

Carbohydrates

Structure and Biological Function

Monosaccharides

Carbohydrates in Cyclic Structures

Reactions of Glucose and Other
Monosaccharides

Polysaccharides

Carbohydrates

Old definition – hydrates of carbon

New definition - Polyhydroxy aldehydes or ketones and their derivatives or as substances that yields one of these compounds

Compounds containing C, H and O

General formula : $C_x(H_2O)_y$

All have C=O and -OH functional groups.

Carbohydrates are the most abundant of all the organic compounds in nature.

- In plants, energy from the Sun is used to convert carbon dioxide and water into the carbohydrate glucose.
- Many of the glucose molecules are made into long-chain polymers of starch that store energy.
- About 65% of the foods in our diet consist of carbohydrates.
- Each day we utilize carbohydrates in foods such as bread, pasta, potatoes, and rice.
- Other carbohydrates called disaccharides include sucrose (table sugar) and lactose in milk

During digestion and cellular metabolism, carbohydrates are converted into glucose, □ which is **oxidized** further in our cells **to provide our bodies with energy** and to provide the cells with **carbon atoms** for building molecules of protein, lipids, and nucleic acids. □ In plants, a polymer of glucose called cellulose builds the structural framework. Cellulose has other important uses, too. □ The wood in our furniture, the pages in your notebook, and the cotton in our clothing are made of cellulose.

Function of Carbohydrates in Cells

- Major source of energy for the cell
- Major structural component of plant cell
- Immediate energy in the form of GLUCOSE
- Reserve or stored energy in the form of GLYCOGEN

Classification of Carbohydrates

- Carbohydrates are classified according to the number of subunits that make them up

3 Types of Carbohydrates

□ Monosaccharides

□ Oligosaccharides

Disaccharides

Trisaccharides

Tetrasaccharides

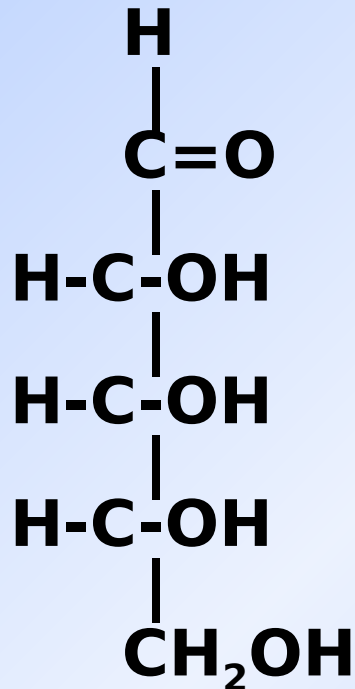
□ Polysaccharides

Monosaccharides

- simple sugars
- compounds which possess a **free aldehyde** (CHO) or **ketone** (C=O) group and two or more hydroxyl (OH) groups.
- They are the simplest sugars cannot be hydrolysed further into smaller units.
- Monosaccharides contain a single carbon chain and are classified on the basis of number of carbon atoms they possess, and as aldoses or ketoses depending upon their groups

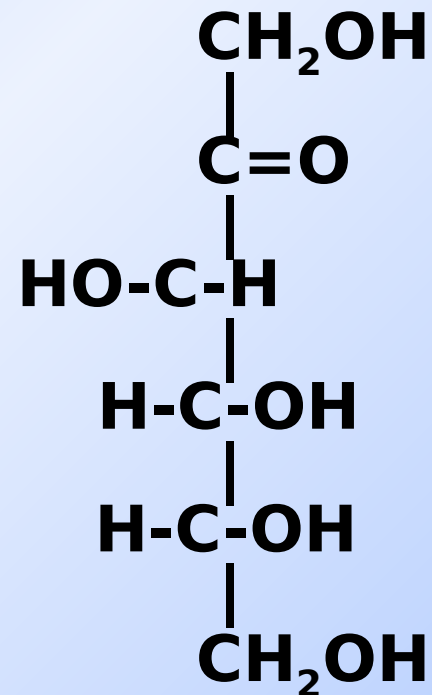
Monosaccharides

Based on location of C=O



Aldose

- aldehyde C=O

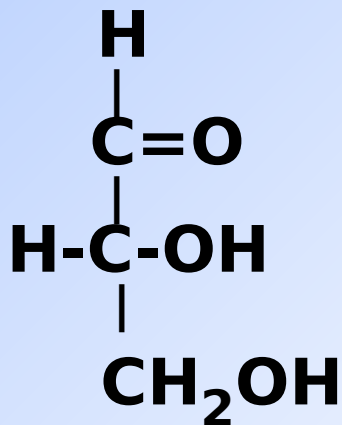


Ketose

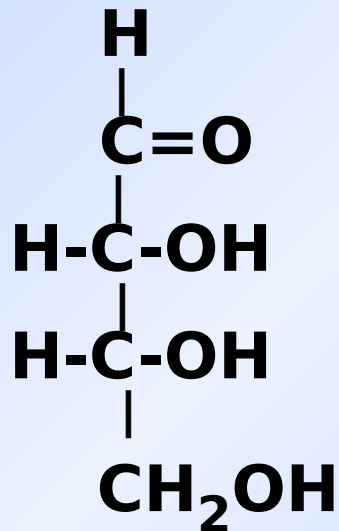
- ketone C=O

Monosaccharide classifications

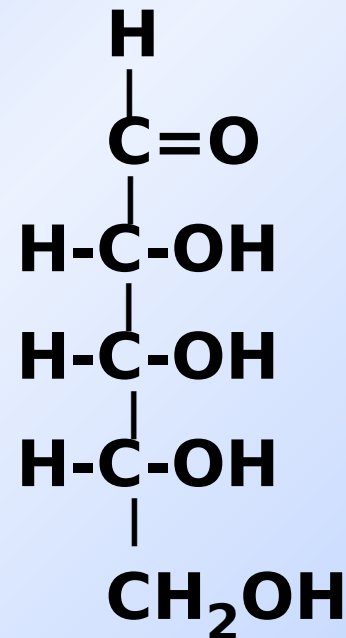
Number of carbon atoms in the chain



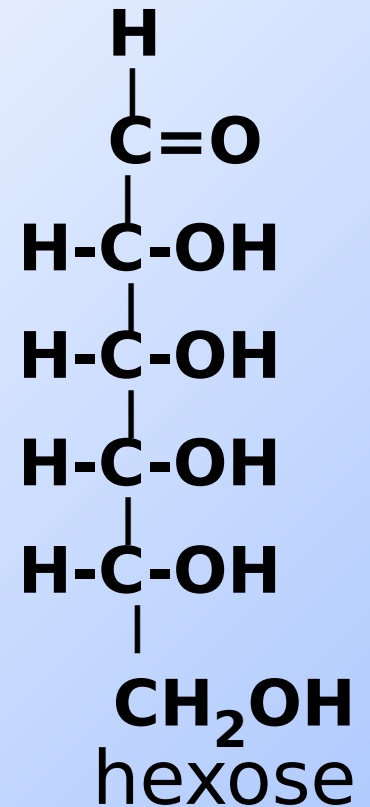
triose



tetrose

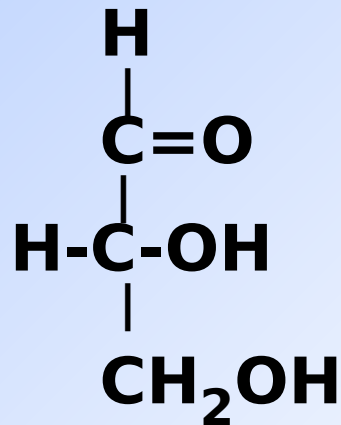


pentose

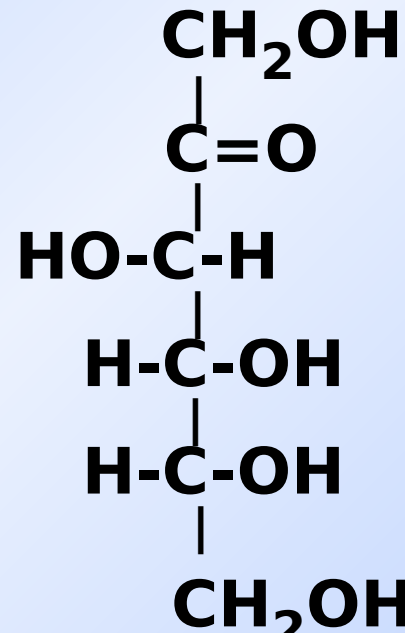


Can be either aldose or ketose sugar.

Examples

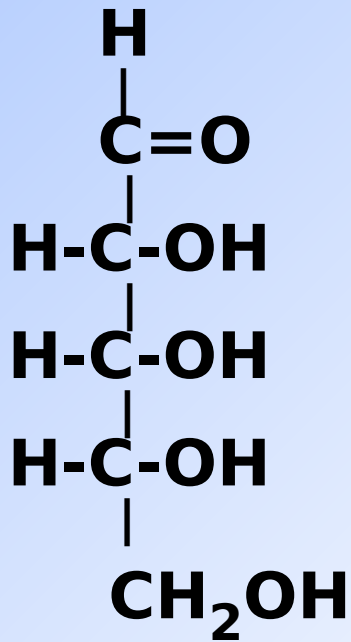


D-glyceraldehyde
triose
aldose
aldotriose sugar

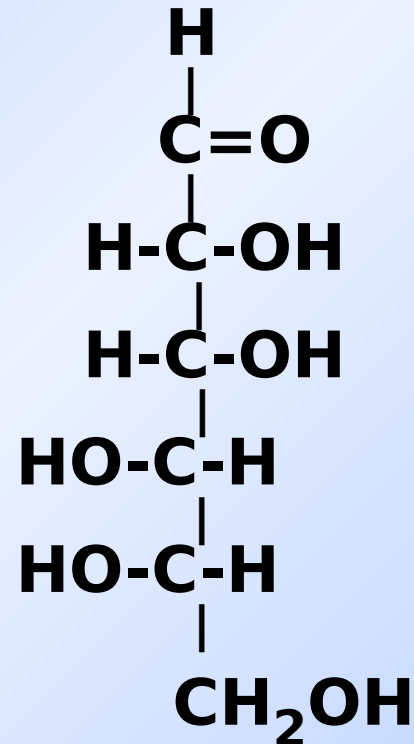


D-fructose
hexose
ketose
ketohehexose sugar

Examples



D-ribose
pentose, aldose
aldopentose sugar



L-mannose
hexose, aldose
aldohexose sugar

Stereoisomers

Stereochemistry

Study of the spatial arrangement of molecules.

Stereoisomers have

- the same order and types of bonds.
- different spatial arrangements.
- different properties.

Many biologically important chemicals, like sugars, exist as stereoisomers. Your body can tell the difference.

Enantiomers

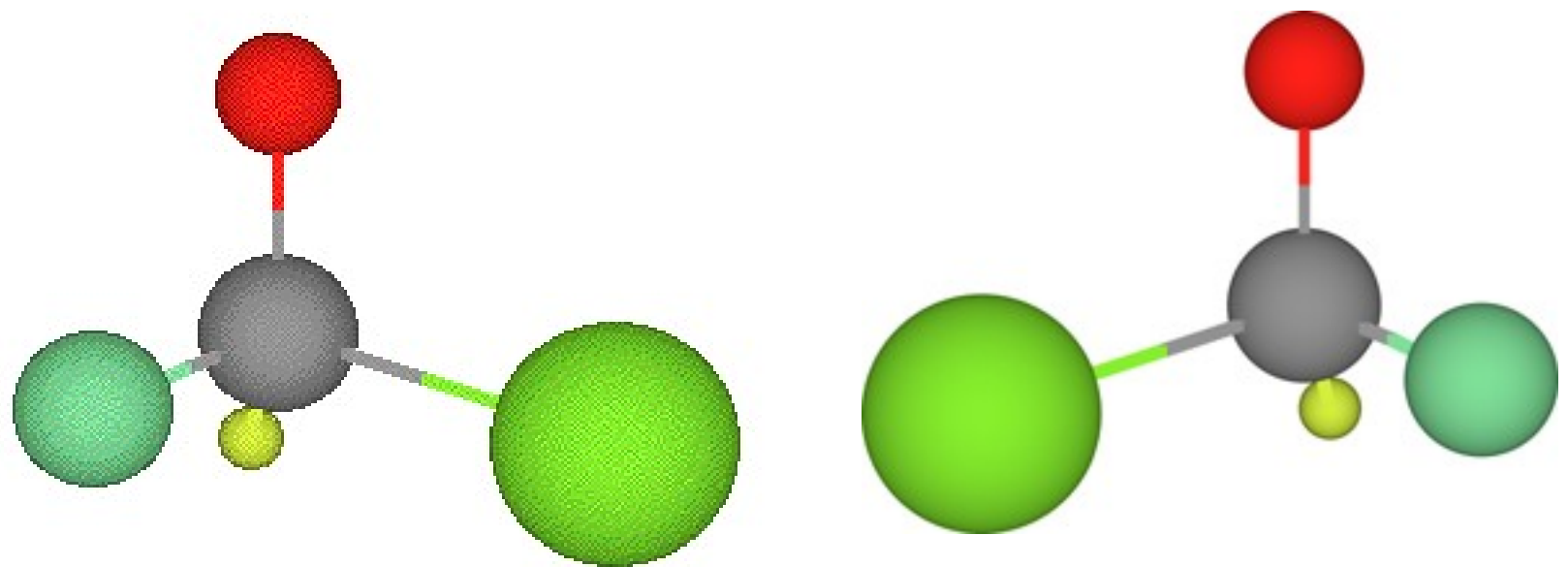
Pairs of stereoisomers

Designated by D- or L- at the start of the name.

