

Carbohydrates
Ref. Biochemistry
By
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What are carbohydrates?

Chemically, carbohydrates are defined as aldehyde or ketone derivatives of polyhydric alcohols or as compounds which yield these derivatives on hydrolysis. Carbohydrates are the 'most abundant bio-organic molecules in nature.

The term 'carbohydrate' is used due to the fact that chemically carbohydrates are the compounds of carbon (C), hydrogen (H) and oxygen (O) and most of the simpler carbohydrates have an empirical formula $(CH_2O)_n$ with hydrogen and oxygen in ratio of 2:1 as in water (H_2O), hence named 'hydrates of carbon'. The common examples of carbohydrates are ribose, glucose, fructose, galactose, sucrose, maltose, lactose, glycogen, starch, cellulose, inulin, etc. Some carbohydrates may also have nitrogen (N) and sulphur (S) in addition to carbon, hydrogen and oxygen, e.g. chitin and mucopolysaccharides such as chondroitin, heparin, dermatan sulphate, hyaluronic acid, etc. The carbohydrates are also called saccharides. The 'saccharide' term is derived from a Greek word 'sakaron' that means 'sugar'.

Occurrence: The carbohydrates are the most abundant bio-organic molecule in nature than any other organic molecule. They are chief source of energy and are widely distributed both in plants and animals. Cellulose, starch and sucrose are the most abundant carbohydrates in plants, whereas glucose and glycogen are the main carbohydrates present in higher animals. Starch and glycogen are most abundant 'storage polysaccharides' in plant and animals, respectively. Cellulose and chitin are most abundant 'structural polysaccharides' in plants and animals, respectively. Chitin is an important and major component of exoskeleton of arthropods, e.g. crabs, lobsters, prawns, insects such as ants, bees, moths, houseflies, bed bug, mosquitoes, etc. Arthropods are largest group of animals in Animal Kingdom. Chitin is believed to be the most abundant carbohydrate in nature after cellulose.

Classification: The carbohydrates are classified in four major groups on the basis of number of monosaccharide units.

1. Monosaccharides
2. Disaccharides
3. Oligosaccharides
4. Polysaccharides

1. Monosaccharides

These are simplest sugars which cannot be hydrolyzed further into simpler compounds. The common examples of monosaccharides are ribose, glucose, fructose, galactose, etc; glucose and fructose are the most abundant monosaccharides in nature. Monosaccharides have a general formula $C_nH_{2n}O_n$. On the basis of number of carbon atoms present (CH), the monosaccharides have been subdivided into trioses containing 3 carbon atoms, e.g. glyceraldehyde, tetroses containing 4 carbon atoms, e.g. erythrose and erythrulose, pentoses containing 5 carbon atoms, e.g.

ribose, ribulose, hexoses containing 6 carbon atoms, e.g. glucose, fructose, galactose, etc. and heptoses containing 7 carbon atoms, e.g. mannoheptose and sedoheptulose.

On the basis of presence of presence of aldehyde (-CHO) or ketone (—CO) group, the monosaccharides are of two types; (i) aldoses containing aldehyde group, e.g. glyceraldehyde, erythrose, ribose, xylose, glucose, mannoheptose, etc. and (ii) ketoses containing ketone group, e.g. dihydroxyacetone, erythrulose, ribulose, fructose, sedoheptulose, etc. Glyceraldehyde, also known as glyceros (an aldotriose) and dihydroxyacetone (a keto-triose) are simplest monosaccharides (Fig 4. 1)

All monosaccharides (both alcloses and ketoses) are reducing sugars due to presence of a free carbonyl group (either aldehyde or ketone group).

