

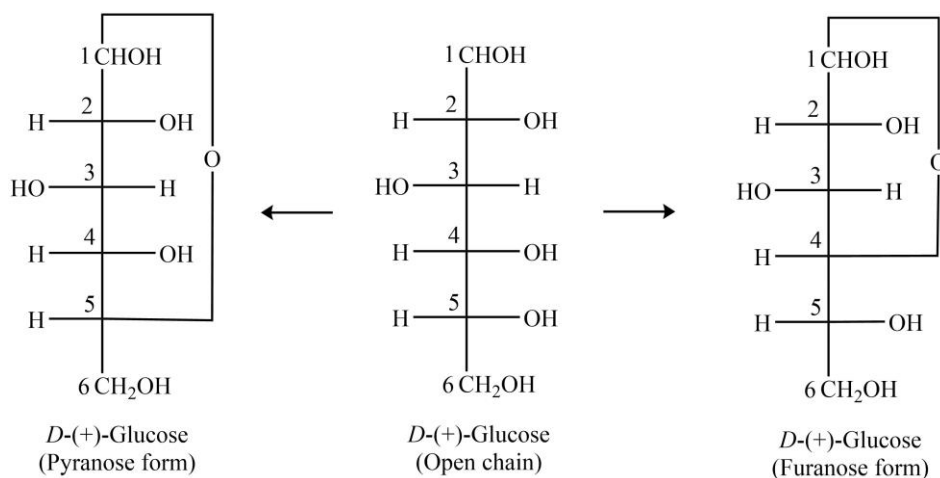
❖ Conformations of Sugars

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 $(\text{CH}_2\text{O})_n$ 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 (dia-, tri-, tetra-saccharides etc.) are crystalline compounds, soluble in water and sweet in taste; and typically labeled as sugars. On the other hand, 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 conformation of different types of sugars i.e. monosaccharides and oligosaccharides. The term "conformation" here refers to the overall three-dimensional structure adopted by a sugar (saccharide) molecule as a result of the through-bond and through-space physical forces it experiences arising from its molecular structure. The physical forces that dictate the three-dimensional shapes of all sugar molecules are sometimes summarily captured by such terms as "steric interactions" and "stereoelectronic effects".

➤ Conformation of Monosaccharides

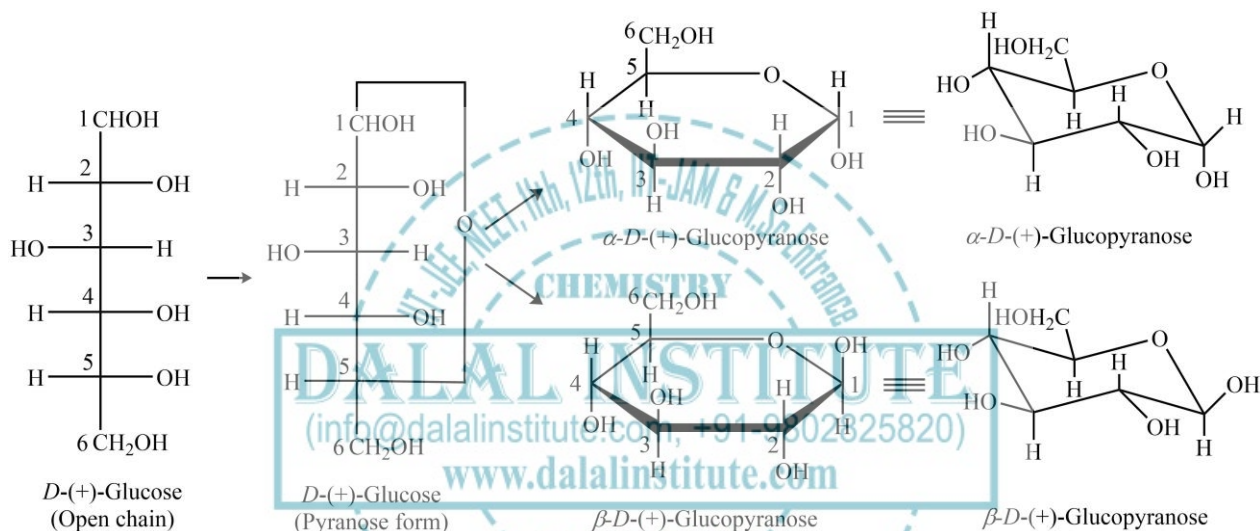
In 1883, Tollan proposed that the glucose molecule does not have a free aldehydic group but a cyclic structure via a hemiacetal carbon. The thought that the terminal aldehydic carbon may participate in hemiacetal formation by using the hydroxyl group of 4th carbon in open-chain glucose molecule, giving rise to a five-membered furan-like ring structure. Later on, in 1926, Haworth proposed that the formation of hemiacetal carbon takes place via 5th carbon, giving rise to a six-membered pyran-like ring structure.



