BCH 101

INTRODUCTION TO BIOMOLECULES

CARBOHYDRATES

BY

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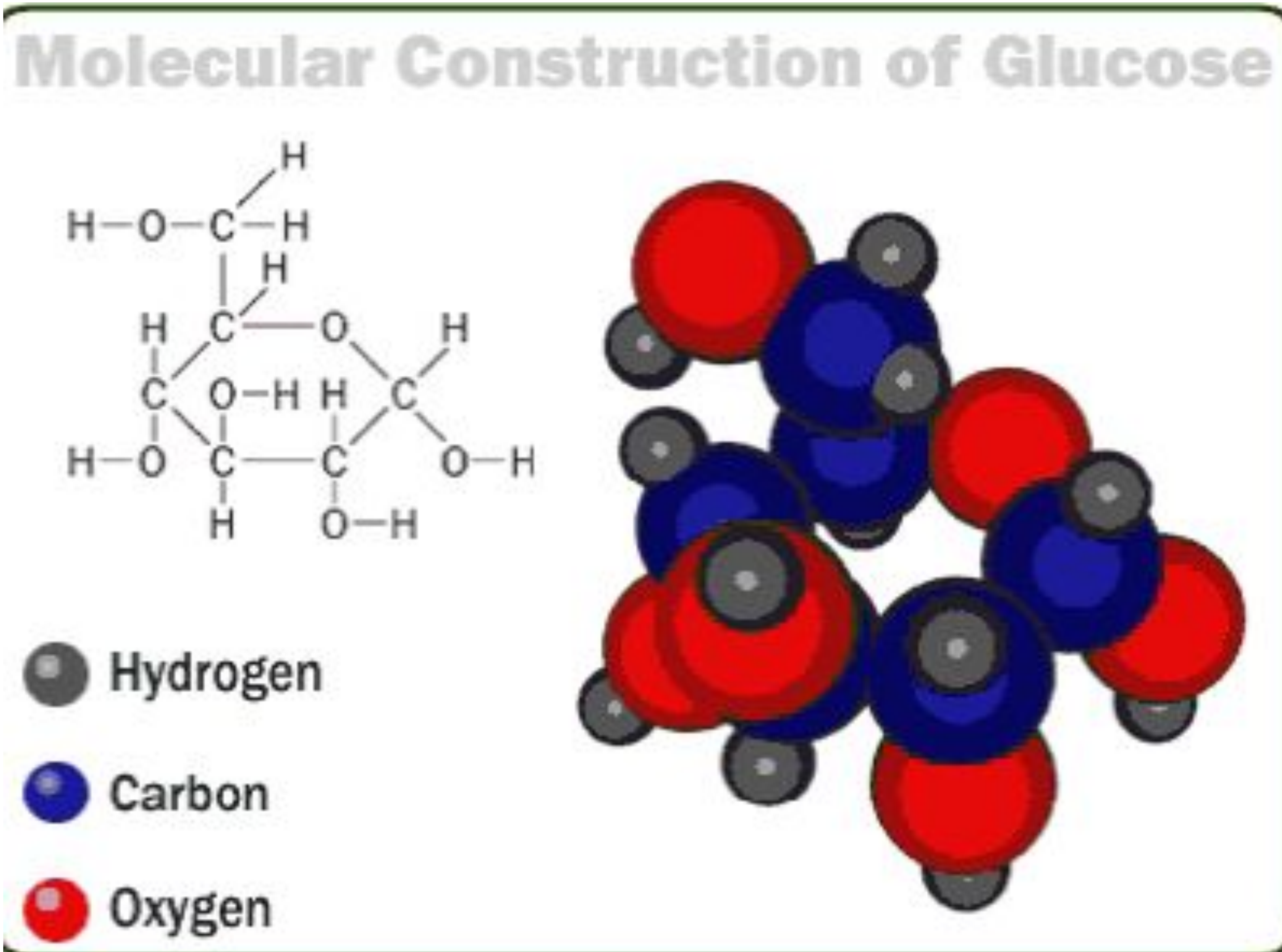
Carbohydrates


Molecular Construction of Glucose
Hydrogen
Carbon
Oxygen

- **DEFINITION**

Carbohydrates are polyhydroxy aldehydes or ketones or compounds which yield these on hydrolysis.

Functions

- sources of energy
- intermediates in the biosynthesis of other basic biochemical entities (fats and proteins)
- associated with other entities such as glycosides, vitamins and antibiotics)
- form structural tissues in plants and in microorganisms (cellulose, lignin, murein)
- participate in biological transport, cell-cell recognition, activation of growth factors, modulation of the immune system

Carbohydrates

- glucose provides energy for the brain and ½ of energy for muscles and tissues
- glycogen is stored glucose
- glucose is immediate energy
- glycogen is reserve energy

Classification of carbohydrates

Carbohydrates – polyhydroxyaldehydes or polyhydroxy-ketones of formula $(CH_2O)_n$, or compounds that can be hydrolyzed to them. (aka sugars or saccharides)

Monosaccharides – carbohydrates that cannot be hydrolyzed to simpler carbohydrates; eg. Glucose or fructose.

Disaccharides – carbohydrates that can be hydrolyzed into two monosaccharide units; eg. Sucrose, which is hydrolyzed into glucose and fructose.

Oligosaccharides – carbohydrates that can be hydrolyzed into a few monosaccharide units.

Polysaccharides – carbohydrates that are are polymeric sugars; eg Starch or cellulose.

Carbohydrates (glycans) have the following basic composition:

$$(CH_2O)_n \quad \text{or} \quad \begin{array}{c} | \\ H - C - OH \\ | \end{array}$$

- 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.

Simple Carbohydrates

- sugars
  - monosaccharides – single sugars
  - disaccharides – 2 monosaccharides

Characteristics of Carbohydrates

- Consist of carbon, hydrogen, & oxygen
- Energy containing molecules
- Some provide structure
- Basic building block is a monosaccharide $(CH_2O)_n$; n = 3,5,6
- Two monosaccharides form a disaccharide

Monosaccharides

- also known as simple sugars
- classified by 1. the number of carbons and 2. whether aldoses or ketoses
- most (99%) are straight chain compounds
- D-glyceraldehyde is the simplest of the aldoses (aldotriose)
- all other sugars have the ending <u>ose</u> (glucose, galactose, ribose, lactose, etc…)

Generic names		Examples
3 carbons:	trioses	Glyceraldehyde
4 carbons:	tetroses	Erythrose
5 carbons:	pentoses	Ribose
6 carbons:	hexoses	Glucose
7 carbons:	heptoses	Sedoheptulose
9 carbons:	nonoses	Neuraminic acid

Figure 7.1
Examples of monosaccharides found in humans, classified according to the number of carbons they contain.

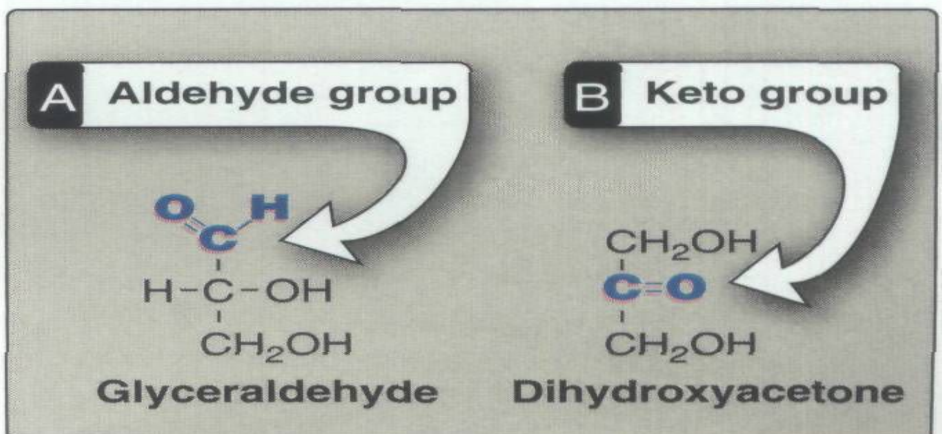
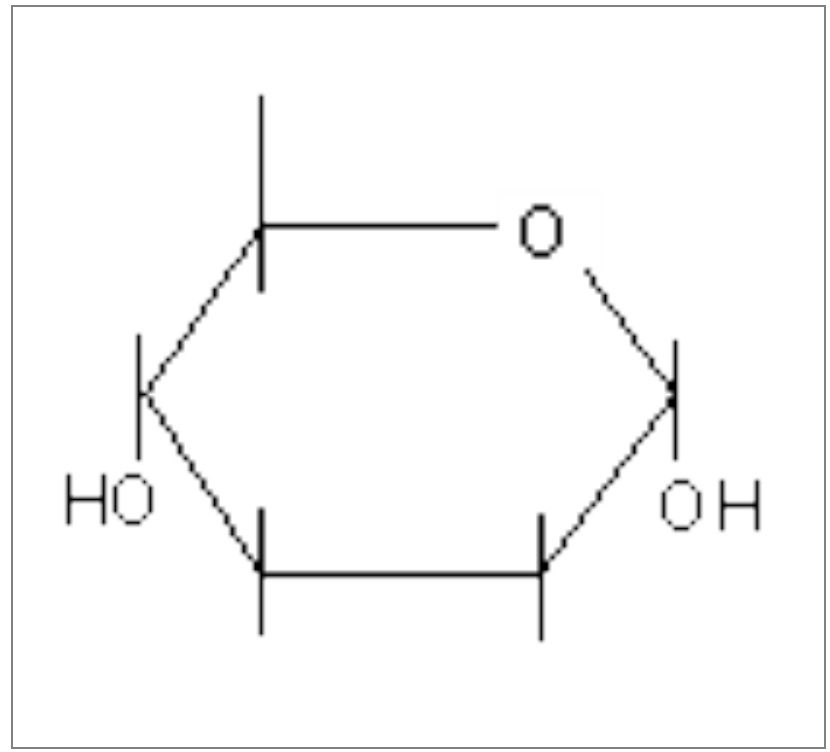


Figure 7.2
Examples of an aldose (A) and a ketose (B) sugar.

Glucose

- The chemical formula for glucose is $C_6H_{12}O_{6.}$
- It is a six sided ring.
- The structure on the left is a simplified structure of glucose



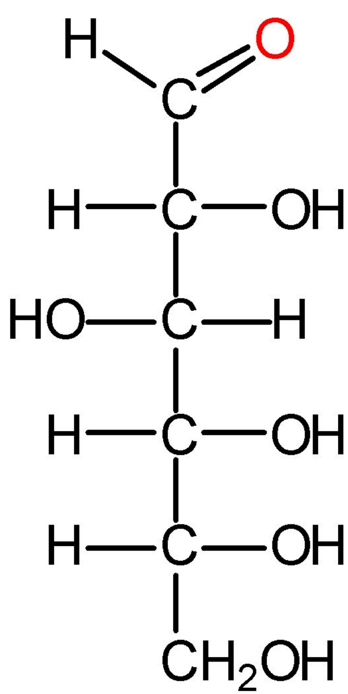
RELATIVE SWEETNESS OF DIFFERENT SUGARS

Sucrose	100
Glucose	74
Fructose	174
Lactose	16
Invert Sugar	126
Maltose	32
Galactose	32

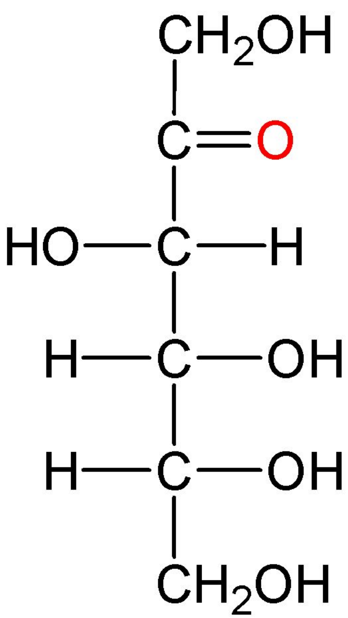
Monosaccharides

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

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



D-glucose



D-fructose

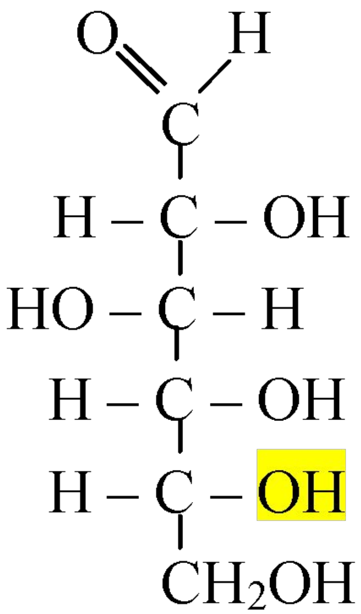
chiral centers by definition are C atoms which have 4 DIFFERENT atoms bonded to it

- **Compounds having same structural formula, but differ in spatial configuration.**
- □
- **Asymmetric Carbon atom:Attached to four different atoms or groups.**
- □
- **Vant Hoff’s rule: The possible isomers (2n) of a given compound is determined by the number of asymmetric carbon atoms (n).**
- □
- **Reference C atom: Penultimate C atom, around which mirror images are formed.**

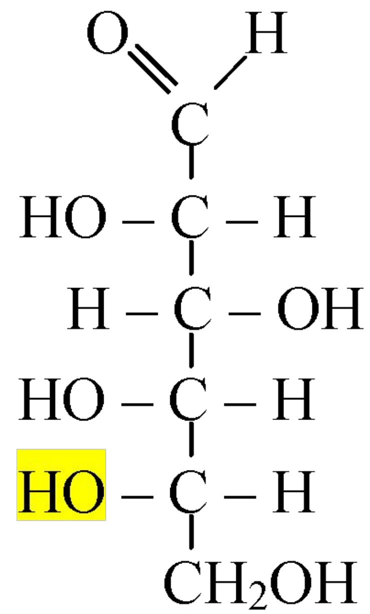
Sugar Nomenclature

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

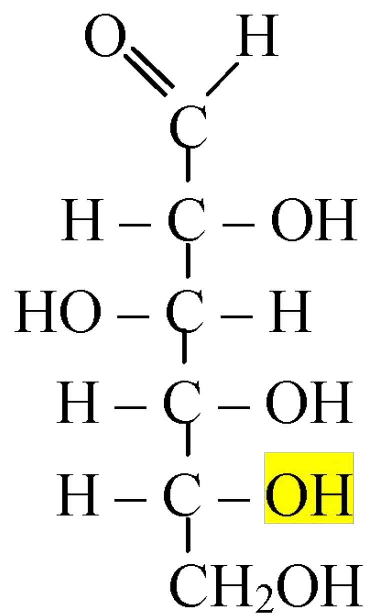


L-glucose

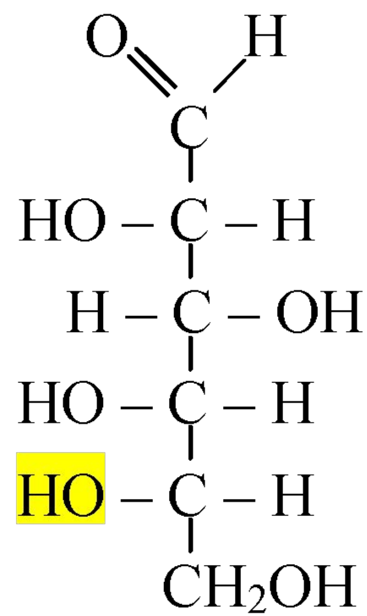
D & L sugars are mirror images of one another.

