Structure and classification of carbohydrates

Introduction

Carbohydrate means the hydrates of carbon. Simple carbohydrates which are soluble in water and sweet in taste are called "Sugars." They are also called as saccharides and are the most abundant biomolecules on Earth. Carbohydrates are synthesized by plants in the process of photosynthesis from carbon dioxide and water. Non-photosynthetic organisms, like animals, derive their energy from the oxidation of carbohydrates. Besides being the central compounds in energy metabolism of all organisms, they also serve as structural and protective elements in the cell walls of bacteria and plants and in the connective tissues of animals. Other carbohydrates lubricate skeletal joints and participate in recognition and adhesion between cells. More complex carbohydrate polymers covalently attached to proteins or lipids to form glycol-conjugates, participate in signaling.

Definition and characteristics

Carbohydrates are polyhydroxylated compounds having at least 3 carbon atoms and a potentially active carbonyl group which may be an aldose or a ketose group. Carbohydrates are made up of carbon, hydrogen and oxygen; most of them have the empirical formula $(CH_2O)_n$. Some carbohydrates also contain nitrogen, phosphorus or sulphur in addition.

Examples- glyceraldehydes, erythrose, ribose, glucose, etc.

Classification of carbohydrates

On the basis of number of saccharides (sugars), carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides.

Monosaccharides

- consist of a single polyhydroxy aldehyde (aldoses) or ketone unit (ketoses).

- These carbohydrates cannot be hydrolyzed into simpler compounds.

- They are divided into different categories on the basis of functional group and number of carbon atoms.

Aldoses: When the functional group is aldehyde (- CHO), they are known as aldoses. E.g. glucose, dihydroxyacetone.

Ketoses: When the functional group is keto (- C=O), they are known as ketoses. E.g. fructose.

Structures of monosacchharides : Pyranose and Furanose structures

- The aldehyde and ketone moieties of the carbohydrates with five and six carbons in aqueous solutions spontaneously react with alcohol groups present in neighboring carbons to produce intramolecular **hemiacetals or hemiketals**, respectively. This results in the formation of five- or six-membered rings. Because the five-member ring structure resembles the organic molecule **furan**, derivatives with this structure are termed **furanoses**. Those with six-membered rings resemble the organic molecule **pyran** and are termed **pyranoses.**

- Such structures can be depicted by either **Fischer** or **Haworth** style diagrams. The numbering of the carbons in carbohydrates proceeds from the carbonyl carbon, for aldoses, or the carbon nearest the carbonyl, for ketoses.

- The rings can open and re-close, allowing rotation to occur about the carbon bearing the reactive carbonyl yielding two distinct configurations -α and β of the hemiacetals and hemiketals. The carbon about in which this rotation occurs is the **anomeric carbon** and the two forms are termed **anomers**. Carbohydrates can change spontaneously between the α and β configurations: this process is known as **mutarotation**. When drawn in the Fischer projection, α configuration places the hydroxyl attached to the anomeric carbon to the right, towards the ring. When drawn in the Haworth projection, α configuration places the hydroxyl downward.

The spatial relationships of the atoms of the furanose and pyranose ring structures are more correctly described by the two conformations- the **chair form** and the **boat form**. The chair form is the more stable of the two. Constituents of the ring that project above or below the plane of the ring are axial and those that project parallel to the plane are equatorial. In the chair conformation, the orientation of the hydroxyl group about the anomeric carbon of α-D-glucose is axial and equatorial in β-D-glucose.

Monosachharides have asymmetric centres

All the monosachharides except dihydroxyacetone contain one or more asymmetric (chiral) carbon atoms and thus occur in optically active isomeric forms. E.g. - Glyceraldehyde contains one chiral centre and therefore has two different **optical isomers** or **enantiomers- D and L forms.** In general, a molecule with n chiral centres can have 2^n stereoisomers. Most of the hexoses of living organisms are D isomers.

Two sugars that differ only in the configuration around one carbon atom are called **epimers**.E.g. D glucose and D mannose which differ in stereochemistry at C 2; D glucose and D galactose which differ at C 4.

Properties & Derivatives of monosaccharides

- Tautomerization/Enolization: Sugars possessing anomeric carbon atom undergo tautomerization in alkaline solution. In this process hydrogen atom is shifted from one carbon atom to another to produce enediols.

- Reducing properties: Due to free aldehyde or keto group of anomeric carbon, sugars can reduce cupric ions of copper sulphate to cuprous ions. Thus, glucose and other sugars capable of reducing ferric or cupric ions are called **reducing sugars**. This property is the basis of qualitative test for sugars in Fehling’s / Benedict’s reaction.

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

- Osazone formation: Phenylhydrazine in acetic acid, when boiled with reducing sugars forms osazones.

Derivatives of monosaccharides

(1) **Amino sugars** – Formed by the replacement of hydroxyl group by amino group e.g. Glucosamine, galactosamine. Sometimes amino groups are acetylated. E.g. N-acetyl D-glucosamine.

