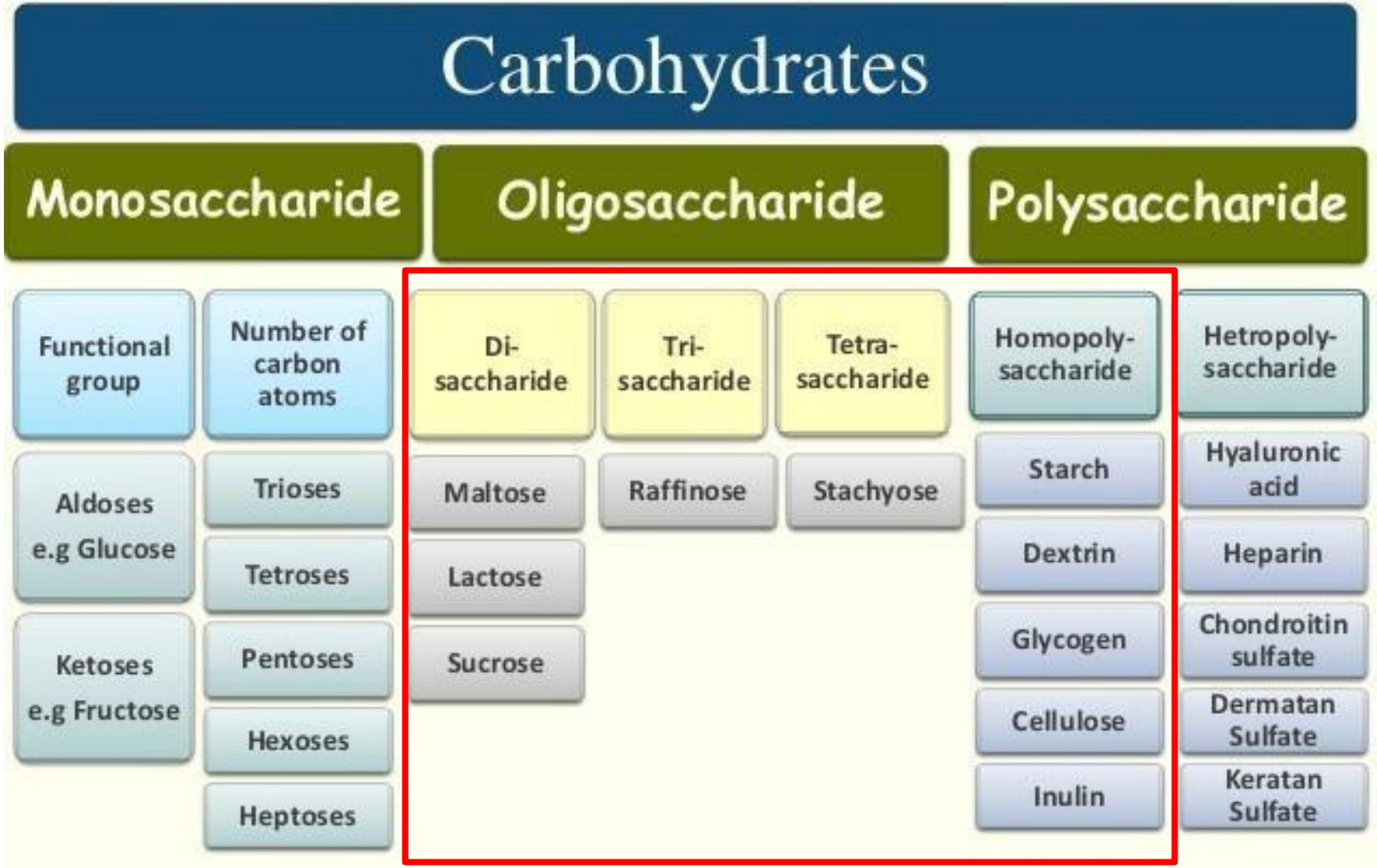
Carbohydrates of biological importance- lecture 3

Ahmed Salem, MBBCH, MSc, PhD, FRCR
asalem@hu.edu.jo

Majority of sides: Dr. Walaa Bayoumie El Gazzar

Classification and Nomenclature



Disaccharides

- Two monosaccharides can be joined by a glycosidic bond (covalent between the hydroxyl group of anomeric carbon) with the loss of a water molecule to make **disaccharides**
- The glycosidic bond always involves the anomeric carbon of one participating sugar. The 2^{nd} sugar participates in this bond by using either:

  - Its anomeric carbon: in this case, the disaccharide (as sucrose) has no free reactive group.
  - A carbon other than the anomeric one. In this case the disaccharide will have a free reactive group and shows reducing character

- The glycosidic linkage is named according to:
  - anomeric carbon to which it is attached (α or β)
  - according to the parent sugar e.g. glucosidic, galactosidic or fructosidic bond

- The most important disaccharides widely distributed in nature are:

Reducing disaccharides:

1. Lactose.

2. Maltose.

3. Isomaltose.

4. Cellobiose (formed of two β glucose)

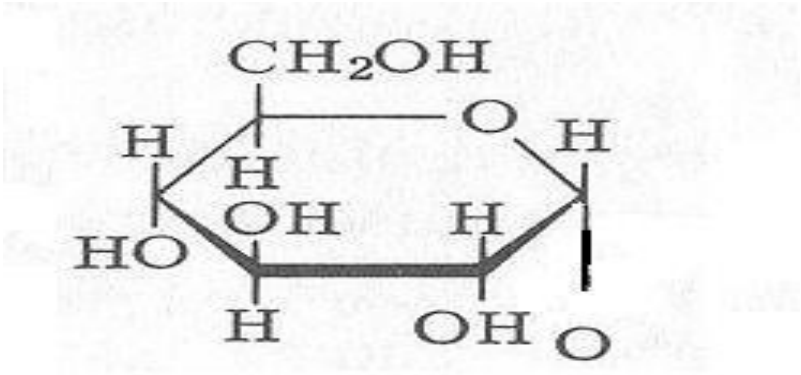
Non-reducing disaccharides:

1. Sucrose.

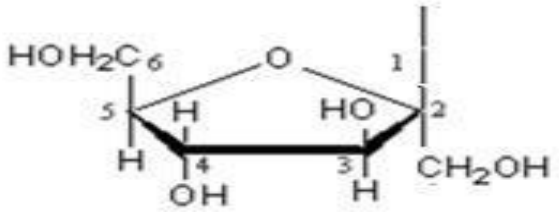
- **1. Sucrose:**
- It is called cane or beet sugar
- It is the common sugar of the table & the kitchen so, it is called table sugar
- It is formed of α-glucose & β-fructose linked together by **α-1, β-2 glucosidic linkage**

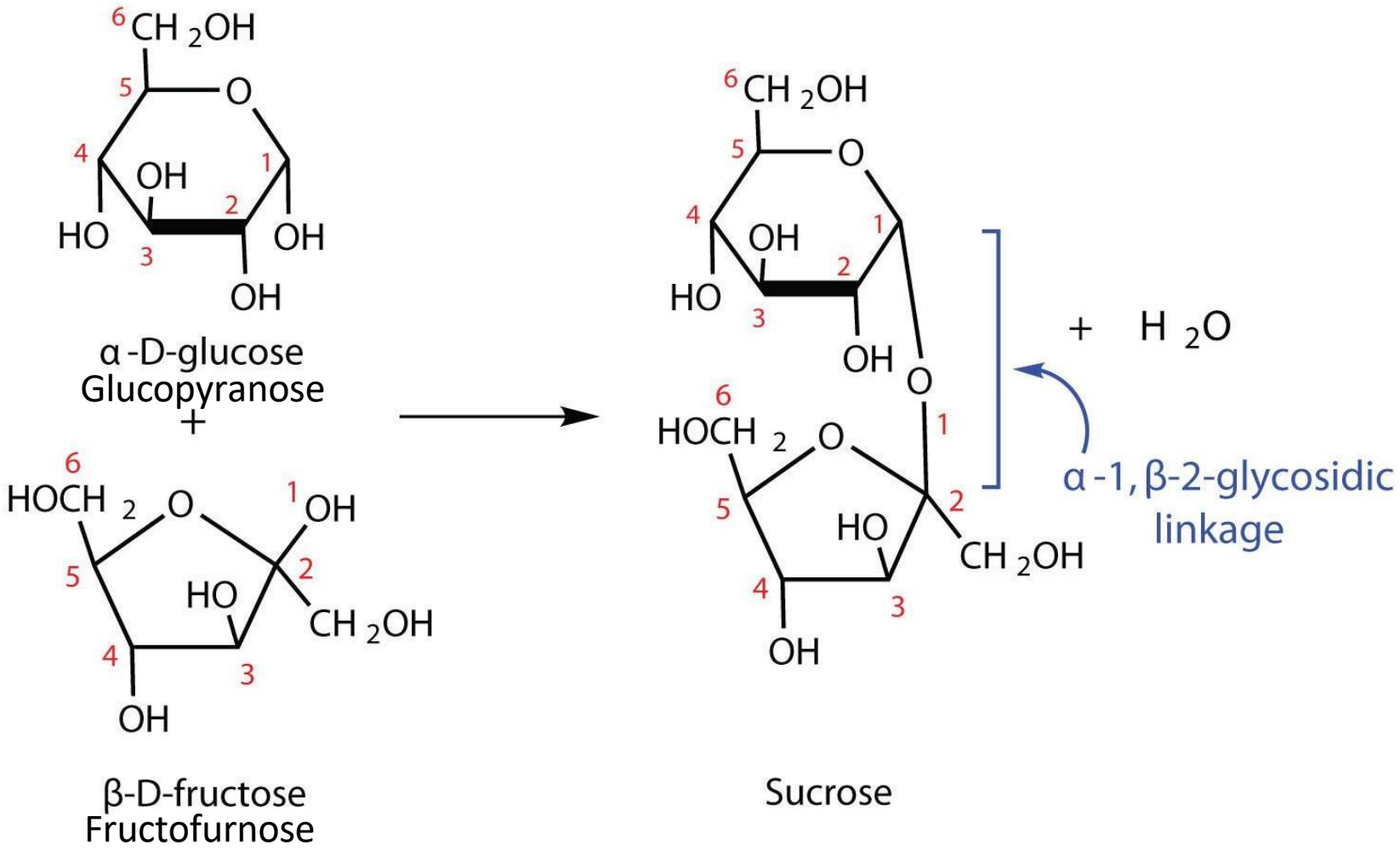
- Sucrose is digested by the enzyme sucrase which is present on the brush border membrane of small intestinal mucosa into glucose and fructose