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

Other stereoisomers have unique names, e.g., glucose, mannose, galactose, etc.



D-glucose



L-glucose

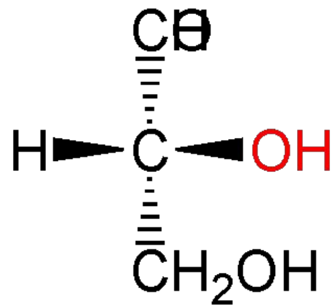
The number of stereoisomers is $\mathbf{2^n}$, where n is the number of asymmetric centers.

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

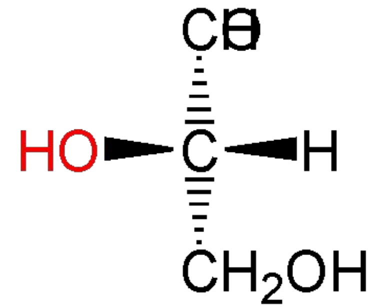
D vs L Designation

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

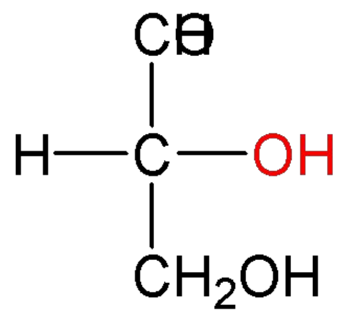
The lower representations are Fischer Projections.



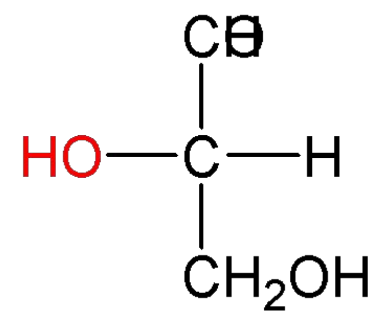
D-glyceraldehyde



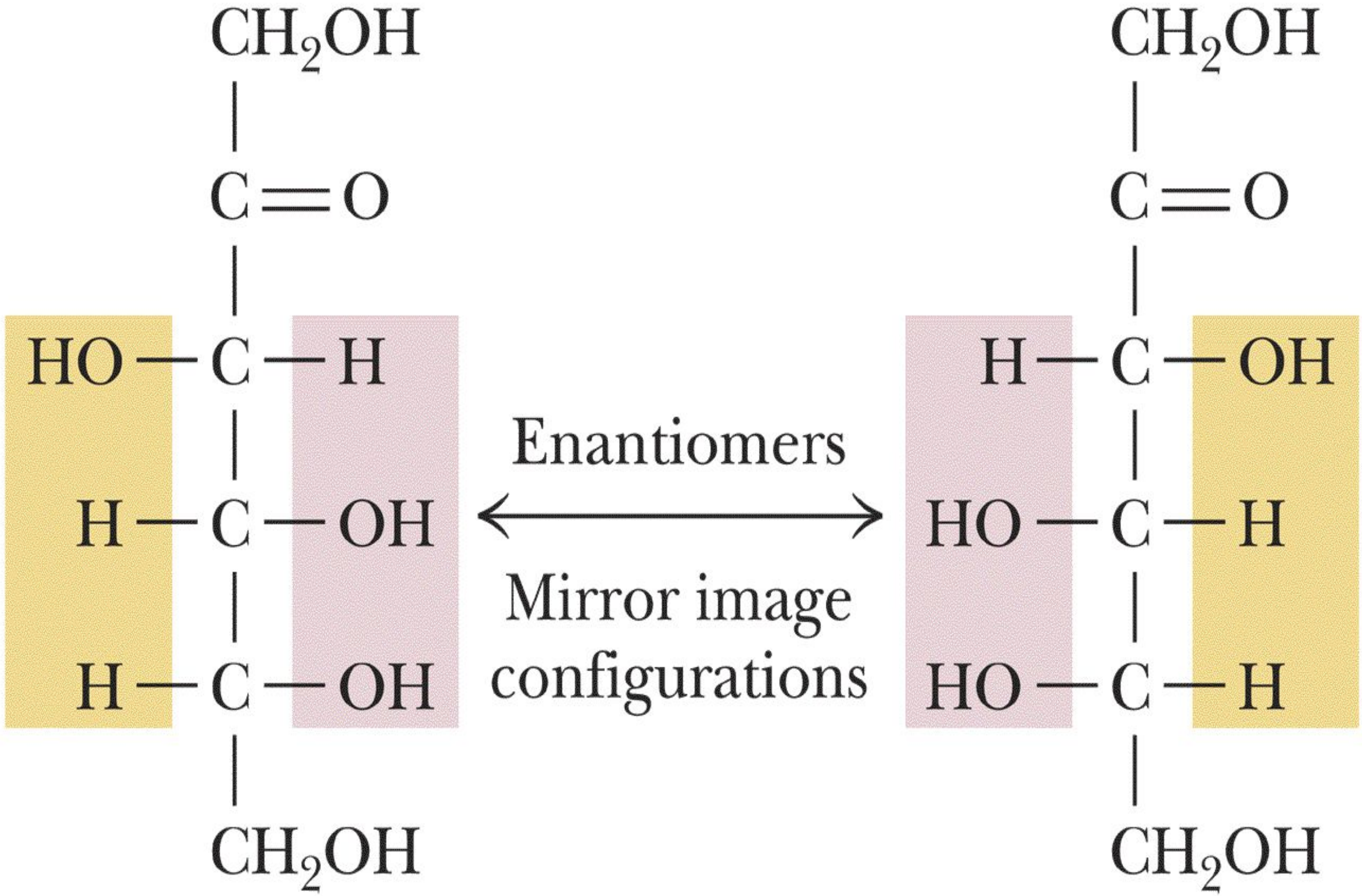
L-glyceraldehyde



D-glyceraldehyde



L-glyceraldehyde



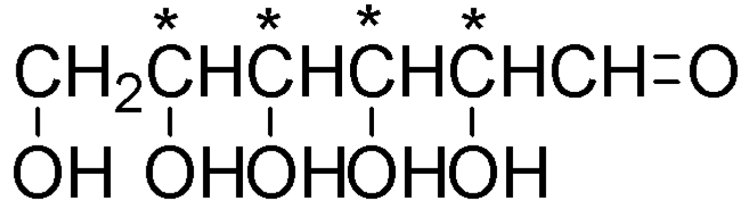
D-Fructose　　　　L-Fructose

Enantiomres

A special type of isomerism is found in the pairs of structures that are mirror images of each other. These mirror images are called **enantiomers, and the two members of the pair are designated as a D- and an L-sugar**

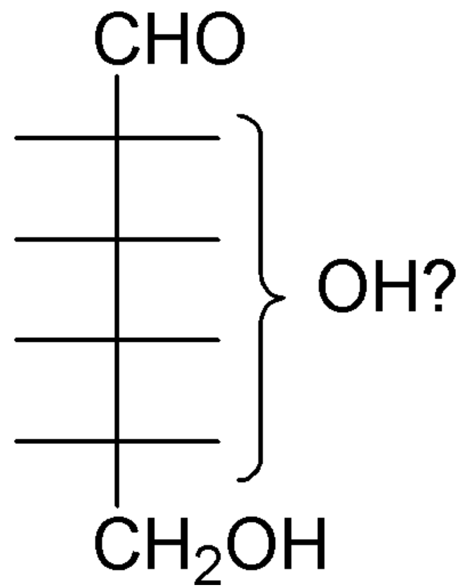
two monosaccharides differ in configuration around only one specific carbon atom (with the exception of the carbonyl carbon, see below), they are defined as **epimers of each other.**

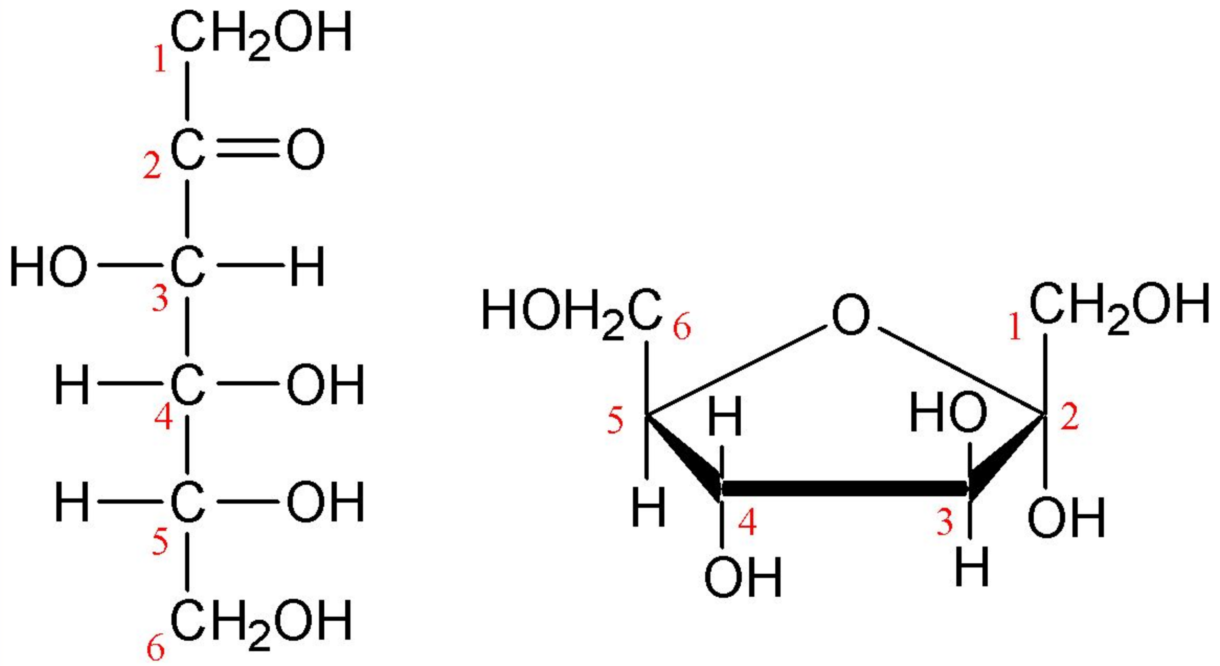
(+)-glucose? An aldohexose



Emil Fischer (1902)

Four chiral centers, $2^4 = 16$ stereoisomers



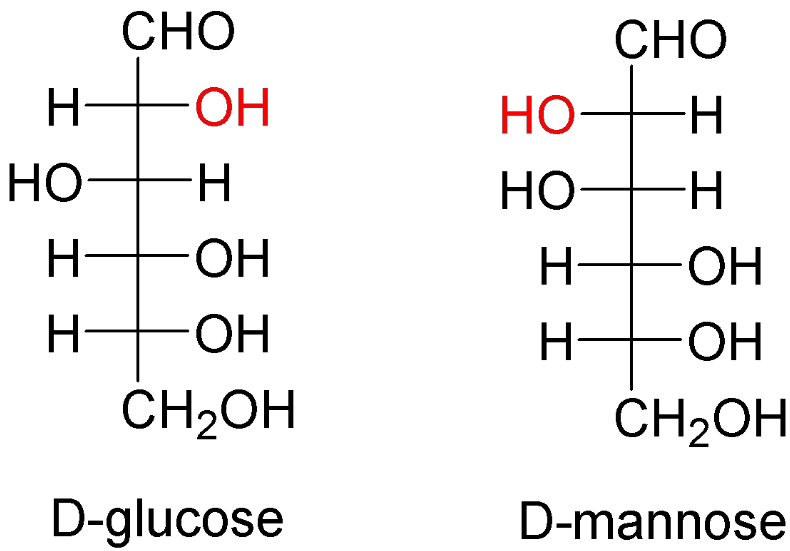


D-fructose (linear) α-D-fructofuranose

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.

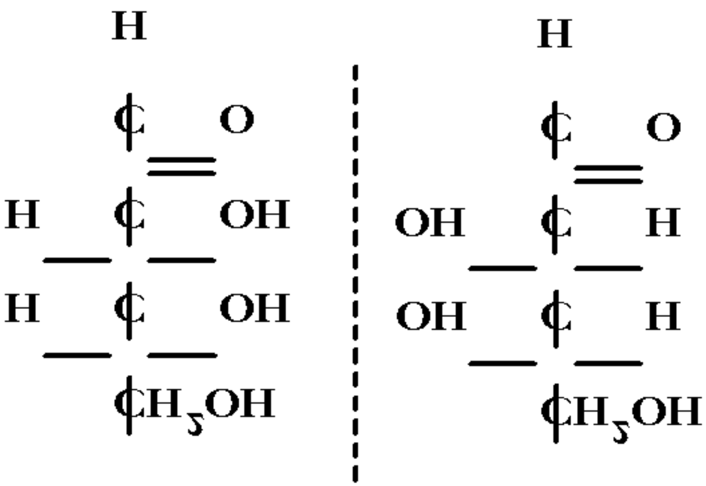
Epimers – stereoisomers that differ only in configuration about <u>one</u> chiral center.



