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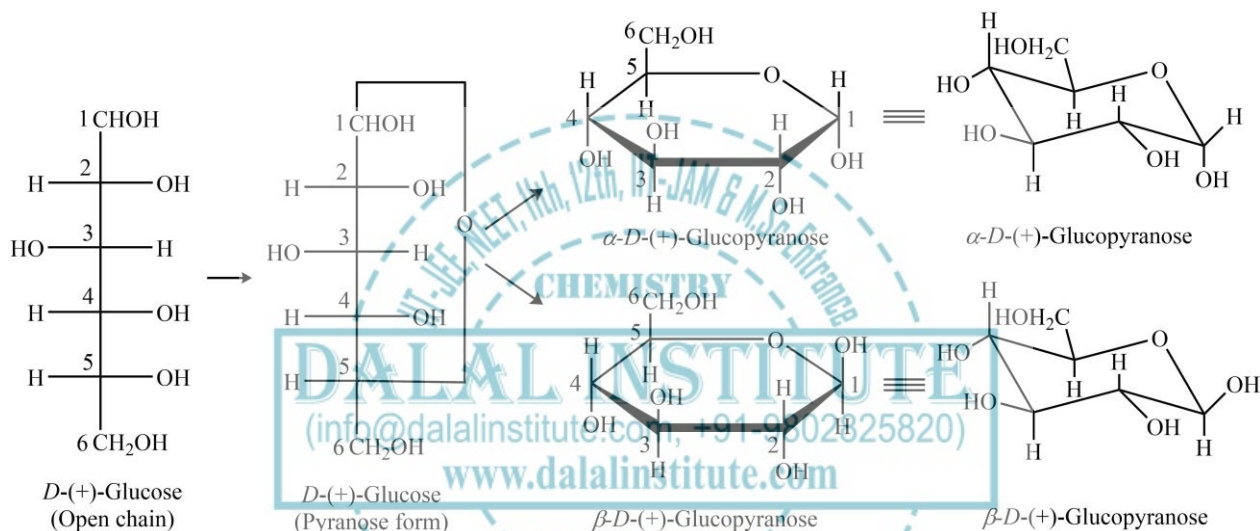
ii) Furanose form: The terminal aldehydic carbon participate in hemiacetal formation by using the hydroxyl group of 4th carbon in open-chain glucose molecule to give furanose form.

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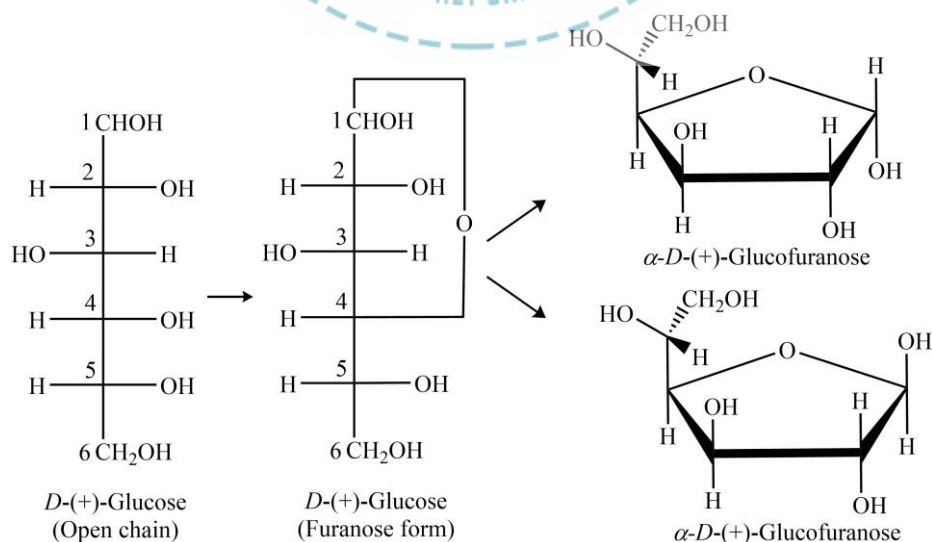
> ➤ *D-(−)-Fructose or Laevulose or Fruit Sugar (C$_6$H$_{12}$O$_6$)*

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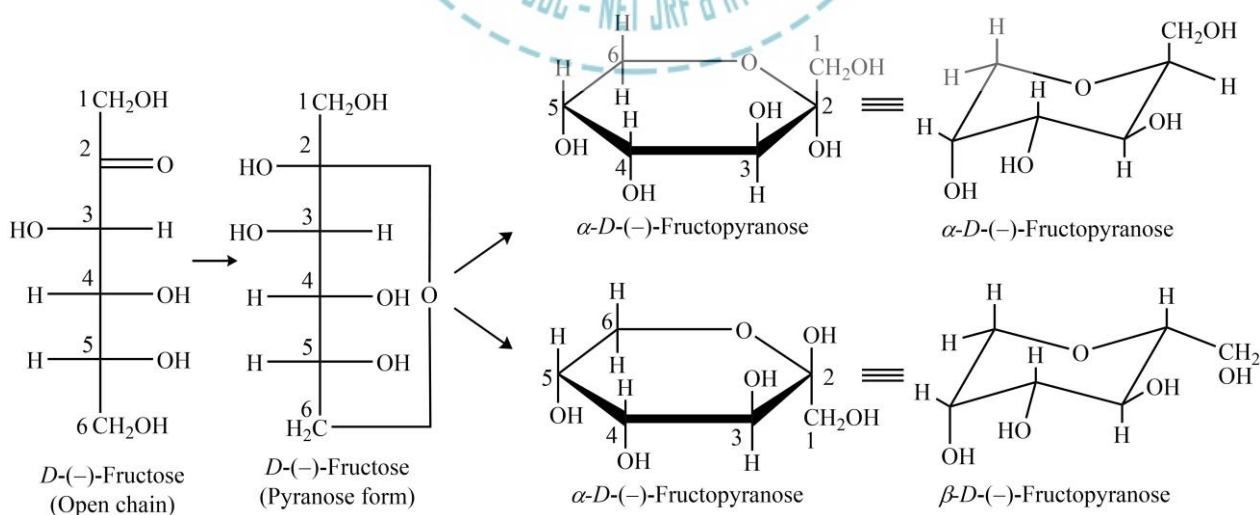
iv) Fructose doesn't react with dilute acids but can give laevulinic acid upon heating with concentrated HCl acid solution.

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.

D-(−)-Fructose (Open chain)

D-(−)-Fructose (Pyranose form)

