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CHEMISTRY



TABLE OF CONTENTS

- 1. Learning outcomes
- 2. Introduction
 - 2.1 Definition of carbohydrates
- 3. Classification
 - 3.1 Based on number of simple sugars (mono, di and polysaccharides)
 - 3.2 Based on carbonyl function (aldose, ketose)
 - 3.3 Based on number of carbon atom
- Graduate Courses 4. Structure and stereochemistry of monosaccharide 4.1 Enantiomers, diastereomers and epimers (isomers)
- 5. Cyclic structure of sugars 5.1 Anomers, racemic mixture, mutorotation
- 6. Chemical properties of monosaccharaides
 - 6.1 Action of acids and alkalis
 - 6.2 Oxidation and reduction of sugars
 - **6.3 Osazone formation**
 - 6.4 Glycoside formation
- 7. Derivatives of monosaccharaides
 - 7.1 Amino sugar, deoxysugars, sugar acids, sugar alcohols, phosphoric acid
 - esters of sugars
- 8. Disaccharides
 - 8.1 Reducing
 - 8.2 Non- reducing
 - 9. Polysaccharides (glycan)
 - 9.1 Homo polysaccharides
 - 9.2 Hetero polysaccharides
 - **10.** Glycoproteins
 - 11. Functions of carbohydrates
 - **12. Summary**

CHEMISTRY



1. Learning Outcomes

After studying this module, you shall be able to

- Know about general definition and basis of classification of carbohydrates
- Know about straight chain and cyclic structures of carbohydrates
- Chemical properties of monosaccharaides and their derivatives
- Types of disaccharides and their properties
- Polysaccharides and its types
- Function of carbohydrates

2. Introduction

The carbohydrates are an important class of naturally occurring organic compounds. They occur naturally in plants (where they are produced photosynthetically), when the word "carbohydrate" was coined, it originally referred to compounds of general formula $C_n(H_2O)_n$. However, only the simple sugars or monosaccharaides fit this formula exactly. The other types of carbohydrates, oligosaccharides, and polysaccharides, are based on monosaccharaides units and have slightly different general formula. Carbohydrates are also called "saccharides" which means sugar in Greek.

Many commonly encountered carbohydrates are polysaccharides, including glycogen, which is found in animals, and starch and cellulose, which occur in plants.

2.1 What is carbohydrate?

The carbohydrates are poly functional compounds. They contain following functional groups:-

- (1). Alcoholic hydroxy group, -OH
- (2). Aldehyde group, -CHO
- (3). Ketone, >C=O

A precise definition of the term 'carbohydrate' can be given as:-

Polyhydroxyaldehydes or polyhydroxy ketones, and large molecules that produce these compounds on hydrolysis.

The above definition of carbohydrate is not entirely satisfactory. It envisages the presence of free carbonyl group in simple carbohydrate molecule which is not true.

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We understand that carbonyl compound (aldehyde or ketone) reacts with an alcohol to form hemiacetal. In carbohydrates, we have an aldehyde group which combines with an alcoholic OH of the same molecule to form an internal hemiacetal. We will also see that it is by elimination of H_2O between the hemiacetal OH group of two sugars molecules that larger carbohydrate molecule are formed. In light of above, the definition of carbohydrate may be improved as: A polyhydoxy compound that has an aldehyde or a ketone function present, either free or as hemiacetal or acetal.

3.Classification of carbohydrates

3.1 Based on number of simple sugars (mono, di and polysaccharides)

The carbohydrates are divided into three major classes depending on the number of simple sugar unit present in their molecule. In other words, the basis of classification of carbohydrate will be the number of simple sugar molecules on hydrolysis. The molecules so obtained may be of same or different sugars

3.1.1 Monosaccharaides (simple sugars)

These are single unit carbohydrate that cannot be broken into simpler glucose and fructose.

Examples:



3.1.2 Oligosaccharides

They are made of 2 to 10 units of monosaccharaides or simple sugars. The oligosaccharides containing two monosaccharaides units are called disaccharide and those containing three units are trisaccharides. Thus sucrose, $C_{12}H_{22}O_{11}$ is disaccharides because on hydrolysis it gives one molecule of glucose and one molecule of fructose.