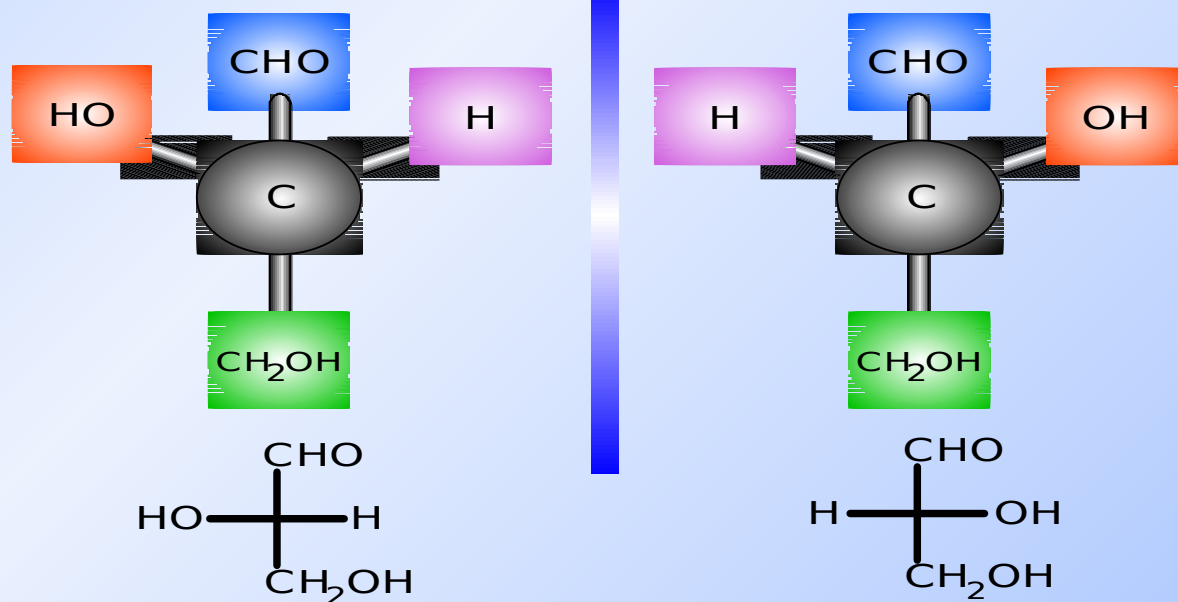
They are mirror images that can't be overlapped.



Enantiomers



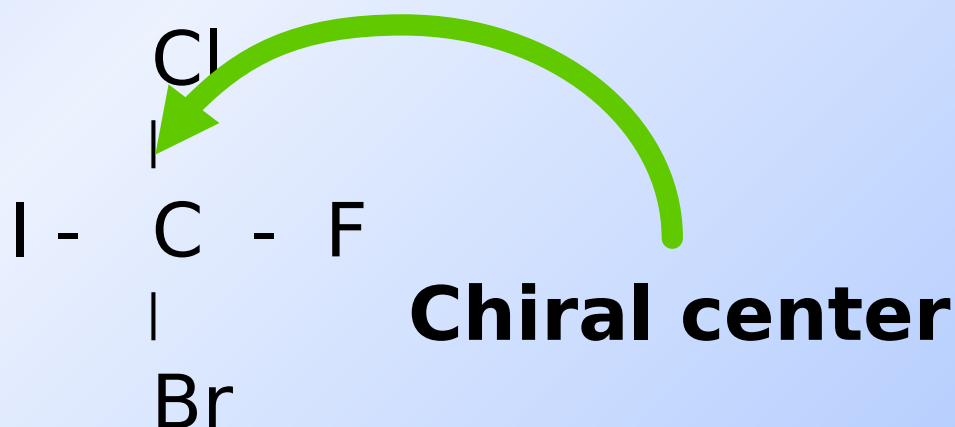
One form in which H atom at carbon 2 is projected to the left side and OH group to the right is designated as D-form and the other form where H atom is projected to the right side and OH group to the left is called as L-form



Enantiomers

Chiral center.

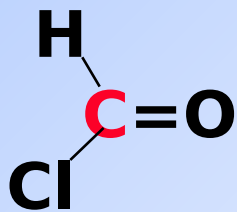
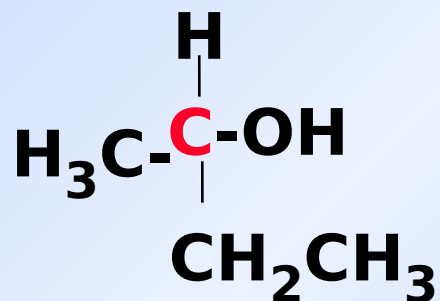
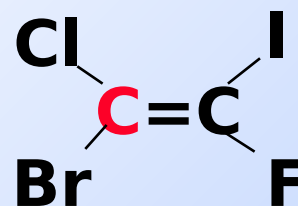
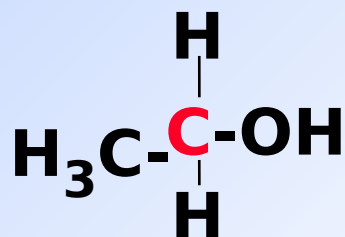
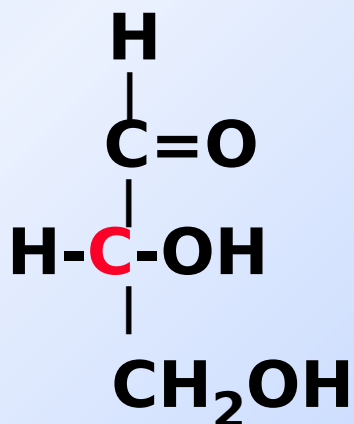
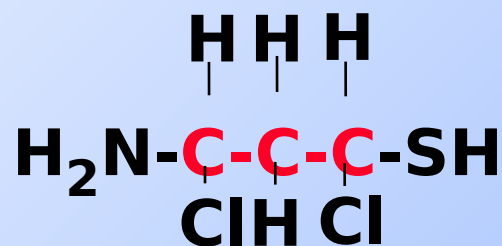
Asymmetric carbon - 4 different things are attached to it.



You must have at least one asymmetric carbon to have stereoisomers.

Examples

Is the 'red' carbon chiral?



Physical properties

Optical activity

ability to rotate plane polarized light.

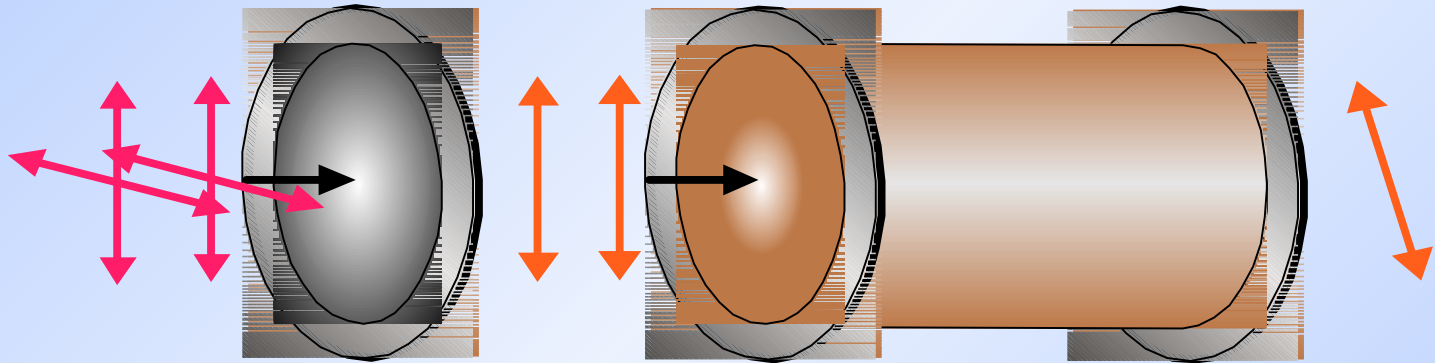
dextrorotatory - rotate to right

- use + symbol
- usually D isomers

levorotatory

- rotate to left
- use - symbol
- usually L isomers

Plane polarized light



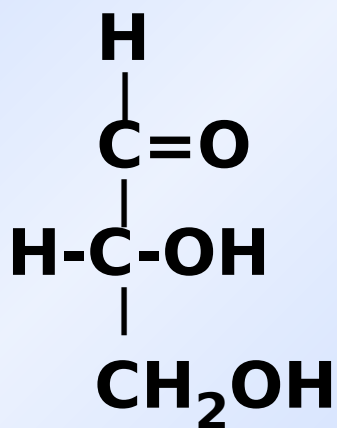
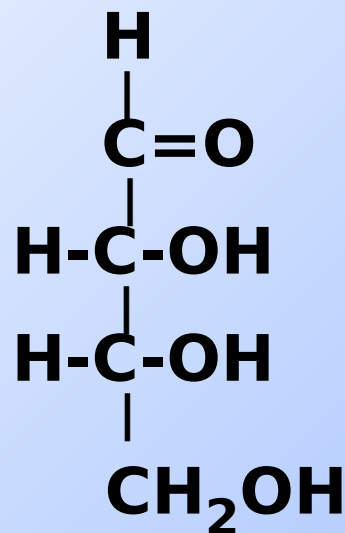
Light is passed through a polarized filter. A solution of an optical isomer will rotate the light one direction.

Stereochemistry

Properly drawing enantiomers in 3-D is hard.

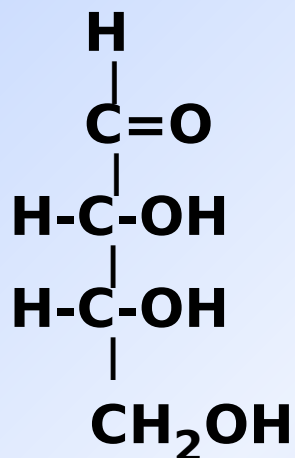
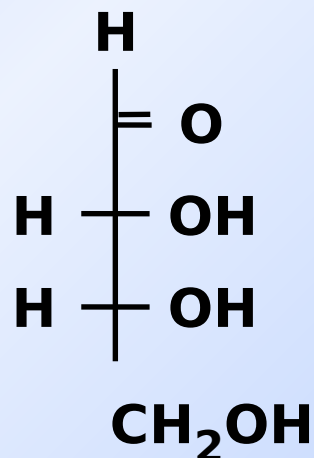
Use **Fischer Projections**

Specific type of formula that designates the orientation of groups.



Fischer projections

With this system, a tetrahedral carbon atom is represented by two crossed lines.



A horizontal bond to an asymmetric carbon designates bonds in the front plane of the page.

Vertical bonds are behind the plane of the page.

