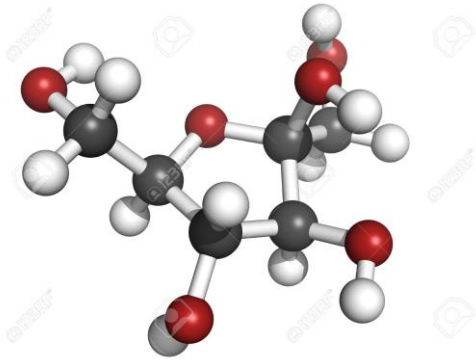
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 7-1

Biomolecules - Carbohydrate



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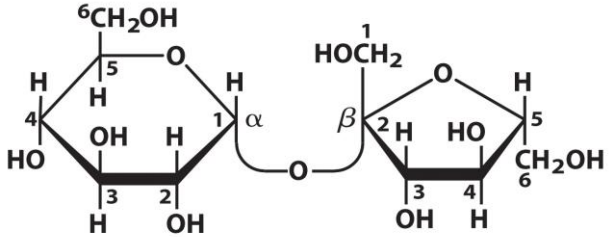
Recommended Textbook:

Chapter 23 and 25 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

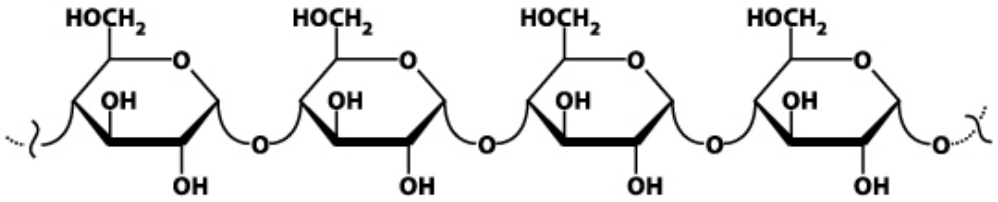
Carbohydrates



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

Sugar

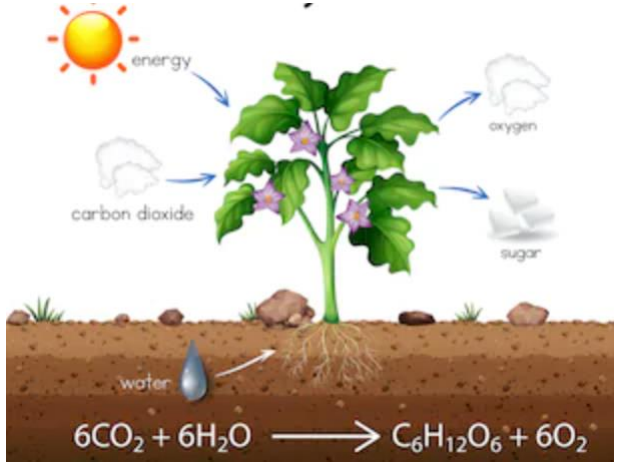
Starch



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**



photosynthesis

Energy is stored.

$$6\,CO_2 + 6\,H_2O \xrightarrow[\text{chlorophyll}]{h\nu} \underset{\text{glucose}}{C_6H_{12}O_6} + 6\,O_2$$

Energy is released.

metabolism

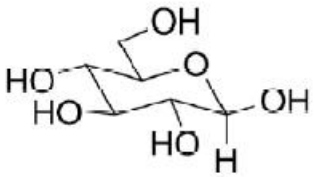
- This energy is released when glucose is **metabolised**

Introduction

- **Carbohydrates** = **carbon** + **water**
- Molecular formula = $C_n(H_2O)_m$

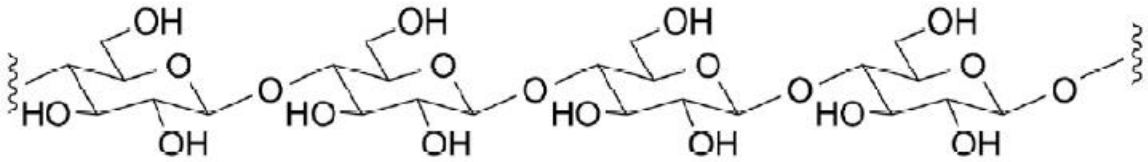
- Our modern definition of carbohydrates includes **polyhydroxyaldehydes**, **polyhydroxyketones**, and compounds that are easily hydrolysed to them.

Monosaccharide

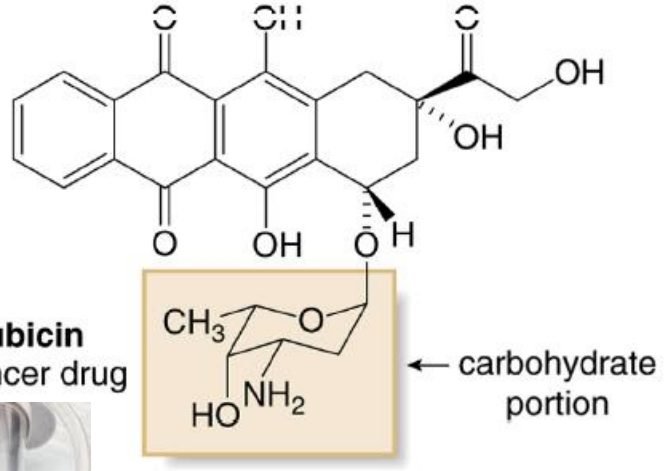


β-D-glucose
most common simple carbohydrate

Polysaccharide

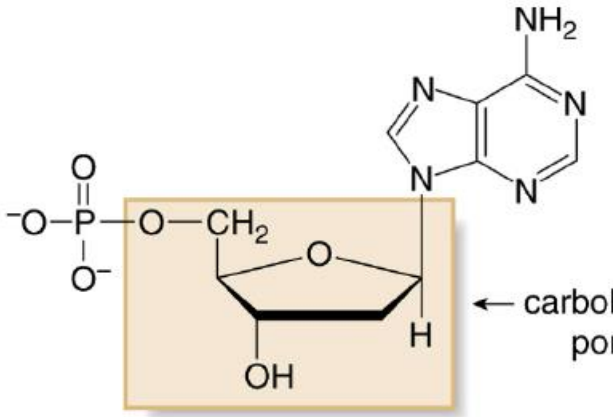


cellulose
main component of wood



doxorubicin
an anticancer drug

← carbohydrate portion



← carbohydrate portion

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

Monosaccharides

- 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**)

