

FOOD CHEMISTRY

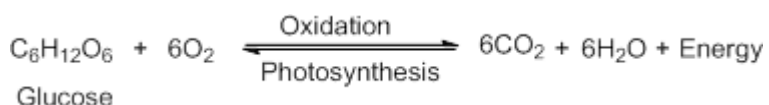
FOR
DIPLOMA STUDENTS

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Carbohydrates I

Introduction

Carbohydrates are polyhydroxy aldehydes or ketones. They are primarily produced by plants and form a very large group of naturally occurring organic substances. Some common examples are cane sugar, glucose, starch, etc. They have general molecular formulas that make them appear to be hydrates of carbon, $C_n(H_2O)_n$, from where the name carbohydrate was derived. Carbohydrates are formed in the plants by photosynthesis from carbon dioxide and water in the presence of sunlight (Scheme 1).



Scheme 1

Classification

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

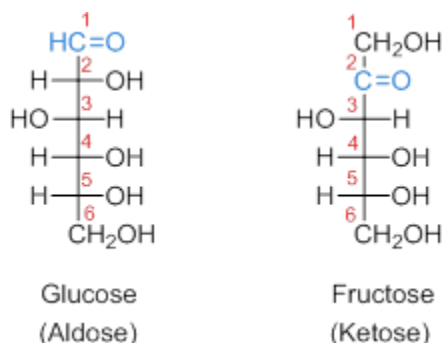
Sugars

Sugars are sweet crystalline substances that are soluble in water. These are further classified on the basis of their behavior on hydrolysis.

Monosaccharides

The simplest form of carbohydrates is the monosaccharide. 'Mono' means 'one' and 'saccharide' means 'sugar'. Monosaccharides are polyhydroxy aldehyde or ketone that cannot be hydrolyzed further to give simpler sugar. They may again be classified on the basis of the nature of carbonyl group.

- Polyhydroxy aldehydes are called aldoses. Example: Glucose (Scheme 2)
- Polyhydroxy ketones are called ketoses. Example: Fructose (Scheme 2)



Scheme 2

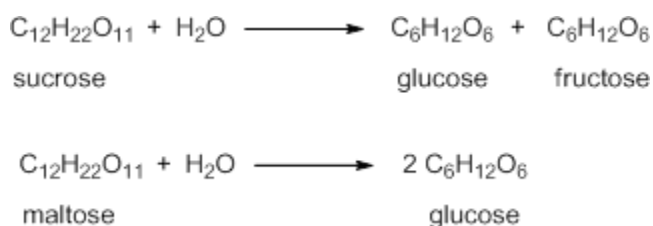
The aldoses and ketoses are further divided based on the number of carbons present in their molecules, as trioses, tetroses, pentoses, hexoses etc. They are referred to as aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses etc.

Number of Carbons	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

Oligosaccharides

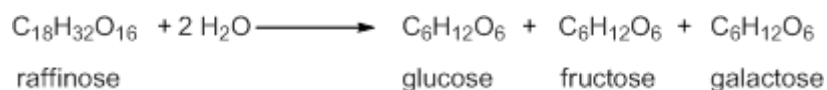
Carbohydrates that produce two to ten monosaccharide units during the hydrolysis are called oligosaccharides. They can be further classified based on the number of monosaccharide units formed on hydrolysis.

Disaccharides: They give two monosaccharide units on hydrolysis, which may be the same or different. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose, whereas maltose gives two molecules of glucose (Scheme 3).



Scheme 3

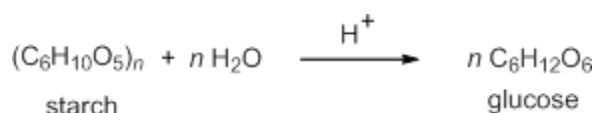
Trisaccharides: These carbohydrates yield three molecules of monosaccharides units on hydrolysis (Scheme 4).



Scheme 4

Polysaccharides

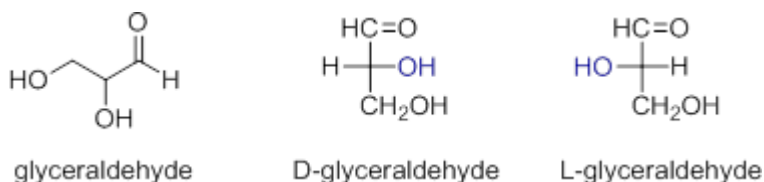
These carbohydrates give a large number of monosaccharide units on hydrolysis. These monosaccharide units are joined together by oxide bridges. These linkages are called glycosidic linkages. The common and widely distributed polysaccharides correspond to the general formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. Polysaccharides are not sweet in taste, so they are called non-sugars. Some common examples are starch, cellulose, glycogen, etc (Scheme 5).



Scheme 5

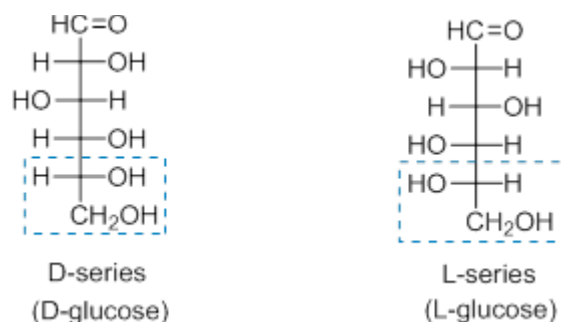
The D and L Notations

The notations D and L are used to describe the configurations of carbohydrates and amino acids. Glyceraldehyde has been chosen as arbitrary standard for the D and L notation in sugar chemistry. Because, this has an asymmetric carbon and can exist as a pair of enantiomers.



Scheme 6

In a Fischer projection, the carbonyl group is always placed on the top position for monosaccharide. From its structure, if the $-\text{OH}$ group attached to the bottom-most asymmetric center (the carbon that is second from the bottom) is on the right, then, the compound is a D-sugar. If the $-\text{OH}$ group is on the left, then, the compound is a L-sugar. Almost all sugars found in nature are D-sugar (Scheme 6).



Scheme 7

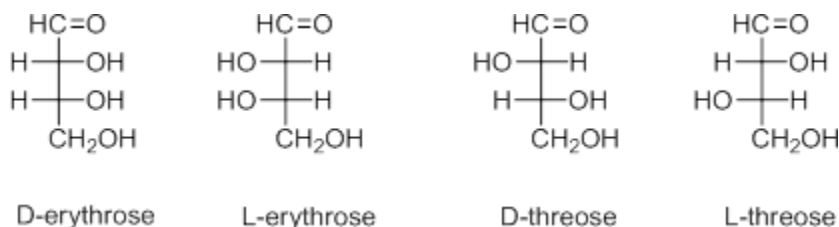
Like R and S, D and L indicate the configuration of an asymmetric carbon, but they do not indicate whether the compound rotates polarized light to the right or to the left. For example, D-glyceraldehyde is dextrorotatory, whereas D-lactic acid is levorotatory. In other words, optical rotation, like melting or boiling points, is a physical property of a compound, whereas "R, S, D, and L" are conventions humans use to indicate the configuration of a molecule (Scheme 7 and 8).



Scheme 8

Configuration of the Aldoses

Aldotetrose : The structural formula of aldotetrose is $\text{CH}_2\text{OH}-\text{CHOH}-\text{CHOH}-\text{CHO}$. There are four stereoisomers (two pairs of enantiomers). Those stereoisomers correspond to D- and L-erythrose and D- and L-threose (Scheme 9).

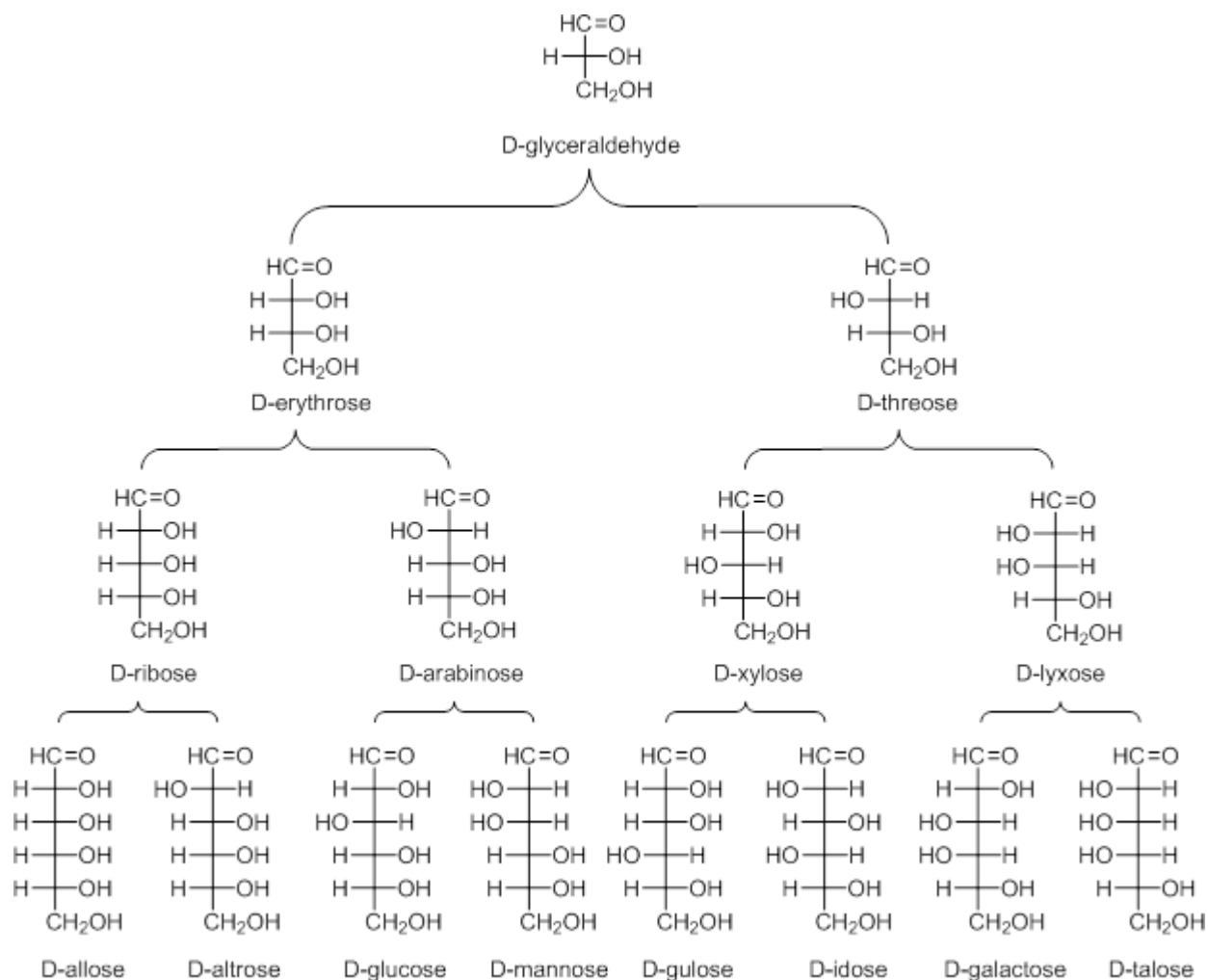


Scheme 9

Aldopentose : The structural formula of aldopentose is $\text{CH}_2\text{OH}-\text{CHOH}-\text{CHOH}-\text{CHOH}-\text{CHO}$. Since it contains three asymmetric carbons and there are eight stereoisomers (four pairs of enantiomers) possible. Those are the D- and L-forms of ribose, arabinose, xylose and lyxose (Scheme 10).

