



Study of Structure, Classification And Functions Of Carbohydrates

Md. Danish Eqbal, Department of Bio- Chemistry, Magadh University.

Dr.M.Z.SHAHZADA, Associate professor, Dept. of Chemistry, K.L.S.College Nawada.

Introduction : Carbohydrates, together with lipids, proteins and nucleic acids, are one of the four major classes of biologically essential organic molecules found in all living organisms. Carbohydrates, all coming from the process of photosynthesis, represent the major part of organic substance on Earth, are the most abundant organic components in the major part of fruits, vegetables, legumes and cereal grains, carry out many functions in all living organisms and are the major energy source in a Mediterranean-type diet. Finally, they provide flavor and texture in many processed foods.

Key Words : Carbohydrates, monosaccharides, oligosaccharides and polysaccharides

Chemical classification of carbohydrates

Carbohydrates, also called Carbs, are defined as aldehydic or ketonic compounds with a some number of oxydrilic groups (so polyhydroxy aldehydes or ketones as well).

Many of them, but not all, have general formula $(CH_2O)_n$ (only molecules with $n > 4$ are considered carbohydrates); some, in addition to carbon (C), oxygen (O) and hydrogen (H), include nitrogen or sulfur.

On the basis of the number of forming units, three major classes of carbohydrates can be defined: monosaccharides, oligosaccharides and polysaccharides.

Monosaccharides or simply sugars are formed by only one polyhydroxy aldehydeidic or ketonic unit. The most abundant monosaccharide is D-glucose, also called dextrose.

Monosaccharide are the simplest carbohydrates which contain free aldehyde (-CHO) and ketone ($>C=O$) groups that have two or more hydroxyl (-OH) groups. The general formula of monosaccharide is $C_n(H_2O)_n$. Monosaccharides are sugars that can not be further hydrolysed into simple carbohydrates. They can be classified on the basis of number of carbon atoms for example triose, tetrose, pentose hexose, heptoses etc. and on the basis of functional group they possess for example, aldoses (those having aldehyde groups) or ketoses (those having ketone groups)



Table1: Classification of monosaccharides

Name of sugar	Aldoses	Ketoses
Trioses (C ₃ H ₆ O ₃)	Glucose	Dihydroxy acetone
Tetroses (C ₄ H ₈ O ₄)	Erythrose	Erythulose
Pentoses (C ₅ H ₁₀ O ₅)	Ribose	Ribulose
Hexoses (C ₆ H ₁₂ O ₆)	Glucose	Fructose

Properties of monosaccharide

Monosaccharide exists in both as straight chain structure and cyclic structure (Figure 2). Sugars with five membered rings and with six membered rings are most stable. Cyclic structures are the result of hemiacetal formation by intermolecular reaction between carbonyl group and a hydroxyl group.

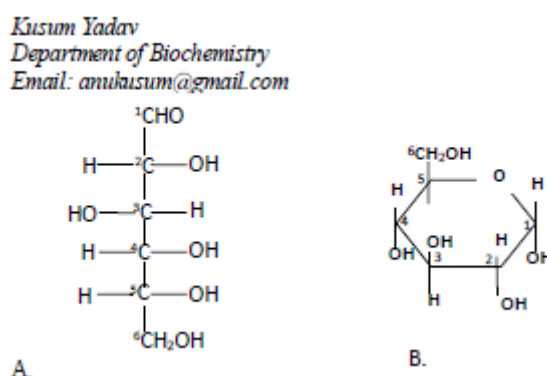


Figure 2: Structure of α -D-glucose. A. Straight chain B. Cyclic form

1. Chiral centre

All monosaccharide except dihydroxy acetone contain one or more asymmetric (chiral) carbon atoms thus are optically active isomers (enantiomers). A molecule with n chiral centres can have 2^n stereoisomers. Glyceraldehydewith one chiral centrehas $2^1=2$ and glucose with four chiral centres, have $2^4=16$ stereoisomers.

2. D and L isomerism

One of the two enantiomers of glyceraldehyde is designated the D isomers and the other L isomers. The orientation of the –OH group that is most distant from the carbonyl carbon determines whether the sugar belongs the D or L sugars. When the –OH group on this carbon is on the right the sugar is D isomers, when is on the left the sugar is L isomers. Most of sugars present in biological system are D sugars. The D and L forms of glucose is shown in Figure 3.

