Carbohydrates
Saccharides

Saccharides (carbohydrates)
- Definition
- Classification

Monosaccharides
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- Classification
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- D and L configuration of sugars
- Cyclization
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- Calculation of optical rotation (Biot's law)
- Mutarotation
- Oxidation of monosaccharides
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  - Oxidation of the aldehyde and primary alcohol functions to a carboxylic acid
  - Oxidation of the primary alcohol group to a carboxylic acid group
- Reduction of aldehyde or ketone groups to alcohol groups
- Amino monosaccharides
- Deoxy-monosaccharides

Disaccharides
- Definition
- Nomenclature
- Sucrose
- Maltose
- Lactose

Polysaccharides
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- Starch
- Glycogen
- Cellulose
- Chitin

Definition

- Carbohydrates or saccharides (Greek: sakcharon, sugar) are essential components of all living organisms and are, in fact, the most abundant class of biological molecules.
- The name carbohydrate, which literally means “carbon hydrate,” stems from their chemical composition, which is roughly (C H2 O)n, where n ≥3.
- The basic units of carbohydrates are known as monosaccharides.

Classification

- Monosaccharides: these are the simplest sugars, composed of a single unit, and cannot be broken down into smaller molecules.
- Oligosaccharides: these are sugars formed by the combination of several monosaccharides (between 2 and 10).
- Polysaccharides: these are sugars formed by the combination of multiple monosaccharides, which can number in the hundreds or thousands.

Monosaccharides

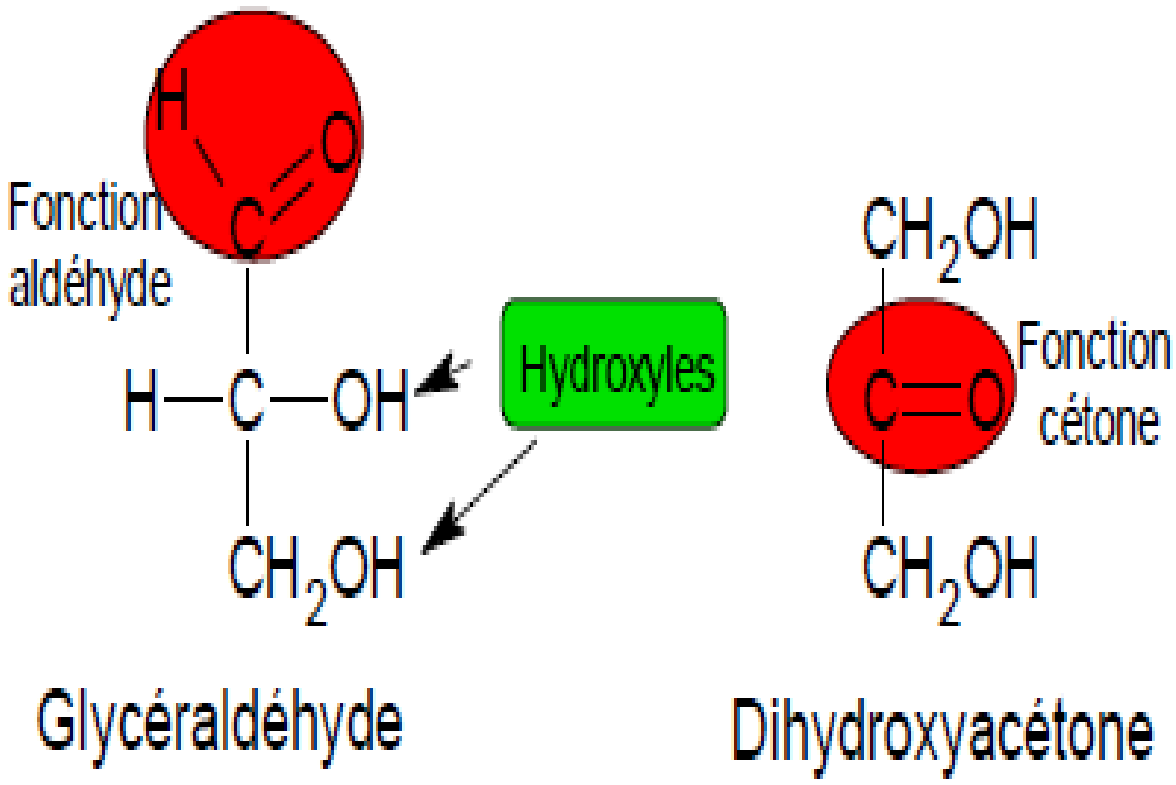
Definition

Monosaccharides or simple sugars are aldehyde or ketone derivatives of straight-chain polyhydroxy alcohols containing at least three carbon atoms.

Example: D-glucose and D-ribulose, cannot be hydrolyzed to form simpler saccharides

The simplest monosaccharides are those with three carbon atoms:

D- or L-glyceraldehyde and dihydroxyacetone



Classification

Monosaccharides are classified according to :

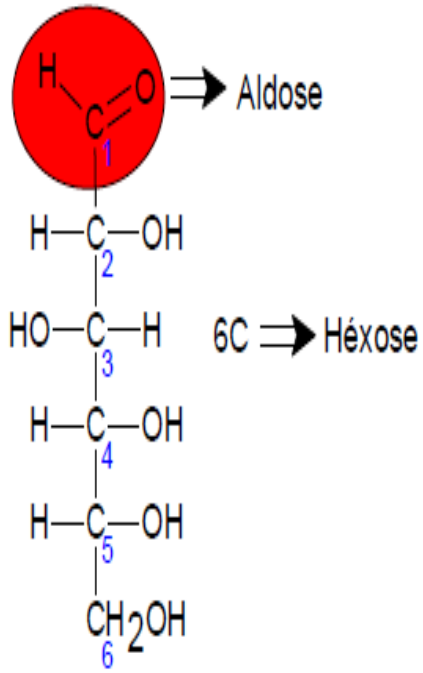
- The chemical nature of their carbonyl group
- The number of their C atoms.

❖If the carbonyl group is an aldehyde, as in glucose, the sugar is an aldose.

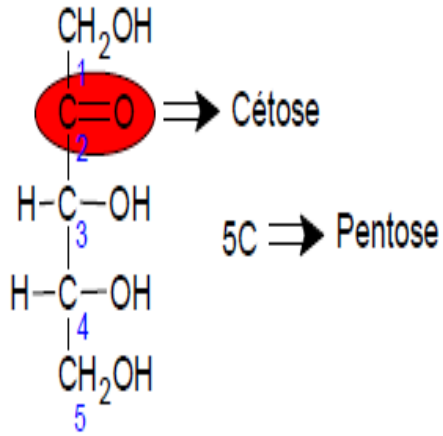
❖If the carbonyl group is a ketone, as in ribulose, the sugar is a ketose.

$C_n(H_2O)_n$

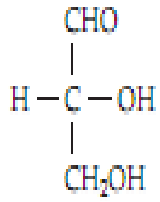
n = 3 : trioses
n = 4 : tétroses
n = 5 : pentoses
n = 6 : hexoses



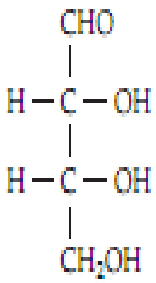
Aldohexose



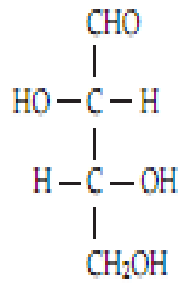
Cétopentose



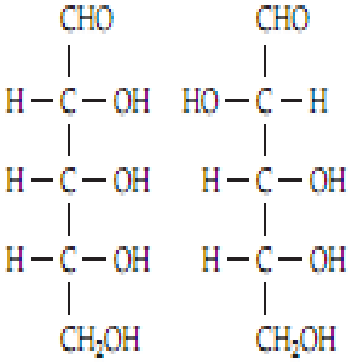
Glyceraldehyde



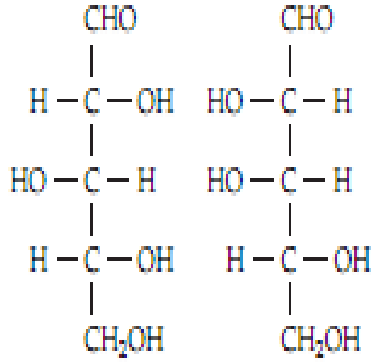
Erythrose



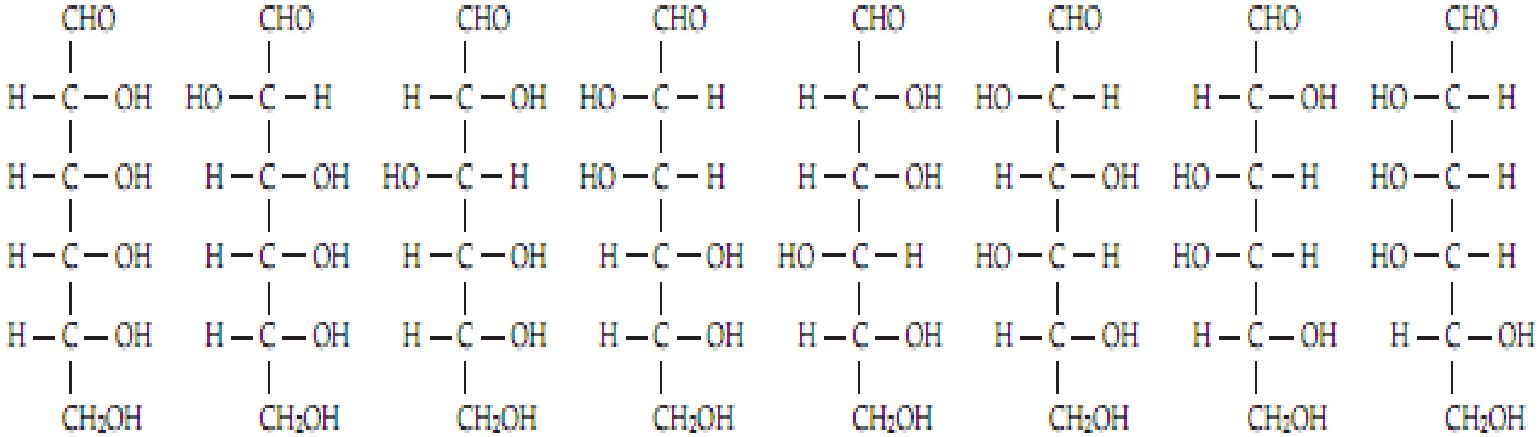
Threose



Ribose (Rib) Arabinose (Ara)

