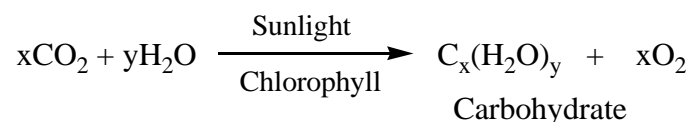


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Module	4(Unit-4, Carbohydrates)
Syllabus	Classification, and General Properties, Glucose and Fructose (open chain and cyclic structure), Determination of configuration of monosaccharides, absolute configuration of Glucose and Fructose, Mutarotation, ascending and descending in monosaccharides. Structure of disacharrides (sucrose, cellobiose, maltose, lactose) and polysacharrides (starch and cellulose) excluding their structure elucidation

Introduction

Carbohydrates are compounds of tremendous biological importance and are ubiquitous in nature. They are primarily produced in plants by photosynthesis and about 75% of the dry weight of plant world is carbohydrate in nature.



Some common examples of carbohydrates are cane sugar, starch, cellulose, dextrin etc.

Chemically, carbohydrates are molecules that are composed of carbon along with hydrogen and oxygen-usually in the same ratio as that found in water (H_2O) and could, therefore, be represented by the general formula $\text{C}_x(\text{H}_2\text{O})_y$ i.e., they appear to be hydrates of carbon. But the above definition has certain limitations as:

1. A variety of compounds such as rhamnose ($\text{C}_6\text{H}_{12}\text{O}_5$), deoxyribose ($\text{C}_5\text{H}_{10}\text{O}_4$) and rhamnohexose ($\text{C}_7\text{H}_{14}\text{O}_6$) etc. are known which are carbohydrates by their chemical behavior but cannot be represented by the general formula $\text{C}_x(\text{H}_2\text{O})_y$.
2. There are other substances like formaldehyde (CH_2O) and acetic acid $\text{C}_2(\text{H}_2\text{O})_2$ which do not behave like carbohydrates but can be represented by the general formula $\text{C}_x(\text{H}_2\text{O})_y$.

New Definition

Carbohydrates are defined as polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis and contain at least one chiral carbon atom. It is pertinent to mention that aldehydic or ketonic groups in carbohydrates are not present as such but usually exist in combination with one of the hydroxyl group of the molecule in the form of hemiacetals and hemiketals respectively.

Importance of carbohydrates

1. Carbohydrates are the source of energy. This energy is stored in the form of glycogen in animals and starch in plants.

2. They supply carbon atoms for the synthesis of other biochemical substances (proteins, lipids and nucleic acids).
3. They serve as a structural component of many organisms including the cell walls of bacteria, the exoskeleton of many insects, and the fibrous cellulose of plants.

Medical importance

1. Erythromycin is an amino sugar used as antibiotic.
2. Streptomycin is a glycoside derivative used as antibiotic.
3. Disorders associated with carbohydrates are: Diabetes mellitus, Galactosemia, Glycogen storage disease.

Classification

Carbohydrates are classified into two main classes, sugars and polysaccharides.

Sugars: Sugars are sweet, crystalline substances that are soluble in water. These are further classified on the basis of their behaviour on hydrolysis as:

1. **Monosaccharides:** The simplest form of carbohydrate is the monosaccharide. 'Mono' means 'one' and 'saccharide' means 'sugar'. Monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones that cannot be hydrolyzed further to give simple sugars. They may again be classified on the basis of carbonyl group as:
 - i) Polyhydroxy aldehydes are called *aldoses*, for example, glucose, ribose etc.
 - ii) Polyhydroxy ketones are called *ketoses*, for example, fructose, ribulose etc.

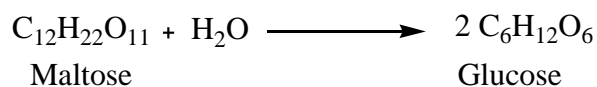
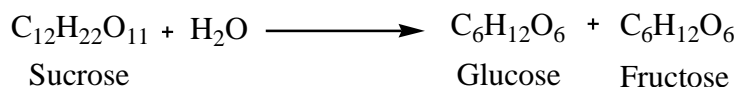
The aldoses and ketoses are further divided based on the number of carbon atoms present in their molecules as trioses, tetroses, pentoses, hexoses, heptoses etc.

Aldehyde	Molecular formula	Structural formula	Examples
Aldotrioses	C ₃ H ₆ O ₃	CH ₂ OH.CHOH.CHO	Glyceraldehyde
Aldotetroses	C ₄ H ₈ O ₄	CH ₂ OH.(CHOH) ₂ .CHO	Erythrose, threose
Aldopentoses	C ₅ H ₁₀ O ₅	CH ₂ OH.(CHOH) ₃ .CHO	Ribose, xylose
Aldohexoses	C ₆ H ₁₂ O ₆	CH ₂ OH.(CHOH) ₄ .CHO	Glucose, mannose
Aldoheptoses	C ₇ H ₁₄ O ₇	CH ₂ OH.(CHOH) ₅ .CHO	Mannoheptose, glucoheptose

Ketone	Molecular formula	Structural formula	Examples
Ketotrioses	C ₃ H ₆ O ₃	CH ₂ OH.CO.CH ₂ OH	Dihydroxyacetone
Ketotetroses	C ₄ H ₈ O ₄	CH ₂ OH.CO.(CHOH). CH ₂ OH	Erythrulose
Ketopentoses	C ₅ H ₁₀ O ₅	CH ₂ OH.CO.(CHOH) ₂ . CH ₂ OH	Ribulose, xylulose
Ketohexoses	C ₆ H ₁₂ O ₆	CH ₂ OH.CO.(CHOH) ₃ . CH ₂ OH	Fructose, sorbose
Ketoheptoses	C ₇ H ₁₄ O ₇	CH ₂ OH.CO.(CHOH) ₄ . CH ₂ OH	Sedoheptulose, mannoheptulose

2. **Oligosaccharides:** Carbohydrates that produce two to ten monosaccharide units during the hydrolysis are called oligosaccharides. They can be further classified based on the number of monosaccharide units formed on hydrolysis. For example :

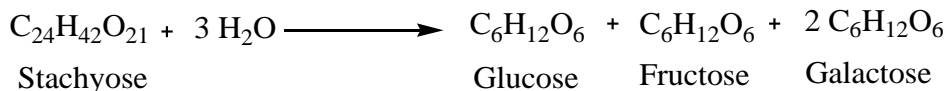
i) **Disaccharides:** These carbohydrates give two monosaccharide units on hydrolysis, which may be same or different. Sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose.



ii) **Trisaccharides:** These carbohydrates yield three molecules of monosaccharide units on hydrolysis. Raffinose upon hydrolysis gives one molecule each of glucose, fructose and galactose.

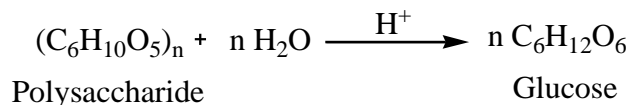


iii) **Tetrasaccharides:** These carbohydrates yield four molecules of monosaccharide units on hydrolysis. Stachyose upon hydrolysis gives one molecule each of glucose and fructose and two molecules of galactose.



3. **Polysaccharides:** These carbohydrates give a large number of monosaccharide units on hydrolysis. These monosaccharide units are joined together by oxide bridges. These linkages are called glycosidic linkages. The common and widely distributed polysaccharides correspond to the general formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$.

Polysaccharides are not sweet in taste, so they are called non-sugars. Some common examples are starch, cellulose, glycogen etc.



Classification on the basis of Reactivity:

1. **Reducing sugars:** Some hemiacetals or hemiketals exist in equilibrium with the open chain sugars in the aqueous solution. These sugars can reduce an oxidizing agent such as Tollen's reagent, Benedict's solution, Fehling's solution or aqueous bromine because of free aldehydic or ketonic group and are thus classified as reducing sugars or carbohydrates. All monosaccharides whether aldoses or ketoses are reducing sugars. For example, glucose, fructose, glyceraldehydes, galactose, etc. Certain disaccharides such as lactose, maltose are also reducing sugars.
2. **Non-reducing sugars:** Some cyclic acetals or ketals do not exist in equilibrium with their open chain carbonyl group containing forms in neutral or basic aqueous solutions. These sugars cannot reduce an oxidizing agent such as Tollen's reagent, Benedict's solution, Fehling's solution or aqueous bromine. All polysaccharides are non-reducing sugars. For example, starch, cellulose, glycogen, dextrin etc.

Note: The disaccharides may be reducing or non-reducing depending upon the position of linkages between the two monosaccharide units. If the glycosidic linkage involves the carbonyl group of both the monosaccharide units, the disaccharide would be non-reducing (for example, sucrose). If one of the carbonyl group in any one of the monosaccharides is free, the disaccharide would be reducing (for example, maltose and lactose).

General Properties of Carbohydrates:

1. Monosaccharides:

- i) Most monosaccharides have a sweet taste (Fructose is sweetest; 73% sweeter than sucrose).
- ii) They are solids at room temperature.

- iii) They are extremely soluble in water.
- iv) They contain one or more chiral carbon atoms and are therefore optically active.
- v) Monosaccharides do not exist in solution in their open chain forms: an alcohol group can add into the carbonyl group in the same molecule to form a pyranose ring containing a stable cyclic hemiacetal or hemiketal.
- vi) In the pyranose form of glucose, carbon-1 is chiral and thus two stereoisomers are possible: one in which the OH group points down (α -hydroxy group) and one in which the OH group points up (β -hydroxy group). These forms are anomers of each other and carbon-1 is called anomeric carbon.
- vii) The hemiacetal and hemiketal forms of monosaccharides can react with the alcohols to form acetal and ketal structure called glycosides. The new carbon-oxygen bond is called glycosidic linkage.
- viii) Phosphate esters can form at the C-6 of aldohexoses and aldoketoses. Phosphate esters of monosaccharides are found in the sugar-phosphate backbone of DNA and RNA and in ATP.
- ix) Once the glycoside is formed, the ring can no longer open up to the open chain form. Glycosides, therefore, are non-reducing sugars.

Disaccharides:

- i) They are crystalline, sweet and water soluble substances.
- ii) They can be hydrolyzed into their monosaccharide building blocks by boiling with dilute acids or reaction with the appropriate enzymes.
- iii) Disaccharides that contain hemiacetal groups are reducing sugars.

Polysaccharides:

- i) They are usually amorphous and tasteless compounds which are insoluble in water.
- ii) Polysaccharides are not reducing sugars, since the anomeric carbons are connected through glycosidic linkages.
- iii) On complete acid or enzymatic hydrolysis, they change into monosaccharides.

Monosaccharides

Monosaccharides, also called simple sugars, are the simplest carbohydrates having general formula $(\text{CH}_2\text{O})_n$ where $n = 3-8$. These are the basic units of carbohydrates that cannot be hydrolyzed further into simpler molecules. They are usually colourless, water-soluble, and crystalline solids. Examples of monosaccharides include glucose, fructose and galactose etc.

D-(+)-Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ [Dextrose/Grape Sugar]

Glucose, also called as *dextrose*, is the most widely distributed monosaccharide. In free form, it is present in abundance in honey, ripe grapes (hence called *grape sugar* also) and most of the sweet fruits including mangoes, apples, peaches etc. In combined form, it forms the component of glycosides, disaccharides and polysaccharides. Glucose constitutes 0.1% of human blood and is the primary source of energy in cell function.

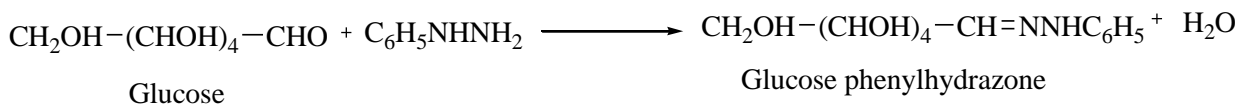
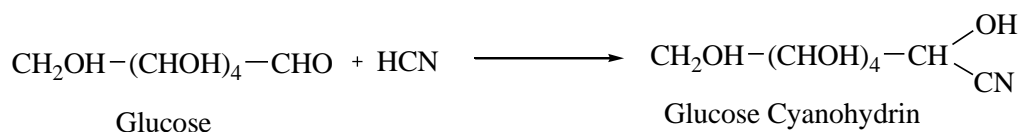
Structure of D-(+)-Glucose

1. Molecular Formula:

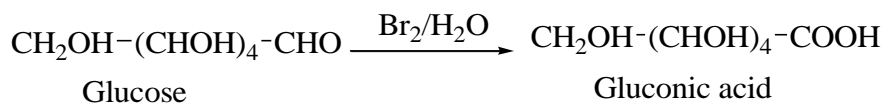
The molecular formula of glucose as established from analytical data and molecular weight determination is $\text{C}_6\text{H}_{12}\text{O}_6$.

2. Presence of aldehydic group:

a. Glucose reacts with hydrogen cyanide to form cyanohydrin, with hydroxylamine to form an oxime and with equimolar quantities of phenylhydrazine to form a phenylhydrazone. These reactions indicate the presence of carbonyl group ($>\text{C}=\text{O}$), in the glucose molecule.

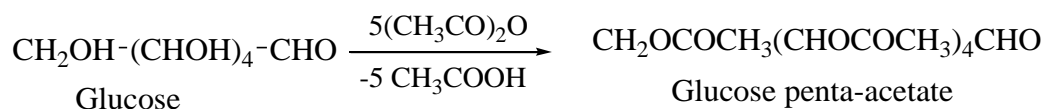


- b. On mild oxidation with bromine water, glucose gives gluconic acid which is a monocarboxylic acid containing the same number of carbon atoms as glucose. This shows that carbonyl group present in glucose must be an aldehydic group.



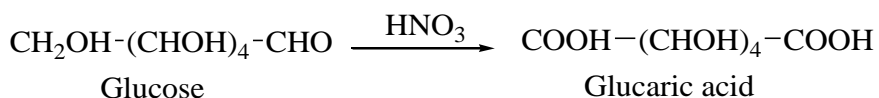
3. *Presence of five hydroxyl groups:*

Glucose reacts with acetic anhydride to form penta-acetate, indicating the presence of five hydroxyl groups in glucose molecule. Further, since glucose does not lose water readily, each hydroxyl group must be present on a different carbon.



4. *Presence of one primary alcoholic group:*

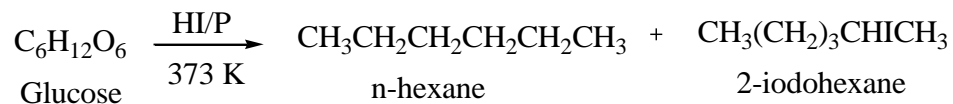
Glucose on oxidation with nitric acid gives glucaric acid, a dicarboxylic acid containing the same number of carbon atoms as glucose.