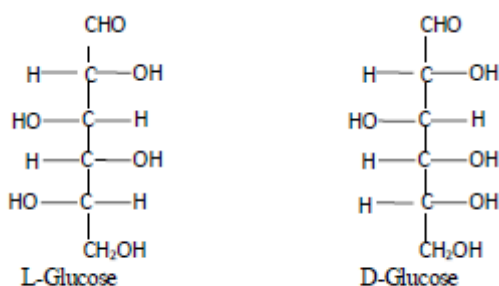


Figure 3: L and D forms of glucose.

3. Anomers

In aqueous solution all monosaccharide with five or more carbon atoms in the backbone occur as cyclic forms. Formation of cyclic structure is result of a reaction between alcohols and aldehydes or ketones to form derivatives called hemiacetal or hemiketals. The ring structure of monosaccharide are either similar to pyran (a six membered ring) or furan (a five membered ring). In linear form of monosaccharide, which is in equilibrium with the cyclic forms, the anomeric carbon is easily oxidised, making the sugar a reducing sugar. D-glucose exists in solution as an intramolecular hemiacetal in which the free –OH at C-5 has reacted with aldehyde C-1 producing two anomers called α and β (Figure 4). D-fructose also forms hemiketal in which –OH at C-5 has reacted with keto at C-2 producing two anomers called α and β (Figure 5).

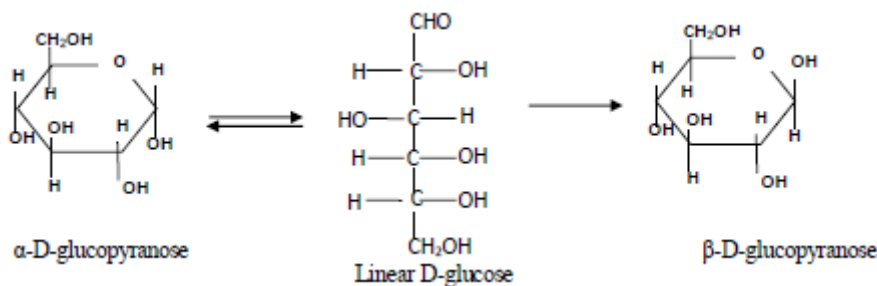


Figure 4: Two cyclic forms of glucose that are interconvertible in aqueous solution (mutarotation).

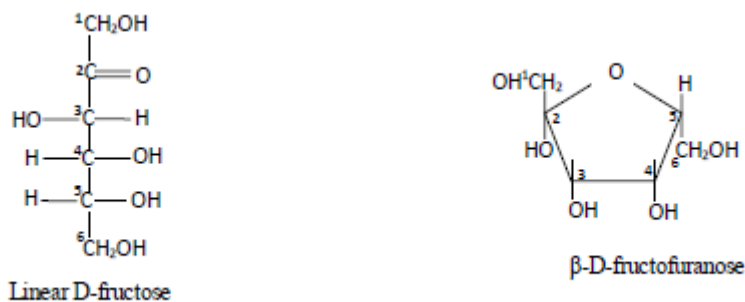


Figure 5: Structure of a ketohexose (fructose) and its cyclic hemiketal fructofuranose.



Oligosaccharides are formed by short chains of monosaccharidic units (from 2 to 20) linked one to the next by chemical bounds, called glycosidic bounds.

The most abundant oligosaccharides are disaccharides, formed by two monosaccharides, and especially in the human diet the most important are sucrose (common table sugar), lactose and maltose. Within cells many oligosaccharides formed by three or more units do not find themselves as free molecules but linked to other ones, lipids or proteins, to form glycoconjugates.

Polysaccharides are polymers consisting of 20 to 107 monosaccharidic units; they differ each other for the monosaccharides recurring in the structure, for the length and the degree of branching of chains or for the type of links between units.

Whereas in the plant kingdom several types of polysaccharides are present, in vertebrates there are only a small number. Depending of the functional roles they play, homopolysaccharides may further be classified as storage polysaccharides and structural polysaccharides. Storage polysaccharides serve as storage form of monosaccharide that is used as fuels. Starch is an example of storage polysaccharide in plants and glycogen is the storage polysaccharide in animals. Structural polysaccharides such as cellulose and chitin serve as structural elements in plant cell wall and animal exoskeleton, respectively. Heteropolysaccharides, unlike the homopolysaccharides, provide extracellular support for organisms. Heteropolysaccharides in the extracellular space of animal tissues form a matrix that holds individual cells together and provides shape, support and protection to the cells and tissues.