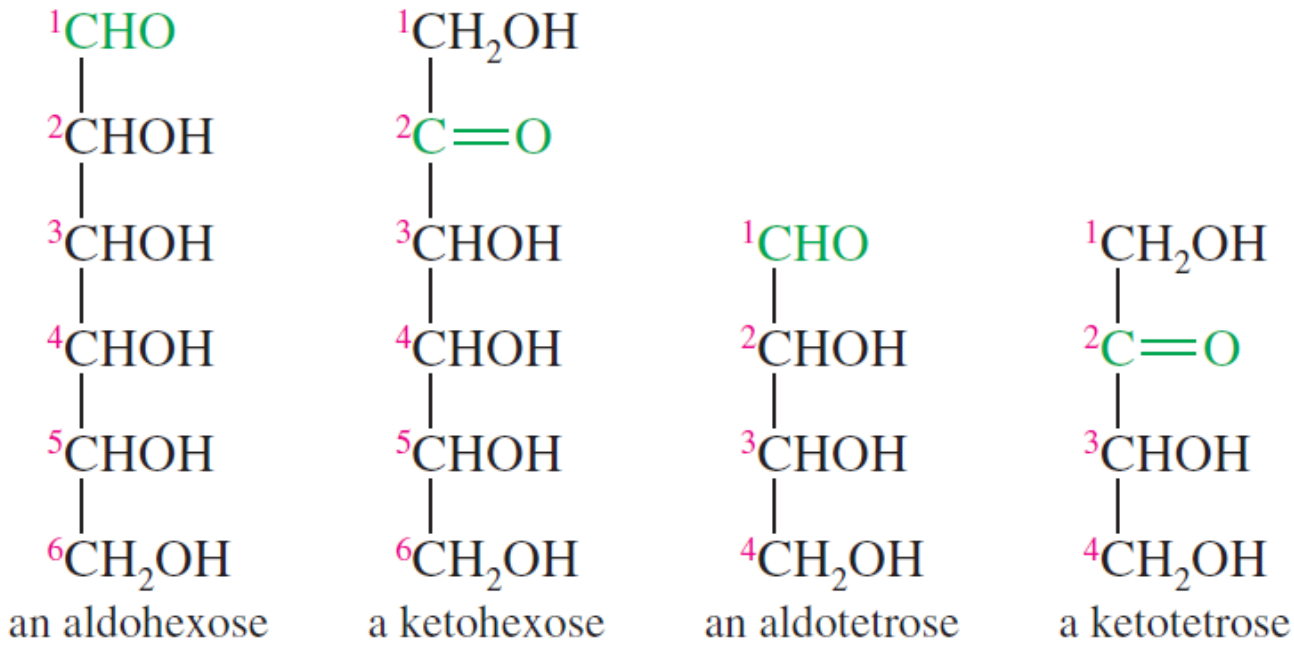
- In most carbohydrates, each of the remaining carbon atoms has a **hydroxy group**

Aldose **Ketose**

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

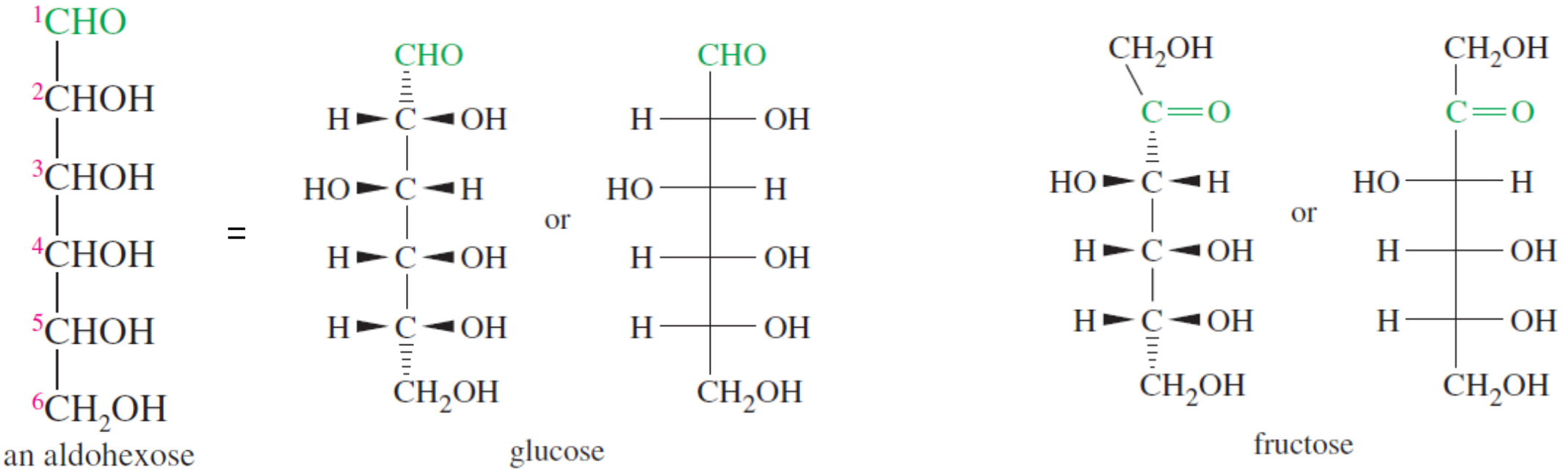
- These terms are then combined with the words **aldose**/**ketose** to indicate both the number of carbon atoms in the monosaccharide, and whether it contains an aldehyde or ketone functionality



Monosaccharides – Fischer Projection

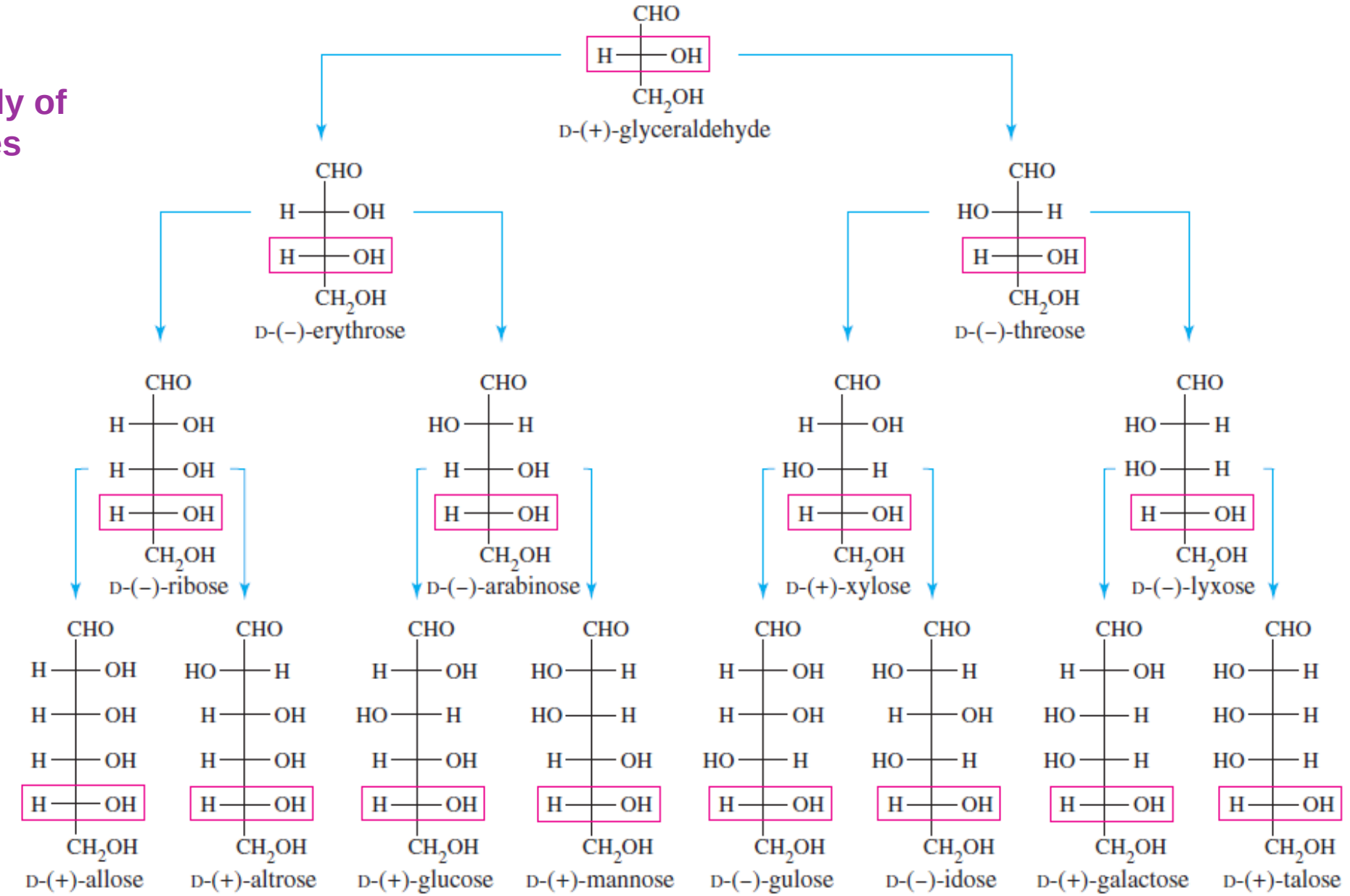
- For monosaccharides with **several stereogenic centres** the molecule is drawn with a **vertical carbon skeleton** and the stereogenic centres are stacked one above another

