SECOND CHAPTER: Structure and physicochemical properties of carbohydrates (Part 2)

IV. Disaccharides

Sugars are readily joined together (and broken apart) in cells. On hydrolysis, disaccharides yield two molecules of either the same or different monosaccharides. The two monosaccharide units are joined by oxide linkage which is formed by the loss of water molecule and this linkage is called glycosidic linkage. The glycosidic bond is formed by condensation reactions between a hydroxyl oxygen atom on carbon on one sugar and the anomeric form of another sugar.

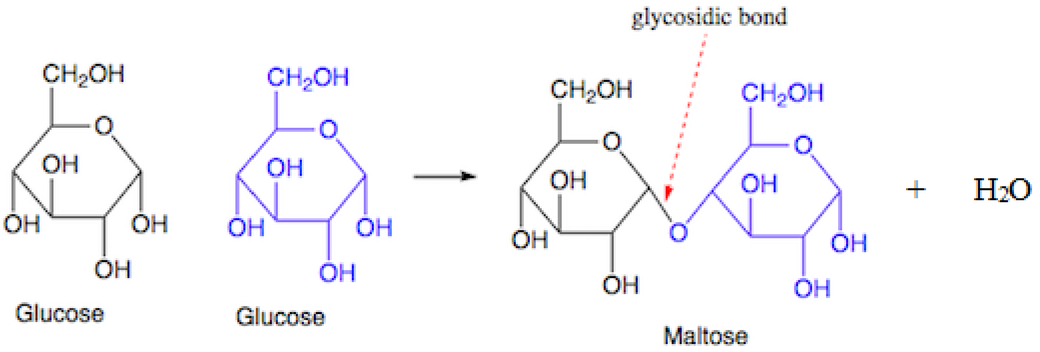
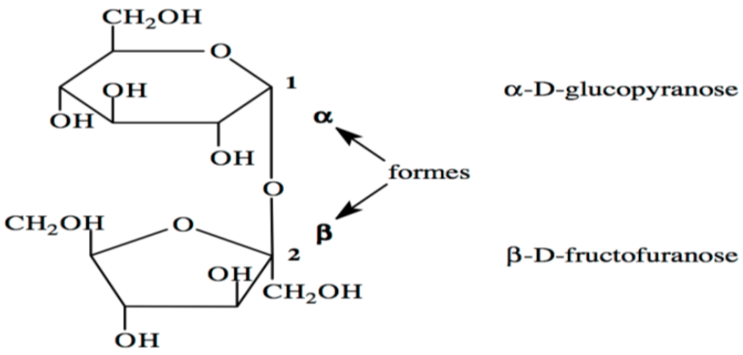


Fig 10. glycosidic linkage.

Sucrose, which is common table sugar, is made by joining the anomeric hydroxyl of alpha-D-glucose to the anomeric hydroxyl of beta-D-fructose. Not all disaccharides join the anomeric hydroxyls of both sugars. For example, lactose (milk sugar) is made by linking the anomeric hydroxyl of galactose in the beta configuration to the hydroxyl of carbon #4 of glucose.



(a)