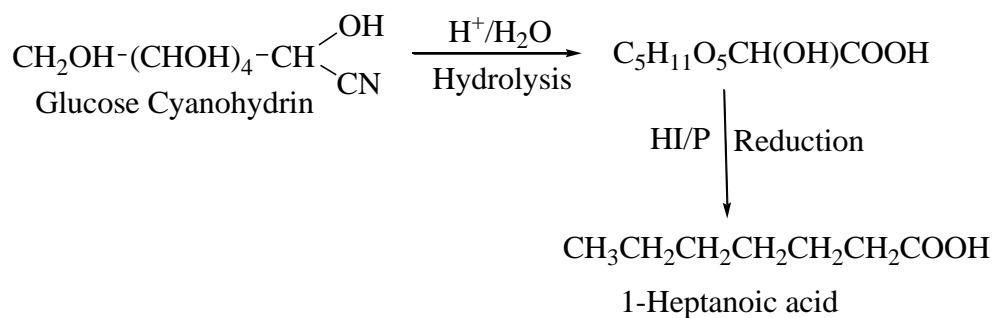
Since the aldehydic group present in glucose can account for the formation of only one carboxylic group, the other carboxylic group must have been formed by the oxidation of primary alcoholic group. Thus, one of the five hydroxyl groups present in glucose must be a primary alcoholic group.

5. *Presence of straight chain of carbon atoms:*

- i. Glucose on reduction with hydrogen iodide and red phosphorus at 373 K, gives a mixture of n-hexane and 2-iodohexane. This indicates that six carbon atoms in glucose are arranged in a straight chain.



- ii. It is further confirmed by the fact that glucose cyanohydrin on hydrolysis and subsequent reduction with HI/Red P gives 1-heptanoic acid.

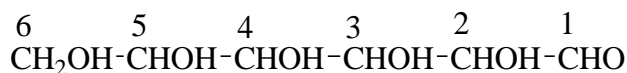


Open chain structure of D-(+)-Glucose

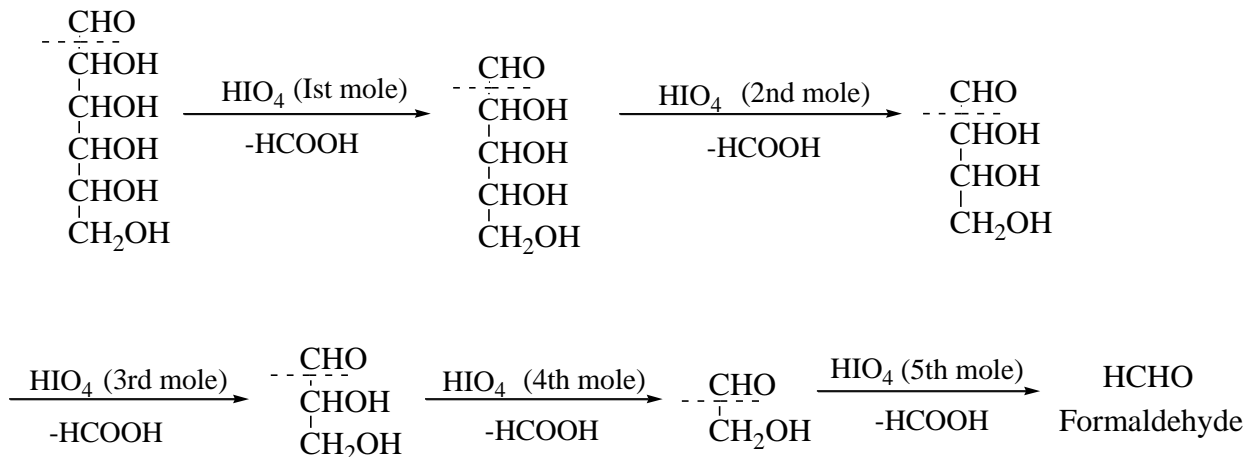
From the above discussion, it can be concluded that:

- Glucose contains a straight chain of six carbon atoms.
- Of the two terminal carbon atoms, one is in the form of aldehydic group and the other end carries a primary alcoholic group (as both aldehydic and primary alcoholic groups are chain terminating groups).
- Each of the remaining four carbon atoms carries a hydrogen atom and a hydroxyl group to account for the presence of five –OH groups and twelve hydrogen atoms in all.

Thus, following open chain structure was proposed for glucose:



The structure is further confirmed by the oxidative cleavage of glucose by periodic acid (Malaprade reagent). Glucose consumes five moles of periodic acid giving 1 mole of formaldehyde and 5 moles of formic acid as shown below:



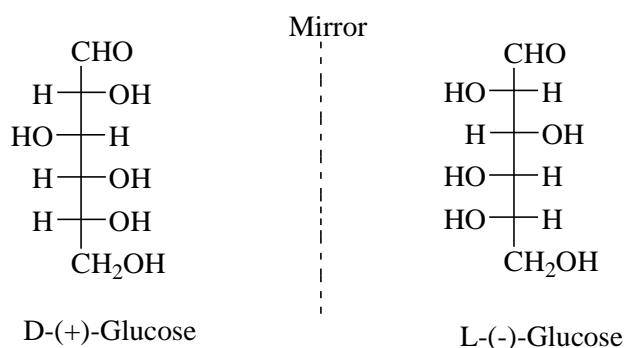
Configuration of D-(+)-Glucose:

The open chain structure of glucose contains four chiral carbon atoms (marked by asterisks). Thus, the number of possible stereoisomers should be 2^4 or 16.



All the 16 stereoisomers are known and exist as eight pair of enantiomers: 8 belonging to D-series and 8 to L-series. These correspond to D- and L- forms of allose, altrose, glucose, mannose, gulose, idose, galactose, and talose.

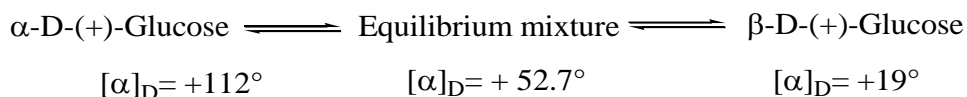
Emil Fischer arbitrarily assigned the following configuration to D-(+)-Glucose by relating it with D-(+)-Glyceraldehyde.



Limitations of Open Chain structure of D-(+)-Glucose

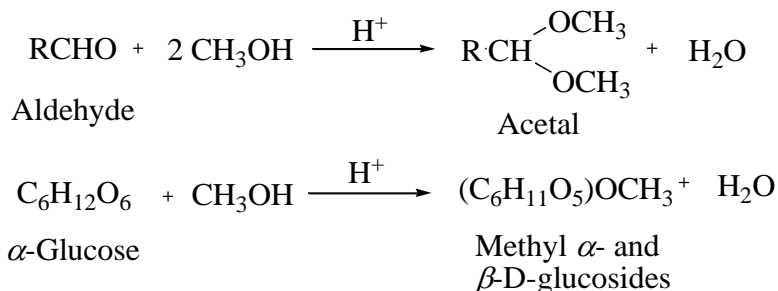
The open chain structure of D-(+)-Glucose explains most of its properties; however it fails to explain the following facts:

1. D-(+)-Glucose does not undergo some characteristic reactions of aldehydes. For instance, D-(+)-Glucose does not form addition compound with sodium bisulphite and doesn't respond to Schiff's test.
2. D-(+)-Glucose exists in two stereo-isomeric forms i.e. α -D-glucose and β -D-glucose. When glucose is crystallized from water or aqueous alcohol at room temperature, α -form of D-glucose is obtained [M. pt. 419 K, Specific rotation $+112^\circ$ in fresh aqueous sol.]. Whereas, when glucose is crystallized from water above 371 K β -form of D-glucose is obtained [M. pt. 423 K, Specific rotation $+19^\circ$ in fresh aqueous sol.].
3. Mutarotation: Although the crystalline forms of α - and β -glucose are quite stable, but in aqueous solution, each form slowly changes into an equilibrium mixture of both. The specific rotation of freshly prepared aqueous solution of α -D-glucose falls gradually from $+112^\circ$ to $+52.7^\circ$ with time and that of β -D-glucose increases from $+19^\circ$ to 52.7° .



The phenomenon of change of specific rotation of an optically active compound, with time, to an equilibrium value is known as *mutarotation*.

4. D-(+)-Glucose forms two isomeric methyl glycosides. Aldehydes normally react with two moles of methanol per mole of aldehyde to form an acetal but D-(+)-Glucose when treated with methanol in presence of dry HCl gas, reacts with only one mole of methanol per mole of glucose to form a mixture of two methyl-D-glucosides, i.e., methyl α -D-glucoside [M. pt. 438 K, Specific rotation $+158^\circ$] and methyl β -D-glucoside [M. pt. 380 K, Specific rotation -33°].



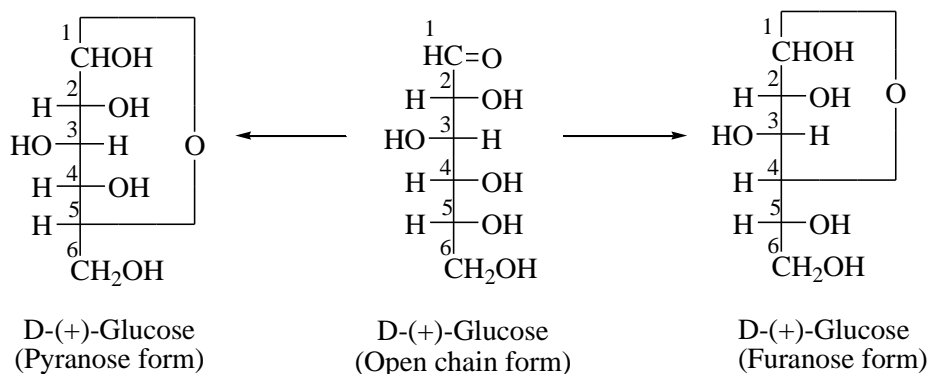
The two methyl D-glucosides behave as full acetals. Like acetals, methyl glucosides change back into glucose and methanol only under acidic conditions. These glucosides do not reduce Fehling solution or Tollen's reagent and do not undergo mutarotation.

5. The U.V spectrum of glucose does not shows the presence of an aldehydic group.

Ring Structure of D-(+)-Glucose

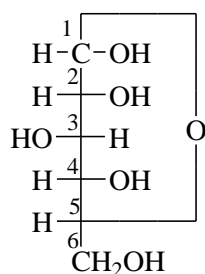
To account for the above facts, Tollen (1883) suggested that aldehydic group does not occur free in glucose. The aldehydic group is tied up by combination with one of the hydroxyl groups to form a *cyclic hemiacetal* structure. He argued, that since –OH and –CHO groups are part of the same molecule, thus any of the –OH groups may be involved in intramolecular hemiacetal formation. Since α -hydroxy acids readily undergo lactonization, he suggested that glucose has a five-membered ring in which C₄-OH is involved in hemiacetal formation. This structure is called α -glucose.

Haworth (1926) later on revised Tollen's structure and suggested that glucose contains a six-membered ring structure in which C₅-OH is involved in hemiacetal formation.

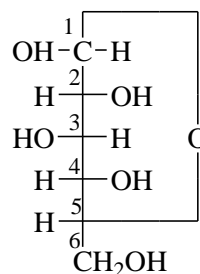


The five-membered ring structure containing an oxygen atom because of its similarity with furan is called the *furanose form*. Similarly, the six-membered ring structure containing an oxygen atom because of its similarity with pyran is called *pyranose form*.

The cyclic hemiacetal structure has a new chiral centre at C₁. As a result, D-(+)-Glucose exists in two diastereoisomeric forms, i.e., α - and β -forms.



α -D-(+)-Glucose



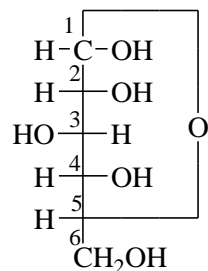
β -D-(+)-Glucose

In α -D-(+)-glucose, the hydroxyl group at C₁ lies on the right hand side while in β -D-(+)-glucose, it lies on the left hand side.

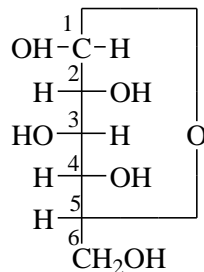
Such pair of diastereomers which differ in configuration only around C₁ are called *anomers* and the C₁ carbon is called the *anomeric carbon* or *the glycosidic carbon*.

Evidence in favour of Ring Structure

1. *Justification of existence of α - and β -forms*: The cyclic hemiacetal structure leads to the formation of a new stereocentre at C-1. Consequently, there are two configurations possible around this carbon, one in which hydroxyl group at C-1 is on the right hand side [α -D-(+)-glucose] and the other in which hydroxyl group is on the left hand side of C-1 [β -D-(+)-glucose].

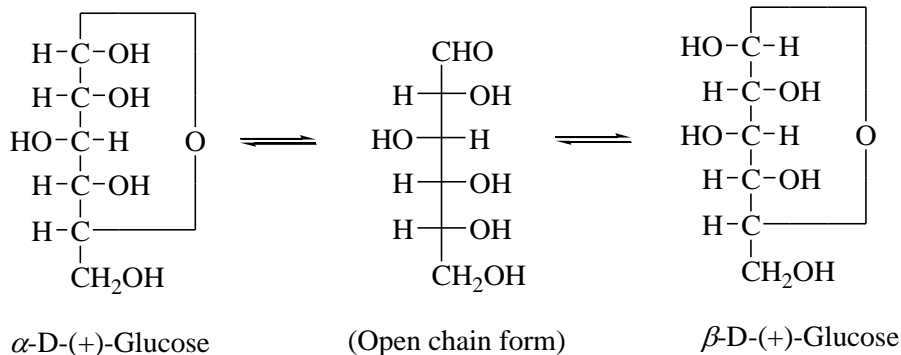


α -D-(+)-Glucose

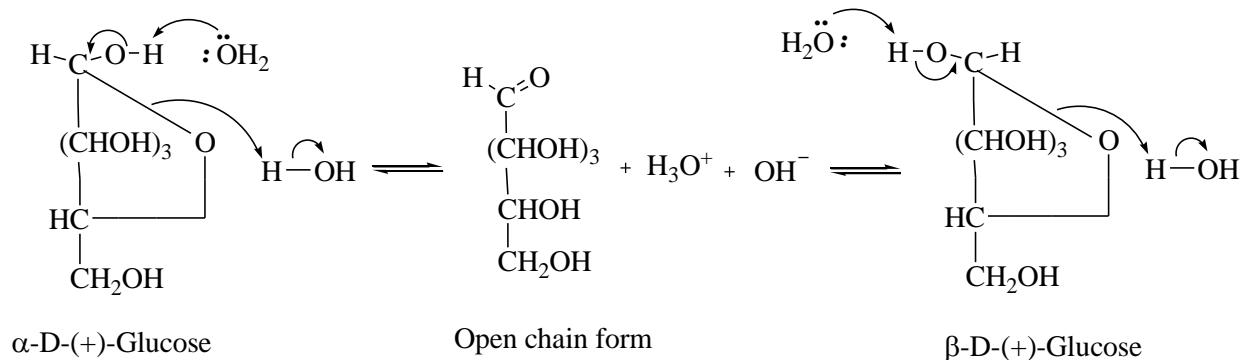


β -D-(+)-Glucose

2. *Explanation of mutarotation:* The phenomenon of mutarotation exhibited by glucose anomers can be easily explained in terms of the cyclic structure. Each of these anomers is a typical hemiacetal and can be easily hydrolyzed in the aqueous solution to give the open chain form of glucose. The open chain form then recloses either in the original position or in the inverted position to form an equilibrium mixture containing both the anomers (36% α -anomer and 64% β -anomer) and a very small amount of open chain form. This equilibrium mixture has a specific rotation of $+52.7^\circ$. Thus the phenomenon of mutarotation is due to the facile opening and closing of hemiacetal ring.



