

# Chapter 7

## Carbohydrates



# Definition of Carbohydrates

carbohydrate: “hydrate of carbon”;  $C_n(H_2O)_m$



Examples: glucose ( $C_6H_{12}O_6$  or  $C_6(H_2O)_6$ ),  
sucrose ( $C_{12}H_{22}O_{11}$  or  $C_{12}(H_2O)_{11}$ )

saccharide: “simple sugar” group

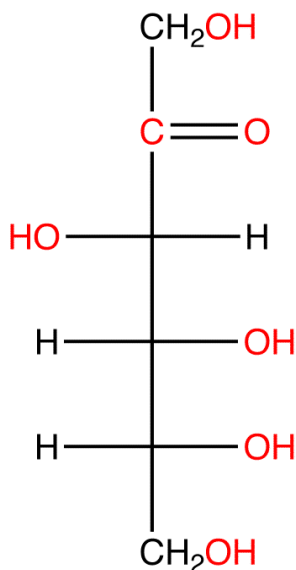
*monosaccharides, disaccharides, polysaccharides...*

monosaccharides are  $C_nH_{2n}O_n$

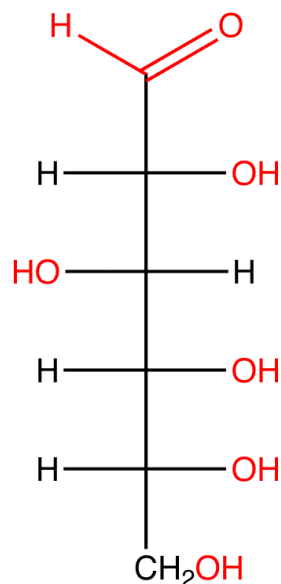
# Functional Groups

Carbohydrates can be classified as:

- Polyhydroxyaldehydes: many alcohols and an aldehyde
- Polyhydroxyketones: many alcohols and a ketone



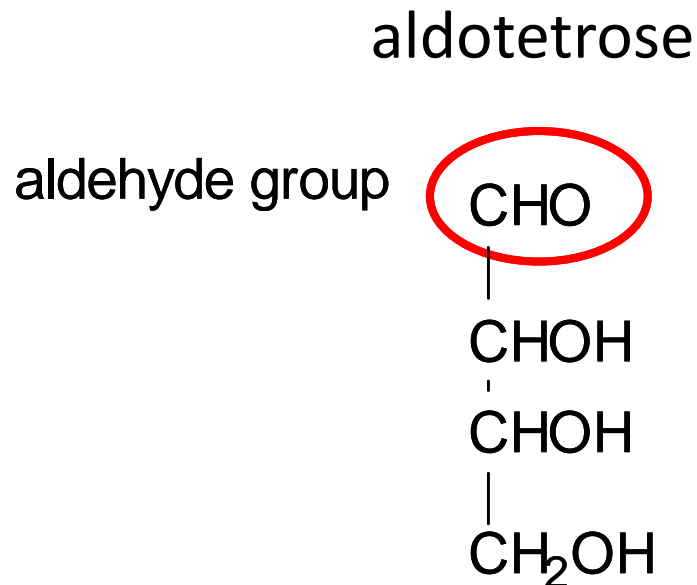
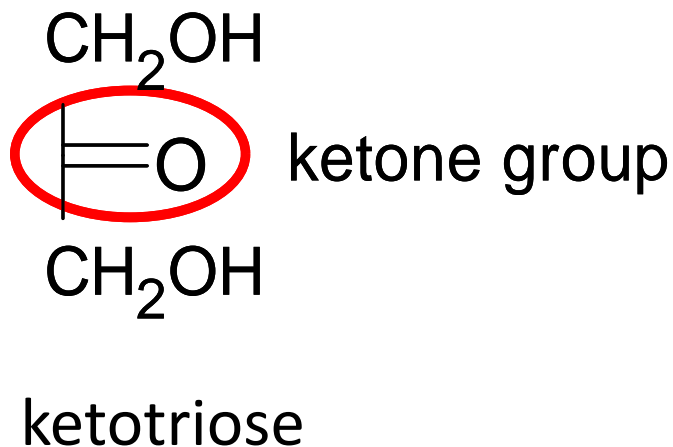
D-fructose  
(a polyhydroxy ketone)



D-glucose  
(a polyhydroxy aldehyde)

# Structure and Nomenclature

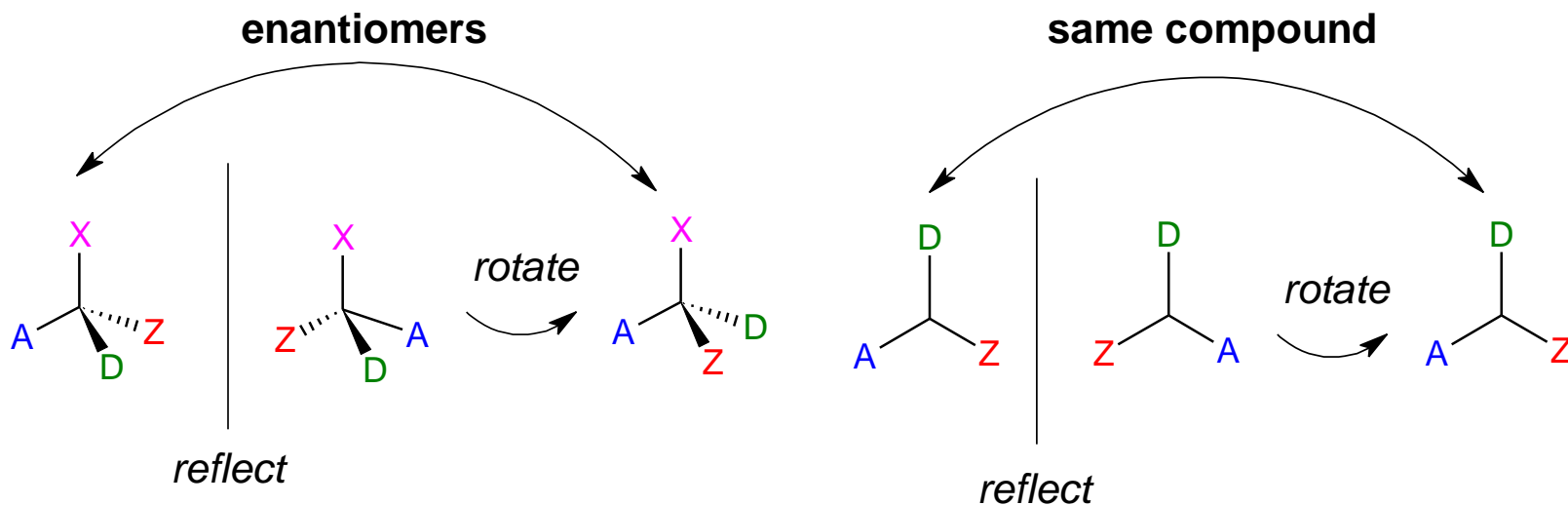
Named by the functional group + number of carbons  
(keto-) or (aldo-) + (tri-, tetr-, pent-) + -ose