- Using this convention, all **horizontal bonds project forward** (on wedges)



Monosaccharides – Stereoisomers

D family of aldoses



Monosaccharides – Cyclic Structures

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

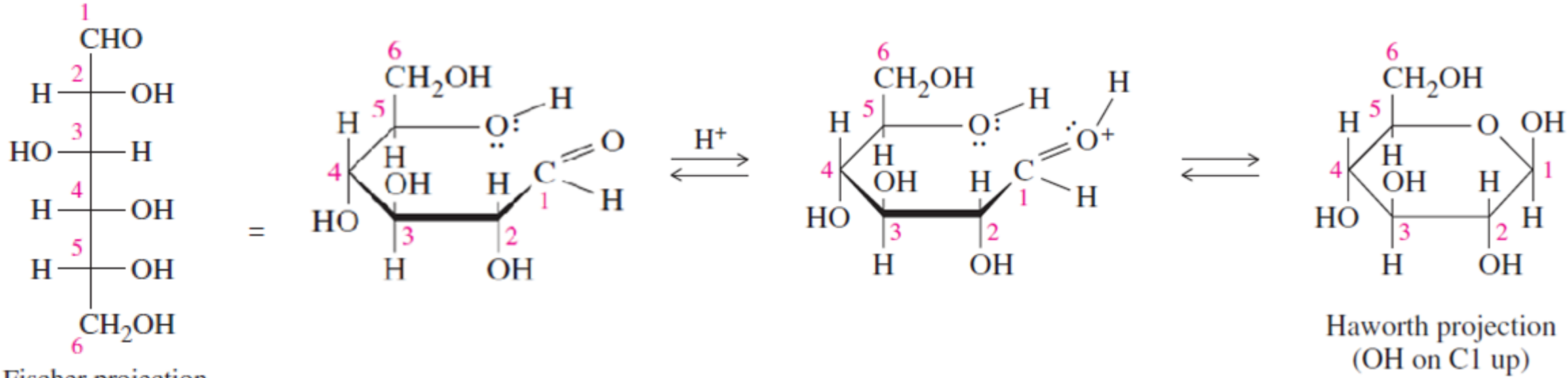
Step 1: Protonation of the carbonyl.

Step 3: Deprotonation gives a cyclic hemiacetal.

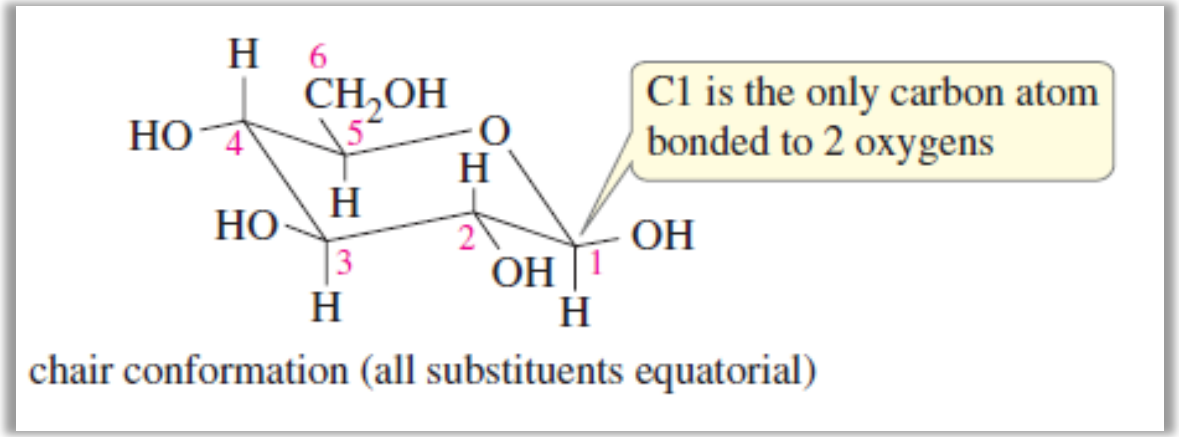
Step 2: The OH group adds as a nucleophile.

