Carbohydrates

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Lecture 10

2020-2021

Lecture Goals

- In this chapter you will learn how to:

- Classification of carbohydrates.
- The major structural features of monosaccharides.
- The cyclic forms of monosaccharides and classify them as α or β isomers.
- Monitoring Glucose Levels
- Recognize the major structural features of disaccharides
- Describe the characteristics of cellulose, starch, and glycogen
- Describe the role that carbohydrates play in determining blood type

Carbohydrates

- Carbohydrates, commonly referred to as sugars and starches, are polyhydroxy, aldehydes and ketones, or compounds that can be hydrolyzed to them.
- Carbohydrates can be **simple** or **complex**, having as **few as three** or as **many as thousands of carbon atoms**.
- They are the largest group of organic molecules in nature, comprising approximately 50% of the earth's biomass.

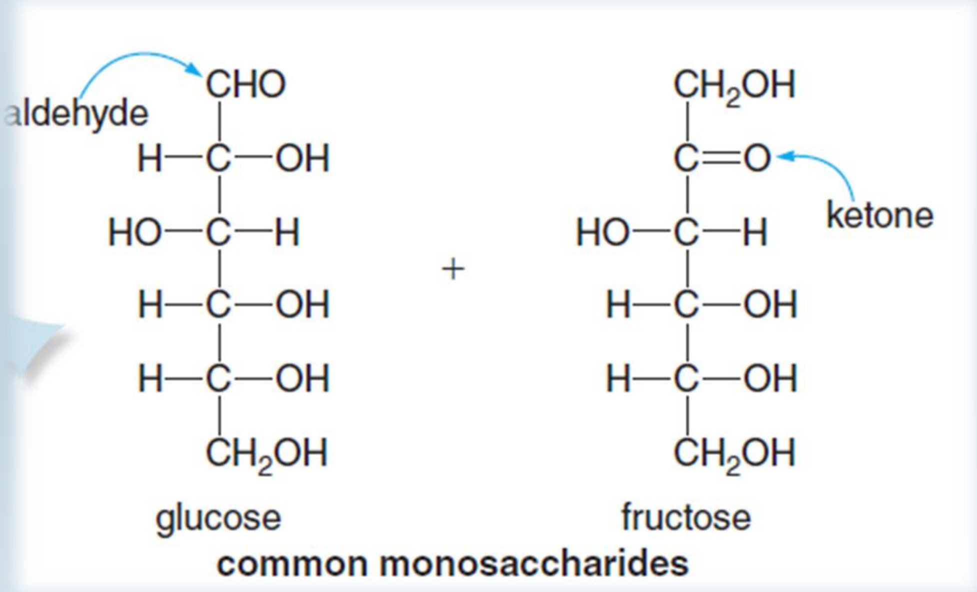
➢ Carbohydrates are classified into three groups:

1. • Monosaccharides
2. • Disaccharides
3. • Polysaccharides

1. Monosaccharides

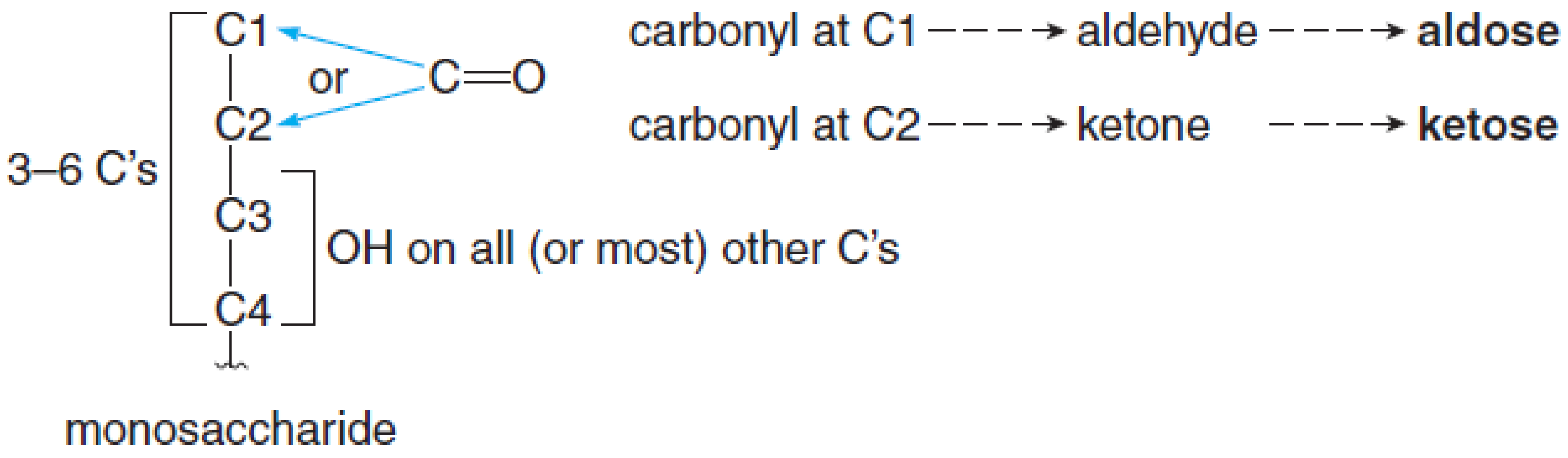
- **Monosaccharides are the simplest carbohydrates**. generally have three to six carbon atoms in a chain, with a carbonyl group at either the terminal carbon.
- **Glucose** and **fructose**, the two major constituents of **honey**, are **monosaccharides**.
- **Glucose** contains an **aldehyde** at one end of a six-carbon chain, and **fructose** contains a **ketone**.
- Every other carbon atom has a **hydroxyl group** bonded to it.

❑ Monosaccharides cannot be converted to simpler compounds by hydrolysis! Why!?

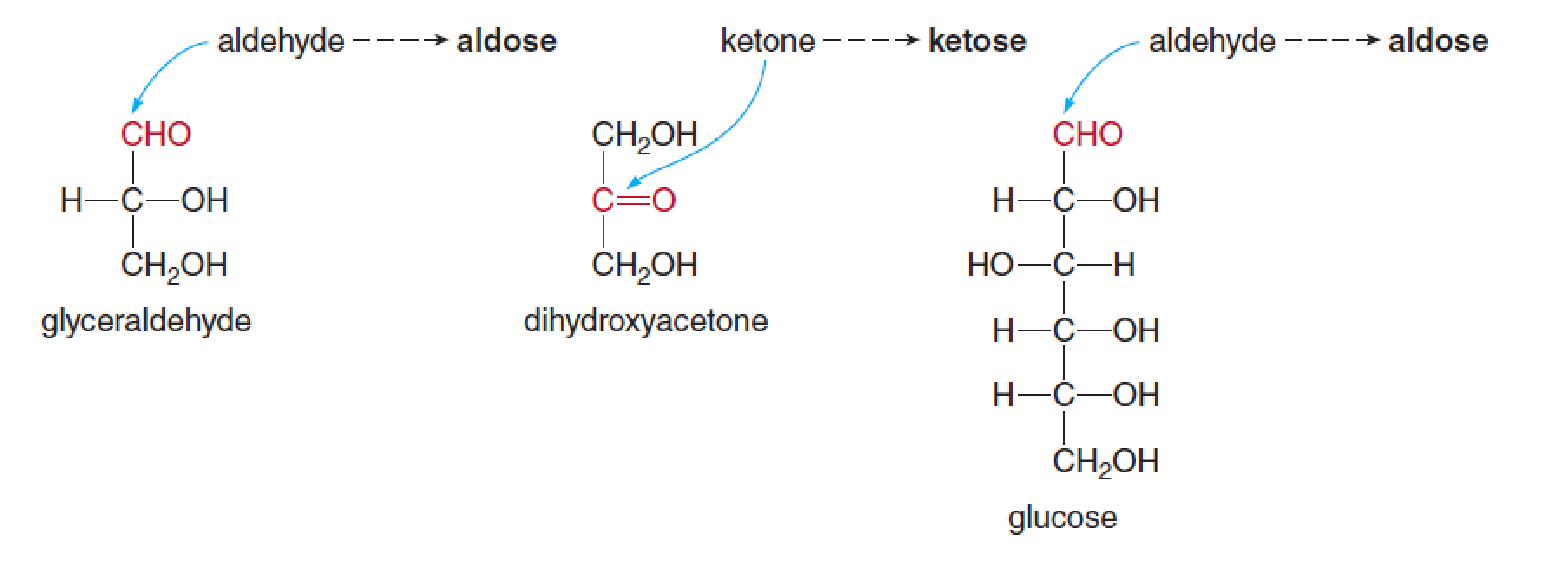


➢ Monosaccharides are drawn vertically, with the carbonyl group at (or near) the top.

✓ • **Monosaccharides with a carbonyl group at C1 are aldehydes called *aldoses.***
✓ • **Monosaccharides with a carbonyl group at C2 are ketones called *ketoses.***



- **Glyceraldehyde** is the simplest **aldose** and **dihydroxyacetone** is the simplest **ketose**.
- ***Glyceraldehyde*** and ***dihydroxyacetone*** both have molecular formula $C_3H_6O_3$, so they are **constitutional isomers;** that is, they have the same molecular formula but a different arrangement of atoms.
- **Glucose** is the most prevalent **aldose**, while **Fructose** is **Ketose**



A monosaccharide is characterized by the number of carbons in its chain.

