

## Structure and Properties of Carbohydrates

Carbohydrates are aldehyde and ketone compounds with multiple hydroxyl groups. They are one of the most abundant classes of biomolecules in nature. They are widely distributed in all life forms and serves many roles, such as

- They serve as energy stores, fuels and metabolic intermediates.
- They are constituent of RNA and DNA backbones as ribose and deoxyribose sugars.
- Polysaccharides are constituents of cell walls of bacteria and plants.
- Carbohydrates are linked to surfaces of proteins and lipids where they play role as informational materials e.g. in cell-cell interaction and interaction between cells with other elements in the cellular environment.

Carbohydrate can be classified into three groups: monosaccharide, oligosaccharides and polysaccharides.

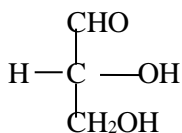
### Monosaccharide

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) (Table 1).

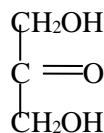
Table1: Classification of monosaccharides.

Name of sugar	Aldoses	Ketoses
Trioses ( $C_3H_6O_3$ )	Glucose	Dihydroxy acetone
Tetroses ( $C_4H_8O_4$ )	Erythrose	Erythulose
Pentoses ( $C_5H_{10}O_5$ )	Ribose	Ribulose
Hexoses ( $C_6H_{12}O_6$ )	Glucose	Fructose

Both the classifications i.e. number of carbon atoms and nature of functional groups may be combined to classify the sugar. For example glycerose (=glyceraldehyde) is an aldotriose, ribose is an aldopentose and fructose is a ketohexose. The smallest monosaccharide are glyceraldehyde and dihydroxyacetone for which  $n=3$  (where  $n$ = number of carbon atoms) (Figure 1).



Structure of glyceraldehyde

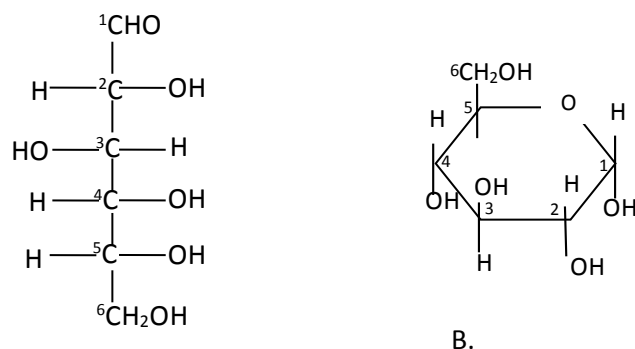


Structure of dihydroxyacetone

Figure 1: Structure of smallest monosaccharides ( $n=3$ ).

### 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.



A.  
 Figure 2: Structure of  $\alpha$ -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.

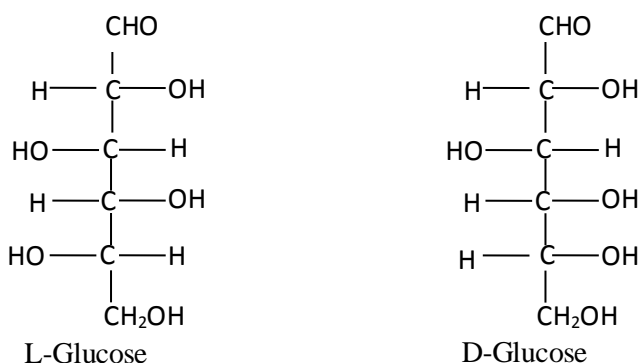


Figure 3: L and D forms of glucose.

### 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  $\alpha$  and  $\beta$  (Figure 4). D-fructose also forms hemiketal in which  $-OH$  at C-5 has reacted with keto at C-2 producing two anomers called  $\alpha$  and  $\beta$  (Figure 5).