α-D-Glucopyranose



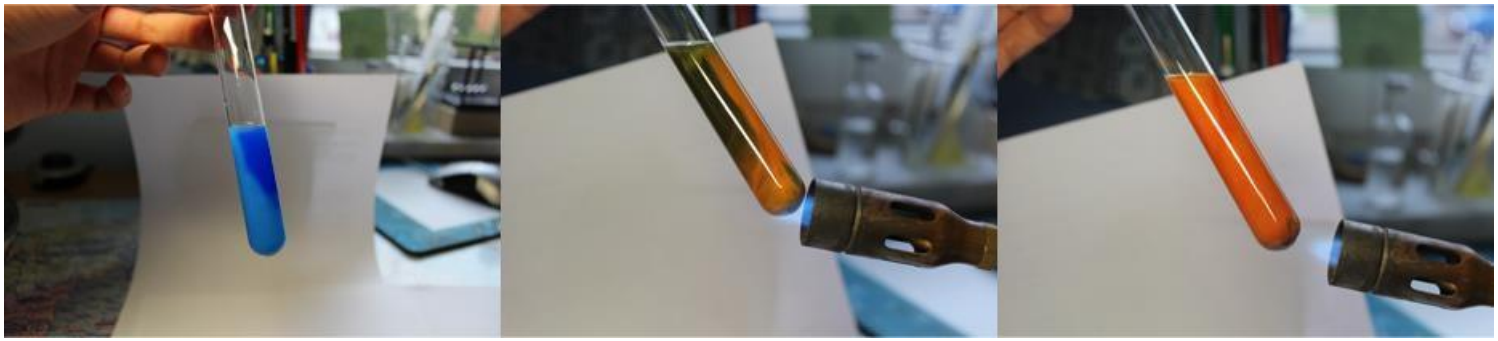
β-D-Fructofuranose

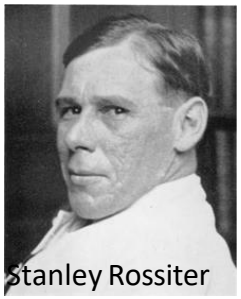



α -D-glucose
Glucopyranose
+
β-D-fructose
Fructofurnose
Sucrose
+ H 2O
α -1, β-2-glycosidic
linkage

Reducing vs non-reducing sugars

- **Benedict's reagent:** Chemical reagent of sodium carbonate, sodium citrate, and copper(II) sulfate pentahydrate
- Detects the presence of aldehydes or ketones (active & **free** carbonyl group)
- If oxygen group on the carbonyl group is not attached to any other structure, the sugar is reducing
- Oxidation of the reducing sugar by the cupric (Cu^{2+}) complex of the reagent produces a cuprous (Cu^{+}), which precipitates as insoluble red copper(I) oxide (Cu_2O)





Stanley Rossiter Benedict

- Sucrose is a **Non-reducing sugar:** because the reducing groups of both glucose & fructose are involved in the linkage between the two sugars. **So,** They cancel the action of each other.

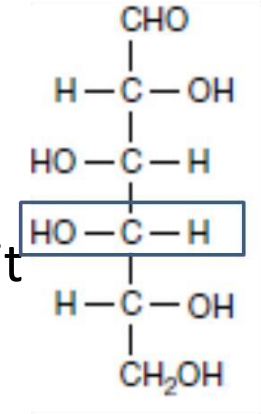
- **Invert sugar:**
- Sucrose before hydrolysis is dextrorotatory

* After hydrolysis by ***sucrase or invertase***, It gives a mixture of D-glucose ($\alpha = +52.5^{\circ}$) and D-fructose ($\alpha = -92^{\circ}$) which is **levorotatory**.

*This change from dextro (before hydrolysis) to levo- (after hydrolysis) called inversion and the sugar is called invert sugar (equimolecular mixture of glucose and fructose is called invert sugar)

2. Lactose:

- It is also called milk sugar
- It is formed of one glucose unit & another one galactose unit
- Usually appear in urine of pregnant female

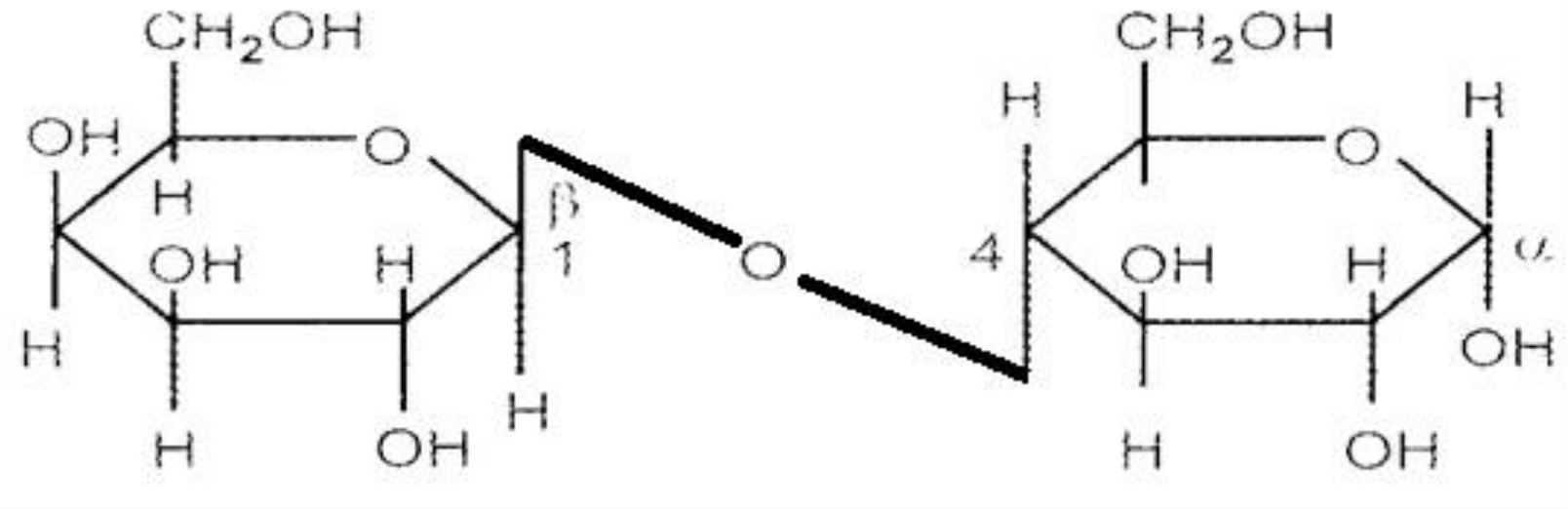


D-Galactose

- Less sweaty → not block the appetite Lactose (appropriate for infants as it is less sweet and babies tolerate large volumes of milk)
- It can be digested by ***lactase enzyme***
- Deficiency of this enzyme leads to **lactose intolerance** which cause distension & diarrhea.

β- D-Galactopyranose

α-D-Glucopyranose



B-1,4 galactosidic linkage

Is lactose a reducing sugar?

