
UNIT 1 CARBOHYDRATES

Structure

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1.1 INTRODUCTION

Nutrition is a relatively new science that evolved from disciplines such as Chemistry and Physiology. Thus, a student who intends to know and practice nutrition and dietetics should not only undertake intense learning and training on the different techniques that relate nutrition with chemistry but they should also understand how nutritional processes are merged with chemistry. Further, it is important to have a clear idea of the chemistry of nutrients for a better understanding of nutrition.

Do you have such knowledge? If the answer is 'No', then it is absolutely necessary that you should learn intensely this unit and you will find that the contents provided in it will serve as the foundation for the other courses such as the Advanced Nutrition, Principles of Food Science and Public Nutrition courses. If your answer is 'Yes', then too you must go through the contents of this unit to assess if you have the correct understanding of the subject and to brush up your previous knowledge and at the same time, to gather any new knowledge that you may discover during study.

This unit will provide you with a broad introduction to metabolic and nutritional aspects of biochemistry. The major focus is on the structure, function and metabolism of carbohydrates.

Objectives

After studying this unit, you will be able to:

- understand the meaning of nutritional biochemistry and discuss its evolution,
- classify carbohydrates, and
- describe the chemical properties, viz. mono, oligo and polysaccharides.

1.2 INTRODUCTION TO NUTRITIONAL BIOCHEMISTRY

Being a student of dietetics, a clear understanding of the term nutritional biochemistry, as well as, its development is pertinent to your knowledge.

Equally important is the applicability of nutritional techniques at the advanced level.

This sub-section, therefore, intends to:

- make the meaning of nutritional biochemistry clear to you, and
- inform you about the evolution of this science over the centuries.

Let us get started then.

1.2.1 Meaning and Importance of Nutritional Biochemistry

Nutrition is a science that cuts across several scientific disciplines, of which one is 'biochemistry'. It is the science that relates food to the functioning of the living organism. Nutrition includes the intake of food, digestion and absorption of food, transport and assimilation of nutrients, metabolism, liberation of energy and elimination of wastes. It, in fact, encompasses all the synthesis essential for growth, maintenance and reproduction. *Biochemistry*, as per definition, is the chemistry of living organisms that covers all the chemical reactions occurring in our body. Biochemistry explores the functioning of living organisms from a molecular and cellular perspective.

As implied by the course, it emphasizes the problems of nutrition and the mechanisms of biochemistry. The reason for this is quite understandable as nutrients are basically chemicals and our body is a chemical machine composed and built up of chemicals. Therefore, the biological function of a nutrient is readily explained in terms of its chemical interaction at the molecular level with the body's endogenous chemicals.

A good understanding of the biochemical basis of nutrient function and of the consequence of nutrient deficiency or excess is important in the clinical and laboratory diagnosis of nutritional diseases, clinical management of the same and in the control of endemic nutritional inadequacies. You, as a student of dietetics, should realize the importance of biochemistry in order to:

- a) understand nutrition properly, and
- b) utilize biochemical tools in solving nutrition-related health problems.

With this basic understanding of biochemistry and its relation with nutrition, let us move on to understanding the development of nutritional biochemistry as a discipline and contemporary interests in this area.

1.2.2 Development of Nutritional Biochemistry

Nutrition, in general, and particularly nutritional biochemistry, has traveled a long way since 1926, when nutrition was first recognized as an independent field of study with the appointment of *Mary Swartz Rose* as Professor of Nutrition at Columbia University. This was actually the culmination of a developmental period stemming from *Antoine Lavoisier's* experiments about 200 years back that formed the basis for the studies on respiratory exchange and calorimetry, the beginning of a new science - Nutrition. About 100 years elapsed before carbohydrates, fats and proteins were identified as the source of energy for animal body. By the end of the nineteenth century, the necessity for certain minerals in the diet was established. But it was not until the decade between 1930 and 1940 that the majority of the vitamins were identified, isolated from different foods, synthesized in the laboratory and received serious attention in order to understand their involvement in various biochemical reactions.

The contemporary interests in nutritional biochemistry are highlighted next.

1.2.3 Contemporary Interests in Nutritional Biochemistry

As newer techniques in biochemistry have emerged from time to time, these were of immense help in the understanding of utilization of different nutrients by the body. Biochemical basis of some of the dreaded nutritional diseases of the past, such as beri-beri, scurvy, pellagra and pernicious anaemia are well understood. Likewise, problems such as protein-energy malnutrition, xerophthalmia, iron deficiency anaemia, iodine deficiency disorders though well understood are still prevalent. Added to these are contemporary problems like diabetes and cardiovascular diseases. Reliable biochemical indicators are also now available to detect the prevalence of sub-clinical deficiency of many nutrients in the population.

Once the generation of free radicals in the body was correlated with the development of different fatal or crippling diseases, the importance of antioxidants increased many folds. In recent times, some nutrients such as vitamin E or selenium are getting special attention from research point of view, as these are potent antioxidants.

Recent biochemical studies have not only revealed the importance of polyunsaturated fatty acids in maintaining the normal lipid profile but these also went further to prove that a desirable ratio of n-3/n-6 fatty acids is essential for preventing *dyslipidemia* (a condition in which an abnormal amounts of lipids and lipoproteins accumulate in the blood).

Importance of nutritional interactions is now being realized. Some nutrients are antagonistic to each other whereas others act synergistically. Examples of uniquely related nutrients include folate and vitamin B₁₂, vitamin E and polyunsaturated fatty acids, vitamin D and calcium, zinc and copper etc. Biochemical research has revealed that certain drugs such as omiprazole, lovastatin, allupurinol, thiouracil and others influence nutrient metabolism.

Not only nutrients, but the importance of non-nutrients such as dietary fiber for healthy living is also understood. Very recently, a group of compounds known as 'phytoestrogens' has created great interest among nutritional biochemists. These substances are considered to protect cancer, besides having other positive roles. As a consequence, many popular, as well as, uncommon foods and beverages are constantly under study to explore the presence of these compounds, as well as, to observe their biochemical effects. Tea and soybean are two good examples.

Neutraceuticals are gaining popularity at an exponential rate. These are classified as foods that provide medical or health benefits. Spirulina is already available in the Indian market besides other countries with high claims. Few uncommon edible oils such as flaxseed oil, primrose oil etc. which are already in use in the western countries for their apparent beneficial effects, may at any time enter the market in India. Though, many of these preparations have proven positive effects on health, a more in-depth biochemical research will definitely help to know about these new generation nutritional substances.

The discussion above presented a good review about nutritional biochemistry, its development and scope in modern times. With this basic understanding, we shall move on to the study of the chemistry of important food constituents, namely carbohydrates, proteins, fats etc. In this unit we shall focus on carbohydrates.

1.3 CHEMISTRY OF CARBOHYDRATES

This is absolutely essential for you, as a student of Dietetics, to have a clear concept on the nature and physico-chemical properties of different nutrients.

After studying this sub-section, you will be able to know the following important aspects of carbohydrates:

- their chemical nature
- their classification, and
- their physico-chemical properties

Let us start by first getting to know what are carbohydrates?

You would realize that the family name ending *-ose* indicates a carbohydrate, for e.g. glucose, fructose, sucrose etc. Carbohydrates are basically *polyhydroxy aldehydes or ketones and their derivatives*. What do we mean by polyhydroxy aldehydes or ketones? Go ahead, read on and you will find the answer to this question soon. Carbohydrates, as you may already know, are found abundantly in both animal and plant tissues in different forms. While plants can produce carbohydrates by photosynthesis, animal cells cannot but are dependent on food for these important sources of energy. Some carbohydrates have highly specific functions in the body. Let us learn about these different carbohydrates.

Carbohydrates are classified into three major groups:

1. Monosaccharides
2. Oligosaccharides
3. Polysaccharides

Monosaccharides and oligosaccharides are also referred to as 'sugars'. Let us get to know about monosaccharides first.

1.4 MONOSACCHARIDES

Monosaccharides consist of a single polyhydroxy aldehyde or ketone unit and are commonly known as simple sugars. These cannot be hydrolyzed into simpler forms.