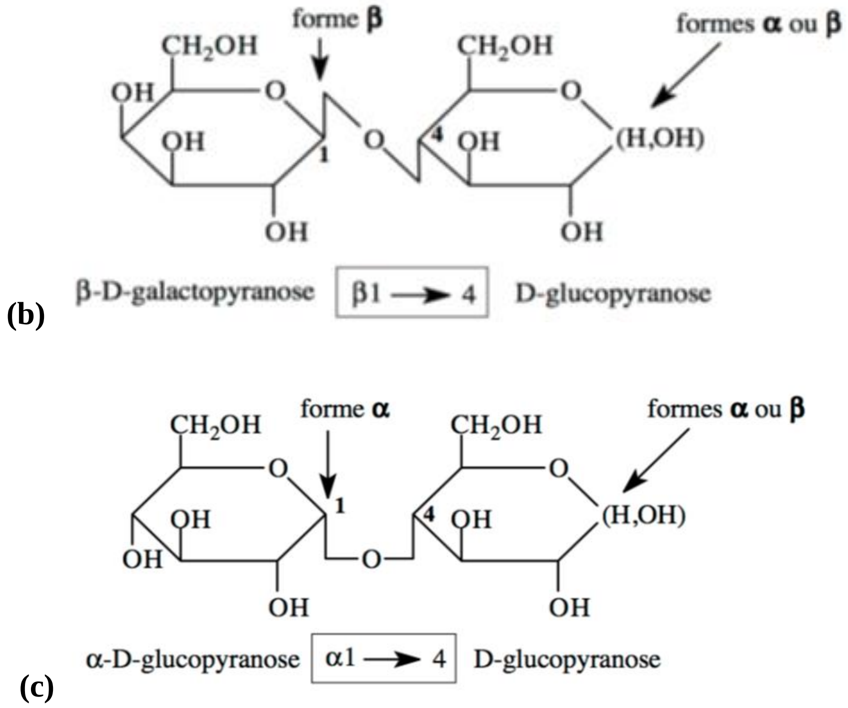


Fig 11. Chemical structures of some disaccharides **[1]**. (a) Saccharose, (b) Lactose, (c) Maltose.

V. Oligosaccharides

The term ‘oligosaccharide’ is used to describe polymers of sugars of 3-15 units, typically. Oligosaccharides are not commonly found free in cells, but instead are found covalently attached to proteins, which are then said to be glycosylated. Oligosaccharides attached to proteins may be N-linked (through asparagine) or O-linked (though serine or threonine).

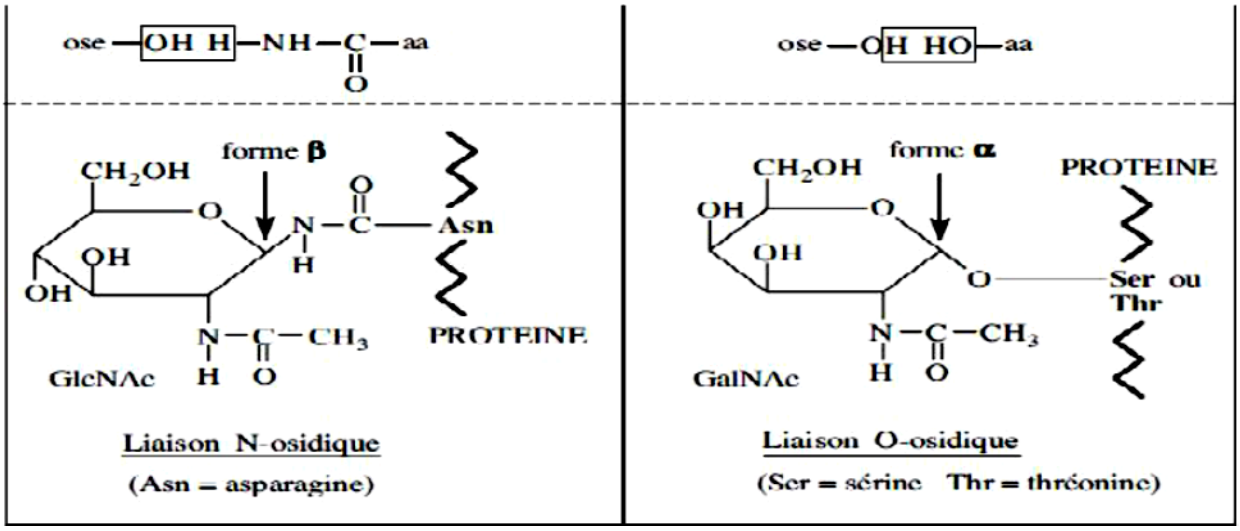


Fig 12. Glycoprotein structures **[5]**.

Oligosaccharides often function as identity markers, both of cells and proteins. On the cell surface, glycoproteins with distinctive oligosaccharides attached establish the identity of each cell. The types of oligosaccharides found on the surface of blood cells is a determinant of blood type. The oligosaccharides that are attached to proteins may also determine their cellular destinations.

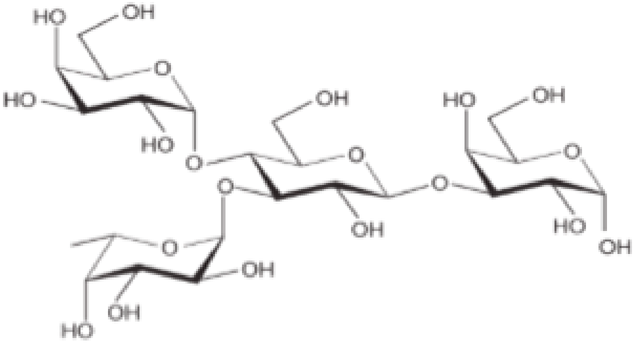


Fig 13. An oligosaccharide.