(2) **Sugar alcohols –** Aldehyde group (–CHO) of the sugar is changed to primary alcohol (–CH_2OH). Sorbitol and Mannitol are respectively formed from glucose and mannose.

(3) **Sugar acids** – They are formed by the oxidation of terminal –CHO or –CH_2OH group of sugar to produce carboxyl group –COOH e.g. Gluconic acid, Galacturonic acid.

(4) **Glycosides** – They are compounds formed by condensation reaction between a sugar (e.g. glucose) and hydroxyl group of another substance which may be a sugar, a sterol, methanol etc. Streptomycin is a glycoside.

Oligosaccharides

Among the oligosaccharides, disaccharides are the most common.

Disaccharides consist of two monosaccharides joined covalently by an O-glycosidic bond. The bond is formed between the hydroxyl group of one sugar with anomeric carbon of the other. Glycosidic bonds can be readily hydrolyzed by acid, but resistant towards cleavage by a base. On acid hydrolysis they yield free monosaccharide components.

- A disaccharide with a free anomeric carbon is called reducing sugar. E.g. maltose.
- All disaccharides are water soluble and sweet in taste, so they are known as **sugars.**

  Maltose is composed of two α-D-glucose units held together by α (1→4) glycosidic bond. It is commonly called as **malt sugar** and is intermediate compound in starch digestion. Cellobiose is another disaccharide similar to maltose, except that it has β (1→4) linkage and is formed during hydrolysis of cellulose.

- **Lactose** is composed of β-D-galactose and β-D-glucose held together by β (1→4) glycosidic bond. It is commonly called as milk sugar and hydrolysed by the intestinal enzyme lactase to glucose and galactose.
- **Sucrose** is made up of α-D-glucose and β-D-fructose held together by α1→ β2 glycosidic bond between C1 of α-D-glucose and C2 of β-D-fructose. The reducing groups of glucose and fructose are involved in glycosidic bond; hence sucrose is a non-reducing sugar. It is commonly called as **cane sugar or table sugar or commercial sugar.** It is the major carbohydrate produced in photosynthesis and is transported to the storage organs of plants, such as, roots, tubers, seeds etc. The intestinal enzyme sucrase/invertase hydrolyzes it into glucose and fructose which are then absorbed.

Sucrose is dextrorotatory, but on hydrolysis it becomes levorotatory, therefore it is also known as **invert sugar.**

Trisaccharides: Trisaccharides have three monosaccharides joined together by glycosidic bonds. E.g.Raffinose (Galactose + Glucose + Fructose)

Polysaccharides

Suffix '–an' is added in their names and they are known as **glycans.** They are **c**omposed of large number of monosaccharide units linked by glycosidic bonds. All polysaccharides are non-reducing and insoluble in water and **do not taste sweet.** They have two important functions, as structural elements and also as energy storing molecules.

On structural basis polysaccharides are of two types-

(1) Homopolysaccharides, which yield a single type of monosaccharide on hydrolysis. They are named on the basis of nature of monosaccharide unit. E.g. glucans are the polymers of glucose; fructosans are the polymers of fructose.

(2) Heteropolysaccharides, which yield a mixture of monosaccharides on hydrolysis.

Homopolysaccharides

Biologically important homopolysaccharides are as follows:

(a) Starch – It is the main reserved food in plants. Starch is a polymer of **α-D-glucose units** held by α glycosidic bond. Starch consists of two types of chains-

- **Amylose** – 15-20% glucose units are arranged in an **unbranched chain** having **α 1→4 linkage.** It is water soluble. It gives blue colour with iodine.
- **Amylopectin** – Approximately 80-85% glucose units are arranged in a **branched chain molecule** where, at the branching point glucose units are linked by **α 1→6 linkage**, and by α 1→4 linkage in a linear chain. It is water insoluble. It gives red colour with iodine.

Starches are hydrolysed by amylases, the enzyme present in human saliva, to liberate dextrins, and finally maltose and glucose units.

(b) Dextrins – They are intermediate substance in the digestion of glycogen and starch. By hydrolysis of dextrin, glucose and maltose are formed. It also occurs as stored food in yeast and bacteria.

(c) Glycogen – storage form of carbohydrate in animals, hence also called as **animal starch**. Storage site of glycogen is **liver** and **muscles.** Its structure is similar to that of amylopectin with more number of branches. Thus, it is highly branched polymer of α-D-glucose with α 1→4 linkage in the linear chain and α 1→6 linkage at branching point. It gives **red colour** with **iodine.**

(d) Inulin – Linear polymer of fructose units linked with β 1→2 linkage. Inulin is found in roots of Dahalia and

Artichoke**.** It is water soluble and smallest storage polysaccharide.

(e) Cellulose - Linear polymer of **α-D-glucose** units (6000 to 10,000) joined by β- 1→4
linkage. Partial digestion yields cellobiose units (disaccharide). Cellulose occurs exclusively in plants and is the main component of plant cell wall. It is totally absent in animal body. In wood, cellulose is 50% and in cotton**,** it is 90%. It is the most abundant organic molecule on earth. Cellulose, though not digested, has great importance in human nutrition, where it is a major constituent of fiber. Grass eating animals, cattle, digest cellulose by the action of the enzyme cellulose, secreted by the bacteria present in the rumen.