The general formula for monosaccharides is $(\text{CH}_2\text{O})_n$ where n is 3 to 7. In biological materials, monosaccharides with 5 and 6 carbon atoms are most common. All the carbon atoms of the monosaccharide contain one hydroxyl group ($-\text{OH}$) except one that contains a carbonyl oxygen (as in $-\text{CHO}$ or $>\text{C}=\text{O}$). If it is present at the terminal position, the monosaccharide is an aldehyde derivative and is called as an 'aldose' sugar position, e.g. glucose. On the other hand, if it is present in any other position, the monosaccharide is a ketone derivative that is known as a 'ketose' e.g. fructose. The carbon atoms are numbered as shown in the Figure 1.1, C-1 atom is an aldehyde functional group and C-2 atom is a ketone functional group as highlighted in Figure 1.1. So now you know how carbohydrates get classified as polyhydroxy aldehyde or ketone.

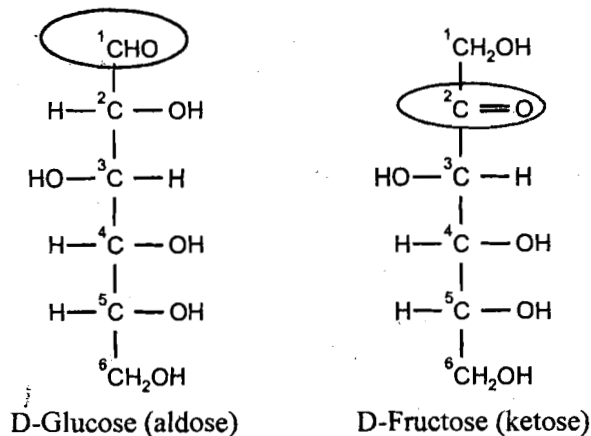


Figure 1.1: Numbering of carbon atoms in monosaccharides

Monosaccharides can further be divided on the basis of the number of carbon atoms they possess. Table 1.1 will be helpful to understand how the monosaccharides are classified, considering the number of carbon atoms in the molecule, as well as, the nature of the carbonyl oxygen with specific examples. The number of carbon atoms in an aldose or ketose may be specified by triose, tetrose, pentose, hexose or heptose. For example, glucose with six carbon atoms is an aldohexose and fructose too with six carbon atoms is a ketohexose.

Table 1.1: Different types of monosaccharides found in foods

Monosaccharides		Specific examples	
No. of carbon atoms	Called as	Aldoses	Ketoses
Three	Trioses	Glyceraldehyde	Dihydroxyacetone
Four	Tetroses	Erythrose	Erythrulose
Five	Pentoses	Ribose, Xylose, Arabinose	Ribulose, Xylulose
Six	Hexoses	Glucose, Galactose, Mannose	Fructose
Seven	Heptoses	Glucoheptose, Galactoheptose	Sedoheptulose

So far we have learnt about the different types of monosaccharides. It is also important to understand that monosaccharides exist as isomers. We shall understand this concept better by learning next about the isomers of monosaccharides.

1.4.1 Isomerism of Monosaccharides

What do we mean by the term isomer? *Existence of different compounds having same molecular form but different structural forms are isomers.* Monosaccharides exhibit a variety of isomerism such as stereoisomerism, optical isomerism, aldose-ketose isomerism etc. These isomerisms are described as follows:

- *Aldose-ketose isomerism*

We have already seen that in a monosaccharide either an aldehyde ($-CHO$) or a ketone ($>C=O$) group is present. The former is called as *aldose* while the latter is known as *ketose*. Glucose and fructose both have the formula $C_6H_{12}O_6$ but glucose is an aldohexose (aldehyde bearing hexose) and fructose is a ketohexose (ketone bearing hexose), so they are isomers to one another. Figure 1.2 graphically represents this isomerism.

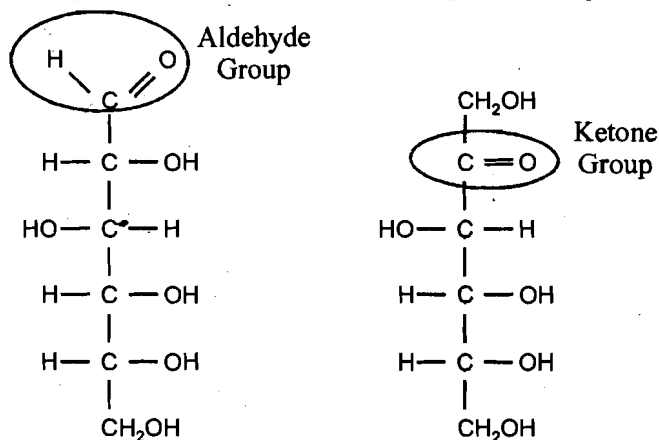


Figure 1.2: Aldose-Ketose isomerism

- *Stereo isomerism*

Stereo isomerism occurs when the same compound due to different spatial arrangement of the groups attached to its asymmetric carbon atom exists in more than one form.

First, let us understand what do we mean by an asymmetric carbon atom?

When any carbon atom of a compound is attached with four different groups or atoms, it is called as an asymmetric carbon atom. Look at Figure 1.3. Why is the C-2 atom the determining factor in this configuration? The carbon atom C-2 (marked here with an *), is unique since it has four different groups (OH, CHO, H, CH₂OH) attached and is therefore an asymmetric carbon. The C-2 atom is also called the *chiral* carbon atom.

According to this observation, monosaccharides may have two different forms namely '*D-sugar*' and '*L-sugar*', depending on their relation to the direction of the -OH group on the number 2 carbon atom as illustrated in Figure 1.3. The D form will have the -OH group next to the bottom carbon atom (primary alcohol group) on the right side while the L form will have it on the left side. The simplest three carbon atoms naturally occurring glyceraldehydes (as indicated in Figure 1.3) lack a plane of symmetry and exist as a pair of enantiomers (stereoisomers that are mirror image of one another) -D and L forms, which are the mirror images of each other. In this context, carbohydrates are chiral molecules since they have carbon atoms carrying four different groups. The majority of the monosaccharides occurring in mammalian metabolism are of D-configuration.

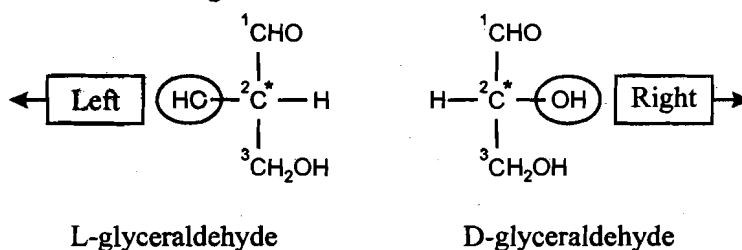


Figure 1.3: Structural isomerism of glyceraldehyde

Another type of stereo isomerism known as *epimerism* occurs with respect to a single asymmetric carbon atom of a monosaccharide possessing more than one asymmetric carbon atom. In Figure 1.4, there are three six carbon (hexose) sugars. Four carbon atoms (C-2, C-3, C-4 and C-5) are chiral atoms. These are structural isomers i.e. they have the same molecular formula of C₆H₁₂O₆, but different structural formula, and consequently they differ in their physical and chemical properties. Actually these isomers are formed as a result of interchange of the -OH and -H on carbon atoms 2, 3 and 4 of glucose. Glucose and galactose differ in the configuration of a single carbon atom (carbon atom 4) while glucose and mannose differ in C atom no. 2, as indicated in Figure 1.4. Compounds that differ in this manner are called as *epimers*.

In general, compounds with 'n' chiral carbon atoms have a maximum of 2ⁿ possible stereoisomers and half that many pair of enantiomers. For example, glucose an aldohexose has four chiral atoms and a total of 2⁴=16 possible stereoisomers (8 pairs of enantiomers).

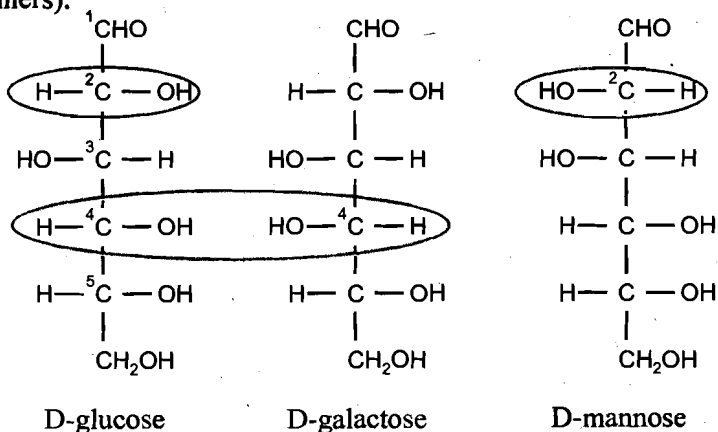


Figure 1.4: Epimerism of glucose, galactose and mannose

- *Optical isomerism*

A compound is said to have optical activity when it rotates the plane of vibration of the rays of polarized light passing through it. This in fact results due to the presence of asymmetric carbon atoms (carbon atom in a compound attached to four different groups or atoms) in the molecule.

