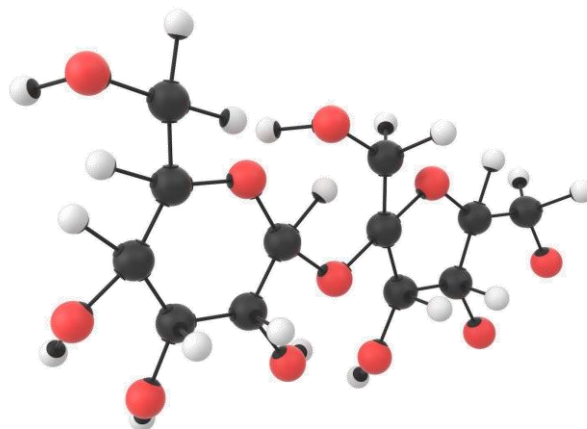


Carbohydrate-1



Instructor: Asst. Prof. Dr. Tanatorn Khotavivattana
E-mail: tanatorn.k@chula.ac.th

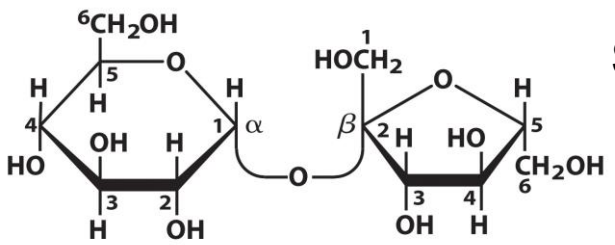
Recommended Textbook:

Chapter 23 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**,
Prentice Hall (Pearson Education)

Key concepts:

- What is carbohydrate?

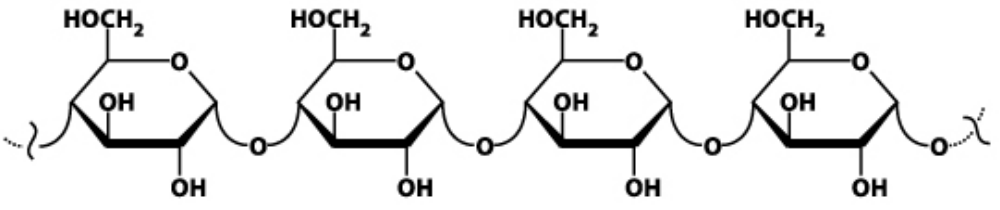
Carbohydrates



Sugar

Sucrose
 α -D-glucopyranosyl β -D-fructofuranoside
 $\text{Glc}(\alpha 1 \leftrightarrow 2\beta)\text{Fru}$

Starch

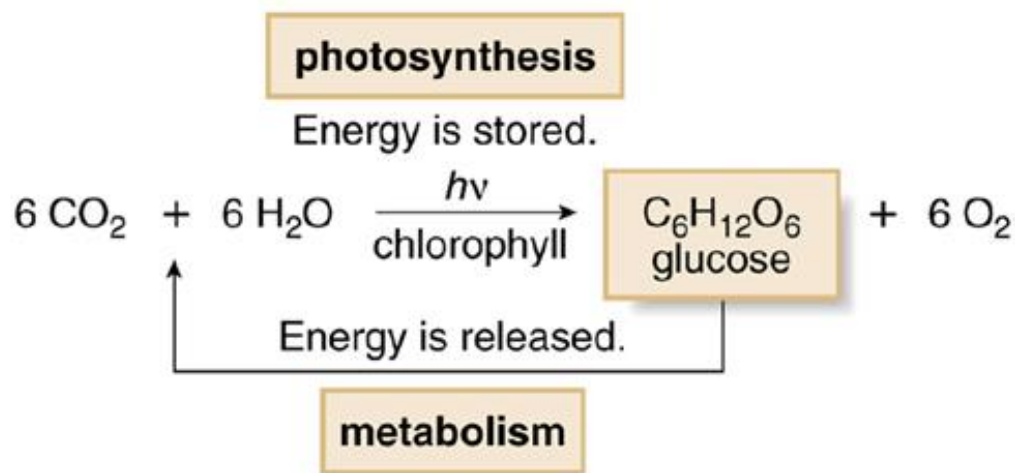


Amylose



Introduction

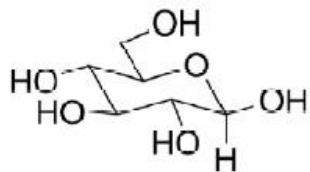
- Carbohydrates are the **most abundant** organic compounds in nature
- Nearly all plants and animals synthesise and metabolize carbohydrates, using them to **store energy** and deliver it to their cells
- Plants synthesise carbohydrates through **photosynthesis**, a reactions that use **sunlight** as the energy source to convert **carbon dioxide** and **water** into **glucose** and **oxygen**



