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Nutrition and Biochemistry *for Nurses*



2nd Edition

Jacob Anthikad

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2 CHAPTER

Chemistry of Carbohydrates

Carbohydrates include a large group of compounds commonly known as starch or sugars, which are widely distributed in plants and animals. Chemically, they are polyhydric alcohols having potentially active aldehyde and ketone groups. Because the ratio of hydrogen to oxygen in these compounds is often 2:1, having the empirical formula $C_n(H_2O)_n$, they are given the name carbohydrates or hydrates of carbon. In general, they are white solids, freely soluble in water with the exception of certain polysaccharides. Carbohydrates of lower molecular weights have a sweet taste.

There are practical reasons for the universal use of carbohydrates in diets. The yield of cereals, the primary source of carbohydrates, is high per unit area. Therefore they are widely available and are economic source of energy. They are easily packed and have a long shelf life when stored dry. They are mild flavored and combine well with other foods. Carbohydrate foods are easy to prepare.

BIOLOGICAL IMPORTANCE

1. Carbohydrates are the main sources of energy in the body. When carbohydrates are oxidized in the body, they liberate CO_2, water and energy. They are the least expensive source of energy to the body for muscular work. Each gram of carbohydrate provides 4 kcal of energy when oxidized. They supply the major portion of energy required by living cells. Brain cells and red blood cells (RBCs) wholly depend on glucose as energy source.
2. The body will use carbohydrates preferably as a source of energy when it is supplied in diet, thus sparing proteins for tissue building purposes.

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3. The main source of energy for central nervous system (CNS) is glucose. Prolonged hypoglycemia results in irreversible damage to brain tissue.
4. All carbohydrates are digested to form glucose before they can be absorbed into bloodsteam and get transported to different tissues of the body.
5. Glucose is the sugar of the blood and is excreted in urine in glycosuria.
6. Glucose is stored as glycogen in liver and muscles.
7. Some carbohydrates are necessary in the diet so that oxidation of fats can proceed normally.
8. Lactose has several functions in the gastrointestinal tract (GIT). It promotes the growth of desirable bacteria, some of which are necessary for the synthesis of vitamin B complex.
9. Though dietary fiber yields no nutrients to the body, it adds to the stimulation of peristaltic movement of GI tract and provides ruffage to avoid constipation.
10. Carbohydrates add flavor and variety to diet.

Sources of Carbohydrates

Carbohydrates, often called starch and sugars are widely distributed in plants and animals. In plants, they are produced by photosynthesis of water from the soil and CO_2 from air. The prefix 'photo' indicates the importance of sunlight in the process. Plants are thus the primary source of food in the world.

In animal cells, carbohydrate serves as an important source of energy. Animal tissues contain glycogen and body fluids contain glucose both of which are carbohydrates. Some carbohydrates have highly specific functions such as ribose in nucleic acids, galactose in some lipids and lactose of milk.

There are three main sources of carbohydrates.

1. *Starch:* These are present in cereals, roots and tubers, e.g. rice, wheat, ragi, pulses, tapioca, yam, colocasia and potatoes.
2. *Sugars:* Disaccharides, e.g. sucrose, lactose, maltose.
3. *Cellulose:* This is the tough fibrous lining found in vegetables, fruits and cereals. It is hard to digest and has no nutrition value. However, cellulose acts as ruffage and prevents constipation.

Glucose also known as dextrose is present in fruits and honey. It is the 'sugar' of the blood. Hydrolysis of cane sugar (sucrose), maltose, lactose and starch yield glucose.

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Fructose also known as levulose, is present in fruit juices and honey. It is obtained by hydrolysis of cane sugar.

Galactose is not found free in nature, its only source being hydrolysis of lactose, milk sugar. It also occurs in cerebrosides (glycolipids) present in brain and nerve tissue. Hence, it is nutritionally important.

Sucrose occurs in sugar cane, beetroot, carrot and pineapple. It is manufactured on large scale from sugar cane and beetroot.

Maltose is obtained from starch, germinating cereals and malt. Lactose is present in the milk of all mammals.

Balanced Diet

Carbohydrates rich in natural fiber should constitute 60% of energy requirements (calorie value). Proteins should give 15%–20% of daily energy needs and fats 20%–30% of the energy needs. Carbohydrates are the cheapest source of energy. Glucose derived from the digestion of carbohydrates is the main source of energy in the body. Hence, diet should contain adequate amounts of carbohydrates to meet a greater part of the energy needs.