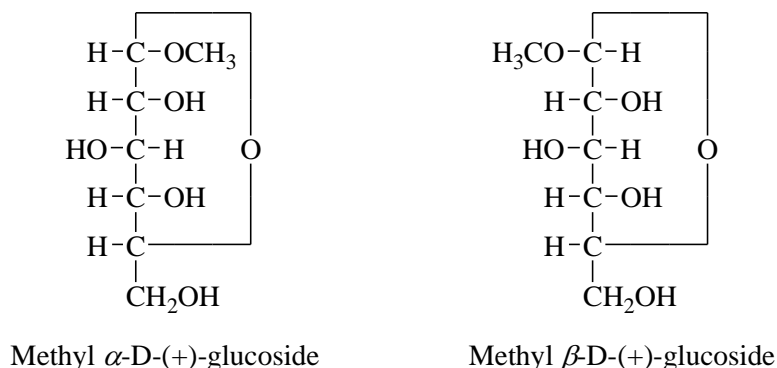
Mechanism of mutarotation: Mutarotation is believed to occur by concerted mechanism. The cyclic hemiacetal ring opens up due to a concerted attack by base and water. The process involves simultaneous removal of a proton (by the base) from hemiacetal hydroxyl group and donation of proton to the ethereal oxygen. The open chain structure thus formed recloses to form an equilibrium mixture of α - and β -anomers. Since water is amphoteric in nature (has both acidic and basic properties), mutarotation takes place readily in aqueous solution.



3. *Occurrence of characteristic reactions of aldehydes*: The typical aldehydic reactions of D-(+)-Glucose such as cyanohydrin, oxime and osazone formation, reduction of Fehling's sol. and Tollen's reagent etc. can be easily explained in terms of the small amount of open chain form present in the equilibrium mixture of two anomers.

On treatment with a particular reagent, the open chain form gets consumed by reaction with that reagent. As a result, the initial equilibrium is disturbed and more of the closed chain form changes into the open chain form to push the reaction forward. Thus, whole of glucose reacts *via* its open chain form. In contrast, the aldehydic reactions of D-(+)-Glucose with Schiff's reagent, sodium bisulphite and ammonia are reversible and the concentration of the open chain form in the equilibrium mixture is too low (less than 0.5 %). Therefore, weak nucleophilic attacking reagents such as sodium bisulphite and Schiff's reagent fail to initiate the attack and are unable to disturb the equilibrium to form more of the open chain form. As a result, glucose does not undergo these reactions.

4. *Formation of glucosides*: The formation of two anomeric methyl glucosides can be explained in terms of cyclic structure. The equilibrium mixture of α - and β -glucose reacts separately with methanol in presence of dry HCl gas to form the corresponding methyl-D-glucosides.

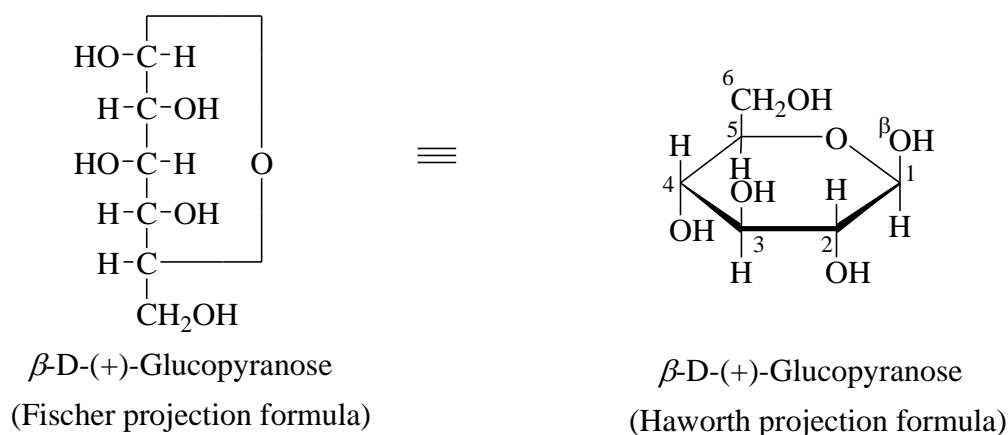
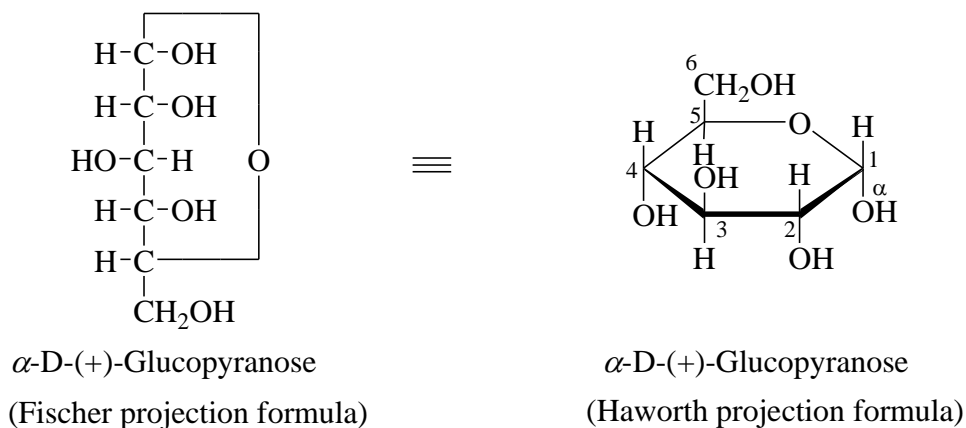


These glucosides are full acetals since they are formed by the further reaction of hemiacetals with methanol. Being acetals, they are hydrolyzed back to methanol and glucose only in the acidic medium. Thus, they are not hydrolyzed in aqueous solution and hence do not undergo mutarotation. Similarly, they are not hydrolyzed by the alkali present in Fehling solution or Tollen's reagent and hence they do not reduce these reagents.

Projection Formulae of α - and β -D-(+)-glucose

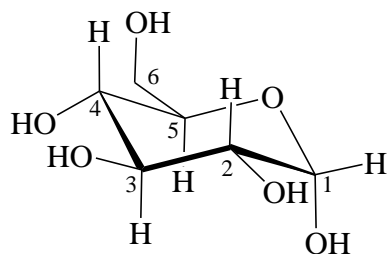
Haworth (1926) proposed the use of projection formulae for better representation of cyclic structures of glucose and other carbohydrates.

To draw the Haworth projection formulae of monosaccharides having six membered rings, firstly a hexagon is drawn in which oxygen atom is written on the right hand side farthest away from the observer. The numbering of atoms is done as shown below. The lower part of the hexagon is thickened to depict that this part is closer to the observer. The terminal $-\text{CH}_2\text{OH}$ group is written on the upper side of hexagon for D-series and on the lower side for L-series. The groups present on the left hand side of the Fischer projection formula are placed on the upper side and groups present on the right hand side are placed on the lower side of the hexagon ring. The Haworth projection formulae of α - and β -D-(+)-glucose are represented as:

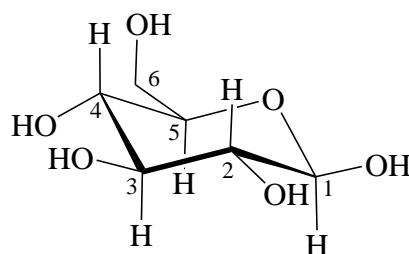


Conformations of α - and β -D-(+)-Glucose

The cyclic structure of glucose and other carbohydrates can be best represented in terms of their conformations. X-ray studies have shown that glucose exists preferentially in more stable chair form (as in cyclohexane). In this conformation, the $-\text{CH}_2\text{OH}$ group, the $-\text{OH}$ groups at C_2 , C_3 and C_4 are all in equatorial positions as it involves lesser crowding between the bulky groups than if they were in axial positions. In addition, the equilibrium mixture of D-(+)-glucose contains more of β -form (36% of α - and 64% of β -form) depicting that β -form is more stable than α -form. As such $-\text{OH}$ group at C_1 in β -form should be equatorial, whereas in α -form, it must be axial. The C_1 $-\text{OH}$ group, therefore, suffers 1,3-diaxial interaction with axial hydrogens at C_3 and C_5 whereas no such interaction is seen in β -form. Thus, β -D-(+)-glucopyranose is thermodynamically more stable than α -D-(+)-glucopyranose. The conformations of glucose in α - and β -form are shown below:



α -D-(+)-Glucopyranose
(Less stable)



β -D-(+)-Glucopyranose
(More stable)

D-(-)-Fructose, C₆H₁₂O₆ [Laevulose or Fruit Sugar]

Fructose or laevulose is a simple reducing sugar (monosaccharide). It is the sweetest, naturally occurring sugar, estimated to be twice as sweet as sucrose. Fructose occurs free along with glucose in honey and sweet fruits (hence the name fruit sugar). In combined form, it is a component of disaccharides and polysaccharides.

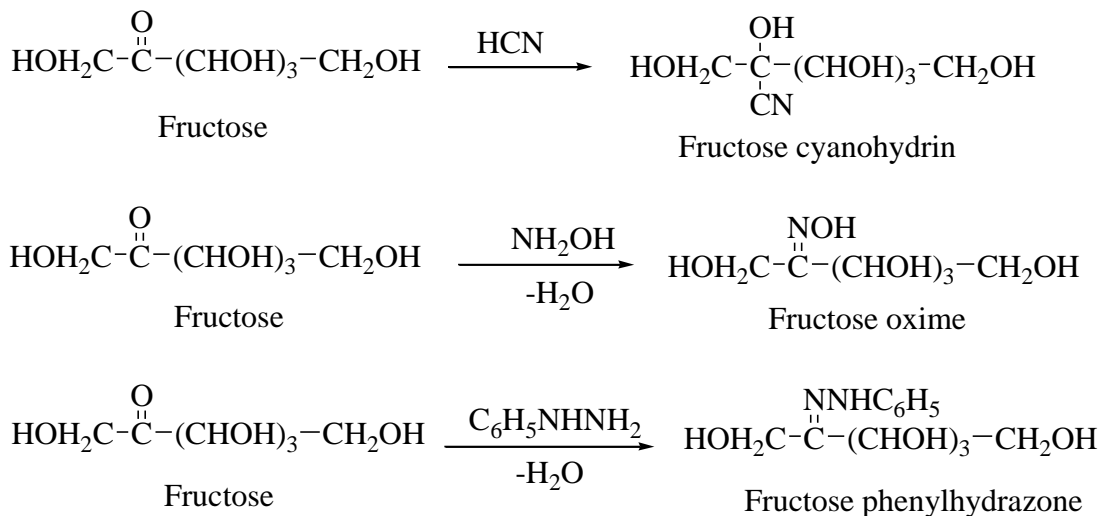
Structure of D-(-)-Fructose

1. *Molecular Formula:*

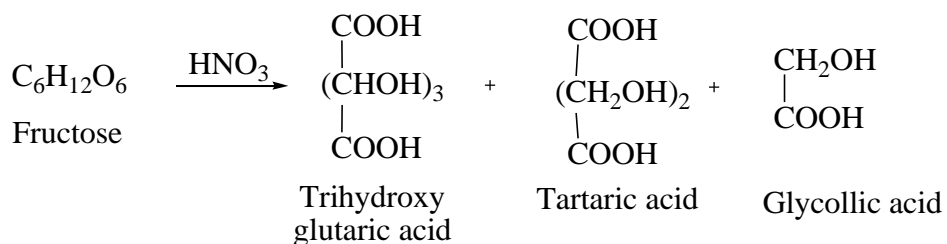
The molecular formula of fructose as determined from elemental analysis and molecular weight determination is C₆H₁₂O₆.

2. *Presence of ketonic group:*

- i. Fructose reacts with hydrogen cyanide to form cyanohydrin, with hydroxylamine to form an oxime and with equimolar amounts of phenylhydrazine to form a phenylhydrazone. These reactions suggest the presence of carbonyl group (>C=O), in the fructose molecule.

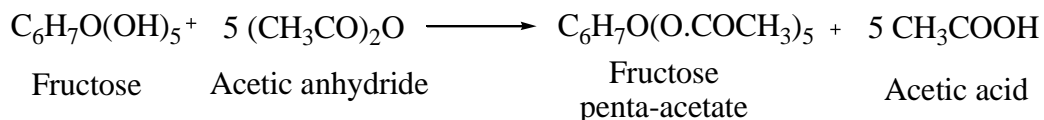


- ii. Fructose on oxidation with nitric acid gives a mixture of trihydroxyglutaric acid, tartaric acid and glycollic acid each of which contains a lesser number of carbon atoms than fructose. This shows that carbonyl group present in fructose is a ketonic group. It is further confirmed by the fact that fructose is not oxidized by bromine water.

