

# CHAPTER 2

## Carbohydrate Chemistry

- Introduction
- Definition, Classification and Functions of Carbohydrates
- Structure of Glucose
- Isomerism
- Mutarotation
- Chemical Properties of Monosaccharides

- Glycoside Formation
- Derivatives of Monosaccharides
- Disaccharides
- Polysaccharides (Glycans)
- Glycoproteins
- Summary
- Exercise

### INTRODUCTION

The carbohydrates are widely distributed both in animal and plant tissues. Chemically, they contain the elements carbon, hydrogen and oxygen. The empirical formula of many simple carbohydrates is  $[\text{CH}_2\text{O}]_n$ . Hence, the name “*carbohydrate*”, i.e. hydrated carbon. They are also called “*saccharides*”. In Greek, *saccharon* means sugar.

Although many common carbohydrates confirm the empirical formula  $[\text{CH}_2\text{O}]_n$ , others like deoxyribose, rhamnohexos do not. Some carbohydrates also contain *nitrogen*, *phosphorus* or *sulfur*.

### DEFINITION, CLASSIFICATION AND FUNCTIONS OF CARBOHYDRATES

Carbohydrates may be defined chemically as *aldehyde* or *ketone* derivatives of polyhydroxy (more than one hydroxy group) alcohols or as compounds that yield these derivatives on hydrolysis.

#### Functions of Carbohydrates

Carbohydrates have a wide range of functions. The following are few of them:

- Source of energy for living beings, e.g. *glucose*

- Storage form of energy, e.g. *glycogen* in animal tissue and *starch* in plants
- Serve as structural component, e.g. *glycosaminoglycans* in humans, *cellulose* in plants and *chitin* in insects
- Non-digestible carbohydrates like cellulose, serve as dietary fibers
- Constituent of nucleic acids RNA and DNA, e.g. *ribose* and *deoxyribose* sugar
- Play a role in lubrication, cellular intercommunication and immunity
- Carbohydrates are also involved in detoxification, e.g. *glucuronic acid*.

### Classification of Carbohydrates

Carbohydrates are classified into three groups:

1. Monosaccharides
2. Oligosaccharides
3. Polysaccharides.

#### Monosaccharides (Greek: *Mono* = one)

Monosaccharides are also called *simple sugars*. The term sugar is applied to carbohydrates that are soluble in water and sweet to taste. They consist of a single polyhydroxy aldehyde or ketone unit, and thus cannot

Table 2.1: Classification of monosaccharides and their examples

No. of Carbon	Empirical formula	Type of sugar	Aldoses	Ketoses
3	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	Trioses	Glyceraldehyde	Dihydroxyacetone
4	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	Tetroses	Erythrose	Erythrulose
5	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	Pentoses	Ribose, Xylose	Ribulose, Xylulose
6	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	Hexoses	Glucose, Galactose and Mannose	Fructose
7	C <sub>7</sub> H <sub>14</sub> O <sub>7</sub>	Heptoses	Glucoheptose	Sedoheptulose

be hydrolyzed into a simpler form. They may be subdivided into two groups as follows:

1. Depending upon the number of carbon atoms they possess, e.g.
  - Trioses
  - Tetroses
  - Pentoses
  - Hexoses
  - Heptoses.
2. Depending upon the functional aldehyde (CHO) or ketone (C=O) group present:
  - Aldoses
  - Ketoses.

Classification of monosaccharides based on the number

of carbon and the type of functional group present with examples is given in **Table 2.1**. *The most abundant monosaccharide in nature is six carbon sugar-D-glucose*. Biologically important monosaccharides are listed in **Table 2.2**.

### Oligosaccharides (Greek: oligo = few)

Oligosaccharides consist of a short chain of monosaccharide units (2 to 10 units), joined together by a characteristic bond called *glycosidic bond* which, on hydrolysis, gives two to ten molecules of simple sugar (monosaccharide) units. Oligosaccharides are subdivided into different groups based on the number of monosaccharide units present (**Table 2.3**).

Table 2.2: Biologically important monosaccharides

Type of monosaccharide	Example	Importance
Trioses	Glyceraldehyde and Dihydroxyacetone	<ul style="list-style-type: none"> <li>• Intermediates in the glycolysis</li> <li>• Precursor of glycerol which is required for the formation of triacylglycerol and phospholipid</li> </ul>
Tetroses	D-Erythrose	<ul style="list-style-type: none"> <li>• Intermediate product of carbohydrate metabolism (Hexose monophosphate pathway)</li> </ul>
Pentoses	D-Ribose	<ul style="list-style-type: none"> <li>• Constituent of nucleic acid RNA and coenzymes, e.g. ATP, NAD, NADP and FAD</li> <li>• Intermediate product of pentose phosphate pathway</li> </ul>
	D-Ribulose	<ul style="list-style-type: none"> <li>• Intermediate product of pentose phosphate pathway</li> </ul>
	D-Xylulose	<ul style="list-style-type: none"> <li>• Constituent of proteoglycans and glycoproteins</li> </ul>
	L-Xylulose	<ul style="list-style-type: none"> <li>• An intermediate in uronic acid pathway</li> </ul>
Hexoses	D-Glucose	<ul style="list-style-type: none"> <li>• The main sugar of the body which is utilized by the tissue for energy purposes</li> </ul>
	D-Fructose	<ul style="list-style-type: none"> <li>• Can be converted to glucose in the liver and so used in the body for energy purpose</li> </ul>
	D-Galactose	<ul style="list-style-type: none"> <li>• Can be converted to glucose in the liver and metabolized</li> <li>• Synthesized in mammary gland to make the lactose of milk</li> <li>• A constituent of glycolipids, proteoglycans and glycoproteins</li> </ul>
	D-Mannose	<ul style="list-style-type: none"> <li>• A constituent of glycoprotein, glycolipids and blood group substances</li> </ul>
Heptoses	Sedoheptulose	<ul style="list-style-type: none"> <li>• An intermediate in the pentose phosphate pathway</li> </ul>

Table 2.3: Classification of oligosaccharides and their examples

Type of oligosaccharide	Number of monosaccharide	Example	Type of monosaccharide present
Disaccharide	Two	Maltose	Glucose + Glucose
		Lactose	Glucose + Galactose
		Sucrose	Glucose + Fructose
Trisaccharide	Three	Raffinose	Glucose + Galactose + Fructose
Tetrasaccharide	Four	Stachyose	2 Molecules of Galactose + Glucose + Fructose
Pentasaccharide	Five	Verbascose	3 Molecules of Galactose + Glucose + Fructose

The disaccharides which have two monosaccharide units are the most abundant in nature. Oligosaccharides with more than three subunits are usually found in glycoproteins; such as blood group antigens.

### Polysaccharides (Greek: Poly = many) or Glycans

Polysaccharides are polymers consisting of hundreds or thousands of monosaccharide units. They are also called *glycans* or *complex carbohydrates*. They may be either *linear*, (e.g. cellulose) or *branched*, (e.g. glycogen) in structure.

