2

CARBOHYDRATES

2.1 INTRODUCTION

A carbohydrate is a large biological molecule, or macromolecule, consisting only of carbon (C), hydrogen (H), and oxygen (O), usually with a hydrogen:oxygen atom ratio of 2:1. Carbohydrates are technically hydrates of carbon, structurally it is more accurate to view them as polyhydroxy aldehydes and ketones.

OBJECTIVES

After reading this lesson, you will be able to:

- define carbohydrates
- classify Common Carbohydrates
- describe the sources and composition of carbohydrates
- explain the Digestion and absorption of carbohydrates.

2.2 DEFINITION

Carbohydrates are polyhydroxy aldehydes or ketones, or compounds that can be hydrolyzed to them. Carbohydrate is an organic compound comprising only carbon, hydrogen, and oxygen, usually with a hydrogen: oxygen atom ratio of 2:1 (as in water). Carbohydrates are technically hydrates of carbon. The empirical formula is $C_n(H_2O)_n$.

2.3 SOURCES OF CARBOHYDRATES

Baked goods commonly contain dietary starch and added sugar. Most dietary carbohydrates come from plants. Sugars and starches are nutritive carbohydrates, meaning they are broken down and utilized by the body, primarily to generate energy. Although dietary fiber is also a carbohydrate, it contributes no calories because it is not digested or absorbed.

2.3.1 Grain Products

Grain products are the leading source of carbohydrates in the diet. Grains naturally contain high concentrations of starch, which our gastrointestinal system breaks down into sugars. Common grains in diet include wheat, oats, rice, barley and cornmeal. Any food that includes grain or grain flour as a primary ingredient contains carbohydrates, such as bread and other baked goods, pasta, cereal, crackers. Choosing whole-grain products instead of those made from refined grains boosts your dietary fiber intake, which supports your heart and digestive health.

2.3.2 Starchy Vegetables and Beans

Beans and starchy vegetables, such as potatoes, yams, green peas, and corn, contain high levels of complex carbohydrates that our body digests into sugars. In addition, starchy vegetables and beans contribute vitamins, minerals and fiber to our diet. Dry beans also serve as a good source of lean dietary protein.

2.3.3 Fruits

All fruit and fruit juices contain carbohydrates in the form of natural sugars, such as glucose and fructose. Fruit sugars contribute nearly all of the calories contained in these foods. With persistently low consumption rates, fruit contributes less than 8 percent of the average daily calories in the diet. Fresh fruit is a healthier option than fruit juice because it provides more dietary fiber and less carbohydrate by volume.

2.3.4 Beverages

Dairy milk is the only significant source of dietary carbohydrates not derived from plants. A cup of unflavored milk contains about 11 to 12 grams of carbohydrate in the form of milk sugar, or lactose. Chocolate milk contains more than twice the amount of carbohydrate per cup compared to plain milk because sugar is added to sweeten the flavor. Sugar-sweetened soda, fruit drinks and sports and energy drinks substantially contribute to dietary carbohydrate intake. Wine, beer and liqueurs also contain carbohydrates. Dessert wines typically contain roughly four times the amount of carbohydrates found in table wines.

2.3.5 Sweets and added Sugars

Eating candy and desserts markedly boosts the number of carbohydrates in our diet. Indulging in a 1.6-ounce milk chocolate bar adds more than 26 grams of carbohydrates to our daily intake; a slice of cherry pie adds approximately 47 to 69 grams. Sugar added to processed foods that you may not consider sweet can be an unrecognized source of carbohydrates in our diet. Commercial pasta sauces, salad dressings, sandwich bread, energy and nutrition bars, cereals, heat-and-eat meals and other convenience foods commonly contain high-fructose corn syrup or another form of sugar for added flavor. Opting for whole, fresh foods rather than processed foods helps us avoid hidden carbohydrates.

2.4 CLASSIFICATION

Carbohydrates are classified into following classes depending upon whether these undergo hydrolysis and if so on the number of products form:

Monosaccharides, Disaccharides, Trisaccharides, Oligosaccharides, Polysaccharides

2.4.1 Monosaccharides

Molecules having only one actual or potential sugar group are called monosaccharides. They are simple carbohydrates that cannot be hydrolyzed further into polyhydroxy aldehydes or ketone unit

Sugars having aldehyde group are called aldoses and sugars with keto group are called ketoses. Depending on the number of carbon atoms monosaccharides are named as triose (C_3), tetrose (C_4), pentose (C_5), hexose (C_6), heptose (C_7) and so on.

