CHAPTER 4

Carbohydrates

❖ Types of Naturally Occurring Sugars

It is quite a well-known fact that carbohydrates can primarily be classified into three categories; monosaccharides, oligosaccharides, and polysaccharides. The monosaccharides are the simplest carbohydrates that cannot be further hydrolyzed to simpler molecules. The general formula of monosaccharides is $(CH_2O)_n$ where n = 3–8. The oligosaccharides are the carbohydrate molecules that can produce 2–10 molecules of monosaccharides. Polysaccharides are carbohydrate molecules that can produce a very large number of monosaccharides' molecules upon hydrolysis.

Furthermore, in addition to the number of hydrolysis produce, the carbohydrates can also be classified on the basis of their taste. It has been found that all the monosaccharides and oligosaccharides (di-, tri-, tetra-saccharides, etc.) are crystalline compounds, soluble in water and sweet in taste; and typically labeled as sugars. On the other hand, the polysaccharides are amorphous compounds, insoluble in water, and don't have any taste; and therefore, these carbohydrates are typically called as non-sugars. In this section, we will discuss the different types of naturally occurring sugars.

➢ *D-(+)-Glucose or Dextrose or Grape Sugar ($C_6H_{12}O_6$)*

The D-(+)-glucose or dextrose is the most abundant monosaccharide in nature; and is also found in the combined state in many disaccharides, polysaccharides, and glycosides. The name grape sugar comes from the fact that D-(+)-Glucose is found in very large amounts in ripe grapes.

Properties: *i)* It is a white solid with crystalline nature that melts at 419K. It is not soluble in ether but may dissolve to some extent in alcohol. However, the sweet solid is highly dissolvable in water. Furthermore, as the name suggests D-(+)-glucose is optically active and is dextrorotatory in nature. The dextrose possesses 75% sweetness to that of table sugar.

ii) Glucose shows most of the aldehydic reactions but does not respond to Schiff's reagent test and is unable to yield addition compounds with sodium bisulfite.

iii) Glucose also reacts with hydroxyl groups. For instance, it reacts with acetic anhydride and methanol to yield glucose penta-acetate and α- or β-methylglucosides, respectively.

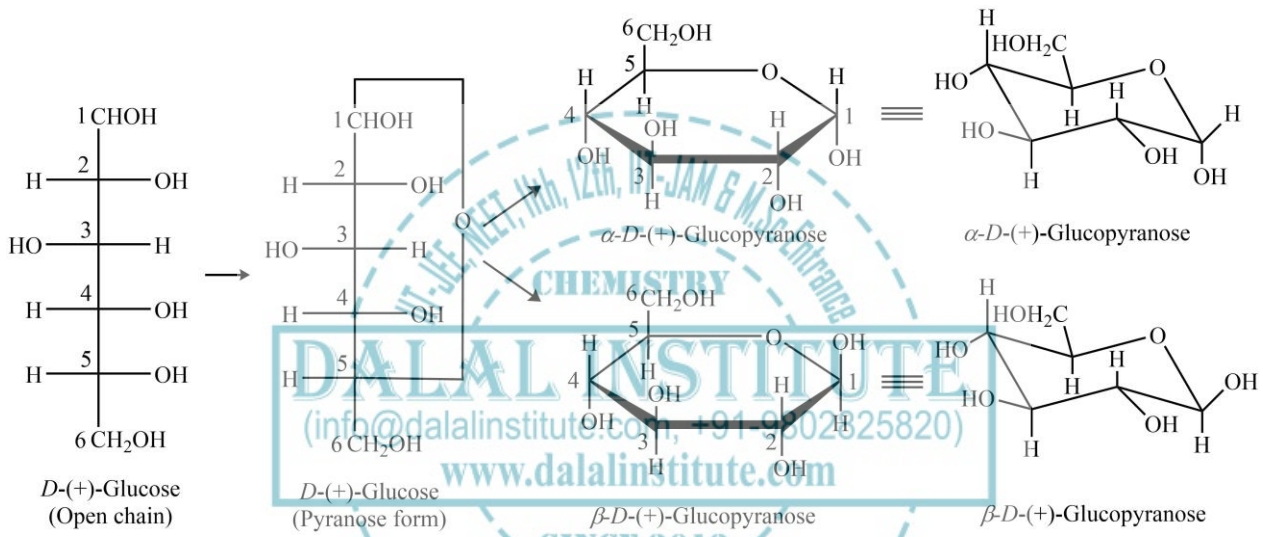
iv) Dextrose doesn't react with dilute acids but can give 5-hydroxymethylfurfural upon heating with concentrated HCl solution.

