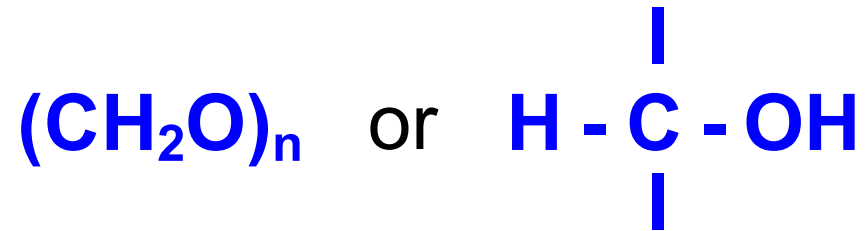


# Carbohydrates

**Carbohydrates** (glycans) have the following basic composition:

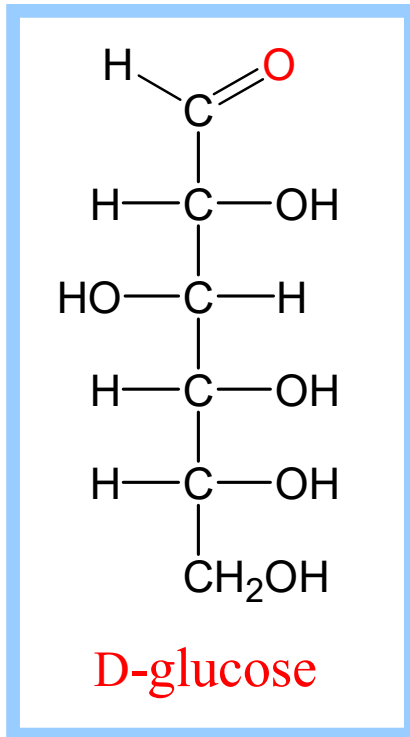


# Classification

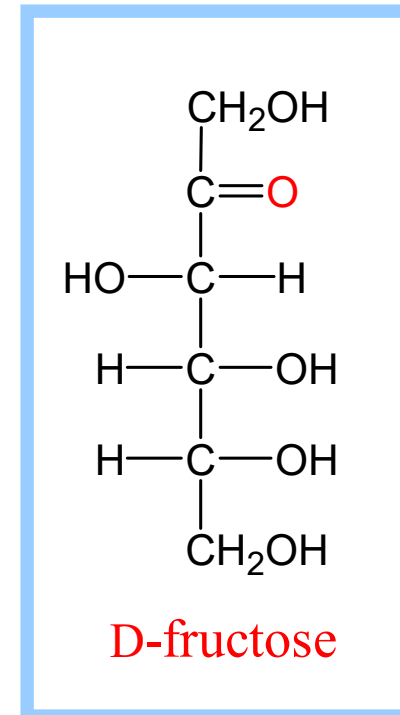
- ♦ **Monosaccharides** - simple sugars with multiple OH groups. Based on number of carbons (3, 4, 5, 6), a monosaccharide is a **triose**, **tetrose**, **pentose** or **hexose**.
- ♦ **Disaccharides** - 2 monosaccharides covalently linked.
- ♦ **Oligosaccharides** - a few monosaccharides covalently linked.
- ♦ **Polysaccharides** - polymers consisting of chains of monosaccharide or disaccharide units.

# Monosaccharides

**Aldoses** (e.g., glucose) have an **aldehyde** group at one end.



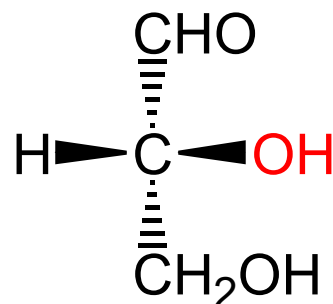
**Ketoses** (e.g., fructose) have a **keto** group, usually at C2.



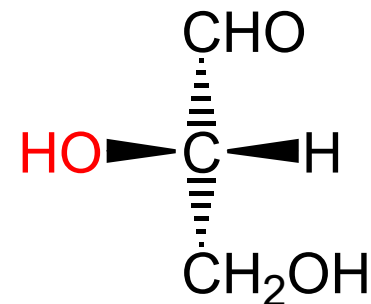
# D vs L Designation

D & L designations are based on the configuration about the single asymmetric C in **glyceraldehyde**.

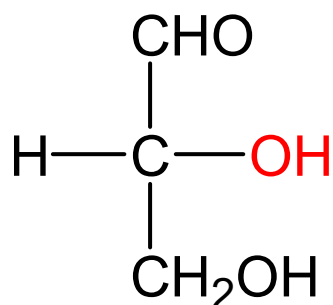
The lower representations are **Fischer Projections**.



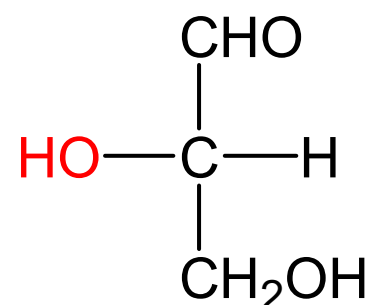
D-glyceraldehyde



L-glyceraldehyde



D-glyceraldehyde

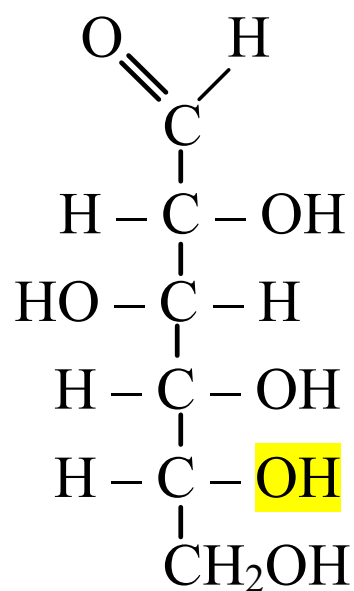


L-glyceraldehyde

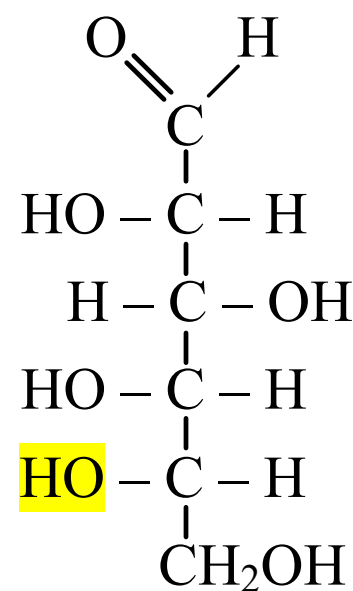
# Sugar Nomenclature

For sugars with more than one chiral center, **D** or **L** refers to the asymmetric **C** farthest from the aldehyde or keto group.