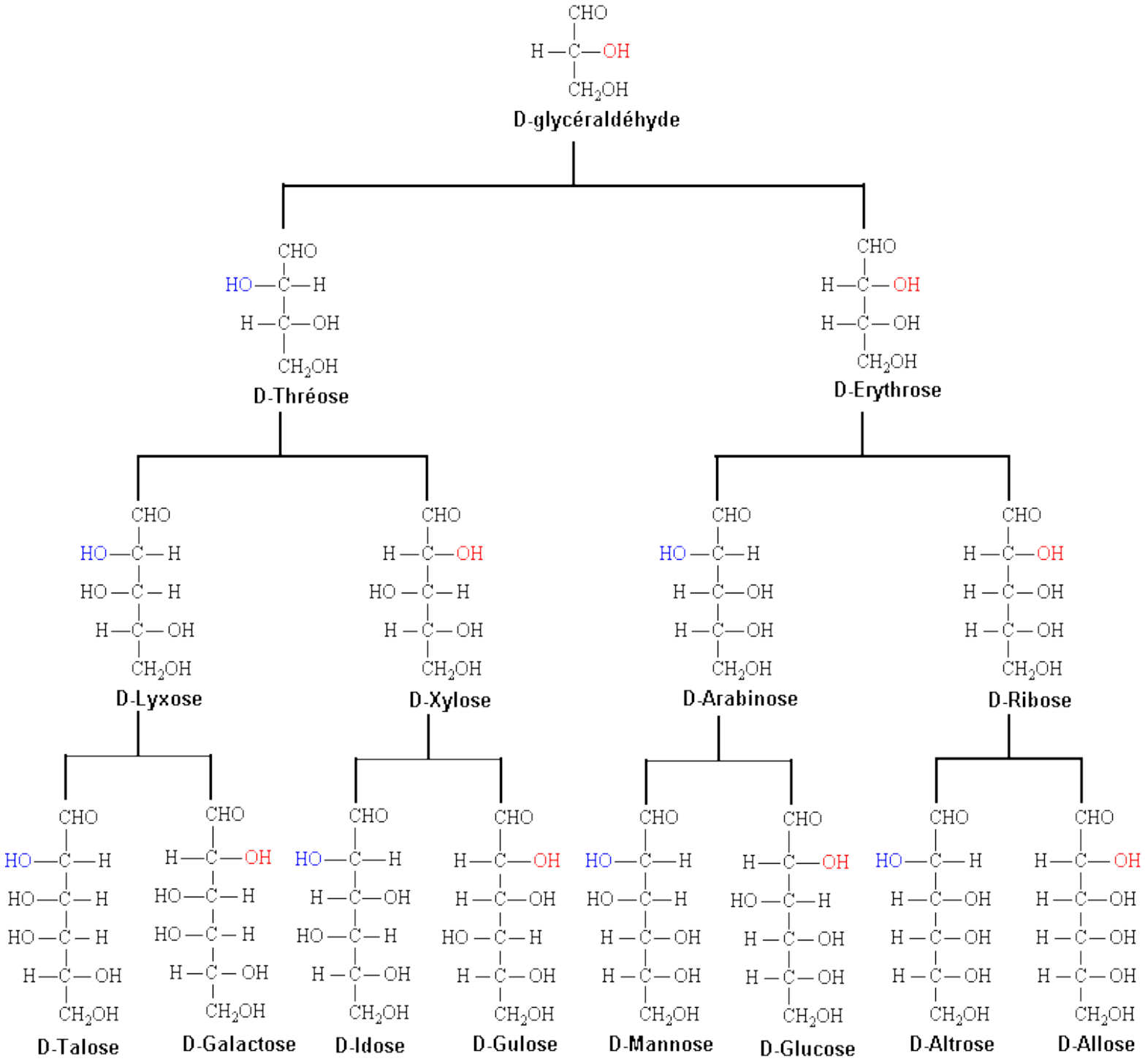


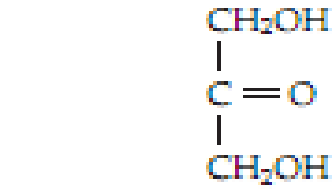
Xylose (Xyl) Lyxose (Lyx)



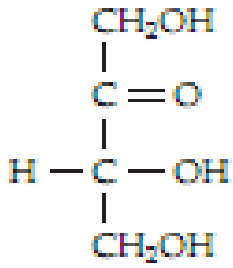
Altrose (Alt) Allose (All) Glucose (Glc) Mannose (Man) Gulose (Gul) Idose (Ido) Galactose (Gal) Talose (Tal)

TABLEAU I : ALDOSES DE LA SERIE D

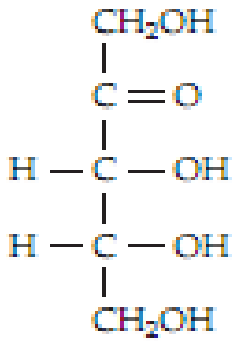




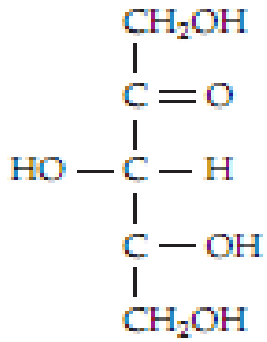
Dihydroxyacetone (not chiral)



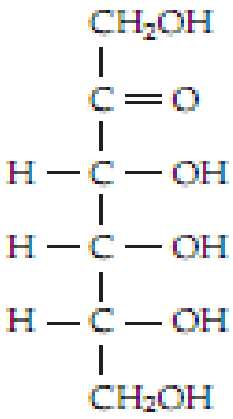
Erythrulose



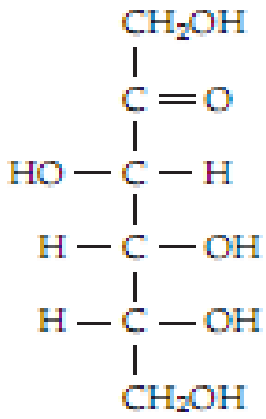
Ribulose



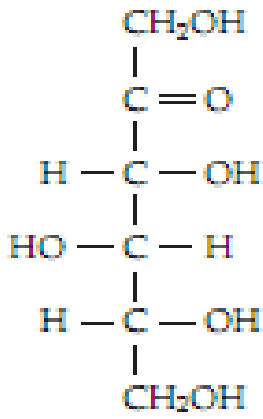
Xylulose



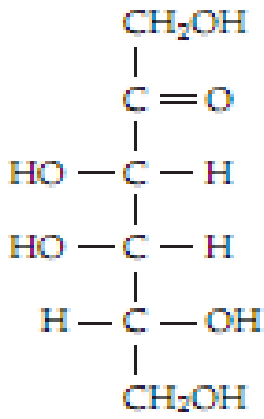
Psicose



Fructose



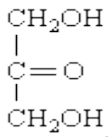
Sorbose



Tagatose

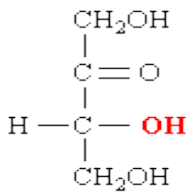
TABLEAU II : CETOSES DE LA SERIE D

CETOTRIOSE



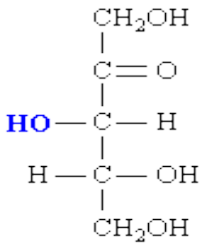
Dihydroxyacétone

CETOTETROSE

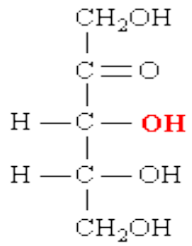


D-Erythrulose

CETOPENTOSES

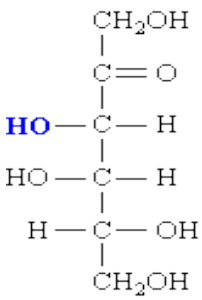


D-Xylulose

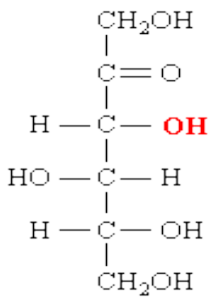


D-Ribulose

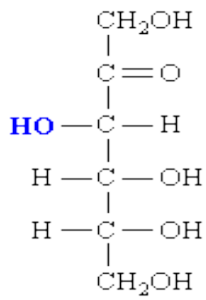
CETO HEXOSES



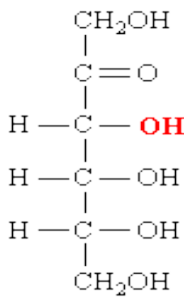
D-Tagatose



D-Sorbose



D-Fructose



D-Psicose

Stereoisomerism

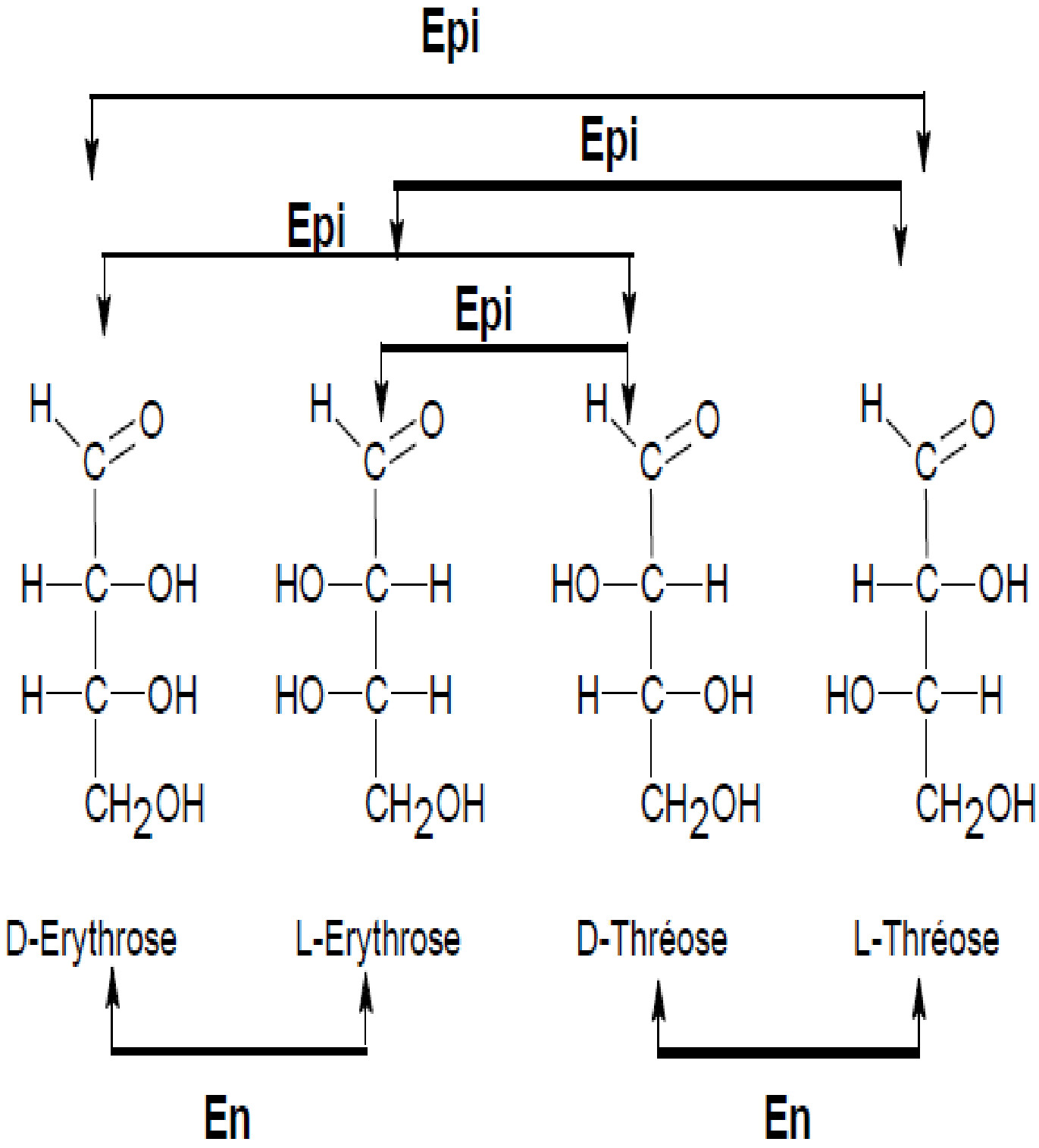
❑Stereoisomers are molecules that have the same molecular formula and the same planar structural formula, but a different spatial arrangement.

