CARBOHYDRATE

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Biochemistry and Oral biochemistry – DENT 293

First Semester

First Week

09/17/2024

➢ **Outlines:**

1. Buffer solution.
2. Carbohydrate.
3. Types of carbohydrate.
4. Drawing Howarth structure for monosaccharides.

- **<u>Objectives:</u>**

1. Knowing the function of buffer solution in human body.
2. Distinguish between monosaccharide, disaccharide, oligosaccharide and polysaccharide.
3. Changing open chain structure to cyclic.

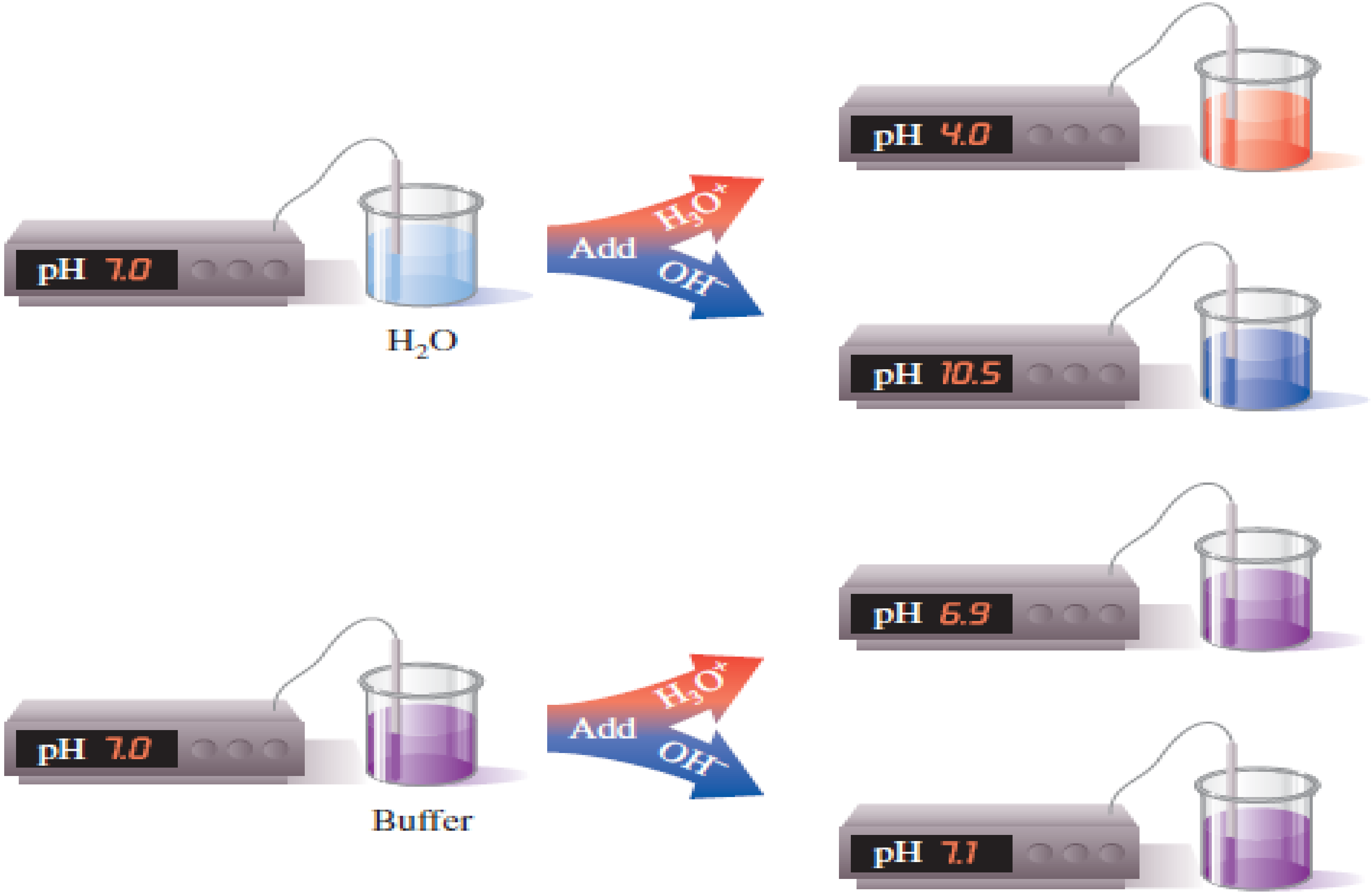
Buffer solution (Buffers)

The pH of water and most solutions changes drastically when a small amount of **acid** or **base** is added. However, if a solution is **buffered**, there is little change in **pH**.

- **Buffer solution:** is a solution that **maintains** pH by neutralizing added **acid** or **base**.

- There are two types of buffer solutions:

1. Acidic buffer solution.
2. Alkaline (or basic) buffer solution.


pH 7.0
H₂O
Add
H_3O^+
OH^-
pH 4.0
pH 10.5
pH 7.0
Buffer
Add
H_3O^+
OH^-
pH 6.9
pH 7.1

Buffer in Blood

When there is a change in pH of blood, cells cannot function properly, and death may result. In our cells, CO_2 is continually produced as an end product of cellular metabolism.

Some CO_2 is carried to the lungs for elimination, and the rest dissolves in body fluids such as **<u>plasma</u>**, forming **carbonic acid**.

As a weak acid, **carbonic acid** dissociates to give **bicarbonate, HCO_3^- and H_3O^+.** More of the anion HCO_3^- is supplied by the kidneys to give an important buffer system in the body fluid: the H_2CO_3/ HCO_3^-

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \underset{}{\overset{H_2O}{\rightleftharpoons}} H_3O^+(aq) + HCO_3^-(aq)$$

Carbohydrates

Carbohydrates are polyhydroxy **aldehydes** or **ketones**, they are the most abundant of all the organic compounds in nature, the general formula is $\mathbf{C_n(H_2O)_n}$.

Carbohydrates such as table sugar, lactose in milk, and cellulose are all made of **carbon, hydrogen, and oxygen**. *In a series of reactions* called photosynthesis, energy from the Sun is used to combine the carbon atoms from carbon dioxide and the hydrogen and oxygen atoms of water (H_2O) into the carbohydrate, glucose.

$$6CO_2 + 6H_2O + \text{energy} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Types of Carbohydrates

1. **Monosaccharides:** The word "saccharide" is derived from the Greek word *"sakkharon"* which means "sugar" or "sweet." monosaccharide is a simplest carbohydrate which cannot be convert or hydrolyzed into smaller carbohydrates.

- Their molecular formula is $[C_nH_{2n}O_n]$.
- **Examples;** glucose, galactose, fructose, ribose…etc.

2. **Disaccharides:** consist of two monosaccharide units joined together. Thus, a disaccharide can be split into two monosaccharide units.

- Their molecular formula is $[C_n(H_2O)_{n-1}]$.

Examples:

- Sucrose = Glucose + Fructose
- Lactose = Glucose + Galactose
- Maltose = Glucose + Glucose
- Cellobiose = Glucose + Glucose

3. **Oligosaccharides:** consist of few carbohydrates that can be hydrolyzed and changes into a few monosaccharide units **(three to ten monosaccharide)**.

Example:

- Raffinose = Glucose + Galactose + Fructose

4. **Polysaccharides:** are polymeric carbohydrates contain many monosaccharide units. In the presence of an acid or an enzyme, a polysaccharide can be completely hydrolyzed to yield many molecules of monosaccharide.

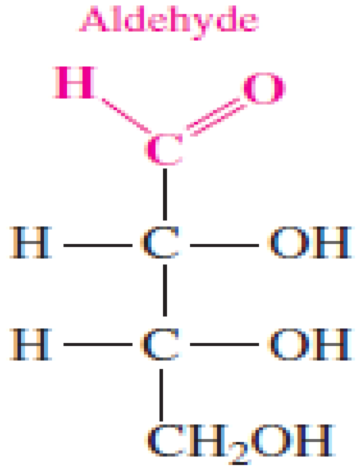
- Their molecular formula is $[C_6H_{10}O_5]_n$.
- Polysaccharides are of two types as follows:

a) **Homopolysaccharides (Homoglycans):** These polysaccharides yield similar monosaccharide units upon hydrolysis.

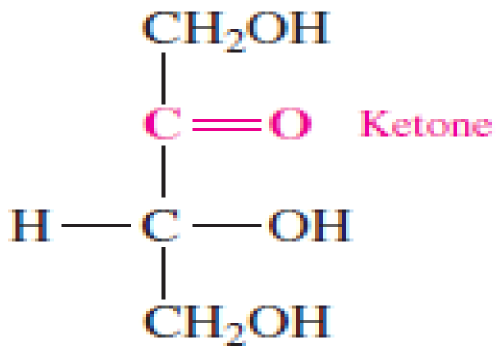
b) **Heteropolysaccharides (Heteroglycans):** These polysaccharides yield different monosaccharide units upon hydrolysis.

Monosaccharides

Monosaccharides are sugars that have a chain of **three** to **eight** carbon atoms, one in a carbonyl group and the rest attached to hydroxyl groups. There are two types of monosaccharide structures. In an **aldose**, the carbonyl group is on the first carbon as an aldehyde, while a **ketose** contains the carbonyl group on the second carbon atom as a ketone.

