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PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA
وزارة التعليم العالي والبحث العلمي
MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH
جامعة باجي مختار - عنابة
BADJI MOKHTAR UNIVERSITY - ANNABA
كلية العلوم
FACULTY OF SCIENCES
قسم البيوكيمياء
DEPARTMENT OF BIOCHEMISTRY

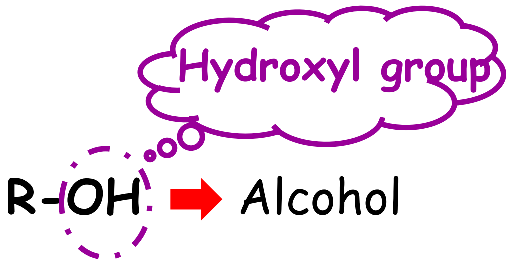
Stuctural and Metabolic Biochemistry

TCSNV 2nd Fondamental unit S3

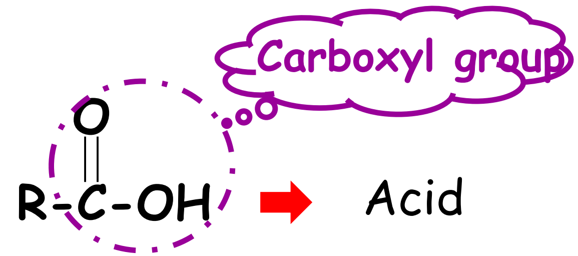
SUGARS / CARBOHYDRATES

Pr. KADI-BIREM

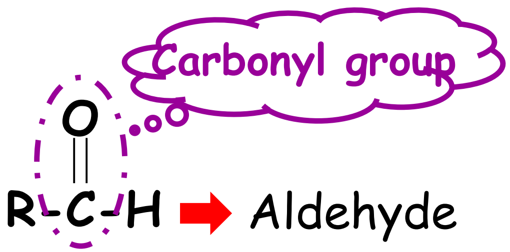
Review of some chemistry concepts



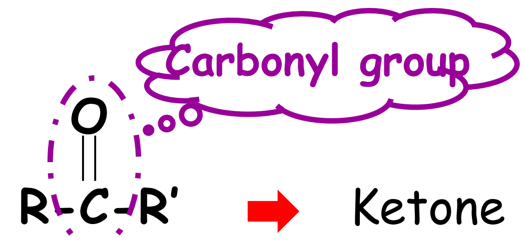
→ Alcohol



→ Acid

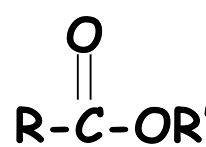


→ Aldehyde



→ Ketone

CH3 → Methyl group



→ Ester

Classification

CARBOHYDRATES

Monosaccharides (Oses)

Simple carbohydrates,
Non-hydrolyzables
(cannot be broken down into smaller carbohydrates).

(Osides)

Complexes carbohydrates,
Composed of two to several hundred sugars that can be released through hydrolysis

Oligosaccharides / Polysaccharides

Composed solely of sugars

Heterosides

Composed of sugar (glycone) and a non-carbohydrate component (aglycone or genin), which can be a lipid, a protein…

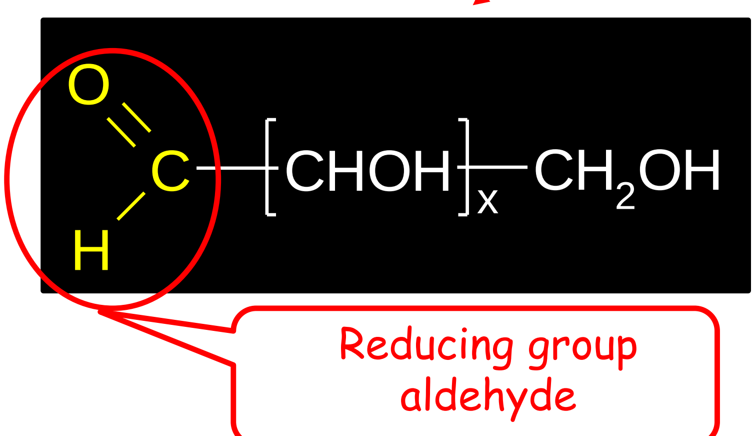
Structure of carbohydrates (monosaccharides)

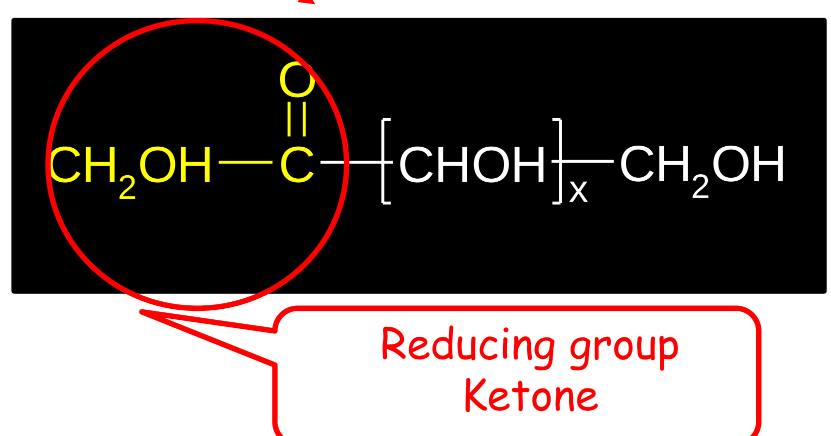
They are composed of carbon and water
➔ $Cn(H_2O)n$, ex: glucose :$C_6(H2O)_6$

They are molécules consisting of:

- **Several hydroxyl groups**
- **Single reducing aldehyde or ketone group.**

This includes aldoses and Ketoses.





Two major families

Aldose **Ketose**

Composed of 3 to 6 carbon atoms

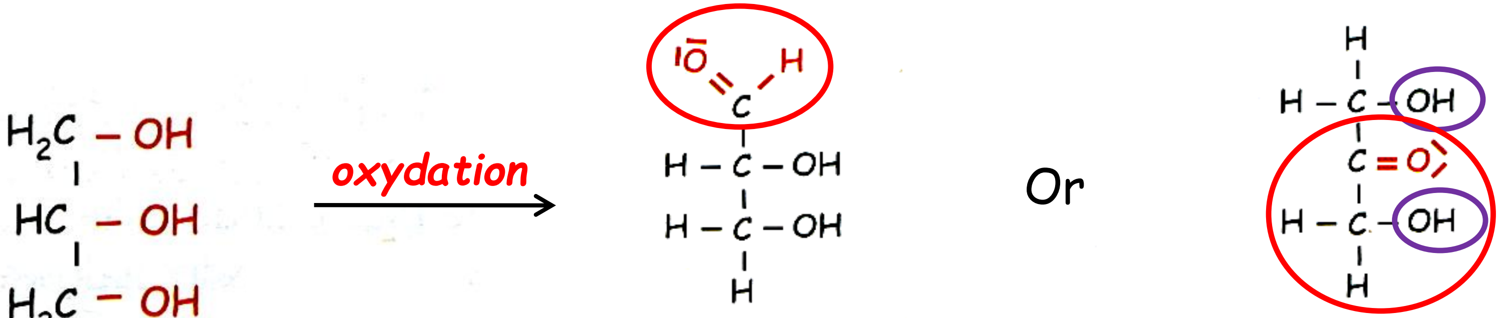
To name them, we combine the type of reducing group with the number of carbon atoms

Type of reducing group – number of carbon atoms– ose

Nb C		Generic term
3	trioses	Aldotrioses, Ketotrioses
4	tetroses	Aldotétroses, Ketotétroses
5	pentoses	Aldopentoses, Ketopentoses
6	hexoses	Aldohexoses, Ketohexoses

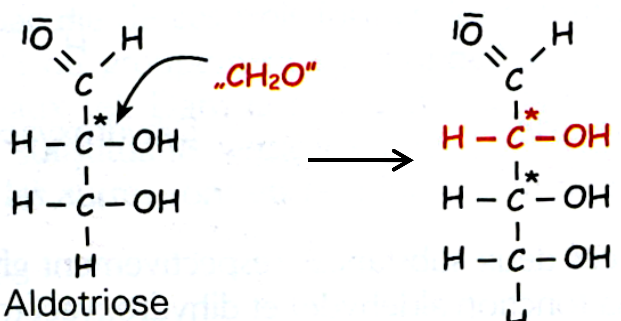
Simple carbohydrates: Monosaccharides

- **The simplest monosaccharides include triose sugars like Glyceraldehyde and dihydroxyacetone, which have only three atoms**



Glycerol — Glyceraldehyde — $C_3(H_2O)_3$ — Dihydroxyacetone

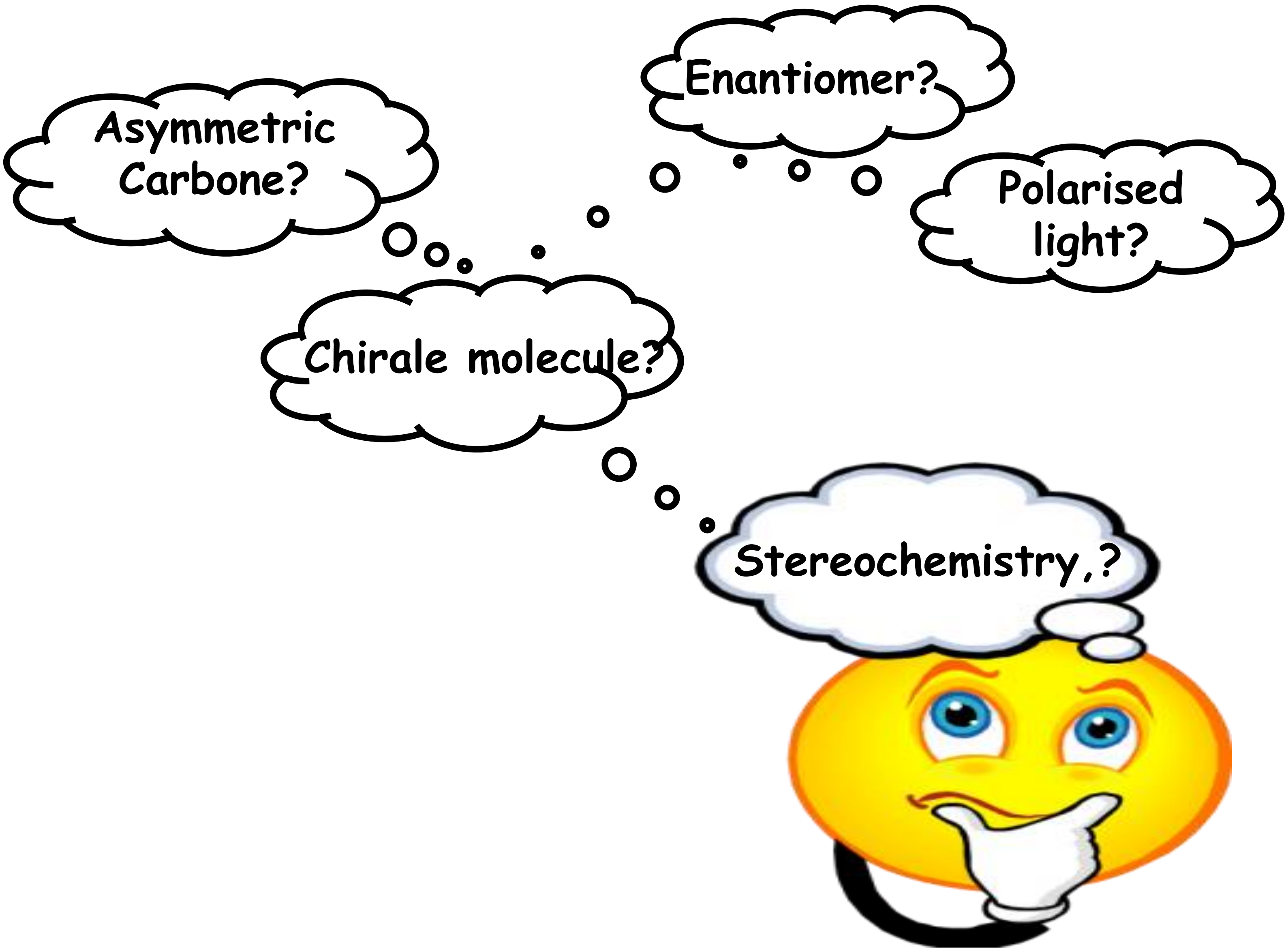
- **They grow by acquiring groups –CH_2O- ou –CHOH- (tetrose, pentose, hexose,…)**



Aldotriose (D-glycéraldéhyde) — Aldotétrose (D-érythrose)

***: asymmetric carbon/chiral carbon**

Simple carbohydrates : <u>Monosaccharides</u>



Simple carbohydrates : Monosaccharides

Stereochemistry

A sub-discipline of chemistry ➔ it involves the study of the spatial arrangement of atoms in a molecule.

Chirale molecules

From the Greec meaning « hand ».
A chiral compound ➔ must contain at least one asymmetric carbone C*.
If a molecule is chirale ➔ it has 2 enantiomers.

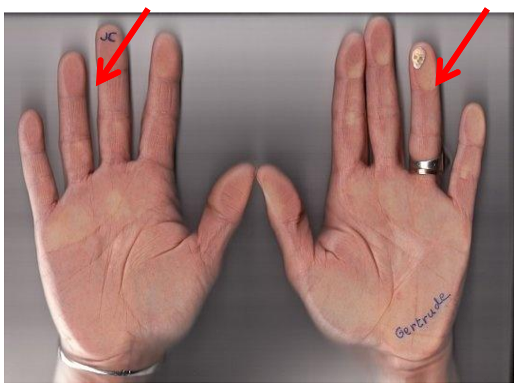
Simple carbohydrates : Monosaccharides

Enantiomers

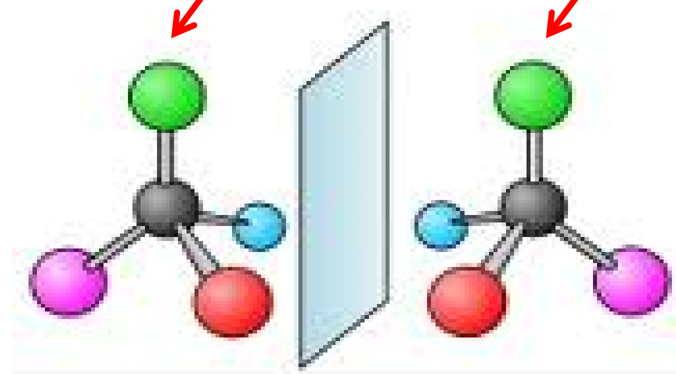
From the Greec *enantios* meaning « opposite ».
These are molecules that have the same physical properties (solubility, boilling point, etc.), but they differ in an optical property ➔ the rotation of polarized light.
One rotates polarized light to the left = levorotatory (lévogyre).
The other rotates polarized light to the right = dextrorotatory (dextrogyre).

2 enantiomers➔ one is the mirror image of the other.