VI. Polysaccharides

Polysaccharides, as their name implies, are made by joining together many sugars. The functions for polysaccharides are varied. They include energy storage (glycogen, starch) and structural strength (cellulose). They are further classified into homopolysaccharides and heteropolysaccharides based on the monomeric units.

- **Homopolysaccharides:** A homopolysaccharide yields the same type of monosaccharide units on hydrolysis. For example starch a homopolysaccharide yields only glucose upon hydrolysis. Similarly glycogen and cellulose also yield glucose on hydrolysis.
- **Heteropolysaccharides:** A heteropolysaccharide yields more than one type of monosaccharide upon hydrolysis. Eg. Hyaluronic acid, heparin, keratan sulphate and chondroitin sulphate.

Polysaccharides involved in energy storage include the plant polysaccharides, amylose and amylopectin. The polysaccharide involved in energy storage in animals is called glycogen and it is mostly found in the muscles and liver.

- **Amylose/Amylopectin**

Amylose is the simplest of the polysaccharides, being comprised solely of glucose units joined in an alpha 1-4 linkage. Amylose is broken down by the enzyme alpha-amylase, found in saliva. Amylopectin is related to amylose in being composed only of glucose, but it differs in how the glucose units are joined together. Alpha 1-4 linkages predominate, but every 30-50 residues, a 'branch' arises from an alpha 1-6 linkage. Branches make the structure of amylopectin more complex than that of amylose.

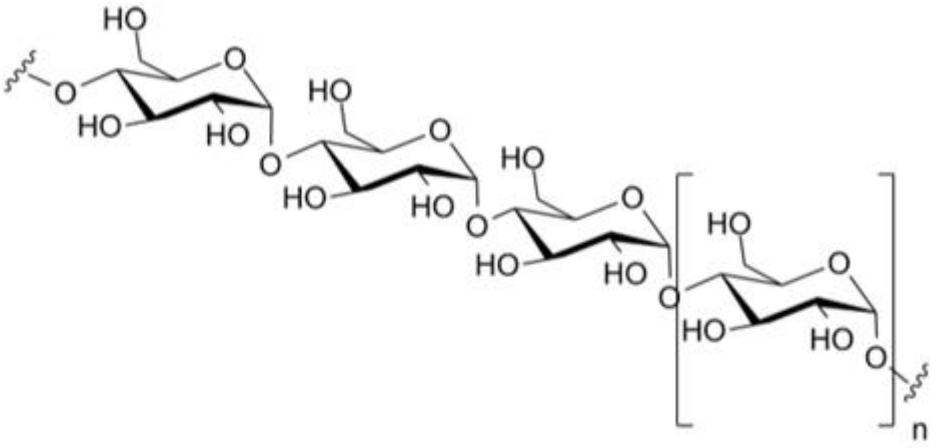


Fig 14. Amylose structure **[1]**.

- **Glycogen**

Glycogen is a polysaccharide that is physically related to amylopectin in being built only of glucose and in having a mix of alpha 1-4 and alpha 1-6 bonds. Glycogen, however, has many more alpha 1-6 branches than amylopectin, with such bonds occurring about every 10 residues.

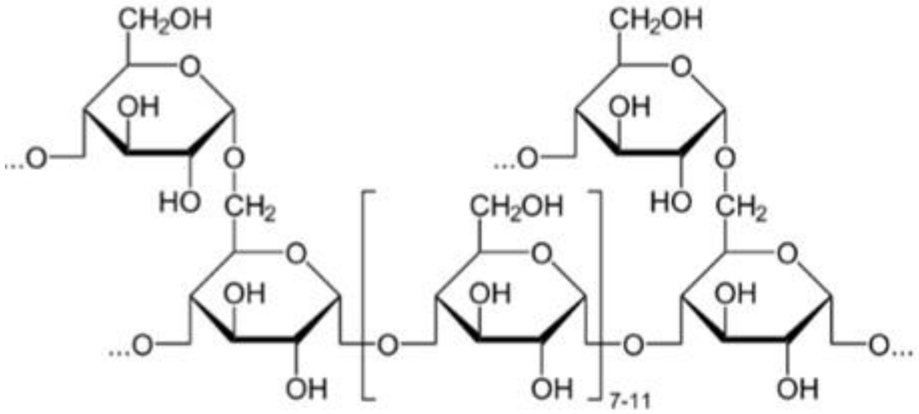


Fig 15. Glycogen structure **[1]**.

