

❖ 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 polysaccharide (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.

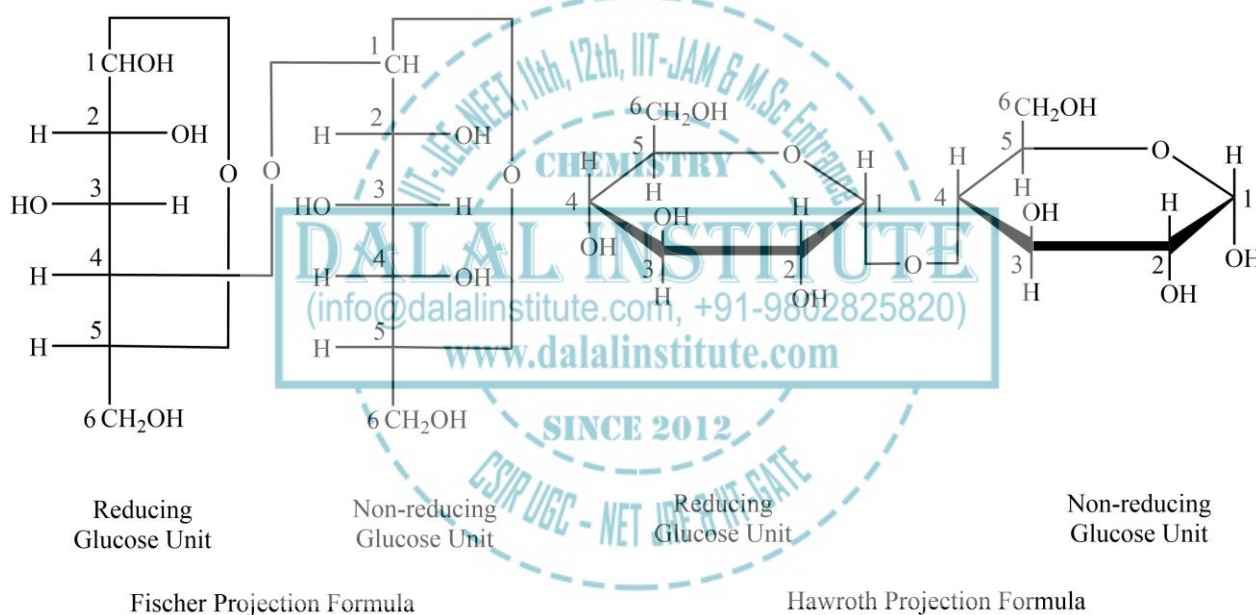
ii) Historical Method: The earliest work to determine the configuration at asymmetric carbon in E. Fisher. He primarily used two routes to study typical monosaccharides; cyanohydrin synthesis and oxidation using nitric acid. In the later period, he used the same approach to get the relative configuration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

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-membered 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 non-reducing, with are joined together by the glycosidic linkage.

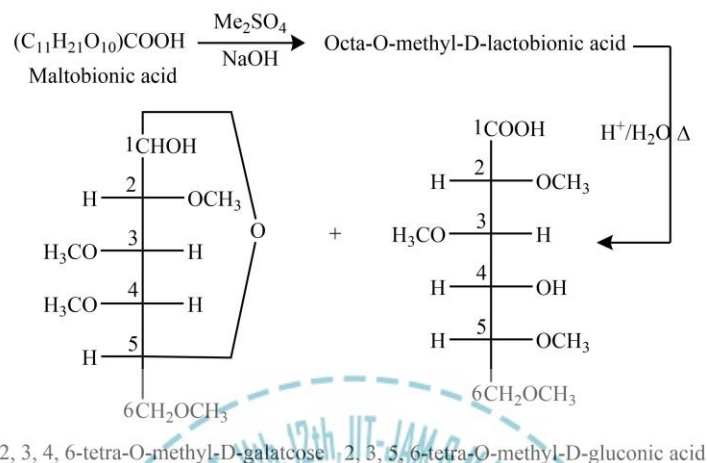


Furthermore, we can also conclude that the α -form of (+)-maltose differs from β -form w.r.t the configuration at anomeric carbon. In other words, the OH group at C_1 in β -form is above the plane whereas it lies below the plane in α -form.

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.