Polysaccharides have high molecular weight and are only sparingly soluble in water. They are not sweetish and do not exhibit any of the properties of aldehyde or ketone group. Polysaccharides are of two types (Table 2.4).

- Homopolysaccharides (homoglycans)
- Heteropolysaccharides (heteroglycans).

### Homopolysaccharides (Homoglycans)

- When a polysaccharide is made up of several units of one and the same type of monosaccharide unit, it is called homopolysaccharide.
- The most common homoglycans are:
  - Starch
  - Dextrins
  - Glycogen

- Inulin
- Cellulose.

- Some homopolysaccharides serve as a storage form of monosaccharides used as fuel, e.g. starch and glycogen, while others serve as structural elements in plants, e.g. cellulose.

### Heteropolysaccharides (Heteroglycans)

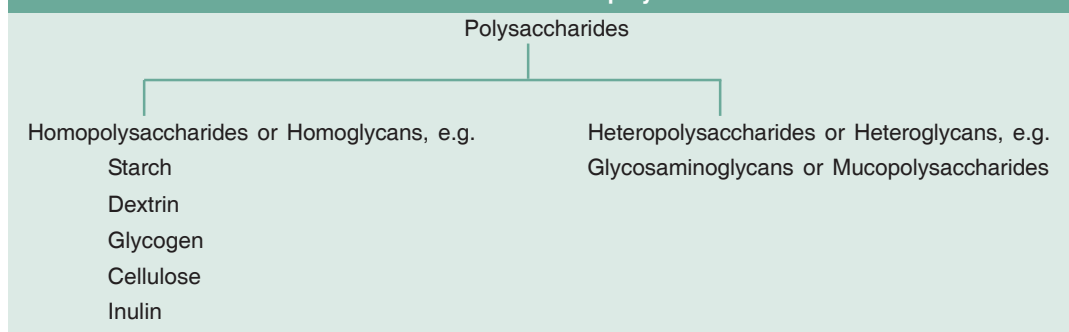
- They contain two or more different types of monosaccharide units or their derivatives.
- Heteropolysaccharide present in human beings is glycosaminoglycans (mucopolysaccharides), e.g.
  - Heparin
  - Chondritin sulfate
  - Hyaluronic acid
  - Dermatan sulfate
  - Keratan sulfate
  - Blood group polysaccharides.

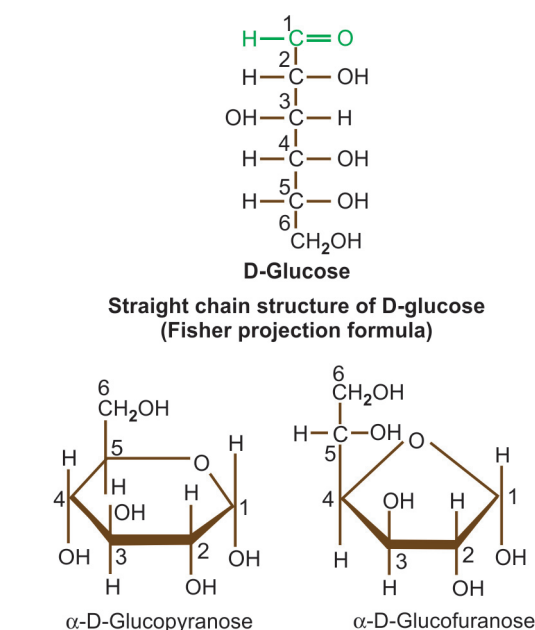
## STRUCTURE OF GLUCOSE

Physiologically and biomedically, glucose is the most important monosaccharide. The structure of glucose can be represented in the following ways (Figure 2.1):

- The straight chain structural formula (Fisher projection).
- Cyclic formula (Ring structure or Haworth projection)

Table 2.4: Classification of polysaccharides





**Figure 2.1:** Structure of D-Glucose

- Monosaccharide in solution is mainly present in ring form. In solution, aldehyde (CHO) or ketone (C=O) group of monosaccharide react with a hydroxy (OH) group of the same molecule forming a bond *hemiacetal* or *hemiketal* respectively.
- The aldehyde group of glucose at C-1 reacts with alcohol (OH) group of C-5 or C-4 to form either six membered ring called **glucopyranose** or five membered ring called **glucofuranose**, respectively. (Figure 2.1)
- However, in case of glucose, the six membered **glucopyranose** is much more stable than the glucofuranose ring. In the case of fructose, the more stable form is **fructofuranose**.

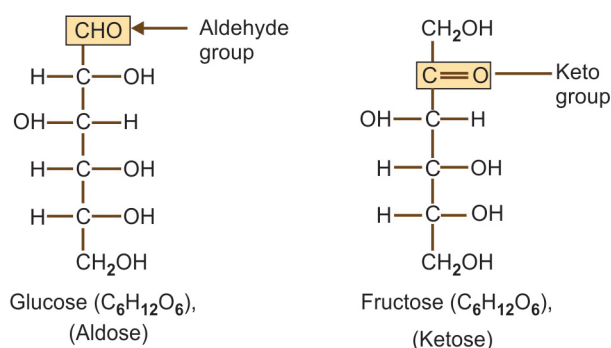
## ISOMERISM

The compounds possessing identical molecular formula but different structures are referred to as **isomers**. The phenomenon of existence of isomers is called **isomerism**. (Greek 'isos' means *equal*, 'meros' means *parts*). The five types of isomerism exhibited by sugar are as follows:

1. Ketose-aldose isomerism
2. D and L isomerism
3. Optical isomerism
4. Epimerism
5. Anomerism.

### Ketose-Aldose isomerism

Glucose and fructose are isomers of each other having the same chemical (molecular) formula  $C_6H_{12}O_6$ , but they differ in structural formula with respect to their

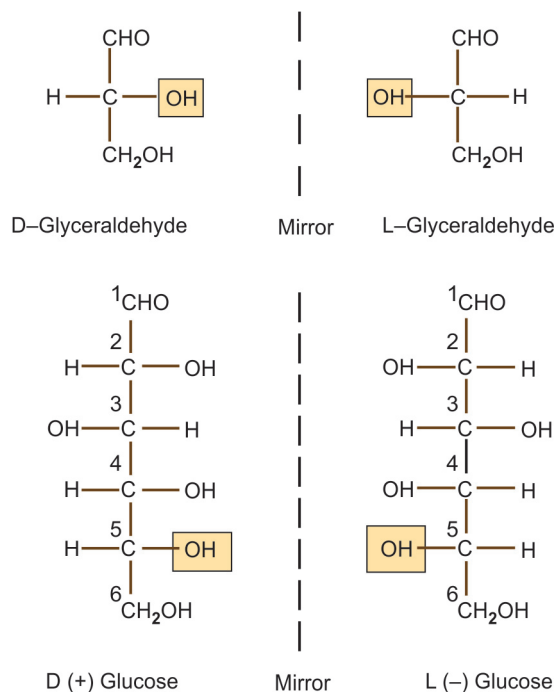


**Figure 2.2:** Ketose-Aldose isomerism

functional groups. There is a **keto** group in position two of fructose and an **aldehyde** group in position one of glucose (Figure 2.2). This type of isomerism is known as **ketose-aldose isomerism**.

