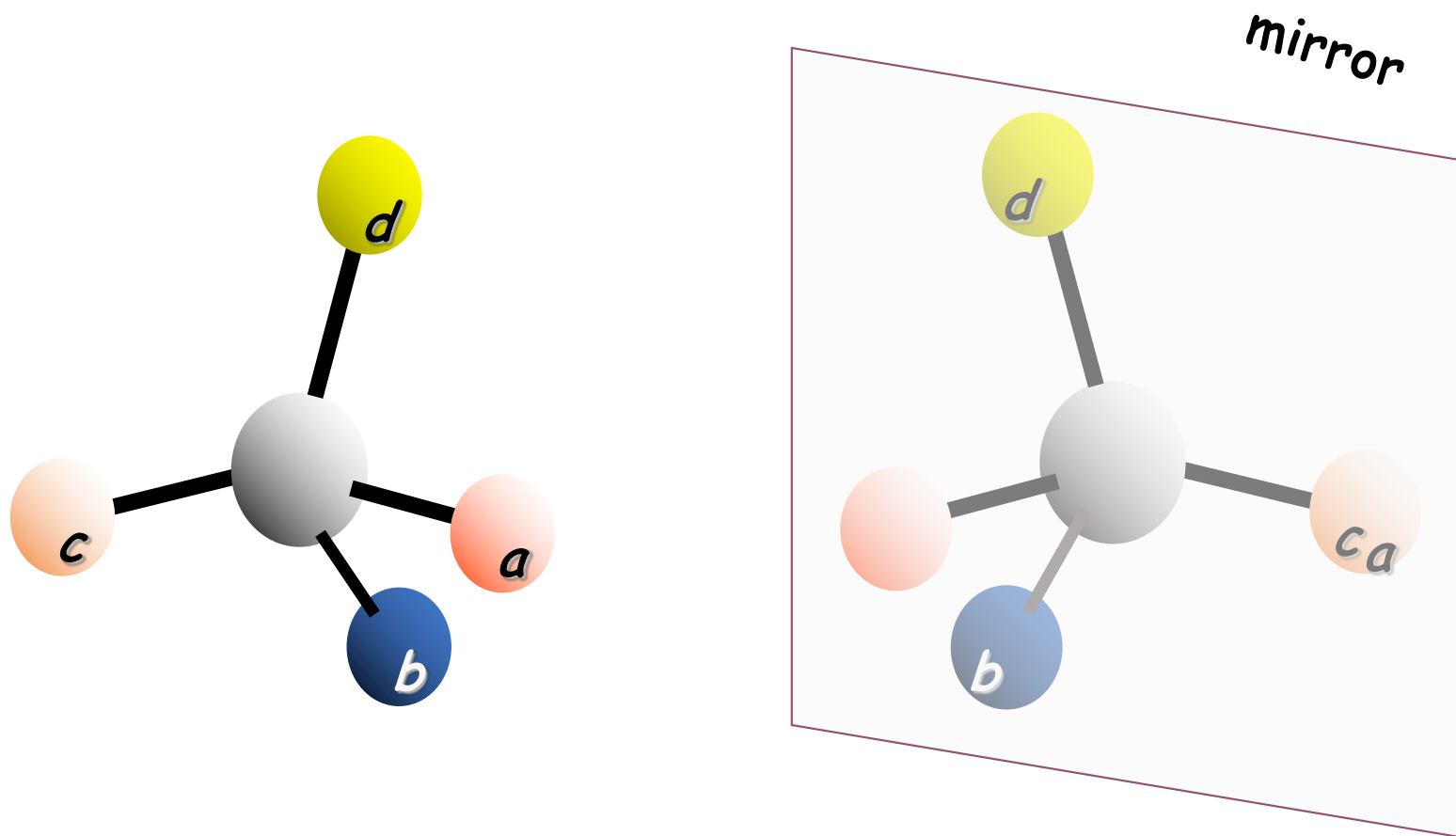


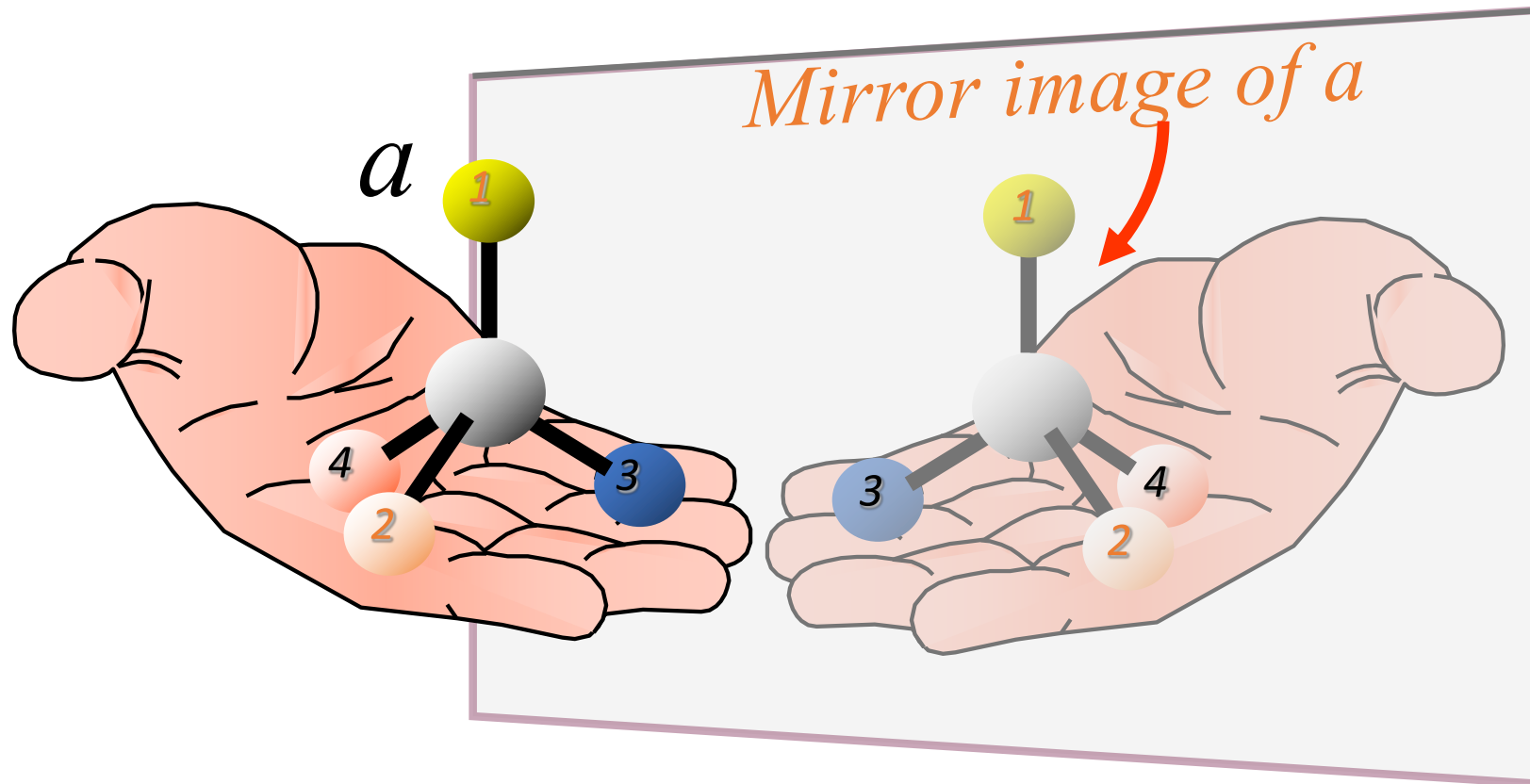
Chiral centers

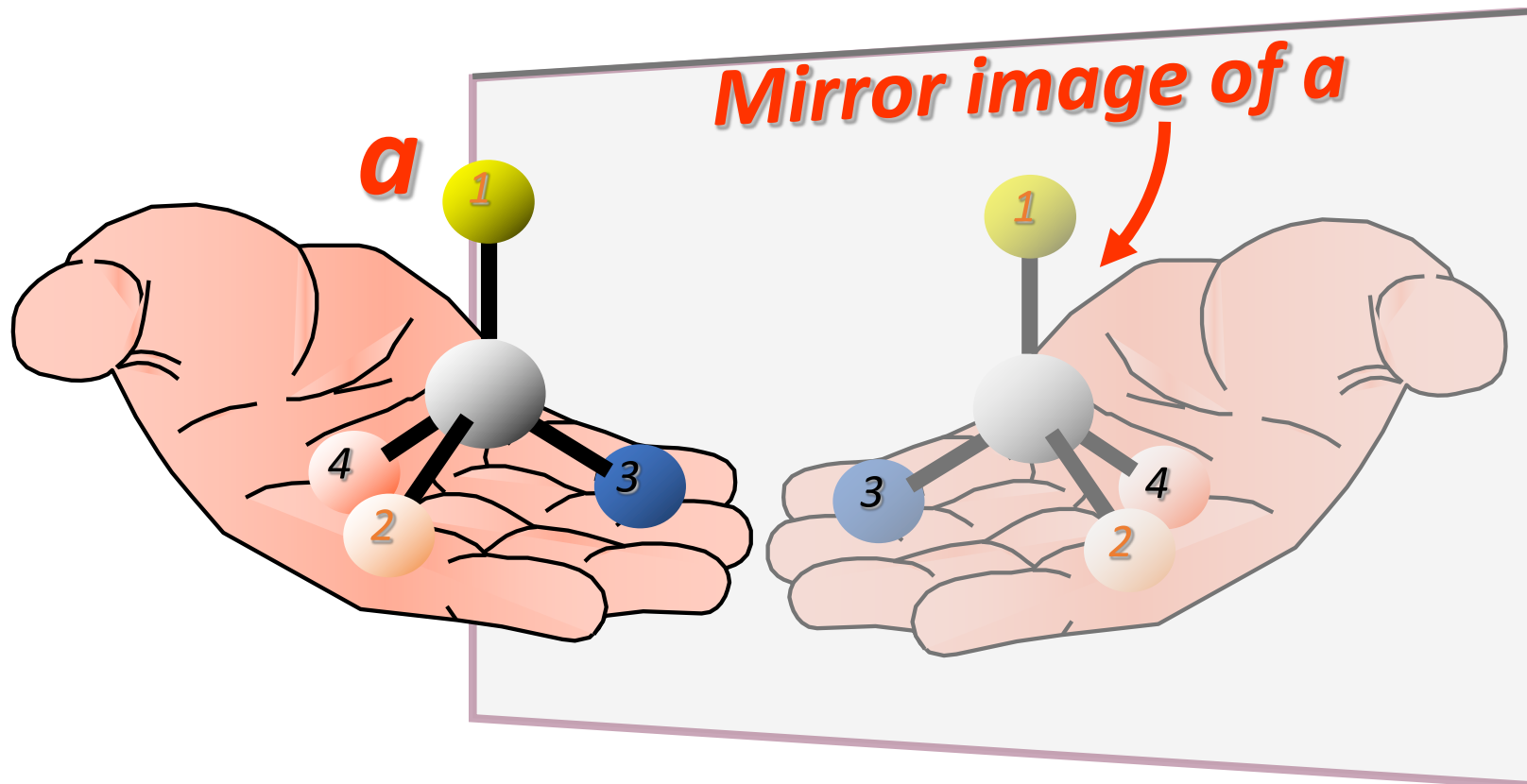
The atom at the centre has sp^3 hybridization and it is bound to four different atoms or groups of atoms. It is called **chiral center** (stereogenic)

We have a second molecule which is the mirror image of the first one

These two molecules are called **enantiomers**.

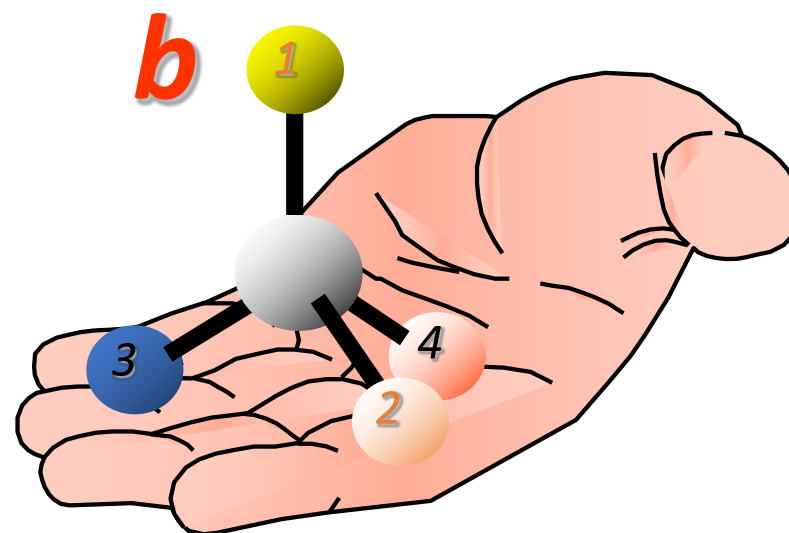






Molecule ***b*** can be superimposed to
The mirror image of molecule ***a***.

When this condition is satisfied
a and ***b*** are called enantiomers.



The **rotational power** α of a solution is proportional to its **concentration** and to the **length** of the tube used for polarimetric measurements

$$[\alpha]_{\text{D}}^{25^{\circ}\text{C}} = \frac{\alpha}{l \cdot c}$$

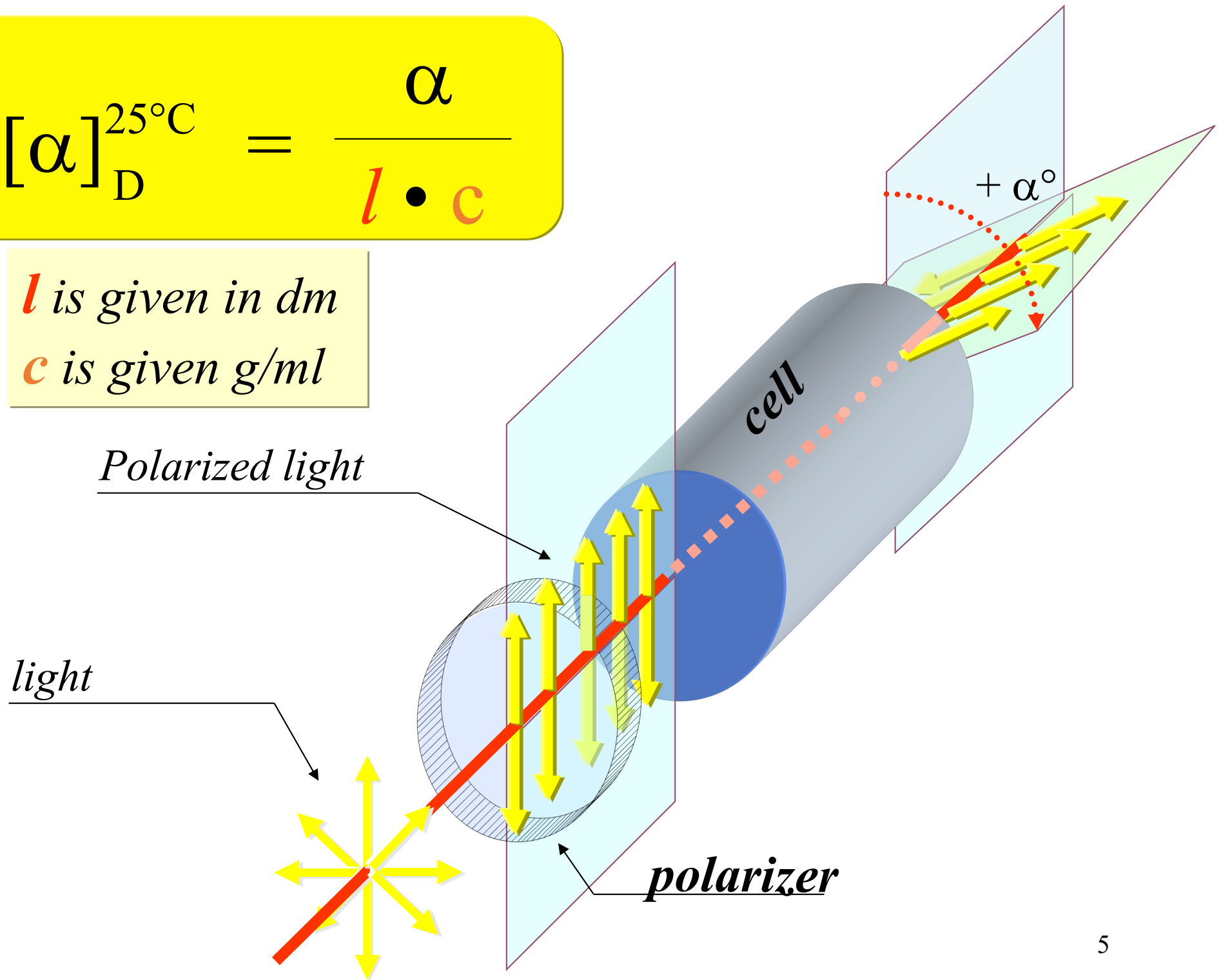
The specific rotational power $[\alpha]$ of a compound is the rotational power of its solution at a concentration 1 g/ml, using an optical path of 1 dm.