α-D-(−)-Fructopyranose

α-D-(−)-Fructopyranose

α-D-(−)-Fructopyranose

β-D-(−)-Fructopyranose

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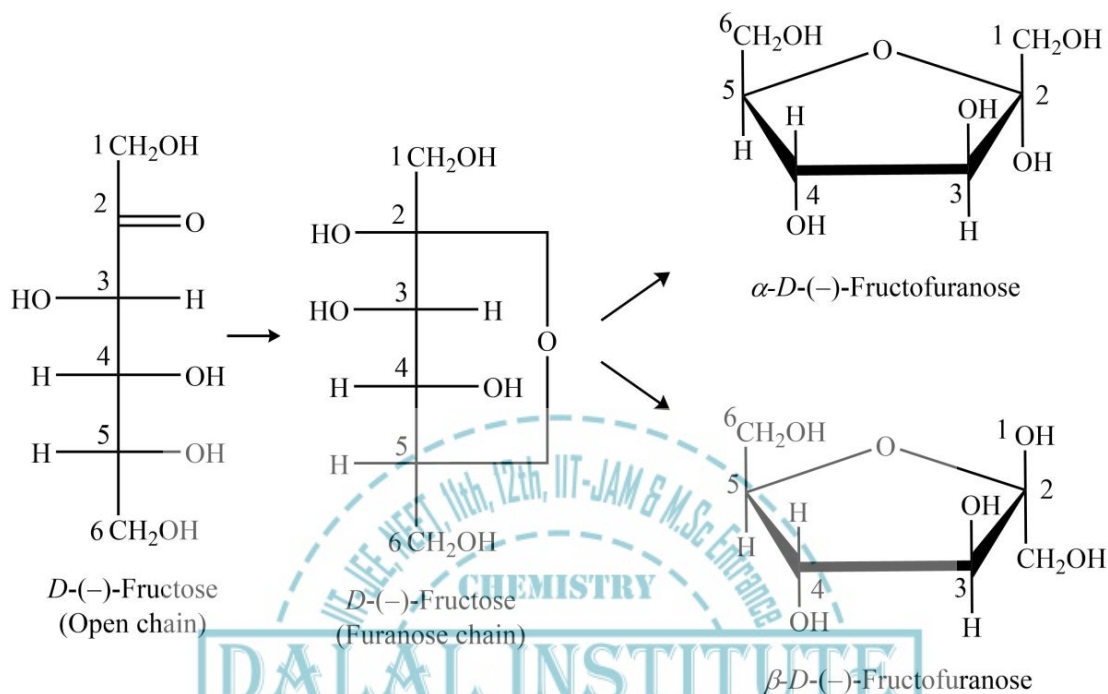
> ➤ *(+)-Sucrose or Cane-Sugar or Table Sugar ($C_{12}H_{22}O_{11}$)*

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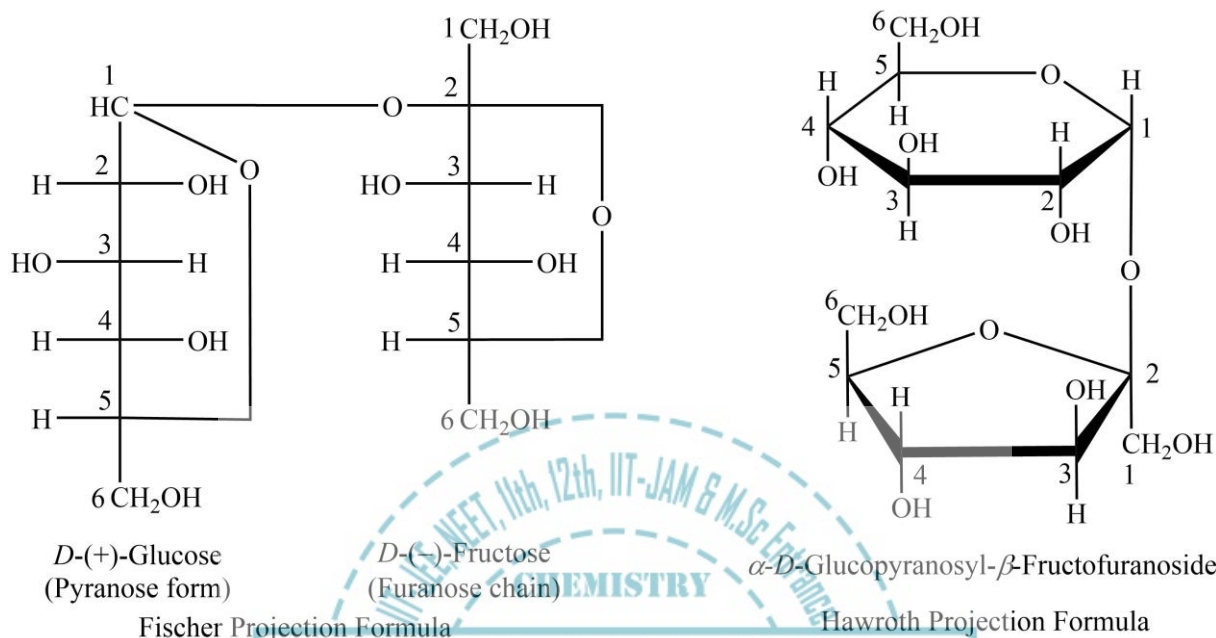
iii) Upon treating with yeast, sucrose yields an equimolar mixture of D-(+)-glucose and D-(–)-fructose which is due to the enzyme invertase.

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.

D-(+)-Glucose
(Pyranose form)

D-(−)-Fructose
(Furanose chain)

α-*D*-Glucopyranosyl-β-Fructofuranoside

Fischer Projection Formula

Hawroth Projection Formula

➤ **(+)-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$_2$O, 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.

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

| Reducing Glucose Unit | Non-reducing Glucose Unit | Reducing Glucose Unit | Non-reducing Glucose Unit |

Fischer Projection Formula   Hawroth Projection Formula
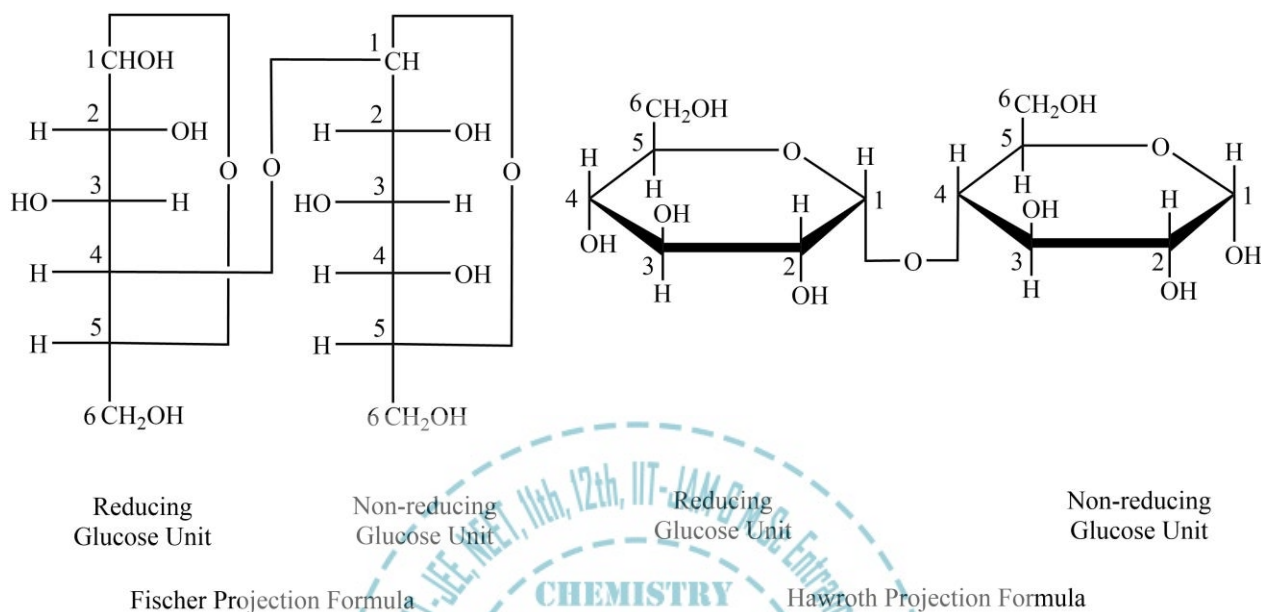
➤ *(+)-Lactose or Milk Sugar (C$_{12}$H$_{22}$O$_{11}$)*

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.