### D and L isomerism

- D and L isomerism depends on the orientation of the H and OH groups around the asymmetric carbon atom adjacent to the terminal primary alcohol carbon, e.g. carbon atom number 5 in glucose determines whether the sugar belongs to D or L isomer.
- When OH group on this carbon atom is on the right, it belongs to **D-series**, when it is on the left, it is the member of the **L-series**. The structures of D and L-glucose based on the reference monosaccharide, D and L glyceraldehyde, a three carbon sugar (Figure 2.3).



**Figure 2.3:** D and L isomers (enantiomeric pairs) of glyceraldehyde and glucose

- D and L isomers are mirror images of each other. These two forms are called **enantiomers**.
- Most of the monosaccharides in the living beings belong to the D-series.

### Optical Isomerism

- The presence of **asymmetric carbon** atoms exhibits **optical activity** on the compound. Optical activity is the capacity of a substance to rotate the plane polarized light passing through it.
- When a beam of plane-polarized light is passed through a solution of an optical isomer, it will be rotated either to the right and is said to be **dextrorotatory (d)** or (+) or to the left and is said to be, **levorotatory (l)** or (-).
- When equal amount of D and L isomers are present, the resulting mixture has no optical activity. Since the activity of each isomer cancel one another, such a mixture is said to be a **racemic** or **dl mixture**.

### Epimerism

When two monosaccharides differ from each other in their configuration around a single **asymmetric carbon** (other than anomeric carbon) atom, they are referred to as **epimers** of each other.

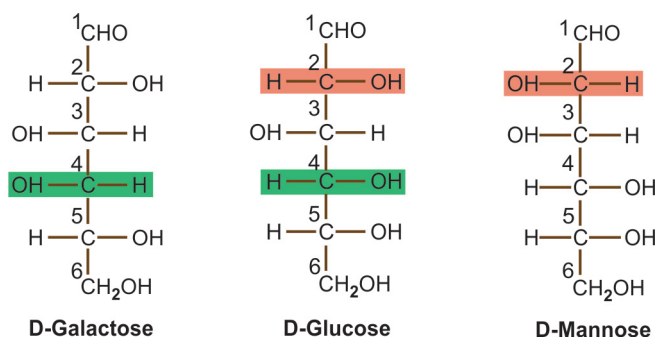


Figure 2.4: Epimers of glucose

For example, galactose and mannose are two epimers of glucose (**Figure 2.4**). They differ from glucose in the configuration of groups (H and OH) around C-4 and C-2 respectively. Galactose and mannose are not epimers of each other as they differ in configuration at two asymmetric carbon atoms around C-2 and C-4.

### Anomerism

#### $\alpha$ and $\beta$ Anomerism

The predominant form of glucose and fructose in a solution are not an open chain. Rather, the open chain

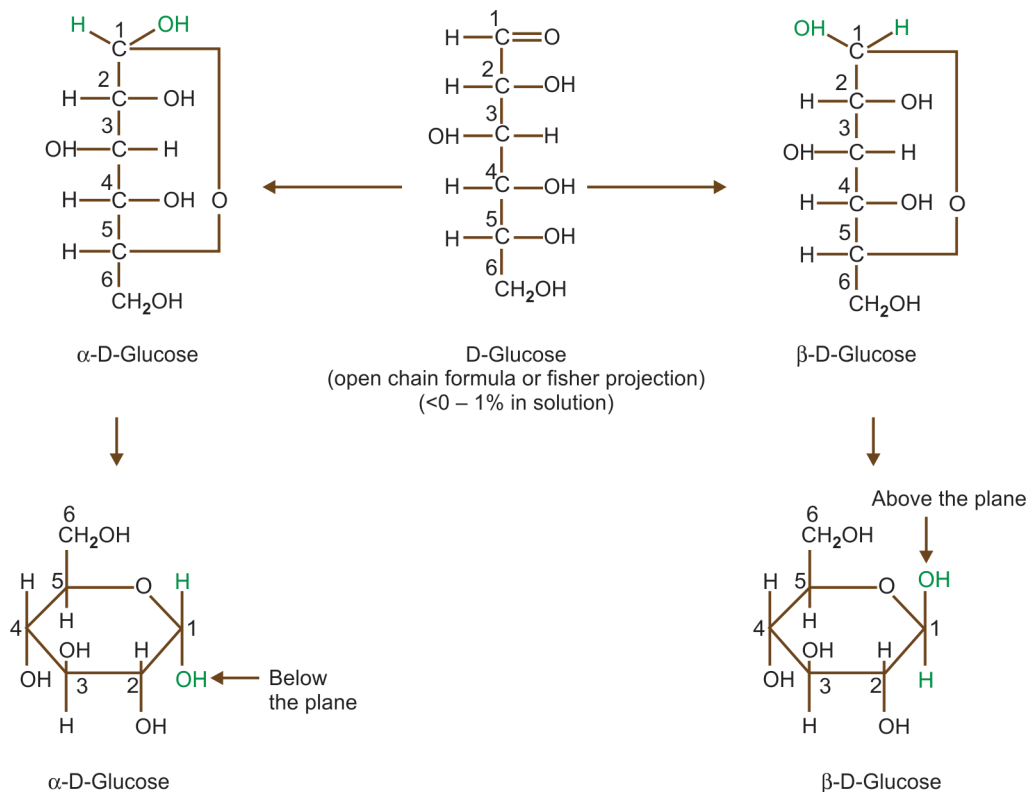


Figure 2.5: Formation of  $\alpha$  and  $\beta$  anomers

form of these sugar in solution cyclize into rings. An additional asymmetric center is created when glucose cyclizes. Carbon-1 of glucose in the open chain form, becomes an asymmetric carbon in the ring form (**Figure 2.5**) and two ring structures can be formed. These are:

- $\alpha$ -D-glucose
- $\beta$ -D-glucose.

The designation  $\alpha$  means that the hydroxyl group attached to C-1 is below the plane of the ring,  $\beta$  means that it is above the plane of the ring. The C-1 carbon is called the *anomeric carbon atom* and so,  $\alpha$  and  $\beta$  forms are *anomers*.

### MUTAROTATION

- Mutarotation is defined as the change in the **specific optical rotation** by the interconversion of  $\alpha$  and  $\beta$  forms of D-glucose to an equilibrium mixture.
- In water,  $\alpha$ -D-glucopyranose and  $\beta$ -D-glucopyranose interconvert through the open chain form of the sugar. This interconversion was detected by optical rotation.
- The specific rotation  $[\alpha]_D$ , of the  $\alpha$  and  $\beta$  anomers of D-glucose are  $+112^\circ$  and  $+18.7^\circ$ . When crystalline sample of either anomers is dissolved in water, specific rotation  $[\alpha]_D$  changes with time until an equilibrium value of  $+52.7^\circ$  is attained (**Figure 2.6**). This change called *mutarotation*, results from the formation of an equilibrium mixture containing about **one-third  $\alpha$ -anomers** and **two-thirds  $\beta$ -anomers**. Very little of the open chain form of glucose is present ( $<1\%$ ).
- Non-reducing sugar cannot show mutarotation due to the absence of the free anomeric OH group.

