Introduction

Carbohydrates are probably **the most common organic substances** in nature. They are found in all organisms and are involved in many vital functions.

In living cells, the carbohydrate ribose is an essential part of nucleic acids (RNA and DNA), but carbohydrates are also elements in many other molecules such as coenzymes, antibiotics and toxins. In plants and algae, carbohydrates are among the first organic compounds formed during photosynthesis. Carbohydrates can be used as an immediate source of energy by largely all cells, but in many photosynthetic organisms a major portion of the carbohydrates will be used for production of structural compounds, e.g., cellulose in cells walls, or for synthesis of storage products such as starch.

1. Nomenclature and structure

Among the four major biomolecules found in all living systems, the most abundant are the carbohydrates (***carbo***-carbon; ***hydro***-water). They were formerly known as hydrates of carbon.

Carbohydrates are called saccharides deriving etymologically from the word “***Saccrose***” which is the *Greek* word for sweet. Carbohydrates are given non-systematic names, although the suffix “ose” is generally used.

Chemically, carbohydrates are made up of carbon, hydrogen, and oxygen with an empirical formula of $(CH_2O)_n$. They have either of the two functional groups, i.e., an aldehyde or a ketone and at least two or more hydroxyl groups, based on this, a carbohydrate is biochemically defined as: “***a molecule that is a polyhydroxy aldehyde or ketone or its derivative***”.

2. Classification

Carbohydrates are divided into four major groups: monosaccharides, disaccharides, oligosaccharides, and polysaccharides.

- **Monosaccharides**, which are the simplest structures that cannot be hydrolyzed further into smaller units, such as glucose for example.
- **Disaccharides** that are made up of two monosaccharides linked together by a covalent bond, called a glycosidic bond (for example: sucrose, or table sugar, which is composed of glucose and fructose).
- **Oligosaccharides** that are made up of three to ten monosaccharides linked together by glycosidic bonds."
- **Polysaccharides** composed of more than ten saccharide units (for example: glycogen)."

2.1.Monosaccharides

Monosaccharides are simple sugars that may become basic units of more complex molecules. They are single chains of carbon atoms bearing multiple adjacent hydroxyl groups. The general overall structure is $(CH_2O)_n$.

Monosaccharides represent the fundamental structure of carbohydrates. They are not susceptible to hydrolysis, which prevents them from being broken down into smaller carbohydrates. They have a vital function in the synthesis of nucleic acids and act as energy sources in glycolysis. Monosaccharides, commonly known as cell sap, are often found inside the cytoplasm. Their content is notably high in some fruits and vegetables, such as maize, peas, and sweet potatoes

- Monosaccharides are organic compounds that may be classified as either aldehydes or ketones, and they include several hydroxyl groups.

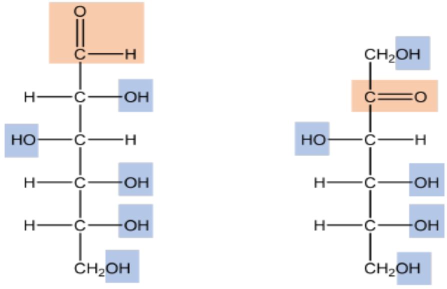


Figure 1: Structures of a polyhydroxy aldehyde (Aldose on the left) and polyhydroxy ketone (Kitose on the right).

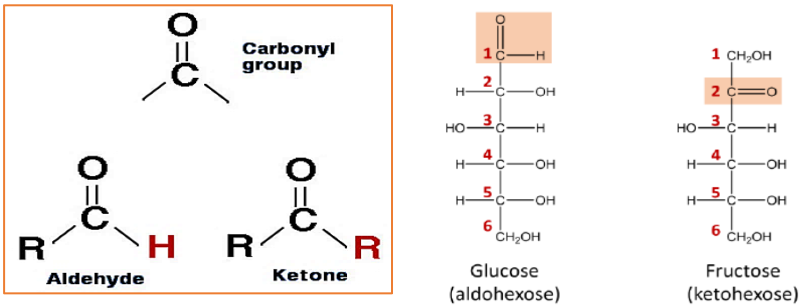
- In the categorizing of monosaccharides, there are three main criteria:

1-The position of the carbonyl group;

2-The total number of carbon atoms;

3- Chiral feature.

- If the **carbonyl group** exists in the form of an aldehyde, then the monosaccharide is classified as an **aldose**. A monosaccharide is classified as a **ketose** if it contains a carbonyl group in the form of a ketone.



Glucose (aldohexose)

Fructose (ketohexose)

Figure 2: Structures of glucose and fructose.