Most naturally occurring sugars are D isomers.



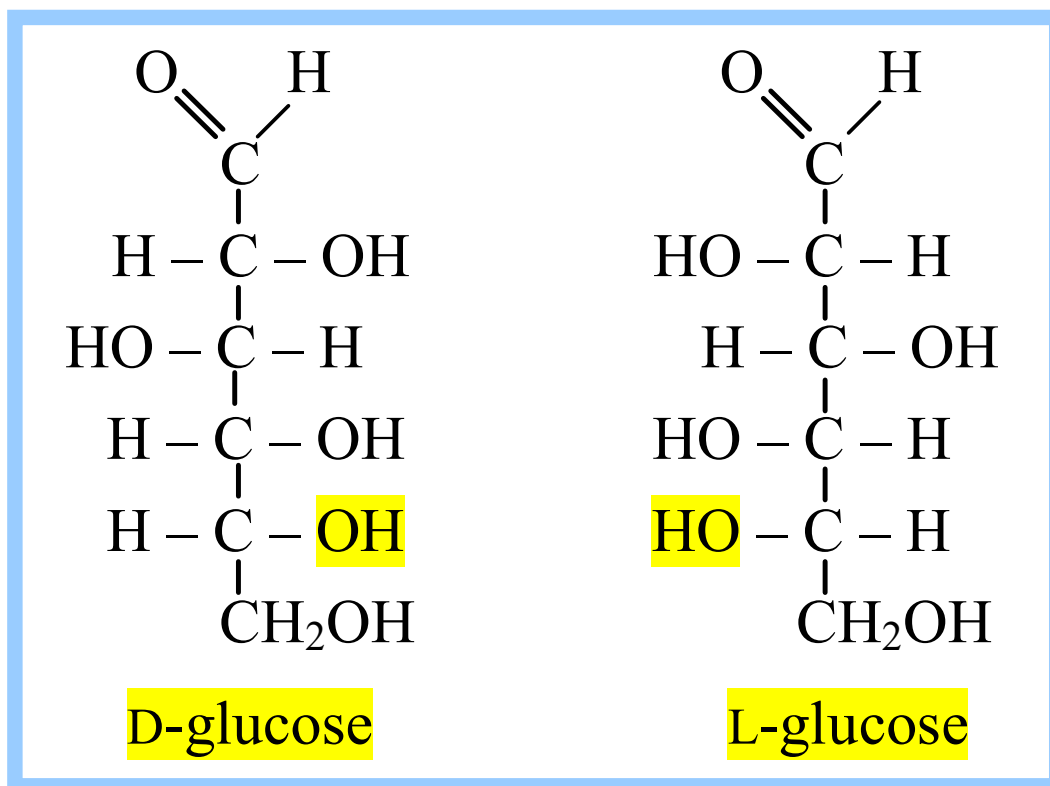
D-glucose



L-glucose

D & L sugars are mirror images of one another.

They have the **same name**, e.g., D-glucose & L-glucose.

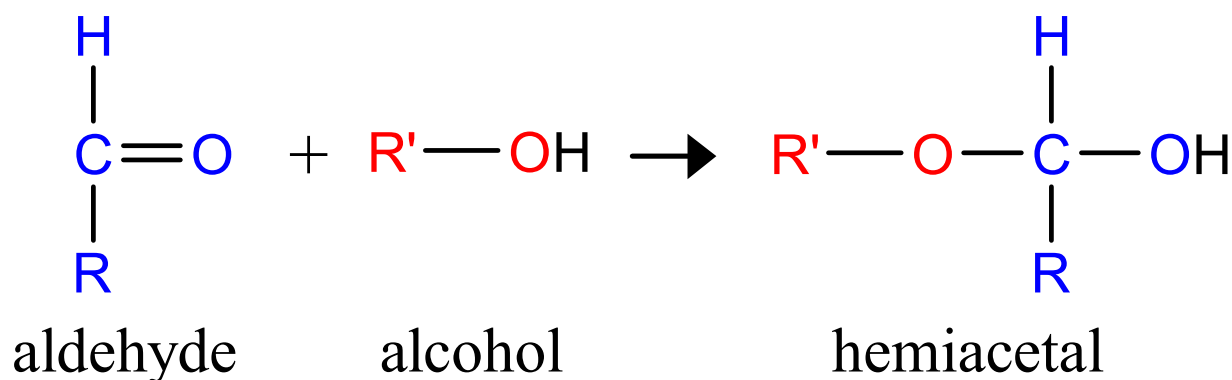


The number of stereoisomers is  $2^n$ , where  $n$  is the number of asymmetric centers.

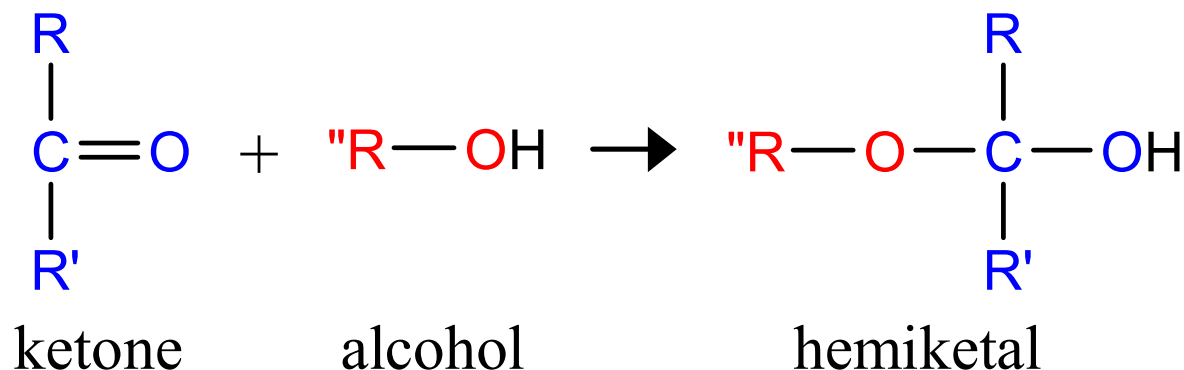
The 6-C aldoses have 4 asymmetric centers. Thus there are **16 stereoisomers** (8 D-sugars and 8 L-sugars).

# Hemiacetal & hemiketal formation

An aldehyde can react with an alcohol to form a **hemiacetal**.