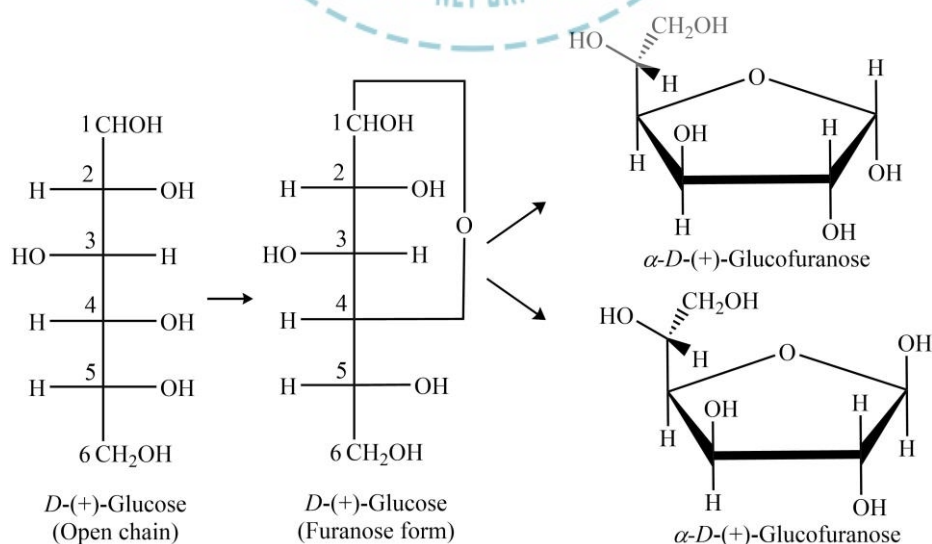
The general discussion on the conformational analysis of some typical monosaccharide sugar molecules is given below.

1. Glucose: 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 solutions, the open-chain form of glucose (either "D-" or "L-") exists in equilibrium with several cyclic isomers, each containing a ring of carbons closed by one oxygen atom. In an aqueous solution, however, more than 99% of glucose molecules, at any given time, exist as pyranose forms. The open-chain form is limited to about 0.25% and furanose forms exist in negligible amounts.

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.