Aldohexose : They have four asymmetric center and therefore 16 stereoisomers (eight pairs of enantiomers). The four D-altopentose and eight D-aldohexose are shown below (Scheme 10).

Configuration of the D-Aldoses

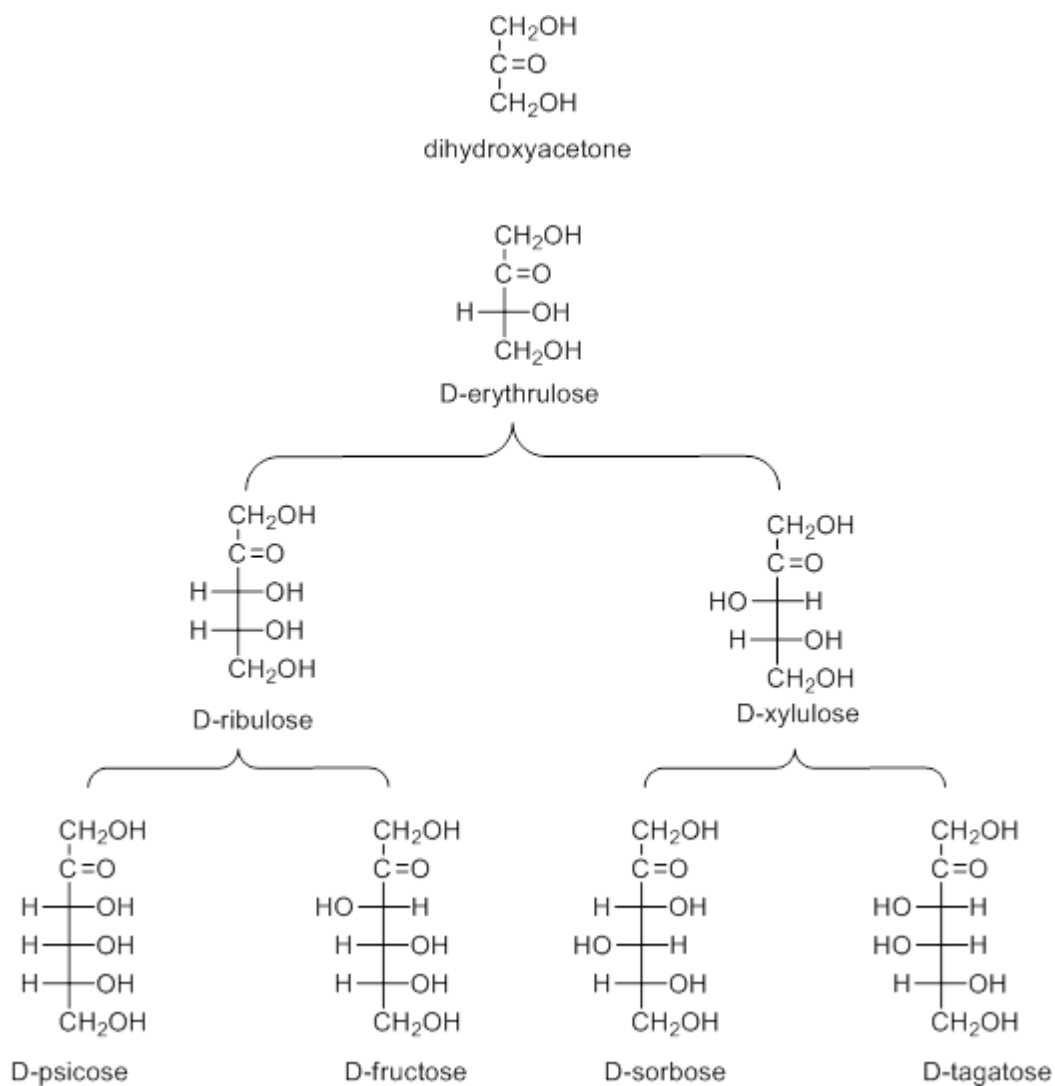


Scheme 10

Configuration of the ketoses

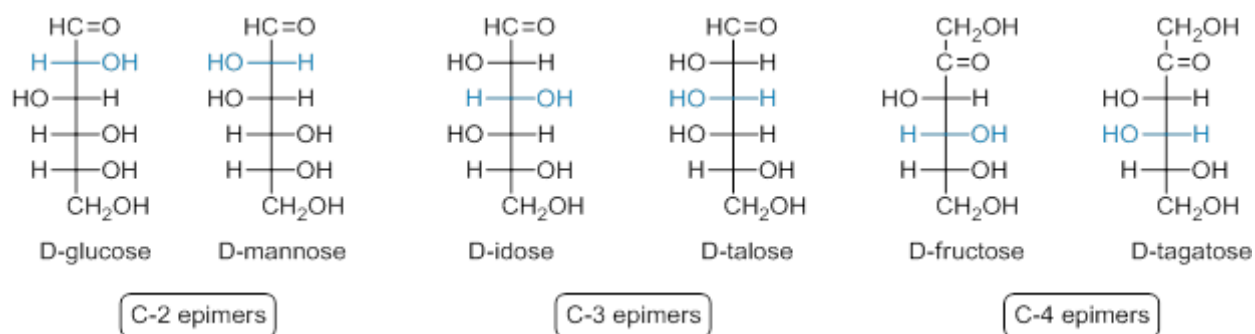
Ketoses have the keto group in the 2-position with one less chiral carbon compared to aldoses. So, ketoses have a half number of stereoisomers compared to aldoses with same number of carbon atoms. For example, aldopentose has three chiral centers with eight stereoisomers, while ketopentose has two chiral centers with four stereoisomers. The configuration of D-2 ketones is illustrated by the following examples. Dihydroxyacetone may not be a sugar, but it is included as the ketose analog of glyceraldehydes (Scheme 11).

Configuration of the Ketoses



Scheme 11

Epimers are stereoisomers that differ in configuration of only one asymmetric carbon of enantiomers or diastereomers. Example, D-glucose and D-mannose are C-2 epimers and D-glucose and D-talose are C-3 epimers. D-fructose and D-tagatose are C-4 epimers of ketohexoses (Scheme 12).



Scheme 12

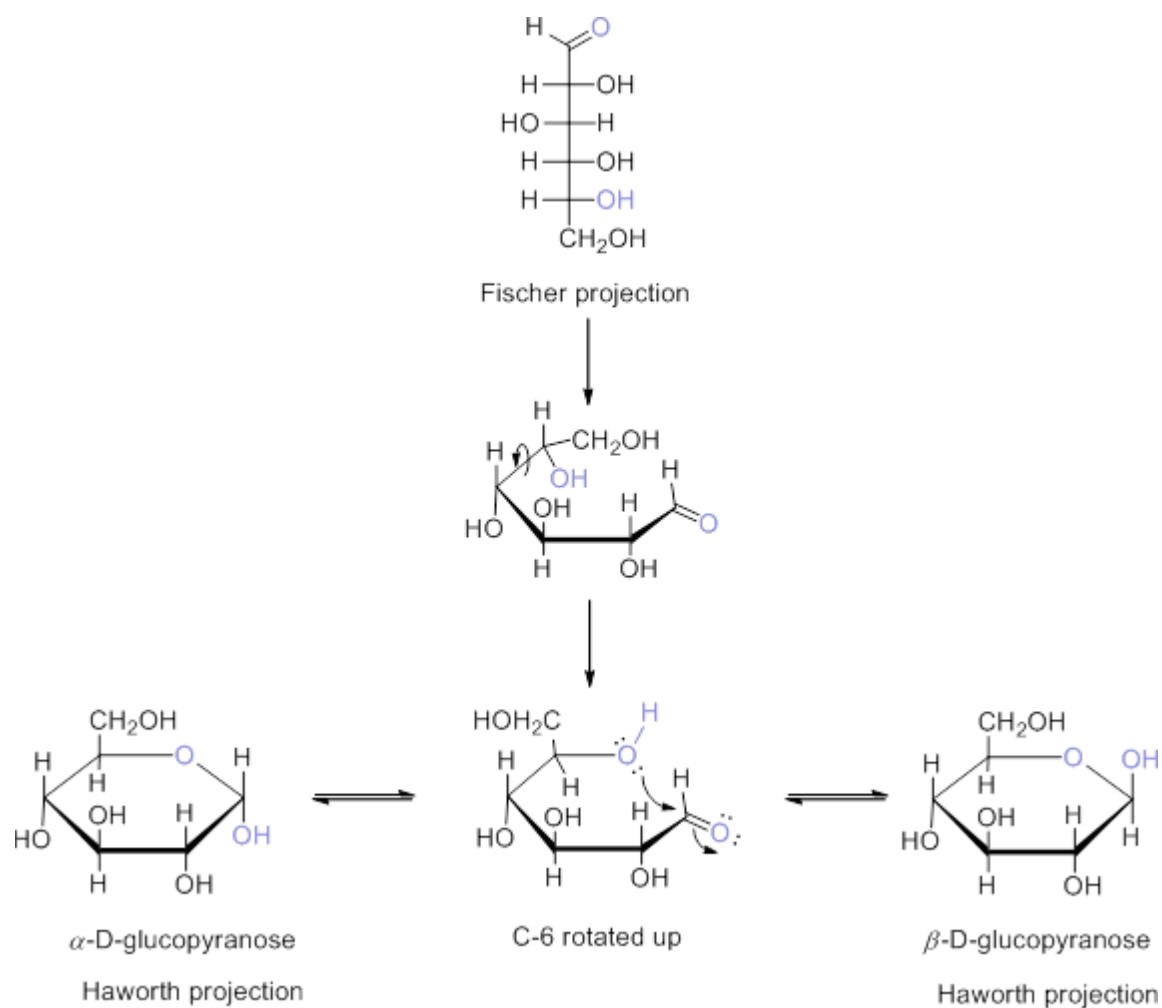
Cyclic Structure of Monosaccharides: Hemiacetal Formation

Aldoses contain an aldehyde group with several alcohol groups. The cyclic forms of D-glucose are six-membered hemiacetals formed by an intramolecular reaction of the –OH group at C-5 with the aldehyde group.

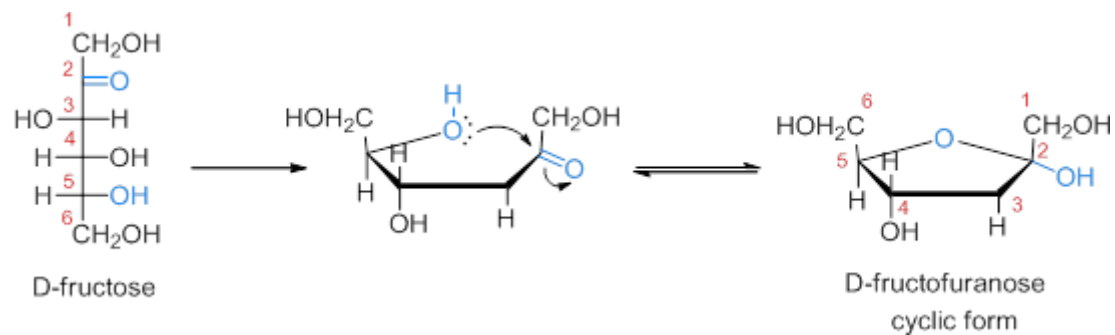
Cyclic structures of monosaccharides are named according to their five- or six-membered rings (Schemes 13 and 14). A six -membered cyclic hemiacetal is called a pyranose , derived from the name of the six-membered cyclic ether pyran . A five-membered cyclic hemiacetal is called a furanose , derived from the name of the five -membered cyclic ether furan . For example, the six-membered ring of glucose is called glucopyranose and the five-membered ring of fructose is called fructofuranose.