Monosaccharides – Cyclic Structure of Glucose

- Glucose forms **six-membered rings**

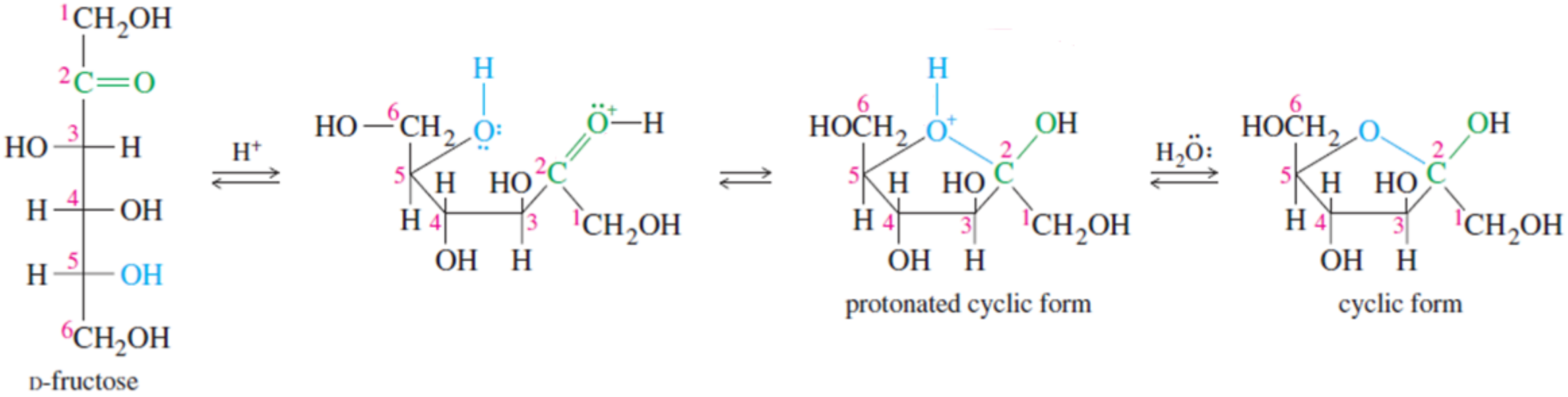


Chair Conformation



Monosaccharides – Cyclic Structure of Fructose

- Many aldopentoses and ketohexoses form **five-membered rings**

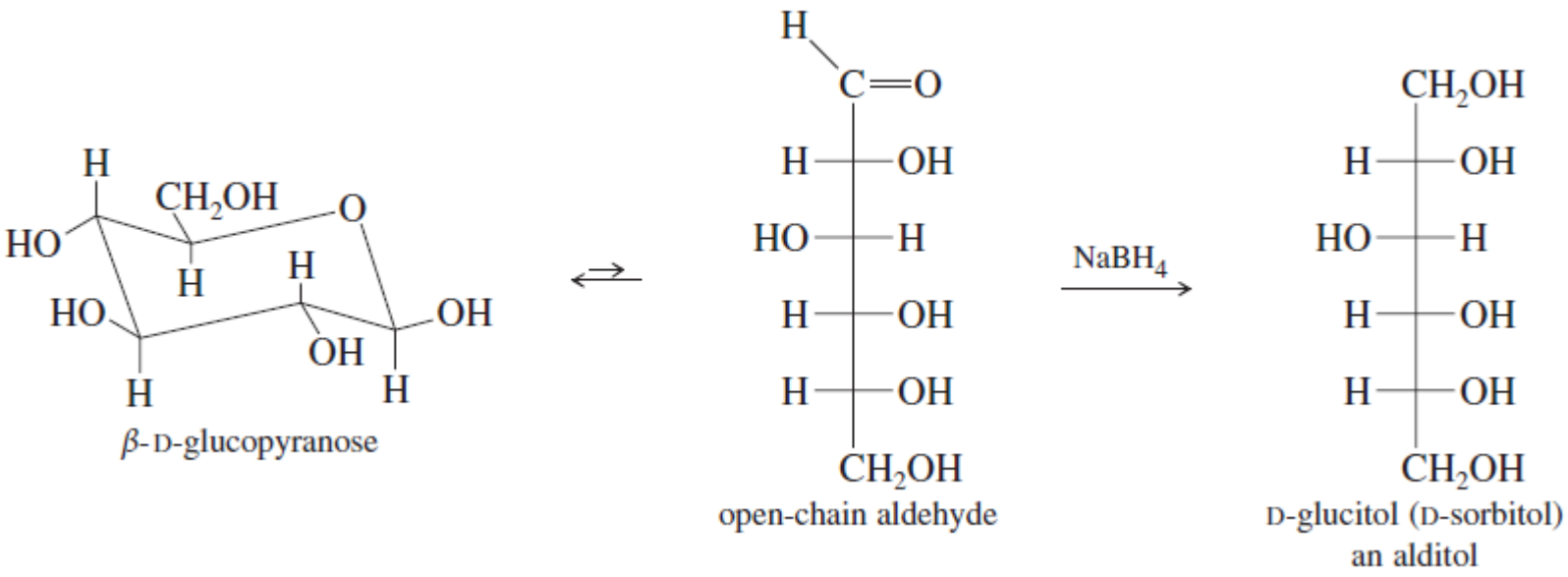


Monosaccharides – Reactions

1) Reduction

- Like other aldehydes and ketones, aldoses and ketoses can be reduced to the corresponding **polyalcohols**, called **sugar alcohols**

- The following equation shows the reduction of glucose to ***glucitol***, sometimes called ***sorbitol***