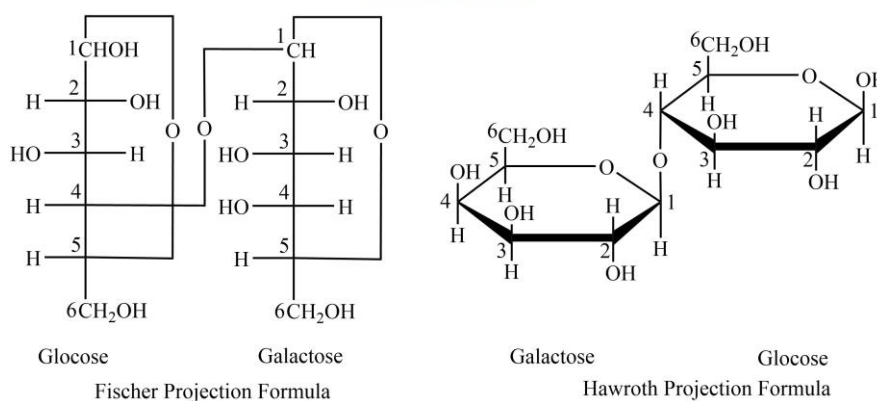
i) Monomeric analysis: The hydrolysis of lactose with lactase or mineral acids yields an equimolar mixture of D-(+)-glucose and D-(+)-galactose. Furthermore, the oxidation of lactose with bromine water results in lactobionic acid. The hydrolysis of lactobionic acid results in D-(+)-gluconic acid and 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 $(\text{CH}_3)_2\text{SO}_4$, 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



The free $-\text{OH}$ 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 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 $-\text{OH}$ 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 lactobionic 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.

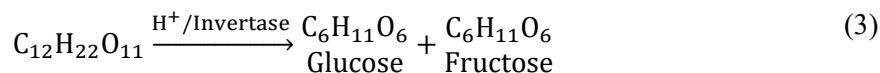
iii) *Nature of linkage:* Since we know that the lactose's hydrolysis by yeast (lactase enzyme) has specificity for the hydrolysis of β -glycosidic linkages, $\beta\text{-C}_1-\text{OH}$ of non-reducing galactose unit must be connected to the C_4-OH of reducing glucose unit.



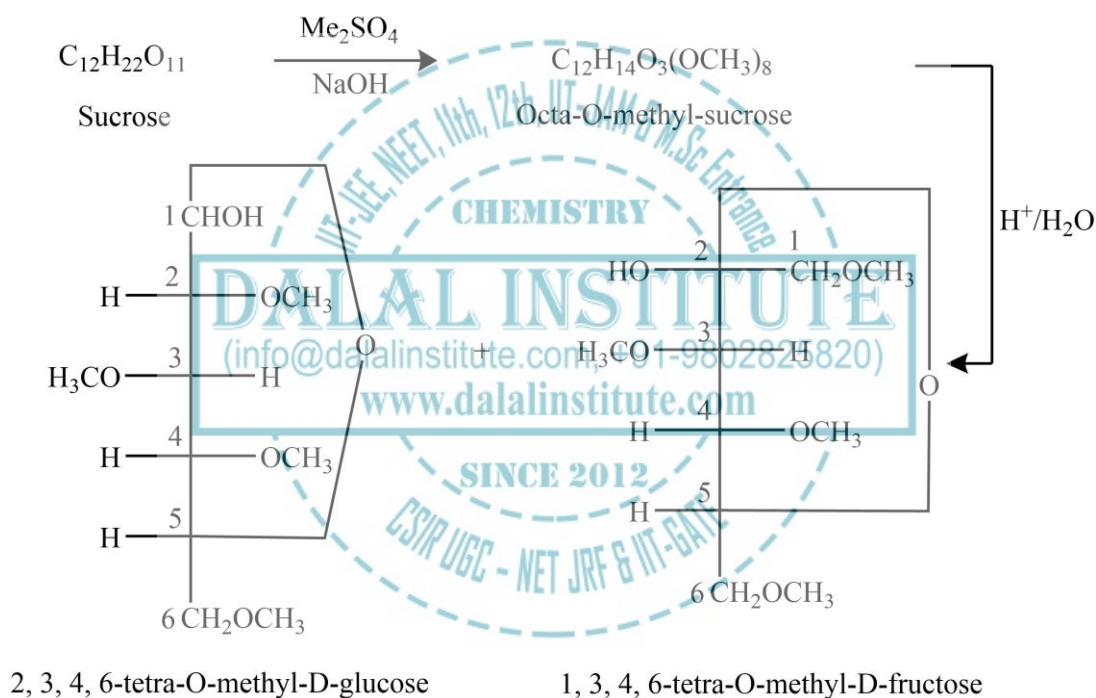
Furthermore, we can also conclude that the α -form of (+)-lactose differs from β -form w.r.t the configuration at anomeric carbon (OH group at C_1 in β -form is above the plane whereas it lies below the plane in α -form).

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.

