranes.

***Superoxide is detoxified as—***



$H_2O_2$  is detoxified as—



***Cytochrome- $a_3$ :***

Cytochrome- $a_3$  is also known as cytochrome oxidase. It has two molecules of heme with long hydrocarbon side chains. To the other end of the heme, two copper atoms are attached which can directly react with oxygen to donate four electrons.

***Inhibitors of ETC:***

Inhibitors of ETC are those which inhibit or stop the flow of electrons in the electron transport chain.

***Some of the inhibitors of ETC are:***

(a) At the first site of ATP formation, rotenone and barbitol inhibit the flow of electrons

(b) At the second site antimycin-A and amytal inhibits the flow of electrons.

(c) At the third site cyanide ( $Cn^-$ ), carbon monoxide (CO) and  $H_2S$  gas inhibit.

### ***Un-couplers of Oxidative Phosphorylation:***

Un-couplers are those substances which prevent oxidative phosphorylation (formation of ATP) though ETC is normally operating. Due to the effect of un-couplers there is a continuous flow of electrons but there is no formation of ATP i.e. ETC is not coupled to the ATP formation, so the energy is dissipated as heat.

#### **Some of the un-couplers are:**

##### **1. 2, 4-Dinitrophenol (DNP):**

It transfers protons across the mitochondrial membrane thereby diverting its flow from  $F_0F_1$  ATPase.

##### **2. Valinomycin:**

It transfers  $K^+$  ions, disturbing the osmotic pressure.

##### **3. Gramicidin:**

It transfers  $Na^+$  ions, across the membrane.

All the above three are known as 'ionophores' i.e. those which disrupt the membrane permeability to ions, thereby uncoupling phosphorylation with ETC.

##### **4. Oligomycin:**

It inhibits  $F_0F_1$ ATPase.

##### **5. Atractyloside:**

It inhibits adenine nucleotide transport protein of the mitochondrial membrane which transport ATP in exchange of ADP.

## Exergonic Reaction

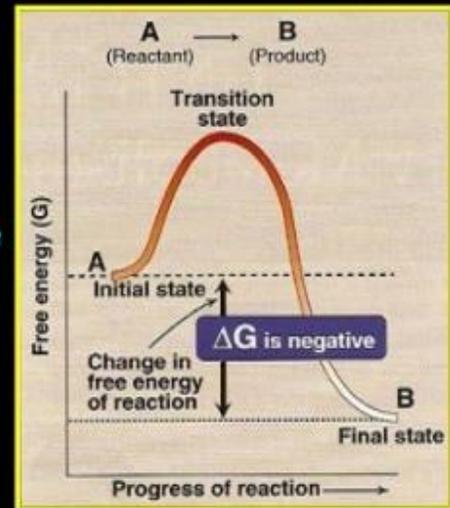


$$\Delta G = G_B - G_A$$

Where  $G_A$  &  $G_B$  are free energy of A & B

- **Negative  $\Delta G$  (A  $\longrightarrow$  B):** If  $\Delta G$  is negative, this means that the energy content of product (B) is less than that of reactant (A)

- There is a **net loss of energy.**
- The reaction proceeds **spontaneously from A  $\longrightarrow$  B**
- The reaction is said to be **exergonic or energy releasing.**
- Exergonic reactions result in **products with less energy than the reactants.**



## Endergonic Reaction



$$\Delta G = G_A - G_B$$

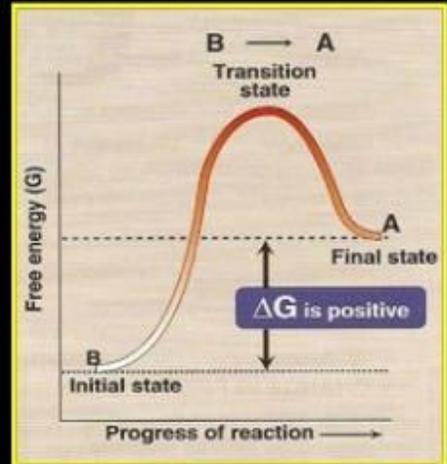
**Positive  $\Delta G$ :** If  $\Delta G$  is positive, this means that the energy content of product (A) is more than that of reactant (B).