Malnutrition for Deficiencies and Overconsumption

If the carbohydrate intake in diet is insufficient, it leads to malnutrition and other metabolic disorders. Tissue protein and fat will be used up for energy purposes. Excess carbohydrates leads to obesity.

TABLE 2.1: Monosaccharides

Simple sugars	*Formula*	*Aldo sugars*	*Keto sugars*
Trioses	$C_3H_6O_3$	Glycerose	Dihydroxyacetone
Tetroses	$C_4H_8O_4$	Erythrose	Erythrulose
Pentoses	$C_5H_{10}O_5$	Ribose	Ribulose
Hexoses	$C_6H_{12}O_6$	Glucose	Fructose

CHARACTERISTICS OF CARBOHYDRATES

Asymmetry

In the formula for glucose, it will be noted that a different group is attached to each of the 4 bonds of carbon atoms 2–5. A carbon atom to

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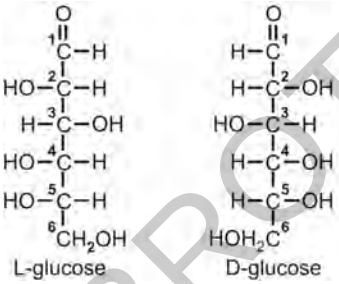
which 4 different atoms or groups of atoms are attached is called asymmetric carbon atom.

Isomerism

The presence of asymmetric carbon atoms in a compound makes possible the isomerism of that compound. Compounds, which are identical in composition and differ only in spatial configuration are called stereoisomers. Two such isomers of glucose, one of which is the mirror image of the other are shown below:



The form in which the hydroxyl group next to the primary hydroxyl is projected to the right of the carbon chain is the D-form, and the form in which it is projected to the left is the L-form.

Optical Isomerism

The presence of asymmetric carbon atoms also gives optical activity in the compound. When a beam of polarized light is passed through a solution exhibiting optical activity, it will be rotated to the right or left in accordance to the type of the compounds, i.e. optical isomer present. A compound, which causes rotation of polarized light to the right is said to be dextrorotatory designated by plus (+) sign. Rotation of beam of light to the left is levorotatory designated by minus (–) sign.

Mutarotation

Mutarotation is defined as a change in specific rotation of optically active solution without any change in other properties.

D-glucose in aqueous solution exists as an equilibrium mixture of five isomers.

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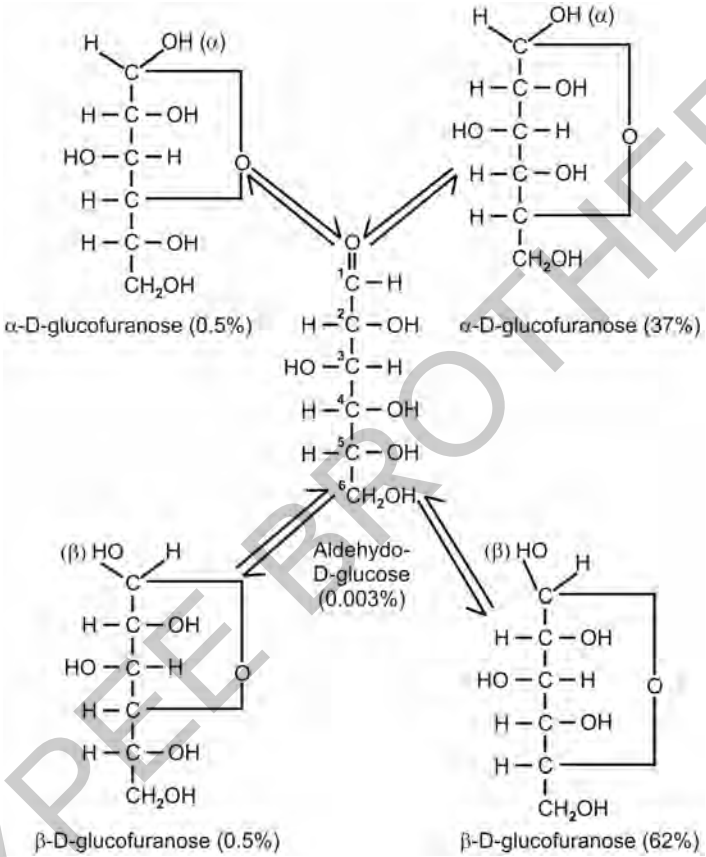
When glucose is dissolved in water, the optical rotation of the solution gradually changes and attains an equilibrium value. This change in the optical rotation is called mutarotation (invert sugar).