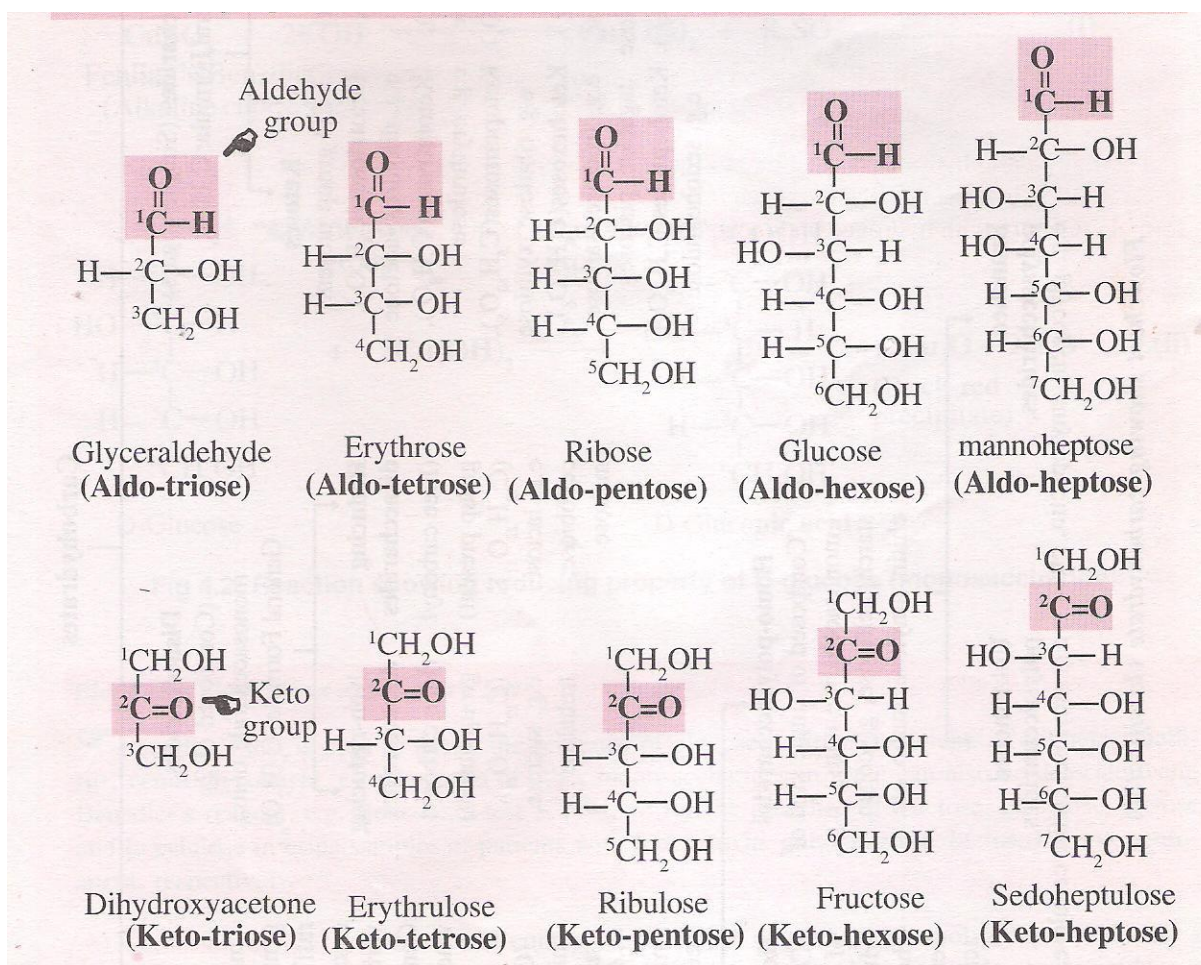


Fig.4.1 acyclic (linear chain) structures of some monosaccharides (aldoses and ketoses)

General properties of monosaccharides (in references to glucose)

(i) Taste and solubility: the monosaccharides are colorless crystalline solid, soluble in water but sparingly soluble in or insoluble in non-polar solvents like alcohols, benzene, ether, etc. Monosaccharides are relatively sweeter than other carbohydrates. Disaccharides are also soluble in water, but the polysaccharides are insoluble in water.