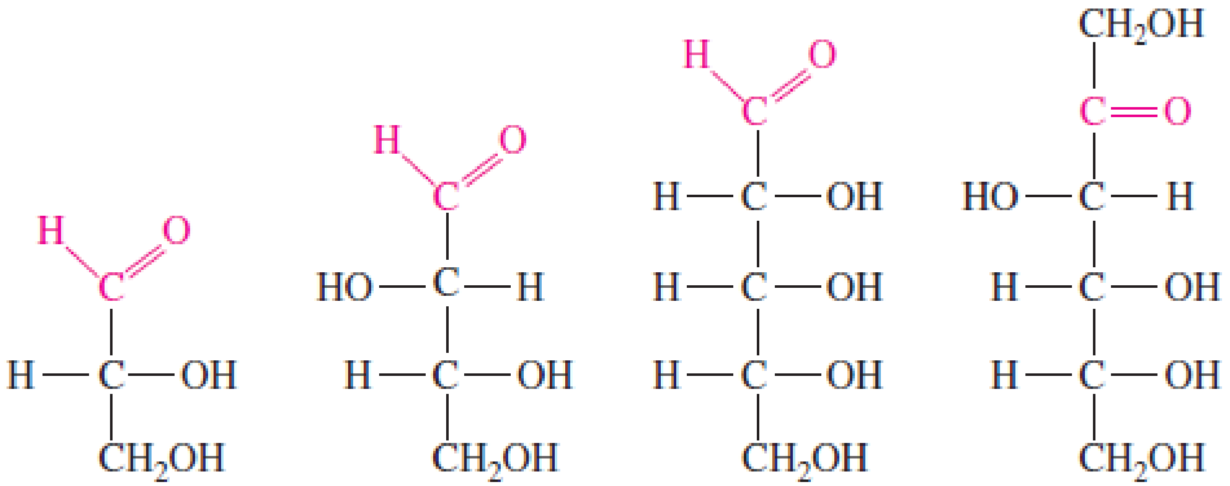


Polyhydroxyaldehyde



polyhydroxyketone

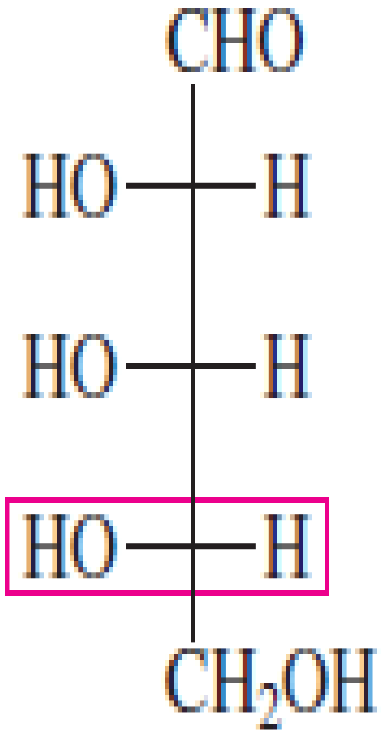
A monosaccharide with ***three, four, five, six, ….etc*** carbon atoms is naming as ***triose, tetrose, pentose, hexose, ….etc***. We can use both classification systems to indicate the type of carbonyl group and the number of carbon atoms. An ***aldopentose*** is a five-carbon monosaccharide that is an aldehyde; a ***ketohexose*** is a six-carbon monosaccharide that is a ketone.



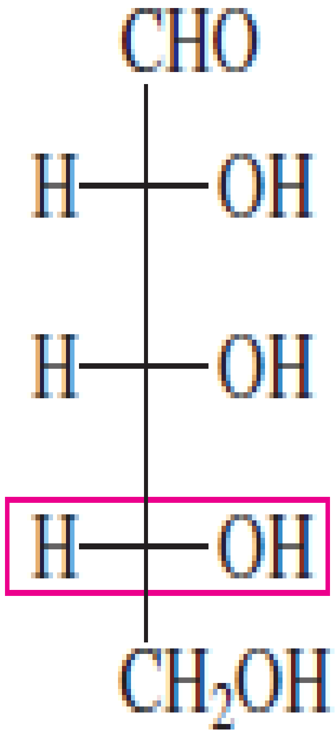
Aldotriose **Aldotetrose** **Aldopentose** **ketohexose**

Fischer Projection

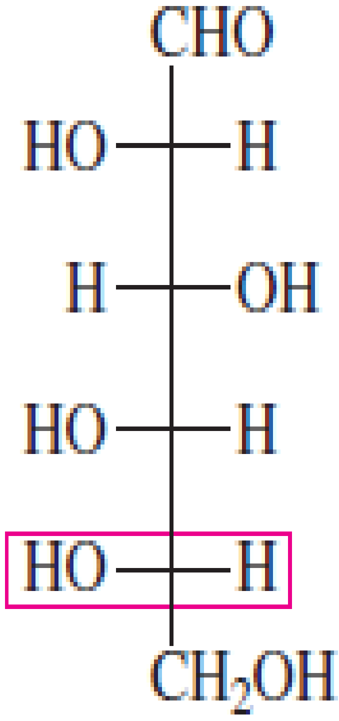
Most of the monosaccharides we will study have five or six carbon atoms with more than one chiral carbon. Then the group on the **chiral** carbon farthest from the carbonyl group is used to determine the D- or L- isomers. The following **(next slide)** are the Fischer projections for the D and L isomers of ribose, a five-carbon monosaccharide, and the D- and L- isomers of glucose, a six-carbon monosaccharide. In each of the mirror images, it is important to understand that the –OH groups on all the chiral carbon atoms are reversed from one side to the other. For example, in L-ribose, the – OH groups are all written on the left side of the horizontal line. In the mirror image, D-ribose, the – OH groups are all written on the right side of the horizontal line.



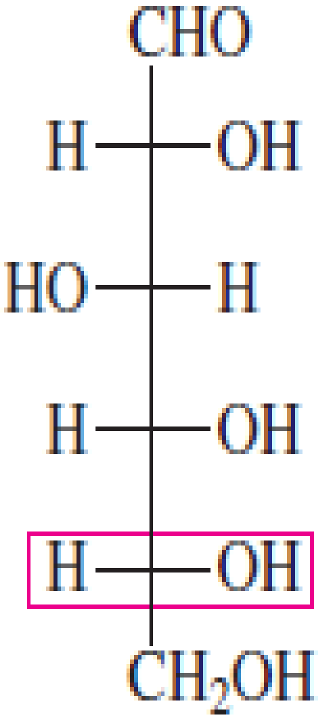
L-aldopentose
L-ribose



D-aldopentose
D-ribose



L-aldohexose
L-glucose



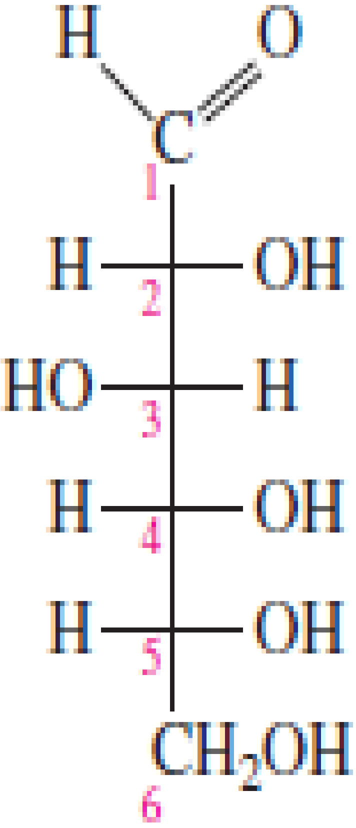
D-aldohexose
D-glucose

➢ Structures of Some Important Monosaccharides:

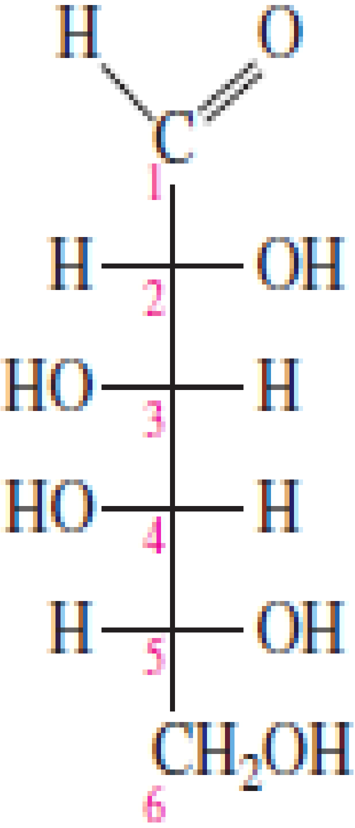
The hexoses **(glucose, galactose, and fructose)** are the most important monosaccharides. They are all hexoses with the molecular formula $\mathbf{C_6H_{12}O_6}$ and are *isomers* of each other.

We can draw Fischer projections for their D- and L- stereoisomers, the D- stereoisomers are commonly found in nature and used in the cells of the body.

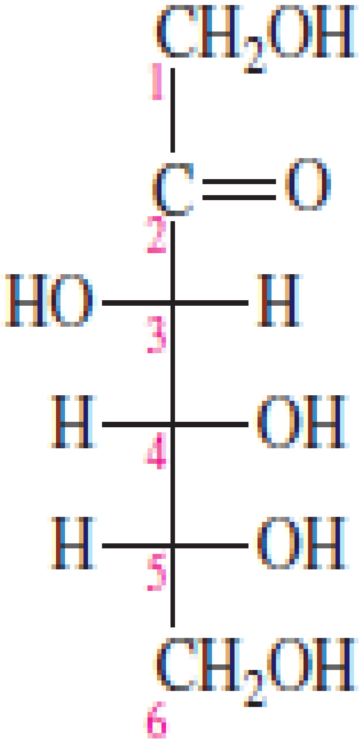
The Fischer projections for the D- stereoisomers are drawn as follows:



D-Glucose

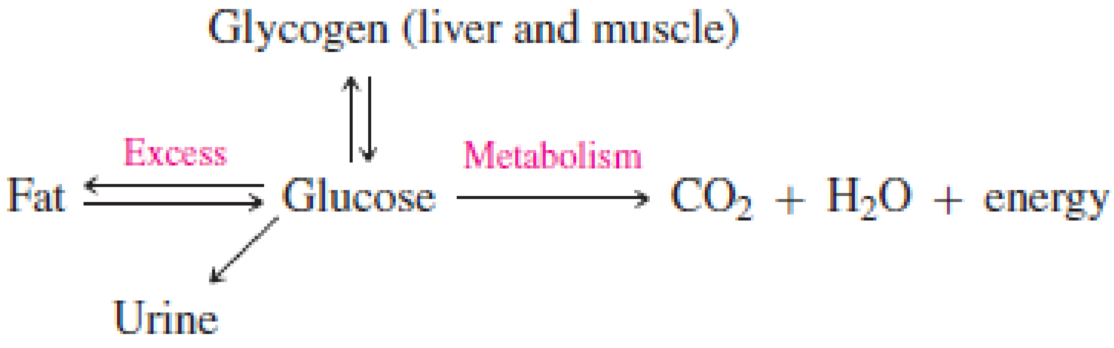


D-Galactose



D-Fructose

The most common hexose, **D-glucose**, $C_6H_{12}O_6$, also known as ***dextrose**** and blood sugar, is found in fruits, vegetables, corn syrup, and honey. D-glucose is a building block of the disaccharides such as; ***sucrose, lactose,*** *and* ***maltose****, and polysaccharides such as* ***amylose, cellulose****, and* ***glycogen***. In the body, **glucose** normally occurs at a concentration of 70–90 mg/dL (1 dL = 100 mL) of blood. Excess glucose is converted to **glycogen** and stored in the liver and muscle. When the amount of glucose exceeds what is needed for energy or glycogen, the excess glucose is converted to **fat**, which can be stored in unlimited amounts.