Haworth projection is "flattened" diagrams used to represent the stereochemistry carbohydrates. The six-membered ring of D-pyranose is represented as flat and is viewed edge on. The ring oxygen is always placed in the back right-hand corner of the ring, with the anomeric carbon (C-1) on the right-hand side and the primary alcohol group drawn up from the back left-hand corner (C-5) (Schemes 13, 14, 15 and 16).

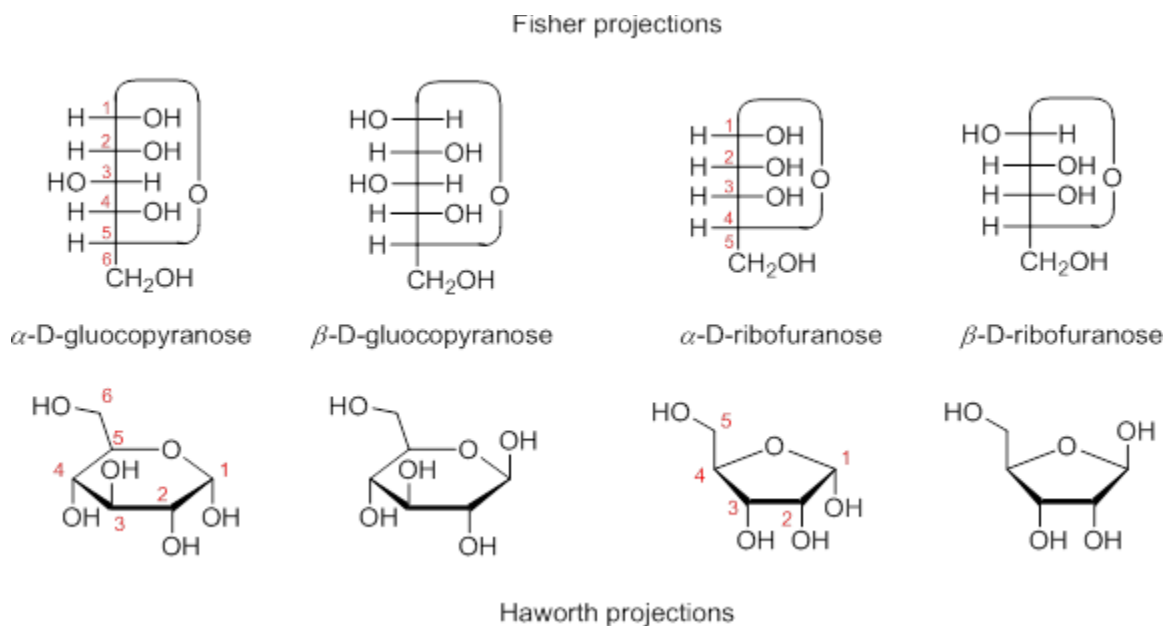
- Groups on the right in a Fischer projection are down (below the ring) in a Haworth projection.
- Groups on the left in a Fischer projection are up (above the ring) in a Haworth projection.



Scheme 13



Scheme 14



Scheme 15

D-Furanose is viewed edge on, with the ring oxygen away from the viewer. The anomeric carbon is on the right-hand side of the molecule, and the primary alcohol group is drawn up from the back left-hand corner (Figure 2).

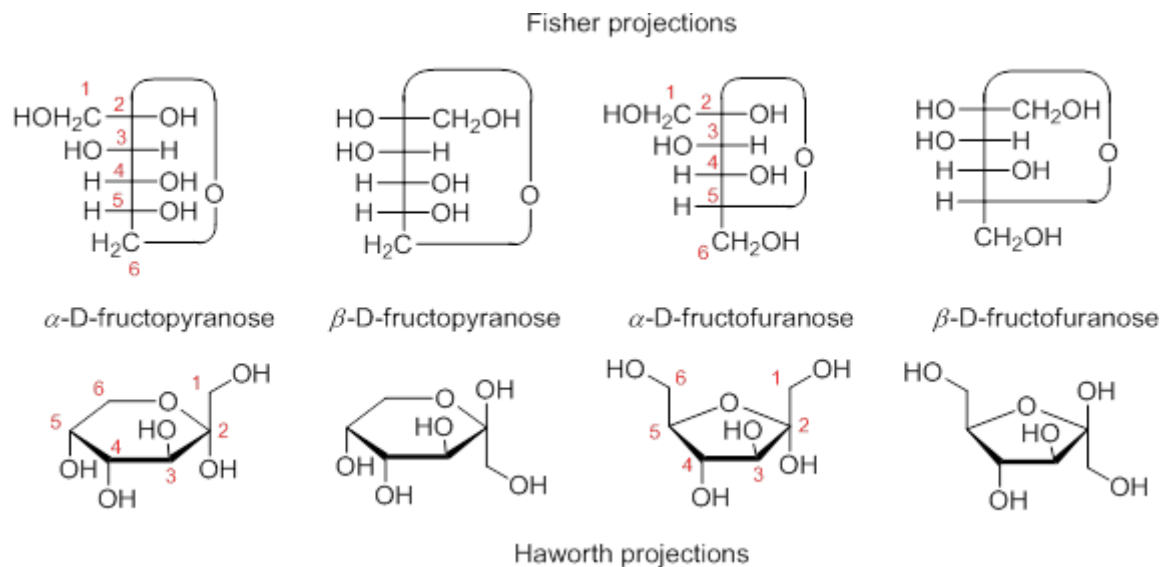
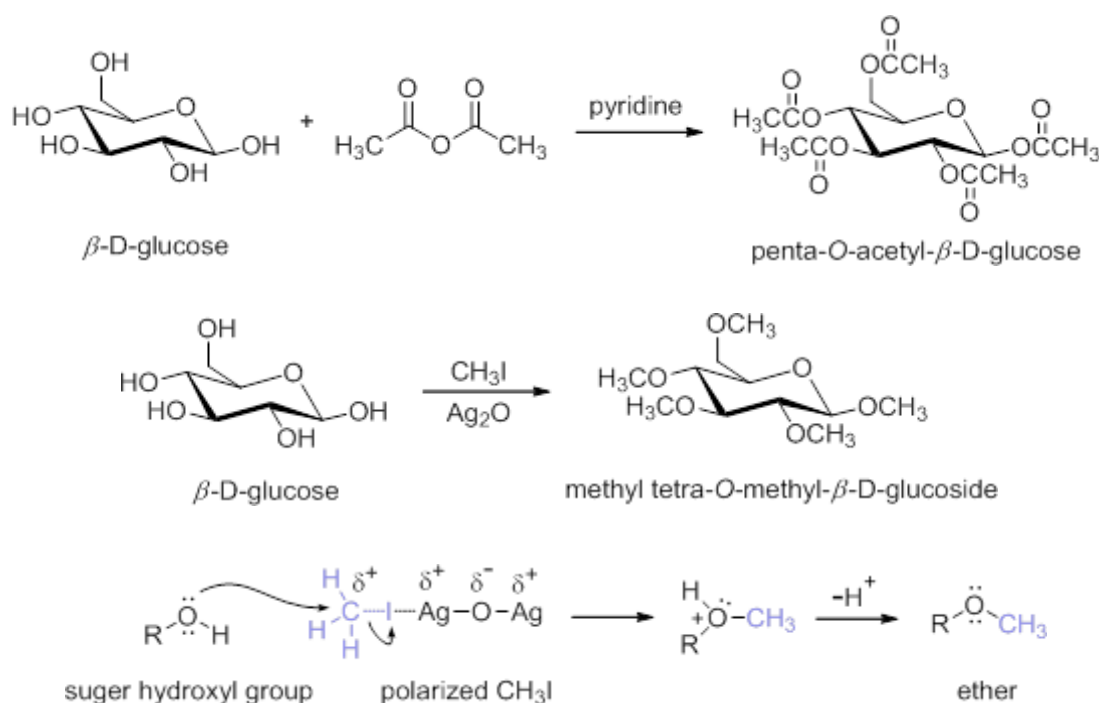


Figure 16

Carbohydrates II

Acylation and Alkylation of Monosaccharides

The -OH group of monosaccharide reacts with acetic anhydride or acetyl chloride to form esters. Similarly, ether can be prepared using methyl iodide/silver oxide. The nucleophilic character of -OH group is relatively poor, so silver oxide is used to increase the leaving tendency of the iodide ion in the $\text{S}_{\text{N}}2$ reaction (Scheme 1).