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

Glocose   Galactose   Galactose   Glocose

Fischer Projection Formula   Hawroth Projection Formula
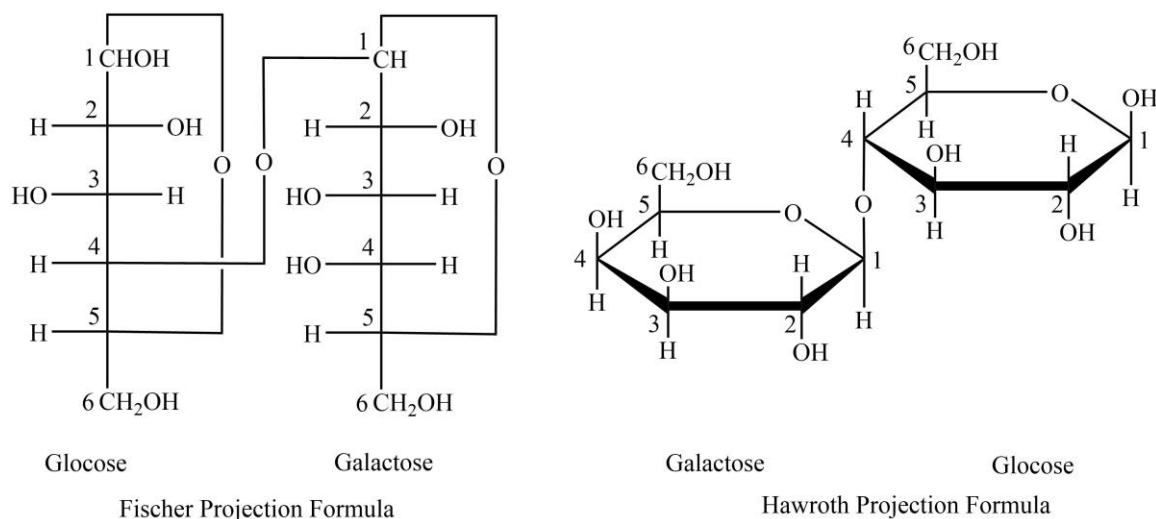
❖ Deoxy Sugars

*Deoxy sugars may simply be defined as the sugars in which at least one hydroxyl group is replaced by a hydrogen atom.*

The common nomenclature of deoxy sugars is carried out by adding the prefix "deoxy" along with the location of carbon at which the displacement has taken place, followed by the common name of parent aldoses or ketoses. On the other hand, the IUPAC nomenclature is done by adding two prefixes before the IUPAC name of parent aldoses or ketoses; the first prefix "deoxy" (along with the location of substituted carbon) and the at which the displacement has taken place followed by the configurational prefix of chiral carbon atoms.
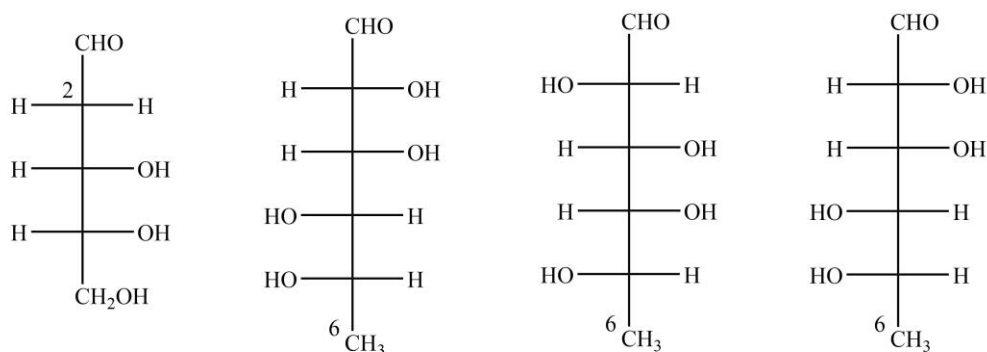
Common Name:	*2-Deoxy-D-(–)-Ribose*	*6-Deoxy-L-(–)-Mannose*	*6-Deoxy-L-(–)-Galactose*	*2, 6-Dideoxy-D-(+)-Allose*
IUPAC Name:	*2-Deoxy-D-*erythropentose	*6-Deoxy-L-*Mannohexose	*6-Deoxy-L-*Galactohexose	*2, 6-Dideoxy-L-*Ribohexose

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The most abundant deoxy sugar is deoxyribose which is a major constituent of DNA. Furthermore, it is also worthy to note that although the replacement of the hydroxyl group (by the hydrogen atom) is feasible at any carbon, most of the deoxy sugars are 6-deoxy type.


(I)   (II)

(III)   (IV)
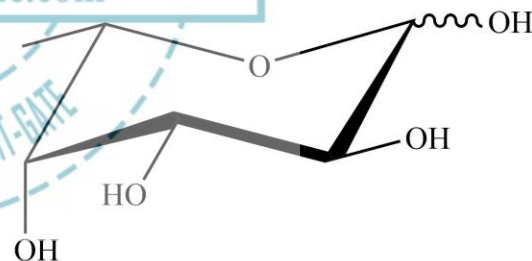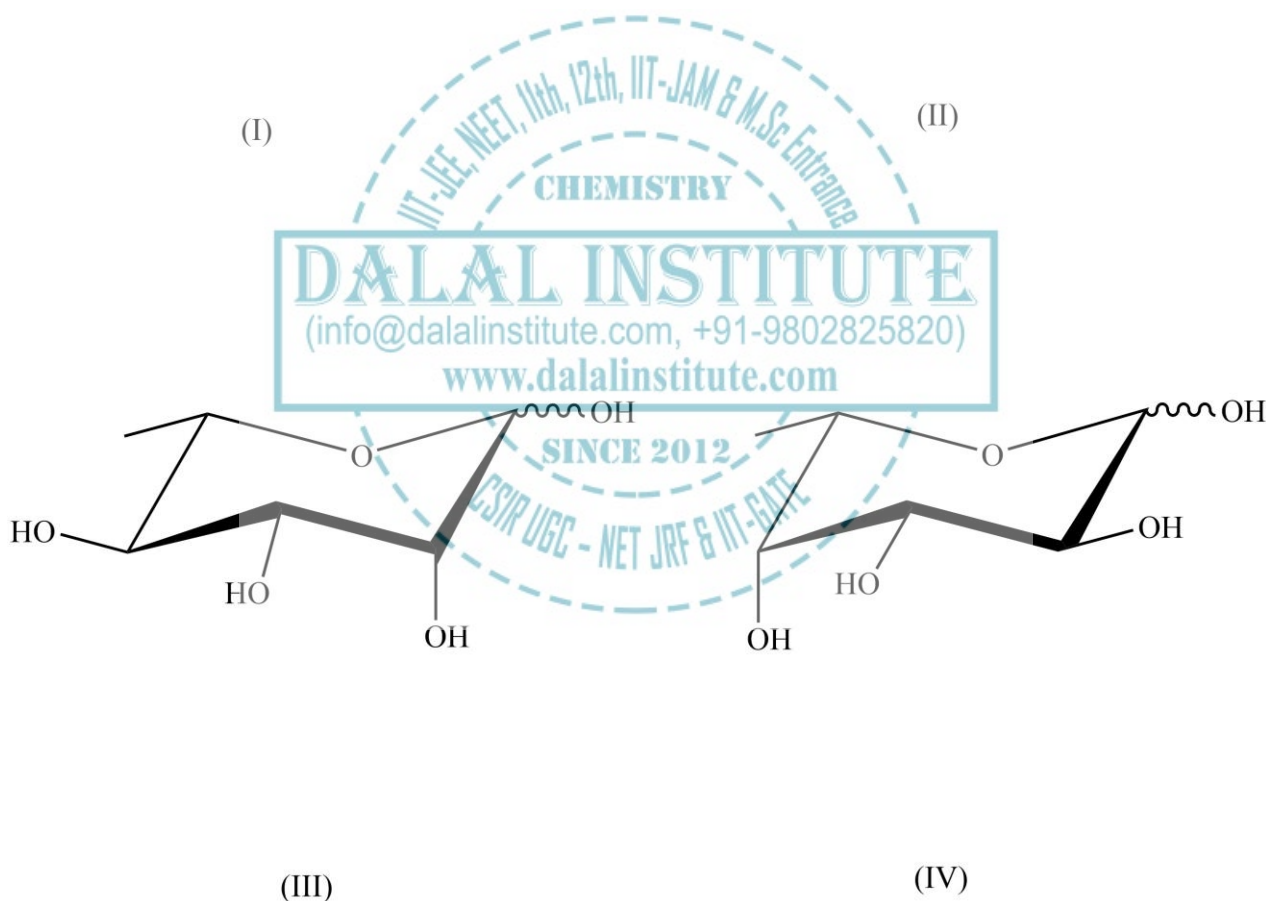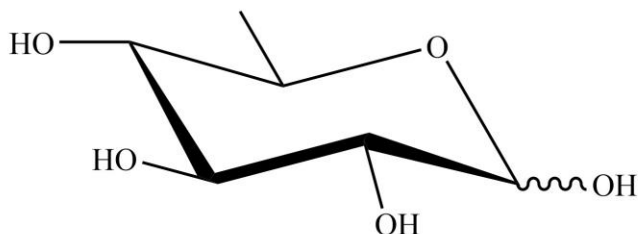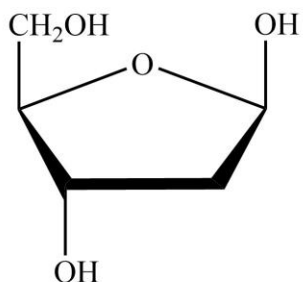
It seems that the deoxygenation at C2 in β-D-ribofuranose enhances the overall stability of the consequential nucleic acid; however, the better hydrophobic interaction at C6 (methyl group) with appropriate receptor sites appears to be the dominant factor in the other three molecules.