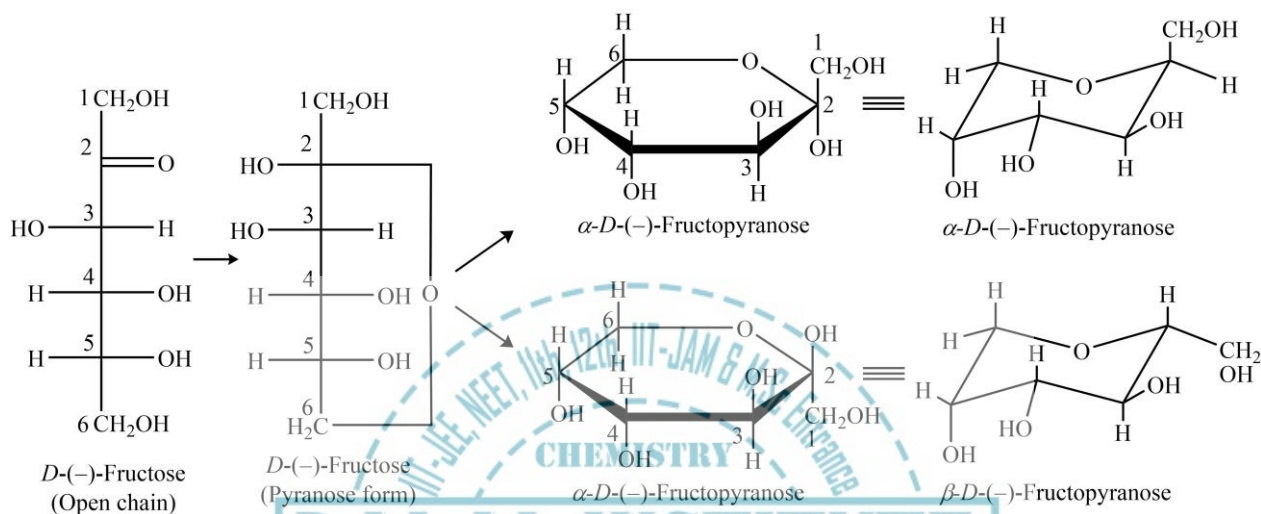


ii) *Furanose form:* The terminal aldehydic carbon participate in hemiacetal formation by using the hydroxyl group of 4th carbon in the open chain glucose molecule to give furanose form.

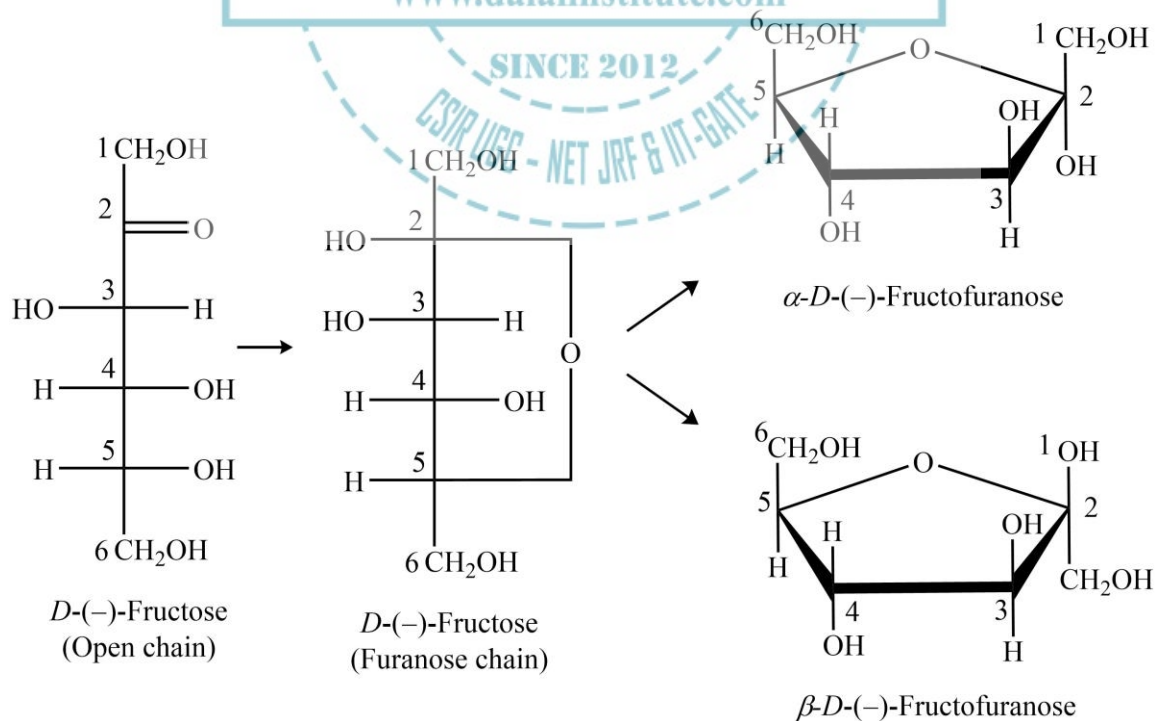


2. Fructose: The ketonic carbon in open-chain fructose molecule may participate in hemiketal formation by using the hydroxyl group of 5th and 6th carbon in open-chain glucose molecule, giving rise to a five-membered furan-like and six-membered pyran-like ring structure, respectively.