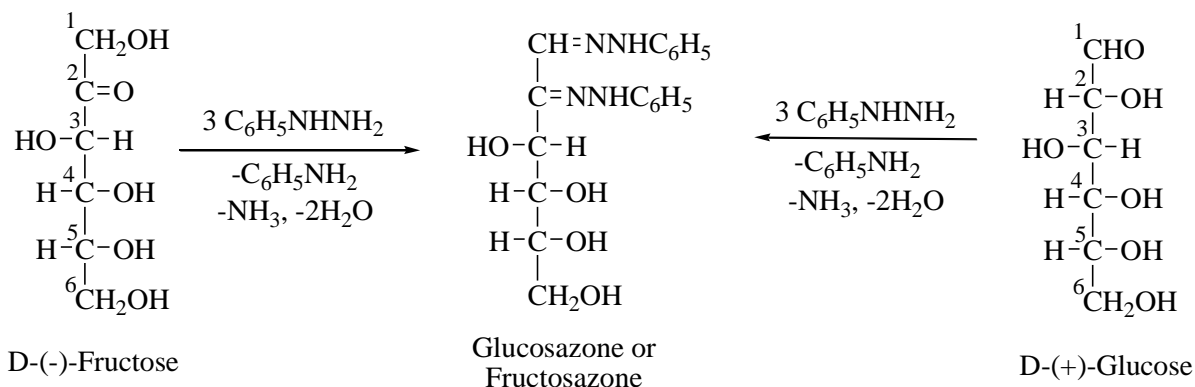


3. *Presence of five hydroxyl groups:*

Fructose reacts with acetic anhydride to form penta-acetate. This shows the presence of five hydroxyl groups in fructose. Further, since fructose does not lose water easily, each hydroxyl group must be present on a different carbon atom.



The naturally occurring fructose is one of the 8 stereoisomers. Its configuration was based upon the fact that fructose forms the same osazone as glucose. As osazone formation involves only first two carbon atoms (none of which is a stereocentre in case of fructose), the configuration at the three stereocentres (C₃, C₄ and C₅) of fructose must be same as that of glucose. Therefore, as in case of glucose, fructose was assigned a D-configuration which may be represented as follows:



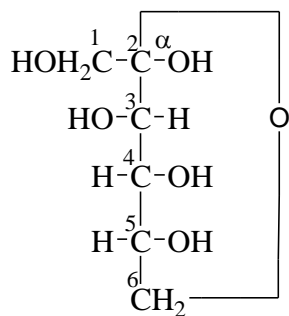
Limitations of Open Chain structure of D-(-)-Fructose

The open chain structure of fructose accounts for most of its properties; however it fails to explain the following facts:

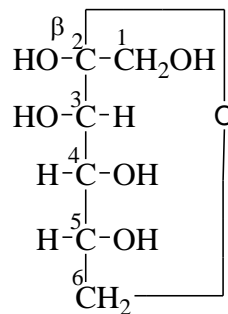
1. D-(-)-Fructose does not react with sodium bisulphite even though it contains a ketonic group.
2. It exists in two stereo-isomeric forms i.e. α -D-fructose and β -D-fructose which show mutarotation.
3. It forms two isomeric methyl fructosides on treatment with methanol in presence of HCl gas.

Ring Structure of D-(-)-Fructose

To explain the above limitations, it was suggested that fructose exists in a cyclic hemiacetal form. It was assigned a six-membered or pyranose hemiacetal ring structure which is formed by combination of C₂ ketonic group and C₆ hydroxyl group to form α - and β -D-fructose as shown:



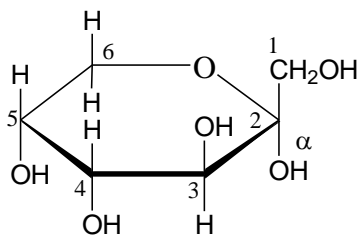
α -D(-)-fructopyranose



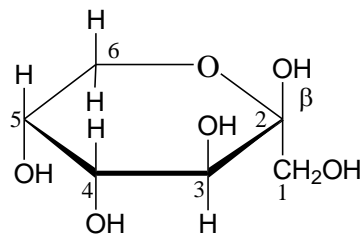
β -D(-)-fructopyranose

Haworth Projection Formulae

The Haworth projection formulae of α - and β -D-fructose may be represented as:



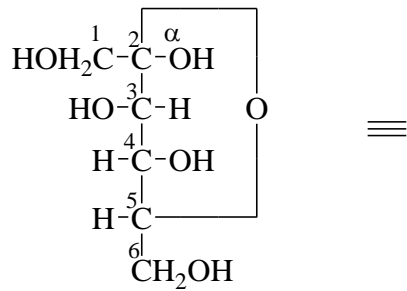
α -D(-)-fructopyranose



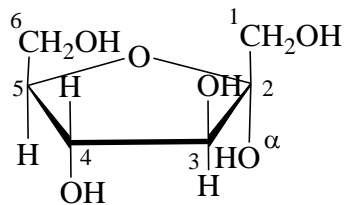
β -D(-)-fructopyranose

Furanose structure of α - and β -D-Fructose

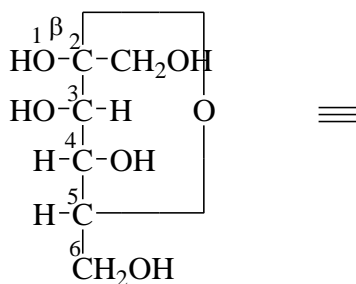
In free state fructose has the six-membered cyclic or the pyranose structure, however, in the combined state such as fructosides, disaccharides like sucrose, etc., fructose always has the five-membered cyclic ring structure or the furanose structure. The Fischer and Haworth projection formulae of α - and β -D-fructofuranose are given below:



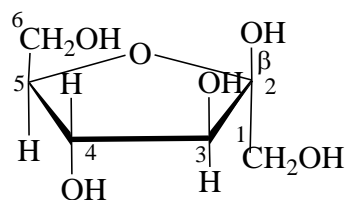
α -D(-)-fructofuranose



α -D(-)-fructofuranose



β -D(-)-fructofuranose

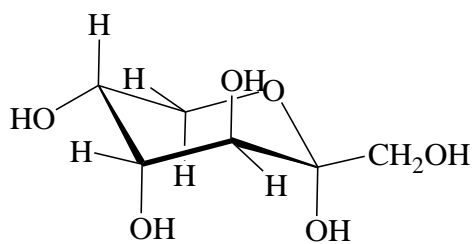


β -D(-)-fructofuranose

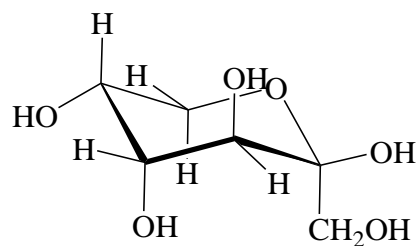
Conformations of α - and β -D(-)-Fructose

Fructose exists preferentially in the chair conformation like glucose due to its greater stability.

The chair conformation of α - and β -D(-)-Fructose is shown as:



α -D(-)-Fructopyranose

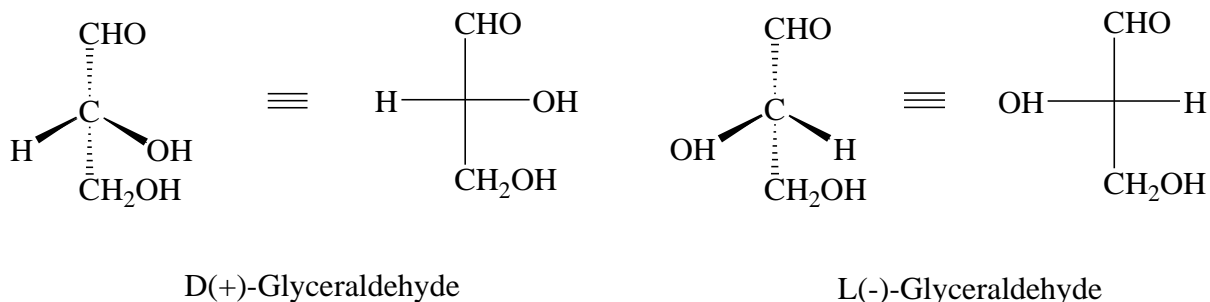


β -D(-)-Fructopyranose

Configuration of Monosaccharides

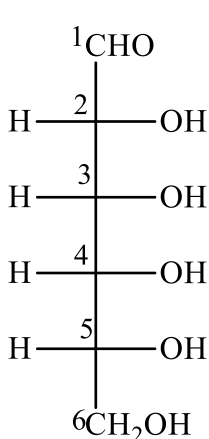
Most applications of stereochemistry, as we know, are based upon the relative configuration of different compounds, not upon their absolute configuration. In the earlier days of the study of stereochemistry, it was not found possible to determine the absolute configuration of the compounds. The chemists were more interested in knowing only the relative configuration. *Relative configuration means the arrangement of atoms/groups in space of a particular stereoisomer relative to the atoms/groups of another compound chosen as arbitrary standard.* To assign relative configuration to various monosaccharides, Emil Fischer chose a standard reference compound and fixed its configuration arbitrarily. The compound chosen was Glyceraldehyde ($\text{CH}_2\text{OH}.\text{CHOH}.\text{CHO}$), a simple aldose having one stereocentre and exists in two enantiomeric forms.

The (+) enantiomer was given symbol D and was assigned configuration in which OH group lies towards right on the penultimate carbon. On the other hand, (-) Glyceraldehyde was given symbol L and was assigned configuration in which OH group lies towards left on the penultimate carbon.

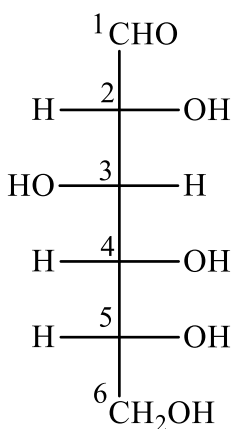


Many other compounds were then assigned the relative configurations by relating their configuration to that of D- and L-Glyceraldehyde. It was only in 1951 when *Bijvoet using X-ray crystallography proved that the arbitrary configurations assigned to glyceraldehydes actually represented their correct absolute configurations.*

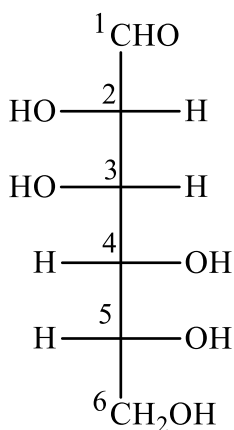
D-Glyceraldehyde and L-Glyceraldehyde act as configurational reference points for all monosaccharides. In monosaccharides containing more than one chiral carbon atoms, the reference point is the **penultimate carbon** i.e., **last but one carbon**. Thus, a monosaccharide is given D-configuration if the –OH group on the penultimate carbon like that in D-(+)-glyceraldehyde lies on the right hand side. On the other hand, a monosaccharide is given L-configuration if the –OH group on the penultimate carbon like that in L-(-)- glyceraldehyde lies on the left hand side. By convention, the open chain formulae of monosaccharides are written vertically with –CHO group at the top and >C=O group near the top. It can be seen in the examples that the penultimate carbon is the highest numbered stereocentre in the molecule.



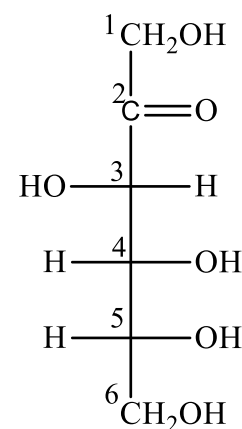
D-Allose



D-Glucose

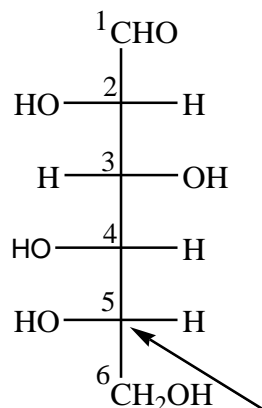


D-Mannose



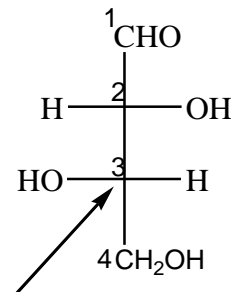
D-Fructose

Carbon-5 is the penultimate carbon



L-Glucose

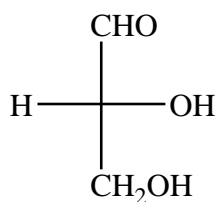
Penultimate carbon



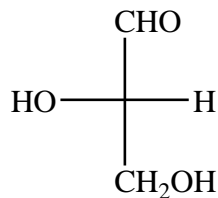
L-Threose

Determination of Absolute configuration of Glucose and Fructose

The precise arrangement of substituents at a stereogenic center is known as the *absolute configuration* of the molecule. Techniques for determining the absolute configuration of chiral molecules were not developed until the 1950's, and so it was not possible for Fischer and his contemporaries to relate the sign of rotation of any substance to its absolute configuration. A system evolved based on the arbitrary assumption, later shown to be correct, that the enantiomers of glyceraldehydes have the signs of rotation and absolute configurations as shown below:



R-(+)-Glyceraldehyde



S-(-)-Glyceraldehyde

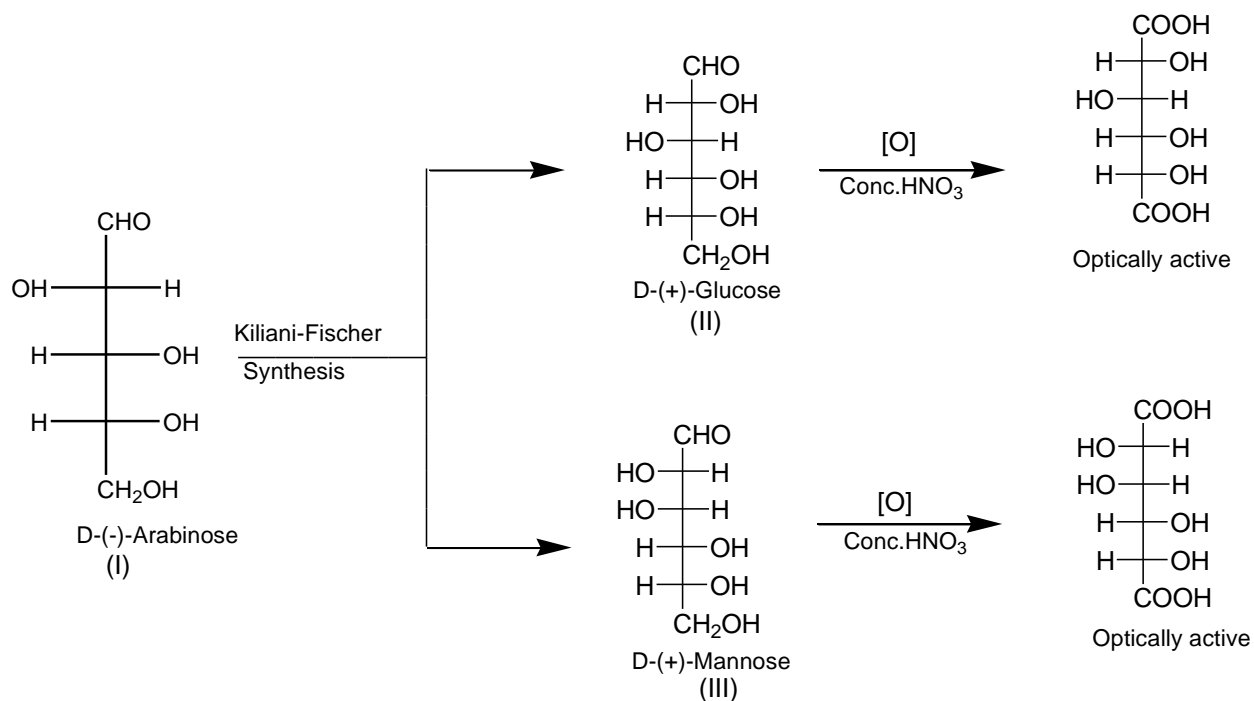
Two stereochemical descriptors were defined: D and L. The absolute configuration of (+)-glyceraldehyde was said to be D and that of its enantiomer, (-)-glyceraldehyde, was said to be L. Compounds that had a spatial arrangement of substituents analogous to D-(+) and L-(-)-glyceraldehyde were said to have the D and L configurations, respectively.