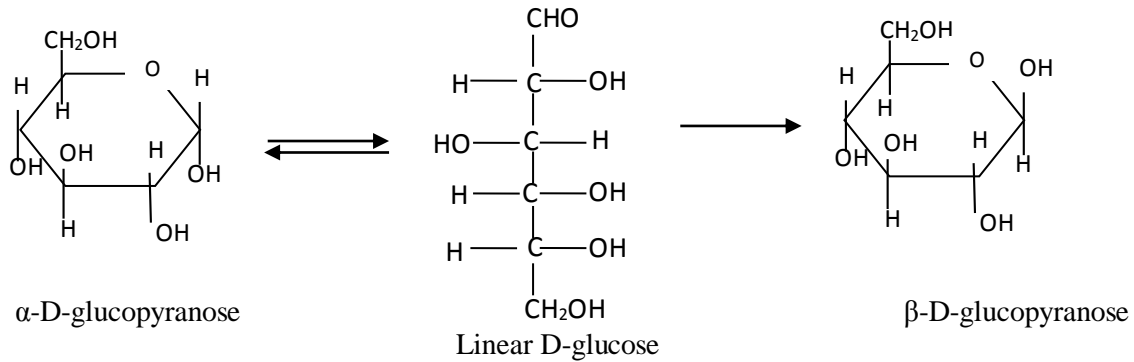


Figure 4: Two cyclic forms of glucose that are interconvertible in aqueous solution (mutarotation).

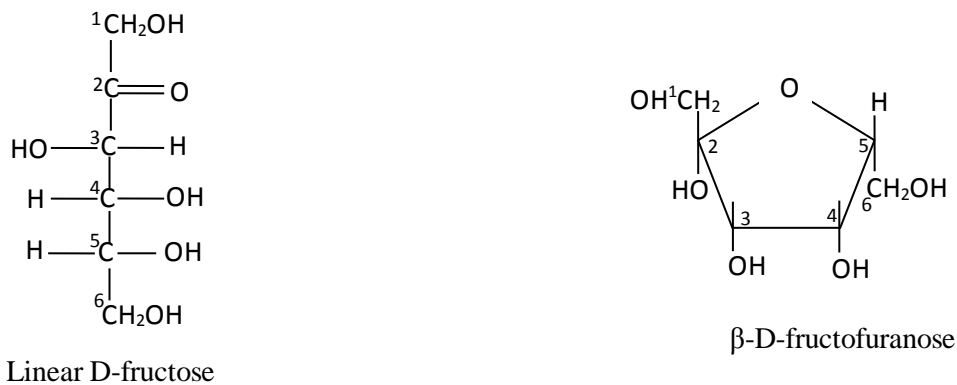


Figure 5: Structure of a ketohexose (fructose) and its cyclic hemiketal fructofuranose.

Isomeric forms of monosaccharide that differ only in their configuration about the hemiacetal or hemiketal carbon atom are called anomers, and the carbonyl carbon atom is called the anomeric carbon. The interconversion of  $\alpha$  and  $\beta$  anomers in aqueous solution is called mutarotation, in which one ring form opens briefly into the linear form, then closes again to produce  $\beta$  anomers. Thus, a solution of  $\beta$ -D-glucose and solution of  $\alpha$ -D-glucose eventually form identical equilibrium mixtures having identical properties. This mixture consists of about one third of  $\alpha$ -isomers and two third  $\beta$ -D-glucose.

#### 4. Epimers

Isomers having different configuration of  $-OH$  only at one carbon atoms are known as epimers. The most important epimers of glucose are mannose (epimers at C-2) and galactose (epimers at C-4) (Figure 6).