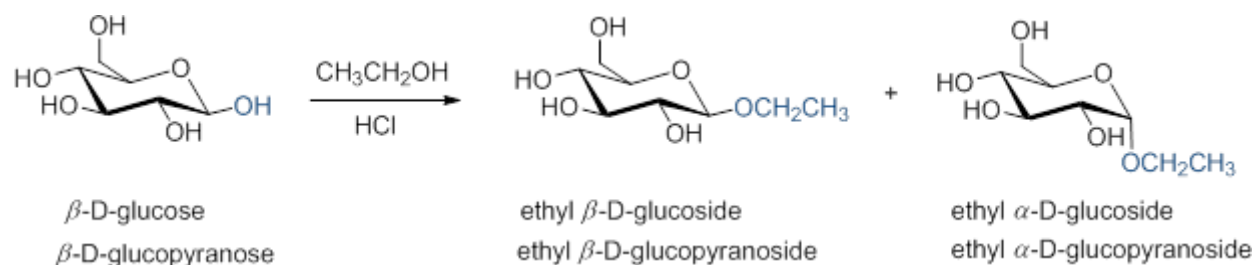


Scheme 1

Glycosides

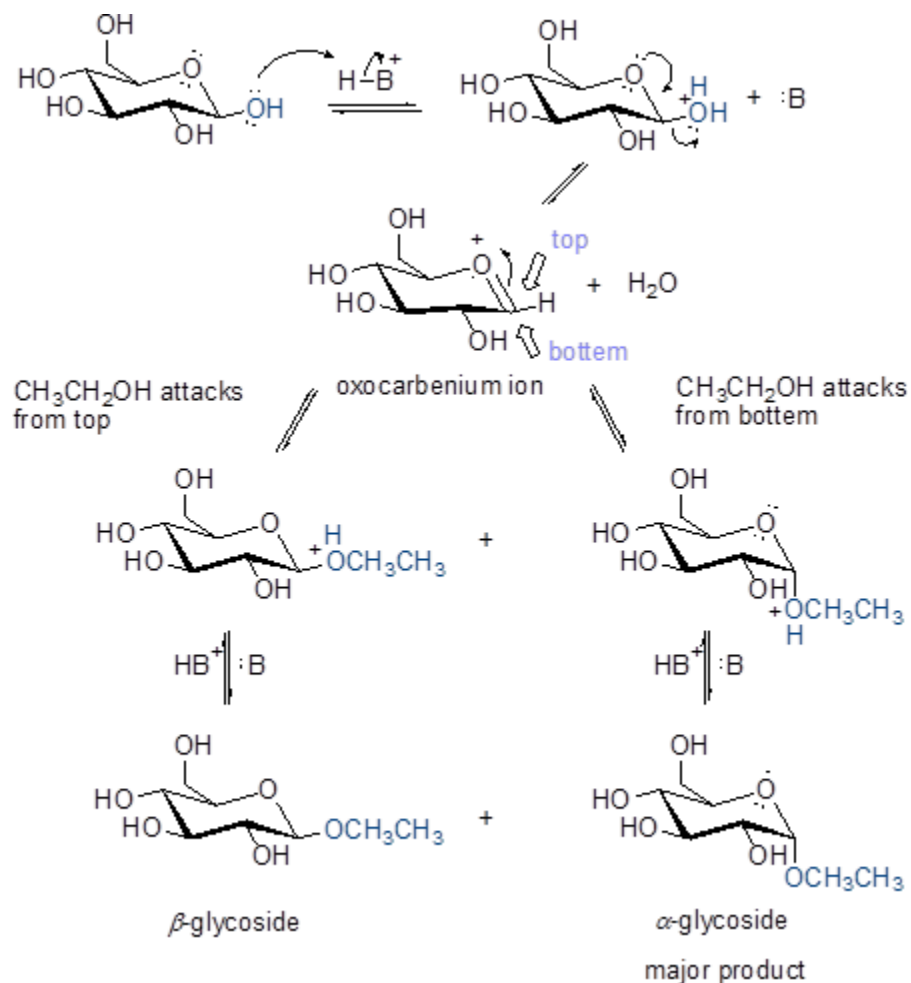
Glycosides are cyclic acetal form of sugars and the bond between the anomeric carbon and the alkoxy oxygen is called a glycosidic bond. They are prepared by the acid-catalyzed reaction of an alcohol with a pyranose or furanose.

Naming of glycosides is done by replacing the "e" of the sugar with "ide". Example, a glycoside of glucose is glucoside and if pyranose or furanose name is used, the acetal is called pyranoside or furanoside. Both α - and β -glycoside obtained from the reaction of a single anomer with an alcohol (Scheme 2).



Scheme 2

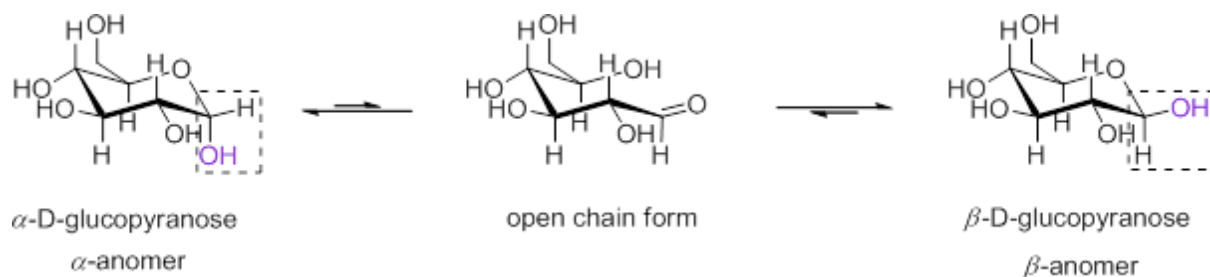
The reason for the formation of both glycosides is shown in Scheme 3. The protonation of the anomeric carbon –OH group followed by elimination of water gives a planar sp^2 hybridized oxocarbenium ion. This can react with alcohol from both faces to give the β -glycoside and the α -glycoside.



Scheme 3

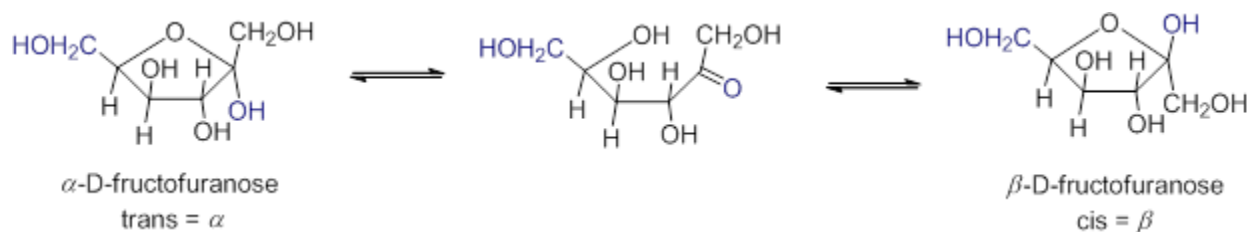
Anomeric Effect

When a pyranose or furanose ring closes, the hemiacetal carbon atom is converted from a flat carbonyl group to an asymmetric carbon. Depending on which face of the (protonated) carbonyl group is attacked, the hemiacetal –OH group can be directed either up or down. These two orientations of the hemiacetal –OH group give diastereomeric products called anomers, and the hemiacetal or acetal carbon atom is called the anomeric carbon atom. The preference of certain substituents bonded to the anomeric carbon for the axial position is called the anomeric effect. Ano is Greek for “upper”; thus, anomers differ in configuration at the upper-most asymmetric carbon. The anomeric carbon is the only carbon in the molecule that is bonded to two oxygen atoms. The anomer with the anomeric –OH group down (axial) is called the α -anomer, and the one with the anomeric –OH group up (equatorial) is called the β -anomer (Scheme 4).



Scheme 4

In fructose, the α -anomer has the anomeric –OH group down, trans to the terminal –CH₂OH group, while the β -anomer has it up, cis to the terminal –CH₂OH group (Scheme 5).

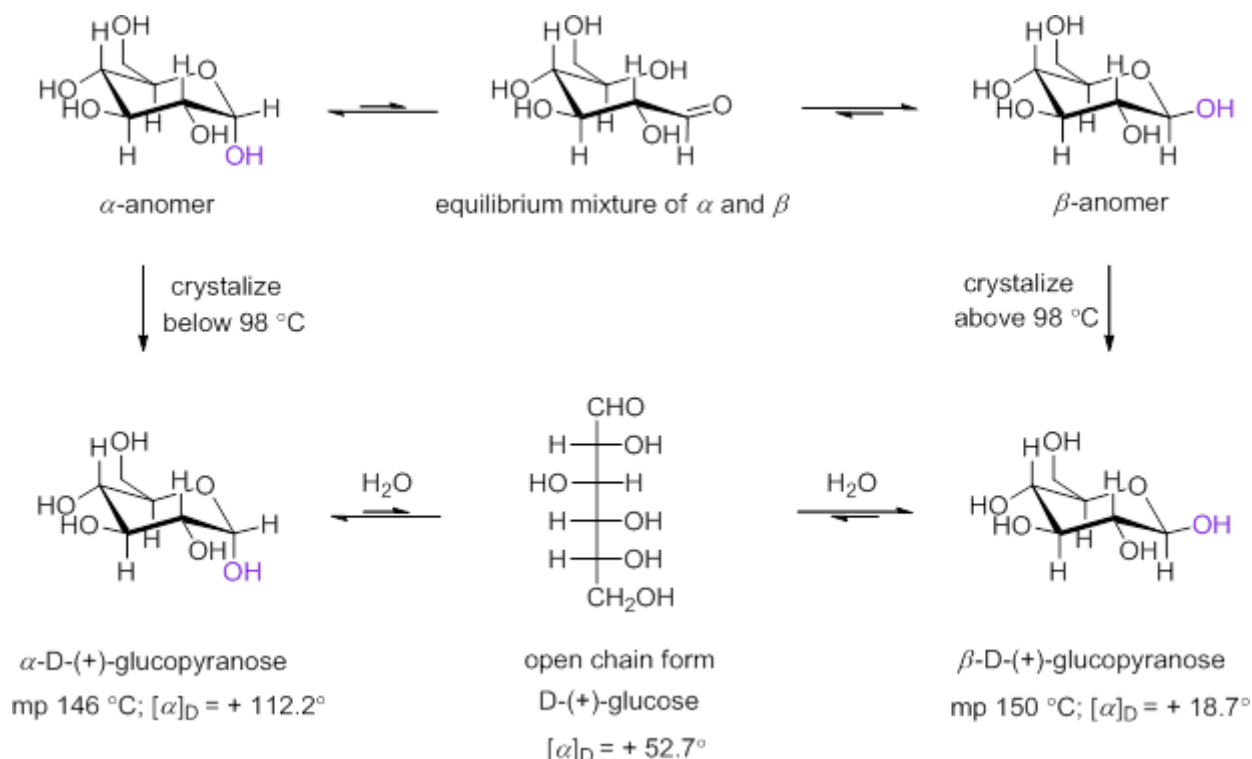


Scheme 5

Mutarotation

Normally D-(+)-glucose has a melting point of 146°C. However, when D-(+)-glucose is crystallized by evaporating an aqueous solution kept above 98°C, a second form of D-(+)-glucose with a melting point of 150°C can be obtained. When the optical rotations of these two forms are measured, they are found to be significantly different, but when an aqueous solution of either form is allowed to stand, its rotation changes. The specific rotation of one form decreases and the other increases, until both solutions show the same value. For

example, a solution of α -D-(+)-glucose (mp 146°C) specific rotation gradually decreases from an initial value of + 112.2° to + 52.7°, while The β -D-(+)-glucose (mp 150°C) specific rotation gradually increases from an initial value of + 18.7° to + 52.7°. The three forms of glucose reach equilibrium concentrations with the specific rotation of +52.7. This change ("mutation") in the specific rotation toward equilibrium is called **mutarotation** (Scheme 6).



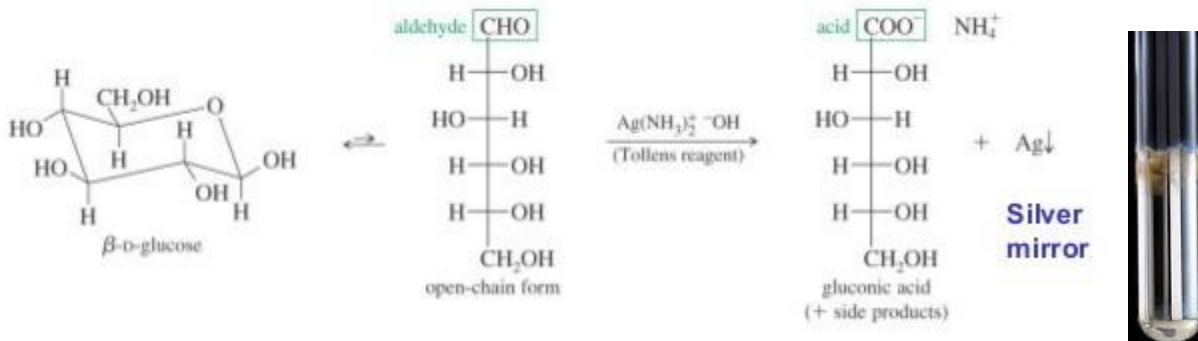
Scheme 6

Reducing and Non-reducing Sugars

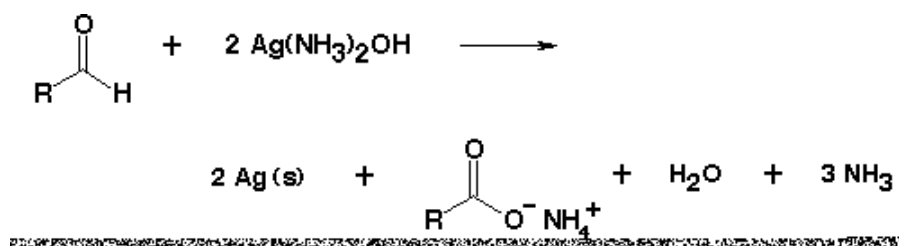
The carbohydrates may also be classified as either reducing or non-reducing sugars.