- There is a **net gain of energy**.
- The reaction **does not proceed spontaneously from B  $\longrightarrow$  A**
- The reaction is said to be **endergonic or energy requiring**.



Carbohydrates  
Lipids, Proteins

- Endergonic reactions result in **products with more energy than the reactants**.



# Carbohydrates- definition, structure, types, examples, functions

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## What are carbohydrates?

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- The carbohydrates are a group of naturally occurring carbonyl compounds (aldehydes or ketones) that also contain several hydroxyl groups.
  - It may also include their derivatives which produce such compounds on hydrolysis.
  - They are the most abundant organic molecules in nature and also referred to as "saccharides".
  - The carbohydrates which are soluble in water and sweet in taste are called as "sugars".
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## Structure of Carbohydrates

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- Carbohydrates consist of carbon, hydrogen, and oxygen.
- The general empirical structure for carbohydrates is  $(\text{CH}_2\text{O})_n$ .
- They are organic compounds organized in the form of aldehydes or ketones with multiple hydroxyl groups coming off the carbon chain.
- The building blocks of all carbohydrates are simple sugars called monosaccharides.
- A monosaccharide can be a polyhydroxy aldehyde (aldose) or a polyhydroxy ketone (ketose).

The carbohydrates can be structurally represented in any of the three forms:

- Open chain structure.
- Hemi-acetal structure.
- Haworth structure.

**Open chain structure** – It is the long straight-chain form of carbohydrates.

**Hemi-acetal structure** – Here the 1st carbon of the glucose condenses with the -OH group of the 5th carbon to form a ring structure.

**Haworth structure** – It is the presence of the pyranose ring structure.

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## Properties of Carbohydrates

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### Physical Properties of Carbohydrates

- **Stereoisomerism** – Compound having the same structural formula but they differ in spatial configuration. Example: Glucose has two isomers with respect to the penultimate carbon atom. They are D-glucose and L-glucose.

- **Optical Activity** – It is the rotation of plane-polarized light forming (+) glucose and (-) glucose.
- **Diastereo isomers** – It the configurational changes with regard to C2, C3, or C4 in glucose. Example: Mannose, galactose.
- **Anomerism** – It is the spatial configuration with respect to the first carbon atom in aldoses and second carbon atom in ketoses.

### **Chemical Properties of Carbohydrates**

- **Osazone formation:** Osazone are carbohydrate derivatives when sugars are reacted with an excess of phenylhydrazine. eg. Glucosazone
- **Benedict's test:** Reducing sugars when heated in the presence of an alkali gets converted to powerful reducing species known as enediols. When Benedict's reagent solution and reducing sugars are heated together, the solution changes its color to orange-red/ brick red.
- **Oxidation:** Monosaccharides are reducing sugars if their carbonyl groups oxidize to give carboxylic acids. In Benedict's test, D-glucose is oxidized to D-gluconic acid thus, glucose is considered a reducing sugar.
- **Reduction to alcohols:** The C=O groups in open-chain forms of carbohydrates can be reduced to alcohols by sodium borohydride, NaBH<sub>4</sub>, or catalytic hydrogenation (H<sub>2</sub>, Ni, EtOH/H<sub>2</sub>O). The products are known as "alditols".