Enantiomer 1 Enantiomer 2



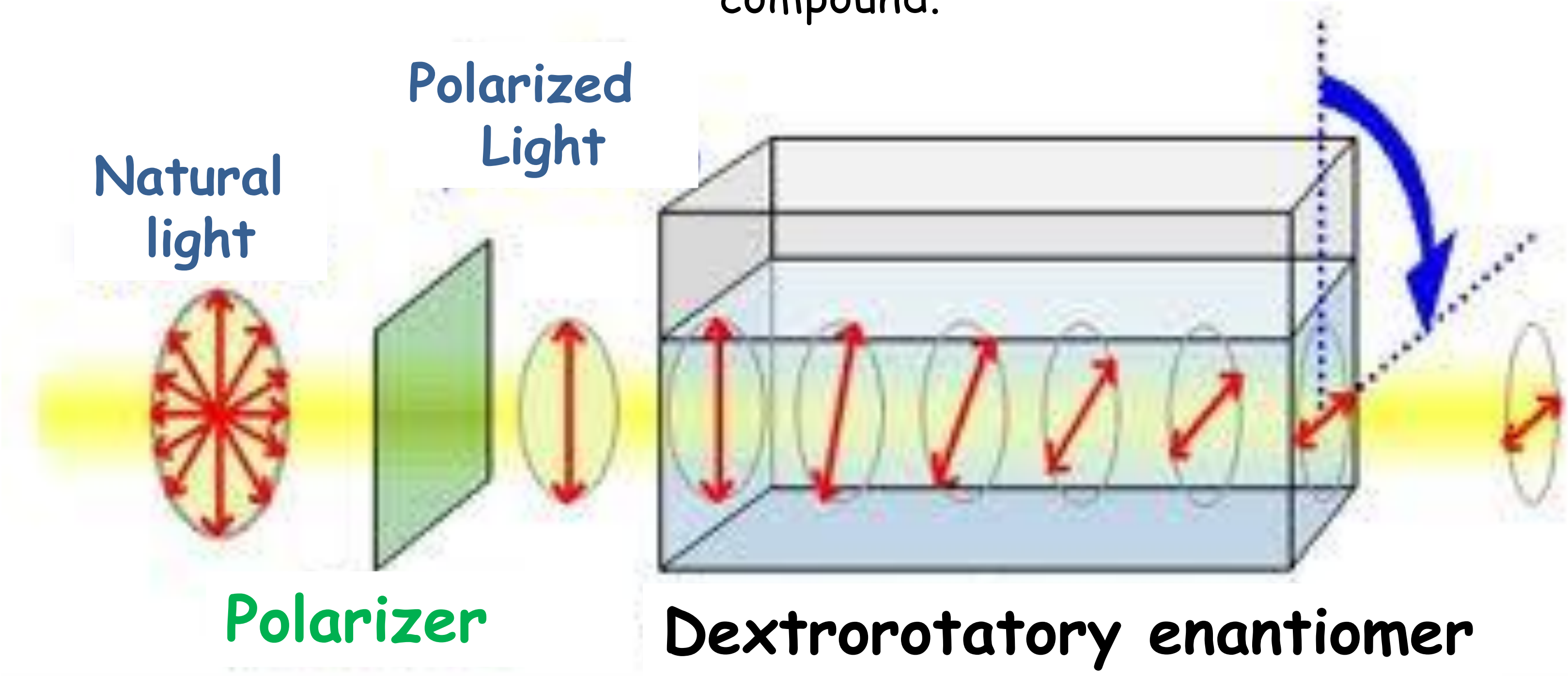
Enantiomer 1 Enantiomer 2



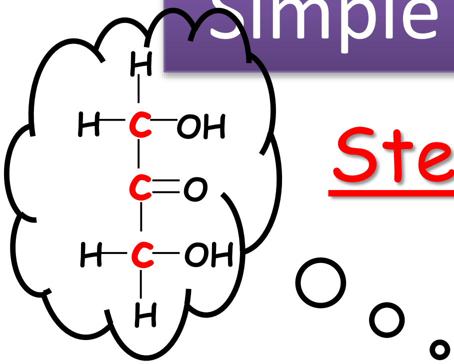
Simple carbohydrates : Monosaccharides

An exemple of polarized light deviation

The polarimeter is used to mesure the optical activity of chiral substances. When polarized light passes through a solution of a chiral compound (as a sugar), the plane of polarization is rotated. The direction and degree of this rotation, either to the right (dextrorotatory) or to the left (levorotatory), can be mesured to identify and characterize the chiral compound.



Simple carbohydrates : Monosaccharides

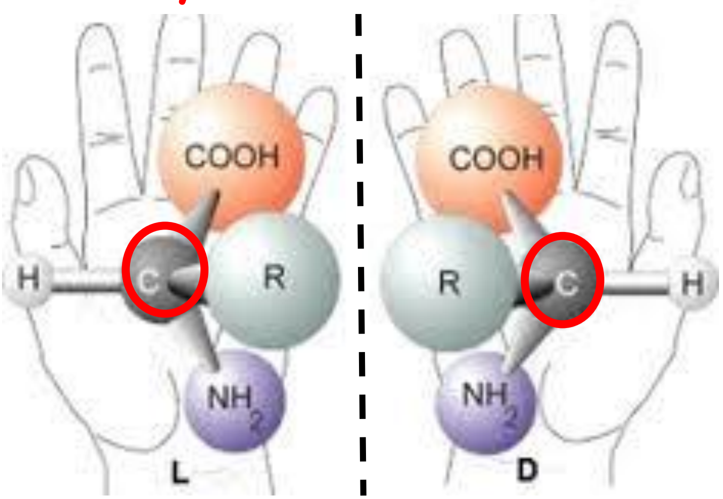


Stereochemistry of carbohydrates

All sugars, except dihydroxyacetone, have a chiral (asymmetric) carbon.

The asymmetric carbon (C*) is a tetrahedral carbon that has four covalent bonds, each connecting to different atoms or groups of atoms ➔ It has no plane of symmetry.

Asymmetric carbon



Non-asymmetric carbon

Two of the four substituants are identical, the carbon is not asymmetric. There is a plane of symmetry in this molecule, and is not chiral.

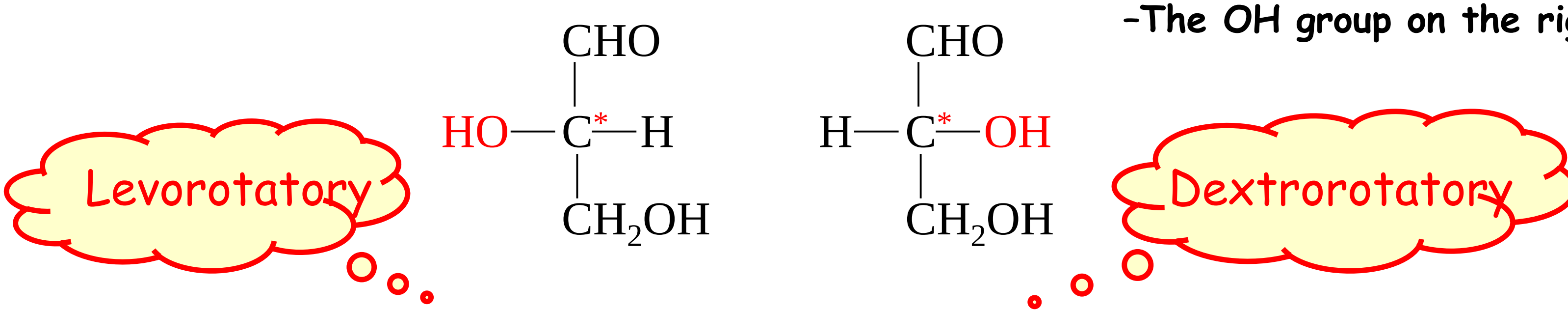
Simple carbohydrates : Monosaccharides

The glyceraldehyde has four covalent bonds at C_2 , each connecting to different groups of atoms.

➔ This carbon is therefore asymmetric, making the molecule chiral and possessing two enantiomers.

Fischer projection

-The OH group on the left : L-ose
-The OH group on the right: D-ose



L-Glyceraldehyde **D-Glyceraldhehyde**

Enantiomers

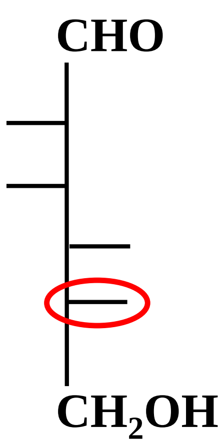
Note: All the sugars in metabolism (biological systems) have the D configuration

Simple carbohydrates : Monosaccharides

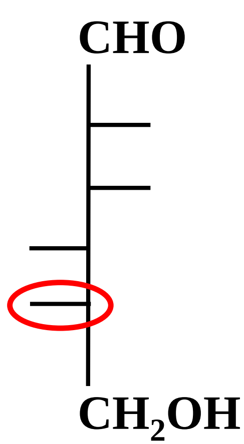
System of naming

To determine the configuration of a sugar, we must base it on the position of the OH group attached to the asymmetric carbon farthest from the aldehyde or ketone group (just before the terminal alcohol group).

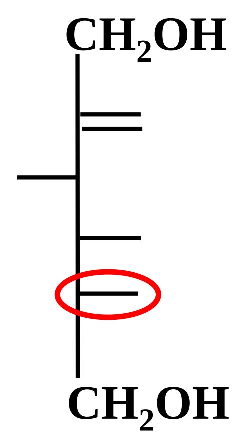
By convention, the H atoms are not shown, and the OH groups are represented by lines.



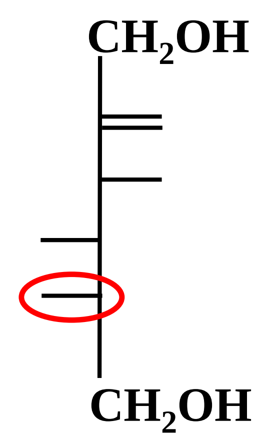
D-aldohexos



L-aldohexose



D-Ketohexos



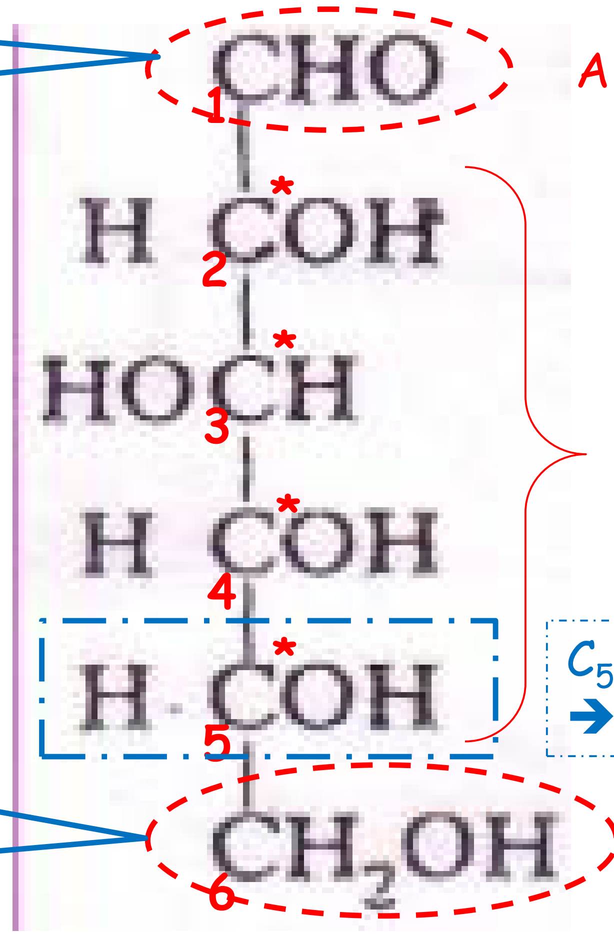
L-Ketohexose

Simple carbohydrates : Monosaccharides

Recapitulation: Exemple of Glucose

This carbon is not asymmetric because it's not tetrahedral

C*: asymmetric carbone



Aldehyde reducing group

Secondary alcohol functions

C_5*Configuration at right
➔ D configuration

Primary alcohol function

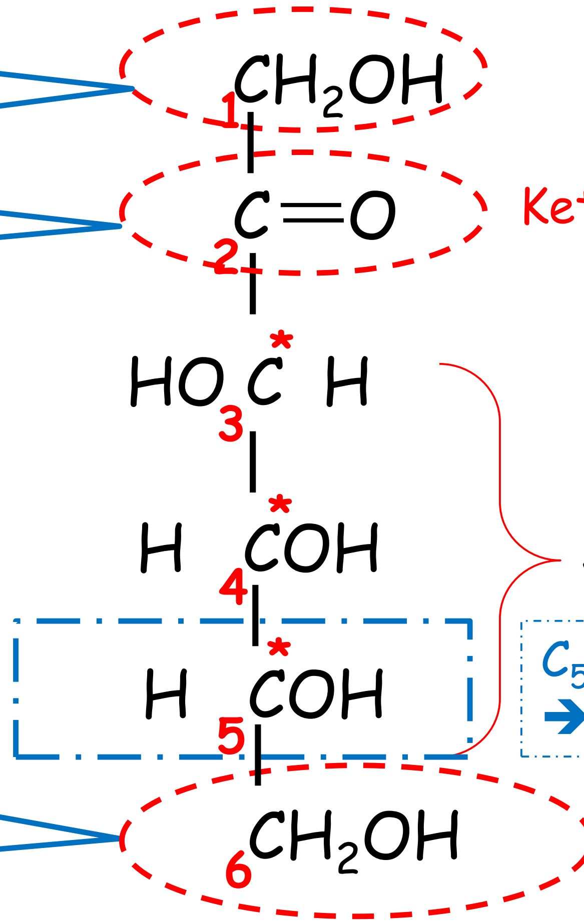
This carbon is not asymmetric because there is a plane of symetrie