Lactose intolerance

- Lactase deficiency:
    - Congenital: due to defect in gene producing enzyme
    - Acquired: after surgery in GI tract or infections

- Lactose accumulates in small bowel

- Osmotic effect of unabsorbed lactose leads to influx of fluid

- Symptoms: Nausea, colic, distention and diarrhoea after milk intake

3. Maltose:

-It is called malt sugar

-The main product of digestion of starch by amylase.

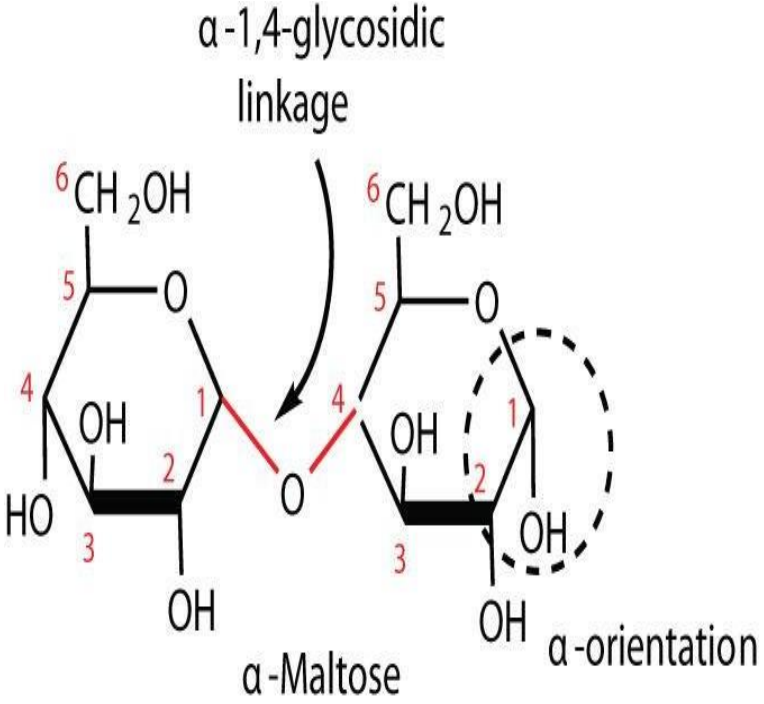
-It is present in 2 forms :

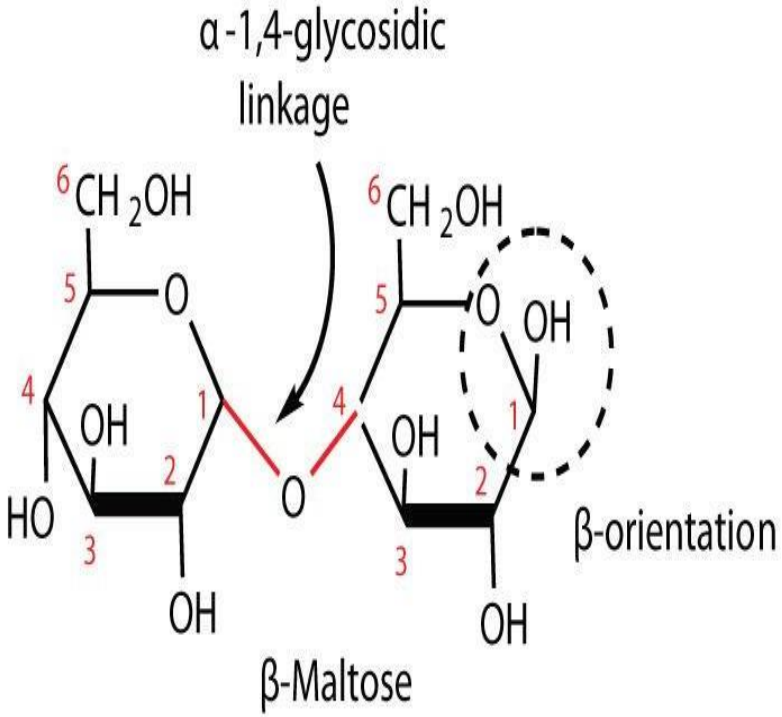
(α- maltose form) = α-glucose + α-glucose

(B-maltose form) = α-glucose + B-glucose

-It is a reducing sugar

Maltose gives the sweet taste that you feel if you **masticate** (chew) bread for a long time

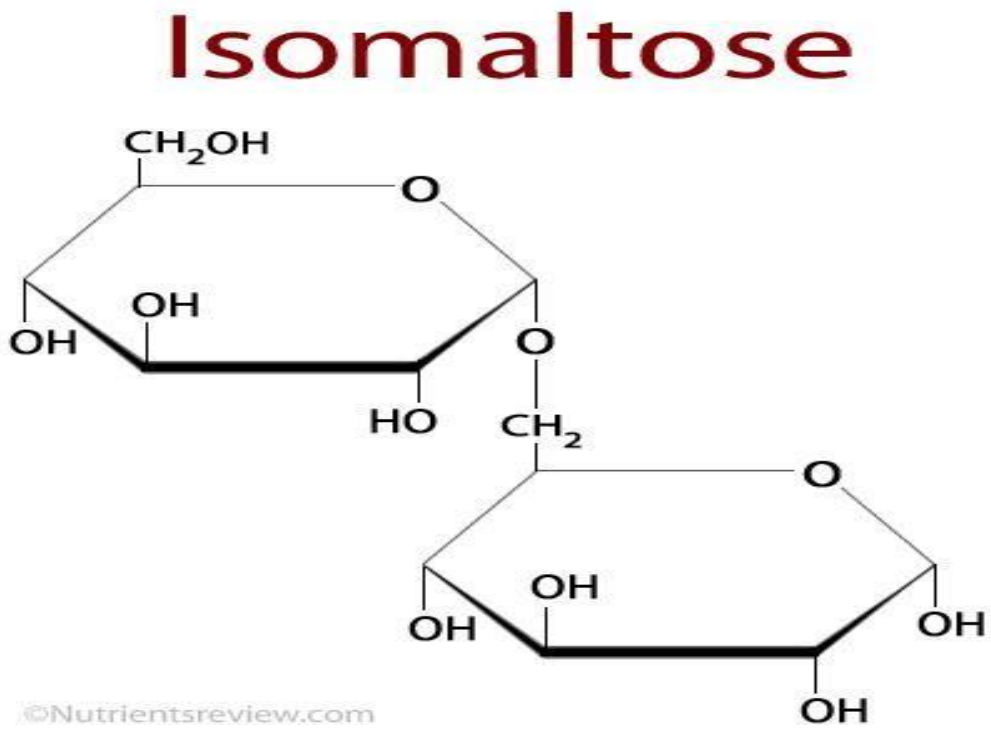


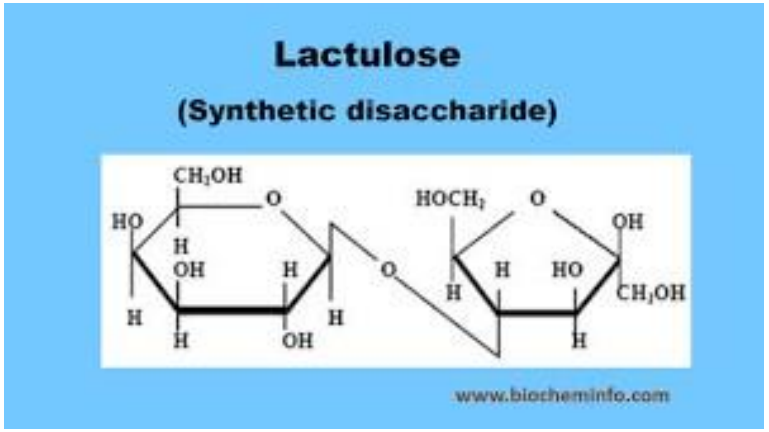


They can be present either in α– or β-form

- This occurs if the second monosaccharide residue of the disaccharide contains a free anomeric carbon atom which has the ability to be present in α or β-form

❖ Isomaltose is similar to maltose but the linkage is α-1,6-glucosidic. It is **one of the hydrolysis products of starch and glycogen by amylase.**





Lactulose

It is a disaccharide composed of galactose and fructose linked through β 1-4 –glycosidic bond, linking β -1 galctosyl carbon to carbon number 4 of fructose.

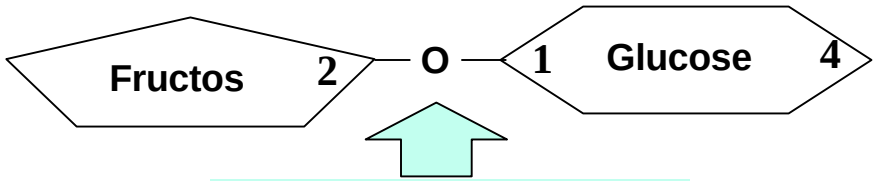
is a laxative used in treating constipation and improving ammonia and bacterial product toxic load in liver failure patients

It works by drawing ammonia from the blood into the colon where it is removed from the body.