❑Enantiomers: These are two molecules that are mirror images of each other and are non-superimposable.

❑Enantiomers share the same physicochemical properties but have different optical rotations (equal in abolute value but opposite in sign); enantiomers are also known as optical isomers.

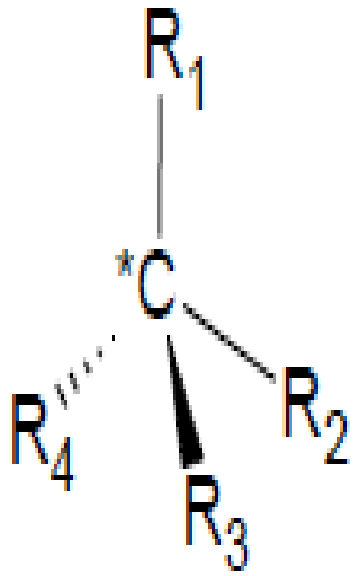
❑Diastereomers: These are all stereoisomers that are not enantiomers-that is, those that are not mirror images.

❑Epimers : are diastereoisomers that differ only in the configuration of the hydroxyl group at a single chiral carbon atom. D-glucose, for example, has two epimers: D-mannose (epimer at C2) and D-galactose (epimer at C4).


Epi
Epi
Epi
Epi
D-Erythrose
L-Erythrose
D-Thréose
L-Thréose
En
En

- The number of stereoisomers of a monosaccharide composed of n asymmetric carbon atoms is equal to 2^n;
- An asymmetric carbon is a carbon atom bearing four different substituents, also known as a chiral center

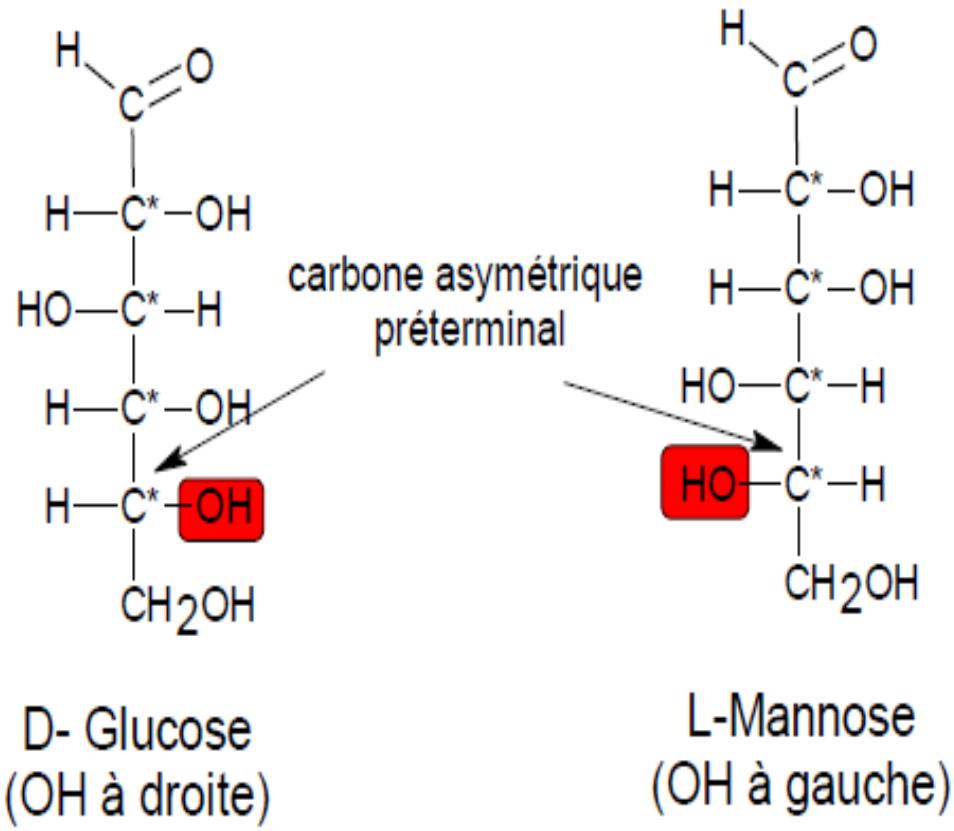
C*= carbone asymétrique
(Centre chiral)



D and L configuration of sugars

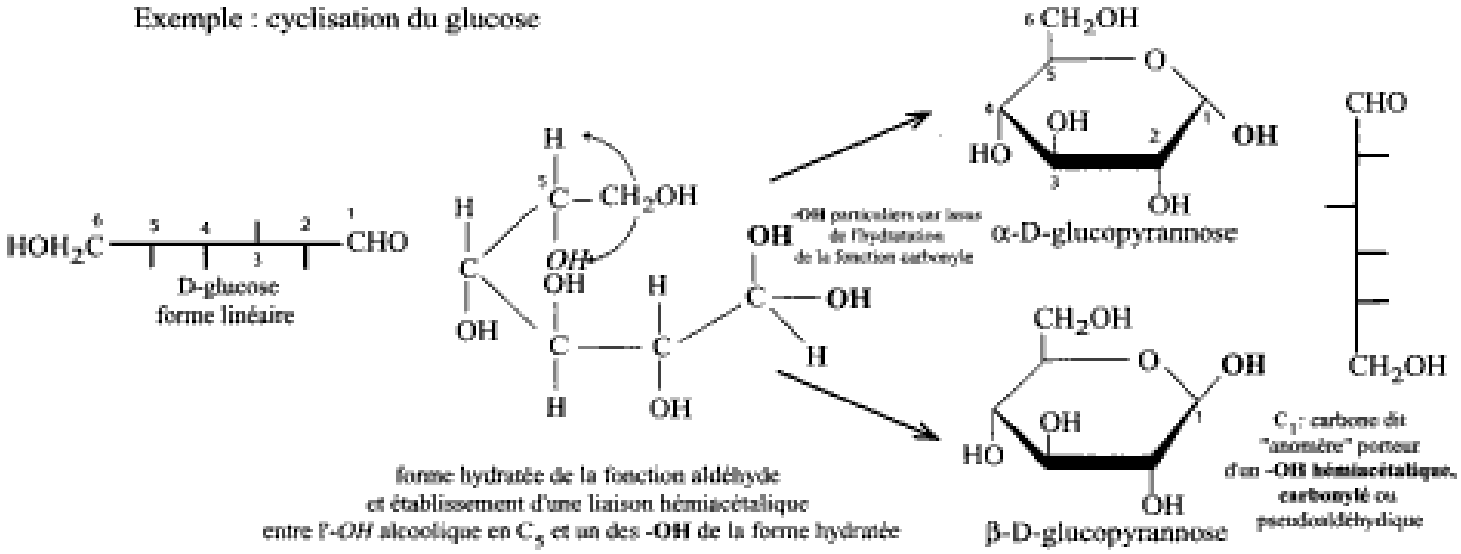
In the Fischer linear structure, assignment to the D or L series is determined by the configuration of the secondary alcoholic hydroxyl group attached to the asymmetric carbon furthest from the carbonyl group (the most oxidized function), that is, the penultimate carbon;

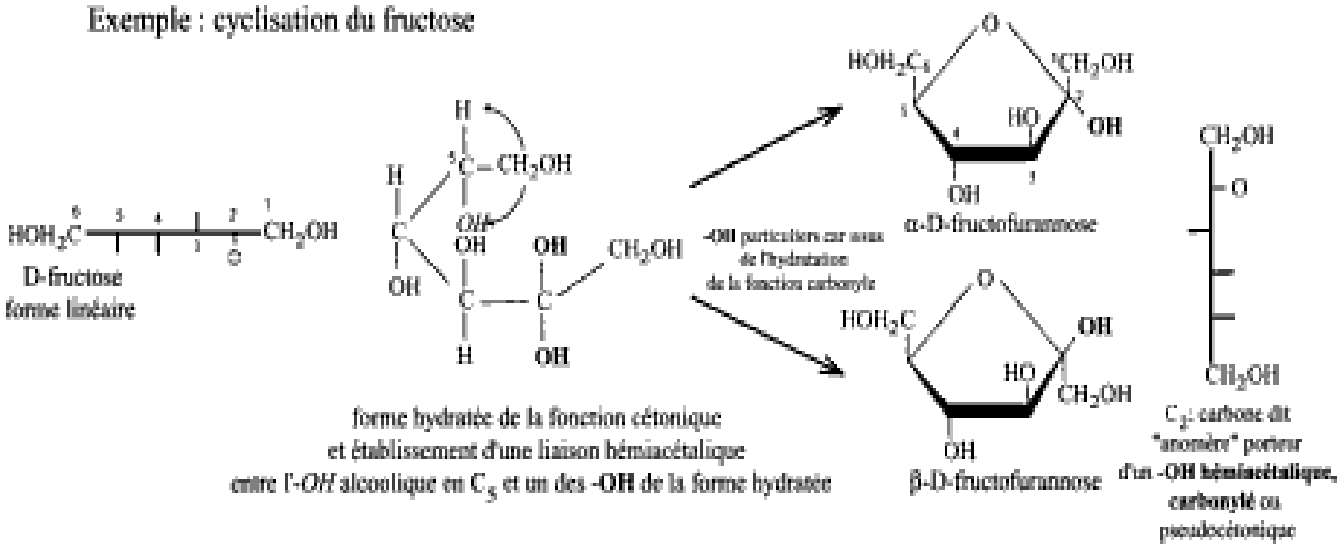
❑If this OH group is located to the right of the carbon chain, the series is designated as D, whereas if it is to the left, it is designated as L



Cyclization

- The transition from the linear form to the cyclic form.
- The cyclization of monosaccharides is an intramolecular reaction between the C1 or C2 carbonyl group and an alcohol group; the resulting functional group is a hemiacetal or hemiketal, respectively.





Two types of stable rings are possible for monosaccharides:

- A furan ring (cyclization between C1 and C4 or between C2 and C5), in which case the monosaccharide is called a furanose.

- A pyran ring (cyclization between C1 and C5 or between C2 and C6), in which case the monosaccharide is called a pyranose

The cyclization of sugars creates a new asymmetric carbon atom (C1 or C2) known as the anomeric carbon; consequently, the number of stereoisomers doubles, giving rise to α and β anomers.