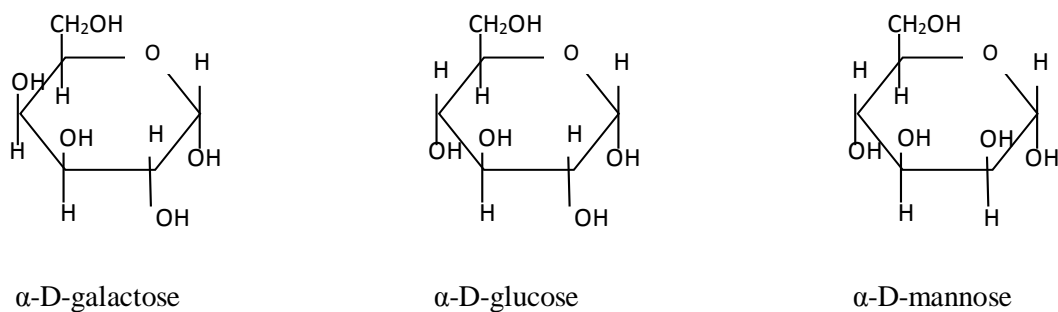


Figure 6: Epimers of glucose.

#### Disaccharides

Two monosaccharides can join covalently when –OH group of one sugar reacts with the anomeric carbon of other to form a disaccharide. The bond formed between the monosaccharide is called O-glycosidic bond. The reaction represents the formation of acetal from a hemiacetal. Glycosidic bond can be hydrolysed by acid but not cleave by the base. Thus disaccharides can be hydrolysed to yield their constituent monosaccharides by boiling with dilute acid. Hydrolysis of sucrose yields a mixture of glucose and fructose called ‘invert sugar’ because fructose is strongly levorotatory and change (converts) the weaker dextrorotatory action of sucrose. Some common disaccharides are given in Table 2.

Table 2: Some common disaccharides.

Disaccharide	Nomenclature	Source
Sucrose	<i>O</i> - $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-fructofuranoside	Cane sugar and beet sugar, sorghum fruits and vegetables
Lactose	<i>O</i> - $\alpha$ -D-galactopyranosyl-(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranose	Milk sugar
Maltose	<i>O</i> - $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 4)- $\alpha$ -D-glucopyranose	Germinating cereals and malt
Isomaltase	<i>O</i> - $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 6)- $\alpha$ -D-glucopyranose	Enzymatic hydrolysis of starch
Trehalose	<i>O</i> - $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 1)- $\alpha$ -D-glucopyranose	Yeast and fungi

When the anomeric carbon is involved in a glycosidic bond, the easy interconversion of linear and a cyclic form is prevented. Because the carbonyl carbon can be oxidised only when the sugar is in its linear form, formation of a glycosidic bond makes the sugar non-reducing. The end of chain in disaccharide and polysaccharide with free anomeric carbon is called the reducing end. The disaccharides maltose contains two D-glucose residues joined by glycosidic linkage and lactose is made up of D-galactose and D-glucose residues. In both the disaccharides C-1 (anomeric carbon) of one sugar makes glycosidic bond with C-4 of another. Since the anomeric carbon of one sugar residue is available for oxidation, maltose and lactose are reducing disaccharides. Whereas in sucrose, the two monosaccharides glucose and fructose are linked via their anomeric carbon (C<sub>1</sub> of glucose and C<sub>2</sub> of fructose form glycosidic bond), no anomeric carbon atom is free, therefore sucrose is a non-reducing sugar (Figure 7).

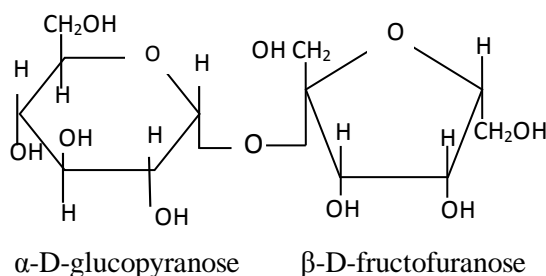


Figure 7: Structure of sucrose [*O*- $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-fructofuranoside

The stability of sucrose makes it ideal molecule for storage and transport of energy in plants. Trehalose, like sucrose is a non-reducing sugar is major constituent of circulating fluid of insects, serving as energy storage compound.