v) Upon treatment with concentrated alkali solution, glucose first turns yellow and then brown resinous mass. On the other hand, reaction with dilute alkali solution gives rise to an equilibrium mixture of glucose, fructose, and mannose.

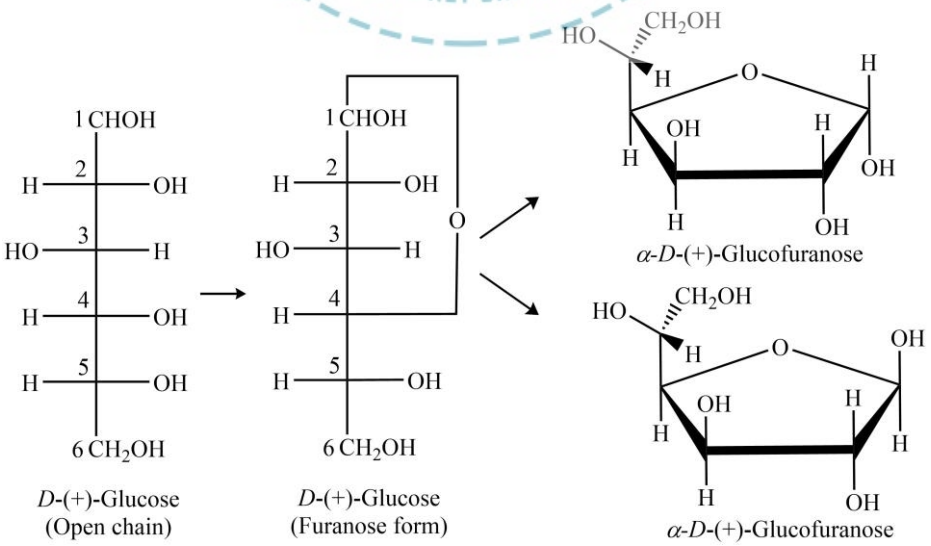
vi) Glucose gets fermented to ethanol when mixed with yeast due to enzyme zymase.

Structure: The terminal aldehydic carbon in open-chain glucose molecule may participate in hemiacetal formation by using the hydroxyl group of 4th and 5th carbon in open-chain glucose molecule, giving rise to a five-membered furan-like and six-membered pyran-like ring structure, respectively. In the solution phase, the open-chain type of glucose (either "L-" or "D-") happens to be in equilibrium with numerous cyclic isomers, where each contains a cycle of carbons closed by one O atom. Nevertheless, in an aqueous phase, greater than 99% of glucose amount, at any given time, exists as the pyranose form; on the other hand, furanose form exists in negligible concentration with the open-chain type is restricted to 0.25% only.

i) Pyranose form: The terminal aldehydic carbon participate in hemiacetal formation by using the hydroxyl group of 5th carbon in open-chain glucose molecule to give pyranose form.



ii) Furanose form: The terminal aldehydic carbon participate in hemiacetal formation by using the hydroxyl group of 4th carbon in open-chain glucose molecule to give furanose form.



➢ *D-(−)-Fructose or Laevulose or Fruit Sugar ($C_6H_{12}O_6$)*

The D-(−)-fructose or laevulose is the most important ketoses monosaccharide in nature. It exists freely in honey and is also found in the combined state in many disaccharides, polysaccharides, and glycosides. The name fruit sugar comes from the fact that D-(−)-fructose is found in very large amounts in sweet fruits.