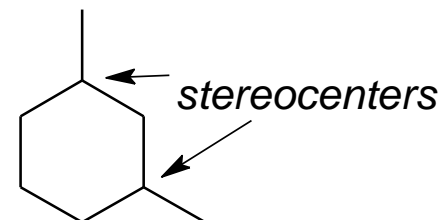
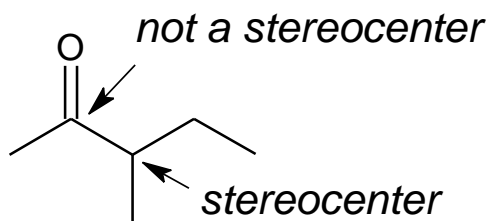
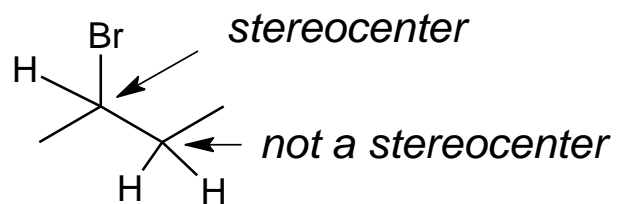
# Chirality

Stereocenter: tetrahedral carbon with four different substituents

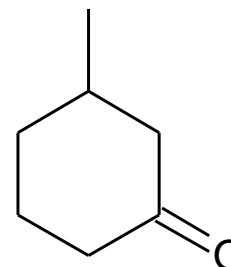
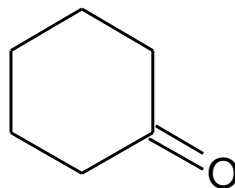
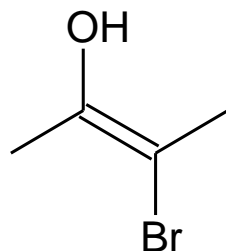
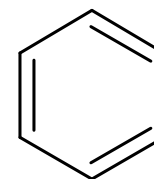
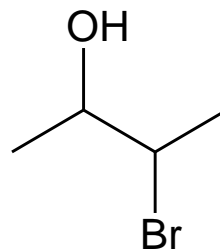
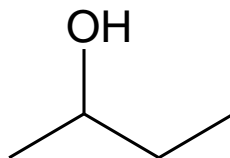
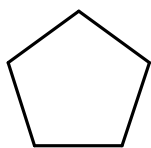
*chiral carbon*  
or *asymmetric center*



# Stereocenters

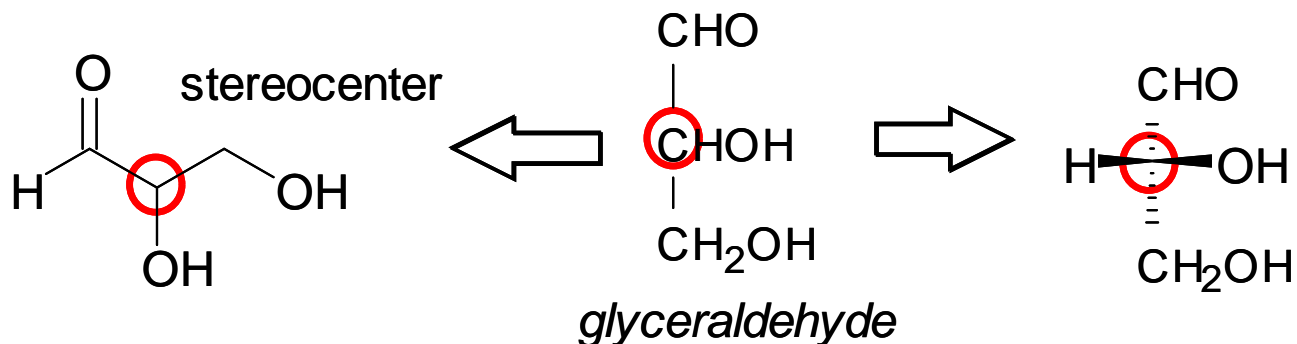


How many chiral carbons are in:



# Fisher Projections

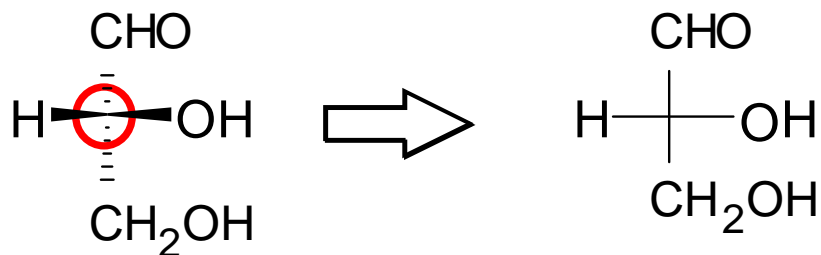
Glyceraldehyde: an aldotriose



Fisher Projection: two-dimensional representation of stereocenters as the only atoms in plane