 $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ Glucose Fructose

Oligosaccharides with more than three subunits are normally found in glycoproteins, such as blood group antigens.

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3.1.3 Polysaccharides

They contain more than ten monosaccharide units in molecule. Thus one molecule of starch or cellulose on hydrolysis gives very large number of glucose units.

$(C_6H_{10}O_5)_n + H_2O \xrightarrow{H^+} n C_6H_{12}O_6$ Glucose

3.2 Further classification of monosaccharides

3.2.1 Based on carbonyl function

Those containing the aldehyde function, -CHO are called aldoses and other containing keto group -Co are, called ketoses.



Fig1. Structure of glucose and fructose

3.3 Based on number of carbon atom

The monosaccharaides containing 3, 4, 5, 6 etc carbon atoms are designated as trioses, tetroses, pentoses, hexoses and so on as shown in table1.

For example, glucose a six carbon sugar with aldehyde function is aldohexose, fructose, a six carbon having ketone function is a ketohexose.

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No of carbon	Empirical Formula	Types	Aldoses	Ketoses
3	C ₃ H ₆ O ₃	Trioses	Glyceraldehydes	Dihydroxyacetone
4	C4H8O4	Tetroses	Erythrose	Erythrulose
5	C5H10O5	Pentoses	Ribose, Xylose	Ribulose, Xylulose
6	C ₆ H ₁₂ O ₆	Hexoses	Glucose, Galactose and Mannose	Fructose
7	C7H14O7	Heptoses	Glucoheptose	Sedoheptalose

Table1. Classification of monosaccharaides

4. Structure and stereochemistry of monosaccharide

4.1 Enantiomers, diastereomers and epimers (isomers)

The building blocks of all carbohydrates are simple sugars called monosaccharaides, which can be an aldose or ketose. The simplest aldose, glyceraldehyde, has only one asymmetric carbon atom or chiral centre (carbon-2) (Figure 2)and only two possible of OH and H of the CH_2OH unit are possible. If the OH group is shown as projecting to left on penultimate carbon atom in the straight chain representation of the molecule, then by convention the molecule is called L isomer, while if OH group is represented as projecting to right it is known as D isomer.



Glyceraldehyde and D-Glyceraldehyde

These two stereoisomers to same carbohydrates are enantiomers or mirror images of one another.





4.1.2 Diastereomers

Glyceraldehyde has only one asymmetric centre (*) and the designation of D or L is determined by the orientation of H and OH groups about the carbon atoms. For carbohydrates with more than one asymmetric carbon atom, the prefix D or L, refers only to configuration about the highest numbered asymmetric carbon atom.

For higher carbohydrate structures, each time number of carbon is increased by one (with the addition of CHOH group), a new carbohydrate is produced, which has a chemically distinct form and completely different name because this group may be added as either OH-C-H or H-C-OH, an extra asymmetric (chiral) centre is created within the molecule, so aldotetroses have two chiral carbon C-2 and C-3, and there are 2^2 or four possible stereoisomer.

Two of isomers have the D-configuration, and the two have L-configuration the two D isomers have same configuration at C-3 but they differ in configuration (arrangement of the -OH group) at other chiral carbon, C-2. These two isomers are called D-erythrose and D-threose. They are not superimposable on each other, but neither is they mirror images of each other. Such non superimposable, non-mirror image stereoisomers are called diastereomers.



Fig3. D-Erythrose and D-Threose

4.1.3 Epimers (isomers)

The two L isomers or L-erythrose, and L-threose is the enantiomer of D-threose. L-threose is a diastereomer of both D and L-erythrose, and L-erythrose is a diastereomer of both D and L-threose. Diasteromers that differ from each other in configuration at only one chiral carbon are called epimers; erythrose and D-threose are epimers. Glucose, galactose are also examples of epimers.

Aldopentoses have three chiral carbons and there are 2^3 or 8 possible stereoisomers - four D form and four L- form, similarly aldohexoses will have 16 stereoisomers. Some of the possible

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stereoisomers are much more common in nature than others. For example D sugars rather than L sugars, predominate in nature. Most sugars present in nature, especially in foods, contain either five or six carbon atoms. We shall discuss D - glucose (an aldohexose) because it is most abundant monosaccharide in nature.