Dextrans

Dextrans are formed when some microorganisms like yeast and bacteria are grown in sucrose solution. It is made up of D-glucose residues but the molecular structure varies with type and strain of the microorganism forming them. Dextrans formed by majority of microorganisms is made up of $\alpha(1 \rightarrow 6)$ linked glucosides. All dextrans contain $\alpha(1 \rightarrow 3)$ branching points and some also contain $\alpha(1 \rightarrow 2)$ or $\alpha(1 \rightarrow 4)$ branches. Dextrans provide a source of glucose for bacterial metabolism. Synthetic dextrans are used in several commercial products (e.g. sephadex) that are used in the fractionation of proteins by size exclusion chromatography. The dextrans in these products are chemically cross-linkes to form insoluble materials of various sizes

Chitin



Chitin is the second most abundant polysaccharide in nature after cellulose. Chitin is main structural component of the exoskeleton of invertebrates such as crustaceans, insects and spiders. It is also main component of cell walls of most fungi. It is a linear polysaccharide of $\beta(1\rightarrow4)$ linked N-acetyl-D-glucosamine residues. Chitin and cellulose have similar structures except that C₂-OH group of cellulose is replaced by an acetamido group in chitin. Extensive hydrogen bonding of N-acetyl side chains makes chitin tough, and insoluble polymer. Like cellulose chitin is not degraded by vertebrate animals. Chitinases (enzyme present in gastric juice of snails or from bacteria) decompose the chitin to N-acetyl-D-glucosamine.

Functions

- They are used as material for energy storage and production.
- Starch and glycogen, respectively in plants and animals, are stored carbohydrates from which glucose can be mobilized for energy production. Glucose can supply energy both fueling ATP synthesis (ATP, the cell's energy currency, has inside a phosphorylated sugar) and in the form of reducing power as NADPH. It should be noted that glucose, used as energy source, “burns” without yielding metabolic wastes, being turned in CO₂ and water, and of course releasing energy.
- Monosaccharides supply 3.74 kcal/g, disaccharides 3.95 kcal/g, while starch 4.18 kcal/g; on average it is approached to 4 kcal/g.
- They exert a protein-saving action: if present in adequate amount in daily nourishment, the body does not utilize proteins for energy purpose, an anti-economic and “polluting” fuel because it will need to eliminate nitrogen (ammonia) and sulfur present in some aminoacids.
- Their presence is necessary for the normal lipid metabolism. More than 100 years ago Pasteur said: “Fats burn in the fire of carbohydrates“. This idea continues to receive confirmations from the recent scientific studies. Moreover, excess carbohydrates may be converted in fatty acids and triglycerides (processes that occur mostly in the liver).
- Glucose is indispensable for the maintenance of the integrity of nervous tissue (some central nervous system areas are able to use only glucose for energy production) and red blood cells.
- Two sugars, ribose and deoxyribose, are part of the bearing structure, respectively of the RNA and DNA and obviously find themselves in the nucleotide structure as well.



- They take part in detoxifying processes. For example, at hepatic level glucuronic acid, synthesized from glucose, combines with endogenous substances, as hormones, bilirubin etc., and exogenous substances, as chemical or bacterial toxins or drugs, making them atoxic, increasing their solubility and allowing their elimination.
- They are also found linked to many proteins and lipids. Within cells they act as signals that determine the metabolic fate or the intracellular localization of the molecules which are bound. On the cellular surface their presence is necessary for identification processes between cells that are involved e.g. in the recognition between spermatozoon and oocyte during fertilization, in the return of lymphocytes in the lymph nodes of provenance or still in the leukocyte adhesion to the lips of the lesion of a blood vessel.
- Two homopolysaccharides, cellulose (the most abundant polysaccharide in nature) and chitin (probably, next to cellulose, the second most abundant polysaccharide in nature), serve as structural elements, respectively, in plant cell walls and exoskeletons of nearly a million species of arthropods (e.g. insects, lobsters, and crabs).
- Heteropolysaccharides provide extracellular support for organisms of all kingdoms: in bacteria, the rigid layer of the cell wall is composed in part of a heteropolysaccharide contained two alternating monosaccharide units while in animals the extracellular space is occupied by several types of heteropolysaccharides, which form a matrix with numerous functions, as hold individual cells together and provide protection, support, and shape to cells, tissues, and organs.

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