- This energy is released when glucose is **metabolised**

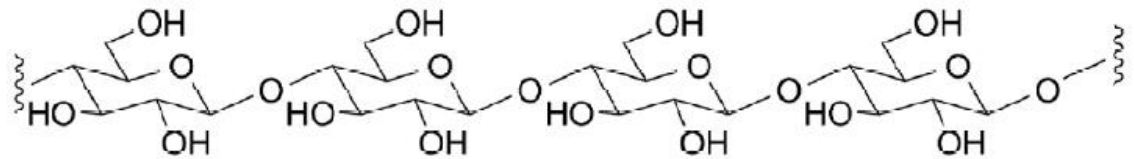
Introduction

- **Carbohydrates** = **carbon** + **water**
- Molecular formula = $C_n(H_2O)_m$
- Our modern definition of carbohydrates includes **polyhydroxyaldehydes**, **polyhydroxyketones**, and compounds that are easily hydrolysed to them.



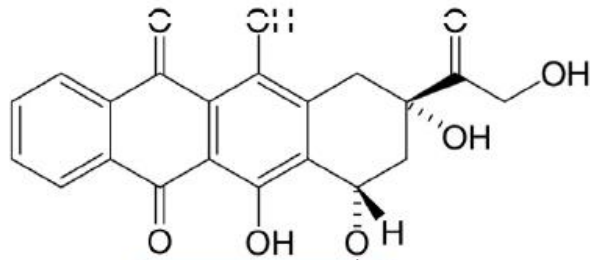
β -D-glucose

most common simple carbohydrate

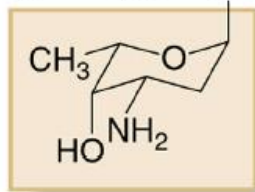


cellulose

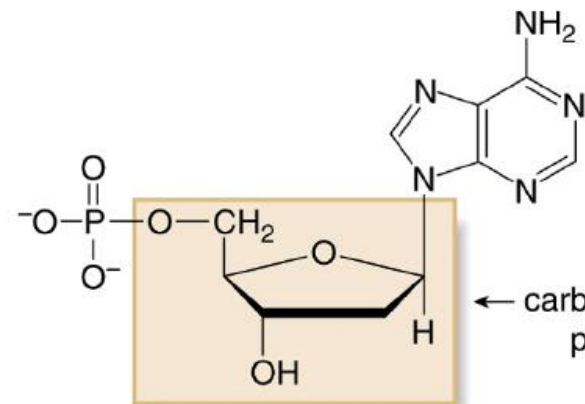
main component of wood



doxorubicin
an anticancer drug



← carbohydrate portion



← carbohydrate portion

2'-deoxyadenosine 5'-monophosphate
a nucleotide component of DNA

Key concepts:

- What is monosaccharide? What's the open-chain structure
- How do we classify monosaccharide based on functional group and number of carbon

Monosaccharides

- **Cannot be hydrolysed** to simpler compounds
- They have **3 to 7 carbon atoms** in a chain, with a **carbonyl group** at either the terminal carbon (**C1; aldehyde = aldose**) or the adjacent carbon (**C2; ketone = ketose**)
- In most carbohydrates, each of the remaining carbon atoms has a **hydroxy group**