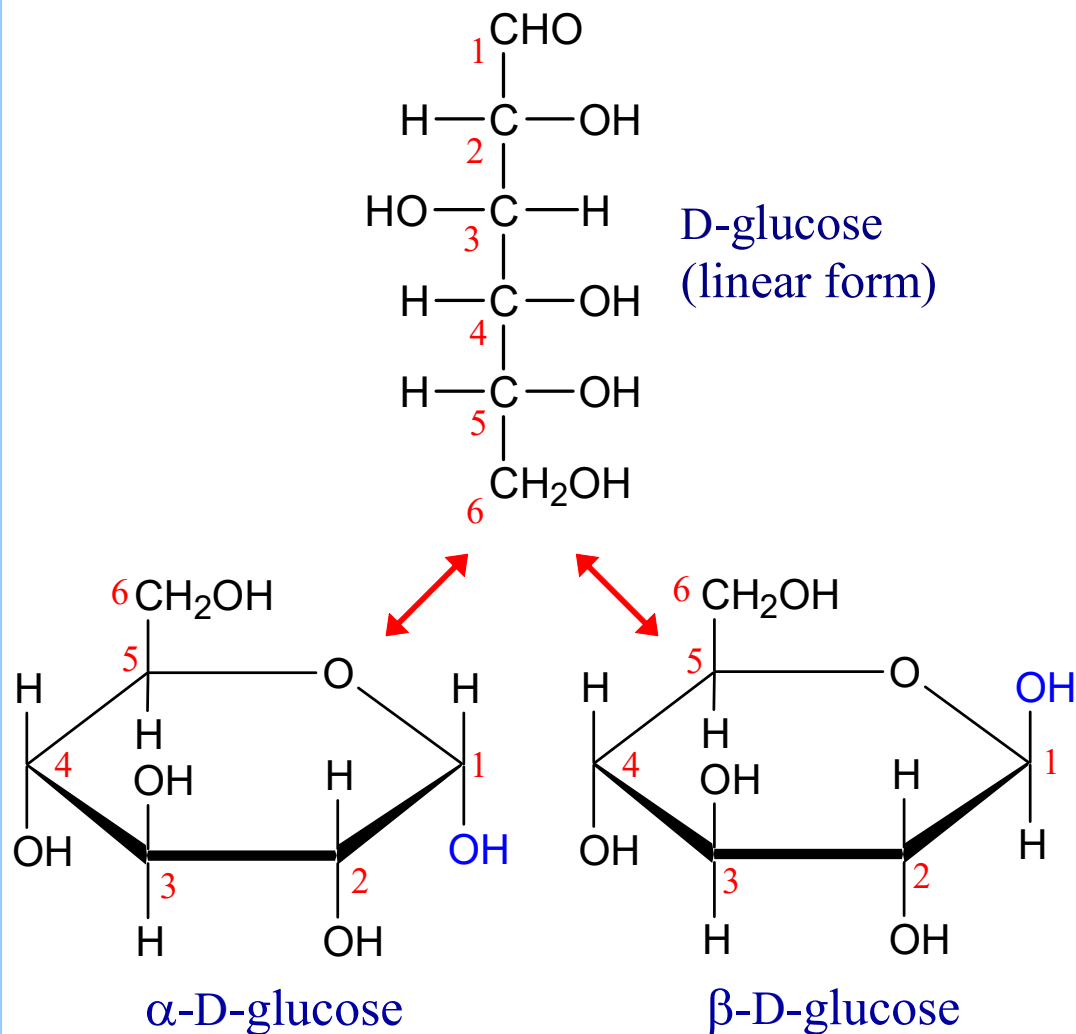


A ketone can react with an alcohol to form a **hemiketal**.



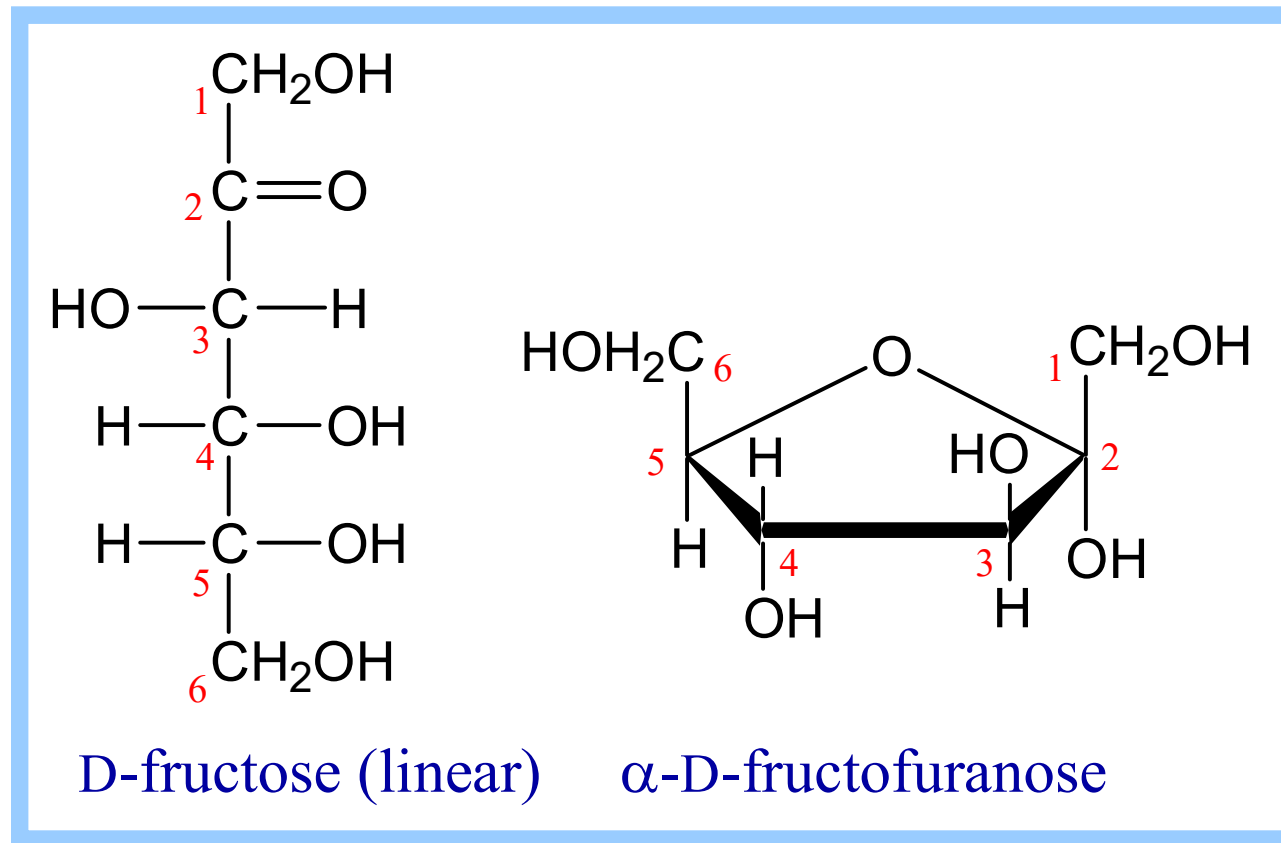
Pentoses and hexoses can cyclize as the ketone or aldehyde reacts with a distal OH.

Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.



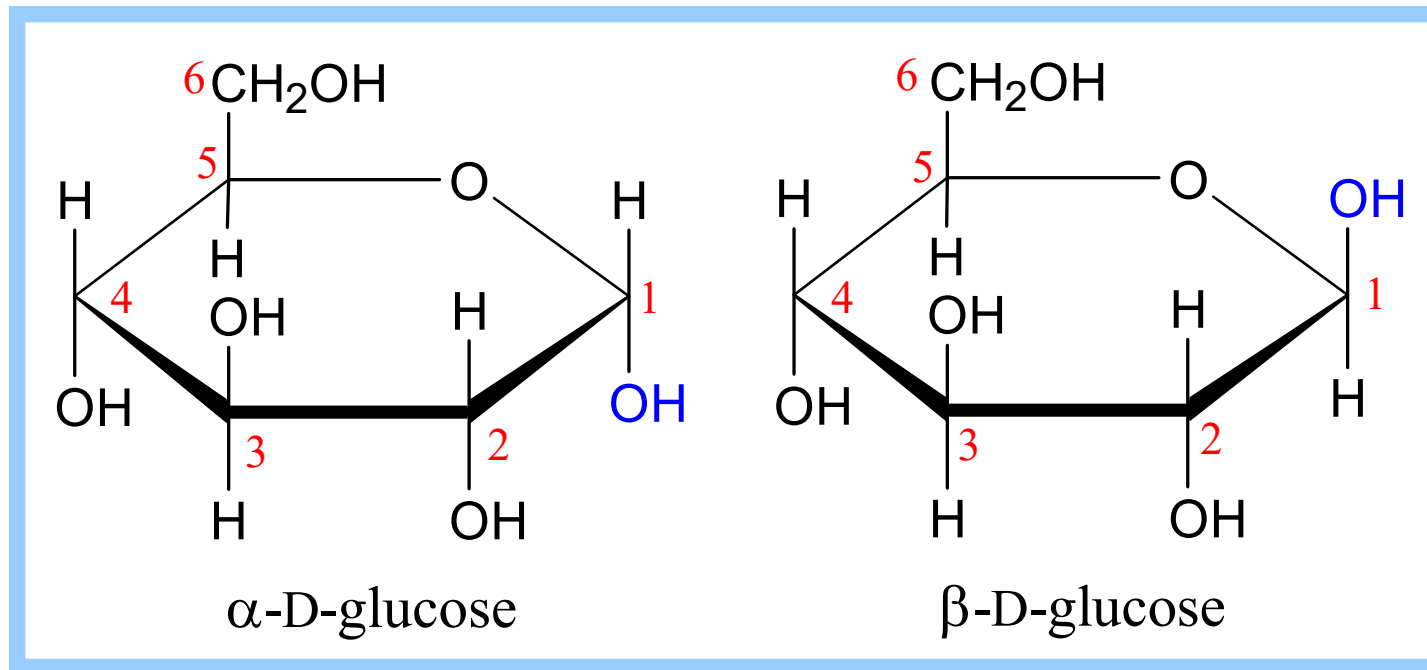
These representations of the cyclic sugars are called **Haworth projections**.





Fructose forms either

- ♦ a 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or
- ♦ a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.



Cyclization of glucose produces a new **asymmetric center** at **C1**. The 2 stereoisomers are called **anomers**,  $\alpha$  &  $\beta$ .

Haworth projections represent the cyclic sugars as having essentially planar rings, with the OH at the anomeric C1:

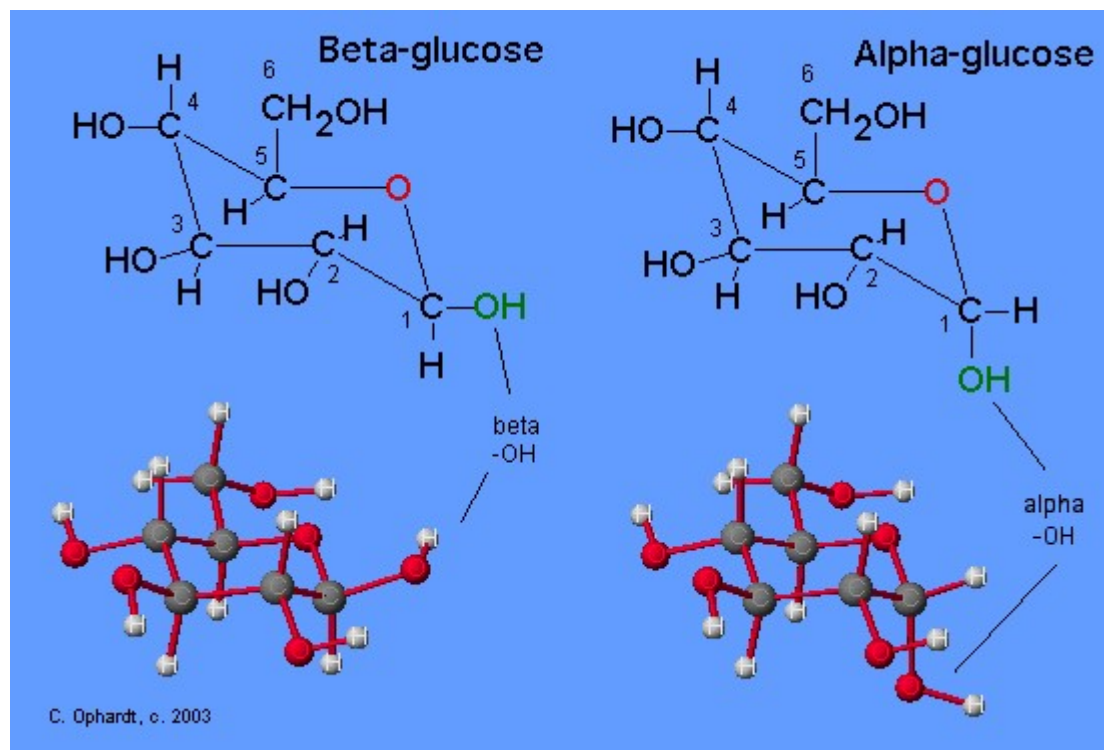
- ♦  $\alpha$  (OH **below** the ring)
- ♦  $\beta$  (OH **above** the ring).