### CHEMICAL PROPERTIES OF MONOSACCHARIDES

Some of the important chemical properties of monosaccharides are:

1. Action of Strong Acids: Furfural formation
2. Action of Alkalies: Enolization
3. Oxidation: Sugar acid formation
4. Reduction: Sugar alcohol formation
5. Action of phenylhydrazine: Osazone formation.

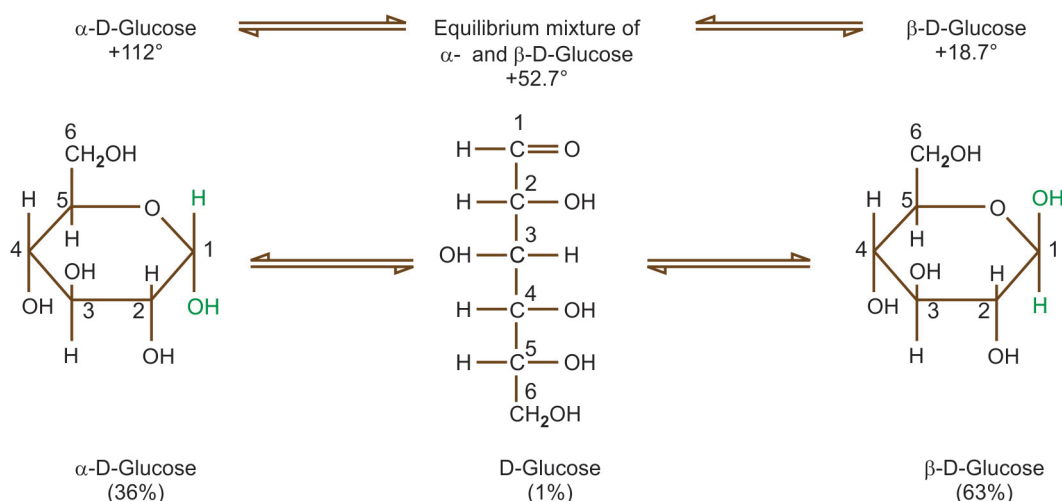
#### Action of Strong Acids (Furfural Formation)

On heating a sugar with mineral acids ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ), the sugar loses water and forms *furfural derivatives*. These may condense with  $\alpha$ -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.

#### Action of Alkalies (Enolization)

- On treatment with dilute aqueous alkalies, both aldoses and ketoses are changed to **enediols**. Enediol is the enol form of sugar because two OH groups are attached to the double bonded carbon (**Figure 2.7**).
- 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 (**Figure 2.7**).



**Figure 2.6:** Mutarotation of glucose



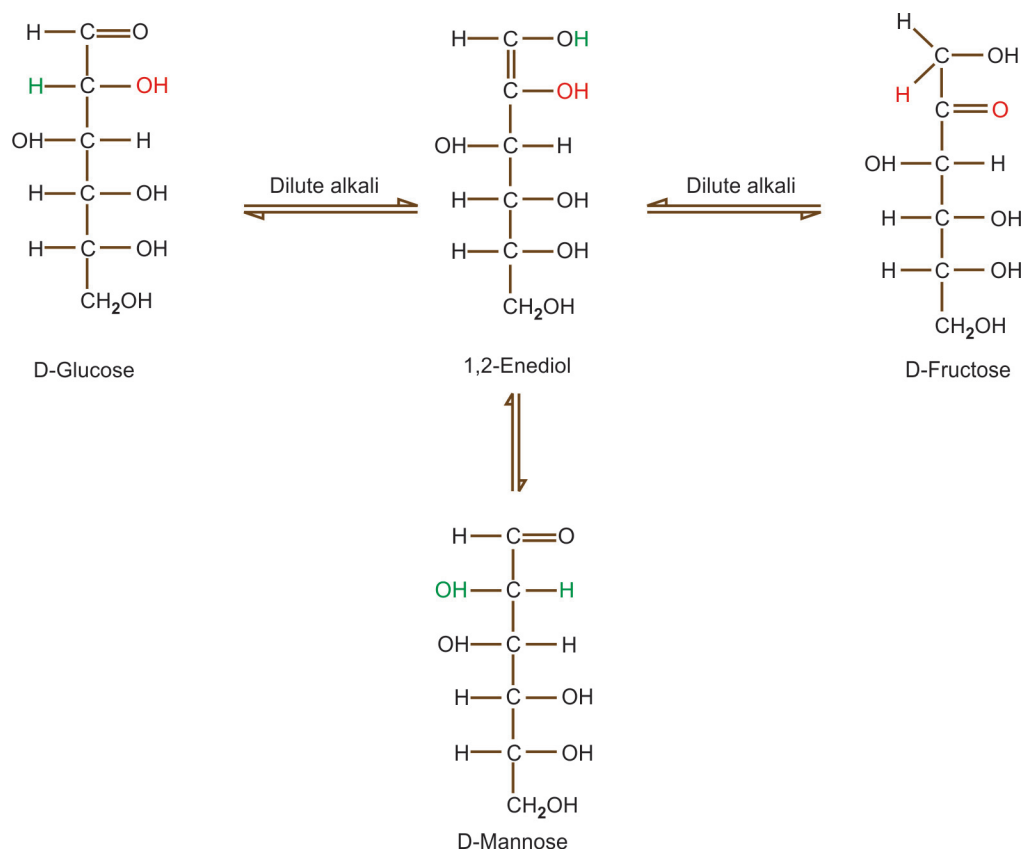


Figure 2.7: Action of alkali on reducing sugar

### Oxidation (Sugar Acid Formation)

- When aldoses oxidize under proper conditions they may form:
  - Aldonic acid
  - Saccharic acids
  - Uronic acid.
- Oxidation of an aldose with hypobromous acid (HOBr), which acts as an oxidizing agent gives **aldonic acid**. Thus, glucose is oxidized to gluconic acid (Figure 2.8).
- Oxidation of aldoses with nitric acid under proper conditions convert 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), a uronic acid is formed (Figure 2.8).

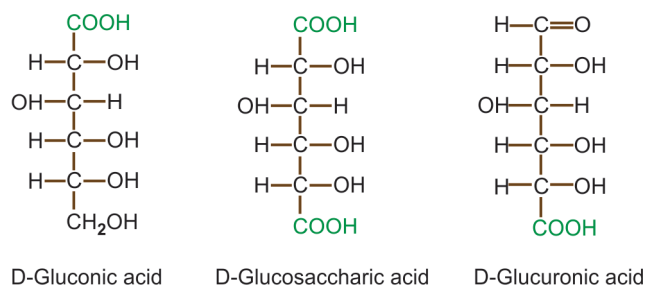


Figure 2.8: Sugar acids produced by oxidation of glucose

### Reduction to Form Sugar Alcohol

Both aldoses and ketoses may be reduced by enzymes or non-enzymatically to the corresponding polyhydroxy alcohols. The alcohols formed from glucose, mannose, fructose and galactose are given in Figure 2.9.