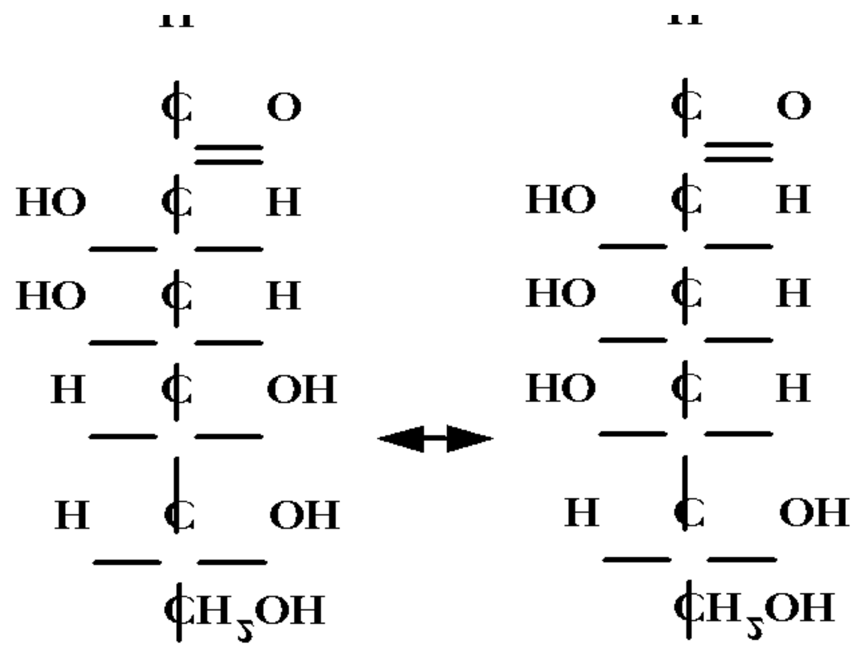
epimers

Sugars are different from one another, only in configuration with regard to a single C atom (other than the reference C atom).

Enantiomers and epimers



these two aldotetroses are enantiomers. They are stereoisomers that are mirror images of each other.

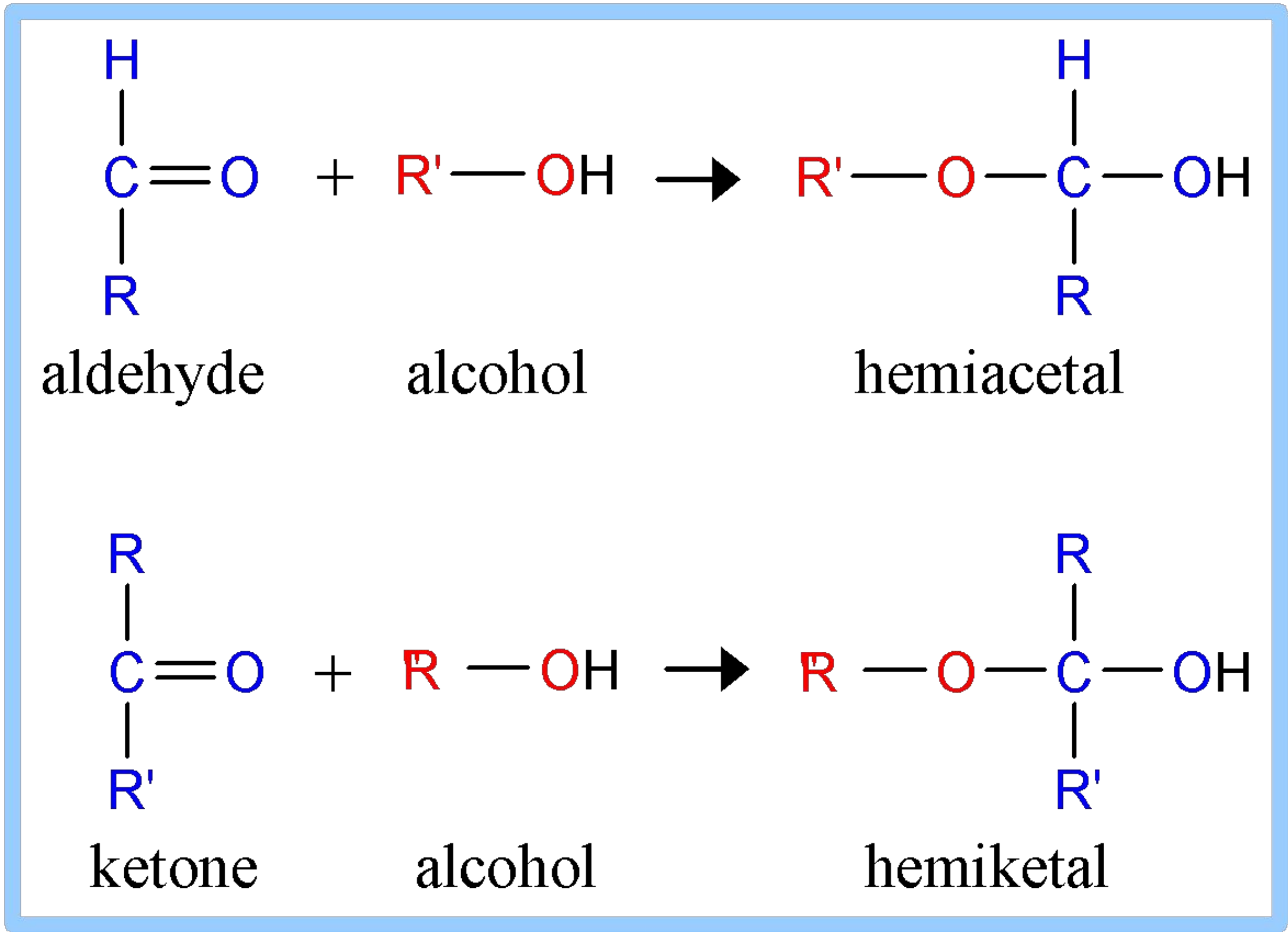


these two aldohexoses are C-4 epimers. they differ only in the position of the hydroxyl group on one asymmetric carbon (carbon 4)

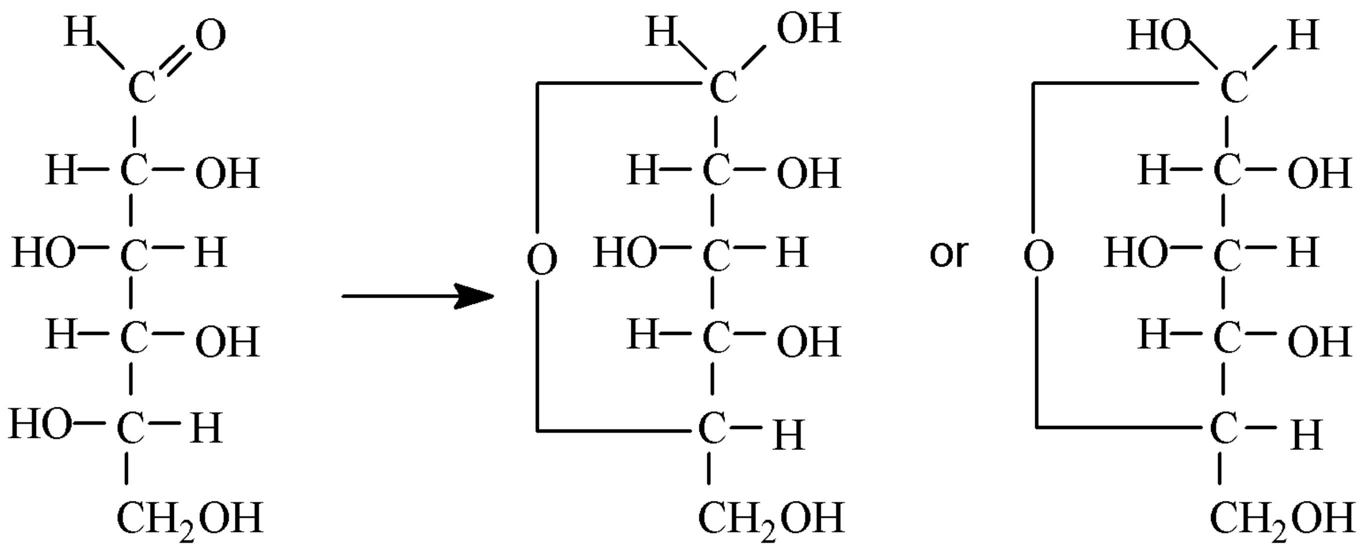
Hemiacetal & hemiketal formation

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

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



<u>Anomers</u>: Stereoisomers formed when ring is formed (α, β).



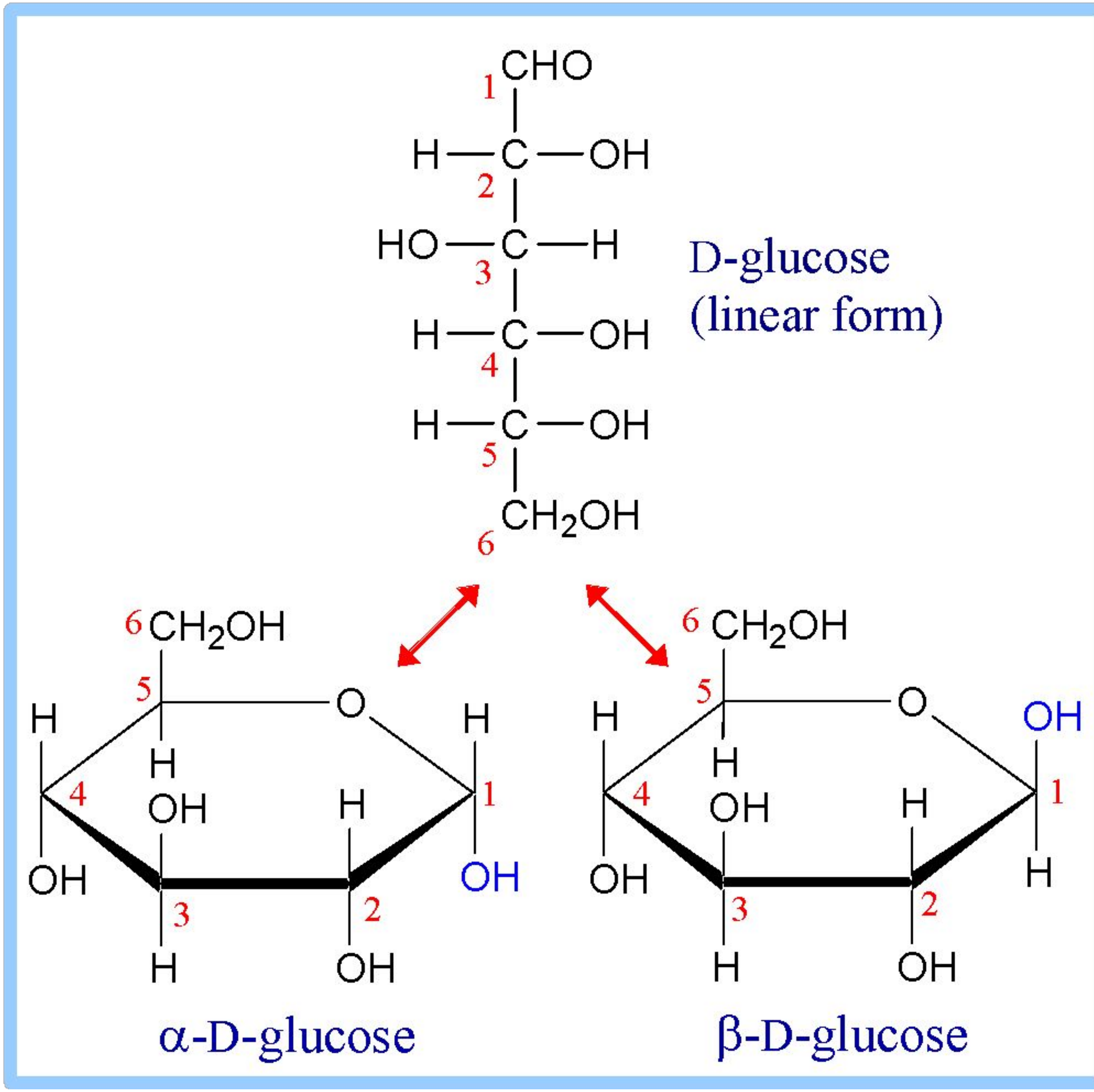
α is same side with ring

Rules for drawing Haworth projections

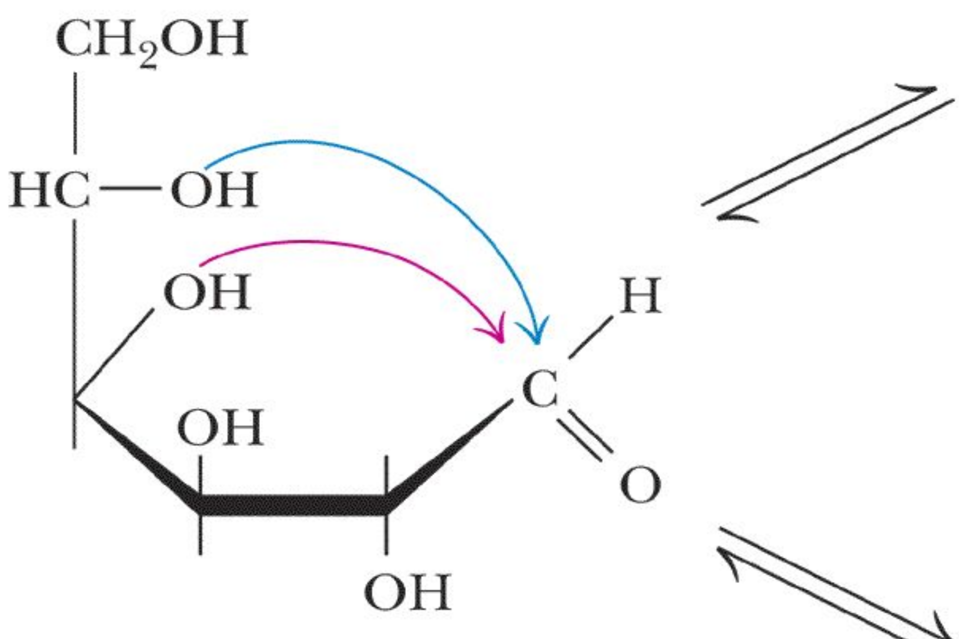
- for D-sugars the highest numbered carbon (furthest from the carbonyl) is drawn up. For L-sugars, it is drawn down
- for D-sugars, the OH group at the anomeric position is drawn down for α and up for β. For L-sugars α is up and β is down

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

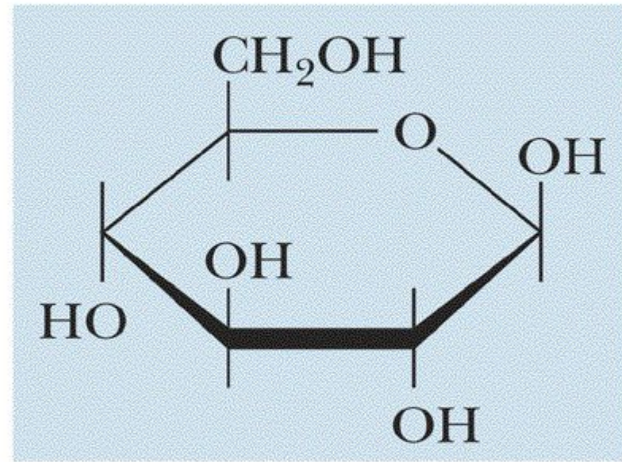
Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.