- The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes maybe indicated by names composed of a stem denoting the number of carbon atoms and the suffix ***-ose***.

1- Three carbons atoms (3 C): **triose**, the smallest monosaccharides;
2- Four carbons atoms (4 C): **tetrose**;
3- Five carbons atoms (5 C): **pentose**;
4- Six carbons atoms (6 C): **hexose**;
5- Seven carbons atoms (7 C): **heptose**, and so on.

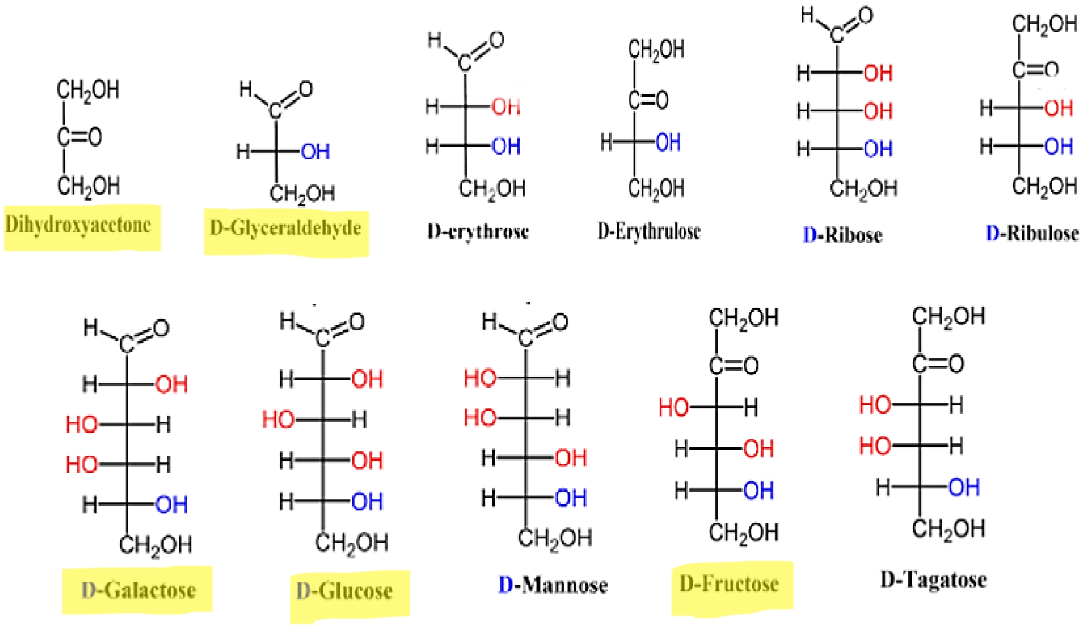


Figure 3: Structures of some aldoses and ketoses

- **Fischer projections**, use horizontal and vertical lines to indicate the three–dimensional structure of a molecule.

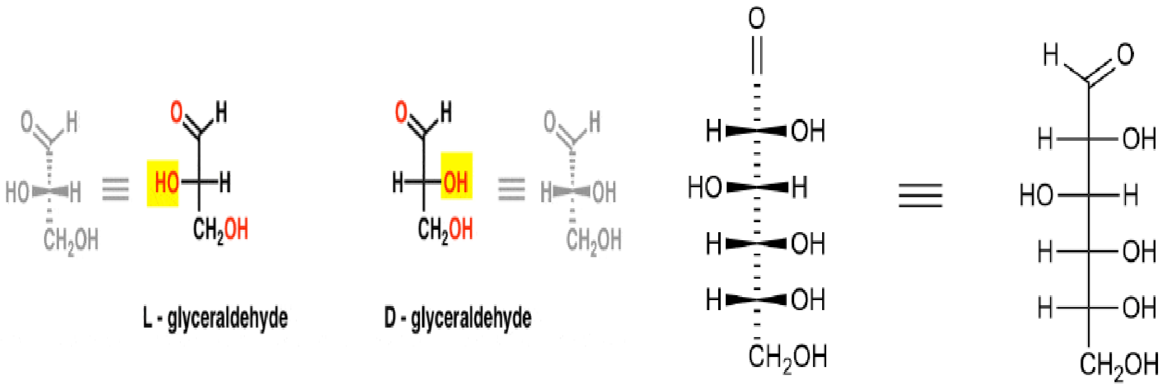


Figure 4: Fischer projections of glyceraldehyde and glucose

- **D- and L- monosaccharide:**
  - if the OH on the chiral carbon farthest from the aldehyde or ketone functional group to the right, the monosaccharide is D.
  - if the OH on the chiral carbon farthest from the aldehyde or ketone functional group to the left, the monosaccharide is L.