## Alpha and beta position

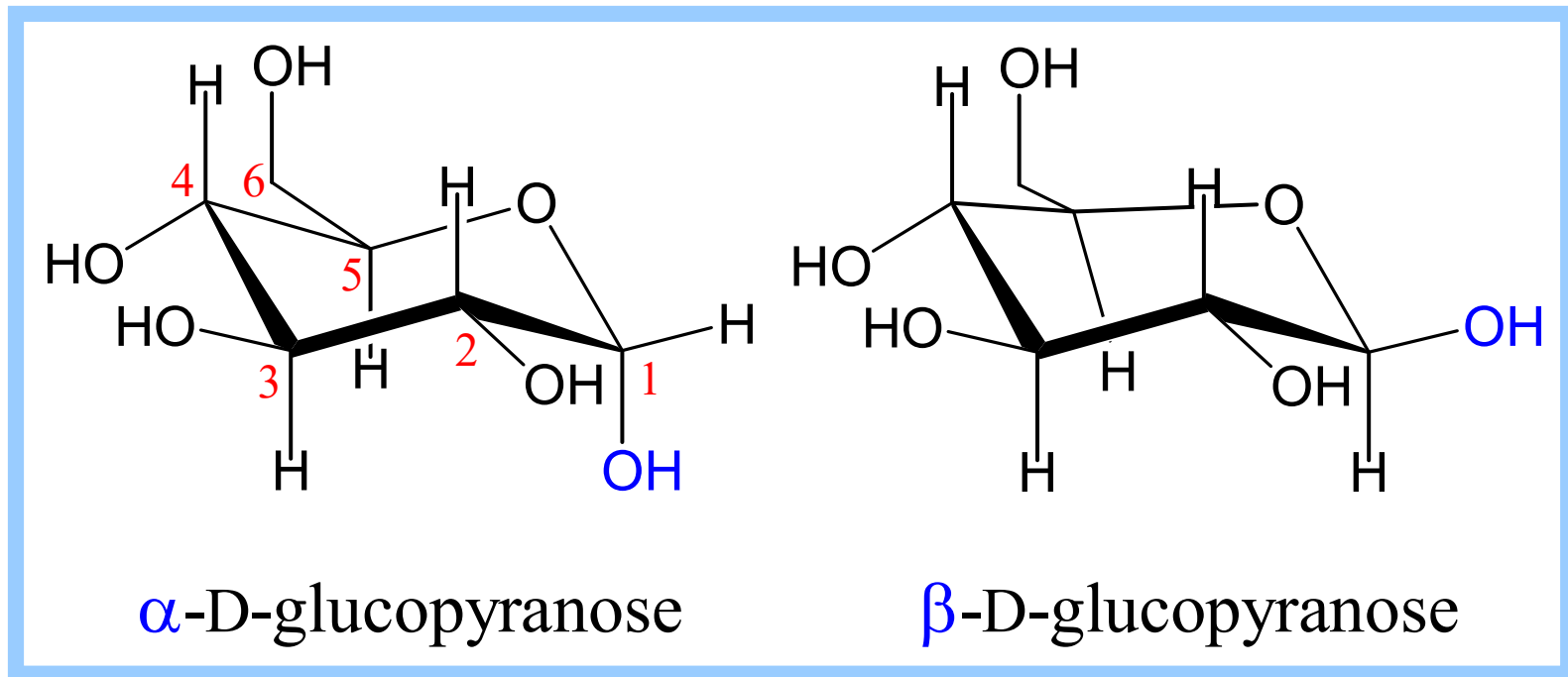
The position of the -OH group on the anomeric carbon (#1) is an important distinction for carbohydrate chemistry.

**$\beta$  position** -OH being on the same side of the ring as the C#6. In the chair structure this results in a **horizontal projection**.

**$\alpha$  position** -OH being on the opposite side of the ring as the C # 6. In the chair structure this results in a **downward projection**.



**The alpha and beta label is not applied to any other carbon – only the anomeric carbon, in this case # 1.**



Because of the tetrahedral nature of carbon bonds, pyranose sugars actually assume a "**chair**" or "**boat**" configuration, depending on the sugar.

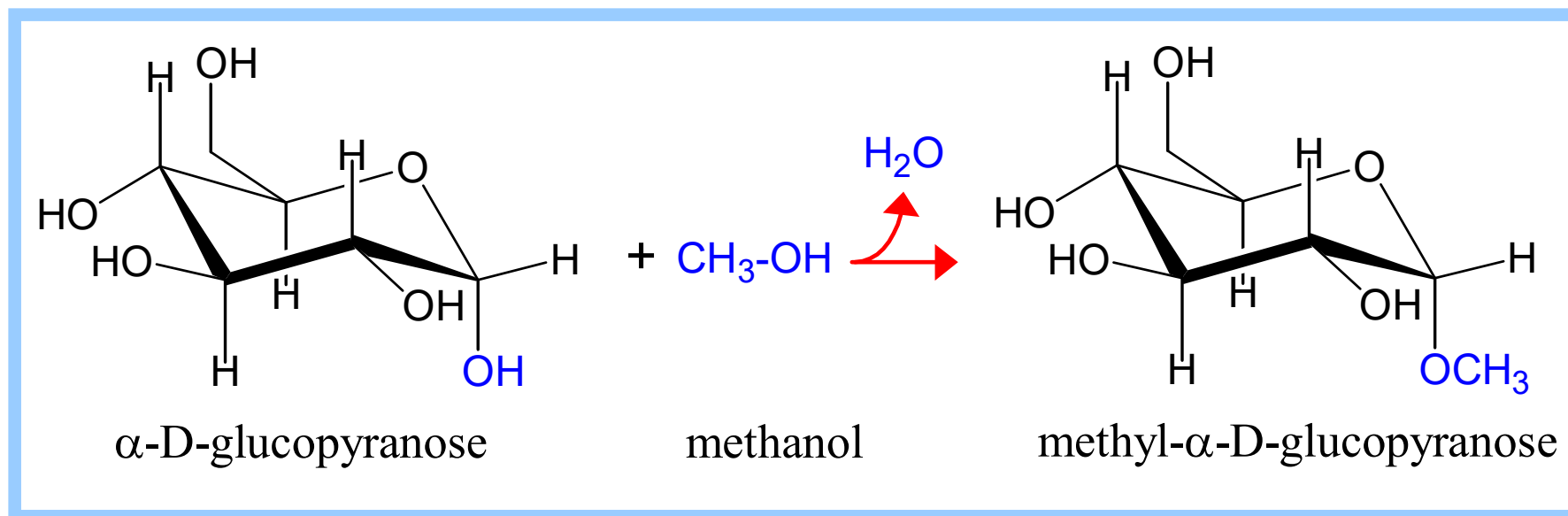
The representation above reflects the chair configuration of the glucopyranose ring more accurately than the Haworth projection.