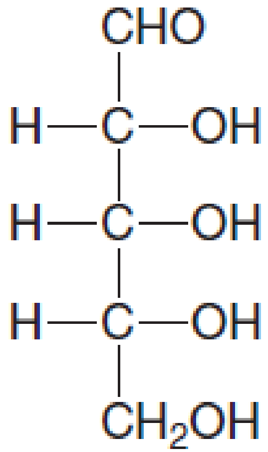
- A triose has three carbons.
- A tetrose has four carbons.
- A pentose has five carbons.
- A hexose has six carbons.

- These terms are then combined with the words ***aldose*** and ***ketose*** to indicate both the number of carbon atoms in the monosaccharide and whether it contains an aldehyde or ketone.
- Thus, **glyceraldehyde** is an **aldotriose** (three carbons and an aldehyde),
- **Dihydroxyacetone** is a **ketotriose** (three carbons and a ketone),
- **Glucose** is an **aldohexose** (six carbons and an aldehyde).

PROBLEM

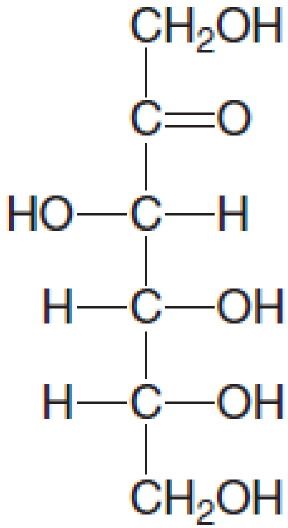
- Classify each monosaccharide by the type of carbonyl group and the number of carbons in the chain.

a.



ribose

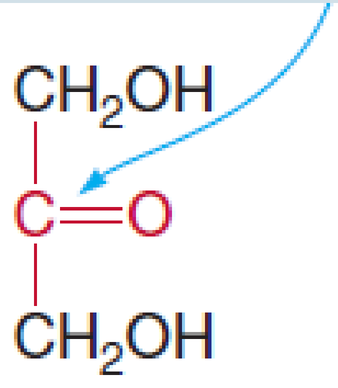
b.



fructose

2. Fischer Projection Formulas

- All carbohydrates except for **dihydroxyacetone** contain **one or more chirality centers**.
- The simplest aldose, **glyceraldehyde**, has one chirality center
- **What mean chirality center**?! one carbon atom bonded to four different groups.
- Thus, there are two possible enantiomers—mirror images that are not superimposable.



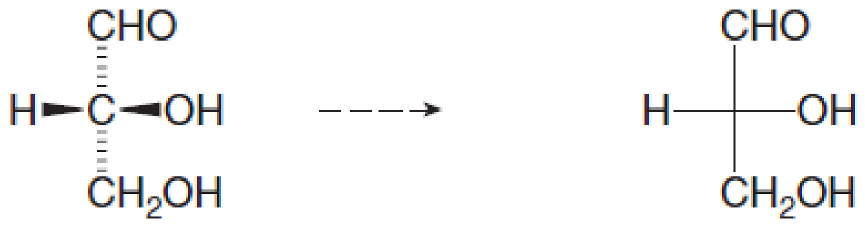
dihydroxyacetone

naturally occurring isomer
D-glyceraldehyde

unnatural isomer
L-glyceraldehyde

- Only one enantiomer of glyceraldehyde occurs in nature. When the carbon chain is drawn vertically with the aldehyde at the top, the naturally occurring enantiomer has the OH group drawn on the right side of the carbon chain.
- **To distinguish the two enantiomers, the prefixes D and L precede the name.** Thus, the naturally occurring enantiomer is labeled D-glyceraldehyde, while the unnatural isomer is L-glyceraldehyde.
- **Fischer projection formulas** are commonly used to depict the chirality centers in monosaccharides. A Fischer projection formula uses a cross to represent a tetrahedral carbon.

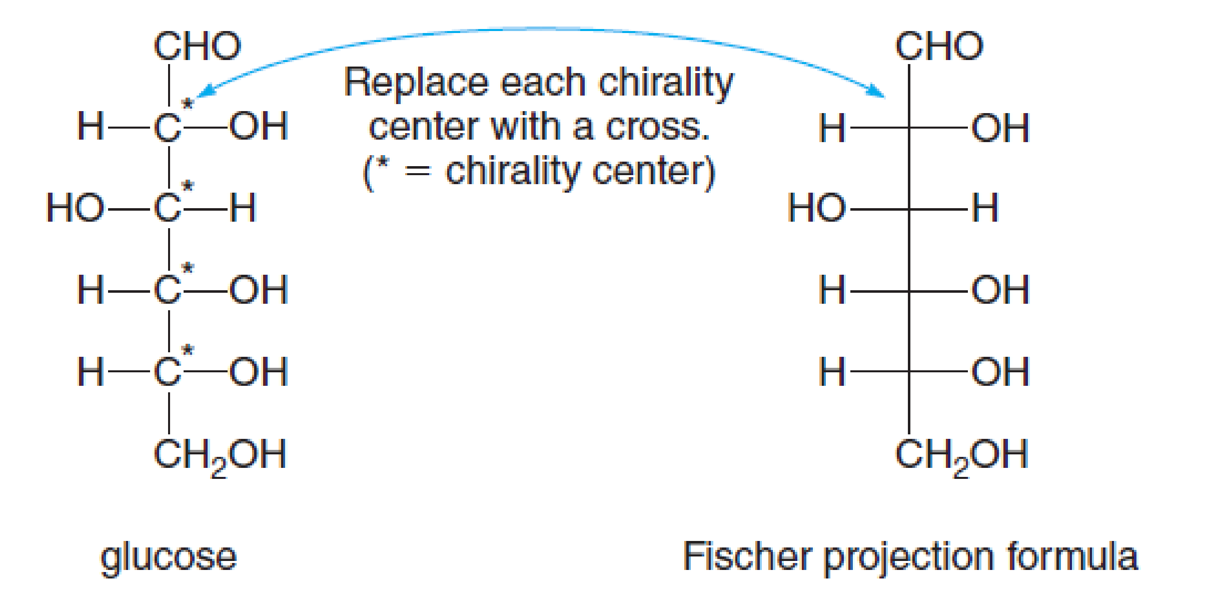
Using a Fischer projection formula, D-glyceraldehyde becomes:



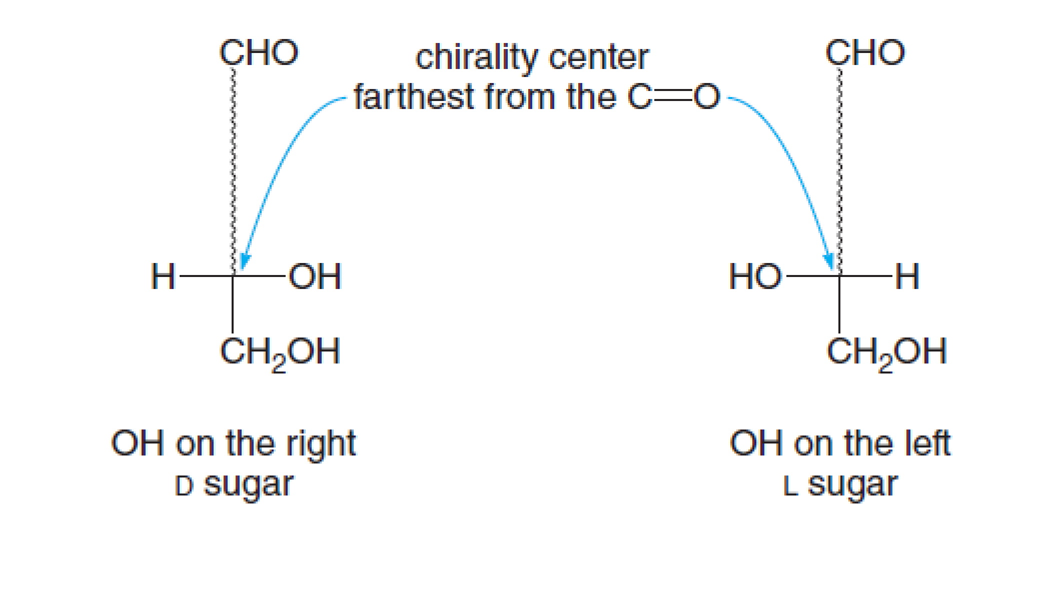
D-glyceraldehyde — Fischer projection formula