Simple carbohydrates : Monosaccharides

Recapitulation: Exemple of Fructose

This carbon is not asymmetric because there is a plane of symetrie

This carbon is not asymmetric because it's not tetrahedral



Ketone reducing group

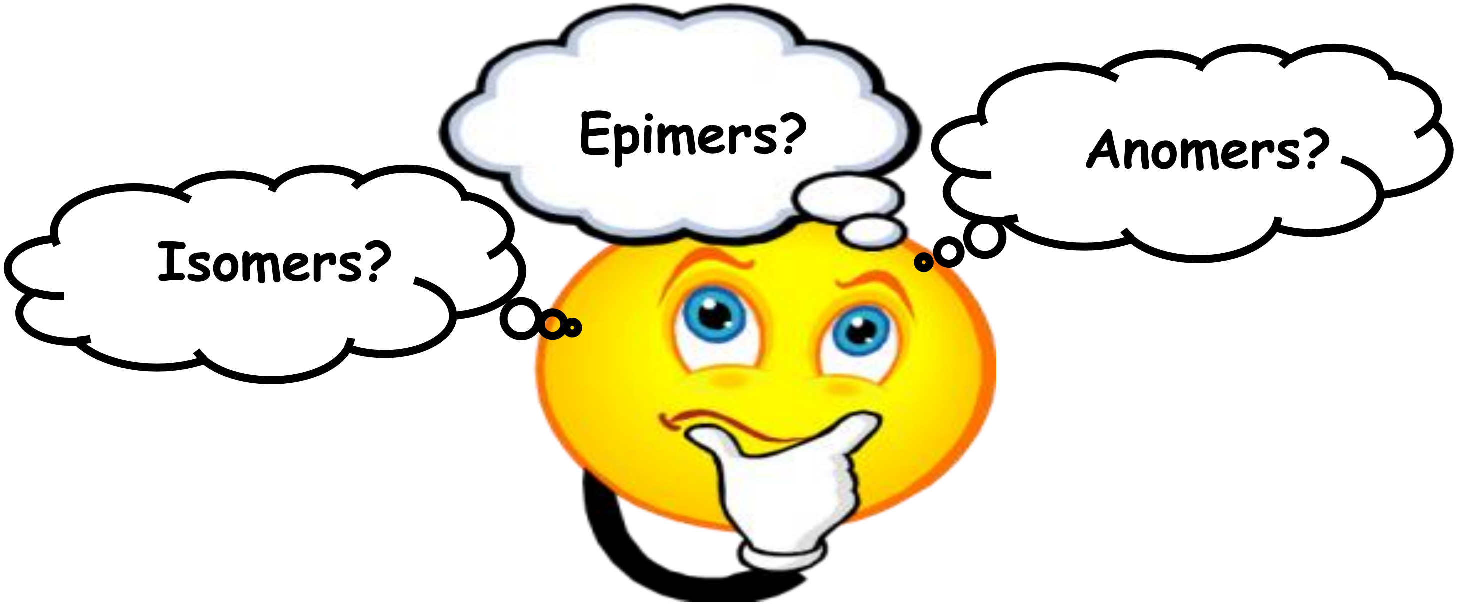
Secondary alcohol functions

C_5*Configuration at right ➔ D configuration

Primary alcohol function

This carbon is not asymmetric because there is a plane of symetrie

Simple carbohydrates : Monosaccharides



Simple carbohydrates : Monosaccharides

Isomers

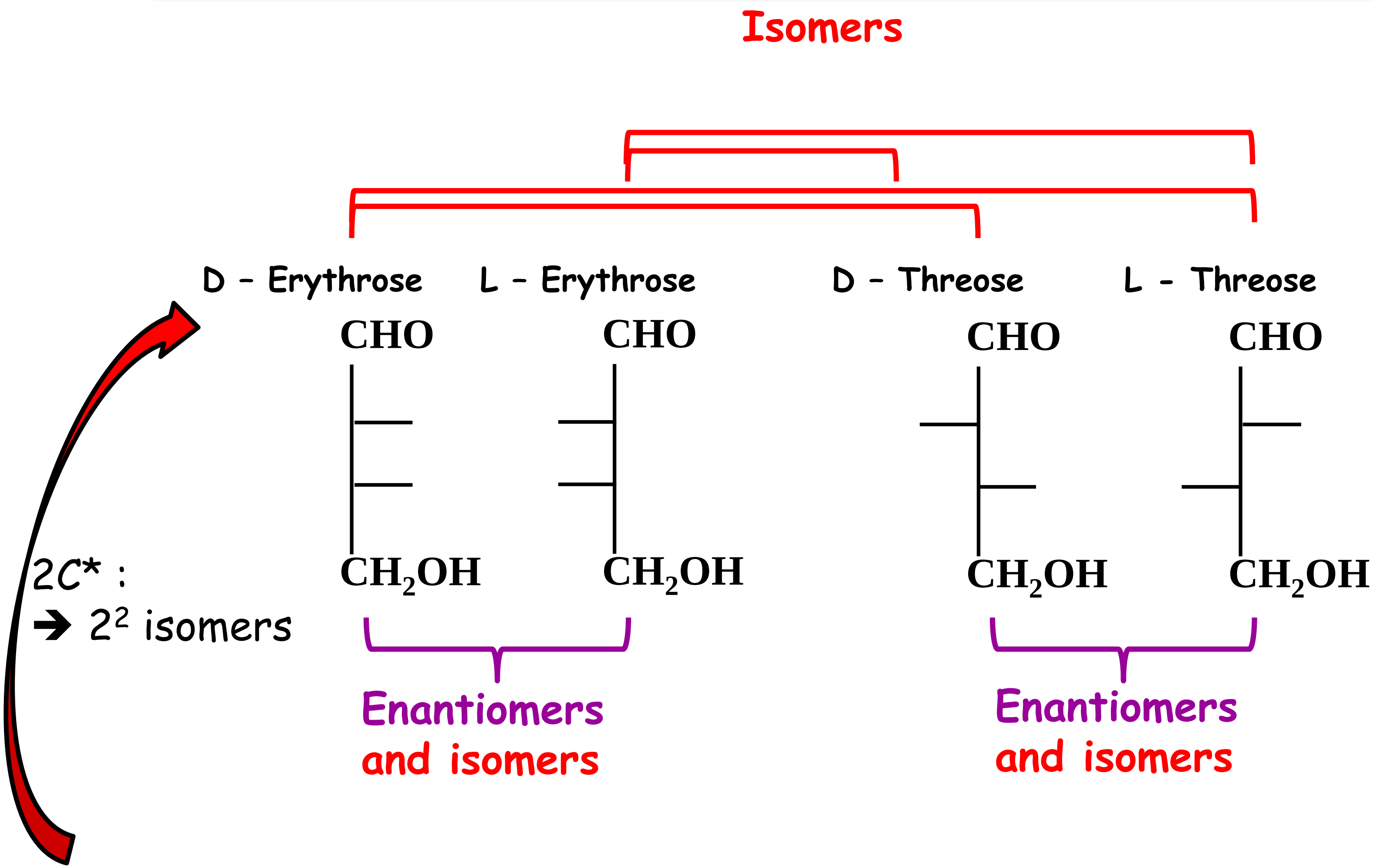
From Greec (*isos* = identical) and (*meros* = part).

1/ Molecules with the same molecular formula (carbon atoms number),

2/ Vary in their spatial arrangement around one or more chiral center (C*) (OH configuration).

Unlike enantiomers, isomers have different physical, chemical and biological properties.

Simple carbohydrates : Monosaccharides



For a sugar containing xC*, there is 2^x isomères

Simple carbohydrates : Monosaccharides

Number of isomers n = 2^x

Aldoses

Nbre of C	xC asymmetric	D configuration	L configuration	Total
3C	1	1	1	2
4C	2	2	2	4
5C	3	4	4	8
6C	4	8	8	16

Ketoses

Nbre of C	xC asymmetric	D configuration	L configuration	Total
3C	0	-	-	1
4C	1	1	1	2
5C	2	2	2	4
6C	3	4	4	8

Simple carbohydrates : Monosaccharides

Epimers

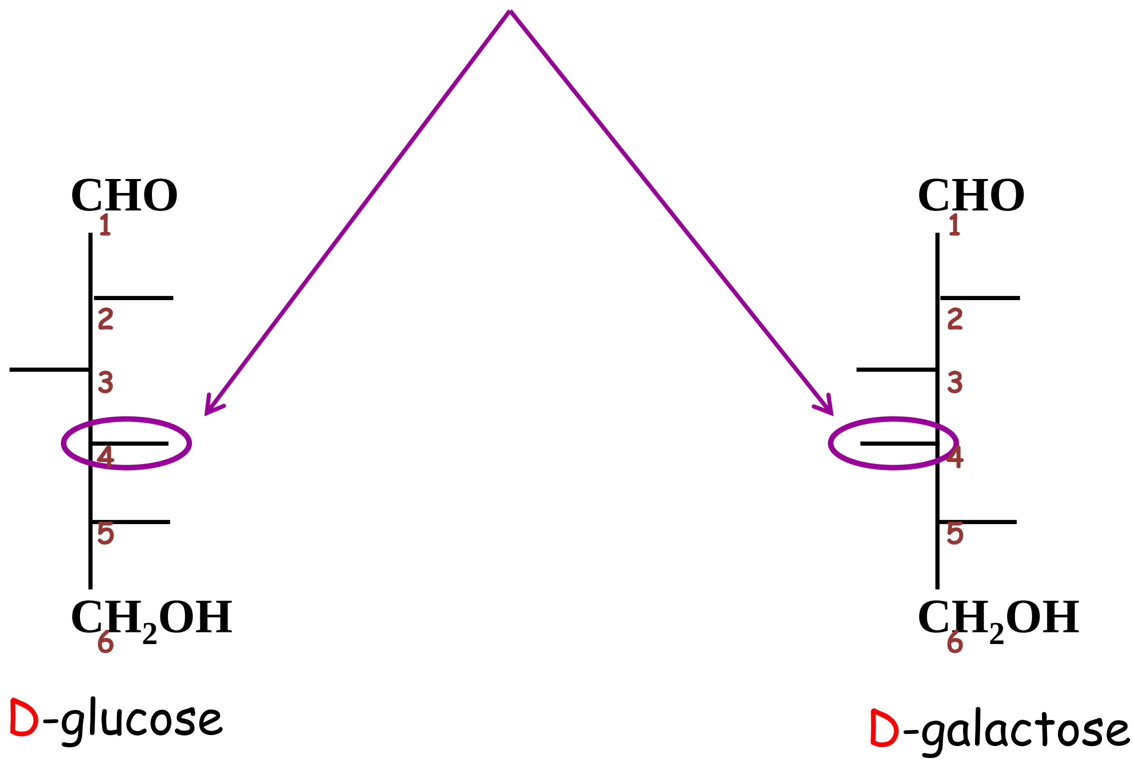
Are a spécific type of isomer

1/ Molecules with the same molecular formula (carbon atoms number),

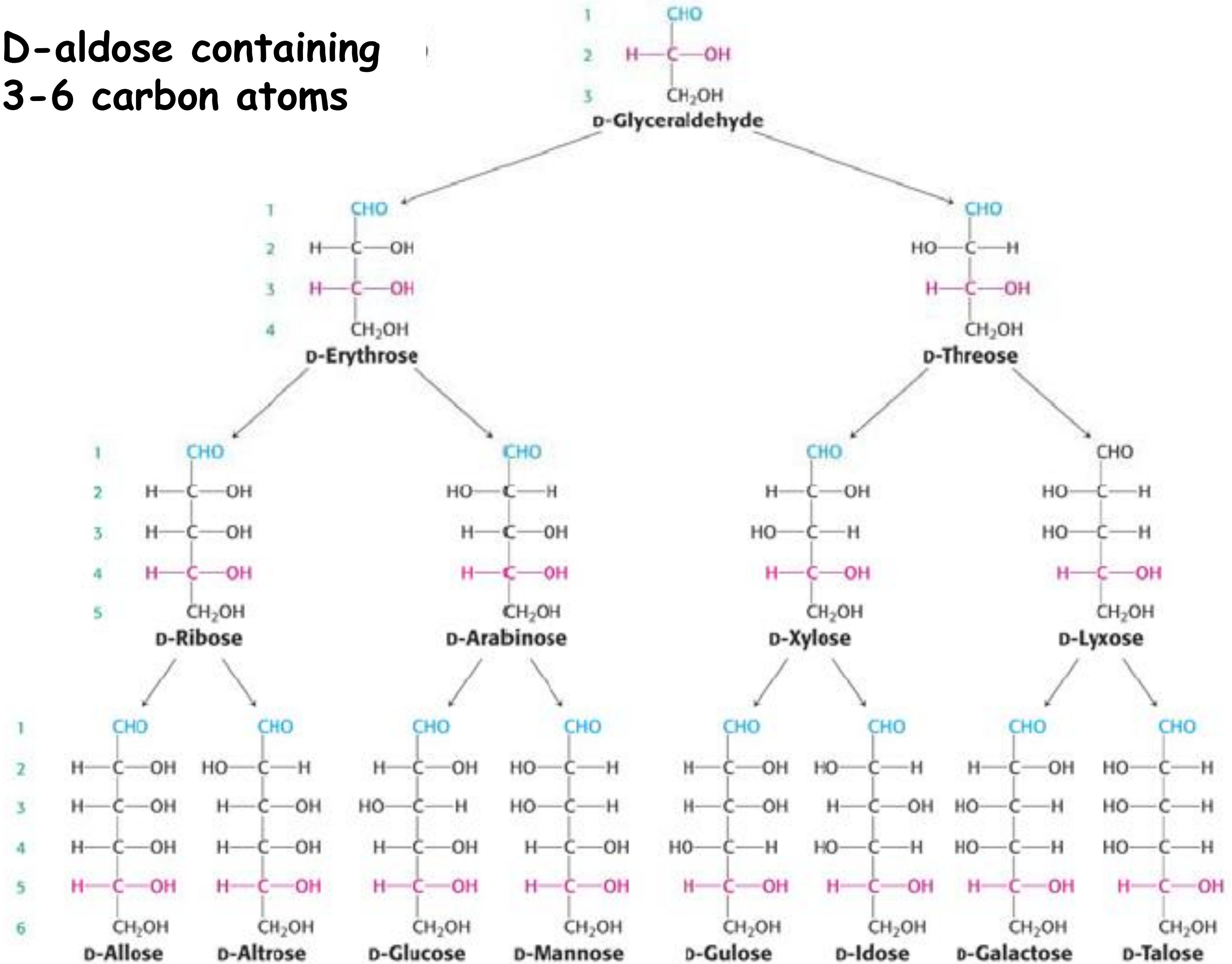
2/ Vary in their spatial arrangement around a single unique chiral center (C*) (OH configuration).

Simple carbohydrates : Monosaccharides

The galactose and glucose are epimers at C*4

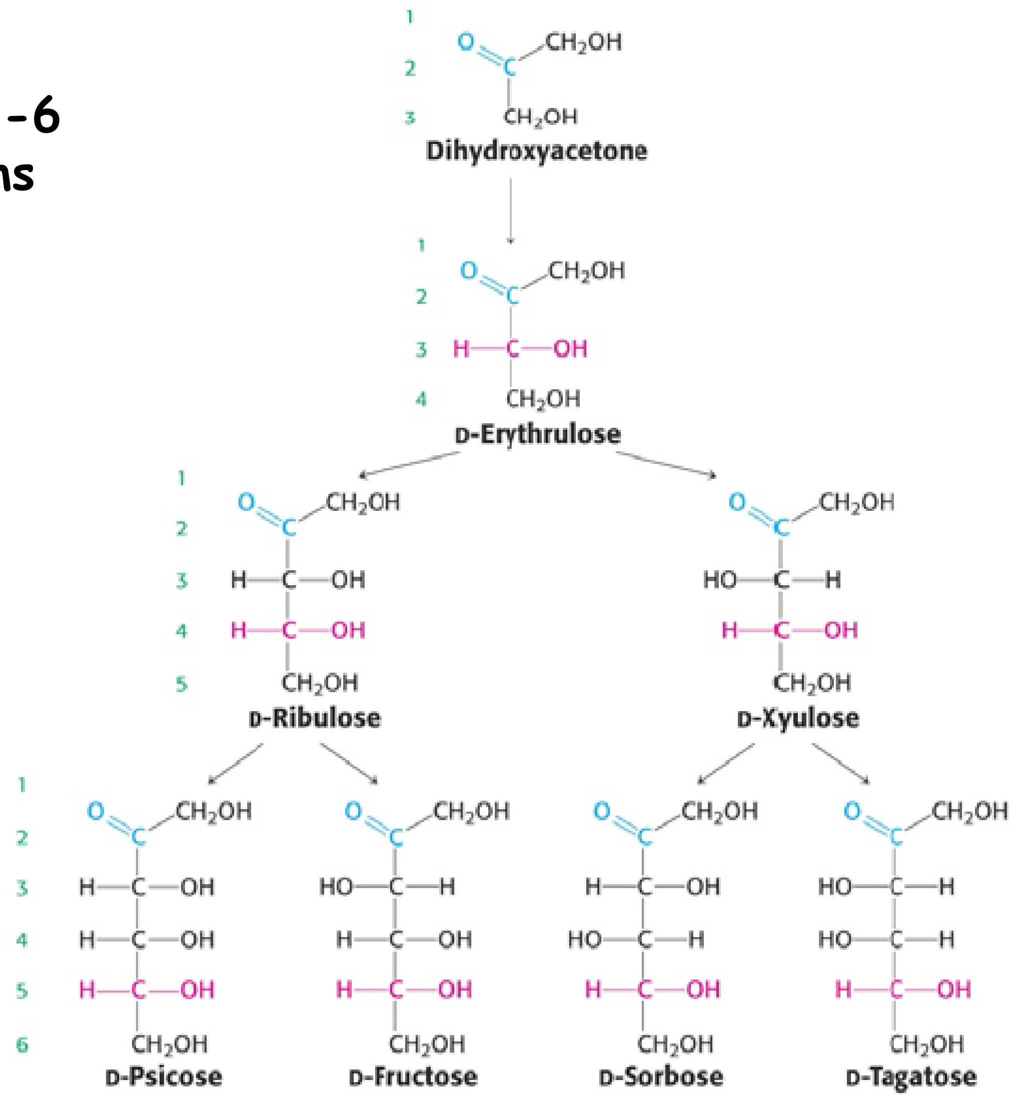


D-aldose containing 3-6 carbon atoms



Nomenclature is defined based on the position of the hydroxyl group attached to the asymmetric carbon adjacent to the primary alcohol function with reference to glyceraldehyde

D-ketose containing 3-6 carbon atoms



Nomenclature is defined based on the position of the hydroxyl group attached to the asymmetric carbon adjacent to the primary alcohol function that in farthest from the kenone group, with reference to the ketotetrose

Simple carbohydrates : Monosaccharides

Cyclic structure of sugars

When sugars dissolve in water, they often adopt the ring structures due to the reaction between their carbonyl group (C=O) (aldehyde or kenone) and a hydroxyl group within the molecule to form a hemiacetal.