The transition from the linear Fischer form to the cyclic Haworth form proceeds according to the following steps

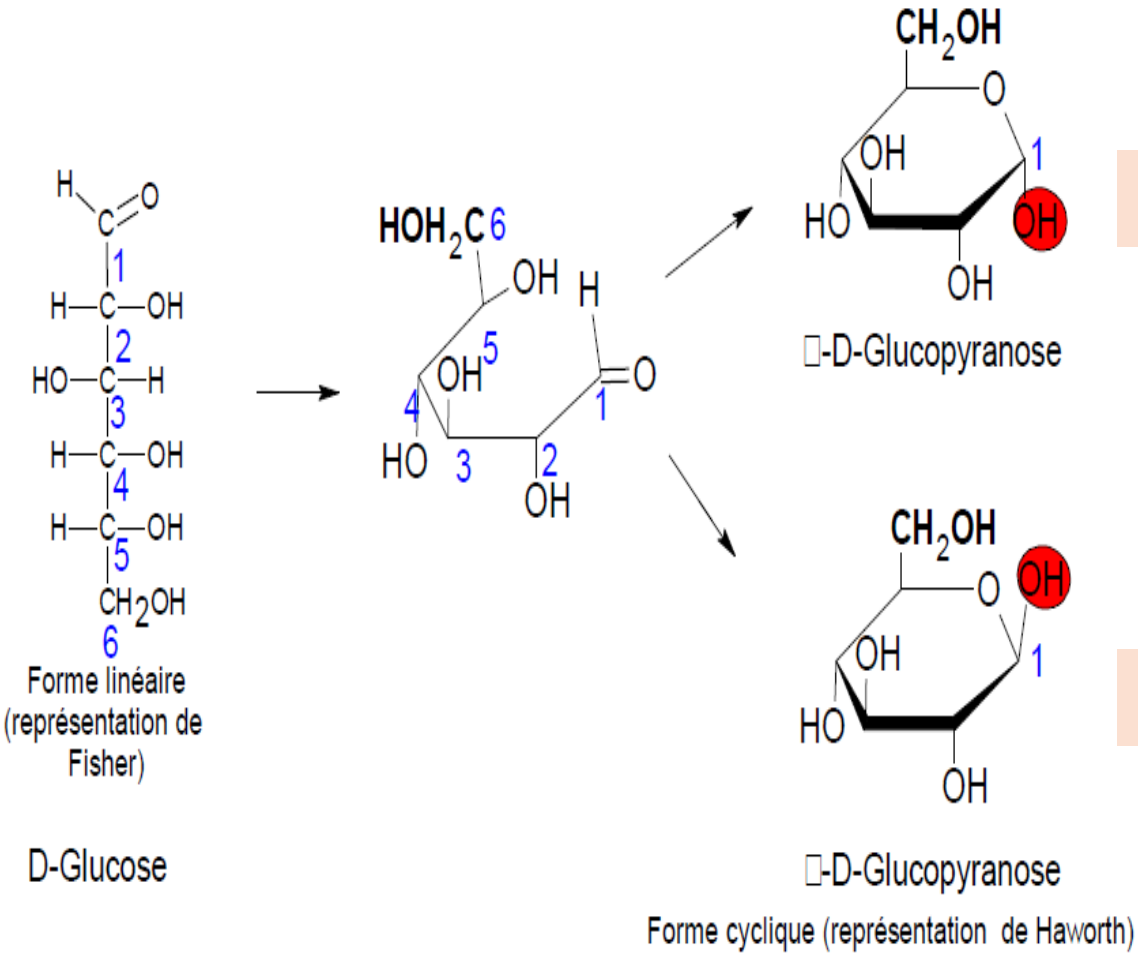
- The Haworth projection is a perspective representation of furanose and pyranose rings.

- Ring bonds projecting towards the viewer are represented by bold lines, while those projecting away are represented by thin lines.

- By convention, the anomeric carbon (1 or 2) is positioned on the right

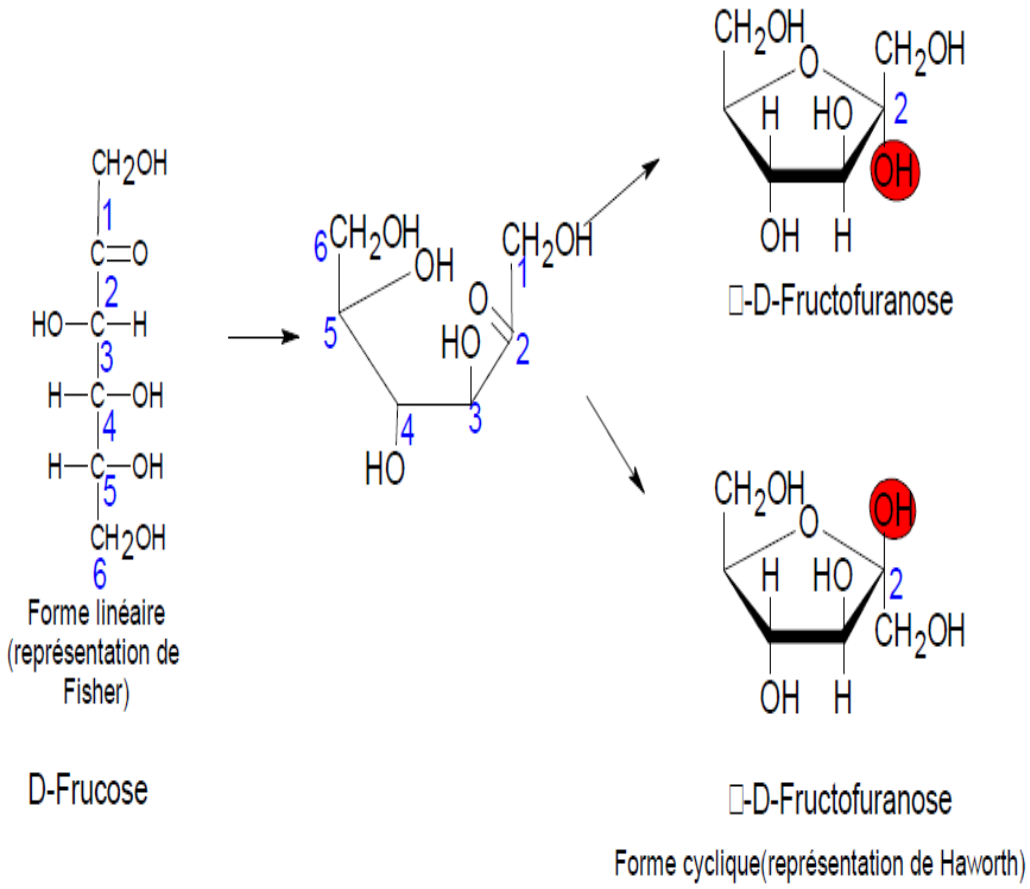
- Hydroxyl groups may be located below (or above) the plane of the ring, depending on whether they appear on the right (or left) of the carbon chain in the linear Fischer projection.

- The position of the anomeric carbon's hydroxyl group determines whether the sugar is an α or β anomer; in D-sugars, the hydroxyl group on the anomeric carbon is below the ring to yield an α anomer, and above the ring to form a β anomer. The reverse applies to L-sugars.



α- D-glucopyranose

β- D-glucopyranose

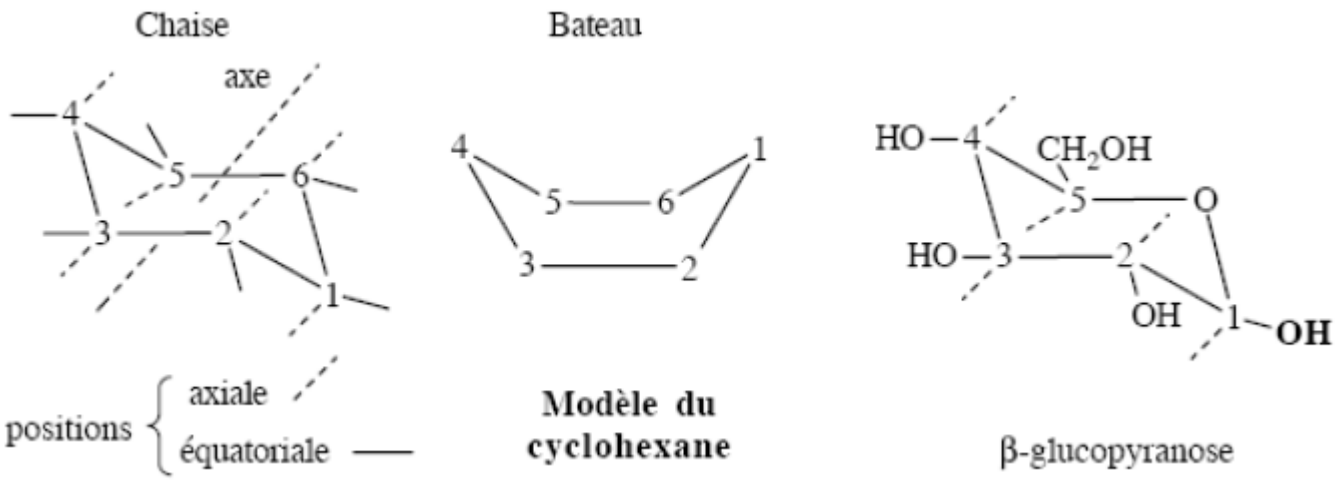


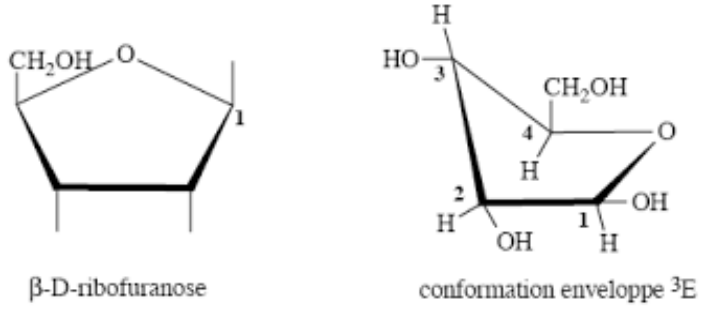
α- D-Fructofuranose

β- D-Fructofuranose

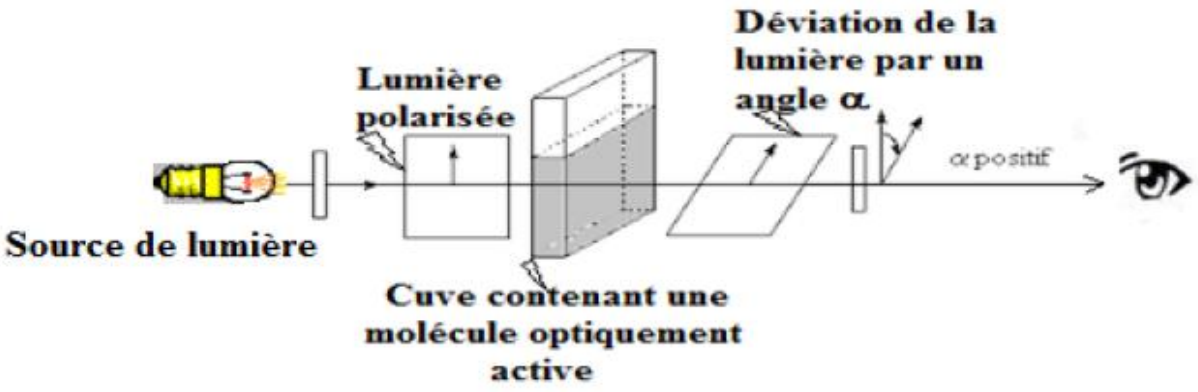
Spatial conformations of monosaccharides

- The conformation of the heterocycles is not planar but adopts various three-dimensional shapes.
- The pyran ring can exist in two main forms: the chair form and the boat form.
- These forms are equilibrium states; the chair form is generally considered the most stable conformation (the form adopted by sugars in solution).
- The furan ring adopts an envelope (E) conformation.