❖ Amino Sugars

Amino sugars may simply be defined as the sugars in which at least one hydroxyl group is replaced by an amine group.

Since amino sugars play key roles in the structure and proper functioning of glycoproteins many biologically significant polysaccharides, these types of sugars are absolutely vital components for the well-functioning of humans and other organisms. The primary cause of such behavior lies in the good polarity to the molecule due to the positively charged ammonium ion or the acetamido group which can be created from the protonation of a free amine in a monosaccharide residue. Two of the most popular members of amino sugars are given below.

(I)

(II)

(III)

(IV)
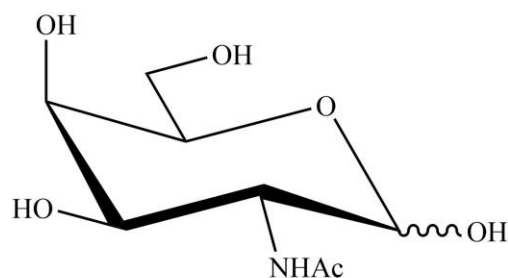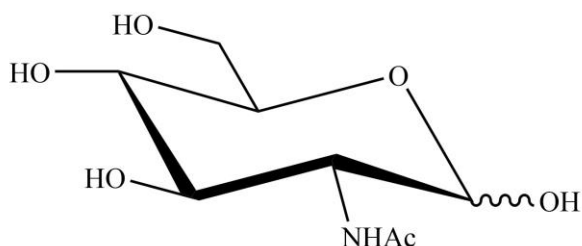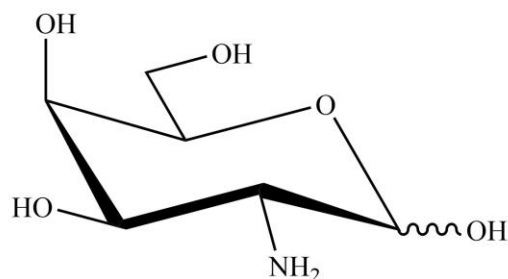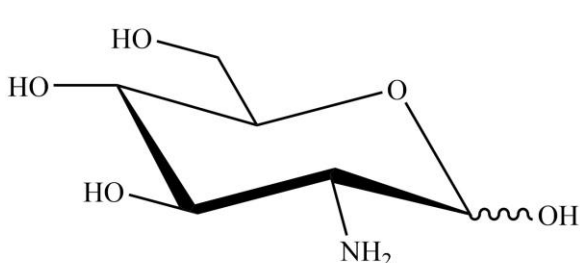
Out of more than 60 types of known amino sugars, N-Acetyl-d-glucosamine the most abundant (main component of chitin). It is also worthy to note that the derivatives of many amine-containing sugars like sialic acid or N-acetylglucosamine are also considered amino sugars, despite the fact that nitrogens in them are part of more complex functional groups rather than formal amines. Furthermore, aminoglycosides (conjugates of amino sugars and aminocyclitols) form a group of antimicrobial substances that hinder the synthesis of bacterial proteins.

❖ Branch Chain Sugars

Branched-chain sugars may simply be defined as the sugars in which at least one hydrogen atom or hydroxyl group is replaced by a carbon group.

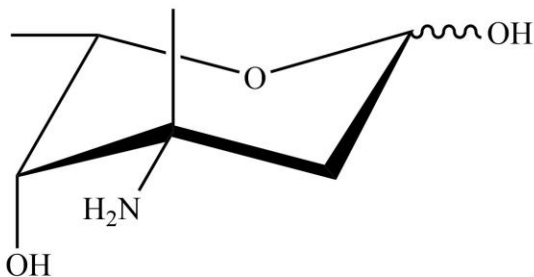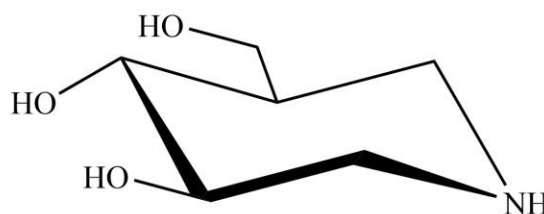The common types of branched-chain sugars (both kinds) are found in biomolecules. Some typical examples are given below.
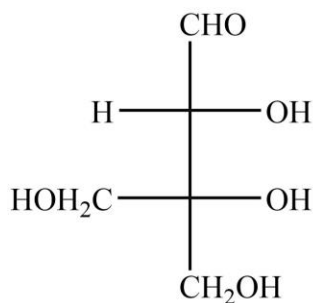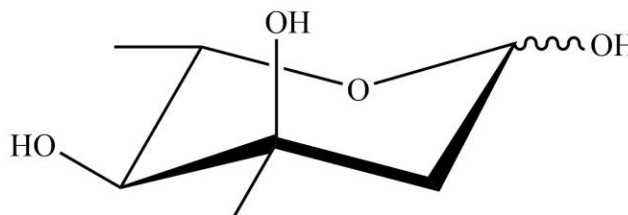
(I)   (II)

(III)   (IV)

It is also worthy to note that branched-chain sugars were considered as "rare" until 1960; however, after the confirmation of their presence in many antibiotics (in form of their glycosidic component), many synthetic chemists put effort to widen the availability domain. Branched-chain sugars are generally obtained from uloses or by the opening of epoxides.