Properties: *i)* It is a white solid with crystalline nature that melts at 375K. It has a higher solubility in water and alcohol than glucose. Furthermore, as the name suggests D-(−)-fructose is optically active and is laevorotatory in nature.

ii) Fructose gives rise to most of the typical ketonic chemical reactions including oxidation and reduction types as well.

iii) Fructose also gives many typical reactions of hydroxyl groups like acetylation or the formation of fructosates etc.

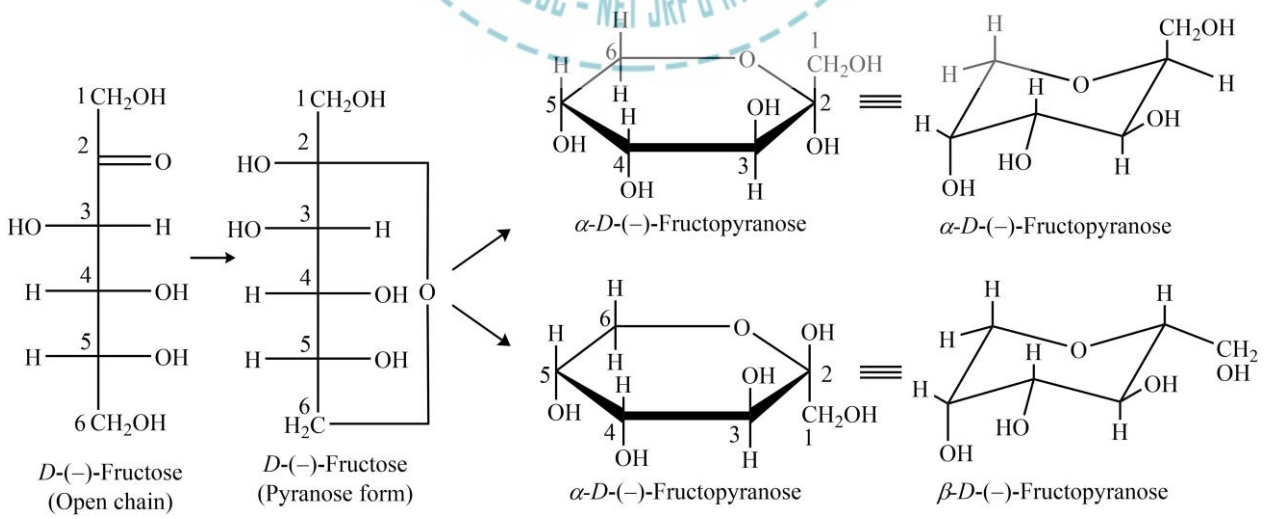
iv) Fructose doesn't react with dilute acids but can give laevulinic acid upon heating with concentrated HCl acid solution.

v) Upon treatment of fructose with dilute alkali solution, we get an equilibrium mixture of glucose, fructose, and mannose.

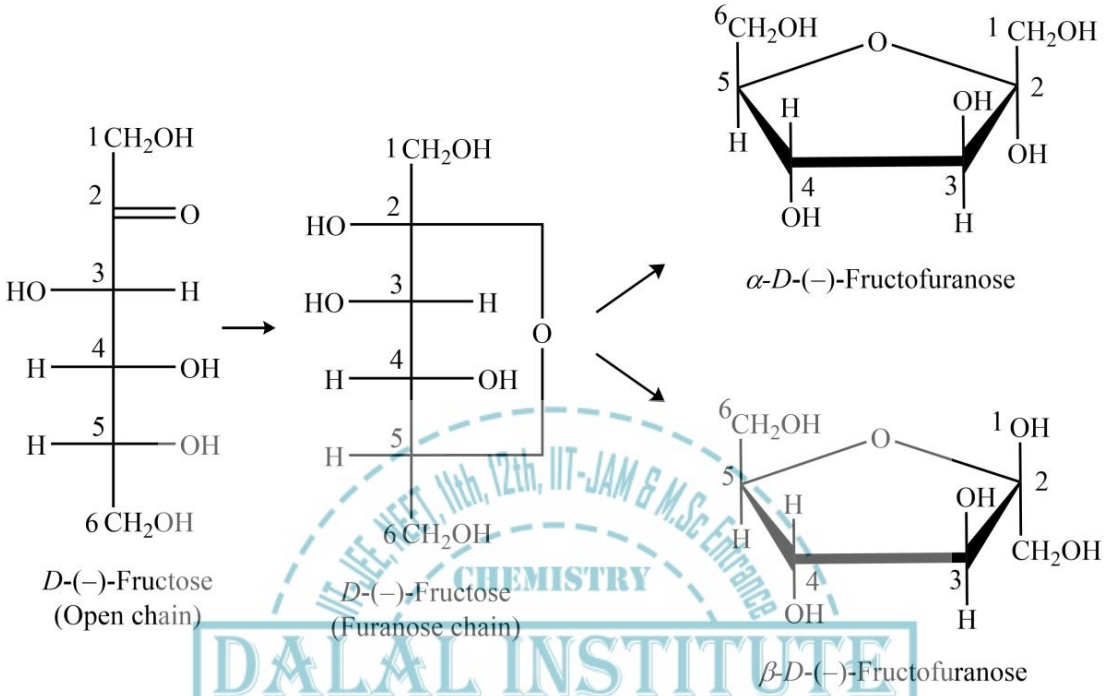
vi) Like glucose, the fructose also gets fermented to ethyl alcohol when mixed with yeast due to enzyme zymase.

