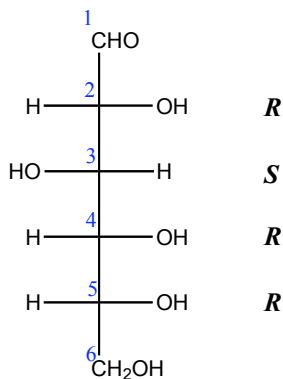


Review from last lecture

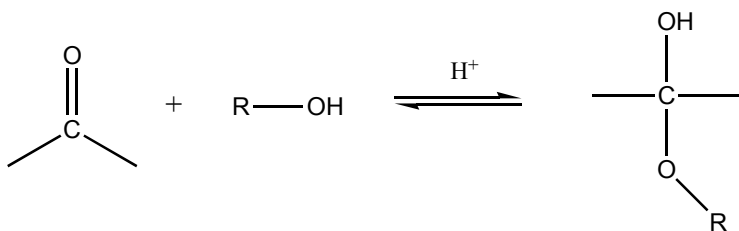
D-glucose has the structure shown below (you are responsible for its structure on the exam). It is an aldohexose (“aldo” since it contains aldehyde functionality and “hexose” since it is a six carbon sugar, numbered on structure).



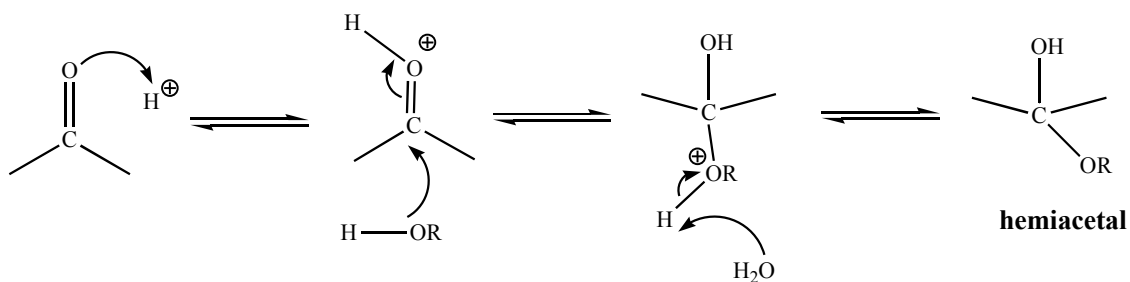
It contains 4 stereogenic carbons (C2, C3, C4 and C5). Recall from last lecture, the highest numbered stereogenic center gives you the designation of sugar, whether D (if it is R configuration at that stereogenic center) or L (if it's S configuration at that stereogenic center). For glucose, the highest numbered stereogenic center is C5. It has an R configuration. By convention, it is designated as a “D” sugar. Configurations of other stereogenic centers are also shown next to the structure.

Hemiacetal Formation

You know from previous lectures that carbonyl react with all kinds of nucleophiles. Hydration and hemiacetal formation are typical examples.



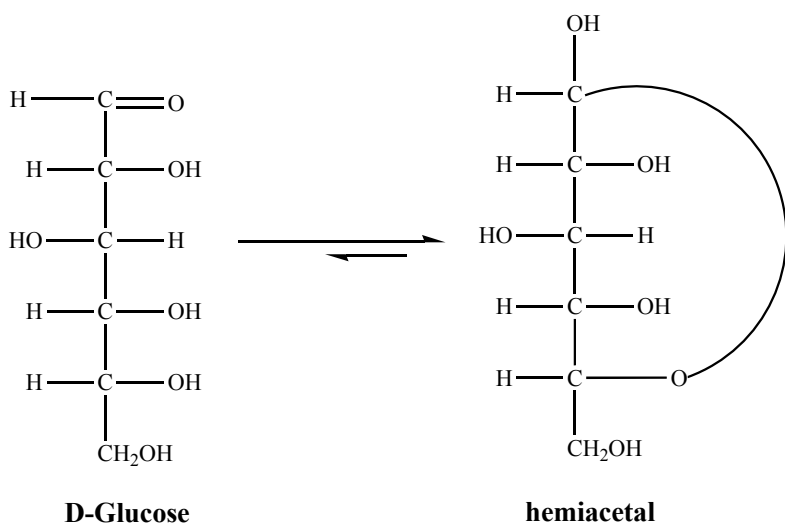
Mechanism (this should be review from previous lecture):