It is a non-digestible, and therefore non-absorbable

It produces an osmotic effect that retains water in the gut which softens stools

Molecular Structures of Some Important Sugars: Disaccharides



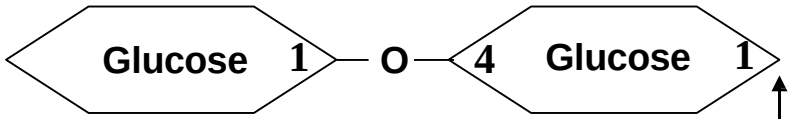
Sucrose

(table or cane sugar)

Non-reducing sugar

1-α, 2β-glycosidic bond

Bond between aldehyde group of glucose on CA No 1 and ketone group of fructose on CA No 2, blocks the two groups and hence sucrose is a non-reducing sugar.



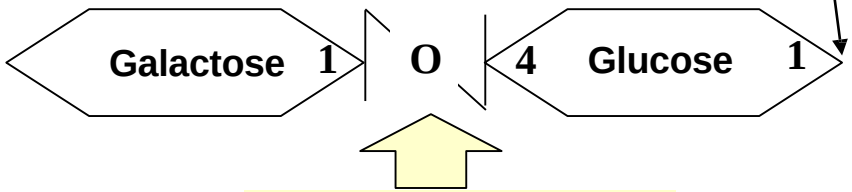
Maltose

(malt sugar)

Reducing sugar

α-1,4-glucosidic bond

Free aldehyde group



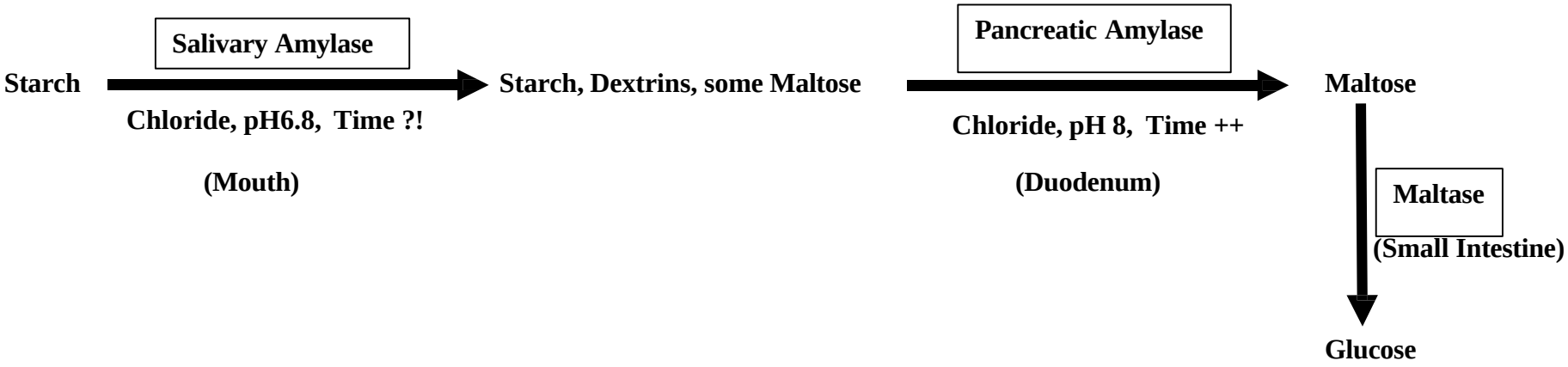
Lactose

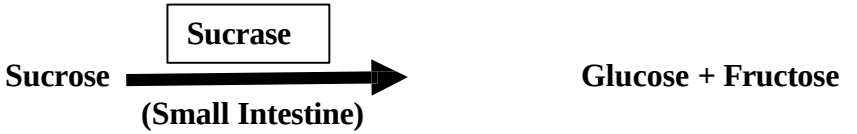
(milk sugar)

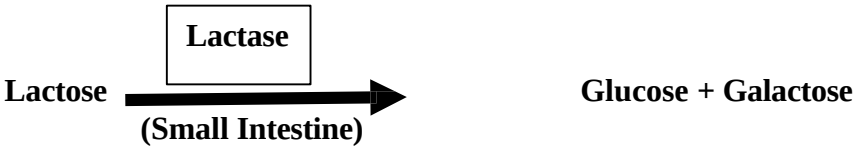
Reducing sugar

β-1,4-glycosidic bond

Digestion of Starch:







N.B: There is no digestion of cellulose in Man as humans lack β-1,4-glucosidase the enzyme needed to digest cellulose

Oligosaccharides

- 3-10 monosaccharide units
- Most are indigestible
- Present in glycolipids/ glycoproteins
- Raffinose: non-reducing trisaccharide (galactose, glucose, fructose), fermented by bacteria, used for their identification

Polysaccharides

- Polysaccharides are carbohydrates of high molecular weight
- 10 or more monosaccharide units linked by glyosidic bond
- They are widely distributed in nature
- As condensation involves carbonyl group, they are non-reducing
- Upon hydrolysis by acid or specific enzyme, monosaccharides or its derivatives are produced.

- **Polysaccharides are classified chemically & functionally as follows:**

- **1- Homogeneous polysaccharides:** These are polysaccharides which **give single type of sugar on hydrolysis** as D-glucose units or D- fructose units.

- **2-Heterogeneous polysaccharides:** These are polysaccharides which **give on hydrolysis different type of sugars associated with other substances.** **e.g.** D-Glucosamine, D-glucuronic acid, N-acetyl neuraminic acid. etc.

Different homopolysaccharides of biological importance:

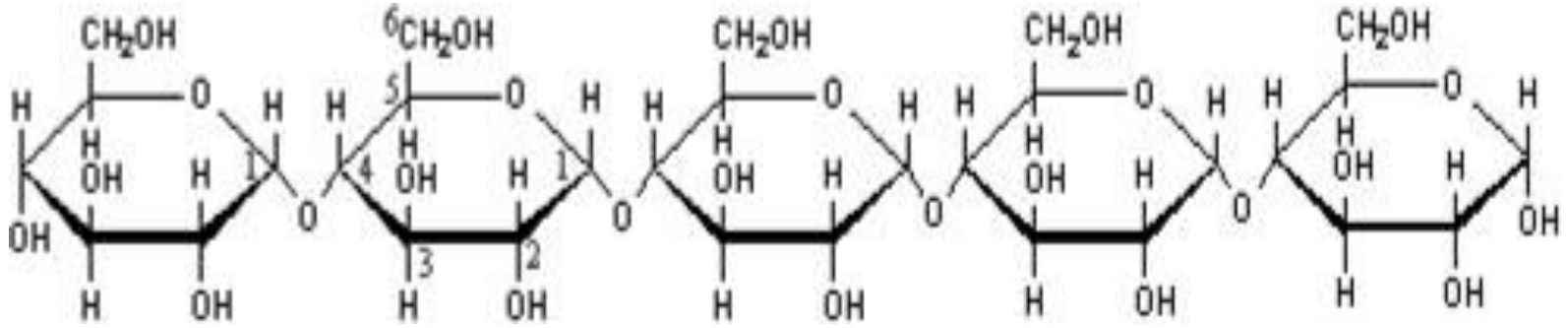
- **1- Starch:**

- It is the storage form of carbohydrates in plants (never present in animals)

- On hydrolysis, it gives only glucose and so it is called **glucosans**.

- It consists of two types of molecules, **amylose** and **amylopectin**

Structure of amylose:

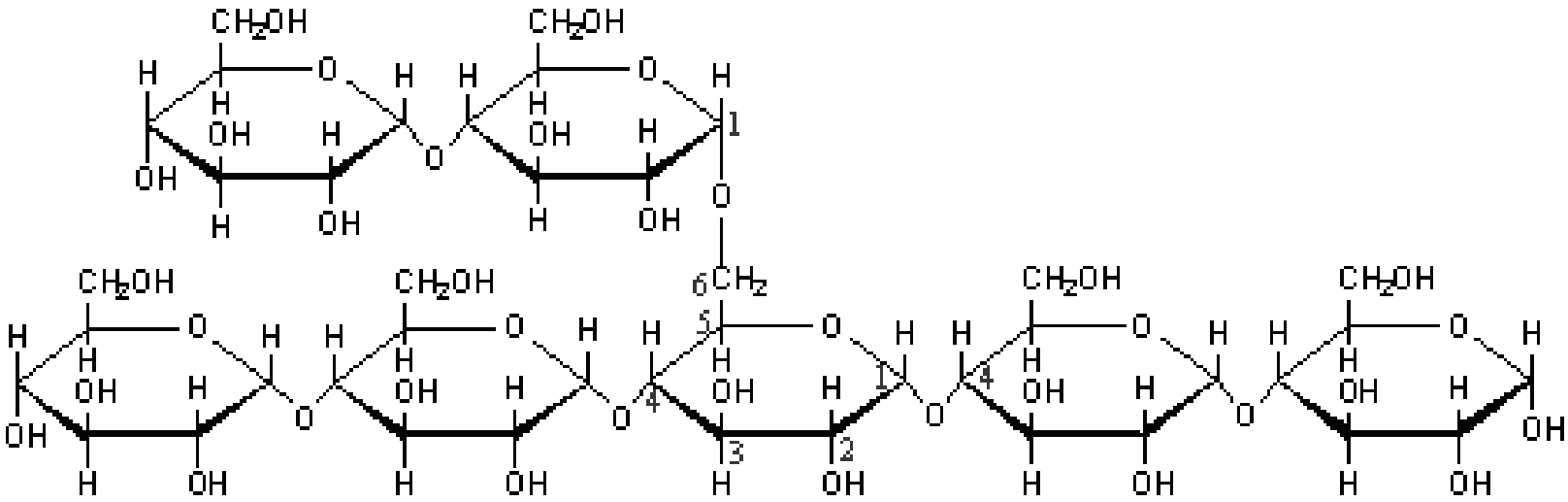


Long, **non-branched** chain of 300-400 (up to 1000) **α glucose units** linked together by α-1,4 glucosidic bond.