The procedure for the determination of the absolute configuration of aldoses and ketoses is as follows:

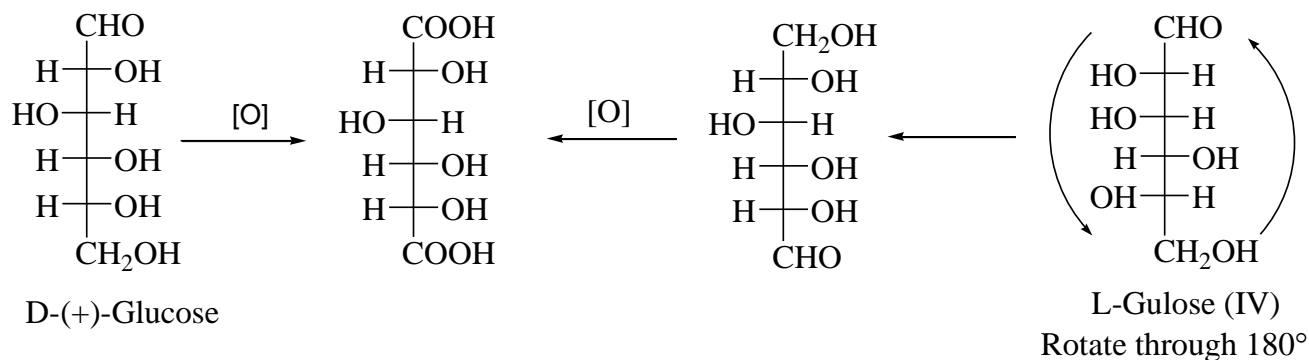
1. Glyceraldehyde of known absolute configuration is subjected to Kiliani-Fischer synthesis when a pair of diastereomeric *tetroses* is obtained.
2. The *tetroses* thus obtained are converted into dicarboxylic acids by oxidation with conc. HNO_3 .
3. The identification of dicarboxylic acids helps to assign the configuration of *tetroses*.
4. Similarly, the configurations of pentoses are established from the configuration of *tetroses* and those of *hexoses* from the configuration of *pentoses*.

Absolute configuration of D-(+)-Glucose

D-(-)-Arabinose(I) (aldopentose with established configuration) on Kiliani-Fischer synthesis gives two aldoses (II and III), one of which is D-(+)-glucose while the other is D-(+)-mannose. Since both these aldohexoses, on oxidation with conc. HNO_3 , give optically active dicarboxylic acids. We can determine their configuration if we can identify which acid is obtained from D-(+)-glucose and which acid is obtained from D-(+)-mannose.

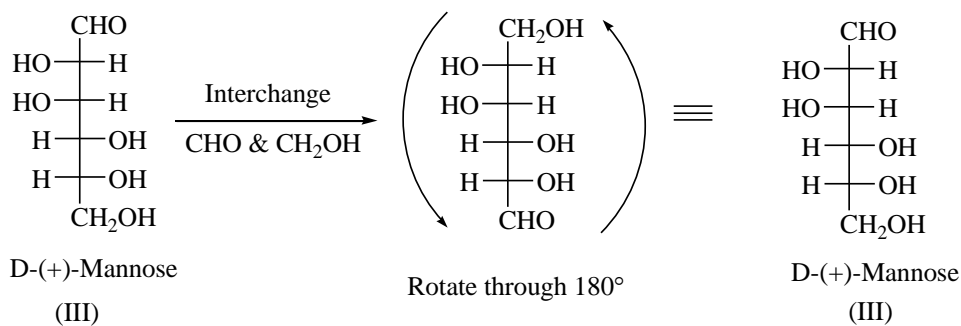


For this purpose, we make use of another aldohexose, L-(+)-Gulose (IV). L-(+)-gulose on oxidation gives the same dicarboxylic acid as is obtained from D-(+)-glucose. D-(+)-glucose and L-(+)-gulose must have the same relative stereochemistry at all the four chiral carbon atoms since during oxidation only the terminal aldehydic and primary alcoholic groups are oxidized. These two aldohexoses must differ in the position of $-\text{CHO}$ and $-\text{CH}_2\text{OH}$ groups which should be interchanged. Oxidation converts the $-\text{CHO}$ and $-\text{CH}_2\text{OH}$ groups of both glucose and gulose into $-\text{COOH}$ groups so that the same diacid is obtained.

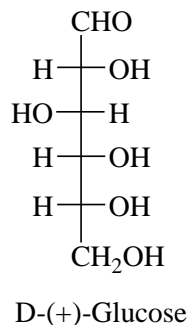


This is possible only if D-glucose has the structure (II).

If we consider the structure (III), the dicarboxylic acid obtained from it cannot be formed from any other aldohexose. Even if we interchange the $-\text{CHO}$ and $-\text{CH}_2\text{OH}$ groups of structure (III), we do not get a different aldohexose.



It is therefore clear that structure (II) represents D-(+)-glucose and structure (III) represents D-(+)-mannose. Therefore, the absolute configuration of D-(+)-glucose may be represented as

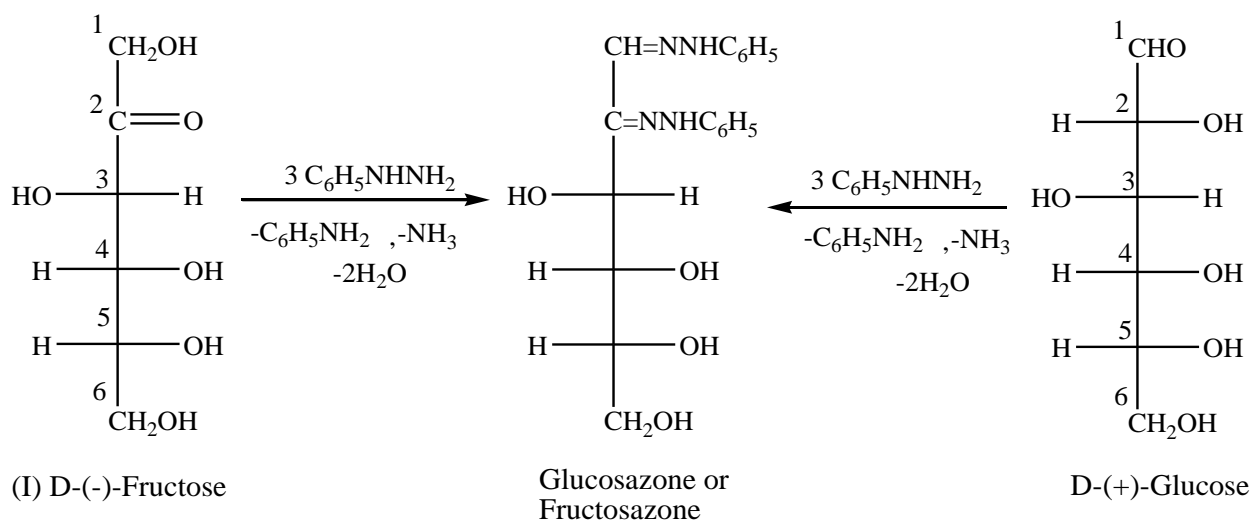


Absolute configuration of Fructose

The absolute configuration of fructose has been derived by following the same guidelines as in case of glucose. As we know that any compound that can be prepared from, or converted into D-(+)-glyceraldehyde will belong to D-series. Although the ketoses are distinct isomers of the aldose monosaccharides, the chemistry of both classes is linked due to their facile interconversion in the presence of acid or base catalysts.

The open chain structure of fructose contains three chiral atoms. Therefore, the number of stereoisomers possible is 8. The naturally occurring D-(-)-Fructose is one of these 8 isomers. Both D-(+)-glucose and D-(-)-Fructose forms the same osazone. Since osazone formation involves only C₁ and C₂ carbon atoms (none of which is chiral in Fructose). Therefore, the configuration at C₃, C₄ and C₅ in both D-glucose and fructose must be the same. Moreover, D-(+)-glucose and D-(-)-Fructose are interconvertible.

The configuration of fructose is shown in structure (I).

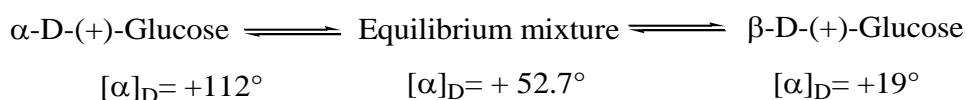


Mutarotation

Monosaccharides that contain five or more carbon atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can be formed from each straight chain monosaccharide,

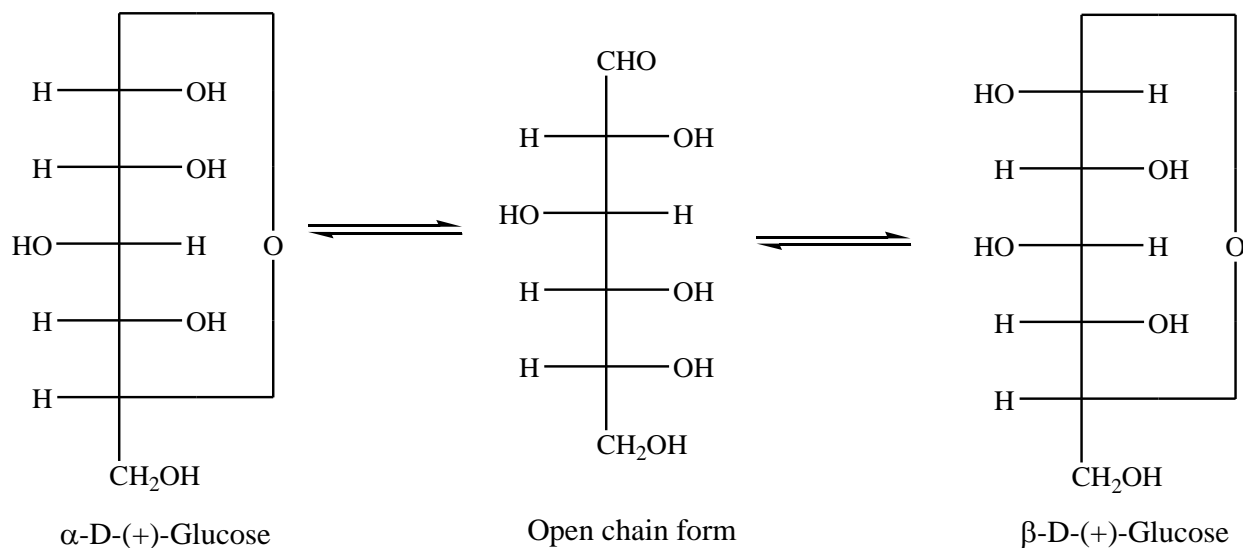
which are called anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight chain structure of a monosaccharide in a process known as mutarotation.

In case of Glucose, the alpha (α) anomer of D-glucose has a specific rotation of $+112^\circ$ in water and the beta (β) anomer of D-glucose has a specific rotation of $+19^\circ$ in water. When either anomer is dissolved in water, the value of specific rotation changes over time, eventually reaching the same value of $+52.7^\circ$. The equilibrium mixture consists of 36% of α -form and 64% of β -form.



Mutarotation is thus defined as the change in the specific rotation of an optically active compound, with time, to an equilibrium value.

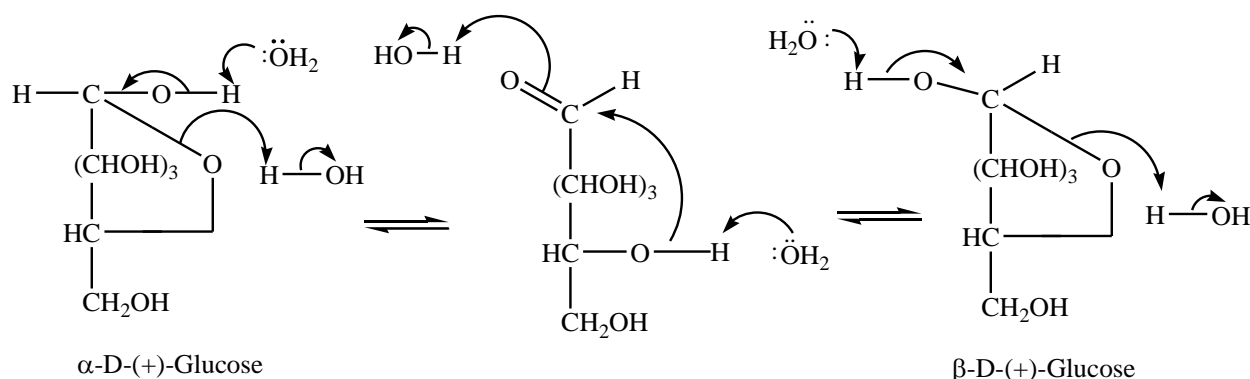
Mutarotation is a consequence of ring-chain tautomerism. It is a general property of sugars, as well as chiral cyclic hemiacetals in general.



Mechanism

Mutarotation occurs by opening of the ring to the free carbonyl form. The mechanism shown in the scheme begins as the reverse of hemiacetal formation, i.e., cyclic hemiacetal ring opens up due to a concerted attack by base and water. There is simultaneous removal of proton by the base from hemiacetal –OH group and donation of proton to the ethereal oxygen. The open chain form then recloses to form an equilibrium mixture of α and β anomers.

Mutarotation takes place in amphoteric solvents. As water is an amphoteric solvent, mutarotation takes place readily in aqueous solution.

