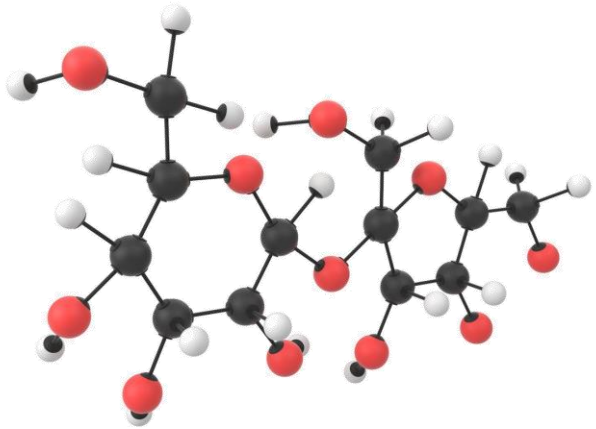
2302272 – Org Chem II – Part IV

Lecture 3

Carbohydrate-1



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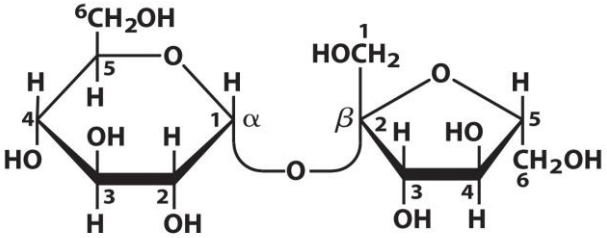
Recommended Textbook:

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

Key concepts:

1) Carbohydrate คืออะไร?

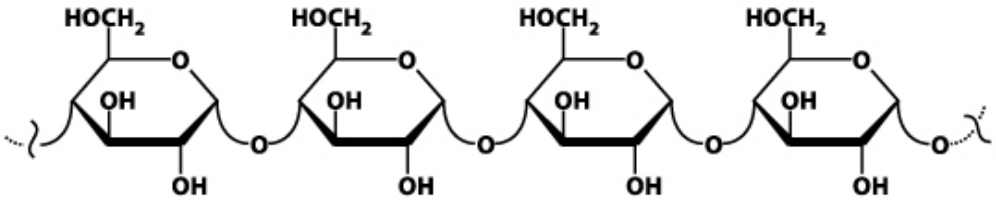
Carbohydrates



Sucrose
α-D-glucopyranosyl β-D-fructofuranoside
Glc(α1↔2β)Fru

Sugar

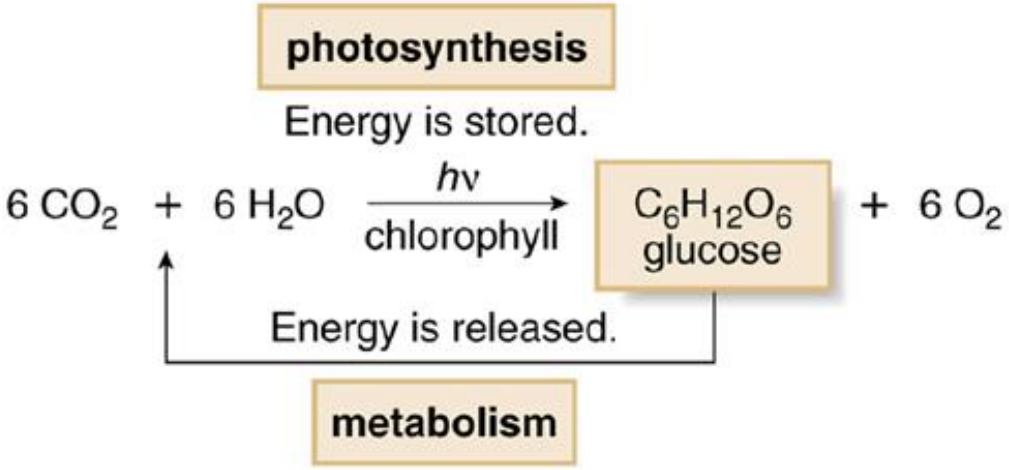
Starch



Amylose

Introduction

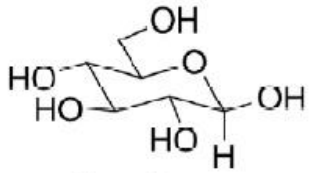
- Carbohydrates are the **most abundant** organic compounds in nature
- Nearly all plants and animals synthesise and metabolize carbohydrates, using them to **store energy** and deliver it to their cells
- Plants synthesise carbohydrates through **photosynthesis**, a reactions that use **sunlight** as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



