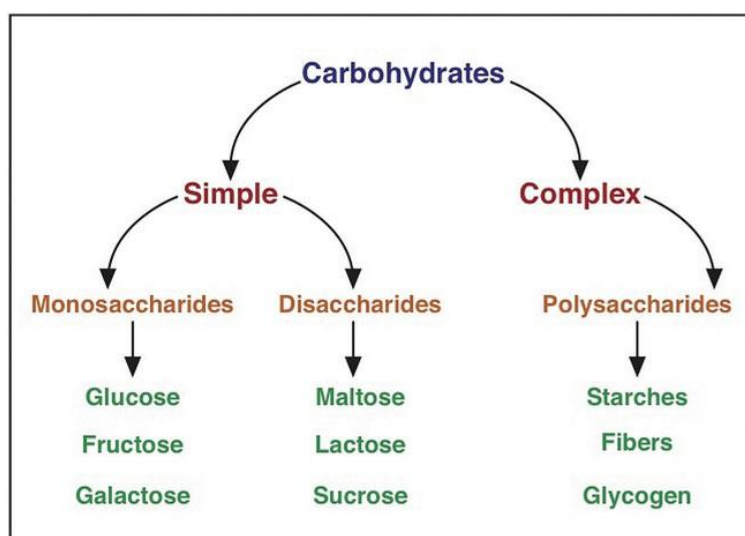


Carbohydrates are often known as sugars, they are the 'staff of life' for most organisms. They are the most abundant class of biomolecules in nature, based on mass. Carbohydrates are also known as saccharides, in Greek *sakcharon* mean sugar or sweetness. They are widely distributed molecules in plant and animal tissues. In plants, and arthropods, carbohydrates form the skeletal structures, they also serve as food reserves in plants and animals. They are important energy source required for various metabolic activities, the energy is derived by oxidation. Plants are richer in carbohydrates than animals.

Carbohydrates Definition:

Carbohydrate is an organic compound, it comprises of only oxygen, carbon and hydrogen. The oxygen: hydrogen ratio is usually is 2:1. The empirical formula being $C_n (H_2O)_n$ (where n can be different from n). Carbohydrates are hydrates of carbon; technically they are polyhydroxy aldehydes and ketones.

Carbohydrates constitute 80% of dry weight of plants and 1-2% in animals. Carbohydrates are the first product of photosynthesis which serve as the major source of energy and perform structural roles. Further carbohydrates provide the carbon skeleton for most if not all organic compounds that make up the plant.



General properties of carbohydrates:

- ✓ Carbohydrates act as energy reserves, also stores fuels, and metabolic intermediates.
- ✓ Ribose and deoxyribose sugars form the structural frame of the genetic material, RNA and DNA.

- ✓ Polysaccharides like cellulose are the structural elements in the cell walls of bacteria and plants.
- ✓ Carbohydrates are linked to proteins and lipids that play important roles in cell interactions.
- ✓ Carbohydrates are organic compounds; they are aldehydes or ketones with many hydroxyl groups.

Physical Properties of Carbohydrates:

- ✓ Stereoisomerism - Compound having same structural formula but they differ in spatial configuration. Example: Glucose has two isomers with respect to penultimate carbon atom. They are D-glucose and L-glucose.
- ✓ Optical Activity - It is the rotation of plane polarized light forming (+) glucose and (-) glucose.
- ✓ Diastereoisomers - It is the configurational changes with regard to C2, C3, or C4 in glucose. Example: Mannose, galactose.
- ✓ Anomerism - It is the spatial configuration with respect to the first carbon atom in aldoses and second carbon atom in ketoses.

Chemical Properties of Carbohydrates:

- ✓ Osazone formation with phenyl hydrazine.
- ✓ Benedict's test.
- ✓ Oxidation
- ✓ Reduction to alcohols

Classification of Carbohydrates:

Carbohydrates are classified into three major classes on the basis of complexity and behavior on hydrolysis

- 1) Mono saccharides
- 2) Oligosaccharides
- 3) Polysaccharides

1) Mono saccharides:

Simple sugars cannot be hydrolyzed into smaller units. Depending upon no. of carbon in a unit, mono saccharides are subdivided into aldoses to decaoses. More common subclasses of mono saccharides are:

Aldoses:

- ✓ Aldotrioses e.g. Glycerose,
- ✓ Aldotetroses e.g. Erythrose,
- ✓ Aldopentoses e.g. Ribose,
- ✓ Aldohexoses e.g. Glucose, Galatose
- ✓ Aldoheptose e.g. Glucoheptose.

Ketoses:

- ✓ Ketotrioses e.g. Dihydroxyacetone,
- ✓ Ketotetroses e.g. Erythrulose,
- ✓ Ketopentoses e.g. Ribulose,
- ✓ Ketohexoses e.g. Fructose,
- ✓ Ketoheptose e.g. Sedoheptulose.

Properties of Mono saccharides:

- 1) Muta-rotation
- 2) Glycoside Formation
- 3) Reducing Power
- 4) Reduction
- 5) Oxidation with mild and strong oxidizing agent
- 6) Methylation / Esterification
- 7) Dehydration
- 8) Form osazone with phenyl hydrazine.

9) Functions of Small Carbohydrates:

10) Some of the important function of small carbohydrates are listed below:

- 11)** 1. Trioses, glyceraldehyde and dihydroxy acetone, are important intermediates of both respiratory and photosynthetic pathways.
- 12)** 2. Erythrose, a tetrose monosaccharide, is not only an intermediate of respiratory and photosynthetic pathways but is also a raw material for the synthesis of lignin, anthocyanin's and some amino acids (e.g., phenylalanine, tyrosine) and a few aromatic compounds.
- 13)** 3. Pentose sugars, arabinose and xylose form polymers (arabans and xylans) which are constituents of hemicellulose.

- 14)** 4. Ribose is an important pentose sugar which is found in a variety of chemicals like CoA, FAD (flavin adenine dinucleotide), NAD (nicotinamide adenine dinucleotide), NADP and ATP besides being a constituent of nucleotides that form RNA (ribonucleic acid). Deoxyribose ($C_5H_{10}O_4$) is part of nucleotides that form DNA (deoxyribonucleic acid).
- 15)** 5. Ribulose 1, 5 bi-phosphate or RuBP (a phosphorylated pentosan) is the acceptor of carbon dioxide in photosynthesis.
- 16)** 6. Glucose is the main respiratory substrate. Fructose can also function similarly.
- 17)** 7. Fats and amino acids are formed from glucose and other sugars.
- 18)** 8. Oligosaccharides attached to cell membranes form cell coat or glycocalyx.
- 19)** **They are important for:**
- 20)** (a) Cell recognition
- 21)** (b) Cell attachment
- 22)** (c) Receptor molecules (for receiving and responding to external stimuli)
- 23)** (d) Antigen specificity for human blood groups (A, B, Rh)
- 24)** (e) Components of antibodies which are large molecules with attached carbohydrates
- 25)** (f) Glycoproteins of some viral coats for attaching to and invading host cells.
- 26)** 9. Some plants store oligosaccharides as reserve food, e.g., sucrose (sugarcane and sugar beet).
- 27)** 10. Monosaccharide's are polymerized to form structural carbohydrates (e.g., cellulose, ligncellulose) and storage carbohydrates, starch in plants and glycogen in animals.