Structure: The ketonic carbon in open-chain fructose molecule may participate in hemiketal formation by using the hydroxyl group of 5th and 6th carbon in open-chain glucose molecule, giving rise to a five-membered furan-like and six-membered pyran-like ring structure, respectively.

i) Pyranose form: The ketonic carbon participate in hemiketal formation by using the hydroxyl group of 6th carbon in open-chain glucose molecule to give pyranose form.



i) Furanose form: The ketonic carbon participate in hemiketal formation by using the hydroxyl group of 6th carbon in open-chain glucose molecule to give furanose form.



➢ ***(+)-Sucrose or Cane-Sugar or Table Sugar ($C_{12}H_{22}O_{11}$)***

Sucrose is the most important disaccharide in nature and is the most widely produced pure chemical. The name cane sugar comes from the fact that (+)-sucrose is found in very large amounts in sugar cane and sugar beets.

Properties: *i*) It is a white solid with crystalline nature that melts at 453K. It is not soluble in ether and alcohol. However, the sweet solid is highly dissolvable in water. Furthermore, as the name suggests (+)-sucrose is optically active and is dextrorotatory in nature.

ii) Upon heating above its melting point, it gets converted to caramel, a brown amorphous solid which is beverage coloring and confectionery. The further heating of the same produces charring with burnt sugar's smell.

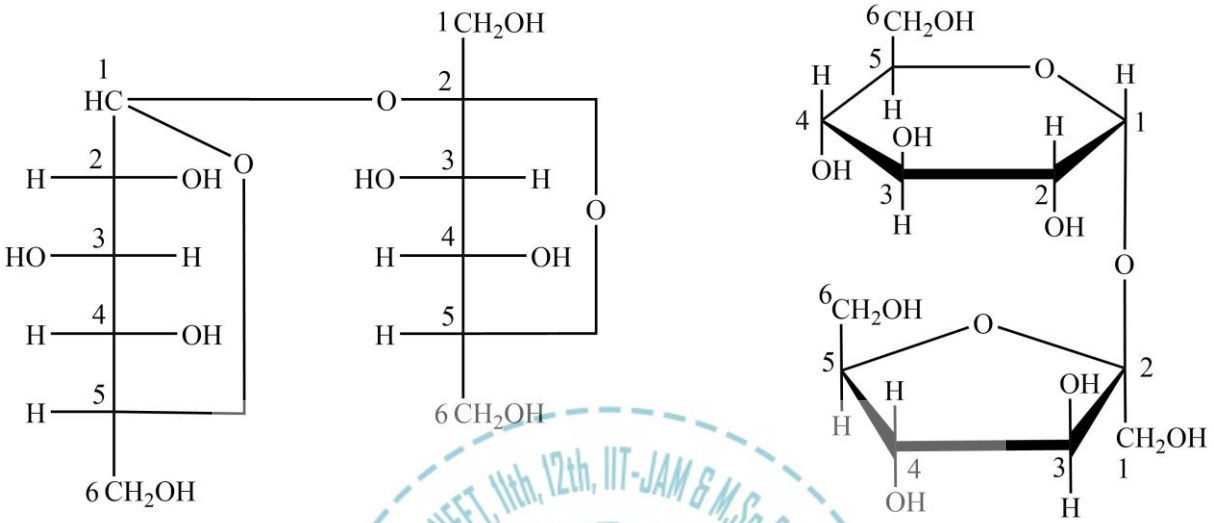
iii) Upon treating with yeast, sucrose yields an equimolar mixture of D-(+)-glucose and D-(–)-fructose which is due to the enzyme invertase.