Forms 15-20% of the starch granules.

It is found in the inner part of the molecule

Structure of amylopectin



Branched chain of α glucose units linked together by α-1,4 glucosidic bond while at the branching point, it forms α- 1, 6 glucosidic bond

Forms 80-85% of the starch granules.

It is found in the outer part of the starch molecule

- **Hydrolysis of starch occurs either by:**
  - Dilute mineral acids and called acid hydrolysis which results in complete hydrolysis to α glucose units .
  - Enzymes as **α-amylase** (salivary & pancreatic) which results in partial hydrolysis producing smaller molecules called dextrins and maltose.

- The products of starch hydrolysis occur according to the following sequence:
- **Starch → Amylodextrin (the earliest dextrin produced; blue with iodine) → Erythrodextrin (red) → Achrodextrin (no colour) → Isomaltose & Maltose → Glucose.**

- Dextrins are a group of low-molecular-weight polysaccharides produced by the hydrolysis of starch or glycogen

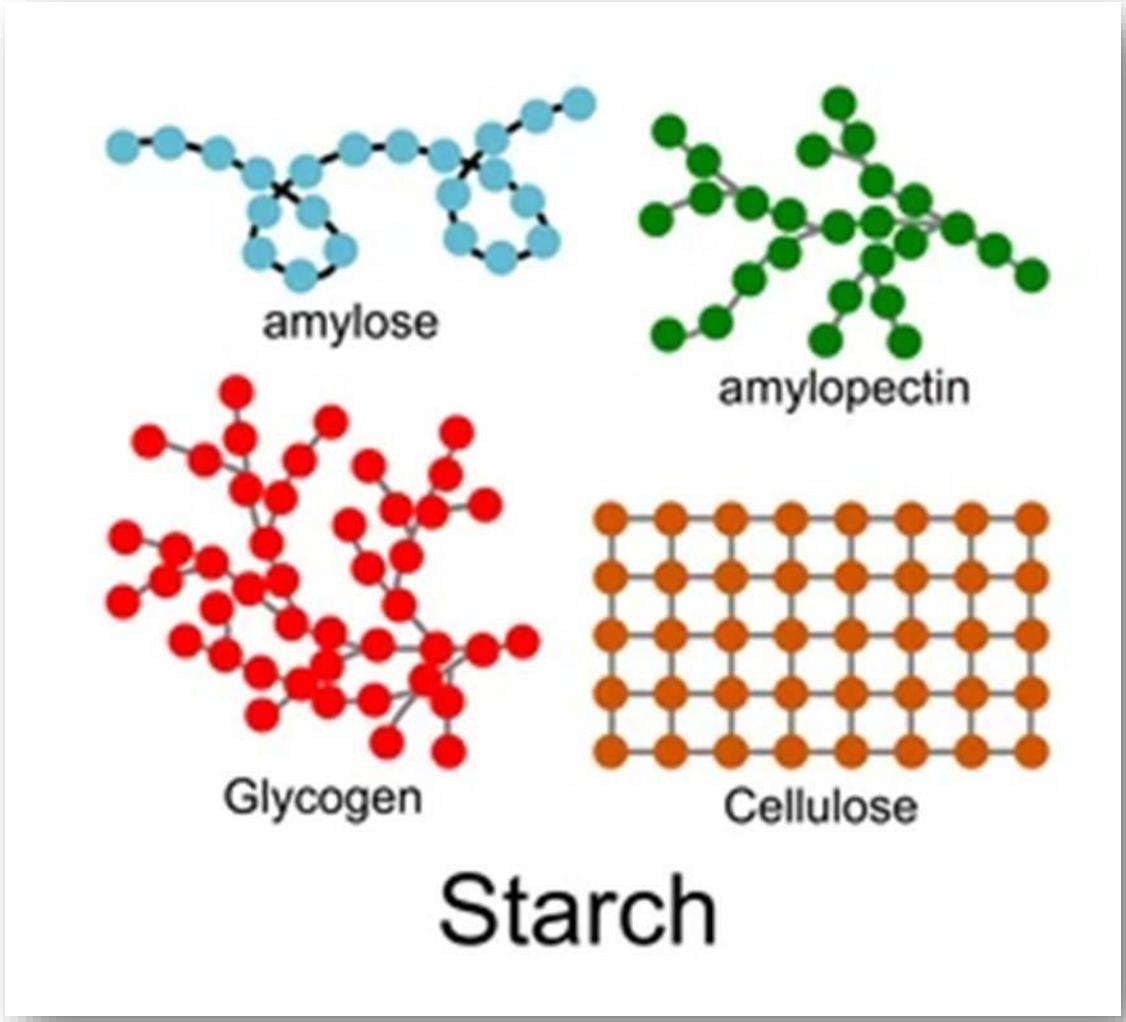
- **Question: which is produced more, isomaltose or maltose?**

- **(N.B.***)*: The difference between maltose and isomaltose in the bond position as it is α-1, 4 in maltose but α-1, 6 in isomaltose (i.e. at the point of branching of starch).

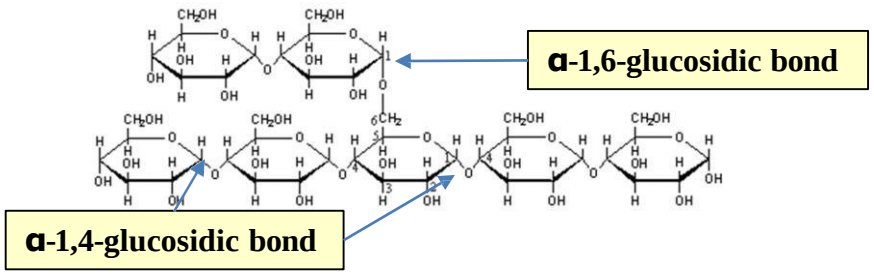
- It is to be noted that hydrolysis of starch by boiling with dilute acids ends in the formation of glucose.

2- Glycogen (animal starch):

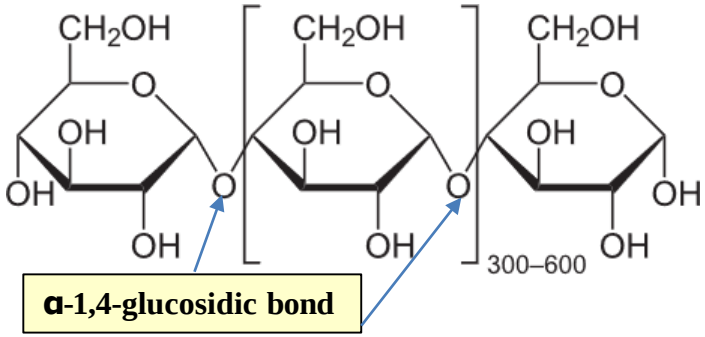
- It is the reserve carbohydrate of animals, and hence the name **animal starch**
- It is similar in its structure to amylopectin
- It is **highly branched** formed of **α** 1, 4 link and 1, 6 at the site of branching.
- Each branch is made of **12-14 glucose units**.
  (It has shorter and more numerous chains)
- Inner chains are branched, outer chains are not
- **It is stored in liver & muscle.**


amylose
amylopectin
Glycogen
Cellulose
Starch

Starch (amylopectin form)



Starch (amylose form)