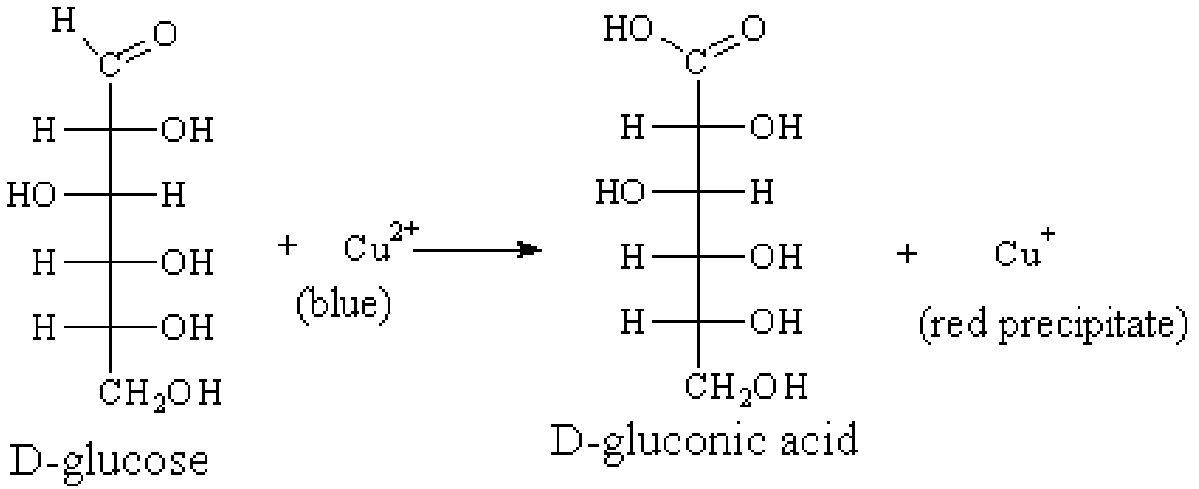


- Sorbitol is used as a **sugar substitute**

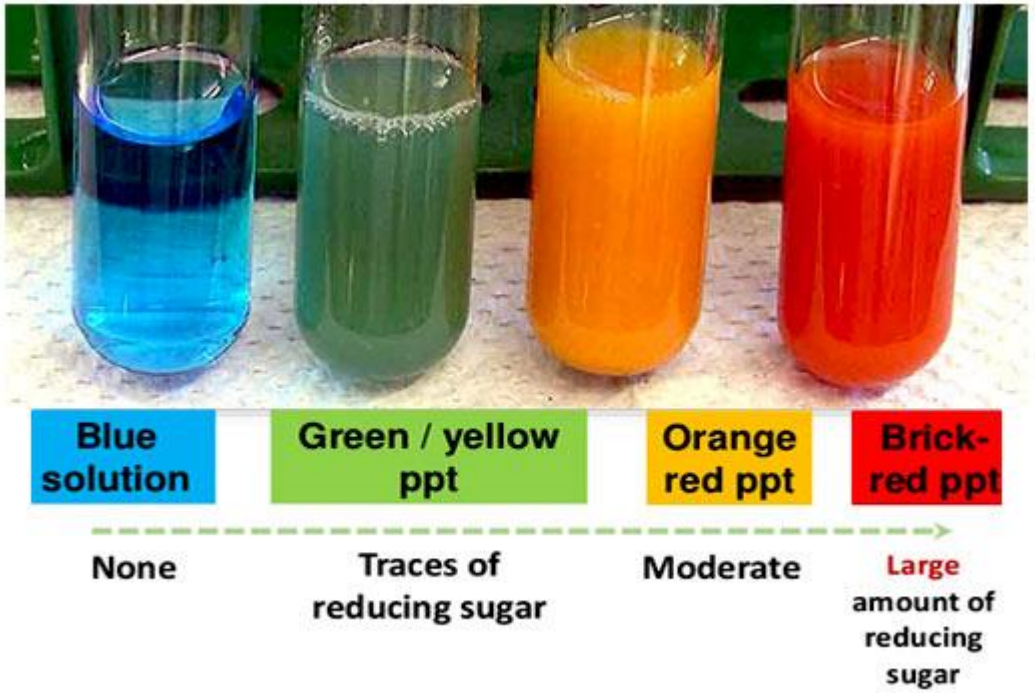
Monosaccharides – Reactions

2) Oxidation

- **Benedict's test** is a complex mixture of sodium carbonate, sodium citrate and **copper(II)** sulfate pentahydrate



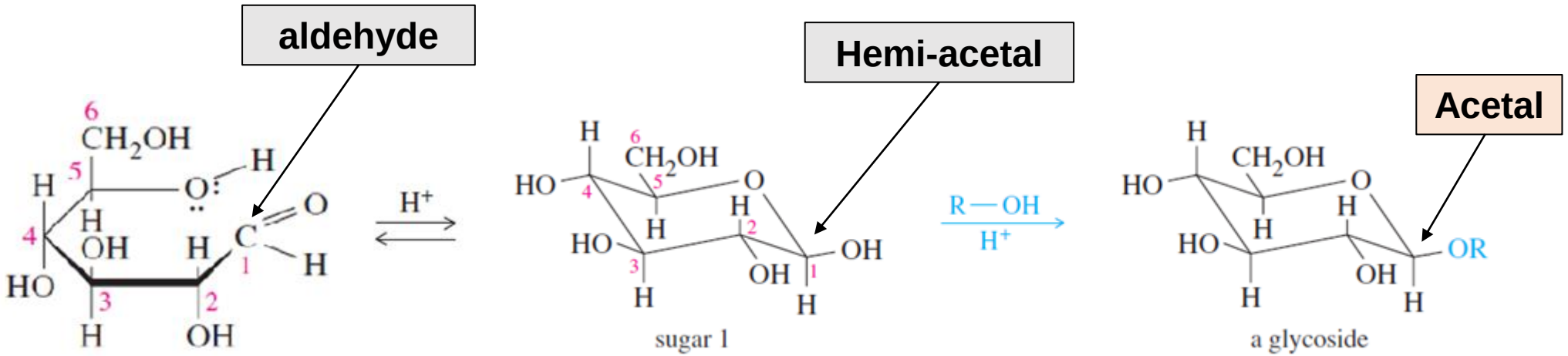
- It is commonly used to detect the presence of **reducing sugars**



Disaccharides

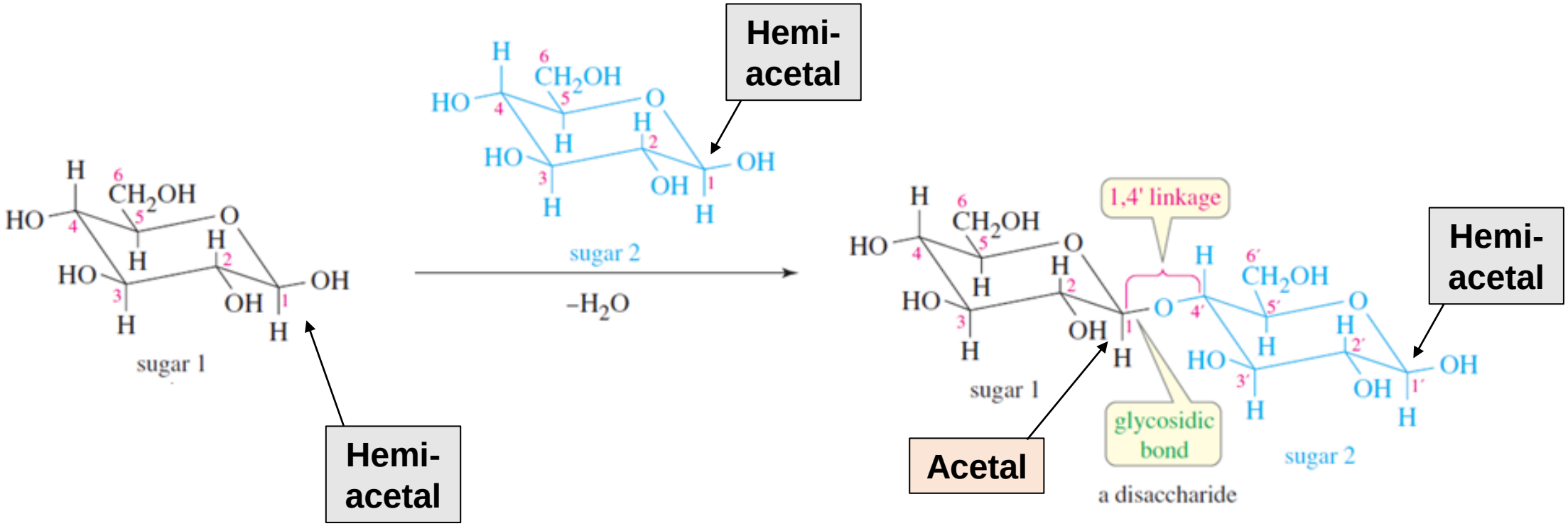
Reaction of aldehyde/ketone with aldehyde -> hemiacetal -> acetal

Compared with monosaccharide:



Disaccharides

- Contains two monosaccharides joined together by a **glycosidic linkage**

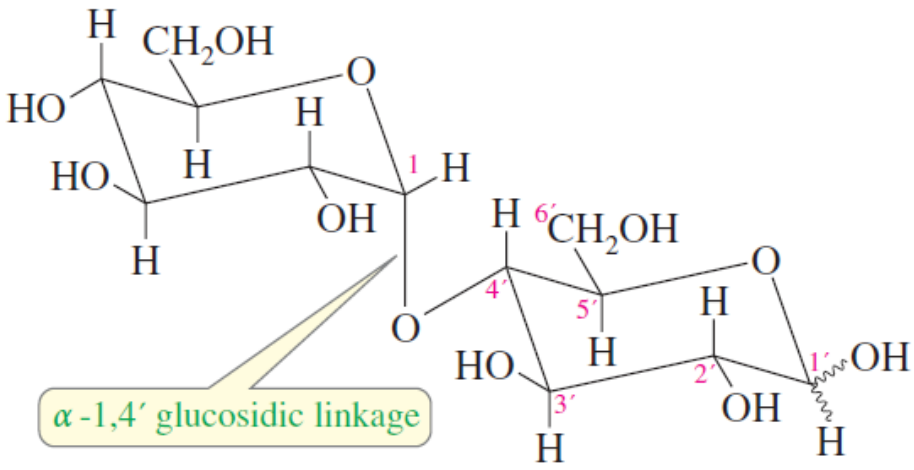


Disaccharides

- In naturally occurring disaccharides, there are **three common glycosidic bonding arrangements**

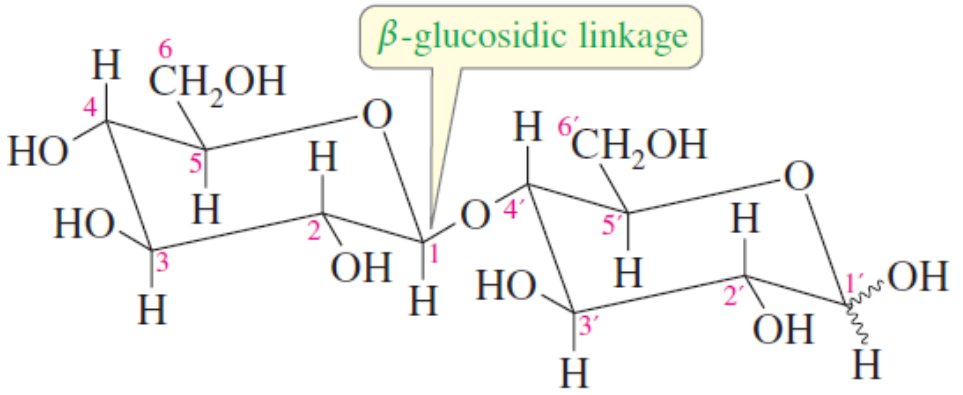
1) 1,4’ Linkage

1.1) *α*-1,4’ Linkage



Maltose, 4-O-(α-D-glucopyranosyl)-D-glucopyranose

1.2) *β*-1,4’ Linkage

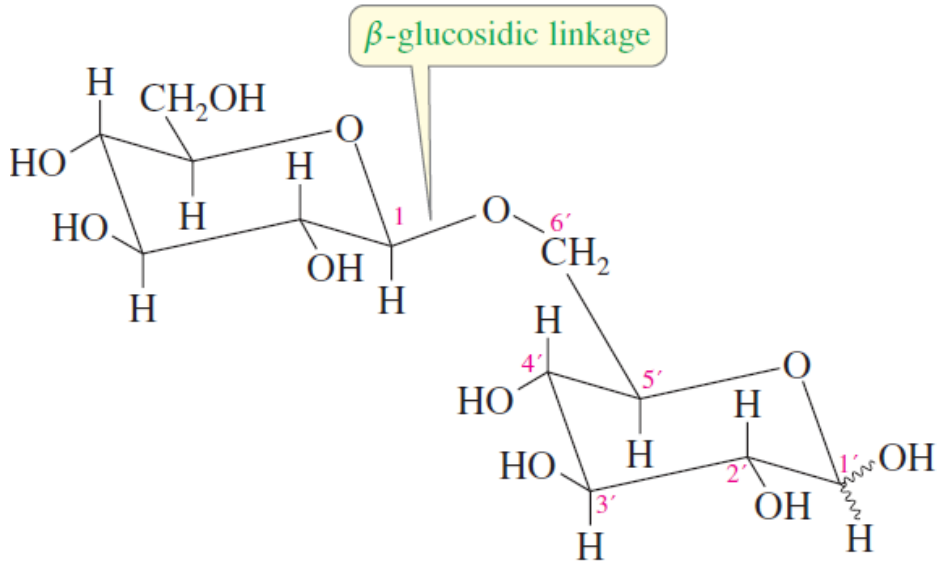


Cellobiose, 4-O-(β-D-glucopyranosyl)-D-glucopyranose

Disaccharides

2) 1,6’ Linkage

The anomeric carbon of one sugar is linked to the oxygen of the terminal carbon (C6) of another

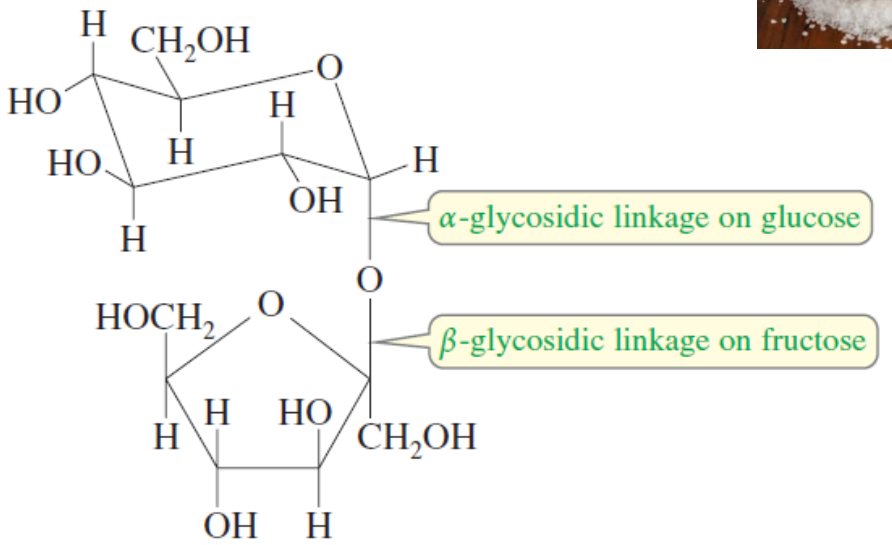


Gentiobiose, 6-O-(β-D-glucopyranosyl)-D-glucopyranose

3) 1,1’ Linkage

Joined by a direct glycosidic linkage between two anomeric carbon atoms

Both monosaccharide units in sucrose are present as **acetals**; **sucrose doesn’t reduce Benedict reagent; (non-reducing sugar)**