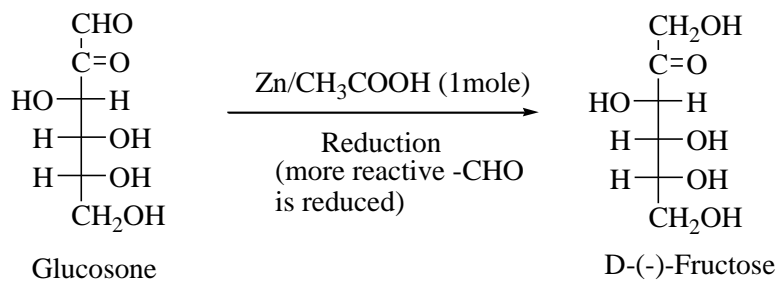
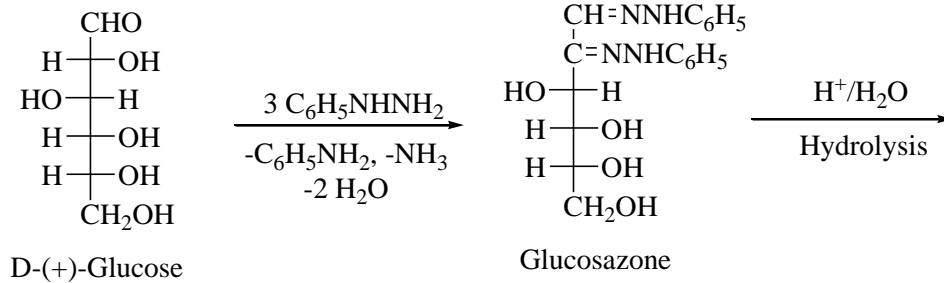


Scheme: Mechanism of mutarotation

Interconversion of Glucose and Fructose

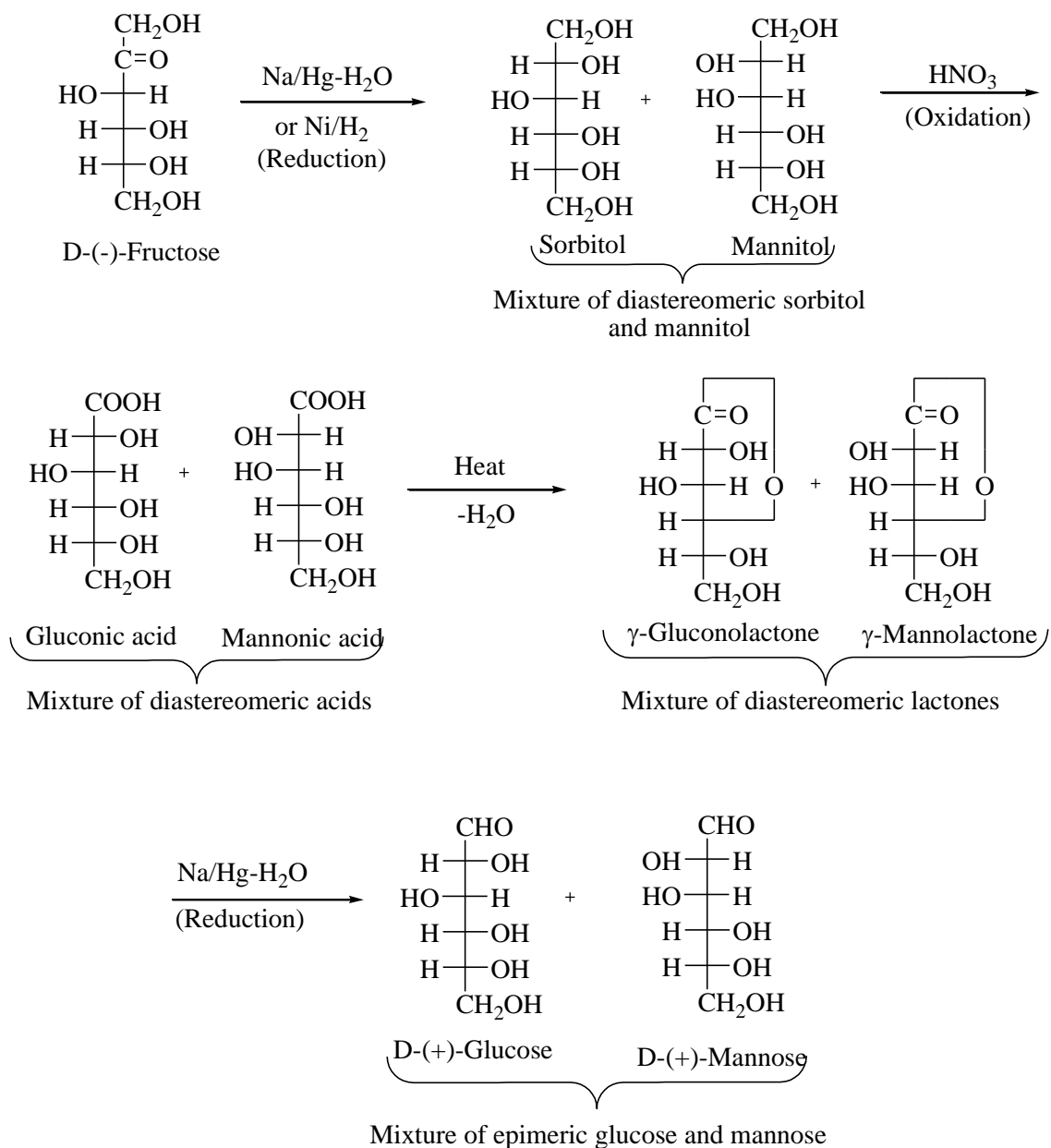
1. Conversion of an Aldose into Isomeric Ketose—Conversion of Glucose into Fructose

Aldose such as glucose can be converted into an isomeric ketose such as fructose via its osazone as illustrated below:



2. Conversion of Ketose into an isomeric Aldose: Conversion of Fructose into Glucose and Mannose

Ketose such as fructose can be converted into a mixture of epimeric aldoses, i.e., glucose and mannose by the following procedure:



Ascending and descending in Monosaccharides

A. Ascending or lengthening of Carbon chain: Conversion of Aldopentose into Aldohexose:

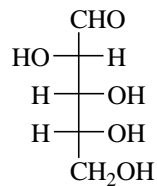
An aldose can be converted into next higher aldose containing one more carbon atom by Killiani-Fischer synthesis. The process involves four steps as discussed below:

1. Reaction of given aldose with hydrogen cyanide when a mixture of two diastereomeric cyanohydrins is obtained. This is because cyanohydrin formation gives rise to a new stereocentre.
2. Hydrolysis of cyanohydrin mixture to obtain a mixture of two corresponding acids which are separated from each other.
3. Action of heat on each of these acids to form the corresponding lactones.
4. Reduction of the lactones by sodium amalgam to get the higher aldoses containing one carbon atom more than the starting aldose.

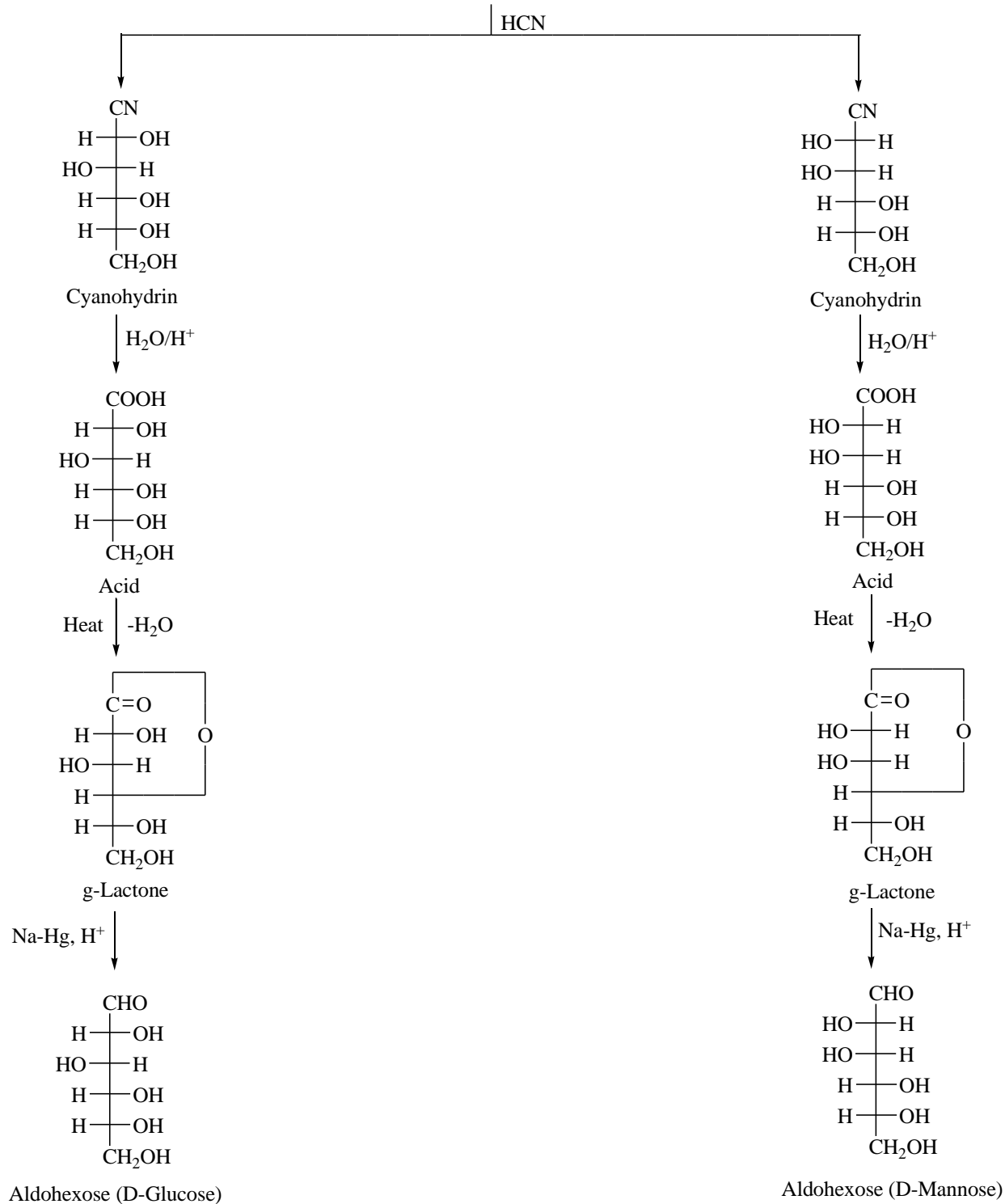
It is pertinent to mention here that the diastereomeric aldoses produced as a result of Kiliani-Fischer synthesis differ in configuration only about C₂. Such pair of diastereomeric aldoses which differ in configuration only at one of the chiral carbon atoms are called *epimers*.

Kiliani-Fischer synthesis cannot be used to convert a ketose into next higher ketose. This is because the ketonic group is not present in terminal position. Thus, formation of nitrile and its hydrolysis does not lead to overall lengthening of the carbon chain.

Kiliani-Fischer synthesis has been illustrated for the *conversion of aldopentose (D-arabinose) into a mixture of two aldohexoses (D-glucose and D-mannose)* as shown:



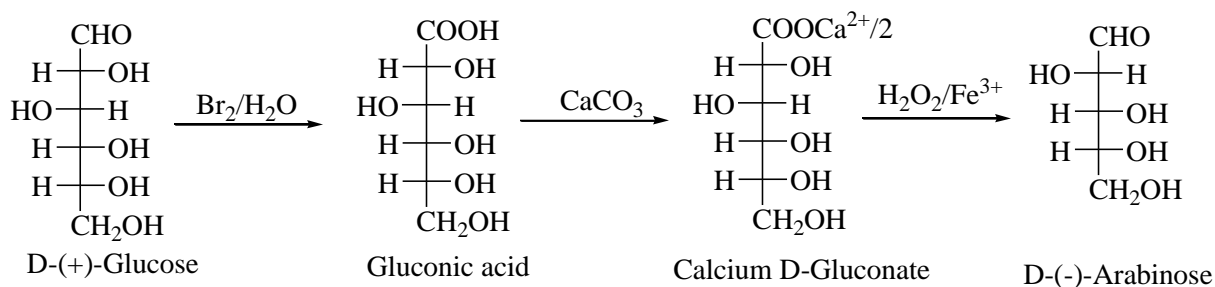
Aldopentose (D-Arabinose)



B. *Descending or Shortening of Carbon chain: Degradation:* An aldose can be converted into next lower aldose containing one carbon atom less by the following two methods:

1. **The Ruff degradation:** This method involves the oxidation of starting aldose into the corresponding aldonic acid using bromine water. The acid is converted into its corresponding calcium salt by treatment with calcium carbonate. The calcium salt, is then, treated with Fenton's reagent (H_2O_2 in presence of Fe^{3+} ions) when the oxidative cleavage occurs between $\text{C}_1\text{-C}_2$ bond to give the lower aldose.

This method may be illustrated by considering the degradation of D-glucose into D-arabinose.

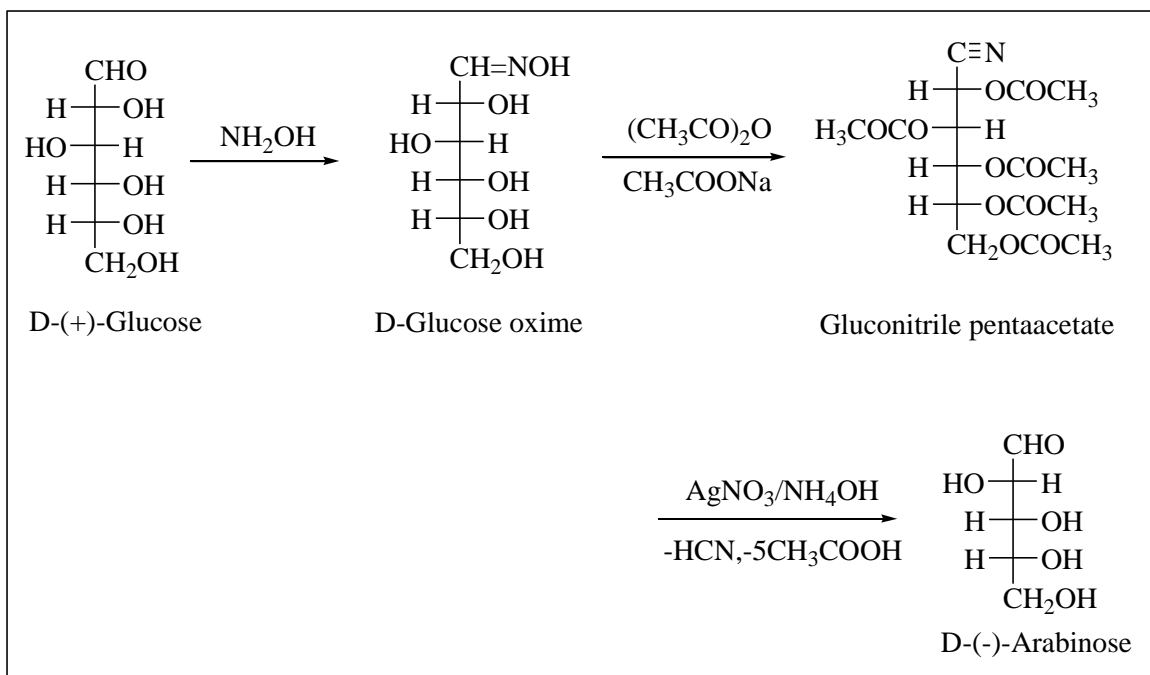


It is to be noted that since the chirality is lost at C_2 during the degradation, therefore two aldohexoses which differ in configuration only at C_2 , i.e., C_2 -epimers give the same aldopentose. For example, when mannose is subjected to ruff degradation, it also gives arabinose.