### Polysaccharides

Polysaccharides are polymers composed of ten or more monosaccharide units. These monosaccharide units are joined together by glycosidic linkages. Polysaccharides made up of a single type of monosaccharide units are called as homopolysaccharides, whereas polysaccharides composed of two or more types of monosaccharides are called heteropolysaccharides. Some polysaccharides are made up of sugar derivatives like, for example glucosamine, a glucose derivative, is the repeating monosaccharide in chitin. Polysaccharides differ from each other in the type of repeating monosaccharide unit, in the number of repeating units, in the degree of branching, and in the type of glycosidic linkage between the monomeric units.

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.

### Homopolysaccharides

Homopolysaccharides yield a single type of monosaccharide on hydrolysis. They serve as both storage (e.g., starch, glycogen, dextran, inulin) and structural (e.g., cellulose, chitin, xylan, pectin) polymers. The structures and properties of some homopolysaccharides are given in Table 3.

Table 3: Structures and properties of some homopolysaccharides.

Name	Constituent monosaccharide	Glycosidic linkage	Size (no. of monosaccharide residues)	Biological significance
Starch	$\alpha$ -D-glucose	$\alpha(1\rightarrow4)$ glucoside (in amylose) $\alpha(1\rightarrow4)$ glucoside; $\alpha(1\rightarrow6)$ glucoside linkage at branch points (in amylopectin) Branches at every 24-30 residues	50-5000  Upto $10^6$	Energy storage in plants
Glycogen	$\alpha$ -D-glucose	$\alpha(1\rightarrow4)$ glucoside; $\alpha(1\rightarrow6)$ glucoside linkage at branch points Branches every 8-14 residues	Upto 50000	Energy storage in bacteria and animals
Cellulose	$\beta$ -D-glucose	$\beta(1\rightarrow4)$ glucoside	Up to 15000	Structural role: provide rigidity and strength to cell wall
Chitin	N-acetyl-D-glucosamine	$\beta(1\rightarrow4)$ glucoside	Very large	Structural role: provide rigidity and strength to exoskeleton of insects
Dextran	$\alpha$ -D-glucose	$\alpha(1\rightarrow6)$ glucoside with $\alpha(1\rightarrow3)$ glucoside at branching points	Wide range	Structural: extracellular adhesive in bacteria
Inulin	$\beta$ -D-fructose	$\beta(2\rightarrow1)$ fructoside	30-35	Energy storage in plants
Pectin	$\alpha$ -D-galacturonic acid	$\alpha(1\rightarrow4)$ galactoside		Structural: holds cellulose fibrils together in plant cell walls
Xylan	$\beta$ -D-xylose	$\beta(1\rightarrow4)$ xylose	30-100	Storage and supporting roles in plants

### Starch

Starch occurs in plants as reserve carbohydrate in tubers, seeds, fruits and roots. It is deposited in the cytoplasm of plant cells as insoluble granules composed of two homopolysaccharides; amylose (15-20%) and amylopectin (80-85%). Amylose is a linear polymer of  $\alpha$ -D-glucose monomers linked by  $\alpha(1\rightarrow4)$  bonds (Figure 8). The linkage in amylose is thus  $\alpha(1\rightarrow4)$  glycoside, similar to that in maltose. The molecular weight of amylose ranges from 10,000 to 50,000 Da.

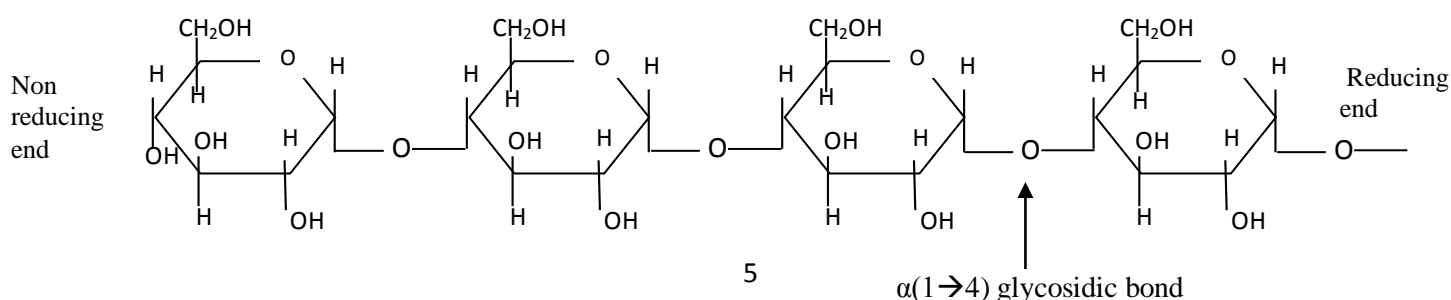


Figure 8: Structure of amylose.

