

CARBOHYDRATES

Carbohydrates are the most abundant organic molecules in nature. They are primarily composed of the elements carbon, hydrogen and oxygen. The name carbohydrate literally means 'hydrates of carbon.' Carbohydrates may be defined as polyhydroxy- aldehydes or ketones or compounds which produce them on hydrolysis. The term 'sugar' is applied to carbohydrates soluble in water and sweet to taste.

Functions of carbohydrates:

Carbohydrates participate in a wide range of functions:

1. They are the most abundant dietary source of energy (4 Cal/g) for all organisms.
2. Carbohydrates are precursors for many organic compounds (fats, amino acids).
3. Carbohydrates (as glycoproteins and glycolipids) participate in the structure of cell membrane and cellular functions such as cell growth, adhesion and fertilization.
4. Carbohydrates also serve as the storage form of energy (glycogen) to meet the immediate energy demands of the body.

Classification of Carbohydrates:

Carbohydrates are often referred to as saccharides (Greek: sakcharon-sugar). They are broadly classified into 3 groups—monosaccharide's, oligosaccharides and polysaccharides. This categorization is based on the number of sugar units. Mono- and oligosaccharides are sweet to taste, crystalline in character and soluble in water, hence they are commonly known as sugars.

Monosaccharide's:

Monosaccharide's (Greek: mono-one) are the simplest group of carbohydrates and are often referred to as simple sugars. They have the general formula $C_n(H_2O)_n$, and they cannot be further hydrolysed. Based on the number of carbon atoms, the monosaccharide's are regarded as trioses (3C), tetroses (4C), pentoses (5C), hexoses (6C) and heptoses (7C). These terms along with functional groups are used while naming monosaccharide's. For instance, glucose is an aldohexose while fructose is a ketohexose.

Oligosaccharides:

Oligosaccharides (Greek: oligo-few) contain 2-10 monosaccharide molecules which are liberated on hydrolysis. Based on the number of monosaccharide units present, the oligosaccharides are further subdivided to disaccharides, tri- saccharides etc.

Polysaccharides:

Polysaccharides (Greek: poly-many) are polymers of monosaccharide units with high molecular weight (up to a million). They are usually tasteless (non-sugars) and form colloids with water. Polysaccharides are of two types—homopoly- saccharides and heteropolysaccharides.

Monosaccharide's:

Stereoisomerism is an important character of monosaccharide's. Stereoisomers are the compounds that have the same structural formulae but differ in their spatial configuration. A carbon is said to be asymmetric when it is attached to four different atoms or groups. The number of asymmetric carbon atoms (n) determines the possible isomers of a given compound which is equal to 2^n . Glucose contains 4 asymmetric carbons and thus has 16 isomers.

Glyceraldehyde— the reference carbohydrate:

Glyceraldehyde (triose) is the simplest monosaccharide with one asymmetric carbon atom. It exists as two stereoisomers, and has been chosen as the reference carbohydrate to represent the structure of all other carbohydrates.

D- and L-isomers:

The D- and L-isomers are mirror images of each other. The special orientation of —H and —OH groups on the carbon atom (C₅ for glucose) that is adjacent to the terminal primary alcohol carbon determines whether the sugar is D- or L-isomer. If the —OH group is on the right side, the sugar is of D-series, and if on the left side, it belongs to L-series. The structures of D- and L-glucose based on the reference monosaccharide, D- and L-glyceraldehyde (glycerose) are depicted in Fig. 65.1

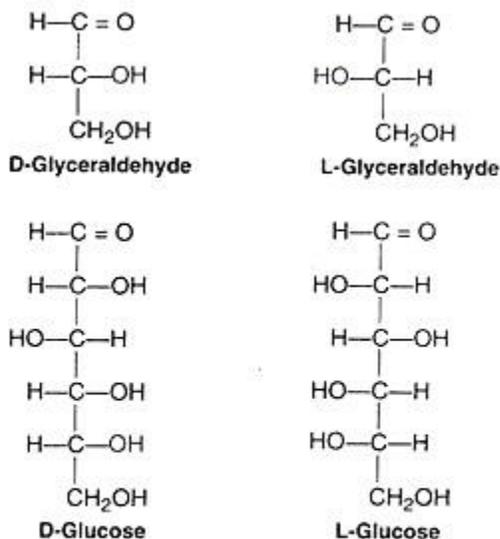


Fig. 65.1 : D- and L-forms of glucose compared with D- and L-glyceraldehydes (the reference carbohydrate).

It may be noted that the naturally occurring monosaccharide's in the mammalian tissues are mostly of D-configuration. The enzyme machinery of cells is specific to metabolize D-series of monosaccharide's.

Optical activity of sugars:

Optical activity is a characteristic feature of compounds with asymmetric carbon atom. When a beam of polarized light is passed through a solution of an optical isomer, it will be rotated either to the right or left. The term dextrorotatory (+) and levorotatory (-) are used to compounds that respectively rotate the plane of polarized light to the right or to the left.