Monosaccharides with More Than One Chirality Center

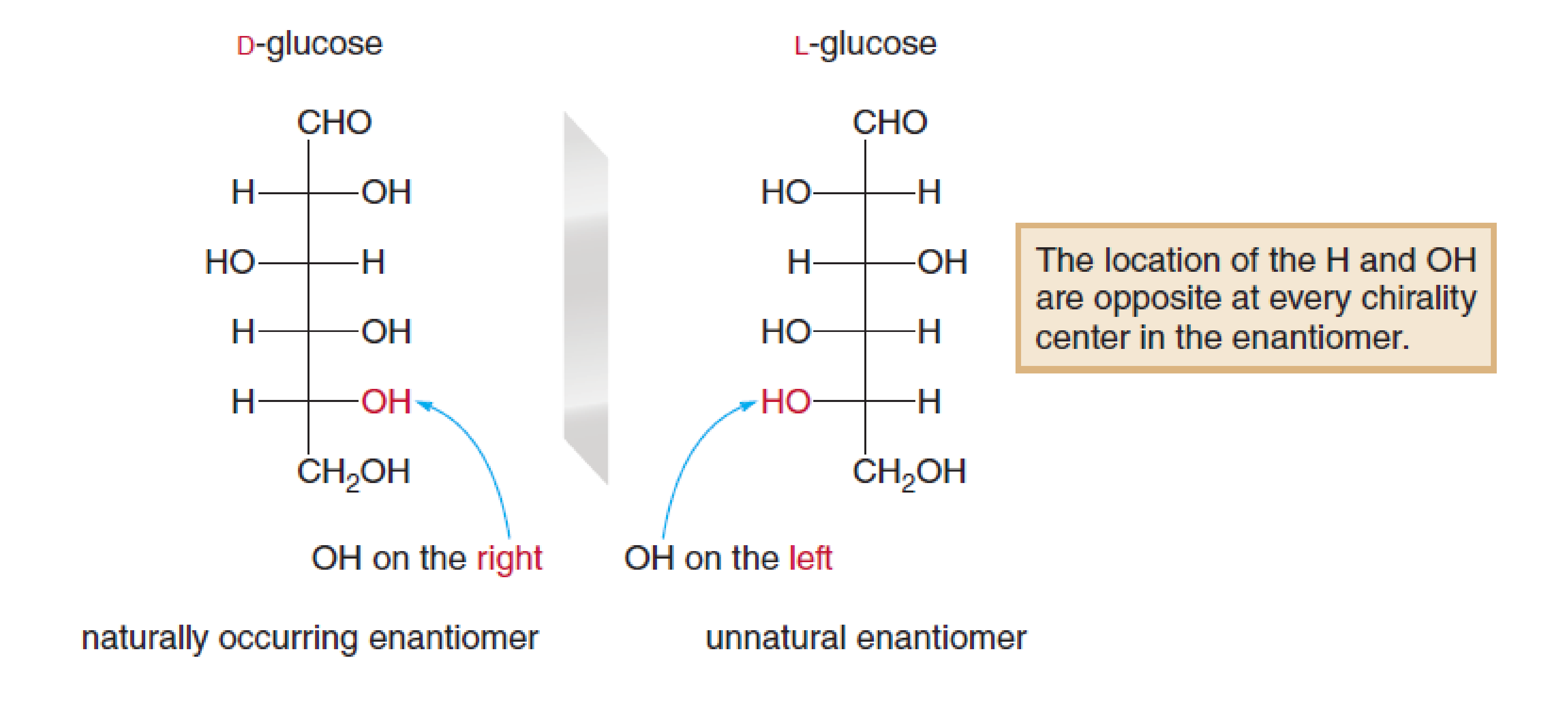
- Fischer projection formulas are also used for compounds like aldohexoses that contain several chirality centers.
- **Glucose**, for example, contains **four chirality centers** labeled in the structure below.
- To convert the molecule to a Fischer projection, the molecule is drawn with a vertical carbon skeleton with the aldehyde at the top, and the horizontal bonds are assumed to come forward (on wedges). In the Fischer projection, each chirality center is replaced by a cross.



- The letters d and l are used to label all monosaccharides, even those with many chirality centers.
- The configuration of the chirality center farthest from the carbonyl group determines whether a monosaccharide is *D* or *L*.
- • A D monosaccharide has the OH group on the chirality center farthest from the carbonyl on the right (like D-glyceraldehyde).
- • An L monosaccharide has the OH group on the chirality center farthest from the carbonyl on the left (like L-glyceraldehyde).

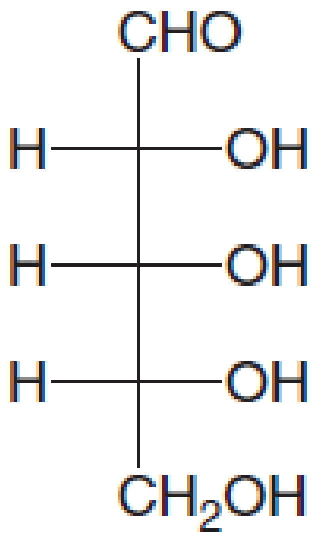


- **Glucose and all other naturally occurring sugars are D sugars**.
- L-Glucose, a compound that does not occur in nature, is the enantiomer of D-Glucose.
- L-Glucose has the opposite configuration at every chirality center.



PROBLEM

- Consider the aldopentose ribose. (a) Label all chirality centers. (b) Classify ribose as a D or L monosaccharide. (c) Draw the enantiomer.

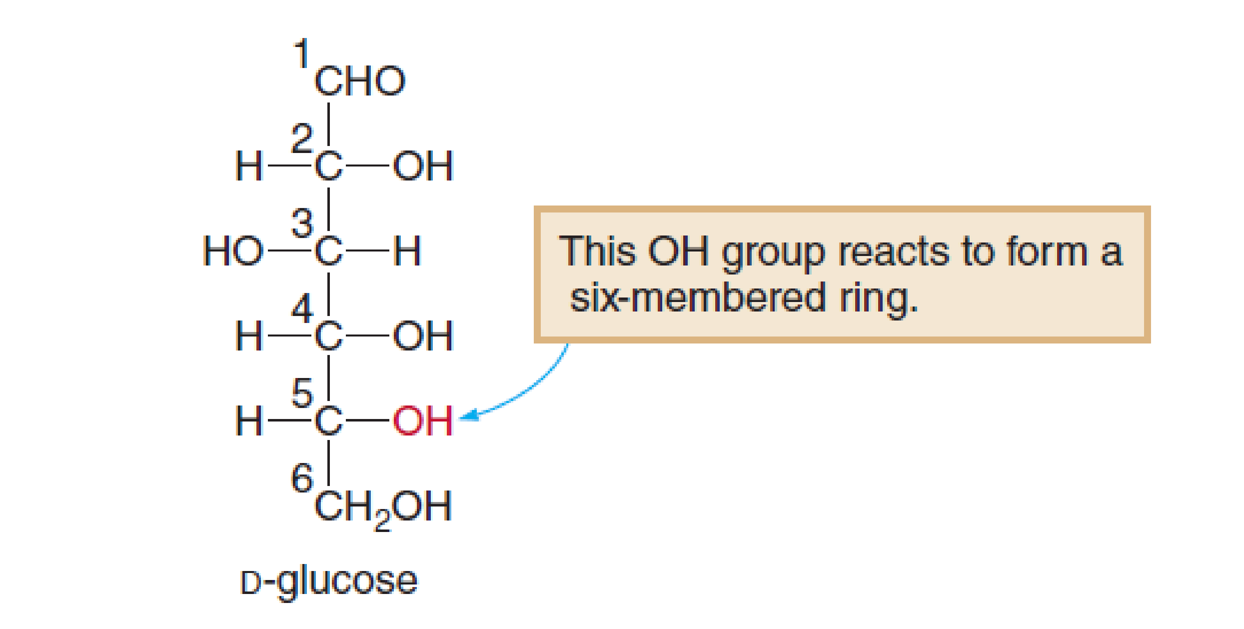


ribose

3. The Cyclic Forms of Monosaccharides

- Although the monosaccharides were drawn as acyclic (chain) carbonyl compounds, the hydroxyl (OH) and carbonyl (C=O) groups can react together to form a ring. Let's illustrate the process with d-glucose, and then learn a general method for drawing the cyclic forms of any aldohexose.

- Which of the five OH groups reacts with the aldehyde carbonyl? In glucose, the OH group on C5 reacts with the carbonyl carbon to form a six-membered ring.



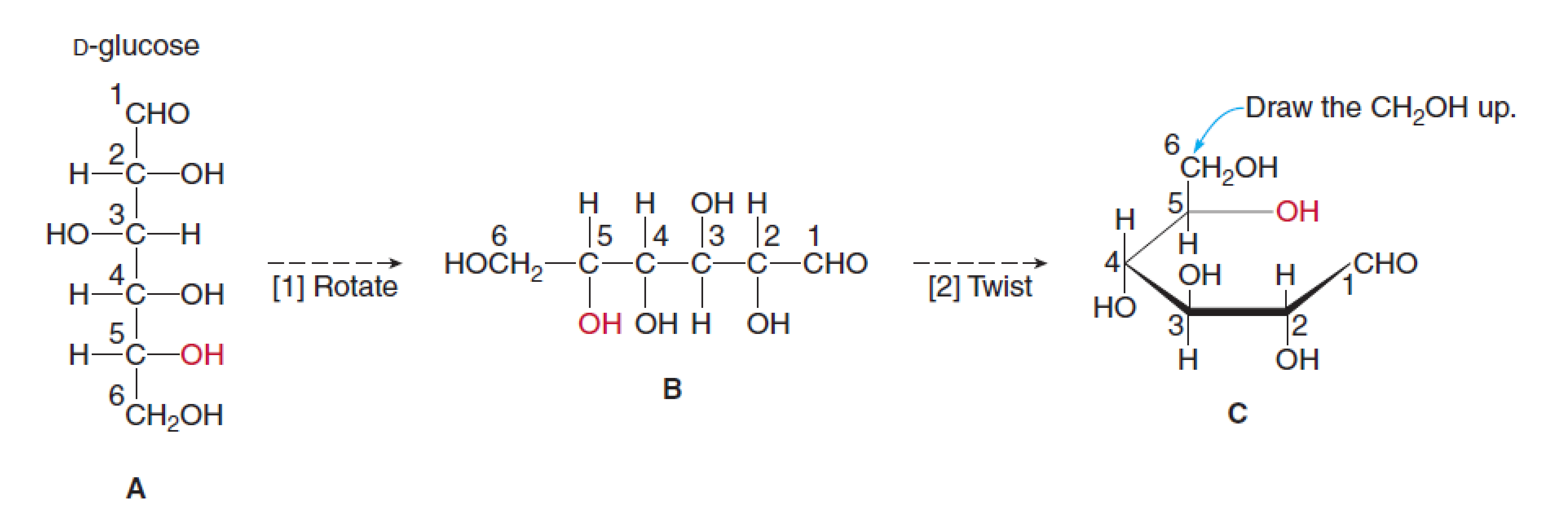
Learn a general method for drawing the cyclic forms of any aldohexose