Two compounds having a similar molecular formula may have different optical activity. When an optically active substance rotates the plane of polarized light in a clockwise direction, it is called as *dextrorotatory* or 'd isomer' of the substance and when it rotates the plane of polarized light in the anticlockwise direction, it is *laevorotatory* or 'l isomer' of the substance. The d and l isomers are also expressed as (+) and (-), respectively. If you look at Figure 1.3, the two forms of glyceraldehydes (D and L forms) rotate plane of polarized light in the opposite direction by the same amount. As it turns out, D-glyceraldehyde rotates the plane of polarized light to the right and is therefore, dextrorotatory, labeled as (+).

So far we have learnt about the different isomers of monosaccharides. You would notice that certain cyclic forms of monosaccharides are also present. These are explained next.

- *Cyclic form of monosaccharides*

Aldohexoses (eg. glucose and galactose), ketohexoses (eg. fructose) and aldopentoses (eg. ribose) in solution undergo cyclization when treated with equivalent amounts of alcohol and form a hemiacetal or a hemiketal in the aldose or ketose, respectively, linking the carbonyl carbon atom with the other carbon atom by a C-O-C linkage. This results in ring formation that is either a six membered ring with one oxygen atom (for aldohexoses) or five membered ring with one oxygen atom (for ketohexoses). The former is known as pyranose and the latter as furanose, as illustrated in Figure 1.5.

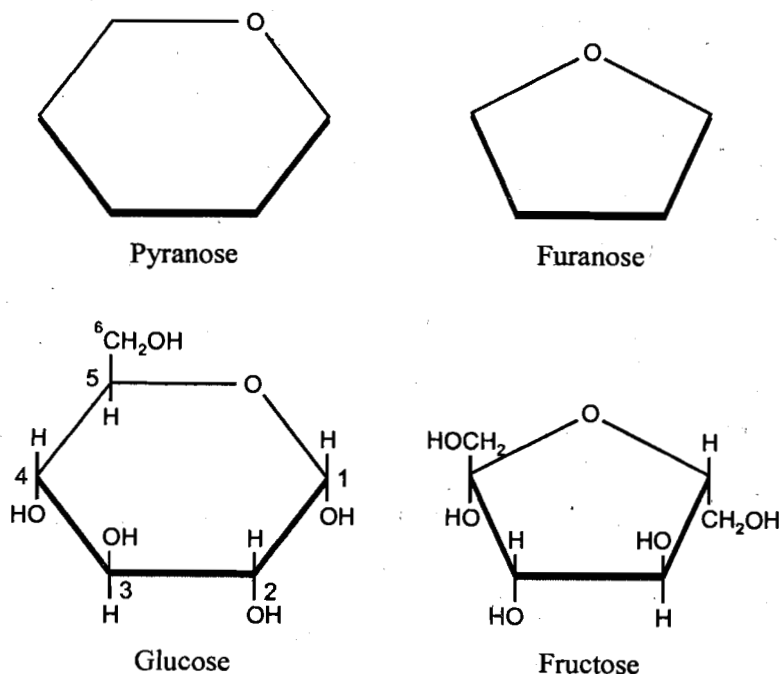


Figure 1.5: Ring structure of monosaccharides

Glucose, like all other monosaccharides, exists in two forms; the open chain form and the ring form, as illustrated in Figure 1.6.

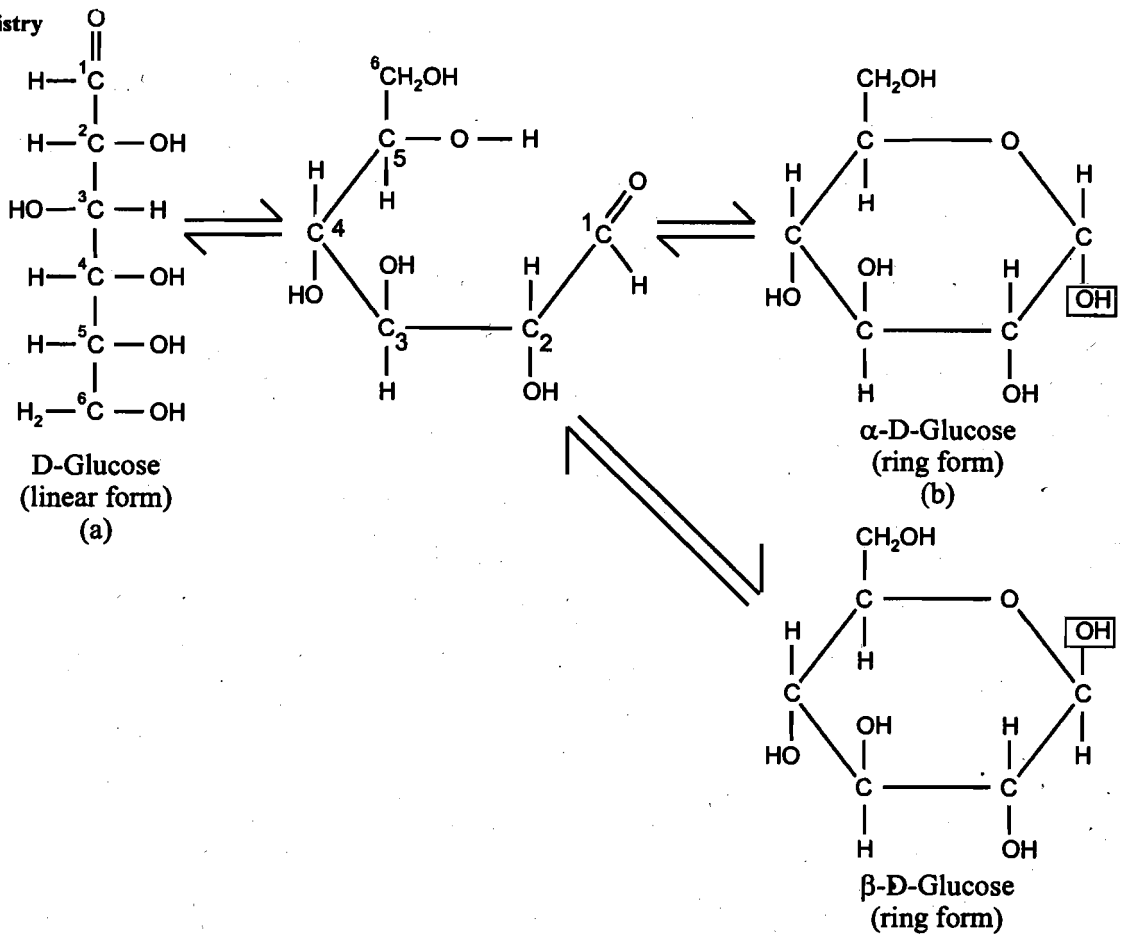


Figure 1.6: Open and ring form of glucose

The ring form has an additional asymmetric carbon atom called the 'anomeric carbon atom'. The asymmetry of C-1 makes possible the two ring forms, α and β , with different optical rotations (mutarotation). *Mutarotation is the process, whereby, the configuration of an anomeric carbon converts from α and β and vice-versa.* The α -form has the $-\text{OH}$ group on the reverse side in comparison to β -form at C-1, as highlighted in Figure 1.6. Thus ring form of sugars (hemiacetals) containing an asymmetric carbon atom can exist in α and β anomers. Anomers are *cyclic sugars that differ only in position of substituents at the hemiacetal carbon*; the α -form has the $-\text{OH}$ group on the opposite side from the $-\text{CH}_2\text{OH}$; the β -form has the $-\text{OH}$ group on the same side as the $-\text{CH}_2\text{OH}$ group, as is evident in Figures 1.6 and 1.7. Glucose in its pyranose form is called as α -D Glucopyranose. Fructose in its furanose form is called α -D Fructofuranose as shown in Figure 1.8.