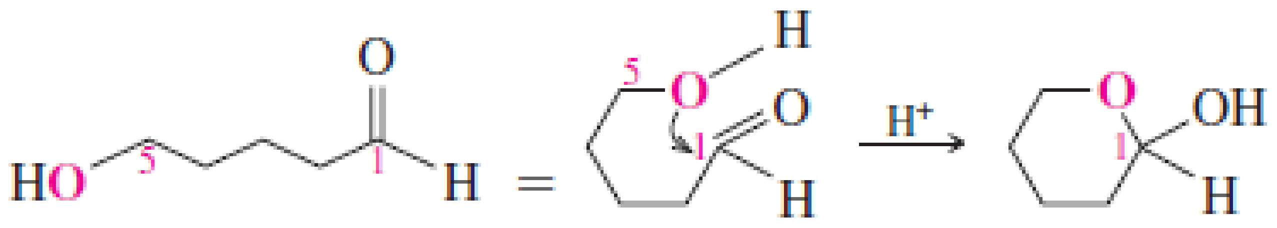


Galactose is an aldohexose that is obtained from the disaccharide lactose, which is found in milk and milk products. Galactose is important in the cellular membranes of the brain and nervous system. The only difference in the Fischer projections of D-glucose and D-galactose is the arrangement of the -OH group on **carbon 4**.

In contrast to glucose and galactose, fructose is a ketohexose. Fructose is the sweetest of the carbohydrates, almost twice as sweet as sucrose. This characteristic makes fructose popular with dieters because less fructose, and therefore fewer calories, is needed to provide a pleasant taste. Fructose, also called ***levulose**** and fruit sugar, is found in fruit juices and honey.

Drawing Haworth Structures for Cyclic Forms

Until now, we have drawn the Fischer projections of monosaccharides as open chains. However, the most stable form of pentoses and hexoses are five- or six-atom rings. These rings, known as **Haworth structures**, are produced from the reaction of a carbonyl group and a hydroxyl group in the *same* molecule, which forms a *cyclic hemiacetal*. For example, the following diagram shows that the oxygen atom in the hydroxyl group on carbon 5 of an aldohexose bonds with carbon 1 in the carbonyl and produces a six-atom cyclic ***hemiacetal****.

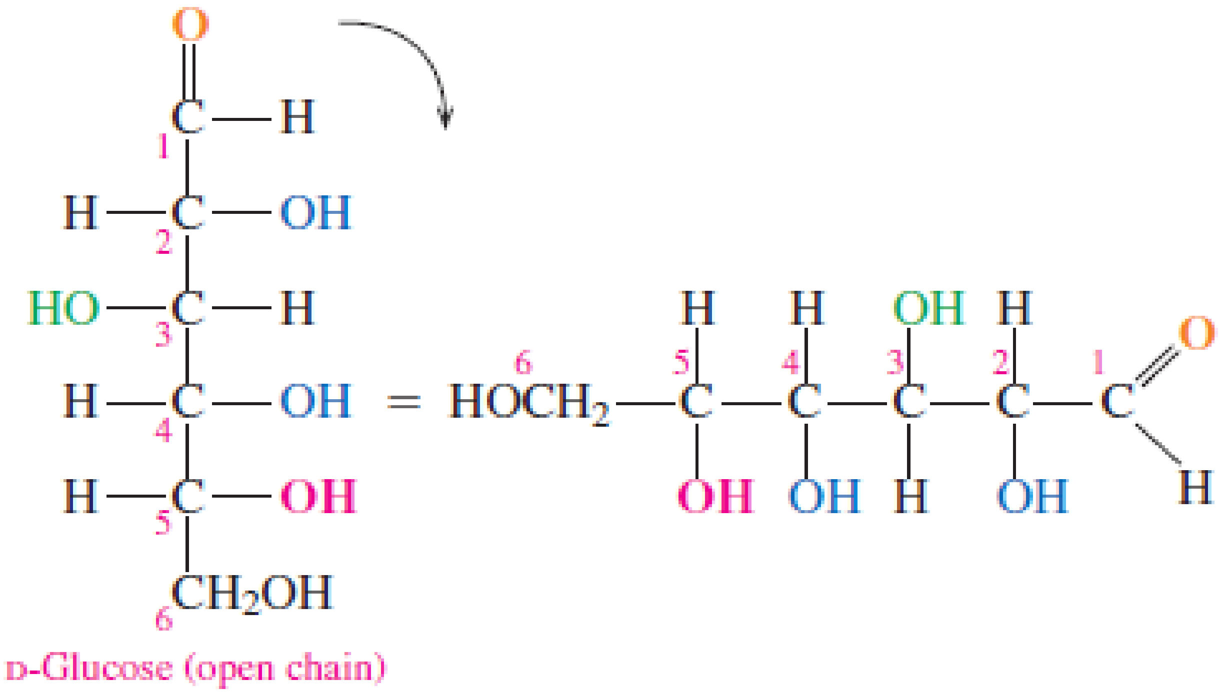


Open chain

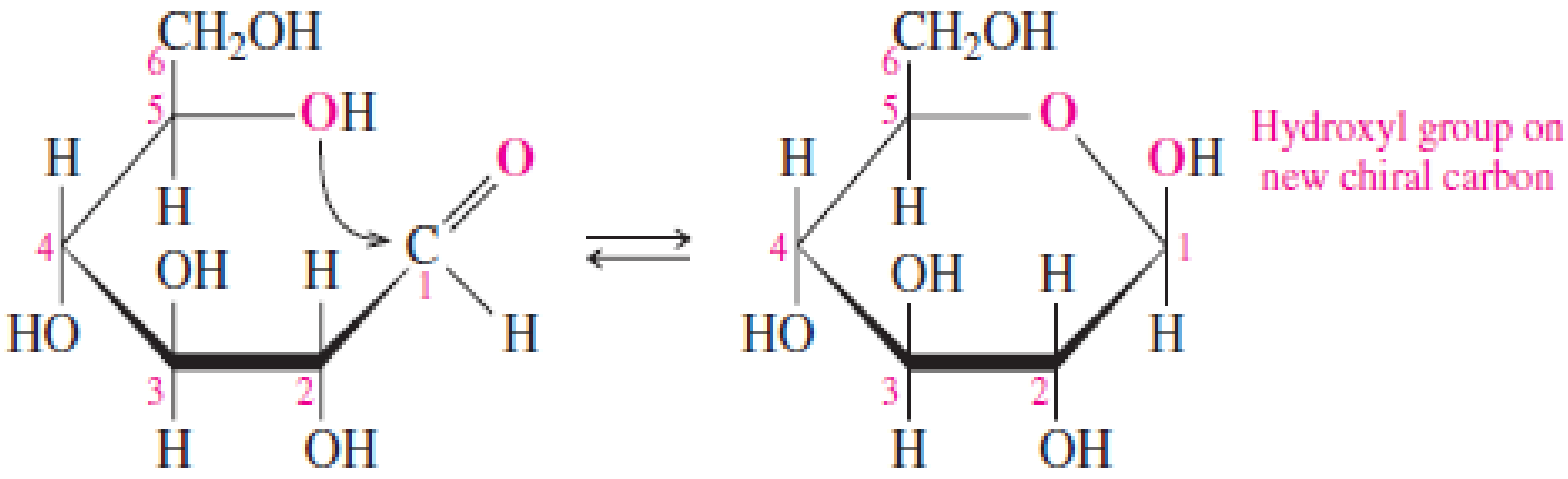
Cyclic hemiacetal

Haworth Structures of Glucose

Step 1: Turn the open-chain clockwise 90°. This places the (OH) groups on the right of carbons 2 and 4 and carbon 5 of the vertical open chain below the carbon atoms. The group on the left of the open chain is drawn above carbon 3.



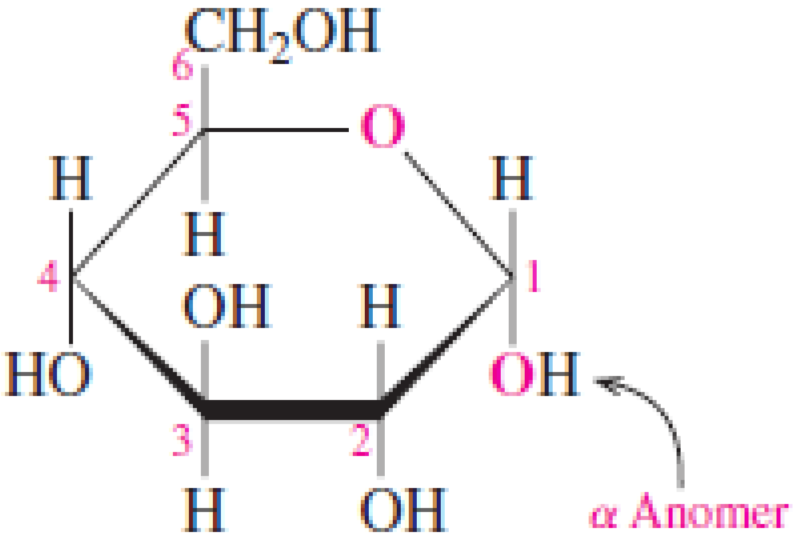
Step 2: Fold the carbon chain into a hexagon and bond the Oxygen on carbon 5 to the carbonyl group. With carbon 2 and 3 as the base of a hexagon, move the remaining carbons upwards. The reacting (OH) group on carbon 5 is drawn next to the carbonyl carbon, which moves carbon 6 in above carbon 5. To complete the Haworth structure, draw a bond from the oxygen of the reacting (OH) group (carbon 5) to the carbonyl carbon.



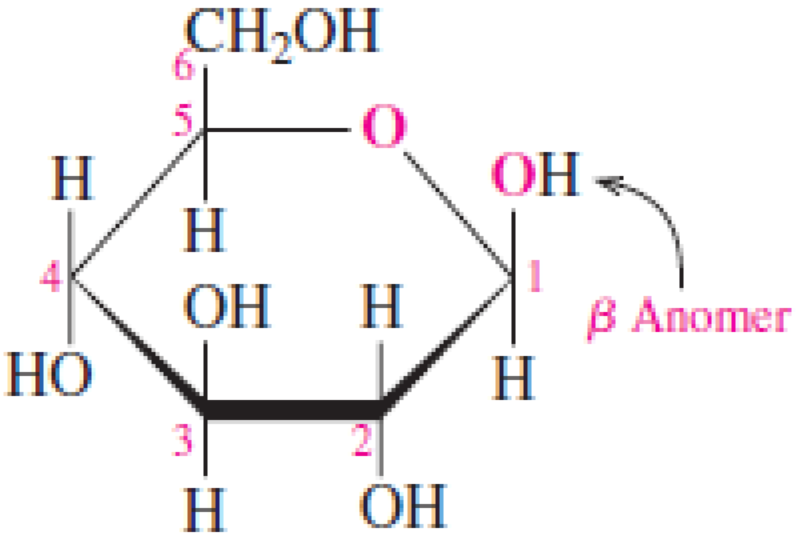
Carbon-5 oxygen bonds to carbonyl

Cyclic hemiacetal structure

Step 3: Draw the new (OH) group on carbon 1 down to give the α-isomer or up to give β-isomer. In a Haworth structure, the corners of the ring represent carbon atoms. There are two ways to draw the new (OH) either up or down, which gives two possible stereoisomers of D-glucose.