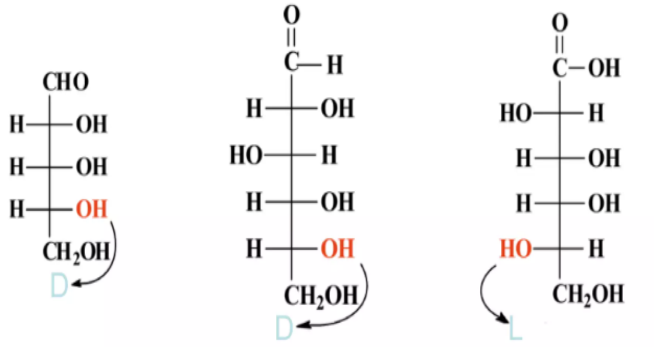


Figure 5: illustration of D and L monosaccharides

- Chiral carbon center has four unique groups attached to it.

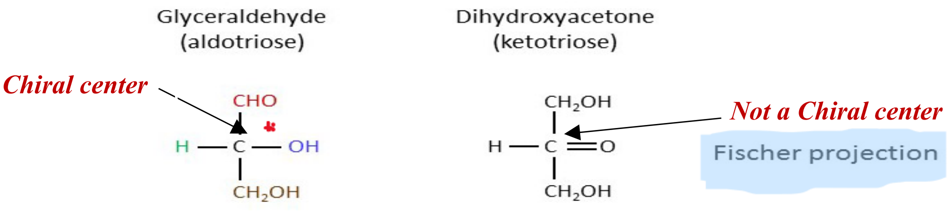
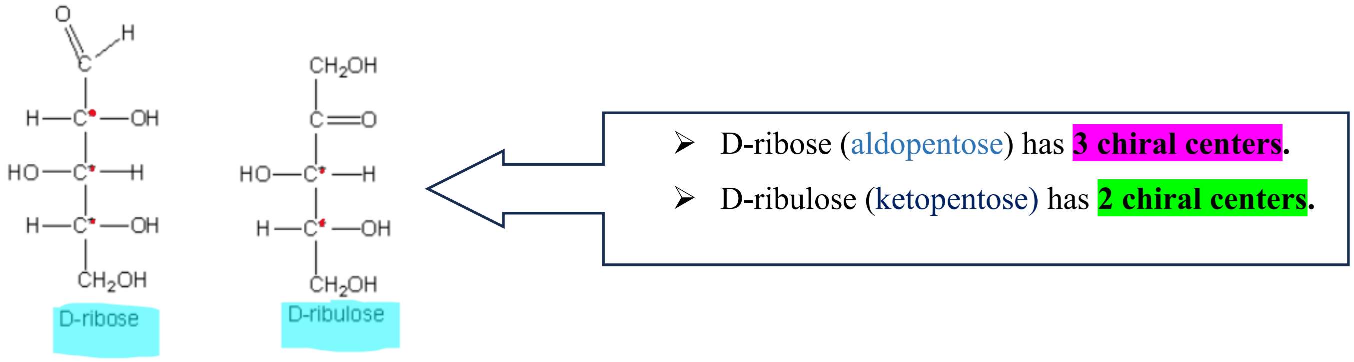


Figure 6: Chiral carbon center

- ***The number of chiral carbons*** present in a ketose is always one less than the number found in the same length aldose. Number of possible steroisomers = 2^n (n = the number of chiral carbons).



- D-ribose (aldopentose) has **3 chiral centers**.
- D-ribulose (ketopentose) has **2 chiral centers**.

Figure 6: Number of chiral carbons

Stereochemistry:

- **Enantiomers** = mirror images;
- Pairs of isomers that have opposite configurations at one or more chiral centers but are NOT mirror images are **diastereomers**;
- **Epimers** = Two sugars that differ in configuration at only one chiral center.

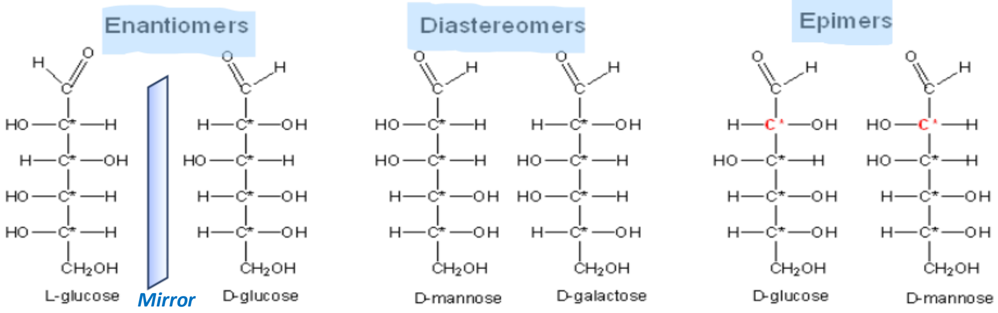


Figure 7: Epimers

Cyclic Structures of Monosaccharides (Ring structure): The cyclic forms of sugars are commonly depicted as **Haworth projections**.