Amylopectin is very high molecular weight (up to 200 million Da) molecule consisting of glucose units linked by  $\alpha(1\rightarrow4)$  glycoside linkage like amylose, but it is highly branched. Branch points occur every 24 to 30 glucose residues and linkage at the branch points is  $\alpha(1\rightarrow6)$  glycosidic (Figure 9).

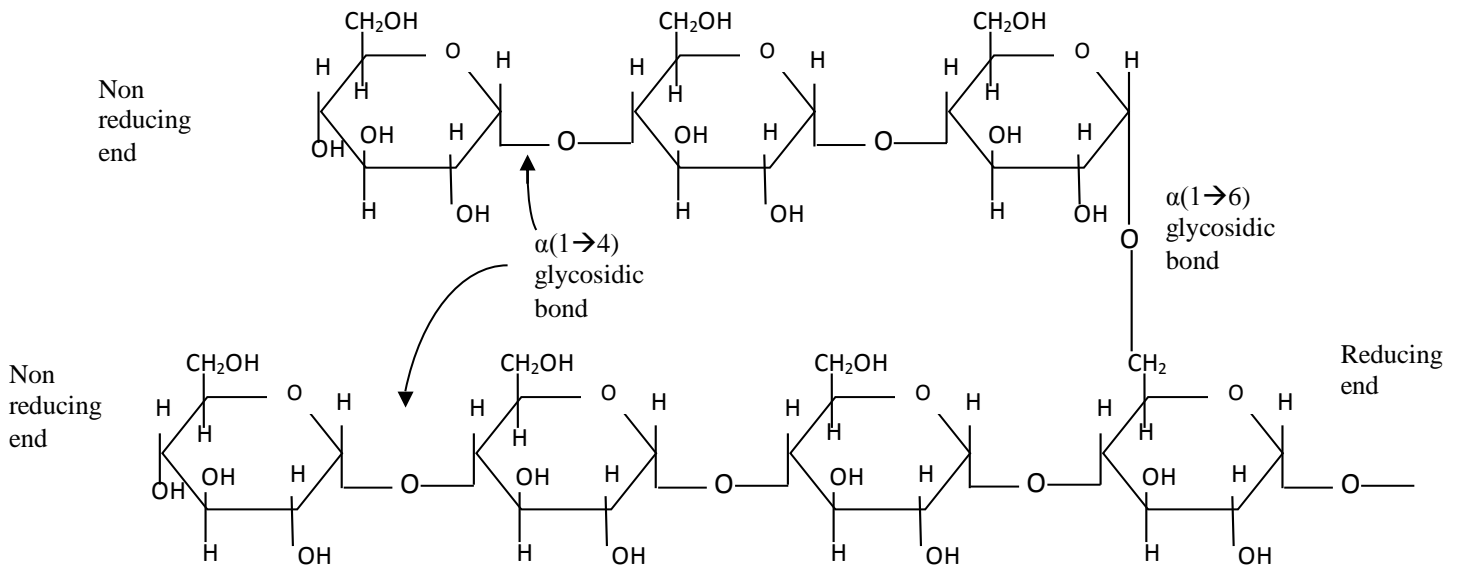


Figure 9: Structure of amylopectin.