- To convert this chain form (**A**) into a cyclic monosaccharide,

A. First rotate the carbon skeleton clockwise 90° to form **B**.

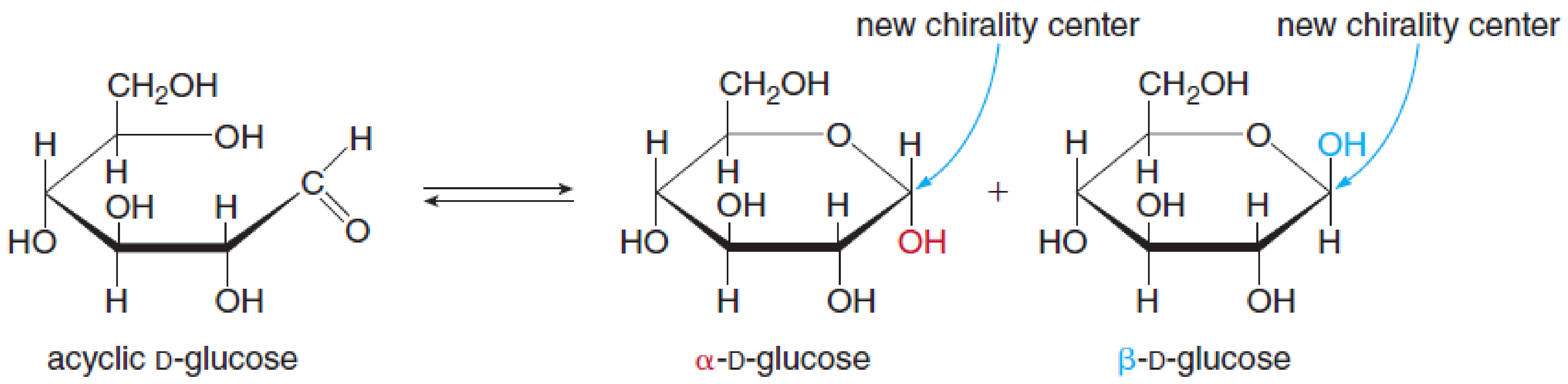
B. Note that groups that were drawn on the right side of the carbon skeleton in A end up below the carbon chain in B.

C. Then twist the chain to put the OH group on C5 close to the aldehyde carbonyl, forming **C**. In this process, the CH_2OH group at the end of the chain ends up above the carbon skeleton.



D. To draw the cyclic form, the OH group on C5 reacts with the aldehyde carbonyl to form a six membered ring with a new chirality center.

E. Cyclization yields two isomers, since the OH group on the new chirality center can be located **above** or **below** the six-membered ring.



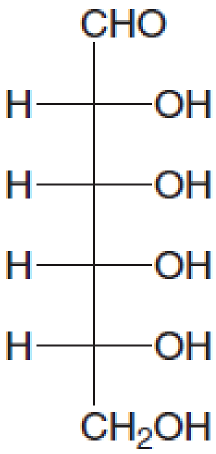
- ✓ The **α** isomer, called **α**-D-glucose, has the OH group on the new chirality center drawn down (shown in red).
- ✓ The **β** isomer, called **β**-D-glucose, has the OH group on the new chirality center drawn up (shown in blue).

- These flat, six-membered rings used to represent the cyclic forms of glucose and other sugars are called **Haworth projections**.

PROBLEM

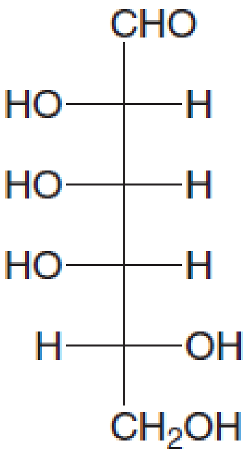
Convert each aldohexose to the indicated isomer using a Haworth projection.

a.



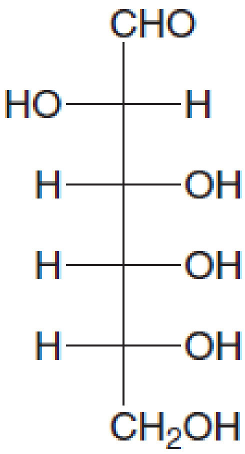
α isomer

b.



β isomer

c.