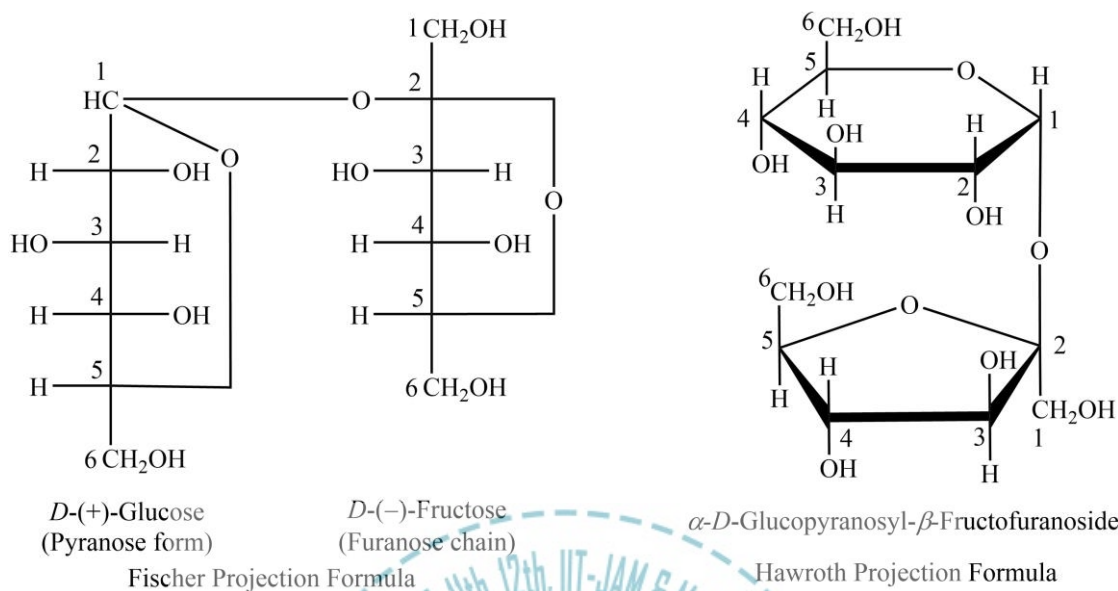


ii) *Study of the monosaccharide units:* The full methylation of sucrose with sodium hydroxide and $(CH_3)_2SO_4$, and then carrying out acid hydrolysis results in a mixture of 2, 3, 4, 6-tetra-O-methyl-D-glucose and 1, 3, 4, 6-tetra-O-methyl-D-fructose.



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).

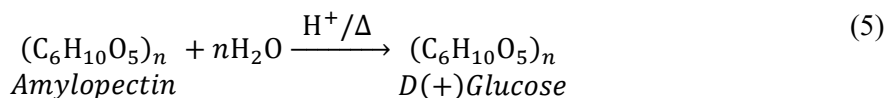
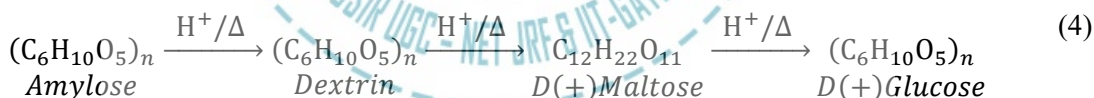
iii) *Nature of linkage:* Owing to the non-reducing nature of sucrose, we can conclude that glucose and fructose units must be connected via corresponding glycosidic or reducing sites. Now, the overall structure of sucrose can be visualized by considering two important experimental results. First is 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.



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

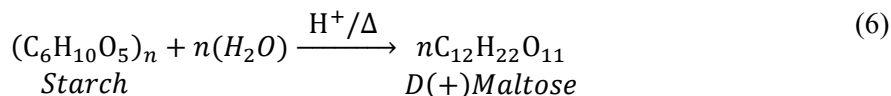
4. Structure determination of starch: Starch is the most abundant carbohydrates' source for human-kind which is primarily found in seeds, plant roots, fruits, and tubers. Moreover, it is also very important to note that starch is not a single compound but a mixture of two; amylose (20%) and amylopectin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

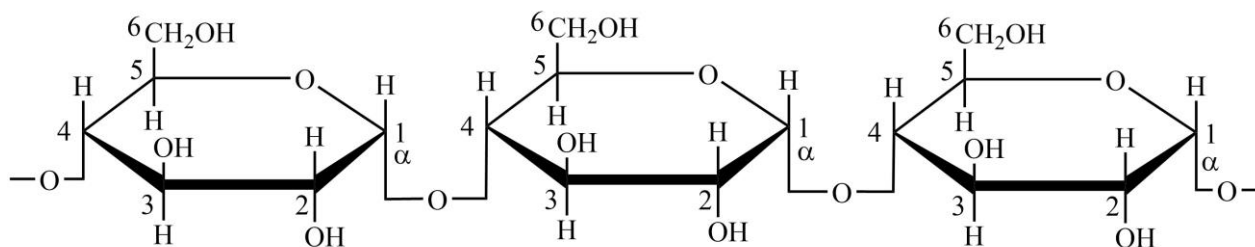


Hence, we can say that amylose, as well as amylopectin, both are made-up of *D*-(+) glucose units. Furthermore, it is also worthy to note that *n* has a range of 200–300 and 1000–3000 for amylose and amylopectin, respectively.