2) **Oligosaccharide:**

Oligosaccharides are polymers of mono saccharides containing two to ten residues accumulate in vacuole while polysaccharides in plastids, they are classified as

- a) **Disaccharides:** Yield two mono saccharides on hydrolysis.
 - ✓ **Reducing Disaccharides:** e.g. Maltose (Glucose + Glucose), Lactose (Galactose + Glucose), other examples are Isomaltose, cellobiose.
 - ✓ **Non Reducing Disaccharides:** Sucrose (Glucose + Fructose)
 - b) **Tri saccharides:** e.g. Raffinose (Glucose + Fructose + Galactose) found in cotton seed and sugar beet.
 - c) **Tetra saccharides:** Yield 4 mono saccharides on hydrolysis e.g. stachyose (Glucose + Fructose + Galactose + Galactose) (only tetra saccharide known to exist in plant).
- ## 3) **Polysaccharides:** Polysaccharides are polymeric anhydrides of mono saccharides. The long chain polymers are either straight chain or branched. They are also called glycans.
- ## 4) **Classification of Polysaccharides:**
- a) **On the Basis of Function:**
 - ✓ Storage e.g. Starch, glycogen
 - ✓ Structural e.g. Cellulose, Pectin
 - b) **On the Basis of Composition:**
 - ✓ Homo polysaccharides
 - ✓ Hetero polysaccharides.

Homo Polysaccharides:

On hydrolysis gives single monosaccharide units

- i) **Pentosans:** Contains pentoses (C₅ H₈ O₄).
- ii) **Hexosans:** Contains hexoses (C₆ H₁₀ O₅) subdivided in to
 - i. **Glucosans:** Polymer of glucose e.g. Starch, Glycogen
 - ii. **Fructosans:** Polymer of fructose e.g. Inulin
 - iii. **Galactans:** Polymer of galactose e.g. Galactan
 - iv. **Mannans:** Polymer of mannose e.g. Mannans.

Hetero Polysaccharide: e.g. Hyaluronic acid, Chondroitin sulphates.

- ✓ **Gum:** Consist of arabinose, rhamnose, galactose and glucuronic acid.
- ✓ **Agar:** The sulphuric acid esters of galactans consist of galactose, galactouronic acid.

- ✓ **Pectins:** Fundamental unit is pectic acid; consist of arabinosc, galactose, galactouronic acid.

Functions of Polysaccharides:

- ✓ They serve as structural components of the cells
- ✓ They serve as stored form of energy
- ✓ They serve as nutrient.

Structure and Properties of Starch:

Consist of two components, Amyloses and Amylopectin. Amylose is a long chain polysaccharides containing α - D glucose molecules linked by 1- 4 glycosidic linkages, produce blue colour with iodine. Amylopectin is a branched chain polysaccharides consisting α -D glucose molecules linked by 1- 4 glycosidic linkage and branches by 1-6, linkage produce purplish colour with iodine and forms a gel with hot water.

Cellulose:

It is structural polysaccharide found in cell walls of plants, made up of long chains of a-D-Glucose molecules linked by 1-4 linkages, no branching, yield on hydrolysis crystalline D-glucose.

Pectin:

Present in apple, lemon, form gel with sugar sole, contains galactouronic acid, galactose and arabinose.

Types of Carbohydrates:

Carbohydrates are of two types, small and complex.

I. Small Carbohydrates:

Small carbohydrates are soluble and have low molecular weight. Commonly they are sweet to taste and are called sugars. Small carbohydrates are further differentiated into monosaccharides, derived monosaccharides and oligosaccharides.

1. Monosaccharides:

They are those sugars or simple carbohydrate monomers which cannot be hydrolysed further into smaller components. They have a general formula of $C_nH_{2n}O_n$.

Depending upon the number of carbon atoms, monosaccharides are of five types:

- (a) Trioses (having 3 carbon atoms, $C_3H_6O_3$), e.g., Glyceraldehyde, dihydroxyacetone.
- (b) Tetroses (having four carbon atoms, $C_4H_8O_4$), e.g., Erythrose, Threose.
- (c) Pentose's (having five carbon atoms, $C_5H_{10}O_5$), e.g., Ribose, Xylose, Deoxyribose, Arabinose, Ribulose. Deoxyribose is an exception because it has a formula of $C_5H_{10}O_4$.
- (d) Hexoses (having six carbon atoms, $C_6H_{12}O_6$), e.g., Glucose, Fructose, Galactose, Mannose.
- (e) Heptoses (having seven carbon atoms, $C_7H_{14}O_7$), e.g., Sedoheptulose, Glucoheptose.

(2) According to the nature of the reducing group they contain, viz.

(a) Aldoses:

E.g., glucose. Here, the reducing group is an aldehyde ($-CHO$) radicle.

(b) Ketoses:

These contain. Ketone ($C=O$) group, viz., fructose. The general formula of monosaccharides is $C_n(H_2O)_n$.

General Properties:

(a) They are colourless crystalline compounds having a sweet taste,

(b) Chemically they are derivatives of polyhydric alcohols. The aldoses are derived from primary alcohols and the ketoses from secondary alcohols.

(c) Formation of Esters:

By virtue of the alcohol group they easily form esters with acids, e.g., acetates, benzoates, etc. Such esters, having great physiological importance, are those of phosphoric acid, viz., hexose phosphates, which play an important role in carbohydrate metabolism; pentose phosphates, present in the nucleic acid and such others,

(d) Reducing Power:

By virtue of the aldehyde ($-CHO$) or the ketone ($C=O$) groups, the simple sugars are powerful reducing agents. They easily reduce alkaline copper, bismuth or silver solutions,

(e) Isomerism:

Due to the presence of asymmetric carbon atom in the molecule, monosaccharides may remain in different isomeric forms,

(f) Optical Rotation:

Simple sugars rotate the plane of polarised light and therefore may exist in either dextro or laevo forms,

(g) Condensation:

Simple sugars condense and form bigger carbohydrate molecules, viz., polysaccharides,

(h) Formation of Glycosides:

When replaceable hydrogen atom of a hydroxyl group from sugar is substituted with other radicles it is 'called a glycoside; that formed from glucose is a glucoside, from galactose a galactoside and the like. A good number of glycosides occur in leaves, roots, etc. of plants and are bitter solids. Phlorizin (glucose-phloretin), digitonin (galactose+xylose+digitogenin), indican (glucose + indoxyl) are-a few examples of them,

(i) Sugar Acids:

Either carbon atom one or six in a hexose molecule may be oxidised to carboxyl group. That formed from oxidation of number one is named hexonic acid (glucose → gluconic acid), and from six called uronic acid (glucose → glucuronic acid). Many drugs and a number of hormones combine with glucuronic acid in the body and are excreted as glucuronides.

(j) Formation of Hexosamine:

Replacement of hydroxyl group in hexose sugar with amino one produces amino sugar or hexosamine, that formed from glucose is glucosamin. They occur in some complex polysaccharides.