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 cannot be oxidized by reagents such as Tollen's reagent (Ag^+ , NH_3 , OH^-) or Br_2 . So, these are referred as non-reducing sugars.

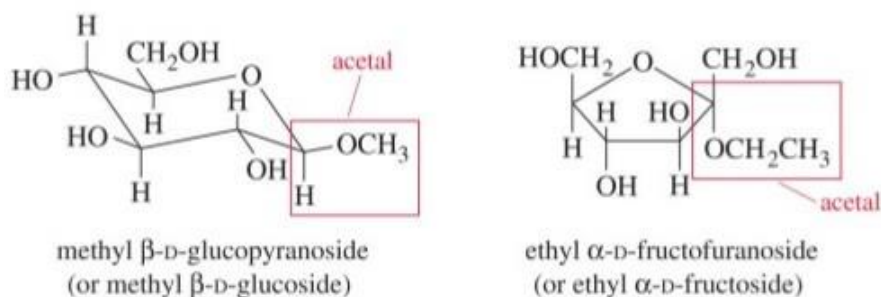
Whereas, some hemiacetals or hemiketals exist in equilibrium with the open-chain sugars in aqueous solution such as glucose. These sugars can reduce an oxidizing agent such as Tollens reagent or aqueous bromine and are thus classified as a reducing sugars. Infact, all aldehyde bearing compounds can reduce tollens reagent and this includes aldoses such as glucose.



Aldoses have a aldehyde group that can get oxidized to carboxylic acid and it turn can reduce tollens reagent to precipitate silver. In a test tube, the silver precipitates to form a silver mirror on the sides of the tube. This is used as a qualitative test for aldehydes which includes reducing sugars.



The reaction with tollen's reagent used as a qualitative test for aldehydes is provided above.

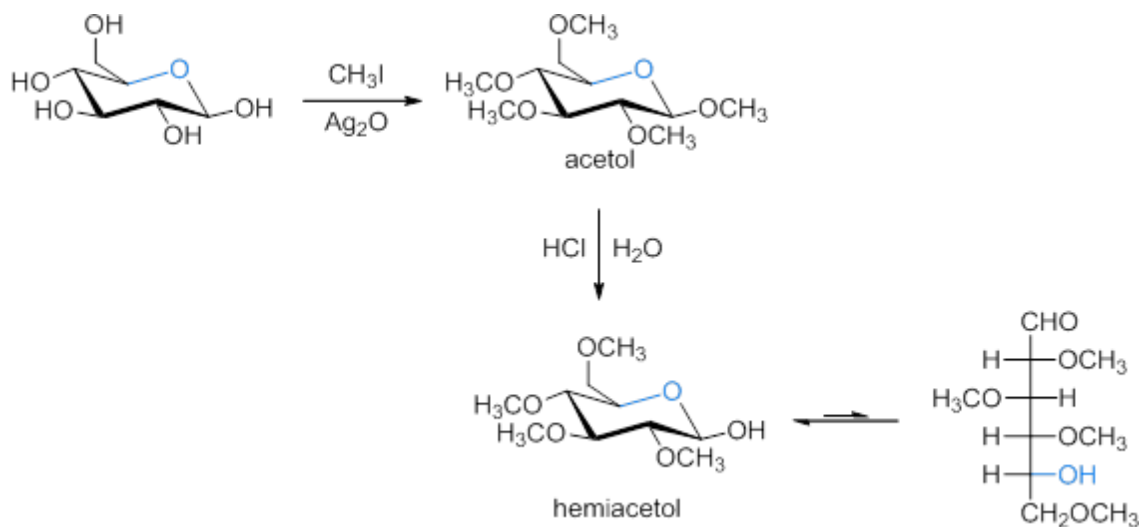


Infact, glucosides and fructosides as shown above, where the anomeric carbon is not free to form an open chain with aldehyde moiety and therefore cannot reduce tollen's reagent. Hence, these are termed non-reducing sugars. This includes di and higher order saccharides as well. Ketoses which do not possess an aldehyde group also not reduce tollen's reagent.

Determination of Ring Size

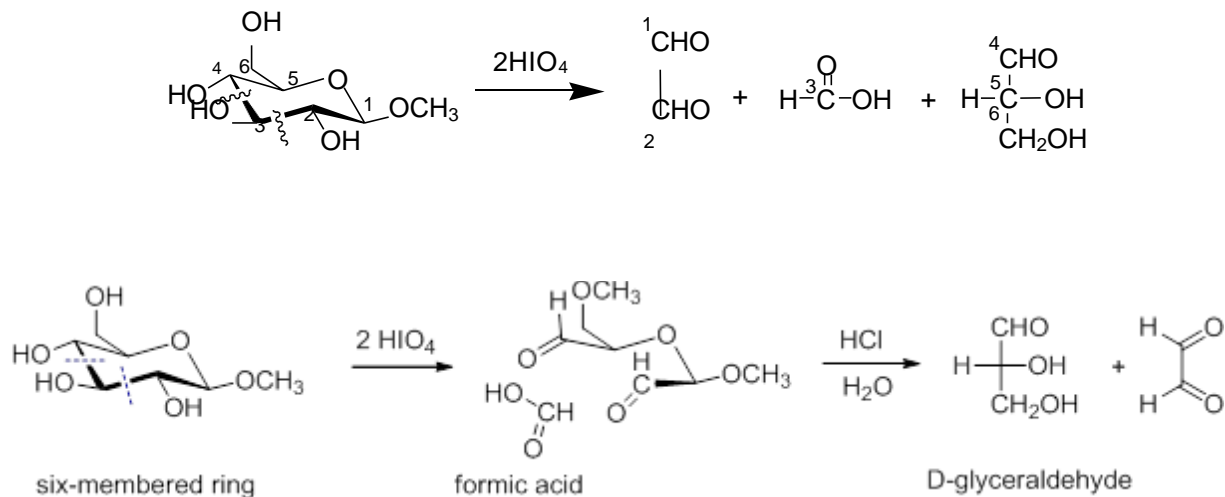
The anomeric carbon can be found via methylation of the -OH groups, followed by hydrolysis. In the first step, all the -OH groups are transformed to -OCH₃ groups with

excess methyl iodide and silver oxide. The hydrolysis of the acetal then forms a hemiacetal in presence of acid. This pyranose structure is in equilibrium with its open-chain form. From the open-chain form we can determine the size of the ring because the anomeric carbon attached -OH group is the one that forms the cyclic hemiacetal (Scheme 7).

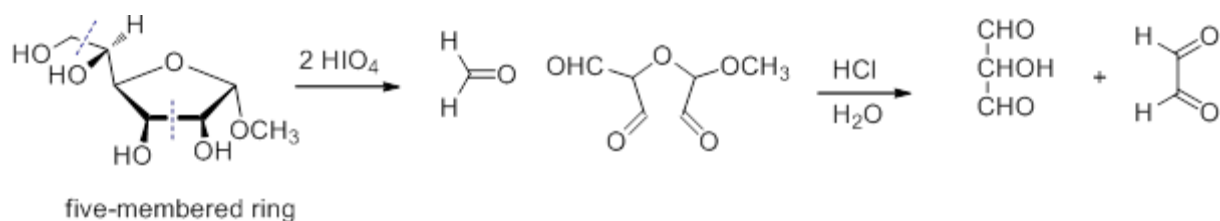


Scheme 7

A monosaccharide's ring size can be determined by the oxidation of an acetal of the monosaccharide with excess periodic acid. The products obtained from periodate cleavage of a six-membered ring acetal are different from those obtained from cleavage of a five-membered ring acetal (Scheme 8-9).



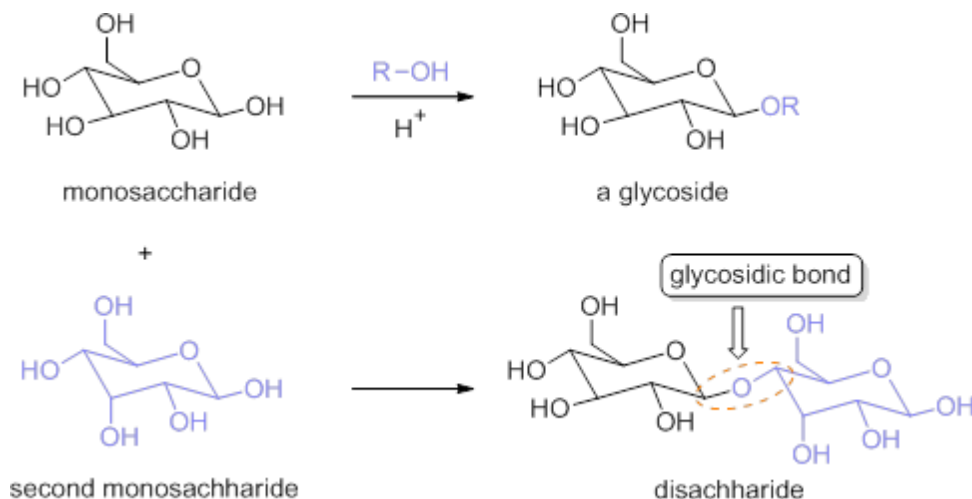
Scheme 8



Scheme 9

Disaccharides

If the glycoside or acetol is formed by reaction of the anomeric carbon of a monosaccharide with OH group of another monosaccharide molecule, then the glycoside product is a disaccharide (Scheme 10).



Scheme 10

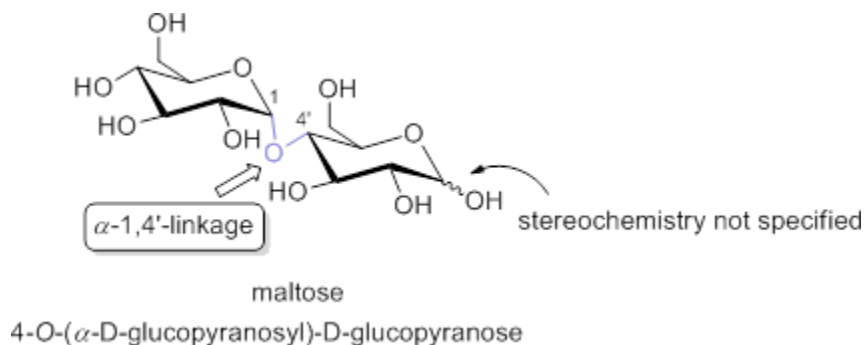
The anomeric carbon can react with any of the hydroxyl groups of another monosaccharide unit to form a disaccharide. Disaccharides can be categorized by the position of the hydroxyl group of another monosaccharide making up the glycoside.