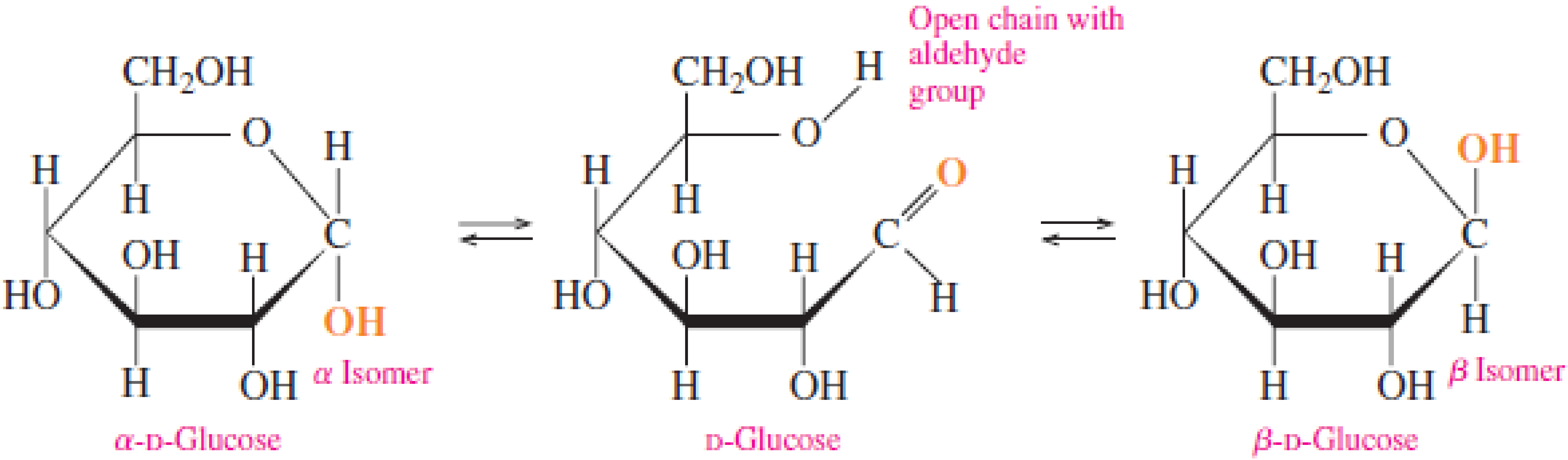


α-D-Glucose



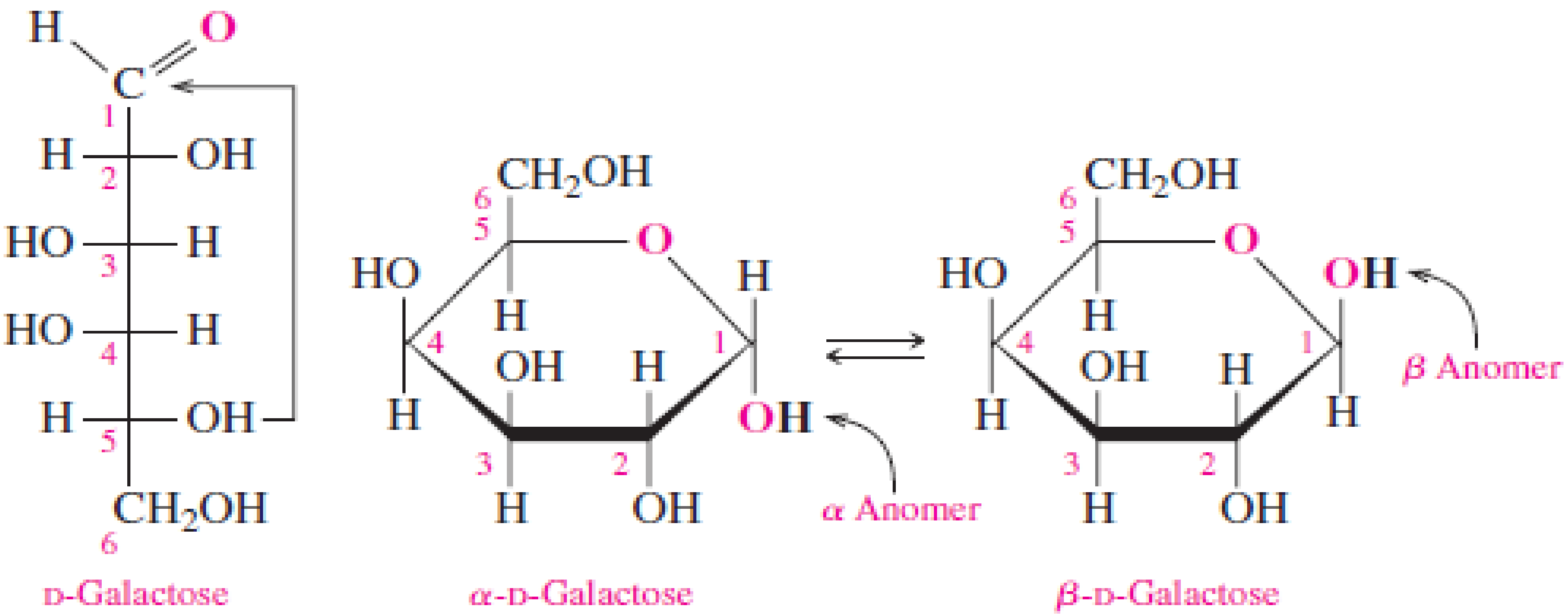
β-D-Glucose

Mutarotation of α- and β- D -Glucose



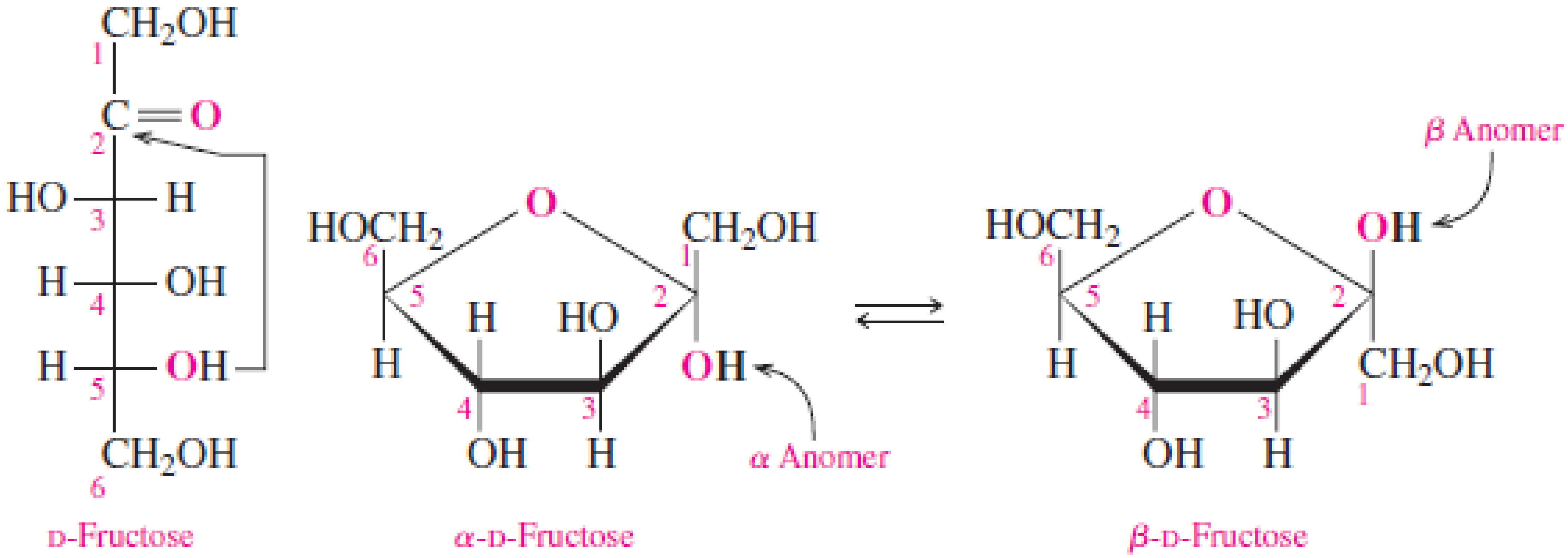
Haworth Structures of Galactose

Its Haworth structure is similar to glucose, except that the on carbon 4 is drawn up. Galactose also exists as α- and β-isomers.