(k) Osazone Formation:

All reducing sugars condense with phenylhydrazine and produce osazone compounds. The crystalline forms of those osazone compounds are so characteristic that they can be used for the

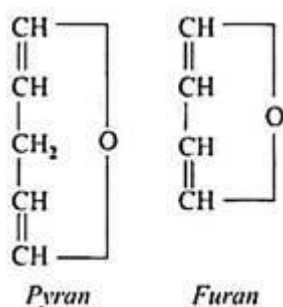
identification of the particular sugar. However glucose, glucosamine and fructose form similar osazones.

(l) Ring Structures of the Sugars:

Sugars not only remain as straight chain compounds but may also remain in the form of rings. This ring may include six members (five carbon atoms and one oxygen atom) or five members (4 carbon atoms and 1 oxygen atom). Haworth has suggested all sugars having six-membered rings to be called pyranoses (from their relation to pyran) and those forming five-membered rings, furanoses (from furan) (vide below), and

(m) Fermentation:

Sugars, in general, undergo fermentation by yeast and other microorganisms.

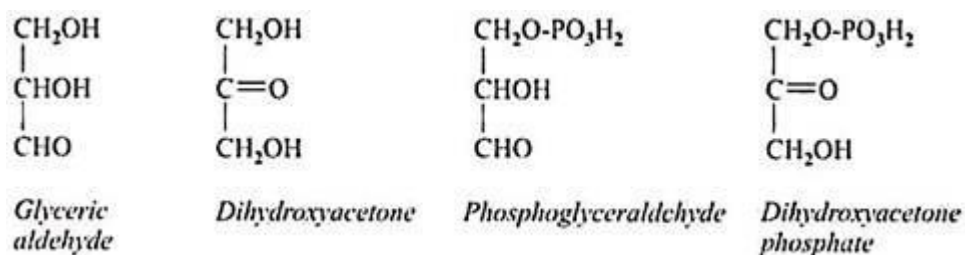


Physiologically Important Monosaccharides:

i. Trioses (Three-Carbon Sugars):

Two trioses are of great physiological importance, glyceric aldehyde and dihydroxyacetone. The corresponding phosphoric acid esters-phosphoglyceraldehyde and dihydroxyacetone phosphate are of great physiological value.

Formation of these triosephosphates is an essential step in the metabolism of sugar.



ii. Pentoses (Five-Carbon Sugars):

(a) Two different pentoses are present in two nucleic acids, RNA and DNA. Sugar ribose is present in the RNA, whereas that present in DNA is deoxyribose. In the Free State both the sugars exist in the pyranose form. In combination with nucleic acids they exist as deoxyribofuranose and ribofuranose.

(b) Arabinose:

It is also a pentose commonly found in gum Arabic—chiefly as l-arabopyranose.

iii. Hexoses (Six-Carbon Sugars):

The following hexoses are of physiological importance:

a. Glucose (Dextrose, Grape Sugar):

It is found in grapes, dextrorotatory and is an aldose. Glucose is found in nature in 'free form', in the form of disaccharides (maltose, sucrose, etc.), in the form of polysaccharides (starch, glycogen, etc.) and in combination with proteins (glycoproteins). It may remain both as a straight chain compound and as well as, in various ring forms, α - and β -glucose are the isomeric forms.

The optical reaction of glucose is peculiar. As soon as dextrose is dissolved in water it gives a specific rotation of $+112^\circ$. On standing the rotation gradually diminishes and finally remains constant at $+52.5^\circ$. This phenomenon is called mutarotation. If however, dextrose be first recrystallised from boiling pyridine, its solution in water at first gives a rotation of $+19^\circ$ and not $+112^\circ$.

This solution on standing also shows mutarotation in which the specific rotation gradually increases and finally becomes constant at the same value, $+52.5^\circ$. This shows that when in solution one particular variety changes into the other, until an equilibrium mixture of the two forms is produced with a constant rotation of $+52.5^\circ$.

Due to asymmetrical nature of carbon atom 1 in ring form of glucose, it can exist in two forms. The α -glucose has a rotation of $+112^\circ$ and the β form, $+19^\circ$. A solution of glucose is an equilibrium mixture between the straight chain and both α and β -ring forms, the percentage of β being more than α . Glucose forms esters with phosphoric acid.

b. Fructose (Laevulose, Fruit Sugar):

It is laevorotatory and is a ketone. Free fructose is present in honey and nearly in all sweet fruits. In combination it is found in cane sugar and inulin. In the human body normally it does not occur in Free State and rapidly converted into glucose in the liver and intestine. In contrast with other sugars, fructose is soluble in hot absolute alcohol. Like glucose it also forms phosphoric acid ester which plays an important role in carbohydrate metabolism.

c. Galactose:

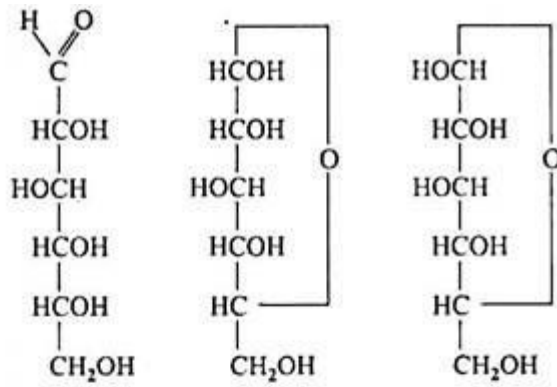
It does not occur free in nature. In the body it is found as a constituent of lactose (milk sugar) and cerebrosides (galactolipids). As polysaccharide (galactan) it is present in lichens, mosses, seaweeds, etc.

d. Mannose:

It does not occur free in nature. It is found as a constituent of certain animal proteins and converted to glucose in the body. It is also found as a polysaccharide known as mannan specially found in the ivory nuts.

iv. Heptoses (Seven-Carbon Sugars):

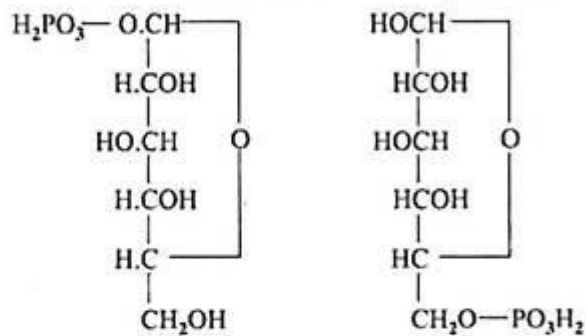
In the metabolic pathway of pentose phosphate by hexose monophosphate shunt, a seven-carbon keto sugar, sedoheptulose is formed as an ester with phosphoric acid (vide Metabolism).