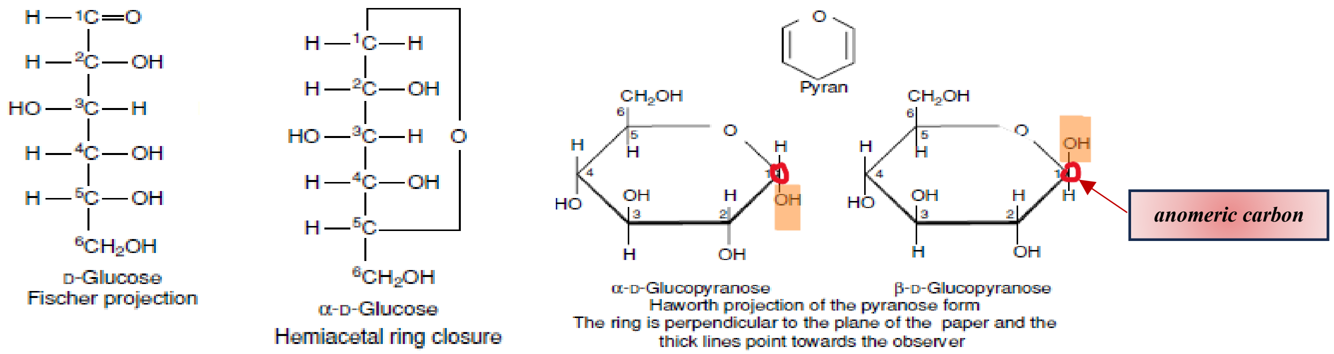


Figure 8 of Cyclic hemiacetal formation between carbon 5 and carbon 1 of glucose. The anomeric carbon 1 is chiral, and two positions are possible for the OH group, which can be below (a-form) or above (b-form) the pyranose ring, or right and left.

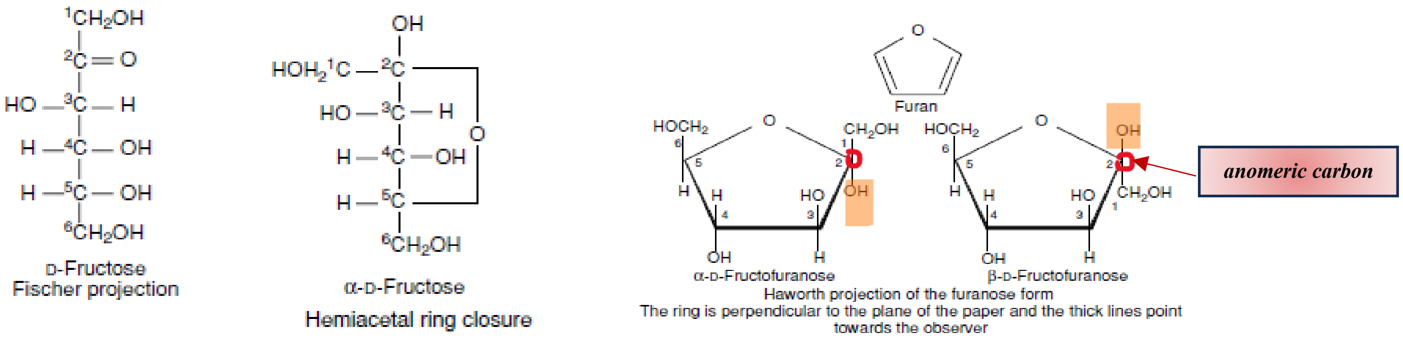


Figure 9 Cyclic hemiacetal (hemiketal) formation between carbon 5 and carbon 2 of fructose leads to the furanose structure

2.2.Disaccharides

Disaccharide consists of two monosaccharide units linked together by a **glycosidic bond** which is formed by condensation reaction between hydroxyl group of one monosaccharide with the hydrogen of another monosaccharide.

The most abundant disaccharides are sucrose, lactose and maltose which are known as table sugar, milk sugar and malt sugar respectively.