❖ General Methods of Determination of Structure and Ring Size of Sugars with Particular Reference to Maltose, Lactose, Sucrose, Starch and Cellulose

Almost all of the oligo- or polysaccharides are white powdery substances that cannot be dissolved in a typical organic solvent but show good solubility in water; so, we cannot tell how the atoms are connected with each other just by looking at it or by other simple routes. Also, owing to the presence of a large number of atoms (especially in the case of polysaccharides), the routine procedure for the "structure elucidation of organic compounds" cannot be employed. Therefore, instead of studying the entire molecule via mass spectrometry or NMR spectroscopy at once, a very sophisticated route has been developed by the researchers over the years in which building blocks of the same carbohydrate are studied. In this section, we will study the general route for the structure determination of oligo- and polysaccharides and then we will apply the same to evaluate the structure of maltose, lactose, sucrose, starch, and cellulose.

➢ General Route to Find the Structure of Oligo- or Polysaccharides

The structure elucidation of complex carbohydrates is based on the principle that an oligo- or polysaccharides can be disconnected into monosaccharide units, which in turn can be studied, and finally can be recombined to produce intact molecule mentally. The general route for the structure determination of oligo- and poly-saccharides involves the following steps.

1. Monomeric analysis: This is the first step which involves the disconnection of a given oligo- or poly-saccharide (typically at glycosidic linkages) into its monosaccharide components. This is typically achieved by the acid hydrolysis of glycosidic bonds. The rate of acid hydrolysis of glycosidic joints differs for the size of the cycle, nature of the bond, and the corresponding configuration also.

2. Study of the monosaccharide units: Once the monosaccharides are obtained, we need to study those building blocks (such as chain length or ring size) by conventional modern spectroscopic techniques like NMR or X-ray analysis. The necessary and optional subtypes of this step are given below.

i) Identification: The identification of methylated sugars or monosaccharides means that we try to identify the building block by search-match its experimental parameters (like the melting point or specific rotation) to previously reported literature i.e., handbooks.

ii) Historical Method: The earliest work to determine the configuration at asymmetric carbon in E. Fisher. He primarily used two routes to study typical monosaccharides; cyanohydrin synthesis and oxidation using nitric acid. In the later period, he used the same approach to get the relative configuration of many other pentoses and hexoses.

iii) Mass spectrometry: The step employs mass spectrometry to find out the structural data of the monosaccharide but gives no information about the stereochemical notation.

iv) NMR analysis: Once the structure of the monosaccharide is known, NMR spectroscopy is used to determine the configuration at the asymmetric center.

3. Finding the nature of linkage: The monomeric analysis and study of monosaccharide units tell us the nature of the cyclic form of monosaccharide units, the bonding poisons, and whether the polysaccharide is branched or unbranched. Therefore, the complete structure of the polysaccharide can be known only after the configuration of glycosidic bonds and the absolute sequence of monosaccharide units in the complete chain. This can be achieved by cleavage selectivity of glycosidic bonds and theoretical mono- or disaccharide yield. In other words, acid hydrolysis's selectivity for most of the polysaccharides is quite unique and can successfully be employed to find out the nature of the linkage.

➢ *Structure Determination of Maltose, Lactose, Sucrose, Starch and Cellulose*

The general route of structure determination of some typical oligosaccharides and polysaccharides is given below.

1. Structure determination of maltose: Maltose is a natural sugar with formula $C_{12}H_{22}O_{11}$ that reduces Tollens' reagent and Fehling solution which indicates its reducing character. The structure of maltose is obtained as given below.

i) Monomeric analysis: The hydrolysis of maltose with maltase or mineral acids yields two molecules of D-(+)-glucose. Furthermore, the oxidation of maltose with bromine water results in the maltobionic acid inferring that one of the two glucose units has reactive hemiacetal form at aldehydic carbon.

$$(C_{11}H_{21}O_{11})CHO \xrightarrow{\text{Br}_2/\text{H}_2\text{O}} (C_{11}H_{21}O_{11})COOH \tag{1}$$

ii) Study of the monosaccharide units: The full methylation of maltobionic acid with sodium hydroxide and $(CH_3)_2SO_4$, and then carrying out acid hydrolysis results in a mixture of 2, 3, 4, 6-tetra-O-methyl-D-glucose and 2, 3, 5, 6-tetra-O-methyl-D-gluconic acid.

2, 3, 4, 6-tetra-O-methyl-D-glucose   2, 3, 5, 6-tetra-O-methyl-D-gluconic acid

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The free –OH present at C_4 in 2, 3, 5, 6-tetra-O-methyl-D-gluconic acid infers that methylation was not possible in maltobionic acid, which in turn proves that C_4–OH must be engaged in glycosidic bonding in maltobionic acid, and therefore in maltose too. Now we are left with the possibility of C_5–OH participating in the formation 6-membe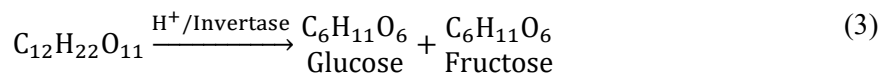red ring structure (pyranose form) in reducing glucose unit. On the other hand, the free –OH present at C_5 in 2, 3, 5, 6-tetra-O-methyl-D-glucose infers that methylation was not possible in maltobionic acid, which in turn proves that C_5–OH must be engaged in glycosidic bonding in maltobionic acid, and therefore in maltose too. Now we are left with the possibility of C_5–OH participating in the formation 6-membered ring structure (pyranose form) in a non-reducing glucose unit.

iii) Nature of linkage: Since we know that the maltose's hydrolysis by yeast (maltase enzyme) has specificity for the hydrolysis of α-glucosidic linkages, α-C_4–OH of reducing glucose unit must be connected to the α-C_1–OH of non-reducing glucose unit. The maltose is made up of two glucose units, one reducing and one none reducing, with are joined together by the glycosidic linkage.

Fischer Projection Formula   Hawroth Projection Formula
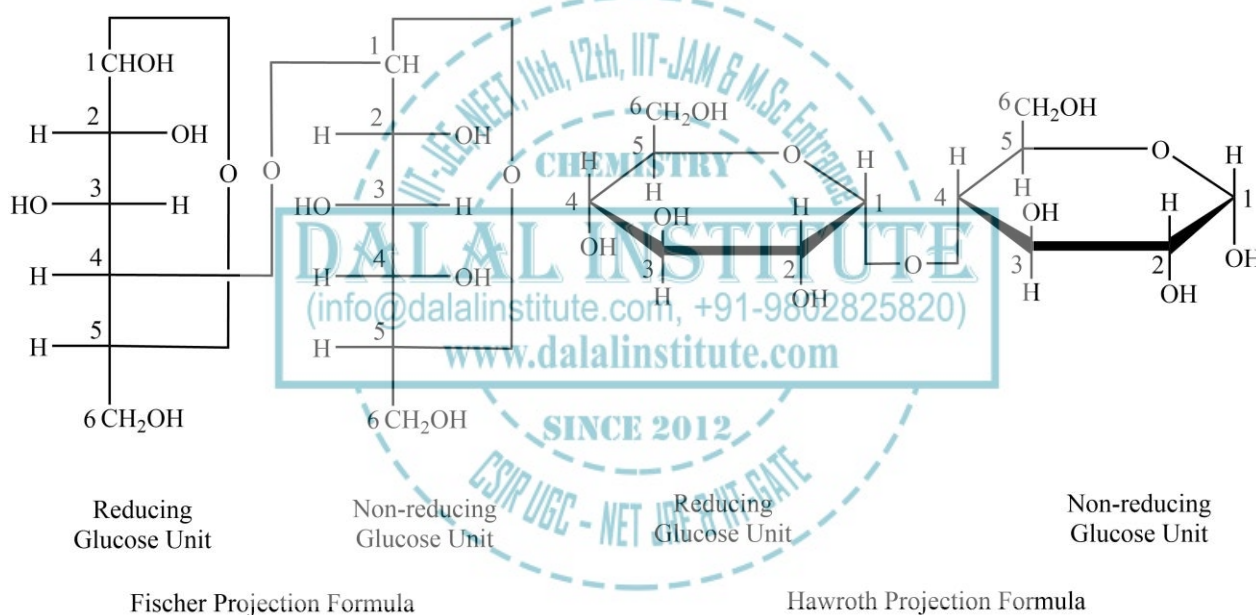
Furthermore, we can also conclude that the α-form of (+)-maltose differs from β-form w.r.t the configuration at anomeric carbon. In other words, the OH group at C_1 in β-form is above the plane whereas it lies below the plane in α-form.