Disaccharides have three naturally occurring glycosidic linkages

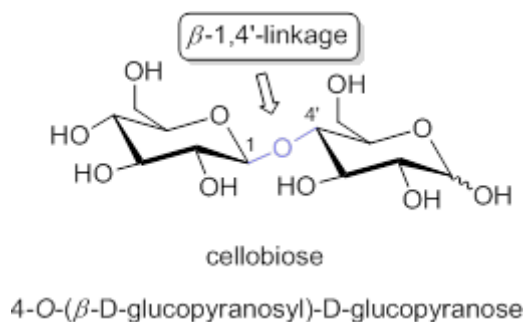
- 1-4' link: The anomeric carbon is bonded to oxygen on C-4 of second monosaccharide.
- 1-6' link: The anomeric carbon is bonded to oxygen on C-6 of second monosaccharide.
- 1-2' link: The anomeric carbons of the two monosaccharide unit are bonded through an oxygen.

The "prime" superscript indicates that –OH group bonded carbon position of the second monosaccharide unit, α - and β -configuration given by based on the configuration at the anomeric carbon of the first monosaccharide unit.

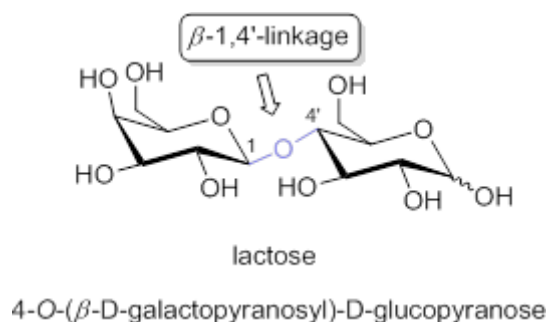
1-4' Glycosides : These represent the most common naturally occurring disaccharides. The linkage is between C-1 of one sugar subunit and C-4 of the other. For example, maltose is a disaccharide with two D-glucose units bearing 1,4'-glycosidic linkage. The stereochemistry of this linkage is α . So, the glycosidic linkage is called α -1,4'-glycosidic linkage.



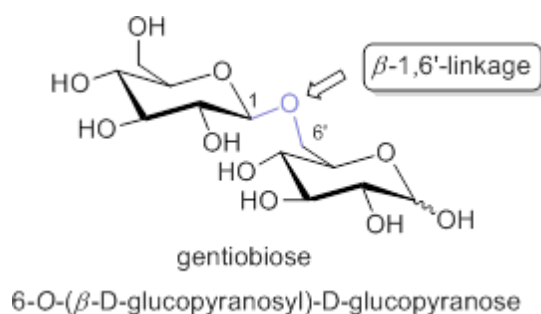
Cellobiose also contains two D-glucose subunits. The only difference from maltose is that the two glucose subunits are joined through a β -1,4'-glycosidic linkage.



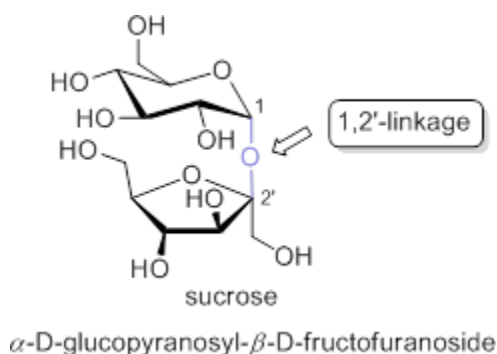
Lactose , a disaccharide present in milk, contains D-galactose (non-reducing) and D-glucose (reducing) monosaccharide units. These units are hooked together by a β -1,4'-glycosidic linkage.



1-6' Glycosides : The anomeric carbon of one unit hooked by the oxygen of the terminal carbon (C-6) of another monosaccharide unit. Example, gentiobiose is a sugar with two glucose units joined by a β -1,6'-glucosidic linkage.



1-2' Glycosides : The glycosidic bond is hooked between the two anomeric carbon of the monosaccharide units. For example, sucrose contains a D-glucose subunit and a D-fructose subunit, which have been joined by a glycosidic bond between C-1 of glucose (in the α - position) and C-2 of fructose (in the β - position).



Polysaccharides

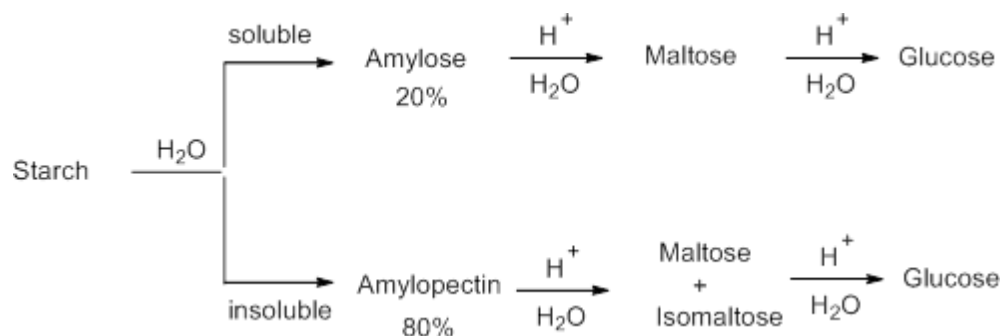
Polysaccharides are carbohydrates that contain many monosaccharide units joined by glycosidic bonds. All the anomeric carbon atoms of polysaccharides are involved in acetal

formation. So, polysaccharides do not react with Tollen's reagent, and they do not mutarotate.

Polysaccharides that are polymers of a single monosaccharide are called homopolysaccharides. If they are made by more than one type of monosaccharide are called heteropolysaccharides. Example, a glucan is made by glucose units and galactan, which is made by galactose units. There are three important polysaccharides, which are starch, glycogen and cellulose.

Starch is a glucose polymer that is the principal food storage carbohydrate in plants. It is found in roots, rhizomes, seeds, stems, tubers and corms of plants, as microscopic granules having characteristic shapes and sizes. Most animals, including humans, depend on these plant starches for nourishment. The intact granules are insoluble in cold water, but grinding or swelling them in warm water causes them to burst.

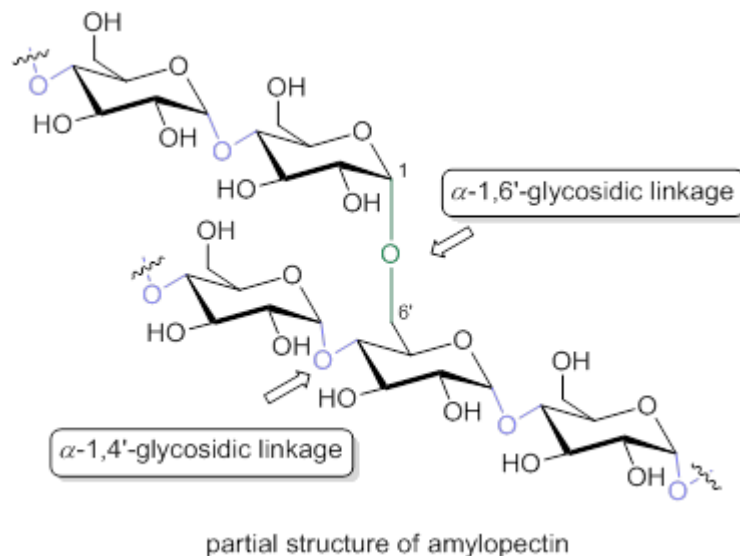
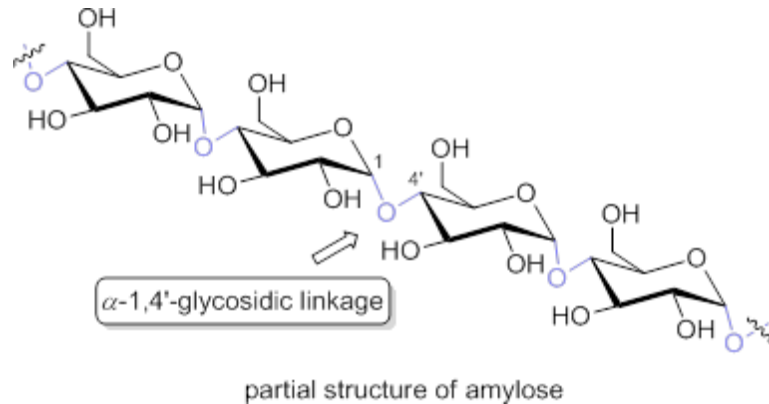
The released starch consists of two fractions. About 20% is a water soluble material called **amylose**. The majority of the starch is a much higher molecular weight substance, consisting of nearly a million glucose units, and called **amylopectin**.



Amylose is a linear polymer of D-glucose units joined by α -1,4'-glycosidic linkages. They are linear chains of several thousand glucose units joined by alpha C-1 to C-4 glycoside bonds. Amylose solutions are actually dispersions of hydrated helical micelles.

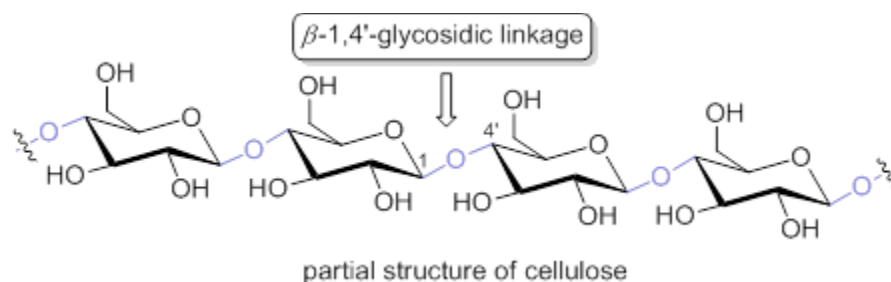
Amylopectin is a branched polymer of D-glucose units hooked by α -1,4'-glycosidic linkages and the branches are created by α -1,6'-glycosidic linkages. (branched networks built from C-1 to C-4 and C-1 to C-6 glycoside links). It is essentially water insoluble. On an average, branches occur every twenty five glucose units.

Hydrolysis of starch, usually by enzymatic reactions, produces a syrupy liquid consisting largely of glucose. When cornstarch is the feedstock, this product is known as **corn syrup**. It is widely used to soften texture, add volume, prohibit crystallization and enhance the flavor of foods. It is a mixture of two components that can be separated on the basis of water solubility.



Glycogen functions as a carbohydrate storage form for animals. Like amylopectin, it is non-linear polymer of D-glucose units joined by α -1,4'-glycosidic linkages and α -1,6' - glycosidic linkages at branches. The structure of glycogen is similar to that amylopectin, but it has more branches. On an average, branches occur every ten glucose units. The highly branched structure of glycogen provides many available glucose end groups for immediate hydrolysis to provide glucose needed for metabolism.

Cellulose serves as structural material in plants, providing structural strength and rigidity to plants. It is a linear polymer of D-glucose units joined by β -1,4'-glycoside bonds. Humans and other mammals do not have the β -glucosidase enzyme needed to hydrolyze cellulose, so they cannot obtain glucose directly from cellulose.