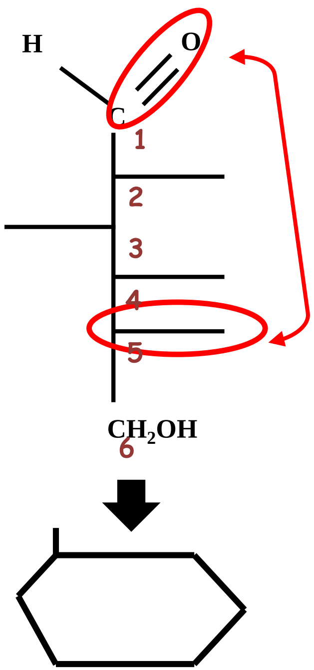
Glucose
(Aldohexose)

C=O / OH of C_5
(Hexoses)

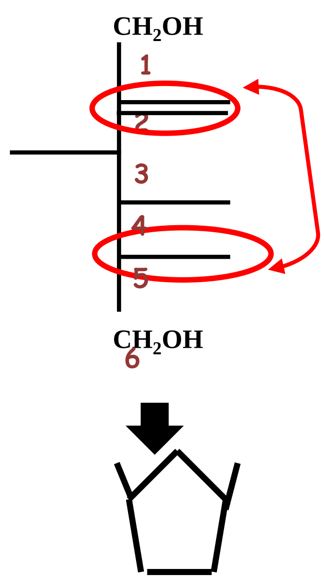
Fructose
ketohexose

C=O / OH of C_4
(Pentose)

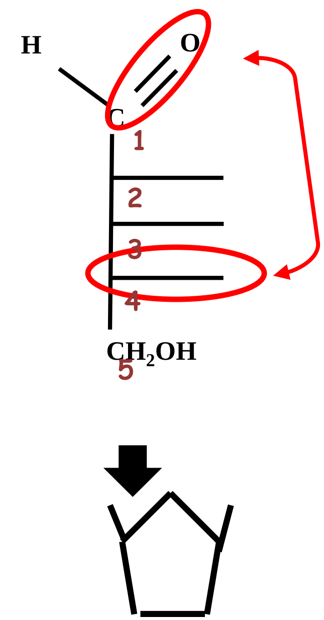
Ribose
(Aldopentose)



Six-membered ring
(pyranose)



Five-membered ring
(Furanose)



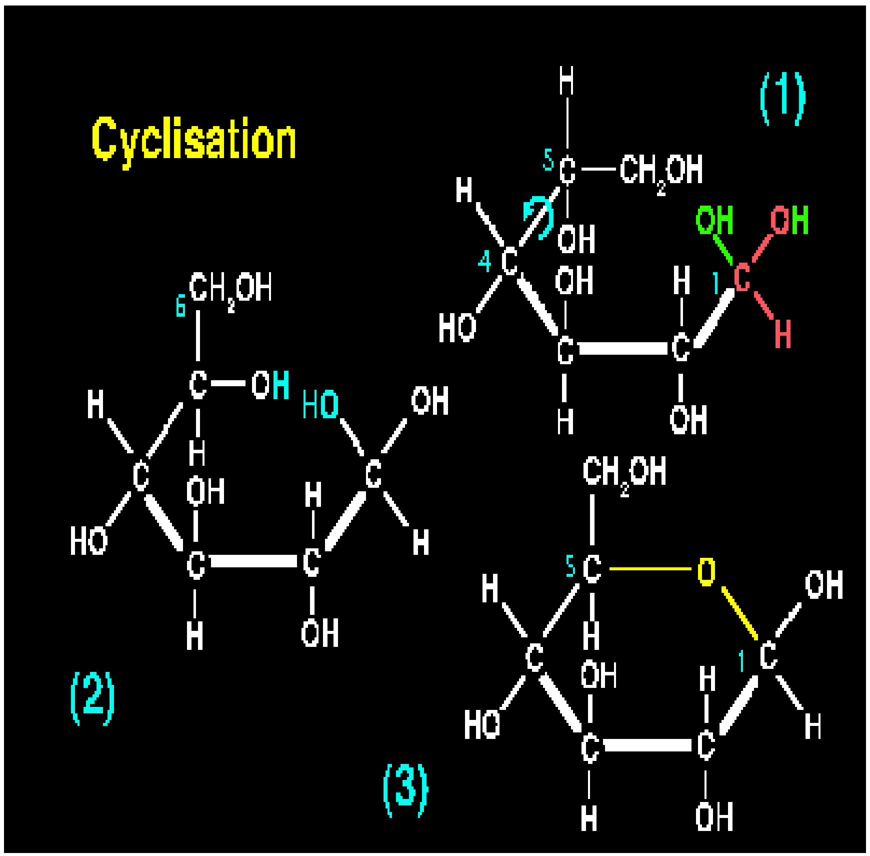
Five-membered ring
(Furanose)

Simple carbohydrates : Monosaccharides

Cyclic structure of sugars

Cyclization reaction of Glucose

This reaction involves the formation of a cyclic structure from linear glucose. In aqueous solution, glucose can cyclize to form either pyranose or furanose form depending on the reaction conditions.



1) - Aldehyde hydration: the aldehyde group react with water to form a diol (molecule with two hydroxyl groups).
- C4-C5 Bond rotation.

3) The two hydroxyl groups attached by (C1 and C5) come close together leading to a chemical reaction.

4) Dehydration reaction: involves the formation of a cyclic structure where an oxygen atom forms a bridge connecting C1 and C5.

Simple carbohydrates : Monosaccharides

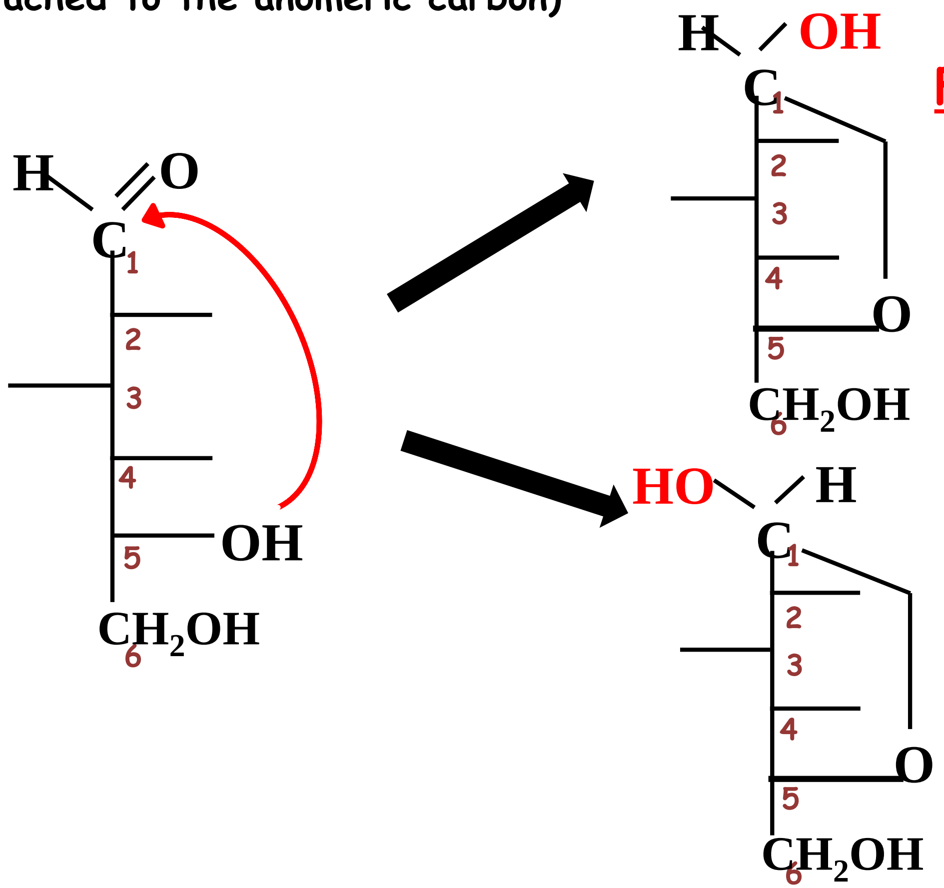
Cyclic structure of sugars

Cyclization reaction of Glucose

➔ The interaction between C=O/OH creates a new chiral C* (C n° 1),

➔ It is called the anomeric carbon

➔ This results in two isomers α or β called anomers (based on the position of the OH group attached to the anomeric carbon)



For a sugar of the D configuration

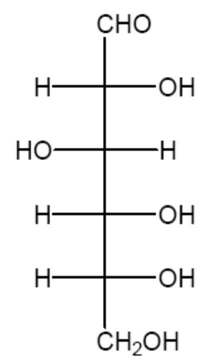
OH du C anomérique à droite:
➔ Anomère α

OH du C anomérique à gauche:
➔ Anomère β

Simple carbohydrates : Monosaccharides

Expended formula

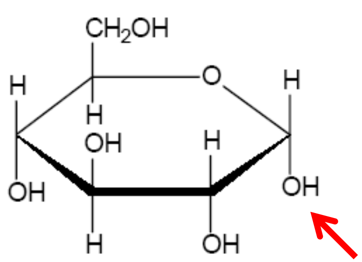
Linear représentation
Fischer



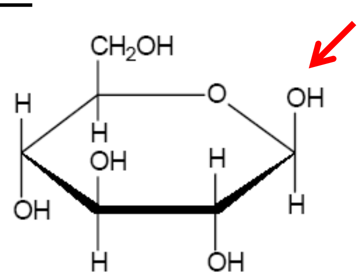
D-Glucose

Cyclic représentations

Haworth

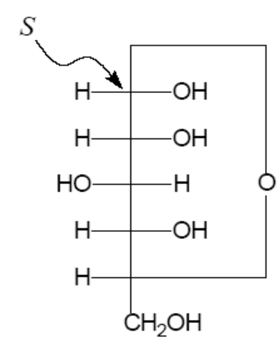


α-D-Glucopyrannose

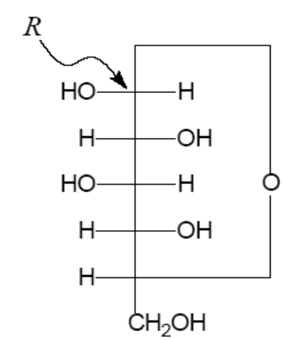


β-D-Glucopyrannose

Tollens



α-D-Glucopyrannose



β-D-Glucopyrannose

Simple carbohydrates : Monosaccharides

Haworth projection

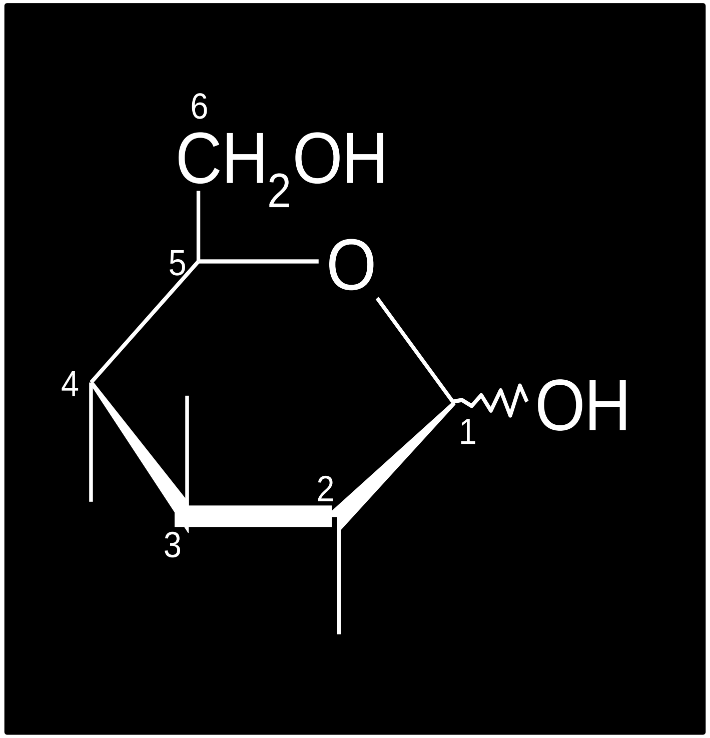
- The cycle is considered as a plane perpendicular to the paper.

- The oxygen bridge is behind the plane.

- The carbons are arranged in a clockwise direction bonds not belonging to the cycle are placed above or below the plane, respecting the absolute configuration of the chiral carbons (C*).

- The OH groups that were on the right in the Fischer projection are found below the plane of the cycle, and the OH groups that were on the left are above the plane of the cycle.

- the OH groups are represented by a line, and the OH atoms are not shown.

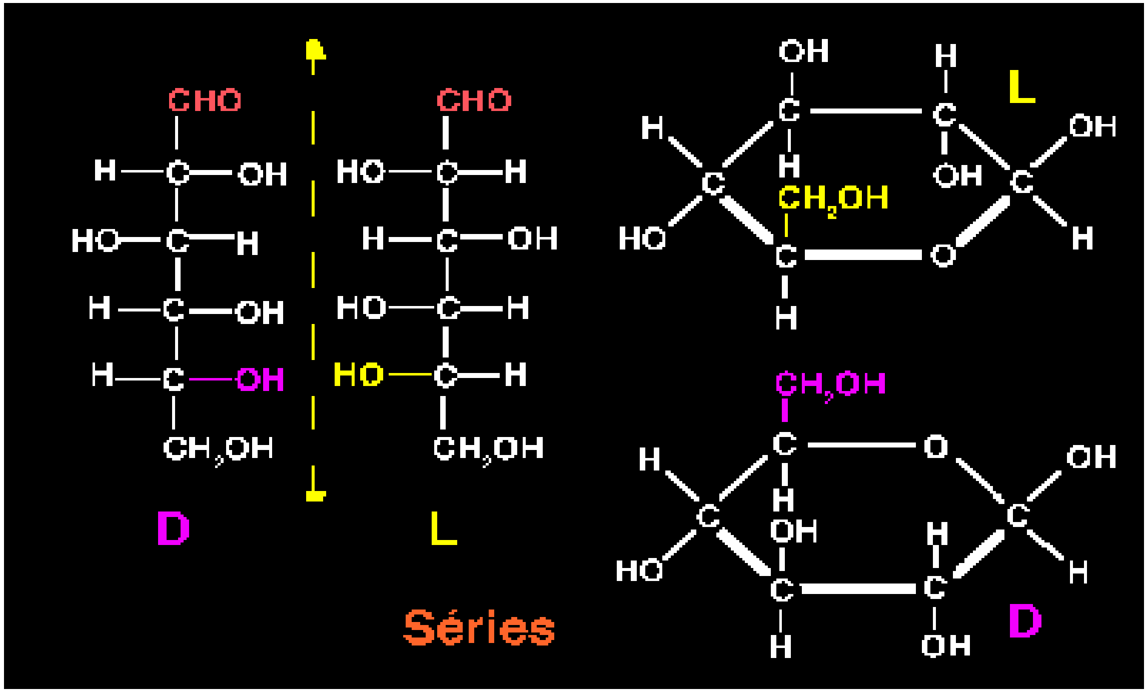


Simple carbohydrates : Monosaccharides

Haworth projection
Exemple: glucose

How to recognize the D or L series of sugars?

- If the CH_2OH (of C6) is situated above the cycle → D configuration,
- if the CH_2OH (of C6) is situated below the cycle → L configuration



Simple carbohydrates : Monosaccharides

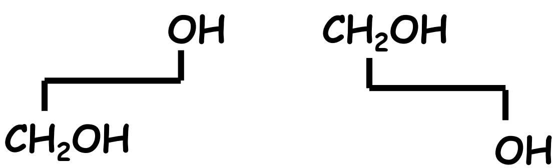
Haworth projection

Exemple: glucose

As a general rule:

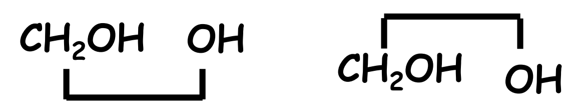
Anomer α

When OH of the C1 and CH_2OH of the C6 are in opposition



Anomer β

When OH of the C1 and CH_2OH of the C6 are located on the same side



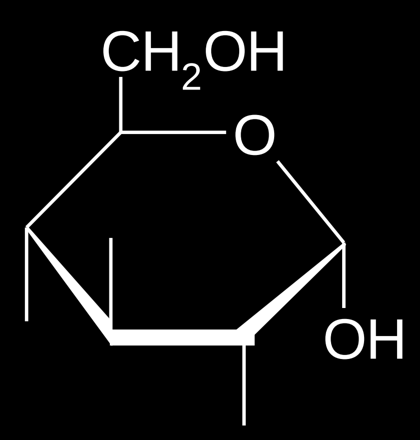
Simple carbohydrates : Monosaccharides

Haworth projection

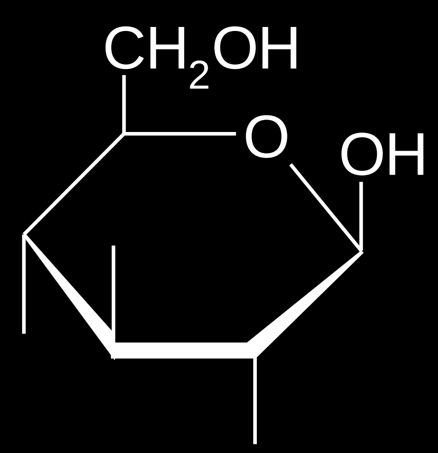
So, for a D-series sugar (CH_2OH on top):

→If the hemiacetal hydroxyl group (OH attached to the anomeric C) is located below the plane of the ring, the sugar is on the α anomeric form.

