

Mutarotation

The α and β anomers are diastereomers of each other and usually have different specific rotations. A solution or liquid sample of a pure α anomer will rotate plane polarised light by a different amount and/or in the opposite direction than the pure β anomer of that compound. The optical rotation of the solution depends on the optical rotation of each anomer and their ratio in the solution.

For example, if a solution of β -D-glucopyranose is dissolved in water, its specific optical rotation will be $+18.7^\circ$. Over time, some of the β -D-glucopyranose will undergo mutarotation to become α -D-glucopyranose, which has an optical rotation of $+112.2^\circ$. Thus the rotation of the solution will increase from $+18.7^\circ$ to an equilibrium value of $+52.7^\circ$ as some of the β form is converted to the α form. The equilibrium mixture is actually about 64% of β -D-glucopyranose and about 36% of α -D-glucopyranose, though there are also traces of the other forms including furanoses and open chained form. The α anomer is the major conformer, although somewhat controversially; this is due to the anomeric effect with the stabilization energy provided by n- σ^* hyperconjugation.

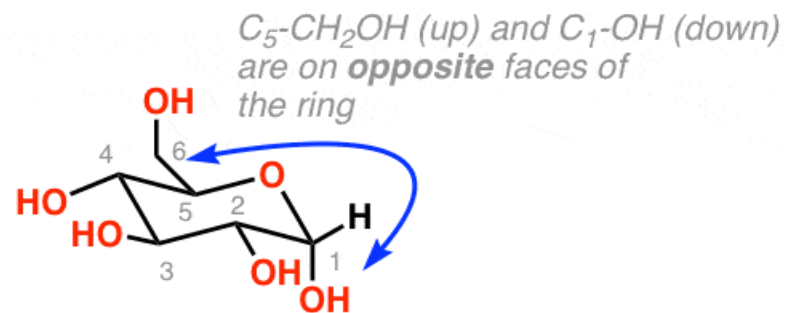
The observed rotation of the sample is the weighted sum of the optical rotation of each anomer weighted by the amount of that anomer present.

Therefore, one can use a polarimeter to measure the rotation of a sample and then calculate the ratio of the two anomers present from the enantiomeric excess, as long as one knows the rotation of each pure anomer. One can monitor the mutarotation process over time or determine the equilibrium mixture by observing the optical rotation.

Alpha (α) and beta (β) isomers ("anomers") differ in the orientation of the OH at the C-1 hemiacetal carbon

Example: D-glucose

"alpha" (α) isomer:

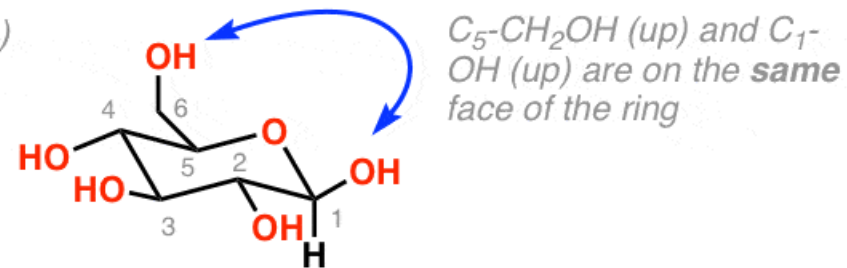


α -D-Glucose

drawn as "chair"

Specific rotation: $[\alpha]_D^{20} + 112^\circ$

"beta" (β) isomer:



β -D-Glucose

drawn as "chair"

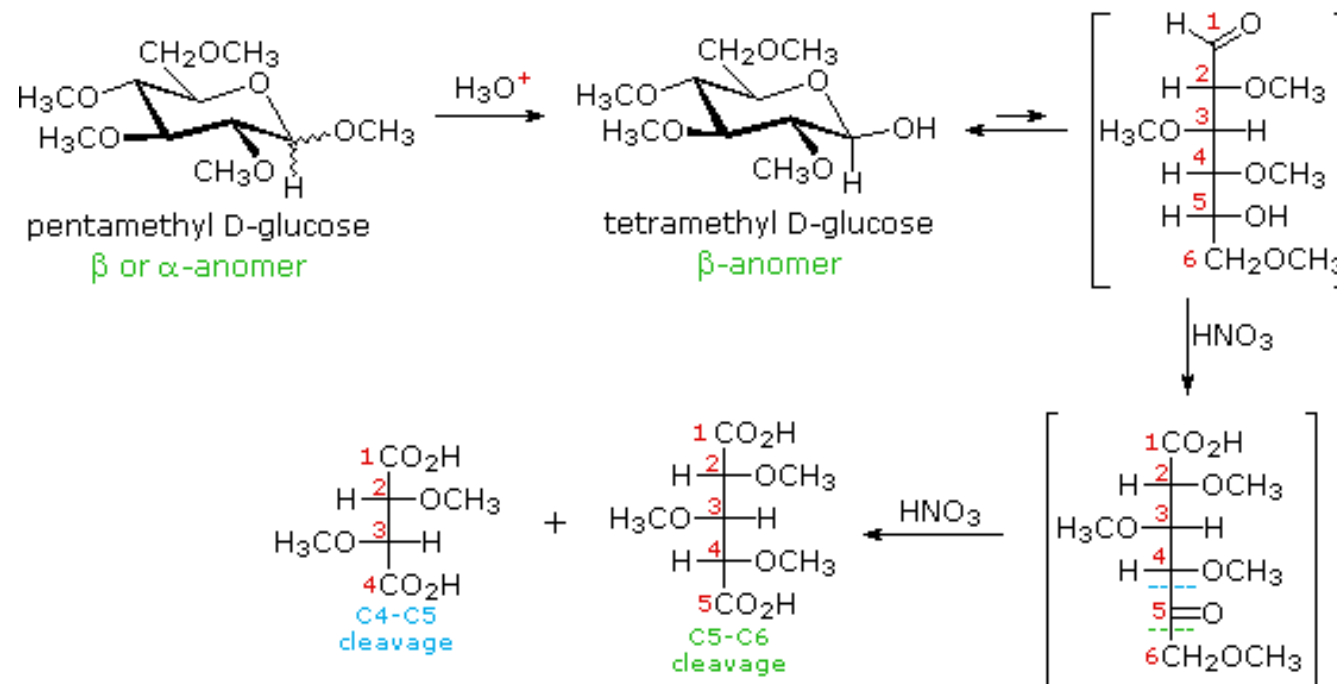
Specific rotation: $[\alpha]_D^{20} + 18.7^\circ$