Glucose

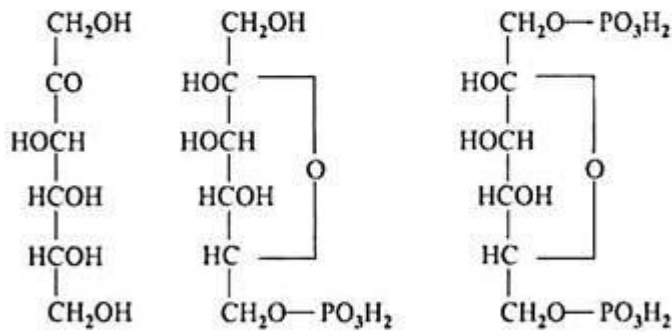
α-Glucose

β-Glucose



Glucose-1-Phosphate

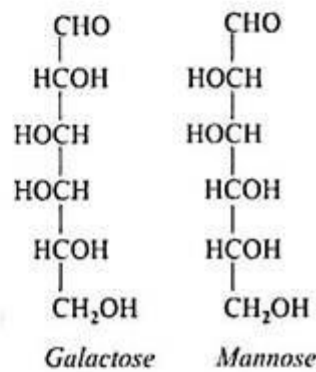
Glucose-6-Phosphate



Fructose

Fructose-6-Phosphate

Fructose-1, 6-Phosphate



Essay # 2. Compound Carbohydrates:

These are made up of from two to one thousand or more than thousand monosaccharide units either with or without non-carbohydrate units. Thus, on hydrolysis these may give rise to monosaccharide and non-carbohydrate units.

These are principally of two types:

i. Simpler Compound:

The simpler compound carbohydrates contain only a few monosaccharide units and are crystalline, water-soluble and give sweet taste. These simpler compounds are generally called oligosaccharides. Oligosaccharides on hydrolysis give rise to at least two to ten mono-saccharide units. Thus oligosaccharides are composed of disaccharides (two monosaccharide units), trisaccharides (three monosaccharide units) and tetrasaccharides (four monosaccharide units).

ii. More Complex Compound:

These carbohydrates include glycogen (glucan), cellulose, starch and also dextrans which are composed of ten or more monosaccharide units. These are mostly tasteless (dextrans are slightly sweet) and are amorphous solid substance. As these compounds are composed of many monosaccharide units, these are called polysaccharides (glycans) which are composed of ten or more monosaccharide units, held together by glycosidic linkages.

Those polysaccharides are composed of monosaccharides are called homoglycans (e.g., glycogen (glucan), starch, cellulose, etc.) whereas those are made up of two or more different types of monosaccharides are named as heteroglycans (e.g., mucopolysaccharides).

Simpler compound carbohydrates:

Oligosaccharides include:

- (a) Disaccharides;
- (b) Trisaccharides;
- (c) Tetrasaccharides.

(a) Disaccharides:

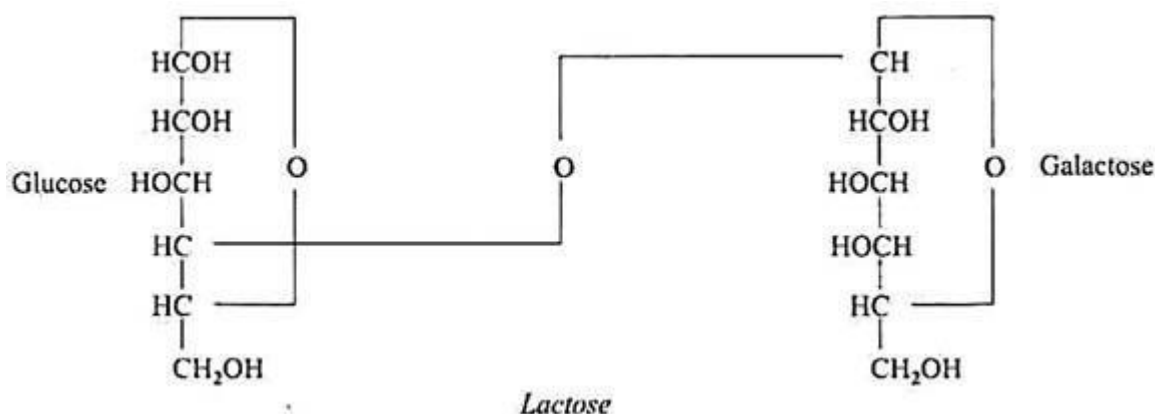
These can be regarded as condensation products of two monosaccharide units with the elimination of one molecule of water. Their general formula is $C_n(H_2O)_{n-1}$. During union the active groups (aldehyde or ketone) become engaged. In lactose only one aldehyde group becomes engaged and one aldehyde group (reducing group) remains free.

Similar is the case with maltose. But in cane sugar both the active radicals ($-CHO$ of glucose and $-CO$ of fructose) become engaged. For this reason lactose and maltose can reduce alkaline copper (although much less than monosaccharides), form characteristic osazone crystals and exhibit mutarotation. Cane sugar, on the other hand, in which both the active radicals are engaged, show no reducing power, does not form any osazone nor shows any mutarotation. In nature about 16 disaccharides are present.

Of these only the following are of physiological importance:

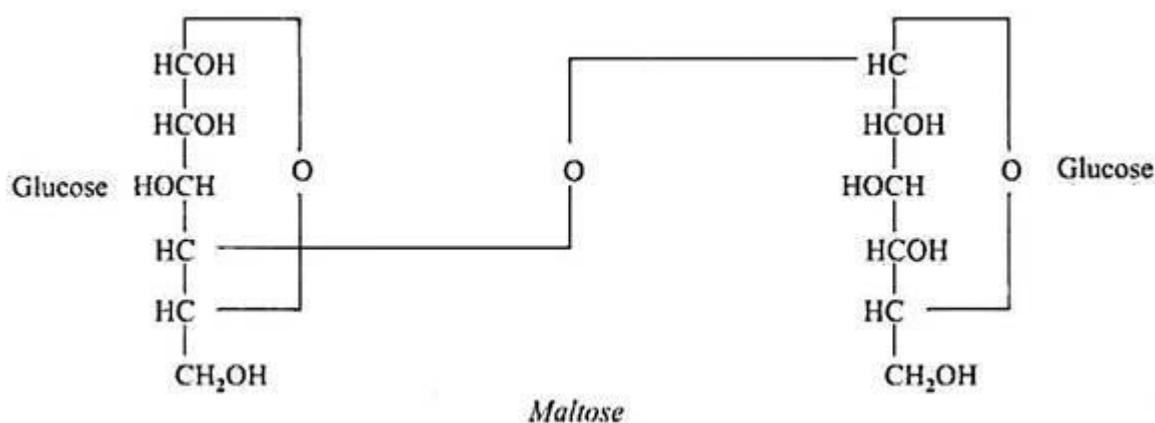
i. Lactose (Milk Sugar):

Composed of one molecule of glucose and one of galactose, found in the milk of mammals.



ii. Maltose (Malt Sugar):