Glycosides:

Glycosides are formed when the hemiacetal or hemiketal hydroxyl group (of anomeric carbon) of a carbohydrate reacts with a hydroxyl group of another carbohydrate or a non-carbohydrate (e.g. methyl alcohol, phenol, and glycerol). The bond so formed is known as glycosidic bond and the non-carbohydrate moiety (when present) is referred to as aglycone.

Derivatives of Monosaccharide's:

There are several derivatives of monosaccharide's, some of which are physiologically important:

1. Amino sugars:

When one or more hydroxyl groups of the monosaccharide's are replaced by amino groups, the products formed are amino sugars e.g. D-glucosamine, D-galactosamine. They are present as constituents of heteropoly- saccharides.

2. Deoxysugars:

These are the sugars that contain one oxygen less than that present in the parent molecule. The groups —CHOH and —CH₂OH become —CH₂ and —CH₃ due to the absence of oxygen. D-2-Deoxyribose is the most important deoxysugar since it is a structural constituent of DNA (in contrast to D-ribose in RNA).

3. L-Ascorbic acid (vitamin C):

This is a water- soluble vitamin, the structure of which closely resembles that of a monosaccharide.

Disaccharides:

Among the oligosaccharides, disaccharides are the most common. As is evident from the name, a disaccharide consists of two monosaccharide units (similar or dissimilar) held together by a glycosidic bond. They are crystalline, water-soluble and sweet to taste.

The disaccharides are of two types:

1. Reducing disaccharides with free aldehyde or keto group e.g. maltose, lactose.
2. Non-reducing disaccharides with no free aldehyde or keto group e.g. sucrose, trehalose.

Polysaccharides:

Polysaccharides (or simply glycans) consist of repeat units of monosaccharide's or their derivatives, held together by glycosidic bonds. They are primarily concerned with two important functions-structural, and storage of energy.

Polysaccharides are of two types:

1. Homopolysaccharides which on hydrolysis yield only a single type of monosaccharide. They are named based on the nature of the monosaccharide unit. Thus, glucans are polymers of glucose whereas fructosans are polymers of fructose.
2. Heteropolysaccharides on hydrolysis yield a mixture of a few monosaccharide's or their derivatives.

Homopolysaccharides:

Starch:

Starch is the carbohydrate reserve of plants which is the most important dietary source for higher animals, including man. High content of starch is found in cereals, roots, tubers, vegetables etc. Starch is a homopolymer composed of D-glucose units held by α -glycosidic bonds. It is known as glucosan or glucan.

Starch consists of two polysaccharide components-water soluble amylose (15-20%) and a water insoluble amylopectin (80-85%). Chemically, amylose is a long unbranched chain with 200-1,000 D-glucose units held by α (1 \rightarrow 4) glycosidic linkages. Amylopectin, on the other hand, is a branched chain with α (1 \rightarrow 6) glycosidic bonds at the branching points and α (1 \rightarrow 4) linkages everywhere else. Amylopectin molecule containing a few thousand glucose units looks like a branched tree (20-30 glucose units per branch).

Glycogen:

Glycogen is the carbohydrate reserve in animals, hence often referred to as animal starch. It is present in high concentration in liver, followed by muscle, brain etc. Glycogen is also found in plants that do not possess chlorophyll (e.g. yeast, fungi). The structure of glycogen is similar to that of amylopectin with more number of branches. Glucose is the repeating unit in glycogen joined together by α (1 \rightarrow 4) glycosidic bonds, and α (1 \rightarrow 6) glycosidic bonds at branching points.

Cellulose:

Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of plant cell wall. Cellulose is totally absent in animal body. Cellulose is composed of β -D-glucose units linked by β (1 \rightarrow 4) glycosidic bonds. Cellulose cannot be digested by mammals—including man— due to lack of the enzyme that cleaves β -glycosidic bonds (α amylase breaks α bonds only).

Certain ruminants and herbivorous animals contain microorganisms in the gut which produce enzymes that can cleave β -glycosidic bonds. Hydrolysis of cellulose yields a disaccharide cellobiose, followed by β -D-glucose.

Cellulose, though not digested, has great importance in human nutrition. It is a major constituent of fiber, the non-digestible carbohydrate. The functions of dietary fiber include decreasing the absorption of glucose and cholesterol from the intestine, besides increasing the bulk of feces.

Heteropolysaccharides:

When the polysaccharides are composed of different types of sugars or their derivatives, they are referred to as heteropolysaccharides or heteroglycans.

Mucopolysaccharides:

These are heteroglycans made up of repeating units of sugar derivatives, namely amino sugars and uronic acids. Mucopolysaccharides are more commonly known as glycosaminoglycan's (GAG). Acetylated amino groups, besides sulfate and carboxyl groups are generally present in GAG structure.

Some of the mucopolysaccharides are found in combination with proteins to form mucoproteins or mucoids or proteoglycans. Mucoproteins may contain up to 95% carbohydrate and 5% protein. Mucopolysaccharides are essential components of tissue structure.

The extracellular spaces of tissue (particularly connective tissue-cartilage, skin, blood vessels, and tendons) consist of collagen and elastin fibers embedded in a matrix or ground substance. The ground substance is predominantly composed of GAG. The important mucopolysaccharides include hyaluronic acid, chondroitin 4-sulfate, heparin, dermatan sulfate and keratan sulfate.