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.

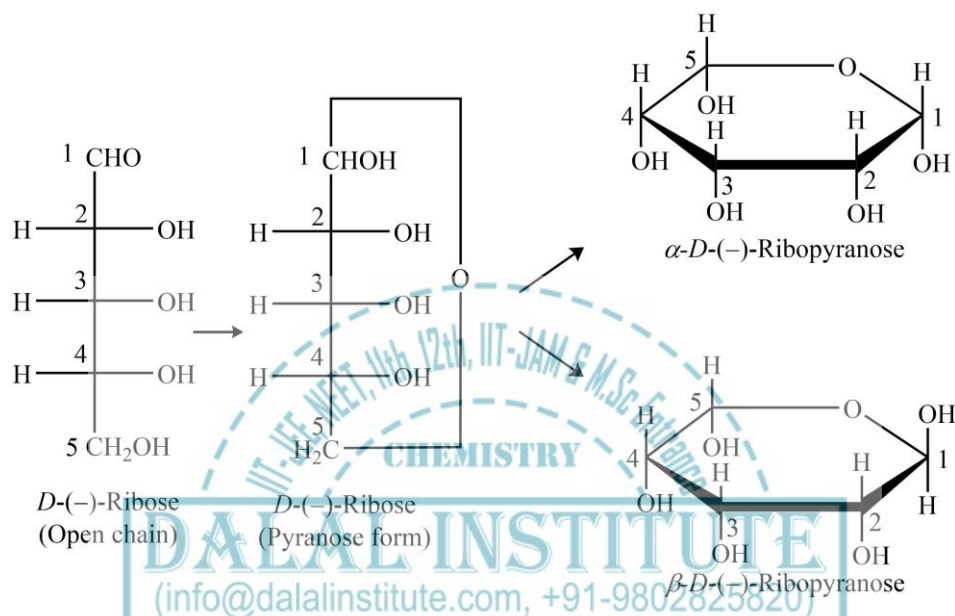


ii) *Furanose form:* The ketonic carbon participate in hemiketal formation by using the hydroxyl group of 5th carbon in open-chain glucose molecule to give furanose form.