In the definition of $[\alpha]$ the **temperature** and the wavelength λ *Must be indicated.*

$$[\alpha]_{\text{D}}^{25^{\circ}\text{C}} = \frac{\alpha}{l \cdot c}$$

l is given in dm

c is given g/ml

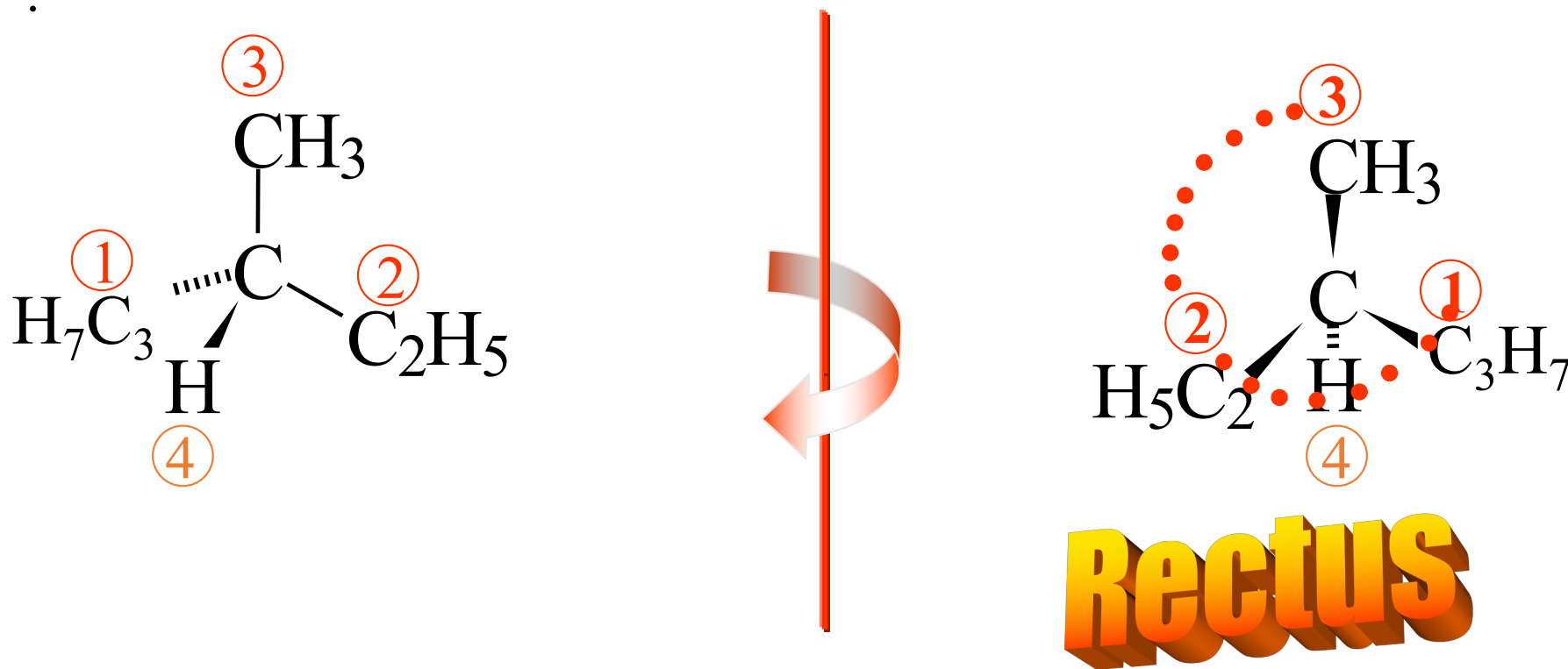


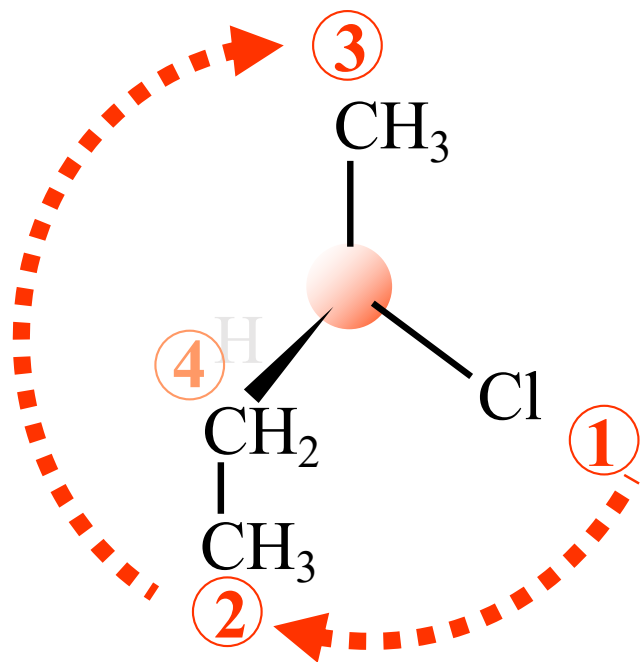
In the Cahn-Ingold-Prelog convention, first the priority is assigned (according to decreasing values of the atomic number).

The molecule is then analysed from the opposite side with respect to the lower priority substituent

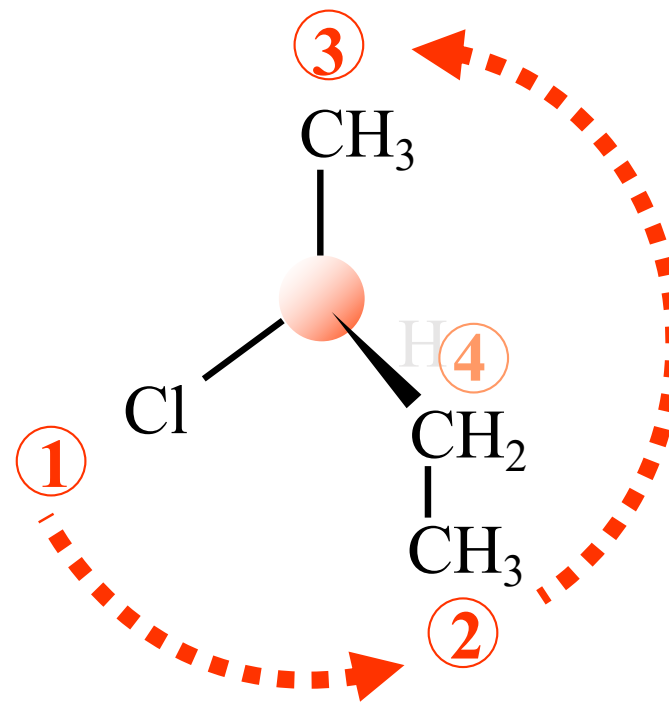
If the rotation from higher priority to lower priority is clockwise the chiral centre is Rectus.

If it is counter-clockwise it is Sinister.

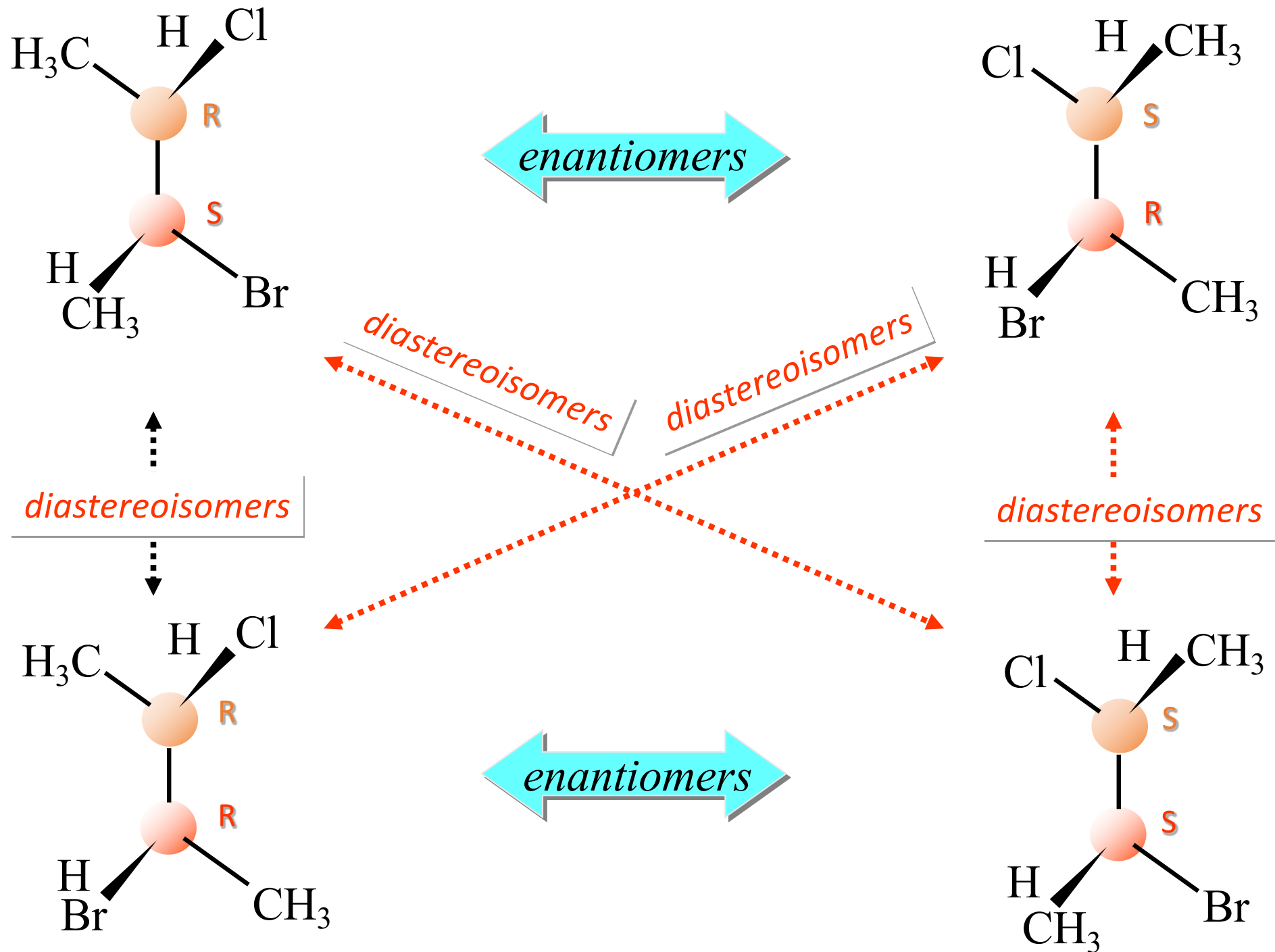




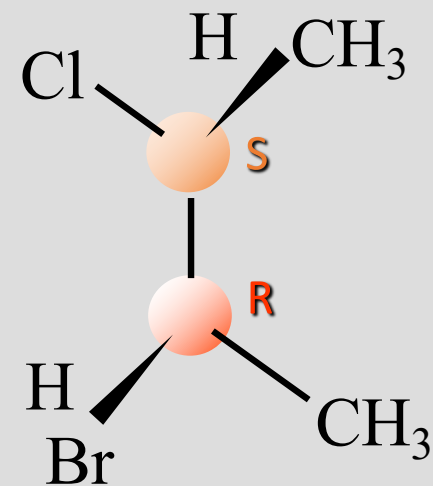
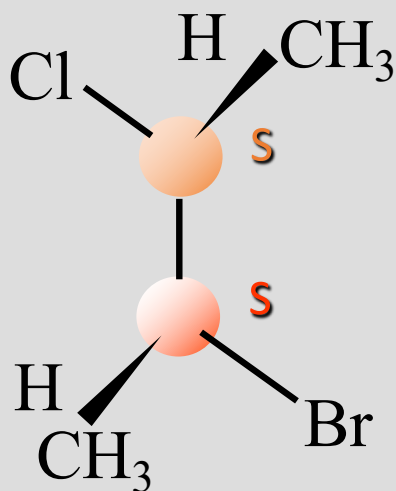
(R)-2-clorobutane



(S)-2-clorobutane



The two compounds differ for the configuration of a single asymmetrical carbon and are therefore called diastereomers.



Mesoform

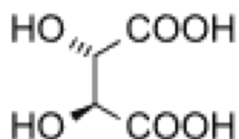
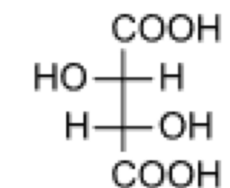
It is a chemical compound which contains stereocenters but it is not optically active, due to the presence of symmetry plane in the molecule.

Such compounds generally also have enantiomers.

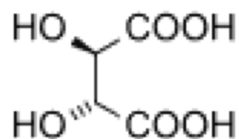
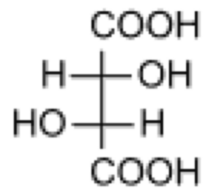
A **racemic mixture** is an equimolar mixture of a couple of enantiomers, it has **no optical activity**.

A mesoform is a compound that has no optical activity due to an "intrinsic compensation".

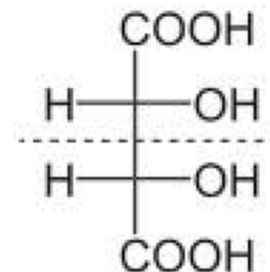
D(-)tartaric Acid
(S,S)

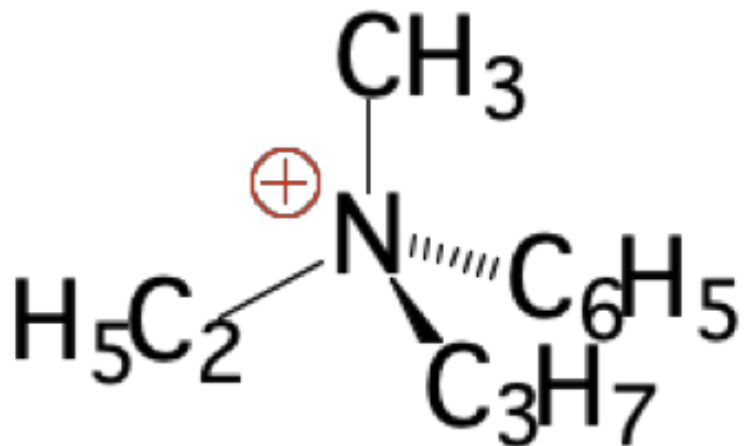


L(+)-tartaric Acid
(L,L)



Mesotartaric acid
(L,S)

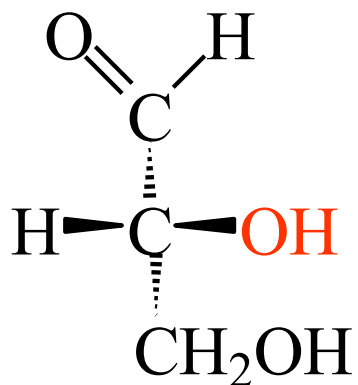




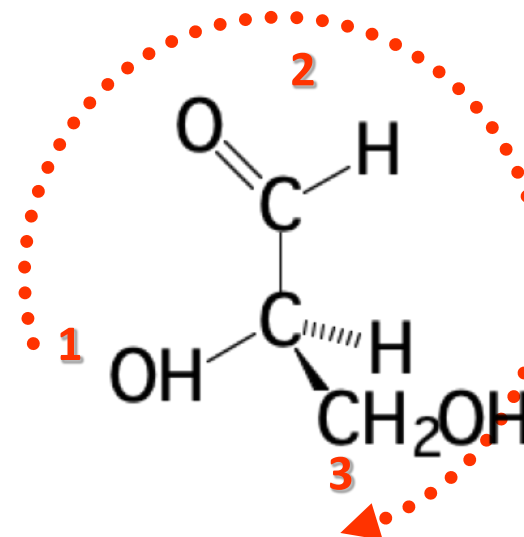
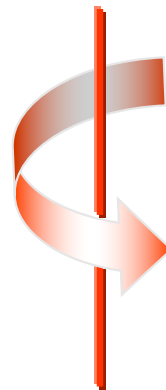
This tetra-alkyl ammonium ion is chiral because all alkylic groups are different

D-glyceraldehyde according to Fischer, the **OH** bound to the chiral carbon is on the **right** side of the carbon chain

If now we rotate the compound according to the Cahn-Ingold-Prelog convention we observe that the absolute configuration is R.



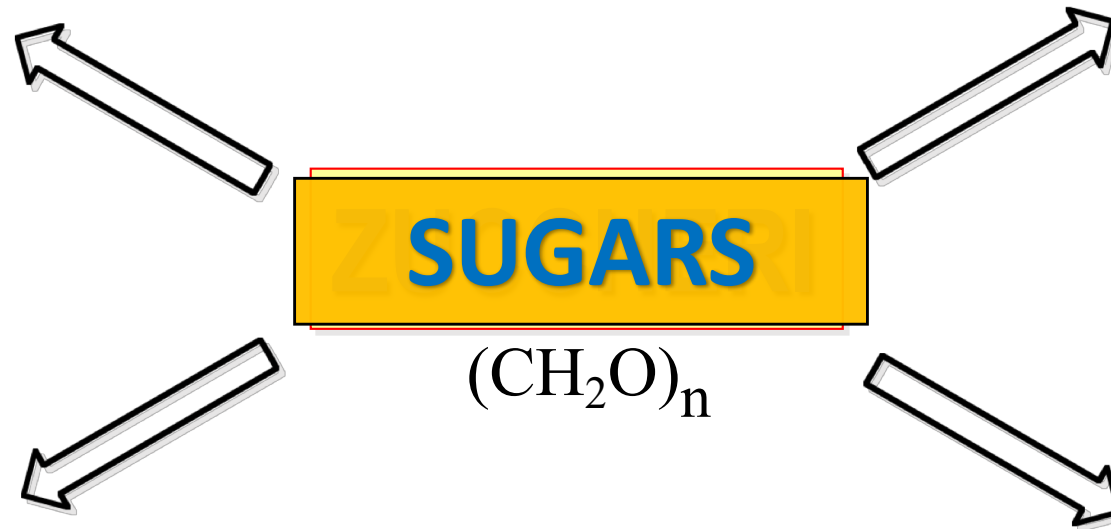
D-gliceraldeide



(2R)-2,3-diossipropanale

Energy source

Cell wall

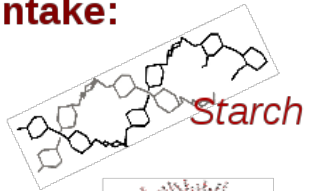


DNA and RNA

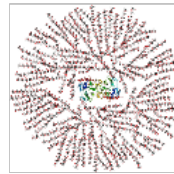
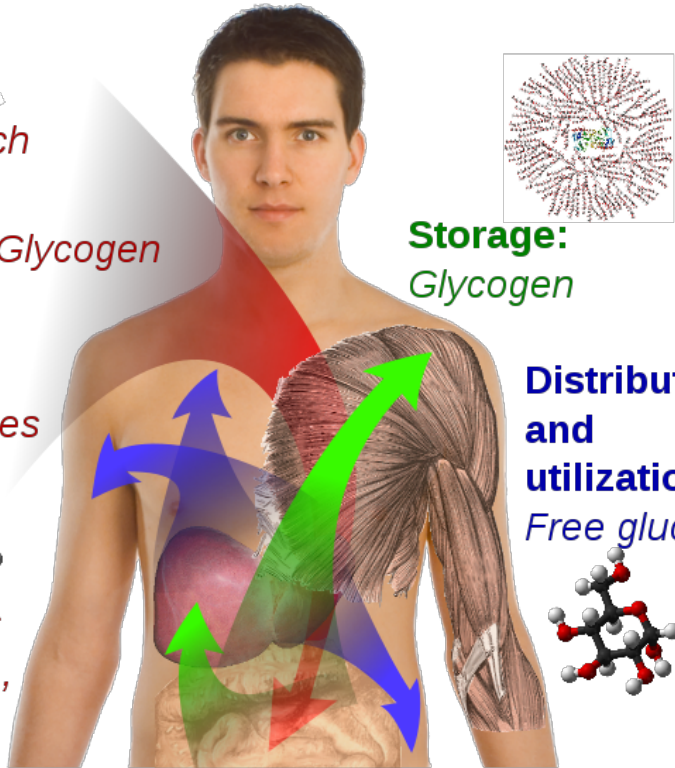
Molecular recognition

Glucose metabolism

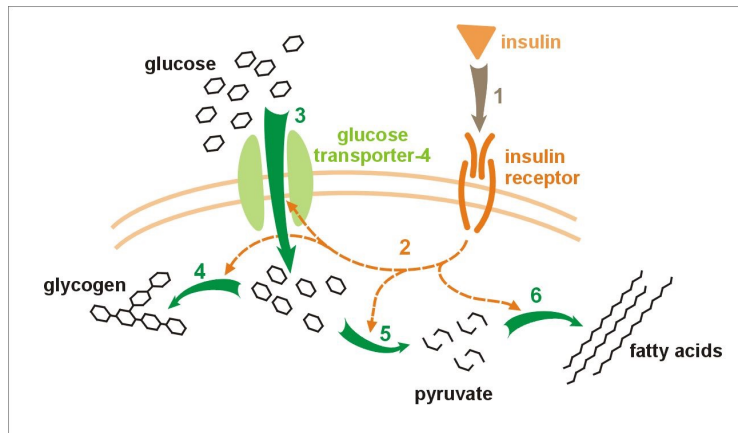
Intake:



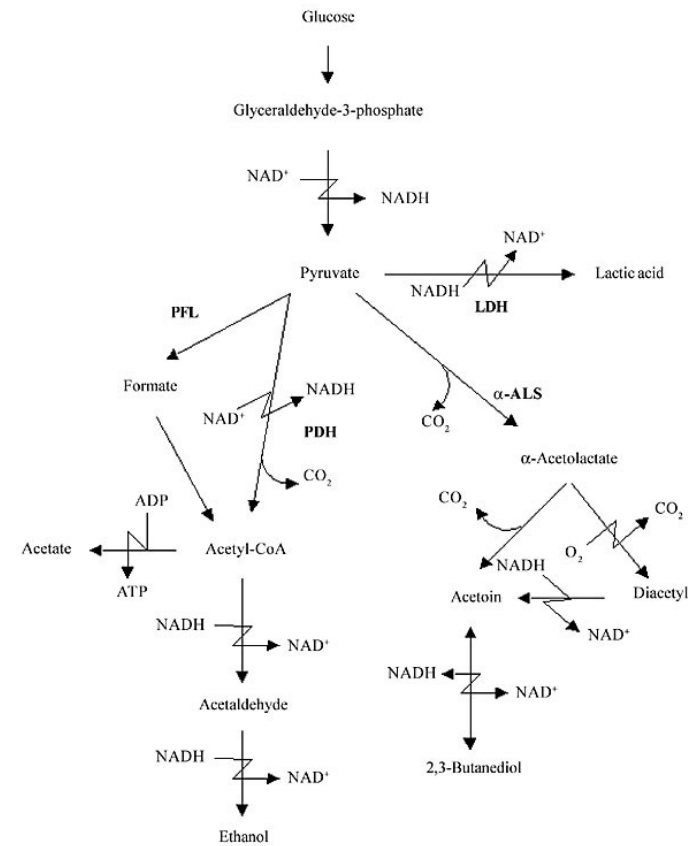
Monosaccharides
(glucose, fructose, galactose)



Distribution and utilization:
Free glucose



Energy source



Molecular recognition

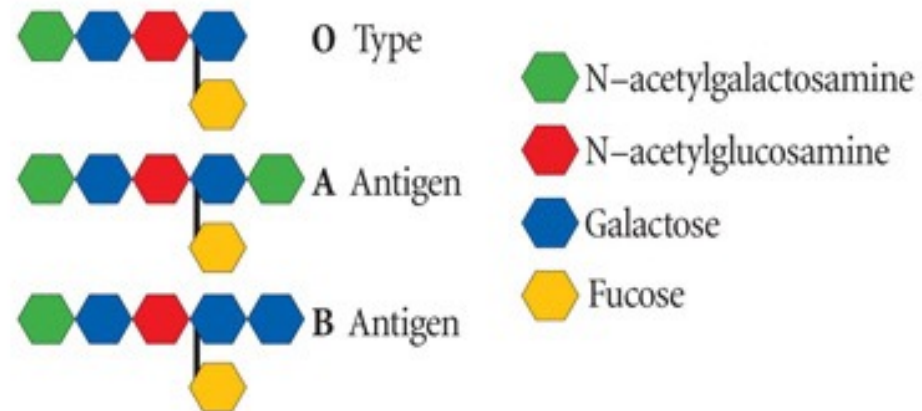
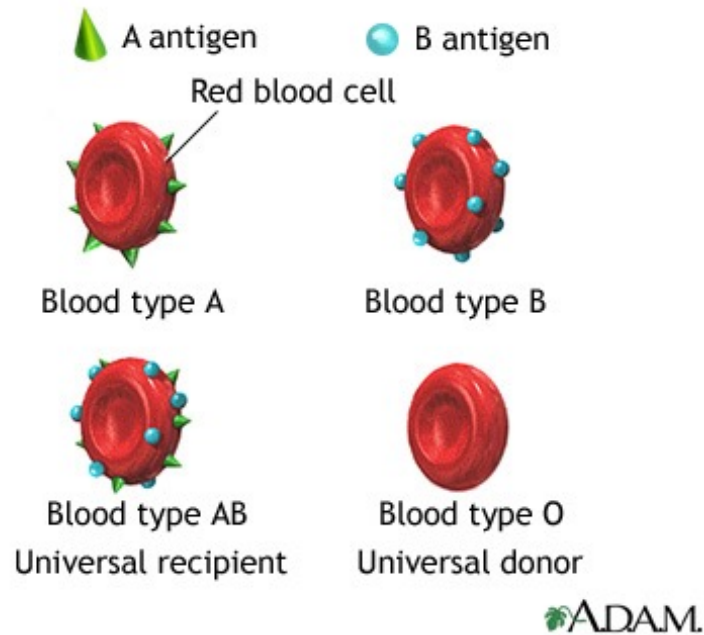
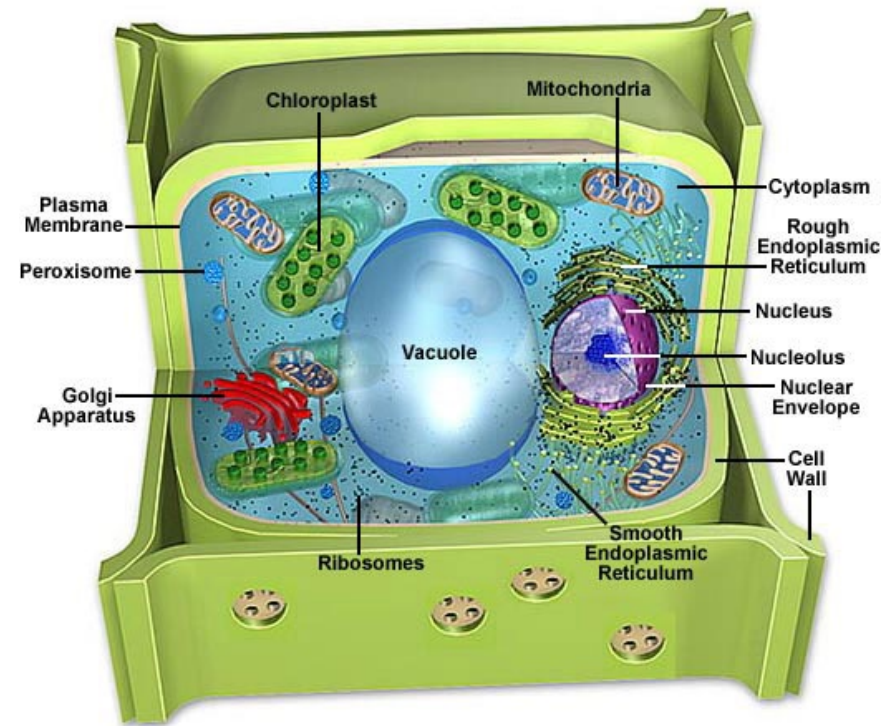


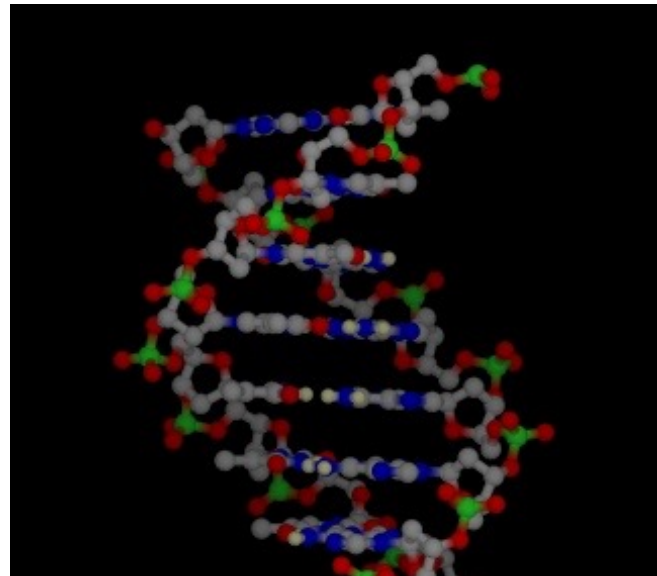
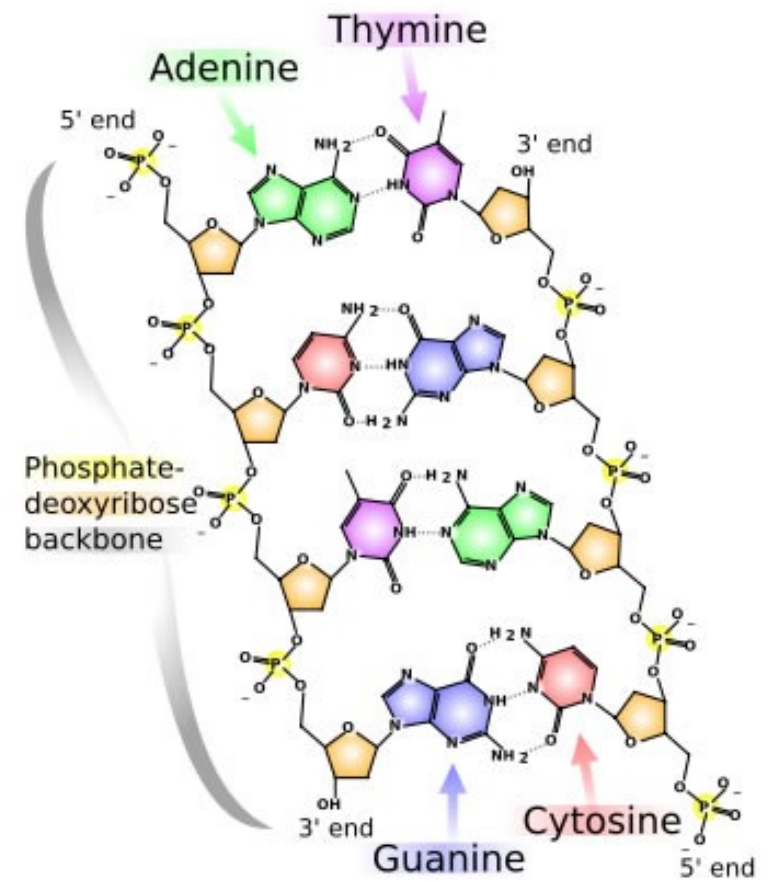
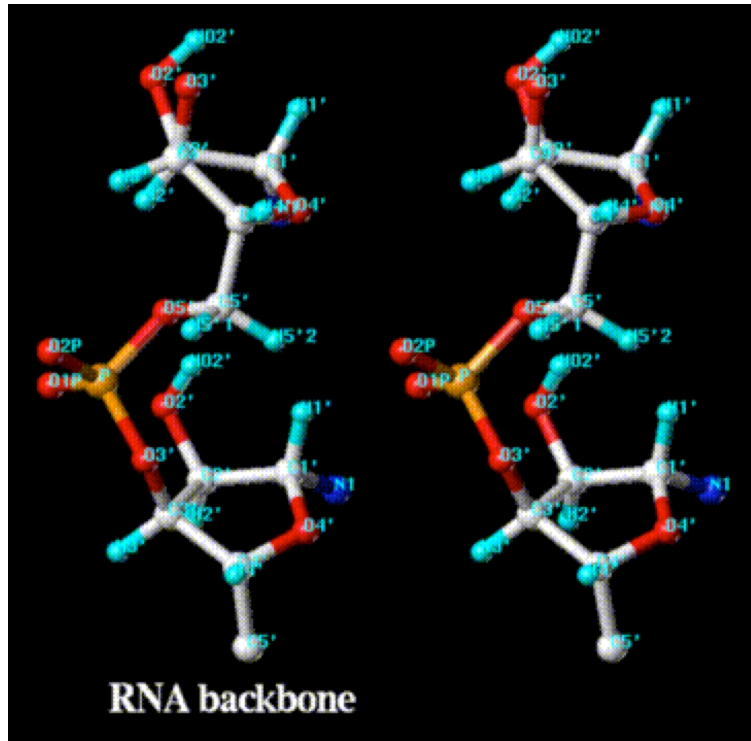
Figure 1. ABO antigen specificity. The ABO antigens differ by just one sugar at the antigen terminus. Only the carbohydrate portion of the antigen is illustrated.

Cell wall (cellulose)



Exoskeleton (chitin)

DNA and RNA



NOMENCLATURE

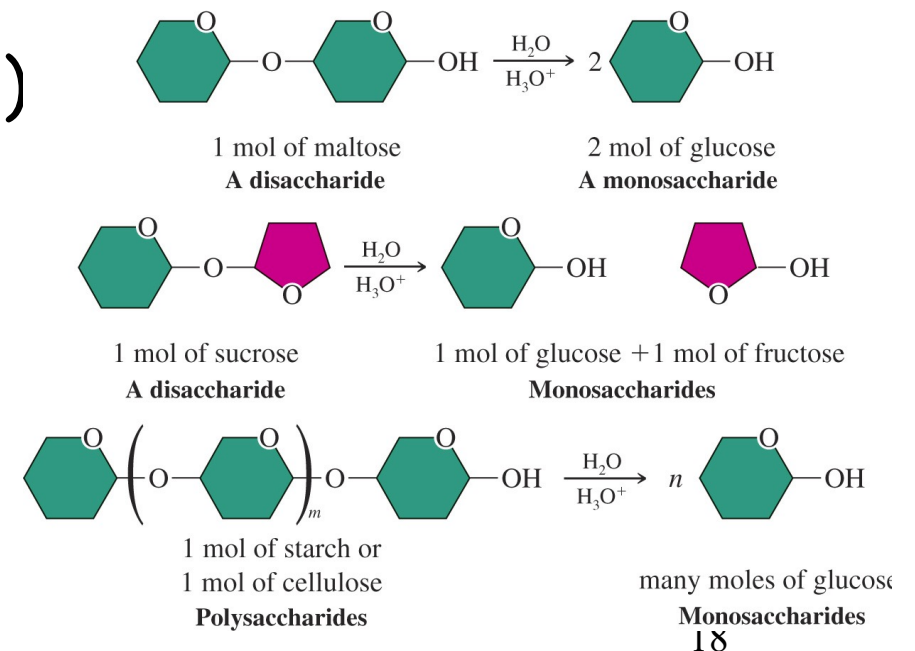
- MONOSACCHARIDES: molecules made up 3 to 9 C atoms

Monosaccharides are MONOMERS and they can form:

- DISACCHARIDES (2 units)

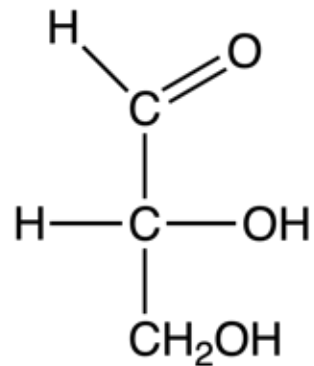
- OLIGOSACCHARIDES (3 - 20 units)

- POLYSACCHARIDES (more than 20)



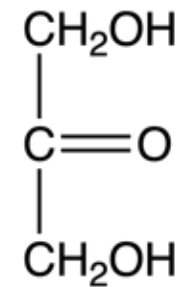
Classes of monosaccharides

Aldoses
(aldehydes)



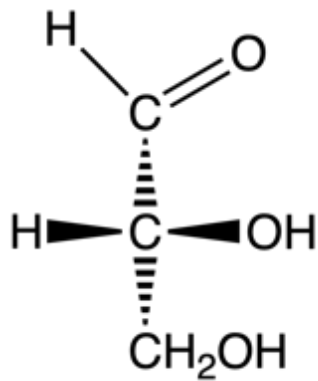
D-glyceraldehyde

Chetoses
(ketons)

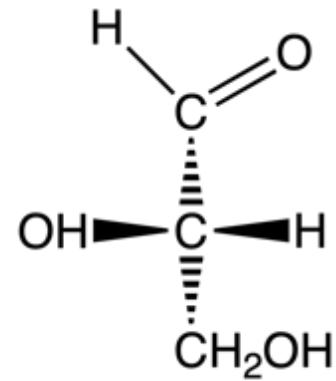


Di-hydroxyacetone

Chirality



D-Glyceraldehyde



L-Glyceraldehyde

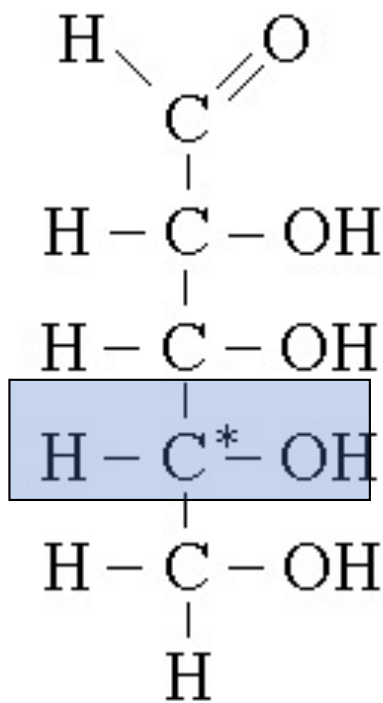
The Fisher convention is used.

The molecule is drawn with the most oxidized carbon on top.

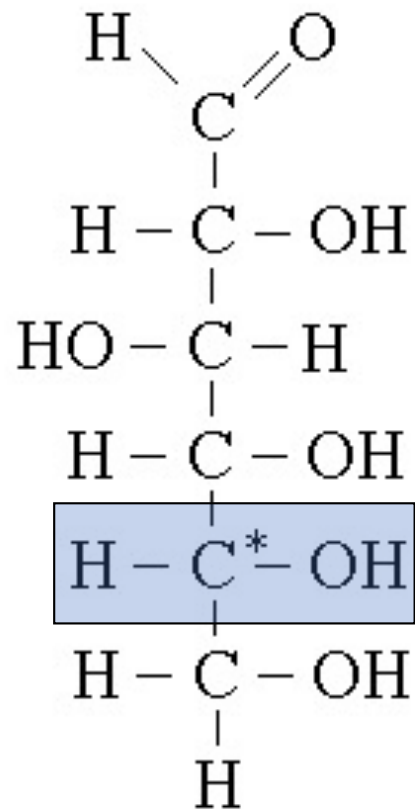
Vertical bonds are below the plane and horizontal ones are out of the plane.

The position of the -OH group at the bottom assign the D or L type.