2. **Wohl degradation:** This method is essentially the reverse of Kiliani-Fischer synthesis. It involves the following steps:

- a) The given aldose is converted into its oxime by reaction with hydroxylamine.
- b) The oxime is then treated with acetic anhydride. As a result, the oxime gets dehydrated into a nitrile and simultaneously various hydroxyl groups are acetylated.
- c) The acetylated cyano compound thus produced is treated with Tollen's reagent to get an aldose containing one carbon atom less than the starting aldose.

This method is illustrated by the conversion of an aldohexose (D-glucose) into an aldopentose (D-arabinose).



Disaccharides

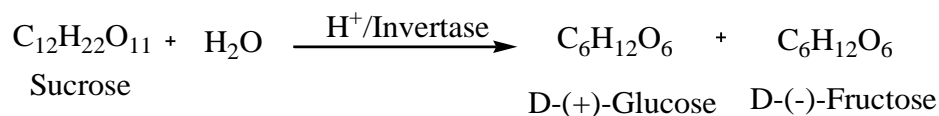
Disaccharides are the carbohydrates which on hydrolysis give two same or different monosaccharides. Their general formula is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. The important members belonging to disaccharides are sucrose, cellobiose, maltose and lactose. In disaccharides, the two monosaccharide units are joined together by acetal or glycosidic formation. The hemiacetal $-\text{OH}$ of one monosaccharide and an $-\text{OH}$ of second monosaccharide dehydrates to establish the bond (called glycosidic bond) between the two monosaccharides.

Sucrose

It is commonly known as cane-sugar or table sugar. Its main sources are sugarcane, sugar beet and sorghum. Sucrose is dextrorotatory with a specific rotation of $[\alpha]_{\text{D}} = +66.5^\circ$. Sucrose on hydrolysis gives dextrorotatory glucose, $[\alpha]_{\text{D}} = +52.7^\circ$ and laevorotatory fructose, $[\alpha]_{\text{D}} = -92.4^\circ$. The hydrolysis of sucrose is accompanied by change in sign of optical rotation from dextrorotatory to laevorotatory; the overall process is called inversion of sugar.

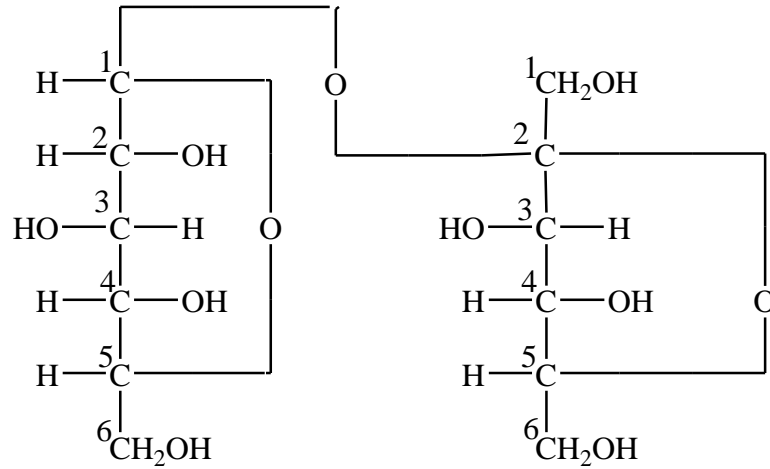
Structure of Sucrose

1. *Molecular formula:* The molecular formula of sucrose is $C_{12}H_{22}O_{11}$ (On the basis of elemental analysis and molecular weight determination).
2. *Nature of monosaccharide units:* Sucrose on hydrolysis with dilute mineral acids or the enzyme invertase (present in yeast), gives an equimolar mixture of D-(+)-Glucose and D-(-)-Fructose.

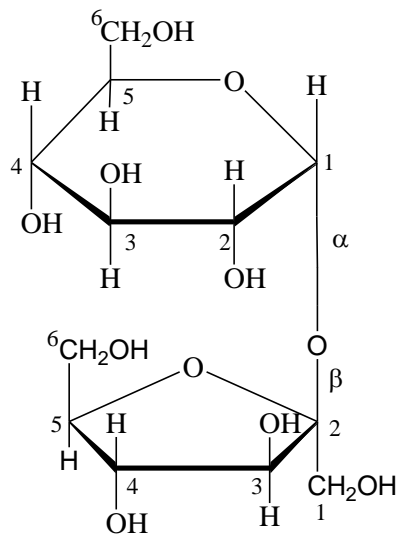


3. *Non-reducing character:* Sucrose does not reduce Tollen's reagent and Fehling's solution. It does not form an osazone and does not undergo mutarotation. This behaviour of sucrose suggests the non-reducing character. It also indicates that combination between glucose and fructose units occurs in such a way that the hemiacetal forms of both the constituent units do not exist as such in sucrose. This is possible only if there is glycosidic linkage between **C-1** of glucose and **C-2** of fructose.
4. *Nature of linkages:* Sucrose is hydrolyzed by the enzyme maltase which can hydrolyse only α -glucopyranosides. Therefore, glucose is present in the α -form. The enzyme invertase or sucrase which is specific for the hydrolysis of β -fructofuranosides also hydrolyses sucrose. Therefore, fructose is present in the β -form.

In view of the above mentioned facts, the sucrose has been assigned the following structure:



Fischer formula of Sucrose



Haworth Projection Formula of Sucrose

Chemical name: α -D-glucopyranosyl- β -D-fructofuranose

Cellulose

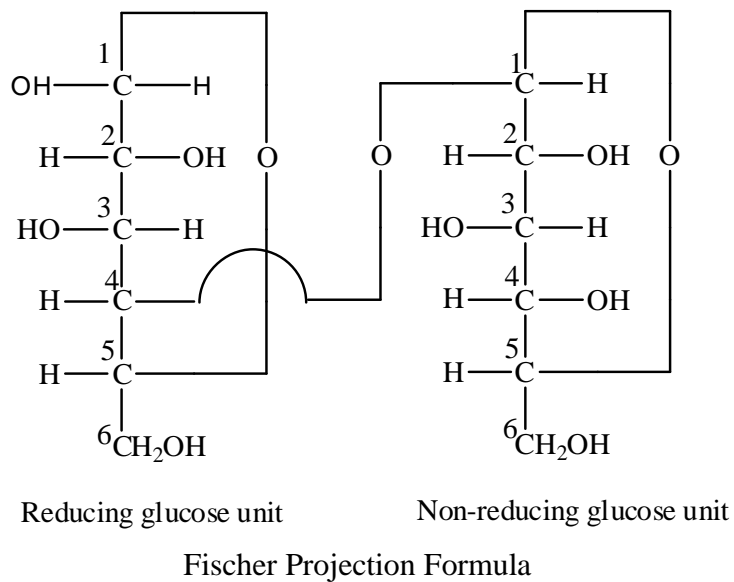
Cellulose is obtained from the partial hydrolysis of cellulose. Its molecular formula is $C_{12}H_{22}O_{11}$. It consists of two molecules of glucose that are linked by β -(1,4') glycosidic bond. Cellulose thus differs from maltose by its configuration at the glycosidic bond.

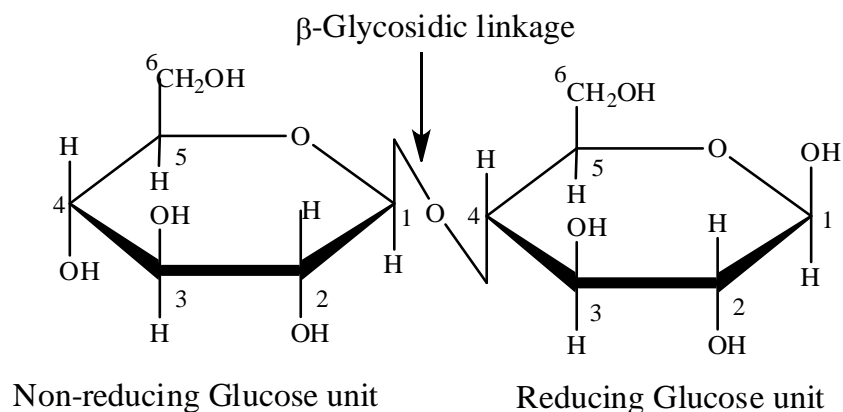
Structure of cellobiose

1. Cellobiose on hydrolysis with dilute acids gives two molecules of β - D-(+)-Glucose.
2. Cellobiose reduces Tollen's reagent and is a reducing sugar. It forms an osazone, exists in α - and β -forms and undergoes mutarotation.
3. Cellobiose is hydrolyzed by emulsion (which is specific for β -glycosidic linkages) but not by maltase or β -amylase (which is specific for α -glycosidic linkages).

Thus, cellobiose is made up of two D-(+)-Glucopyranose units linked together by β -glycosidic linkage involving C-1 of one glucose unit and C-4 of the other.

The structure of cellobiose is given as:





Haworth Projection Formula of cellobiose

Chemical name: 4-O-β-D-Glucopyranosyl-β-D-glucopyranose

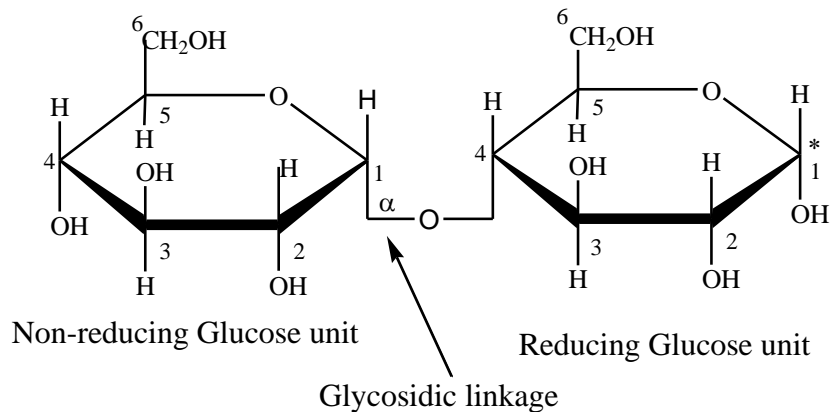
Maltose

Maltose is commonly known as malt sugar and is present in germinating seeds; particularly cereals. It is prepared by the partial hydrolysis of starch either with dilute acids or with enzyme diastase (β -amylase) present in malt.

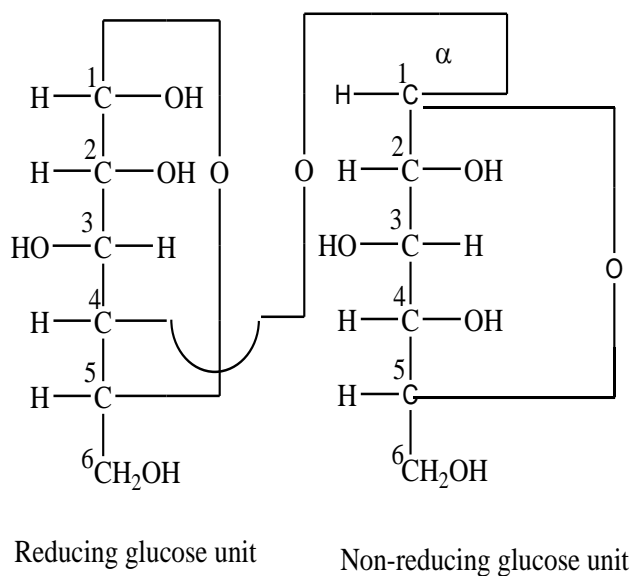
Structure

1. The molecular formula of maltose is $C_{12}H_{22}O_{11}$.
2. Maltose is a reducing sugar as it reduces Fehling's solution and Tollen's reagent. It forms oxime, phenylhydrazone, an osazone and its aqueous solution shows mutarotation.
3. Maltose gives two molecules of α -D-(+)-Glucose on hydrolysis with dilute acids or enzyme maltase.
4. Maltose is oxidized by bromine water to maltobionic acids which is monocarboxylic acid having the same number of carbon atoms as maltose. This indicates that the two D-(+)-Glucose units of maltose are linked in such a way that one of the glucose molecules has the hemiacetal form and acts as the reducing unit.

The linkage between the two units is α -glucoside linkage involving the hemiacetal carbon (**C-1**) of one unit and -OH group on **C-4** of the other unit. The α - and β - forms of (+)-maltose differ in their configuration only at the anomeric carbon marked by asterisk.



Haworth Projection Formula (α -form)



Fischer projection formula (α -anomer)

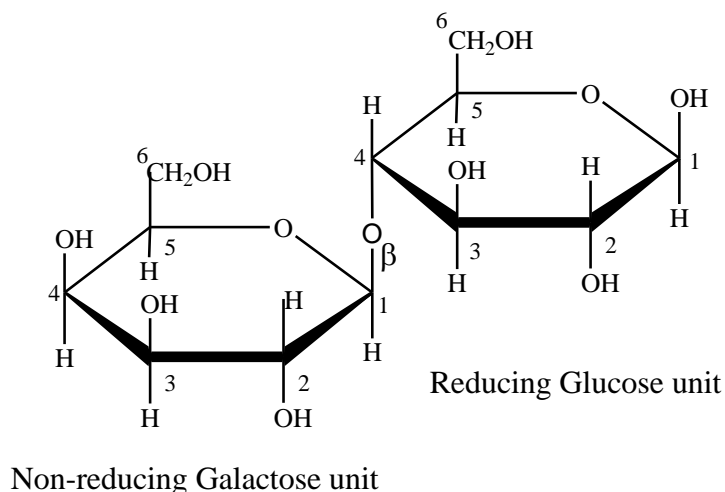
Chemical name: 4-O-(α -D-Glucopyranosyl)-D-glucose

Lactose

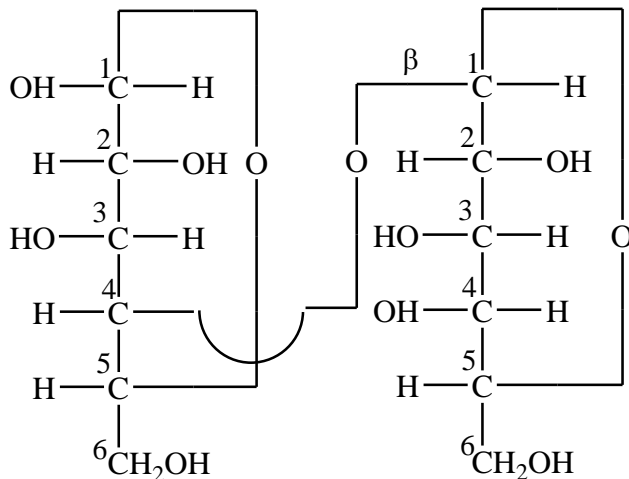
Lactose, also called milk sugar, occur in milk of mammals. It is prepared commercially as a by-product of the cheese manufactured from milk. Milk turns sour when lactose is converted into lactic acid by bacterial action.