Some important monosaccharides

D-glyceraldehyde

Simplest sugar

D-glucose
diet

Most important in

D-fructose
sugars

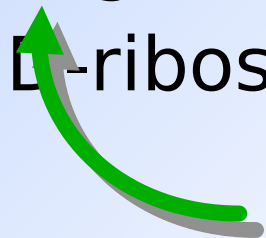
Sweetest of all

D-galactose

Part of milk sugar

D-ribose

Used in RNA



note that each is a D-

enantiomer

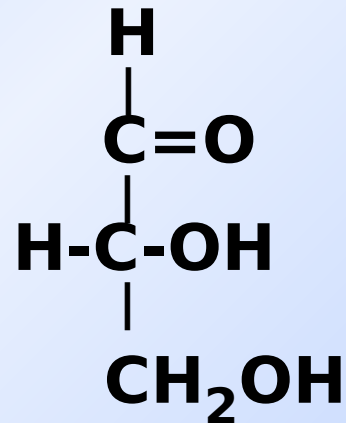
D-glyceraldehyde

Three carbon sugar

Aldose sugar

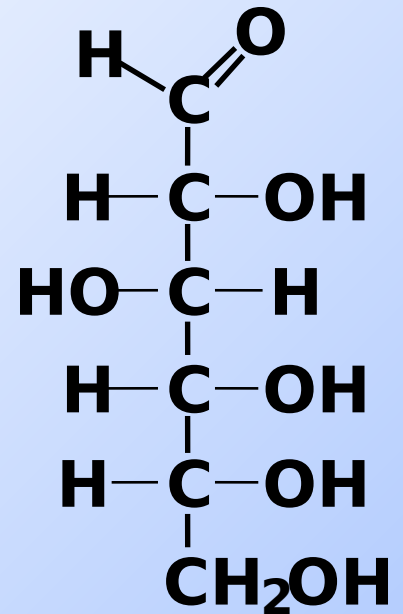
Triose sugar

aldotriose



D-glucose

- Glucose is an aldohexose sugar.
- Common names include dextrose, grape sugar, blood sugar.
- Most important sugar in our diet.
- Most abundant organic compound found in nature.
- Level in blood can be as high as 0.1%



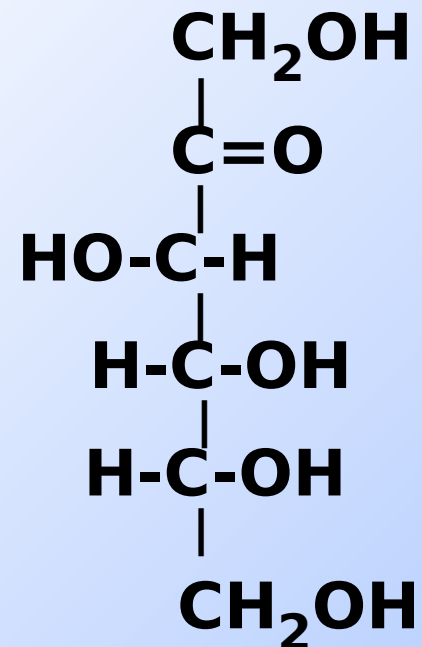
D-fructose

Another common sugar.

It is a ketohexose.

Sweetest of all sugars.

1.5 X sweeter than
sucrose

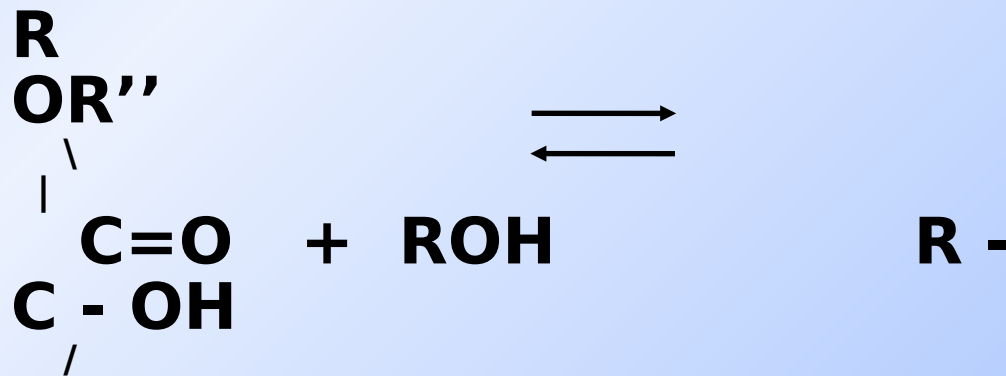


Carbohydrates in cyclic structures

If optical isomers weren't enough, sugars also form rings. For many sugars, it's the most common form.

hemiacetal - forms from alcohol and aldehyde

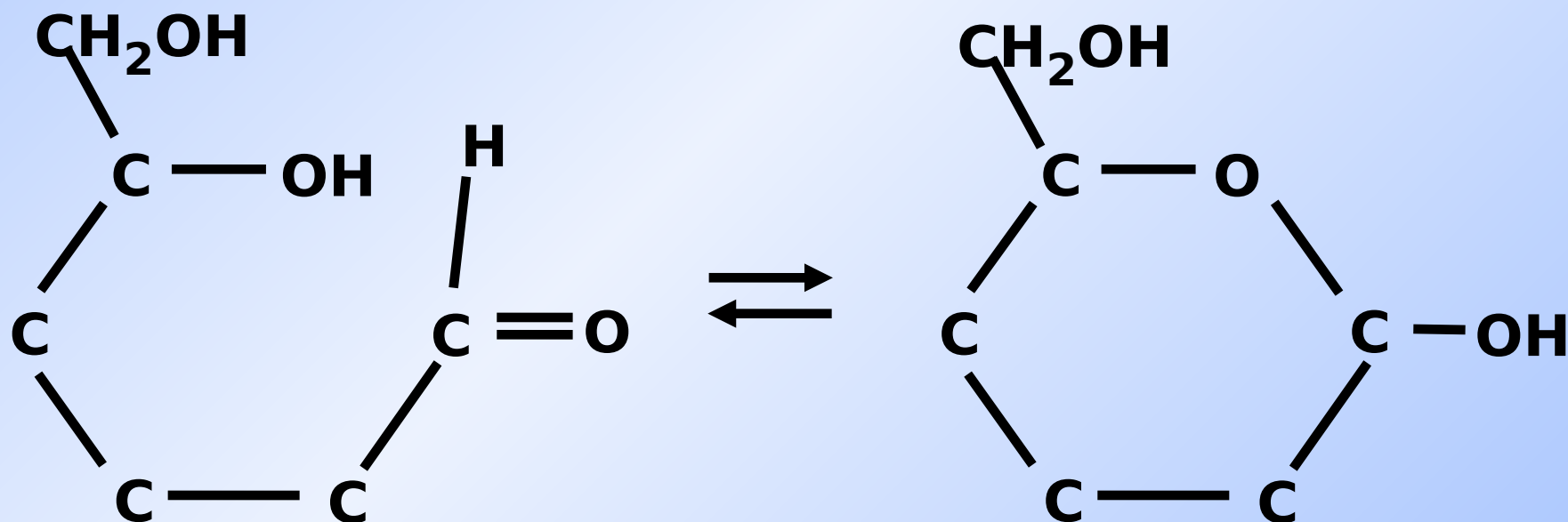
hemiketal - forms from alcohol and ketone



Intramolecular cyclization

Cyclization.

Remember - chains can bend and rotate.



Intramolecular cyclization

The -OH group that forms can be above or below the ring resulting in two forms

- anomers

□ and □ are used to identify the two forms.

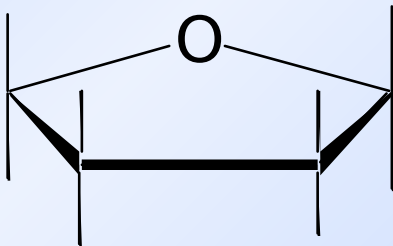
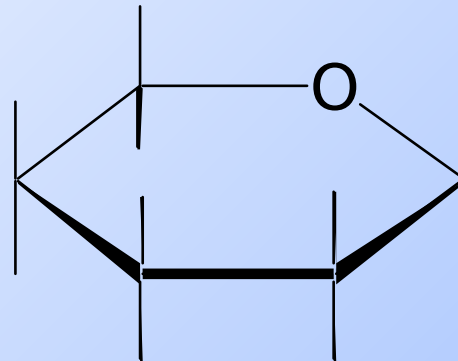
- □ - OH group is down compared to CH_2OH (trans).
- □ - OH group is up compared to CH_2OH (cis).

Intramolecular cyclization

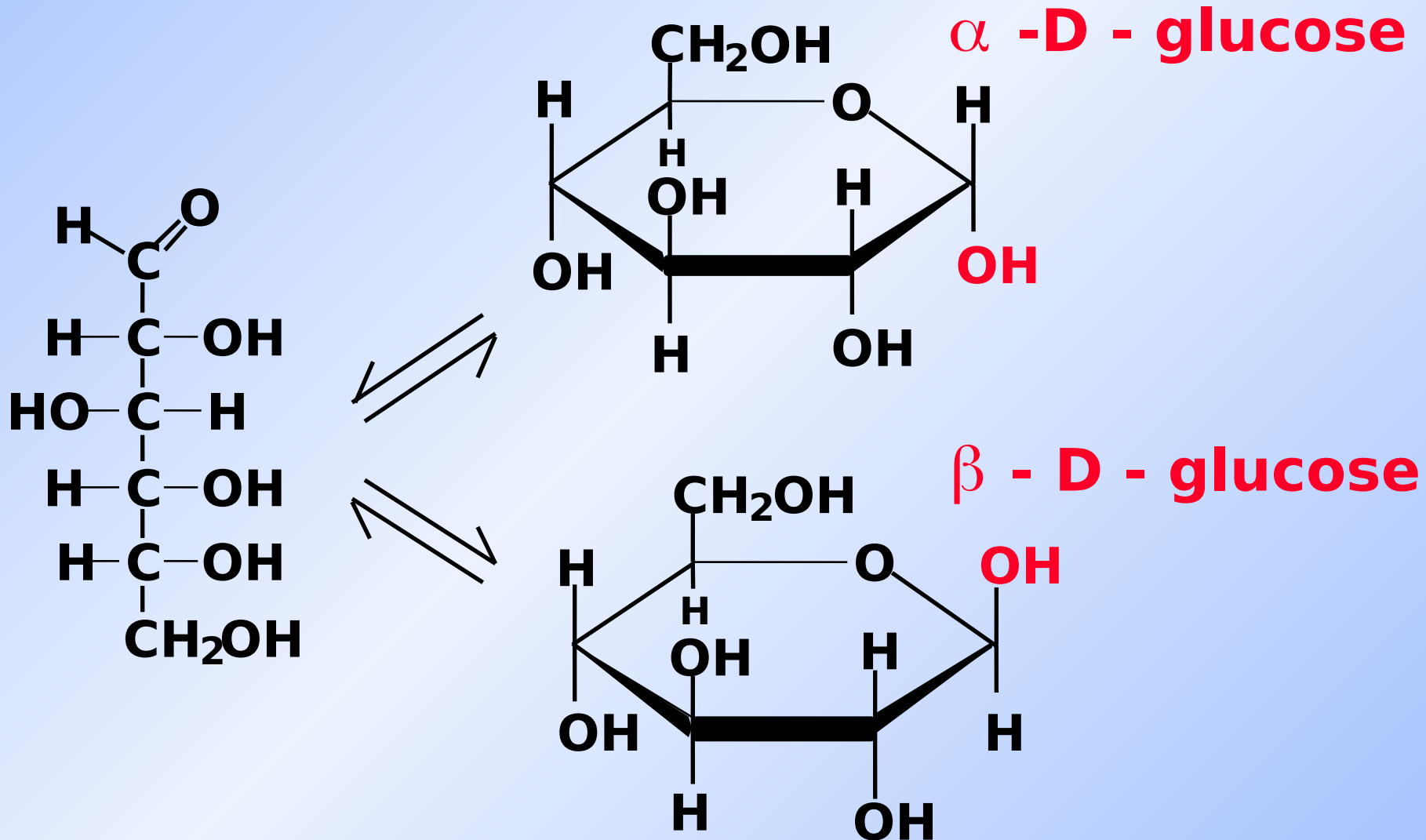
The α and β forms are in equilibrium so one form can convert to the other - **mutarotation**.

Haworth projections can be used to help see α and β orientations.

This process occurs more rapidly in the presence of cellular enzymes called *mutarotases*.