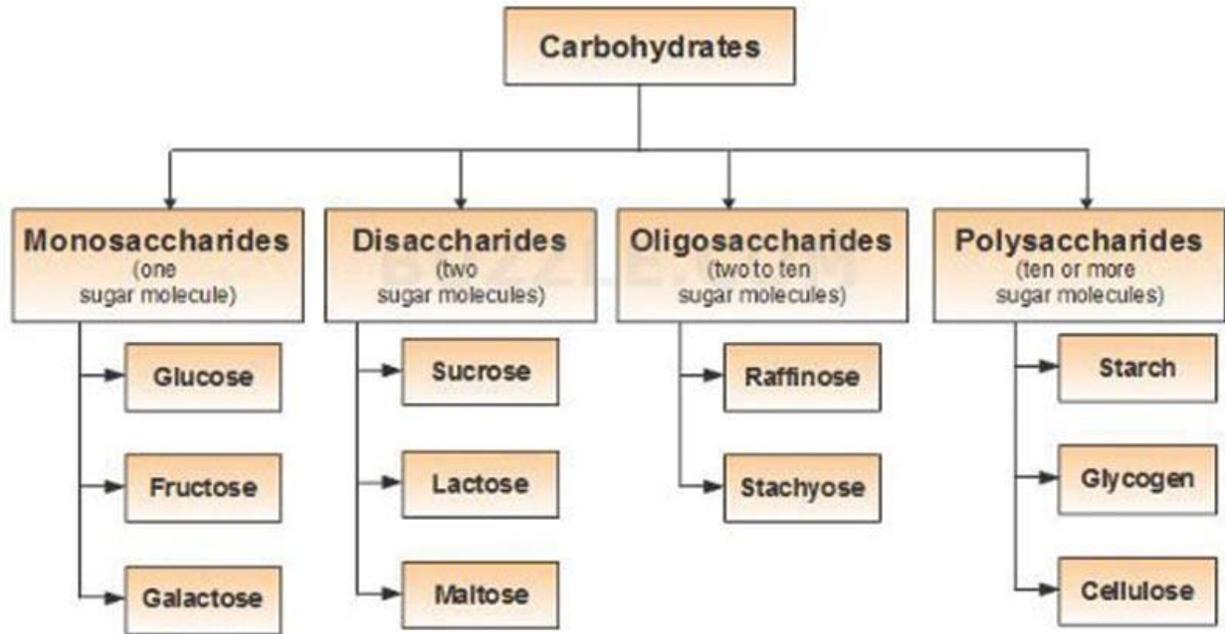
### **Properties of Monosaccharides**

- Most monosaccharides have a sweet taste (fructose is sweetest; 73% sweeter than sucrose).
- They are solids at room temperature.
- They are extremely soluble in water: – Despite their high molecular weights, the presence of large numbers of OH groups make the monosaccharides much more water-soluble than most molecules of similar MW.
- Glucose can dissolve in minute amounts of water to make a syrup (1 g / 1 ml H<sub>2</sub>O).

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## **Classification of Carbohydrates (Types of Carbohydrates)**

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The simple carbohydrates include single sugars (monosaccharides) and polymers, oligosaccharides, and polysaccharides.

### Monosaccharides

- Simplest group of carbohydrates and often called simple sugars since they cannot be further hydrolyzed.
- Colorless, crystalline solid which are soluble in water and insoluble in a non-polar solvent.
- These are compound which possesses a free aldehyde or ketone group.
- The general formula is  $C_n(H_2O)_n$  or  $C_nH_{2n}O_n$ .
- They are classified according to the number of carbon atoms they contain and also on the basis of the functional group present.
- The monosaccharides thus with 3,4,5,6,7... carbons are called trioses, tetroses, pentoses, hexoses, heptoses, etc., and also as aldoses or ketoses depending upon whether they contain aldehyde or ketone group.
- Examples: **Glucose, Fructose, Erythrulose, Ribulose.**

### Oligosaccharides

- Oligosaccharides are compound sugars that yield 2 to 10 molecules of the same or different monosaccharides on hydrolysis.
- The monosaccharide units are joined by glycosidic linkage.
- Based on the number of monosaccharide units, it is further classified as disaccharide, trisaccharide, tetrasaccharide etc.

- Oligosaccharides yielding 2 molecules of monosaccharides on hydrolysis is known as a disaccharide, and the ones yielding 3 or 4 monosaccharides are known as trisaccharides and tetrasaccharides respectively and so on.
- The general formula of disaccharides is  $C_n(H_2O)_{n-1}$  and that of trisaccharides is  $C_n(H_2O)_{n-2}$  and so on.
- Examples: **Disaccharides include sucrose, lactose, maltose, etc.**
- Trisaccharides are Raffinose, Rabinose.