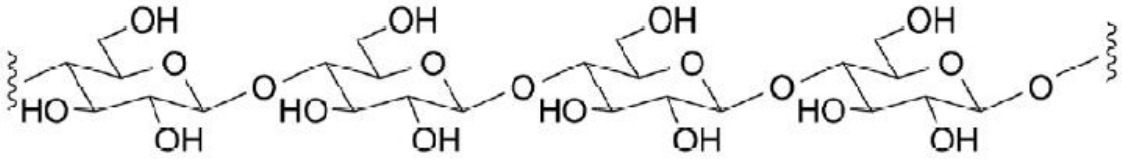
- This energy is released when glucose is **metabolised**

Introduction

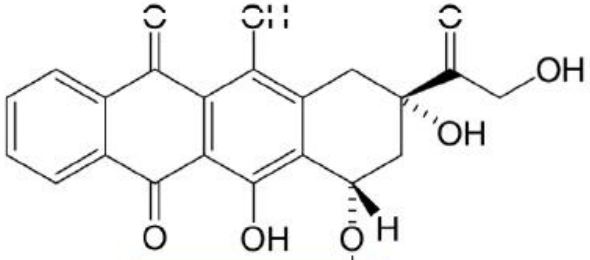
- **Carbohydrates** = **carbon** + **water**
- Molecular formula = $C_n(H_2O)_m$
- Our modern definition of carbohydrates includes **polyhydroxyaldehydes**, **polyhydroxyketones**, and compounds that are easily hydrolysed to them.



β-D-glucose
most common simple carbohydrate

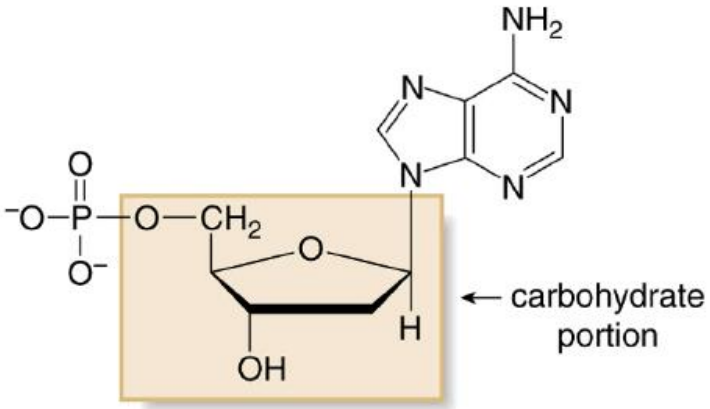


cellulose
main component of wood



doxorubicin
an anticancer drug

← carbohydrate portion



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

← carbohydrate portion

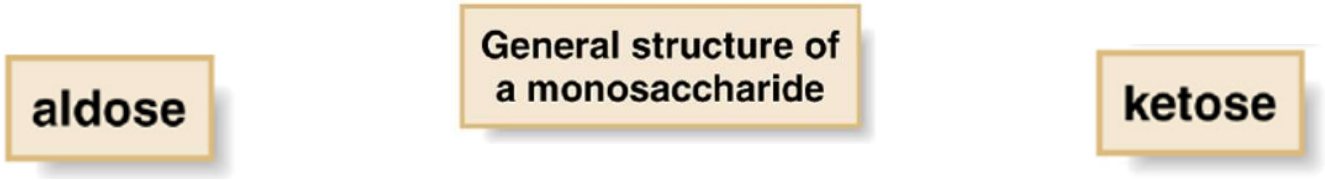
Key concepts:

2) Monosaccharide คืออะไร? มีโครงสร้างพื้นฐานแบบโซ่เปิดอย่างไร?