Monosaccharide classifications based on the number of carbons

Number of Carbons	Category Name	Examples
4	Tetrose	Erythrose, Threose
5	Pentose	Arabinose, Ribose, Ribulose, Xylose, Xylulose, Lyxose
6	Hexose	Allose, Altrose, Fructose, Galactose, Glucose, Gulose, Idose, Mannose, Sorbose, Talose, Tagatose
7	Heptose	Sedoheptulose, Mannoheptulose

INTEXT QUESTIONS 2.1

1. Carbohydrate consists of ...., ... & .... molecule
2. Hydrogen Oxygen atom ratio in Carbohydrate is ....
3. Molecules having only one actual sugar group is called as ....
4. Sugars having aldehyde group is called as ....
5. Sugars with keto group is called as ....
6. Match the following

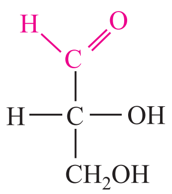
1.	Monosaccharides with six carbons	(a)	Tetrose
2.	Monosaccharides with four carbons	(b)	Heptose
3.	Monosaccharides with five carbons	(c)	Hexose
4.	Monosaccharides with seven carbons	(d)	Pentose

7. Match the following

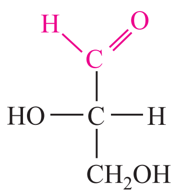
1.	Hexose	(a)	Erythrose
2.	Heptose	(b)	Ribose
3.	Tetrose	(c)	Mannoheptulose
4.	Pentose	(d)	Fructose

2.4.2 Sterioisomers

Compounds having same structural formula but differing in spatial configuration are known as sterioisomers. While writing the molecular formula of monosaccharides, the spatial arrangements of H and OH groups are important, since they contain asymmetric carbon atoms. Asymmetric carbon means four different groups are attached to the same carbon. The reference molecule is glyceraldehyde which has a single asymmetric carbon.



D (+)



L (–)

glyceraldehyde

The number of possible sterioisomers depends on the number of asymmetric carbon atoms by the formula 2^n where n is the number of asymmetric carbon atoms

Reference carbon atom of sugars

The configuration of H and OH at the second carbon of glyceraldehyde will form two mirror images, they are denoted as D and L varieties. All monosaccharides are molecules derived from glyceraldehyde by successive addition of carbon atoms. Therefore the penultimate carbon atom is the reference carbon atom for naming the mirror images. This is also referred to as absolute configuration.

Optical activity

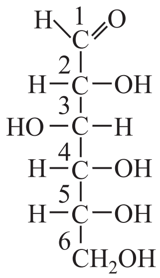
The presence of asymmetrical carbon atom causes optical activity. When a beam of plane polarized light is passed through a solution of carbohydrates, it will rotate the light either to right or to left. Depending on the rotation, molecules are called dextrorotatory (+) (d) or levorotatory (–).

Racemic mixture

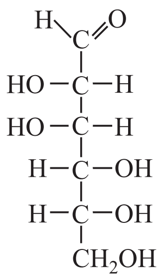
Equimolecular mixture of optical isomers has no net rotation and hence it is called as racemic mixture.

Epimers

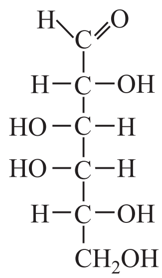
When sugars are different from one another, only in configuration with regard to the single carbon atom, other than the reference carbon atom, they are called Epimers. Example Glucose and Mannose are an epimeric pair which differ only with respect to C_2. Similarly galactose is the fourth epimer of glucose



D-Glucose



D-Mannose

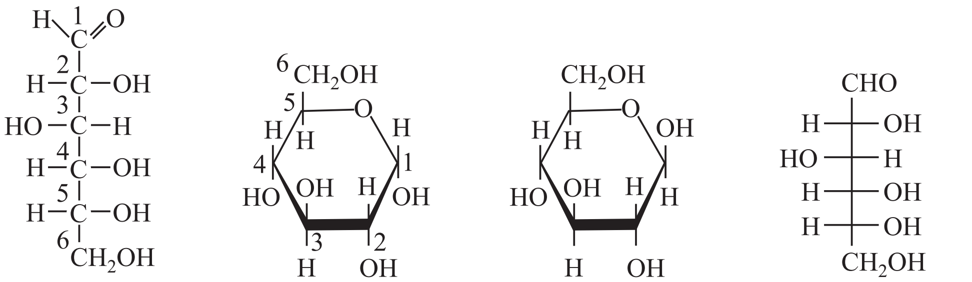


D-Galactose

Anomers

When D glucose is crystallized at room temperature and a fresh solution is prepared, its specific rotation of polarized light is +112°; but after 12-18 hours it changes to +52.5°. If initial crystallization is taking place at 98° C and then solubilized, the specific rotation is found to be +19°, which also changes to+52.5° within few hours. This change in rotation with time is called **mutarotation**.