(ii) Reducing; property: Due to presence of a free carbonyl group (either —CHO or —CO group), all monosaccharides (both aldoses and ketoses) are reducing in nature and are called reducing sugars. All monosaccharides reduce the Fehling's and Benedict's reagents (alkaline CuSO_4) to cuprous oxide (Cu_2O), a brick-red precipitate. In this reaction, the cupric ions (Cu^{++}) of Fehling's and Benedict's reagents are reduced to cuprous ions (Cu^+) and the aldehyde group (—CHO) of D-glucose is oxidized to carboxylic group (—COOH) yielding D-gluconic acid (Fig 4.2); the aldoses are oxidized to yield aldonic acids.

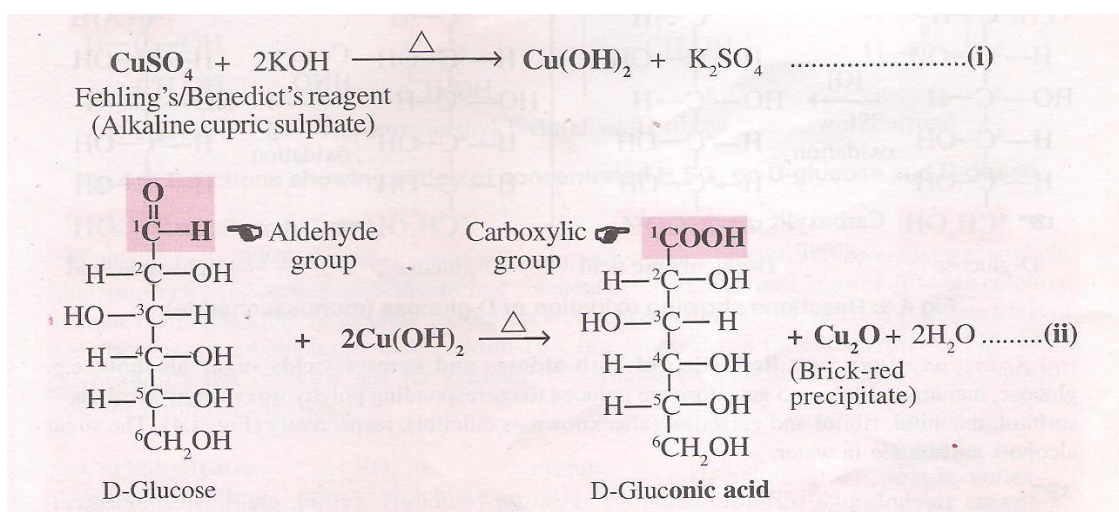
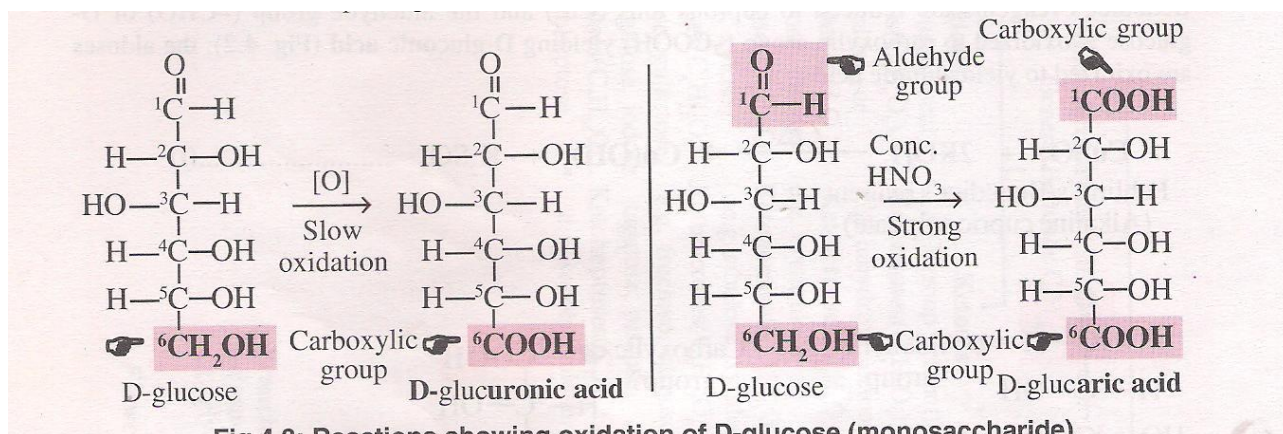


Fig. 4.2 reaction showing reducing property of D-glucose (monosaccharide)

Benedict's test is used to detect the presence of glucose in urine in patients of diabetes mellitus, renal glycosuria, etc. Presence of other monosaccharides in urine can also be detected using Benedict's reagent, e.g. Benedict's test is positive for the presence of fructose, galactose, lactose and L-xylulose in urine samples of patients with fructosuria, galactosernia, lactosuria and pantosuria, respectively.