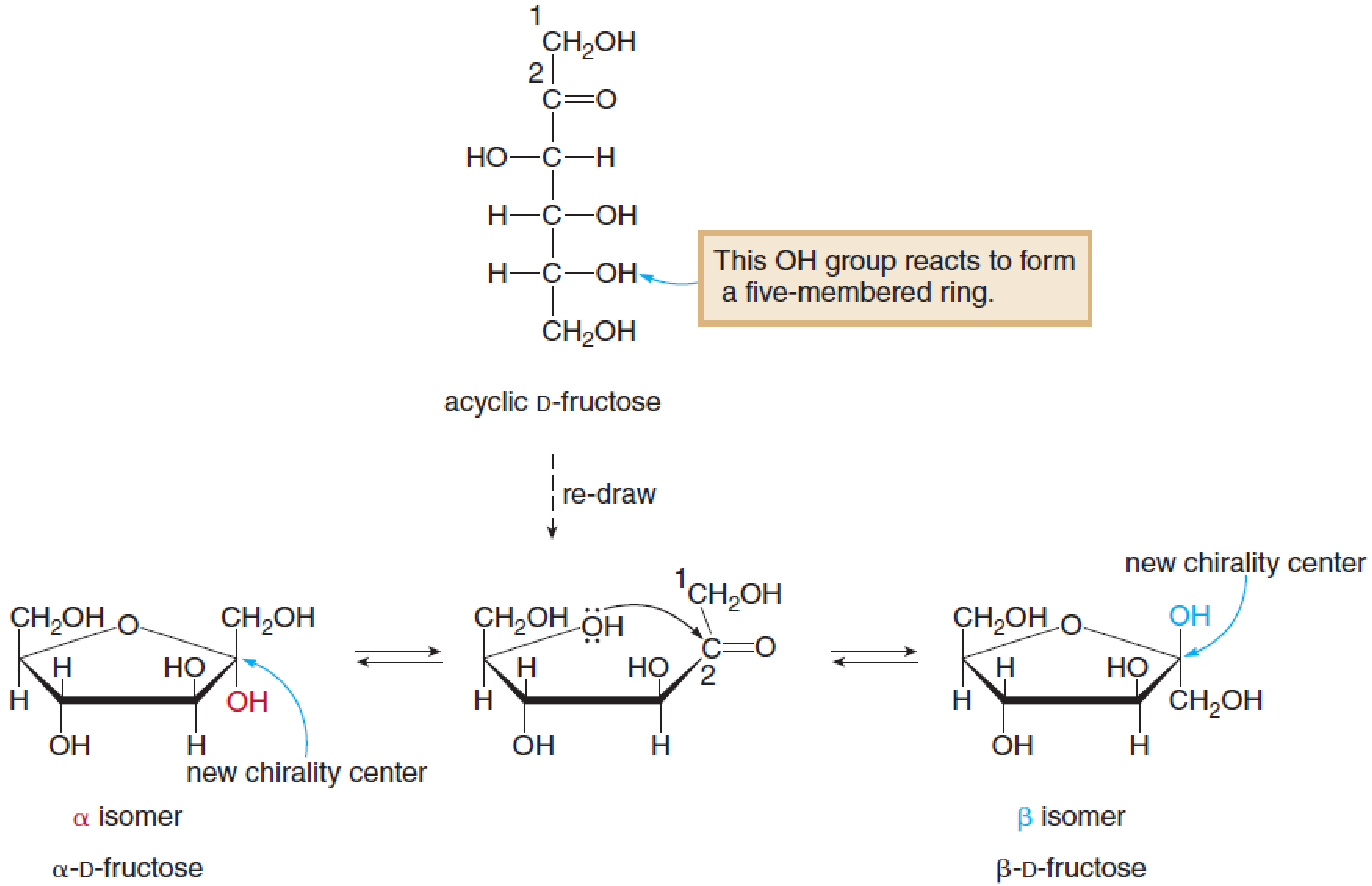


α isomer

4. The Cyclic Forms of Fructose, a Ketohexose

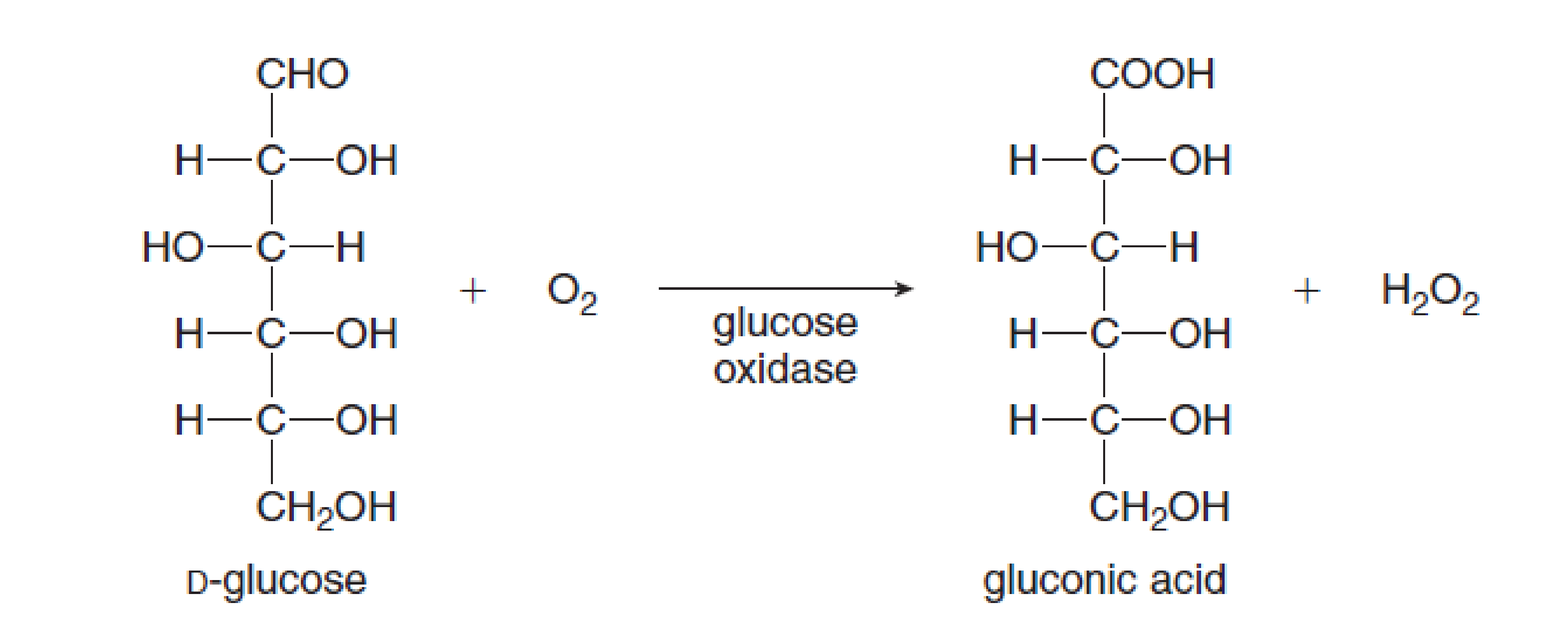
- Certain monosaccharides—notably aldopentoses and ketohexoses—form five-membered rings, not six-membered rings, in solution. The same principles apply to drawing these structures as for drawing six-membered rings, except the ring size is one atom smaller.

- Cyclization forms two isomers. For a D sugar, the OH group is drawn down in the **α** isomer and up in the **β** isomer.


1
CH2OH
2
C=O
HO—C—H
H—C—OH
H—C—OH
CH2OH
This OH group reacts to form a five-membered ring.
acyclic D-fructose
re-draw
new chirality center
α isomer
α-D-fructose
β isomer
β-D-fructose

5. Monitoring Glucose Levels
(FOCUS ON HEALTH & MEDICINE)

- In order to make sure that their blood glucose levels are in the proper range, individuals with diabetes frequently measure the concentration of glucose in their blood.
- A common method for carrying out this procedure today involves the oxidation of **glucose** to **gluconic** acid using the enzyme **glucose oxidase**.

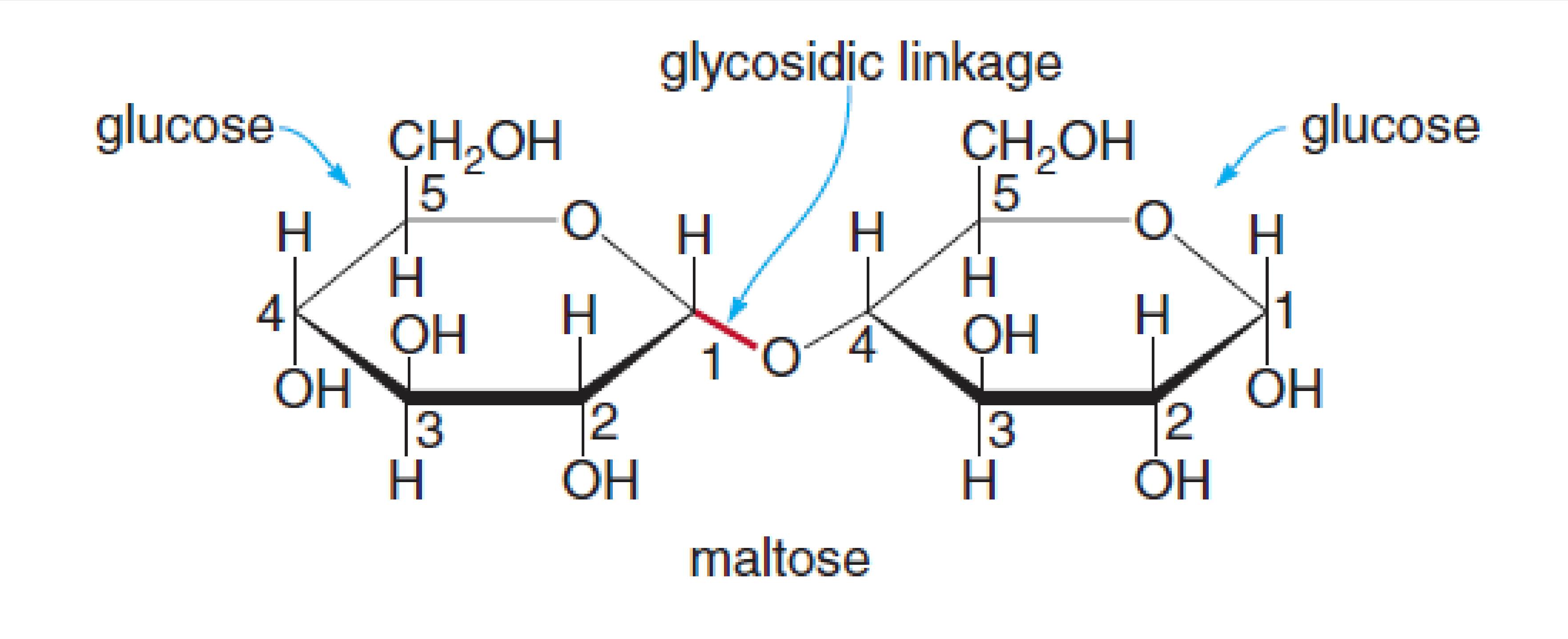


- In the presence of glucose oxidase, oxygen (O_2) in the air oxidizes the aldehyde of **glucose** to a **carboxyl group**. The O_2, in turn, is reduced to hydrogen peroxide, H_2O_2.
- **In the first generation of meters for glucose monitoring**, the H_2O_2 produced in this reaction was allowed to react with another organic compound to produce a **colored product**. The intensity of the colored product was then correlated to the amount of glucose in the blood. Test strips used for measuring glucose concentration in the urine are still based on this technology.
- **Modern glucose meters are electronic devices** that measure the amount of oxidizing agent that reacts with a known amount of blood. This value is correlated with blood glucose concentration and the result is displayed digitally.
- A high blood glucose level may mean that an individual needs more insulin, while a low level may mean that it is time to ingest some calories.

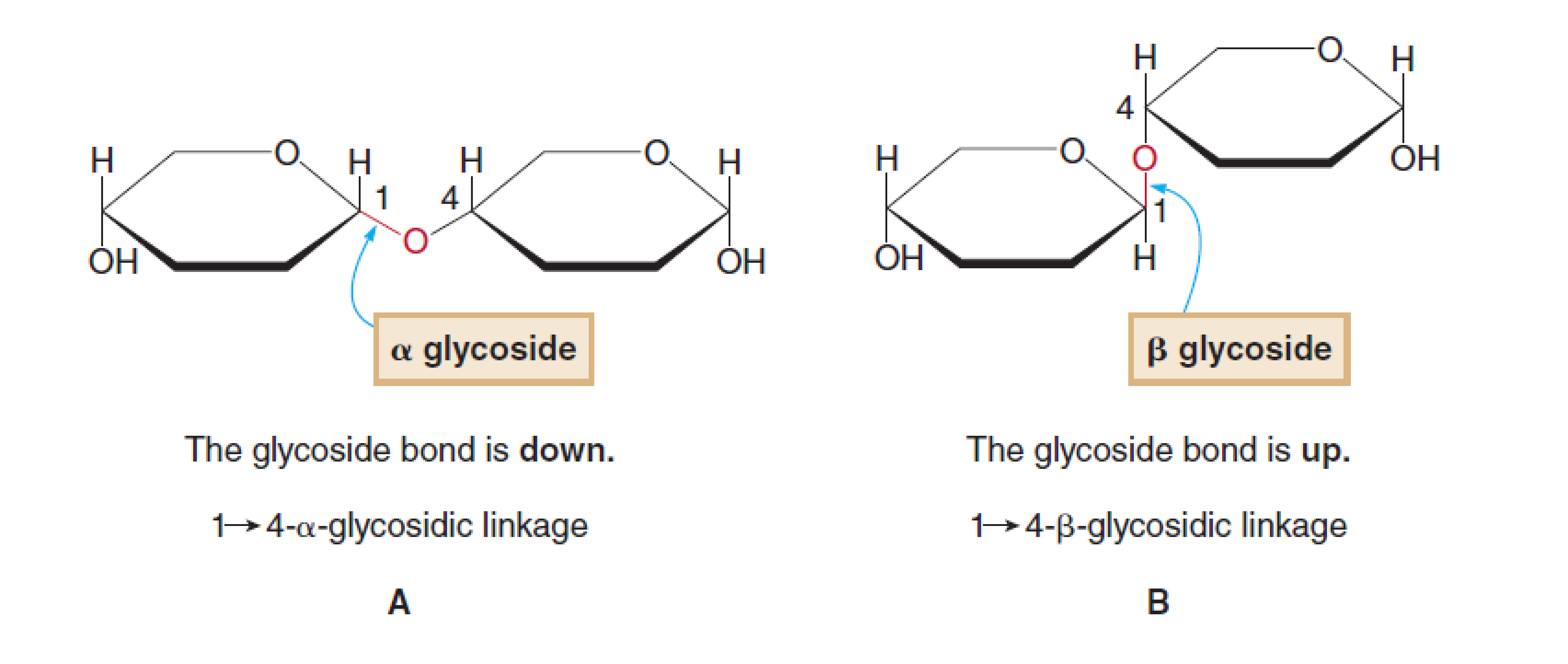
6. Disaccharides

- **Disaccharides are carbohydrates composed of two monosaccharides**.
- **A disaccharide** is formed when a hydroxyl group of one monosaccharide reacts with a hydroxyl group of a second monosaccharide.
- The new C-O bond that joins the two rings together is called a **glycosidic linkage**. The carbon in a glycosidic linkage is bonded to two O atoms.
- One O atom is part of a ring, and the other O atom joins the two rings together.