This is explained by the fact that D-glucose has two anomers, alpha and beta varieties. These anomers are produced by the spatial configuration with reference to the first carbon atom in aldoses and second carbon in ketoses. Hence these carbons are called anomeric carbon atoms. Thus α-D-glucose has specific rotation of +112° and β=D-glucose has specific rotation of +19°. Both undergo mutarotation and at equilibrium one-third molecules are alpha type and two-third are beta variety to get the specific rotation +52.5°

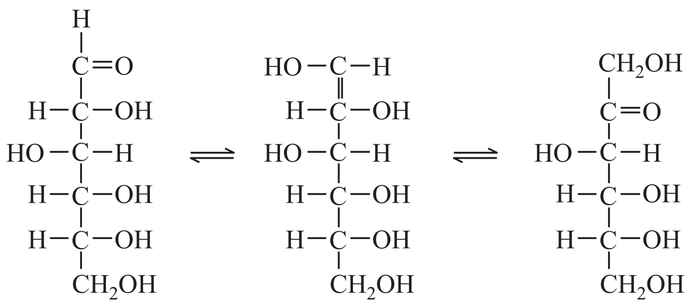


D-Glucose α-D-Glucose β-D-Glucose Cyclation of Glucose

2.5 REACTIONS OF MONOSACCHARIDES

2.5.1 Enediol formation

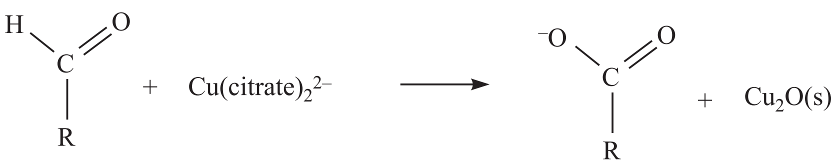
In mild alkaline solutions, carbohydrates containing free sugar group (aldehyde or keto group) will tautomerise to form enediols, where two hydroxyl groups are attached to the double-bonded carbon, in mild alkaline conditions, glucose is converted into fructose and mannose.



aldose D-Glucose enediol ketose D-fructose

Benedict's Reaction

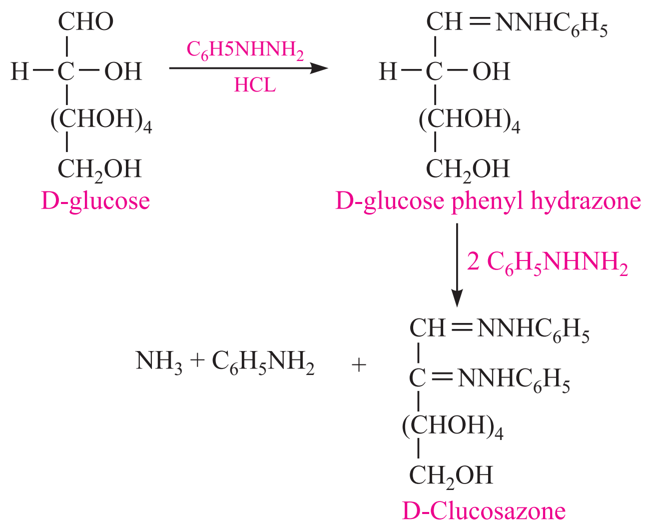
Benedict's reagent contains sodium carbonate, copper sulphate and sodium citrate. In alkaline medium, sugars form enediols which will reduce cupric ions and correspondingly the sugar is oxidized. Any sugar with free aldehyde or keto group will reduce benedict's reagent and called as reducing sugars.



An aldose Benedict's reagent (blue solution) Carboxylate anion Brick-red precipitate

Osazone Formation

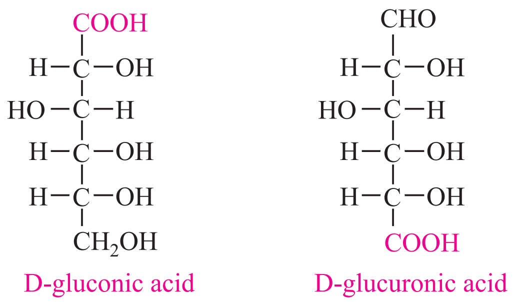
All reducing sugars will form osazone with excess of phenylhydrazine when kept at boiling temperature. Osazones are insoluable. Each sugar will have characteristic crystal form of osazone



Oxidation of Sugars

Under mild oxidation conditions the aldehyde group is oxidized to carboxyl group to produce aldonic acid. Ex: Glucose to Gluconic acid

When aldehyde group is protected and the molecule is oxidized the last carbon becomes COOH group to produce uronic acid. Ex: Glucose to Glucuronic acid.



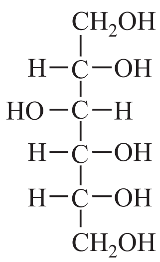
Under strong oxidation conditions the first and last carbon atoms are simultaneously oxidized to form dicarboxyllic acids, known as saccharic acids. Ex: Glucose to Glucosaccharic acid.