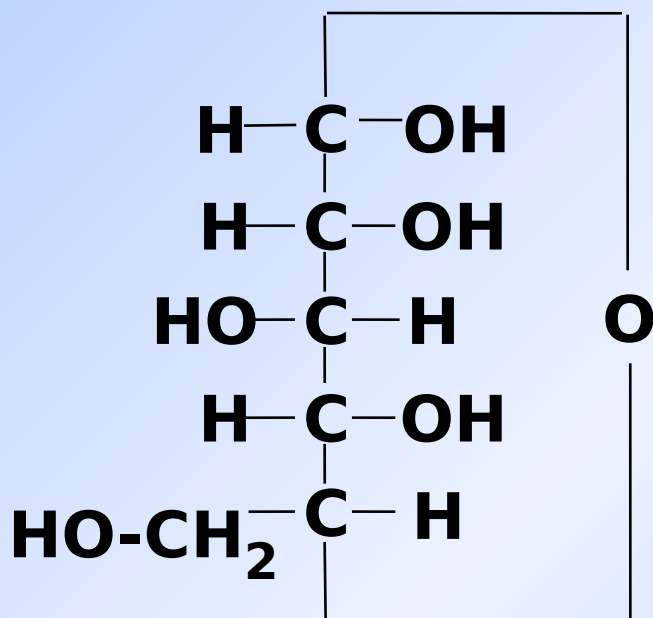
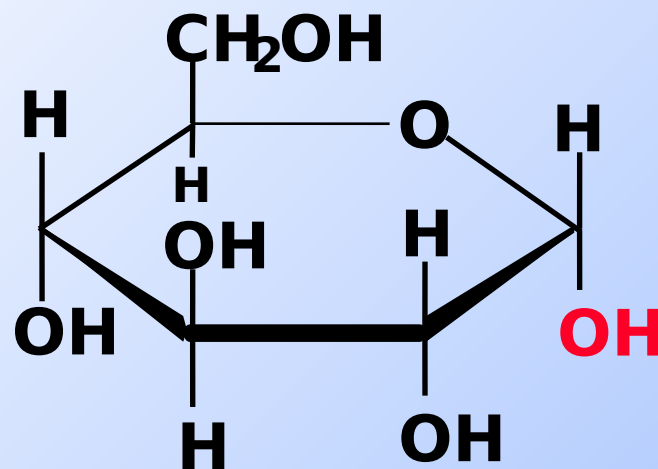


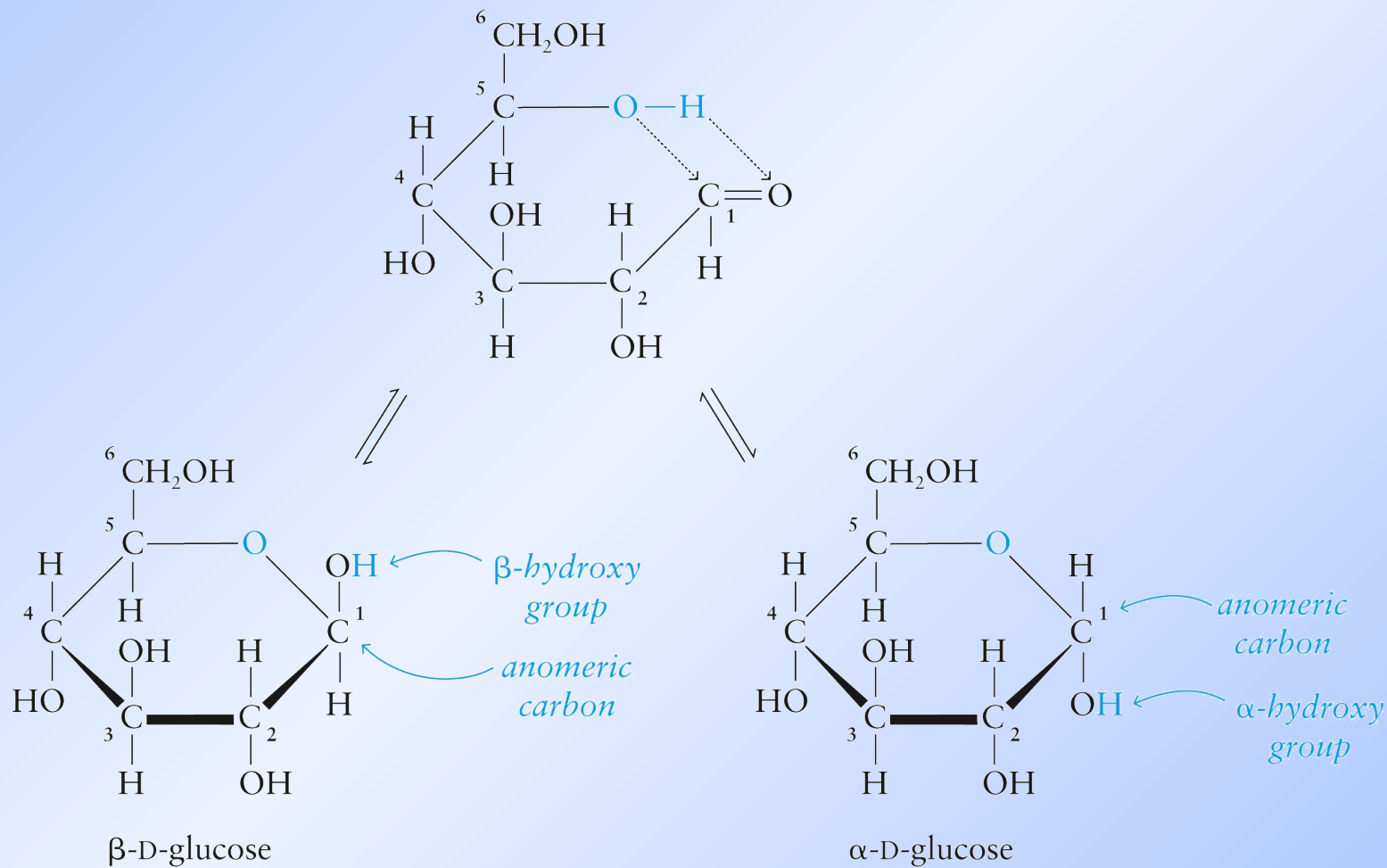
Cyclization of D-glucose



Fischer vs. Haworth projections

α -D-glucose



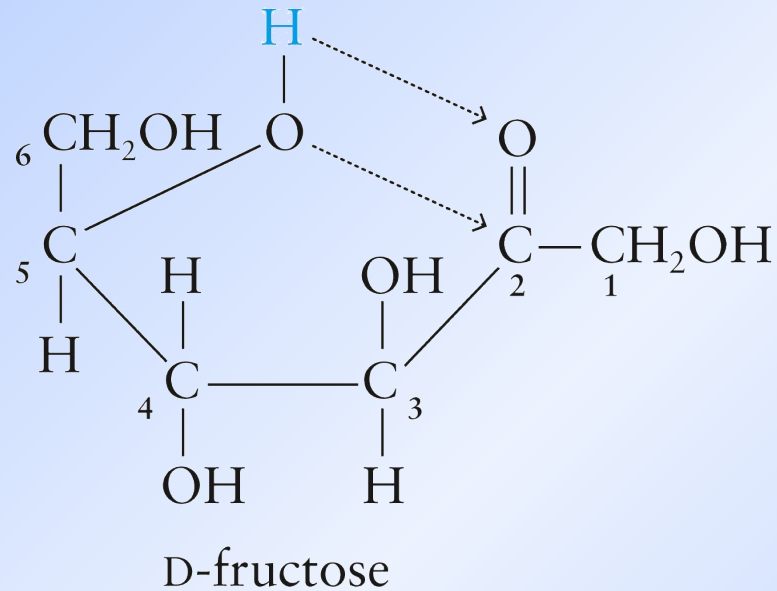
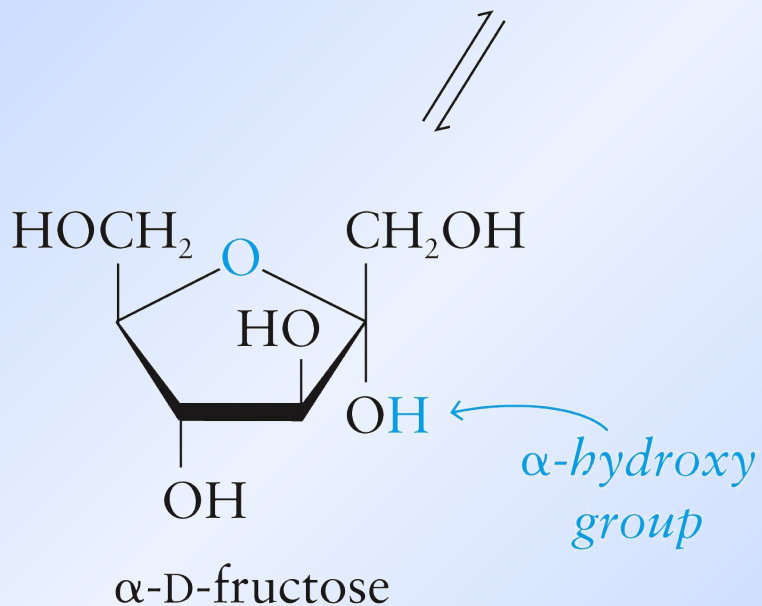
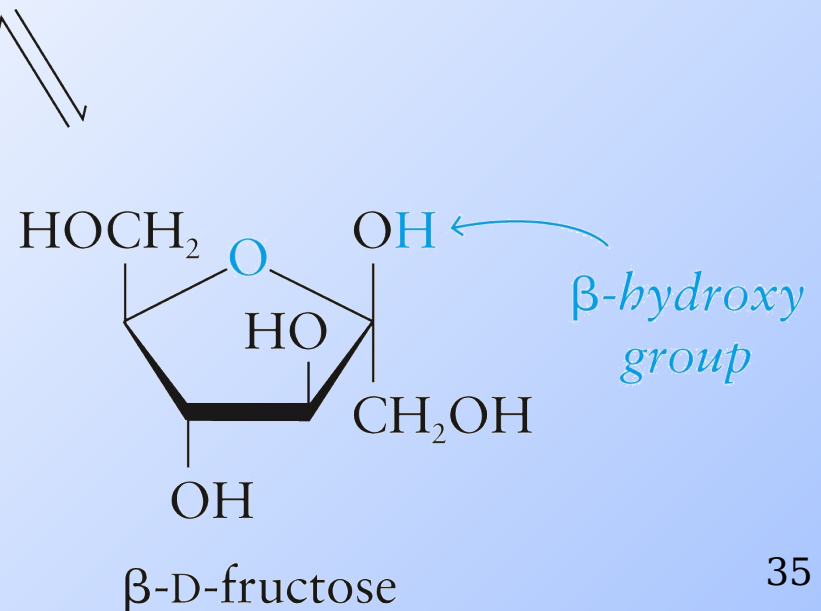


- The open-chain structure is numbered starting at the end closest to the carbonyl carbon atom.
- The alcohol group on the next to the last carbon atom adds to the carbonyl group.
- In the case of glucose, the alcohol group on carbon 5 adds to the aldehyde group on carbon 1 and a **pyranose** (six-membered ring containing an oxygen atom) forms.
- In the case of fructose, the alcohol group on carbon 5 adds to the ketone group on carbon 2 and a **furanose** (five-membered ring containing an oxygen atom) forms.
- The former carbonyl carbon atom is now **chiral** and called the **anomeric carbon** atom.



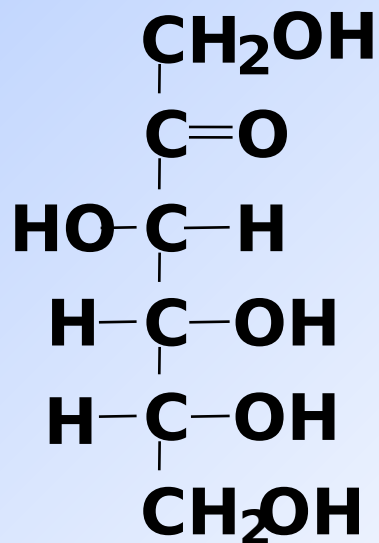
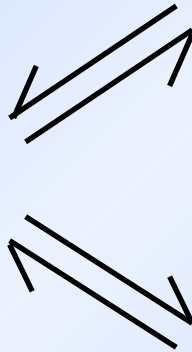
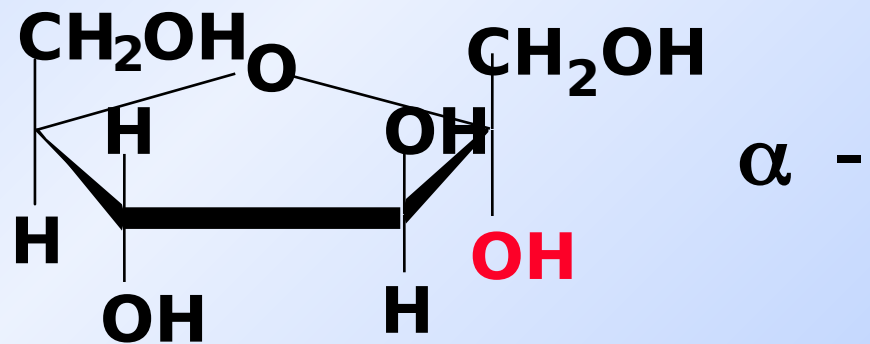
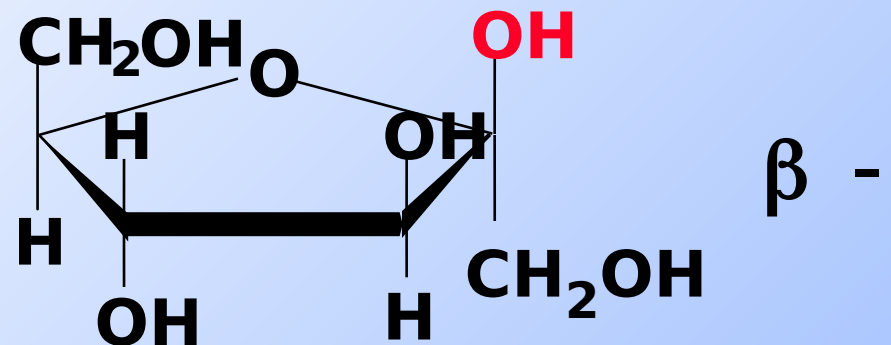
- Because the **anomeric carbon** atom is **chiral**, two possible stereoisomers can be formed during cyclization.
 - An **anomer** (-OH on the **anomeric carbon** pointing down)
 - A **anomer** (-OH on the **anomeric carbon** pointing up)
- **Anomers** are stereoisomers that differ in the 3-D arrangement of groups at the **anomeric carbon** of an acetal, ketal, hemiacetal, or