- **Cellulose**

Another important polysaccharide containing only glucose is cellulose. It is a polymer of glucose used to give plant cell walls structural integrity and has the individual units joined solely in a beta 1-4 configuration.

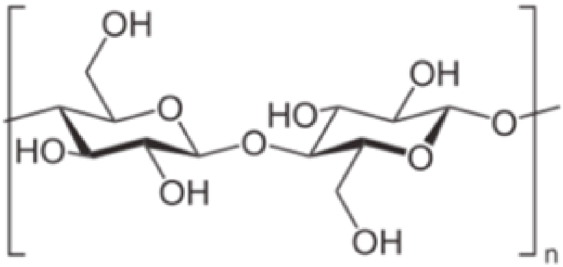


Fig 16. Repeating structure of cellulose **[1]**.

VII. Physical and chemical properties of carbohydrates

- **Physical properties of carbohydrates:**

- Carbohydrate like monosaccharides are soluble in water, because they have several OH groups, but insoluble in organic solvents example chloroform.
- Carbohydrates comprising monosaccharides, oligosaccharides and polysaccharides are solid at room temperature, their structure is thermodegradable (caramelization).
- Crystallization is facilitated by adding alcohol (methanol or ethanol) where the sugars are poorly soluble.
- Majority of monosaccharides and few diasaccharideslike sucrose are sweet to taste.
- Monosaccharides, diasaccharides and polysaccharides are odorless.
- Sugars do not show absorption in the visible or ultraviolet but they absorb in the infrared.

- **Chemical proprieties:**

Their chemical properties are characteristic of alcoholic hydroxyl groups and carbonyl groups.

- In a concentrated acidic environment and under heat, the carbohydrates undergo dehydration with cyclization.

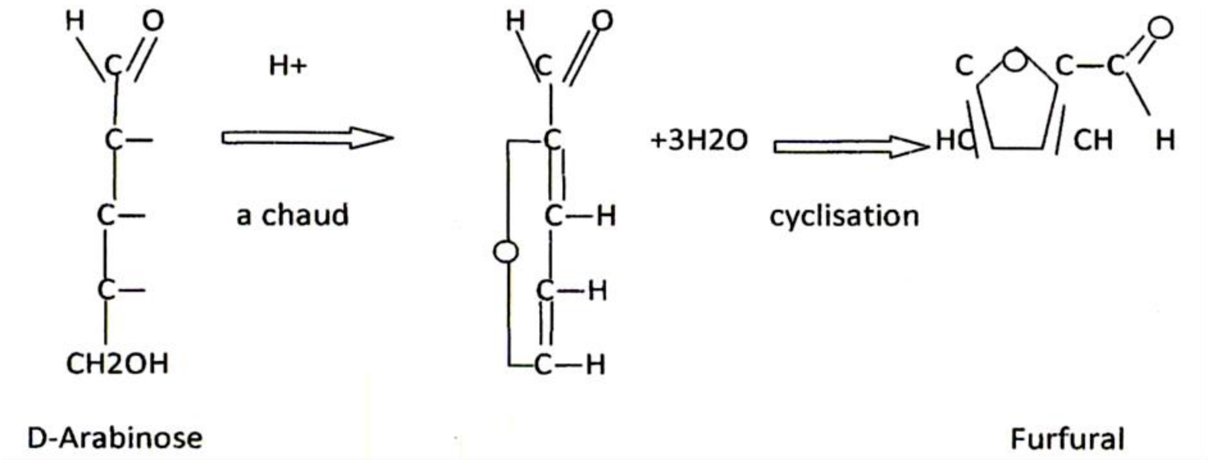
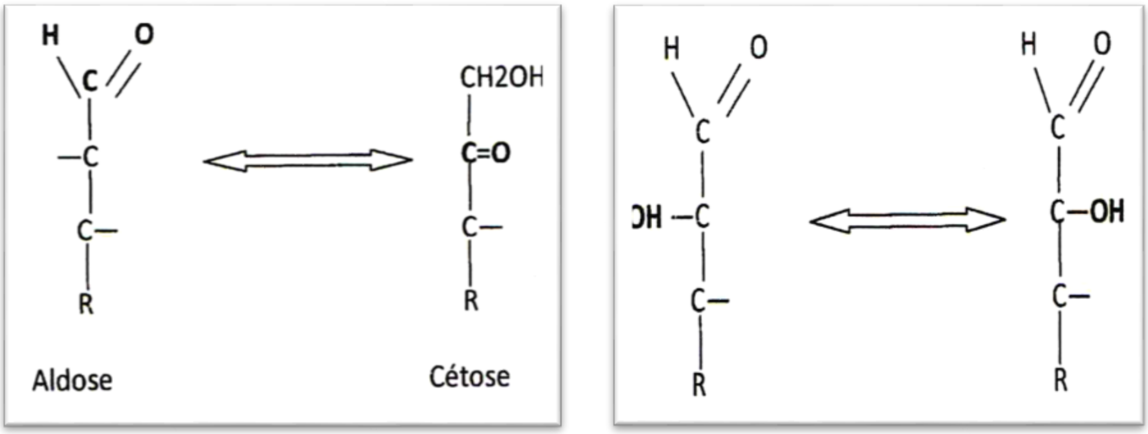