Structure of Lactose

1. The molecular formula of lactose is $C_{12}H_{22}O_{11}$.
2. Lactose is a reducing sugar as it reduces Fehling's solution and Tollen's reagent. It forms oxime, phenylhydrazone, an osazone and its aqueous solution shows mutarotation.
3. On hydrolysis with mineral acids or enzyme lactase, it gives an equimolar mixture of β -D-(+)-Glucose and β -D-(+)-Galactose.
4. It undergoes oxidation with bromine water to form lactobionic acid which on hydrolysis gives D-(+)-Galactose and D-Gluconic acid. It indicates that D-(+)-Glucose unit is the reducing half while D-(+)-Galactose unit is the non-reducing half.
5. As lactose is hydrolysed by the enzyme lactase which is specific for the hydrolysis of β -glycosidic linkages, therefore, C_1 - β of galactose unit is connected to C_4 -OH of the glucose unit. The structure of (+)-lactose is as shown below. It may be noted that α and β forms of (+)-lactose differ in their configuration at the anomeric carbon.



Haworth Projection Formula (β -anomer)



Reducing glucose unit

Non-reducing galactose unit

Fischer projection formula (β -anomer)

Chemical name: 4-O-(β -D-galactopyranosyl)- β -D-glucopyranose

Polysaccharides

Polysaccharides (also known as glycans) are the naturally occurring condensation polymers comprising of a large number (hundreds to thousands) of monosaccharide units joined together through oxide bridges, also called glycosidic linkages. Polysaccharides are not sweet in taste, so they are called non-sugars. These are also colourless, tasteless, amorphous powders which are insoluble in water, alcohol and ether. On complete acidic or enzymatic hydrolysis, they yield the constituent monosaccharides. The common and widely distributed polysaccharides correspond to the general formula $(C_6H_{10}O_5)_n$. Some common examples of polysaccharides include starch, cellulose, glycogen, etc.

Starch/Amylum

Starch is a glucose polymer that is one of the most abundant sources of carbohydrates in the human diet. It is the major food reserve material of plants and occurs as granules mainly in the seeds, fruits, tubers and roots of the plants. The most important sources of starch are wheat, rice, maize, potatoes, legumes and other vegetables.

For isolating starch, the plant cells are broken by grinding and then extracted with water. The extract is passed over fine sieves when starch granules pass through as a milky liquid. This is

then allowed to settle down. When starch settles, it is separated by decantation and finally dried in hot air.

Properties

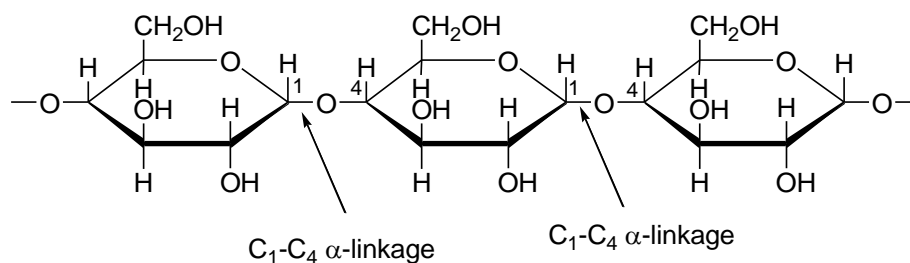
1. Starch granules are insoluble in cold water but if the water suspension is heated, granules swell and ultimately burst to form a paste-like colloidal solution.
2. Starch is composed of two components. The water soluble component is called amylose (20%) while the water insoluble component is called amylopectin (80%).
3. Amylose gives a deep blue colour with iodine solution which disappears on heating but reappears on cooling. This constitutes a delicate test for starch. Amylopectin, on the other hand, gives a red to purple colour with iodine solution.
4. Starch is a non-reducing saccharide. It neither reduces Tollen's reagent or Fehling's solution nor forms an osazone.

Structure

As starch is composed of two components, amylose and amylopectin; its structure can be studied by determining structure of its constituents.

Structure of Amylose

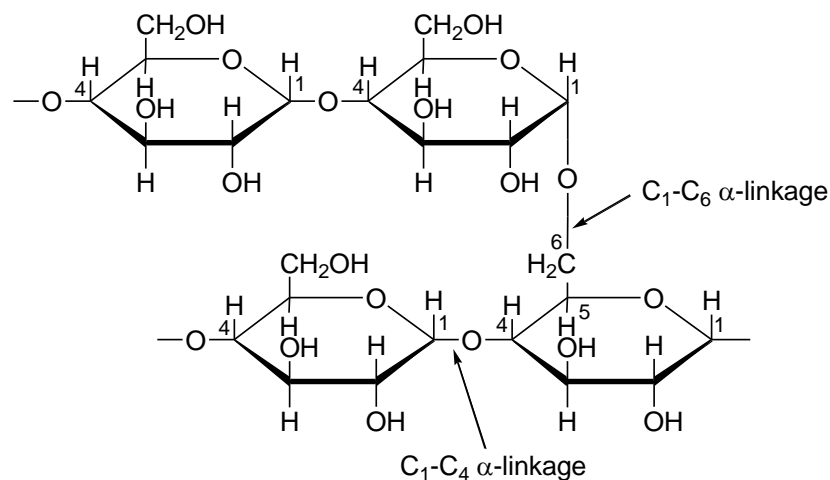
1. The molecular formula of amylose is $(C_6H_{10}O_5)_n$ where n varies from 200-300.
2. On complete hydrolysis, amylose gives the monosaccharide, D-(+)-glucose in quantitative yield. Thus, amylose is made up of only D-(+)-glucose units.
3. It has been found that amylose molecule is composed of a large number of D-(+)-glucose units joined by α -glucosidic linkages involving C_1 of one unit with C_4 of the other. Thus, the structure of amylose may be depicted as follows:



4. Each amylose chain has a terminal reducing glucose unit. Since, this unit is present at the end of a long chain, its properties are masked. Therefore, amylose does not exhibit strong reducing properties of sugars.
5. X-ray analysis has revealed that amylose chain is not linear but gets coiled to produce a helix (like a spiral staircase). Each turn of the helix comprises about 6-7 glucose units.
6. The blue colour produces when iodine solution is treated with starch is due to the formation of an inclusion complex in which iodine molecules are trapped along the axis of the helix.

Structure of Amylopectin

1. Molecular formula of amylopectin is $(C_6H_{10}O_5)_n$ where n varies from 1000-3000 glucose units.
2. Like amylose, amylopectin on hydrolysis with boiling mineral acids finally gives D-(+)-glucose units. Thus, amylopectin is also made entirely of D-(+)-glucose units similar to amylose.
3. Amylopectin has highly branched structure comprising of a large number (several hundreds) of short chains. Each short chain consists of 20-25 glucose units linked through α -glucosidic linkages involving C₁ of one unit with C₄ of the other. The C₁ of the terminal glucose unit in each chain is further linked to C₆ of other glucose units in the next chain through α -1,6-linkage as shown below:



Cellulose

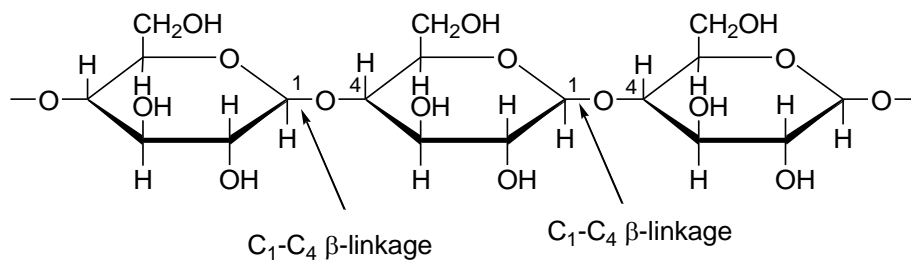
Cellulose is widely distributed in nature and serves as structural material of cell walls in plants, providing structural strength and rigidity to plants. It is also the chief component of cotton (90% cellulose), wood (50% cellulose) and jute.

Properties

1. Cellulose is colourless, tasteless, fibrous solid which is insoluble in water; however, it dissolves in ammoniacal copperhydroxide solution (Schweitzer's reagent) from which it can be precipitated by addition of acids, alkalis. This property is used in the manufacture of artificial silk (rayon) from cotton.
2. Cellulose is also a non-reducing polysaccharide like starch since it does not reduce Tollen's reagent or Fehling's solution. It does not form an osazone and is not fermented by yeast.
3. In contrast to starch, cellulose does not undergo hydrolysis easily. However, on heating with dil. H_2SO_4 under pressure, it undergoes hydrolysis to give D-glucose only.
4. Concentrated sodium hydroxide acts on cellulose to form a gelatinous mass which gives a silky lustre to cotton. This process is known as *mercerization* and the cotton thus treated is termed mercerized cotton.

Structure of Cellulose

Molecular formula of cellulose is $(C_6H_{10}O_5)_n$. Like starch, cellulose is also made up of D-(+)-glucose units only but with a difference that in cellulose D-(+)-glucose units are linked by β -glucosidic linkages (unlike α -glucosidic linkages in starch) as shown below:



X-ray analysis has shown that cellulose is comprised of several long; linear chains each containing about 3000 or more glucose units. These chains lie side by side in bundles held together by H-bonding between C₆-CH₂OH of one chain with C₂-OH of the other chain. These bundles get twisted together to form rope like structures. These ropes may be further grouped together to form fibres or may be embedded in lignin as in case of food.

Problems for Practice

Very Short Answer Type Questions

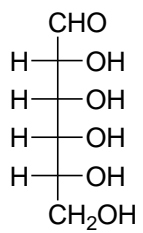
1. Why epimers do not show mutarotation?
2. Why glucose does not react with sodium bisulphite even though it contains an aldehyde group.
3. How many chiral carbon atoms are there in Glucose and Fructose? Also write the number of stereoisomers possible for both of them.
4. Draw the conformations of α - and β -D-(+)-glucopyranose.
5. Of α - and β -D-(+)-glucopyranose, which one is more stable and why?
6. Discuss the significance of symbols (+), (-), D- and L- as used before the names of carbohydrates?
7. Draw the furanose structure of α - and β -D-(-)-Fructose.
8. Write a short note on carbohydrates and their classification?
9. Briefly explain reducing sugars with examples?
10. Why D-(-)-Fructose has a prefix D although it is laevorotatory?
11. Give two examples of non-carbohydrates which conform to the general formula of carbohydrates?
12. Why sucrose is non-reducing in character?
13. Draw Haworth projection formula for sucrose?
14. Which sugars are obtained by epimerization of D-glucose at C-2, C-3 and C-4?
15. Define absolute configuration and relative configuration?
16. Briefly explain about the molecule taken as reference standard by Emil Fischer?

Short Answer Type Questions

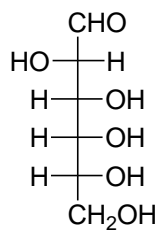
1. Discuss about monosaccharides? Write the names and structure of monosaccharides containing six carbon atoms (any four).
2. What are the limitations of open structure of D-(+)-Glucose?
3. How can you convert Glucose to fructose?
4. How can mannose be obtained from fructose?
5. Discuss briefly evidences in favor of ring structure of D-(+)-Glucose.
6. What are disaccharides? Write the Haworth and Fischer structure of maltose and cellobiose.
7. Discuss in detail the classification of carbohydrates?
8. Discuss the mechanism of mutarotation?
9. Discuss the structure of Lactose?
10. How has the configuration of D-(+)-Glucose been established?
11. Why does Glucose not give the Schiff's reagent test?
12. What is the difference between anomers and epimers? Give one example in each case?
13. Write the structure of sucrose indicating the monosaccharides and type of linkages involved?
14. Briefly explain the structure of cellobiose indicating the monosaccharides and type of linkages involved?
15. Give the main points of difference between starch and cellulose.
16. What are the main components of starch? Briefly discuss structure of each one of them.

Long Answer Type Questions

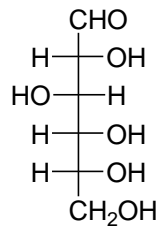
1. Discuss in detail the absolute configuration of Glucose and Fructose.
2. What are the limitations of open structure of D-(+)-glucose? How can these be overcome by cyclic structure?
3. Discuss in detail the open chain and cyclic structure of D-(+)-Glucose.
4. Write short notes on i) Ruff degradation ii) Wohl degradation iii) Kiliani-Fischer synthesis.
5. Discuss the cyclic structure of D-(+)-Fructose. How can it be represented by Fischer and Haworth Projection formulae?
6. Discuss in detail the structure of sucrose and lactose.
7. Draw the Haworth and Fischer structures of i) α -D-Glucose ii) β -D-Glucose iii) Cellobiose
8. Explain the following: i) Mutarotation ii) Anomers iii) Epimers, with suitable examples.
9. What are polysaccharides? Discuss briefly the structure of starch and cellulose
10. Predict the relative configuration of the following molecules and also explain how you arrive at these configurations:



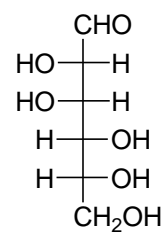
--Allose



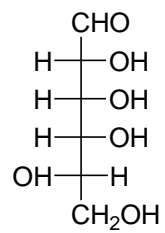
--Altrose



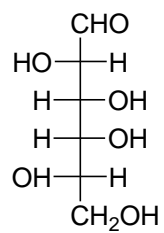
--Glucose



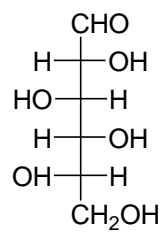
--Mannose



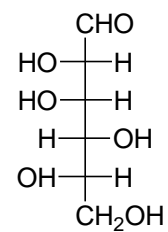
--Allose



--Altrose



--Glucose



--Mannose