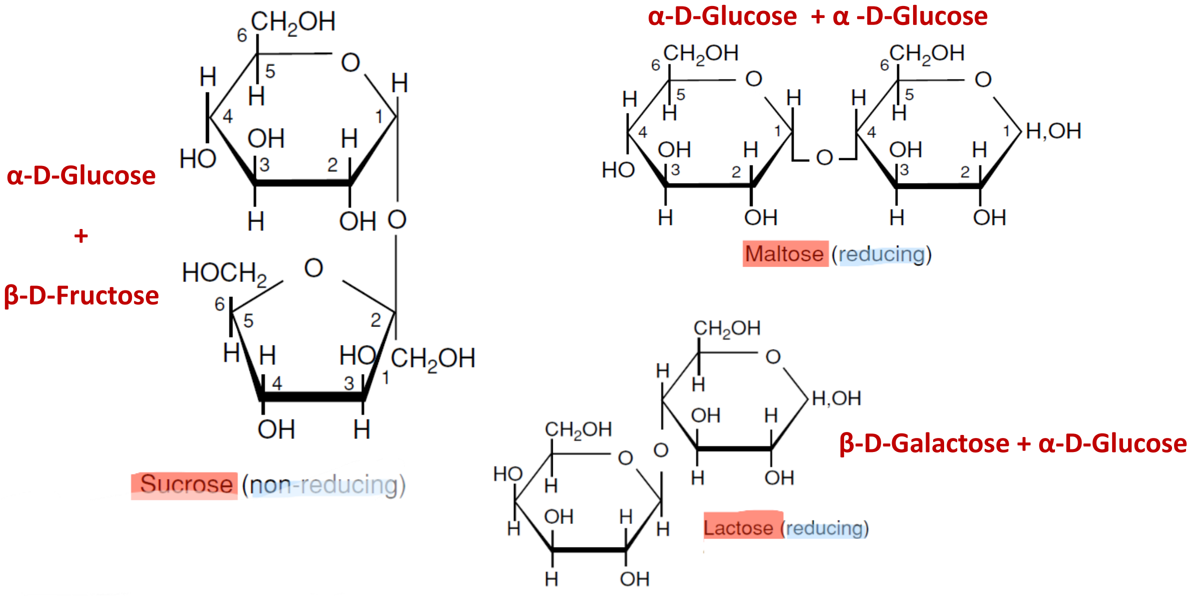


Figure 10: Formulae and nomenclature of three **common disaccharides**. Sucrose does not have a free carbonyl group ***(non reducing).*** The OH group on the anomeric carbon atom of maltose and lactose can acquire either the **α** or the **β** configuration ***(Reducing)***. Both sugars mutarotate when

Table 1: Some common disaccharides.

Disaccharide	Nomenclature	Source
Sucrose	*O*-α-D-glucopyranosyl-(1→2)-β-D-fructofuranoside	Cane sugar and beet sugar, sorghum fruits and vegetables
Lactose	*O*-α-D-galactopyranosyl-(1→4)-β-D-glucopyranose	Milk sugar
Maltose	*O*-α-D-glucopyranosyl-(1→4)-α-D-glucopyranose	Germinating cereals and malt

2.3.Oligosaccharide

Oligosaccharide is a *Greek* word: ***Oligo*** = few, ***sacchar*** = sugar. Oligosaccharide is the short chain of monosaccharide unit which composed of 3-10 molecules connected by **glycosidic linkage**.