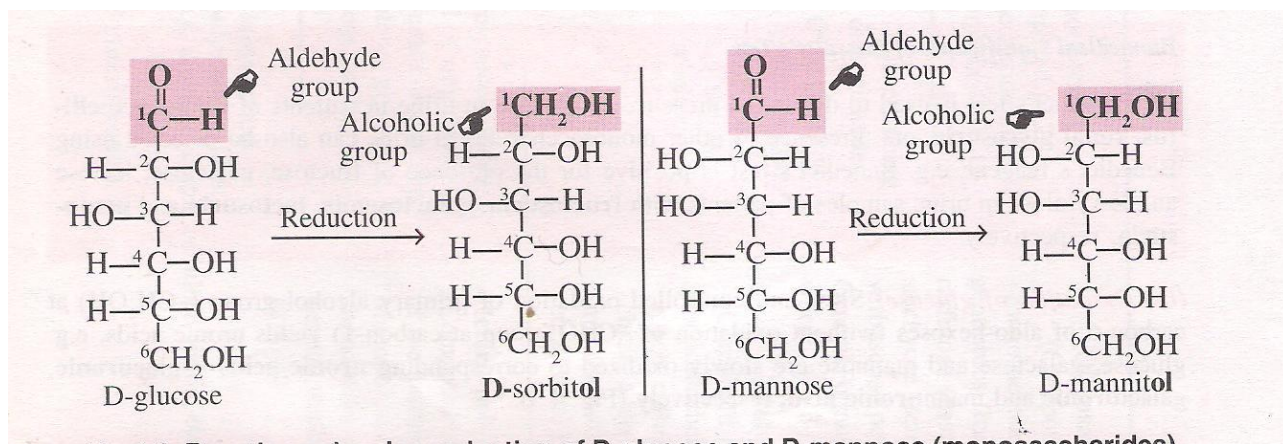
(iii) Oxidation of glucose: slow and controlled oxidation of primary alcohol group (—CH₂OH) at on-6 of aldo-hexoses (Without oxidation of —CHO group at carbon-1) yields **uronic acids**, e.g. glucose, galactose and mannose are slowly oxidized to corresponding **uronic acids**— glucuronic, galacturonic and mannuronic acid, respectively (Fig. 4.3).



Glucuronic, **galacturonic** and **mannuronic** acids are present in natural products, e.g. D-glucuronic acid is a component of mucopolysaccharides and D-galacturonic acid is constituent of pectins, plant gum and mucilages. Alginic acid is a polymer of D-mannuronic acid.

Oxidation of aldohexoses by strong oxidizing agent like concentrated HNO_3 yields sugar acids, known as **aldaric acid** or **saccharic acid**, e.g. glucose, galactose and mannose are oxidized in presence of concentrated HNO_3 to **glucaric acid** (or **glucosaccharic acid**), **galactaric acid** and **mannaric acid**, respectively (Fig. 4.3). Strong oxidation of aldo-hexoses by concentrated HNO_3 involves oxidation of both $-\text{CHO}$ and $-\text{CH}_2\text{OH}$ groups at carbon-1 and carbon-6, respectively. According to the aldaric system, the name of an acid derived from oxidation of a sugar ends with 'aric acid' replacing 'ose'.

(iv) Reduction of glucose: Reduction of both aldoses and ketoses yields sugar alcohols, e.g. glucose, mannose, ribose and galactose are reduced to corresponding polyhydroxy sugar alcohols-sorbitol, mannitol, ribitol and galactitol (also known as dulcitol-), respectively (Fig. 4.4). The sugar alcohols are soluble in water.