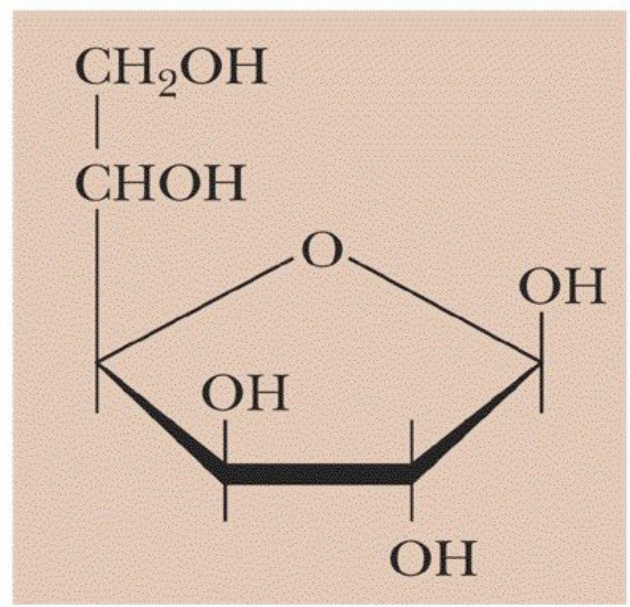
These representations of the cyclic sugars are called Haworth projections.



D-Glucose

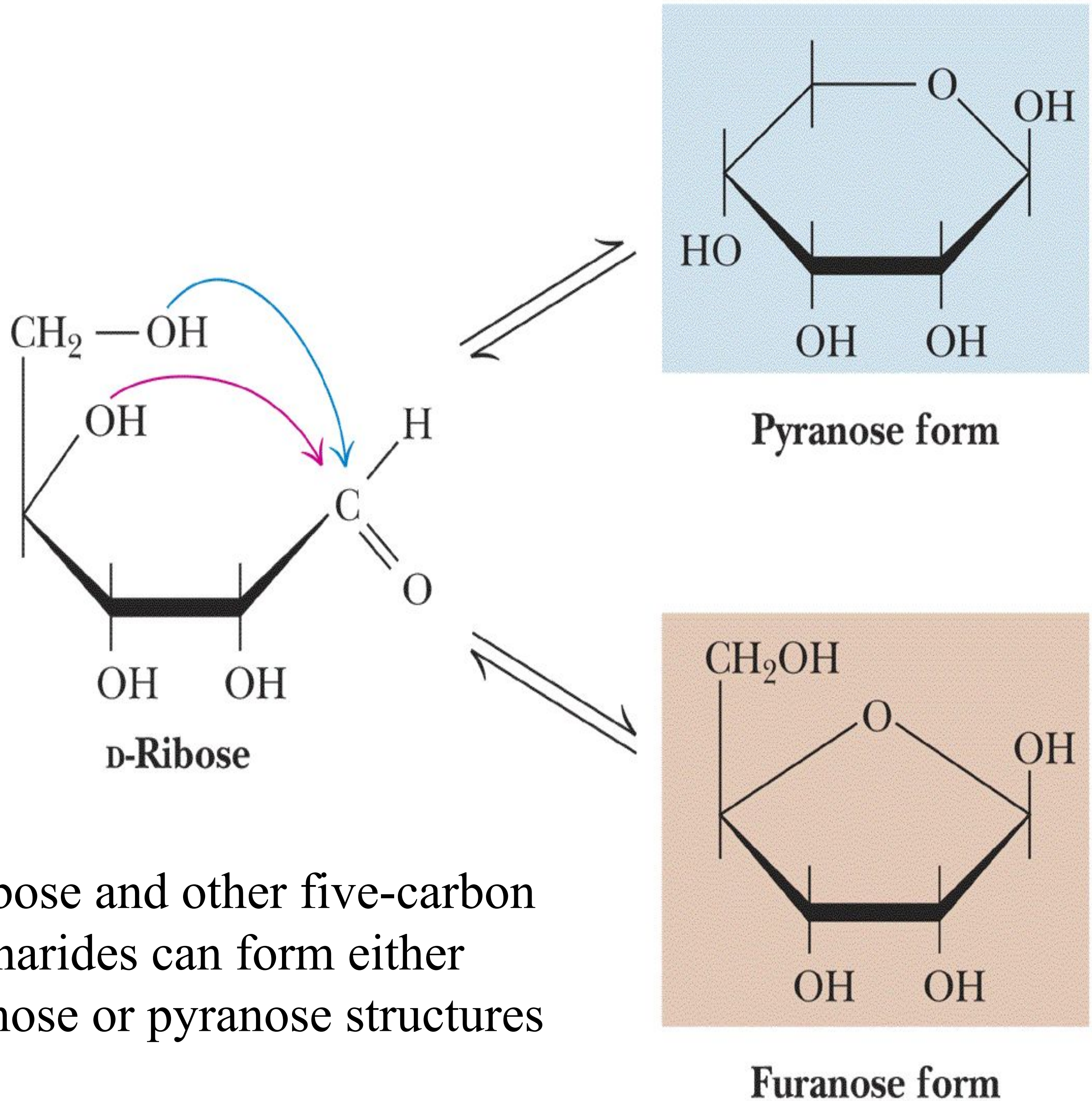


Pyranose form



Furanose form

D-glucose can cyclize in two ways forming either furanose or pyranose structures

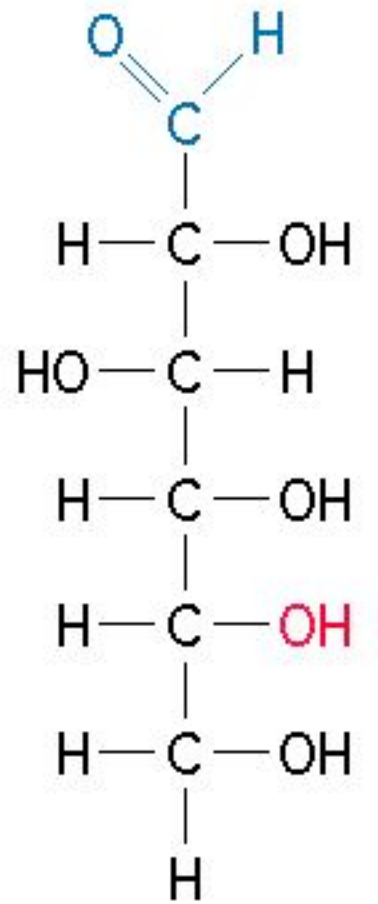


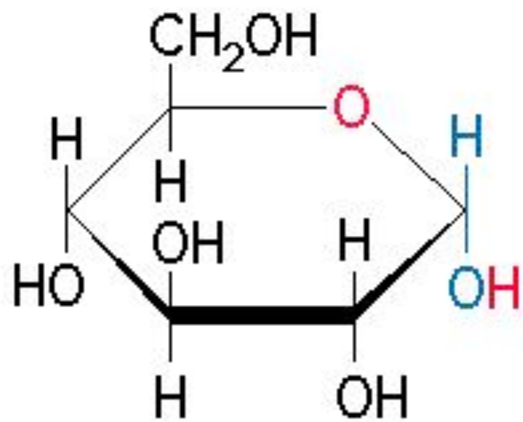
D-ribose and other five-carbon saccharides can form either furanose or pyranose structures

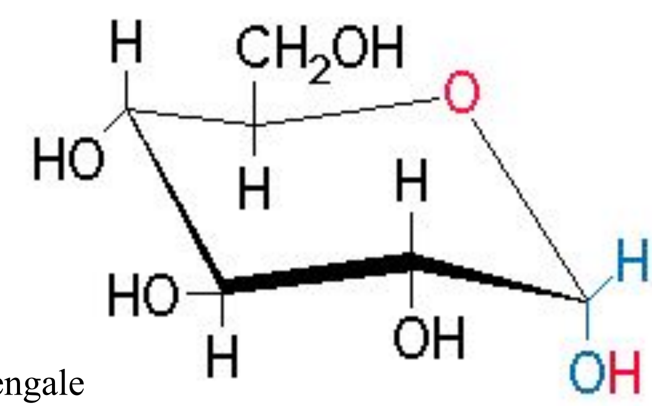
Structural representation of sugars

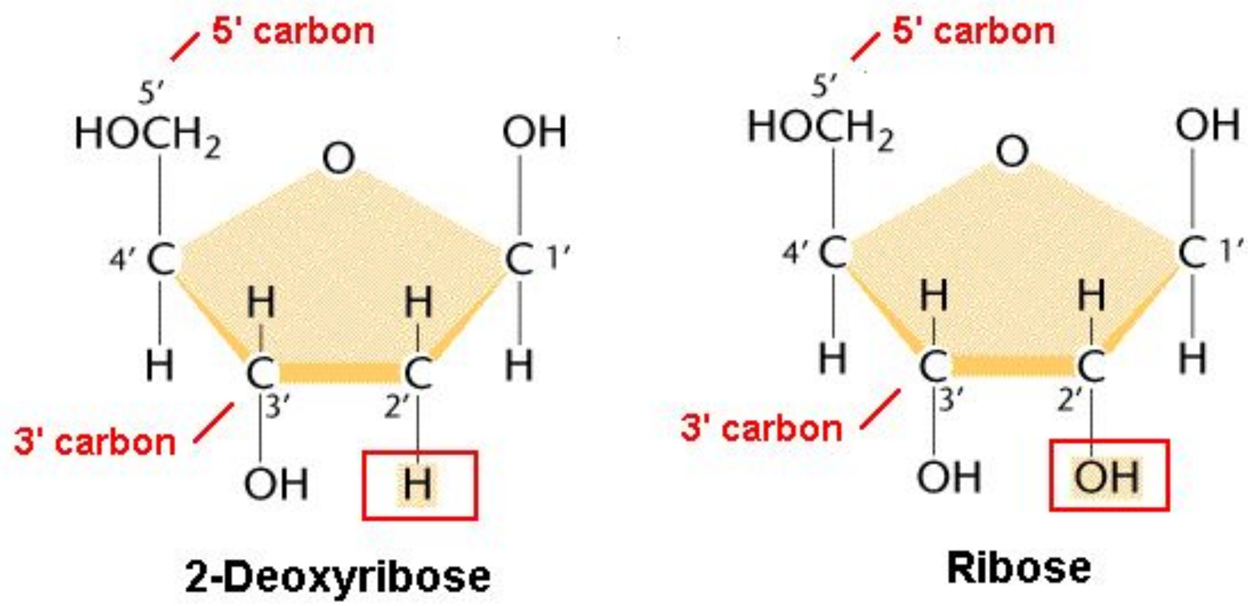
- Fisher projection: straight chain representation
- Haworth projection: simple ring in perspective
- Conformational representation: chair and boat configurations

Different Forms of Glucose







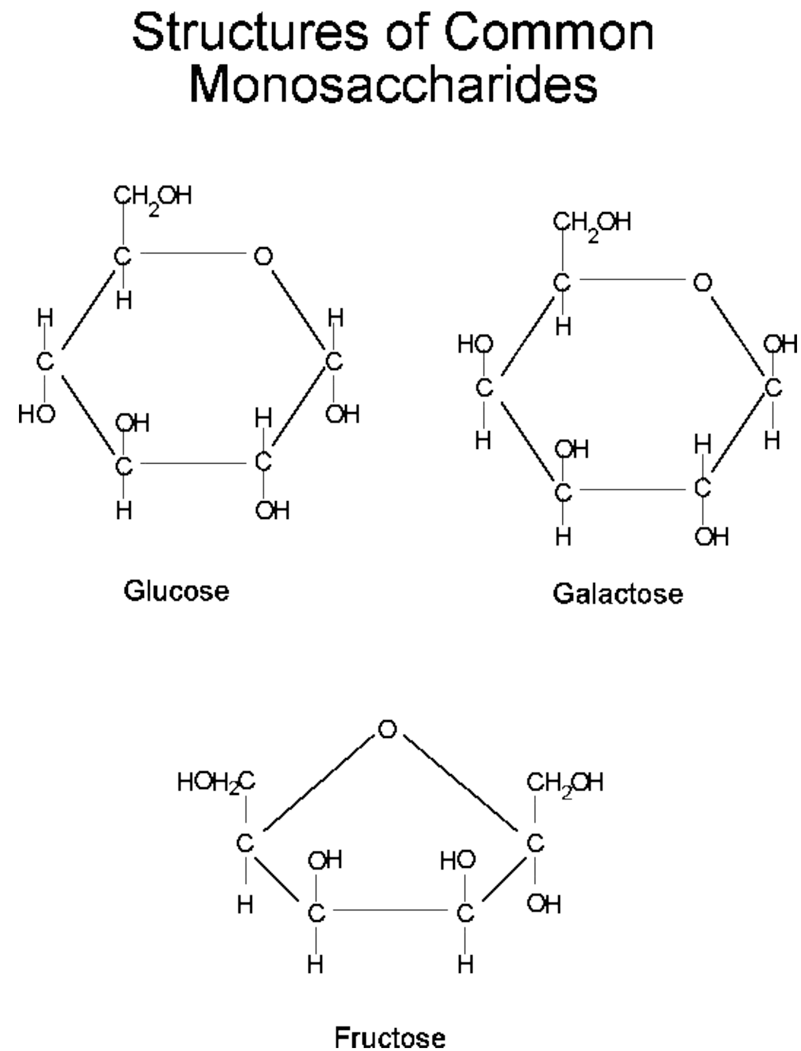


Oxygen of the hydroxyl group is removed to form deoxy sugars.