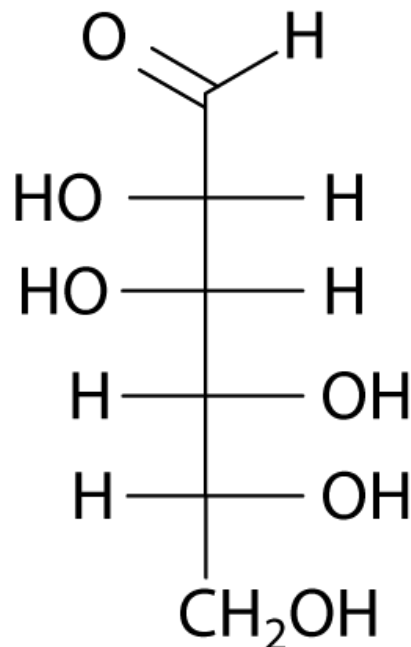
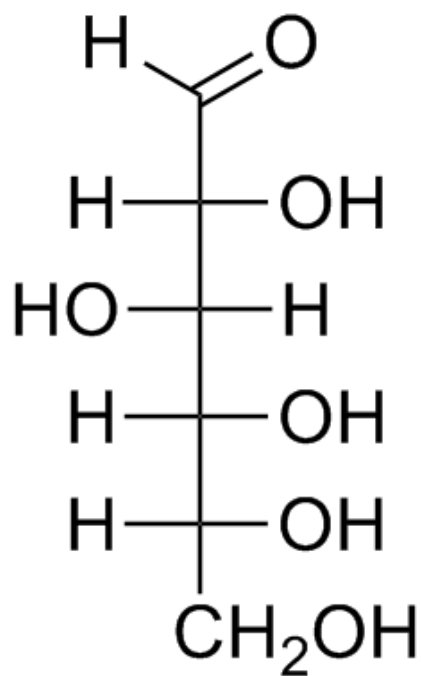
Wedges (toward you) are *horizontal*

Dashes (away from you) are *vertical*



# Chirality in Carbohydrates

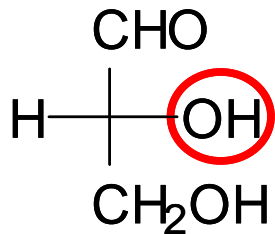
How many chiral carbons are present?



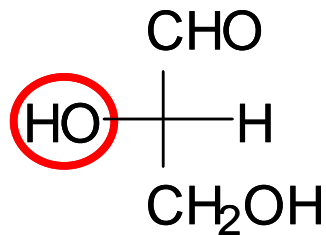
Are these structures (1) enantiomers, (2) constitutional isomers, or (3) neither?

# D and L Configuration

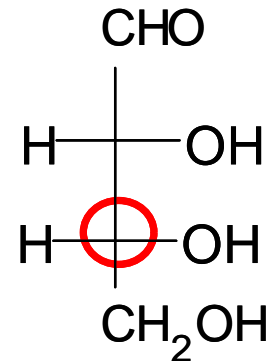
Sugars are designated with **D** (right) and **L** (left).



D-glyceraldehyde

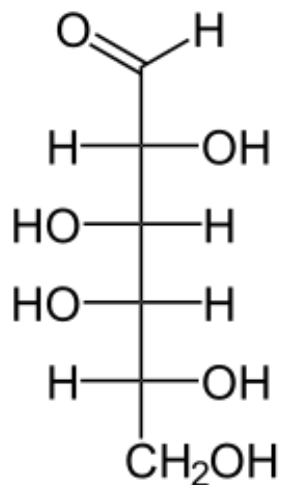


L-glyceraldehyde

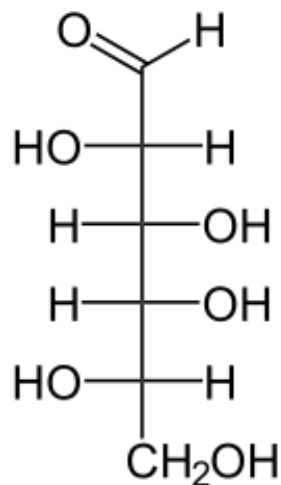


D-erythrose

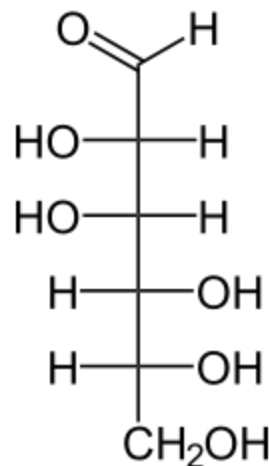
# D and L Configuration



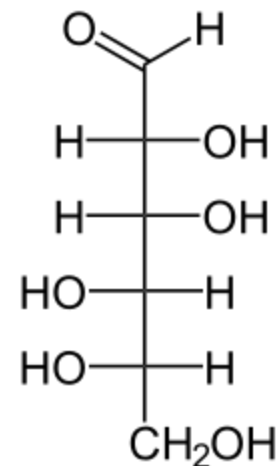
D-Galactose



L-Galactose



D-Mannose



L-Mannose

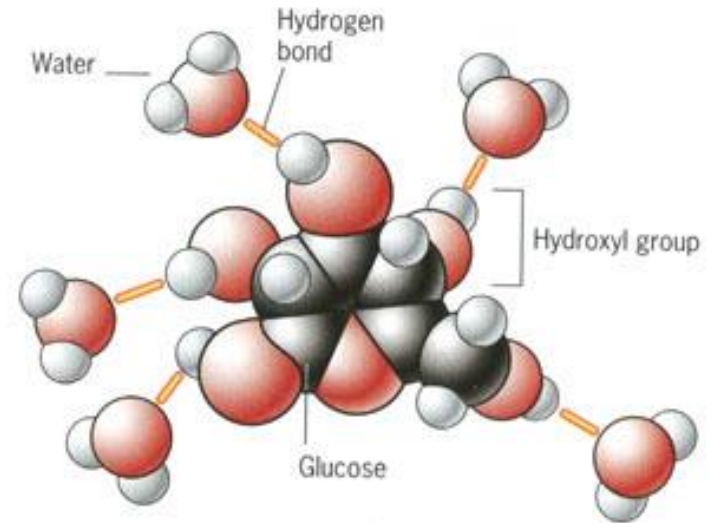
# Physical Properties

Most are colorless,  
crystalline solids with a  
sweet taste (sugars).