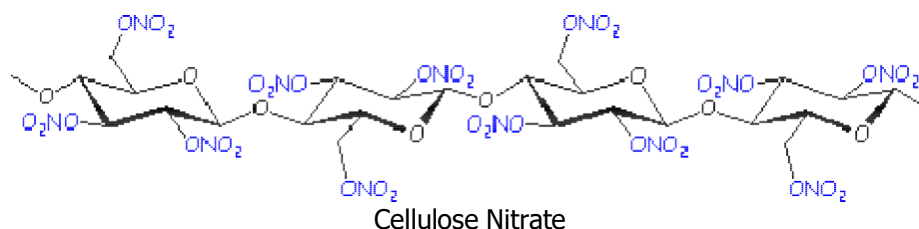


Synthetic Modification of Cellulose

Cotton, probably the most useful natural fiber, is nearly pure cellulose. The manufacture of textiles from cotton involves physical manipulation of the raw material by carding, combing and spinning selected fibers. For fabrics the best cotton has long fibers, and short fibers or cotton dust are removed. Crude cellulose is also available from wood pulp by dissolving the lignan matrix surrounding it. These less desirable cellulose sources are widely used for making paper.

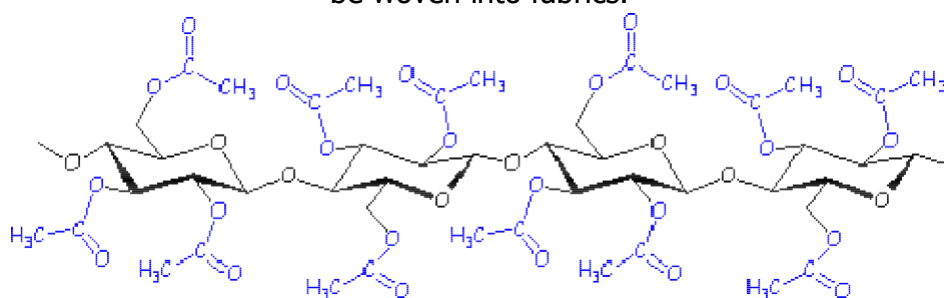
In order to expand the ways in which cellulose can be put to practical use, chemists have devised techniques for preparing solutions of cellulose derivatives that can be spun into fibers, spread into a film or cast in various solid forms. A key factor in these transformations are the three free hydroxyl groups on each glucose unit in the cellulose chain, -- $[C_6H_7O(OH)_3]_n$ --. Esterification of these functions leads to polymeric products having very different properties compared with cellulose itself.

Cellulose Nitrate, first prepared over 150 years ago by treating cellulose with nitric acid, is the earliest synthetic polymer to see general use. The fully nitrated compound, -- $[C_6H_7O(ONO_2)_3]_n$ --, called guncotton, is explosively flammable and is a component of smokeless powder. Partially nitrated cellulose is called **pyroxylin**. Pyroxylin is soluble in ether and at one time was used for photographic film and lacquers. The high flammability of pyroxylin caused many tragic cinema fires during its period of use. Furthermore, slow hydrolysis of pyroxylin yields nitric acid, a process that contributes to the deterioration of early motion picture films in storage.



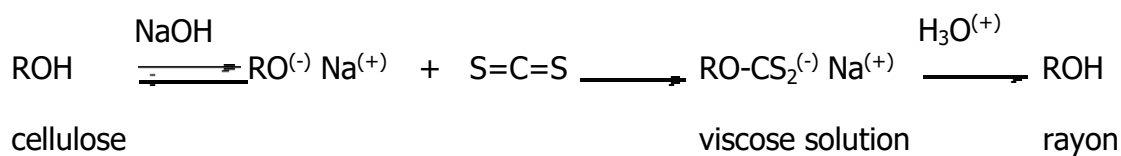
Cellulose Acetate, -- $[C_6H_7O(OAc)_3]_n$ --, is less flammable than pyroxylin, and has replaced it in most applications. It is prepared by reaction of cellulose with acetic anhydride and an acid catalyst. The properties of the product vary with the degree of acetylation. Some chain shortening occurs unavoidably in the preparations. An acetone solution of cellulose acetate may be forced through a spinneret to generate filaments, called **acetate rayon**, that can

be woven into fabrics.



Cellulose Acetate

Viscose Rayon, is prepared by formation of an alkali soluble xanthate derivative that can be spun into a fiber that reforms the cellulose polymer by acid quenching. The following general equation illustrates these transformations. The product fiber is called **viscose rayon**.



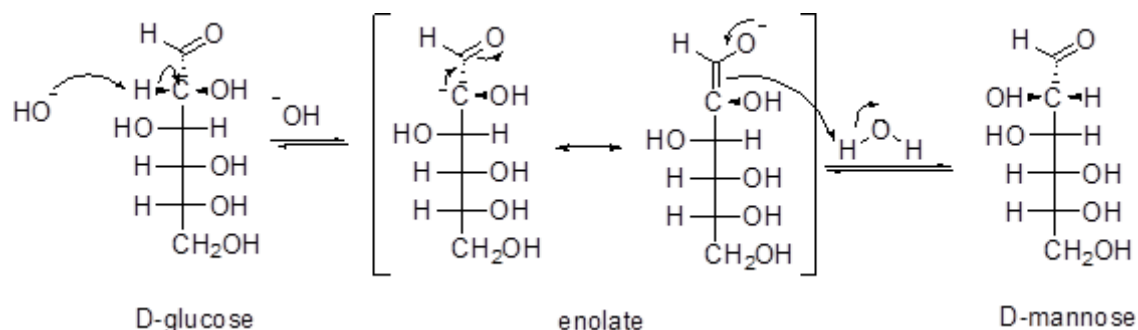
Carbohydrates III

Reactions

Monosaccharides contain carbonyl functional group and alcohol functional groups, so it can be oxidized or reduced and can react with nucleophiles to form corresponding products.

Epimerization

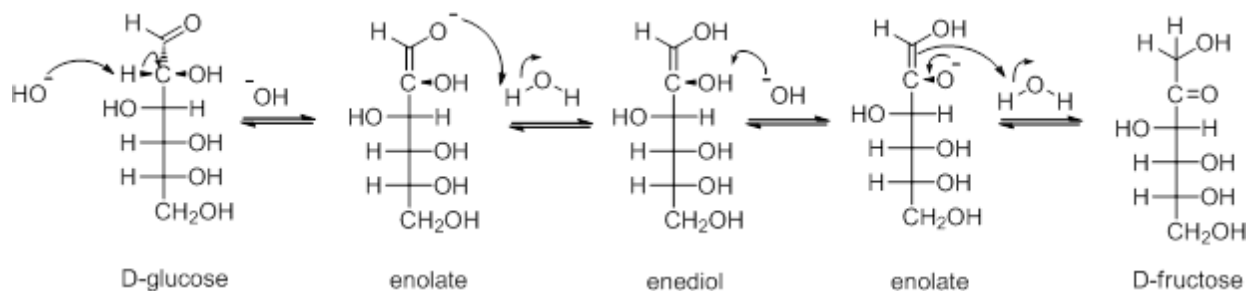
In the presence of base, D-glucose may be converted into D-mannose via the removal of hydrogen at C-2 carbon followed by protonation of the enolate (Scheme 1).



Scheme 1

Enediol Rearrangement

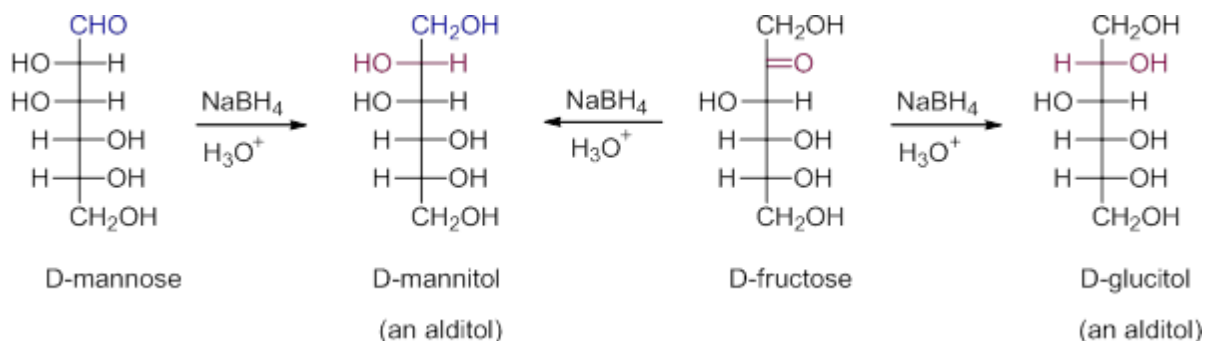
The position of carbonyl group may shift via enediol intermediate under basic condition. For example, rearrangement of D-glucose gives D-fructose (Scheme 2).



Scheme 2

Reduction

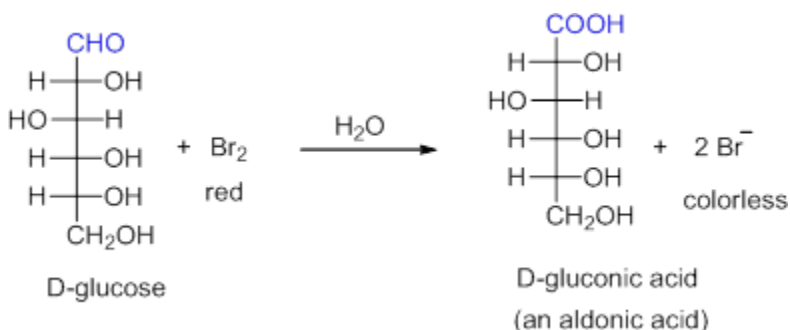
The monosaccharide contains carbonyl group which can be reduced by the reducing agents such as NaBH_4 . Reduction of aldose forms one alditol and ketose forms two alditols (Scheme 3).



Scheme 3

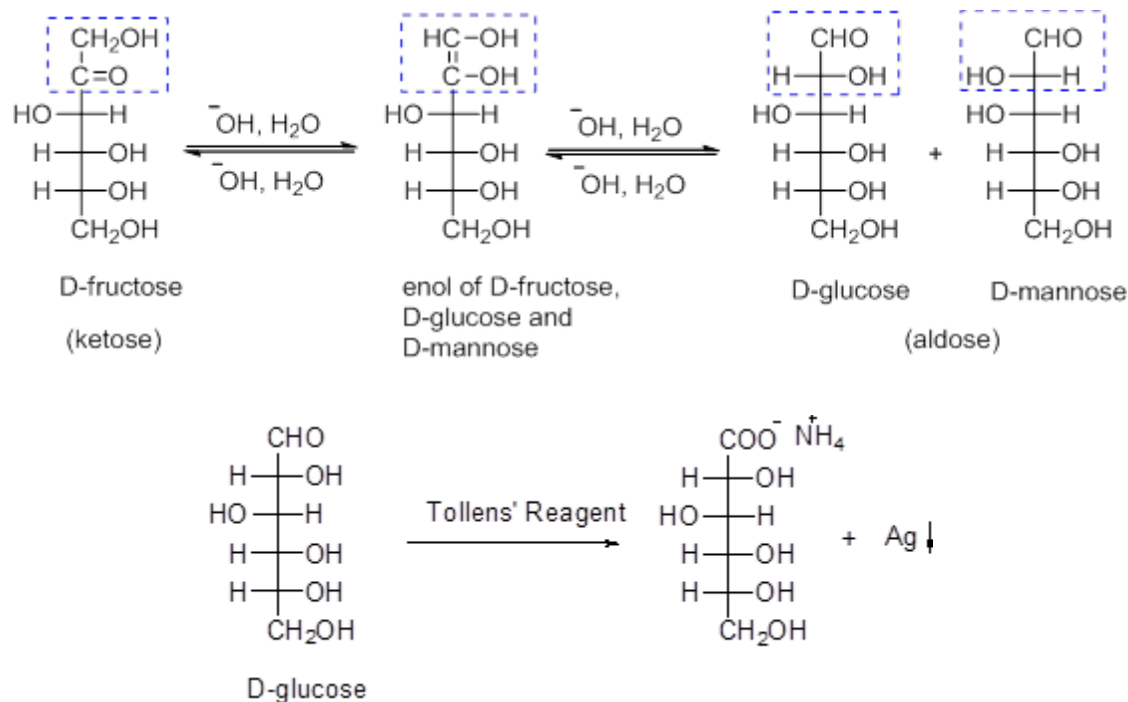
Oxidation

- Bromine water oxidizes aldehyde functional group, but it cannot oxidize ketones or alcohols. Therefore, aldose can be distinguished from ketose by observing reddish-brown colour of bromine. The oxidized product is an aldonic acid (Scheme 4).