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.

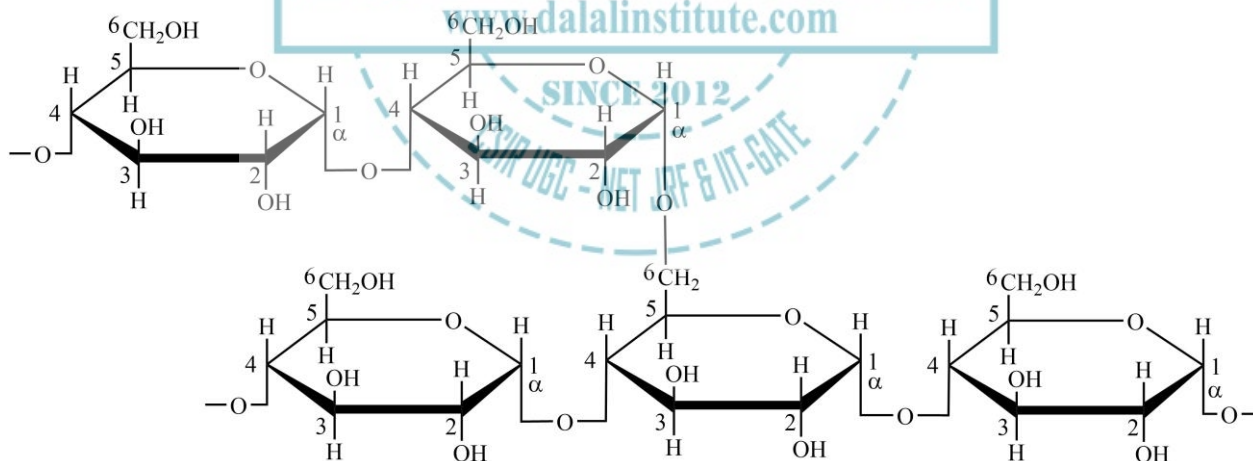


iii) *Nature of linkage:* Since we know that C_4 -OH of reducing glucose unit is connected to the α - C_1 -OH of non-reducing glucose unit i.e., α -glucosidic linkage, amylose can be considered as a chain of D-(+) glucose units connected by α -glucosidic bonds.



Amylose Structure
(Haworth 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.

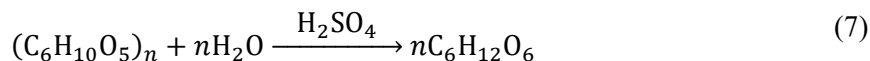


Amylose Structure
(Haworth Projection Formula)

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.

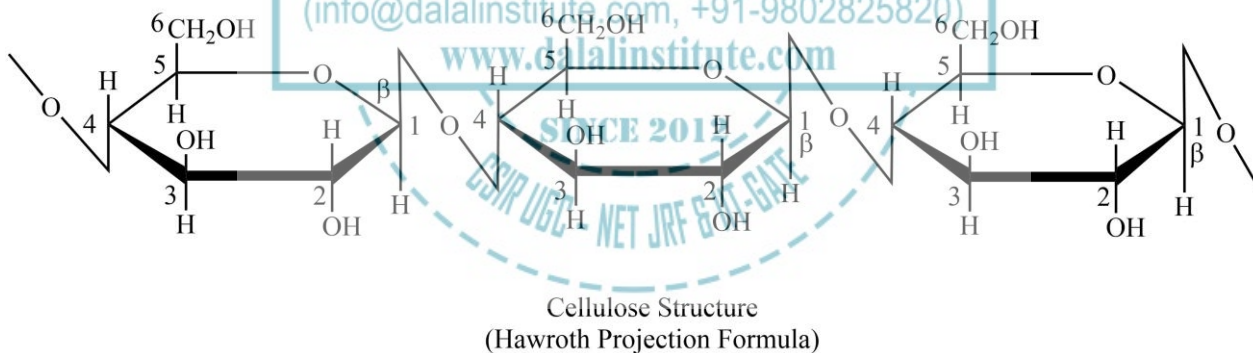
i) *Monomeric analysis:* The complete hydrolysis of cellulose with dilute sulphuric acid yields D-(+)-glucose as the only product. Therefore, one can conclude that cellulose is made up of D-(+)-glucose units (just like the case of starch).



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).



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.



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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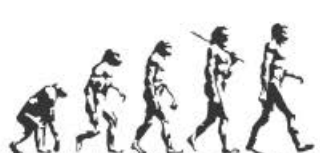
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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