Optical rotation of monosaccharides



A molecule is said to possess optical rotation if it can rotate plane-polarized light by an angle α; such a molecule is optically active.

❑If the light is rotated by an angle +α in a clockwise direction, the molecule is said to be dextrorotatory (+)

❑If the light is rotated by an angle –α in a counter-clockwise direction, the molecule is said to be levorotatory (-). A polarimeter is used to measure the angle of rotation α of a substance.

❑The fact that a molecule is dextrorotatory (+) or levorotatory (-) has no relationship to its classification in the D or L series.

❑A D-series molecule can be (+) or (-), and the same applies to an L-series molecule.

Calculation of optical rotation (Biot's law)

Biot's law allows for the calculation of a molecule's specific optical rotation, measured under specific conditions: a temperature of 25°C and the wavelength of the sodium D-line (λ = 589 nm).

$$[\alpha]_D^{25^\circ C} = \frac{\alpha}{lC}$$

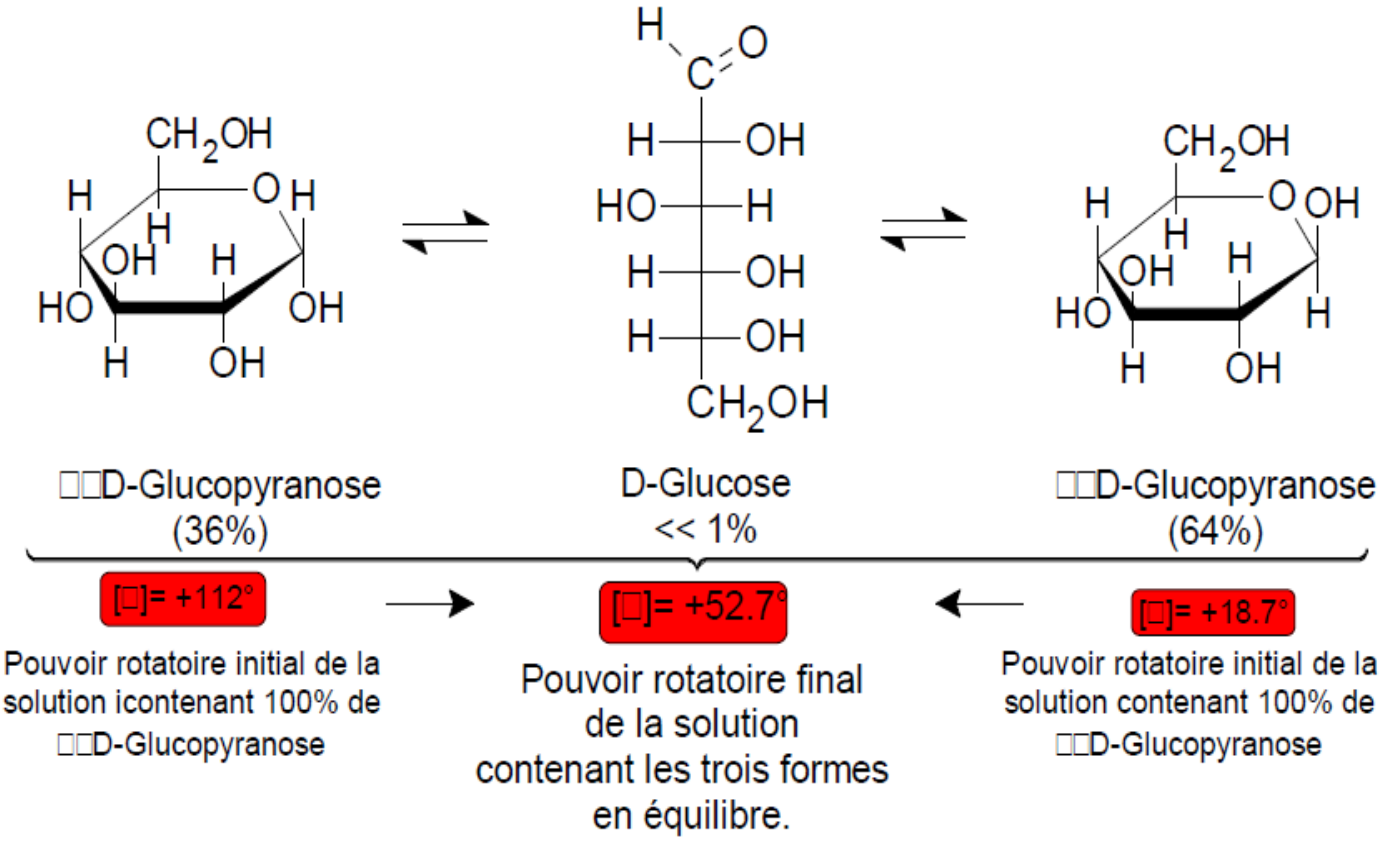
α = observed optical rotation in degrees (measured by the polarimeter).
l = optical path in dm
C = concentration of the molecule (g/ml).

Exercice: Calculer le pouvoir rotatoire d’une solution de mannose 0,65 mol/l traversé sur une longueur de 35 cm à 20°C sachant que la déviation du plan de polarisation est de 0,89°. (PM mannose = 180)

Exercise: Calculate the optical rotation of a 0.65 mol/L mannose solution over a path length of 35 cm at 20°C, given that the rotation of the plane of polarization is 0.89°. (Molar mass of mannose = 180)

Mutarotation

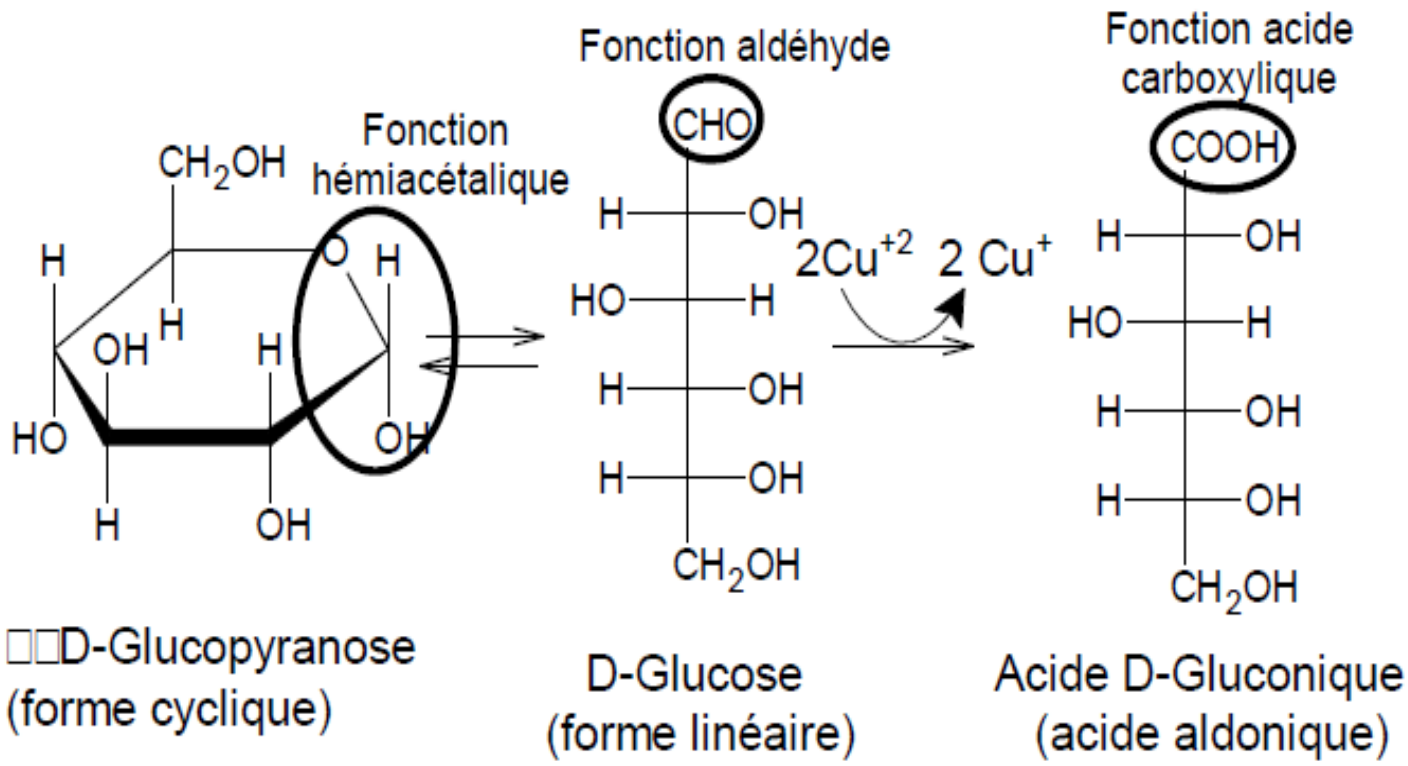
- The specific optical rotations of α-D-glucose and β-D-glucose are +112.2° and +18.7°, respectively.
- Once in aqueous solution, each anomer converts into the other via the linear structure, reaching a specific optical rotation of +52.7° at equilibrium.
- This phenomenon of changing specific optical rotation is called mutarotation



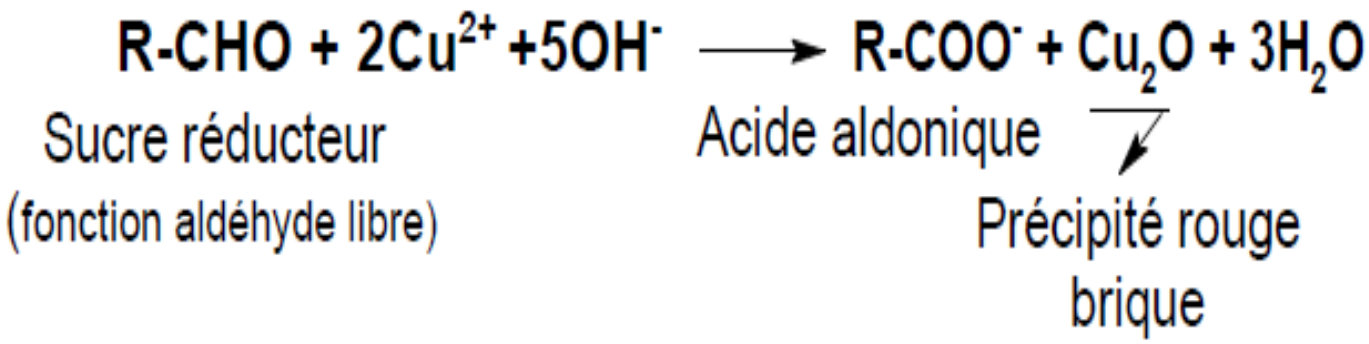
Oxidation of monosaccharides

Oxidation of the aldehyde group to a carboxylic acid group

- In an alkaline medium (OH^-) and under heating, the aldehyde group of monosaccharides is oxidized by metal ions (Cu^{2+} or Ag^+) into a carboxylic acid group, yielding an aldonic acid
- The oxidized monosaccharide is referred to as a reducing sugar.
- Thus, glucose yields gluconic acid, galactose yields galactonic acid, mannose yields mannonic acid, etc.