Fig4. Epimers or isomers

5. Cyclic structure of sugars

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5.1 Anomers, racemic mixture, mutarotation

An aldehyde and alcohol group can react together to form a hemiacetal, and when this occurs within an aldohexose, a five- or six-membered ring structure is formed. Both pentoses and ketohexoses form similar cyclic structures and it is as such that hexoses and pentoses exist predominantly in nature, with only traces of the aldehyde or ketone forms being present at equilibrium. The cyclic hemiacetal of an aldohexose is formed by reaction of the aldehyde at carbon 1 with the hydroxyl group at carbon 4 or 5 producing an oxygen bridge. Similarly the cyclic form of the ketohexose is produced by reaction of the ketone group at carbon 2 with the hydroxyl at carbon 5. (Figure 5)



This introduces a new asymmetric centre at carbon 1 and increases the possible number of isomers by a factor of two. The configuration of this new hydroxyl group (the glycosidic hydroxyl group at carbon 1) relative to the oxygen bridge results in two additional isomers of the original carbohydrate which are designated as either the α form (OH group represented on the same side of the carbon atom as the oxygen bridge) or the β form (OH group represented on the opposite side of the carbon atom to the oxygen bridge). Such monosaccharaides, differing only in this configuration around the carbon atom to which the carbonyl group is attached (the anomeric carbon), are called **anomers.** (Figure 6)

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Figure 6: The α & β anomers are named with reference to the configuration of the glycosidic hydroxyl group associated with oxygen brige

These two possible orientations of the hydroxyl group confer differences in optical properties when the substance is present in the crystalline anhydrous form and α -D-glucose has a specific rotation of +113° whereas that of β -D-glucose is +19.7°. However, either form in aqueous solution gives rise to an equilibrium mixture which has a specific rotation of +52.5°, with approximately 36% being in the α form and 64% in the β form, with only a trace present as the free aldehyde. Because it takes several hours for this equilibrium to be established at room temperature, any standard glucose solution for use with a specific enzyme assay (e.g. glucose by the glucose oxidase which is specific for β -D-glucose) should be allowed to achieve equilibrium before use, so that the proportions of each isomer will be the same in the standard and test solutions. **Mutarotation** is defined as the change in specific optical rotation by inter conversion of α and β form of D-glucose to an equilibrium mixture. Enzymes that accelerate the attainment of this equilibrium are called mutarotases and can be incorporated in assay reagents in order to speed up the equilibrium formation.

The cyclic forms adopted by the hexoses and pentoses can be depicted as symmetrical ring structures called Haworth projection formulae, which give a better representation of the spatial arrangement of the functional groups with respect to one another. The nomenclature is based on the simplest organic compounds exhibiting a similar five- or six-membered ring.

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Figure 7: Structure, namely furan & pyran

The stable ring structures which are adopted by hexoses and pentoses are five or six-membered and contain an oxygen atom. They are named as derivatives of furan or pyran, which are the simplest organic compounds with similar ring structures, e.g. glucofuranose or glucopyranose for five or six-membered ring structures of glucose respectively: (Figure 8)



Figure 8. Five or six-membered ring structures of glucose and fructose

The ring is considered to be planar with the substituent groups projecting above or below the plane. The thickened lines represent the portion of the ring that is directed out of the paper

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towards the reader. The alpha and beta anomeric forms are shown with the hydroxyl group at carbon 1 below or above the plane of the ring respectively. (Figure 8)

Galactose, however, as well as some other aldohexoses, does -exist in appreciable amounts in the furanose form in solution and as a constituent of polysaccharides. Ketoses may also show ring configuration and the ketohexose, fructose, exists as a mixture of furanose and pyranose forms with the latter form predominating in the equilibrium mixture. However, the configuration of fructose when it occurs as a constituent of a disaccharide or a polysaccharide is usually the furanose form.

In the symmetrical ring structures depicted by the Haworth formulae, the ring is considered to be planar and the configuration of each of the substituent groups represented as being either above or below the plane. Those groups that were shown to the right of the carbon backbone in the linear representation are drawn below the plane of the ring and those that, were originally on the left are drawn above the plane. An exception is the hydrogen attached to the carbon 5, the hydroxyl group of which is involved in the formation of the oxygen bridge, which is drawn below the plane of the ring, despite the fact that in the linear representation of the D form it is shown to the left. The orientation of the hydroxyl group at carbon 1 determines the α or β designation, and is shown below the plane for the α form and above the plane for the β form. (Figure 9)

The planar Haworth projection formulae bear little resemblance to the shape of the six-membered pyranoses that actually adopt a non-planar ring conformation comparable to that of cyclohexane. The chair form is the most form of the sugar in solution cyclize into rings.