Fig 17. Cyclization of a carbohydrate in a concentrated acid medium and at heat **[2]**.

- In an alkaline and cold environment carbohydrates give either an interconversion or an epimerization at C2.



Interconversion Epimerization

Fig 18. Interconversion and epimerization at C2 of sugars in an alkaline and cold medium **[2]**.

- In an alkaline and hot environment: total degradation of the sugar.
- Sugar reduction reaction: the reduction of the aldehyde and ketone functions gives polyalcohols.

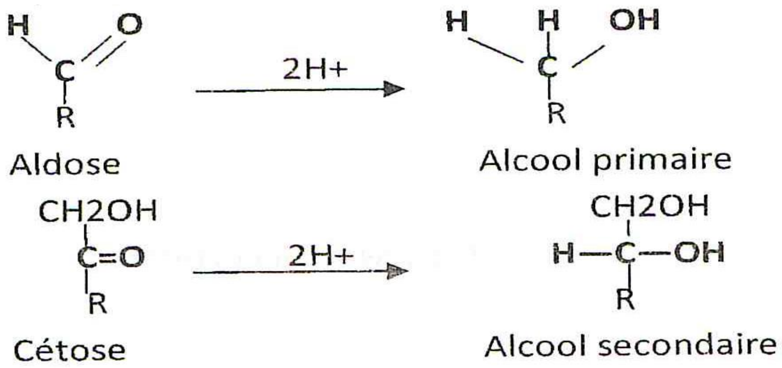


Fig 19. Sugar reduction reaction **[2]**.

- Oxidation reaction of sugars by chemical or enzymatic means: oxidation of the aldehyde function of aldoses and to a lesser degree ketones into a carboxylic group.

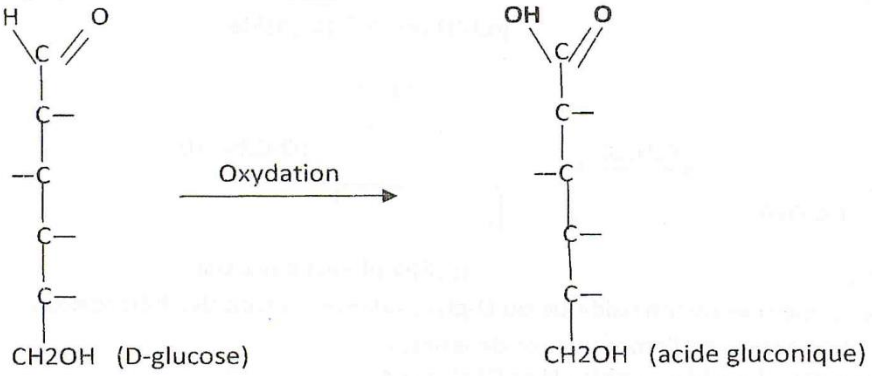


Fig 20. Sugar oxidation reaction **[2]**.