Starch is insoluble in water, alcohol and ether at room temperature. It is highly hydrated since it contains many exposed  $-\text{OH}$  groups. It is non-reducing polysaccharide since the carbonyl groups of all units (except the last unit at the terminus) are involved in glycosidic bond formation. Characteristic blue colour of the starch with iodine is due to amylose. The amylose is an open, helical molecule, the inside diameter of the helix is large enough to accommodate iodine molecule. In contrast, most other polysaccharides including amylopectin, give only dull reddish brown colour with iodine.

### Glycogen

Glycogen is storage homopolysaccharide of animals and is consist of glucose units linked by  $\alpha(1\rightarrow4)$  glycoside linkage like amylopectin in starch. Branching is more extensive as compared to amylopectin, occur every 8 to 14 glucose residues and linkage at the branch points is  $\alpha(1\rightarrow6)$  glycosidic. Each glycogen molecule contains up to 120,000 glucose units. Muscle cells contain glycogen at 1-2% of their dryweight, and liver cells contain up to 10% of their dry weight as glycogen, which is sufficient for >12 hour energy supply for the body. Glycogen granules contain enzymes that catalyze glycogen synthesis and breakdown, as well as enzymes that regulate these processes.

Glycogen's highly branched structure is physiologically significant; it permits glycogen's rapid degradation through the simultaneous release of the glucose units at the end of every branch. In animals the fat is far more abundant in the body and can serve the same purpose as glycogen but still body uses glycogen as storage energy. The reason for that is 1.) muscle can not mobilize fat as rapidly as glycogen, 2.) the fatty acid residues of the fat can not be metabolized anaerobically, and 3.) animals can not convert fatty acids to glucose, so fat metabolism alone cannot adequately maintain essential blood glucose levels. Cells can only metabolize glucose monomers but cannot store glucose within cells.

Storage of glucose monomers in the form of starch (in plants) and glycogen (in animals) greatly reduces the large intracellular osmotic pressure that would result from its storage in monomeric form. Osmotic pressure is proportional to the number of solute molecules in a given volume.

## Cellulose

Cellulose is most abundant extracellular structural polysaccharide of the plants. It is also most abundant of all biomolecules in the biosphere. It is primary structural component of plant cell wall. Cellulose is linear polymer of upto 15000 D-glucose units linked by  $\beta(1 \rightarrow 4)$  glucosidic bonds.

In plant cell walls, the cellulose fibres are embedded in and cross-linked by a matrix of several polysaccharides that are composed of glucose as well as other monosaccharides. In wood this cementing matrix also contains a large proportion of lignin, a plastic like polymer.  $\beta$ -D-glucose monomers in cellulose form extensive hydrogen bonded structure that gives cellulose fibres exceptional strength and make them water insoluble despite their hydrophilicity. Unlike starch it gives no colour with iodine and lacks sweetness. It is of no nutritive value as it is chemically unreactive, however, its non-reactive property make it so useful fibers for paper and cloth.

Vertebrates lack the enzyme that hydrolyse  $\beta(1 \rightarrow 4)$  linkages of cellulose. However, the digestive tracts of herbivores contain symbiotic microorganisms that secrete a series of enzymes called cellulase that readily digests cellulose. Termites also digest cellulose because their gut contains parasitic protozoa, Trichonympha, which secrete cellulase. Cellulase is also produced by wood-rot fungi and bacteria.

Degradation of cellulose is slow process because it is tightly packed and hydrogen bonded polymer chains are not easily accessible to cellulase and do not separate readily even after many of their glycosidic bonds have been cleaved. The digestion of fibrous plants such as grass by herbivores is therefore a more complex and time consuming process than is the digestion of meat by carnivores. Similarly, the decay of dead plants by fungi, bacteria and other microorganisms, and the consumption of wooden houses by termites, often takes years.

## 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  $\beta(1 \rightarrow 4)$  linked N-acetyl-D-glucosamine residues. Chitin and cellulose have similar structures except that C<sub>2</sub>-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.