- For example, **maltose** is a disaccharide formed from **two molecules of glucose**. Maltose, which is found in grains such as barley, is a product of the hydrolysis of starch.
- Each ring in maltose is numbered beginning at the carbon bonded to two oxygen atoms. In maltose, the glycosidic linkage joins C1 of one ring to C4 of the other ring.



- The **glycosidic linkage** that joins the two monosaccharides in a disaccharide can be oriented in two different ways, shown with **Haworth projections** in structures **A** and **B**. (Several OH groups are omitted for clarity.)



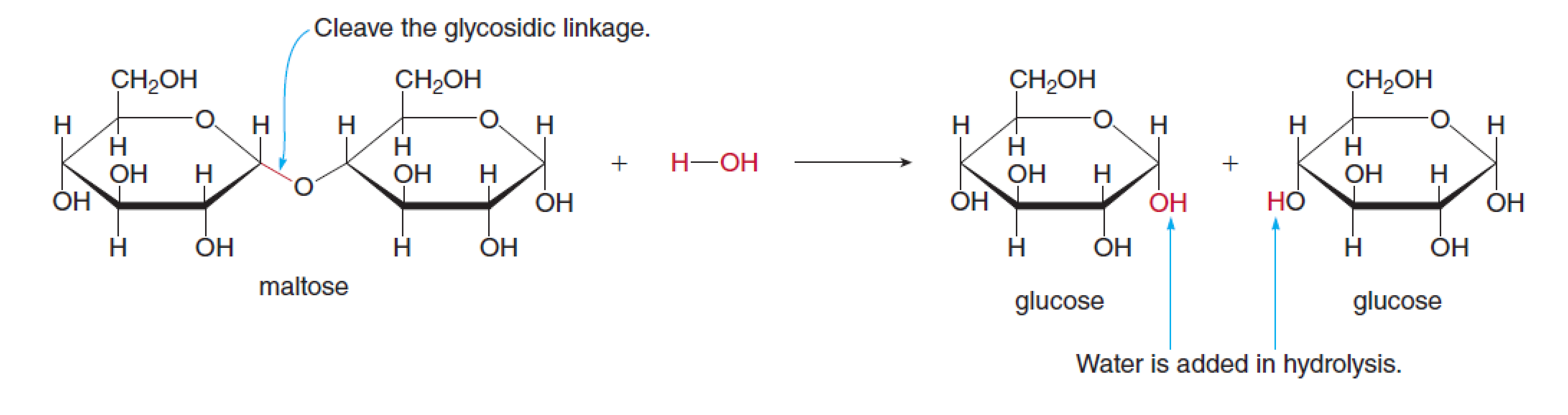
- ✓ • **An α glycoside has the glycosidic linkage oriented down.**
- ✓ • **A β glycoside has the glycosidic linkage oriented up.**

Functions of Disaccharides

- ✓ Disaccharides are carbohydrates found in many foods and are often added as sweeteners.
- ✓ Sucrose, for example, is table sugar, and it is the most common disaccharide that humans eat. It is also found in other foods like beetroot.
- ✓ When disaccharides like sucrose are digested, they are broken down into their simple sugars and used for energy.
- ✓ Lactose is found in breast milk and provides nutrition for infants.
- ✓ Maltose is a sweetener that is often found in chocolates and other candies.

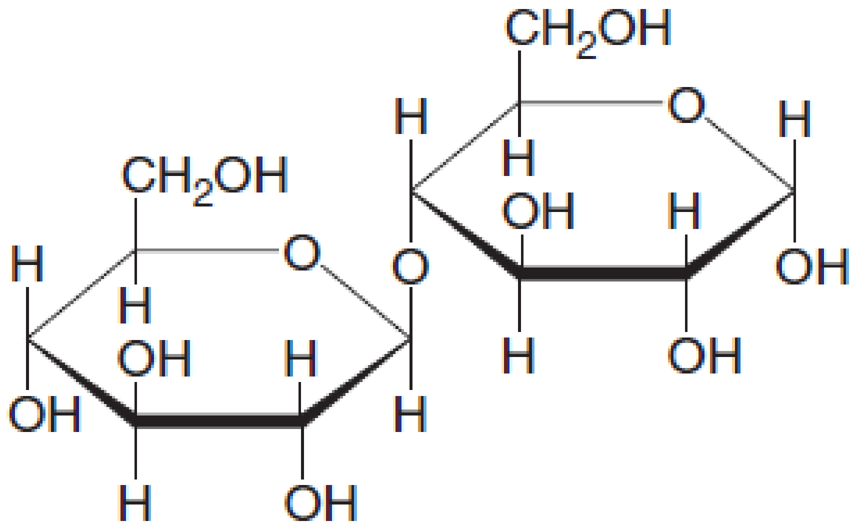
6.1.Hydrolysis of a disaccharide

- **The hydrolysis of a disaccharide cleaves the C-O glycosidic linkage and forms two monosaccharides.**
- For example, hydrolysis of maltose yields two molecules of glucose.



PROBLEM

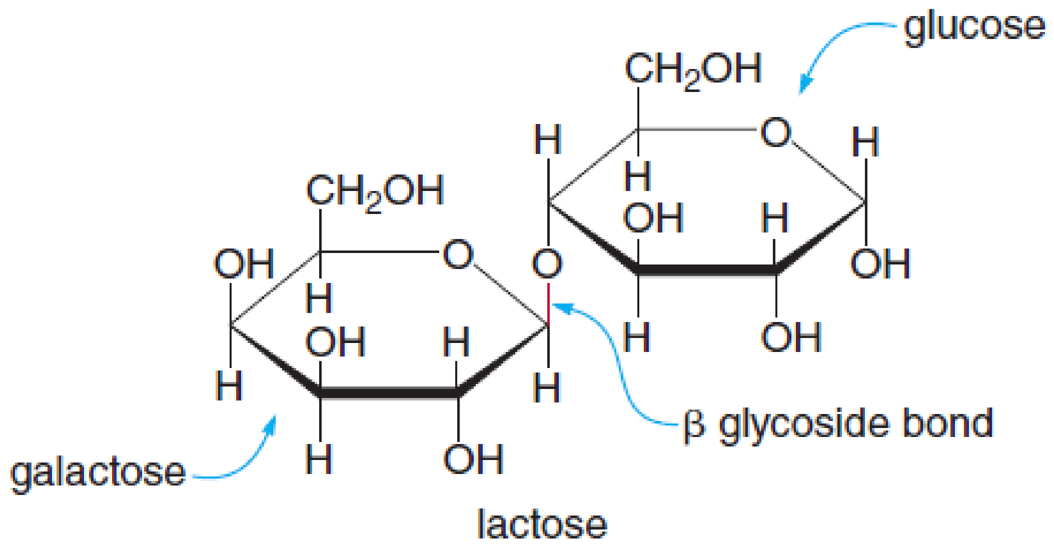
- What monosaccharides are formed when cellobiose is hydrolyzed with water?