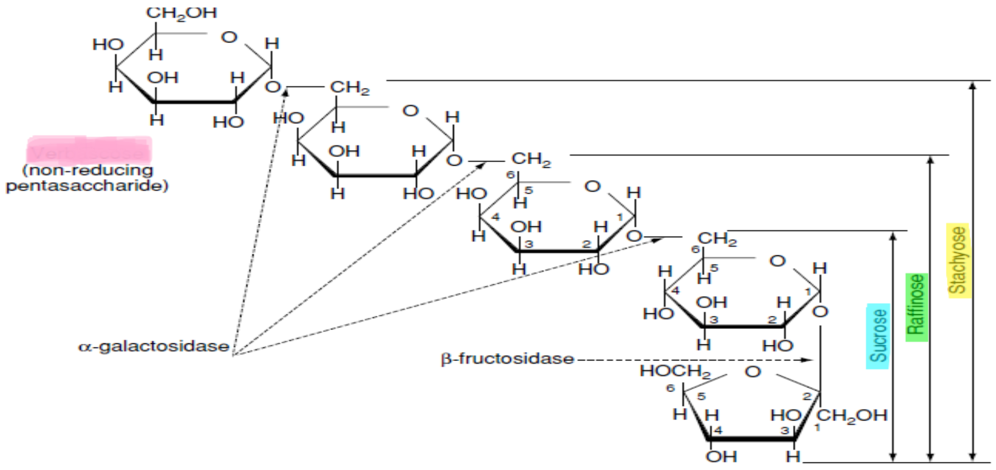


Figure 11: O-a-D-Galactopyranosyl-(1→6)-[O-a-D-galactopyranosyl-(1→6)]2-O-a-D-glucopyranosyl-(1→2) b-D-frutofuranoside. Arrows indicate the points of hydrolysis by enzymes.

2.4.Polysaccharides

Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose.

2.4.1. Nomenclature

- Polysaccharides are also known as '**glycans**' where ***glyc***-means sweet or sugar and ***-an*** means polymer.
- Depending on the **monomeric sugar**, they are described as glucans, fructans, galactans, mannans, xylans, etc., where the first four letters refer to glucose, fructose, galactose, mannose, and xylose, respectively.

2.4.2. Classification

According to their composition (structure), there are two types of polysaccharides:

- ***Homopolysaccharides (homoglycans):*** are formed by the repetition of a monosaccharide.
- ***Heteropolysaccharides (heteroglycans)***: are formed by the orderly repetition of a disaccharide formeby two different monosaccharides.

- **Based on the functionality:**

Homopolysaccharides can be again classified into two types:

- **Storage** homopolysaccharides
- **Structural** homopolysaccharides (maintain mechanical shape and rigidity of the living cells)

Heteropolysaccharides can be classified into:

- **Nitrogen** heteroglycan
- **Non-nitrogen** heteroglycan

Example of *nitrogen heteroglycan* is glycosaminoglycans which is available in different tissues and intracellular cells. For *non-nitrogen heteroglycan* examples are agar (sources are microalgae, seaweeds and coral reefs), gums (seeds, plant exudates and microorganisms), hemicelluloses (plant cell walls), and pectin (plant cell walls, citrus fruits, carrot, apple, and beet).

- Based on monosaccharides and which carbons in the monosaccharides are connected, polysaccharides may again classify as:
  - **Linear** polysaccharide
  - **Branched** polysaccharide

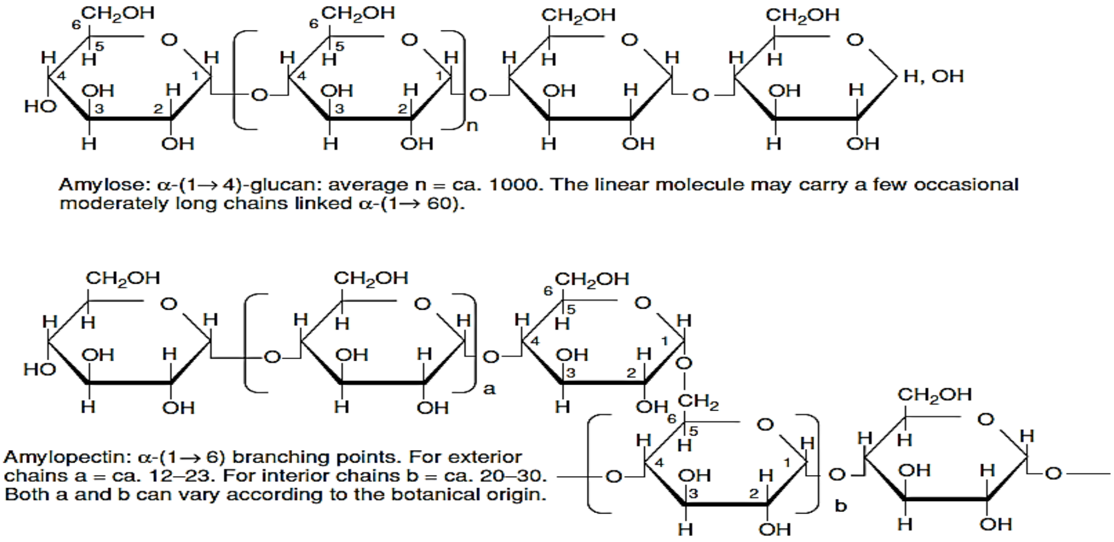
A molecule with a straight chain of monosaccharides connected with a straight chain form a linear polysaccharide whereas branched polysaccharide has a chain that has arms and turns. Branches in polysaccharide may be short, regularly, or irregularly spaced, isolated, or positioned to produce bush-like structures, a branch-on branch structure or clustered.