- **Non reducing and non osazone forming.**
- **Important part of nucleic acids.**

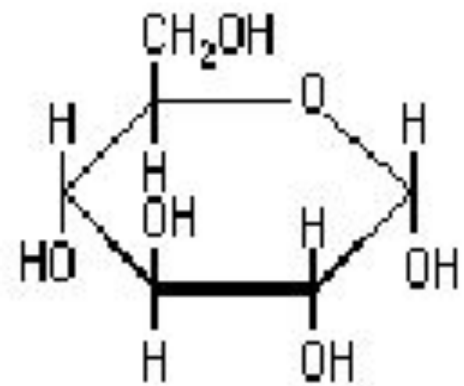
Simple Carbs

- monosaccharides
  - all are 6 carbon hexes
    - 6 carbons
    - 12 hydrogens
    - 6 oxygens
    - arrangement differs
      - accounts for varying sweetness
  - glucose, fructose, galactose

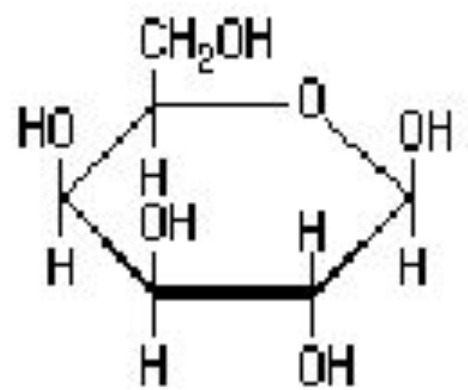


Three Monosaccharides

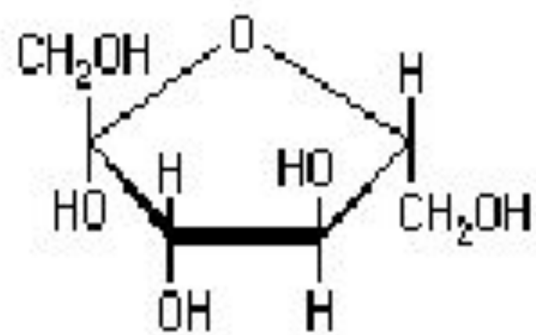
$C_6H_{12}O_6$



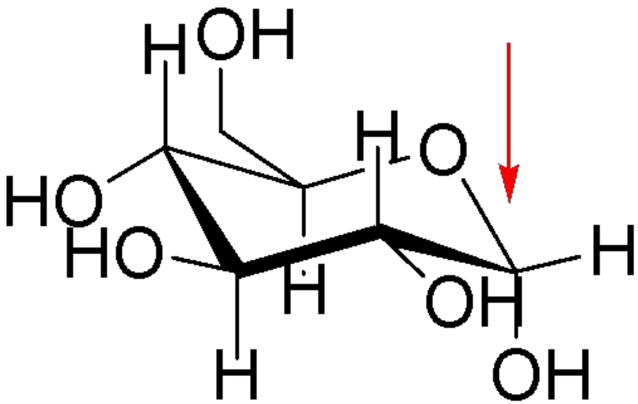
Glucose



Galactose

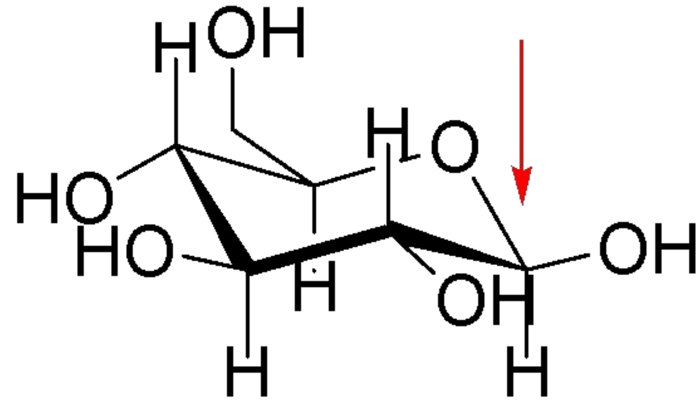


Fructose

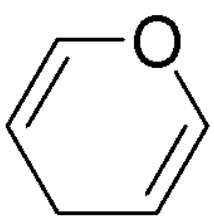


alpha

hemiacetal

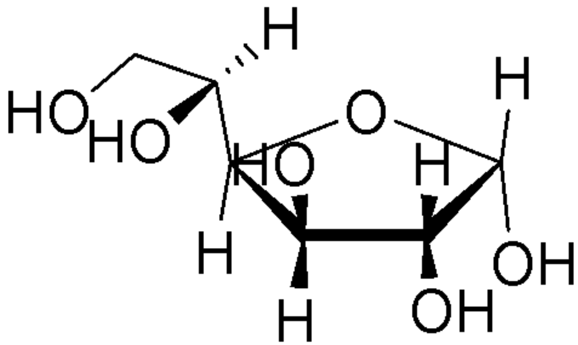


beta

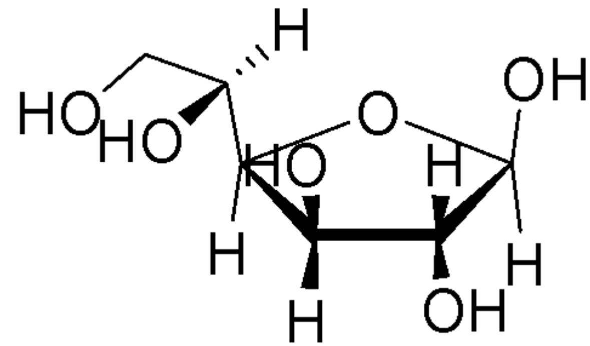


4*H*-Pyran

D-glucopyranoses

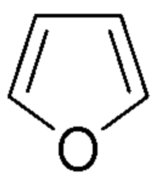


alpha furanose form



beta furanose form

D-glucofuranoses



furan

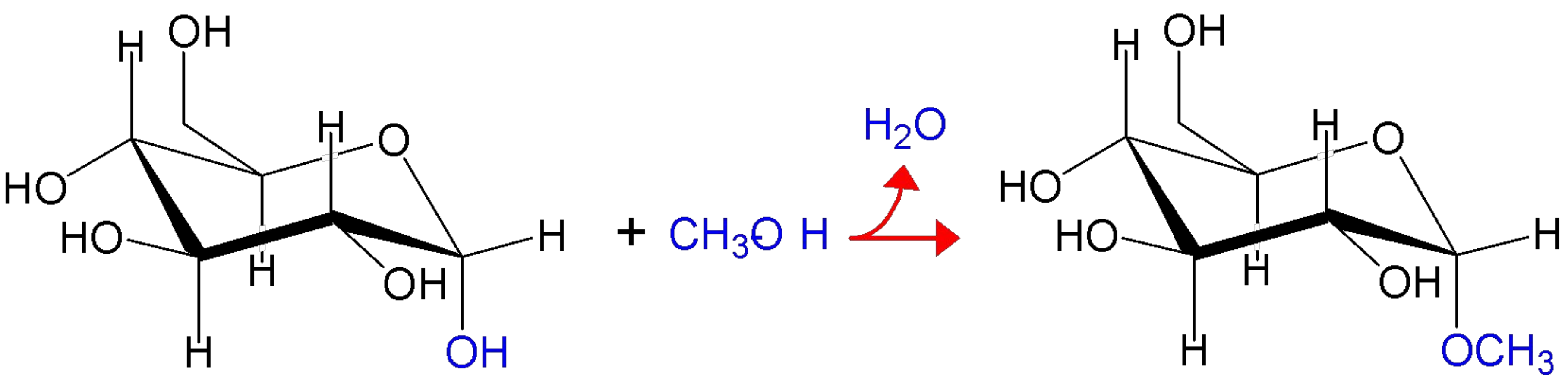
- **OPTICAL ACTIVITY**
- **Dextrorotatory (+) :If the sugar solution turns the plane of polarized light to right.**
-
- **Levorotatory (–) :If the sugar solution turns the plane of polarized light to left.**
-
- **Racemic mixture:Equimolar mixture of optical isomers has no net rotation.**

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:

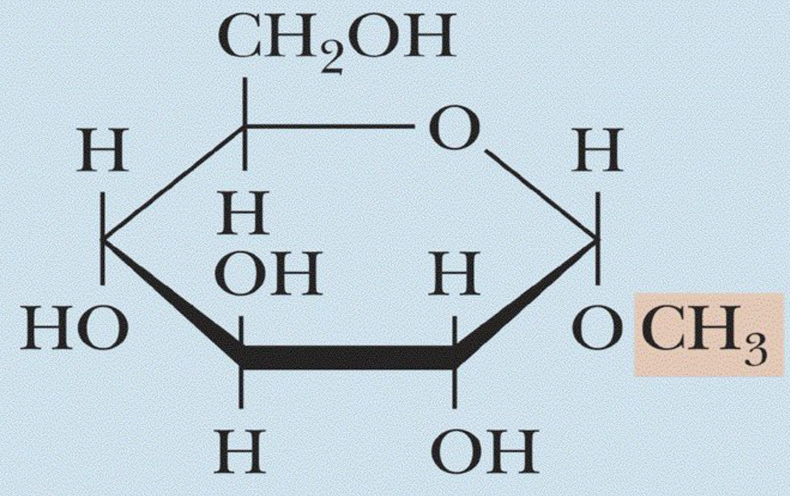
$$\text{R-OH} + \text{HO-R'} \;\square\; \text{R-O-R'} + H_2O$$