Haworth Structures of Fructose

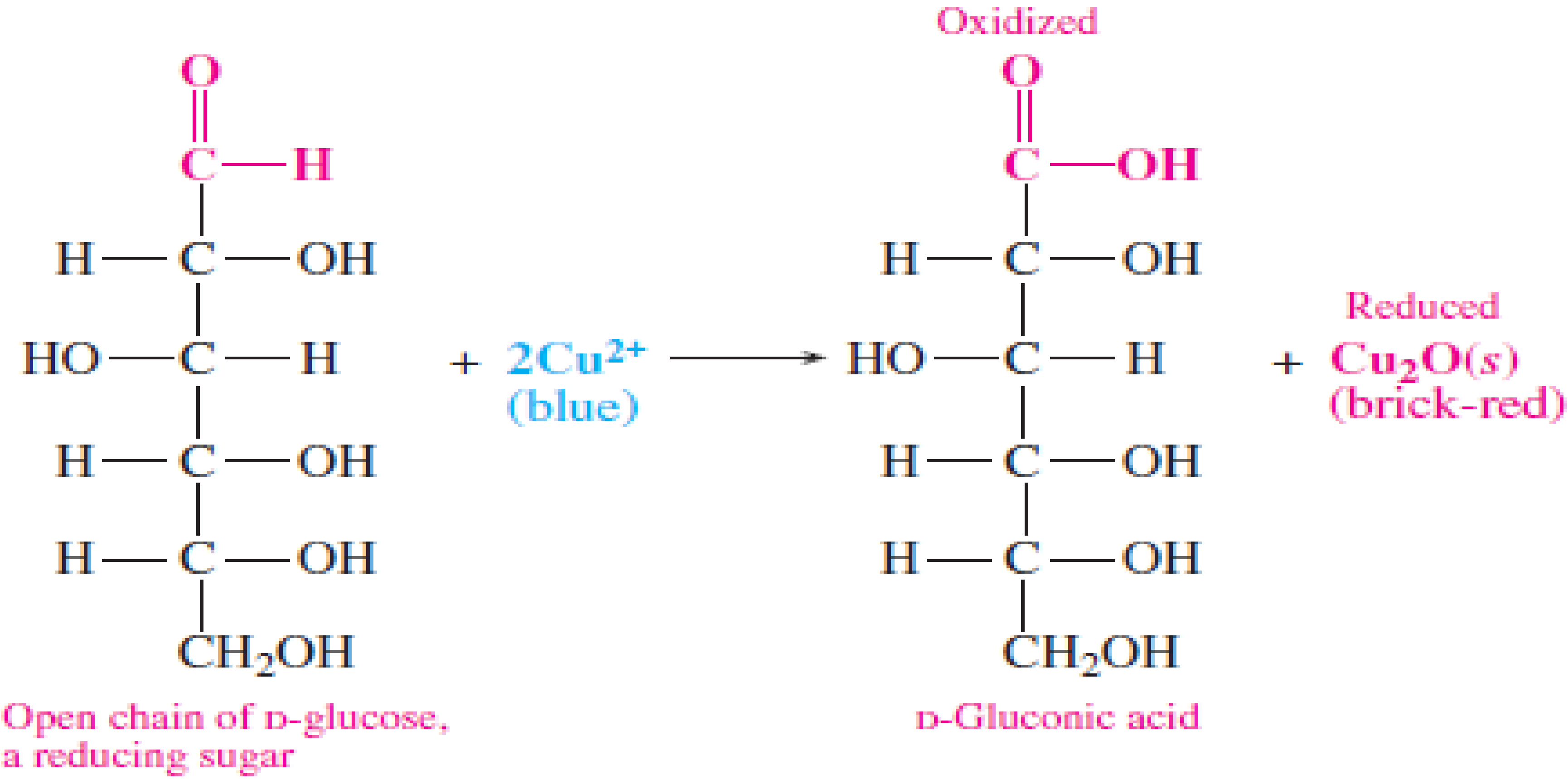
Fructose is a ketohexose. The Haworth structure for fructose is a five-atom ring with carbon 2 at the right corner of the ring. The cyclic structure forms when the hydroxyl group on carbon 5 reacts with carbon 2 in the carbonyl group. The new hydroxyl group on carbon 2 gives the α- and β-isomers of fructose.



Anomers and Epimers??

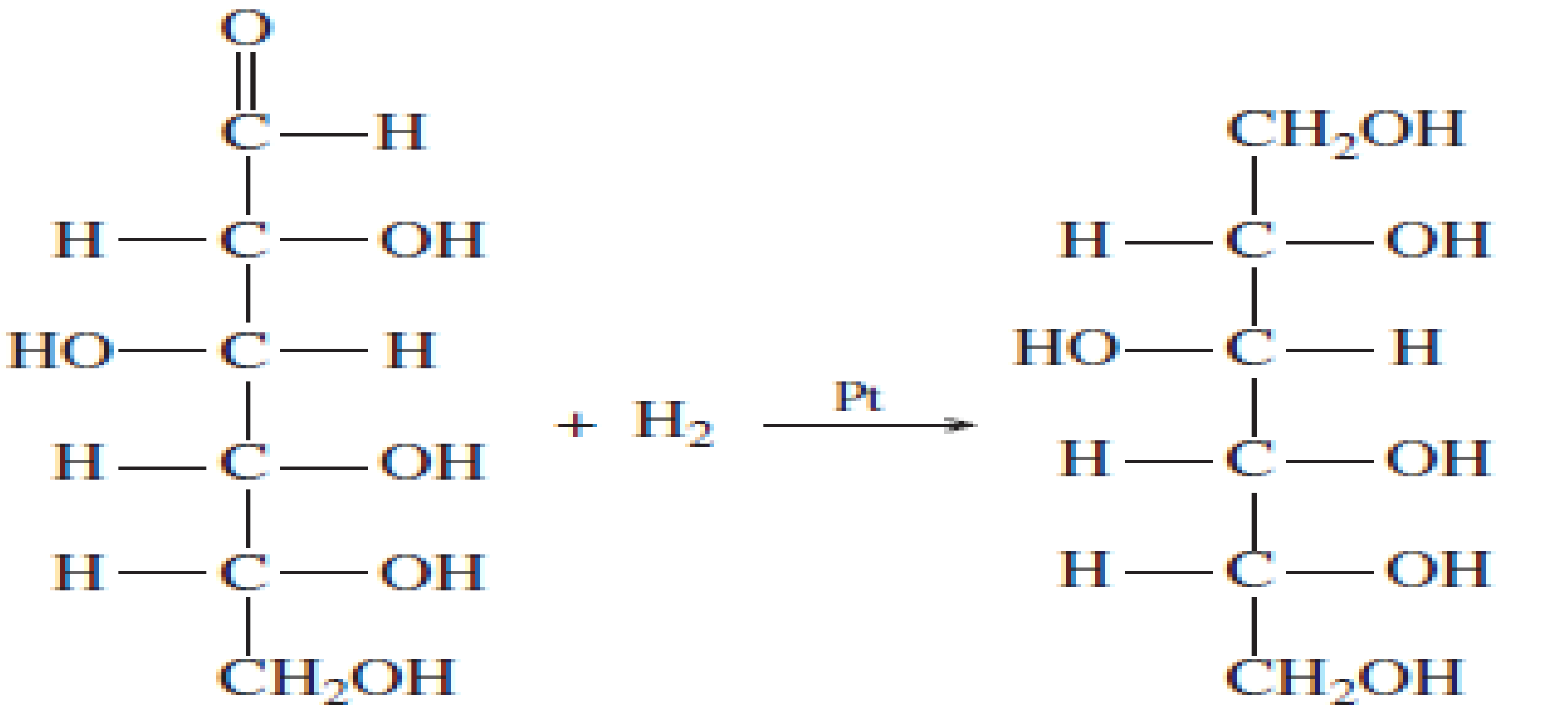
Oxidation of Monosaccharides

Although monosaccharides exist mostly in cyclic forms, we have seen that a small amount of the open-chain form is always present, which provides an aldehyde group.



Reduction of Monosaccharides

The reduction of the carbonyl group in monosaccharides produces sugar alcohols, which are also called *alditols. D-Glucose is reduced to D-glucitol, better known as D-sorbitol.*



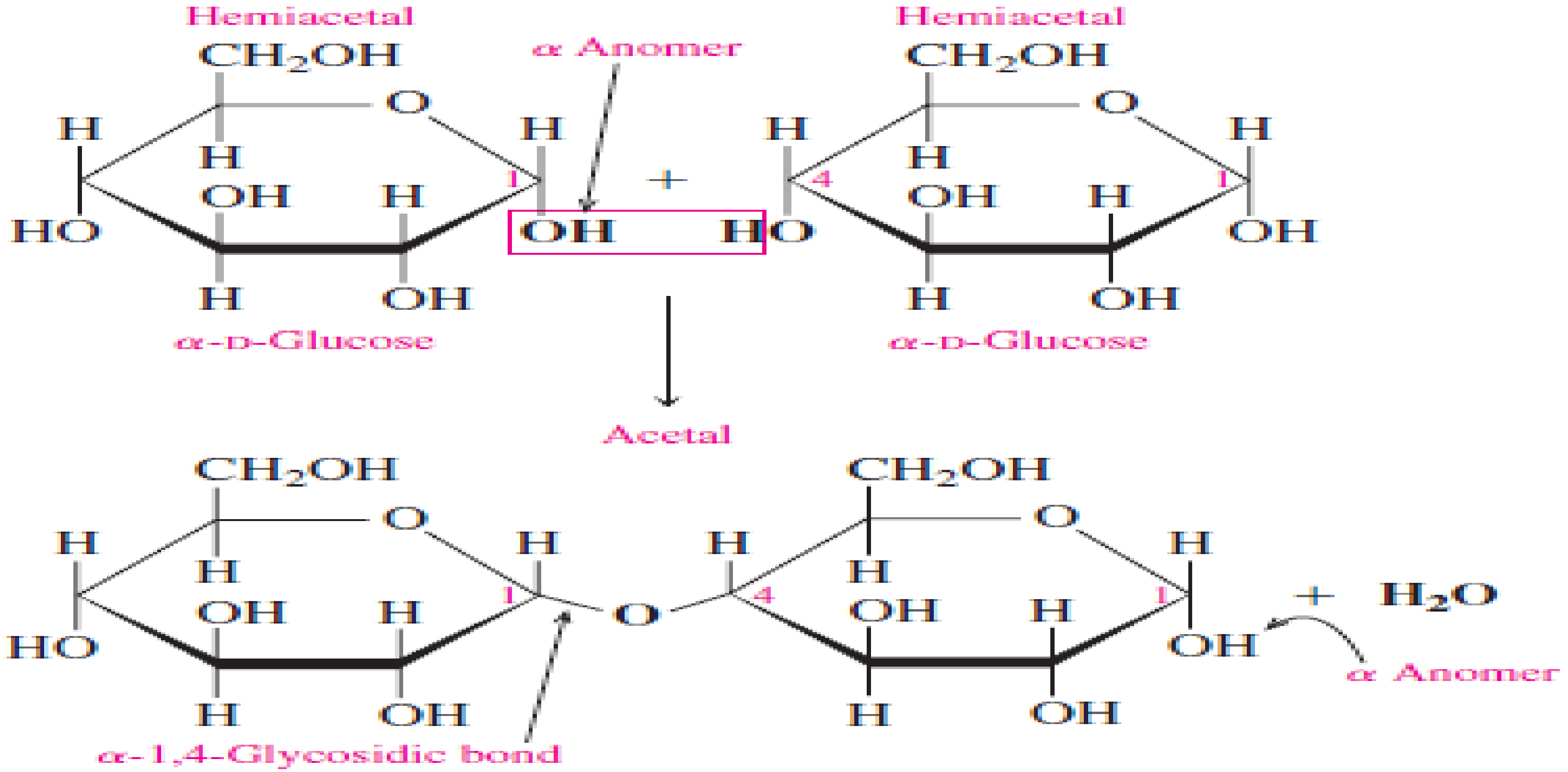
D-Glucose   D-Glucitol or D-Sorbitol

Disaccharides

A **glycosidic bond** is an **ether** bond that connects two monosaccharides.