# Glycosidic Bonds

The anomeric hydroxyl and a hydroxyl of another sugar or some other compound can join together, splitting out water to form a **glycosidic bond**:



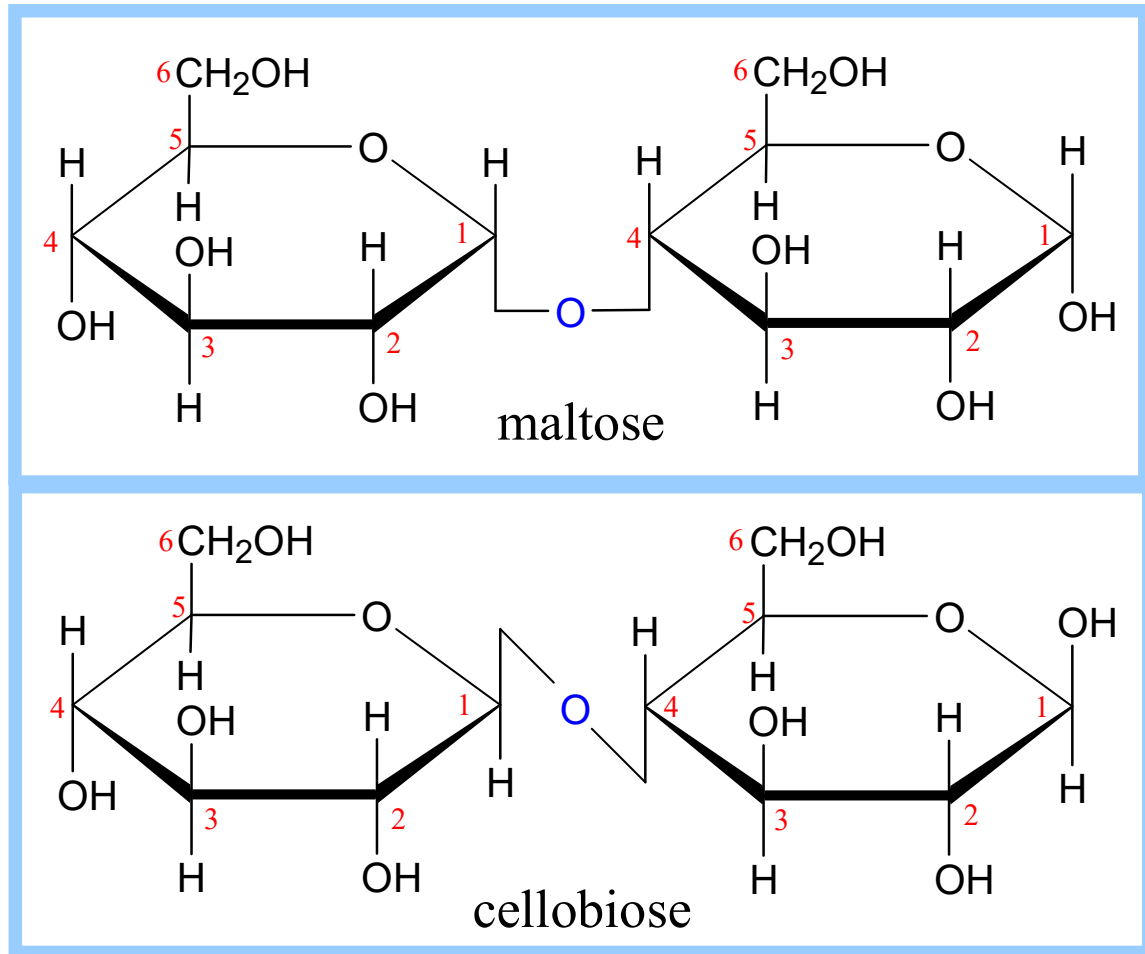
E.g., methanol reacts with the anomeric OH on glucose to form **methyl glucoside** (methyl-glucopyranose).



## Disaccharides:

**Maltose**, a cleavage product of starch (e.g., amylose), is a disaccharide with an  $\alpha(1-4)$  glycosidic link between C1 - C4 OH of 2 glucoses.

It is the  $\alpha$  anomer (C1 O points down).



**Cellobiose**, a product of cellulose breakdown, is the otherwise equivalent  $\beta$  anomer (O on C1 points up).

The  $\beta(1 \rightarrow 4)$  glycosidic linkage is represented as a zig-zag, but one glucose is actually **flipped over** relative to the other.

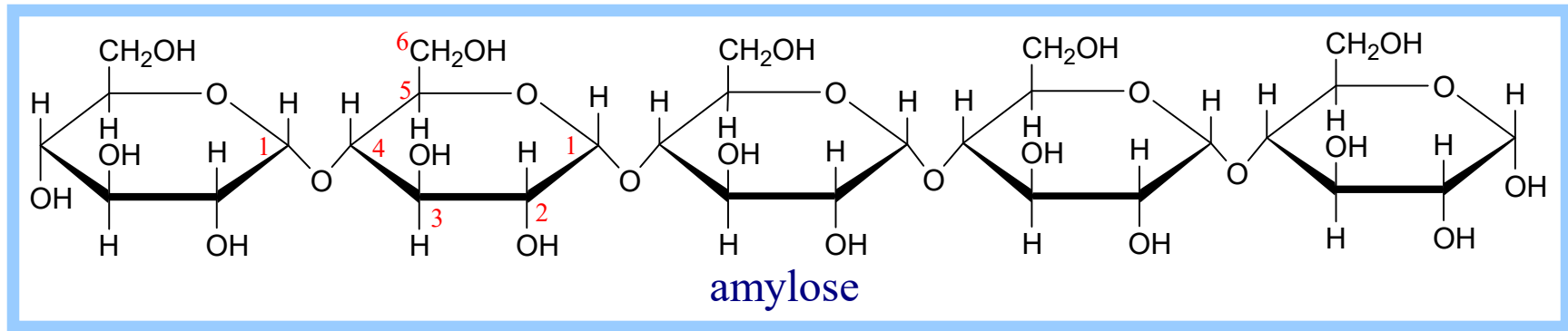
Other **disaccharides** include:

- ♦ **Sucrose**, common table sugar, has a glycosidic bond linking the anomeric hydroxyls of **glucose** & **fructose**.