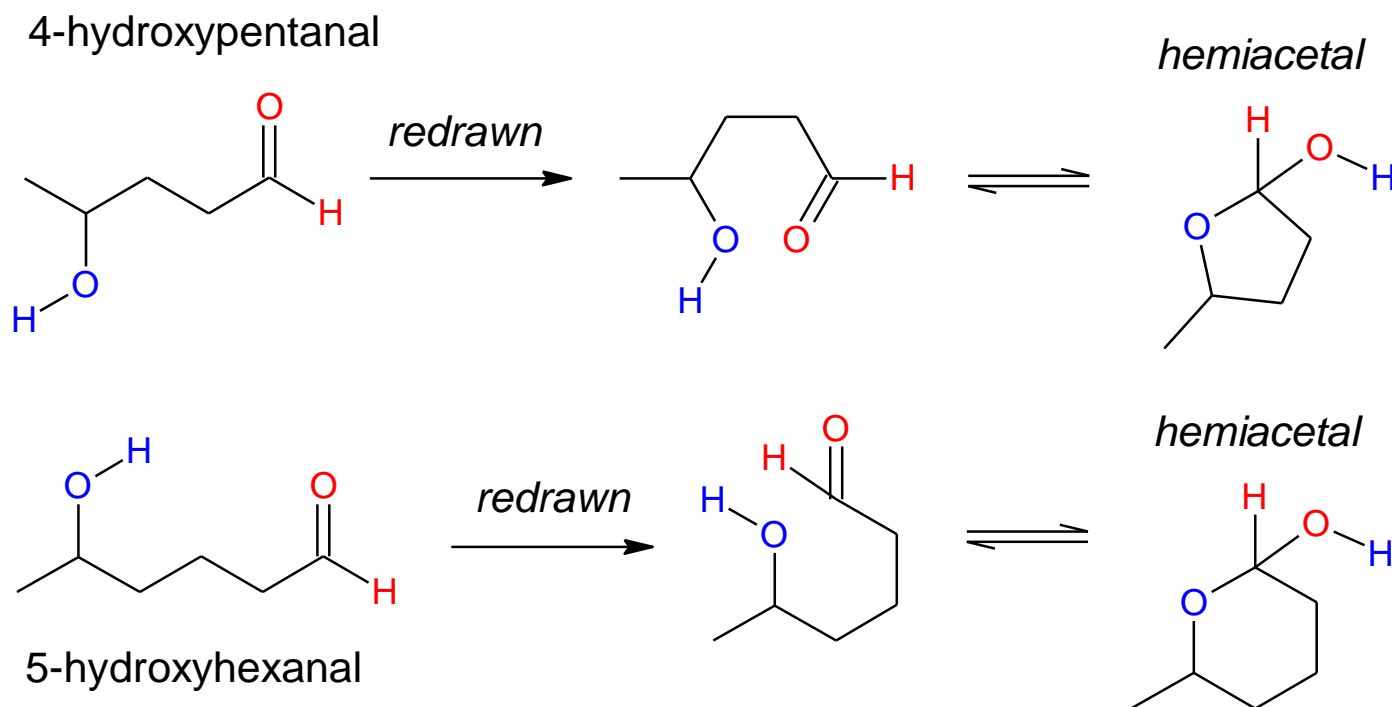
The many alcohols make the  
compounds extremely  
polar.

- All three intermolecular forces
- Very water-soluble



# Hemiacetals

Hydroxyaldehydes will form *hemiacetals*.



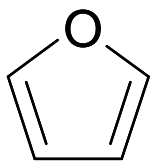
Are these isomers or different compounds?

How many stereocenters are in the hydroxyaldehydes?

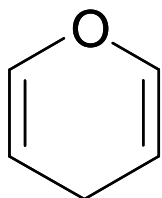
How many are in the hemiacetals?

# Furanose and Pyranose

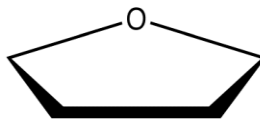
The cyclic hemiacetal forms are *particularly* stable when forming a 5- or 6-membered ring.