3) การจำแนก monosaccharide ตามชนิดของหมู่ฟังก์ชั่น และจำนวนคาร์บอน

Monosaccharides

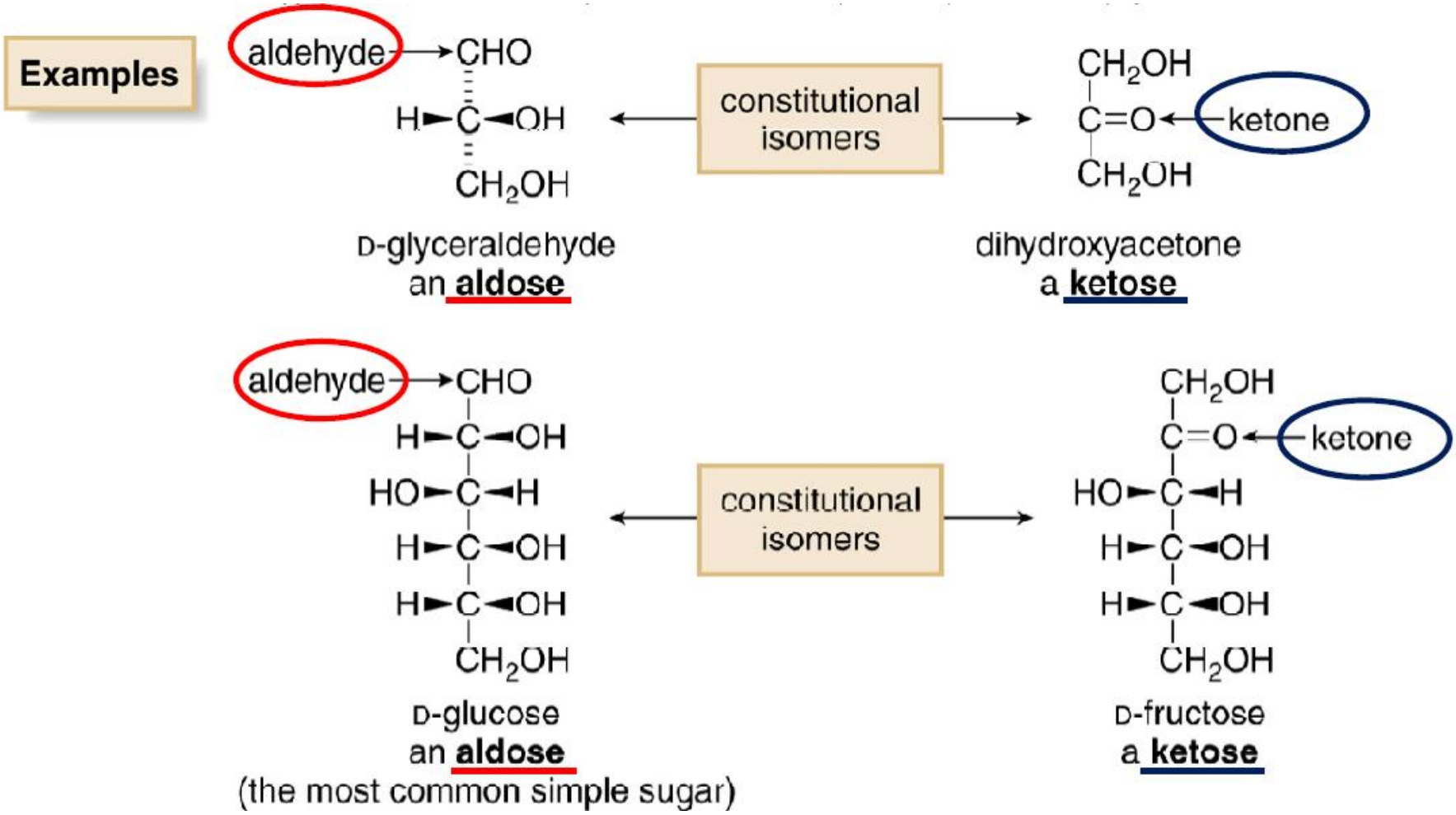
- **Cannot be hydrolysed** to simpler compounds
- They have **3 to 7 carbon atoms** in a chain, with a **carbonyl group** at either the terminal carbon (**C1; aldehyde = aldose**) or the adjacent carbon (**C2; ketone = ketose**)
- In most carbohydrates, each of the remaining carbon atoms has a **hydroxy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