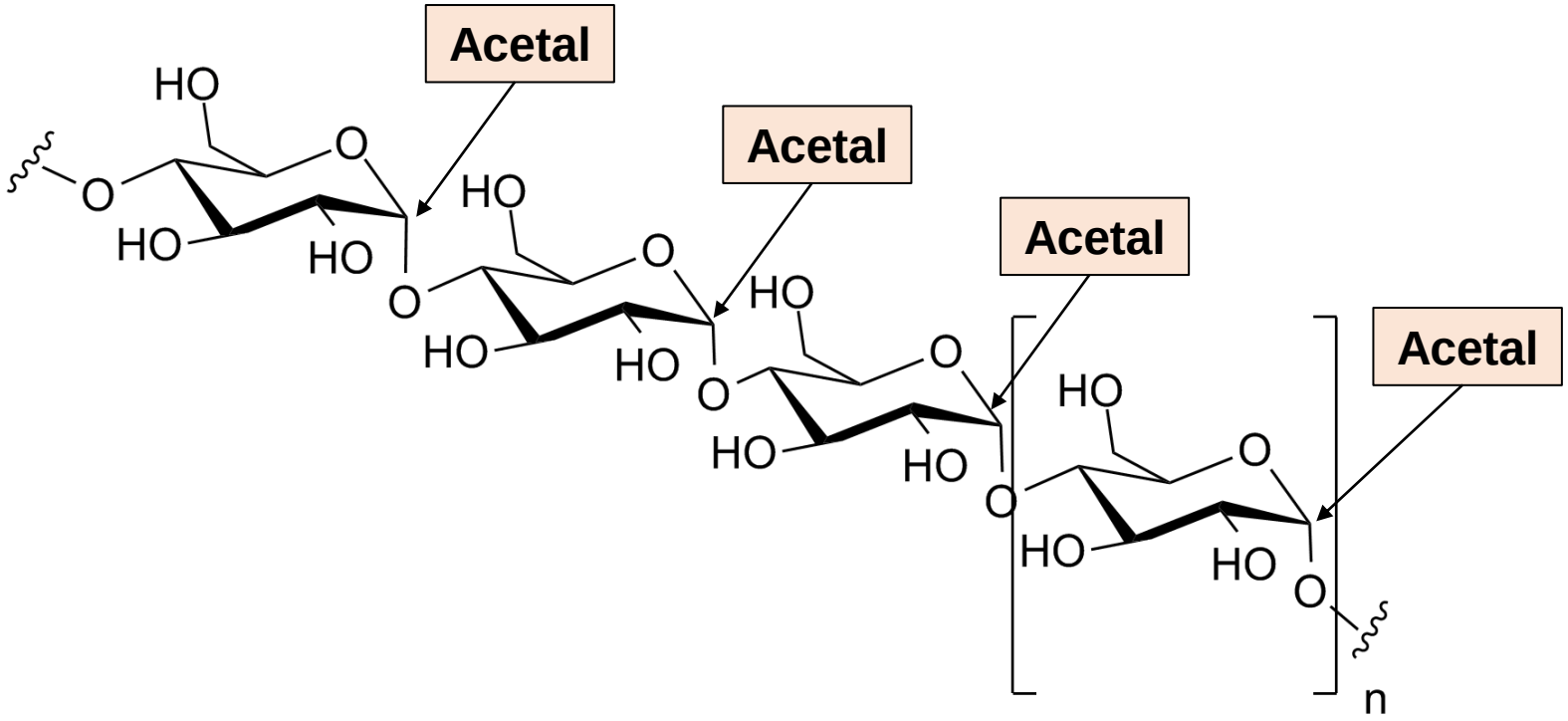


Sucrose, α-D-glucopyranosyl-β-D-fructofuranoside

Polysaccharides

- Contain **many** (usually hundreds or thousands) monosaccharide units joined by glycosidic bonds to form a **polymer chain**

- Smaller polysaccharides, containing about **three to ten** monosaccharide units, are sometimes called **oligosaccharides**

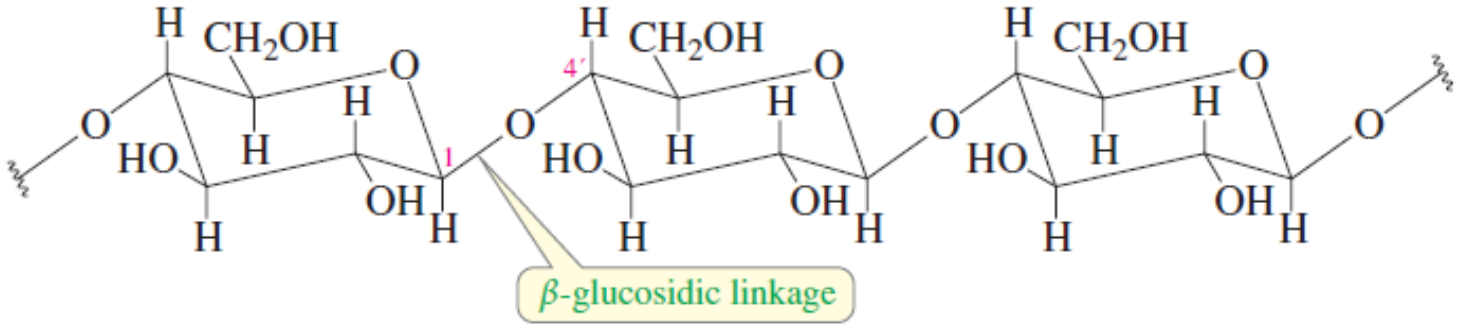


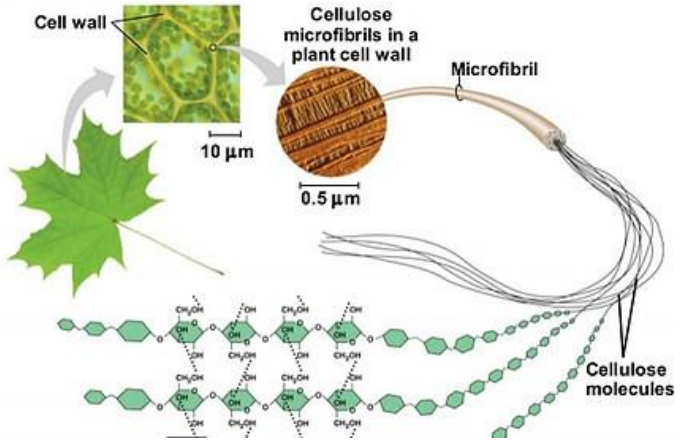
- Except for units at the ends of chains, **all the anomeric carbon** atoms of polysaccharides are involved in **acetal glycosidic links**. Therefore, polysaccharides give **no noticeable reaction with Tollens reagent**