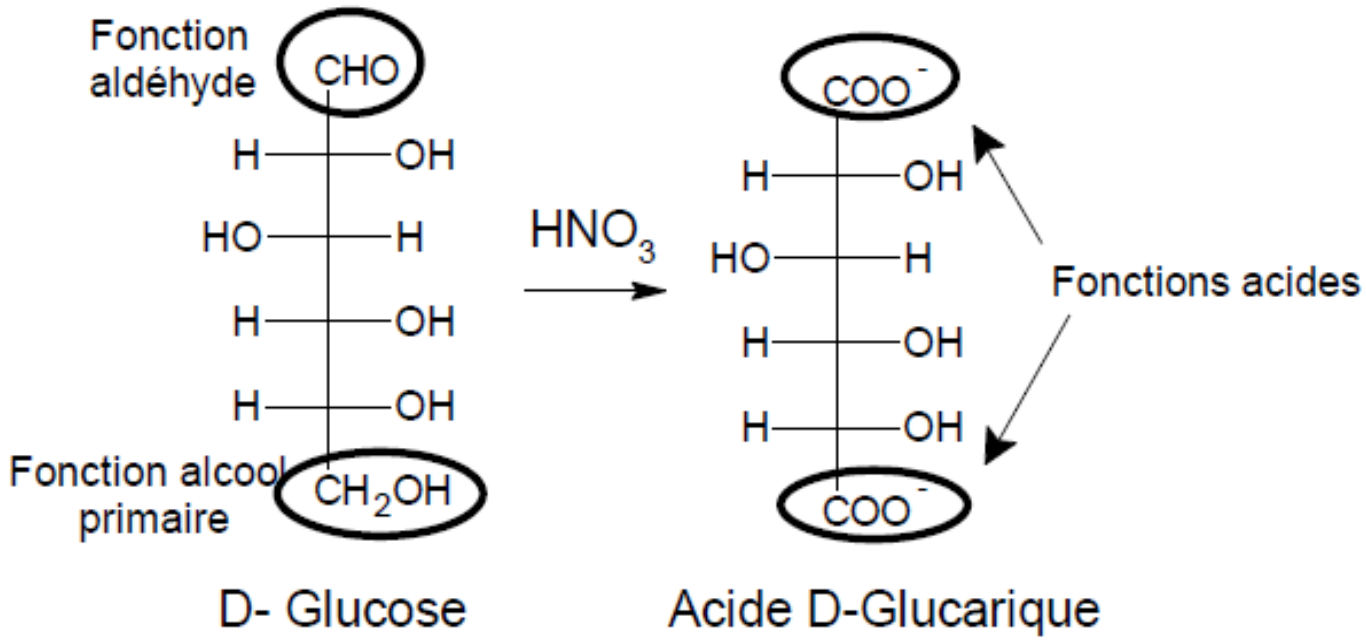


- Fehling's solution is a blue solution containing copper sulfate (CuSO4); when added to a reducing sugar such as glucose, it yields a brick-red precipitate of copper (I) oxide (Cu2O).
- Quantifying this precipitate makes it possible to determine the amount of reducing sugar in the initial solution



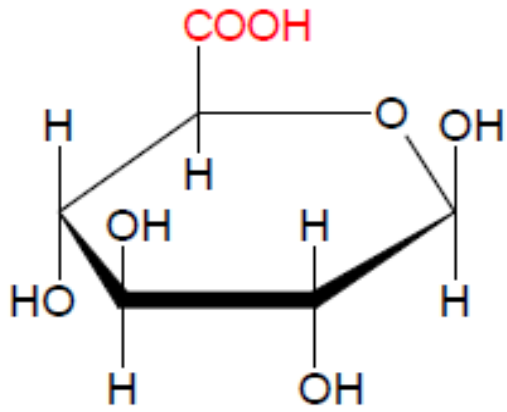
Oxidation of the aldehyde and primary alcohol functions to a carboxylic acid

- Upon heating in the presence of nitric acid (HNO3)-a powerful oxidizing agent-two functional groups of the monosaccharide are oxidized to carboxylic acid groups: the aldehyde group and the primary alcohol group.
- The resulting acid is called an aldaric acid.
- Thus, glucose yields glucaric acid, and galactose yields galactaric acid.



Oxidation of the primary alcohol group to a carboxylic acid group

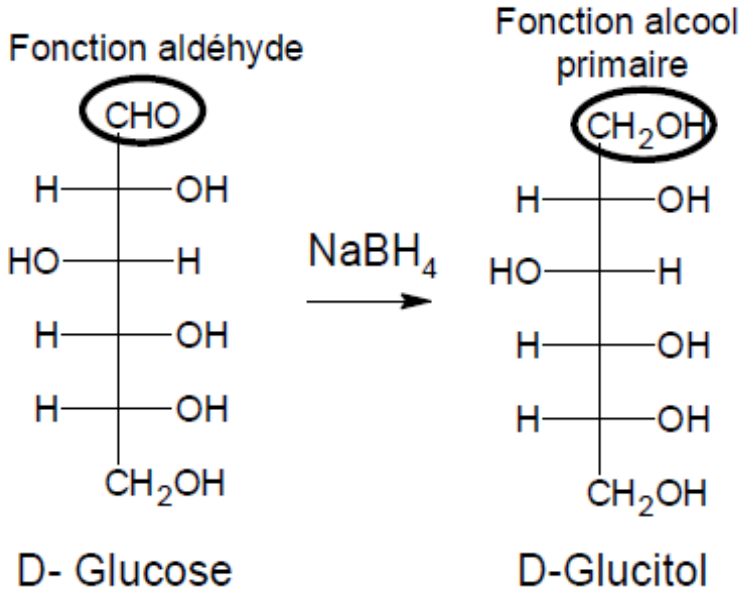
- In the presence of enzymes, the primary alcohol groups of monosaccharides such as glucose, mannose, and galactose are oxidized to form uronic acids-specifically glucuronic acid, mannuronic acid, and galacturonic acid, respectively.
- These acids are constituents of animal glycolipids and glycoproteins.



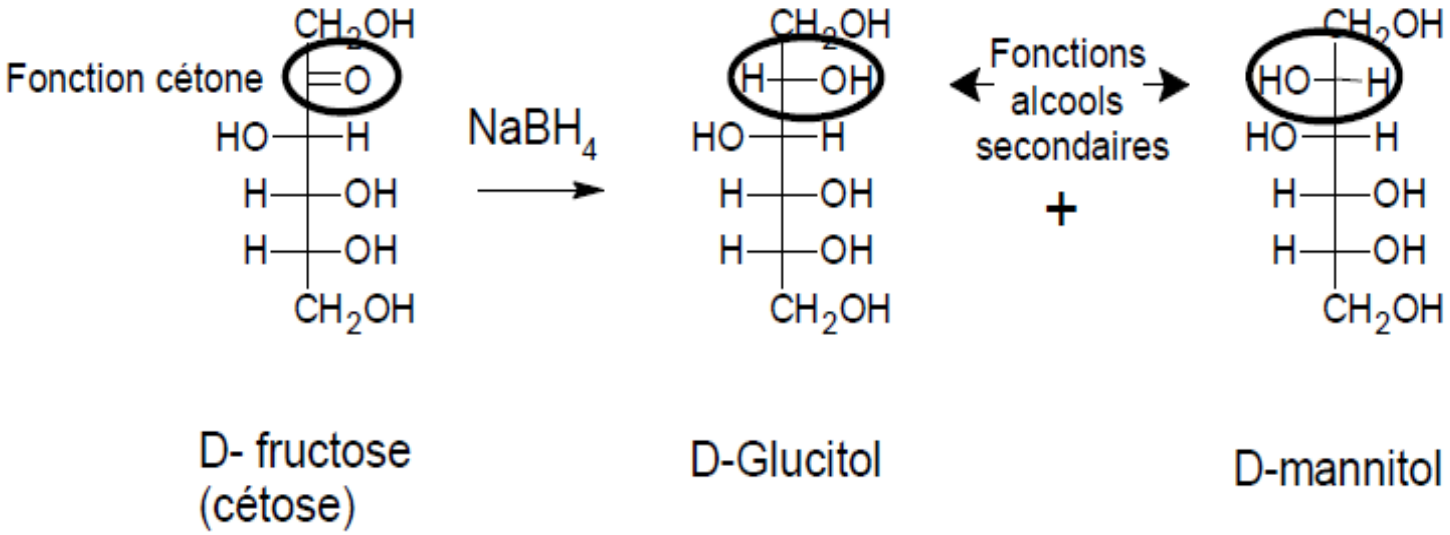
Reduction of aldehyde or ketone groups to alcohol groups

- Aldehyde and ketone groups can be reduced to alcohols by catalytic hydrogenation or in the presence of chemical agents such as sodium amalgam (NaBH4).
- The reduction of monosaccharides yields polyalcohols (also known as polyols or alditols).

- The reduction of D-glucose yields D-glucitol

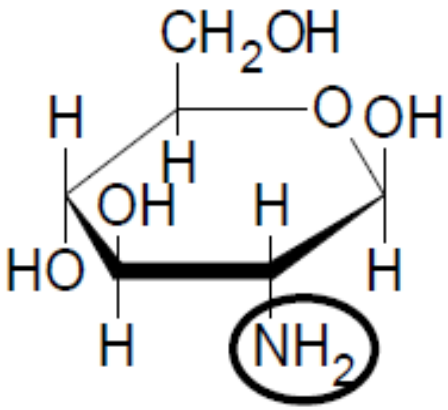


- The reduction of D-fructose yields two polyalcohols that are epimers at C2

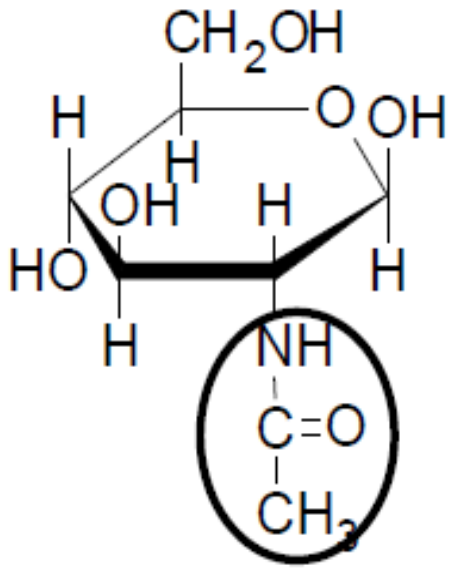


Amino monosaccharides

- This involves the replacement of the hydroxyl group (-OH) on carbon 2 of the monosaccharide with an amino group (-NH2); this group is almost always condensed with acetic acid.
- Amino sugars are important constituents of various macromolecules, such as those found in the bacterial cell wall.