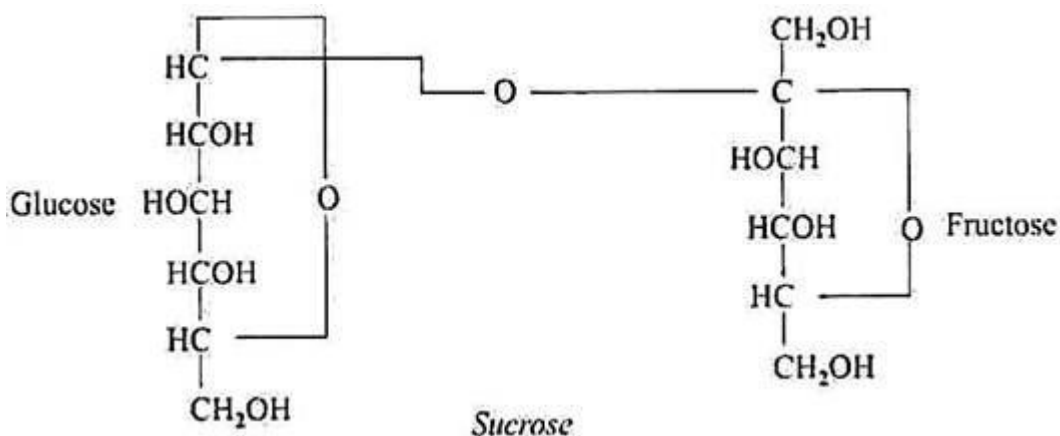
Composed of two glucose units. It is an intermediate product in the digestion of starch.



Sucrose (Cane Sugar):

On hydrolysis it gives rise to one molecule of glucose and one of fructose. It is the chief form of sugar taken in diet. It is widely distributed in many plant juices, such as sugar cane, sugar maple, and pine apple and also in sugar beets.

Sucrose is dextrorotatory but on hydrolysis the resulting mixture becomes laevorotatory owing to the liberation of fructose. The laevorotation of fructose is greater than the dextro rotation of glucose. For this reason the mixture is known as invert sugar and the enzyme (sucrase) which hydrolyse sucrose is also called invertase.



iii. Trehalose (Composed of Two Units of Glucose):

It is present in the haemolymph of insects as the principal sugar, also occurs in yeast and fungi.

(b) Trisaccharides:

These types of oligosaccharides on hydrolysis give rise to two monosaccharide units.

These trisaccharides are:

- i. Mannotriose giving rise to two molecules of galactose and one molecule of glucose on hydrolysis.
- ii. Robinose on hydrolysis gives rise to galactose and two molecules of rhamnose.
- iii. Rhamninose on hydrolysis gives rise to galactose and two molecules of rhamnose.
- iv. Raffinose on hydrolysis gives rise to fructose, glucose and galactose.
- v. Gentianose on hydrolysis gives rise to fructose and two molecule of glucose.
- vi. Melibiose (melezitose) on hydrolysis gives rise to fructose and two molecules of glucose.

Among six trisaccharides described, the first three are reducing and the rest three are non-reducing. The general formula of trisaccharides is $C_n(H_zO)_{n-2}$.

(c) Tetrasaccharides:

Only two tetrasaccharides are known.

These are:

- (1) Stachyose which is composed of D-glucose, galactose and fructose found in Stachys tubrifera, and
- (2) Scorodose in the bulbs of garlic and onion.

**More Complex Compound Carbohydrates
(Polysaccharides):**

Polysaccharides are made up of a large number of monosaccharide units. During condensation all the active radicals become engaged, so that they do not show any reducing power, do not produce any osazone and are generally not sweet to taste. They are soluble in water excepting cellulose. The molecules are large and hence, show colloidal properties. The empirical formula of polysaccharides is $(C_6H_{10}O_5)_n$.

Polysaccharides are classified according to the nature of the constituent units. For instance, those made up of pentose units are called pentosans, those of hexose unit's hexosans, etc., more specifically they are described after the name of the particular units of which they are composed.

For instance, glucosans (dextrans) are made of glucose, galactans of galactose, fructosans (laevans) of fructose and such others. Starch, glycogen and cellulose are glucosans. Inulin is a fructosan. Agar is a galactosan (galactan). Gums are mixtures of both pentosans and hexosans.

i. Starch:

This is the chief form of carbohydrate taken in diet. It is manufactured by the plants and plays the same role in them as glycogen does in animals, i.e., an easily available sugar store. It is the main constituent of food grains. Starch from different sources can be identified from their microscopic peculiarities. It is insoluble in cold water due to the presence of another cellulose layer around the granule.

On boiling the insoluble cellulose covering ruptures and starch enters into a colloidal solution. It is a glucosan and on hydrolysis breaks down into glucose. It gives blue colour with iodine. It has got no reducing power and is tasteless. Starch is a mixture of two substances having similar structure – amylose (mol. wt. 60,000) and amylopectin (mol. wt. 300,000) both being composed of chains of 24 to 30 glucopyranose units.

ii. Glycogen:

It is called animal starch; because it is in this form that glucose remains stored in the liver and muscles of animal body. Glycogen is also found in those plants which do not possess any chlorophyll, such as yeast, fungi, etc., but not in green plants. There is probably more than one type of glycogen.

When rabbit is fed with glucose, it synthesises a glycogen containing 12 glucose units, but if fed with galactose it forms a glycogen with 18 glucose units. But curiously enough, mixtures of glycogens with 12

and 18 units are not found. Glycogen is soluble in water, makes an opalescent solution and gives reddish colour with iodine. The glycogen molecule contains many glucose units. The units are joined by linkage between carbons 1 of one unit to carbon 4 of the next one; branches involving 1, 6 linkages are frequently present.

iii. Dextrins:

They do not occur naturally, but are the split product of starch resulting from hydrolysis. For this reason they ought to have been described as derived carbohydrates. The term dextrin is a group name including several varieties of dextrins. The earlier products of hydrolysis of starch are all called dextrins. The names of the different dextrins are given according to their colour reaction with iodine.

The first dextrin formed is amylopectin giving blue colour with iodine, the next product is called erythro-dextrin giving red colour with iodine and the next product gives no colour with iodine and is called achroodextrin. As these products become smaller and smaller, they develop more and more the characteristic properties of monosaccharide, such as the reducing power, a sweet taste and the others.

iv. Cellulose:

It is a stable, insoluble compound, found in the plants and never present in the animal body. Cellulose is taken with vegetable food. It cannot be digested by the human beings. Herbivorous animals can digest cellulose with the help of bacteria. Although indigestible, yet cellulose is of considerable importance.

In human dietetics because it adds 'bulk' to the intestinal contents, stimulate peristalsis and thereby help in the formation and evacuation of faeces. Filter papers, commonly used in the laboratories, are almost pure cellulose.

v. Inulin:

It is a polysaccharide composed of D-fructose units. It is a white crystalline powder and is readily soluble in hot water. It does not give any such characteristic colour with iodine.

Other polysaccharides (heterosaccharides) containing carbohydrate and non-carbohydrate units are:

(a) Heteropentosans (mucilages, gums, peptic substances, etc.).

(b) Heterohexosans (hignocellulose, pectocellulose, etc.).

(c) Mucopolysaccharides (mucin and mucoids) are composed of two to six different monosaccharide units including amino sugar and uronic acid.