(v) Action of strong mineral acids on glucose: In presence of strong mineral acids like H_2SO_4 and HCl , monosaccharides are dehydrated to their furfurals, e.g. pentoses and hexoses are dehydrated to furfural and hydroxymethyl furfural, respectively (Fig. 4.5). Disaccharides, oligosaccharides - or polysaccharides, when treated with concentrated H_2SO_4 or HCl , also form furfurals. Actually, they are first hydrolyzed to their constituent monosaccharides and then the monosaccharides are dehydrated to corresponding furfurals.

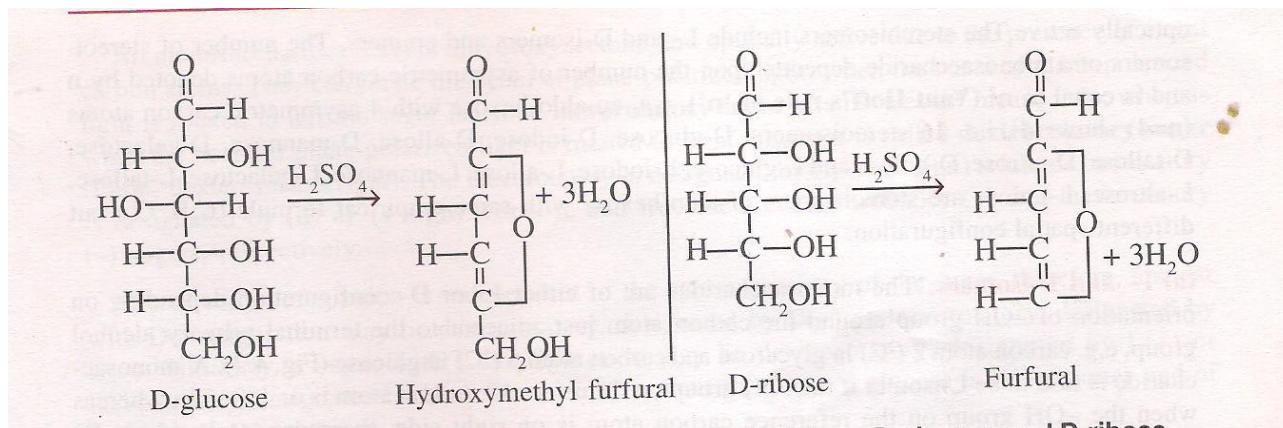


Fig.4.5 reactions showing action of concentrated H_2SO_4 on D-glucose and D-ribose

The furfural and hydroxymethylfurfural react with various phenol compounds, e.g naphthol, resorcinol and orcinol to yield different colored complex. The formation of different colored complex with phenolic compounds (in presence of concentration H_2SO_4 or $I-ICI$) form the basis of certain tests of carbohydrates such as Molisch's test (general test for carbohydrates; Fig. 4.6a), Seliwanoff's test (specific test for keto sugar D-fructose; Fig. 4.6b) and Bial's test (specific test for D-ribose; Fig. 4.6c).

- Carbohydrates $\xrightarrow{H_2SO_4}$ furfural $\xrightarrow{\alpha\text{-naphthol}}$ Deep-red/cherry
(Mono-,di-,oligo and polysacch.)

Fig. 4.6a: Formation of colored complex in **Molisch's test**.

- D-fructose $\xrightarrow[HCl]{\Delta}$ Hydroxymethylfurfural $\xrightarrow{\text{Resorcinol}}$ Deep red-cheery/red colored complex

Fig. 4.6b: Formation of colored complex in **Seliwanoff's test**.

- D-ribose $\xrightarrow[HCl]{\Delta}$ Furfural $\xrightarrow{\text{Orcinol}}$ Green color

Fig. 4.6c: Formation of colored complex in **Bial's test**.