- 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)

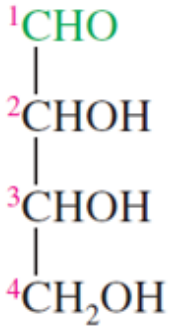


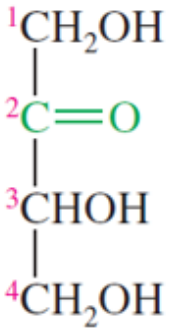
- **Constitutional isomers**: **same molecular formula** but **different connectivity**

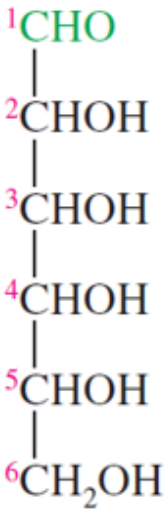
Monosaccharides – Classification

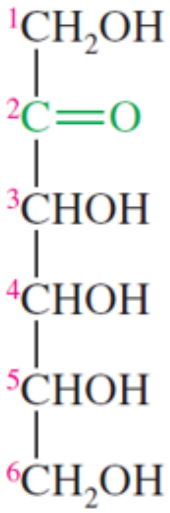
- A monosaccharide is called
  - **Triose** if it has **3** C's
  - **Tetrose** if it has **4** C's
  - **Pentose** if it has **5** C's
  - **Hexose** if it has **6** C's
  - **Heptose** if it has **7** C's

- 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:

4) Monosaccharide แต่ละชนิดแตกต่างกันอย่างไร?

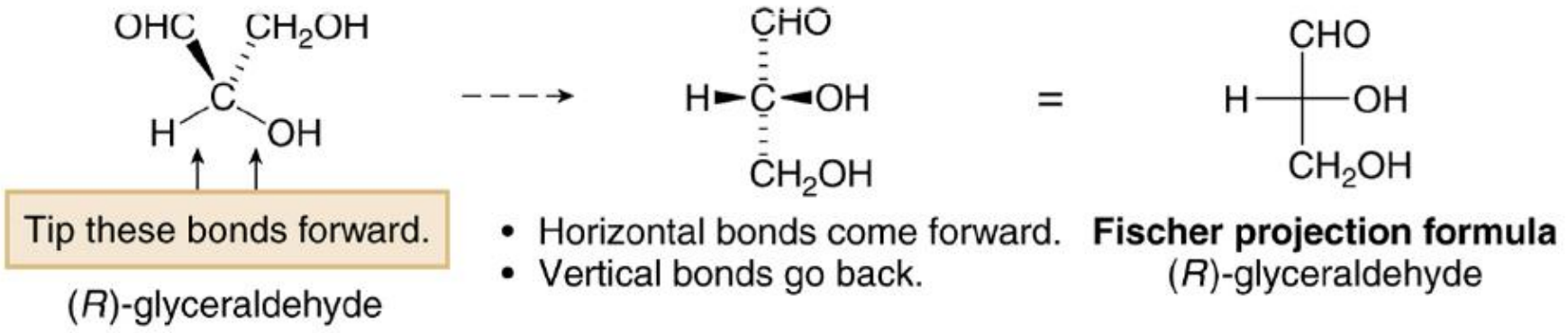
5) Stereogenic center ใน monosaccharide และวิธีการเขียน Fischer projection

Monosaccharides – Fischer Projection

Example: Glyceraldehyde (an aldotriose)

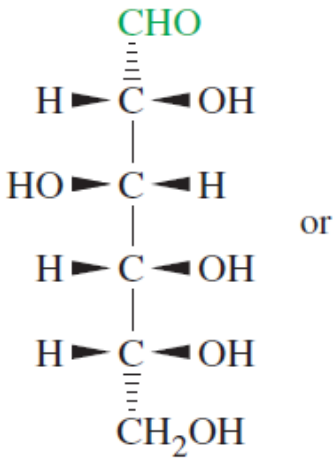
- The **stereogenic centres in sugars** are often depicted following a different convention than is usually seen for other stereogenic centres
- The **tetrahedron** carbon is tipped so that **horizontal bonds come forward** (drawn on wedges) and **vertical bonds go behind** (on dashed lines)