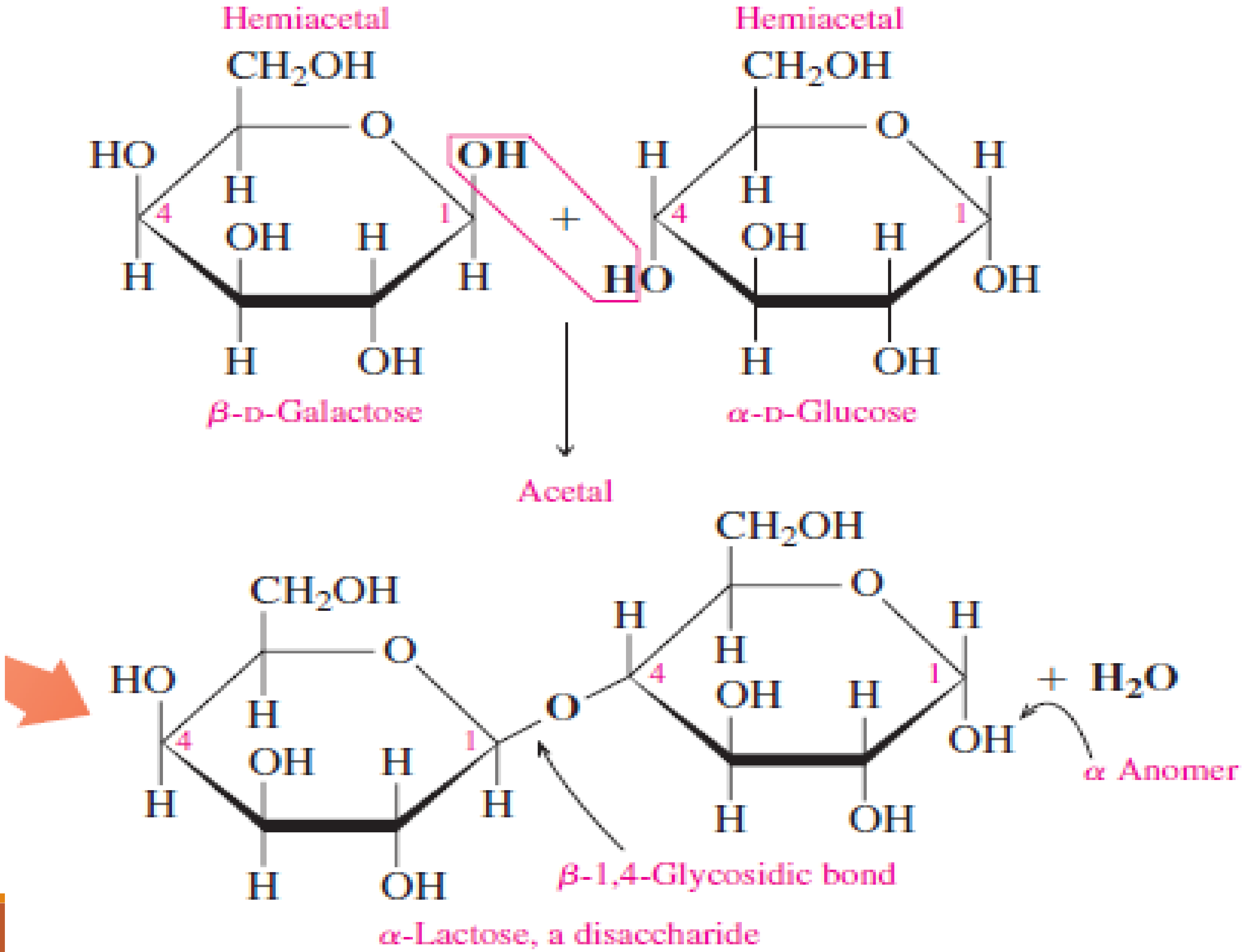
- **Maltose or malt sugar:** used in cereals and candies. Maltose has a glycosidic bond, which is an ***acetal***, between two glucose molecules. To form maltose, the -OH group on **carbon 1** of the hemiacetal in the first glucose forms a bond with the -OH group on **carbon 4** in a second glucose molecule, which results in a **1,4-glycosidic bond**. Because the -OH group on carbon 1 of the hemiacetal of the first glucose is the **α-anomer**, it is an **α-1,4-glycosidic bond**.

For maltose, it is the free -OH group in the hemiacetal on **carbon 1** of the ***second glucose*** molecule that determines if maltose is the **α- or β- anomer.**



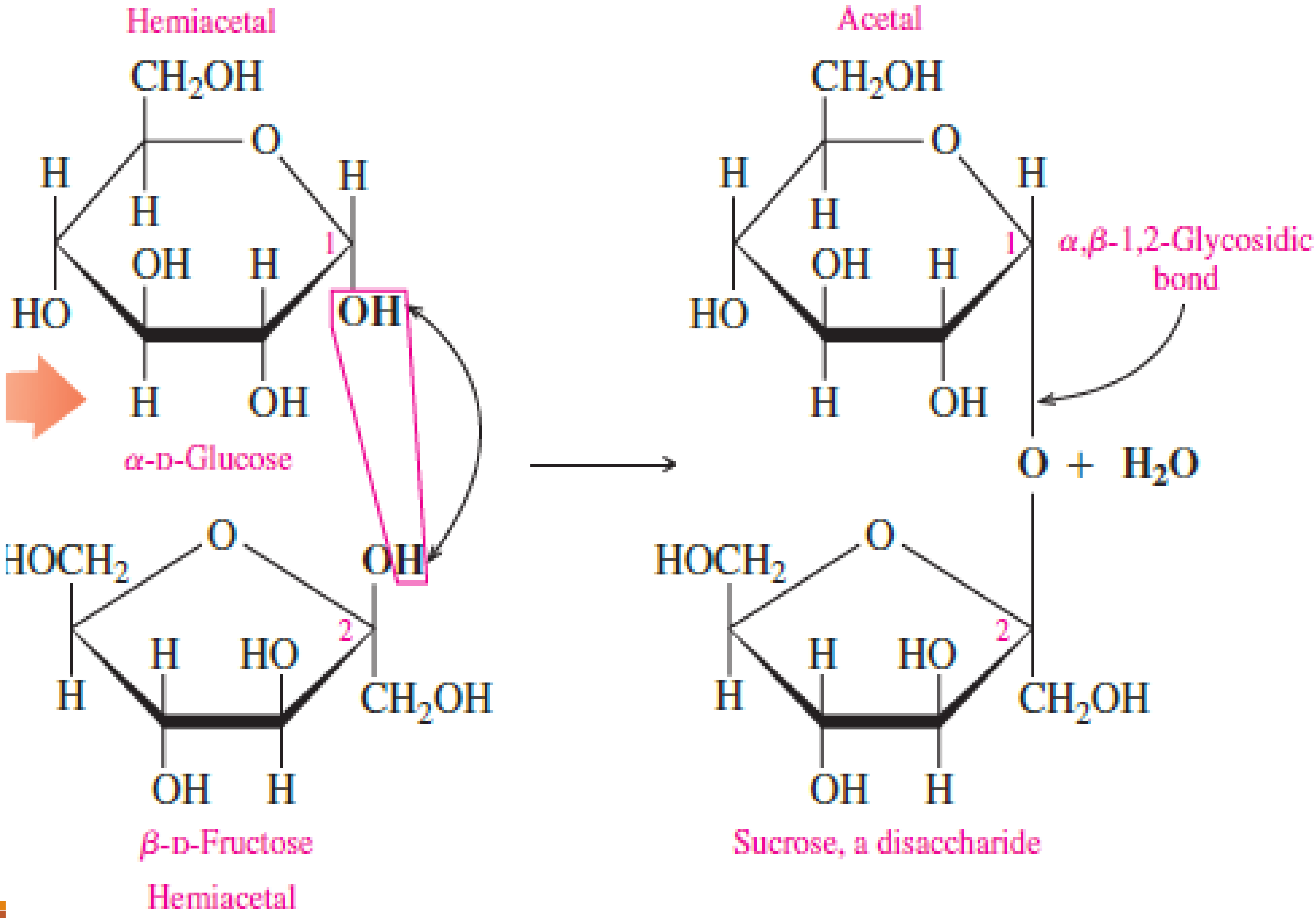
α-Maltose, a disaccharide

- **Lactose (milk sugar):** is a disaccharide found in milk and milk products. The acetal bond in lactose is a ***β-1,4-glycosidic*** *bond because it is the -OH group of a β-anomer of galactose that forms an acetal with the -OH group on carbon 4 of glucose*. In lactose, the hemiacetal of glucose undergoes ***mutarotation********, which gives **α- and β- anomers**. Therefore, lactose is a reducing sugar because the hemiacetal can open to give an aldehyde that can reduce other substances.


Hemiacetal
CH2OH
O
HO
OH
H
4
1
+
OH
H
H
H
HO
H
OH
β-D-Galactose
Hemiacetal
CH2OH
O
H
H
4
1
OH
H
OH
H
OH
α-D-Glucose
Acetal
CH2OH
O
HO
H
4
1
OH
H
H
H
OH
O
CH2OH
O
H
H
H
4
1
OH
H
OH
H
OH
+ H2O
α Anomer
β-1,4-Glycosidic bond
α-Lactose, a disaccharide