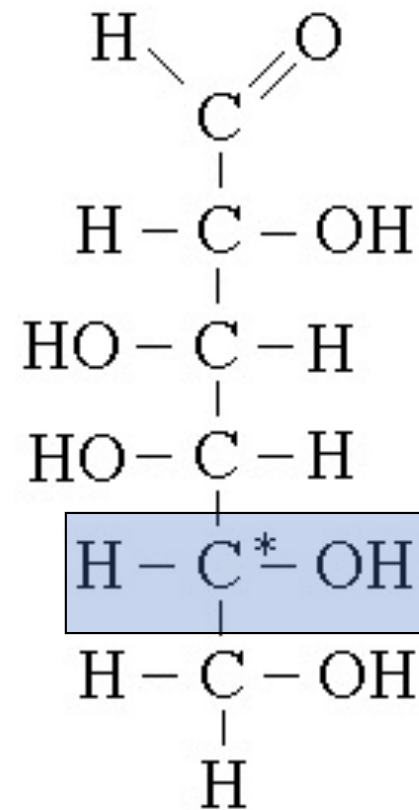
All sugars naturally present in our metabolism are members of the D series



Ribose



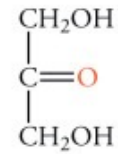
Glucose



Galactose

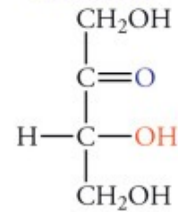
Family of the D-ketoses from 3 to 6 C atoms

Ketotriose

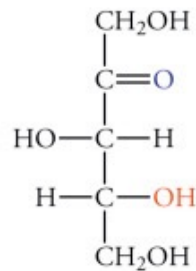


dihydroxyacetone

Ketotetrose

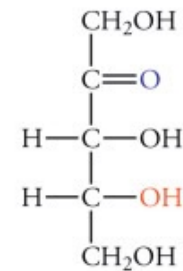


D-erythulose



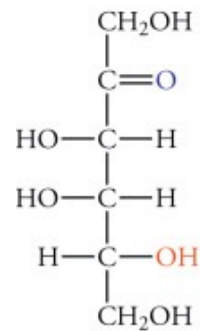
D-xylulose

Ketopentoses

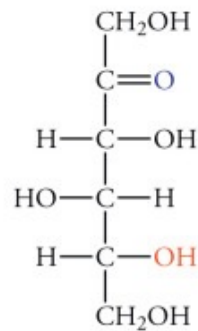


D-ribulose

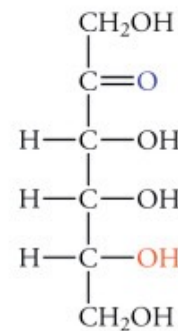
Ketohexoses



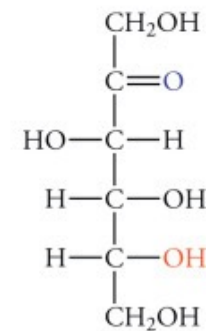
D-tagatose



D-sorbose

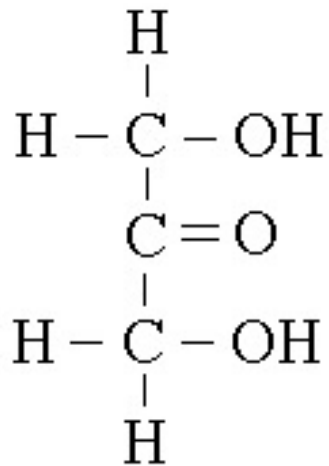


D-psicose

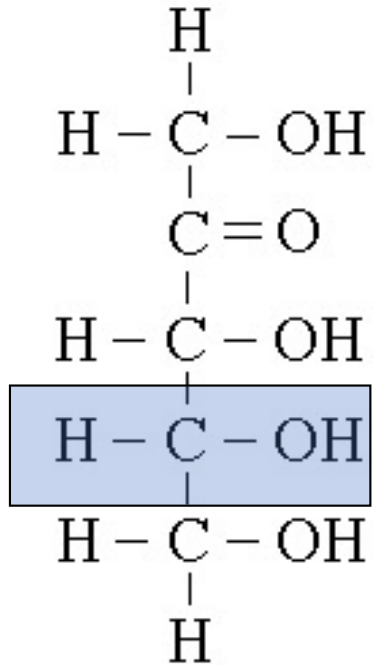


D-fructose

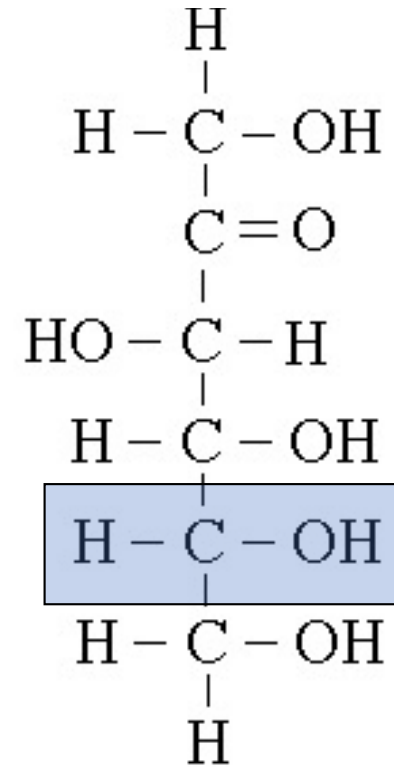
KETOSES



dihydroxyacetone

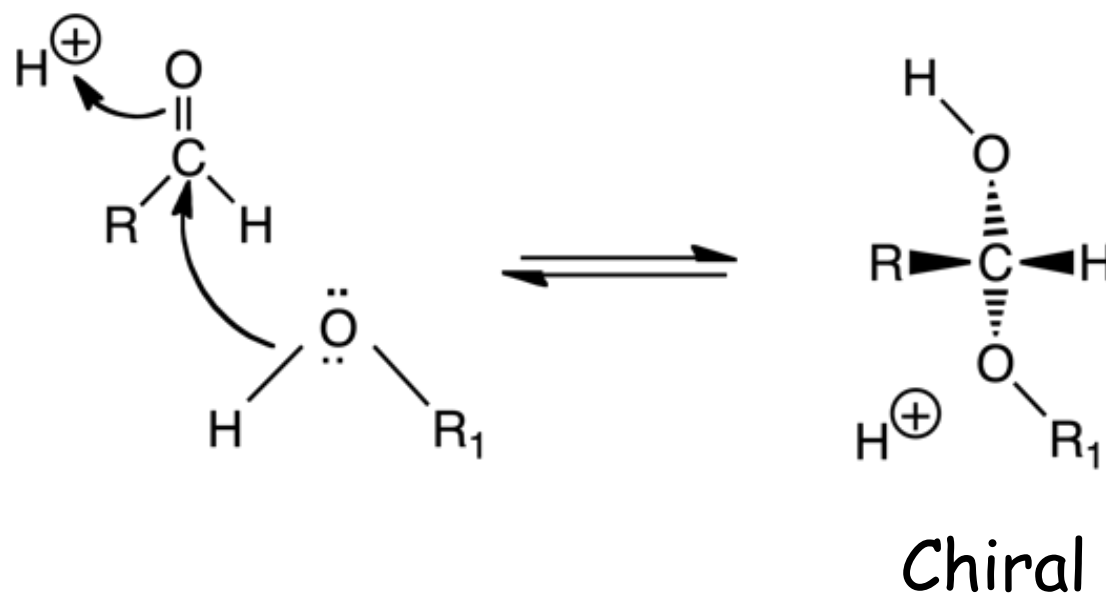


ribulose

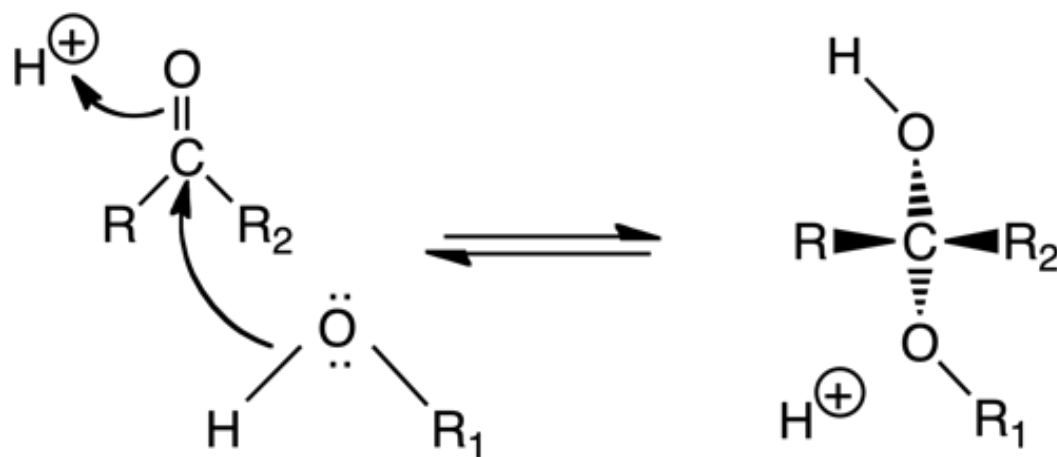


fructose

Hemiacetal formation



Hemiketal formation



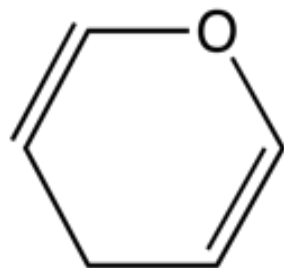
Chiral

The new chiral centre is called
anomeric carbon

It is a **reversible** reaction that
cause **mutarotation**.

Nomenclature

Pyranoses



pyran

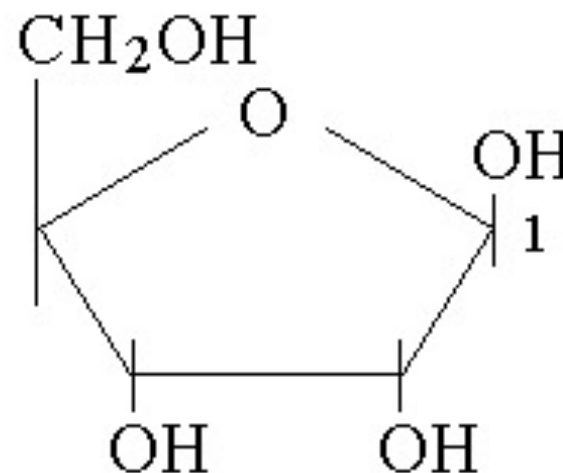
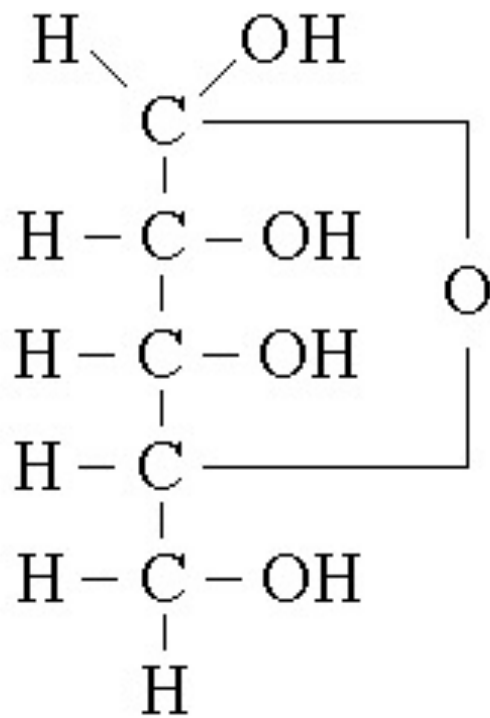
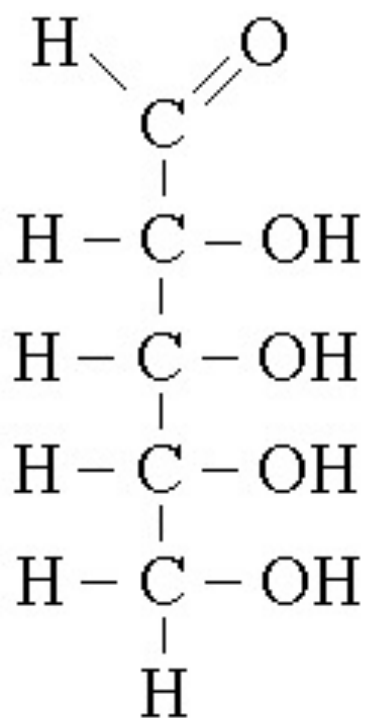
Furanoses



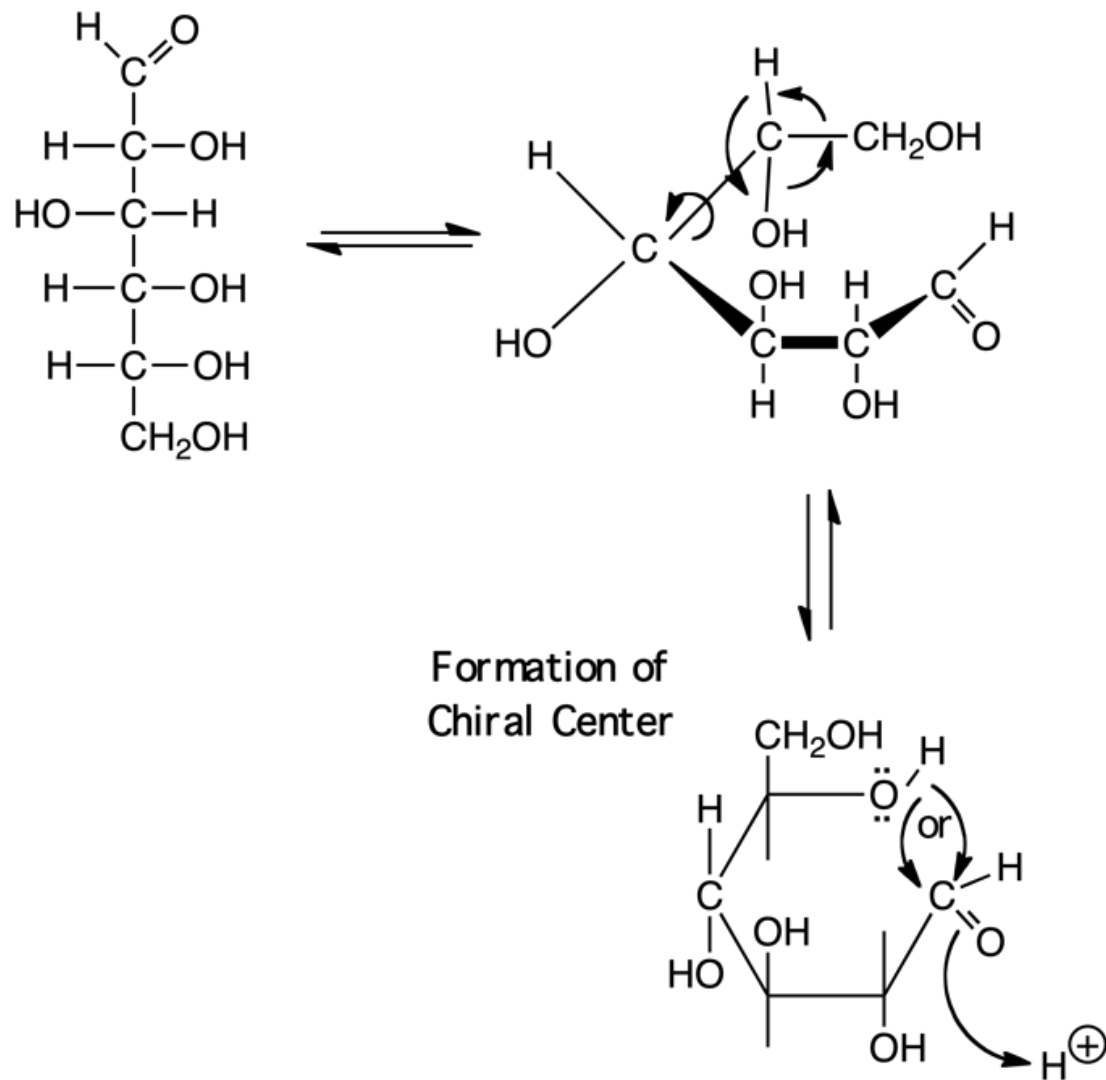
furan

HEMIACETAL FORMS OF ALDOSES

Aldoses with more than three C atoms can form internal hemiacetals and become cyclic. This is the most common form in water solution



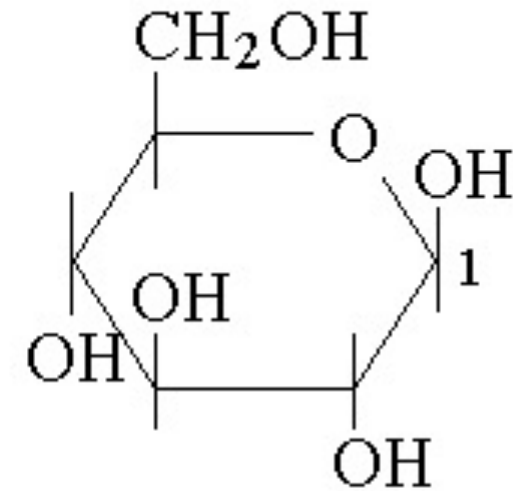
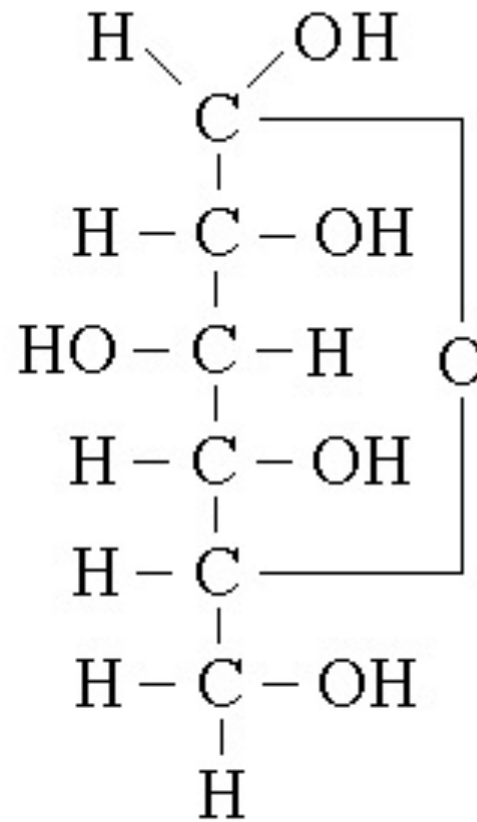
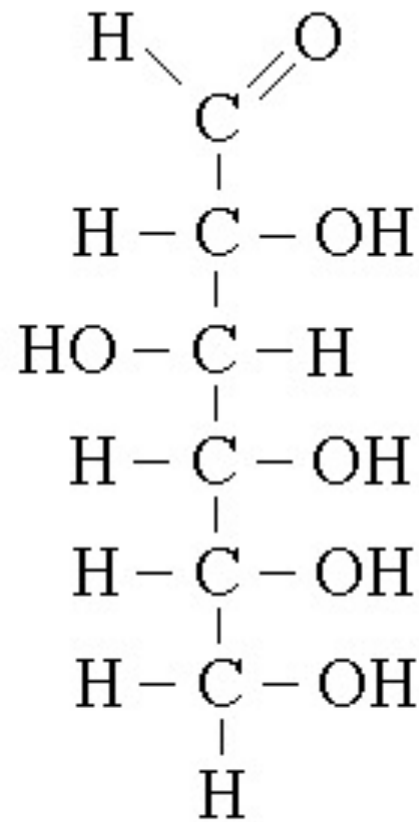
D-ribose in the open and closed form (furanosic)



Reaction of nucleophilic addition between -OH group and carbonyl C

The addition of the -OH in C5 to the aldehydic group 2 can happen from opposite sides (free rotation around C1-C2).