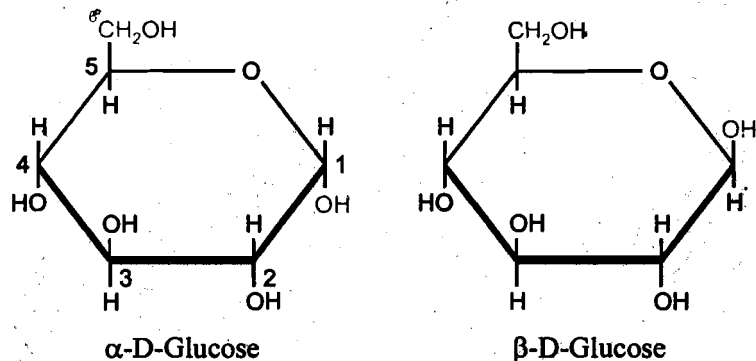


Figure 1.7: α and β anomers of D-glucose

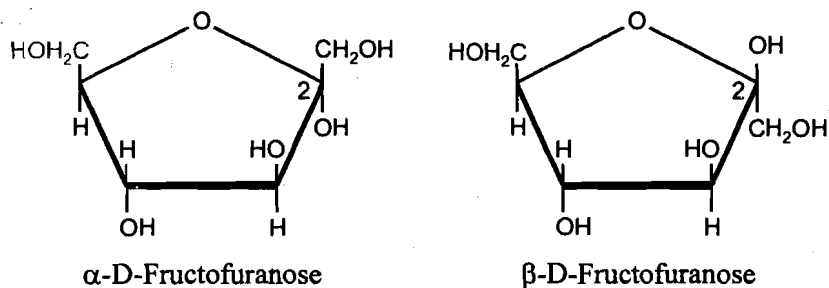


Figure 1.8: α and β anomers of Fructose

We have observed that monosaccharides can exist in different forms. Why do you think the study of these forms was important? The structure or the form in which monosaccharide is present influences the properties of monosaccharides. We shall learn about the properties of monosaccharides after answering the check your progress exercise 1.

Check Your Progress Exercise 1

- 1) What are simple sugars? Give their general formula.

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- 2) What do you understand by the term 'isomer'?

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Give examples of the following:

- a) Aldose-Ketose isomers

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- b) Epimers

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- 3) How would you classify a sugar as 'D' or 'L'?

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- 4) What is meant by the following terms? Explain by giving examples.

- a) Chiral carbon atom

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- b) Mutarotation

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1.4.2 Properties of Monosaccharides

Monosaccharides form water soluble, colourless, odourless, sweet crystals and show specific reactions of the aldehyde, or ketone and hydroxyl groups, which help to identify these compounds.

Some of the important reactions of monosaccharides are elucidated here.

- *Esterification*

As monosaccharides possess hydroxyl groups (–OH), they form esters with acids. Phosphoric acid esters of glucose and fructose have a great significance in nutritional biochemistry, as these are the metabolic intermediates of glucose or fructose. For example, Fructose-1, 6-bisphosphate. We will learn more about this later in Unit 6.

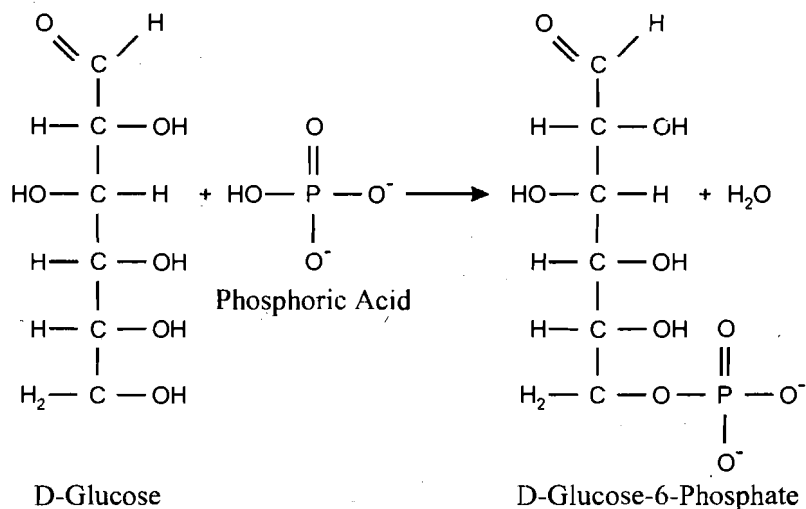


Figure 1.9: Esterification of glucose to Glucose-6-Phosphate

- *Oxidation reactions*

Mild oxidizing agents such as sodium hypiodite (NaOI) and bromine water oxidize aldoses to aldonic acids when –CHO (aldehyde group) of the aldose is converted to –COOH (carboxylic group). Glucose is oxidized to gluconic acid as shown in Figure 1.10.

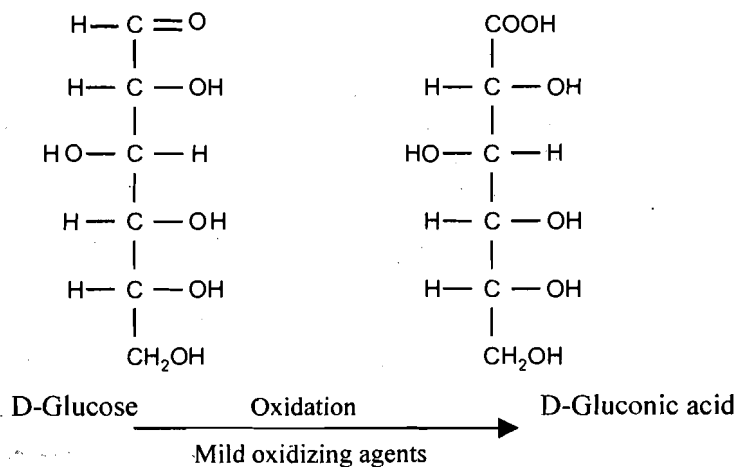


Figure 1.10: Oxidation of glucose to gluconic acid

On the other hand, strong oxidizing agents, such as nitric acid oxidizes aldose to glucaric acid (aldaric acid). See Figure 1.11 for reaction. Here both –CHO and –CH₂OH are oxidized to –COOH. Glucose is oxidized to glucaric acid. As ketoses do not undergo oxidation, this reaction may be used to distinguish an aldose from a ketose.

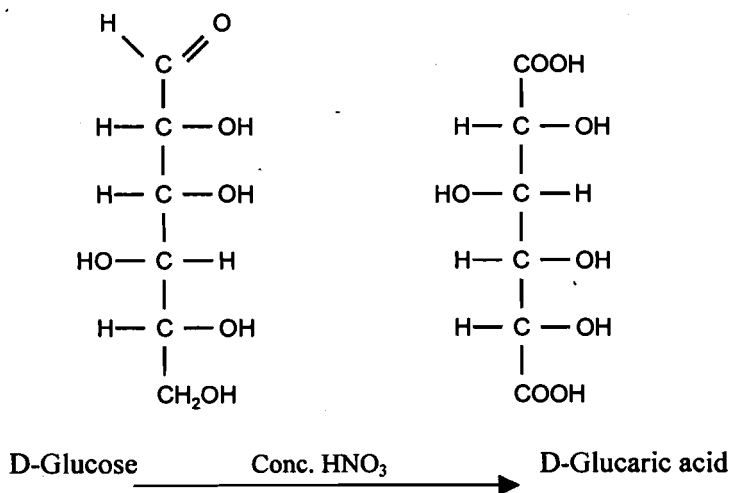


Figure 1.11: Nitric acid oxidation of glucose to glucaric acid

Dilute hydrochloric acid (HCl) oxidizes only the terminal $-\text{CH}_2\text{OH}$ group with the formation of uronic acid. Glucose is thus oxidized to glucuronic acid.