→ If the hemiacetal hydroxyl group is located above the plane of the ring. The sugar is on the β anomeric form.



α-D-glucopyranose

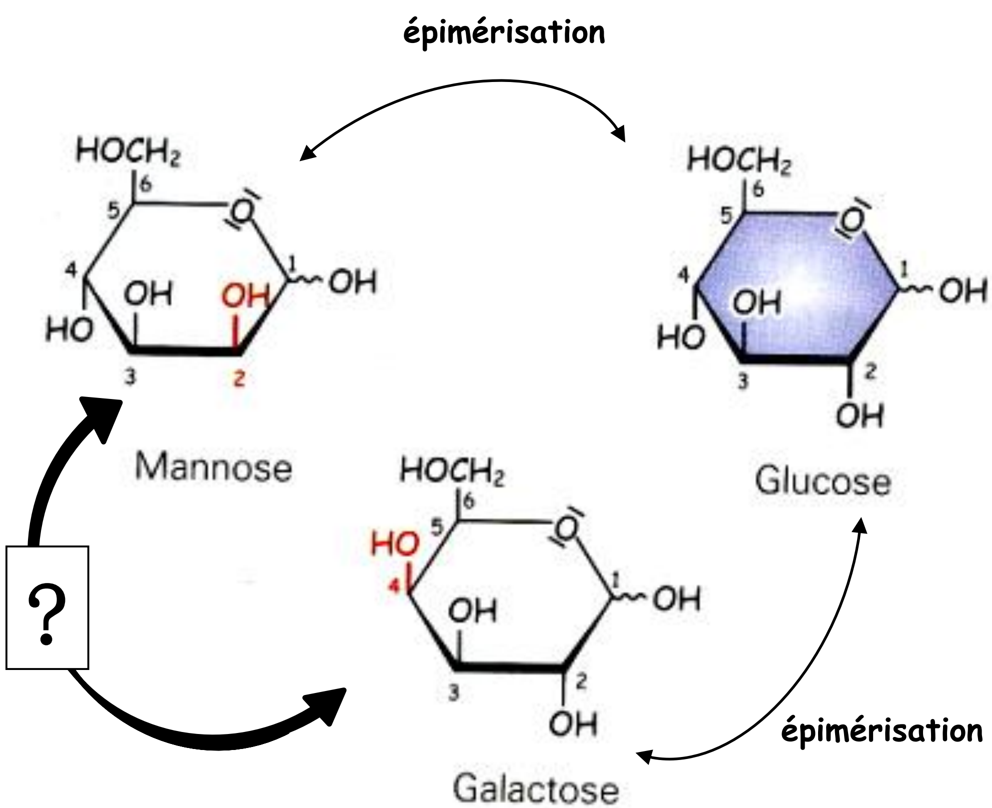


β-D-glucopyranose

Simple carbohydrates : Monosaccharides

Haworth projection

The concepts of epimers are the same in Haworth projection as in Fischer projection.



Simple carbohydrates : Monosaccharides

Optical rotation of sugars $[\alpha]^{D}_{20°}$

Anomers α and β do not rotate polarized light in the same way,

Ex: α-D glucose ➔ +112°

β-D glucose ➔ +18,7°

The optical rotation of the two sugars is calculated as follows:

Proportion of sugar in the solution

$$[\alpha]^{D}_{20°\ (mixture)} = [\alpha]^{D}_{20°\ (\alpha\ glucose)} * X_{(\alpha\ glucose)} + [\alpha]^{D}_{20°\ (\beta\ glucose)} * X_{(\beta\ glucose)}$$

Ex: When preparing a solution consisting of :
50ml de α-D glucose + 50ml de β-D glucose

$$[\alpha]^{D}_{20°\ (mixture)} = 112° * 0,5 + 18,7° * 0,5 = 65,35° \approx 66°$$

Simple carbohydrates : Monosaccharides

Optical rotation of sugars $[\alpha]^{D}_{20°}$

The mutarotation

- The optical rotation of a α-D glucose solution freshly prepared = +112°

Over time, this optical rotation is not stable ➔ it decreases !

- The optical rotation of a β-D glucose solution freshly prepared = +18,7°

Over time, this optical rotation is not stable ➔ it increases !

- When cristalline glucose is dissolved in water, it undergoes cyclization, resulting in the formation of both α and β anomers in approximately equal proportions ➔ 50% α form and 50% β form ➔ $[\alpha]^{D}_{20° \text{ (initial)}} \approx 66°$

Over time, it is observed that the optical rotation is not stable ➔ it decreases !

⇩

This change in optical rotation over time is called : mutarotation

La mutarotation accompanies the conversion of the anomère α ⟷ anomère β until an equilibrium between the two forms is reached.

Simple carbohydrates : Monosaccharides

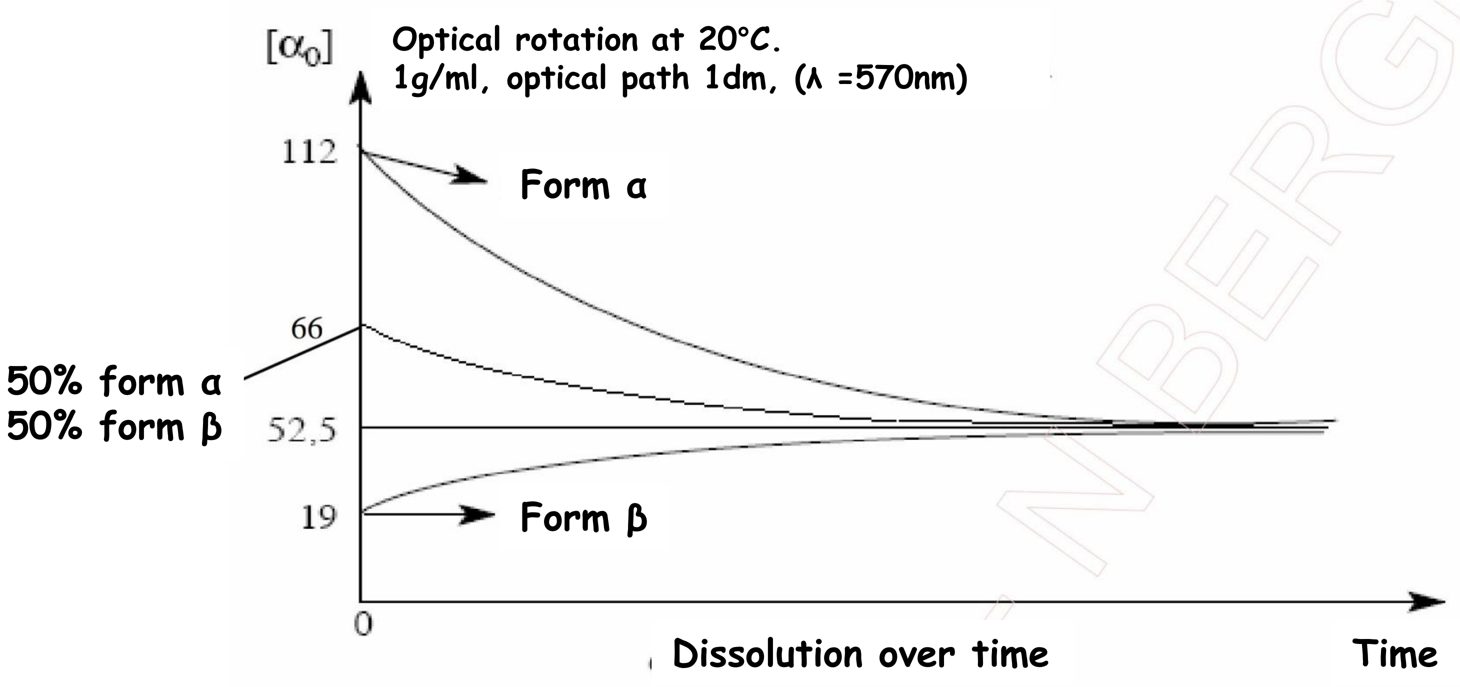
Optical rotation of sugars $[\alpha]^{D}_{20°}$

The mutarotation

Ex: **for the glucose in aqueous solution, there is an equilibrium**

βD-glucopyranose ~ 64% ⟷ Linear Glucose ~ 0,02% ⟷ αD-glucopyranose ~ 36%

$$[\alpha]^{D}_{20° \text{ (mixture)}} = 112° * 0{,}36 + 18{,}7° * 0{,}64 = \underline{52{,}5°}$$



Simple carbohydrates : Monosaccharides

Hexoses (six-carbon sugars)

- **Important role in métabolism**: such as the crucial role of the glucose in energy production and other metabolic process.
- Directly and indirectly interconvertible.
- Almost never in a linear form → Cyclization

- Aldohexoses important:
  - Glucose
  - Mannose
  - Galactose

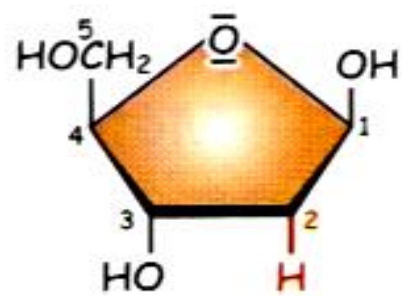
- ketohexose the most important:
  - Fructose (Fruits, honey and some vegetables)

Simple carbohydrates : Monosaccharides

Pentoses (five-carbon sugars)

- Ribose ➔Ribonucleic acid (RNA)
- Desoxyribose ➔ desoxyribonucleic acide (DNA)
- Group of furanoses

Ribose



2-Désoxyribose

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

- The properties due to the hemiacetal function,
- The properties due to the alcohol function,
- The prperties due to the mutual influence of these two types of functions.

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Reduction

It is possible to reduce the aldehyde or ketone group of a sugar to an alcohol function, thereby obtaining:

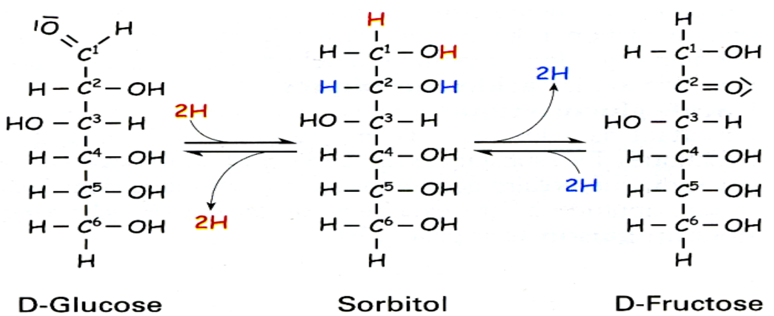
For an aldose ⇩ Un polyol (sugar alcohol)

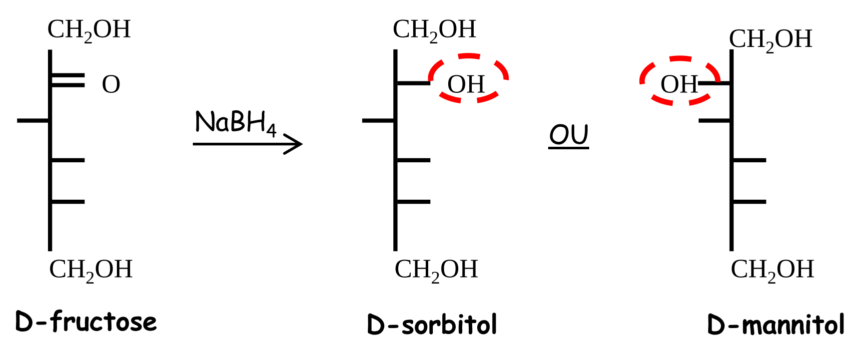
For a ketose ⇩ 2 polyol epimers.

Exemple:
D-Glucose ➔ Sorbitol

Exemple:
D-Fructose ➔ 50% D-Sorbitol + 50% D-Mannitol epimers at C2*

Reduction with sodium borohydride de $NaBH_4$





Simple carbohydrates : Monosaccharides

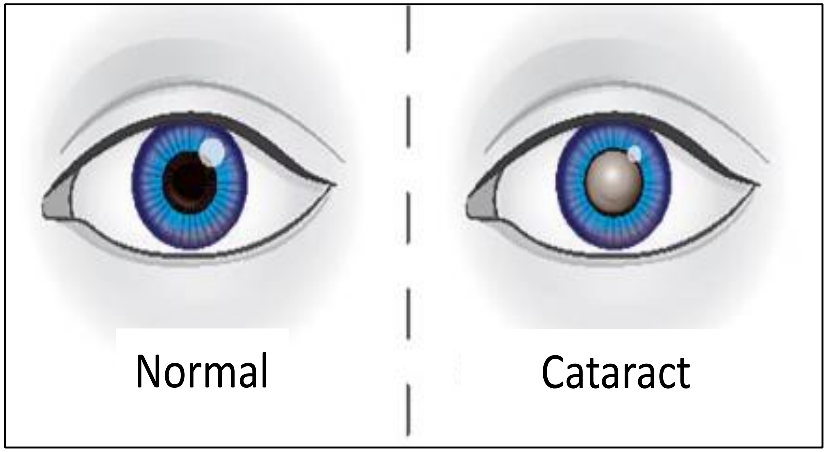
Chemical properties of sugars

Reduction

Biological and practical contexts

⇨ **In metabolism :**

Sorbitol accumulates in certain tissues during chronic hyperglycemia due to the activation of the **polyol pathway**. In this pathway, **glucose is reduced to sorbitol** by the enzyme **aldose reductase**, particularly in insulin-independent tissues such as the **lens of the eye, peripheral nerves, and kidneys**. Since sorbitol does **not easily diffuse across cell membranes**, it tends to **accumulate intracellularly**, increasing **osmotic pressure**. This leads to **cellular swelling, oxidative stress**, and contributes to the development of **diabetic complications** such as: **Cataracts** (due to lens opacity), p**eripheral neuropathy**, and n**ephropathy** (kidney damage).



Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Reduction

Biological and practical contexts

⇨ **In the food industry :**

Sorbitol and Mannitol are widely used as a low-calorie sweetener, particularly in **sugar-free** or **diabetic-friendly** products like: chewing gums, sugarless candies, toothpaste and mouthwash. It provides **about 60% of the sweetness of sucrose** but with **fewer calories** and **a lower glycemic index**, making it suitable for diabetics. However, in high doses, sorbitol and Mannitol can have a **laxative effect** due to there poor absorption in the small intestine.