Linear and cyclic forms (pyranosidic) of glucose

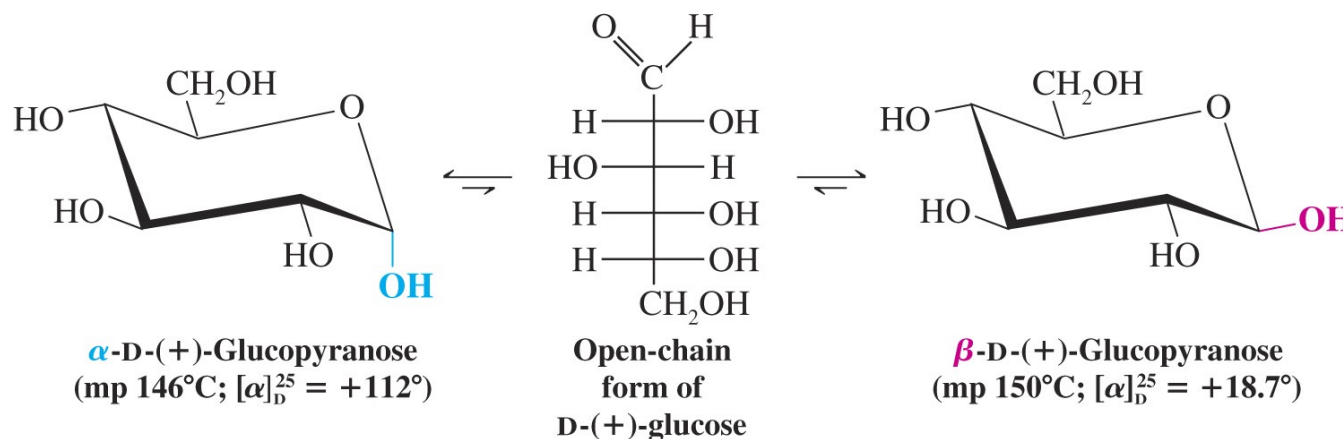


Cyclic glucose has the same conformations of cyclohexane (chair, boat etc)

Mutarotation

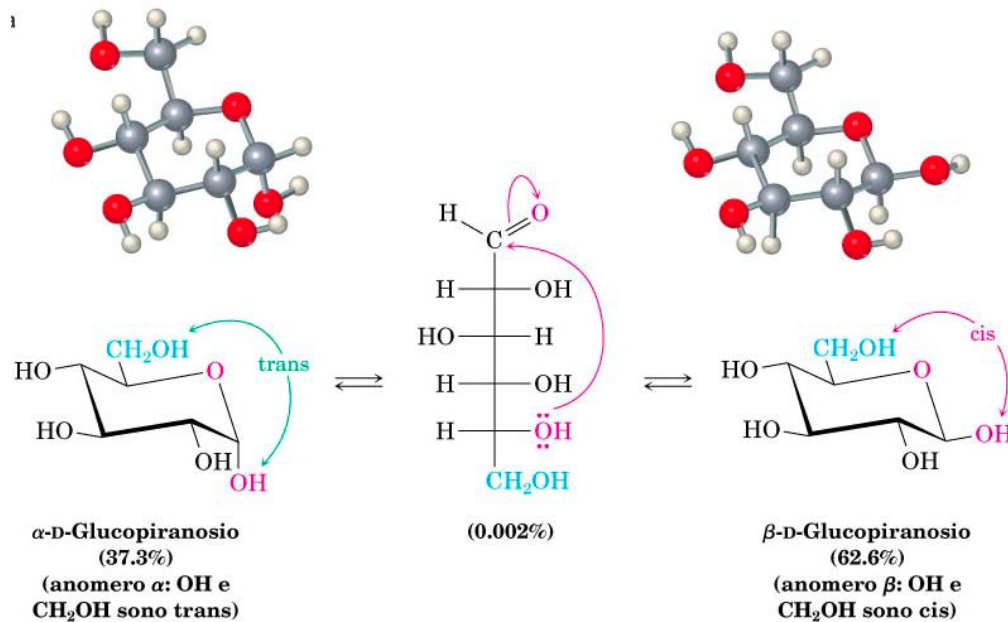
α - and β -glucose can be isolated and they have different specific rotatory properties ($\alpha = +112^\circ$, $\beta = +18,7^\circ$). If one of the two forms is dissolved in water a value of specific rotation of $+52.7^\circ$ is achieved.

- Mutarotation is the change in optical rotatory properties that occurs when a mixture of anomers is formed.

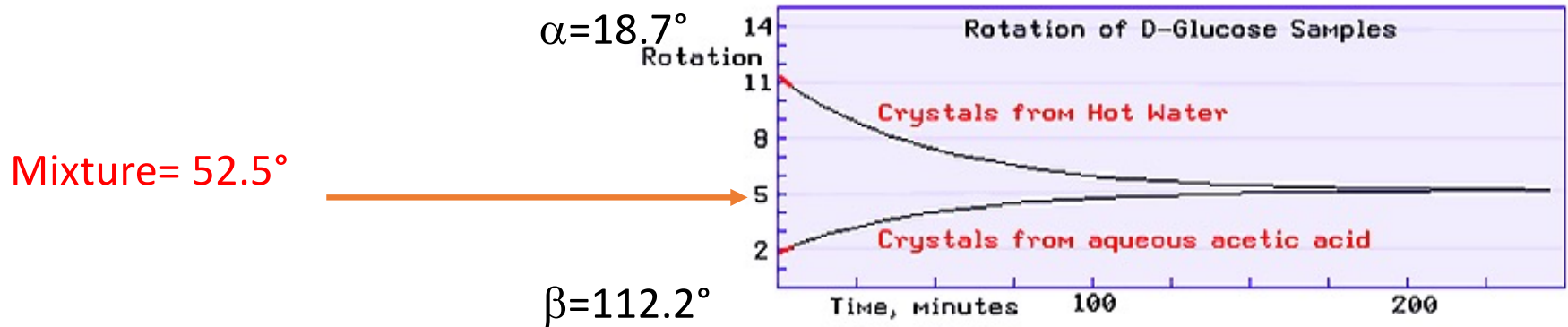


The most stable anomer is more abundant, a small fraction of the open form allows the interconversion.

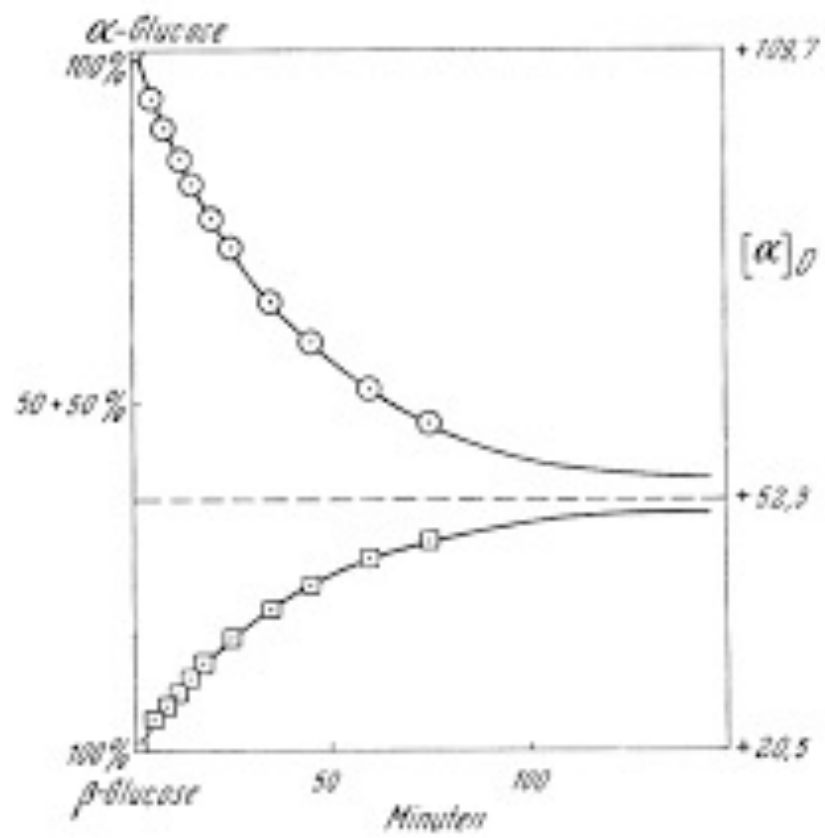
Mutarotation

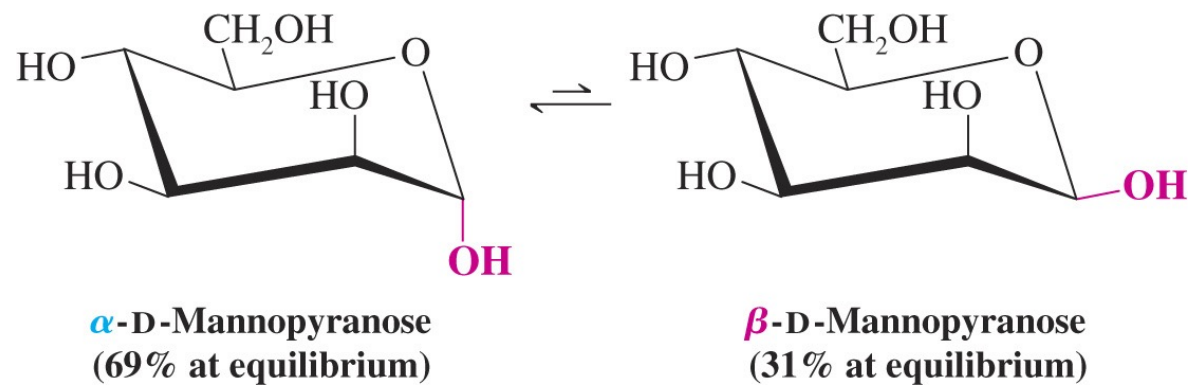
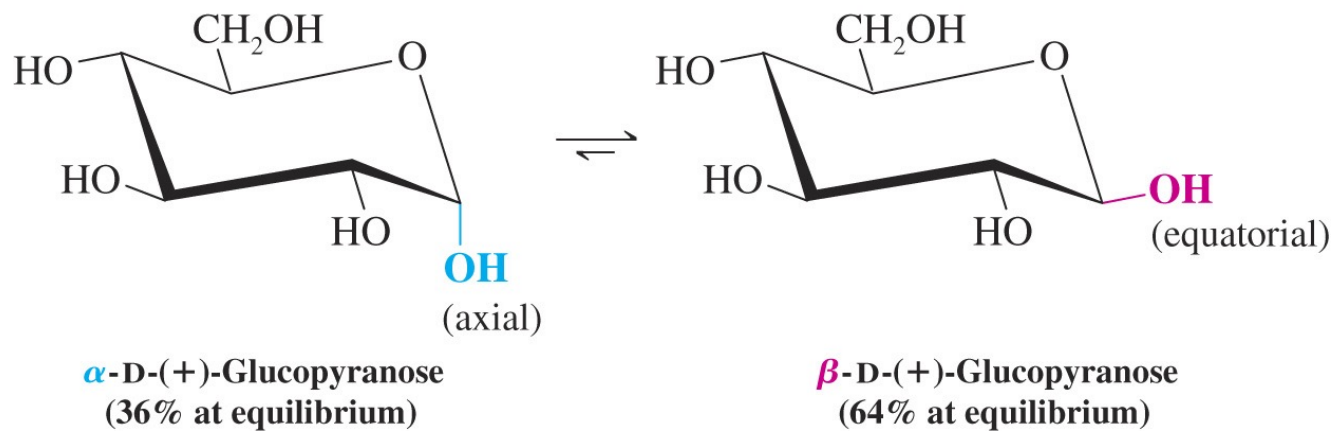


Variation during time of the optical properties of α - and β -glucose

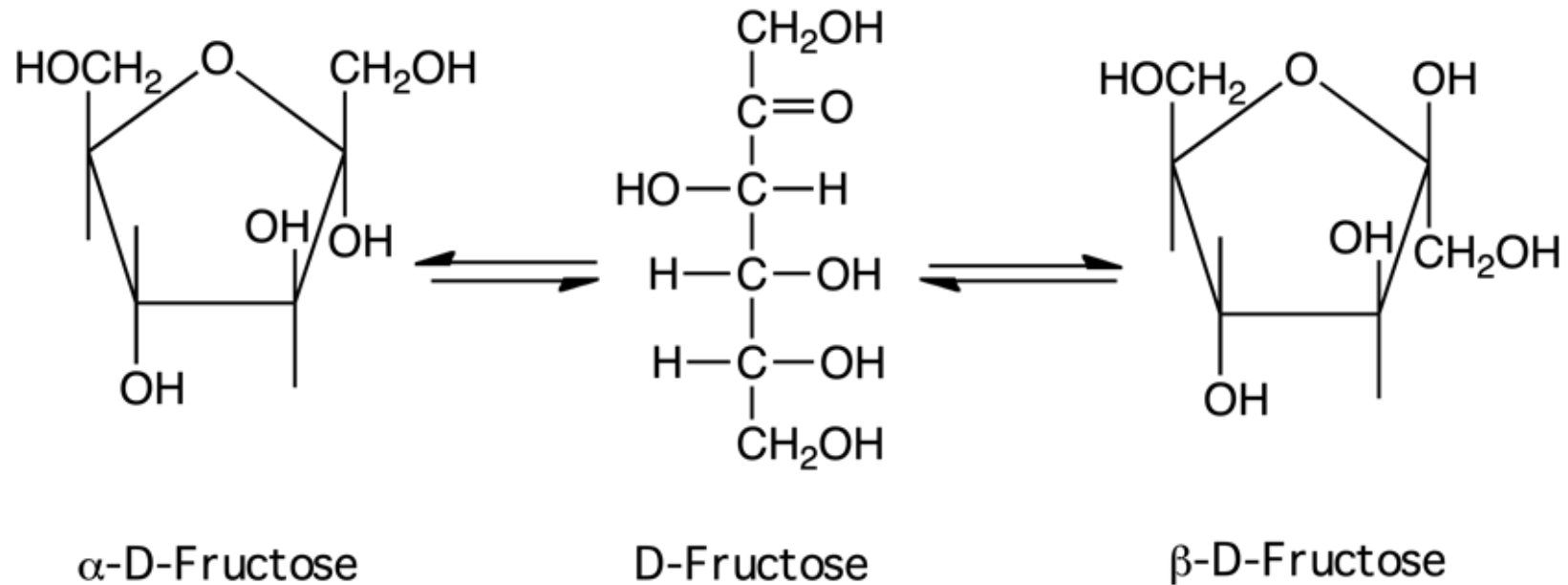


Occurs in all reducing sugars, i.e. sugars that have a free anomeric carbon





Cyclization of D-Fructose (biologically relevant forms)



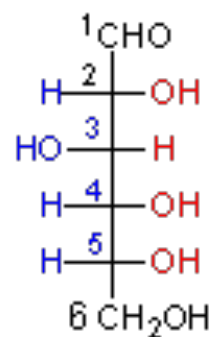
Distribution of the cyclic forms:

- Open chain: 0.4%
- α -D-fructopyranose: 2%
- β -D-fructopyranose : 71%
- α -D-fructofuranose: 5.6%
- β -D-fructofuranose: 21%

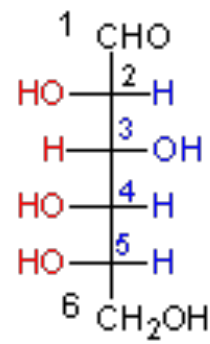
CONFIGURATIONAL ISOMERS

enantiomers

stereoisomers that are mirror images



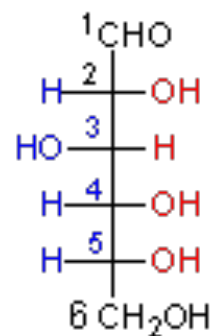
D-glucose



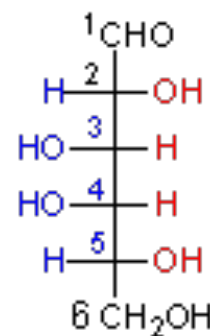
L-glucose

diastereomers

stereoisomers that are not mirror images



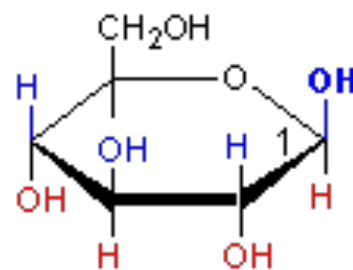
D-glucose



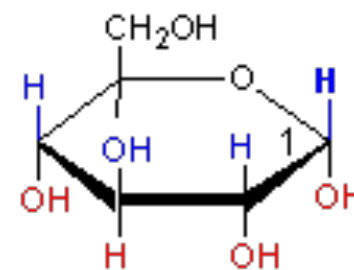
D-galactose

anomers

stereoisomers and diastereomers that differ in config. around anomeric C

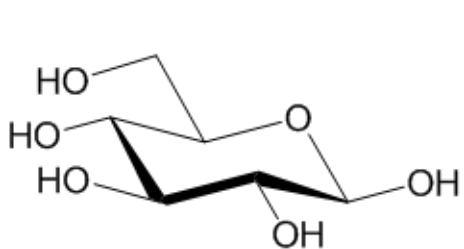


β-D-glucopyranose
OH on C1 point up

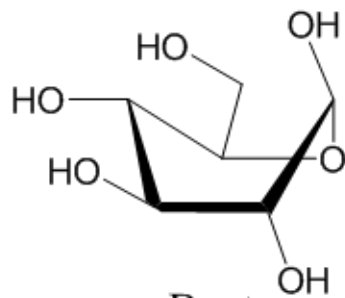


α-D-glucopyranose
OH on C1 point down

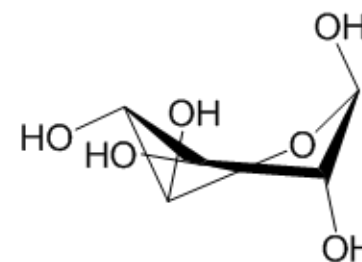
Conformational isomers of glucose.
Same stereochemistry, but different conformations.