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



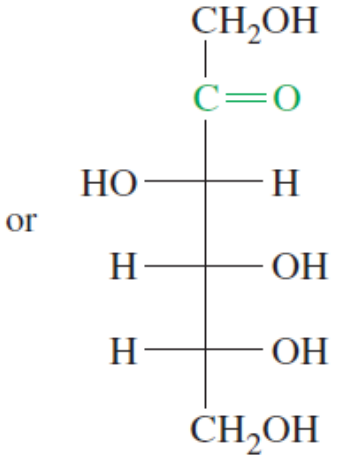
Monosaccharides – Fischer Projection

- 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)



or

glucose



or

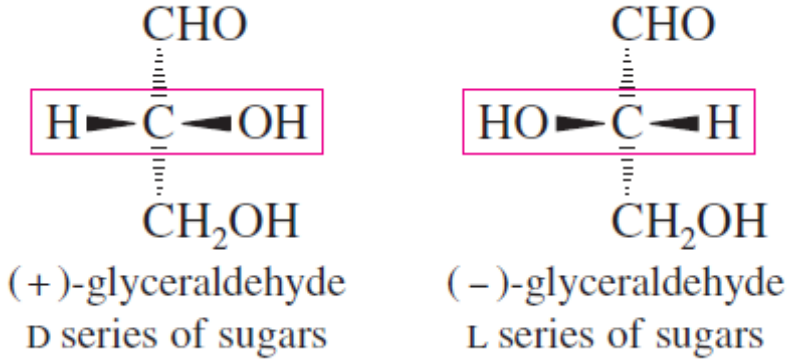
fructose

Monosaccharides – Fischer Projection

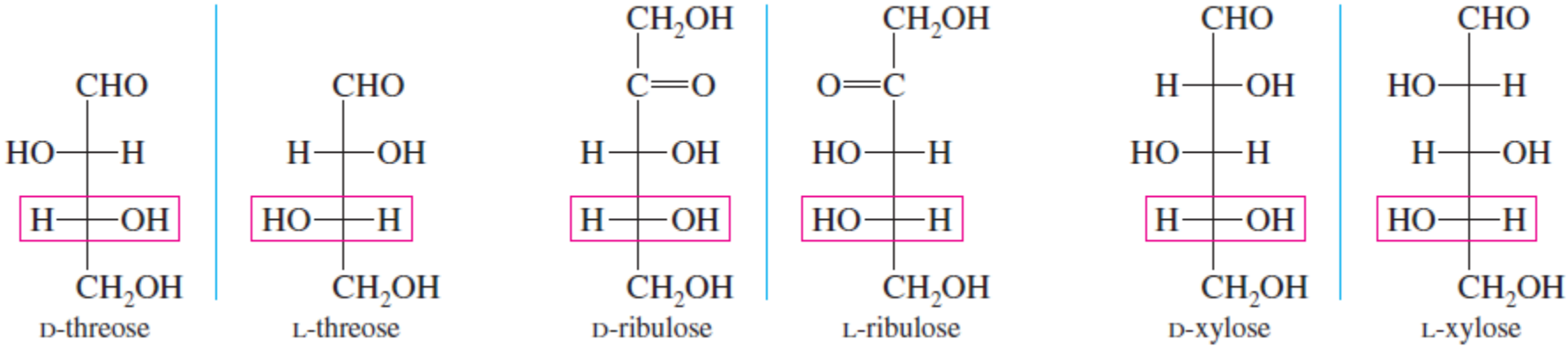
Example: aldotetrose

Monosaccharides – Stereoisomers

- ***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

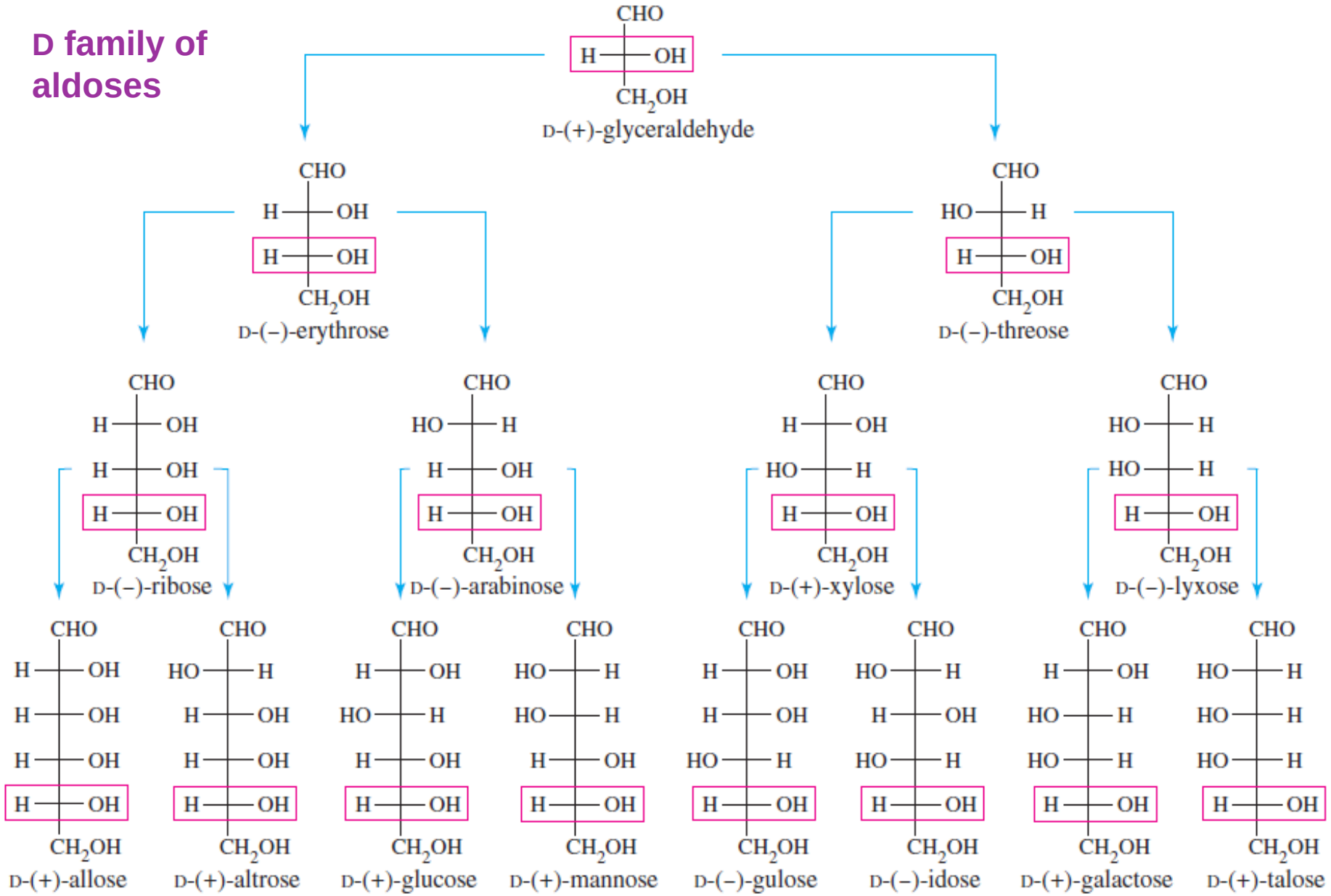


- Sugars of the **D series** have the OH group of the bottom asymmetric carbon on the **right** in the Fischer projection
- Sugars of the **L series** have the OH group of the bottom asymmetric carbon on the **left**



Monosaccharides – Stereoisomers

D family of aldoses



Monosaccharides – Fischer Projection

Example: ketopentose

Key concepts:

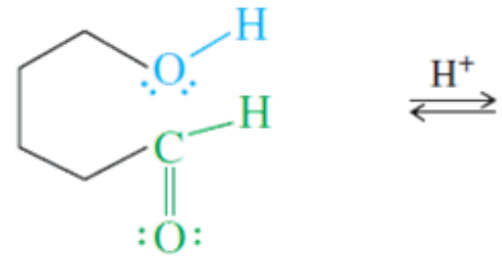
6) ปกติแล้ว monosaccharide จะไม่ได้อยู่ในรูปโซ่เปิด แต่จะปิดเป็นวง 6 เหลี่ยม (pyranose) หรือ 5 เหลี่ยม (furanose)

7) Anomeric carbon คืออะไร?