### **Polysaccharides**

- They are also called as "glycans".
- Polysaccharides contain more than 10 monosaccharide units and can be hundreds of sugar units in length.
- They yield more than 10 molecules of monosaccharides on hydrolysis.
- Polysaccharides differ from each other in the identity of their recurring monosaccharide units, in the length of their chains, in the types of bond linking units and in the degree of branching.
- They are primarily concerned with two important functions ie. Structural functions and the storage of energy.
- They re further classified depending on the type of molecules produced as a result of hydrolysis.
- They may be **homopolysaccharidese**, containing monosaccharides of the same type or **heteropolysaccharides** i.e., monosaccharides of different types.
- Examples of Homopolysaccharides are **starch, glycogen, cellulose, pectin.**
- Heteropolysaccharides are Hyaluronic acid, Chondroitin.

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### **Functions**

Carbohydrates are widely distributed molecules in plant and animal tissues. In plants and arthropods, carbohydrates form the skeletal structures, they also serve as food reserves in plants and animals. They are important energy source required for various metabolic activities, the energy is derived by oxidation.

#### **Some of their major functions include:**

- Living organisms use carbohydrates as accessible energy to fuel cellular reactions. They are the most abundant dietary source of energy (4kcal/gram) for all living beings.
- Carbohydrates along with being the chief energy source, in many animals, are instant sources of energy. Glucose is broken down by [glycolysis](#)/ [Kreb's cycle](#) to yield ATP.
- Serve as energy stores, fuels, and metabolic intermediates. It is stored as glycogen in animals and starch in plants.

- Stored carbohydrates act as an energy source instead of proteins.
- They form structural and protective components, like in the [cell wall](#) of plants and microorganisms. Structural elements in the cell walls of bacteria (peptidoglycan or murein), plants (cellulose) and animals (chitin).
- Carbohydrates are intermediates in the biosynthesis of fats and proteins.
- Carbohydrates aid in the regulation of nerve tissue and is the energy source for the brain.
- Carbohydrates get associated with lipids and proteins to form surface antigens, receptor molecules, vitamins, and antibiotics.
- Formation of the structural framework of RNA and DNA (ribonucleic acid and deoxyribonucleic acid).
- They are linked to many proteins and lipids. Such linked carbohydrates are important in cell-cell communication and in interactions between cells and other elements in the cellular environment.
- In animals, they are an important constituent of connective tissues.
- Carbohydrates that are rich in fiber content help to prevent constipation.
- Also, they help in the modulation of the immune system.

## ISOMERISM IN CARBOHYDRATES

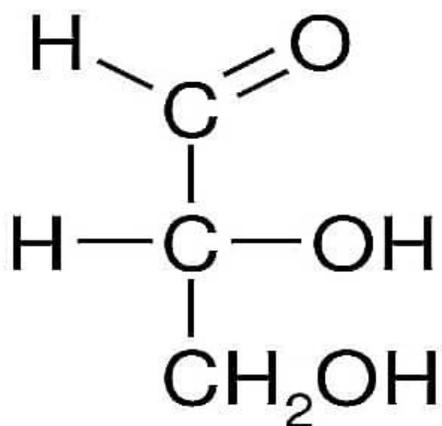
⇒ Isomers are the compounds having same molecular formula but different structural formula and this phenomenon are known as isomerism.

⇒ Isomers are of two types –

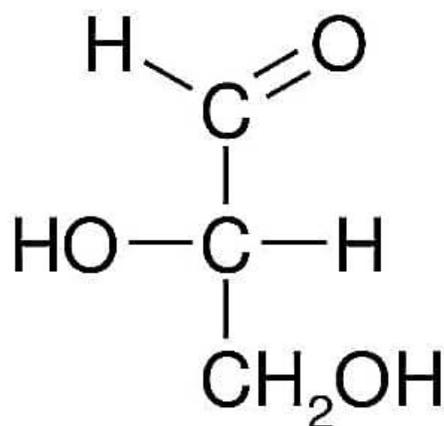
- **Structural isomers** – The isomers having same molecular formula but different structure are called as structural isomers.
- **Stereoisomers** – The compounds having same molecular formula and structure but differs only in the spatial configuration.