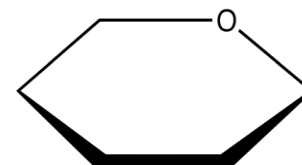
furan



pyran



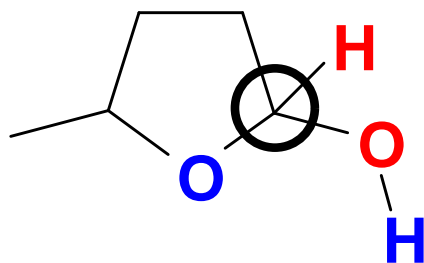
furanose ring



pyranose ring

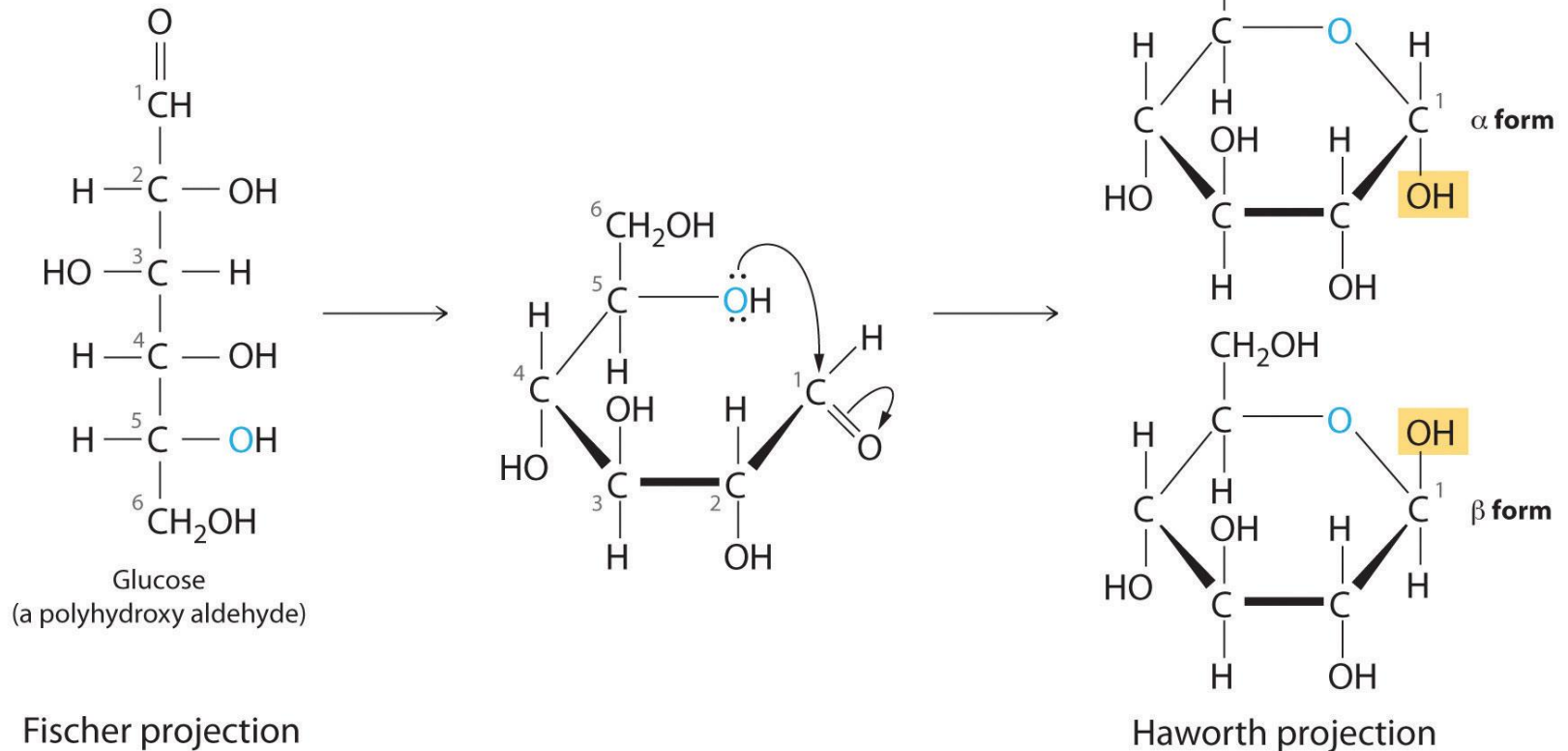
Furanose: 5-membered

Pyranose: 6-membered



anomeric carbon: *new* stereocenter  
created in forming the cyclic hemiacetal

# Haworth Projections

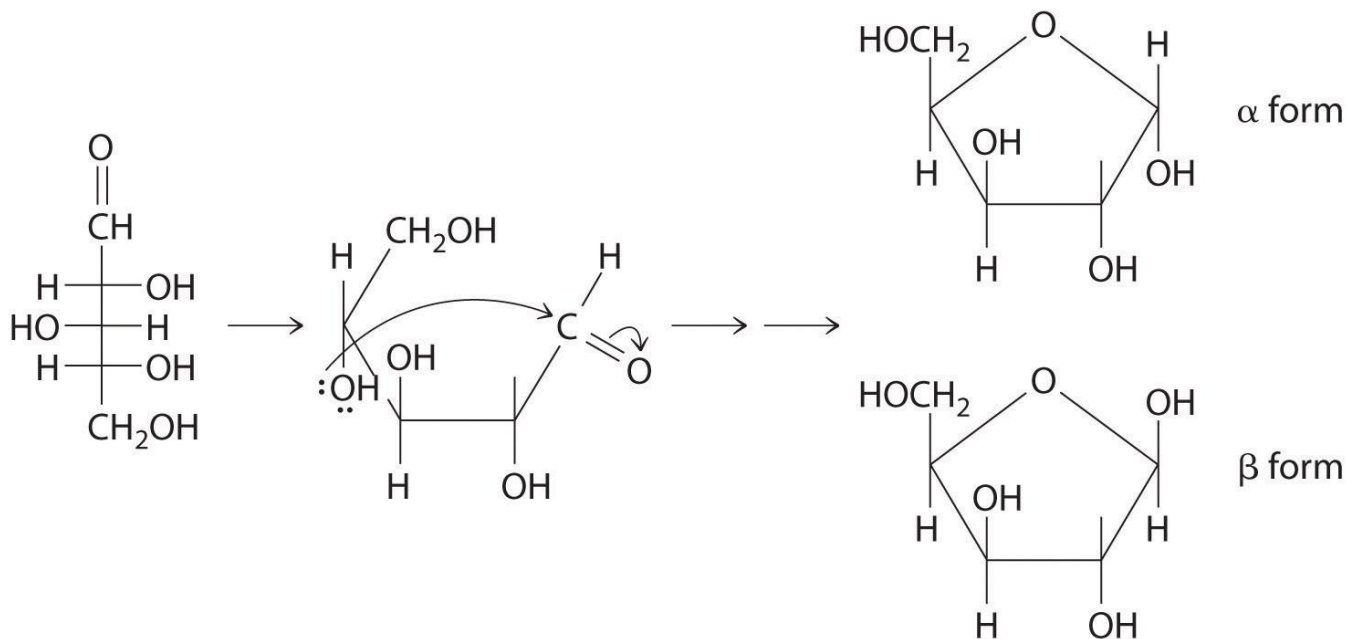


**Left** in Fisher → up from ring

**Right** in Fisher → down from ring

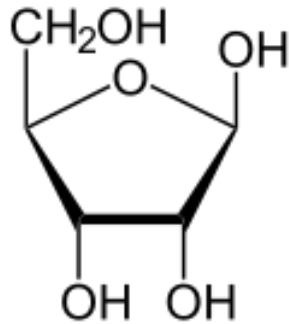
Anomeric carbon's alcohol can be *either* up or down.

# Haworth Projections

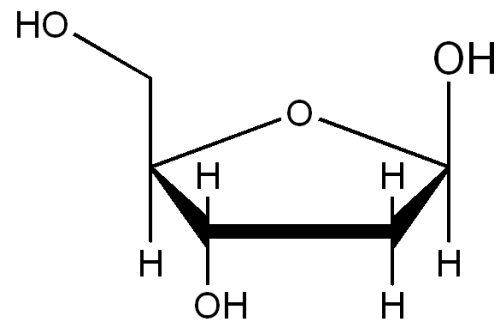


Oxygen in the ring is always pointed *backwards*.  
Anomeric carbon is always to the *right*.  
All three isomers exist in in equilibrium.