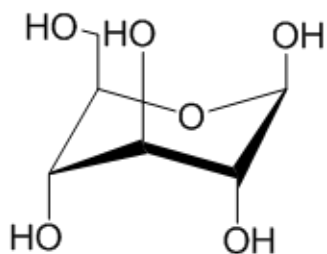
Chair



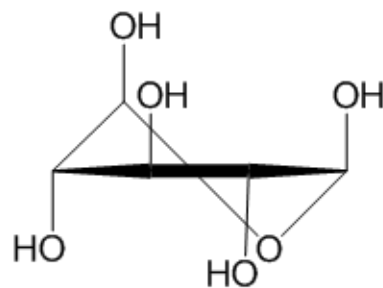
Boat



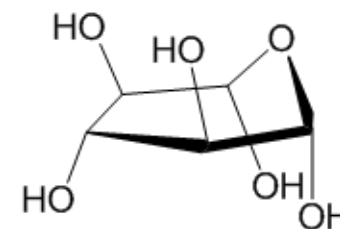
Skew



Chair



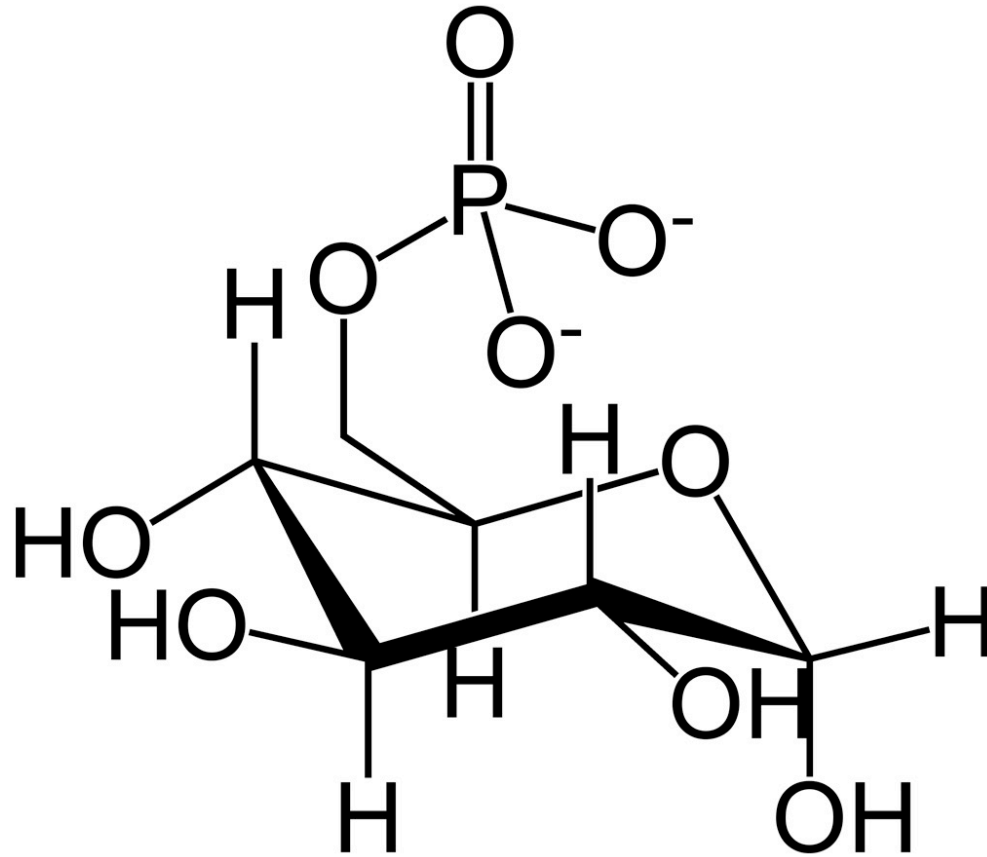
Half-Chair



Envelope

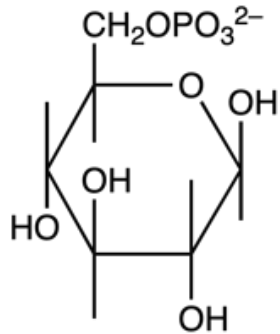
Derivatives of Monosaccharides

Esters with phosphate

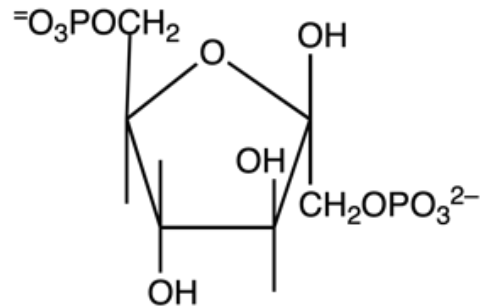


Glucose-6-Phosphate

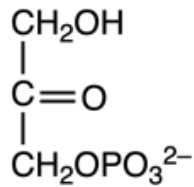
Esters with phosphate



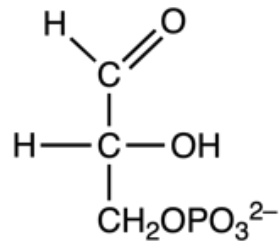
β -D-Glucose-6-P
(Glc-6-P)



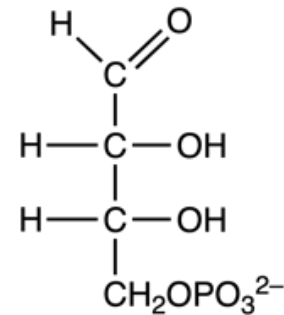
β -D-Fructose-1,6-bisphosphate
(Fru-1,6-bisP)



Dihydroxyacetone
phosphate
(DHAP)

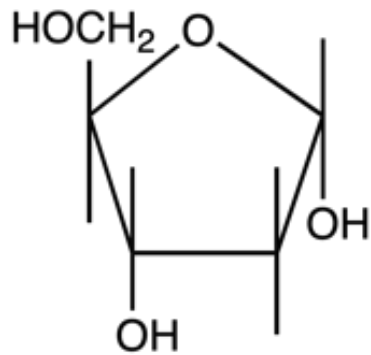


D-Glyceraldehyde
3-phosphate
(G3P)

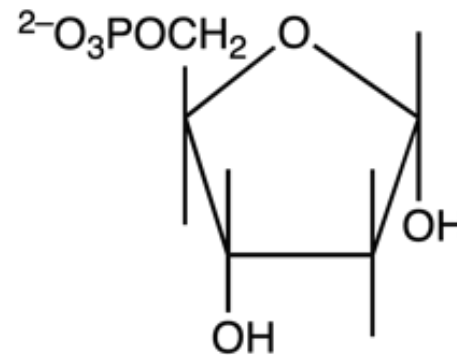


D-Erythrose
4-phosphate
(E4P)

Deoxy sugars



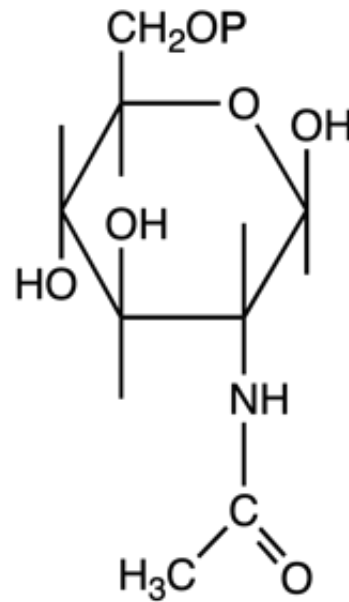
2-Deoxyribose
(dRib)



Deoxyribose 5-phosphate (dRib-5-P)
[Deoxy- α -D-ribofuranose 5-phosphate]

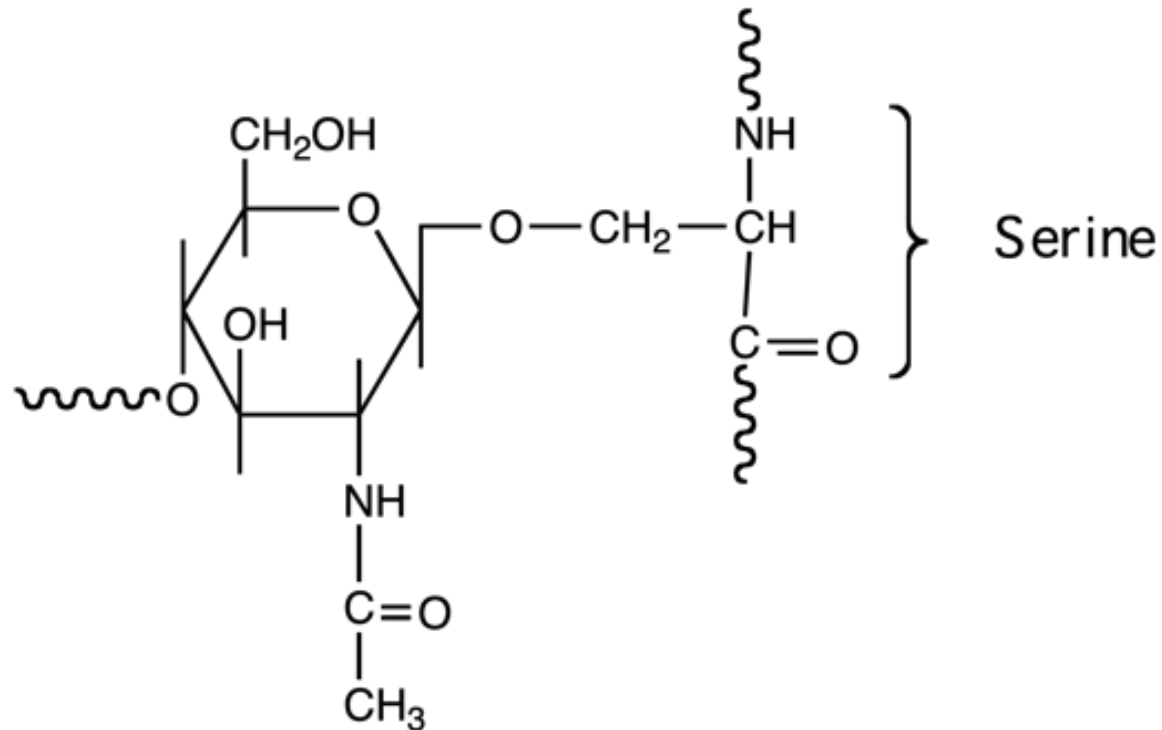
In biological compounds the 5-member ring is found

Amino Sugars (e.g. GlcNAc-6-P)

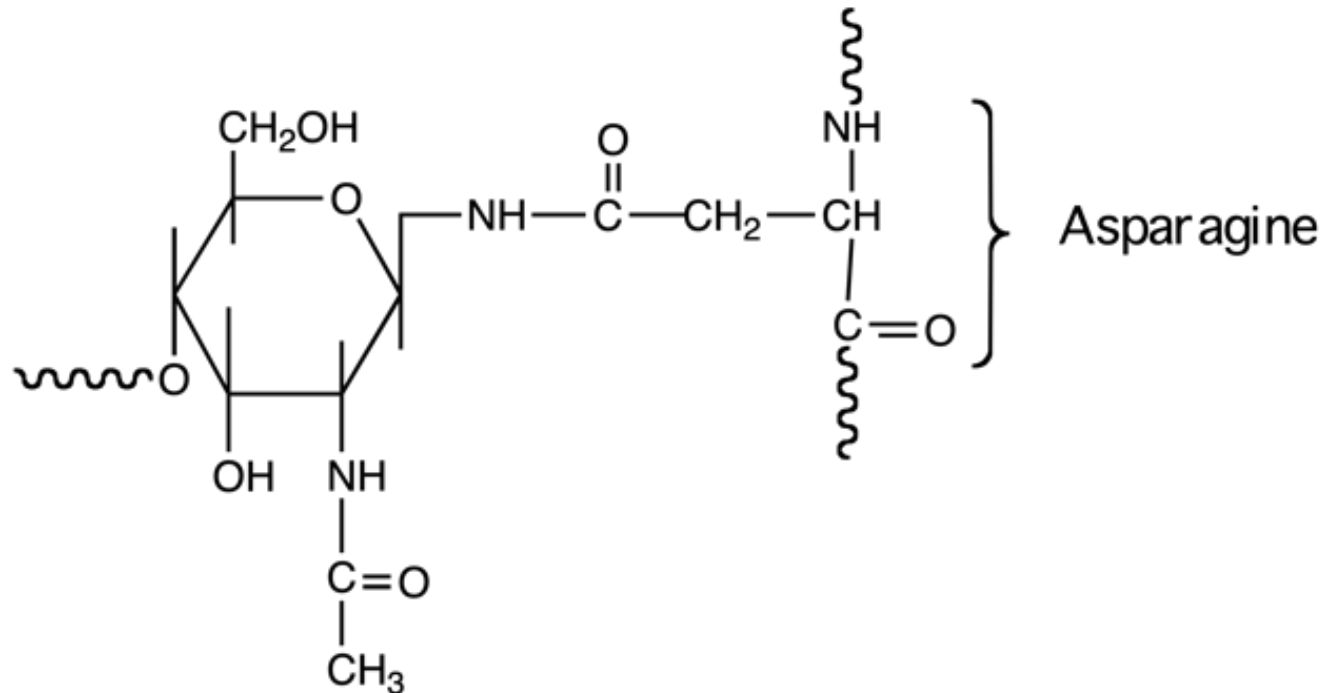


N-Acetyl-D-glucosamine 6-phosphate

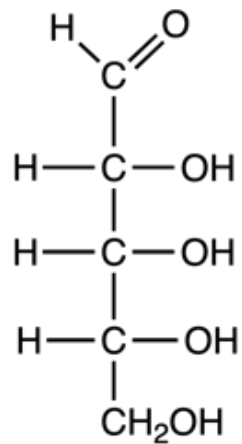
O-glycosylation of proteins with oligosaccharides



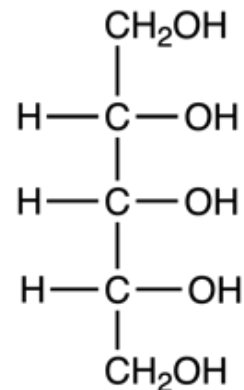
N-glycosylation of proteins with oligosaccharides



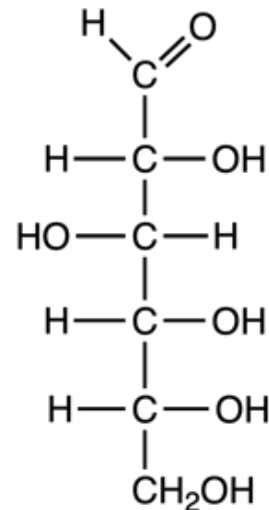
Alcohols derived from sugars (reduced)



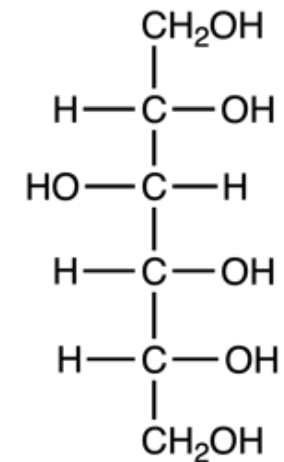
D-Ribose



Ribitol



D-Glucose



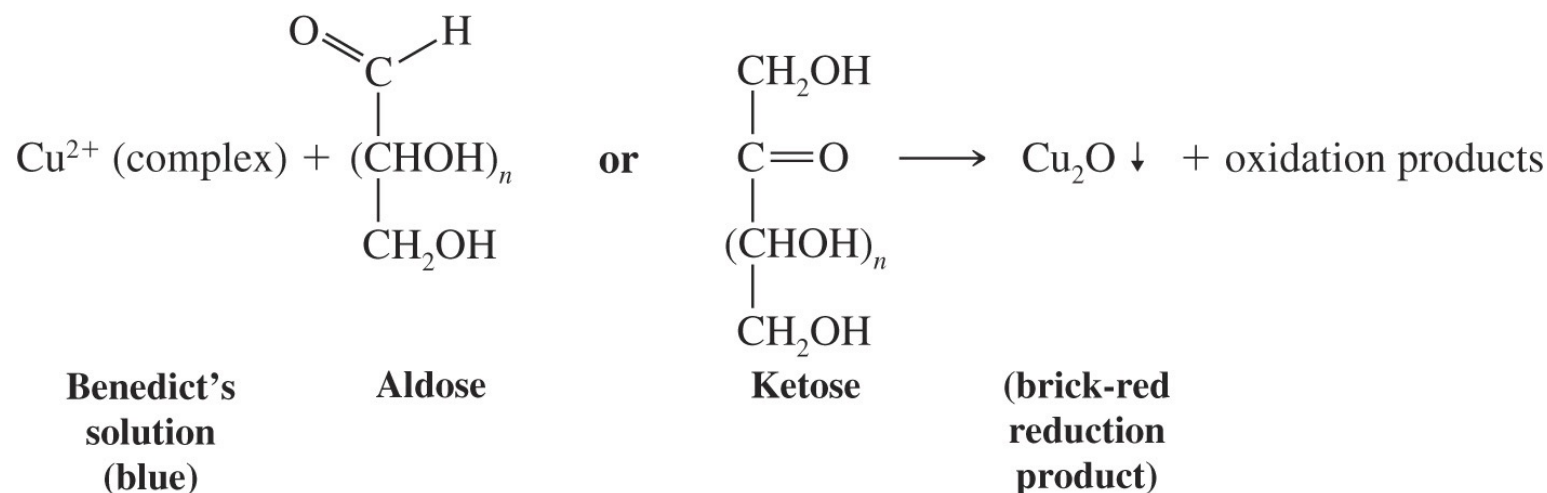
Sorbitol

- Oxidation of monosaccharides**

Tollens or Benedict reagents: active on reducing sugars

Tollens reagent $[Ag(NH_3)_2OH]$ yields a "silver mirror" when $Ag^+ \rightarrow Ag^0$

Benedict reagent (alkaline solution of rameic citrate) yields a red precipitate of Cu_2O

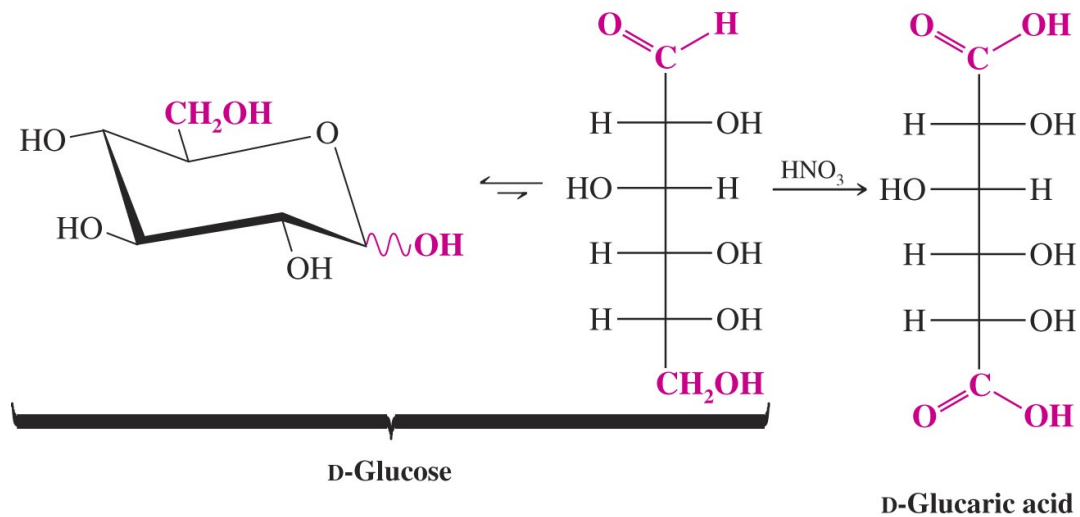
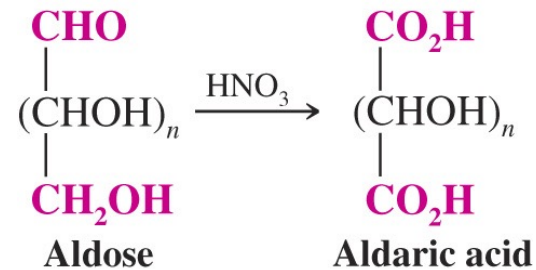
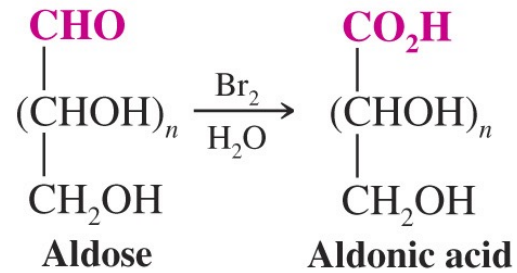


In an alkaline solution a ketose can be converted into an aldose.