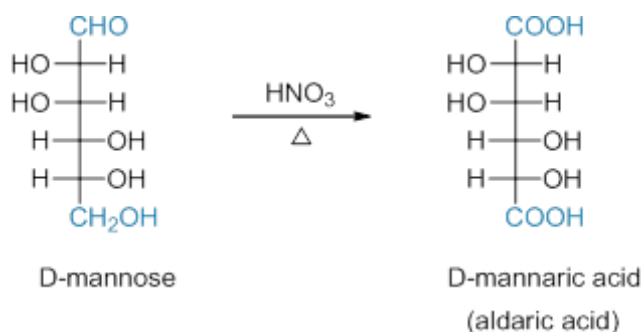
Scheme 4

- Tollen's reagent can oxidize both aldose and ketose to aldonic acids. For example, the enol of both D-fructose and D-glucose, as well as the enol of D-mannose are same (Scheme 5).



Scheme 5

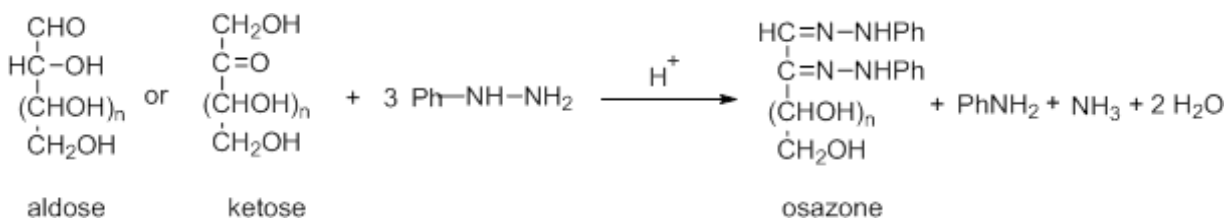
Both aldehyde and primary alcohol groups of an aldose are oxidized by strong oxidizing agent such as HNO_3 . The oxidized product called an aldonic acid. Ketose also reacts with HNO_3 to give more complex product mixtures (Scheme 6).



Scheme 6

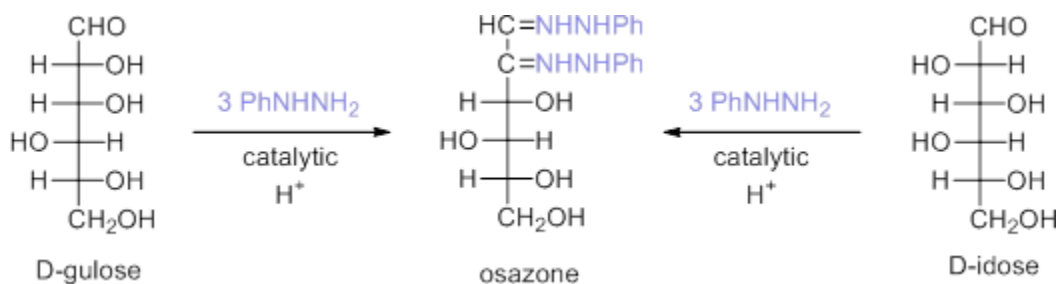
Osazone Formation

Aldose and ketose react with one equiv of phenylhydrazine to produce phenylhydrazones. In contrast, both C-1 and C-2 react with three equivalent of phenylhydrazine to form a bis-hydrazone known as an osazone (Scheme 7).



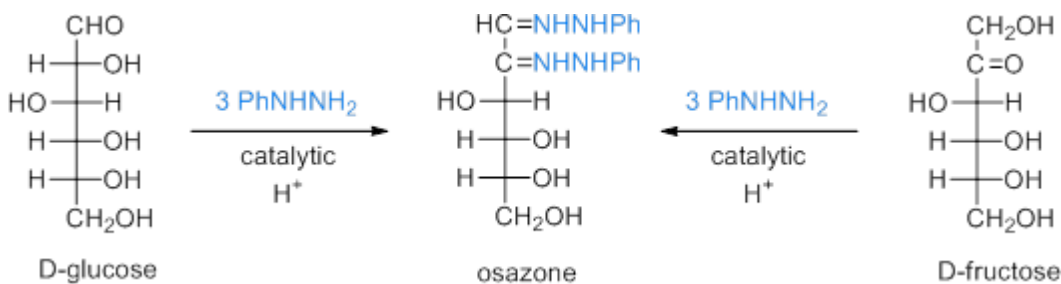
Scheme 7

The configuration at C-1 or C-2 is lost in the formation of osazone, C-2 epimers form identical osazones. For example, D-glucose and D-idose are C-2 epimers; both form the same osazone (Scheme 8).



Scheme 8

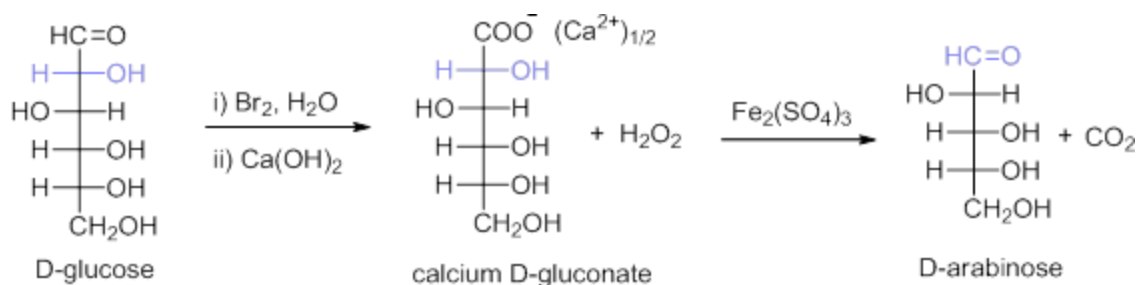
Ketose reacts with phenylhydrazine at C-1 and C-2 position to form osazone. D-Glucose and D-fructose form the same osazone (Scheme 9).



Scheme 9

The Ruff Degradation

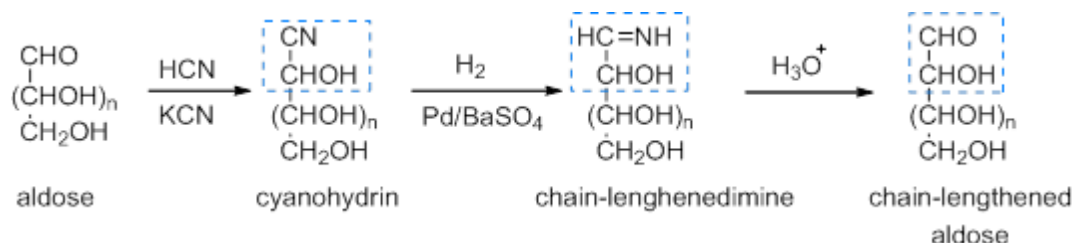
Aldose chain is shortened by oxidizing the aldehyde to -COOH , then decarboxylation. In the Ruff degradation, the calcium salt of an aldonic acid is oxidized with hydrogen peroxide. Ferric ion catalyzes the oxidation reaction, which cleaves the bond between C-1 and C-2, forming an aldehyde. The calcium salt of the aldonic acid prepared from oxidation of an aldose with an aqueous solution of bromine and then adding calcium hydroxide to the reaction mixture (Scheme 10).



Scheme 10

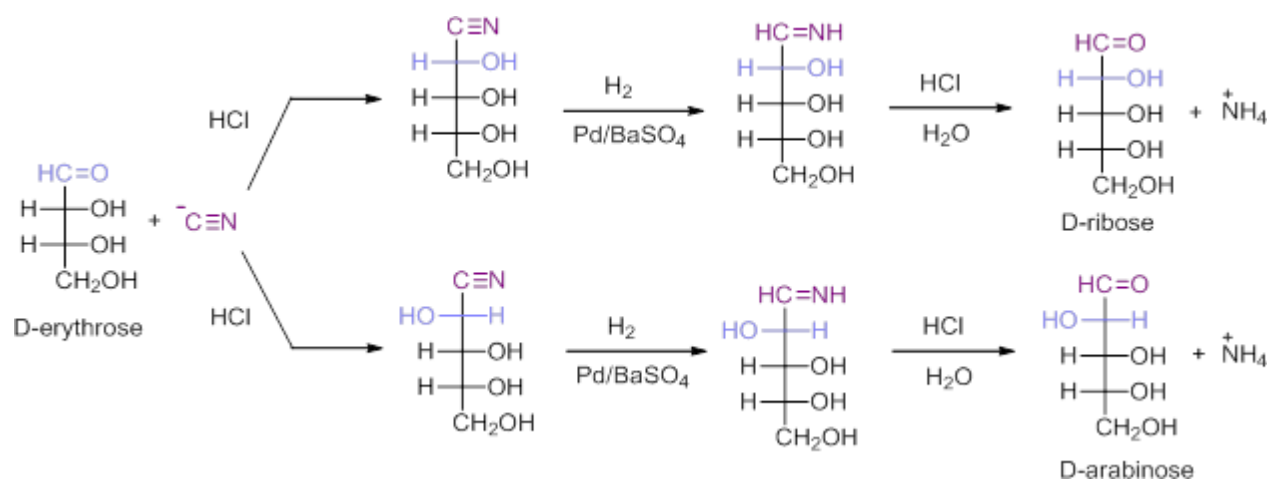
The Kiliani–Fischer Synthesis

An aldose carbon chain can be increased by one carbon in a Kiliani–Fischer synthesis (Scheme 11). It is the opposite of Ruff Degradation reaction. This synthesis leads to formation of a pair of C-2 epimers.



Scheme 11

D-Erythrose gives the corresponding chain lengthened products D-ribose and D-arabinose (Scheme 12).



Scheme 12

Text Books

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- R. R. Morrison, R. N. Boyd and S. K. Bhattacharjee, Organic Chemistry , Dorling Kindersley (India) Pvt. Ltd, New Delhi, 2011.
- C. M. Loudon , Organic Chemistry , Oxford University Press, New Delhi, 2002.