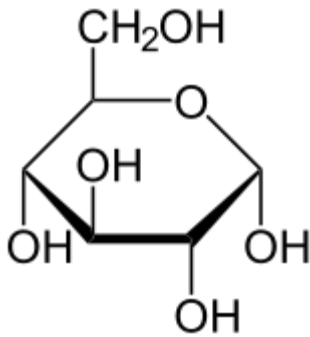
# Important Monosaccharides



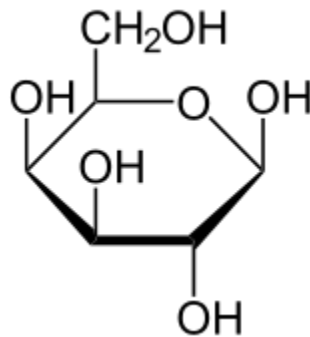
$\beta$ -ribose



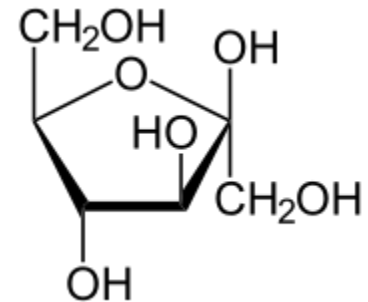
$\beta$ -deoxyribose



$\beta$ -glucose



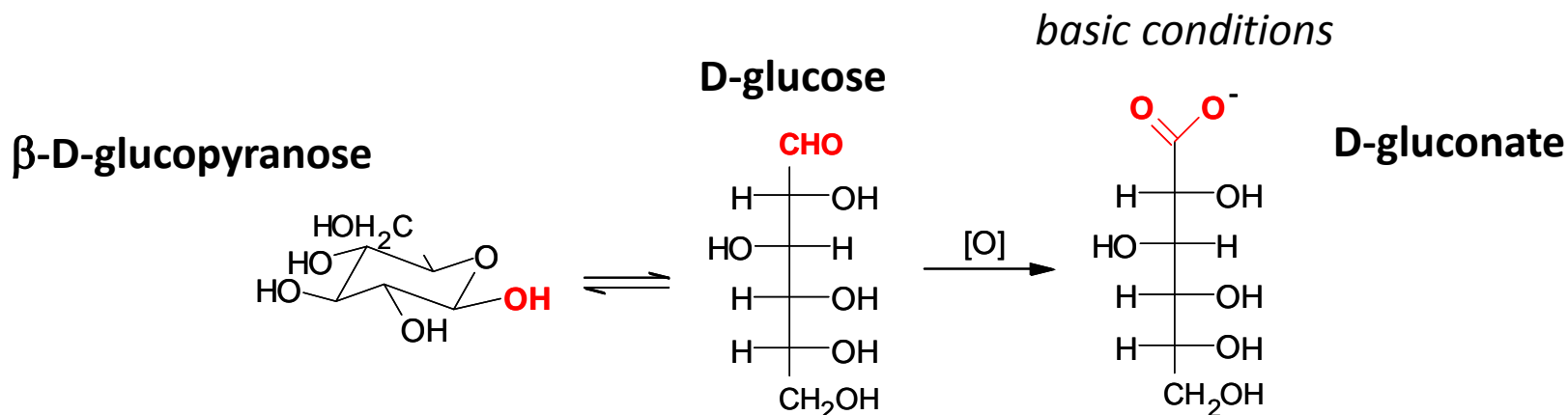
$\beta$ -galactose



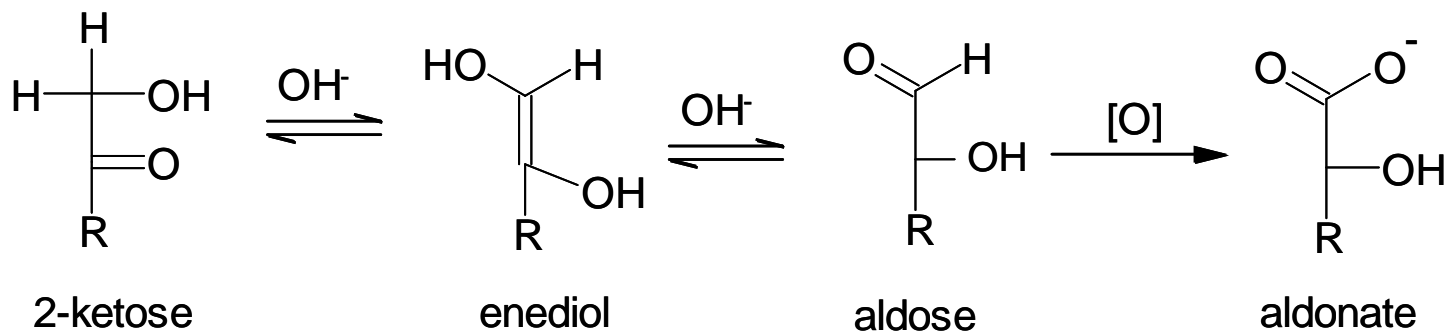
$\beta$ -fructose

# Oxidation

reducing sugar: carbohydrate that reacts with an oxidizing agent



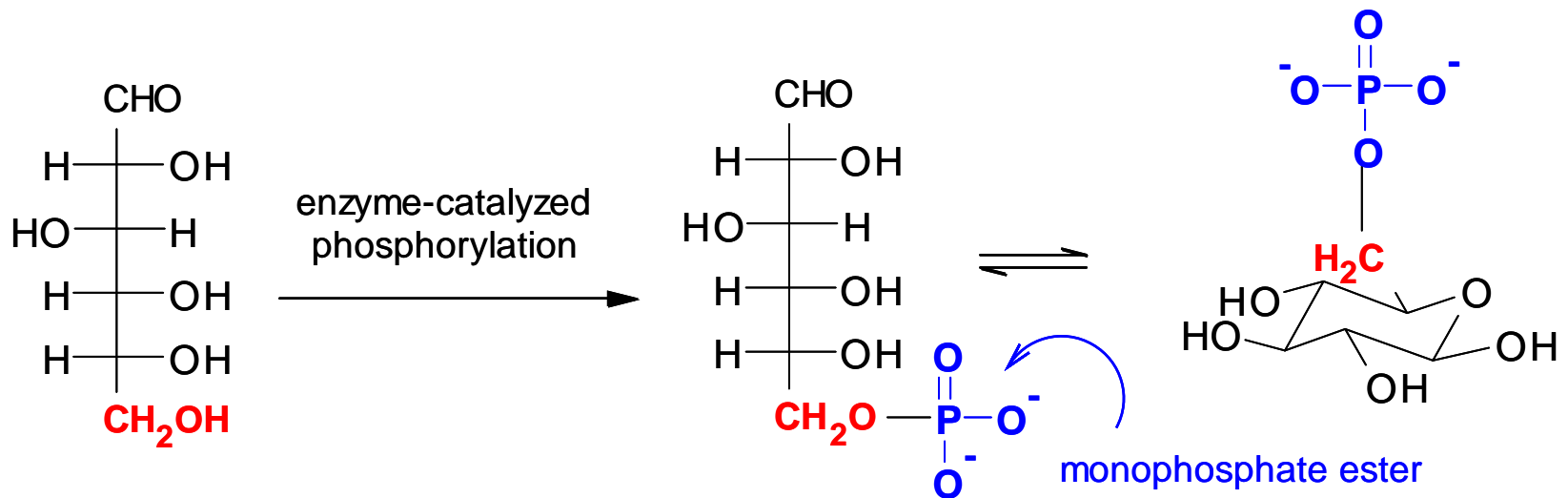
2-ketoses are also reducing sugars.