Cyclic Forms of Sugars

The close proximity of an aldehyde (or ketone) group and an alcohol group in the carbohydrate facilitates their reaction to give cyclic hemiacetals (or hemiketals). This can occur with the alcohol group of either carbon 4 or carbon 5.

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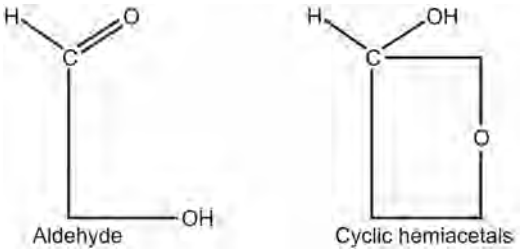
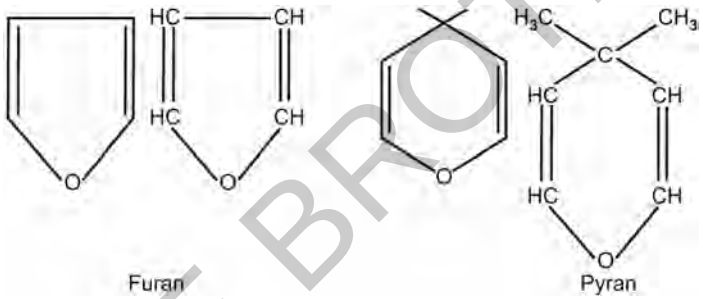
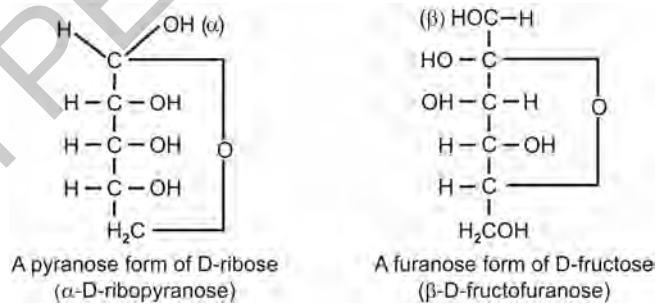


In the first case, a ring consisting of 4 carbon atoms and one oxygen atom is created. This is called furanose ring. In the second case, the ring contains 5 carbon atoms in addition to oxygen. This is called pyranose ring.



Because of the asymmetry present in the terminal carbon, 2 forms of each ring structure can exist.



Haworth Projections

Sir Walter Haworth in 1925 established that glucose is existing in biological systems not as a rectangle, but as a pyranose ring and was awarded

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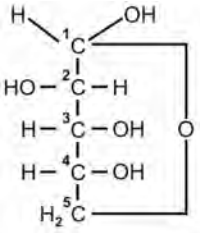
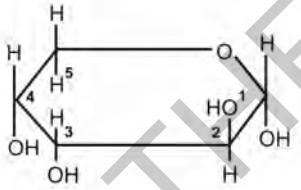
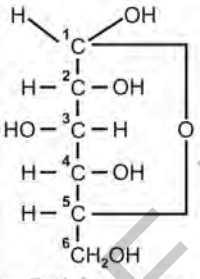
the Nobel Prize in 1937. To accurately represent the ring structure, the Haworth projections are used.

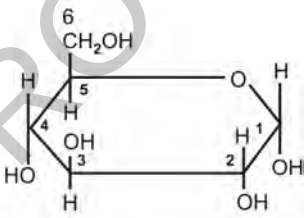
In Haworth projection, any group to the right of the carbon chain is written down and those to the left are written up. When there are more carbon atoms in the sugar than are involved in the ring formation, the rule is that if the ring is to the right, the extra carbon or carbon will be up.

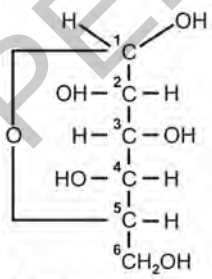




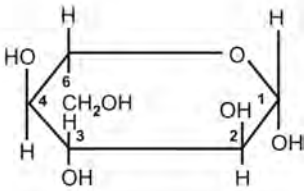


α-D-glucopyranose





β-L-glucopyranose



REACTIONS OF CARBOHYDRATES

The carbohydrates, being polyhydroxy aldehydes and ketones, generally are capable of undergoing all of the normal reactions of aldehydes

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and ketones, e.g. oxidation, reduction, dehydration, esterification, ether formation and addition to the carbonyl double bond.