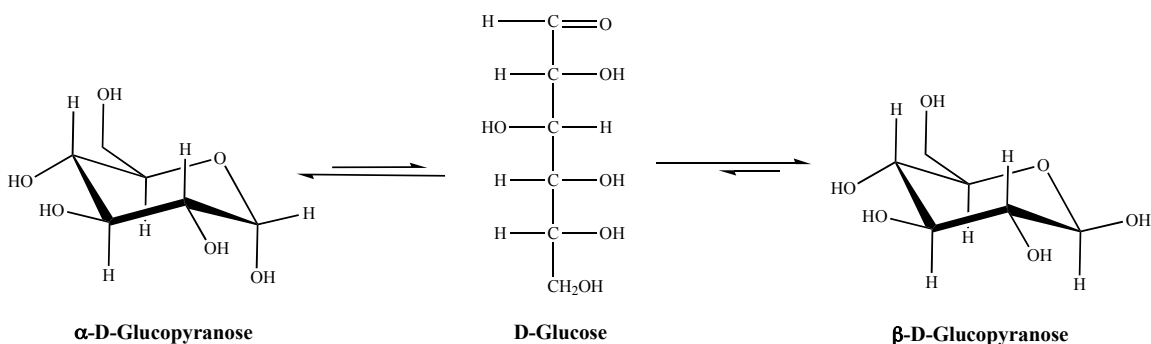
In nature, formations of 5- and 6-member rings are favored, and if possible, a molecule will form such a ring when it can.

In sugars, the cyclic forms with 5-member rings are called furanose, and 6-member rings are called pyranose. For most aldohexoses, the five membered furanose and six-membered pyranose can be formed. However, with D-glucose the six-membered pyranose usually predominates.

For example, glucose can react internally to form a hemiacetal (an intramolecular cyclization).



The molecule is predominantly in the cyclic form; however, it is still in equilibrium with a small amount of acyclic form. The cyclic 6-membered rings exist in energy minimum chair forms (shown in figure below). This is also depicted in the handouts given.



The cyclic forms are indicated in the name by combining the simple name of the sugar with “furanose” or “pyranose” to indicate the size of the ring. Therefore, glucose in its cyclic form with 6-member ring is called glucopyranose.

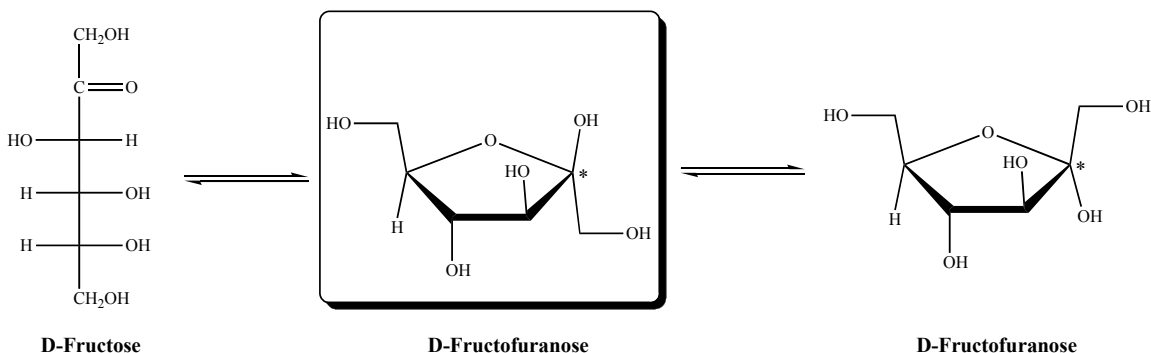
The intramolecular cyclization reaction creates a new stereogenic carbon that can be either R or S configuration, with OH group in equatorial or axial position. The terms α and β refers to position of OH at C1 relative to CH₂OH group of C6.

When the OH group attached to C1 is down relative to CH₂OH group that is up (they are *trans* to each other), The configuration is α . When they are on the same side (both are up), the configuration is β .

The two stereoisomers are interconverting structural isomers called **anomers**. They differ only in stereochemistry at C1 position, which is known as the **anomeric carbon**.

The α and β anomers can equilibrate through the small amount of the open form present at equilibrium.

Formation of 5-member ring is possible for D-Glucose, but it exist predominantly as 6-membered ring. Fructose, on the otherhand, exists predominantly as 5-member ring.