2. Structure determination of lactose: Lactose is a natural sugar with formula $C_{12}H_{22}O_{11}$ that reduces Tollens' reagent and Fehling solution which indicates its reducing character. The structure of lactose is obtained as given below.

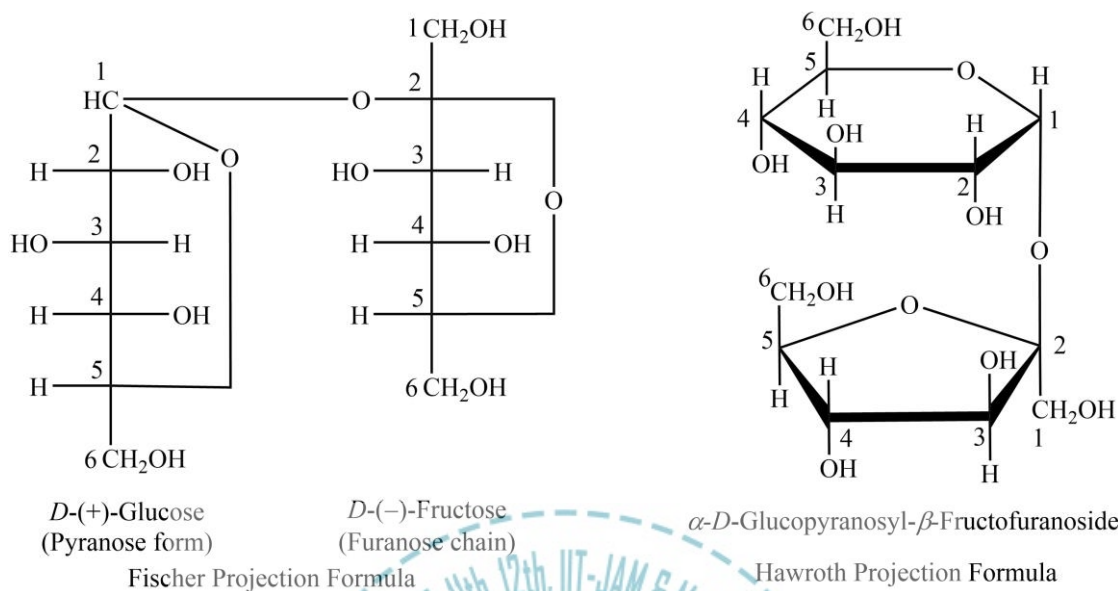*i) Monomeric analysis:* The hydrolysis of lactose with lactase or mineral acids yields an equimolar mixture of D-(+)-glucose and D-(+)-galactose. Furthermore, the oxidation of lactose with bromine water results in lactobionic acid. The hydrolysis of lactobionic acid results in D-(+)-gluconic acid and D-(+)-galactose inferring that D-(+)-galactose is non-reducing while D-(+)-glucose must be reducing in nature.

ii) Study of the monosaccharide units: The full methylation of lactobionic acid with sodium hydroxide and $(CH_3)_2SO_4$, and then carrying out acid hydrolysis results in a mixture of 2, 3, 4, 6-tetra-O-methyl-D-galactose and 2, 3, 5, 6-tetra-O-methyl-D-gluconic acid
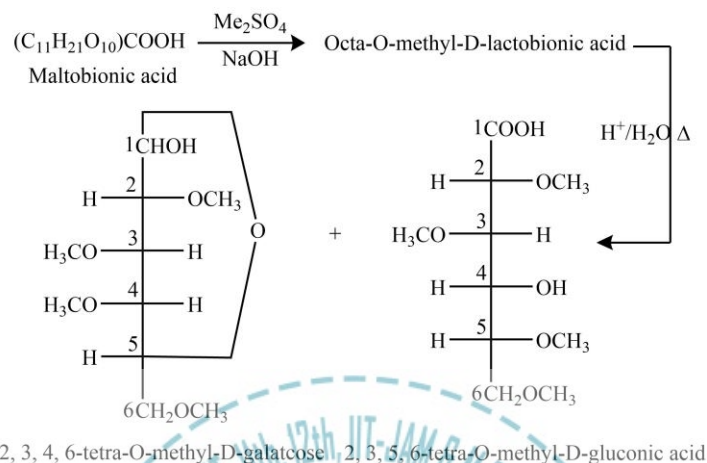
2, 3, 4, 6-tetra-O-methyl-D-galatcose   2, 3, 5, 6-tetra-O-methyl-D-gluconic acid

The free –OH present at C_4 in 2, 3, 5, 6-tetra-O-methyl-D-gluconic acid infers that methylation was not possible in lactobionic acid, which in turn proves that C_4–OH must be engaged in glycosidic bonding in lactobionic acid, and therefore in lactose too. Now we are left with the possibility of C_5–OH participating in the formation 6-membered ring structure (pyranose form) in reducing glucose unit. On the other hand, the free –OH present at C_5 in 2, 3, 4, 6-tetra-O-methyl-D-galactose infers that methylation was not possible in lactobionic acid, which in turn proves that C_5–OH must be engaged in glycosidic bonding in latobionic acid, and therefore in maltose too. Now we are left with the possibility of C_5–OH participating in the formation 6-membered ring structure (pyranose form) in a non-reducing galactose unit.

iii) Nature of linkage: Since we know that the lactose's hydrolysis by yeast (lactase enzyme) has specificity for the hydrolysis of β-glycosidic linkages, β-C_1–OH of non-reducing galactose unit must be connected to the C_4–OH of reducing glucose unit.
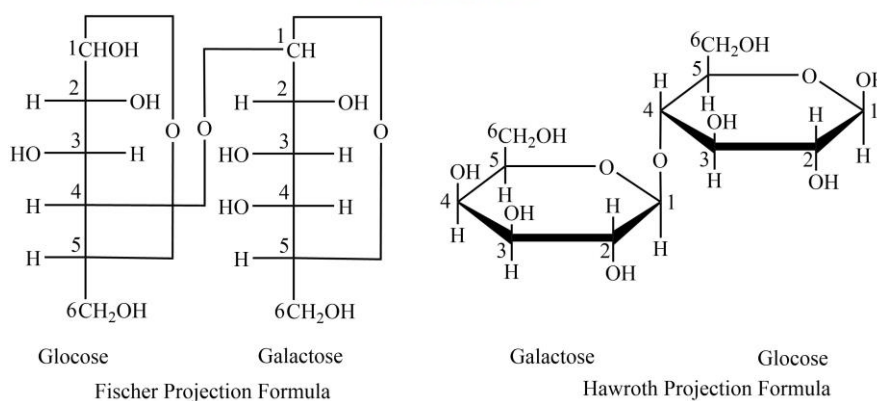
Furthermore, we can also conclude that the α-form of (+)-lactose differs from β-form w.r.t the configuration at anomeric carbon (OH group at C_1 in β-form is above the plane whereas it lies below the plane in α-form).