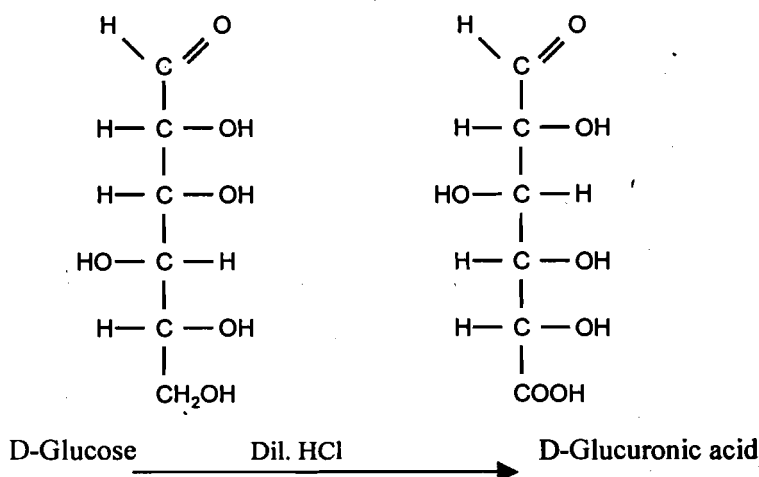


Figure 1.12: Oxidation of glucose to glucuronic acid

This is the basis of Fehling's test and explains the term *reducing sugar*. In Fehling's test, the free sugar group (aldehyde or ketone) reduces the Cu^{2+} (cupric) ions in an alkaline environment to form Cu_2O (cuprous oxide) and the sugar is itself oxidized to a carboxylic acid (mixture of sugar acids). The Cu_2O is red and precipitates. Carbohydrates that react in basic solution with oxidizing agents are classified as *reducing sugars*. In basic solution, all monosaccharides whether aldoses or ketoses, are reducing sugars. Simple sugars can act as reducing agents because the aldehyde or ketone group is readily oxidized to carboxylic acid.

• Reduction reaction

Aldoses and ketoses are reduced to the corresponding polyhydroxy alcohols by sodium borohydride, sodium amalgam, etc. So, in this reaction, as given in Figure 1.13, glucose is reduced to glucitol (sorbitol).

Polyhydric alcohols are also called sugar alcohols and are the hydrogenated forms of the aldoses or ketoses. Glucitol, also known as sorbitol, has the same linear structure as the chain form of glucose, but the aldehyde ($-\text{CHO}$) group is replaced with a $-\text{CH}_2\text{OH}$ group (at C-1). Sugar alcohols have about half the calories of sugars and are frequently used in low-calorie or "sugar-free" products.

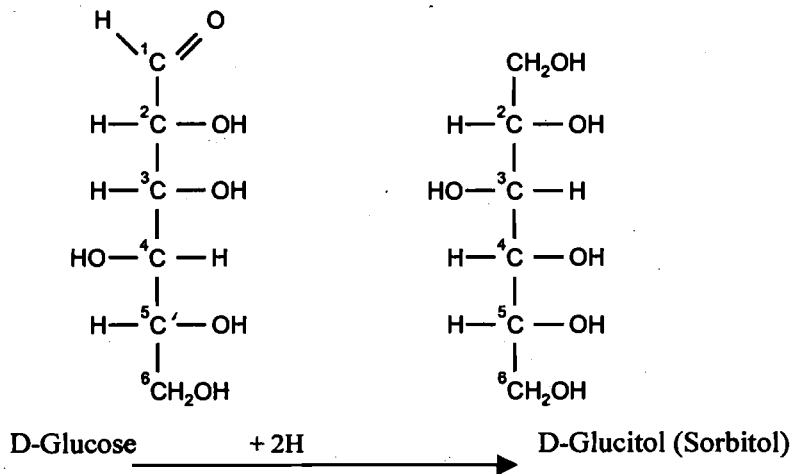


Figure 1.13: Reduction reaction of glucose

• *Osazone reaction*

When a monosaccharide (or a reducing disaccharide) is heated with phenylhydrazine (a mild oxidizing agent) in acetic acid, the carbonyl group of the monosaccharide reacts with phenylhydrazine to form a compound known as *osazone*. Osazones have characteristic yellow or orange microscopic crystals of specific melting points. This reaction can thus be utilized to identify different sugars.

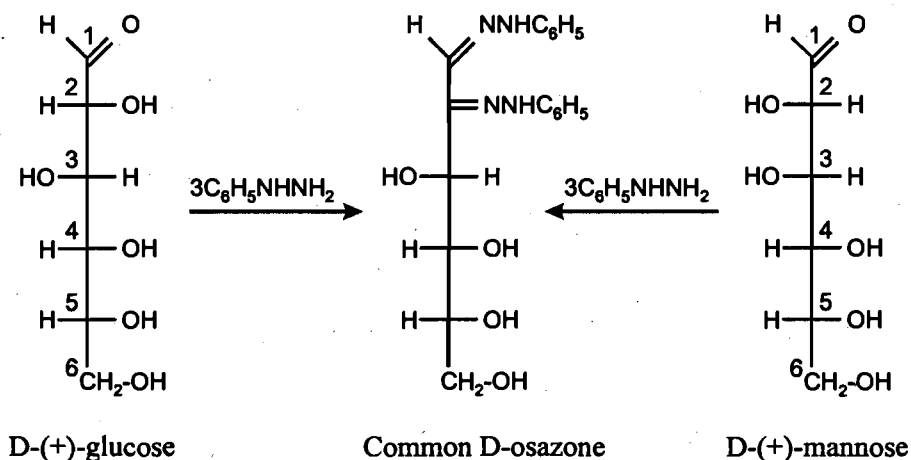


Figure 1.14: Formation of osazone

• *Furfural formation*

When treated with concentrated mineral acids, monosaccharides are transformed to a class of compounds known as furfurals.

Check Your Progress Exercise 2

1) Give any one test to distinguish a reducing sugar from a non-reducing sugar.

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2) What is the product formed by reduction of glucose? Also, give the corresponding reaction?

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- 3) Give a test that can be used to identify different sugars. Indicate the reaction involved using glucose as an example.
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We have studied about monosaccharides in last section. Next, let us get to know about the oligosaccharides, their structure and chemical properties.

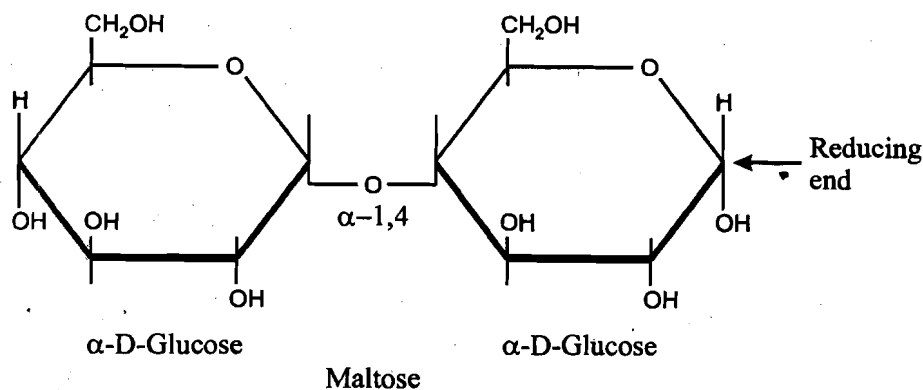
1.5 OLIGOSACCHARIDES

Oligosaccharides contain 2 to 6 monosaccharide units joined by a linkage known as *glycosidic (acetal) linkage*. On the basis of number of monosaccharides present, these are divided into disaccharides, trisaccharides etc. Disaccharides are the most important compounds in this group. These consist of two monosaccharide units/molecules joined by a glycosidic linkage. Depending on the nature of monosaccharides present, different disaccharides are formed as highlighted in the Table 1.2.

Table 1.2: Constituents of disaccharides

Disaccharides	Monosaccharides present
Maltose	Glucose (two molecules)
Lactose	Glucose, Galactose
Sucrose	Glucose, Fructose

The glycosidic linkage or bond is formed through a reaction between a $-OH$ group on the anomeric carbon of one unit and a $-OH$ group contributed by the other unit. In sucrose, the second $-OH$ group is also contributed by an anomeric carbon atom but in maltose and lactose, it is contributed by carbon atom 4. The configuration of the disaccharide glycosidic linkage depends on the anomeric form of the unit contributing the anomeric carbon atom. Thus exists $\alpha(1\rightarrow2)$ glycosidic linkage in sucrose (carbon 1 of glucose in the alpha orientation to carbon 2 in the beta form of fructose), $\alpha(1\rightarrow4)$ in maltose (2 glucose units joined from C1 to C4) and $\beta(1\rightarrow4)$ lactose. The figures in the brackets indicate the position of the glycosidic linkage between the two monosaccharide units. The configuration of the glycosidic linkage affects the chemical properties of the disaccharide. Disaccharides with free anomeric carbon atoms like monosaccharides, exhibit the characteristic reduction reaction of carbonyl group with Fehling's reagent and Benedict's reagents (an alkaline solution containing a cupric citrate complex ion). Sugars which reduce these reagents are called as '*reducing sugars*'. Sucrose, having no free anomeric carbon atom, does not respond to this reaction. Linkage of the disaccharides are shown in Figure 1.15.