- 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.



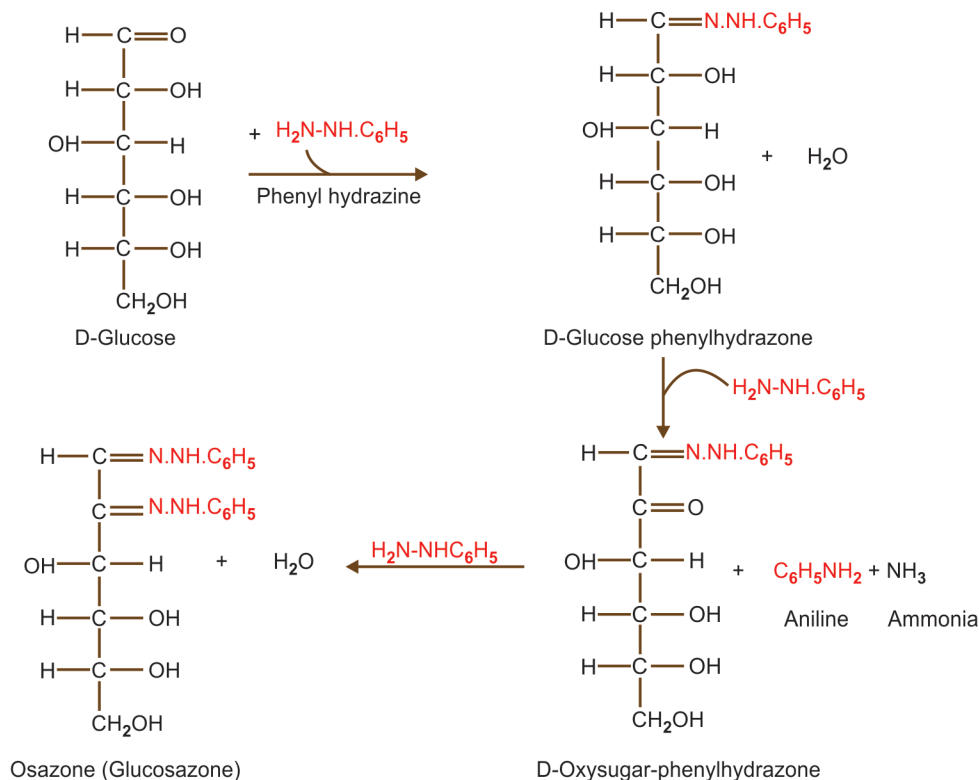
**Figure 2.9:** Reduction of sugar to form alcohol

### Action of Phenylhydrazine (Osazone Formation)

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

The reactions of glucose with phenylhydrazine are shown in **Figure 2.10**.

- 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 and maltose differ in forms (**Figure 2.11**):



**Figure 2.10:** Formation of glucosazone

- 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 ( $\text{CHO}$  or  $\text{C}=\text{O}$ ) group in them.

### 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**.
- The monosaccharides are joined by glycosidic bonds to form **disaccharides**, **oligosaccharides** and **polysaccharides**.
- In disaccharides, the glycosidic linkage may be either  $\alpha$  or  $\beta$  depending on the configuration of the atom attached to the anomeric carbon of the sugar (**Figure 2.16**).

### Therapeutic importance of glycosides

- Glycosides are found in many drugs, e.g. in antibiotic *streptomycin*.



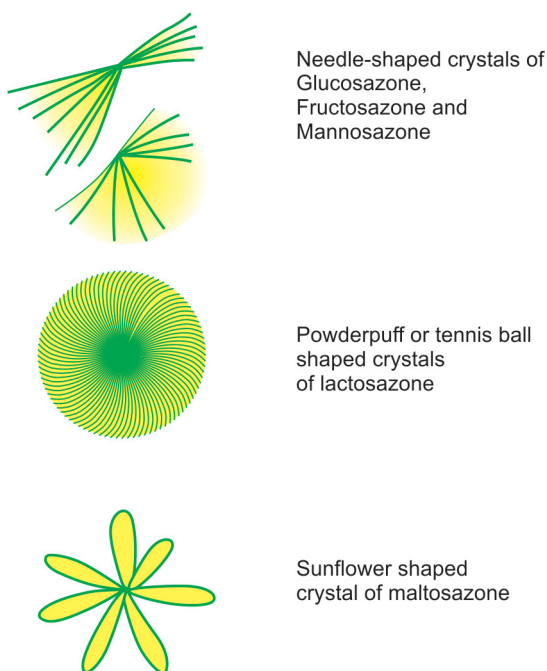


Figure 2.11: Structure of different osazones

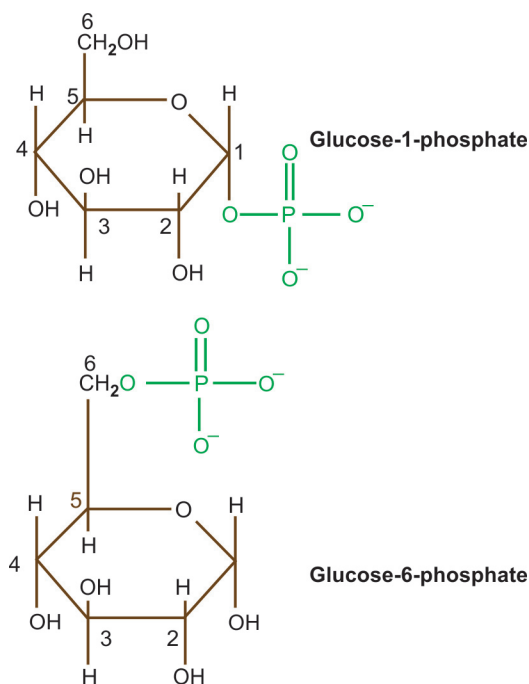


Figure 2.12: Phosphoric acid ester of glucose

- Cardiac glycosides such as *Ouabain* and *digoxin* increase heart muscle contraction and are used for treatment of congestive heart failure.
- *Anthracycline* glycosides (daunorubicin and doxorubicin), *Daunorubicin* is used to treat leukemia. *Doxirubicin* is used to treat a wide range of cancers.

### DERIVATIVES OF MONOSACCHARIDES

Some important sugar derivatives of monosaccharides are:

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

#### Phosphoric Acid Ester of Monosaccharides

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 2.12).

##### Importance

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

- 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 amino (acetamino) group. For example, glucosamine, N-acetyl glucosamine (Figure 2.13), galactosamine and mannosamine.

##### Importance of amino sugar

- Amino sugars are components of glycolipid (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 (Figure 2.14), e.g. 2-deoxyribose found in nucleic acid DNA.