Figure 9. Chair forms of Glucose

The pyranoses adopt a non-planar ring conformation and the chair form with-the highest number if equatorial rather than axial hydroxyl groups are favored. It should be noted that a-D-glucopyranose, in contrast to β -D-glucopyranose has an axial hydroxyl group.

The designation a means that the hydroxyl group attached to C-1 is below the plane of the ring, β means that it is above the plane of the ring. The C-1 carbon is called the anomeric carbon atom and so, α and β forms are anomers.

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6. Chemical properties of monosaccharaides

Some of the important chemical properties of monosaccharaides are:

6.1 Action of acids and alkalis

6.1.1 Action of acids

On heating a sugar with mineral acids (H_2SO_4 or HCI), the sugar loses water and forms furfural derivatives. These may condense with α -naphthol, thymol or resorcinol to produce colored complexes. This is the basis of the:

- Molisch's test
- Seliwanoff's test -
- Bial's test
- Tollen's-phloroglucinol-HCl test.

6.1.2 Action of alkalis

On treatment with dilute-aqueous alkalies, both aldoses and ketoses are changed to ehediols. Enediol is the enol form of sugar because two OH groups are attached to the double bonded carbon. Enediols are good reducing agents and form basis of the Benedict's test and Fehling's test.Thus, alkali enolizes the sugar and thereby causes them to be strong reducing agents. Through the formation of a common 1, 2-enediol, glucose, fructose and mannose may isomerize into each other in a dilute alkaline solution

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6.2 Oxidation and reduction of sugars

6.2.1 Oxidation of sugars

When aldoses oxidize under proper conditions they may form:

- Aldonic acid •
- Saccharic acids
- Uronic acid •

Oxidation of an aldose with hyprobromous acid (HOBr), which acts as an oxidizing agent gives aldonic acid. Thus, glucose is oxidized to gluconic acid.

Oxidation of aldoses with nitric acid under proper conditions converts both aldehyde and terminal primary alcohol groups to carboxyl groups, forming saccharic acid.

When an aldose is oxidized in such a way that the terminal primary alcohol group is converted to carboxyl without oxidation of the aldehyde group (usually by specific enzymes), auronic acid is formed

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Figure 10. Structure of D-Gluconic acid, D-Glucosaccharic acid and D-Glucuronic acid

Oxidation of α -D-glucose hemiacetal to give a lactone. Deposition of free silver as silver mirror indicates reaction has taken place.



6.2.2 Reduction of sugars

Both aldoses and ketoses may be reduced by enzymes or non-enzymatically to the corresponding polyhydroxy alcohol called alditols. Manitol, the sugar alcohol derived from mannose, is frequently used medically as an osmotic diuretic to reduce cerebral edema.

Sorbitol, the sugar alcohol, derived from glucose, often accumulates in the lenses of diabetics and produces cataracts.

In the cyclic form, the compound produced by oxidation of aldose iso-lactone (a cyclic ester linking the carboxyl group and one of the sugar alcohols)

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6.3 Osazone formation

Osazones are yellow or orange crystalline derivatives of reducing sugars with phenylhydrazine

(Figure 11) and have a characteristic crystal structure, which can be used for identification and characterization of different sugars having closely similar properties (like maltose and lactose).



Figure 11. Osazone formation

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Osazone formed from glucose, mannose and fructose are identical because these are identical in the lower four carbon atoms. The osazone crystals of glucose and of the reducing disaccharides, lactose arid maltose differ in forms.





Needle-shaped crystals of Sunflower shaped Glucosazone and crystal of maltosazone of lactosazone Mannosazone

Powderpuff or tennis ball shaped crystals

Figure 12: Structure of different osazones

- Glucosazone are needle shaped
- Lactosazone are powder puff or tennis ball shaped
- Maltosazone are sunflower shaped.