Furfural Derivatives

Monosaccharides when treated with concentrated sulphuric acid undergo dehydration with removal of 3 molecules of water. Therefore hexoses give hydroxymethyl furfural and pentoses give furfural. These furfural derivatives can condense with phenolic compounds to give coloured products. This forms the basis of Molisch test, a general test for carbohydrates.

Reduction to form Alcohols

When treated with reducing agents such as sodium amalgam, hydrogen can reduce sugars. Aldose yields corresponding alcohols. But ketose forms two alcohols, because of appearance of a new asymmetric carbon atom. Ex: Glucose forms sorbitol and fructose forms sorbitol and mannitol.



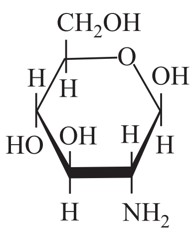
Glucitol or Sorbitol
(a sugar alcohol)

Glycosides: When the hemi-acatal group of a monosaccharide is condensed with an alcohol or phenol group, it is called glycoside.

Formation of esters: Hydroxyl groups of sugars can be esterified to form acetates, propionates, benzoates, phosphates, etc

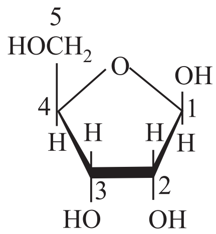
Amino sugars

Amino groups may be substituted for hydroxyl groups of sugars to give rise to amino sugars. Ex: Glucose to Glucosamine. Generally the amino group is added to the second carbon atom of hexoses. The amino group may be further acetylated to form N-acetylated sugars such N-acetyl-glucosamine.

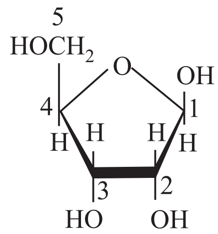


Glucosamine
(an amino sugar)

Deoxy sugars: Oxygen of the hydroxyl group may be removed to form deoxy sugars.



Ribose

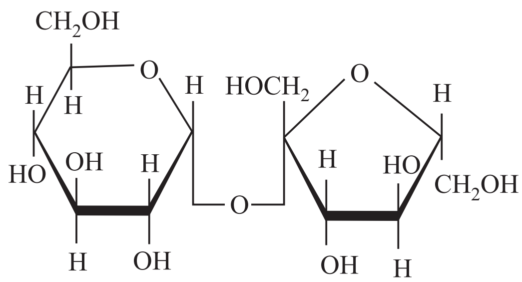


Deoxyribose

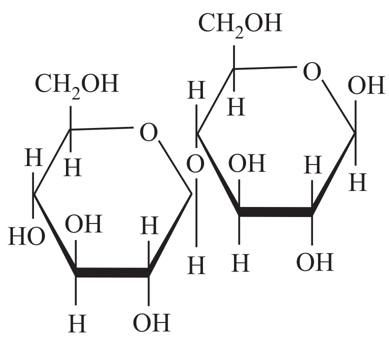
Disaccharides

When two monosaccharides are combined together with elimination of a water molecule it is called disaccharide. Monosaccharides are combined by glycosidic bond.

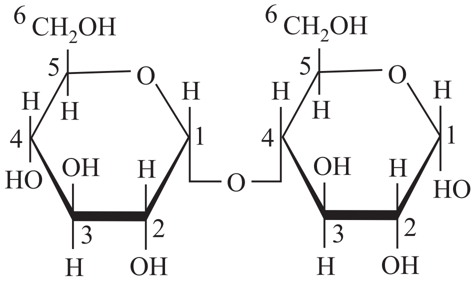
Disaccharide	Description	Component monosaccharides
Sucrose	common table sugar	glucose $\alpha 1 \rightarrow 2$ fructose
Maltose	product of starch hydrolysis	glucose $\alpha 1 \rightarrow 4$ glucose
Trehalose	found in fungi	glucose $\alpha 1 \rightarrow 1$ glucose
Lactose	main sugar in milk	galactose $\beta 1 \rightarrow 4$ glucose
Melibiose	found in legumes	galactose $\beta 1 \rightarrow 6$ glucose



Sucrose



Lactose



Maltose

Sucrose

Sucrose also called saccharose, is ordinary table sugar refined from sugar cane or sugar beets. Sucrose is not a reducing sugar. This is because the glycosidic linkage inolves first carbon of glucose and second carbon of fructose, and hence there is no free reducing groups. When sucrose is hydrolyzed the resulting products have reducing property. Hydrolysis of sucrose (optical rotation +66.5°) will produce one molecule of glucose (+52.5°) and one molecule of fructose (-92°). Therefore the products will change the dextrorotation to levorotation, or the plane of rotation is inverted. Equimolecular mixture of glucose and fructose thus formed is called invert sugar.