#### 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.

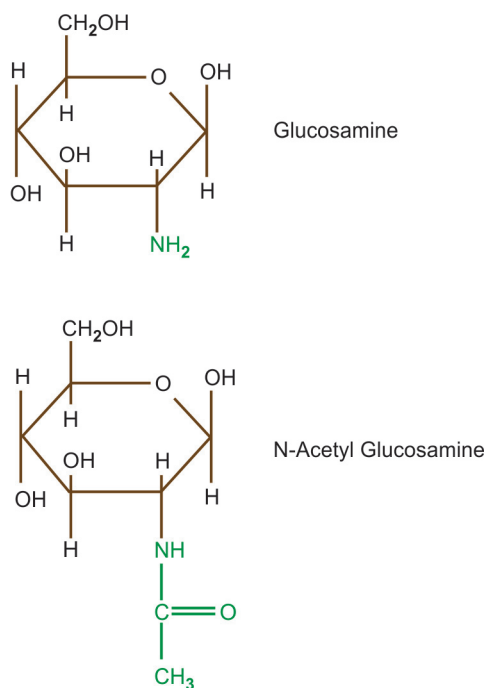


Figure 2.13: Structure of amino sugars

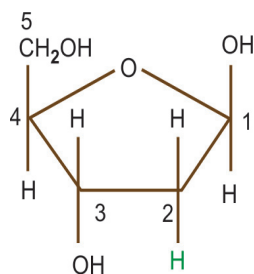


Figure 2.14: Structure of 2-deoxyribose sugar

- Glucuronic acid (uronic acid) (See properties of monosaccharide-oxidation).

### 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  $\longrightarrow$  Neuraminic acid

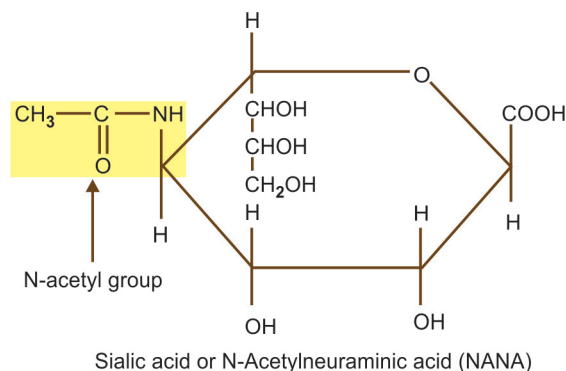


Figure 2.15: Structure of sialic acid or NANA

### Sialic Acid

Sialic acids are acetylated derivatives of neuraminic acid in which amino ( $\text{NH}_2$ ) or hydroxy ( $\text{OH}$ ) group is acetylated (Figure 2.15).

### Importance

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

### DISACCHARIDES

- Disaccharides consist of two monosaccharide units.
- They are crystalline, water soluble and sweet to taste.
- They are subclassified on the basis of the presence or absence of free reducing (aldehyde or ketone) group (Table 2.5).
  - Reducing disaccharides with free aldehyde or keto group, e.g. maltose, lactose
  - Non-reducing disaccharides with no free aldehyde or keto group, e.g. sucrose.

### 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**.
- The numerical description like (1  $\rightarrow$  4) of glycosidic bond represents the number of carbon atoms that connect the two sugars as shown in Figure 2.16. 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  $\alpha$ -amylase.

Table 2.5: Classification of disaccharides

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

### 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*.

### Lactose (Milk sugar)

- It is present in milk. Lactose contains one unit of  **$\beta$ -galactose** and one unit of  **$\beta$ -glucose** that are linked by a  **$\beta$  (1  $\rightarrow$  4) glycosidic linkage (Figure 2.16).**
- 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* enzyme in human beings.

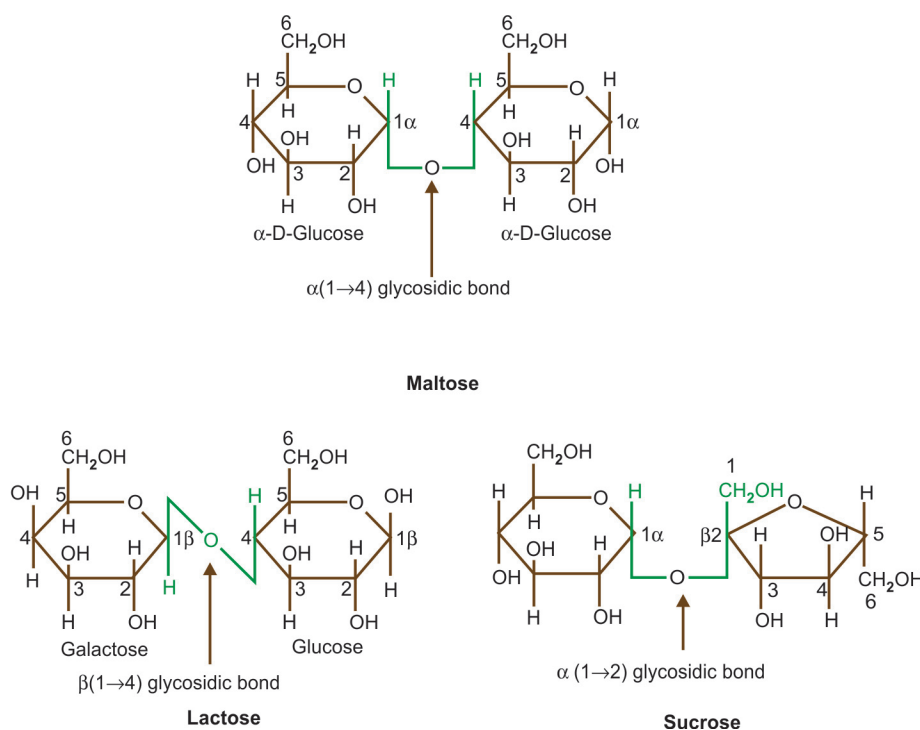


Figure 2.16: Structure of disaccharides

### 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 (**Figure 2.16**). Sucrose is therefore, a non-reducing sugar.
- Sucrose is hydrolyzed to fructose and glucose by an enzyme *sucrase* which is also called *invertase*.

### POLYSACCHARIDES (GLYCANS)

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 (**Table 2.4**).

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

### 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  $\alpha$ -1  $\rightarrow$  4 glycosidic linkages (**Figure 2.17**).

#### Amylopectin

Amylopectin is structurally identical to those of amylose ( $\alpha$ -1  $\rightarrow$  4 glycosidic linkages) but with side chains joining them by  $\alpha$ -1  $\rightarrow$  6 linkages (**Figure 2.18**).

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  $\alpha$ -1  $\rightarrow$  6 bonds and occur at an interval of 20 to 30 units of glucose. **Figures 2.17** and **2.18** represent diagrammatically the difference in the amylose and amylopectin molecules.

#### Dextrin

Partial hydrolysis of starch by acids or  $\alpha$ -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.