aldose

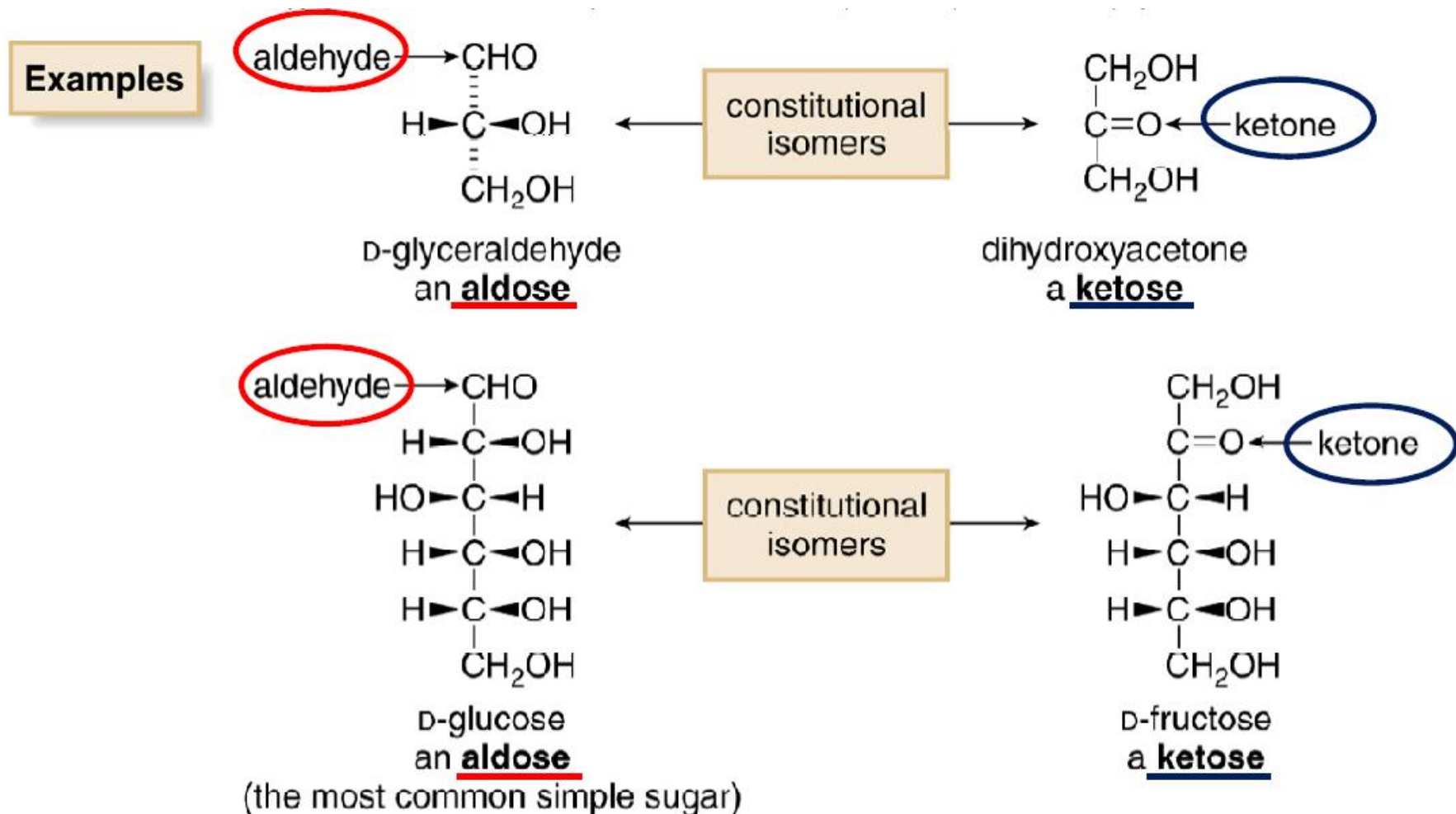
General structure of
a monosaccharide

ketose

- Monosaccharides are usually drawn **vertically**, with the **carbonyl group at the top**

Monosaccharides – Aldose vs. Ketose

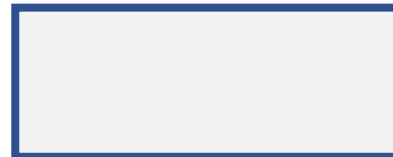
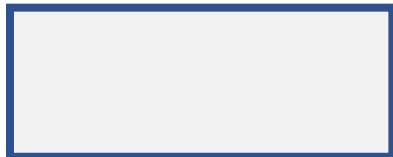
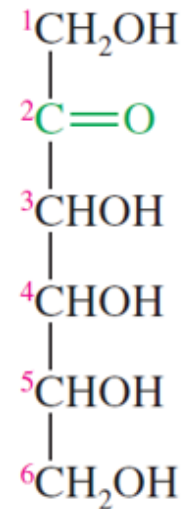
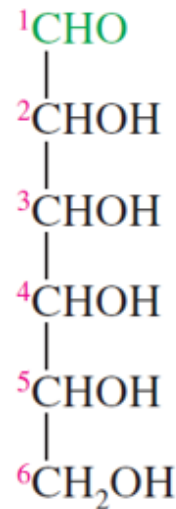
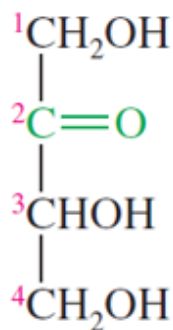
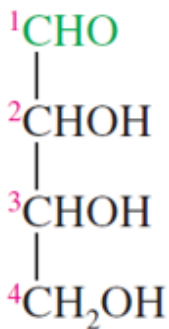
- The simplest **aldose** is **glyceraldehyde** (C=3), and the simplest **ketose** is **dihydroxyacetone** (C=3)