3. Structure determination of sucrose: Sucrose is a natural sugar with formula $C_{12}H_{22}O_{11}$ that does not reduce Tollens' reagent and Fehling solution which indicates its non-reducing character. The structure of sucrose is obtained as given below.

i) Monomeric analysis: The hydrolysis of sucrose with invertase or mineral acids yields an equimolar mixture of D-(+)-glucose and D-(+)-fructose.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{H}^+/\text{Invertase}} \underset{\text{Glucose}}{C_6H_{11}O_6} + \underset{\text{Fructose}}{C_6H_{11}O_6} \tag{3}$$

ii) Study of the monosaccharide units: The full methylation of sucrose with sodium hydroxide and $(CH_3)_2SO_4$, and then carrying out acid hydrolysis results in a mixture of 2, 3, 4, 6-tetra-O-methyl-D-glucose and 1, 3, 4, 6-tetra-O-methyl-D-fructose.

2, 3, 4, 6-tetra-O-methyl-D-glucose   1, 3, 4, 6-tetra-O-methyl-D-fructose
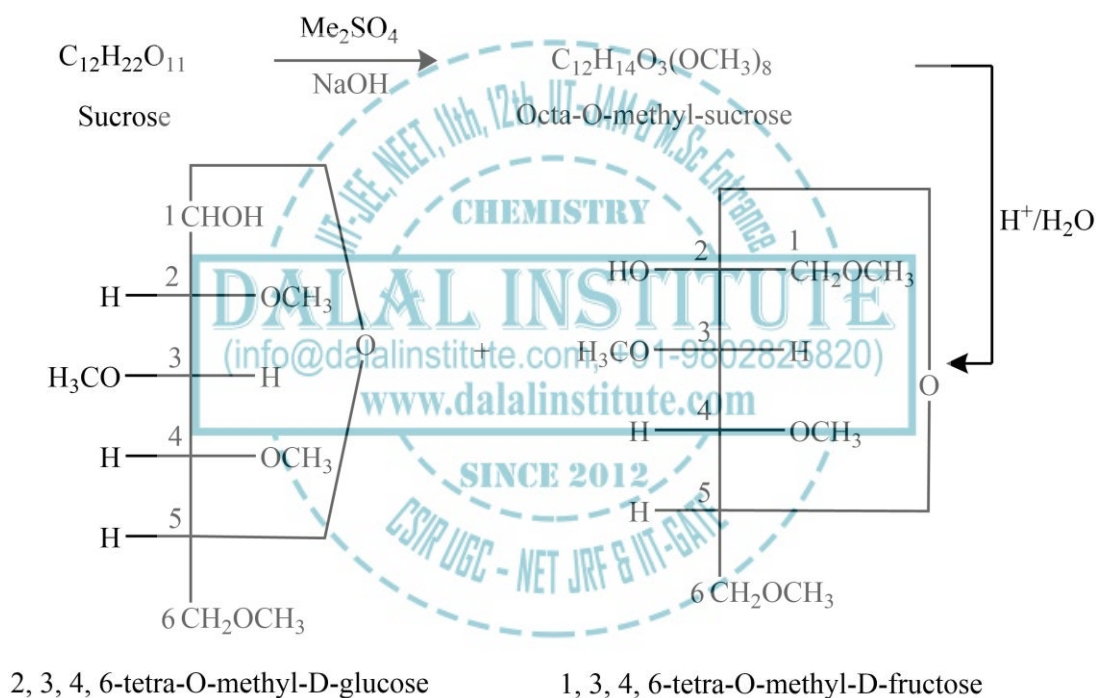
The NMR analysis and Fisher method showed that C_1–OH and C_5–OH in 2, 3, 4, 6-tetra-O-methyl-D-glucose are involved in hemiacetal formation unveiling a six-membered ring structure (pyranose form). On the other hand, C_2–OH and C_5–OH in 1, 3, 4, 6-tetra-O-methyl-D-fructose are involved in hemiacetal formation unveiling a five-membered ring structure (furanose form).

iii) Nature of linkage: Owing to the non-reducing nature of sucrose, we can conclude that glucose and fructose units must be connected via corresponding glycosidic or reducing sites. Now, the overall structure of sucrose can be visualized by considering two important experimental results. First is that maltase hydrolyses α-glucopyranosides and sucrose showing that the glucose unit must be in α-form. The second one is that invertase hydrolyses β-fructofuranosides and sucrose showing that the fructose unit must be in β-form.

D-(+)-Glucose   *D*-(−)-Fructose α-*D*-Glucopyranosyl-β-Fructofuranoside
(Pyranose form)   (Furanose chain)
Fischer Projection Formula   Hawroth Projection Formula

Hence, we can say that sucrose is made up of one glucose and one fructose unit, which are joined together by the glycosidic linkage.

4. Structure determination of starch: Starch is the most abundant carbohydrates' source for human-kind which is primarily found in seeds, plant roots, fruits, and tubers. Moreover, it is also very important to note that starch is not a single compound but a mixture of two; amylose (20%) and amylopectin (80%). The structure of maltose is obtained as given below.

i) Monomeric analysis: The hydrolysis of both compounds of starch (amylose and amylopectin) with boiling mineral acids yields D-(+) glucose units.

$$\underset{Amylose}{(C_6H_{10}O_5)_n} \xrightarrow{H^+/\Delta} \underset{Dextrin}{(C_6H_{10}O_5)_n} \xrightarrow{H^+/\Delta} \underset{D(+)Maltose}{C_{12}H_{22}O_{11}} \xrightarrow{H^+/\Delta} \underset{D(+)Glucose}{(C_6H_{10}O_5)_n} \tag{4}$$

$$\underset{Amylopectin}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+/\Delta} \underset{D(+)Glucose}{(C_6H_{10}O_5)_n} \tag{5}$$
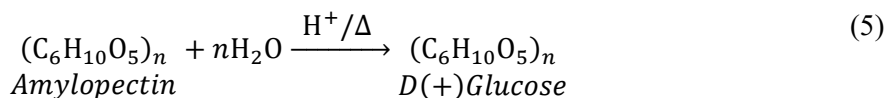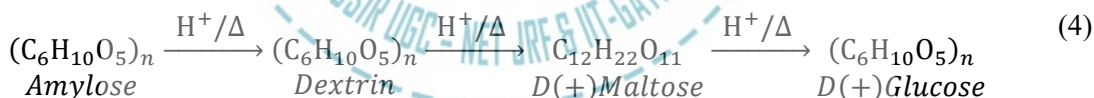
Hence, we can say that amylose, as well as amylopectin, both are made-up of D-(+) glucose units. Furthermore, it is also worthy to note that *n* has a range of 200–300 and 1000–3000 for amylose and amylopectin, respectively.

ii) Study of the monosaccharide units: The partial hydrolysis of amylose and amylopectin with β-amylase (diastase enzyme) results in the D-(+)-maltose i.e. a single disaccharide.