# Formation of Phosphate Esters

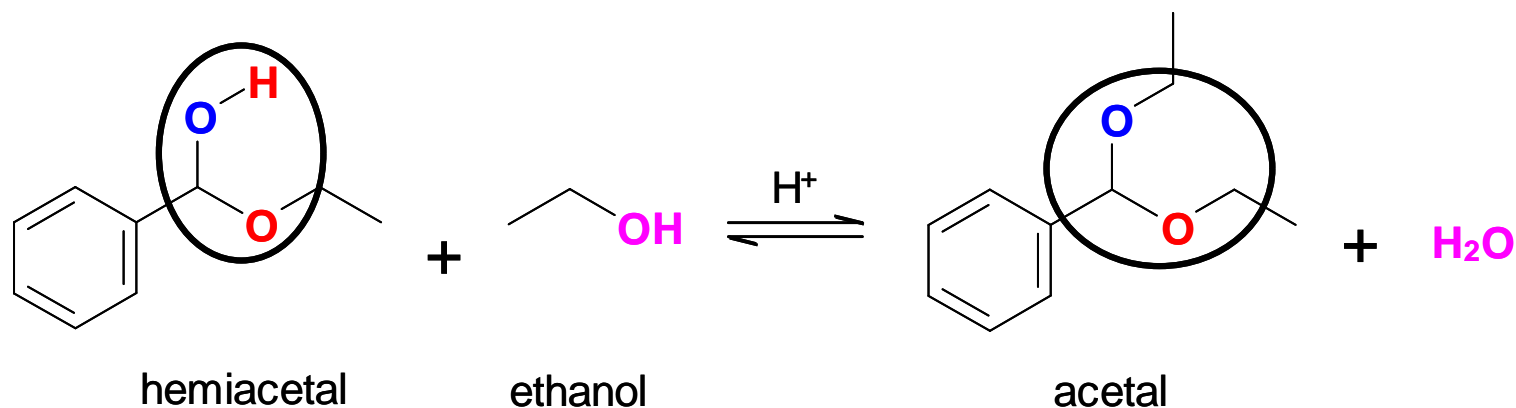
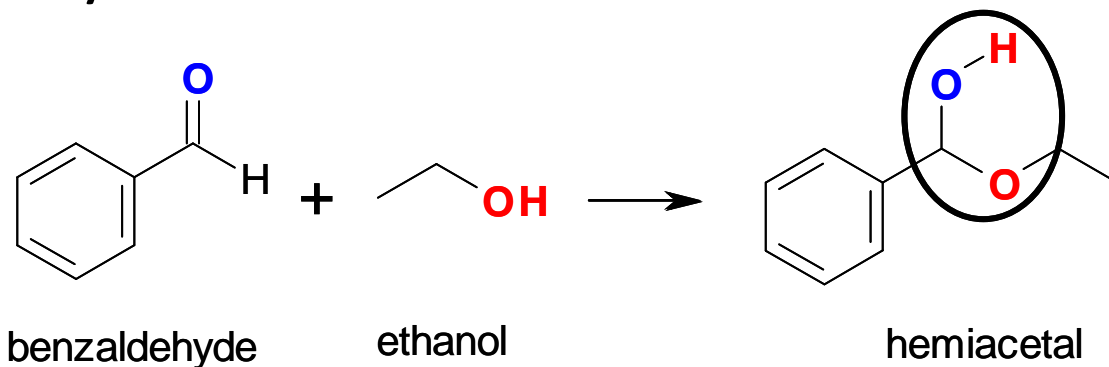
Mono- and diphosphoric esters serve as intermediates in the metabolism of monosaccharides.

phosphorylation: addition of a phosphate ester



# Formation of Acetals

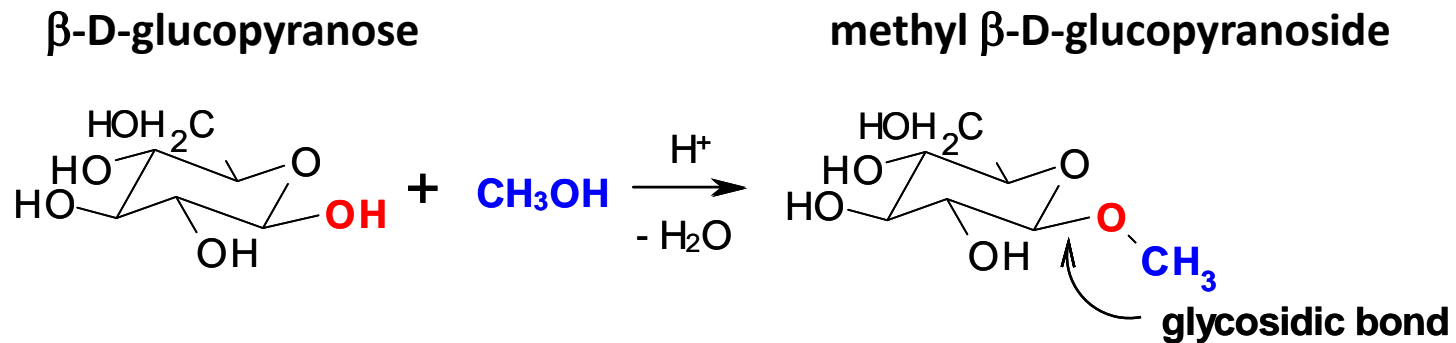
Recall: aldehyde or ketone + alcohol  $\rightarrow$  hemiacetal



# Glycosides

Addition of an alcohol to a monosaccharide in acidic conditions will form a *glycoside*.