cellobiose

6.2. Lactose Intolerance
(FOCUS ON HEALTH & MEDICINE)

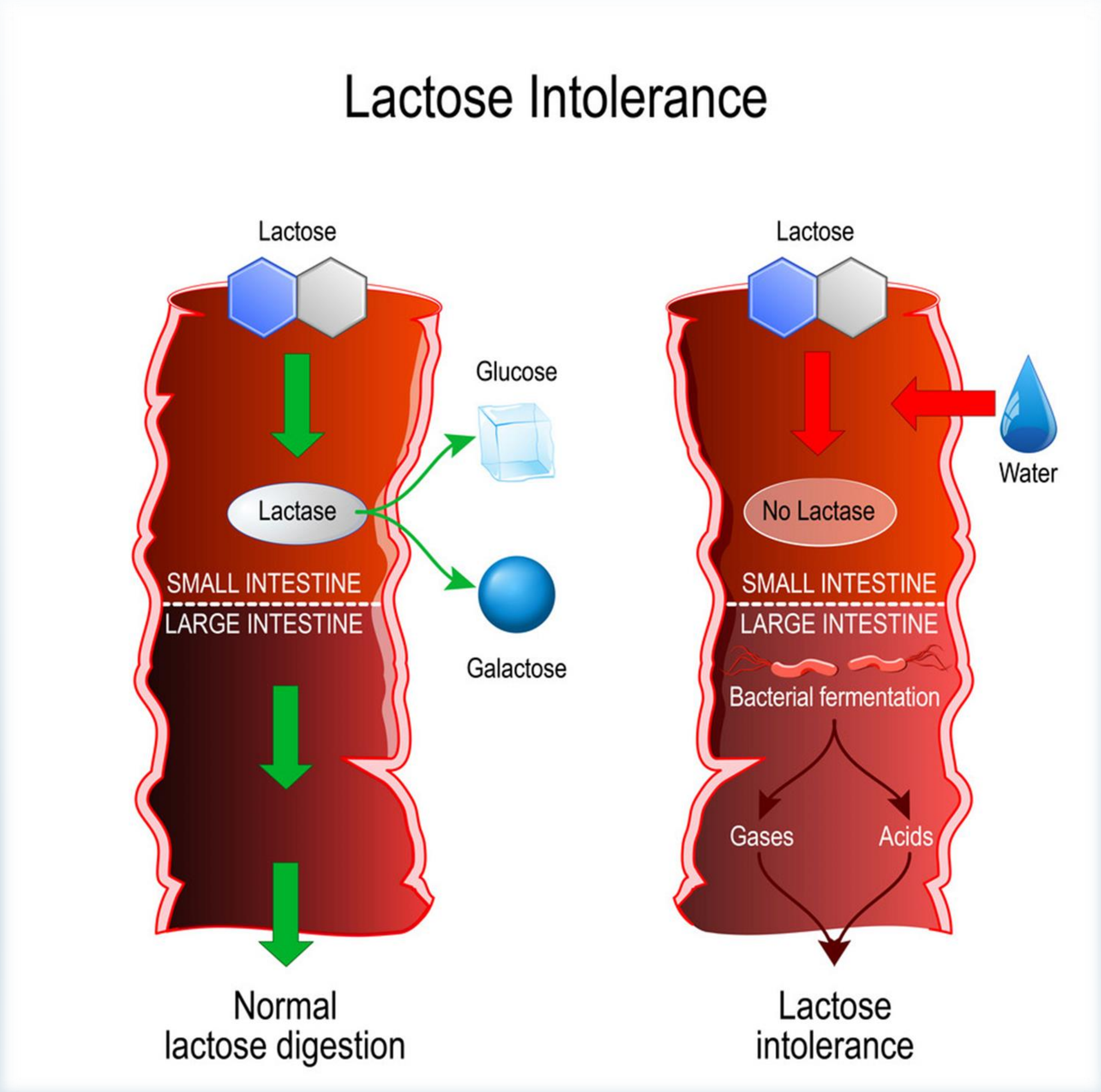
- **Lactose is the principal disaccharide found in milk from both humans and cows.**
- Unlike many mono- and disaccharides, lactose is not appreciably sweet. Lactose consists of one galactose ring and one glucose ring, joined by a 1→4-β-glycoside linkage.



- **Lactose** is digested in the body by first cleaving the **1→4-β-glycoside bond** using the enzyme **lactase**.
- Individuals who are lactose intolerant no longer produce this enzyme, and so lactose cannot be properly digested, ***causing abdominal cramps and diarrhea***. Lactose intolerance is especially prevalent in Asian and African populations whose diets have not traditionally included milk beyond infancy.

- Individuals who are lactose intolerant can drink lactose-free milk. Tablets that contain the lactase enzyme can also be taken when ice cream or other milk products are ingested.

✓ What products are formed when lactose is hydrolyzed with water?


Lactose Intolerance
Lactose
Glucose
Lactase
Galactose
SMALL INTESTINE
LARGE INTESTINE
Normal
lactose digestion
Lactose
Water
No Lactase
SMALL INTESTINE
LARGE INTESTINE
Bacterial fermentation
Gases
Acids
Lactose
intolerance

6.3. Sucrose and Artificial Sweeteners

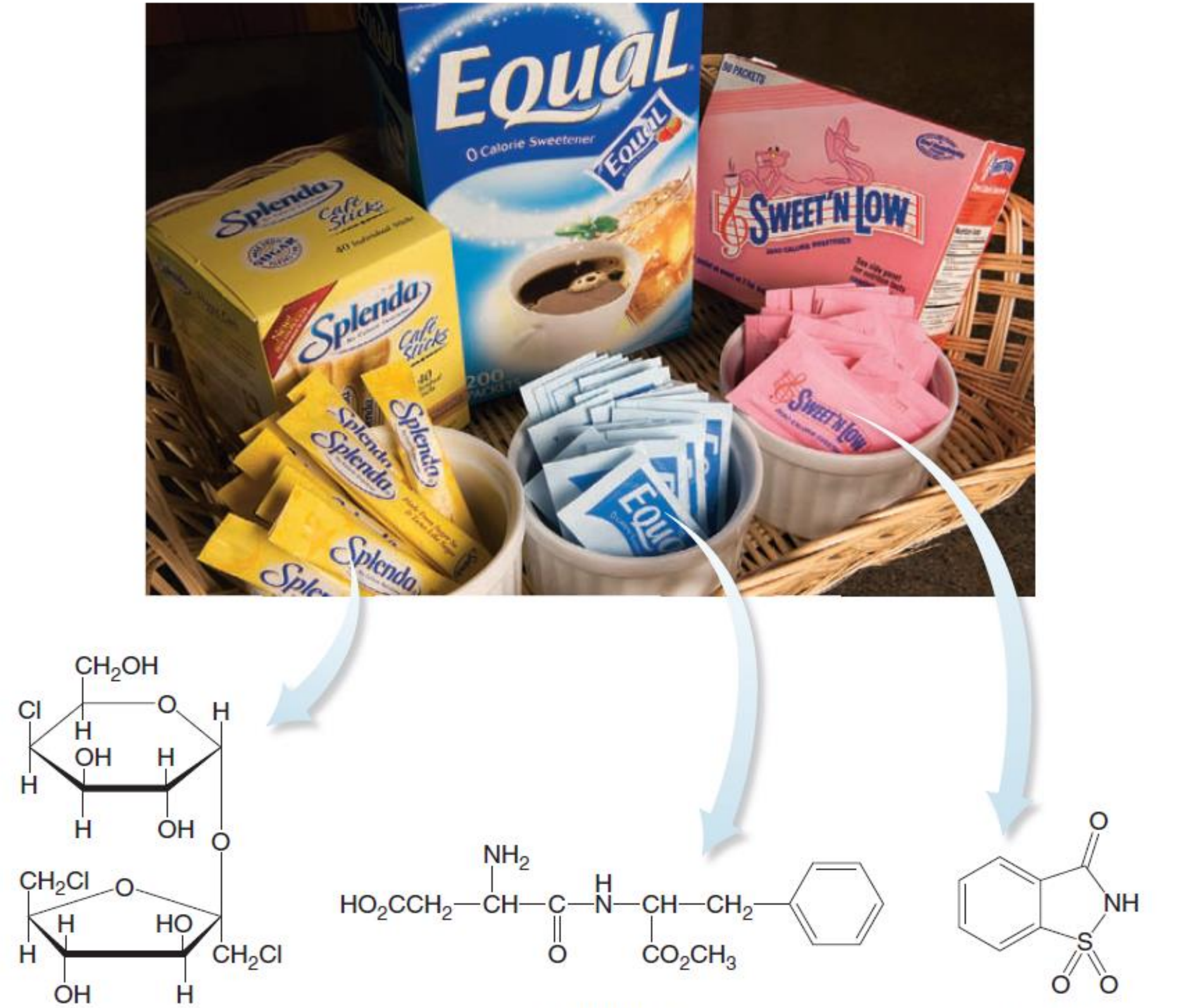
(FOCUS ON HEALTH & MEDICINE)

- **Sucrose**, the disaccharide found in sugarcane and the compound generally referred to as "sugar," **is the most common disaccharide in nature**. It contains one glucose ring and one fructose ring.

- **Unlike maltose and lactose**, which contain only six-membered rings, **sucrose** contains one six membered and one five-membered ring.

sugarcane | two varieties of refined sugar | sucrose

- Sucrose’s pleasant sweetness has made it a widely used ingredient in baked goods, cereals, bread, and many other products.
- Like other carbohydrates, however, sucrose contains many calories.
- To reduce caloric intake while maintaining sweetness, **a variety of artificial sweeteners have been developed**.
- These include **aspartame**, **saccharin**, and **sucralose** . These compounds are much sweeter than sucrose, so only a small amount of each compound is needed to achieve the same level of perceived sweetness.



sucralose
(Trade name: Splenda)

aspartame
(Trade name: Equal)

saccharin
(Trade name: Sweet'n Low)

7. Polysaccharides

- **Polysaccharides contain three or more monosaccharides joined together by glycosidic linkages**.
- Three prevalent polysaccharides in nature are cellulose, starch, and glycogen, each of which consists of repeating glucose units joined by glycosidic bonds.
- This carbohydrate can react with water (**hydrolysis**) using **amylase enzymes** at catalyst, which produces constituent sugars (monosaccharides, or disaccharides).