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

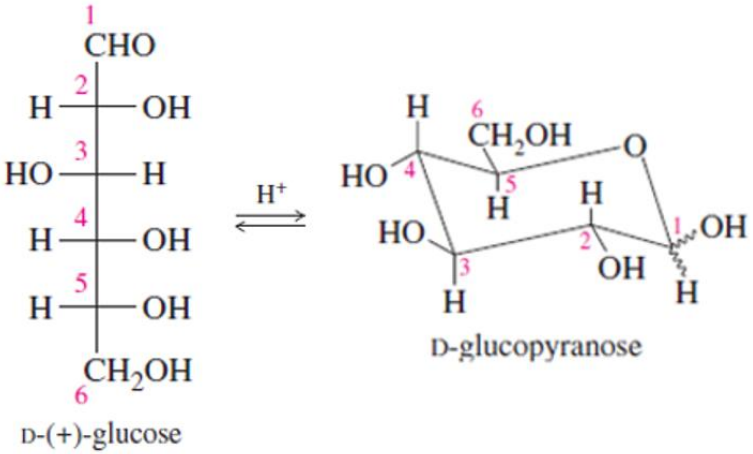
Step 1: Protonation of the carbonyl. ***Step 2:*** The OH group adds as a nucleophile.

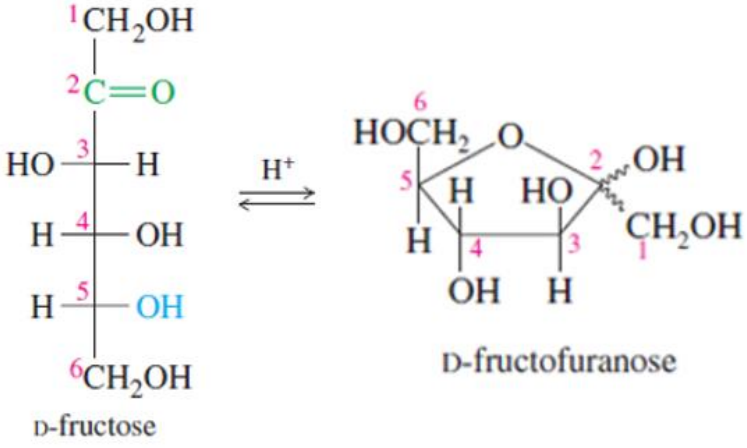


δ-hydroxyaldehyde

Step 3: Deprotonation gives a cyclic hemiacetal.

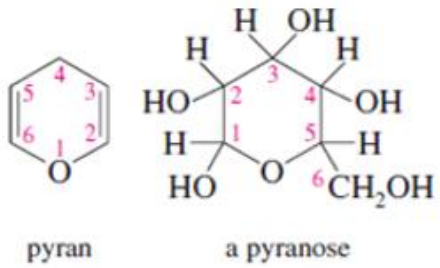
Monosaccharides – Cyclic Structure

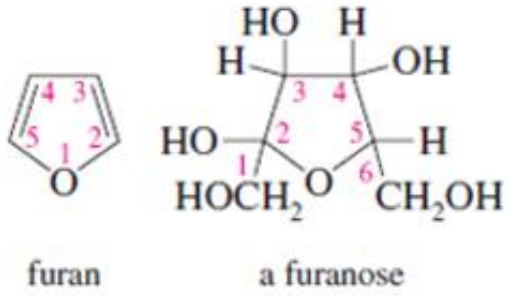




- **Six-membered** cyclic hemiacetal is called a **Pyranose**

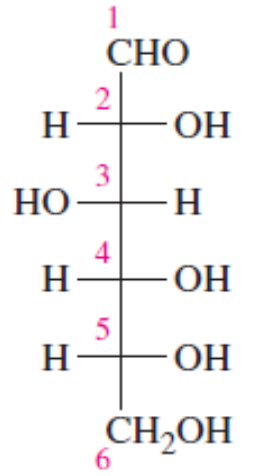
- **Five-membered** cyclic hemiacetal is called a **Furanose**