Lactose

Lactose is the sugar present in milk. It is reducing disaccharide.

Maltose

Maltose consists of two α-D-glucose molecules. It is a reducing disaccharide

Polysaccharides

Polysaccharides are polymerized products of many monosaccharide units. They may be homo or hetero polysaccharides. Many polysaccharides, unlike sugars, are insoluble in water. Dietary fiber includes polysaccharides and oligosaccharides that are resistant to digestion and absorption in the human small intestine but which are completely or partially fermented by microorganisms in the large intestine.

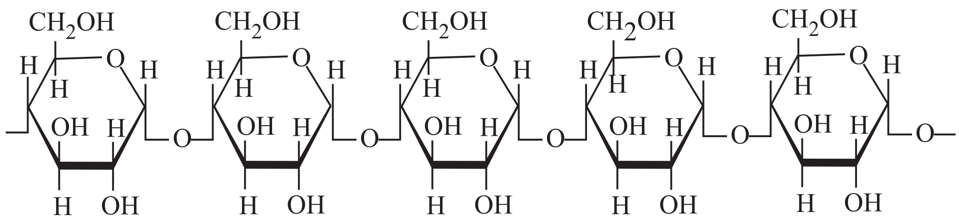
Homopolysaccharides

They have only one type of monosaccharide units.

Starch

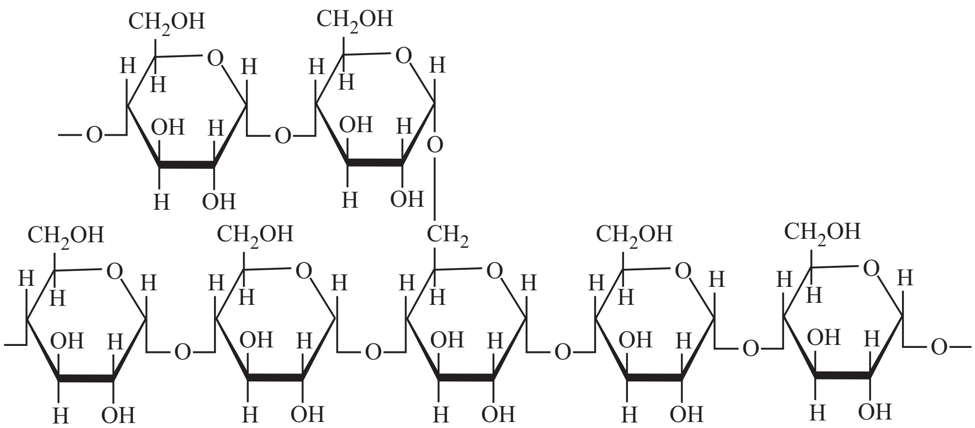
Starch is the major form of stored carbohydrate in plants. Starch is composed of a mixture of two substances:amylose, an essentially linear polysaccharide, and amylopectin, a highly branched polysaccharide. Both forms of starch are polymers of α-D-Glucose. Natural starches contain 10-20% amylose and 80-90% amylopectin. Amylose forms a colloidal dispersion in hot water (which helps to thicken gravies) whereas amylopectin is completely insoluble.

- Amylose molecules consist typically of 200 to 20,000 glucose units which form a helix as a result of the bond angles between the glucose units.



Amylose

- Amylopectin differs from amylose in being highly branched. Short side chains of about 30 glucose units are attached with 1α→6 linkages approximately every twenty to thirty glucose units along the chain. Amylopectin molecules may contain up to two million glucose units.



Amylopectin

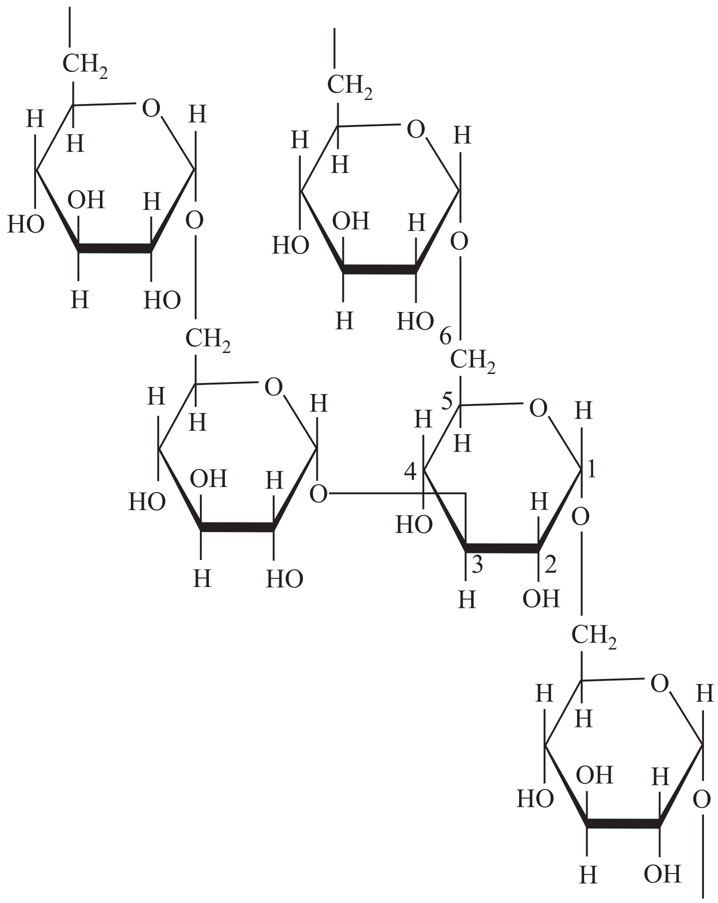
The side branching chains are clustered together within the amylopectin molecule