CYCLIZATION OF FRUCTOSE



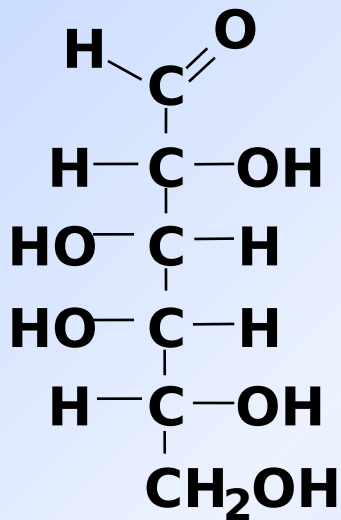
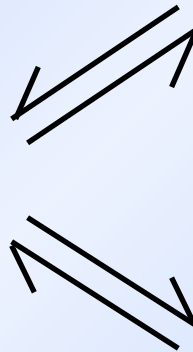
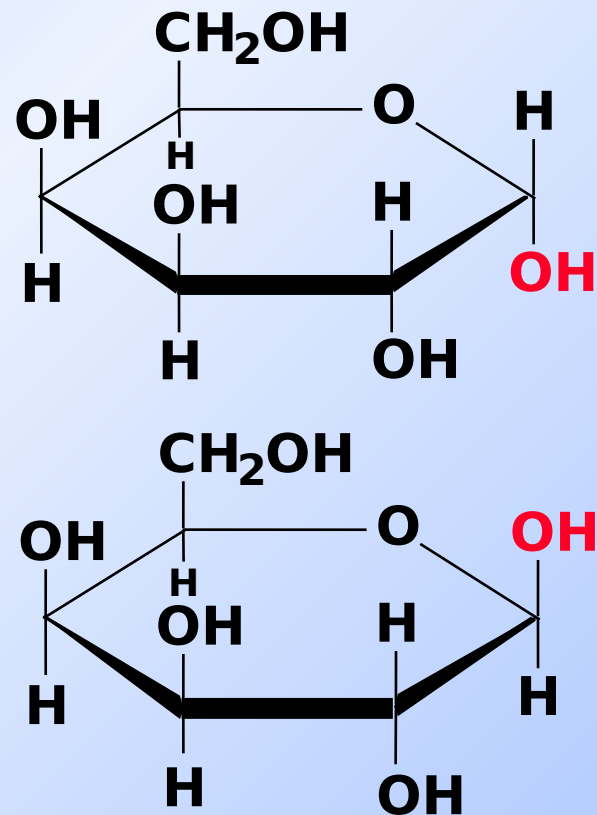
Cyclization of D-fructose

This can also happen to ketose sugars.



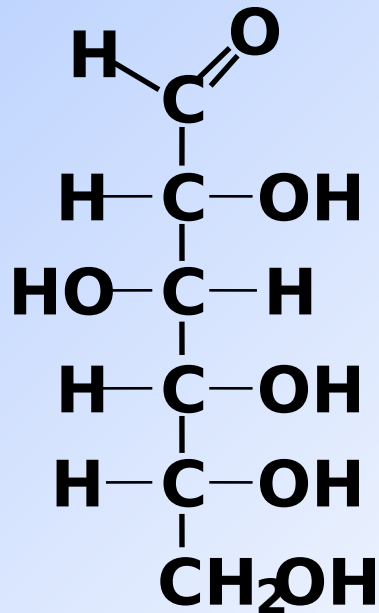
D-galactose

- Not found in many biological systems
- Common part of lactose - disaccharide

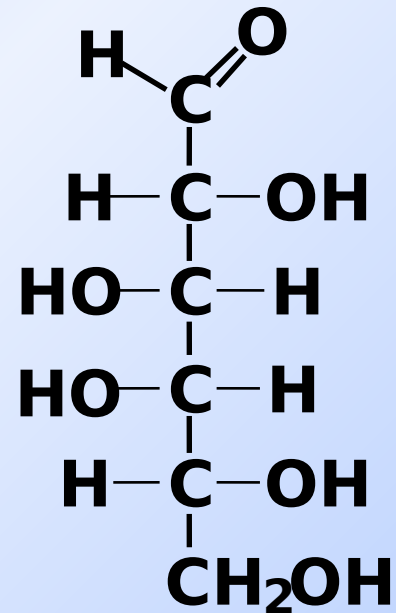


D-glucose vs. D-galactose

D-glucose



D-galactose



Can you find a difference? Your body can!

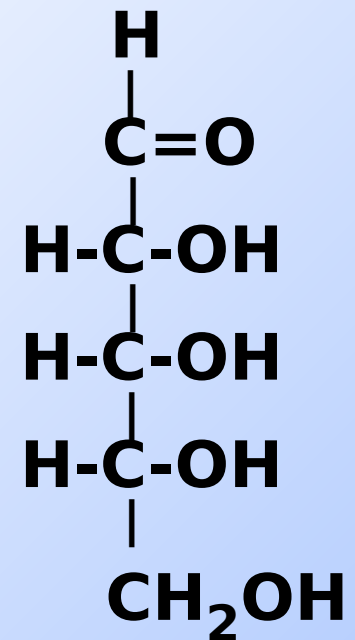
You can't digest galactose - it must be converted to glucose first.

D-ribose

An important sugar used in genetic material.

This sugar is not used as an energy source but is a part of the backbone of RNA.

When the C-2 OH is removed, the sugar becomes **deoxyribose** which is used in the backbone of DNA.



Reactions of glucose and other monosaccharides

Oxidation-Reduction. Required for their complete metabolic breakdown.

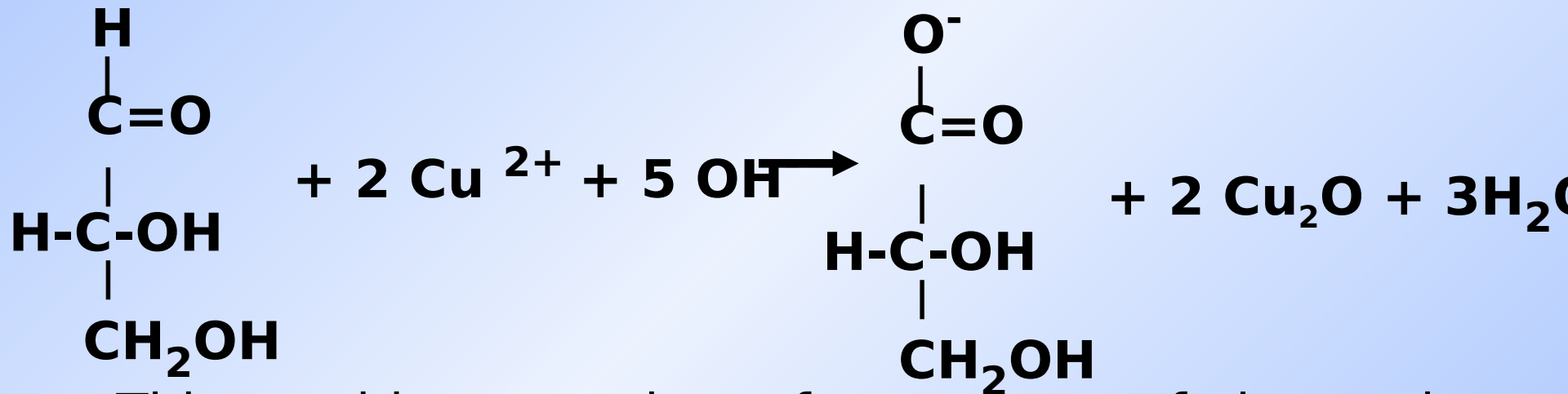
Esterification. Production of phosphate esters.

Amino derivatives. Used to produce structural components and glycoprotein.

Glycoside formation. Linkage of monosaccharides to form polysaccharides.

Oxidation-Reduction.

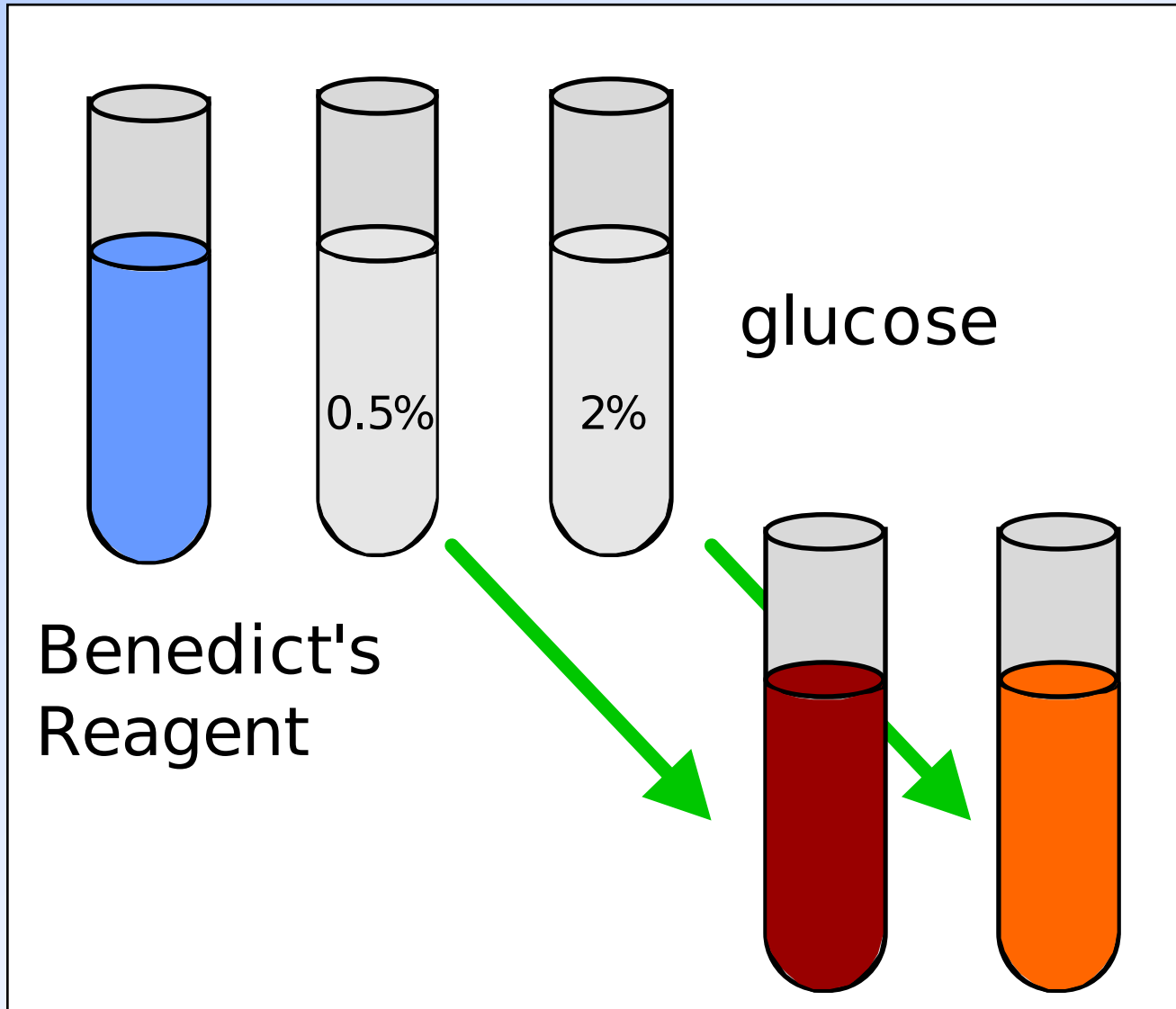
Aldehyde sugars (reducing sugars) are readily oxidized and will react with Benedict's reagent.



This provides a good test for presence of glucose in urine - forms a red precipitate.

Other tests - Tollen's or Fehling's solutions.