⇒ **Enantiomers** – They are non-superimposed mirror images of each other. D- and L- isomers are mirror images of each other. When the hydroxyl group is present on the right side the sugar is D- isomer and if it

is on the left side it is L- isomer. For e.g. D-Glyceraldehyde and L-Glyceraldehyde.

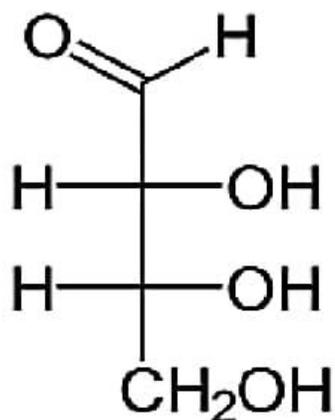


*D- GLYCERALDEHYDE*

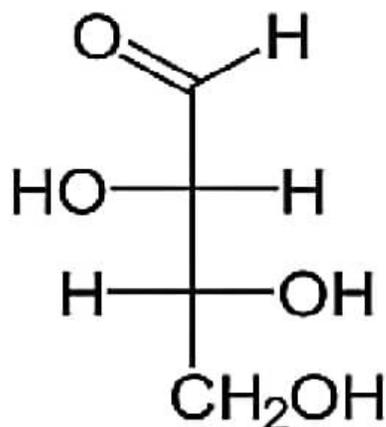


*L- GLYCERALDEHYDE*

⇒ **Diastereomers** – The stereoisomers having the different configuration at two or more stereocenters are not the mirror images of each other they are called as diastereomers.



*D- ERYTHROSE*



*D- THREOSE*

⇒ **Optical activity** – The substances which rotate the plane polarised light either towards right or towards left are said to be optically active substances and the property is known as optical activity. Those compounds which rotate light towards the right are called as ***Dextro-rotatory*** and the compounds which rotate plane polarised light towards left are known as ***Laevo-rotatory***.

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## **Reducing and non-reducing sugars**

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### **What are Reducing sugars?**

- Reducing sugar is a sugar or a carbohydrate molecule with a free aldehyde group or a free ketone group which causes the molecule to act as a reducing agent.
- All monosaccharides, along with some disaccharides and polysaccharides, are reducing sugars.
- In the case of other polysaccharides and disaccharides, the aldehyde and ketone groups remain bound in the cyclic form.
- Most reducing sugars are sweet in taste. These sugars can be detected by tests like Benedict's test and Fehling's test as they give a positive result to these tests.
- Examples of reducing sugars include monosaccharides like galactose, glucose, glyceraldehyde, fructose, ribose, and xylose, disaccharides like cellobiose, lactose, and maltose, and polymers like glycogen.

### **What are Non-reducing sugars?**

- A non-reducing sugar is a sugar or carbohydrate molecule that doesn't have a free aldehyde or ketone group and thus cannot act as a reducing agent.
- Non-reducing sugars have aldehyde and ketone groups, but they are involved in the cyclic form of the sugar molecule.
- Some disaccharides and all polysaccharides are non-reducing sugars.
- Non-reducing sugars have a less sweet taste than the reducing sugars. These sugars can also be detected by tests like Benedict's test and Fehling's test as they give a negative result to these tests.
- Examples of non-reducing sugars include disaccharides like sucrose, maltose, and lactose and polysaccharides like starch and cellulose.

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### **Formation of a glycosidic bond by condensation**

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- The process of formation of glycosidic bonds in carbohydrates is a condensation reaction which means that a molecule of [water](#) is formed during the process.
- The condensation reaction is formed between the OH group and the anomeric carbon of a sugar.
- These glycosidic bonds are formed in a dehydration synthesis reaction.
- When the alcohol attacks the anomeric carbon, the OH group of the carbon is replaced by the oxygen atom of the alcohol molecule. The OH group of the carbon and the remaining H atom of the alcohol are released in the form of a water molecule.
- The glycosylation reaction involves nucleophilic displacement at the anomeric center. As the reaction takes place at the secondary carbon atom by the attack of weak nucleophiles (sugar acceptors), it often follows a unimolecular SN<sup>1</sup> mechanism.
- The result of a glycosidic bond is a sugar molecule bound to another molecule by an ether group.
- The ether bond formed has an oxygen atom bonded to two carbon atoms which result in a relatively stable structure than with the alcohol group. As a result, a glycosidic bond results in a more stable structure of the sugar.