Non-reducing sugars like the disaccharide sucrose cannot form osazone due to the absence of a free carbonyl (CHO or C=O) group in them.

6.4 Glycoside formation

Glycosides are formed when the hydroxyl group of anomeric carbon of a monosaccharide reacts with OH or NH group of second compound that may or may not be a carbohydrate. The bond so formed is known as glycosidic or glycosyl bond or hemiacetal carbon can react with an alcohol to give a full acetal or glycoside. The newly formed bond is called glycosidic bond.

The monosaccharides are joined by glycosidic bonds to form disaccharides, oligosaccharides and polysaccharides. In disaccharides, the glycosidic linkage may be either $\alpha \& \beta$ depending on the configuration of the atom attached to the anomeric carbon of the sugar.

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Two types of glycosides are there (1) O-glycosides, with each sugar bonded to an oxygen atom of another molecule. (2) N-glycosides in which sugar is bonded to nitrogen atom. Glycosides derived from furanoses are called furanosides, and those derived from pyranoses called pyranosides. Glycosides are found in many drugs e.g. in antibiotic streptomycin.

7. Derivatives of monosaccharaides

Some important sugar derivatives of monosaccharaides are:

- Phosphoric acid ester of monosaccharaides
- Amino sugar
- Deoxy sugars
- Sugar acids
- Sugar alcohols
- Neuraminic acid
- Sialic acid

Phosphoric acid ester of monosaccharaides

These are formed from the reaction of phosphoric acid with hydroxyl group of the sugar, e.g. glucose-1-phosphate or glucose-6-phosphate. (Figure 13)



Figure 13. Structure of Glucose-6-phosphate and Glucose-1-phosphate

Importance

Phosphorylation of sugar within cells is essential to prevent the diffusion of the sugar out of the cell.

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Nucleic acids (RNA and DNA) of cell nuclei also contain sugar phosphates of ribose and deoxyribose.

Amino Sugar

Amino sugars have a hydroxyl group replaced by an amino or an acetylated ammo (acetylammino) group. For example, glucosamine, N-acetyl glucosamine, galactosamine and mannosamine. (Figure 14)



Figure 14. N-Acetyl Glucosamine

Importance of amino sugar

Amino sugars are components of glycolipids (ganglioside), glycoprotein and proteoglycans (glycosaminoglycans). Several antibiotics, e.g. erythromycin, carbomycin contain amino sugar.

Deoxy sugars

Deoxy sugars possess a hydrogen atom in place of one of their hydroxy groups e.g. 2deoxyribose found in nucleic acid DNA.

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Figure 15. 2-deoxyribose

Sugar Acids

Sugar acids are produced by oxidation of the monosaccharides, for example:

• Ascorbic acid or vitamin C (not synthesized by human beings.) is required for the synthesis of collagen. It acts as water soluble antioxidant.

• Glucuronic acid (uronic acid).

Sugar Alcohols

Discussed in properties of monosaccharide-reduction. They are not metabolically very active but have some medical importance in that they are used as non-glucose forming sweeteners in food stuffs for diabetics, sorbitol and xylitol are the most commonly used.

Neuraminic Acid

Neuraminic acid is a nine carbon sugar derived from mannosamine (an epimer of glucosamine) and pyruvate.

Mannosamine + Pyruvate ----- Neuraminic acid

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Sialic acid or N-Actylneuraminic acid (NANA)

Sialic Acid

Sialic acids are acetylated derivatives of neuraminic acid in which amino (NH₂) or hydroxy (OH) group is acetylated

Importance

Sialic acids are constituents of both glycoproteins and glycolipids (ganglioside).

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8. Disaccharides

Disaccharides consist of two monosaccharide units.

• They are crystalline, water soluble and sweet to taste.