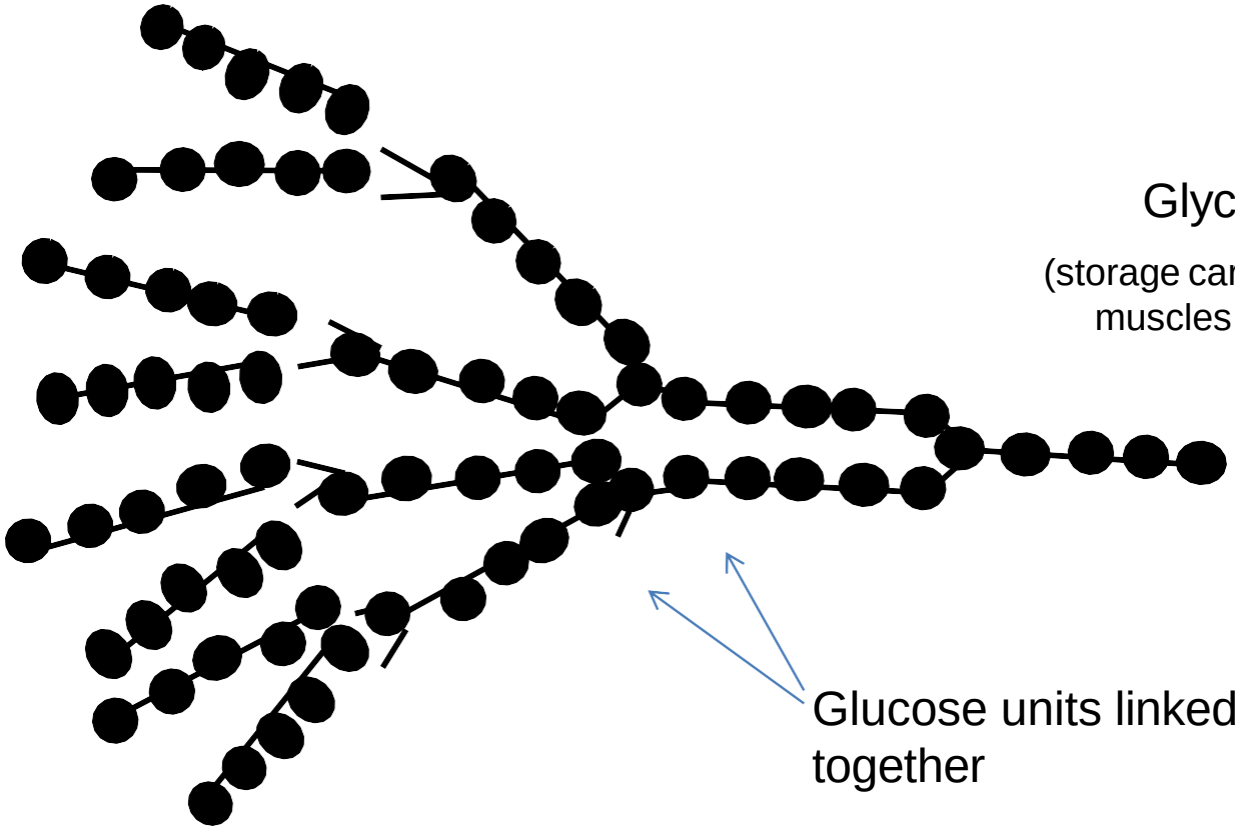


Glycogen in animals is a more branched version of amylopectin.

Amylose was traditionally thought to be completely unbranched, but it is now known that some of its molecules contain a few branch points.

Although only about one quarter of the starch granules in plants consists of amylose, there are about 150 times more amylose molecules than amylopectin molecules because they have smaller masses.

Starch is digested briefly by salivary amylase in the mouth but is mainly digested in the duodenum and jejunum by pancreatic amylase in alkaline medium in the presence of chloride ions to gradually break into dextrins and finally produces maltose.

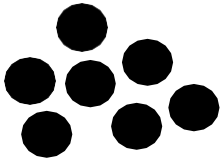


Glycogen

(storage carbohydrate in muscles and liver)

Glucose units linked together

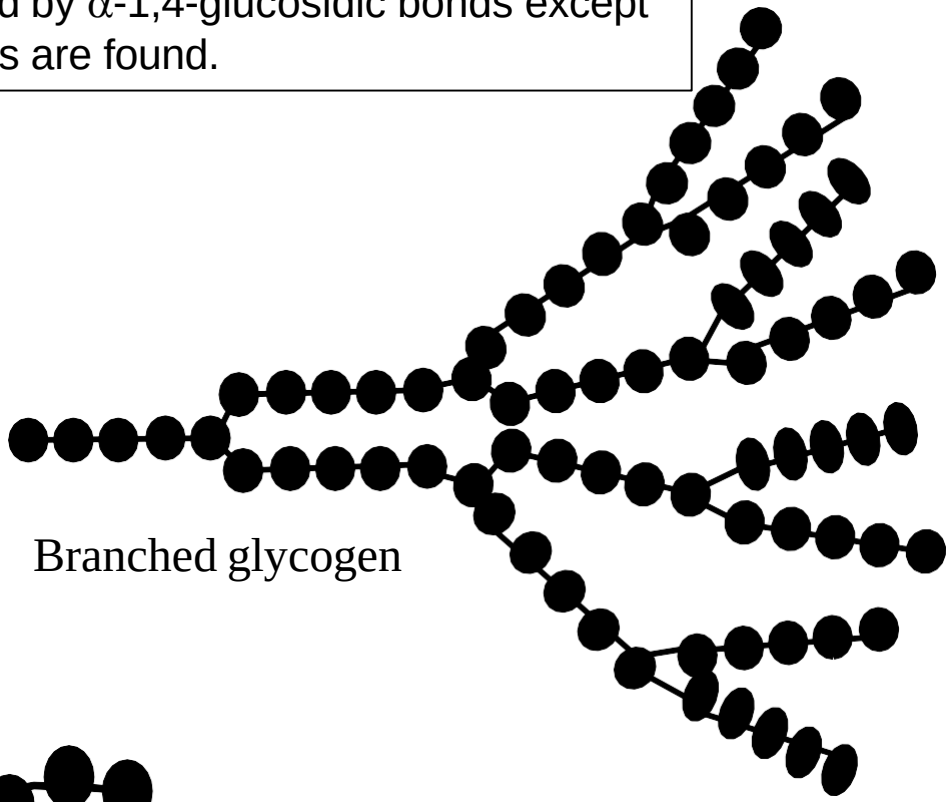
The Homo-polysaccharides glycogen (in animals) and starch (in plants) are made of repeated α-D glucose residues linked by α-1,4-glucosidic bonds except at branch points where α-1,6-glucosidic bonds are found.



Separate α-D-glucose monomers

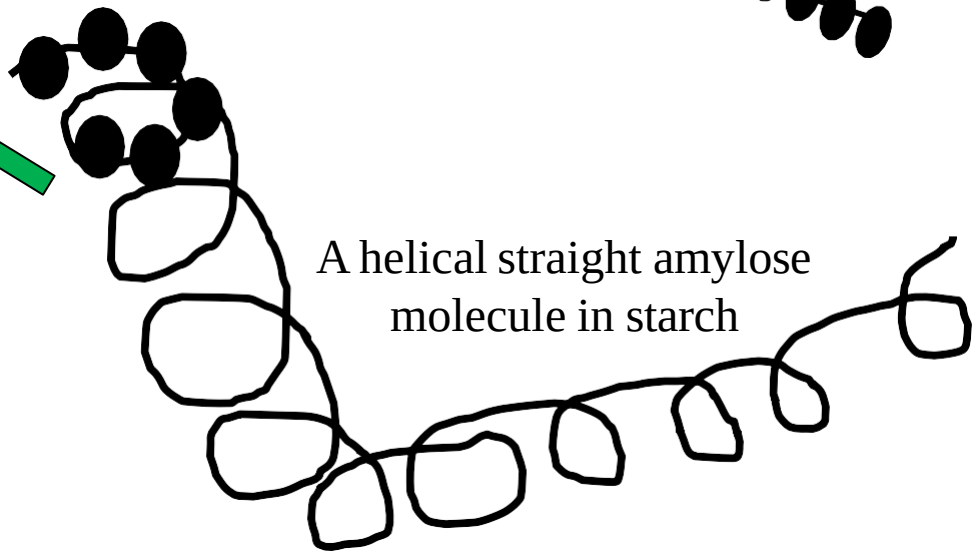
Glycogenesis in liver and muscles

Glycogenolysis in liver (muscles produce lactate)