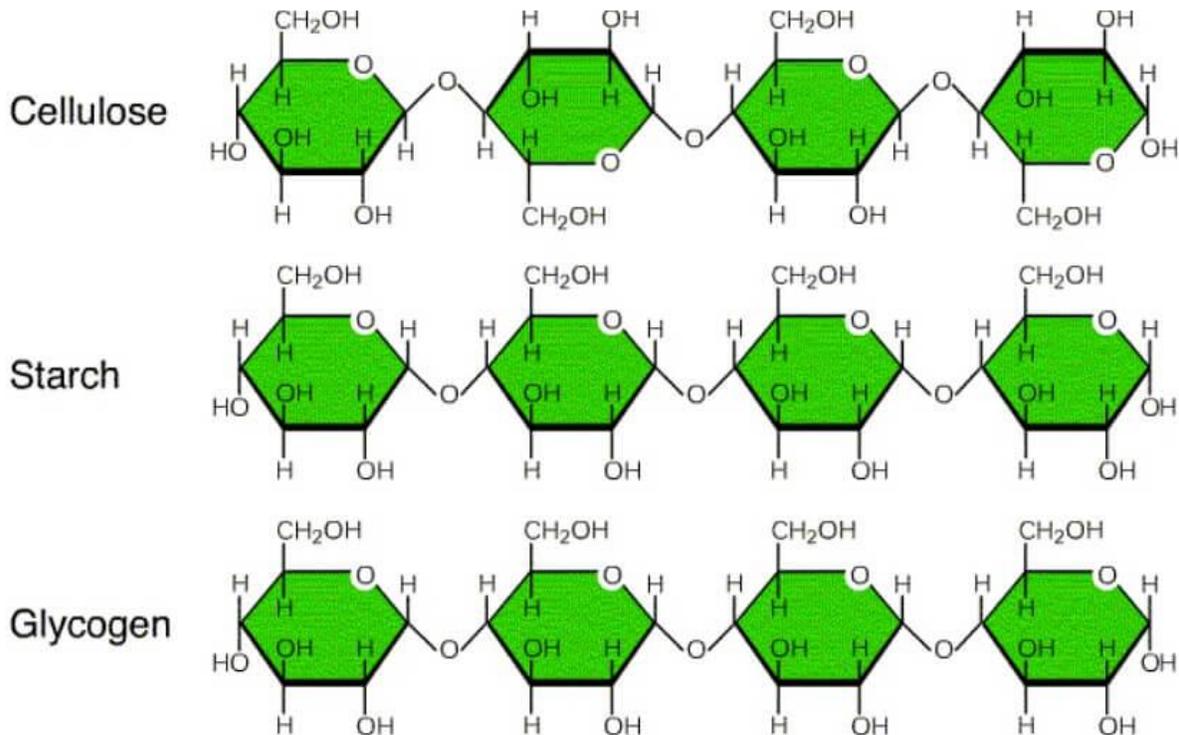
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### **Breakage of a glycosidic bond by hydrolysis**

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- The breakage of a glycosidic bond occurs by the process of hydrolysis by the addition of a water molecule.
- Hydrolysis of glycosidic bond occurs both in the presence of acid or an alkali.
- The OH group from the water molecule attacks the carbon atom involved in the glycosidic linkage.
- In acid-catalyzed hydrolysis, the hydrogen atom binds to the oxygen atom of the ether bond separating the monomeric units.
- In the case of polysaccharides, hydrolysis results in smaller polysaccharides or disaccharides, or monosaccharides.
- In the living system, hydrolysis of polysaccharides occurs in the presence of a group of enzymes termed hydrolases that catalyze the hydrolysis process.

# Polysaccharides



## Examples of Polysaccharides

### 1. Starch

Starch is a polysaccharide comprising glucose monomers joined together by glycosidic linkages. Starch is an organic compound found in all living plants which is manufactured from the excess glucose produced during photosynthesis. Starch is the form of reserve food in plants stored in chloroplasts in the form of granules and storage organs like roots, tuber, stem, and seeds.