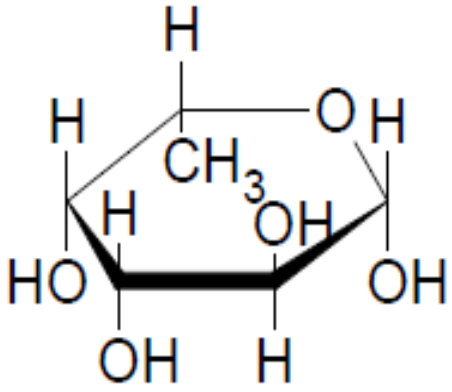
□-D-Glucosamine



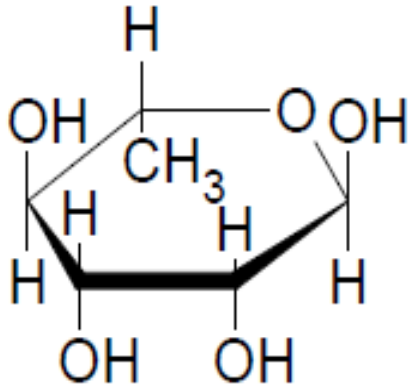
N-acétyl-□-D-Glucosamine

Deoxy-monosaccharides

❑Substitution of the hydroxyl group on carbon 6 of L-galactose and L-mannose with a hydrogen atom yields L-fucose and L-rhamnose.



□-L-Fucose



□-L-Rhamnose

Disaccharides

Defintion

❑Disaccharides (or diholosides) are molecules formed by two monosaccharides (either identical or different) linked by an O-glycosidic bond-also known simply as a glycosidic bond.

❑In a disaccharide, the bond forms between the anomeric carbon atom of the first sugar and the oxygen atom of either an alcohol group or an anomeric carbon on the second sugar.

This results in two possible situations:

➢Anomeric carbon + oxygen of an anomeric carbon = non-reducing disaccharide.

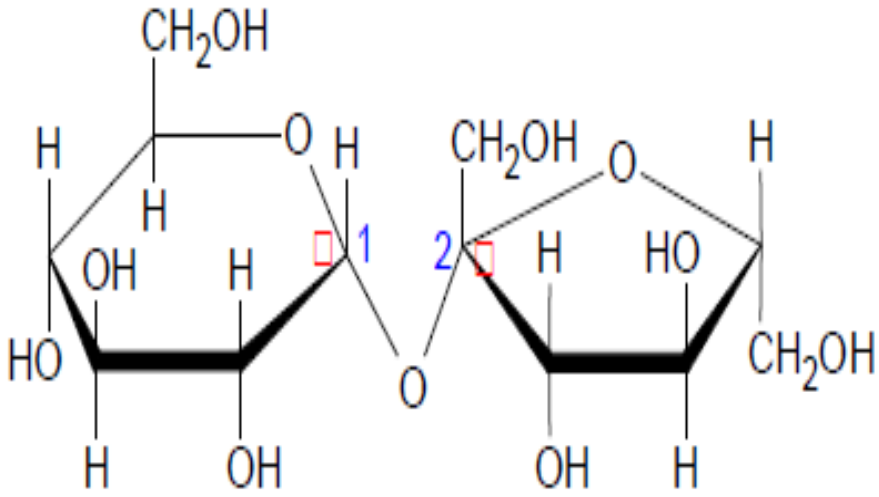
➢Anomeric carbon + oxygen of an alcohol group = reducing disaccharide.

Nomenclature

- Start with the first monosaccharide involved in the glycosidic bond.
- State its α or β configuration.
- Give its name, including the D or L series.
- Specify the ring form: ‘pyrano’ or ‘furano’.
- Indicate in parentheses the numbers of the carbons linked by the glycosidic bond, using an arrow (e.g., 1→4).
- Give the name of the second monosaccharide (α or β configuration, D or L series, and ring form).

Sucrose

Sucrose, known as table sugar, is found in fruits and vegetables. It is a non-reducing sugar that is hydrolyzed by sucrase.

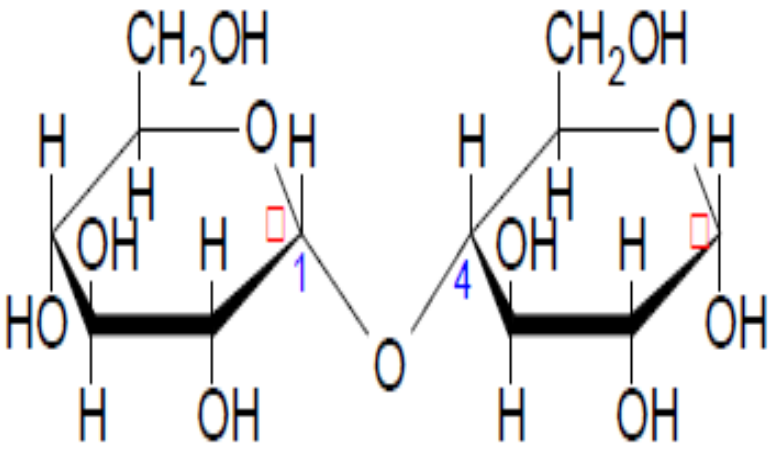




α-D-glucopyranosyl-(1→2)-ß-D fructofuranoside

Maltose

Maltose is the product of the partial hydrolysis of starch by the enzyme amylase; it is a reducing sugar that is hydrolyzed by maltase.

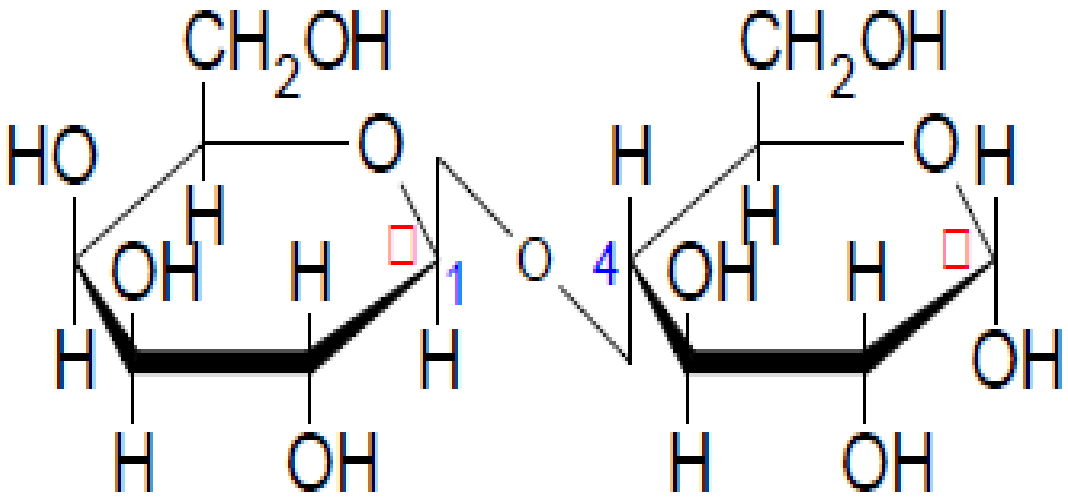




α-D-glucopyranosyl-(1→4)-D-glucopyranose

Lactose

Lactose is known as milk sugar; it is a reducing sugar that is hydrolyzed by lactase.





ß-D-galactopyranosyl-(1→4)-D-glucopyranose

Polysaccharides

Definition and classification

Polysaccharides are polymers with medium to high molecular weights, composed of a chain of multiple monosaccharide units (monomers).

Polysaccharides differ based on:

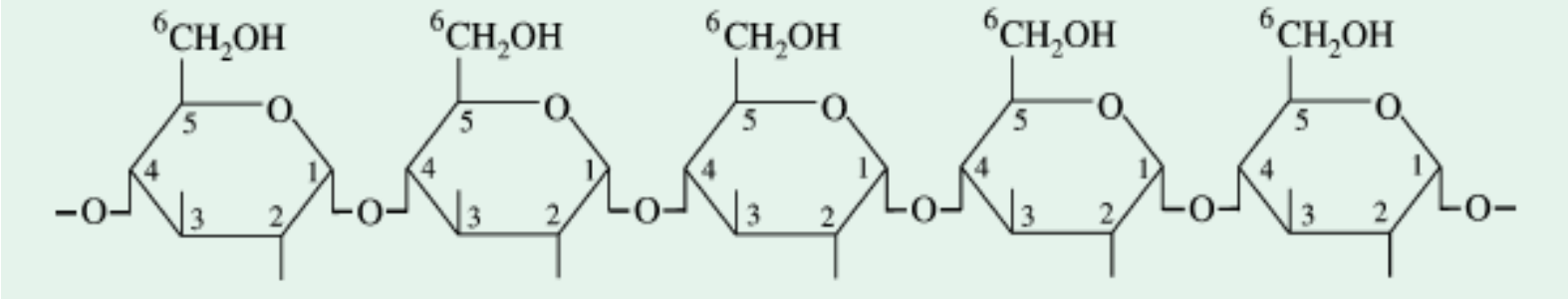
- ❖The nature of the monosaccharide
- ❖The chain length (number of units)
- ❖The nature of the linkage between units
- ❖The degree of branching

There are two types of polysaccharides:

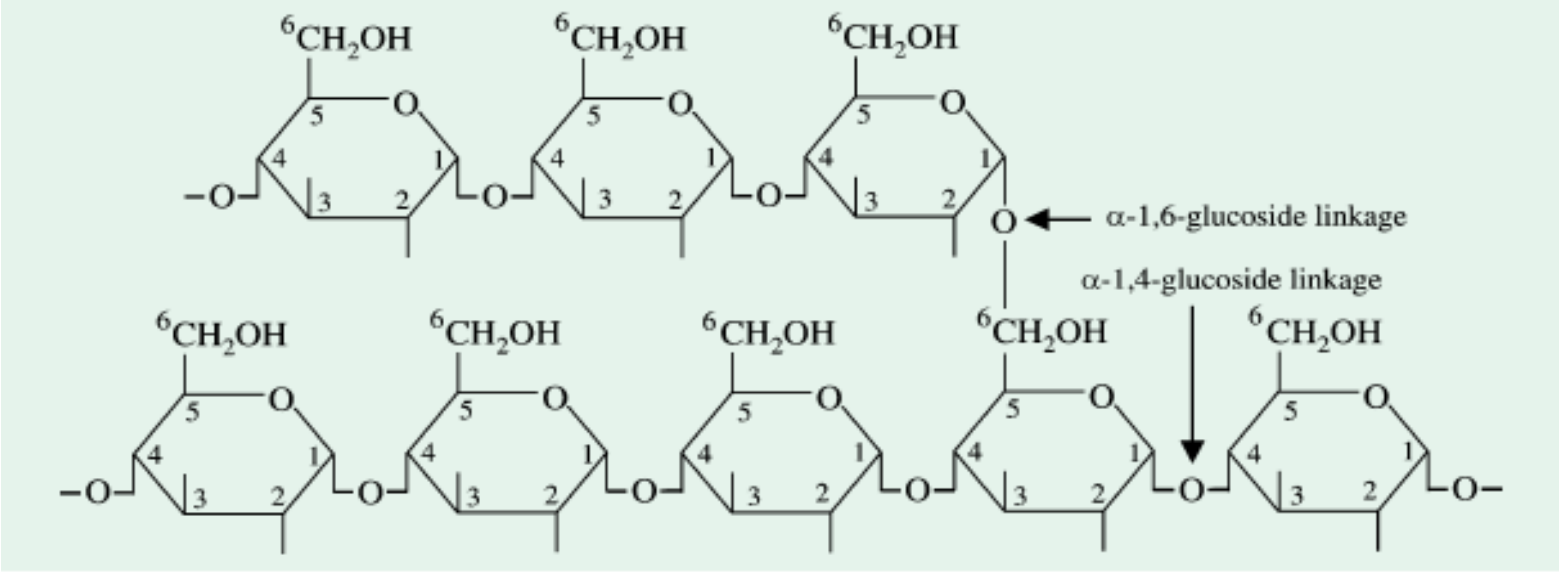
- ❑Homopolysaccharides: Molecules that contain only a single type of monosaccharide.
- ❑Heteropolysaccharides: Molecules that contain two or more types of monosaccharides.