- Constitutional isomers: same molecular formula** but **different connectivity**

Monosaccharides – Classification

- A monosaccharide is called
 - **Triose** if it has **3** C's
 - **Tetrose** if it has **4** C's
 - **Pentose** if it has **5** C's
 - **Hexose** if it has **6** C's
 - **Heptose** if it has **7** C's
- These terms are then combined with the words **aldose/ketose** to indicate both the number of carbon atoms in the monosaccharide, and whether it contains an aldehyde or ketone functionality



Key concepts:

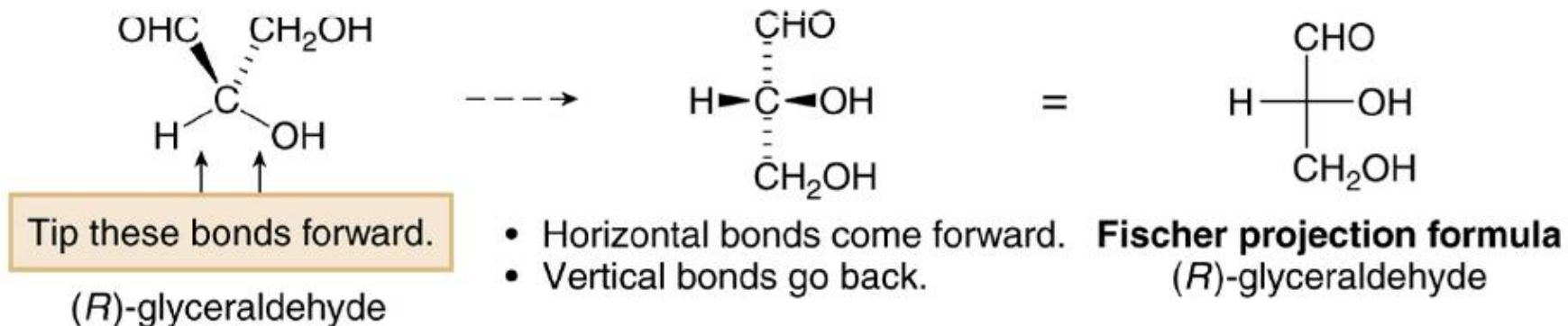
- What is the difference between each type of monosaccharide?
- What are stereogenic centers in monosaccharide and how to represent them as “Fischer Projection”?

Monosaccharides – Fischer Projection

Example: Glyceraldehyde (an aldotriose)

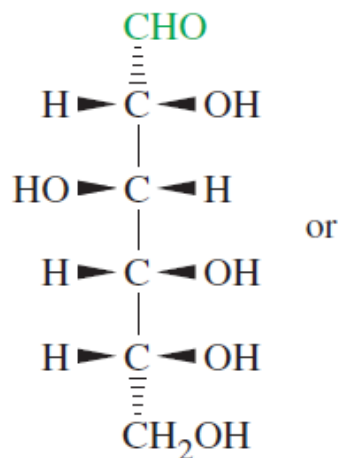
- The **stereogenic centres in sugars** are often depicted following a different convention than is usually seen for other stereogenic centres
- The **tetrahedron** carbon is tipped so that **horizontal bonds come forward** (drawn on wedges) and **vertical bonds go behind** (on dashed lines)

Using a Fischer projection formula, (*R*)-glyceraldehyde becomes:

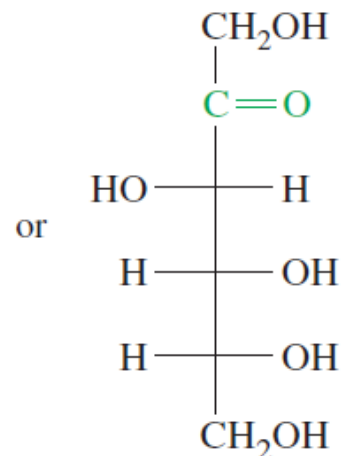


Monosaccharides – Fischer Projection

- Fischer projection formulas are also used for compounds like aldohexoses that contain **several stereogenic centres**
- In this case, the molecule is drawn with a **vertical carbon skeleton** and the stereogenic centres are stacked one above another
- Using this convention, all **horizontal bonds project forward** (on wedges)



glucose



fructose

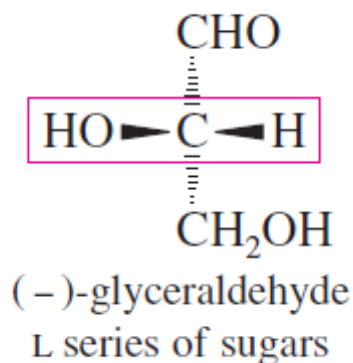
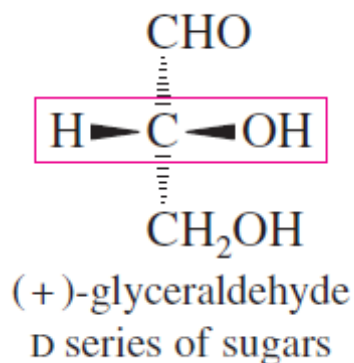
Monosaccharides – Fischer Projection

Example: aldotetrose

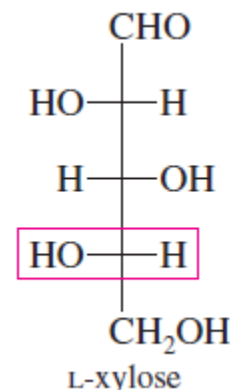
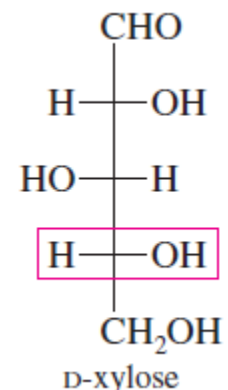
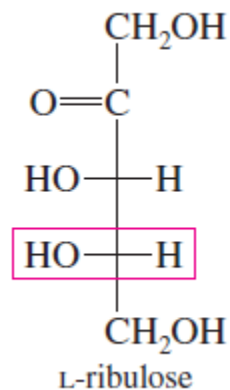
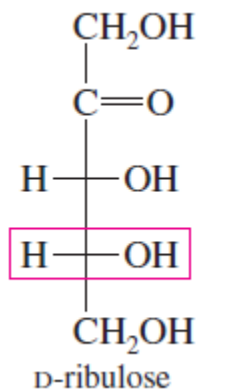
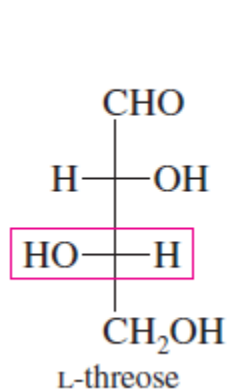
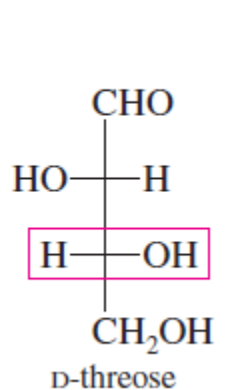
- **Fischer–Rosanoff convention**

- Uses **D** to designate the sugars that degrade to **(+)**-glyceraldehyde
- Uses **L** to designate the sugars that degrade to **(-)**-glyceraldehyde

- Later, chemists identified the absolute configuration of the **D** and **L** sugars



- Sugars of the **D series** have the OH group of the bottom asymmetric carbon on the **right** in the Fischer projection
- Sugars of the **L series** have the OH group of the bottom asymmetric carbon on the **left**



Monosaccharides – Fischer Projection

Example: ketopentose

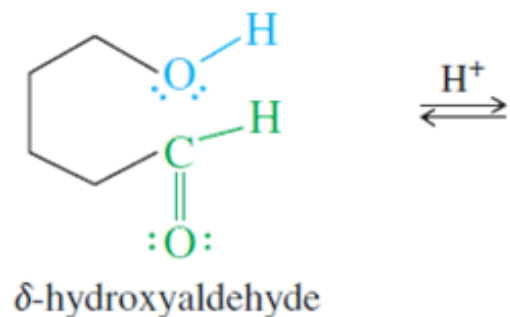
Key concepts:

- What is the cyclic structures of monosaccharide
- What is anomeric carbon?