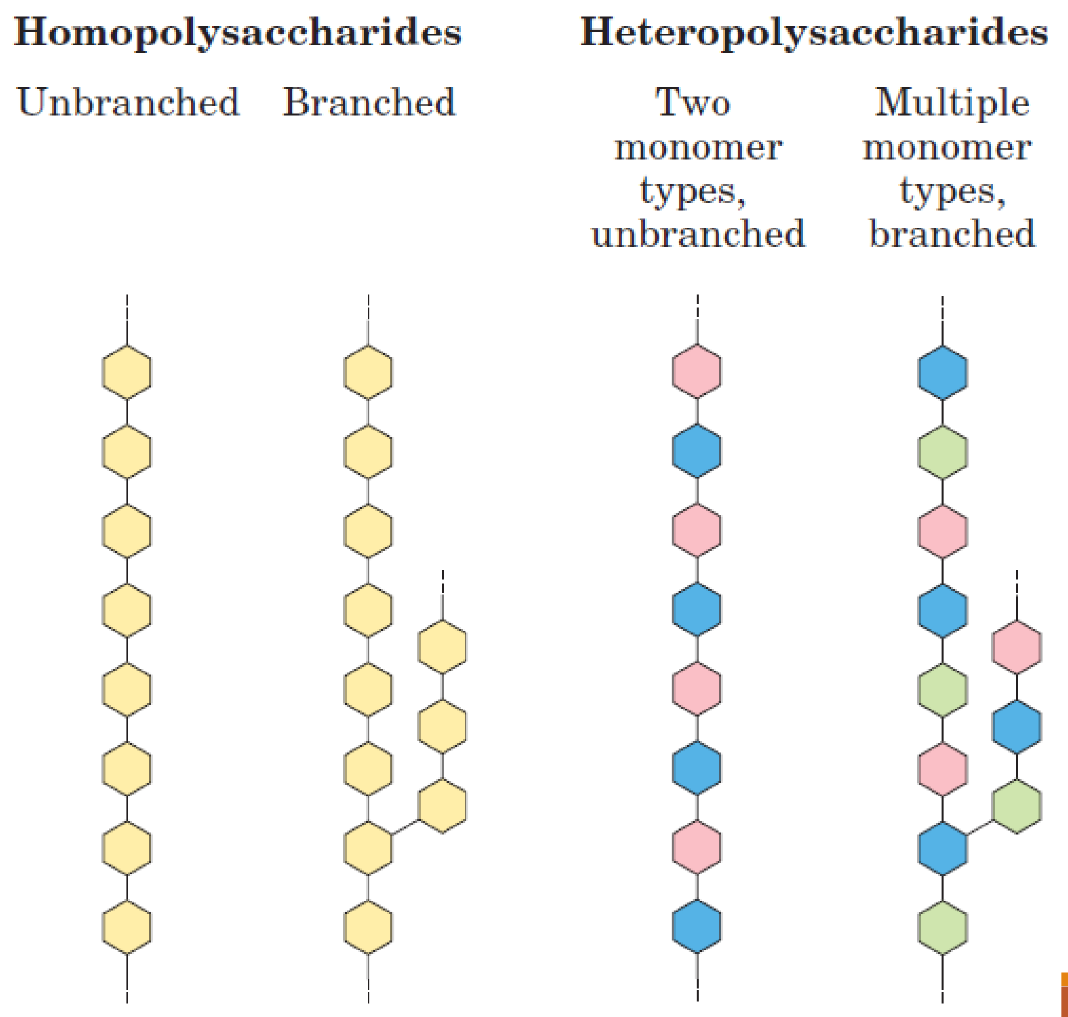
Lactose makes up 6–8% of human milk and about 4–5% of cow's milk, and it is used in products that attempt to duplicate mother's milk. When a person does not produce ***sufficient quantities of the enzyme lactase***, which is needed to hydrolyze lactose, it remains undigested when it enters the colon. Then bacteria in the colon digest the lactose in a fermentation process that creates large amounts of gas including ***carbon dioxide and methane***, which cause bloating and abdominal cramps. In some commercial milk products, lactase has already been added to break down lactose.

- **Sucrose:** consists of an α-D-glucose and a β-D-fructose molecule joined by an **α, β - 1,2-glycosidic bond**. Unlike maltose and lactose, the glycosidic bond in sucrose forms between the -OH groups in the hemiacetals of glucose and fructose. As a result, sucrose does not have any hemiacetals and cannot undergo ***mutarotation**** to an aldehyde. *Thus, sucrose is not a reducing sugar.*


Hemiacetal
CH_2OH
α-D-Glucose
HOCH₂
β-D-Fructose
Hemiacetal
Acetal
α,β-1,2-Glycosidic bond
O + H_2O
Sucrose, a disaccharide

Polysaccharide

A polysaccharide is a polymer of many monosaccharides joined together. Four important polysaccharides are amylose, amylopectin, cellulose, and glycogen. They are all polymers of D-glucose that differ only in the type of glycosidic bonds and the amount of branching in the molecule.



1. Homopolysaccharides:

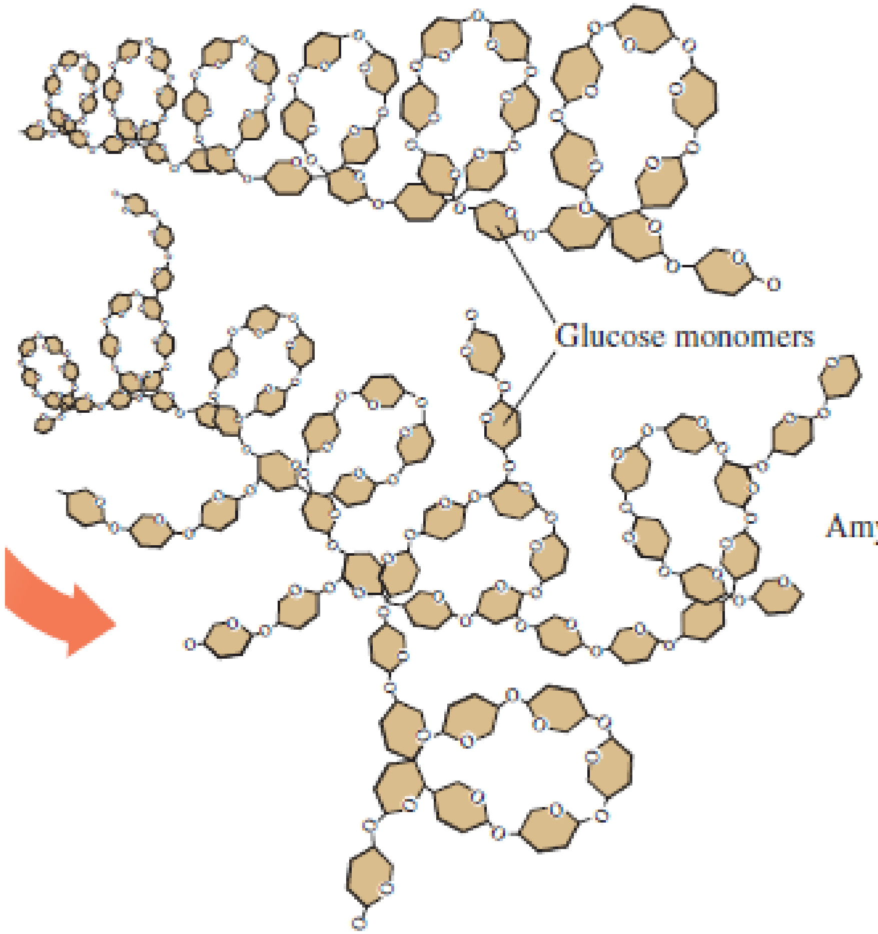
- **Amylose:** which makes up about 20% of **starch**, consists of 250–4000 α-D-glucose molecules connected by **α-1,4-glycosidic** bonds in a continuous chain. Sometimes called a straight-chain polymer, polymers of amylose are *coiled in helical fashion.*

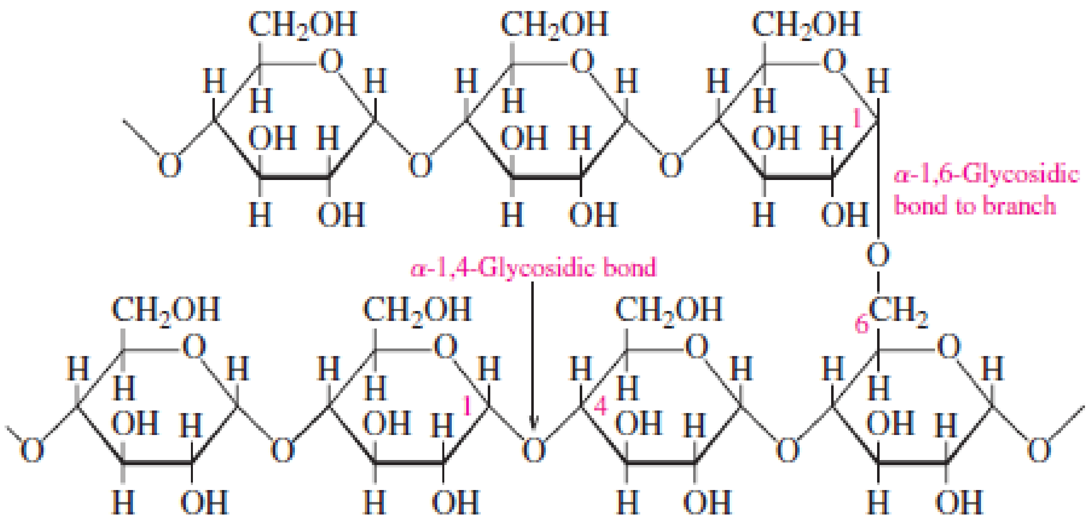
- **Amylopectin:** which makes up as much as 80% of **starch**, is a branched-chain polysaccharide. Like amylose, the glucose molecules are connected by ***α-1,4-glycosidic*** bonds. However, at about every **25** glucose units, there is a branch of glucose molecules attached by an ***α-1,6-glycosidic*** bond between carbon 1 of the branch and carbon 6 in the main chain.

Starches hydrolyze easily in water and acid to give shorter glucose chains called **Dextrin**, which then hydrolyze to **maltose** and finally **glucose**. In our bodies, these complex carbohydrates are digested by the enzymes; amylase (in saliva) and maltase (in the intestine). The glucose obtained usually provides about 50% of our nutritional calories.

$$\text{Amylose, amylopectin} \xrightarrow[\text{amylase}]{H^+ \text{ or}} \text{dextrins} \xrightarrow[\text{amylase}]{H^+ \text{ or}} \text{maltose} \xrightarrow[\text{maltase}]{H^+ \text{ or}} \text{many D-glucose units}$$