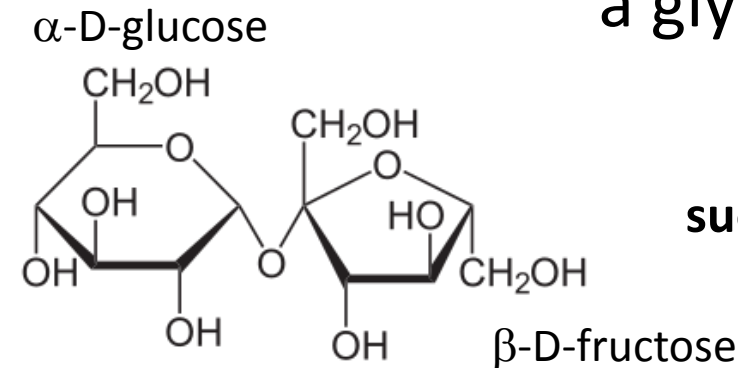
glycoside: cyclic acetal derived from a monosaccharide



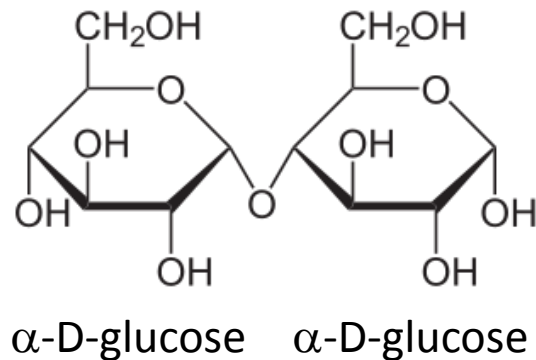
glycosidic bond: bond between the anomeric carbon and the new  $-\text{OR}$  group formed during the conversion to an acetal

# Disaccharides

disaccharide: two sugar units linked through a glycosidic bond

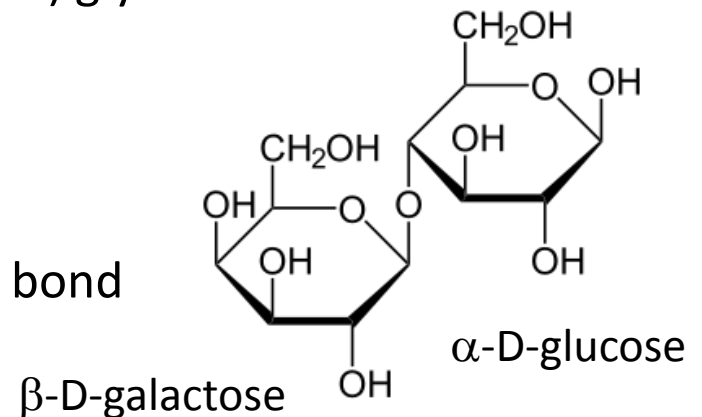


**sucrose:**  $\alpha(1 \rightarrow 2)$  glycosidic bond

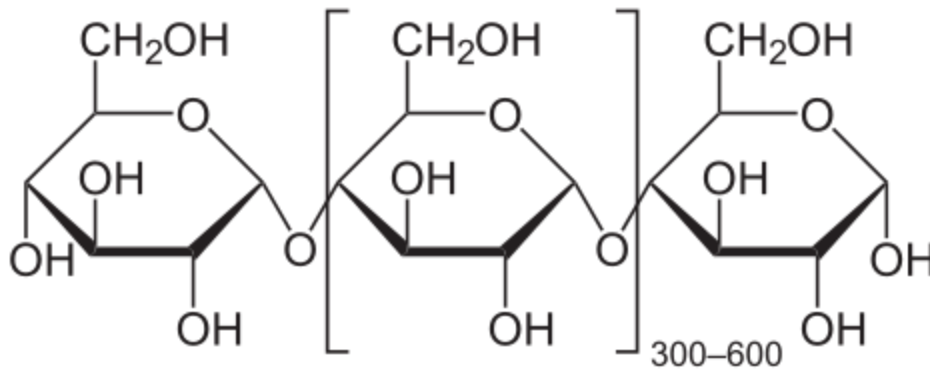


**maltose:**  $\alpha(1 \rightarrow 4)$  glycosidic bond

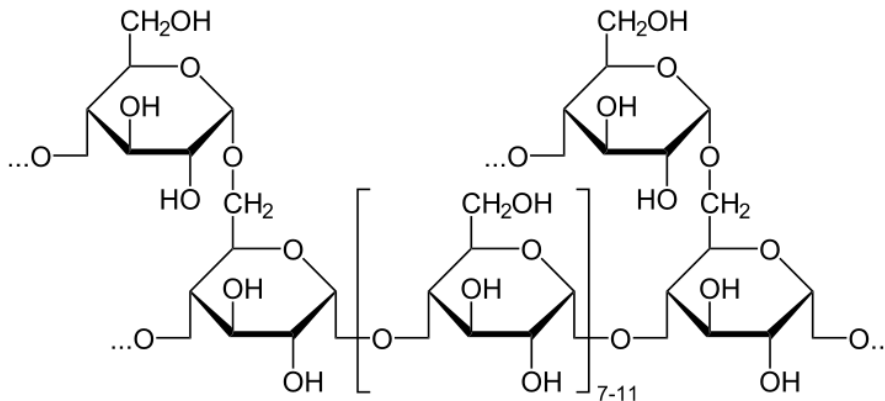
**lactose:**  $\beta(1 \rightarrow 4)$  glycosidic bond



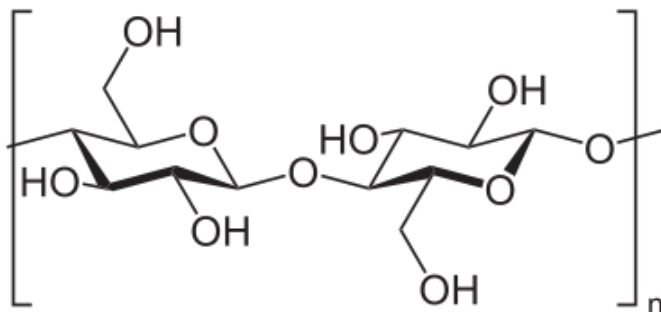
# Polysaccharides



**starch:** polymer of D-glucose units connected with  $\alpha(1\rightarrow4)$  linkages



**glycogen:** polymer of D-glucose units connected with  $\alpha(1\rightarrow4)$  and  $\alpha(1\rightarrow6)$  linkages



**cellulose:** polymer of D-glucose units connected with  $\beta(1\rightarrow4)$  linkages