Monosaccharides – Cyclic Structure of Glucose

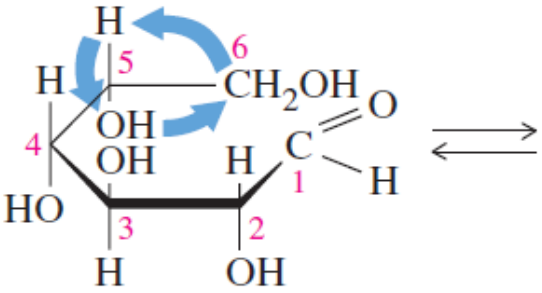
1) Mentally lay the Fischer projection over on its **right side**. The groups that were on the **right** in the Fischer projection are **down** in the cyclic structure, and the groups that were on the **left** are **up**. C5 and C6 curl back away from you



Fischer projection

Monosaccharides – Cyclic Structure of Glucose

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

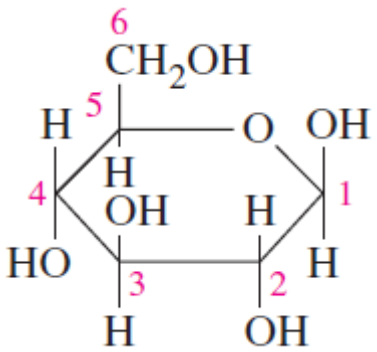


3) **Close the ring**.

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)

Monosaccharides – Cyclic Structure of Glucose

Haworth Projection



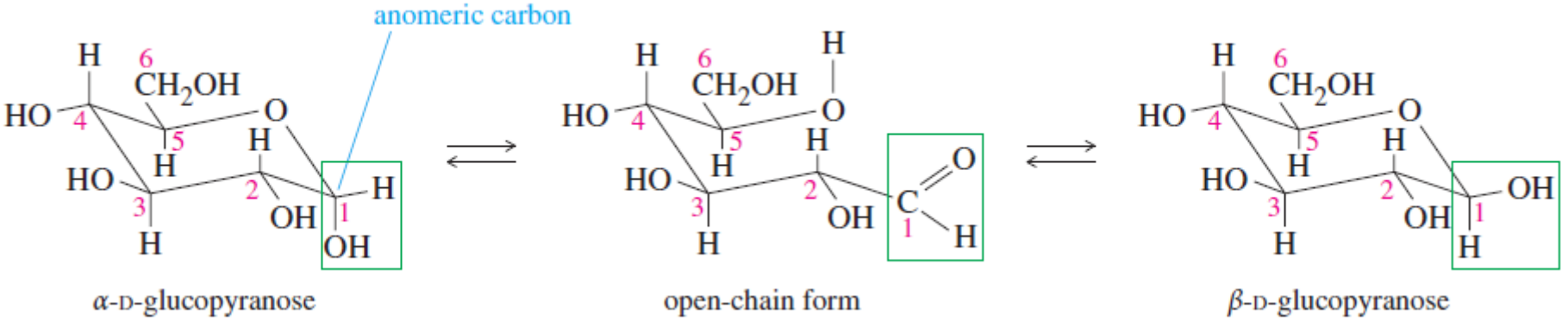
Chair Conformation

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

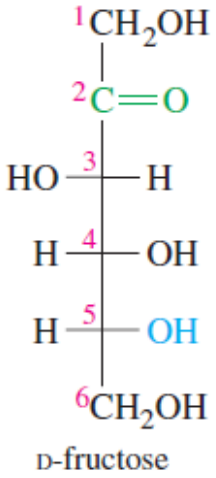


- The structure with the anomeric group **down** (axial) is called the **α (alpha) anomer**
- The structure with the anomeric group **up** (equatorial) is called the **β (beta) anomer**

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**



D-fructose