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

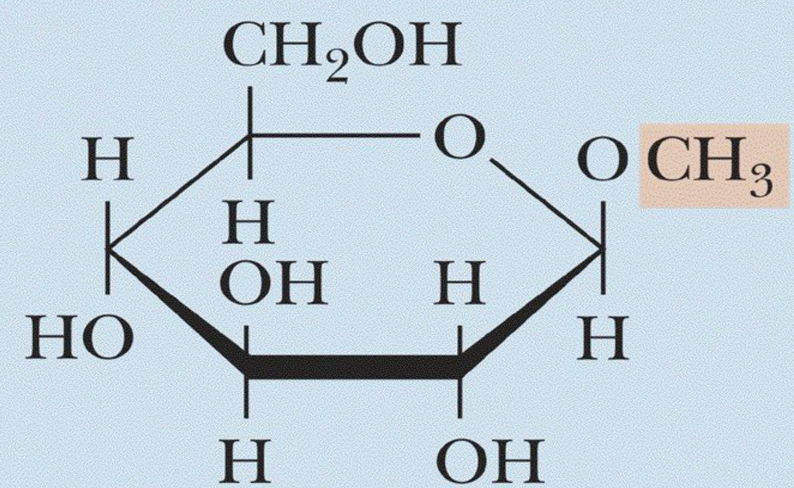


α-D-glucopyranose methanol methyl-α-D-glucopyranose

The anomeric forms of methyl-D-glucoside

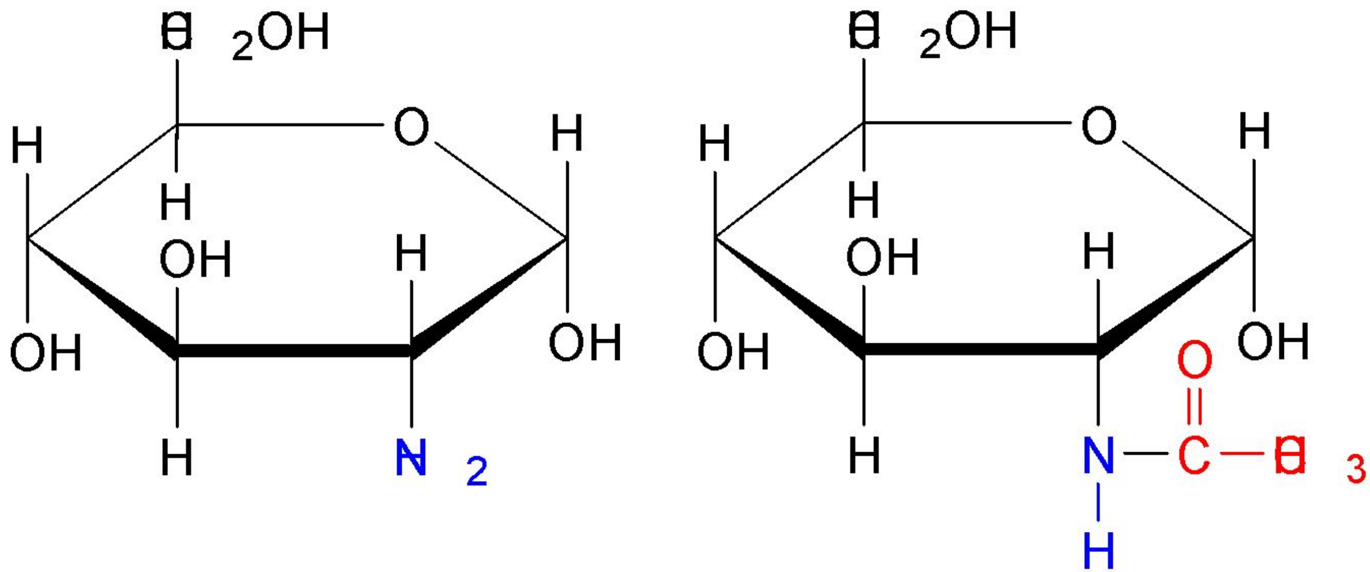


Methyl-α-D-glucoside



Methyl-β-D-glucoside

Sugar derivatives



α-D-glucosamine α-D-*N*-acetylglucosamine

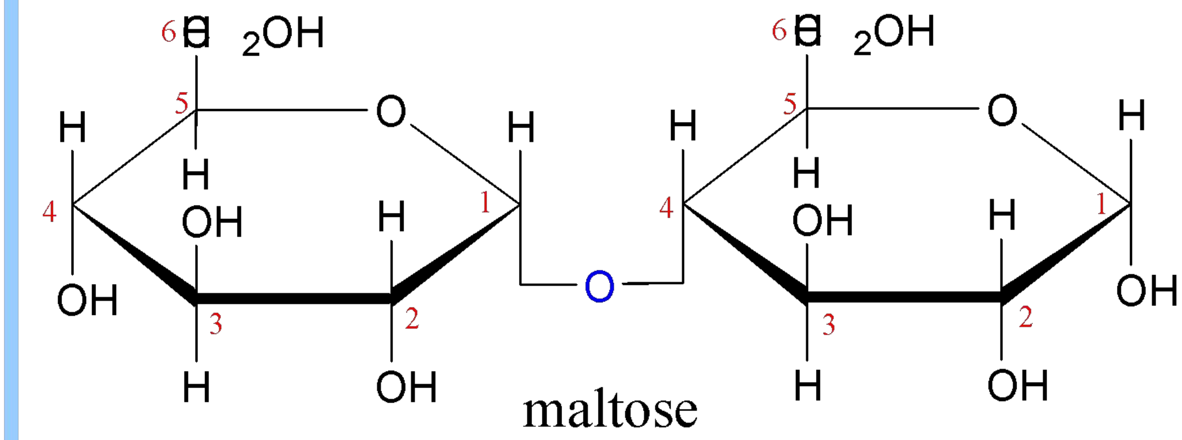
amino sugar - an amino group substitutes for a hydroxyl. An example is glucosamine.

The amino group may be acetylated, as in *N*-acetylglucosamine.

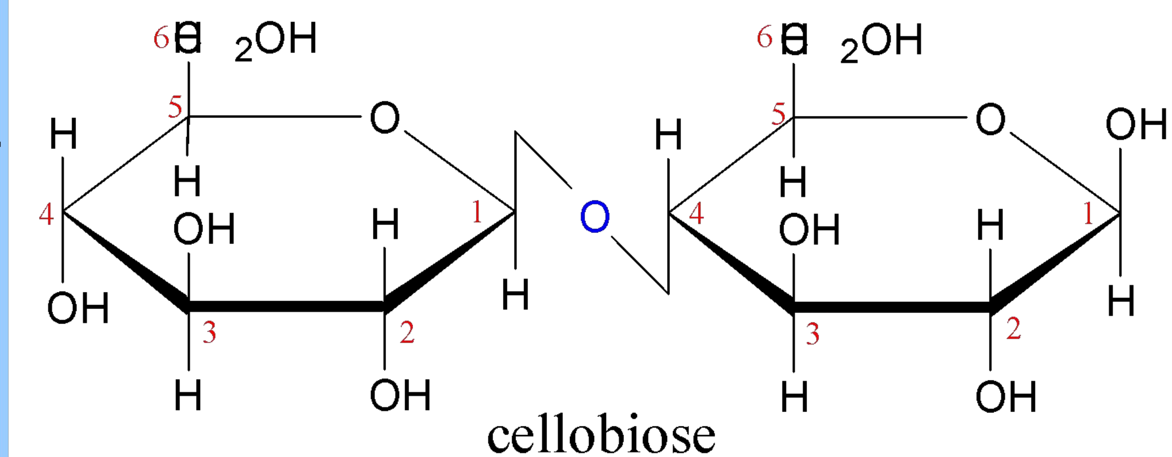
Disaccharides:

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

It is the **α** anomer (C1 O points down).



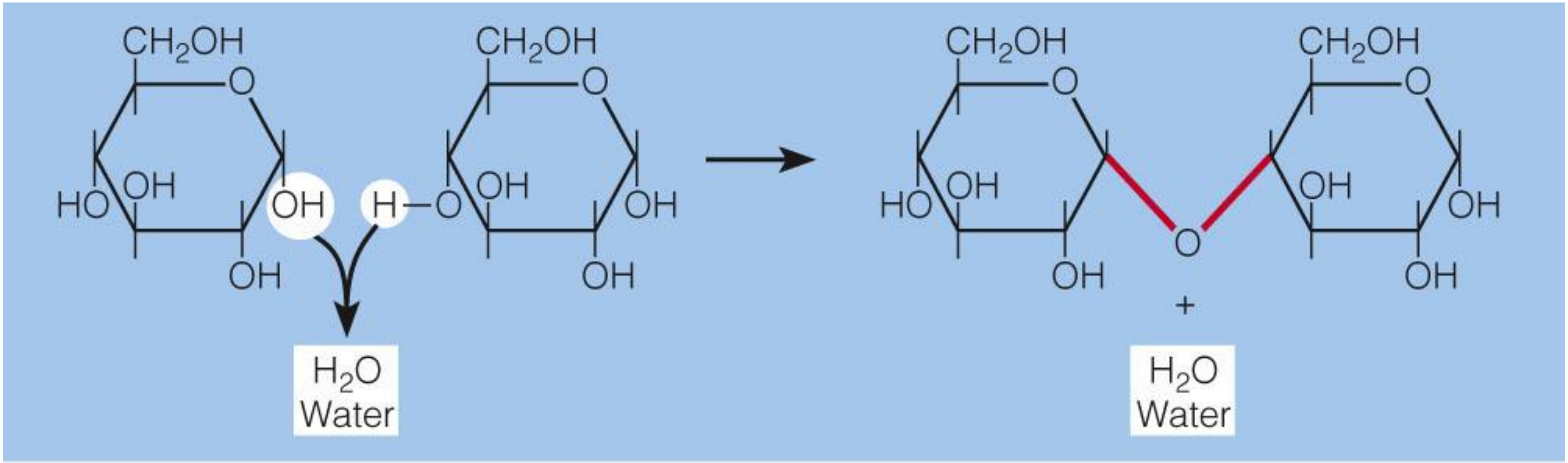
maltose



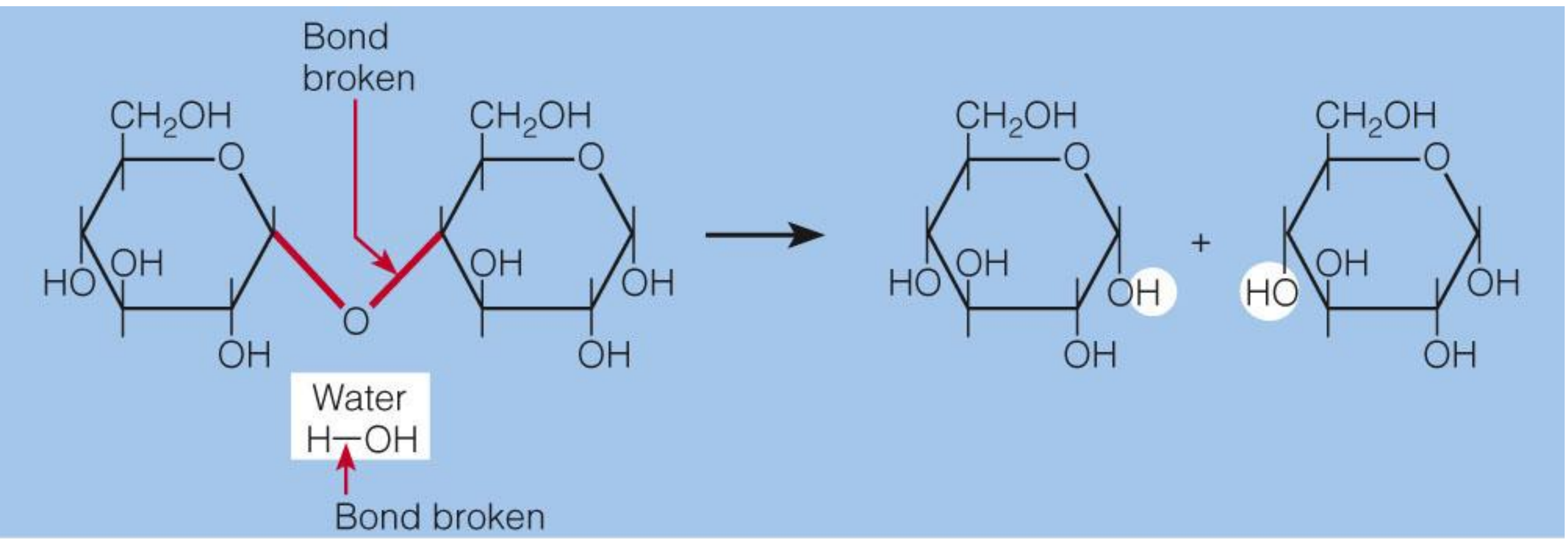
cellobiose

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

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



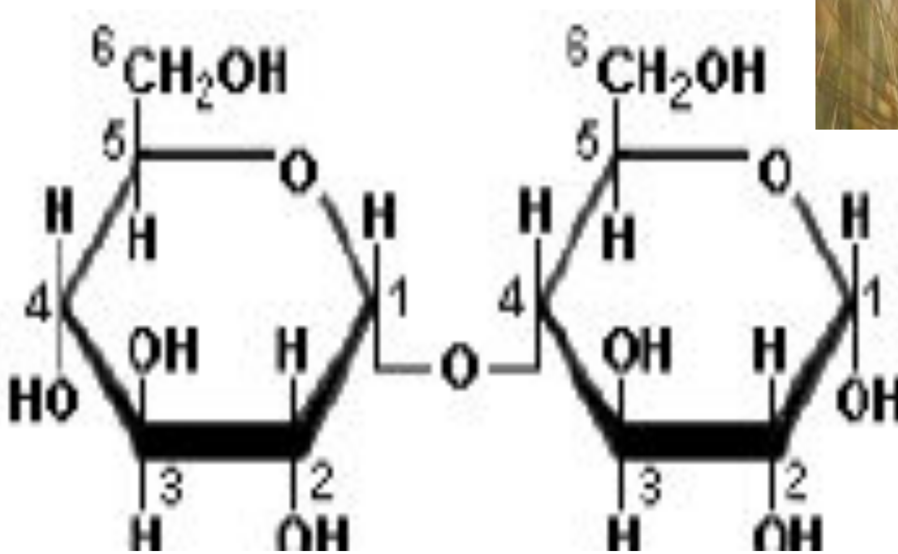
Glucose + glucose → Maltose



Maltose → Glucose + glucose

MALTOSE

- Malt sugar.
- Produced during the course of digestion of starch by the enzyme amylase.
- Two α-D-glucose units held together by α(1→4) glycosidic bond.



Other **disaccharides** include:

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

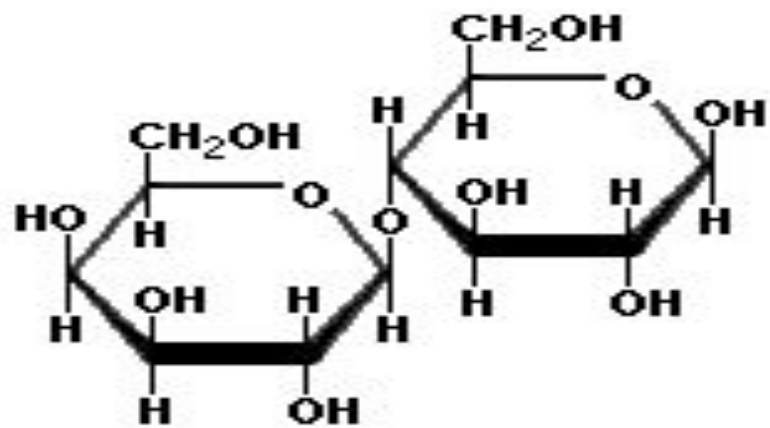
  Because the configuration at the anomeric C of glucose is α (O points down from ring), the linkage is α(1→2).

  The full name of sucrose is α-D-glucopyranosyl-(1→2)-β-D-fructopyranose.)