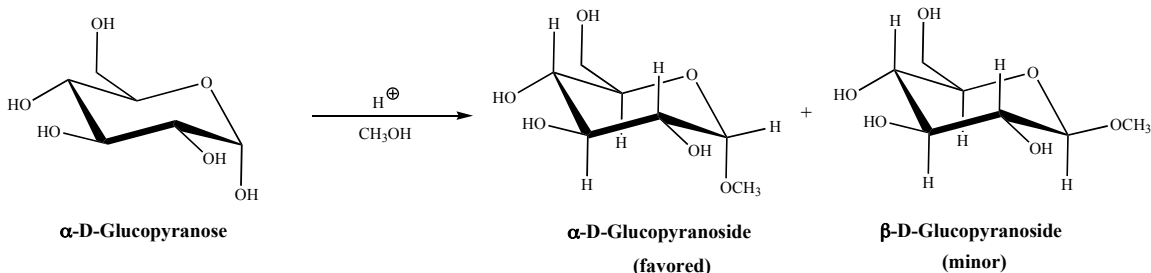


D-fructose is a ketohexose (“keto” since it contains ketone). Its cyclized form, D-fructofuranose is a hemiacetal since the anomeric carbon (marked by asterisk) has a free OH group and a OR group attached. An easy way to find the anomeric carbon is to find a carbon with 2 oxygen atoms attached directly.

Is the fructofuranose highlighted in box an α or β sugar?

Answer: It is β . The rule is to find CH_2OH group and the OH substituent of the anomeric carbon, and see if they are on the same or opposite side. Since the OH group and the CH_2OH group are on the opposite side of each other, the ring is β .

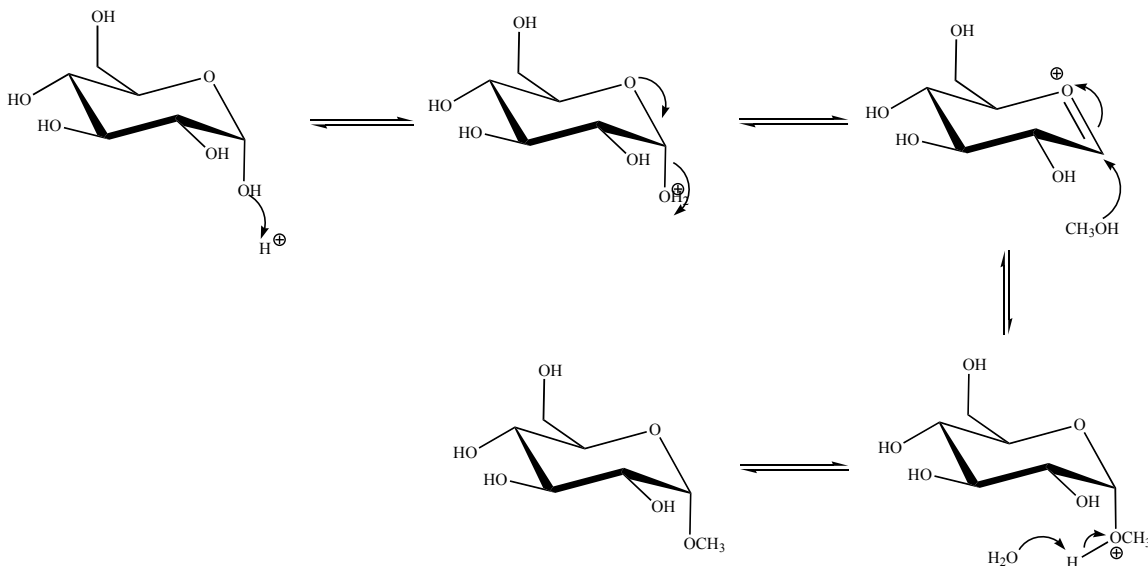
Reaction of Sugars



Treatment with dilute acid and alcohol converts only the OH at the anomeric position into an acetal called a glycoside. Specific glycosides are named by replacing the “ose” of the simple sugar’s name with “oside”. When glucopyranose is reacted, its product is called glucopyranoside.

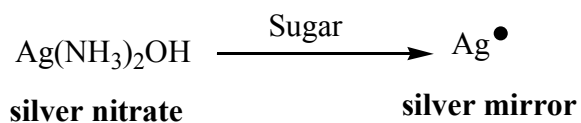
The α anomer with the methoxy group in axial position is favored due to anomeric effect.

Mechanism:

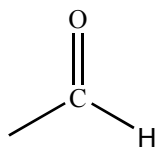


Reducing or non-reducing sugars

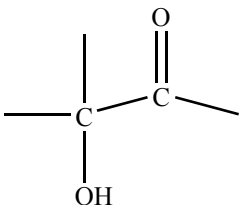
We can perform chemical reactions on the sugar to find out if it’s a reducing or non-reducing sugar, such as silver mirror reaction. Silver nitrate in ammonia is allowed to react with sugar. If a silver mirror is observed, then the sugar is reducing.