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Attachment of an amine group

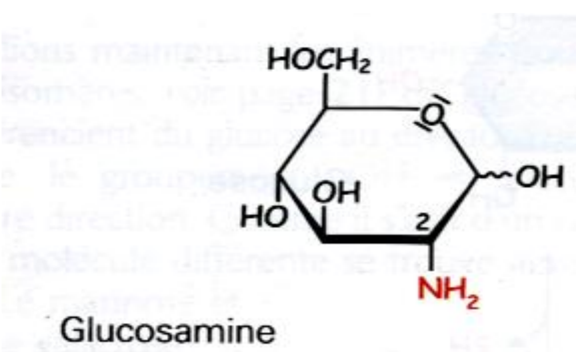
➔ **Osamines**

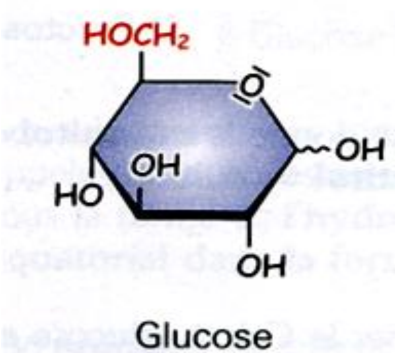
- Amino sugar where an amino group replaces a hydroxyl group in the sugar molecule.
- Important in various biological processes and are component of polysaccharides and glycoprotéines of the cell membrane and the extracellular matrix (glycosaminoglycans/GAGs)

Glucose → glucosamine

Mannose → mannosamine

Galactose → galactosemine





Simple carbohydrates : Monosaccharides

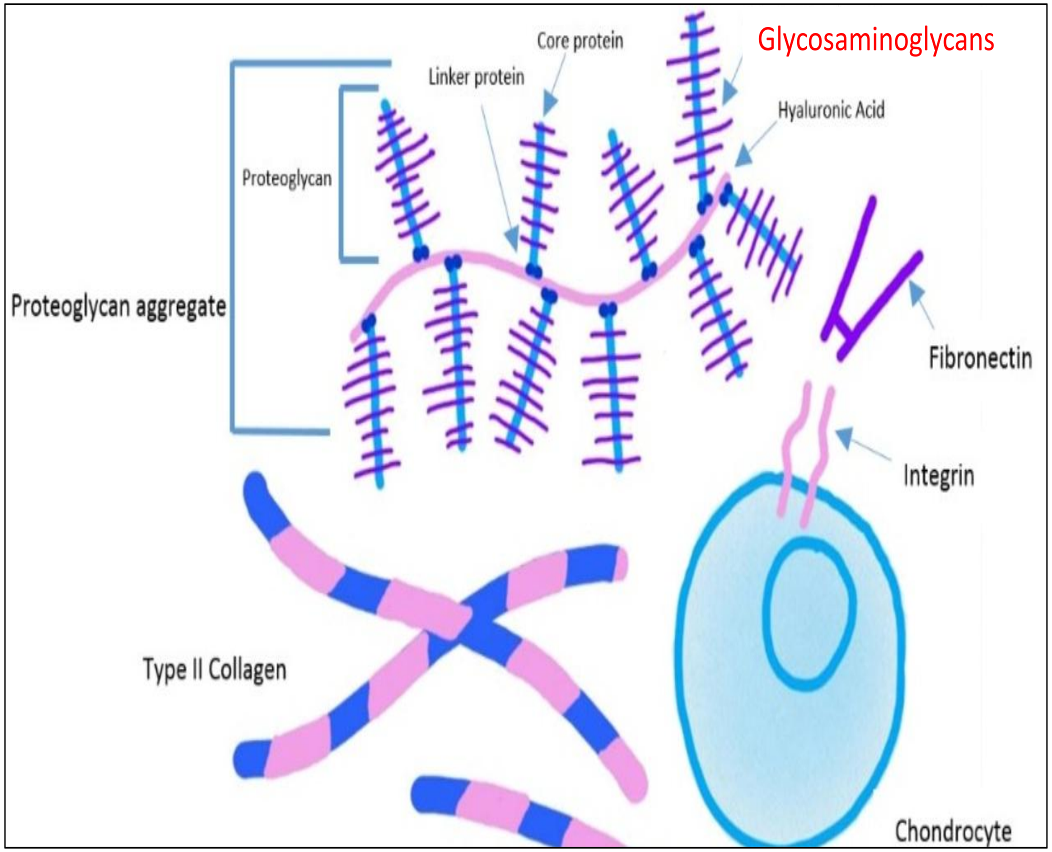
Chemical properties of sugars

Attachment of an amine group

Biological and practical contexts

Amino sugars play significant roles in biological recognition, cellular communication, and structural integrity of tissues. The glucosamine is an essential component of **Glycosaminoglycans (GAGs)** such as **hyaluronic acid**, found in articular cartilage, tendons, ligaments, and the extracellular matrix.

It is commercially available as a **dietary supplement**, widely used to potentially **slow cartilage degradation**.



Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

Mild oxidation

Controlled and less agressive oxidation which only affectes one function of the sugar

Oxidation of the aldehyde fonction

- With Bromine (Br_2) or l'Iodine (I_2) in an alkalin medium
- Oxidize aldoses but not ketoses (ketone fonction does not oxidize)
- transformation into aldonic acide.

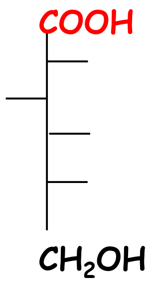
-Glucose→gluconic acide
- Mannose→ mannonic acide
- Galactose→galactonic acide.

Oxidation of the primary alcohol fonction

- The reducing group must be protected
- The pimary alcohol group ($-CH_2OH$) is oxidized to form a carboxylic acide ($-COOH$).
- transformation into uronic acide.

-Glucose→glucuronic acide
- Galactose→galacturonic acide.

Simple carbohydrates : Monosaccharides



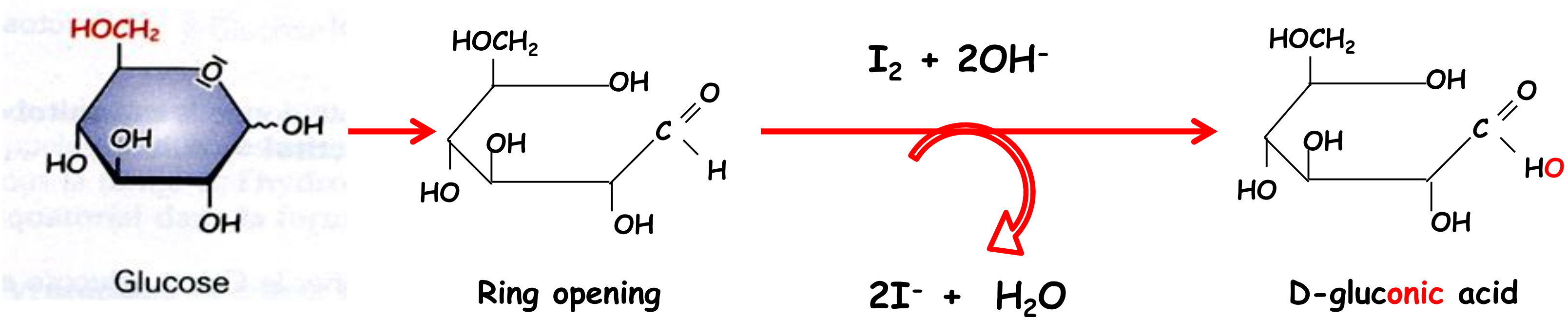
Chemical properties of sugars

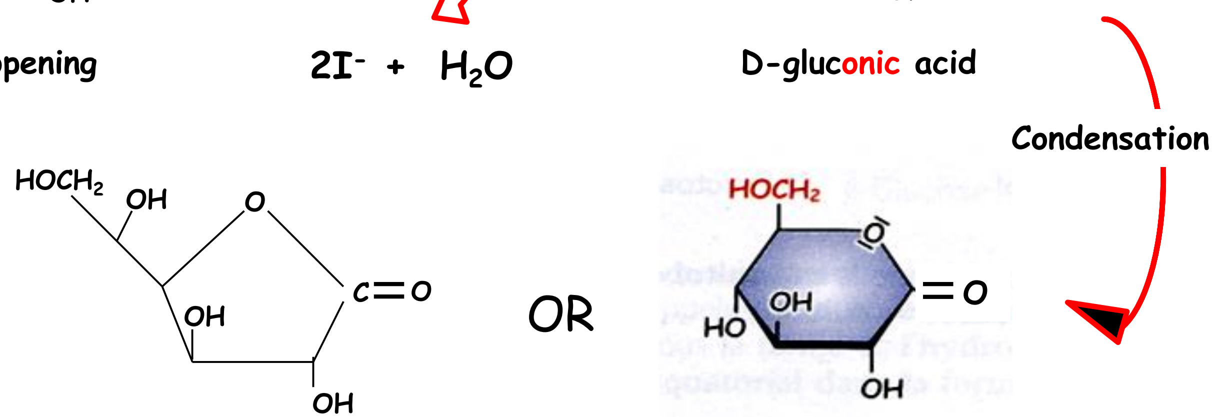
Oxidation

Glucose oxidation with Iodine (I_2) or Bromine (Br_2)

➔ **Gluconic Acide**

Obtained by the oxidation of the aldehyde group of glucose (on C n° 1)





γ-gluconolactone acide
Furan ring (C1-C4)

δ-gluconolactone acid
Pyran ring (C1-C5)

- Antimicrobial/anti-inflammatory,
- Intermediate for drug synthesis.

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

Glucose oxidation with Iodine (I_2) or Bromine (Br_2)

Biological and practical contexts

⇨ **In biochemistry :**

Glucose oxidase is used to **quantify glucose** by measuring the production of gluconic acid and hydrogen peroxide. This principle is used in **blood glucose meters** (glucometers).

Simple carbohydrates : Monosaccharides

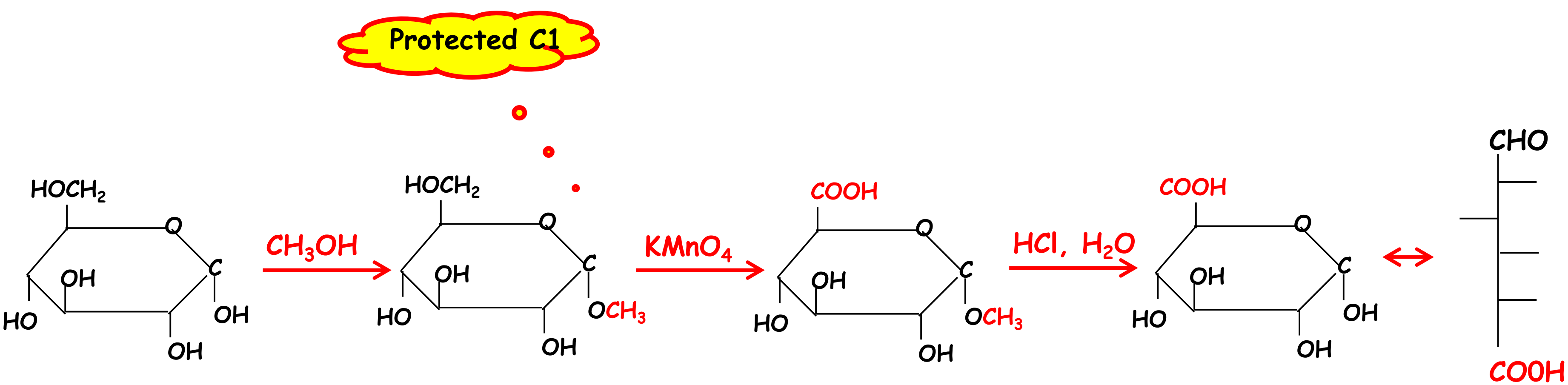
Chemical properties of sugars

Oxidation

Glucose oxidation

➔ Glucuronic acide

- Oxidation of the primary alcohol fonction to a carboxylic acid yields an uronic acide with potassium permenganates ($KMnO_4$).
- Produced glucuronic acid, which is a component of glycosaminoglycans (GAGs) such as heparin and hyaluronic acid. It's also a precursor in the synthesis pathway of vitamin C.



D-glucose

Glucuronic acide

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

Glucose oxidation

Biological and practical contexts

- **In structural polysaccharides :** Glucuronic acid is a component of glycosaminoglycans (GAGs) such as heparin and hyaluronic acid.

- **In detoxification :** Glucuronic acid is used to conjugate toxic substances, drugs, and hormones (bilirubin, paracetamol, steroid hormones) in the liver, making them more hydrophilic and excretable in bile or urine.

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

Action of a strong oxydants

These reactions are caused by strong oxidizing agents, which can simultaneously oxidize several functional groups

With hot nitric acid HNO_3

Case of aldoses

➢ Simultaneous oxydation of the two terminal functions of the molecule (aldehyde and primary alcohol group) leading to the formation of two carboxyl groups and resulting in the formation of an aldaric acid.

-Glucose➔glucaric acid
-Galactose➔galactaric acide

Case of ketoses

➢ Cleavage of the carbon chain at the ketone function and formation of a mixture of carboxylic acids.

With periodic acid HIO_4

Oxidizes molecules that possess:

➢ Two free and adjecent hydroxyl groups.

➢ a free hydroxyl group and a free aldehyde function, adjacent.

➢ This causes the cleavage of the C-C bond between the two groups, we obtain:

➢ Formaldehyde (methanal) (CH_2O) from primary alcohol function ($-CH_2OH$),

➢ Formic (methanoic) acid ($HCOOH$) from secondary alcohol functions and aldehydes.

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

Action of a strong oxydants

The strong oxidation of monosaccharides by nitric acid (HNO_3) or periodic acid (HIO_4) is a **purely chemical reaction** used in laboratory settings to analyze or characterize sugar structures. These reactions **do not occur in the human body** and have **no known biological or metabolic role.**

Simple carbohydrates : Monosaccharides

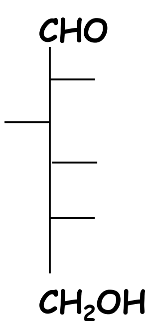
Chemical properties of sugars

Oxidation

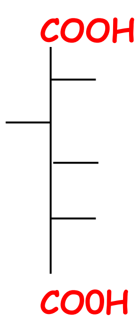
Action of a strong oxydants
Nitric acid HNO_3

Aldoses
Case of glucose

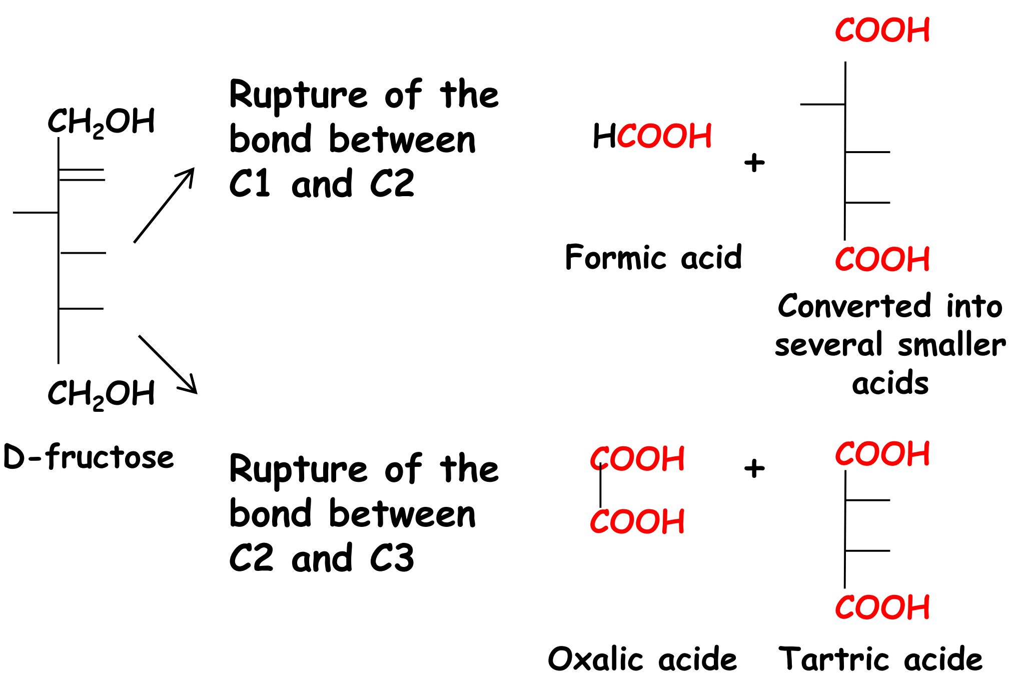
ketoses
Case of fructose



D-glucose



Acide D-glucaric



D-fructose

Simple carbohydrates : Monosaccharides

Chemical properties of sugars

Oxidation

General principle

Action of a strong oxydants
Periodic acid HIO_4

1. $R - CHOH - CHOH - R' + HIO_4 \rightarrow R - CHO + R' - CHO + HIO_3 + H_2O$

   2 alcohols II → 2 aldehydes

2. $R - CHOH - CHO + HIO_4 \rightarrow R - CHO + HCOOH + HIO_3$

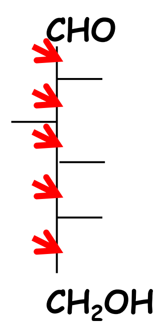
   alcohols II and aldehyde → Aldehydes + formic acid