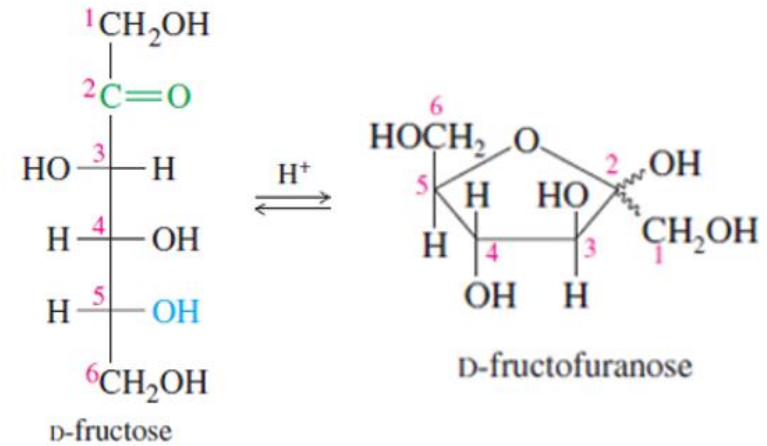
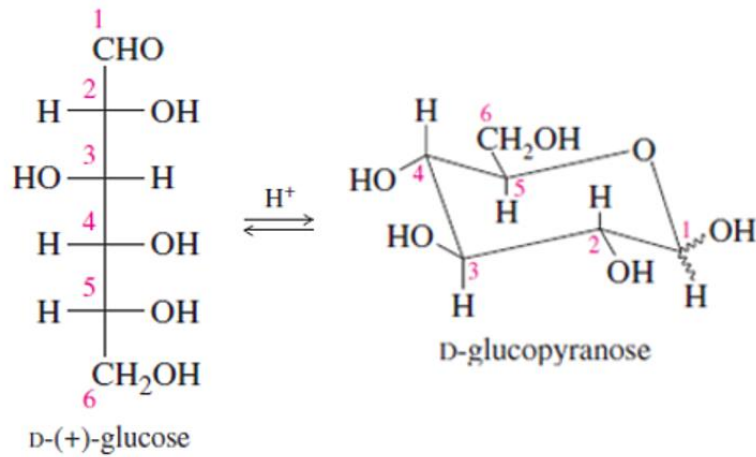
Cyclic Hemiacetals

- An **aldehyde** reacts with one molecule of an **alcohol** to give a **hemiacetal**; and with a second molecule of the alcohol to give an **acetal**
- If the aldehyde group and the hydroxyl group are **part of the same molecule**, a **cyclic hemiacetal** results

Step 1: Protonation of the carbonyl. *Step 2:* The OH group adds as a nucleophile.

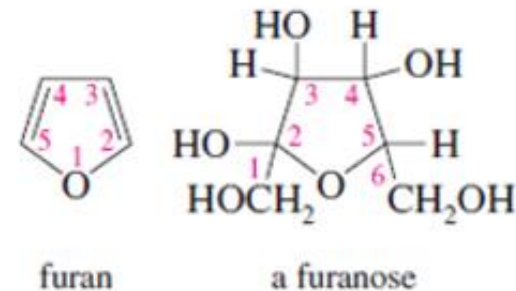
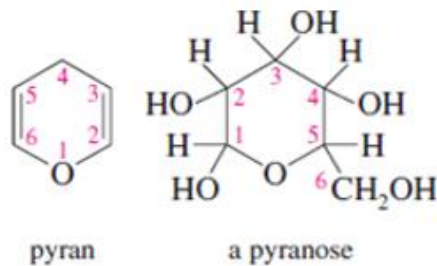


Step 3: Deprotonation gives a cyclic hemiacetal.