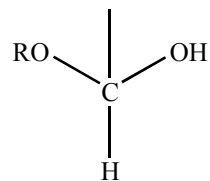
Usually, reducing sugars contain one of the three functional groups:



aldehyde

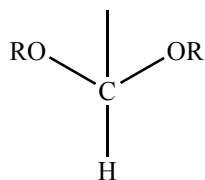


α-hydroxyketone



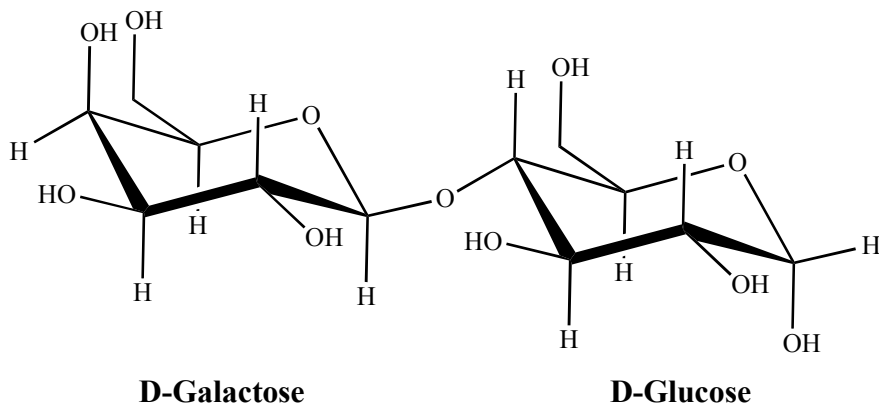
hemiacetal

The non-reducing sugars do NOT contain the above functionality, but may contain an acetal functionality:



acetal

Example:

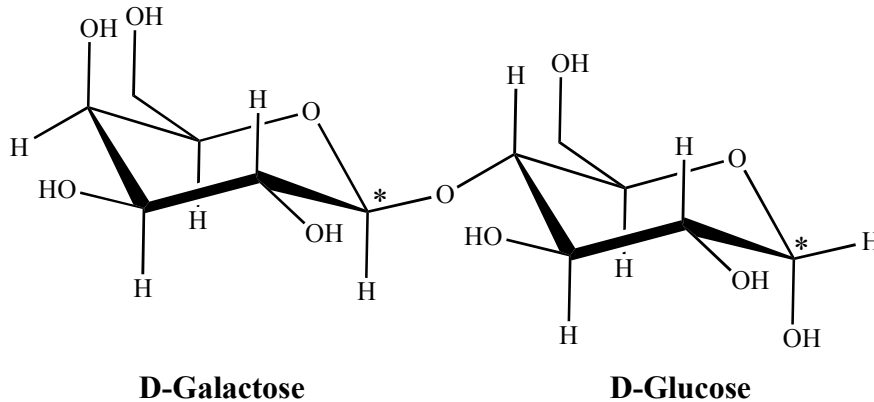


The molecule shown as a whole is a disaccharide (made from 2 sugars) known as lactose. It is made up of galactose and glucose sugars connected by an acetal linkage

Can you spot the difference between galactose and glucose?

The OH groups at C4. In galactose, the OH group at C4 position is axial, whereas in glucose the corresponding C4 OH group is equatorial.

Identify the anomeric carbon in each sugar.
 These are highlighted with asterisks.



Is galactose shown above α or β sugar?

It is β . The OH at the anomeric carbon is on the same side as its CH₂OH group.

Is glucose α or β ?

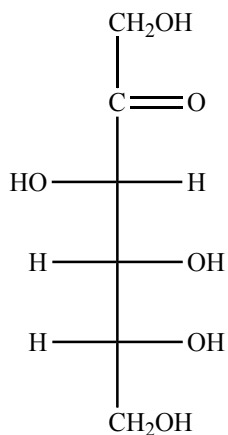
It is α . The OH group at the anomeric carbon is down, on the opposite side as its CH₂OH group.

Is this a reducing sugar?

Yes. It contains hemiacetal functionality at anomeric carbon of glucose.

Note: for large polysaccharides, there would be a lot of sugars linked together through acetal functionality and only the end sugar would have free OH group. Then the polysaccharide would be said to be non-reducing.