3. $R - CHOH - CH2OH + HIO_4 \rightarrow R - CHO + HCOH + HIO_3 + H_2O$

   alcohols I and II → Aldehydes + methanal

Exemple

Case of Glucose



D-glucose

$+ 5\ HIO_4 \longrightarrow HCHO + 5HCOOH + 5HIO_3$

HCHO	5HCOOH
Methanal C6	Formic acid C1 à C5

Simple carbohydrates : Monosaccharides

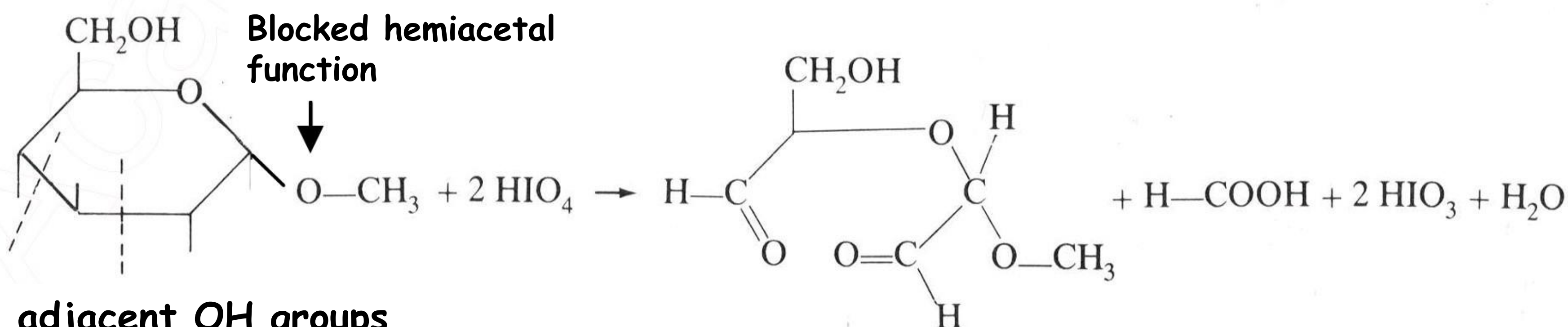
Chemical properties of sugars

Action of a strong oxydants

Application of periodic oxydation to the determination of the cyclic structure of a sugar

If the D-glucose in in pyranose form

Blocked hemiacetal function



3 adjacent OH groups
➔2 cleavages
➔ 2 HIO_4 consumed

Oxidized C2 and C4
➔Aldehyde function

1 Formic acid (C3)

Simple carbohydrates : Monosaccharides

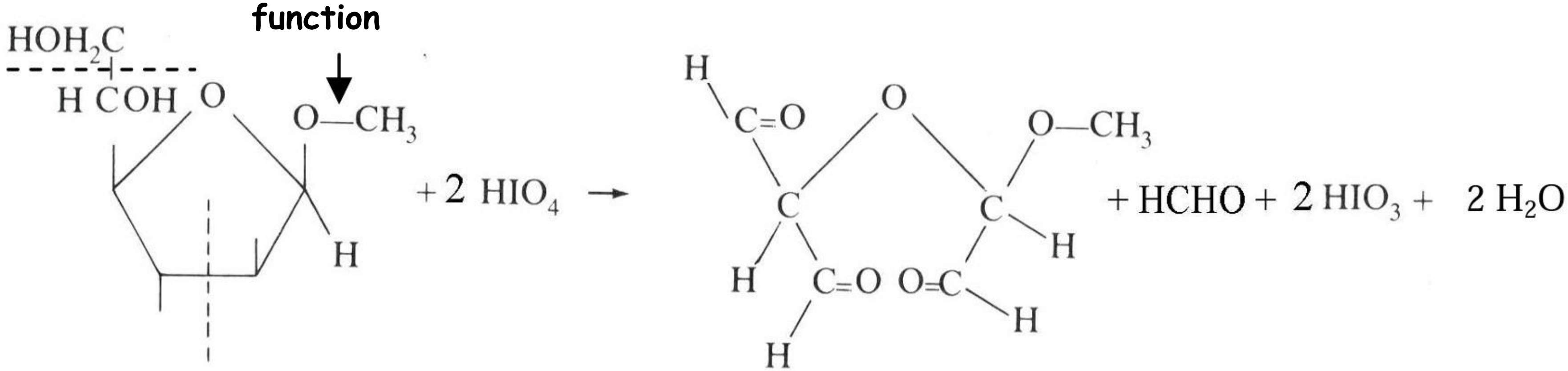
Chemical properties of sugars

Action of a strong oxydants

Application of periodic oxydation to the determination of the cyclic structure of a sugar

If the D-glucose in furanose forme

Blocked hemiacetal function



2 x 2 adjacent OH groups
➔2 cleavages
➔ 2 HIO_4 consumed

Oxidized C2 and C3
➔Aldehyde function

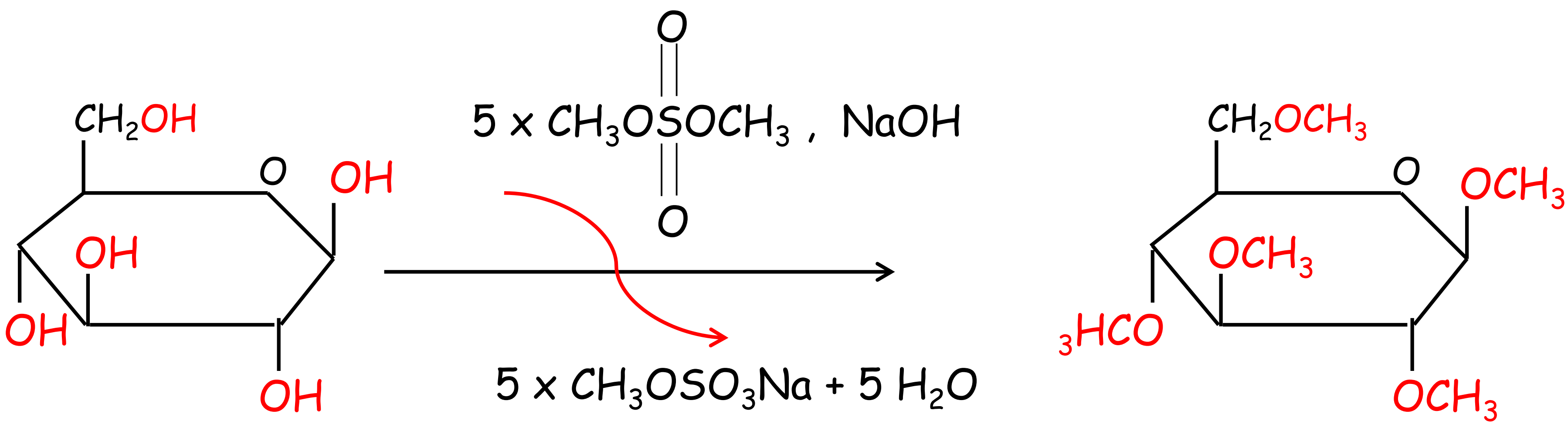
1 methanal (C3)

Simple carbohydrates : Monosaccharides

The reactions of monosaccharides

Permethylation with methyl iodide (CH_3I) or dimethyl sulfate $(CH_3)_2SO_4$

Permethylation refers to the prolonged reaction leading to the methylation of all accessible hydroxyl groups of a sugar.



β-D glucopyranose

1,2,3,4,6 penta-O- methyl-β-D-glucopyranose

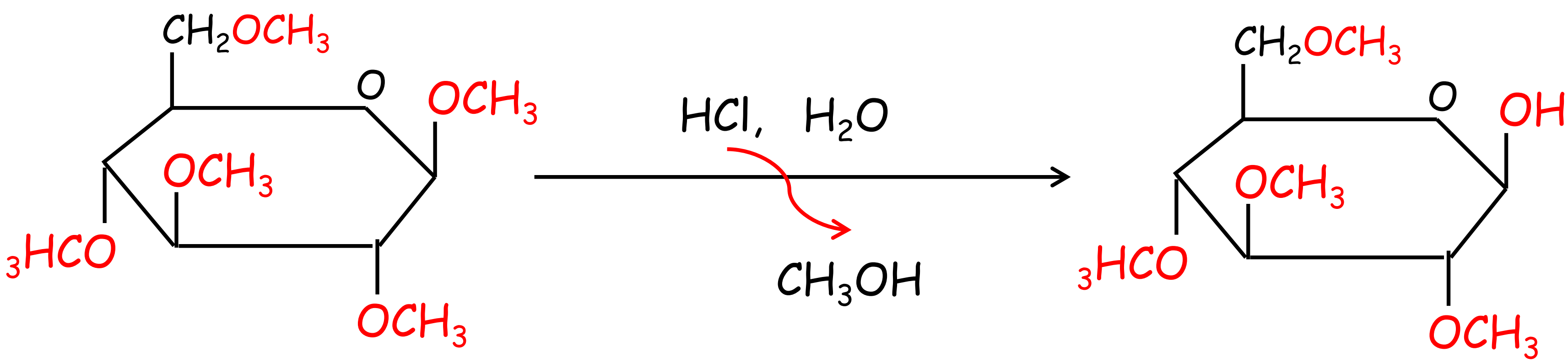
Simple carbohydrates : Monosaccharides

The reactions of monosaccharides

Permethylation with methyl iodide (CH_3I) or dimethyl sulfate $(CH_3)_2SO_4$

Among the hydroxyl groups of a sugar, there is the hemiacetal hydroxyle (OH attached to the anomeric carbon), which has different properties from those of other hydroxyl groups.

Il is sensitive to acid hydrolysis:



1,2,3,4,6 penta-O- methyl-β-D-glucopyranose

2,3,4,6 tetra-O- methyl-β-D-glucopyranose

Simple carbohydrates : Monosaccharides

The reactions of monosaccharides

Effet of methylation on optical rotation

In a mixture of anomers α-D glucose et β-D glucose, the angle of light deviation is calculated using the formula :

$$[\alpha]^{D}_{20°\ (mixture)} = [\alpha]^{D}_{20°\ (\alpha\ glucose)} * X_{(\alpha\ glucose)} + [\alpha]^{D}_{20°\ (\beta\ glucose)} * X_{(\beta\ glucose)}$$

After a few hours, an equilibrium is established between the forms α and β and the angle of deviation changes.

Methylation (formation of $COCH_3$ bond) at the C1 position leads to the permanent fixation of the anomeric configuration α and β.

⬇

The angle of deviation remains the same because the initial proportion (X) of α-D glucose and β-D glucose do not change.

Disaccharides: diholosides

- Sugars composed of two monosaccharide units
- 4 disaccharides are important in human :
  - [Maltose, isomaltose], lactose, saccharose

- Liaison O-glycosidic bond (α ou β)
- The bond between two sugars is made by an oxygen atom.

$$R\text{-}OH + R'\text{-}OH \rightarrow R\text{-}O\text{-}R' + H_2O$$

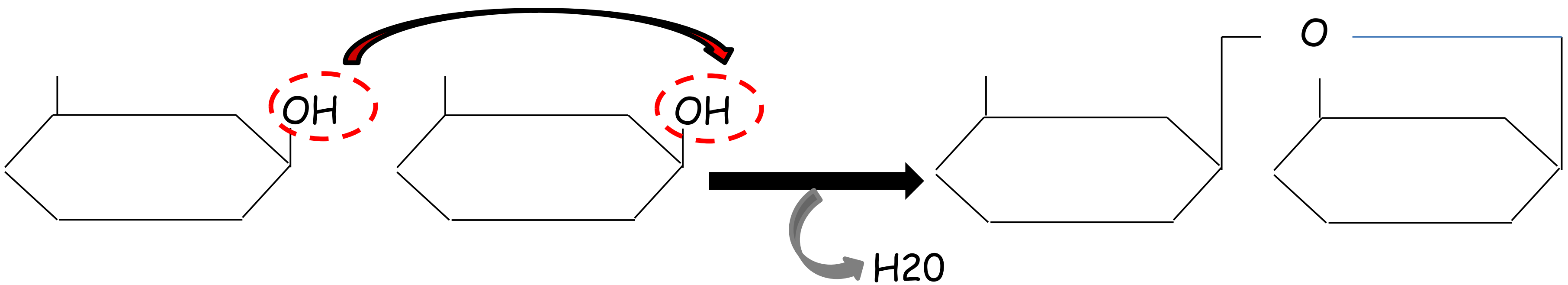
Disaccharides: diholosides

Non-reducing diholoside

Osidic-Osidic bond

OH lié au carbone anomérique

2 sugars linked by the hemiacetal OH groups through a Osidic-Osidic bond.



Both hemiacetal OH groups are involved in the glycosidic bond

The diholoside is non-reducing

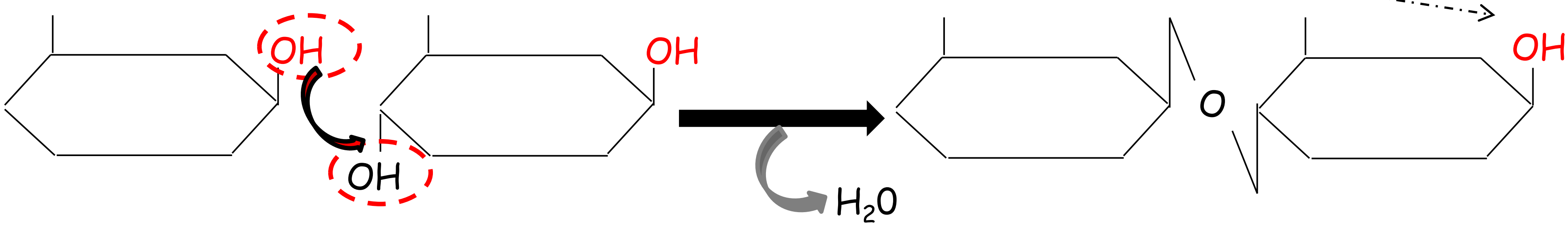
Disaccharides: diholosides

Reducing diholoside

Liaison Osidic-Ose

2 sugars interact via a hemiacetal hydroxyl group of one sugar and an alcohol function Osido-Ose.

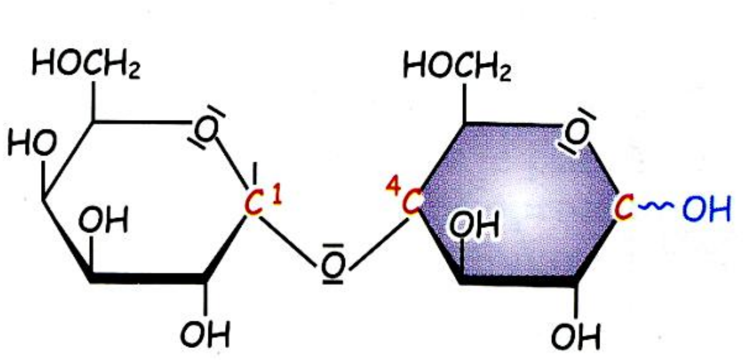
The remaining free hemiacetal hydroxyl group is responsible for the reducing ability of the diholoside.



Disaccharides: diholosides

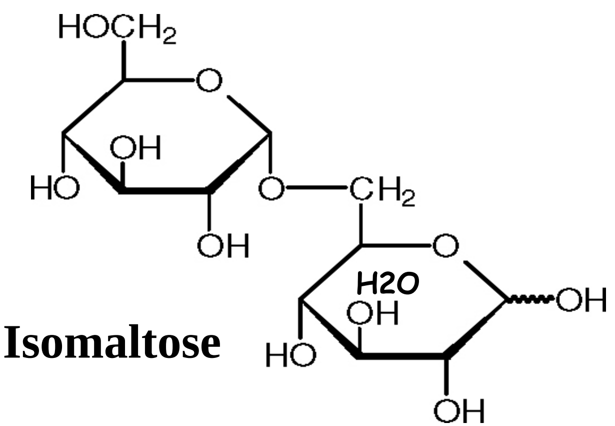
Maltose and Isomaltose

- sucres of malt
- Hydrolysis $\rightarrow$ 2 molécules of glucose
- basic constituent of starch and glycogen



Maltose

2 glucoses α (1,4))-glycosidic bond



Isomaltose

2 glucoses α (1,6)-glycosidique bond

α D glucopyranosyl (1,4) glucopyranose

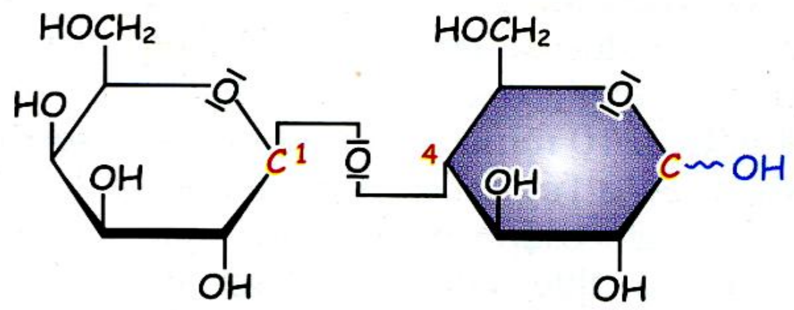
α D glucopyranosyl (1,6) glucopyranose

Reducing sugars because each has a free hemiacetal hydroxyl group

Disaccharides: diholosides

Lactose

- Milk sugar from mammals
- Composed of glucose and galactose
- Substrate for lactic acid fermentation by lactobacilli, fundamental to cheese fermentation.