• They are sub classified on the basis of the presence or absence of free reducing (aldehyde or ketone) group

	Disaccha 	rides	
Reducing (with free aldehyde or ketone group)		Non-reducing (absence of free aldehyde or ketone group	
Example	Constituent	Example	Constituent
Maltose Lactose Isomaltose	Glucose+Glucose Galactose+Glucose Glucose+Glucose	Sucrose Trehalose	Glucose+Fructose Glucose+Glucose

1. Reducing disaccharides with free aldehyde or keto group, e.g. maltose, lactose.

2. Non-reducing disaccharides with no free aldehyde or keto group, e.g. sucrose.

8.1 Reducing sugars

8.1.1 Maltose

Maltose contains two glucose residues, joined by glycosidic linkage between C-1 (the anomeric carbon) of one glucose residue and C-4 of the other, leaving one free anomeric carbon of the second glucose residue, which can act as a reducing agent. Thus, maltose is a reducing disaccharide. (Figure 16)

The numerical description like $(1 \rightarrow 4)$ of glycosidic bond represents the number of carbon atoms that connect the two sugars as shown in. The sugar contributing anomeric carbon is written first.

Maltose is produced as an intermediate product in the digestion of starch and glycogen by the action of the enzyme α -amylase.

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Maltose

Figure 16 Structure of Maltose

8.1.2 Isomaltose

It consists of two glucose molecules linked by an $(\alpha - 1 \rightarrow 6)$ glycosidic bond.

Isomaltose is a disaccharide derived from the digestion of starch or glycogen. It is hydrolyzed to glucose in the intestinal tract by an enzyme called isomaltase.

8.1.3 Lactose (Milk sugar)

It is present in milk. Lactose contains one unit of β -galactose and one unit of β -glucose that are linked by a β (1 \rightarrow 4) glycosidic linkage. (Figure 17)

The anomeric carbon of the glucose unit is available for oxidation and thus lactose is a reducing disaccharide. Lactose is hydrolyzed to glucose and galactose by lactase eneyzme in human beings.

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8.2 Non- reducing sugars

8.2.1 Sucrose (Common Table Sugar)

Sucrose is a disaccharide of glucose and fructose. It is formed by plant but not by human beings. Sucrose is an intermediate product of photosynthesis. Sucrose is the commonly used table sugar. In contrast to maltose and lactose, sucrose contains no free anomeric carbon atom. The anomeric carbon of both glucose and fructose are involved in the glycosidic bond. Sucrose is therefore, a non-reducing sugar. Sucrose is hydrolyzed to fructose and glucose by an enzyme sucrase which is also called invertase. (Figure 18)



Figure 18 α-Glucose and -βGlucose

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9. Polysaccharides

Carbohydrates composed of ten or more monosaccharide units or their derivatives (such as amino sugars and uronic acids) are generally classified as polysaccharides. Polysaccharides are colloidal in size. In polysaccharides, monosaccharide units are joined together by glycosidic linkages. Another term for polysaccharides is a "glycans". Polysaccharides are subclassified in two groups.

1. Homopolysaccharides- (Homoglycans): When a polysaccharide is made up of several units of one and the same type of monosaccharide unit only; it is called homopolysaccharide.

2. Heteropolysaccharides (Heteroglycans): They contain two or more different types of monosaccharide units or their derivatives.

9.1 Homopolysaccharides or Homoglycans

Starch

It is the storage form of glucose in plants, e.g, in potato, in grains and seeds and in many fruits. Starch is composed of two constituents viz. *amylose* and amylopectin.

Amylose

Amylose is a linear polymer of D-glucose units joined by α -1 \rightarrow 4 glycosidic linkages. (Figure 19)

o_o_o_o_o_o_o_o_o_o

Glucose unit

α-(1→4)glycosidic linkage



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Figure 19. Structure of Amylose

Amylopectin

Amylopectin is structurally identical to those of amylose ($\alpha \rightarrow 4$ glycosidic linkages) but with side chains joining them by $\alpha \rightarrow 6$ linkages. Thus, amylopectin is a branched polymer having both $\alpha (1\rightarrow 4)$ and $\alpha (1\rightarrow 6)$ linkages. The branch points in amylopectin are created by $\alpha \rightarrow 1\rightarrow 6$ bonds and occur at an interval of 20 to 30 units of glucose. Figure 20







Figure 20. Structure of Amylopectin

Dextrin

Partial hydrolysis of starch by acids or α -amylase (enzyme) produces substances known as dextrins. These also occur in honey. All dextrins have few free aldehyde groups and can show mild reducing property. They are not fermented by yeast.