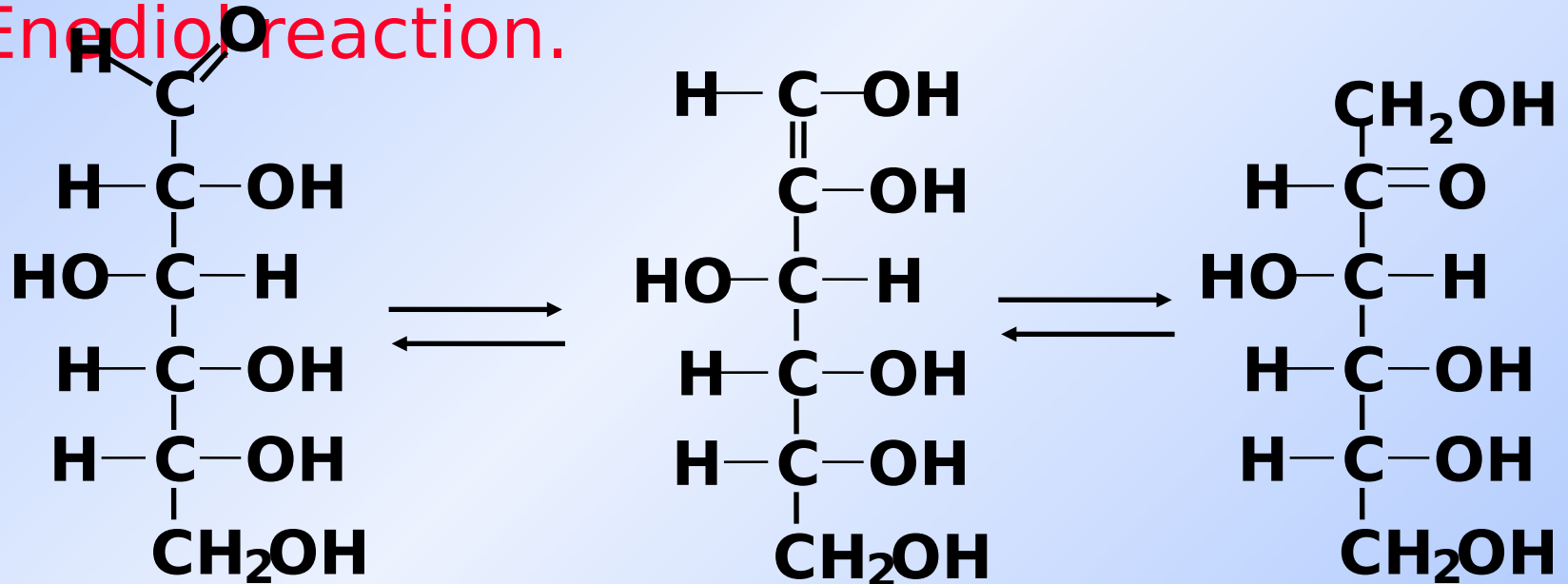
Benedict's reagent



Ketone sugars

Ketones are not easy to oxidize except ketoses.

Enediol reaction.



So all monosaccharides are reducing sugars.

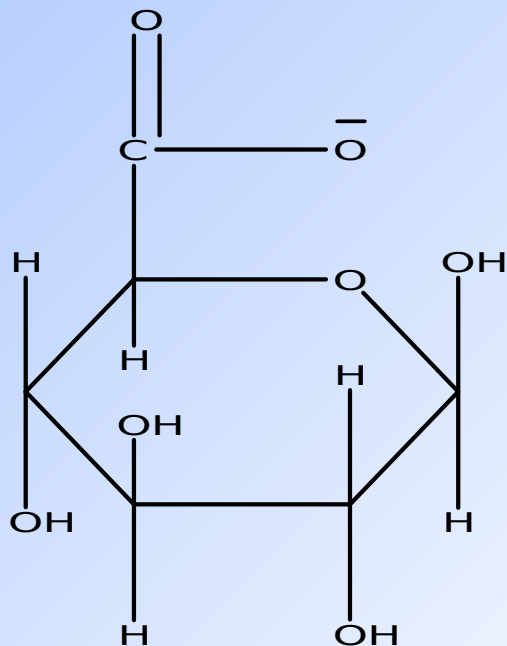
Technically, the compound is no longer a sugar, and the ending on its name is changed from “-ose” to “-onic acid” or “-onate” (e.g., glu**conic** acid).

If the carbon containing the terminal hydroxyl group is oxidized, the sugar is called a *uronic acid* (e.g., gluc**uronic** acid).

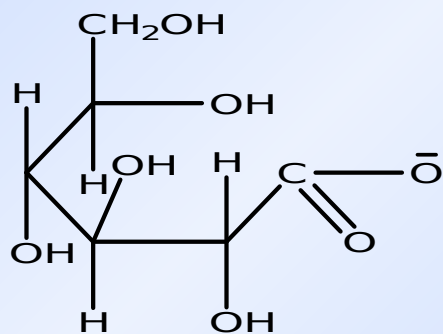
If the aldehyde of a sugar is reduced, all of the carbon atoms contain alcohol (hydroxyl) groups, and the sugar is a poly**ol** (e.g., sorbit**ol**)

If one of the hydroxyl groups of a sugar is reduced so that the carbon contains only hydrogen, the sugar is a deoxysugar, such as

oxidized sugars

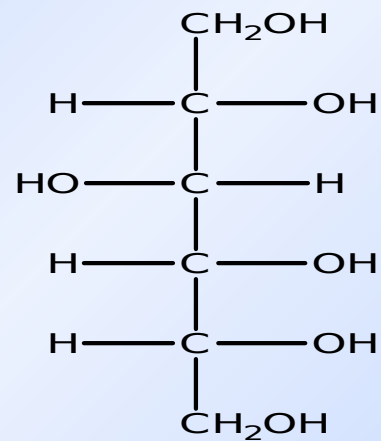


β -D-glucuronate

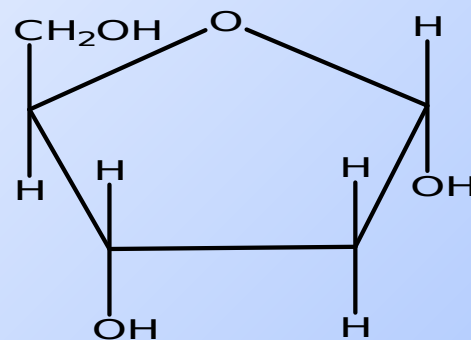


D-glucuronate

Reducing sugars



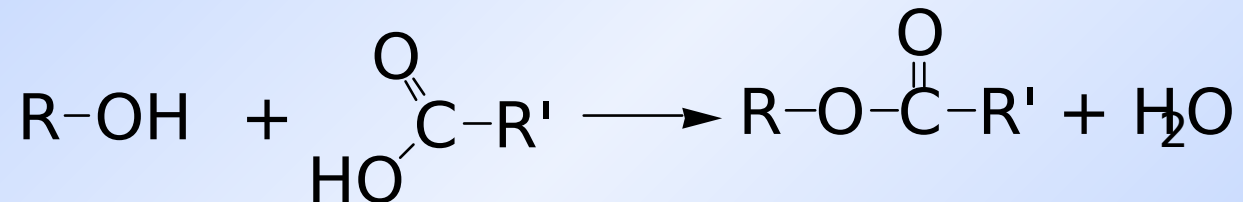
D-sorbitol



Deoxyribose

Esterification

Esters are formed by reaction of hydroxyl groups (alcohols) with acids.

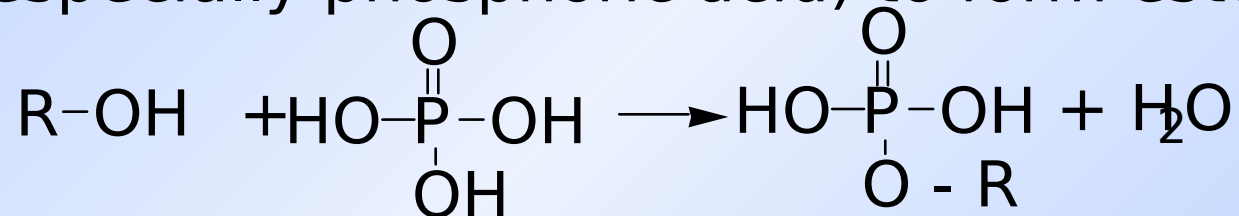


The hydroxyl groups of carbohydrates react similarly to alcohols.

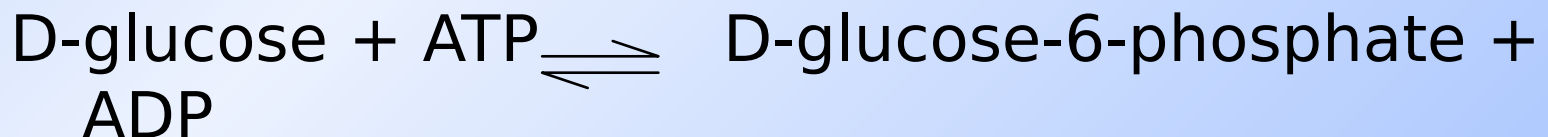
Esterification

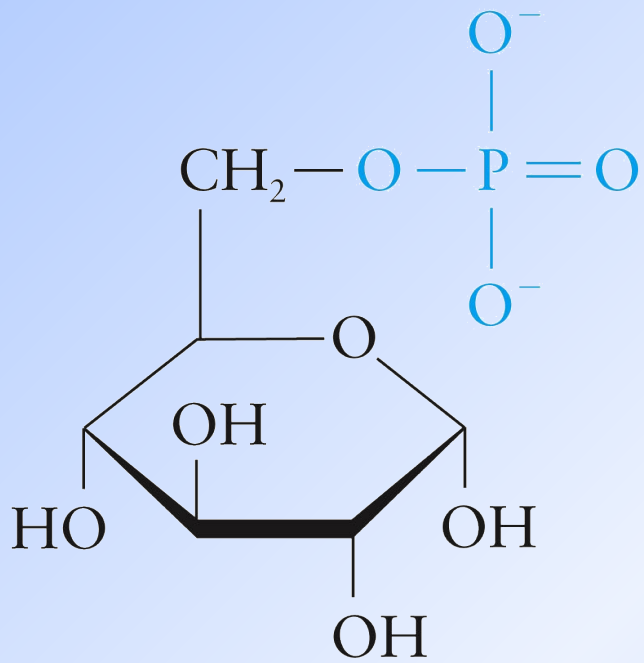
The most important biological esters of carbohydrates are **phosphate esters**.

The -OH groups of **monosaccharides** can behave as alcohols and react with acids (especially phosphoric acid) to form esters.

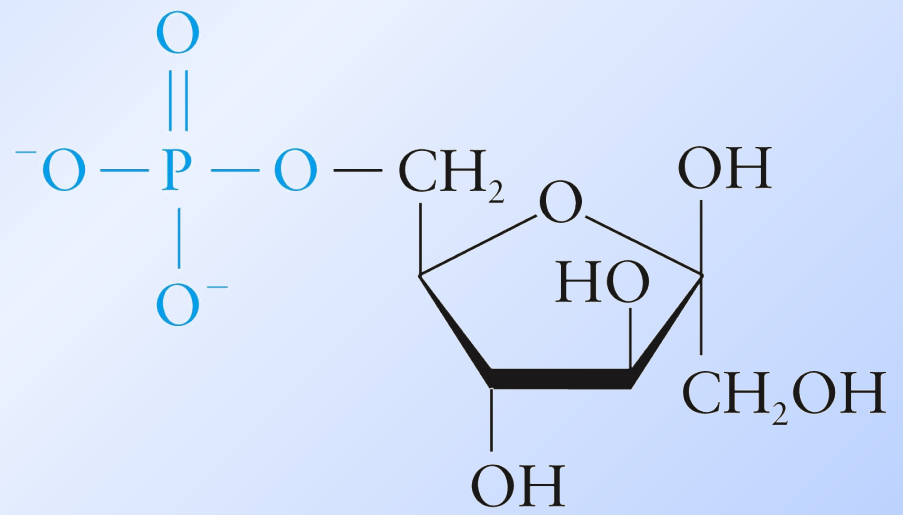


Example. Phosphoryl group from ATP forms an ester with D-glucose, catalyzed by kinases





glucose 6-phosphate

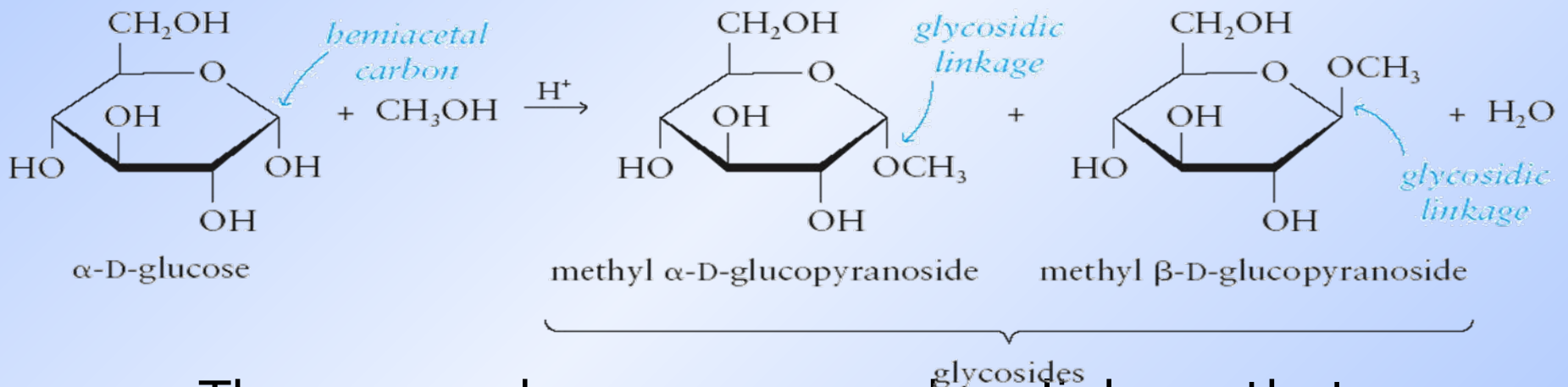


fructose 6-phosphate

Glycoside formation

- The hydroxyl group on the anomeric carbon of a monosaccharide can react with an MOH or an MNH group of another compound to form a glycosidic bond. The linkage may be either α or β , depending on the position of the atom attached to the anomeric carbon of the sugar.
- **N-glycosidic bonds** are found in nucleosides and nucleotides. For example, in the adenosine moiety of **adenosine triphosphate (ATP)**, the nitrogenous base adenine is linked to the sugar ribose through a β -N-glycosidic bond
- In contrast, **O-glycosidic bonds**, such as those found in lactose, join sugars to each other or attach sugars to the hydroxyl group of an amino acid on a protein.