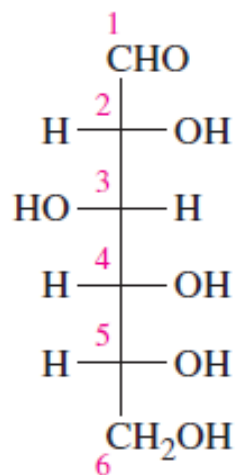
- **Six-membered** cyclic hemiacetal is called a **Pyranose**

- **Five-membered** cyclic hemiacetal is called a **Furanose**



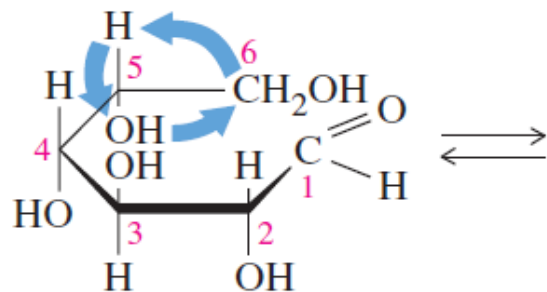
Monosaccharides – Cyclic Structure of Glucose

1) Mentally lay the Fischer projection over on its **right side**. The groups that were on the **right** in the Fischer projection are **down** in the cyclic structure, and the groups that were on the **left** are **up**. C5 and C6 curl back away from you



Fischer projection

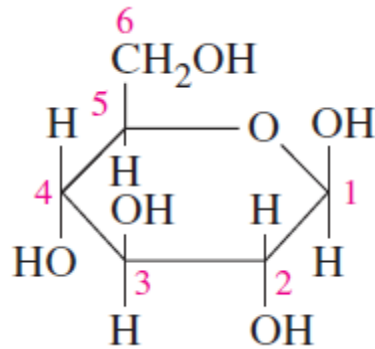
2) The bond must be rotated so that the **C5 hydroxyl group can form a part of the ring**. For a sugar of the D series, this rotation puts the terminal (C6 in glucose) upward



3) **Close the ring.**

Always draw the **Haworth projection** or chair conformation with the **oxygen at the back, right-hand corner**, with **C1 at the far right**. (C1 is easily identified because it is the hemiacetal carbon—the only carbon bonded to two oxygens)

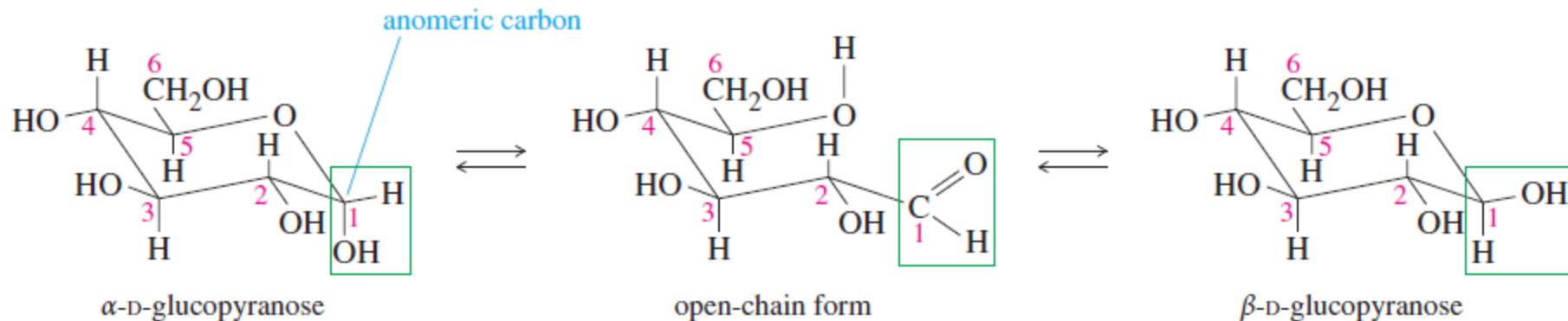
Haworth Projection



Chair Conformation

Monosaccharides – Anomers

- When a pyranose or furanose ring closes, the flat carbonyl group is converted to an **asymmetric carbon** in the hemiacetal
- Hemiacetal O—H group can be directed either **up or down**. These two orientations of the hemiacetal O—H group give diastereomeric products called **anomers**
- The hemiacetal carbon atom is called the **anomeric carbon**, easily identified as the only carbon atom bonded to two oxygens



- The structure with the anomeric group **down** (axial) is called the **α (alpha) anomer**
- The structure with the anomeric group **up** (equatorial) is called the **β (beta) anomer**

Monosaccharides – Cyclic Structure of Fructose

- Many aldopentoses and ketohexoses form **five-membered rings**
- Usually drawn with the ring **oxygen in back** and the **hemiacetal carbon** (the one bonded to two oxygens) **on the right**