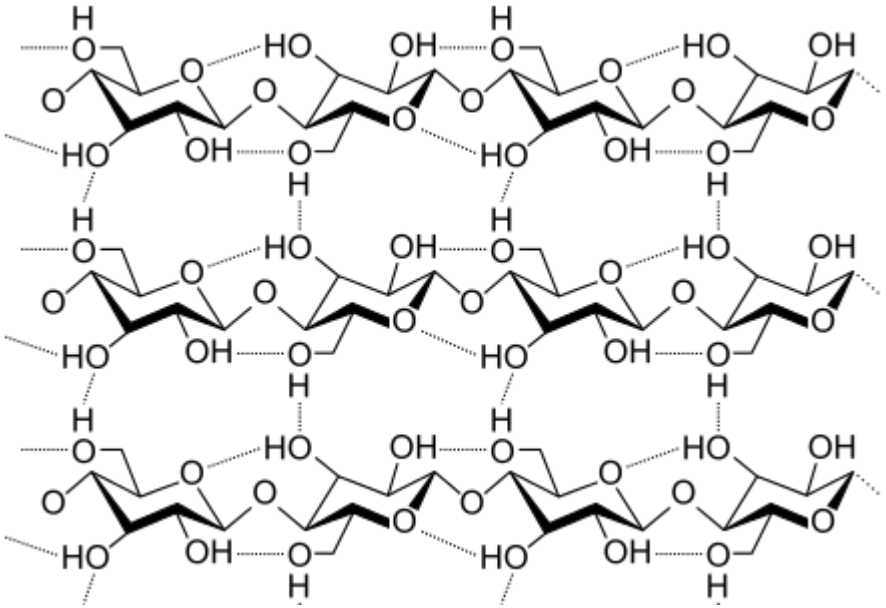
Polysaccharides

1) Cellulose

- a polymer of **D-glucose**, is the **most abundant** organic material. Cellulose is synthesised by plants as a structural material to support the weight of the plant







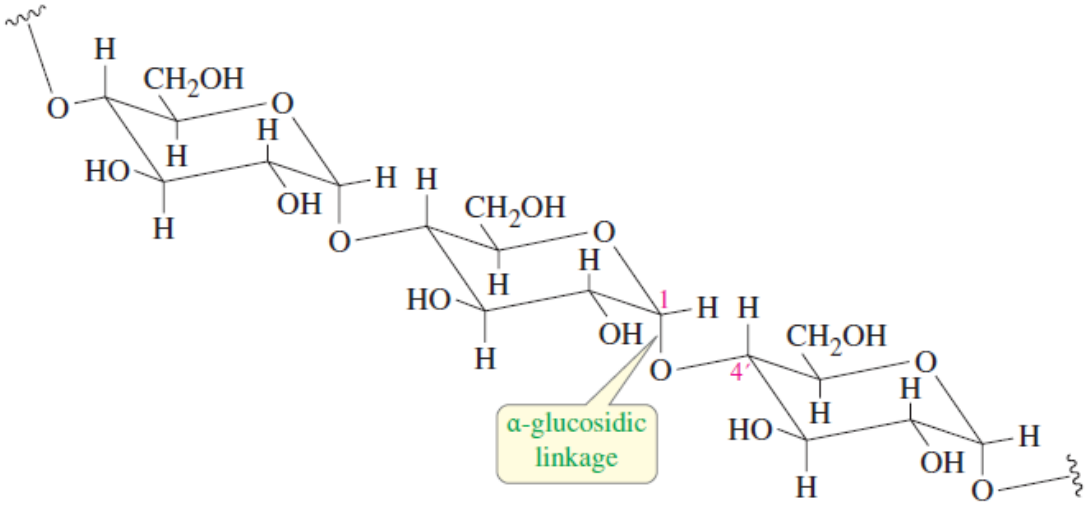
- Cellulose is composed of D-glucose units linked by ***β*-1,4' glycosidic bonds**. This bonding arrangement is rather rigid and very stable, giving cellulose desirable properties for a structural material

Polysaccharides

2) Starches

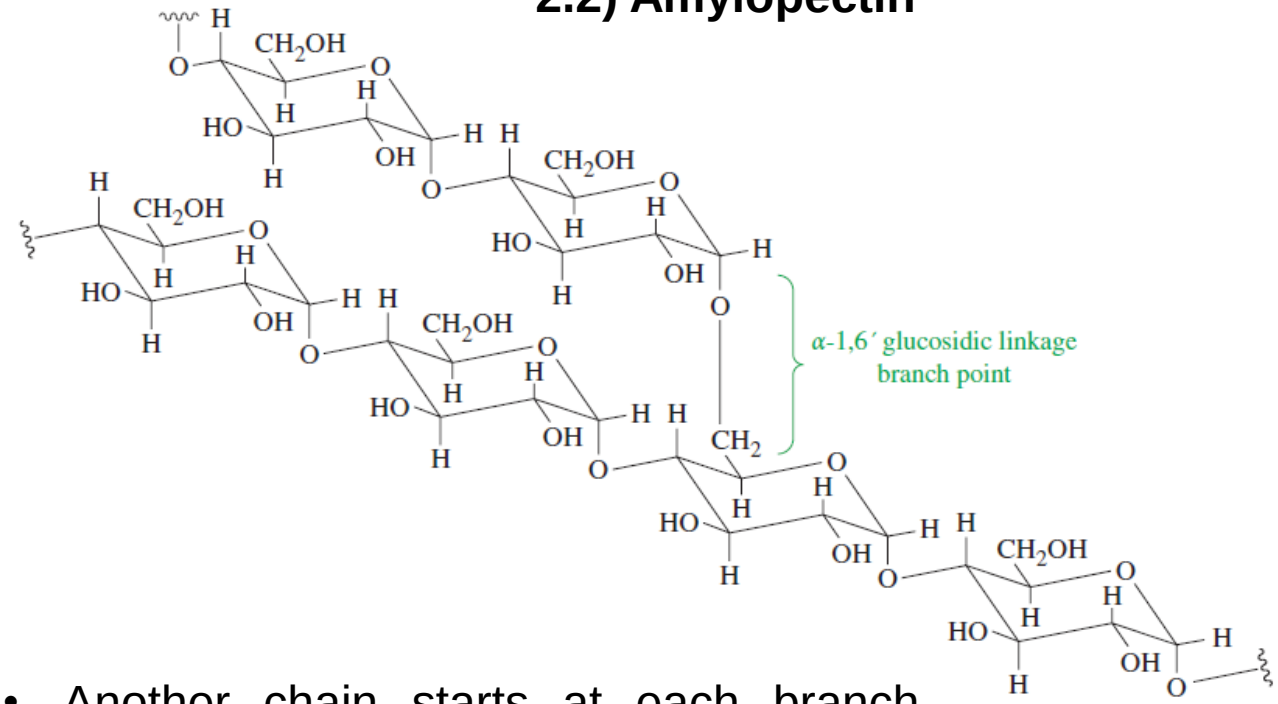
- About 20% of the starch is water-soluble ***amylose***, and the remaining 80% is water-insoluble ***amylopectin***

2.1) Amylose



- Amylose is a linear polymer of glucose with **α-1,4' glycosidic linkages**

2.2) Amylopectin



- Another chain starts at each branch point, connected to the main chain by an **α-1,6' glycosidic linkage**

Keywords:

Monosaccharide

- **Aldose / Hexose**
- **Triose / Tetrose / Pentose / Hexose / Heptose**
- **Stereogenic centers**
- **Open chain / Ring structure (hemiacetal)**
- **Reduction / Oxidation**

Disaccharide & Polysaccharide

- **Glycosidic bond (acetal) [1,4’] / [1,6’] / [1,1’]**