Glycogen

Glucose is stored as glycogen in animal tissues by the process of glycogenesis. When glucose cannot be stored as glycogen or used immediately for energy, it is converted to fat. Glycogen is a polymer of α-D-Glucose identical to amylopectin, but the branches in glycogen tend to be shorter (about 13 glucose units) and more frequent. The glucose chains are organized globularly like branches of a tree originating from a pair of molecules of glycogenin, a protein with a molecular weight of 38,000 that acts as a primer at the core of the structure. Glycogen is easily converted back to glucose to provide energy.

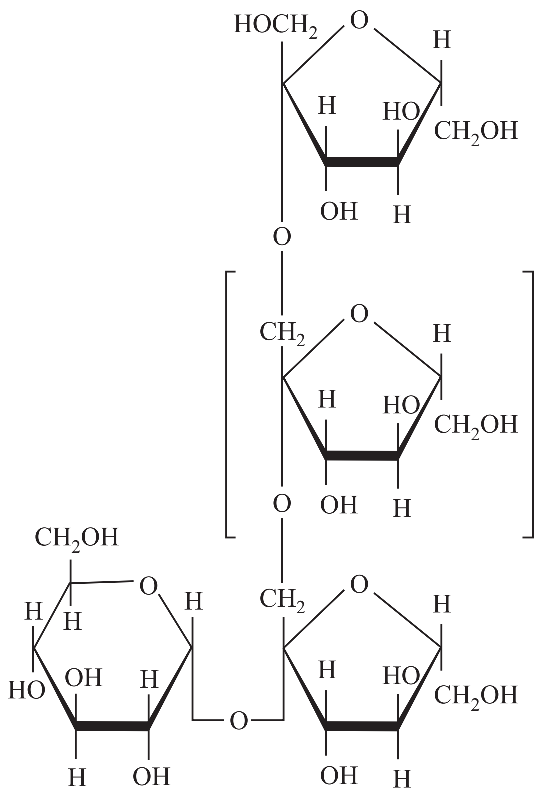
Dextran

Dextran is a polysaccharide similar to amylopectin, but the main chains are formed by 1α→6 glycosidic linkages and the side branches are attached by 1α→3 or 1α→4 linkages. Dextran is an oral bacterial product that adheres to the teeth, creating a film called plaque. It is also used commercially in confections, in lacquers, as food additives, and as plasma volume expanders.



Dextran

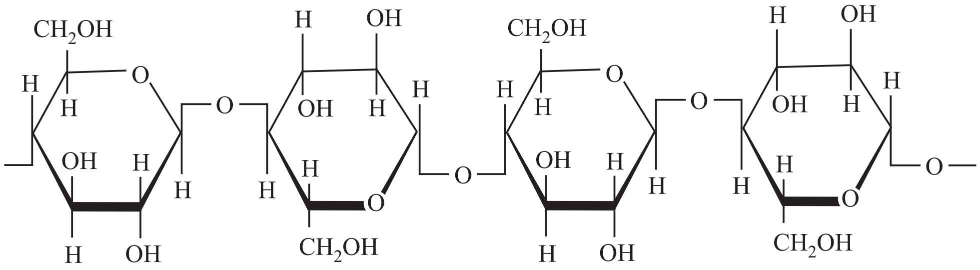
Inulin: Inulins, also called fructans, are polymers consisting of fructose units that typically have a terminal glucose. Oligofructose has the same structure as inulin, but the chains consist of 10 or fewer fructose units. Oligofructose has approximately 30 to 50 percent of the sweetness of table sugar. Inulin is less soluble than oligofructose and has a smooth creamy texture that provides a fat-like mouthfeel. Inulin and oligofructose are nondigestible by human intestinal enzymes, but they are totally fermented by colonic microflora. The short-chain fatty acids and lactate produced by fermentation contribute 1.5 kcal per gram of inulin or oligofructose. Inulin and oligofructose are used to replace fat or sugar and reduce the calories of foods like ice cream, dairy products, confections and baked goods.