- According to **source (origin)**, polysaccharides can be classified in to four main categories, which are:
  - Polysaccharides of **plant** origin;
  - Polysaccharides of **algal** origin;
  - Polysaccharides of **animal** origin;
  - Polysaccharides from **microorganisms.**

2.4.3. Common polysaccharides

- **Starch**
  - The *main storage polysaccharide* is **starch** which is plant's food reserve material it is stored in the chloroplasts of plant cells as insoluble granules. Also, it is widely available in foods; such as in potato, rice, wheat, maize, egumes, and other vegetables.

- It is composed of linear α-amylose and branched amylopectin materials.
- The **α-Amylose** polymer is made of several thousands of glucose monomers linked by ***α-(1, 4) bonds.***
- The amylopectin branched molecule composed of ***α-(1, 4) linked*** glucose residues with ***α-(1, 6) branch*** points at every 24–30 glucose residues in average.
- **The helical structure** of amylopectin is disrupted by the branching of the chain.



Amylose: α-(1→ 4)-glucan: average n = ca. 1000. The linear molecule may carry a few occasional moderately long chains linked α-(1→ 60).

Amylopectin: α-(1→ 6) branching points. For exterior chains a = ca. 12–23. For interior chains b = ca. 20–30. Both a and b can vary according to the botanical origin.

Figure 12 : Basic structure of amylose and amylopectin

Glycogen

- **Glycogen** is the *energy storage* carbohydrate of animals. Like starch in plants, glycogen is found as granules in liver and muscle cells. Practically all mammalian cells contain some stored glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%).
- Glycogen is structurally *quite similar to amylopectin*, although glycogen *is more highly branched* (8–12 glucose units between branches) and the *branches are shorter*.
- Glycogen can be *broken down* into its D-glucose subunits by acid hydrolysis or by enzyme.

Cellulose

- **Cellulose**, a *fibrous carbohydrate* found in all plants, is the *structural component* of plant cell walls. Because the earth is covered with vegetation, cellulose is *the most abundant* of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom.
- Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose.

- Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose. This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers.
- Humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose.

- certain microorganisms *can digest* cellulose because they make *the enzyme cellulase*, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of ***herbivorous animals*** (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy.

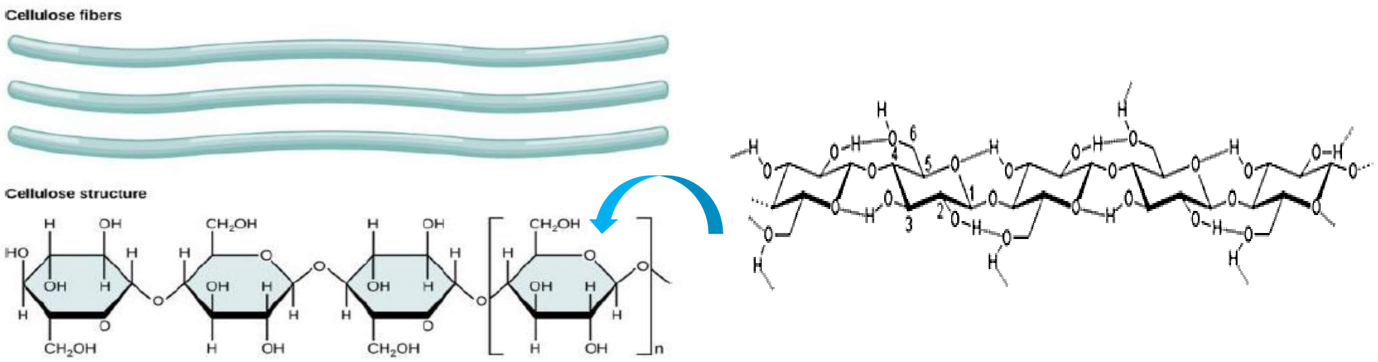


Figure 13: Cellulose. In cellulose, glucose monomers are linked in unbranched chains by *β-1,* glycosidic linkages. Because of the way the glucose subunits are joined, every glucose monomer is flipped relative to the next one resulting in a linear, fibrous structure.

Table 2: Structures and properties of some polysaccharides.