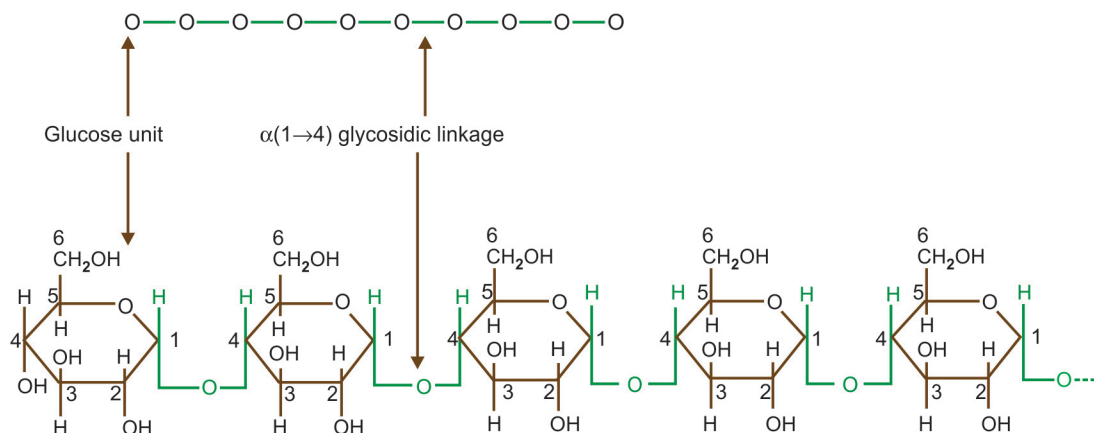
#### Glycogen (Animal Starch)

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, (**Figure 2.19**) having  $\alpha$ -(1  $\rightarrow$  6) linkages at intervals of about 8 to 10 glucose units.

#### Function

- 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.



**Figure 2.17:** Structure of amylose

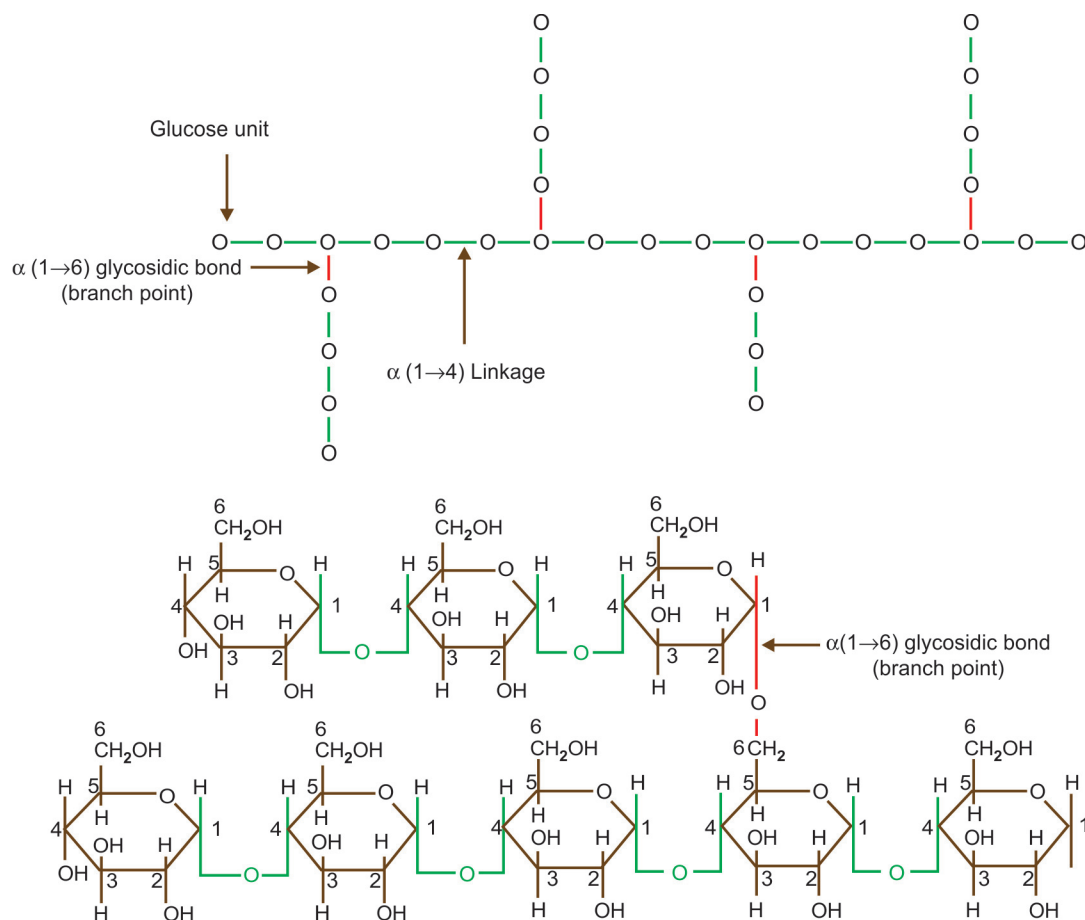


Figure 2.18: Structure of amylopectin

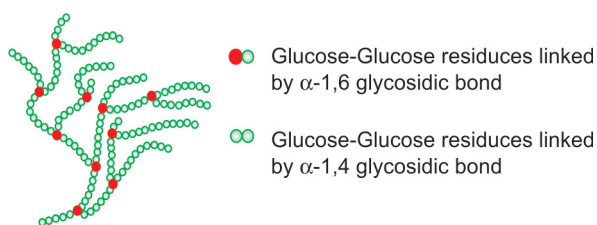


Figure 2.19: Diagrammatic representation of glycogen molecule

### 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  **$\beta(1 \rightarrow 4)$  glycosidic linkages** and not  $\alpha(1 \rightarrow 4)$  as in amylose (Figure 2.20).

Since humans lack an enzyme **cellulase** that can hydrolyze the  $\beta(1 \rightarrow 4)$  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.

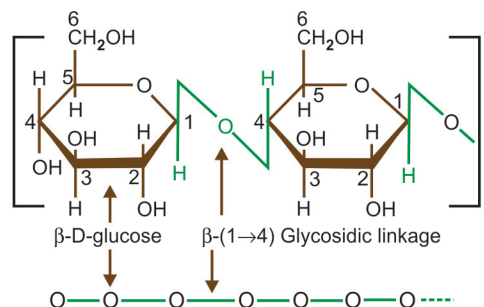


Figure 2.20: Structure of cellulose

### 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  $\beta$ -(1  $\rightarrow$  2) glycosidic linkage. It occurs in the tubers of some plants, e.g. chicory, bulb of onion and garlic. Inulin is not hydrolyzed by  $\alpha$ -amylase but is hydrolyzed by *inulinase*, which is not present in the humans and so it is not utilized as food.

### Clinical importance of Inulin

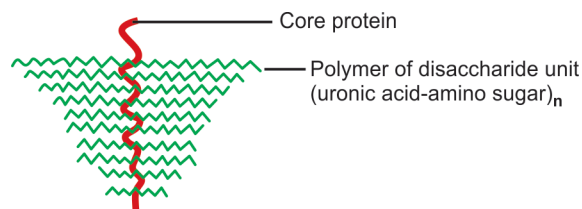
Inulin has clinical importance as it is used in the studies of *glomerular filtration rates (kidney function test)*.