Oxidation products of sugars:

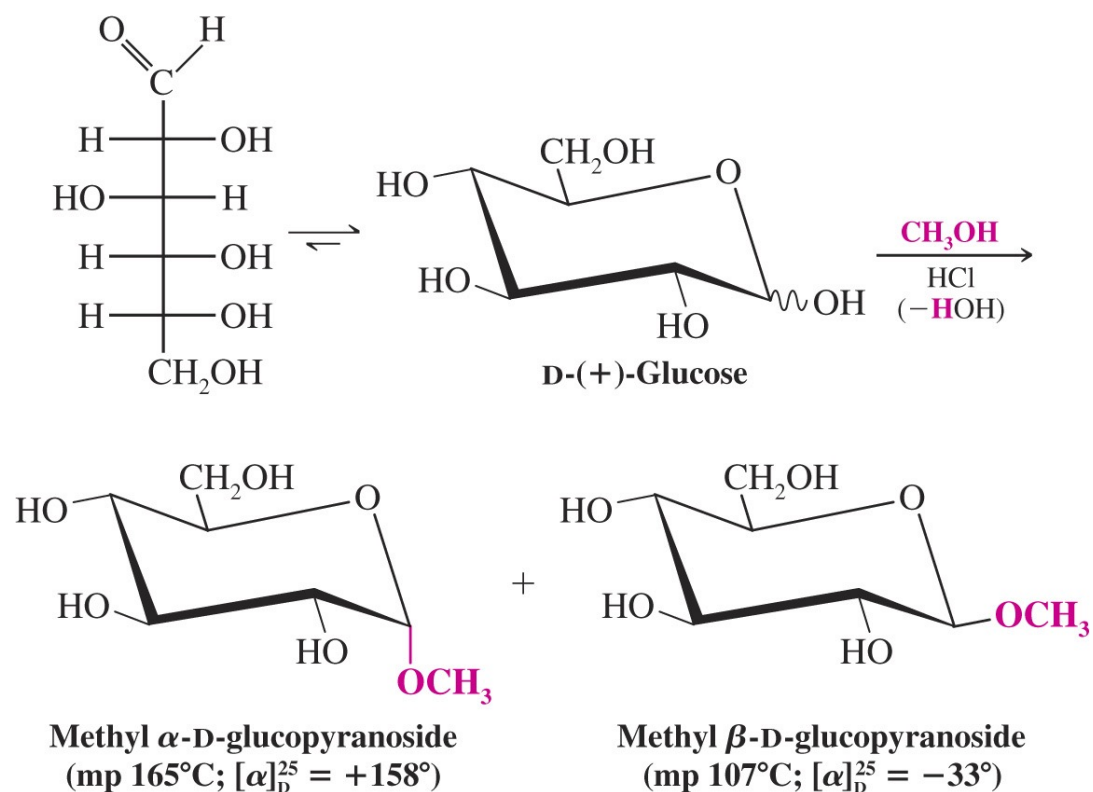
Aldonic Acids

Aldaric Acids

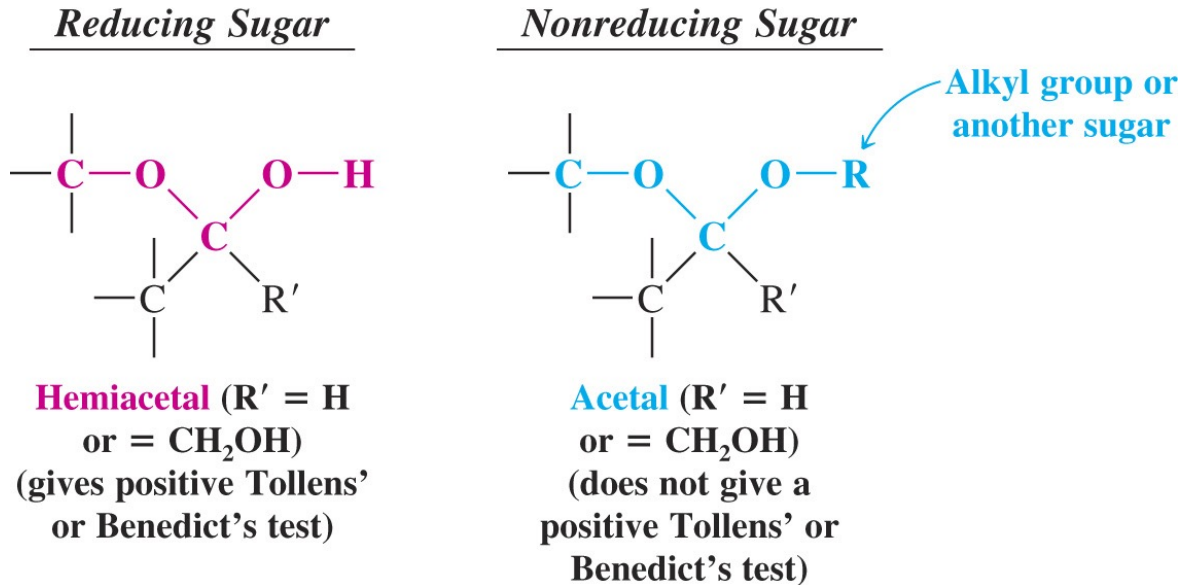


Formation of glycosides

- Glycosides are acetals of the anomeric carbon
- When glucose reacts with methanol a methyl glucoside is formed
- A glycoside derived from glucose is called glucoside.

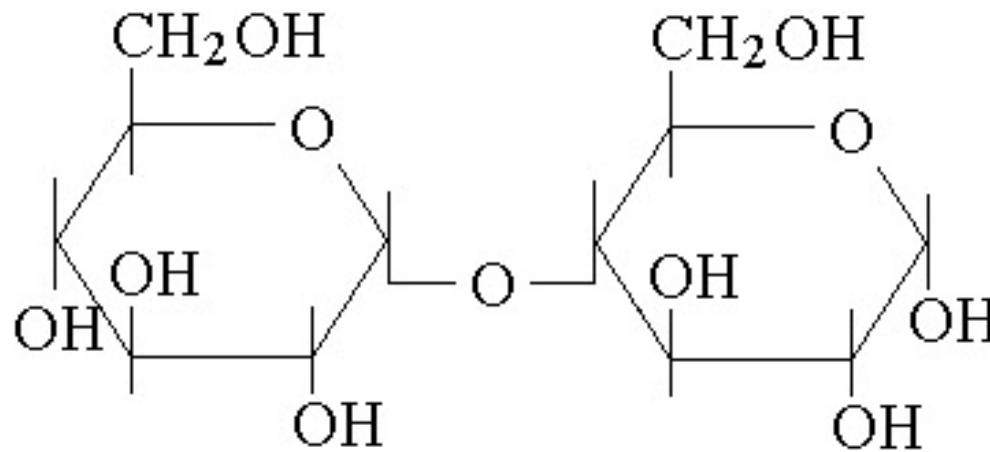


- Sugars in hemiacetal form are **reducing** since they are in equilibrium with the open form and can react with Benedict and di Tollens reagents.
- Sugars with glycosidic bonds are **non-reducing** since they have no free aldehydic groups.



GLYCOSIDIC BOND

It is a peculiar form of acetal, formed between the hemiacetalic carbon of a cyclic sugar and a carbon from another sugar.



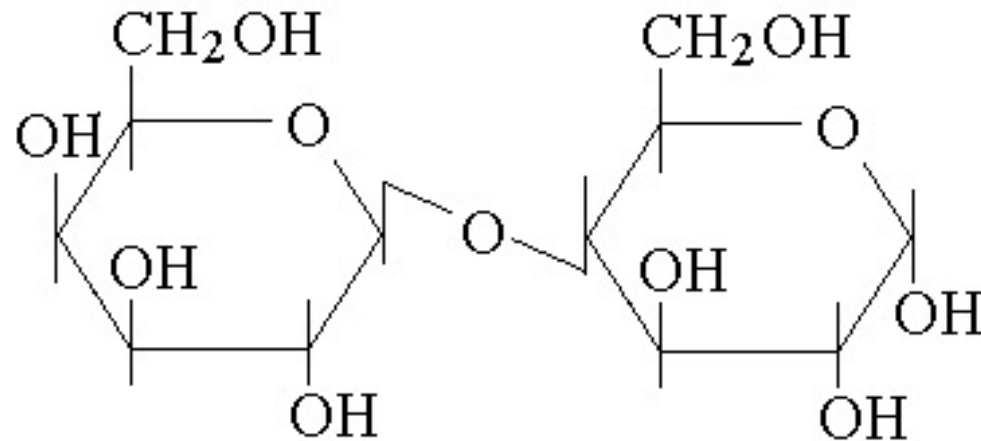
Reducing

Maltose (dimer of α -glucopyranose)

α -D-glucopyranosil - (1- 4) - D- glucose

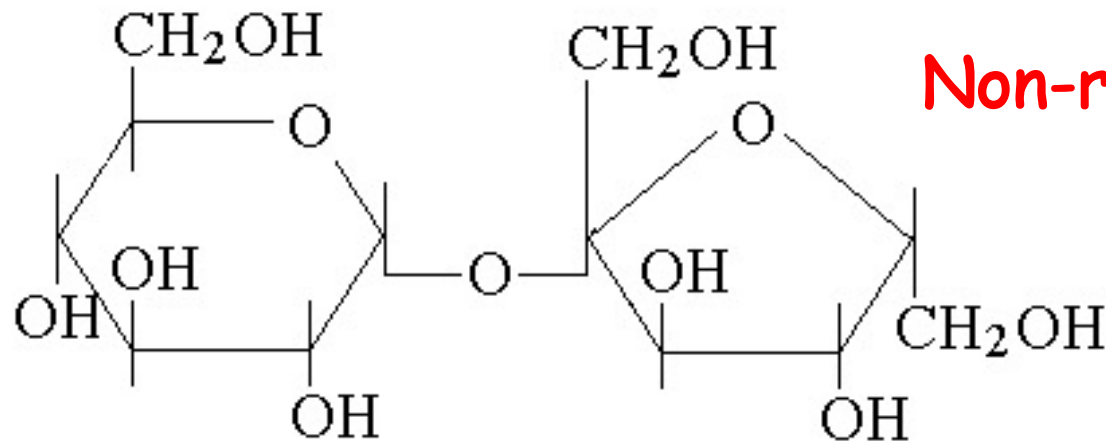
Reducing

β -D-galactopyranose (1- 4) α -D-glucopyranose



β -galactosidase and
lactose intolerance

Lactose (galactose-glucose)

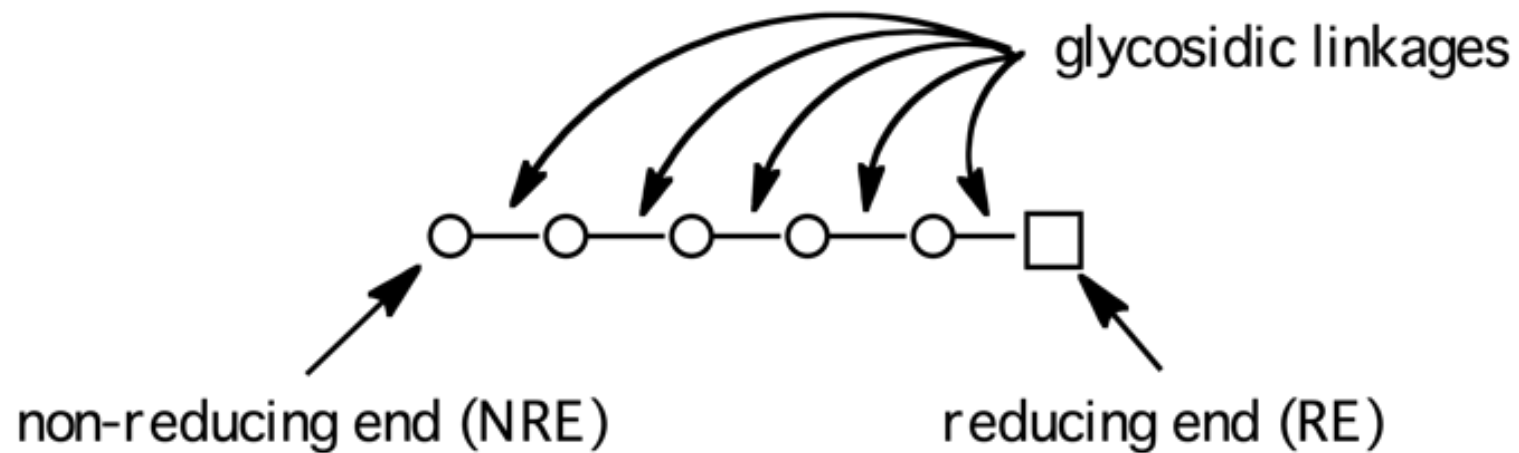


Non-reducing

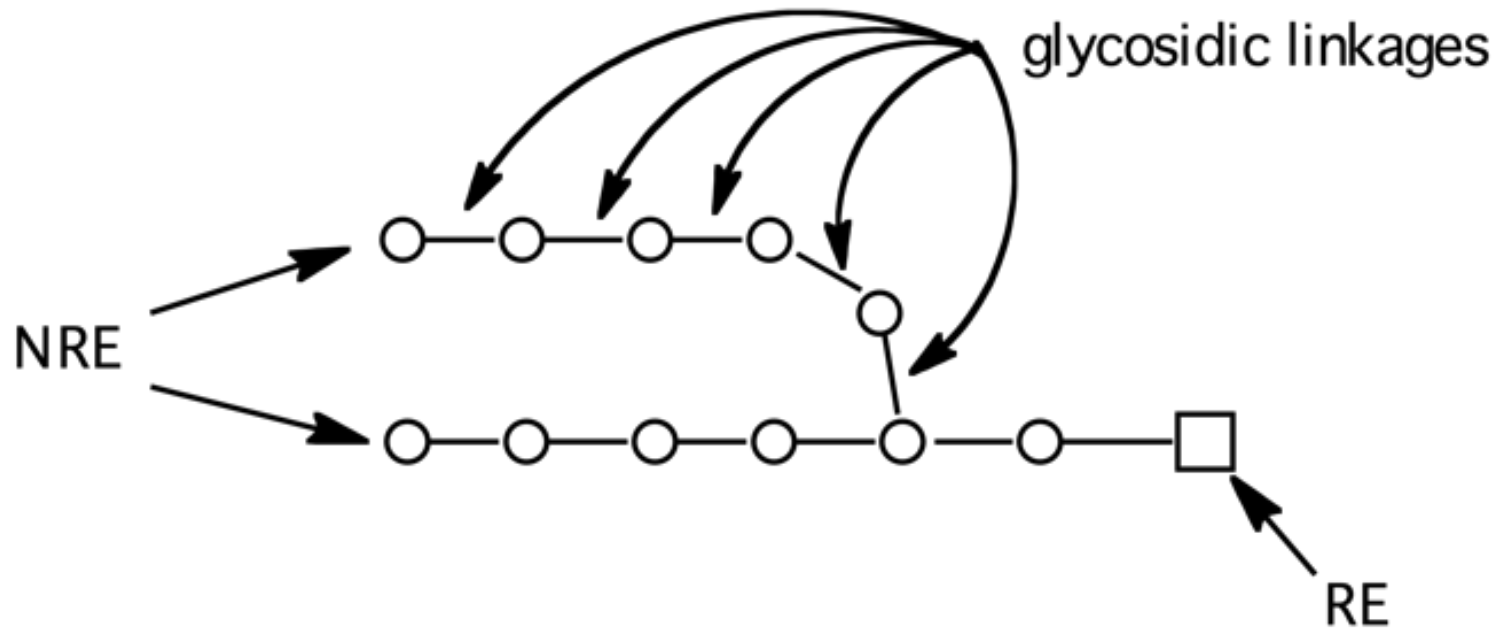
Sucrose (glucose-fructose)