(f) Chitin – Linear polymer of N-acetyl-D-glucosamine with β 1→4 glycosidic linkage.
It is an important component of exoskeleton of Arthropods and cell walls of fungi.

Heteropolysaccharides

(a) Mucopolysaccharides- They are heteroglycans, made up of repeating units of sugar derivatives namely, amino sugars and uronic acids. These are more commonly called as glycosaminoglycans. Acetyl, sulfate and carboxyl groups are generally present in their structure, which contributes to their acidity making them acid mucopolysaccharides. Some of the mucopolysaccharides are found in combination with proteins to form mucoproteins or mucoids or proteoglycans. They are essential components of tissue structures found in extracellular spaces.

The important mucopolysaccharides are:

(1) Hyaluronic acid – Found in vitreous humor of eyes, umbillical cord, synovial fluid of joints and connective tissue in the form of lubricating agent and shock absorbant. It is made up of D-glucouronic acid and N-acetyl–D-glucosamine arranged in alternate orders. These two molecules form disaccharides units held together by β 1→3 glycosidic bond. The enzyme hyaluronidase hydrolyzes hyaluronic acid, present in high concentration in testes, seminal fluid and in certain snake and insect venoms.

(2) Chondroitin sulphate – A major constituent of cartilages, tendons and bones. Consist of repeating disaccharide units of D-glucuronic acid and N-acetyl D-galactosamine 4 sulphate.

(3) Heparin – It is anticoagulant of blood, made up of repeating disaccharide unit of D- glucosamine and uronic acid linked by 1→4 inter glycosidic bond. The uronic acid residue could be either D-glucuronic acid or L-iduronic acid. Few hydroxyl groups on each of these monosaccharide residues may be sulfated giving rise to a polymer which is highly negatively charged.

(4) Dermatan sulphate- Mostly occurs in the skin. It is structurally related to chondroitin sulphate with the difference in an inversion in configuration around C5 of D-glucuronic acid to form L-iduronic acid.

(5) Keratan sulphate- A heterogenous glycosaminoglycan with a variable sulfate content, and small amount of mannose, fructose, sialic acid etc.

(6) Pectins – Methylated galacturonic acid + galactose + arabinose. It is found in cell wall where it binds cellulose fibrils in bundles. Salts of pectin i.e. Ca and Mg-pectates form **middle lamella** in plants.It is also called Plant cement**.**

Peptidoglycan – Present in cell wall of bacteria. Composed of N-acetyl Glucosamine + N-acetyl muramic acid + peptide chain of 4-5 amino acids.

A**gar-Agar** – Obtained from some red algae – Gracilaria, Gelidium, Chondrus. It is composed of **D-galactose** and **L-galactose** unit and after every 10^{th} unit a sulphate group is present. Used for preparing **culture medium.**

Glycoconjugates

In addition to their important roles as stored fuels (starch, glycogen) and as structural materials (cellulose, chitin), polysaccharides and oligosaccharides are information carriers, where they are involved in cell-cell recognition and adhesion, cell migration, blood clotting, wound healing etc. Informational carbohydrates are covalently joined to a protein or lipid to form glycol-cojugates. E.g. proteoglycans, glycoproteins and glycolipids.

- In proteoglycans core protein is attached covalently to one or more large glycans, such as, heparan sulphate, chondroitin sulphate, keratan sulphate. They are bound to the plasma membrane by a peptide or lipid and provide points of adhesion, recognition etc.
- Glycoproteins contain covalently linked oligosaccharides that are smaller but structurally more complex.
- Glycolipids and lipopolysaccharides are components of the plasma membrane with covalently attached oligosaccharide chains exposed on the cell's outer surface.

Conclusion

Carbohydrates are commonly called as sugars, particularly those which are soluble in water and sweet in taste. Chemically nature of carbohydrates is polyhydroxy aldehydes or ketones, or compounds which produce them on hydrolysis. They are mainly involved in energy generation, in cell structure and protection. Carbohydrates are broadly classified into three groups-monosaccharides, oligosaccharides and polysaccharides. The monosaccharides are further divided into aldoses or ketoses. D-glucose is the most predominant naturally occurring monosaccharide. Among the oligosaccharides, disaccharides are the most common, such as, lactose maltose, sucrose etc. Polysaccharides are the polymers of monosaccharides held together by glycosidic bonds. Homoglycans are composed of a single monosaccharide e.g. starch, glycogen etc. which are the carbohydrate reserves of plants and animals respectively. Heteroglycans are mixture of monosaccharides e.g. mucopolysaccharides, such as, hyaluronic acid, heparin, chondroitin sulphate etc. Glycoproteins, glycolipids and proteoglycans are important informational carbohydrates involved in cell-cell adhesion, interaction, recognition, blood clotting etc.