Name	**Constituent monosaccharide**	**Glycosidic linkage**	**Size (no. of monosaccharide residues)**	**Biological significance**
Starch	α-D-glucose	α(1→4) glucoside (in amylose) α(1→4) glucoside; α(1→6) glucoside linkage at branch points (in amylopectin) Branches at every 24-30 residues	50-5000 Upto 10^6	Energy storage in plants
Glycogen	α-D-glucose	α(1→4) glucoside; α(1→6) glucoside linkage at branch points Branches every 8-14 residues	Upto 50000	Energy storage in bacteria and animals
Cellulose	β-D-glucose	β(1→4) glucoside	Up to 15000	Structural role: provide rigidity and strength to cell wall

3.Physicochemical properties

Physical Properties

- **Solubility in Water**: Carbohydrates, especially simple sugars (monosaccharides and some disaccharides), are indeed highly soluble in water due to their multiple hydroxyl (–OH) groups, which can form hydrogen bonds with water molecules.
- **Viscosity of Concentrated Solutions**: When carbohydrates are dissolved in high concentrations, they form iscous solutions (syrups), which is common with substances like glucose or fructose syrups.
- **Crystallization with Alcohol**: The crystallization of sugars is often facilitated by adding alcohol, like methanol or ethanol, as sugars have limited solubility in these solvents. This encourages sugar to precipitate out of solution, forming crystals.
- **Optical activity:** Carbohydrates contain multiple chiral centers and thus rotate plane-polarized light. The direction of light rotation depends on the specific stereochemistry of the sugar. D-glucose, for example, rotates light to the right (dextrorotatory), while L-glucose would rotate it to the left (levorotatory), although L-glucose is rarely found in nature.

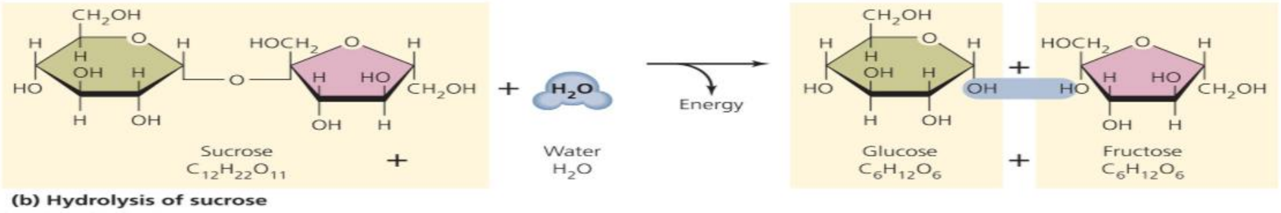
Chemical properties

1. Hydrolysis and Condensation Reactions

- **Hydrolysis**: Carbohydrates, particularly disaccharides and polysaccharides, can undergo hydrolysis, where they are broken down into simpler sugar units (monosaccharides) by the addition of water. This reaction is catalyzed by enzymes (such as amylase for starch) or acid catalysts.

$$\text{Disaccharide} + H_2O \rightarrow \text{Monosaccharide} + \text{Monosaccharide}$$

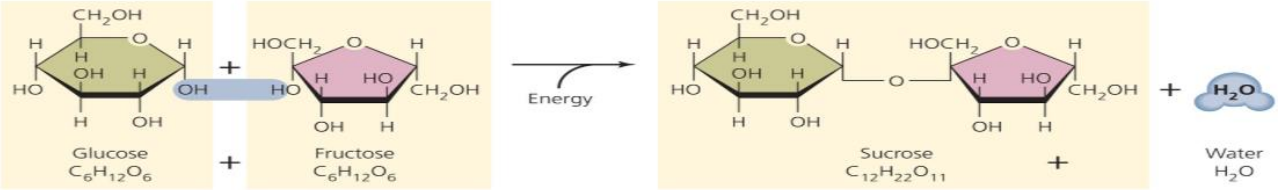
Example:



- **Condensation (Dehydration)**: Conversely, monosaccharides can join to form disaccharides or polysaccharides through condensation reactions, where a water molecule is removed. This type of reaction requires energy and is facilitated by enzymes like glycosyltransferases.

Monosaccharide1+ Monosaccharide2 → Disaccharide + H_2O

Example:



(a) Dehydration synthesis of sucrose

2. Reducing property

- Sugars arc classified as either reducing or non-reducing depending upon the presence of potentially free aldehyde or keto groups.
- The reducing property is mainly due to the ability of these sugars to reduce metal ions such as copper or silver under alkaline conditions. This reducing property is the basis of Fehling’s and Benedict’s tests. In these tests, cupric ion in copper sulphate is reduced to red cuprous oxide.

$$\underset{\text{Benedict's solution (blue)}}{Cu_2^{+}\text{ complex}} + \text{Aldose or Ketose} \longrightarrow \underset{\text{Cuprous oxide (red precipitate)}}{Cu_2O} + \text{Oxidation products}$$