iv) Sucrose reacts with acetic anhydride to give sucrose octaacetate.

v) Sucrose yields oxalic acid when treated with concentrated HCl.

vi) It gives sugar charcoal when treated with concentrated sulphuric acid with a large amount of SO_2 and CO_2 release.

Structure: The sucrose is made up of one glucose and one fructose unit which are joined together by the glycosidic linkage.



- ***(+)-Maltose** or Malt Sugar ($C_{12}H_{22}O_{11}$)*

Maltose in nature is primarily present in germinating seeds especially cereals. Originally, Augustin-Pierre Dubrunfaut discovered Maltose; nevertheless, his finding was well accepted in 1872 after the confirmation by Irish brewer and chemist Cornelius O'Sullivan. The name maltose comes from malt, combined with the suffix '-ose' which is used in sugars' nomenclature.

Properties: *i*) It is a white solid with crystalline nature that melts at 438K. It is not soluble in ether and alcohol. However, the sweet solid is well dissolvable in water. Furthermore, as the name suggests (+)-maltose is optically active and is dextrorotatory in nature.

ii) Upon treating with Br_2/H_2O, maltose yields maltobionic acid, an organic compound with the same number of carbon atoms as maltose.

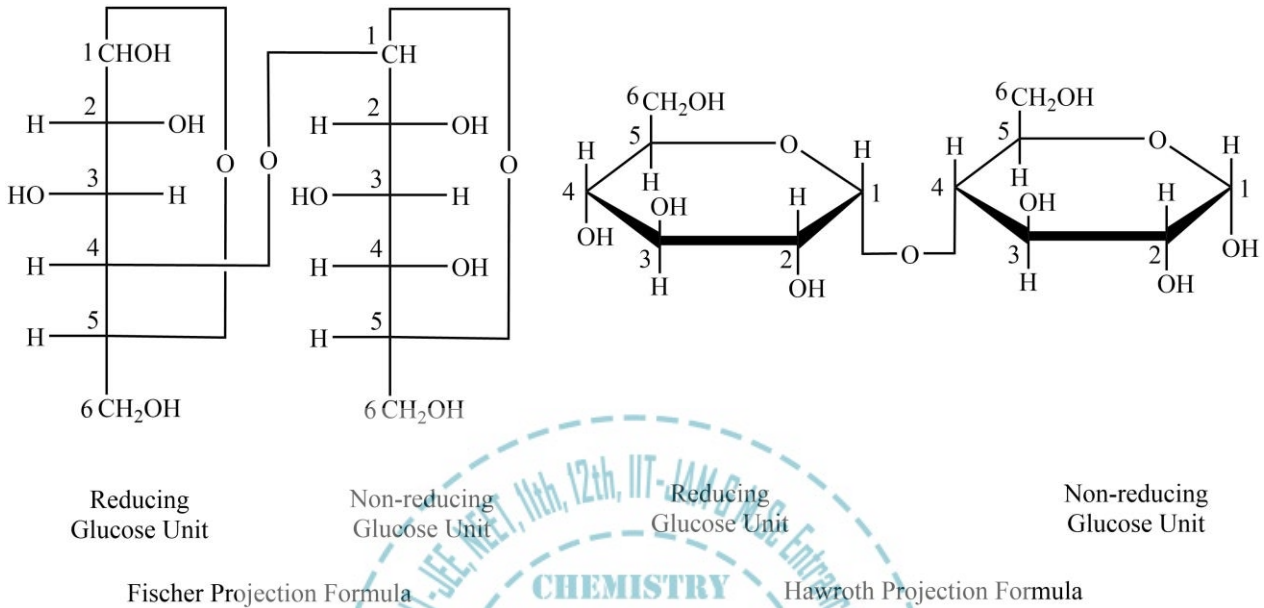
iii) Upon treating with dilute acids or yeast, maltose yields to moles of D-(+)-glucose which is due to the enzyme maltase.