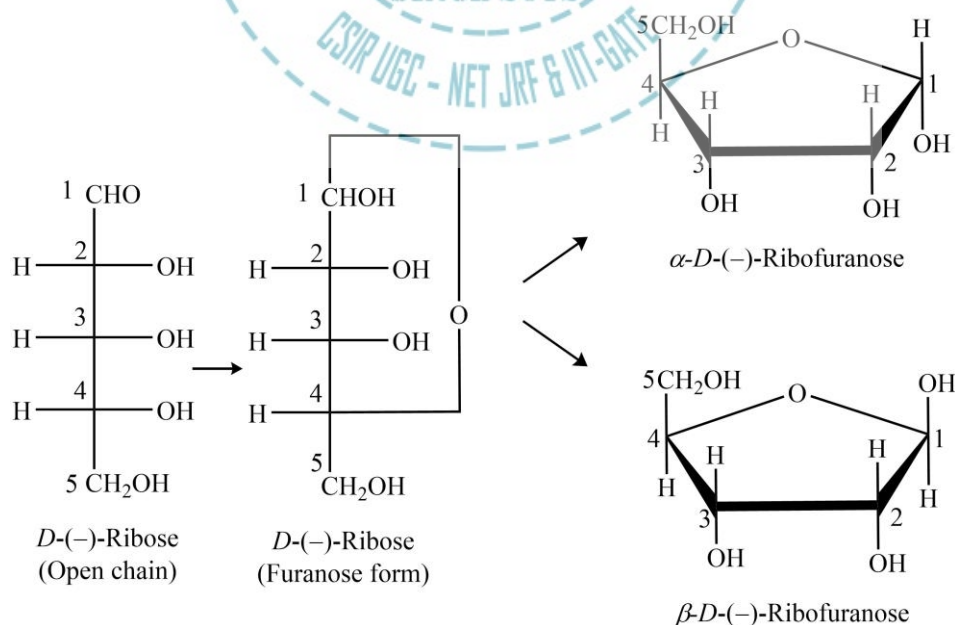


3. Ribose: The aldehydic carbon in open-chain ribose molecule may participate in hemiacetal formation by using the hydroxyl group of 4th and 5th carbon, giving rise to a five-membered furan-like and six-membered pyran-like ring structure, respectively.

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

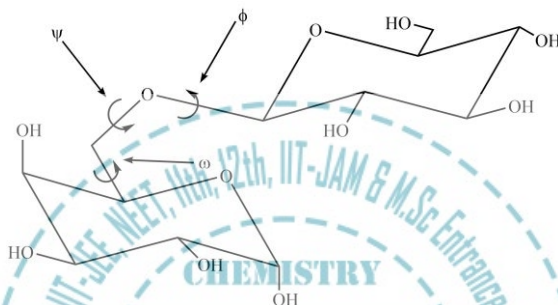


i) *Furanose form:* The aldehydic carbon participate in hemiacetal formation by using the hydroxyl group of 4th carbon in open chain ribose molecule to give furanose form.



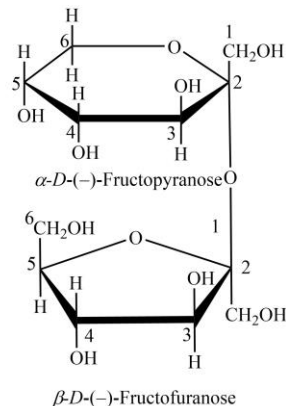
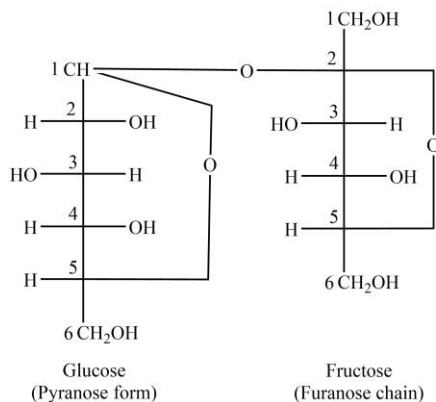
➤ Conformation of Oligosaccharides

In addition to the factors affecting monosaccharide residues, conformational analysis of oligosaccharides requires the consideration of some additional factors. One such major factor is the exo-anomeric effect, which is similar to the endo-anomeric effect. The difference is that the lone pair being donated is coming from the substituent at C-1. However, since the substituent can be either axial or equatorial there are two types of exo-anomeric effects, one from axial glycosides and one from equatorial glycosides as long as the donating orbital is anti-periplanar to the accepting orbital. The other one is Glycosidic torsion angles which angles are described by ϕ , ψ , and ω (in the case of glycosidic linkages via O-6). Steric considerations and anomeric effects need to be taken into consideration when looking at preferred angles.

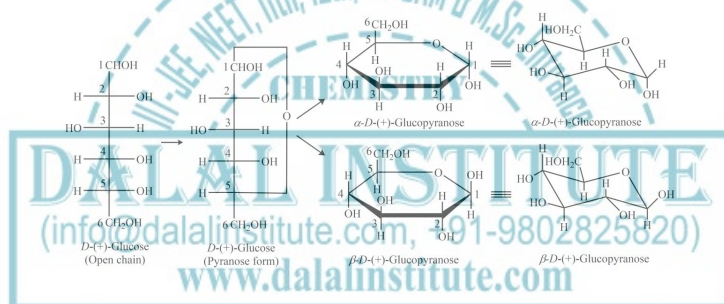


The general discussion on the conformational analysis of some typical monosaccharide sugar molecules is given below.