Branched glycogen

Salivary and pancreatic amylase followed by intestinal maltase Digestion



A helical straight amylose molecule in starch

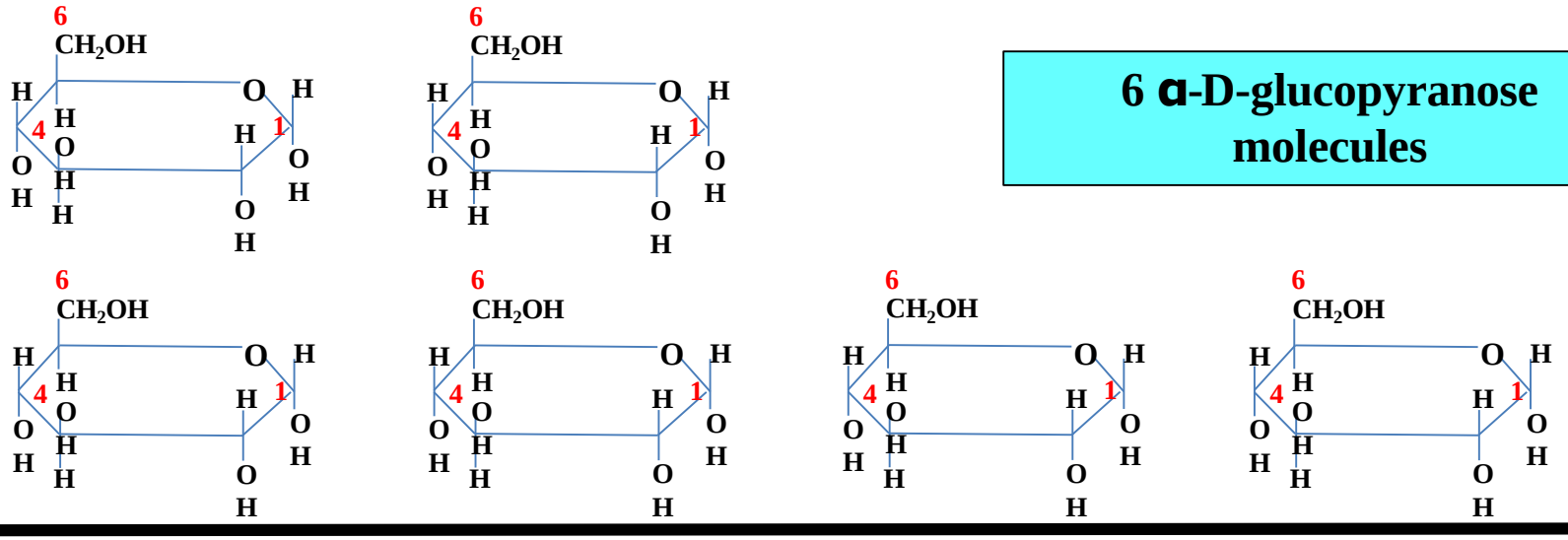
AMYLOPECTIN

VERSUS

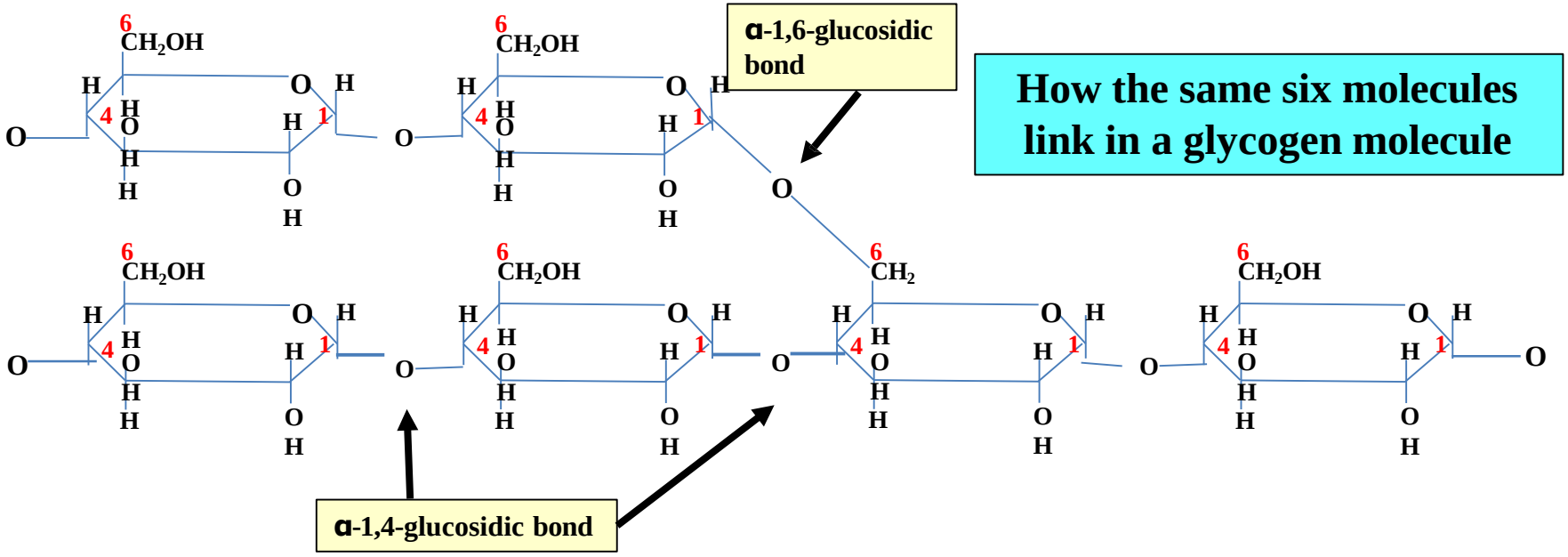
GLYCOGEN

AMYLOPECTIN	GLYCOGEN
Amylopectin is a branched-chain polysaccharide, which is found in plants	Glycogen is the storage polysaccharide of animals and fungi
Storage polysaccharide in plants	Storage polysaccharide in animals
Formed by the polymerization of glucose	Formed by a combination of amylose and amylopectin
A branched polymer	Highly branched when compared to amylopectin
Can be broken down by amylase	Hydrolyzed when it is dissolved in water

Basic Structure for Glycogen and Starch (Amylopectin)



6 α-D-glucopyranose molecules



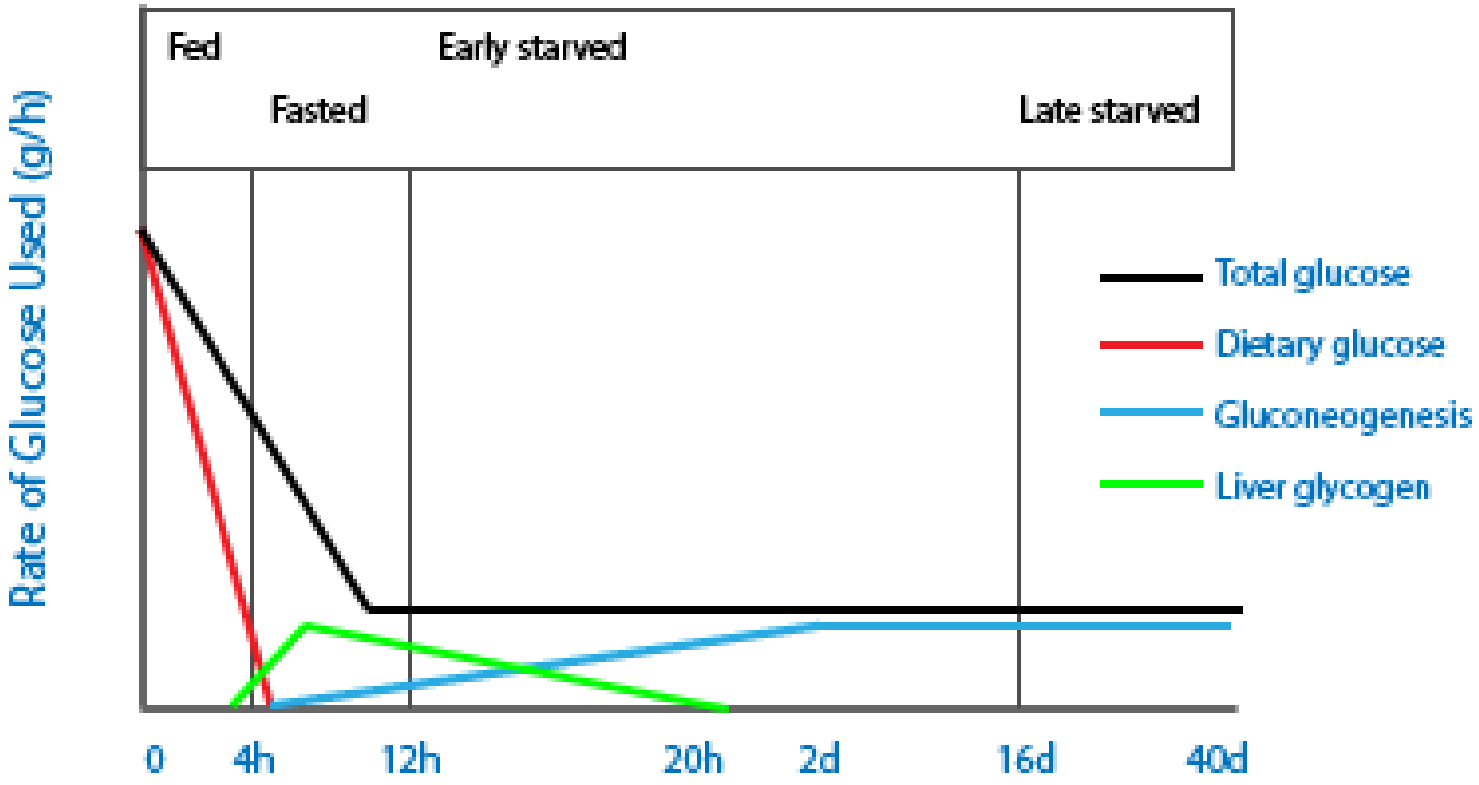
How the same six molecules link in a glycogen molecule

Functions of glycogen :

- Liver glycogen maintains normal blood glucose concentration especially during the early stage of fasting (between meals)

- After 12 -18 hours fasting, liver glycogen is depleted

- Muscle glycogen acts as a source of energy within the muscle itself especially during muscle contraction.