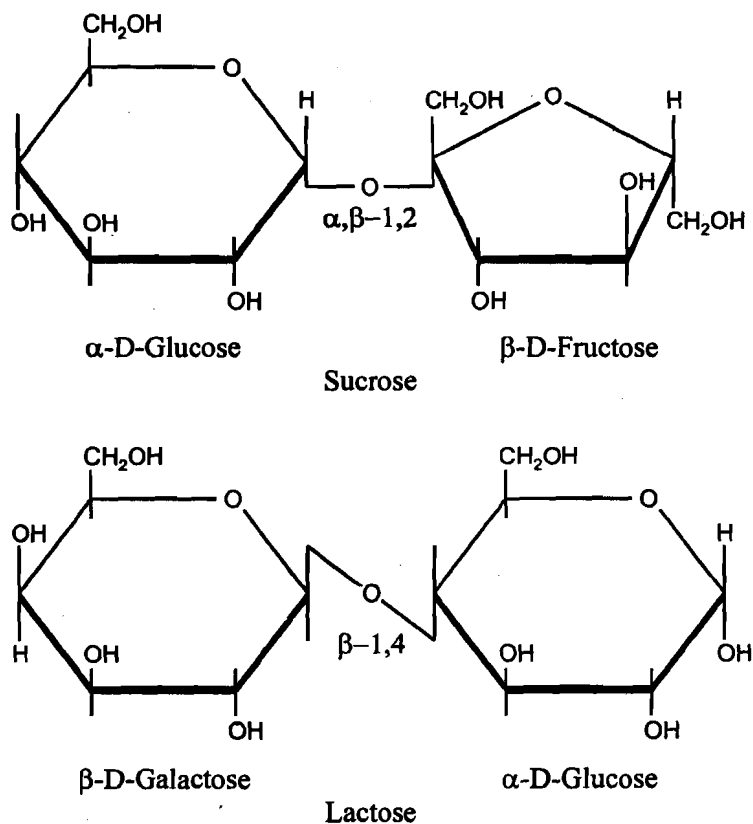


Figure 1.15: Structure of disaccharides

Besides disaccharides, some trisaccharides (possessing three monosaccharide units) are also freely available in nature. One important member of this group is raffinose, which is made up of the derivatives of galactose, glucose and fructose.

Disaccharides consist of characteristic anomeric forms of monosaccharide units. Sucrose consists of α -D-glucose and β -D-fructose, maltose consists of two α -D-glucose units while lactose consists of β -D-galactose and α or β -D-glucose units as shown in Figure 1.15.

Disaccharide molecules in which the second hexose unit has a free anomeric carbon atom may undergo mutarotation and the free anomeric carbon is capable of existing in α and β forms. Sucrose, however, is an exception as it has no free anomeric carbon.

Next, let us learn about polysaccharides.

1.6 POLYSACCHARIDES

Polysaccharides are produced when many monosaccharide units are joined together by glycosidic linkage. Chemically, polysaccharides are of two types:

- a) *Homopolysaccharides* or *homoglycans* which possess only one type of monosaccharides, such as starch, cellulose etc., and
- b) *Heteropolysaccharides* or *heteroglycans* which are formed by more than one type of monosaccharides, such as hyaluronic acid, heparin.

Table 1.3 lists the commonly occurring polysaccharides of different types.

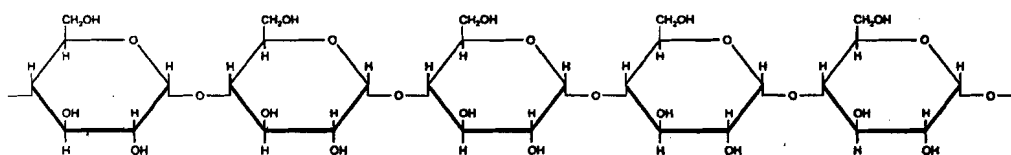
Table 1.3: Constituents of common polysaccharides

Polysaccharides	Monosaccharides present	
Homopolysaccharides	Starch	Glucose
	Cellulose	Glucose
	Glycogen	Glucose
	Dextrins	Glucose
	Inulin	Fructose
	Pectin	Methyl D-galacturonate
Heteropolysaccharides	Hyaluronic acid	Glucuronic acid, N-acetyl glucosamine
	Chondroitin sulphates	Glucuronic acid, 2-N-acetylamino galactose
	Heparin	Glucosamine, glucuronic acid

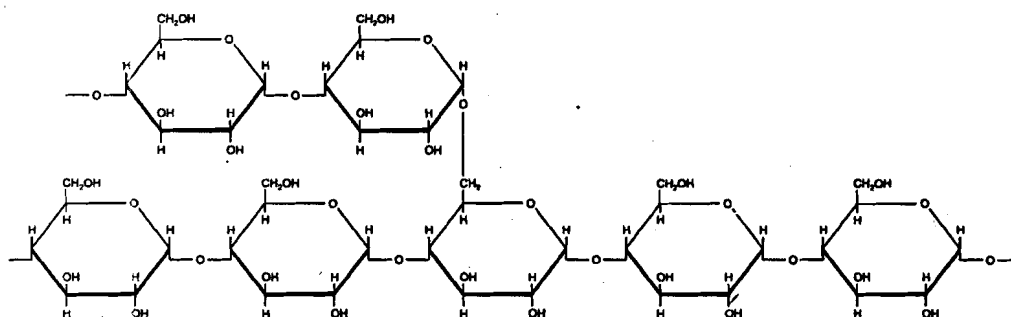
Let us move on to studying each of these polysaccharides – their components and structure. We shall begin our discussion with the most commonly known of these – starch.

• *Starch*

Starch is a plant polysaccharide synthesized by the plant through photosynthesis and stored mainly in grains, legumes, roots and tubers. Its molecular formula is $(C_6H_{10}O_5)_n$. Starch consists of two forms, amylose and amylopectin. Normally, 65-85% of the starch is amylopectin and only 15-35% is amylose. Amylose has a straight chain structure formed by 250-300 glucose residues linked together by $\alpha(1,4)$ glycosidic linkage as shown in Figure 1.16. In aqueous medium, it assumes a folded conformation. Amylopectin, on the other hand, is a highly branched polymer of glucose. In amylopectin molecule, branching occurs at intervals of 24-30 glucose residues. Glucose units of the main chain are joined by $\alpha(1,4)$ glycosidic linkage (similar to amylose) and the glucose units at the branch are joined by $\alpha(1,6)$ glycosidic linkages to the main chain (Figure 1.16). Amylopectin generally has about 3000-6000 glucose residues.



Amylose
(Glucose- $\alpha(1,4)$ -Glucose)



Amylopectin
(Glucose- $\alpha(1,4)$ and $\alpha(1,6)$ -Glucose)

Figure 1.16: Schematic diagram of amylose and amylopectin

Starch is not soluble in water and forms colloid in aqueous medium called as *micelles*. Iodine reacts with both amylose and amylopectin, but the former produces a complex that gives an intense blue colour and masks the violet colour of the complex formed by the latter. As a result, we observe a blue colour when starch reacts with iodine. This colour complex dissociates on heating and reforms again after cooling.

Starch is a non-reducing substance, as except one carbonyl group, all other carbonyl groups are involved in glycosidic bond formation. It may be hydrolyzed by boiling with hydrochloric acid or by the action of enzyme amylase ultimately to free glucose.

Now, we move on to cellulose – most abundant polymer of glucose, found only in plants.

- *Cellulose*

It is the main constituent of plant cell walls and the most common and abundant of the D-glucose polymers. This does not occur in the animal body. It is a homopolymer of glucose like starch, except the linkages joining the glucose units are $\beta(1 \rightarrow 4)$ rather than $\alpha(1 \rightarrow 4)$. Hence, cellulose is made up of β -glucose molecules linked by $\beta(1,4)$ glycosidic linkage as shown in Figure 1.17.

Due to the difference in the chemical structure, it is not acted upon by the enzyme amylase of the digestive juice. Strong hydrochloric acid hydrolyzes cellulose to glucose.