Note different specific rotations!

Determination of Ring Size of Glucose Ring

The anomeric carbon can be found via methylation of the -OH groups, followed by hydrolysis. In the first step, all the -OH groups are transformed to -OCH_3 groups with excess methyl iodide and silver oxide. The hydrolysis of the acetal then forms a hemiacetal in presence of acid. This pyranose structure is in equilibrium with its open-chain form. From the open-chain form we can determine the size of the ring because the anomeric carbon attached -OH group is the one that forms the cyclic hemiacetal.

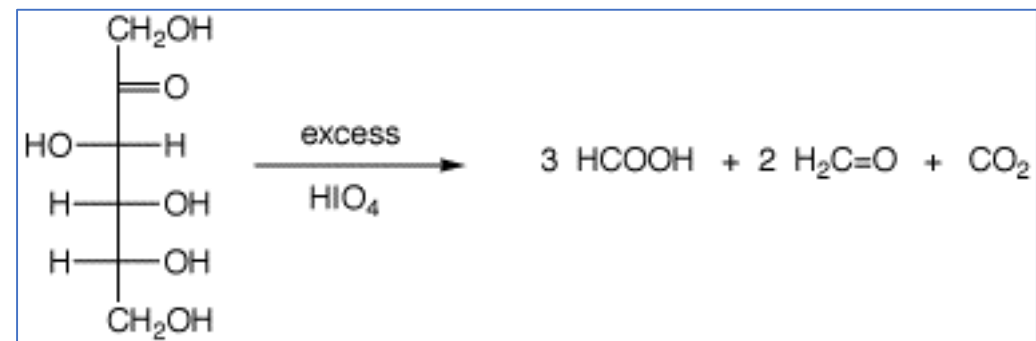
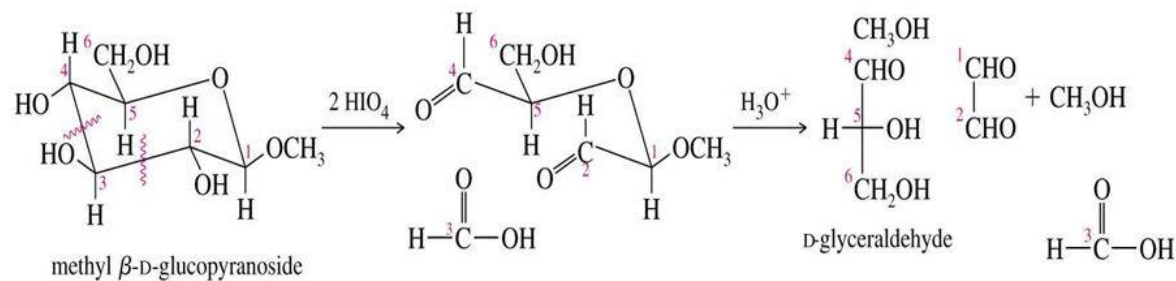
Reaction Sequence for Determining Ring Size of Cyclic Monosaccharides



A monosaccharide's ring size can be determined by the oxidation of an acetal of the monosaccharide with excess periodic acid. The products obtained from periodate cleavage of a six-membered ring acetal are different from those obtained from cleavage of a five-membered ring acetal.

Use of Periodic Acid Cleavage

- Separation and identification of the products determine the size of the ring.



Cyclic Structure of Monosaccharides: Hemiacetal Formation

- ❖ Aldoses contain an aldehyde group with several alcohol groups.
- ❖ The cyclic forms of D- glucose are six-membered hemiacetals formed by an intramolecular reaction of the –OH group at C-5 with the aldehyde group.
- ❖ Cyclic structures of monosaccharides are named according to their five- or six-membered rings.
- ❖ A six-membered cyclic hemiacetal is called a *pyranose*, derived from the name of the six-membered cyclic ether *pyran*.
- ❖ A five-membered cyclic hemiacetal is called a *furanose*, derived from the name of the five-membered cyclic ether *furan*.
- ❖ For example, the six-membered ring of glucose is called glucopyranose and the five- membered ring of fructose is called fructofuranose.