Because the configuration at the anomeric C of glucose is  $\alpha$  (O points down from ring), the linkage is  $\alpha(1\rightarrow2)$ .

The full name of sucrose is  $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-fructopyranose.)

- ♦ **Lactose**, milk sugar, is composed of **galactose** & **glucose**, with  $\beta(1\rightarrow4)$  linkage from the anomeric OH of galactose. Its full name is  $\beta$ -D-galactopyranosyl-(1 $\rightarrow$ 4)- $\alpha$ -D-glucopyranose



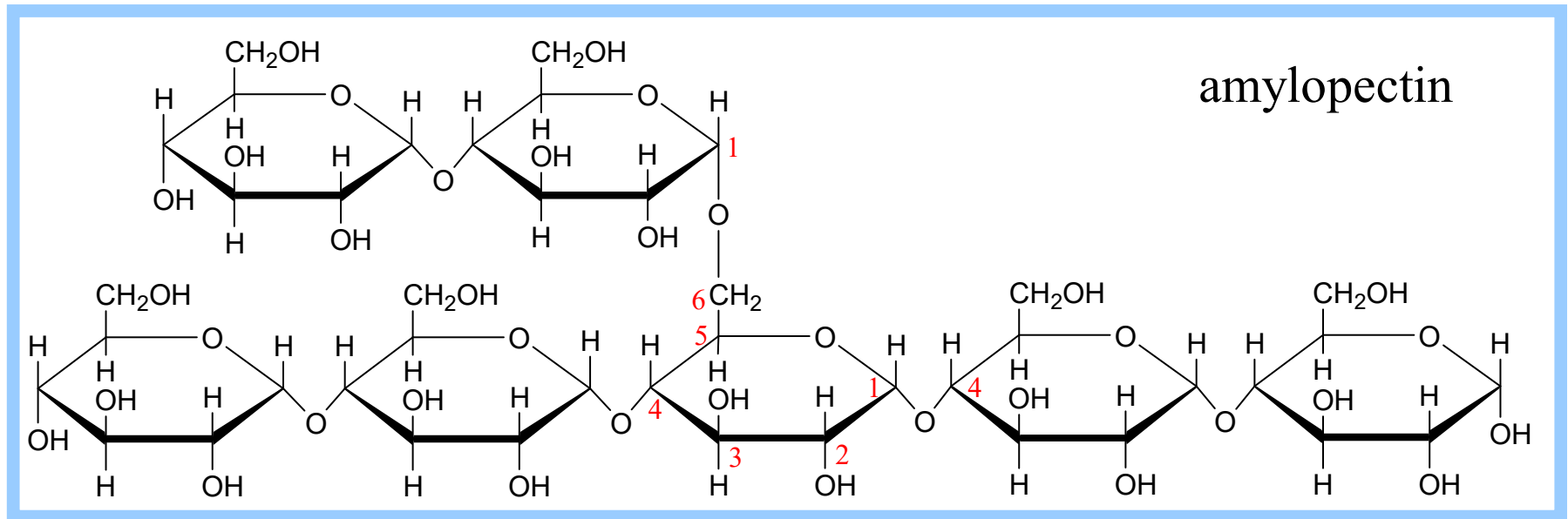
## Polysaccharides:

**Plants** store glucose as **amylose** or **amylopectin**, glucose polymers collectively called starch.

**Amylose** is a glucose polymer with  $\alpha(1 \rightarrow 4)$  linkages.

The end of the polysaccharide with an anomeric C1 not involved in a glycosidic bond is called the **reducing end**.

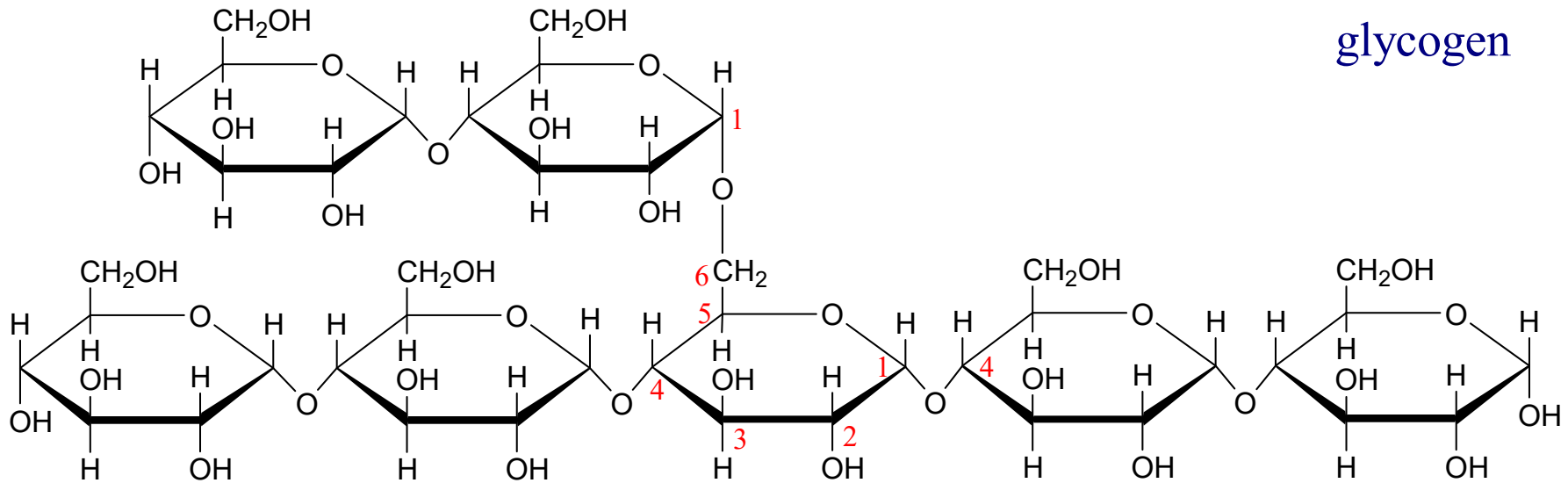




**Amylopectin** is a glucose polymer with mainly  $\alpha(1\rightarrow4)$  linkages, but it also has **branches** formed by  $\alpha(1\rightarrow6)$  linkages. Branches are generally longer than shown above.