(vi) Isomerism: All monosaccharides, except keto-triose, dihydroxyacetone have one or more asymmetric carbon atoms or chiral carbon atoms. The simplest sugar aldo-triose (glyceraldehyde, i.e. glycerose) contains one asymmetric carbon atom whereas aldo-tetroses (erythrose), -pentoses (ribose, xylose), aldo-hexoses (glucose, galactose) and aldo—heptose (mannoheptose) two, three, four and five asymmetric carbon atoms, respectively. Presence of asymmetric carbon atoms in monosaccharides allows the formation of isomers (stereoisomers and optical isomers). The compounds which have same empirical formula but differ in their spatial configuration are called stereoisomers whereas optical isomers are optically active. The stereoisomers include L- and D-isomers and epimers. The number of stereoisomers of a monosaccharide depends upon the number of asymmetric carbon atoms denoted by n and is equal to n^2 (Vant Hoff's rule of 'n'), e.g. an aldohexose with 4 asymmetric carbon atoms ($n=4$) shows 4^2 , i.e. 16 stereoisomers. D-glucose, D-iodose, D-allose, D-mannose, D-galactose, D-tallose, D-altrose, D-gulose and L-glucose, L-iodose, L-allose, L-mannose, L-galactose, L-tallose, L-altrose, L-gulose are stereoisomers of aldo-hexose with same empirical formula ($C_6H_{12}O_6$) but different spatial configuration.

(a) L- and D-isomers: The monosaccharides are of either L- or D- configuration depending on orientation of —OH group around the carbon atom just adjacent to the terminal primary alcohol group, e.g. carbon atom 2 (C₂) in glycerose and carbon atom 5 (C₅) in glucose (Fig. 4.7). A monosaccharide is said to be L-isomer if the OH group on the reference carbon atom is on left side, whereas when the OH group on the reference carbon atom is on right side, the monosaccharide is D- isomer (Fig. 4.7).

The D— and L-isomers of a sugar are mirror images of each other and are called enantiomers (Fig. 4.7). The marking of an isomer as D- or -L isomer is determined by its three-dimensional relationship to glyceraldehyde (glycerose), which is the parent compound of the carbohydrate family.

Majority of the monosaccharides present in mammals are D-isomers except L-xylulose (a metabolite of glucuronic acid pathway), L-fucose, 6-deoxy-L-galactose (constituents of glycoproteins) and L-iduronic acid (component of mucopolysaccharides, e.g. dermatan sulphate). In mammals, enzymes of carbohydrate metabolism are specific for D-isomers of sugars.

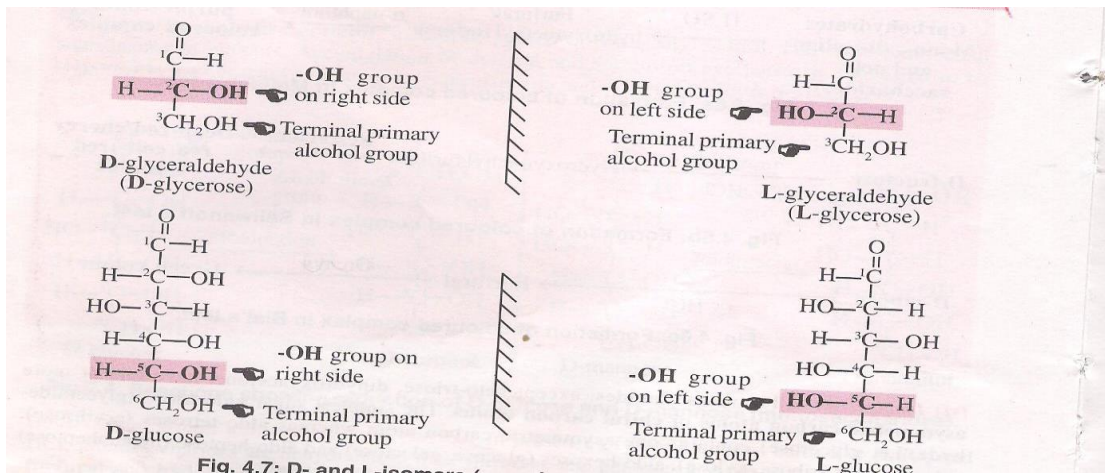


Fig. 4.7 showing D- and L- isomers of glycerose and glucose