$$\underset{Starch}{(C_6H_{10}O_5)_n} + n(H_2O) \xrightarrow{H^+/\Delta} \underset{D(+)Maltose}{nC_{12}H_{22}O_{11}} \tag{6}$$
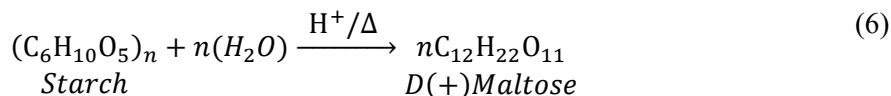
iii) Nature of linkage: Since we know that C_4–OH of reducing glucose unit is connected to the α-C_1–OH of non-reducing glucose unit i.e., α-glucosidic linkage, amylose can be considered as a chain of D-(+) glucose units connected by α-glucosidic bonds.
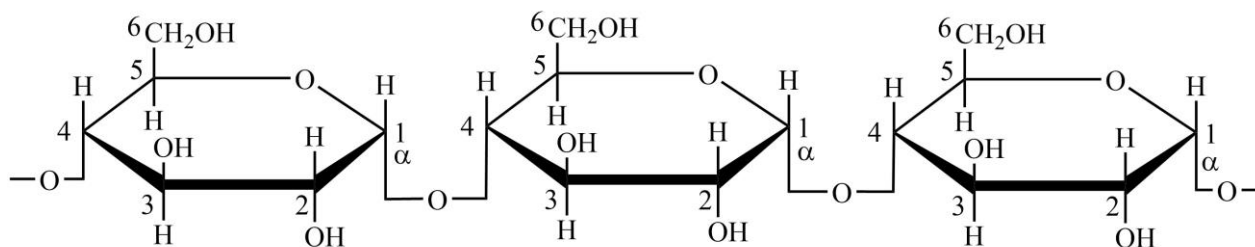
Amylose Structure
(Hawroth Projection Formula)

Just like the case of amylose, the C_4–OH of the reducing glucose unit is connected to the α-C_1–OH of the non-reducing glucose unit (α-glucosidic linkage) to form a chain of D-(+) glucose units. However, unlike amylose, the generation of D-(+)-maltose by hydrolysis of amylopectin with β-amylase (diastase enzyme) is feasible only up to fifty percent. This infers that amylopectin also has some other kind of bonds that are immune to the diastase enzyme. The acid hydrolysis of fully methylated amylopectin yields 2, 3, 6-tri-O-methyl-D-glucose (90%), 2, 3, 4, 6-tetra-O-methyl-D-glucose (5%) and 2, 3-di-O-methyl-D-glucose (5%); which infer α-1, 4-linkages, some non-reducing ends and α-1, 4-linkages, respectively.
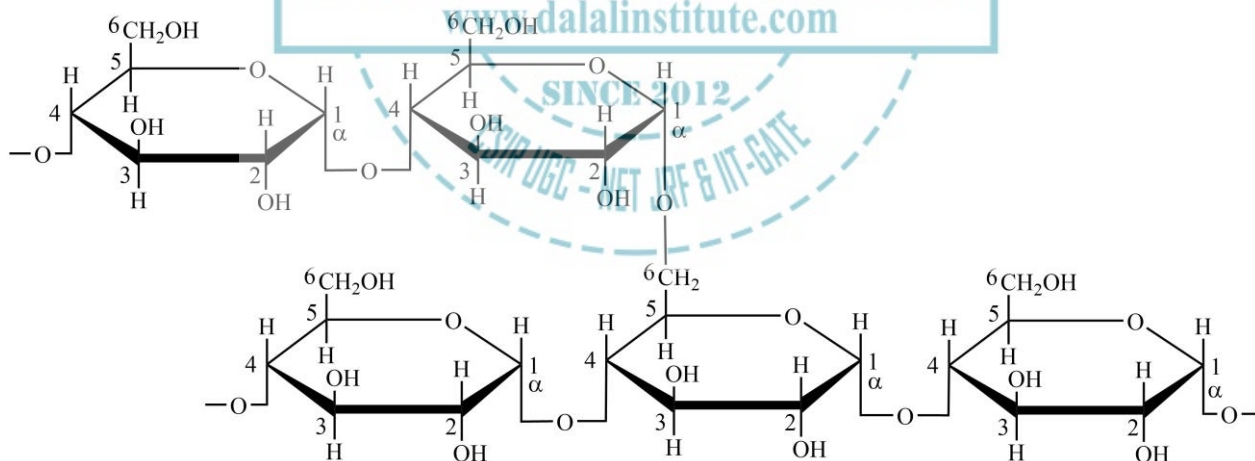
Amylose Structure
(Hawroth Projection Formula)

Finally, it is also worthy to note that unlike amylose, a very large extent of branching has been observed in amylopectin in which short-chain (about 25 glucose units) with α-linkage.

5. Structure determination of cellulose: The most abundant organic compound on earth is cellulose which forms all plants' cell walls. It is the primary component of jute, wood (50%), and cotton (95%). The structure of maltose is obtained as given below.

i) Monomeric analysis: The complete hydrolysis of cellulose with dilute sulphuric acid yields D-(+)-glucose as the only product. Therefore, one can conclude that cellulose is made up of D-(+)-glucose units (just like the case of starch).

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H_2SO_4} nC_6H_{12}O_6 \tag{7}$$
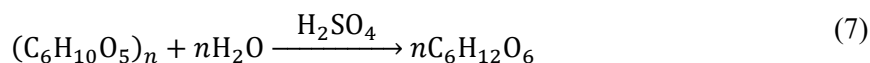
ii) Study of the monosaccharide units: The reaction of cellulose with a mixture of sulphuric acid and acetic anhydride results in hydrolysis and acetolysis simultaneously to produce cellobiose (a disaccharide).

$$(C_6H_{10}O_5)_n \xrightarrow{(MeCO)_2/H_2SO_4} \text{Cellobiose} \tag{8}$$
$$\text{\textit{Cellulose}}$$

iii) Nature of linkage: The cellobiose's structure resembles to the structure of maltose excepting the fact that its hydrolysis is carried out by 'emulsin' instead of β-amylase or maltase. Emulsin enzyme is specific for β-glycosidic linkage whereas β-amylase is specific for α-glycosidic bonds. Hence, we can conclude that D-(+)-glucose units joined together via β-glucosidic linkage to form cellobiose. All this information infers that cellulose can be considered as glucose units' chain via β-1, 4-glucosidic bonds.
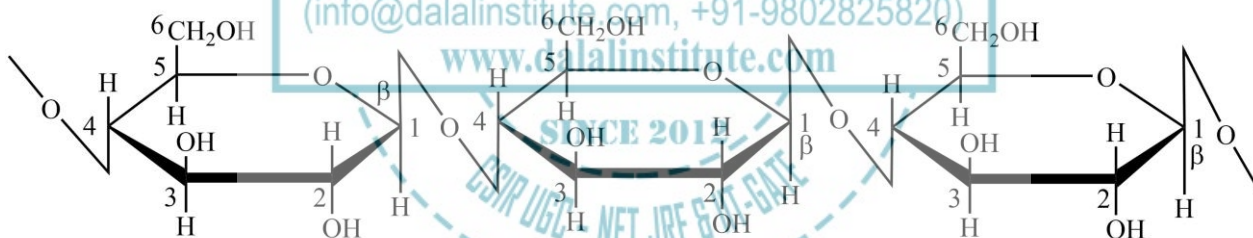
Cellulose Structure
(Hawroth Projection Formula)

One of the glaring differences between amylose and cellulose is that the glucose units in amylose are connected by α-1, 4-glucosidic bonds; whereas in cellulose, glucose units bind together via β-1, 4-glucosidic bonds.

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❖ Problems

Q 1. What are natural sugars? Discuss the structure properties of Maltose.

Q 2. What do you mean by deoxy sugars? Explain with suitable examples.

Q 3. Define amino sugars?

Q 4. What do you understand by branched chain sugars? How they are different from normal sugars?

Q 5. Discuss the primary methods of structure determination of disaccharide with special refence to maltose, lactose, sucrose.

Q 6. Discuss the structure determination of starch.

Q 7. What is cellulose? How would you find its structure?

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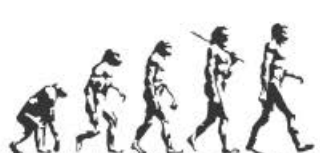
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