Inulin n = approx. 35

Cellulose

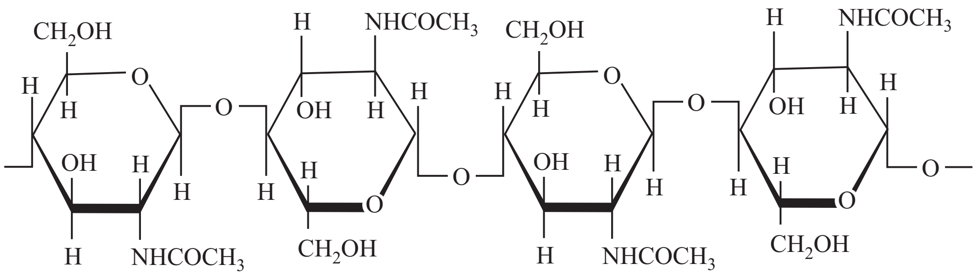
Cellulose is a polymer of β-D-Glucose, which in contrast to starch, is oriented with $-CH_2OH$ groups alternating above and below the plane of the cellulose molecule thus producing long, unbranched chains. The absence of side chains allows cellulose molecules to lie close together and form rigid structures. Cellulose is the major structural material of plants. Wood is largely cellulose, and cotton is almost pure cellulose. Cellulose can be hydrolyzed to its constituent glucose units by microorganisms that inhabit the digestive tract of termites and ruminants. Cellulose may be modified in the laboratory by treating it with nitric acid (HNO_3) to replace all the hydroxyl groups with nitrate groups (-ONO_2) to produce cellulose nitrate (nitrocellulose or guncotton) which is an explosive component of smokeless powder. Partially nitrated cellulose, known as pyroxylin, is used in the manufacture of collodion, plastics, lacquers, and nail polish.



Cellulose

Chitin

Chitin is an unbranched polymer of N-Acetyl-D-glucosamine. It is found in fungi and is the principal component of arthropod and lower animal exoskeletons, e.g., insect, crab, and shrimp shells. It may be regarded as a derivative of cellulose, in which the hydroxyl groups of the second carbon of each glucose unit have been replaced with acetamido (–NH(C=O)CH_3) groups.



Chitin

2.6 HETEROPOLYSACCHARIDES

Heteropolysaccarides contain two or more different kind of monosaccharides. Usually they provide extracellular support for organisms of all kingdoms: the bacteria cell envelope, or the matrix that holds individual cells together in animal tissues, and provides protection, shape and support to cells, tissues and organs.

Heteropolysaccharides provide extracellular support to very different organisms, from bacteria to humans; together with fibrous proteins, like collagen, elastin, fibronectin, laminin and others, heteropolysaccharides are the most important components of the extracellular matrix. Hyaluronic acid, condroitin sulfates and dermatan sulfates are important heteropolysaccharides in the extracellular matrix. These heteropolysaccharides usually are formed by the repetition of a disaccharide unit of an aminosugar and an acid sugar.

Other common constituents are sulfate groups linked to certain monosaccharides. Usually heteropolysaccharides are associated with proteins forming proteoglycans, glycosaminoglycans or mucopolysaccharides (since they are abundant in mucous secretions). As a group, they perform diverse functions: structural, water metabolism regulation (as a reservoir of water), cellular cement, biological sieve, biological lubricant, docking sites for growth factors, among other functions.

Established specific functions of some glycosaminoglycans are:

Hyaluronic Acid (Hyaluronate): It is a lubricant in the synovial fluid of joints, give consistency to vitreous humor, contributes to tensile strength and elasticity of cartilages and tendons (Answer to C-O6)

Chondroitin Sulfates: contributes to tensile strength and elasticity of cartilages, tendons, ligaments and walls of aorta.

Dermatan sulfate (former chondroitin sulfate B) is found mainly in skin, but also is in vessels, heart, lungs. It may be related to coagulation and vascular diseases and other conditions.

Keratan sulfate: Present in cornea, cartilage bone and a variety of other structures as nails and hair.

Digestion and absorption

All carbohydrates absorbed in the small intestine must be hydrolyzed to monosaccharides prior to absorption. The digestion of starch begins with the action of salivary alpha-amylase/ptyalin, although its activity is slight in comparison with that of pancreatic amylase in the small intestine. Amylase hydrolyzes starch to alpha-dextrin, which are then digested by gluco-amylase (alpha-dextrinases) to maltose and maltotriose. The products of digestion of alpha-amylase and alpha-dextrinase, along with dietary disaccharides are hydrolyzed to their corresponding monosaccharides by enzymes (maltase, isomaltase, sucrase and lactase) present in the brush border of small intestine. In the typical Western diet, digestion and absorption of carbohydrates is fast and takes place usually in the upper small intestine. However, when the diet contains carbohydrates not easily digestible, digestion and absorption take place mainly in the ileal portion of the intestine.