- Cyclic **monosaccharide** hemiacetals and hemiketals react with alcohols to form acetals and ketals, referred to as **glycosides**.

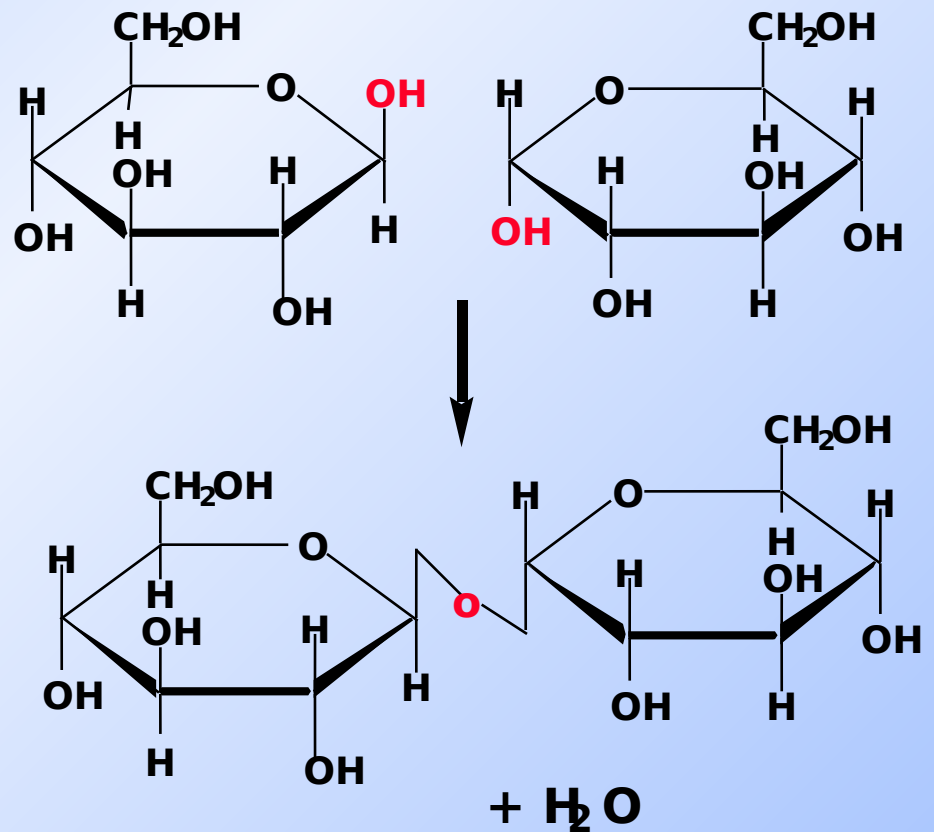


- The new carbon-oxygen-carbon linkage that joins the components of the **glycoside** is called a **glycosidic linkage**.
- Glycosides** do not exhibit open-chain forms.
- Glycosides** are not **reducing sugars**.

glycosidic bond

sugar -O- sugar

oxygen bridge



Glycosidic bonds

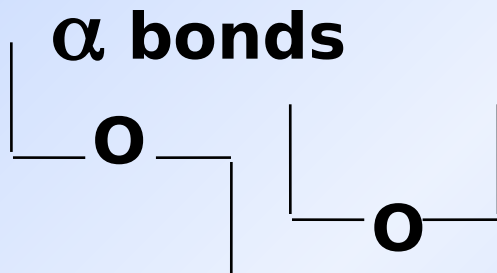
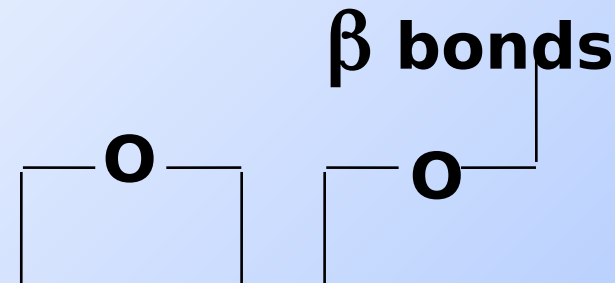
Type is based on the position of the C-1 OH

α glycosidic bond

- linkage between a C-1 α OH and a C-4 OH

β glycosidic bond

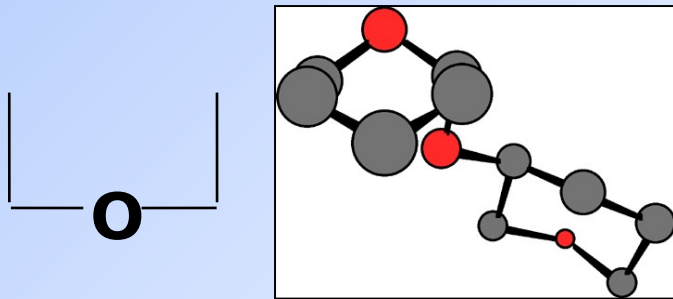
- linkage between a C-1 β OH and a C-4 OH



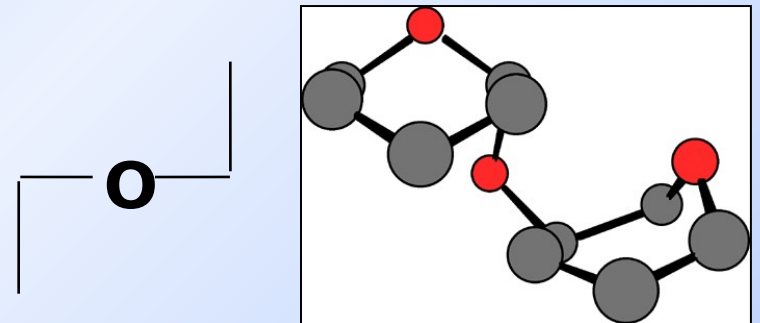
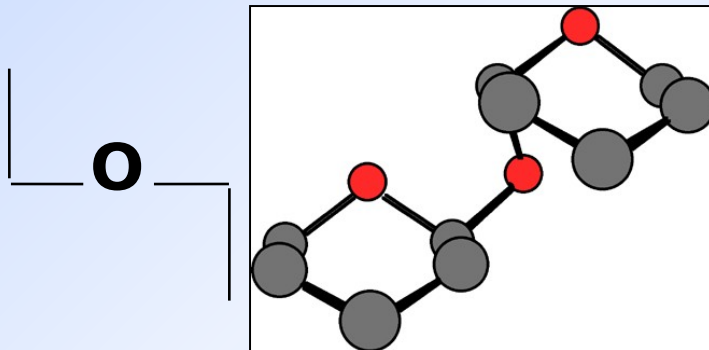
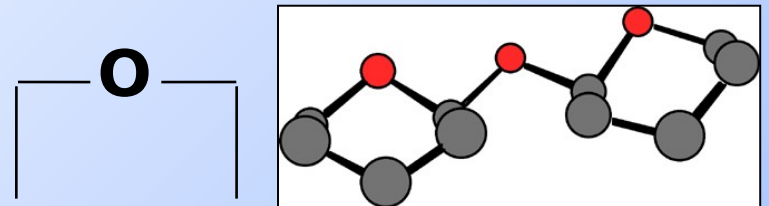
C-4 end can be either up or down depending on the orientation of the monosaccharide.

Glycosidic bonds

α bonds



β bonds



Glycosidic bonds

General format used to describe bond.

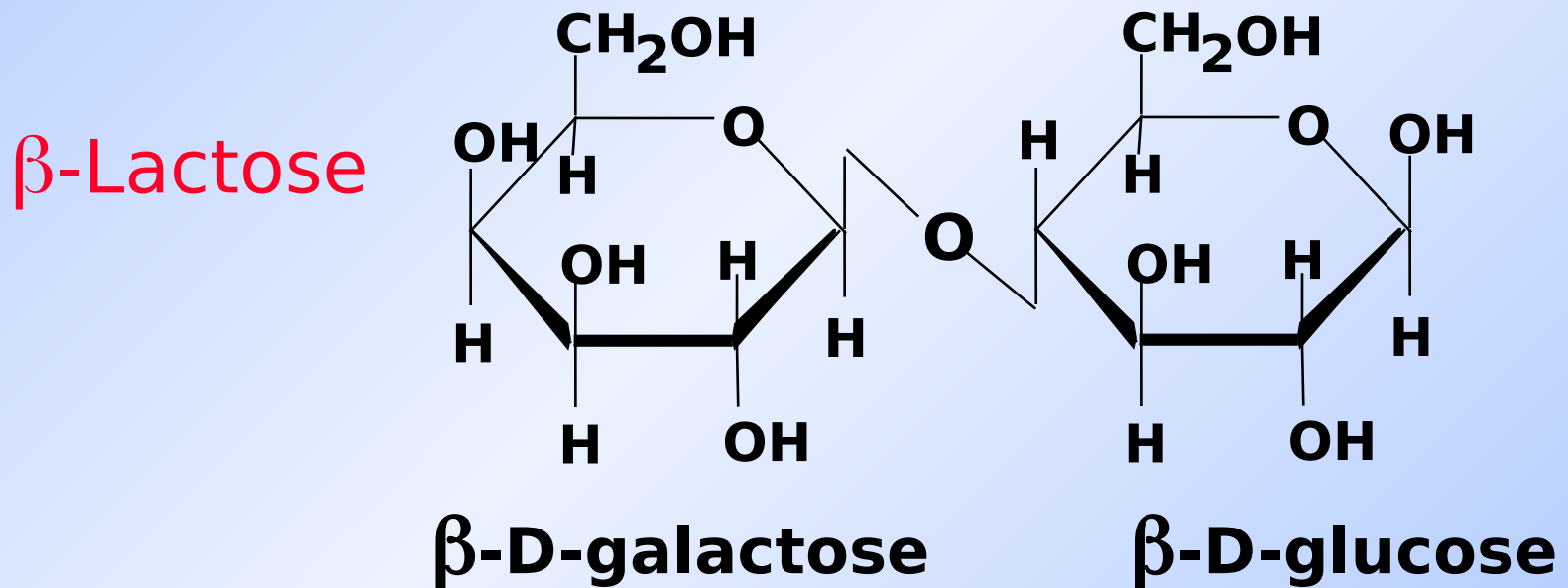
OH type (α or β) (carbon# of first sugar → carbon# of second sugar)

As we work through the next few examples this will become clear.

For disaccharides - the sugar is either α or β based on form of the remaining C-1 OH.

Lactose

Milk sugar - dimer of β -D-galactose and either the α or β - D-glucose.



β (1 — 4) linkage, β disaccharide.