Glycogen (Animal Starch)

Glycogen is the major storage form of carbohydrate (glucose) in animals, found mostly in liver and muscle. It is often called animal starch. The structure of glycogen is similar to that of amylopectin, except that it is more highly branched, having α (1 \rightarrow 6) linkages at intervals of about 8 to 10 glucose units. (Figure 21)

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Figure 21. Structure of Glycogen (Animal starch)

The main difference between glycogen and amylopectin is that glycogen is more highly branched. Branches point occur every 10 residues in glycogen and about every 25 residues in amylopectin. In glycogen average chain length 13 glucose residues. At the heart of every glycogen molecule is a protein called glycogenin.

Functions

The function of muscle glycogen is to act as a readily available source of glucose for energy within muscle itself. Liver glycogen is concerned with storage and maintenance of the blood glucose.

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Cellulose

Cellulose is the chief constituent of cell wall of plants. It is an unbranched polymer of glucose and consists of long straight chains which are linked by β (1 \rightarrow 4) glycosidic linkages and not α $(1 \rightarrow 4)$ as in amylose. (Figure 22)



Figure 22. Structure of Cellulose

Since humans lack an enzyme cellulase that can hydrolyze the β (1 \rightarrow 4) glycosidic linkages, cellulose cannot be digested and absorbed and has no food value unlike starch. However, the ruminants can utilize cellulose because they have in their digestive tract microorganisms whose enzymes hydrolyze cellulose.

Importance of Cellulose

For human cellulose has nutritional significance. Cellulose is a component of fiber in the diet.

Although there is no known metabolic requirement for fiber, yet high fiber diet is associated with reduced incidence of a number of diseases like:

- Cardiovascular disease
- Colon cancer
- Diabetes
- Diverticulosis

Cellulose is present in unrefined cereals. It increases bulk of stool, aids intestinal motility, acts as a stool softener and prevents constipation.

Inulin

Inulin is a polymer of D-Fructose (Fructosans) linked together by β (l \rightarrow 2) glycosidic linkage. It occurs in the tubers of some plants, e.g. chicory, bulb of onion and garlic. Inulin is not hydrolyzed

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by α -amylase but is hydrolyzed by inulinase, which is not present m the humans and so it is not utilized as food.

Clinical importance of Inulin

Inulin has clinical importance as it is used in the studies of glomerular filtration rates (kidney function test).

9.1 Heteropolysaccharides or Heteroglycans

9.1.1 *Glycosaminoglycans (GAGs) or Mucopolysaccharides*

Structure of GAG

GAG is an unbranched heteropolysaccharide, made up of repeating disaccharides.

One component of which is always an amino sugar (hence the name glycosaminoglycans) either D-glucosamine or D-galactosamine. The other component of the repeating disaccharide (except in the case of keratan sulfate) is auronic acid, either L-glucuronic acid or its epimer L-iduronic acid. Thus, GAG is a polymer of [uronic acid-amino sugar]_n. This polymer is attached covalently to extracellular proteins called core protein (except hyaluronic acid) to form proteoglycans. A resulting structure resembles a "bottle brush". (Figure 23)





The proteoglycan monomer associates with a molecule of hyaluronic acid to form proteoglycan aggregates.

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The association is stabilized by additional small proteins called link proteins. With the exception of hyaluronic acid, all the GAGs contain sulfate group. The amount of carbohydrates in proteoglycans is usually much greater than is found in a glycoprotein and may comprise upto 95 percent of its weight.

Occurrence-of-GAGs

Glycosaminoglycans are found in the:

- Synovial fluid of joints
- Vitreous humor of the eye
- Arterial wails
- Bones
- Cartilage.

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Functions of GAGs

They are major components of the extracellular matrix or ground substance.GAGs carry sulfate and carboxyl groups which give them a negative charge and have special ability to bind large amounts of water, thereby producing a gel-like matrix which functions as a cushion against mechanical shocks. They act as "molecular sieves', determining which substances enter and leave cells. They also give resilience (elasticity) to cartilage, permitting compression and re-expansion.

They lubricate joints both at the surface of cartilage and in synovial fluid. The viscous lubricating properties of mucous secretions are also due to the presence of glycosaminoglycans, which led to st Graduate Courses the original naming of these compounds as mucopolysaccharides. (Table 2)

Types of GAGs 9

The different types of GAGs are:

- Hyaluronic acid
- Condroitin sulfate
- Keratan sulfate
- Dermatan sulfate
- Heparin
- Heparin sulfate.