## Heteropolysaccharides or Heteroglycans

### Glycosaminoglycans (GAGs) or Mucopolysaccharides (Table 2.6)

### Structure of GAG

- A 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 a **uronic acid**, either **L-glucuronic acid** or its epimer **L-iduronic acid**.
- Thus, GAG is a polymer of **[uronic acid-amino sugar]<sub>n</sub>**.
- 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 2.21**).
- The proteoglycan monomer associates with a molecule of hyaluronic acid to form **proteoglycan aggregates** (**Figure 2.22**).



**Figure 2.21:** Bottle brush structure of proteoglycan monomer

**Table 2.6: Structure and functions of glycosaminoglycans (GAGs)**

GAG	Disaccharide unit	Function
Hyaluronic acid	N-Acetyl glucosamine -Glucuronic acid	Serves as lubricant and shock absorber, facilitates cell migration in embryogenesis, morphogenesis, wound healing
Chondroitin sulfate	N-Acetyl-galactosamine-Glucuronic acid	Provides an endoskeletal structure helping to maintain their shape. Has a role in compressibility of cartilage in weight bearing
Keratan sulfate	N-Acetyl-glucosamine-Galactose (no uronic acid)	Transparency of cornea
Dermatan sulfate	N-Acetyl-galactosamine-L-Iduronic acid	Transparency of cornea and maintains the overall shape of the eye
Heparin	Glucosamine-Glucuronic acid or Iduronic acid	Serves as an anticoagulant, causes release of lipoprotein lipase from capillary walls
Heparan sulfate	Same as heparin except that some glucosamine are acetylated	Component of plasma membrane where it may act as receptor and may also participate in the mediation of cell growth, cell-to-cell communication



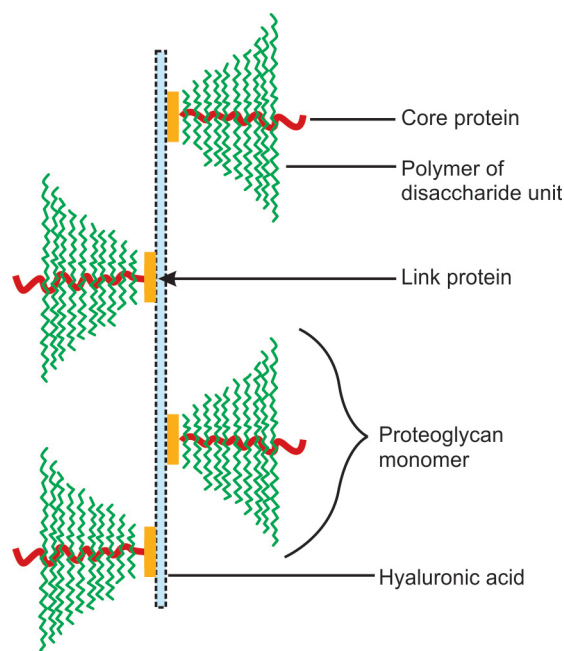


Figure 2.22: Proteoglycan aggregate

- 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 walls
- Bones
- Cartilage.

### 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 the original naming of these compounds as *mucopolysaccharides*.

### Types of GAGs

- The different types of GAGs are:
  - Hyaluronic acid
  - Chondroitin 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 amino sugar and uronic acid
  - Chain length of the disaccharide polymer
  - Presence or absence of sulfate groups and their position of attachment to the sugar
  - The nature of the core protein to which they are attached
  - Their tissue and subcellular distribution and their biological function.

Table 2.6 describes structure and functions of different types of glycosaminoglycans.

### 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

- 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.

- Glycoproteins serve as **lubricant** and **protective agent**, e.g. mucin of gastrointestinal and urogenital tracts.
- Glycoproteins also serve as transport molecules, such as **transferrin** and **ceruloplasmin**.

### SUMMARY

- Carbohydrates are polyhydroxy aldehydes or ketones.
- Carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides.
- Sugars with free, oxidizable anomeric carbons are called reducing sugars.
- Disaccharides consists of two monosaccharides joined by the glycosidic bond, e.g. lactose, maltose and sucrose.
- Polysaccharides (glycans) contain many monosaccharide units in glycosidic linkage. Some function as storage forms of carbohydrates, e.g. starch in plants and glycogen (animal starch) in animals.
- Glycogen is branched polymer of glucose having  $\alpha$ -(1  $\rightarrow$  4) linkages in the main chain and  $\alpha$ -(1  $\rightarrow$  6) linkages at the branch points.
- Proteoglycans and glycosaminoglycans contains sugar derivatives such as amino sugar, uronic acids and sialic acids, which are associated with structural components of the tissues.
- Glycoproteins are proteins attached to oligosaccharides. Many cell surface proteins and extracellular proteins are glycoproteins.

### EXERCISE

#### Multiple Choice Questions (MCQs)

1. All the following are composed exclusively of: glucose, *except*:
  - a) Glycogen
  - b) Starch
  - c) Lactose
  - d) Maltose
2. The sugar residues of glycogen are:
  - a) In  $\alpha$ -(1  $\rightarrow$  4) and  $\alpha$ -(1  $\rightarrow$  6) linkages
  - b) In  $\beta$ -(1  $\rightarrow$  4) linkages
  - c) Fructosans
  - d) None of the above
3. Which of the following statements is true for fructose?
  - a) It is an aldose sugar
  - b) It usually exists in the pyranose form
  - c) It is involved in the formation of sucrose
  - d) Carbon 1 is the anomeric carbon atom
4. D-galactose and D-glucose are:
  - a) Epimers of each other
  - b) Enantiomers of each other
  - c) Anomers of each other
  - d) Mirror images of each other
5. Which of the following carbohydrate is dietary fiber?
  - a) Cellulose
  - b) Starch
  - c) Glycogen
  - d) Inulin
6. Glycosaminoglycans are:
  - a) Disaccharide
  - b) Homoglycans
  - c) Heteroglycans
  - d) None of the above
7. Which of the following glycosaminoglycans is unsulfated?
  - a) Chondroitin sulfate
  - b) Heparin
  - c) Hyaluronic acid
  - d) Keratan sulfate
8. Which of the following GAGs does not contain uronic acid?
  - a) Hyaluronic acid
  - b) Keratan sulfate
  - c) Heparin
  - d) Heparan sulfate
9. Inulin is:
  - a) Fructosans
  - b) Glycans
  - c) Mannans
  - d) Xylans
10. Which of the following is not hydrolyzed by  $\alpha$ -amylase?
  - a) Starch
  - b) Glycogen
  - c) Cellulose
  - d) Dextrin

#### Correct Answers for MCQs

1-c	2-a	3-c	4-a
5-a	6-c	7-c	8-b
9-a	10-c		