iv) Just like the case of (+)-sucrose (cane sugar) Maltose reacts with acetic anhydride to give maltose octaacetate.

v) Tollens' reagent and Fehling's solution are well reduced by maltose.

vi) The maltose molecules react with hydroxylamine to yield phenylhydrazine or oxime to form phenylhydrazone.

Structure: The maltose is made up of two glucose units, one reducing and one none reducing, with are joined together by the glycosidic linkage.



- ***(+)-Lactose or Milk Sugar ($C_{12}H_{22}O_{11}$)***

Lactose is a disaccharide which is a sugar composed of galactose and glucose subunits and has the molecular formula $C_{12}H_{22}O_{11}$. Lactose is mainly found in mammals' milk; and therefore, it is also called as milk sugar. The milk gets sour if the bacterial action turns (+)-lactose into lactic acid. Lactose makes up around 2–8% of milk (by weight).

Properties: *i*) Lactose is a mildly sweet, non-hygroscopic, water-soluble, white solid with α- and β- forms which melt at 496K and 525K, respectively. Furthermore, as the name suggests (+)-lactose is optically active and is dextrorotatory in nature.

ii) Upon treating with dilute acid or yeast, lactose yields an equimolar mixture of D-(+)-glucose and D-(+)-galactose which is due to the enzyme lactase.

iii) Tollens' reagent and Fehling's solution are well reduced by lactose. This confirms the reducing nature of lactose like maltose.

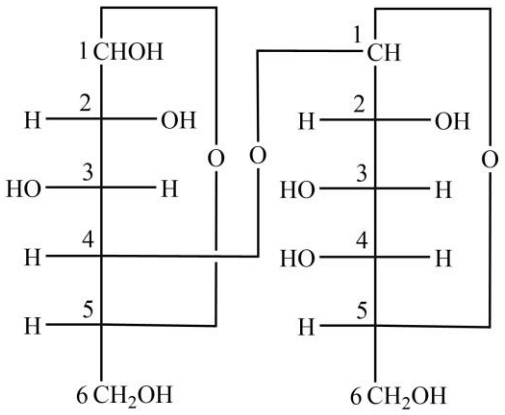
iv) The lactose molecules or milk sugar react with hydroxylamine to yield oxime, and with phenylhydrazine gives osazone.

vi) Upon treating with Br_2/H_2O, lactose yields lactobionic acid, an organic compound with the same number of carbon atoms as lactose.

vii) Lactose has relatively low cariogenicity among sugars.

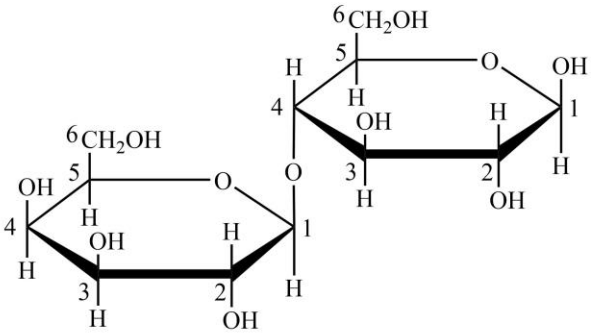
viii) Undigested lactose acts as dietary fiber.

Structure: The sucrose is made up of one glucose and one galactose unit with are joined together by the glycosidic linkage.



Glocose Galactose

Fischer Projection Formula



Galactose Glocose

Hawroth Projection Formula

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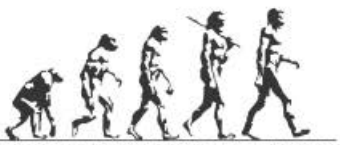

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