The branches produce a compact structure & provide multiple chain ends at which enzymatic cleavage can occur.

glycogen

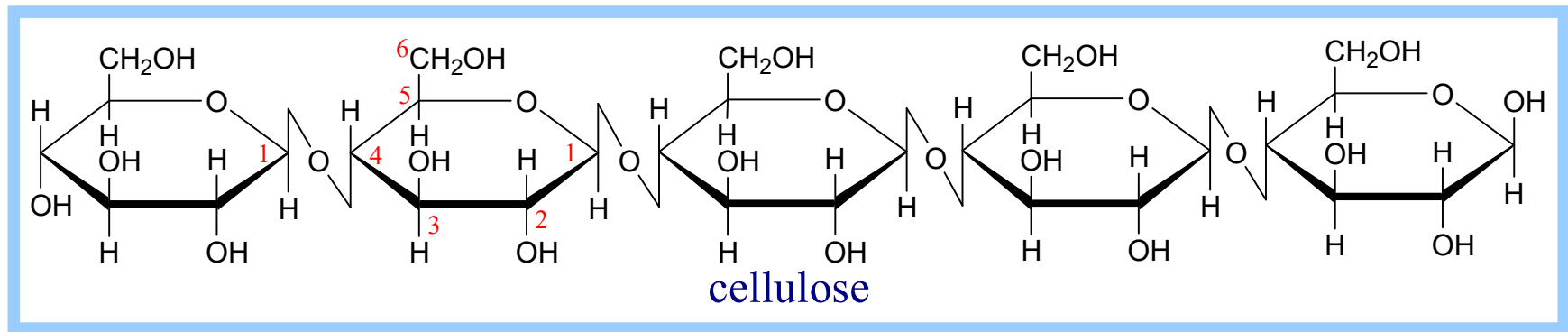


**Glycogen**, the glucose storage polymer in **animals**, is similar in structure to amylopectin.

But glycogen has **more  $\alpha(1 \rightarrow 6)$  branches**.

The highly branched structure permits rapid glucose release from glycogen stores, e.g., in muscle during exercise.

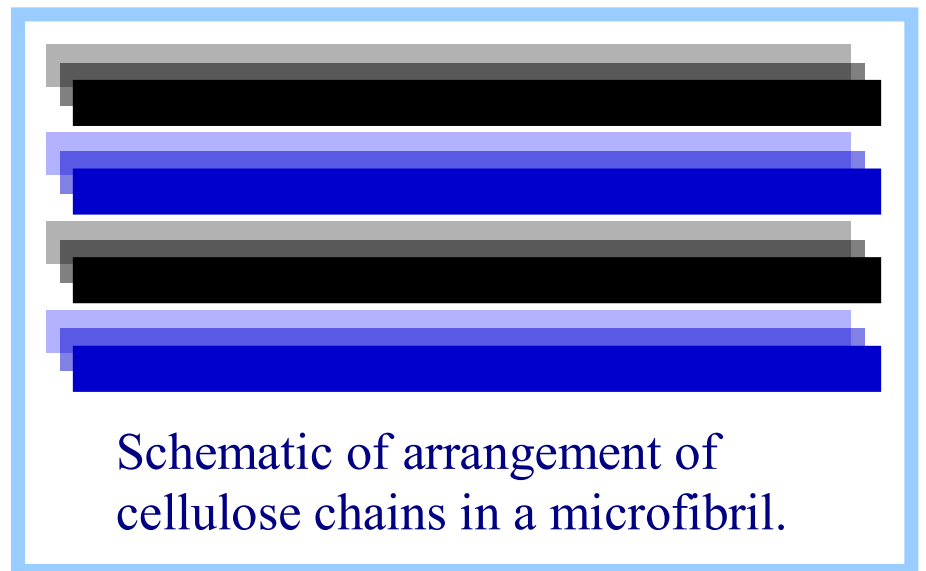
The ability to rapidly mobilize glucose is more essential to animals than to plants.



**Cellulose**, a major constituent of **plant cell walls**, consists of long linear chains of glucose with  $\beta(1\rightarrow4)$  linkages.

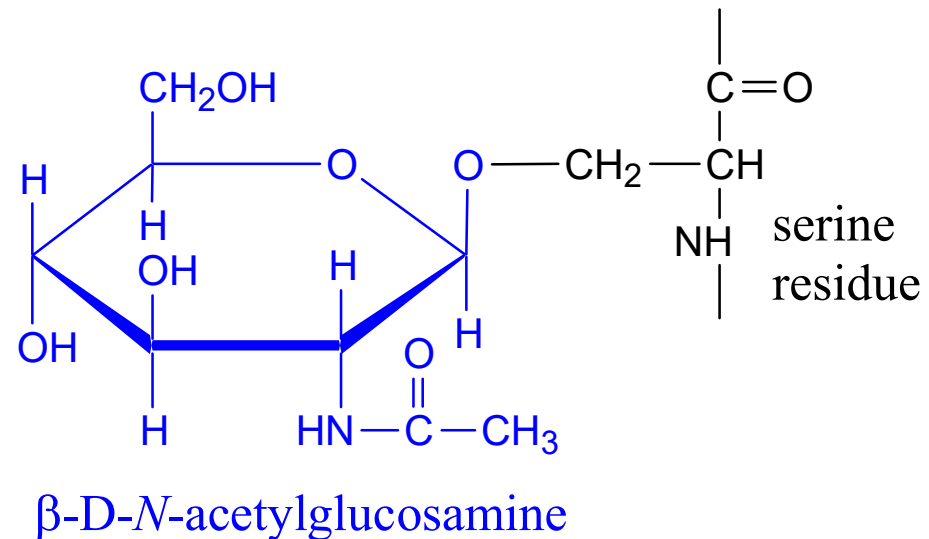
**Every other glucose is flipped over**, due to  $\beta$  linkages.

This promotes intra-chain and inter-chain H-bonds and van der Waals interactions, that cause cellulose chains to be straight & rigid, and pack with a crystalline arrangement in thick bundles - **microfibrils**.



## Oligosaccharides

that are covalently attached to proteins or to membrane lipids may be linear or branched chains.



**O-linked oligosaccharide** chains of glycoproteins vary in complexity.

They link to a protein via a glycosidic bond between a sugar residue & a **serine or threonine OH**.

O-linked oligosaccharides have roles in **recognition**, **interaction**, and **enzyme regulation**.