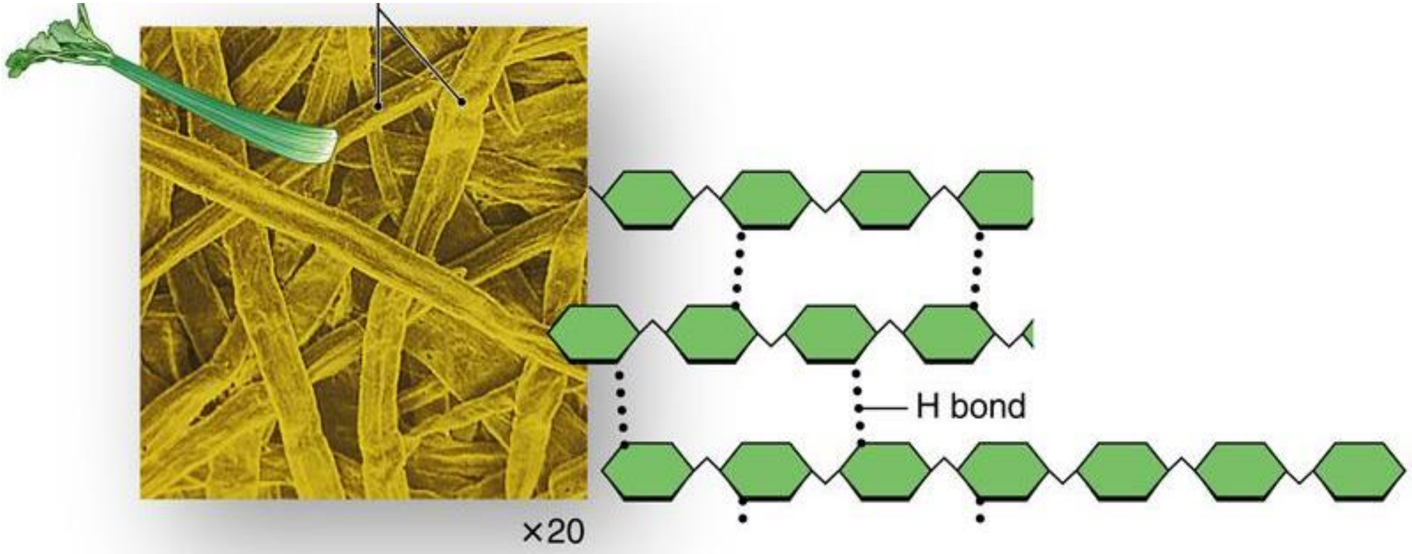
- **Glycogen:** is a non-linear polymer of glucose that is stored in the liver and muscle of animals. It has up to 50,000 ***α***-D-Glucose units . The structure of glycogen is very similar to that of amylopectin, found in plants, except that glycogen is *more highly branched*. In glycogen, ***α-1,4-glycosidic*** bonds join the glucose units, and branches occurring about every **10 to 15** glucose units are attached by ***α*** **-1,6-glycosidic** bonds.





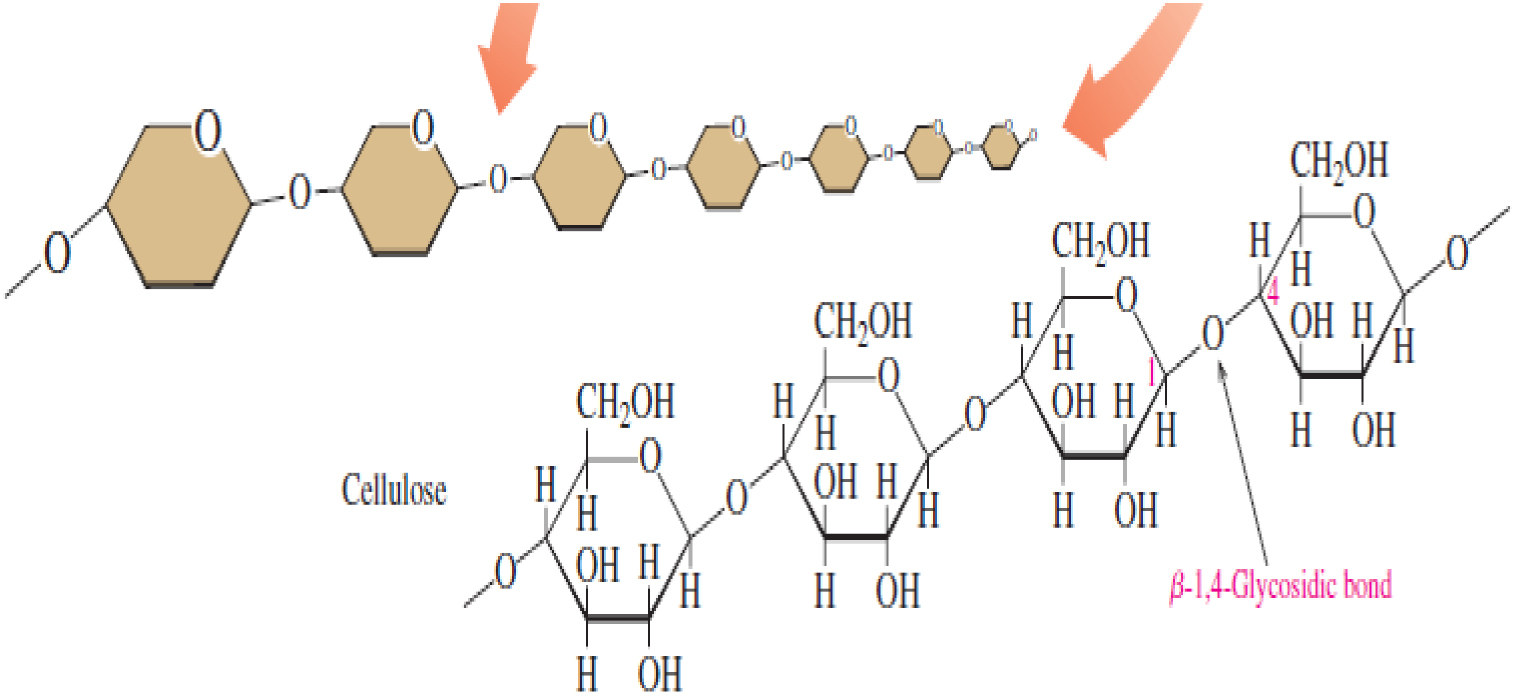
(b) Branched chain of amylopectin

- **<u>Cellulose:</u>** is the major structural material of wood and plants. Cotton is almost pure cellulose. In cellulose, there are nearly 15,000 ***β***-glucose units and they form a long unbranched chain similar to that of amylose. However, the glucose units in cellulose are linked by ***β-1,4-glycosidic*** bonds.



Cellulose structure

- Humans have enzymes called **α-amylase** in saliva and pancreatic juices that hydrolyze the **α-1,4-glycosidic** bonds of starches, but not the **β-1,4-glycosidic** bonds of cellulose.

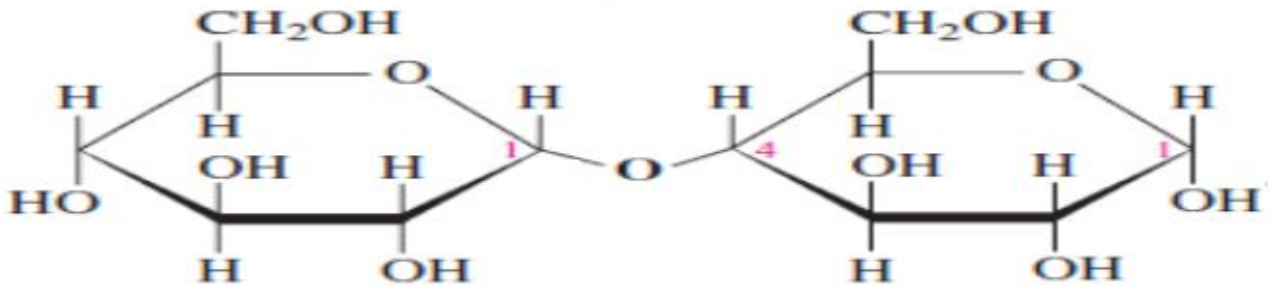


2. Heteropolysaccharide:

- **Heparin:** is an anticoagulant (prevents blood clotting) that occurs in blood, lung, liver, kidney and spleen etc. Heparin is composed of alternating units of N-sulfo-D-glucoseamine-6-sulfate and glucuronate 2-sulfate.
- **Keratan sulfate:** consists of alternating units of D-galactosamine and N-acetylglucosamine 6-sulfate.
- **Mucopolysaccharide:** is made up of repeating units of sugar derivatives, namely amino-sugars and more commonly known as glycosaminoglycans (GAG).

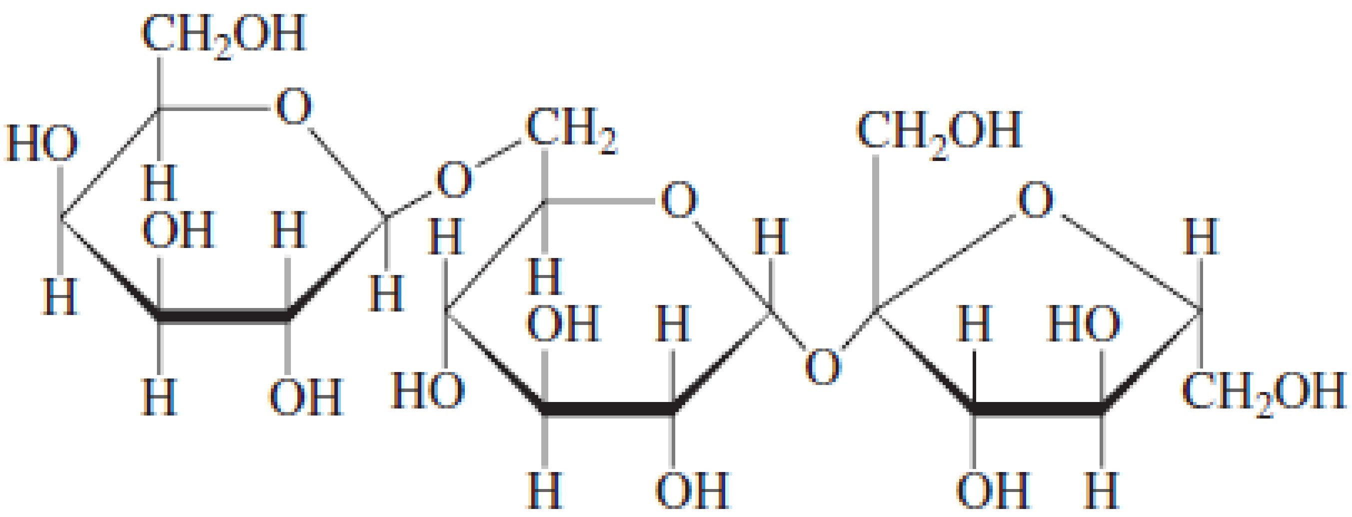
Homework:

1. Alpha-Cellobiose is a disaccharide obtained from the hydrolysis of cellulose. It is quite similar to maltose except it has a beta-1,4-glycosidic bond. Draw the Haworth structure of a-cellobiose.



Maltose

2. Write down types and positions of glycosidic bon for the following trisaccharide?



3. What are the differences in the Fischer projections of D-galactose and L-galactose?

4. What are the differences in the Haworth structures of alpha-D-glucose and beta-D-glucose?

5. Why are lactose and maltose reducing sugars, but sucrose is not?

➢ References:

1. Lehinger principles of biochemistry, 5th edition.
2. W.H. Freeman and company harpers illustrated biochemistry,28th edition.
3. An introduction to general, organic and biological chemistry by Timberlake, 11th edition.