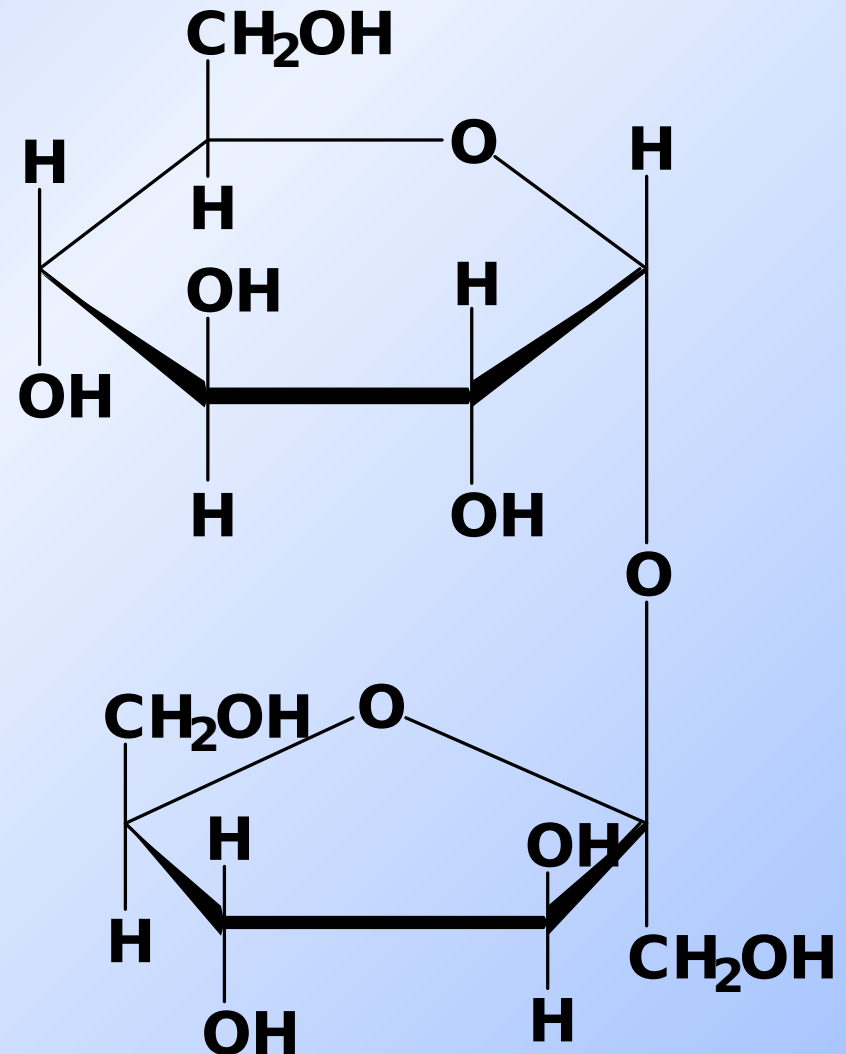
Sucrose

Table sugar - most common sugar in all plants.

Sugar cane and beet, are up to 20% by mass sucrose.

Disaccharide of α -glucose and β -fructose.

α (1 $\rightarrow$ 4) linkage



How sweet it is!

relative Sugar	Sweetness to sucrose
lactose	0.16
galactose	0.32
maltose	0.33
sucrose	1.00
fructose	1.73
aspartame	180
saccharin	450

Polysaccharides

Containing 10 or more monosaccharide units attached together

- Examples

- 1. Starch- digestible**

- 2. Glycogen- digestible**

- 3. Fiber- indigestible**

Long chains of glucose units form these polysaccharides

- Cellulose gives structure to plants, fiber to our diet

- Glycogen is an energy storage sugar produced by animals

- Liver cells synthesize glycogen after a meal to maintain blood glucose levels

A great majority of carbohydrates of nature

occur as polysaccharides

Chemically, the polysaccharides may be distinguished into

homopolysaccharides, which yield, on hydrolysis, a single monosaccharide and

heteropolysaccharides, which produce a mixture of monosaccharides on hydrolysis.

Based on their **functional aspect**, the polysaccharides may be grouped under two heads :

(a) **Nutrient (or digestible)**

polysaccharides. These act as metabolic reserve of monosaccharides in plants and animals, e.g., starch, glycogen and insulin.

(b) **Structural (or indigestible)**

polysaccharides. These serve as rigid mechanical structures in plants and animals, e.g., cellulose, pectin and chitin and also hyaluronic acid and chondroitin.

Starch

Energy storage used by plants

Long repeating chain of α -D-glucose

Chains up to 4000 units

Amylose

straight chain
major form of

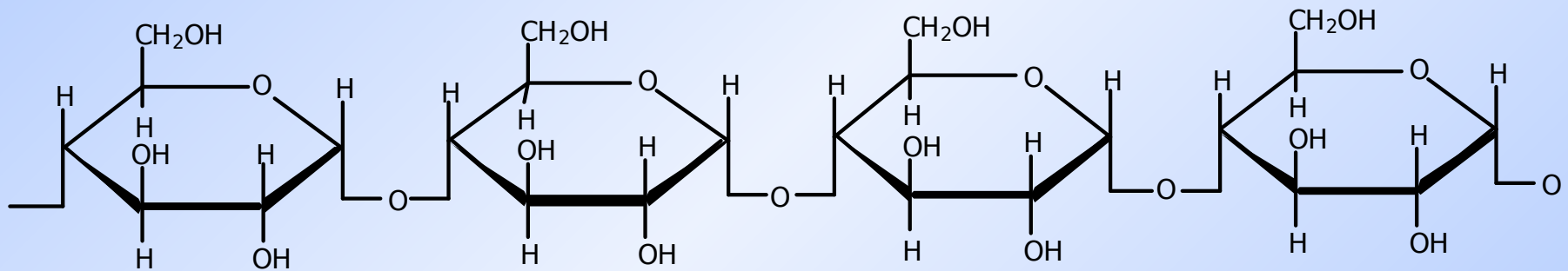
starch

Amylopectin

branched structure

Amylose starch

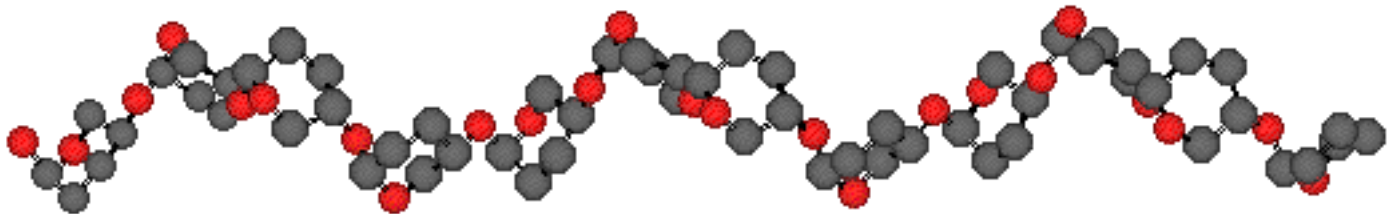
Straight chain that forms coils α ($1 \rightarrow 4$) linkage. Most common type of starch.



Amylose starch

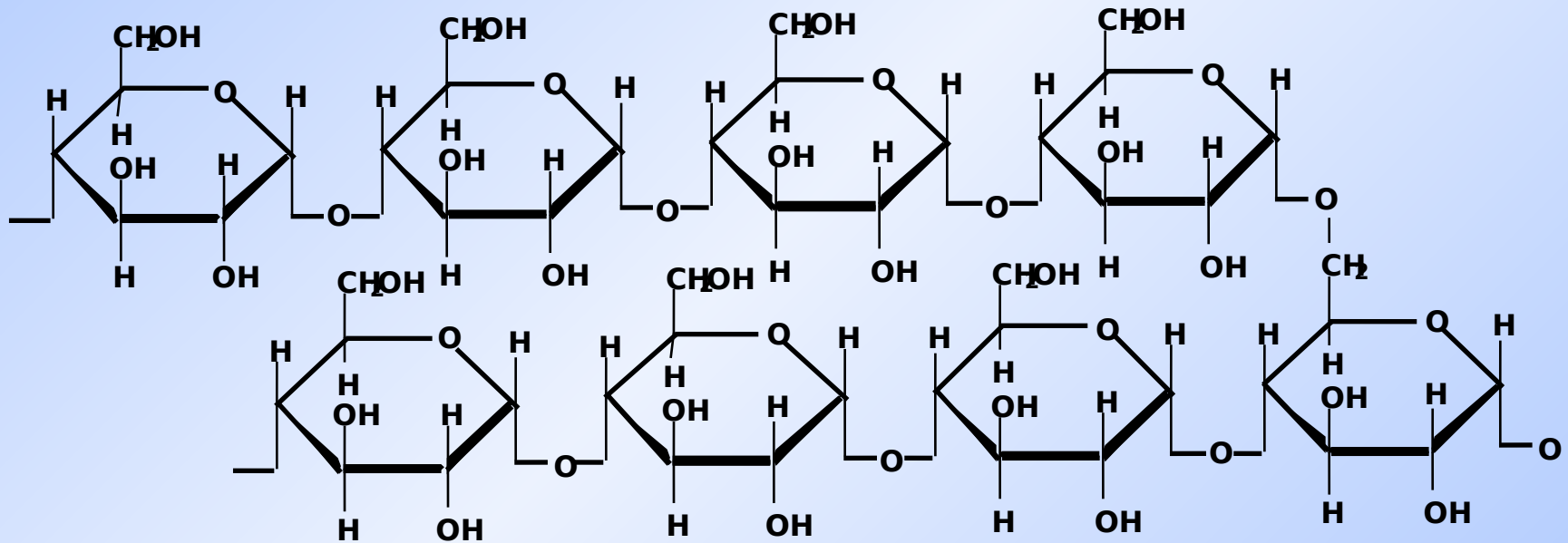
Example showing coiled structure

- 12 glucose units
- hydrogens and side chains are omitted.



Amylopectin starch

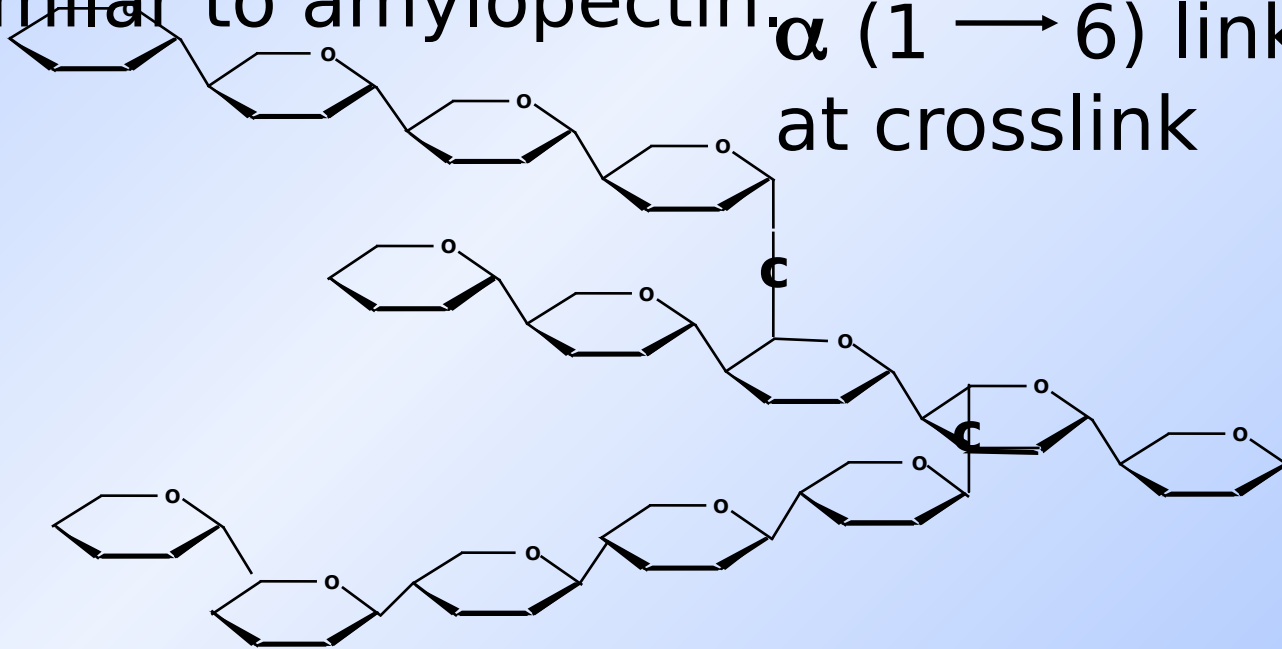
Branched structure due to crosslinks.



**$\alpha(1 \rightarrow 6)$ linkage
at crosslink**

Glycogen

- Energy storage of animals.
 - Stored in liver and muscles as granules.
 - Similar to amylopectin.
- α (1 $\rightarrow$ 6) linkage at crosslink



Cellulose

- Most abundant polysaccharide.
- β (1 $\rightarrow$ 4) glycosidic linkages.
- Result in long fibers - for plant structure.