α -D-glucopyranose (1- 2) β -D-fructofuranose

Linear polysaccharides



Branched polysaccharides



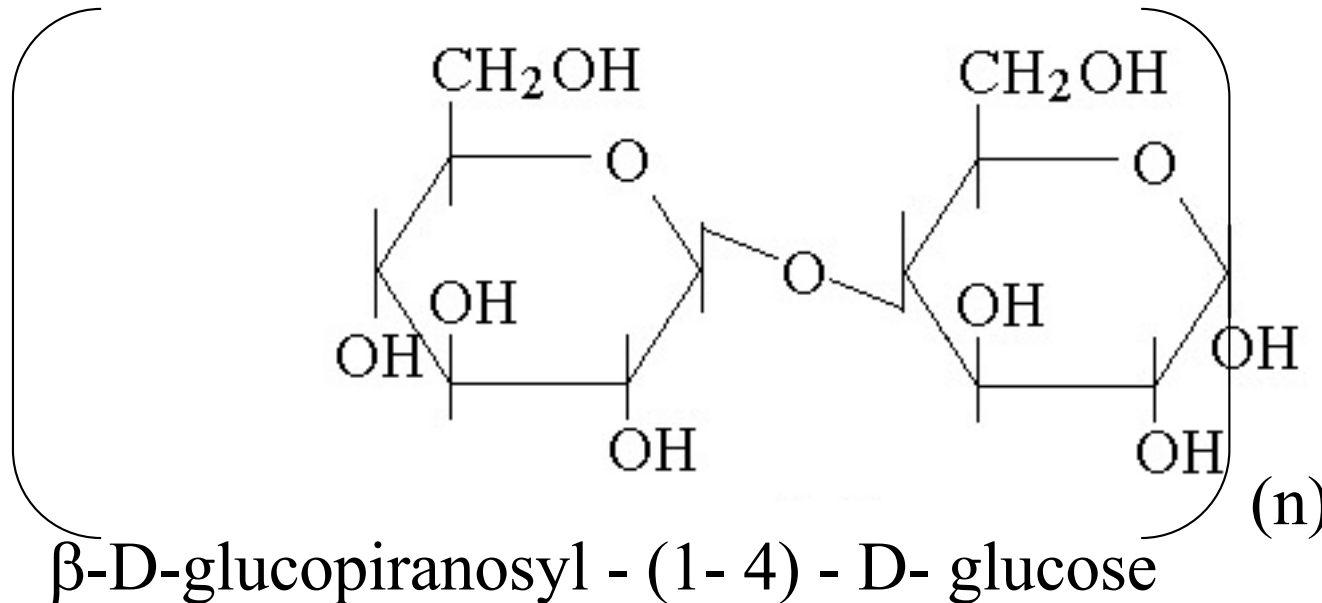
STRUCTURAL POLYSACCHARIDES

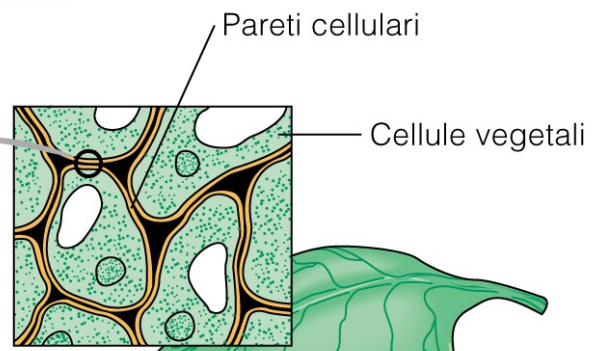
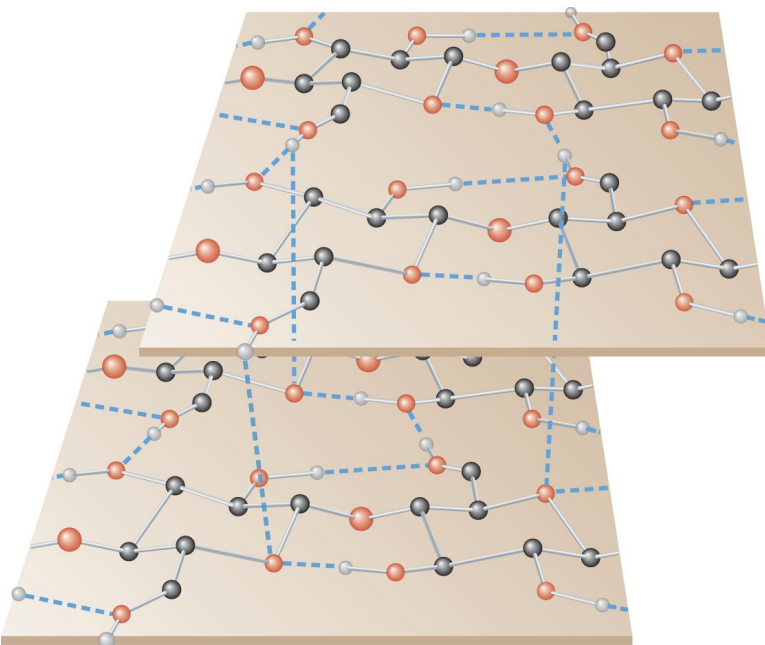
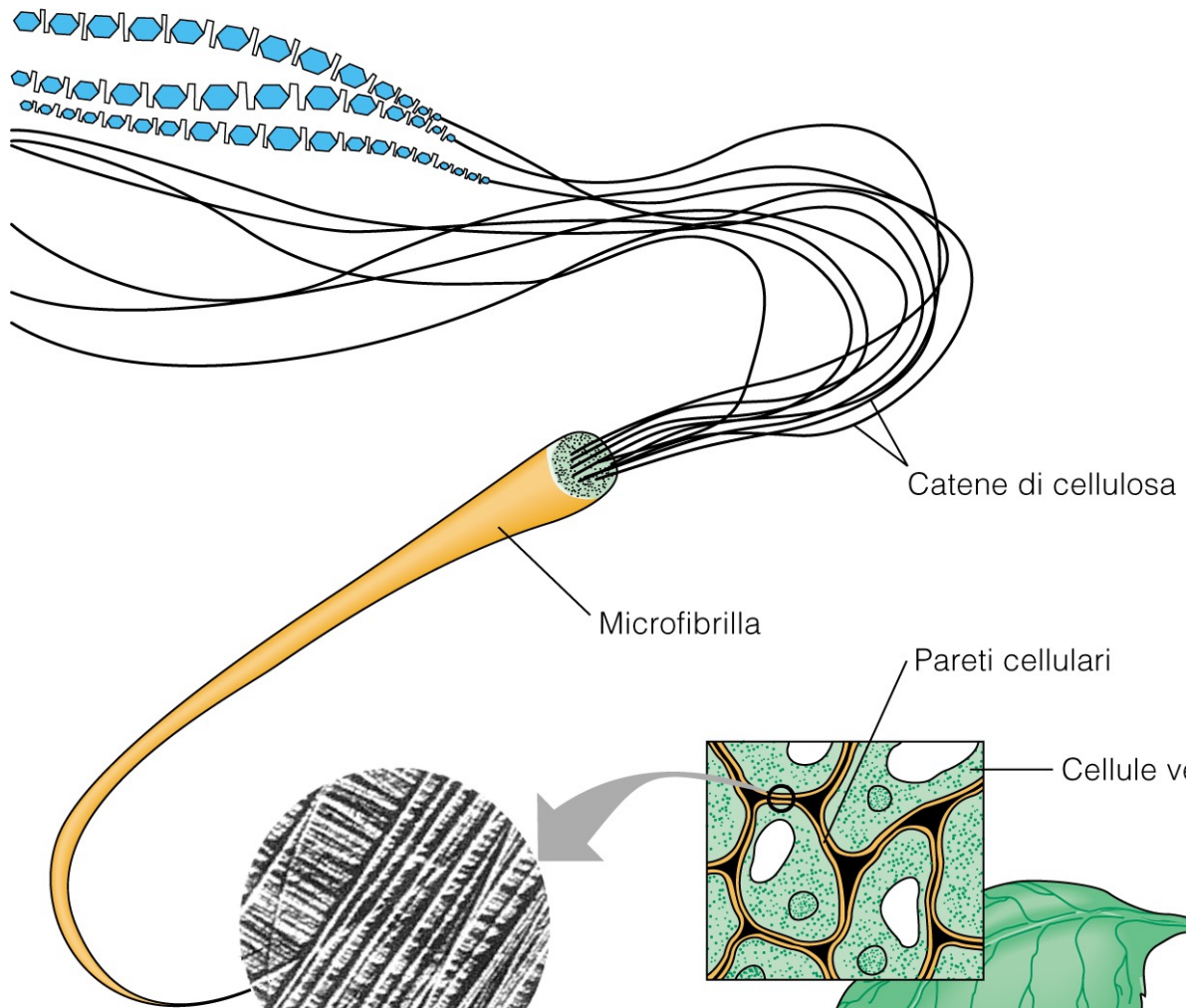
CELLULOSE

an example of of isomerism in sugars is cellulose, that has a β -glycosidic bond.

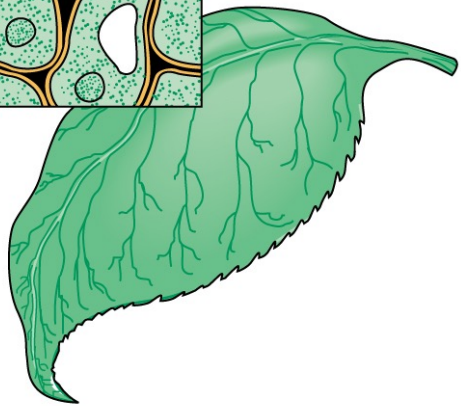
The disaccharide from cellulose is very similar to maltose, but it is usable in human metabolism, since we do not have enzyme that can break the bond between the two glucose molecules.

Cellulose



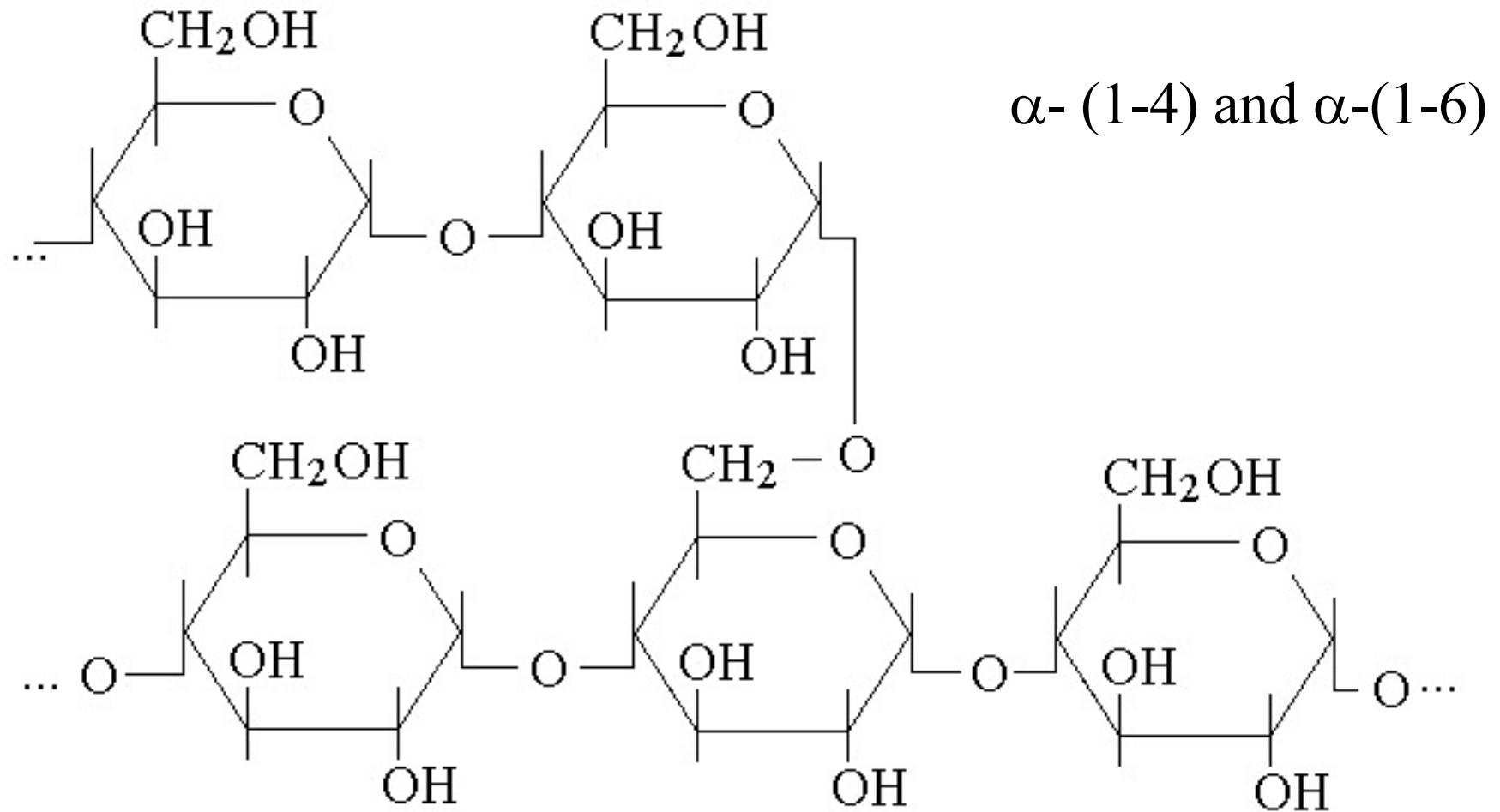


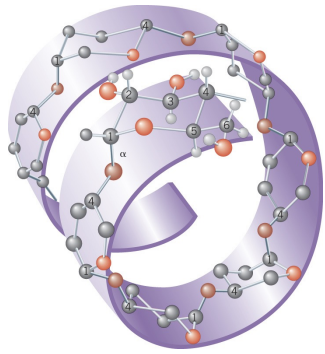
Microfibrille di cellulosa nella parete delle cellule vegetali



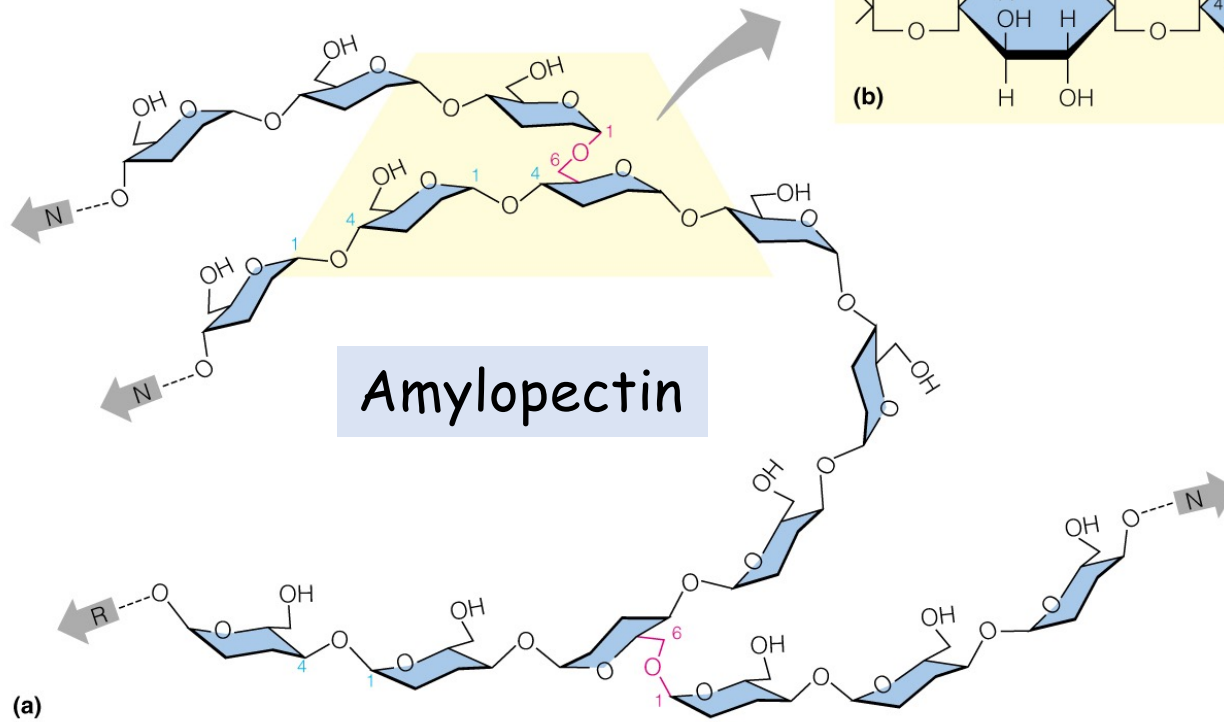
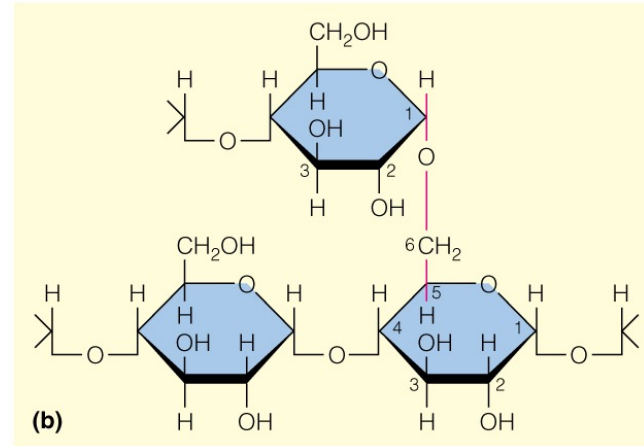
Storage Polysaccharides

Starch (amilose -linear, and amylopectin- branched) in plants.



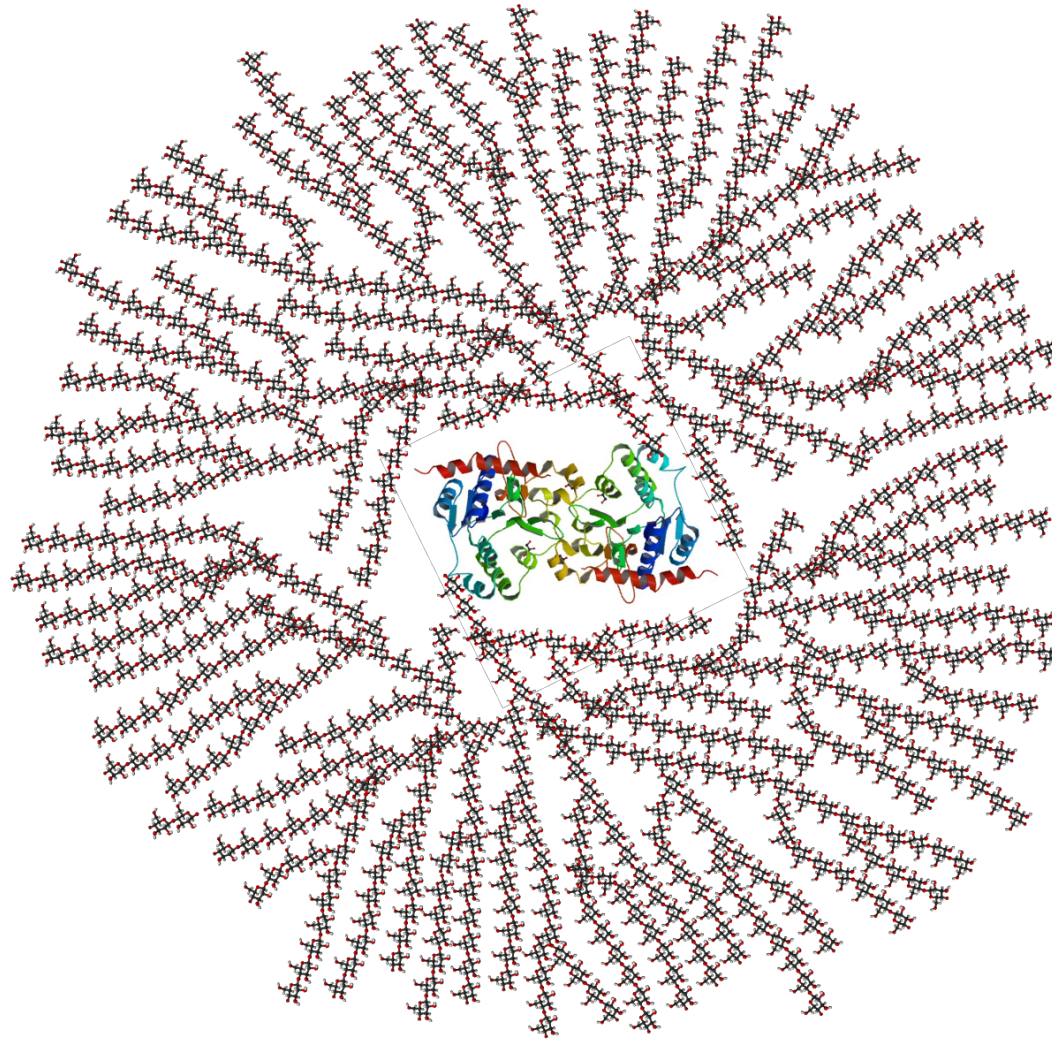


Amylose



Amylopectin

Glycogen is highly branched



Fast release of sugar from liver and muscles