Many important biological compounds are included in this group; they are hyaluronic acid, chondroitin sulphate, heparin, blood group substances, etc. The first three are called acid mucopolysaccharides due to their acidic character. The mucopolysaccharides in tissues are usually present in combination with protein and are called glycoproteins (mucoproteins, mucoids).

Functions of Polysaccharides:

Some of the important functions of Polysaccharides are listed below:

1. Starch and glycogen are the major storage foods of organic world.
2. On hydrolysis storage carbohydrates provide both energy and carbon chains.
3. Chitin is the structural carbohydrate of fungal walls and exoskeleton of arthropods.
4. Cellulose is the structural substance of cell walls in most of the plants.
5. Cellulose is economically important in the production of furniture, shelter, fuel, paper, textiles, ropes, rayon, cellophane, plastics, shatter proof glass, propellant explosives, emulsifier and raw material for several fermentation products.
6. For human beings cellulose has a roughage value but it is a food for ruminants, snails and termites.

7. Mucilage present as a protective coating around aquatic plants, bacteria, blue-green algae and some animals is derived from polysaccharides.

8. Mucopolysaccharides in human body have several functions—lubrication of ligaments and tendons, formation of some types of body fluids like cerebrospinal fluid, synovial fluid, vitreous humor, providing strength and flexibility to skin, connective tissue and cartilage, binding of proteins in cell walls and holding water in interstitial spaces.

9. Heparin prevents blood clotting inside blood vessels of animals.

10. Some mucopolysaccharides have medicinal and other commercial importance, e.g., husk of *Plantago ovata*, mucilage of Aloe, and alginic acid, agar, carragenin of marine algae.

11. Pectin's form matrix of cell wall. As calcium pectate they produce middle lamella or cementing layer between adjacent plant cells. Pectin's are commercial jellying agents.

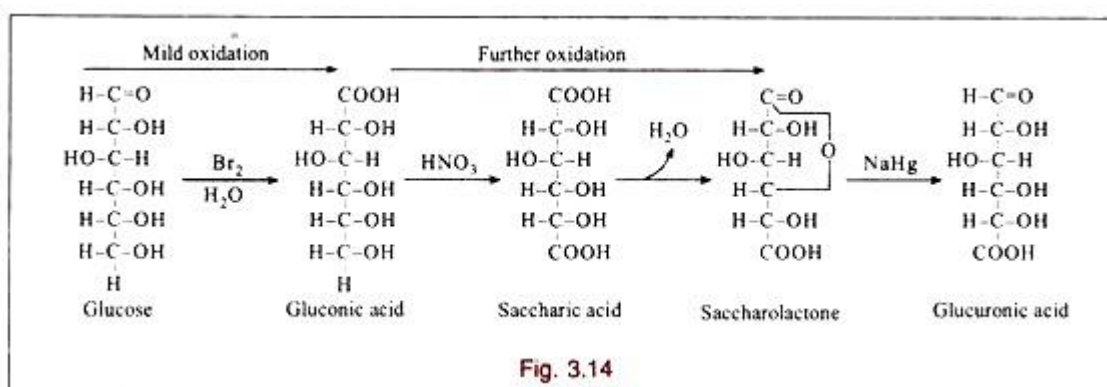
Important Chemical Reactions of Monosaccharides:

(i) Iodo Compounds:

An aldose sugar, when heated with concentrated hydriodic acid (HI), loses all of its oxygen and is converted into an iodo compound (glucose to iodoheptane, $C_6H_{13}I$).

(ii) Ester Formation:

Sugars, by virtue of the alcohol groups, readily form esters with acids. All the free -OH groups are replaceable. The greater biochemical significance is the ester with phosphoric acid and, to a lesser extent, with sulphuric acid. Pentose phosphates are involved in the formation of nucleic acids.



(iii) Acetylation:

The acetylation with acetyl-chloride indicates the presence of -OH group present in the sugar. The presence of 5 OH groups of glucose results in a penta-acetate.

(iv) Oxidation:

Oxidation of the aldehyde group forms “**al-donic acids**”. If the aldehyde group remains intact and the primary alcohol group is oxidized “**uronic acids**” are formed. Oxidation of galactose with concentrated HNO_3 yields the dicarboxylic mucic acid. This compound crystallizes readily.

(v) Reduction:

The monosaccharides are reduced to their corresponding alcohols by reducing agents such as sodium amalgam.

Thus, Glucose yields sorbitol (Protects liver).

Galactose yields dulcitol.

Mannose yields mannitol.

Fructose yields mannitol and sorbitol.

Mannitol:

(a) It is neither reabsorbed nor secreted in tubules.

(b) It is used as force diuretics i.e. to increase the volume of urine.

(vi) With Strong Mineral Acids:

There is a change of hydroxyl groups towards and of hydrogen away from the aldehyde end of the chain.

Reaction products with acids will condense with certain organic phenols to form compounds having characteristic colours.

(vii) Heat:

Gluconic acid on heating produces lactones. These are cyclic structures which resemble pyranoses and furanoses.

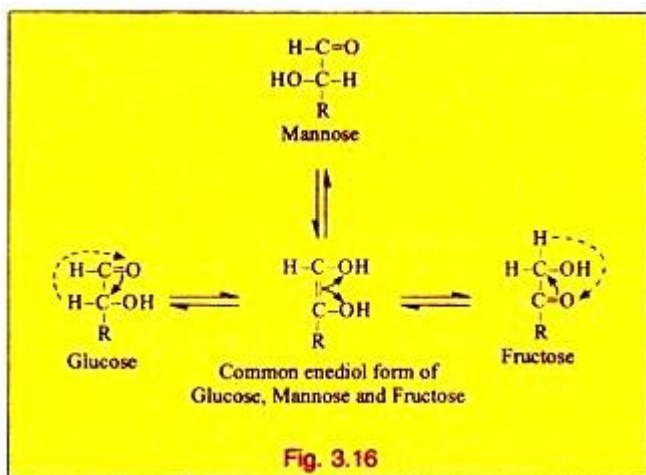
(viii) With Alkali:

Monosaccharides react in various ways:

(a) In dilute alkali the sugar will change to the cyclic alpha and beta structures, with an equilibrium between the 2 isomeric forms.

On standing, a rearrangement will occur which produces an equilibrated mixture of glucose, fructose and mannose through the enediol form.

(b) In concentrated alkali, sugar produces a series of decomposition products. Yellow and brown pigments develop, salts may form, many double bonds between carbon atoms are formed, and carbon-to-carbon bonds may rupture.