The different types of GAGs differ from each other in the following properties:

- Uronic acid composition •
- Amino sugar composition
- Linkage between ammo sugar and uronic acid
- Chain length of the disaccharide polymer ٠
- Presence or absence of sulfate groups and their position of attachment to the sugar ٠
- The nature of the core protein to which they are attached •
- Their tissue and subcellular distribution and their biological function.

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GAG	Disaccharide unit	
Hyaluronic acid	N-Acetyl glucosamine-Glucuronic acid	
Condroitin sulfate	N-Acetyl glucosamine-Glucuronic acid	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Keratan sulfate	N-Acetyl glucosamine-Galactose (no uronic acid)	COUISES
Dermatan sulfate	N-Acetyl glucosamine-L-lduronic acid	le
Heparin	Glucosamine-Glucuronic acid or Iduronic acid	
Heparan sulfate	Same as heparin except that some glucosamine are acetylated	

Table 2

10. Glycoproteins

Glycoproteins are proteins to which oligosaccharides are covalently attached to their polypeptide chain. Glycoproteins contain much shorter carbohydrate chain than proteoglycans. The distinction between glycoproteins and proteoglycans may be based on the amount of carbohydrate. Glycoproteins contain less than 4 percent carbohydrate in the molecule. Proteoglycans contain more than 4 percent carbohydrate.

Functions of Glycoproteins

- The most important reproductive hormones are glycoproteins.
- Almost all the plasma proteins of humans are glycoproteins, except albumin.
- Many integral membrane proteins are glycoproteins.
- Most proteins that are secreted, such as antibodies, hormones and coagulation factors are glycoproteins.





• Two types of glycosides are there (i) o-glyosides with each sugar bonded to an oxygen atom of another molecule. (2) N-glyosides in which sugar is bonded to nitrogen atom. Glyosides derived from furanoses are called furanosides and those derived from pyranoses called pyranosides.

The main difference between glycogen & amylopectin is that glycogen is more highly branched. Branches point occur every 10 residues in glycogen and about every 25 residues in amylopectin in glycogen average chain length 13 glucose residues. At the heart of every glycogen molecule is a protein called glycogenin.

11. Functions of carbohydrates

Carbohydrates have wide range of functions.

- Source of energy for living beings e.g. glucose.
- Storage form of energy e.g. glycogen in animals and starch in plants.
- Serve as structural component e.g. glycosoaminoglycans in humans, cellulose in plants and chitin in insects.
- Non digestable carbohydrates like cellulose, serve as dietary fibres.
- Constituents of nucleic acid RNA and DNA. E.g. Ribose and deoxyribose sugar.
- Carbohydrates are also involved in detoxification, e.g. glucuronic acids.

12. Summary

- Carbohydrates are poly hydroxy aldehydes and ketones.
- Monosaccharides containing an aldehyde group are called aldoses and those with aketo group are called ketoses.
- Carbohydrates can also be classified as disaccharides, oligosaccharides, and polysaccharides consist of monosaccharides linked by glycosidic bonds.
- Sugars with free, oxidizableanomeric carbons are called reducing sugars.
- If two monosaccharides isomers differ in configuration around one specific carbon atom [with exception of carbonyl carbon] they are called epimers of each other.
- If a pair of sugar are mirror images of each other they are called enantiomers and designated as D- and L- sugars.
- When sugar cyclizes and anomeric carbon is created from aldehyde group of an aldose or a keto group of ketose. This carbon has two configuration α or β , if the oxygen on anomeric is not attached to any other structure.
- Disaccharides consist of two monosaccharides joined by glycosidic linkage of lactose, sucrose.
- Polysaccharides [glycans] contain many monosaccharides units in glycosidic linkage e.g. glycogen, starch in plants and glycogen (animal starch) in animals.

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- Proteoglycans and glycosoaminoglycans contains sugar derivative such as amino sugar, uronic acid and sialic acid, which are associated with structural components of tissue proteoglycans are predominately carbohydrate but also contain protein.
- Glycoproteins are proteins to which carbohydrate chains are covalently bound. Many cell surface protein and extracellular proteins are glycoprotein.



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