Example:



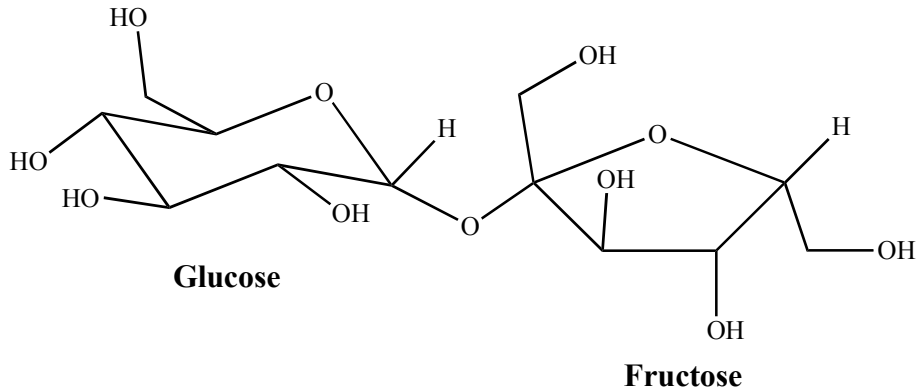
D-Fructose

Fructose is the sweetest sugar of all (sweetness index 180)

Is it a reducing or non-reducing sugar?

It is reducing since it contains a ketone group in open form and the cyclized form is a hemiacetal at anomeric position.

Example:



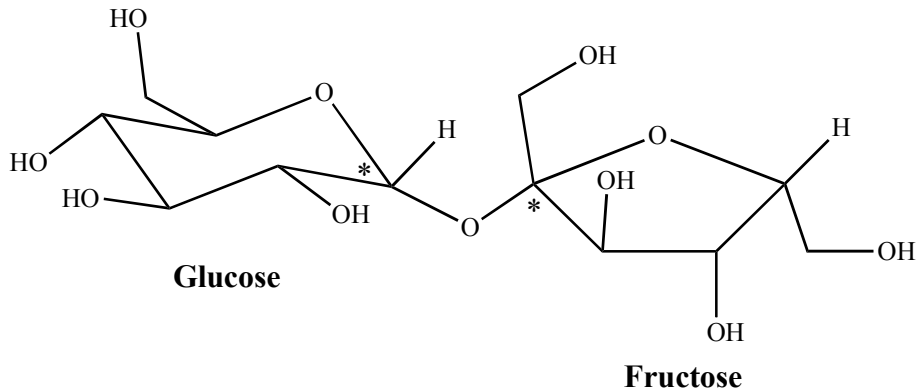
The structure shown is sucrose (table sugar). It is made up of a glucose and a fructose molecule (sweetness index 100)

Does this molecule have anomeric carbon?

Yes.

Identify the anomeric carbon.

They are highlighted with asterisks.



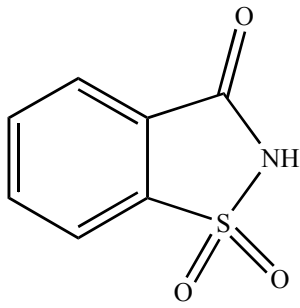
Are they acetals or hemiacetals?

They are acetals. In both cases, the carbon has two OR group attached. There is no free OH group.

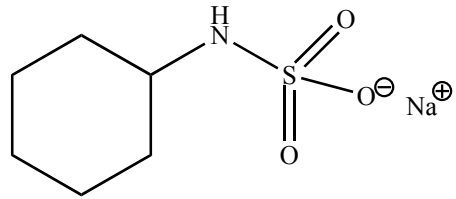
Is this sugar reducing or non-reducing?

Non-reducing since the anomeric carbons has acetal groups.

Some artificial sweeteners are shown below:



saccharin

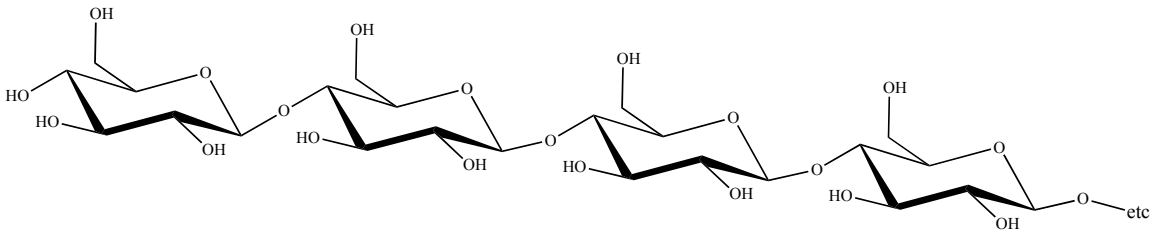


sodium cyclamate

Although a small amount taste a lot sweeter than sugars, these are found to be carcinogenic in very large doses.

Polysaccharides = polymers of sugars

Example: Cellulose



Cellulose is a polymer of simple repeating monosaccharide units (D-glucose). Many mammals cannot digest cellulose directly. Ruminants such as cows or goats have bacteria in their stomach to break it down to its simpler unit. The bacteria have a cellulose hydrolysis enzyme called cellulase which we do not have.