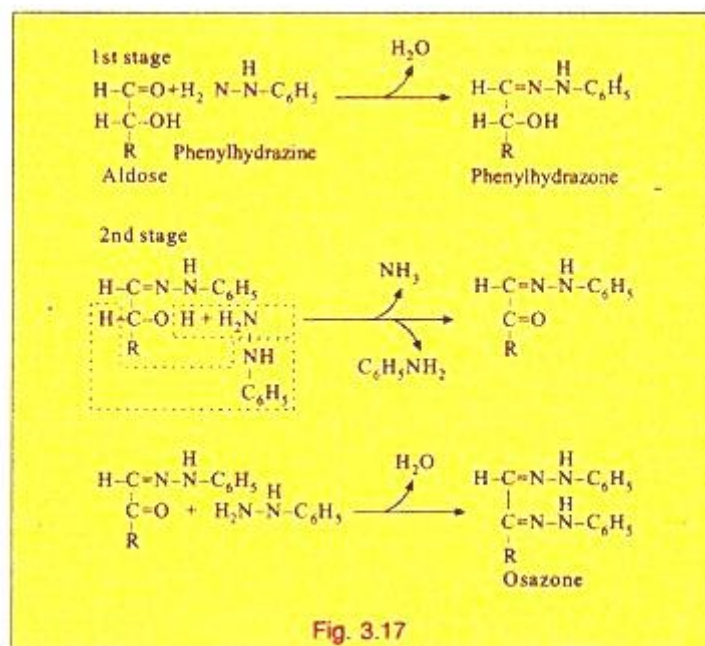
(ix) Osazone Formation:

It is nothing but the formation of crystalline derivatives of the sugars which are valuable in the identification of sugars.

These crystals are obtained by adding a mixture of phenyl hydrazine hydrochloride and sodium acetate to the sugar solution and heating in a boiling water bath.

The carbonyl group (i.e. aldehyde or ketone group) and the next adjacent carbon are involved in this reaction. With an aldose the reaction is shown Fig. 3.17.

The hydrazone then reacts with two additional molecules of phenyl hydrazine to form the osazone. The ketoses also show similar reaction.



From the comparison of their structures it may be noted that glucose, fructose and mannose form the same osazone; whereas galactose forms a different osazone because the part (carbon 4) in the structure of galactose which differs from that of glucose, fructose and mannose remains unaffected in osazone formation.

(x) Other Reactions:

Various other reactions take place due to the presence of aldehyde or ketone groups of the sugars which are important for analytical purposes. The best-known tests are reduction of metallic hydroxides together with oxidation of the sugar.

The alkaline metal is kept in solution with sodium potassium tartrate (Fehling's solution) or sodium citrate (Benedict's solution). Other metallic hydroxides may be used (Bismuth, Ammoniacal silver, Tollen's test, Nylander's test).

Barfoed's test distinguishes between monosaccharides and disaccharides. The copper acetate in dilute acid is reduced in 30 seconds by monosaccharides; whereas reduction of the same takes several minutes by disaccharides.

Carbohydrates: Classification # 2. Disaccharides:

The disaccharides are composed of two monosaccharide units united by a glycosidic linkage.

The physiologically important disaccharides are maltose, lactose and sucrose:

Maltose = 1 mol. glucose + 1 mol. glucose.

Lactose = 1 mol. glucose + 1 mol. galactose.

Sucrose = 1 mol. glucose + 1 mol. fructose.

a. Maltose (Malt sugar):

(i) It does not occur in the body.

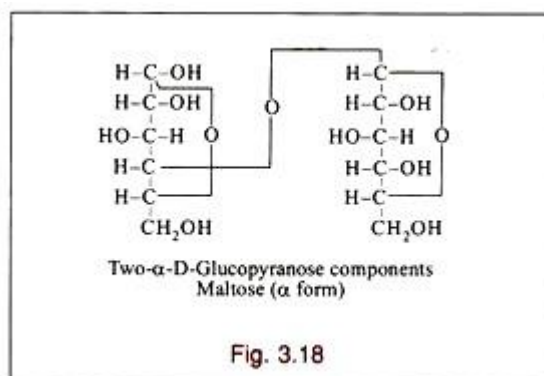
(ii) The sources of it are germinating cereals and malt and it is the intermediate product in the breakdown of starch by amylase in the alimentary canal.

(iii) It is hydrolysed to glucose by the enzyme maltase and the products are absorbed.

(iv) It has one free aldehyde group and hence shows mutarotation and the final rotation of the solution is $+130^\circ$. It can exist in α or β forms.

(v) It can reduce Fehling's and Benedict's solutions since it is a reducing sugar but cannot reduce Barfoed's solution.

(vi) It forms an osazone with phenyl hydrazine.



b. Lactose (Milk Sugar):

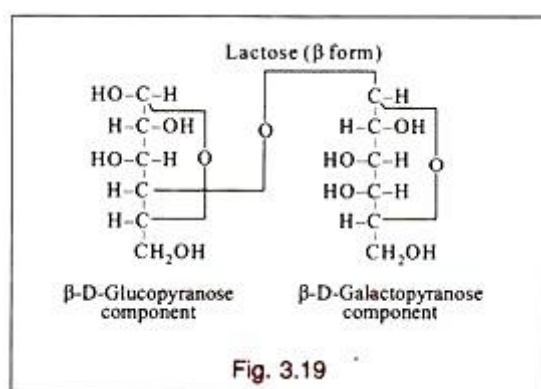
(i) It is present in milk and formed in the lactating mammary gland. It may occur in urine during pregnancy.

(ii) It is hydrolysed to glucose and galactose by the enzyme lactase in the alimentary canal and the products are absorbed.

(iii) It has free aldehyde group and hence shows mutarotation and the final constant specific rotation of the solution is $+55.2^\circ$. It can also exist in α or β forms.

(iv) Since it is a reducing sugar it can reduce Fehling's and Benedict's solutions but cannot reduce Barfoed's solution.

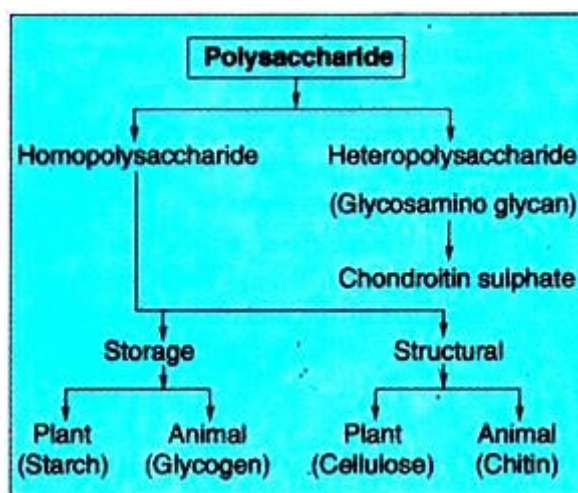
(v) It forms an osazone with phenyl hydrazine.



Carbohydrates: Classification # 3. Polysaccharides:

Polysaccharides are classified as homopolysaccharides and heteropolysaccharides.

The physiological important homopolysaccharides are Cellulose, Glycogen, Starch, Dextrins, and Inulin.



a. Cellulose:

(i) It is the main constituent of the supporting tissues of plants and forms a considerable part of our vegetable food. It does not occur in the animal body.

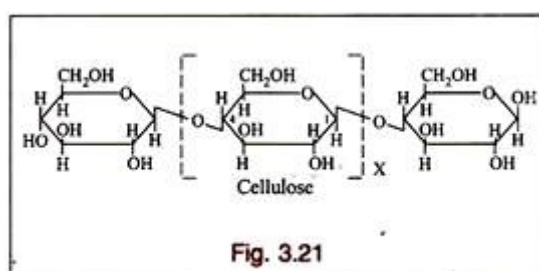
(ii) It is made up of β -glucose molecules which are linked by 1:4 linkages.