Test for Carbohydrates (Molisch's Test)

To 2 mL of the unknown solution, add 2 drops of fresh 1% α-naphthol reagent and mix. Pour 2 mL of concentrated H_2SO_4 so as to form a layer below the mixture. A red violet ring indicates carbohydrate.

Reducing and Non-reducing Sugars

Any free aldehyde or α-hydroxy ketone is capable of being oxidized, thus causing the reduction of some other substances. Any of the sugars in the free aldehyde or ketone form, or in any other form in equilibrium with the free aldehyde or ketone (hemiacetal forms) can be oxidized.

Carbohydrates capable of undergoing oxidation without having to be hydrolyzed first, is a reducing sugar. Sugars like sucrose and trehalose are non-reducing disaccharide.

A variety of reagents can be used to carry out the oxidation of carbohydrates and be themselves reduced. The most common is the cupric ion (Cu^{++}), which is the active ingredient in Fehling's, Benedict's and Barfoed's reagents for the detection of reducing sugars. The reaction is as follows:

$$CuSO_4 \longrightarrow \underset{\text{Cupric}}{Cu^{++}} + SO_4^{--}$$

$$\text{Reducing sugar} + \underset{\text{Blue}}{2Cu^{++}} \longrightarrow \underset{\text{Cuprous}}{\text{Oxidized sugar} + 2Cu^{+}}$$

$$\underset{\text{Cuprous}}{2Cu^{+} + 2OH^{-}} \longrightarrow \underset{\text{Yellow}}{2CuOH} \longrightarrow \underset{\substack{\text{Cuprous}\\ \text{Oxide (red)}}}{Cu_2O\downarrow} + H_2O$$

$$\text{For example, } C_6H_{12}O_6 + 2CuO \longrightarrow C_6H_{12}O_7 + Cu_2O\downarrow$$

The color of the solution or precipitate gives an approximate amount of reducing sugars present in the solution. This can be estimated by the following tests.

Benedict's Test ($CuSO_4$, Sodium Citrate and Sodium Carbonate)

To 5 mL of the reagent in a test tube, add 8 drops of the urine sample. Place in a boiling water bath for 5 minutes. Observe the colors and report:

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Blue color	:	Nil
Green color	:	Up to 0.5% (+)
Yellow color	:	Up to 1.0% (++)
Orange color	:	Up to 1.5% (+++)
Red color	:	Up to 2.0% (++++)
Brick red precipitate	:	More than 2%

Barfoed's Test

Mix 5 mL of Barfoed's reagent (copper acetate in glacial acetic acid) with 0.5 mL of urine sample in a test tube.

Benedict's qualitative reagent contains cupric sulfate, sodium carbonate and sodium citrate, whereas Fehling's solution contains cupric sulfate, sodium carbonate and sodium potassium tartrate.

Sodium citrate in Benedict's reagent and sodium potassium tartrate (Rochelle salt) in Fehling's solution prevent the precipitation of cupric hydroxide or cupric carbonate by forming a deep blue solution, slightly dissociated complexes with the cupric ions. The complexes dissociate sufficiently to provide a continuous supply of readily available cupric ions for oxidation.

Osazone Formation

Heat 100°C phenylhydrazine reagent with 2 mL of a solution of sugar in a test tube for 30 minutes and examine the crystals with a microscope.

Reducing sugars can be distinguished from one another by phenylhydrazine test when characteristic osazones are formed. These osazones have characteristic crystal structures, melting points, precipitation time and show different crystalline form under a microscope.

Glucose, fructose and mannose give the same needle shaped, yellow osazone and they cannot be differentiated from one another by this test. But maltose gives sunflowered osazone while, lactose gives cotton ball-shaped osazone.

Oxidation

Oxidation of aldoses forms acids as end products. Oxidation of the aldehyde group forms aldonic acids. However, if the aldehyde group remains intact and primary alcohol group at the opposite end of the molecule is oxidized, uronic acids are formed. Heat in a boiling water bath for 5 minutes. Appearance of a red precipitation within 5 minutes indicates the presence of monosaccharides.