- **Lactose**, milk sugar, is composed of galactose & glucose, with β(1→4) linkage from the anomeric OH of galactose. Its full name is β-D-galactopyranosyl-(1→ 4)-α-D-glucopyranose

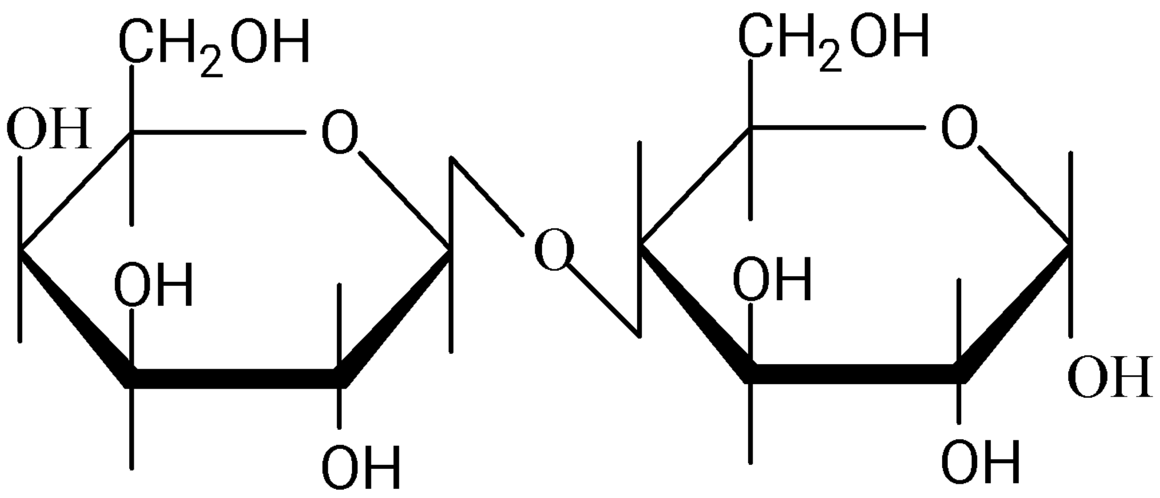
SUCROSE

- **Cane sugar.**
- □
- **α-D-glucose &β-D-fructose units held together by (α1→β2) glycosidic bond.**
- □
- **Reducing groups in both are involved in bond formation, hence non reducing.**



Lactose

Principal sugar in milk

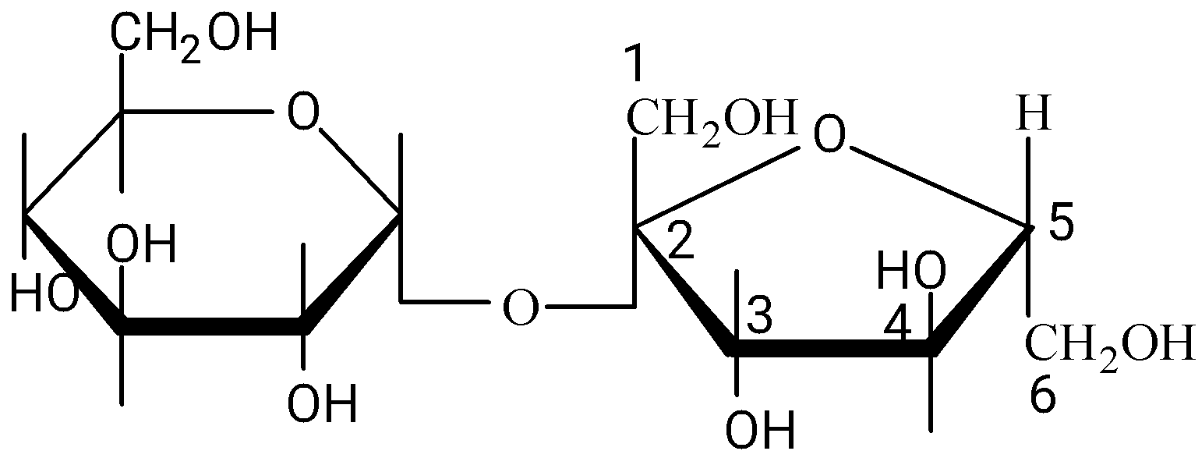


β-D-galactose & β-D-glucose units held together by β(1→4) glycosidic bond.

-
- **Reducing:Maltose, Lactose –with free aldehyde or keto group.**
-
- **Non-reducing:Sucrose, Trehalose –no free aldehyde or keto group.**

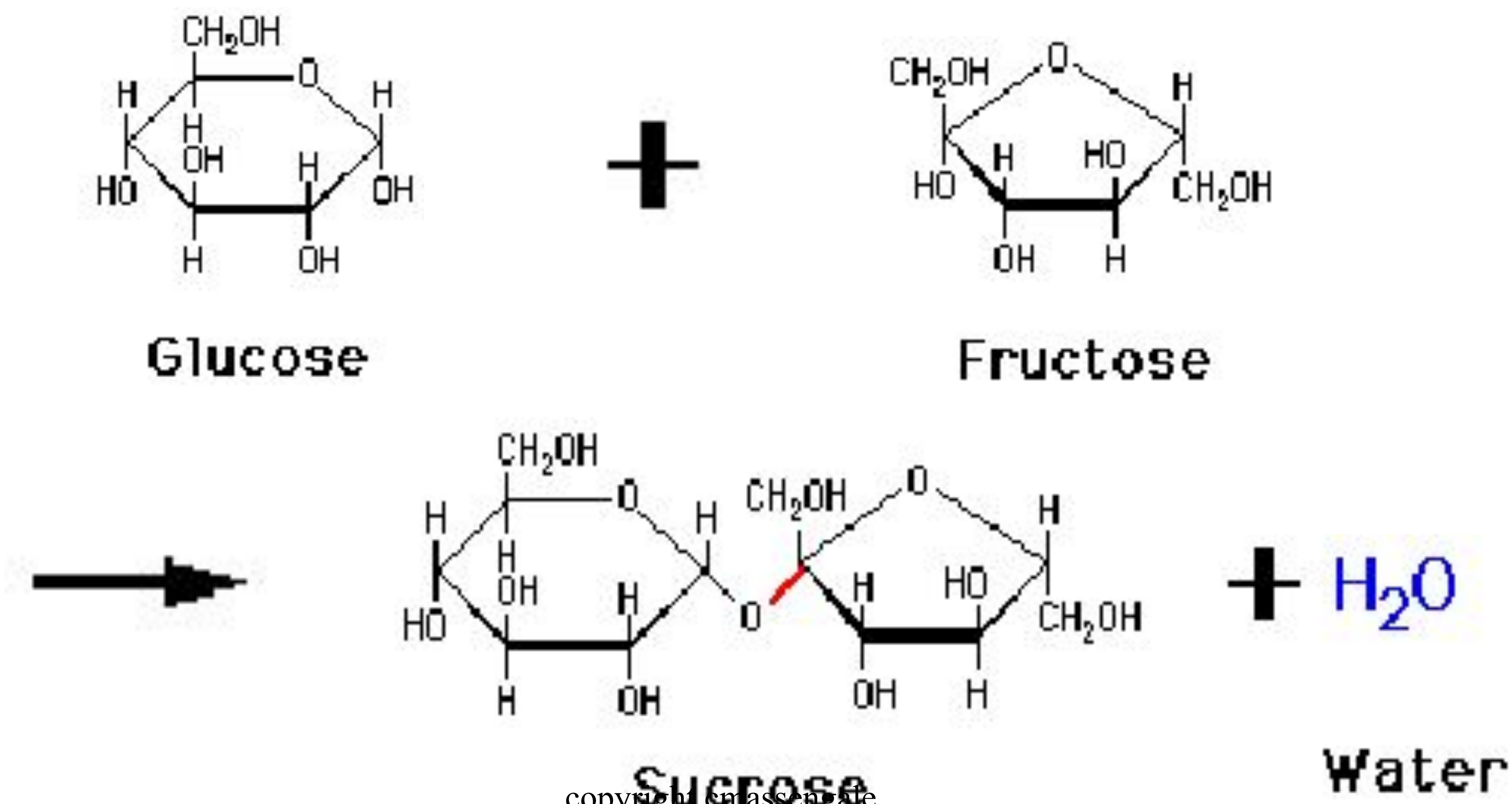
Sucrose

2-0-α-D-Glucopyranosyl β-D-Fructofuranoside

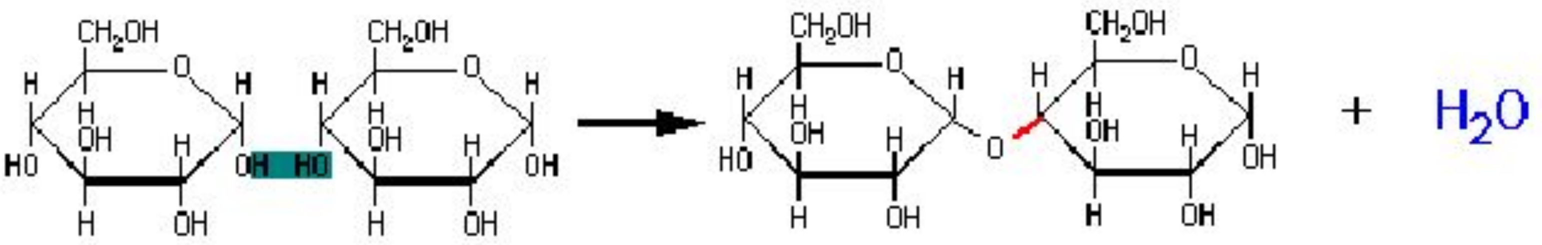


Invert Sugar --- when sucrose in solution, the rotation changes from detrorotatory (+66.5) to levorotatory (-19.8). So, sucrose is called "Invert Sugar". Sucrose has been hydrolyzed into glucose and fructose.

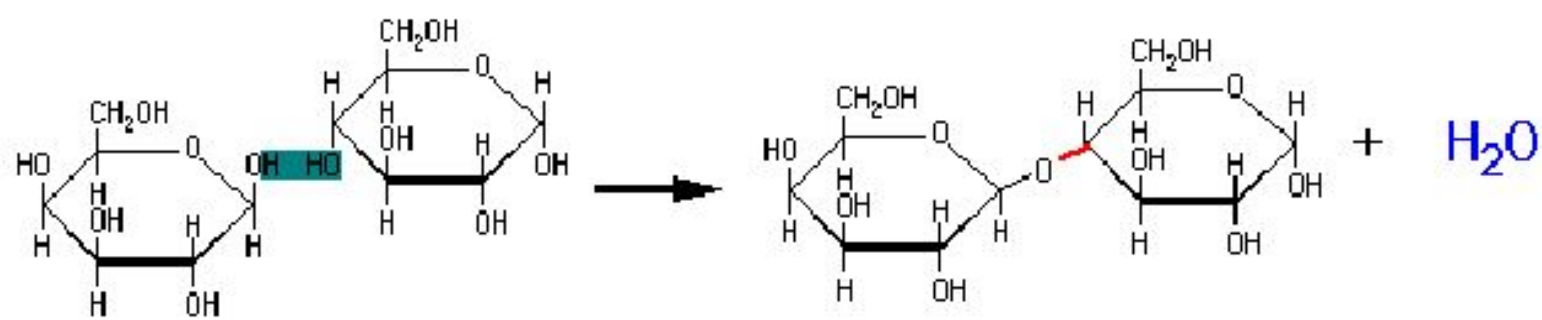
Dehydration Synthesis of a Disaccharide



Formation of Disaccharides



Glucose + Glucose = Maltose + Water



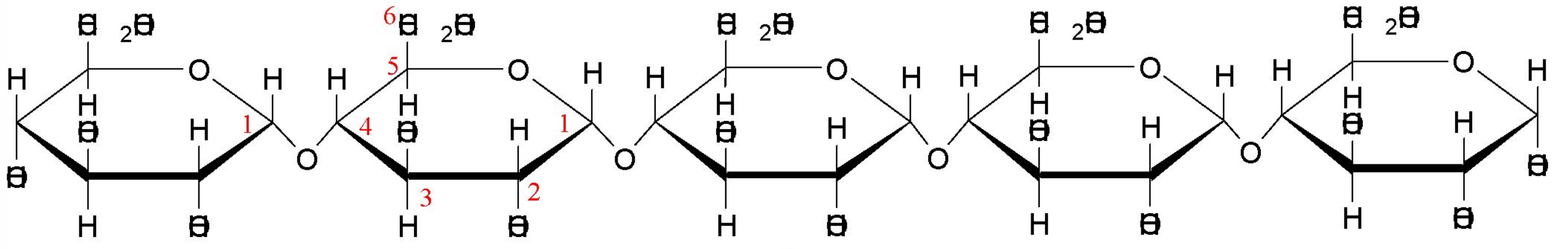
Galactose + Glucose = Lactose + Water

Starches

- stored in plant cells
- body hydrolyzes plant starch to glucose

Starch

- most common storage polysaccharide in plants
- composed of 10 – 30% α−amylose and 70-90% amylopectin depending on the source
- the chains are of varying length, having molecular weights from several thousands to half a million



amylose

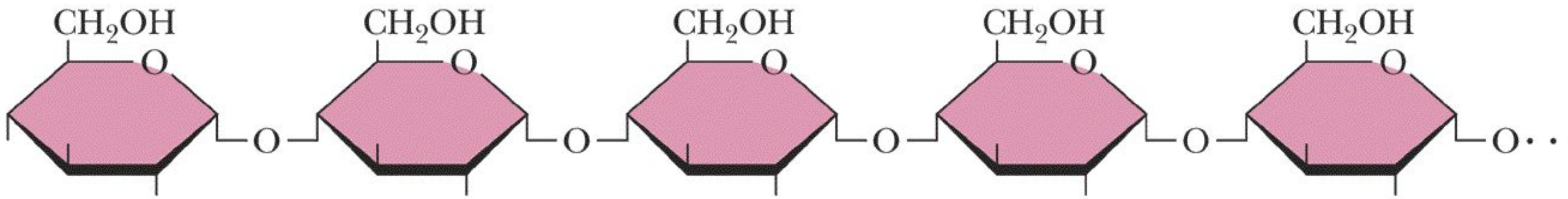
Polysaccharides:

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

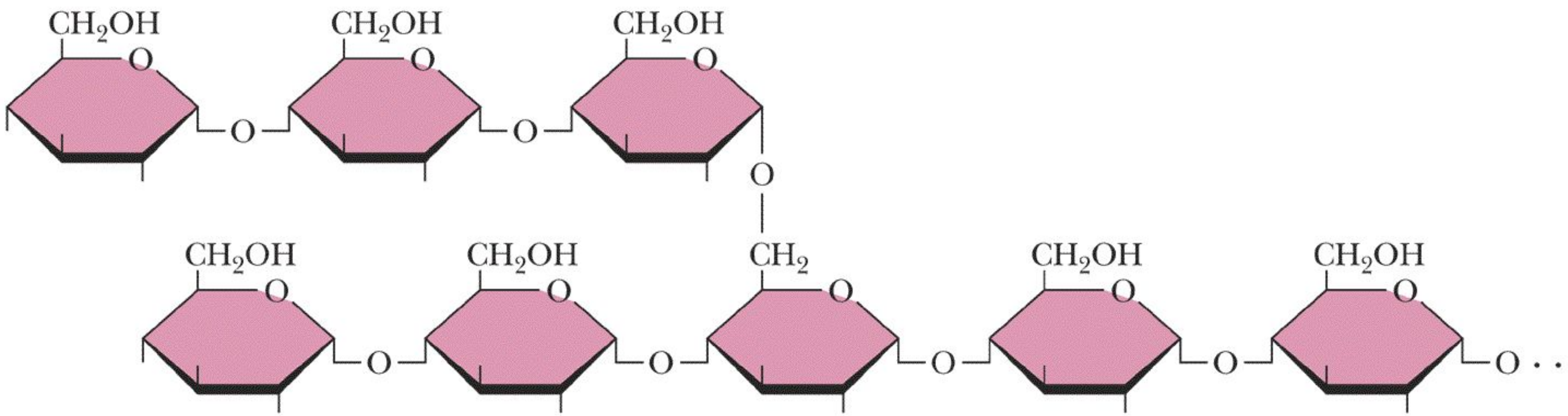
Glucose storage in **polymeric** form **minimizes osmotic effects**.