Digestion of food continues while simplest elements are absorbed. The absorption of most digested food occurs in the small intestine through the brush border of the epithelium covering the villi(small hair-like structure). It is not a simple diffusion of substances, but is active and requires energy use by the epithelial cells.

During the phase of carbohydrate absorption, fructose is transported into the intestinal cell's cytosol, glucose and galactose competes with other Na + transporter required for operation. From the cytosol, monosaccharides pass into the capillaries by simple or facilitated diffusion.

Carbohydrates that are not digested in the small intestine, including resistant starch foods such as potatoes, beans, oats, wheat flour, as well as several non-polysaccharides oligosaccharides and starch, are digested in a variable when they reach the large intestine. The bacterial flora metabolize these compounds in the absence of oxygen. This produces gases (hydrogen, carbon dioxide and methane) and short-chain fatty acids (acetate, propionate, butyrate). The gases are absorbed and excreted by breathing or through the anus. Fatty acids are rapidly metabolized. Thus butyrate, used mainly in the colonic, is an important nutritional source for these cells and regulates their growth, acetate into the blood and taken up by the liver, muscle and other tissues, and propionate, which is an important precursor of glucose in animals, it is not so in humans.

Are polymers made up of two to ten monosaccharide units joined together by glycosidic linkages. Oligosaccharides can be classified as di-, tri-, tetra- depending upon the number of monosaccharides present. Among these the most abundant are the disaccharides, with two monosaccharide units.

INTEXT QUESTIONS 2.2

1. Compounds having same structural formula but differing in spatial configuration are known as ....
2. This change in rotation with time is called ....
3. Equimolecular mixture of glucose and fructose thus formed is called ....
4. Types of Polysaccharides are .... & ....

WHAT HAVE YOU LEARNT

- Carbohydrates are polyhydroxy aldehydes or ketones, or compounds that can be hydrolyzed to Monosacchrides.
- Carbohydrate is an organic compound comprising only carbon, hydrogen, and oxygen, usually with a hydrogen: oxygen atom ratio of 2:1.

- Baked goods commonly contain dietary starch and added sugar. Most dietary carbohydrates come from plants
- Carbohydrates are classified depending on hydrolysis as Monosaccharides, Disaccharides, Trisaccharides, Oligosaccharides, Polysaccharides
- Molecules having only one actual or potential sugar group are called monosaccharides which cannot be hydrolyzed further into polyhydroxy aldehydes or ketone unit
- Sugars having aldehyde group are called aldoses and sugars with keto group are called ketoses. Depending on the number of carbon atoms monosaccharides are named as triose (C_3), tetrose (C_4), pentose (C_5), hexose (C_6), heptose (C_7) and so on.
- Compounds having same structural formula but differing in spatial configuration are known as sterioisomers
- The number of possible sterioisomers depends on the number of asymmetric carbon atoms by the formula 2^n where n is the number of asymmetric carbon atoms
- The presence of asymmetrical carbon atom causes optical activity. Depending on the rotation molecules are called dextrorotatory (+) (d) or levorotatory(-)
- When sugars are different from one another, only in configuration with regard to the single carbon atom are called Epimers
- When two monosaccharides are combined together with elimination of a water molecule it is called disaccharide. Monosaccharides are combined by glycosidic bond
- Sucrose, Maltose, Trehalose, Lactose and Melibose are disaccharide
- Polysaccharides are polymerized products of many monosaccharide units. They may be homo or hetero polysaccharides.
- Homopolysaccharides have only one type of monosaccharide units.
- Homopolysaccharides are starch, Glycogen, Dextran, Inulin, Cellulose, chitin
- Heteropolysaccarides contain two or more different kind of monosaccharides
- Carbohydrates absorbed in the small intestine and are hydrolyzed to monosaccharides prior to absorption.
- The digestion of starch begins with the action of salivary alpha-amylase/ ptyalin, although its activity is slight in comparison with that of pancreatic amylase in the small intestine.

TERMINAL QUESTIONS

1. Classify Monosaccharides with examples
2. Classify Polysaccharides with examples
3. Write short note on absorption of Carbohydrates

ANSWERS TO INTEXT QUESTIONS

2.1

1. Carbon, Hydrogen & Oxygen
2. 2 : 1
3. Monosaccharides
4. Aldoses
5. Ketoses
6.
    1. (c)
    2. (a)
    3. (d)
    4. (b)
7.
    1. (d)
    2. (c)
    3. (a)
    4. (b)

2.2

1. Sterioisomers
2. Mutarotation
3. Invert sugar
4. Homopolysaccharide & Heteropolysaccharide