Lactose

Glucose+galactose β (1,4)-glycosidic bond

⬇

β D galactopyranosyl (1,4) glucopyranose

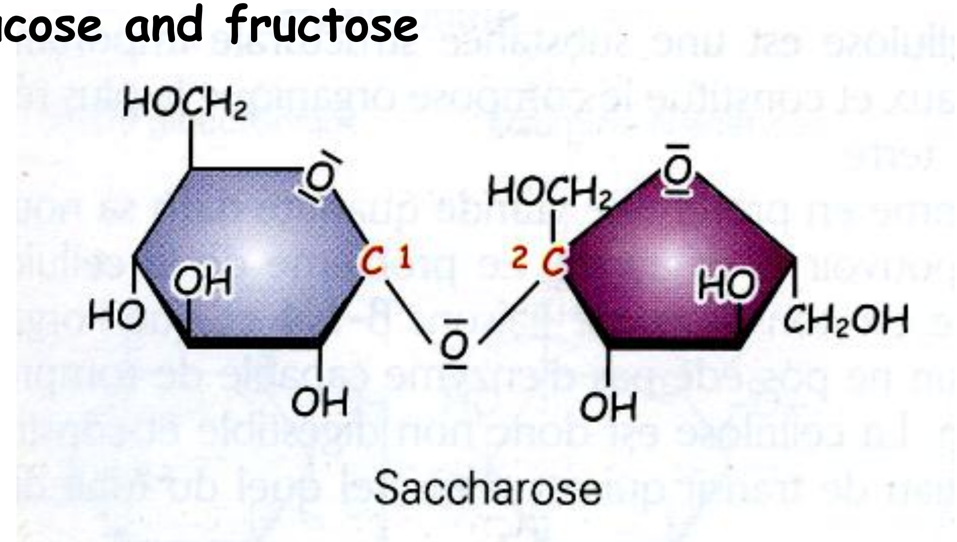
⬇

Reducing because it has a free hemiacetal hydroxyl

Disaccharides: diholosides

Saccharose

- Cane sugar and beet sugar
- Composed of glucose and fructose



Glucose + fructose α (1,2)-glycosidic bond

⇩

α D glucopyranosyl (1,2) α fructofuranoside

⇩

Non-reducing because it does not contain a free hemiacetal hydroxyl
Both are involved in the glycosidic bond

Oligosaccharides: polysaccharides

Homoglycans

- Consisting of a single type of monosaccharides
  - Storage sugar: amidon, glycogène, dextran
  - Structural sugar : cellulose, chitine

Heteroglycans

- Consisting of différents types of monosaccharides
- Often bound to proteins or lipids

Glycoproteins

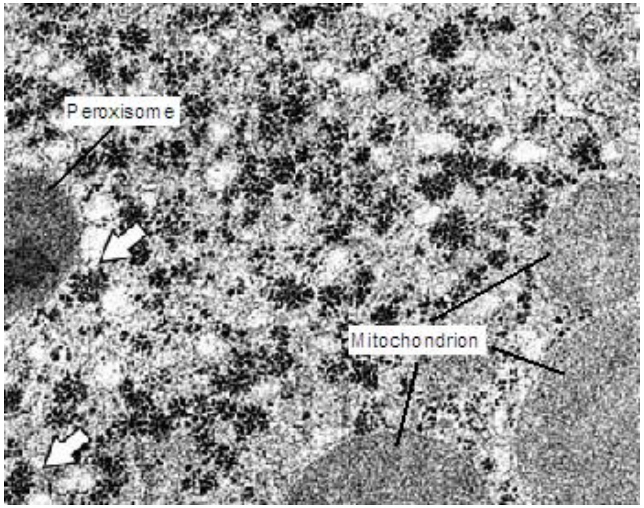
Glycolipids

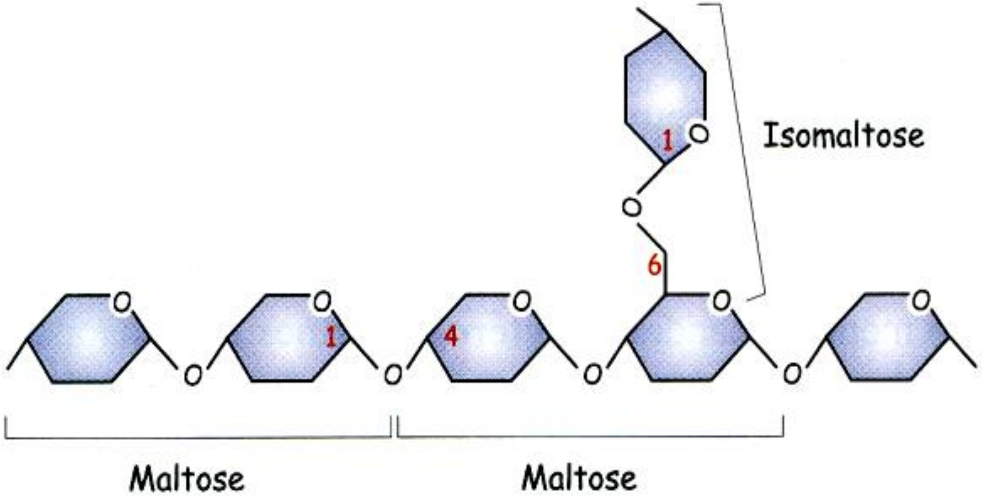
Oligosaccharides: polysaccharides

Storage Homoglycans

Glycogen

- α-1,4 bond and α-1,6 bond
- Primary storage substance in mammals
- Main storage sites in muscle and liver





Glycogen

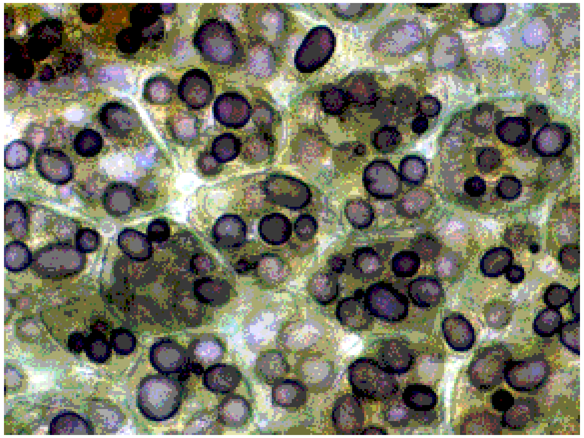
Oligosaccharides: polysaccharides

Storage Homoglycans

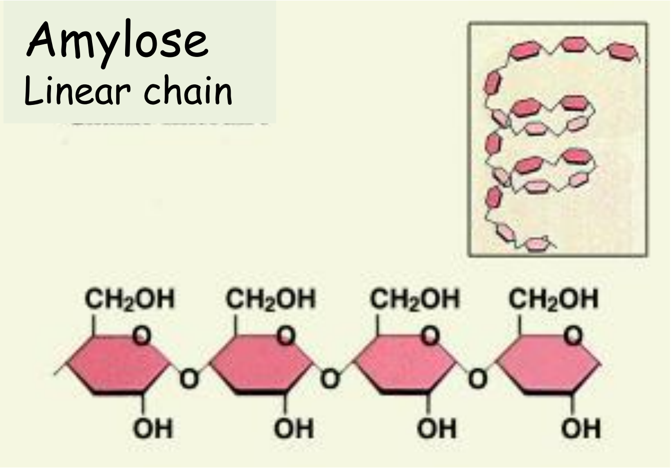
Starch

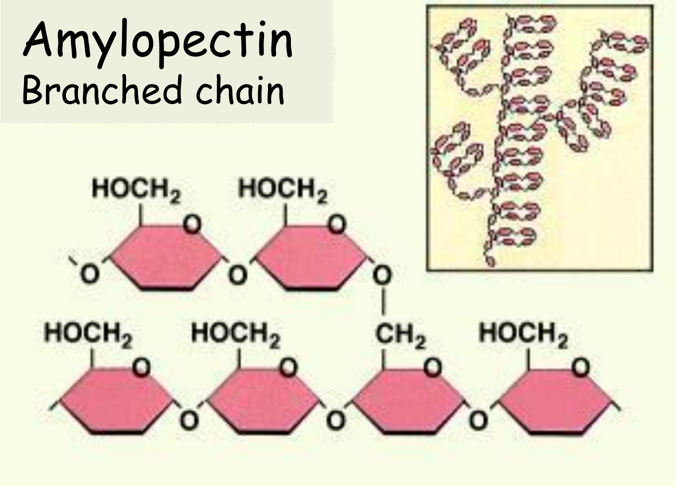
- Composed of two types of glucose polymers :
  - l'amylose (linear chain), α-1,4 bond
  - l'amylopectin (branched chain), α-1,4 and α-1,6 bonds.
- Can contain between 100 and 20 000 glucose units

- Storage sugar of plants (roots, seeds, and fruits).
- Abundant in cereals (rice, wheat, corn, etc.) and tubers (potatoes).



Starch grains in potato cells



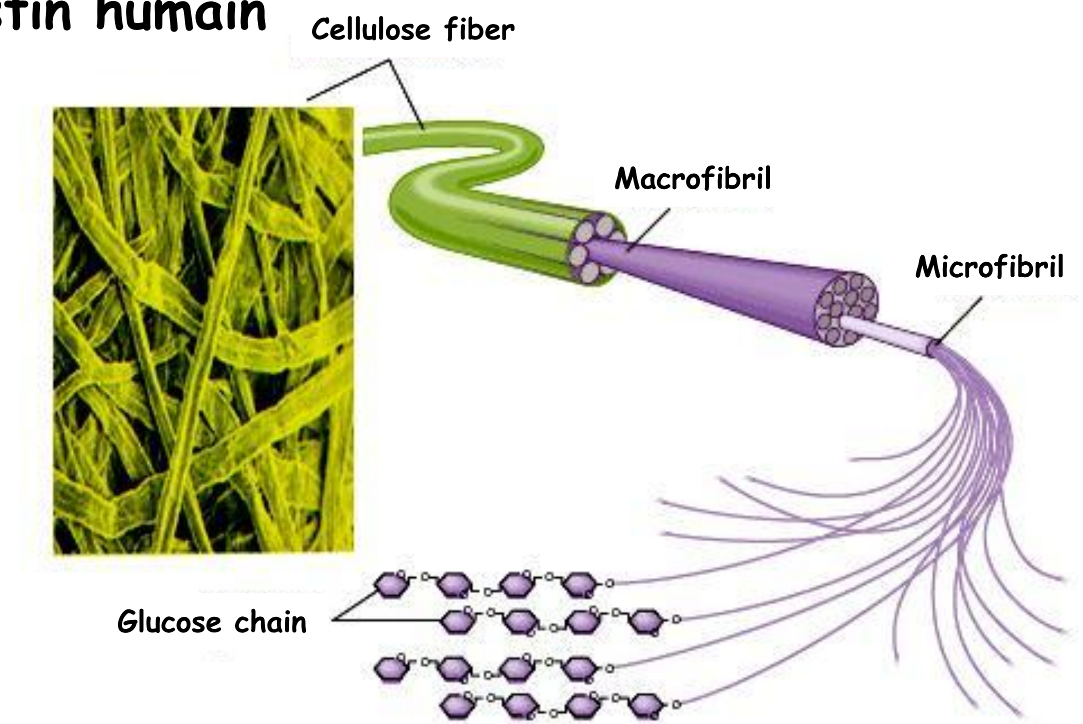


Oligosaccharides: polysaccharides

Structural Homoglycans

Cellulose

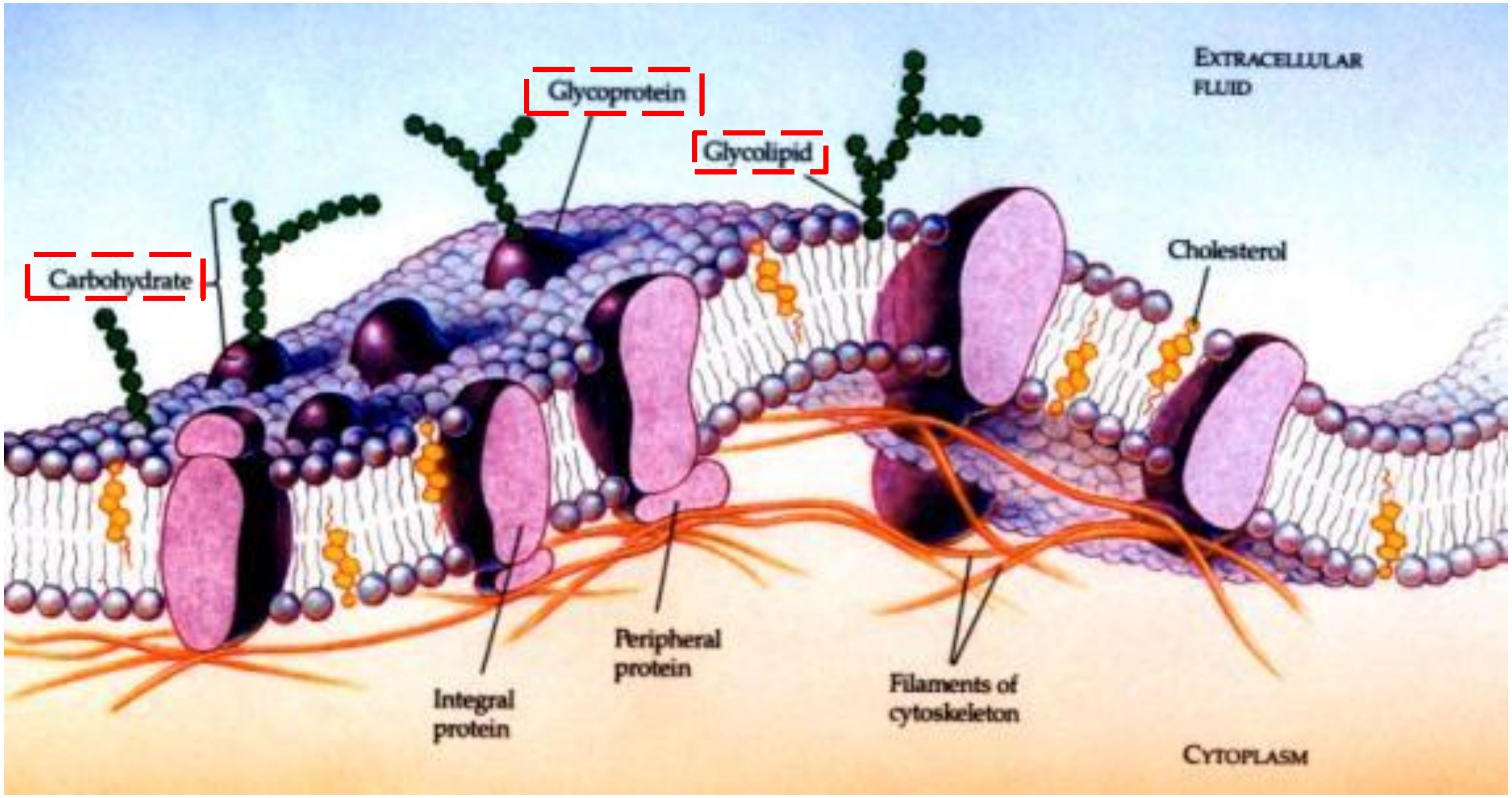
- Linear polymer of glucose, β-1,4 glycosidic bond
- Major component of plant cell walls, providing stuctural support and rigidity.
- pas dégradé dans l'intestin humain



Oligosaccharides: polysaccharides

Heteroglycans

Glycoproteins et Glycolipids of cell membrane



Oligosaccharides: polysaccharides

Type	Sugar	Structure	Function
Homoglycans/ Homopolysaccharids	Starch	Glucose α-1,4; α-1,6	Glucose storage in plants
	Glycogen	Glucose α-1,4; α-1,6	Glucose storage in mammals
	Cellulose	Glucose β-1,4	Plant structure
Heteroglycans/ Heteropolysaccharids	Proteoglycans	Glycoseaminoglycans Repetitive units	Main component of extracellular matrix
	Peptidoglycans	N-acetyl-glucosamin Acid N-acetyt-muramic	Bacterial cell wall
	Glycoproteins	Up to 20 residues monosaccharidic	Plasma proteins
	Glycolipids	Up to 20 residues monosaccharidic	Membrane constituent