(iii) Owing to the difference in chemical structure, cellulose is not acted upon by amylases present in the digestive juices.

(iv) It is of considerable human dietetic value only because it adds “bulk” to the intestinal contents, thereby stimulating peristalsis and elimination of food residues.

(v) It is insoluble in ordinary solvents and gives no colour with iodine.

(vi) Cotton and filter paper are nearly pure cellulose.



b. Glycogen (Animal Starch):

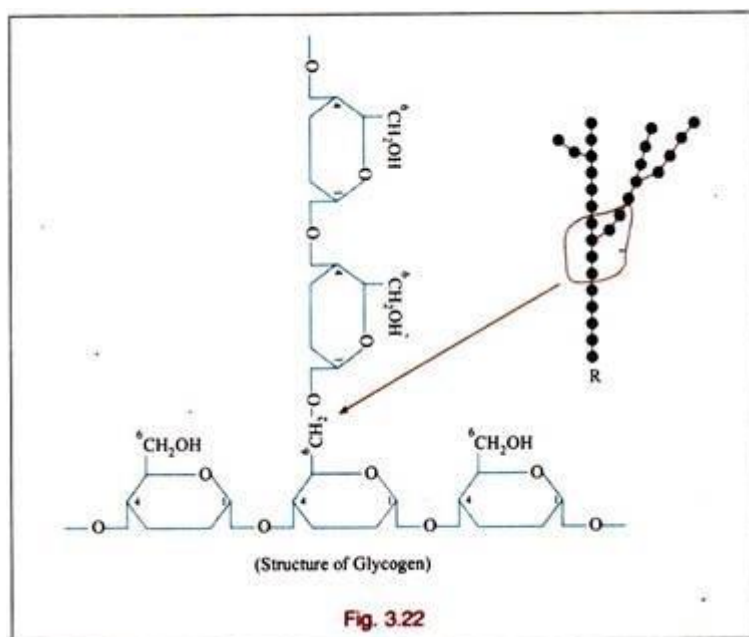
(i) It is the reserve carbohydrate found in liver and muscles of animals and human beings. The glycogen content of liver is more than that of muscle.

(ii) It is also found in plants which have no chlorophyll system (e.g., fungi and yeasts), but not in green plants.

(iii) The molecular weight of glycogen obtained from different sources may range from 10^5 to 10^8 and each molecule contains from 5,000 to 10,000 glucose molecules.

(iv) It has a branched structure with straight chain units of 12- 18- α -D-glucopyranose [in a 1 -4 glucosidic linkage] with branching by means of a [1-6]-glucosidic bonds.

(v) It is non-reducing, readily soluble in water and gives a red colour with iodine.



c. Starch:

(i) It is the stored carbohydrate of chlorophyll-containing plants. In plants, the starch is laid down in the cells in granules. The microscopic form of the granules is characteristic or the source of the starch.

(ii) It is formed by an α -glucosidic chain. Such a compound—which produces only glucose on hydrolysis—is called a glucosan.

(iii) It is the most important source of carbohydrate in our food and is found in cereals, potatoes, legumes and other vegetables in high concentrations.

(iv) It is a mixture of two substances – amylose and amylopectin – both are composed of glucopyranose units.

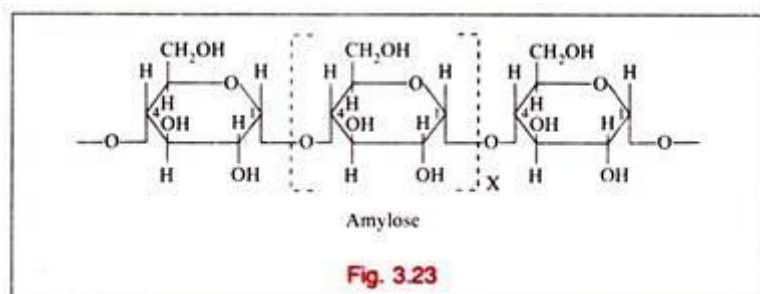
In the amyloses, the glucose units are joined by 1, 4 – α links to form un-branched chains which are in the form of a helix with six glucose units per turn.

Their molecular weights are about 60,000 which are equivalent to about 300 – 400 glucose units and are responsible for the development of blue colour with iodine.

Amylopectins have much larger molecular weights of about 500,000 and the chains have at least 80 branches; each branch is at an interval of 24-30 glucose units. The point of branching is the sixth carbon atom of glucose.

(v) Raw starch is insoluble in cold water owing to the resistance of the outer cellulose layer of the granule.

When this is ruptured by heating in water, starch is soluble. Concentrated solutions gelatinise on cooling and are used as an adhesive-starch paste.



d. Dextrins:

(i) Dextrins are formed by the partial hydrolysis of starch by an enzyme (salivary amylase), dilute mineral acids or heat.

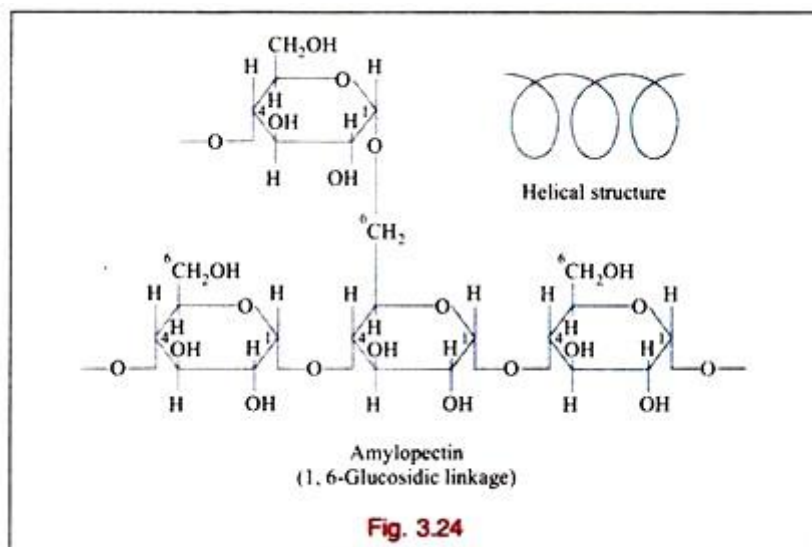
(ii) Amylodextrin, erythrodextrin and achrodextrin give blue, red-brown and no colour, respectively, with iodine, Achrodextrin being the simplest.

(iii) If they have reducing properties at all, they are very feeble.

(iv) They have a faint sweet taste.

(v) They form sticky solutions in water and are frequently used as adhesive, e.g., on postage stamps.

(vi) The final product of hydrolysis of starch by an amylase is maltose which is hydrolysed to glucose by maltase.



e. Inulin:

(i) It is found in tubers and roots of dahlias, and dandelions.

(ii) It is hydrolysed to fructose; hence it is a fructosan.

(iii) It does not produce any colour with iodine.

(iv) It is easily soluble in warm water.

(v) It is used in physiological investigation for the determination of the rate of glomerular filtration.