#### Structure

- Starch is a homoglycan composed of a single type of sugar unit, regardless of the source of the starch.
- A single starch molecule has 300 to 1000 glucose units bound together.
- Most starches are composed of two kinds of polysaccharides, a linear  $\alpha$ -(1 $\rightarrow$ 4) linked glucan, called amylose, and an  $\alpha$ -(1 $\rightarrow$ 4) linked glucan with 4.2 to 5.9%  $\alpha$ -(1 $\rightarrow$ 6) branch linkages, called amylopectin.

- The ratio of amylose to amylopectin also varies, depending on the source of the starch; it ranges from 17 to 70% amylose and a corresponding 83 to 30% amylopectin.
- $\alpha$ -amylose or simply amylose has a molecular weight range of 10,000 to 50,000, which may be formed in plant cells by the elimination of a molecule of water from a glycosidic OH group of one  $\alpha$ -D-glucose molecule and alcoholic OH group on carbon 4 of the adjacent  $\alpha$ -D-glucose molecule.
- The linkage in amylose is, thus, an  $\alpha$ -1, 4-glucoside.
- $\beta$ -amylose or amylopectin has a high molecular weight range of 50,000 to 1,000,000, thus indicating the presence of 300–5,500 glucose units per molecule.
- Additional  $\alpha$ -1,6-glucoside linkages are found in amylopectin in addition to the  $\alpha$ -1,4-glucoside linkages.
- In plants, starch molecules are arranged in the form of semi-crystalline granules.

### **Functions**

- Starch is the most common and essential storage form of carbohydrates in plants.
- It is a major source of energy in a carbohydrate diet where the hydrolysis of starch yields glucose which is further metabolized to produce energy.

## **2. Glycogen**

Glycogen is a branched polysaccharide that is a major form of glucose in animals and humans. It is often termed as 'animal starch' and is stored in the liver and muscles of animals.

### **Structure**

- Glycogen is a branched-chain polysaccharide and resembles amylopectin in its structure.
- Glycogen molecule is composed of glucose subunits that are linked together by  $\alpha$ -1,4 linkages that branch off via  $\alpha$ -1,6 linkages every ten glucose residues.
- These linkages result in a helical polymer structure that exists in the form of granules in the cytoplasm.
- Glycogen is similar to starch but has more branches and is more compact than starch.
- Glycogen is synthesized in the body when there is an excess of glucose produced in the body.

### **Functions**

- The primary function of glycogen is the storage of excess glucose in the body when the blood glucose level increases.
- Glycogen then breaks down into glucose molecules to provide energy to the body when the blood glucose level decreases.
- By allowing the formation and hydrolysis, glycogen helps to maintain the blood glucose level.
- About 6-10% of the weight of the liver is made up of glycogen which is converted into glucose molecules during fasting.
- Reserved glycogen in the muscle cells serves as a fuel or the supply of ATP during muscle contraction.

### **3. Cellulose**

Cellulose is the most abundant extracellular structural polysaccharide in plants and the most abundant of all biomolecules in the biosphere. Cellulose is found in all land plants but is absent in meat, egg, fish, and milk. It, however, cannot be metabolized by the human system. Cellulose occurs in the cell walls of plants where it contributes in a major way to the structure of the organism.

#### **Structure**

- The molecular weight of cellulose ranges between 200,000 and 2,000,000, thus corresponding to 1,250–12,500 glucose residues per molecule.
- It is formed by the glycosidic linkage between the OH group on C1 of one  $\beta$ -D-glucose molecule and the alcoholic OH group on C4 of the adjacent  $\beta$ -D-glucose molecule.
- It resembles in structure with amylose except that the glucose units are linked together by  $\beta$ -1, 4-glucoside linkages.

#### **Functions**

- Cellulose is the major structural polysaccharide in plants that forms the various structure of plant cells, including the cell wall.
- Cellulose has high rigidity and strength that enables the cell to have a solid structure and shape.
- Cellulose can be degraded into smaller monosaccharides like glucose which can then be broken down metabolically to produce energy.
- It is also important for the formation of paper and wood.