## 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-linked to form insoluble materials of various sizes.

## Inulin

Inulin is storage polysaccharide of plants composed of D-fructose residues. It occurs in the tubers of artichoke and dahlias and roots of dandelions. Bulbs of onion and garlic also contain inulin. Inulin is not found in animals. It is composed of straight chain of polyfructose residues of 30-35 number and molecular weight of about 5000. It is formed by glycosidic linkage between -OH group of C-2 one  $\beta$ -D-fructose unit and -OH group on C-1 of adjacent  $\beta$ -D-fructose unit. Inulin therefore contain  $\beta(2 \rightarrow 1)$  glycosidic bond.

It is non-reducing, levorotatory sugar soluble in hot water but does not gelatinize as starch does. Unlike starch it does not give characteristic blue colour with iodine. Inulin is not hydrolysed by amylase but is cleaved by inulinase. It is not hydrolysed by any of the enzymes of the gastrointestinal tract and is therefore not utilized as food. Inulin is used as a source of commercial fructose. It is also administered to animals in studies of glomerular membrane filtration rates.

### **Pectin**

Pectin is structural carbohydrate made up of mixture of polysaccharides that hold cellulose fibrils together. It is found in pulp of ripe fruits such as citrus fruits, apples, guava etc. it is present in cell wall in an insoluble form. Pectic acid is a polysaccharide of  $\alpha$ -D-galacturonic acid. Some of the free  $-\text{COOH}$  groups are esterified with methyl alcohol and others are combined with Ca and Mg ions. Pectin provides stability and solidity to plants. Pectin is used in the fruit conserving industry.

### **Xylan**

Xylans and related substances are collectively known as hemicelluloses. They are abundant in unrefined cereals, vegetables and in some fruits. Hemicelluloses consist of either pentoses (e.g. xylose, arabinose) or hexoses (e.g. glucose, mannose, galactose). Unlike cellulose they are partially soluble in alkali and water. They play storage and supporting role in plants. They absorb water and are partially digestible.

Xylan is a complex polysaccharide and closely associated with cellulose in lignified cell walls of plants. It is a linear polymer of D-xylose linked by  $\beta(1 \rightarrow 4)$  bond having side chain of 4-O-methylglucuronic acid and/or arabinose. The numbers of xylose residues vary from 30 to 100. Microorganisms can degrade xylan more rapidly than cellulose. Many cellulase producing organisms also produce xylanase, thus they can utilize xylan.

### **Heteropolysaccharides**

Heteropolysaccharides yield a mixture of monosaccharide on hydrolysis. They are present in extracellular matrix of plants, animals and bacteria.

### **Agar**

Agar is gelatinous polysaccharide produced in cell wall of marine red algae such as species of *Gelidium*, *Gracilaria*, *Gigartina* etc. It is a mixture of sulphated heteropolysaccharides made up of D-galactose and L-galactose derivatives ether-linked between C<sub>3</sub> and C<sub>6</sub>. Agarose is the agar component with fewest charged groups (sulfates, pyruvates). It has molecular weight of 150000. If agar and agarose are dissolved in hot water they form sol which upon cooling sets to a gel. Agarose gels are used as inert support for the electrophoretic separation of nucleic acids. Agar is used to form a surface for the growth of bacterial and plant tissue cultures.

### **Peptidoglycan**

Peptidoglycan constitutes the rigid component of bacterial cell wall. It is heteropolysaccharide of alternating  $\beta(1 \rightarrow 4)$  linked N-acetyl-D-glucosamine and N-acetyl muramic acid residues. The linear polysaccharide chains are cross linked by short peptides attached to N-acetyl muramic acid. Cross linking by peptide welds the polysaccharide chains into a strong sheath that envelops the entire cell and prevents osmotic rupture of the cell. Lysozyme, which is an enzyme present in human tears kills bacteria by hydrolyzing the  $\beta(1 \rightarrow 4)$  glycosidic linkage of peptidoglycan. Some bacteriophages also produce lysozyme for releasing themselves from the host. An antibiotic penicillin kills bacteria by preventing the cross linking process and therefore making the cell wall weak to resist osmotic lysis.