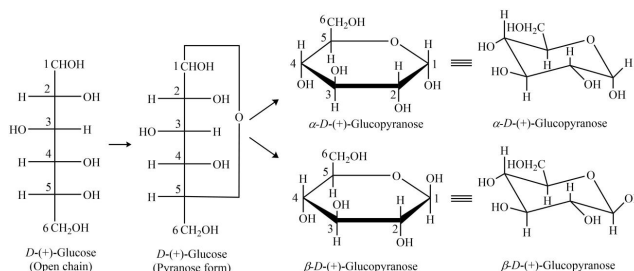
1. Sucrose: In sucrose, the components glucose and fructose are linked via an ether bond between C1 on the glucosyl subunit and C2 on the fructosyl unit. The bond is called a glycosidic linkage. Glucose exists predominantly as two isomeric "pyranoses" (α and β), but only one of these forms links to the fructose. Fructose itself exists as a mixture of "furanoses", each of which having α and β isomers, but only one particular isomer link to the glucosyl unit. What is notable about sucrose is that, unlike most disaccharides, the glycosidic bond is formed between the reducing ends of both glucose and fructose, and not between the reducing end of one and the nonreducing end of the other. This linkage inhibits further bonding to other saccharide units. Since it contains no anomeric hydroxyl groups, it is classified as a non-reducing sugar.



2. Maltose: Maltose is a disaccharide: the carbohydrates are generally divided into monosaccharides, oligosaccharides, and polysaccharides depending on the number of sugar subunits. Maltose, with two sugar units, is an oligosaccharide, specifically a disaccharide, because it consists of two glucose molecules. Glucose is a hexose: a monosaccharide containing six carbon atoms. The two glucose units are in the pyranose form and are joined by an O-glycosidic bond, with the first carbon (C1) of the first glucose linked to the fourth carbon (C4) of the second glucose, indicated as (1→4). The link is characterized as α because the glycosidic bond to the anomeric carbon (C1) is in the opposite plane from the CH₂OH substituent in the same ring (C₆ of the first glucose). If the glycosidic bond to the anomeric carbon (C1) were in the same plane as the CH₂OH substituent, it would be classified as a β (1→4) bond, and the resulting molecule would be cellobiose. The anomeric carbon (C1) of the second glucose molecule, which is not involved in a glycosidic bond, could be either an α - or β -anomer depending on the bond direction of the attached hydroxyl group relative to the CH₂OH substituent of the same ring, resulting in either α -maltose or β -maltose. An isomer of maltose is isomaltose. This is similar to maltose but instead of a bond in the α (1→4) position, it is in the α (1→6) position, the same bond that is found at the branch points of glycogen and amylopectin.



3. Lactose: Lactose is a disaccharide derived from the condensation of galactose and glucose, which form a β -1→4 glycosidic linkage. Its systematic name is β -D-galactopyranosyl-(1→4)-D-glucose. The glucose can be in either the α -pyranose form or the β -pyranose form, whereas the galactose can only have the β -pyranose form: hence α -lactose and β -lactose refer to the anomeric form of the glucopyranose ring alone. Detection reactions for lactose are the Woehlk-[6] and Fearon's test.[7] Both can be easily used in school experiments to visualize the different lactose content of different dairy products such as whole milk, lactose-free milk, yogurt, buttermilk, coffee creamer, sour creme, kefir etc. Lactose is hydrolyzed to glucose and galactose, isomerized in alkaline solution to lactulose, and catalytically hydrogenated to the corresponding polyhydric alcohol, lactitol.[9] Lactulose is a commercial product, used for the treatment of constipation.



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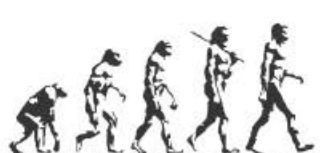
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

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