Amylose is a glucose polymer with **α(1→4)** linkages.

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



Amylose



Amylopectin

Amylose and amylopectin are the 2 forms of starch. Amylopectin is a highly branched structure, with branches occurring every 12 to 30 residues

Polysaccharides

starch

cellulose

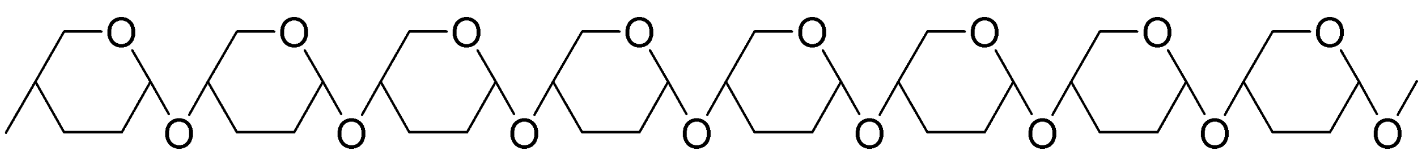
Starch 20% amylose (water soluble)

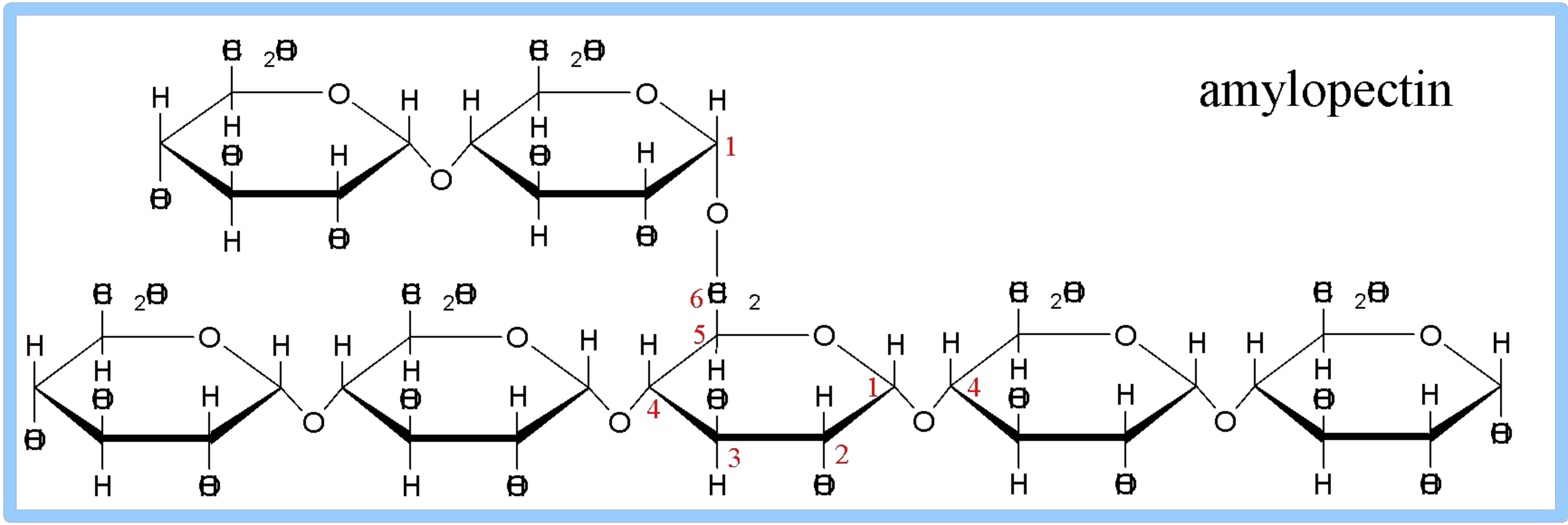
80% amylopectin (water insoluble)

amylose + H_2O □ (+)-maltose

(+)-maltose + H_2O □ (+)-glucose

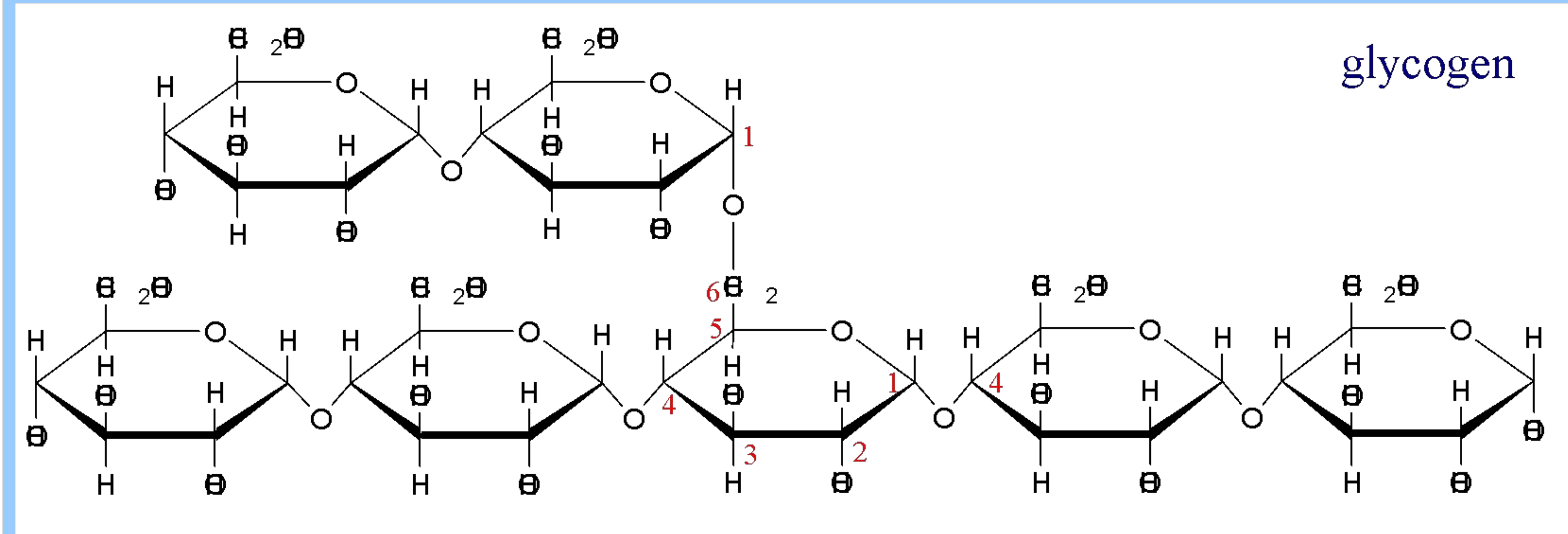
starch is a poly glucose (alpha-glucoside to C-4)





Amylopectin is a glucose polymer with mainly α(1→4) linkages, but it also has **branches** formed by α(1→6) 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, the glucose storage polymer in **animals**, is similar in structure to amylopectin.

But glycogen has **more** α(1→6) **branches**.

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

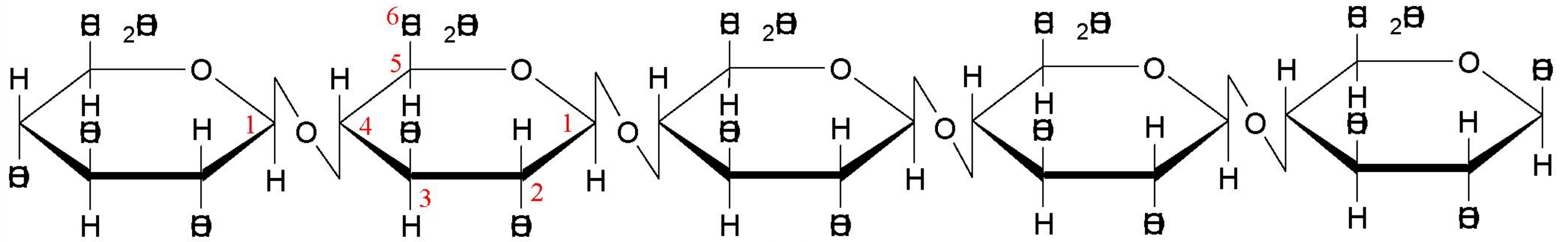
The ability to rapidly mobilize glucose is more essential to animals than to plants.

Glycogen

- also known as animal starch
- stored in muscle and liver (mostly)
- present in cells as granules (high MW)
- contains both α(1,4) links and α(1,6) branches at every 8 to 12 glucose unit (more frequent than in starch)
- complete hydrolysis yields glucose
- glycogen and iodine gives a red-violet color
- hydrolyzed by both α and β-amylases and by glycogen phosphorylase

Cellulose

- Polymer of β-D-glucose attached by β(1,4) linkages
- Only digested and utilized by ruminants (cows, deers, giraffes, camels)
- A structural polysaccharide
- Yields glucose upon complete hydrolysis
- Partial hydrolysis yields cellobiose
- Most abundant of all carbohydrates
    - Cotton flax: 97-99% cellulose
    - Wood: ~ 50% cellulose
- Gives no color with iodine
- Held together with lignin in woody plant tissues



cellulose

Cellulose, a major constituent of plant cell walls, consists of long linear chains of glucose with β(1 → 4) linkages.

Every other glucose is flipped over, due to β linkages.

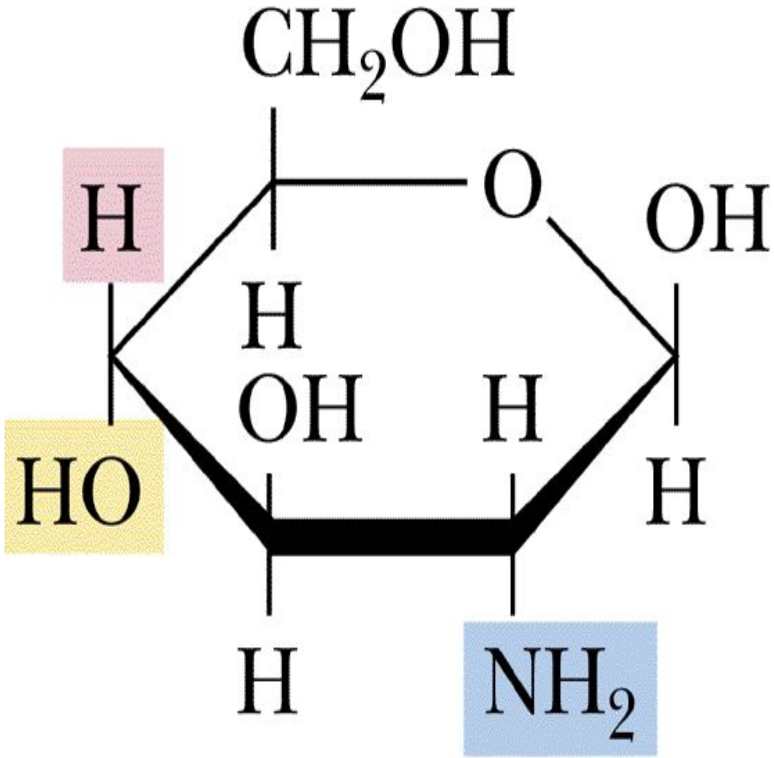
This promotes intra-chain and inter-chain H-bonds and van der Waals interactions, that cause cellulose chains to be straight & rigid, and pack with a crystalline arrangement in thick bundles - microfibrils.

See: Botany *online* website website; website at Georgia Tech

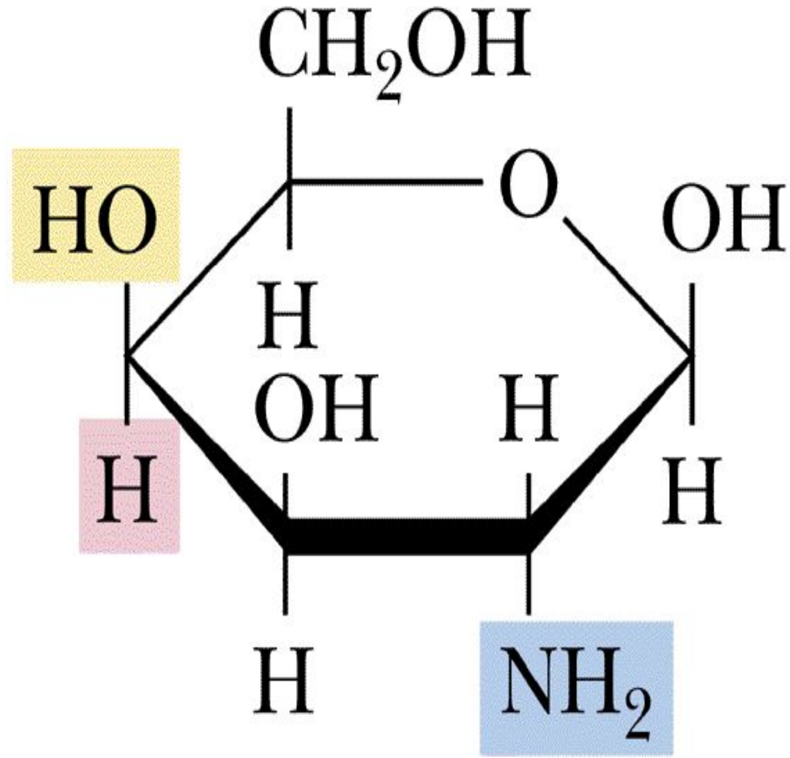
Schematic of arrangement of cellulose chains in a microfibril.

Special monosaccharides: amino sugars

Constituents of mucopolysaccharides



β-D-Glucosamine



β-D-Galactosamine