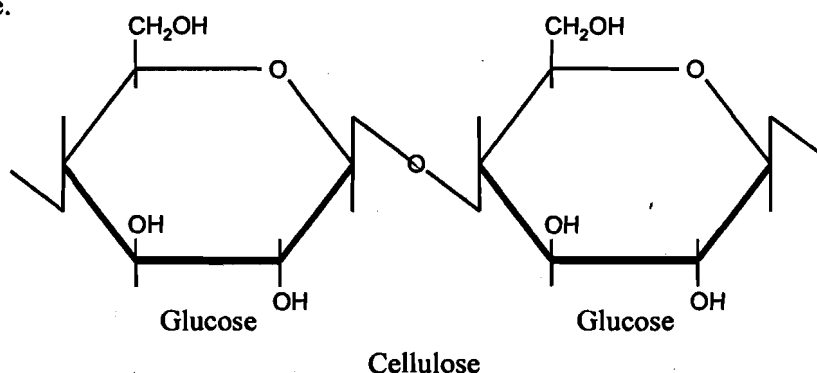


Figure 1.17: $\beta(1, 4)$ glycosidic linkage in cellulose

Glycogen is the storage polysaccharide found in the muscle and liver of animals and humans. It is a branched polymer having about 8 to 10 glucose units in each branch. Like amylopectin, its straight chains are formed by $\alpha(1,4)$ glycosidic linkages and $\alpha(1,6)$ glycosidic linkage exists at branch points. Thus, the chemical structure of glycogen and amylopectin are similar except that the former is more branched.

Each glycogen molecule may contain 5,000 to 10,000 glucose units. It is non-reducing, readily soluble in water and gives a red colour with iodine.

Now, we move on to the not-so-commonly known polysaccharides – dextrins and inulin.

- *Dextrins*

Dextrins are also polymers of D-glucose held by $\alpha(1, 4)$ glycosidic linkages. Dextrins are, in fact, formed due to partial hydrolysis of starch by enzymes such as salivary amylase, dilute mineral acids or heat.

Dextrins form sticky solutions in water and are frequently used as adhesives e.g. on postage stamps. They may have feeble reducing properties and when hydrolyzed, yield maltose and finally glucose.

Inulin is a plant polysaccharide made up of fructose, soluble in warm water and does not give any colour with iodine. Inulins are polymers consisting of fructose units that typically have a terminal glucose. Inulins have a sweet taste and are present in many vegetables and fruits, including onions, leeks, garlic, bananas, asparagus, chicory etc.

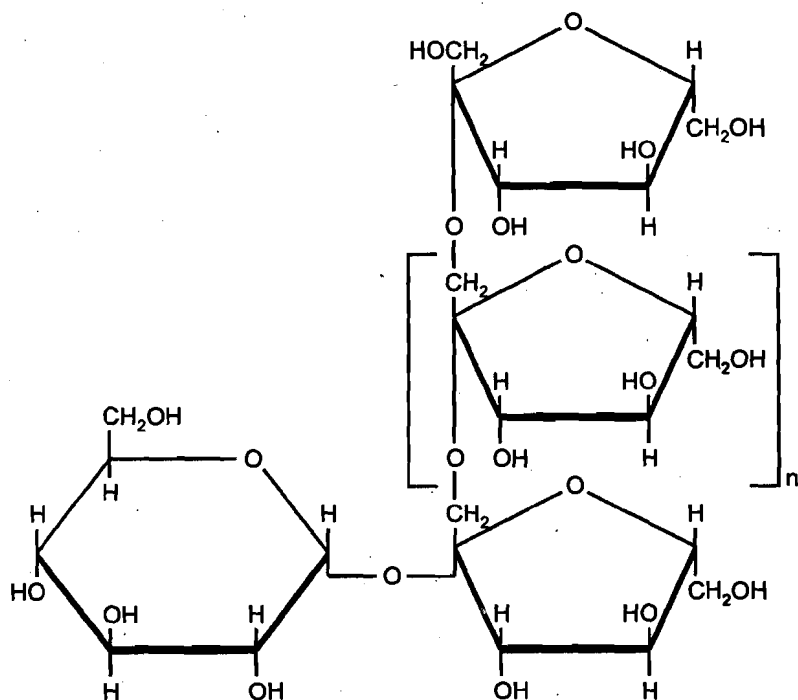


Figure 1.18: Inulin ($n = \text{approx. } 35$)

Check Your Progress Exercise 3

1) What are polysaccharides? What are its types? Explain giving examples.

.....

2) Differentiate between structural differences between amylose and amylopectin.

.....

3) What bonds exist in sucrose, dextrans and cellulose?

.....

4) What is a glycosidic linkage?

.....

Indicate which glycosidic linkage exists in the following compounds:

a) Lactose

b) Sucrose

c) Maltose

5) Explain briefly why sucrose cannot have α and β forms.

.....

With this, we come to an end on our discussion on carbohydrates. In the following units, we will discuss about other proximate principles-proteins and lipids and their characteristic features.

1.7 LET US SUM UP

In this unit, we got introduced to biochemistry as a discipline, its scope and relevance in context to dietetics. We started our discussion on carbohydrates which form an essential part of our diet. This discussion, as you would now know, included definition and classification of carbohydrates along with their structure and properties.

We learnt about various monosaccharides, disaccharides, their structure and chemical properties. We saw how we can distinguish these through different reactions. Finally, we discussed about various types of oligosaccharides and polysaccharides.

1.8 GLOSSARY

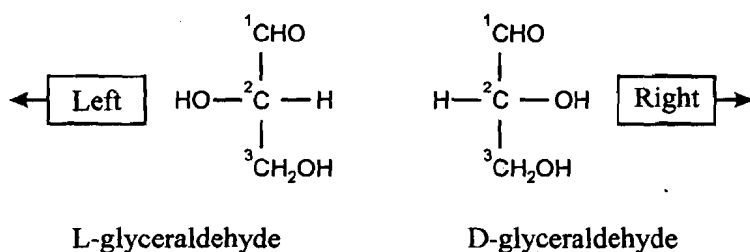
Asymmetric carbon atom	: a carbon atom attached with four different groups or atoms.
Biochemistry	: the chemistry of living organisms that covers all the chemical reactions occurring in our body.
Carbohydrates	: polyhydroxy aldehydes or ketones and their derivatives.
Dextrin	: polymers of D-glucose, formed due to partial hydrolysis of starch by enzymes.
Dextrorotatory	: when an optically active substance rotates the plane of polarized light in a clockwise direction.
Inulin	: plant polysaccharide of fructose units having a terminal glucose.
Isomer	: existence of different compounds having same molecular form but different structural forms.
Monosaccharides	: sugars consisting of a single polyhydroxy aldehyde or ketone unit.
Mutarotation	: the process whereby the configuration of an anomeric carbon converts from α and β and vice-versa.
Oligosaccharides	: compounds containing 2 to 6 monosaccharides units joined by a glycosidic linkage.
Phytoestrogens	: a group of compounds considered to offer protection against cancer.

1.9 ANSWERS TO CHECK YOUR PROGRESS EXERCISES

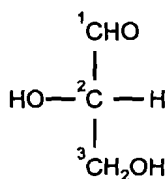
Check Your Progress Exercise 1

- Simple sugars are monosaccharides consisting of a single polyhydroxy aldehyde or ketone unit. Their general formula is $(\text{CH}_2\text{O})_n$ ($n=3$ to 7).
- Isomers are different compounds having same molecular form but different structural forms.
 - Glucose and Fructose
 - Glucose and Galactose