Fed
Fasted
Early starved
Late starved
Rate of Glucose Used (g/h)
Total glucose
Dietary glucose
Gluconeogenesis
Liver glycogen
0
4h
12h
20h
2d
16d
40d

3- Cellulose:

- It is long **unbranched** polysaccharide of **β-glucose units** linked together by **β 1,4glucosidic bond**

- It is the main structural molecules in cell walls of plants. Cotton is almost pure cellulose

- Many mammals including humans cannot digest cellulose of diet because of the **absence of digestive enzyme that attacks β-linkage.**

(β 1,4 linkages are not hydrolized by **α amylase**)

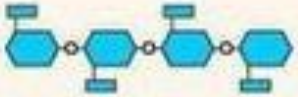
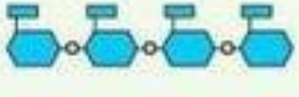
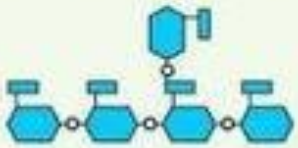
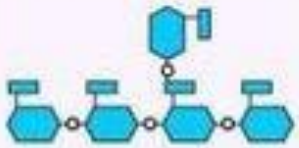
- The presence of cellulose in diet is important because it increases the bulk of stool

- This stimulate intestinal peristalses & prevent constipation (laxative)

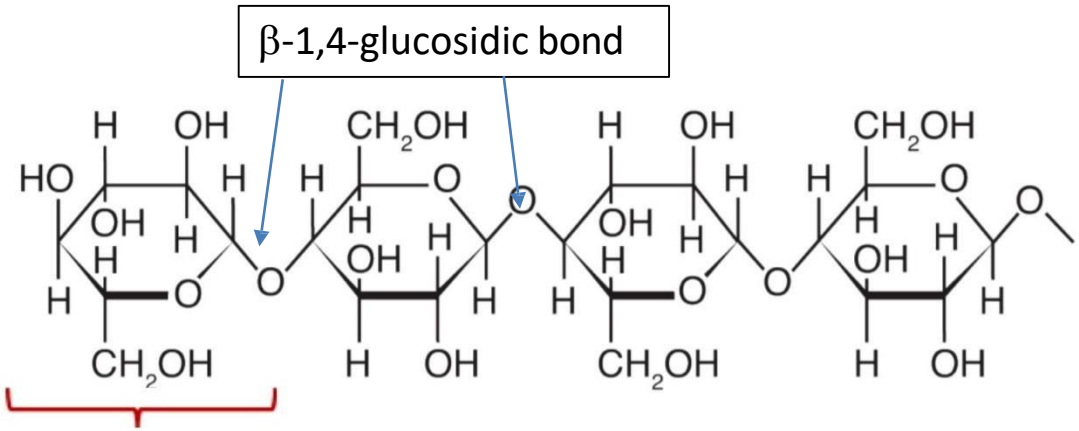
- Cellulose is a constituent of dietary fibers. These fibers help in decreasing absorption of toxic compounds and reduce the incidence of cancer colon

- Cellulose can be utilized & serve as a source of energy in herbivores because their gut contains bacterial enzyme that can attack β-linkage.

BYJU'S The Learning App

	Cellulose	Starch		Glycogen
		Amylose	Amylopectin	
Source	Plant	Plant	Plant	Animal
Subunit	β-glucose	α-glucose	α-glucose	α-glucose
Bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Branches	No	No	Yes (~per 20 subunits)	Yes (~per 10 subunits)
Diagram				
Shape				

Cellulose Structural Units: the units for cellulose are made of β-D-Glucopyranose molecules linked by β-1,4-glucosidic bonds.

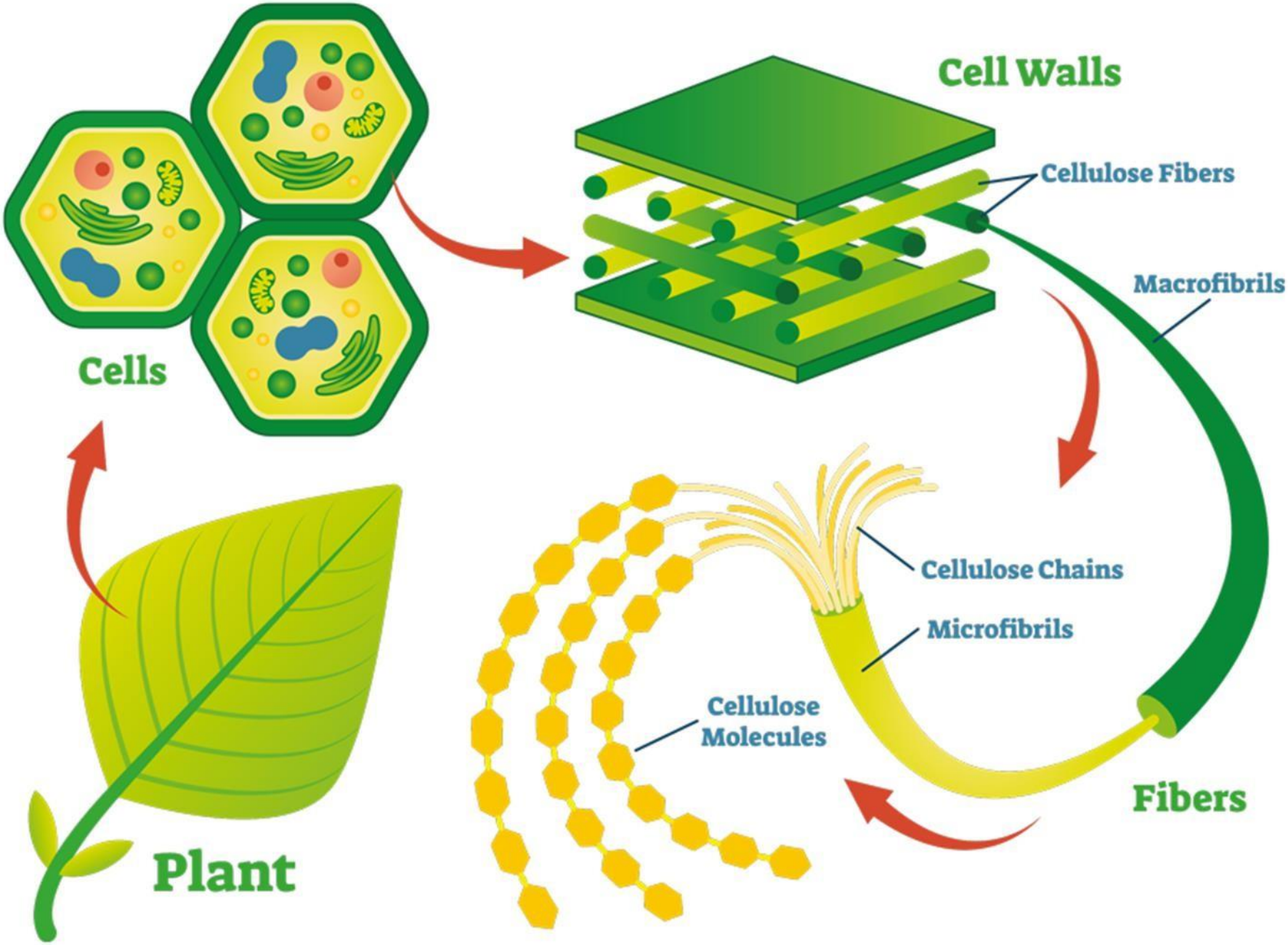


Cellulose is a scaffolding polysaccharide found in plants as microfibrils (2-20 nm diameter and 100 - 40 000 nm long)

These form the structurally strong framework in the cell walls

Due to extensive inter-chain and intra-chain hydrogen bonding cellulose is not water soluble

It is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended stiff rod-like conformation. with high tensile strength.


Cells
Cell Walls
Cellulose Fibers
Macrofibrils
Cellulose Chains
Microfibrils
Cellulose Molecules
Fibers
Plant