Starch

It is a polysaccharide found in plant cells in the form of insoluble granules; it is composed of two polyglucoses ; amylose and amylopectin.



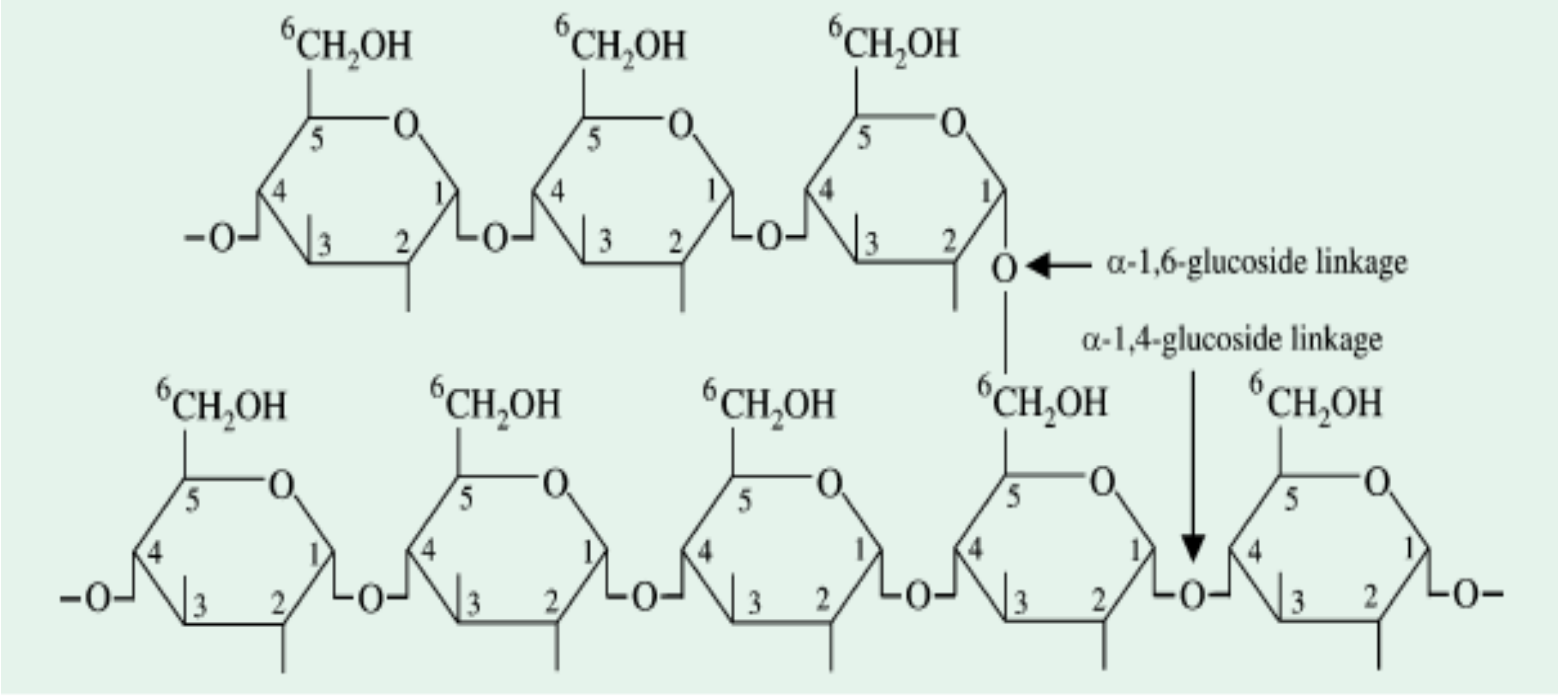
Polymer of D-glucopyranoses linked via α(1→4) bonds



Polymer of D-glucopyranoses linked by α(1→4) and α(1→6) bonds

Glycogen

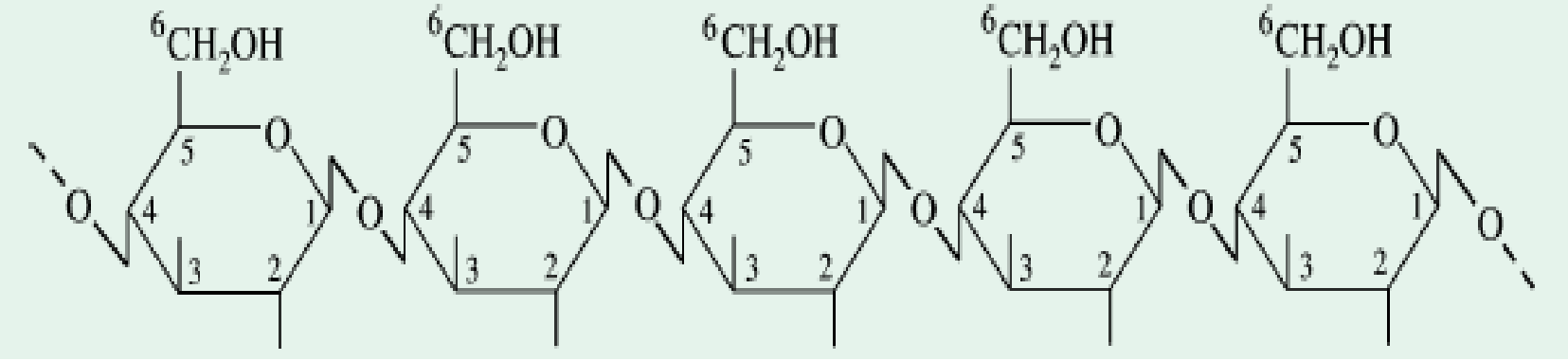
Is composed solely of amylopectin, which is more branched than that found in starch.



Polymer of D-glucopyranoses linked by α(1→4) and α(1→6) bonds

Cellulose

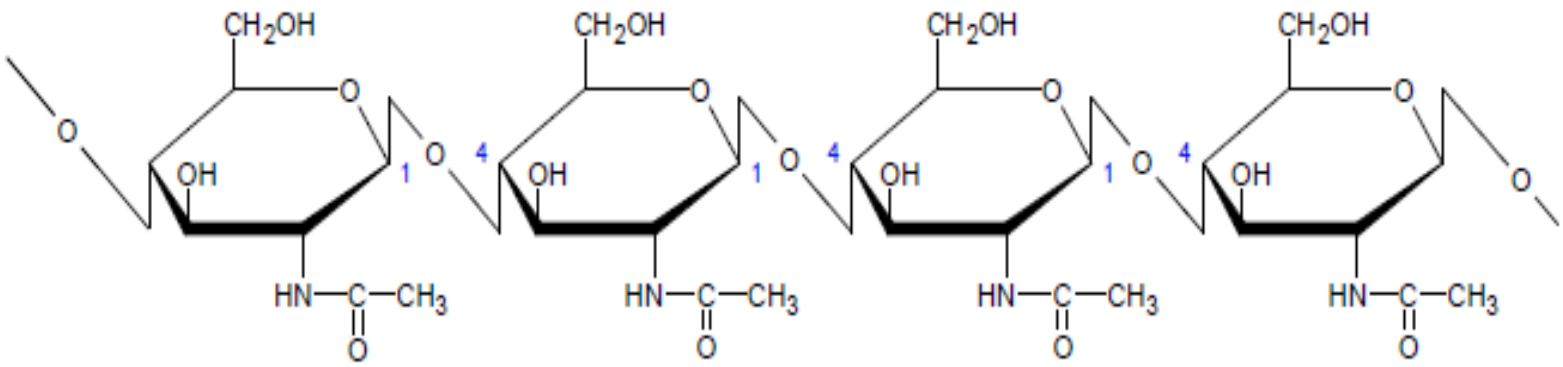
It is a structural polysaccharide composed of D-glucose molecules linked by β(1→4) bonds



Polymer of D-glucopyranoses linked by β(1→4) bonds

Chitin

It is an unbranched structural polysaccharide composed of 100% β-N-acetylglucosamine



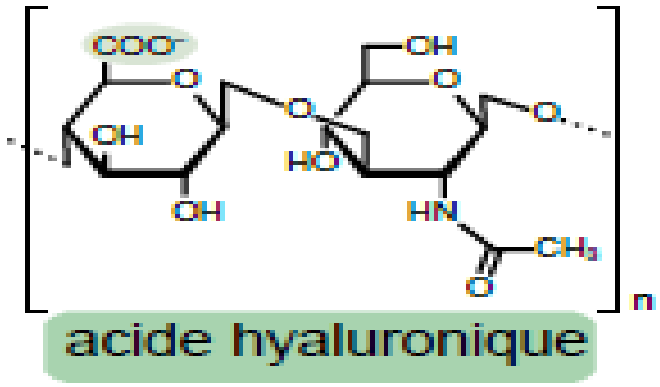
Polymer of β(1→4)-linked N-acetyl-D-glucopyranosamines

Heterosides

- Heterosides are molecules that, upon complete hydrolysis, release sugars and a non-sugar compound (such as a protein or lipid) known as an aglycone.
- Many small heterosides consist of an aglycone and a few sugar units.
- However, there are two major families of polysaccharides that form part of heterosides with distinct functions: the oligosaccharides found in glycoproteins and glycolipids, and the glycosaminoglycans found in proteoglycans.

Proteoglycans

- Proteoglycans consist of long, linear glycosaminoglycan chains attached to a core protein.
- Each chain is composed of a repeating disaccharide unit that is typically negatively charged and contains a hexosamine and a uronic acid.
- Sulfate groups are often present.



acide hyaluronique

Glycoproteins

- Glycoproteins contain smaller polysaccharide chains that are usually branched.

Glycolipids

- Glycolipids belong to the class of sphingolipids