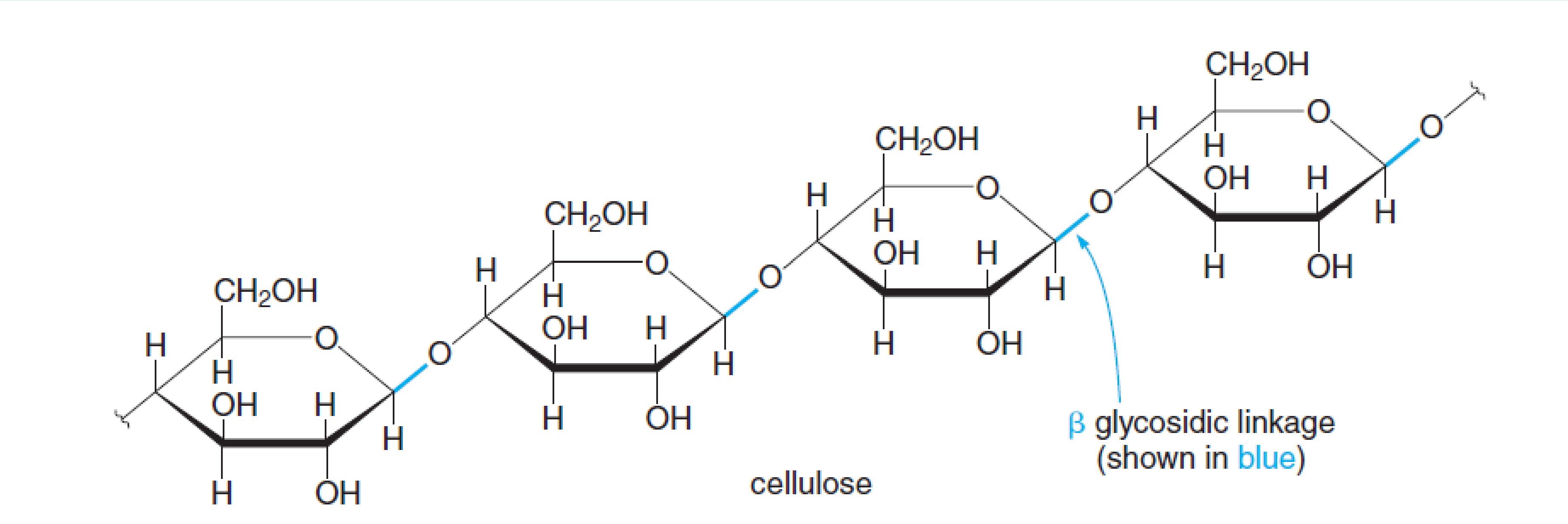
Functions of a Polysaccharide

- Depending on their structure, polysaccharides can have a wide variety of functions in nature. Some polysaccharides are used for **storing energy**, some for **sending cellular messages**, and others for **providing support to cells and tissues**.

7.1. Cellulose

- **Cellulose is found in the cell walls of nearly all plants**, where it gives support and rigidity to wood, plant stems, and grass . Wood, cotton, and flax are composed largely of cellulose.

- **Cellulose is an unbranched polymer composed of repeating glucose units joined in a 1→4-β- glycosidic linkage**. The β glycosidic linkages create long linear chains of cellulose molecules that stack in sheets, making an extensive three-dimensional array.

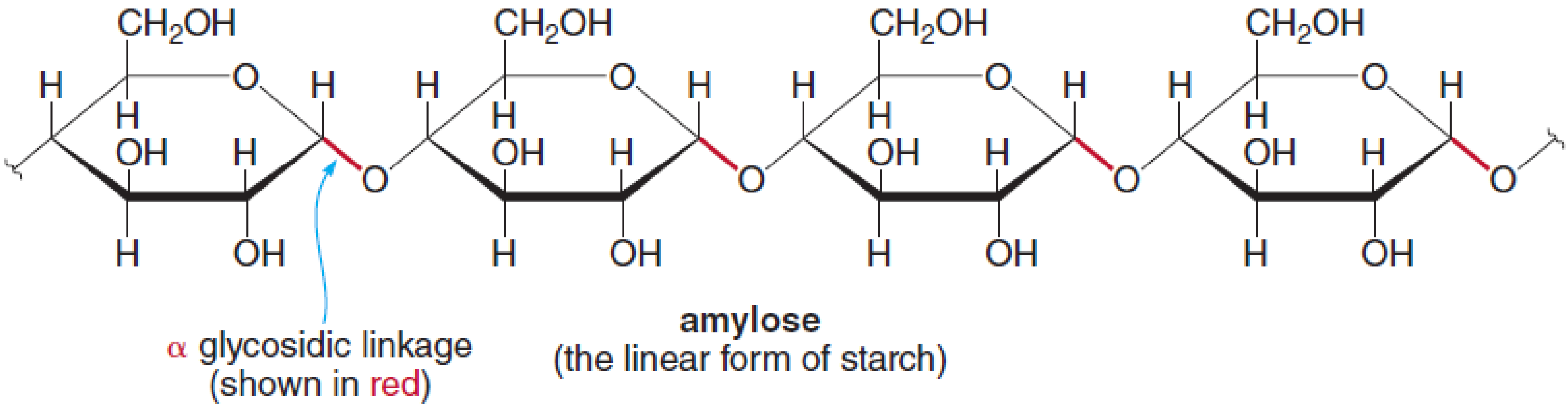


- In some cells, cellulose is hydrolyzed by an enzyme that cleaves all of the β glycoside bonds, **forming glucose. Humans do not possess this enzyme, and therefore cannot digest cellulose**.
- Much of the insoluble fiber in our diet is cellulose, which passes through the digestive system without being metabolized.
- Foods rich in cellulose include whole wheat bread, brown rice, and bran cereals.
- Fiber is an important component of the diet even though it gives us no nutrition; fiber adds bulk to solid waste, so that it is eliminated more readily.

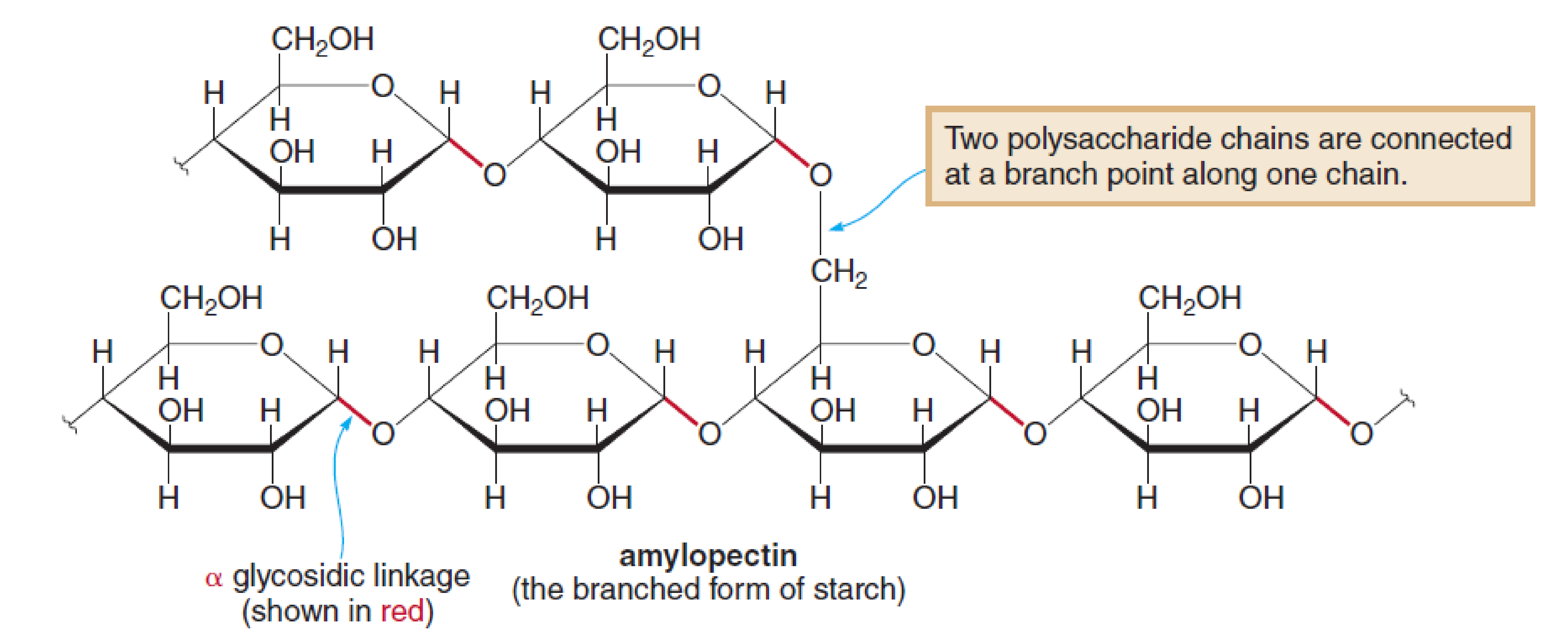
7.2. Starch

- **Starch is the main carbohydrate found in the seeds and roots of plants**. Corn, rice, wheat, and potatoes are common foods that contain a great deal of starch.
- **Starch is a polymer composed of repeating glucose units joined in α glycosidic linkages**. The two common forms of starch are **amylose** and **amylopectin**.
- Both forms of starch are water soluble. Since the OH groups are available for hydrogen bonding with water molecules, **leading to greater water solubility than cellulose**.
- Both amylose and amylopectin are hydrolyzed to glucose with cleavage of the glycosidic bonds. The human digestive system has the necessary amylase enzymes needed to catalyze this process.

- **Amylose**, which comprises about **20% of starch molecules**, has an **unbranched skeleton** of glucose molecules with **1→4-α-glycoside bonds**. Because of this linkage, an amylose chain adopts a helical arrangement, giving it a very different three-dimensional shape from the linear chains of cellulose.



- **Amylopectin,** which comprises about 80% of starch molecules, consists of a backbone of glucose units joined in **α glycosidic bonds,** but it also **contains considerable branching along** the chain.
- The linear linkages of amylopectin are formed by **1→4-α-glycoside bonds,** similar to amylose.



7.3. Glycogen

- **Glycogen is the major form in which polysaccharides are stored in animals**.
- Glycogen, a polymer of glucose containing **α** glycosidic bonds, has a branched structure similar to amylopectin, but the branching is much more extensive.
- Glycogen is stored principally in the liver and muscle.
- When glucose is needed for energy in the cell, glucose units are hydrolyzed from the ends of the glycogen polymer, and then further metabolized with the release of energy. Because glycogen has a highly branched structure, there are many glucose units at the ends of the branches that can be cleaved whenever the body needs them.

End