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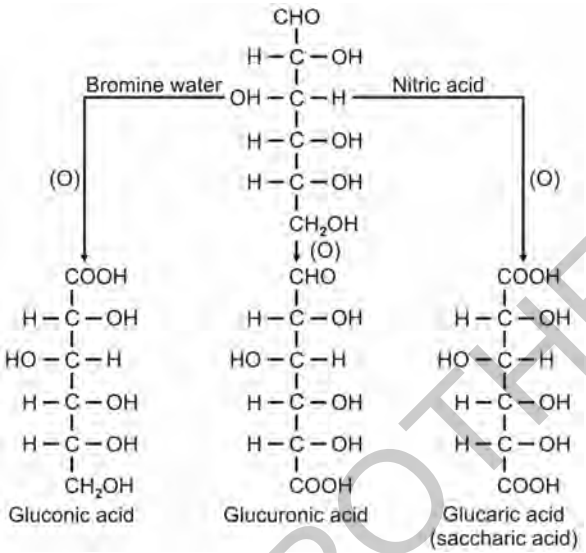
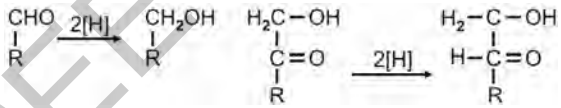


Reduction

The monosaccharides may be reduced to corresponding alcohols by reducing agents like sodium amalgam.



Glucose yields sorbitol, galactose yields dulcitol, and fructose yields mannitol and sorbitol.

CLASSIFICATION

Carbohydrates are classified into four major groups as below.

Monosaccharides

Monosaccharides, called simple sugars, are those which cannot be hydrolyzed into a simpler form. The general formula is $C_nH_{2n}O_n$. The simple sugars may be subdivided into trioses, tetroses, pentoses and hexoses

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N-sulfate, glucuronic acid and their sulfate esters).

Glycosidic linkages involving uronic acids or amino sugars are highly resistant to hydrolysis. Hence, polysaccharides containing these units are extremely stable and are present where chemical resistance and physical strength are needed, e.g. in skin, connective tissues, insect exo-skeletons, umbilical cord, etc.

QUESTIONS

1. **What are carbohydrates? What are their functions in living organisms?**
2. **Classify carbohydrates with examples. What is an asymmetric carbon atom?**
3. **What are the differences between mono, di and polysaccharides?**
4. **What are the differences between cellulose and starch?**
   Ans: In starch, the glucose units are linked by α (1-4) linkages. In cellulose the glucose units are linked by β-1,4 glycosidic linkages.
5. **Write short notes on:**
   A. Mucopolysaccharides.
   B. Mutarotation and its causes.
   C. Benedict's test.
6. **What is the difference between starch and glycogen?**

Starch	*Glycogen*
1. Plant origin.	1. Animal origin.
2. It is a branched molecule. Branching occurs after every 20–24 glucose units.	2. More branched than starch molecules. Branching occurs after every 8–10 glucose units.
3. Blue color with iodine solution.	3. Red color with iodine solution.

MULTIPLE CHOICE QUESTIONS

7. **Carbohydrates are the compounds of:**
   A. C, H, N and O
   B. C, H and O
   C. C, N and H
   D. N, H and O
8. **Which of the following is a monosaccharide?**
   A. Glucose
   B. Lactose
   C. Sucrose
   D. Maltose
9. **Monomer of cellulose is:**
   A. Lactose
   B. Maltose
   C. Fructose
   D. Glucose

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21. Shape of maltosazone is:

A. Sunflower shaped
B. Needle/broom shaped
C. Cotton ball shaped
D. Powder puff shaped

22. One of the following carbohydrates is not digested in the human gastro-intestinal (GI) tract:

A. Starch
B. Cellulose
C. Lactose
D. Sucrose

23. Following polysaccharide is naturally occurring anticoagulant:

A. Hyaluronic acid
B. Chondroitin sulfate
C. Heparin
D. Keratin sulfate

24. Blood group substances consist of N-acetyl-glucosamine, galactosamine, fucose, sialic acid and:

A. Glucose
B. Fructose
C. Galactose
D. Sucrose

25. Following are homopolysaccharides *except:*

A. Cellulose
B. Starch
C. Glycogen
D. Heparin

ANSWERS

7. (B)	8. (A)	9. (D)	10. (B)	11. (D)
12. (B)	13. (D)	14. (D)	15. (D)	16. (B)
17. (C)	18. (D)	19. (B)	20. (C)	21. (A)
22. (B)	23. (C)	24. (C)	25. (D)	

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