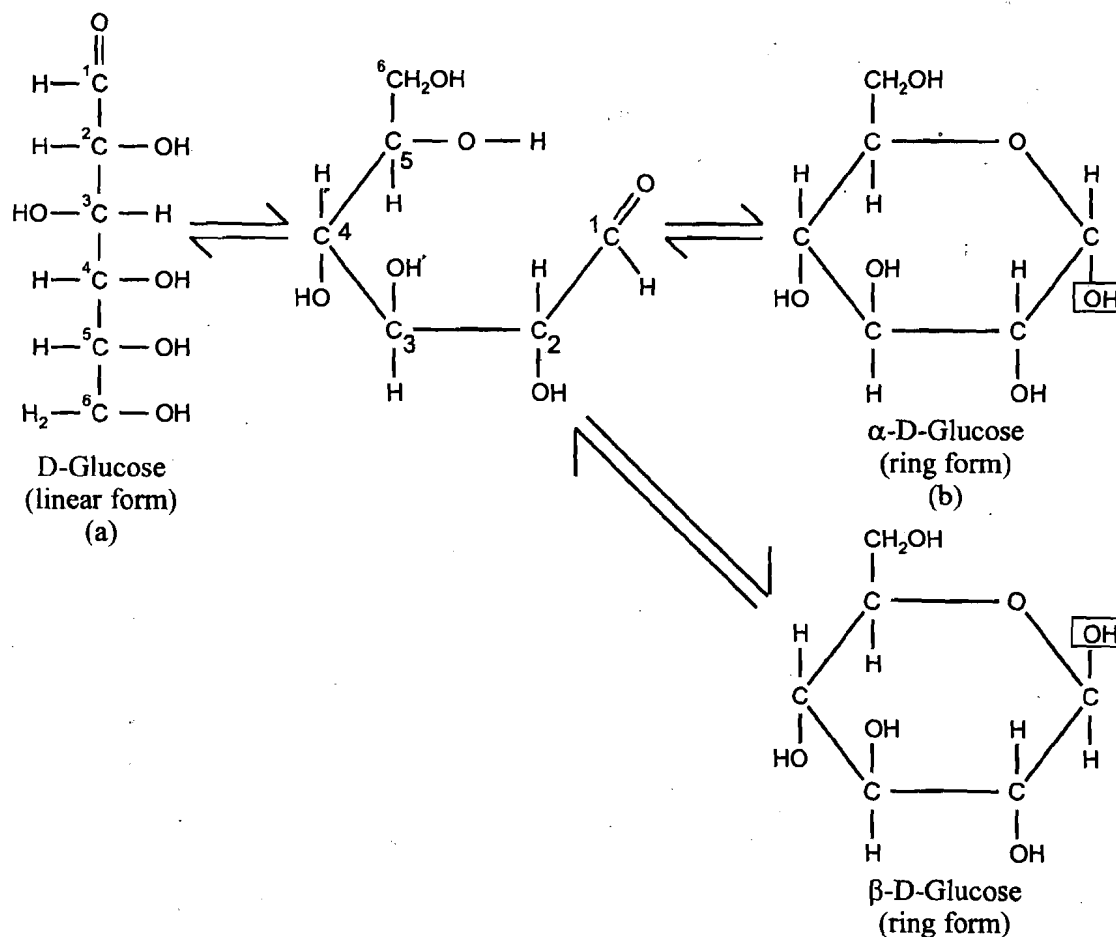
- 3) A sugar can be classified as '*D-sugar*' and '*L-sugar*', depending on their relation to the direction of the OH group on the carbon atom next to the primary alcohol group. The D form will have the -OH group of the bottom carbon atom next to the primary alcohol group on the right side while the L form will have it on the left side.



- 4) a) Any carbon atom of a compound attached with four different groups or atoms is referred to as chiral carbon atom. In the given figure, the C-2 atom is a chiral carbon atom, as it is attached with four different groups.



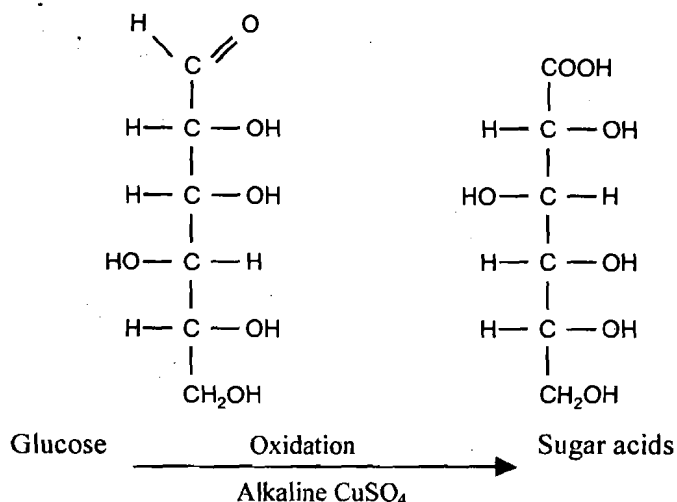
- b) Mutarotation is the process, whereby, the configuration of an anomeric carbon converts from α and β and vice-versa.



Check Your Progress Exercise 2

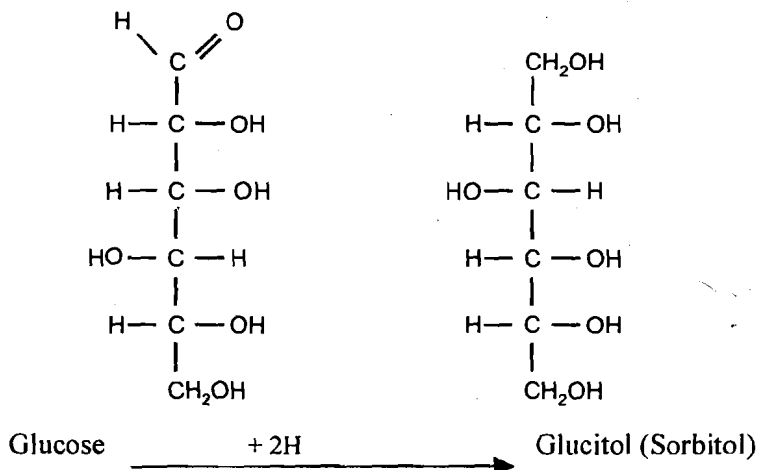
- 1) Fehling's test and osazone test are the tests to distinguish a reducing sugar from a non-reducing sugar. These tests can be discussed as:

- a) Fehling's Test: Fehling's solution (alkaline CuSO_4) oxidizes aldoses to mixture of sugar acids when $-\text{CHO}$ (aldehyde group) of the aldose is converted to $-\text{COOH}$ (carboxylic group).

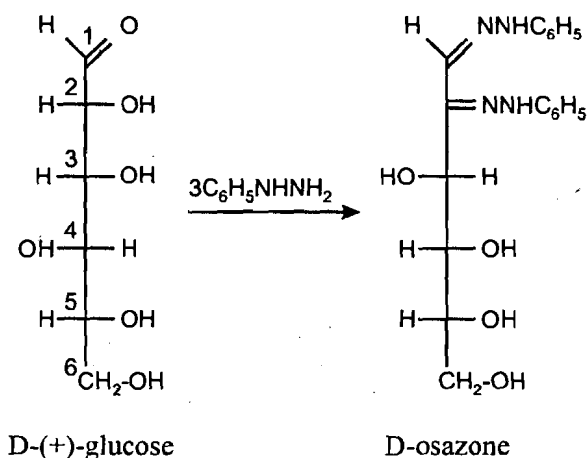


This is the basis of Fehling's test and explains the term *reducing sugar*. In Fehling's test the aldehyde reduces the Cu^{2+} ions in an alkaline environment to form Cu_2O and is itself oxidized to a carboxylic acid. The Cu_2O is red and precipitates. Carbohydrates that react in basic solution and bring about reduction are classified as reducing sugars.

- 2) Sorbitol (glucitol) is the product formed by the reduction of glucose. The reaction includes:



- 3) Osazone reaction can be used to identify different sugars. The reaction involving glucose is given below:



Check Your Progress Exercise 3

- 1) Polysaccharides are produced when many monosaccharide units are joined together by a glycosidic linkage. Chemically, polysaccharides are of two types:
 - a) Homopolysaccharides or homoglycans which possess only one type of monosaccharides, such as starch, cellulose etc., and
 - b) Heteropolysaccharides or heteroglycans which are formed by more than one types of monosaccharides, such as hyaluronic acid, heparin.
- 2) Amylose has a straight chain structure formed by 250-300 glucose residues linked together by $\alpha(1, 4)$ glycosidic linkage. In aqueous medium, it assumes a folded conformation. Amylopectin, on the other hand, is a highly branched polymer of glucose. In amylopectin molecule, branching occurs at intervals of 24-30 glucose residues.
- 3) Sucrose - $\alpha(1, 2)$
Dextrin - $\alpha(1, 4)$ and $\alpha(1, 6)$
Cellulose - $\beta(1, 4)$
- 4) The glycosidic linkage or bond is formed through a reaction between a $-OH$ on the anomeric carbon of one unit and a $-OH$ group contributed by the other unit.
 - a) Lactose - $\beta(1,4)$
 - b) Sucrose - $\alpha(1,2)$
 - c) Maltose - $\alpha(1,4)$
- 5) Sucrose cannot have α and β forms because it has no free anomeric carbon atom.