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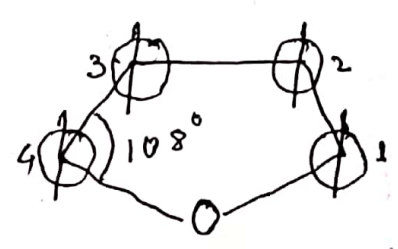
Topic : Conformation of monosaccharides
and their derivatives

For : semester II

Paper : CC VIII Unit : IV

Lecture : 3rd.

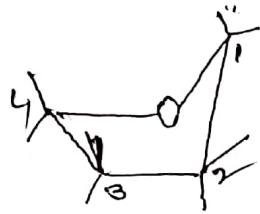
In the case of a furanose ring, i.e. a five membered ring, only two parameters viz, the puckering parameter and an angle is required. The internal angle of a pentagon (108°) is very close to a tetrahedral angle (109.5°) but all atoms/groups of the ring are eclipsed.



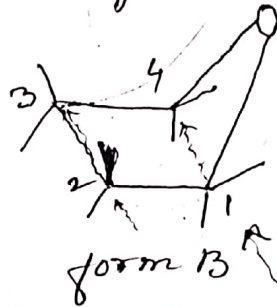
The puckering of the ring results in two energy forms - the envelope and the twist form.

In the envelope form one ring atom lies out of the plane in which the remaining four atoms are present.

Here the angle strain is nearly absent ²⁻ because a tetrahedral angle is maintained at each carbon and the bent angle is observed at oxygen. This form is slightly folded, like the shape of an envelope. This puckered form reduces the eclipsing at the adjacent



form A

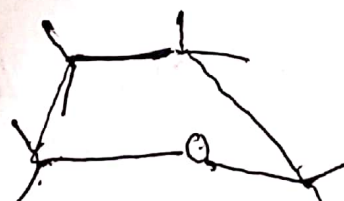
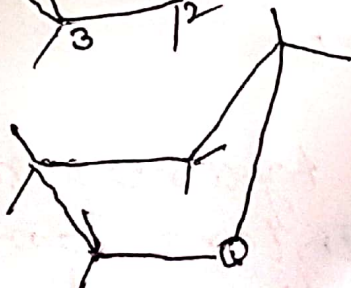
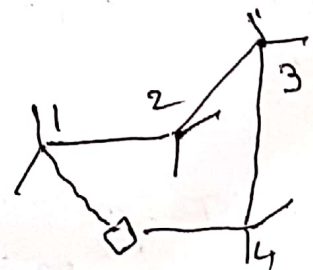
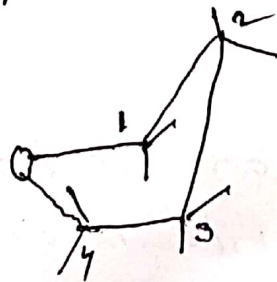
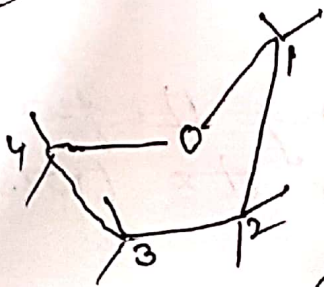


form B

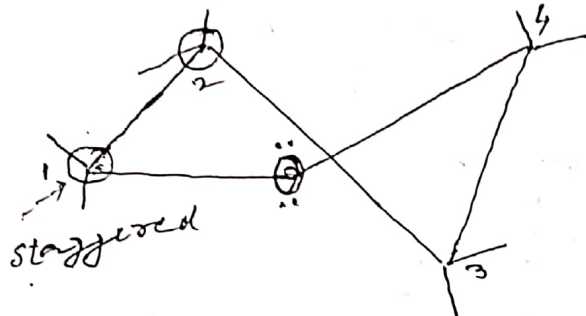
eclipsed
observed

ring carbons

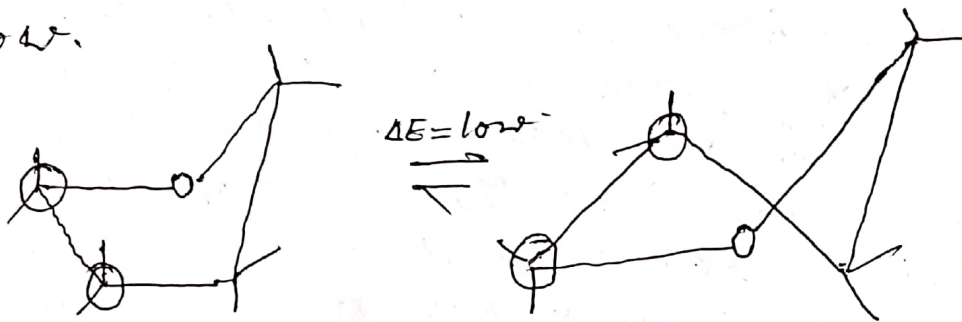
It is further suggested that when the oxygen of the envelope goes out of the plane, it ^{become} slightly less stable (more eclipsing) in comparison to that envelope in which the oxygen remains in the plane of rest those carbon atoms. Now it is possible to draw ten envelope conformation for the furanose ring out of which eight conformations having oxygen atoms in the plane of the ring.



The furanose ring can also acquire half chair/twist form in order to relieve the torsional strain.



Here the conversion between the envelope and the twist form is slightly frequent because the energy difference is quite low.

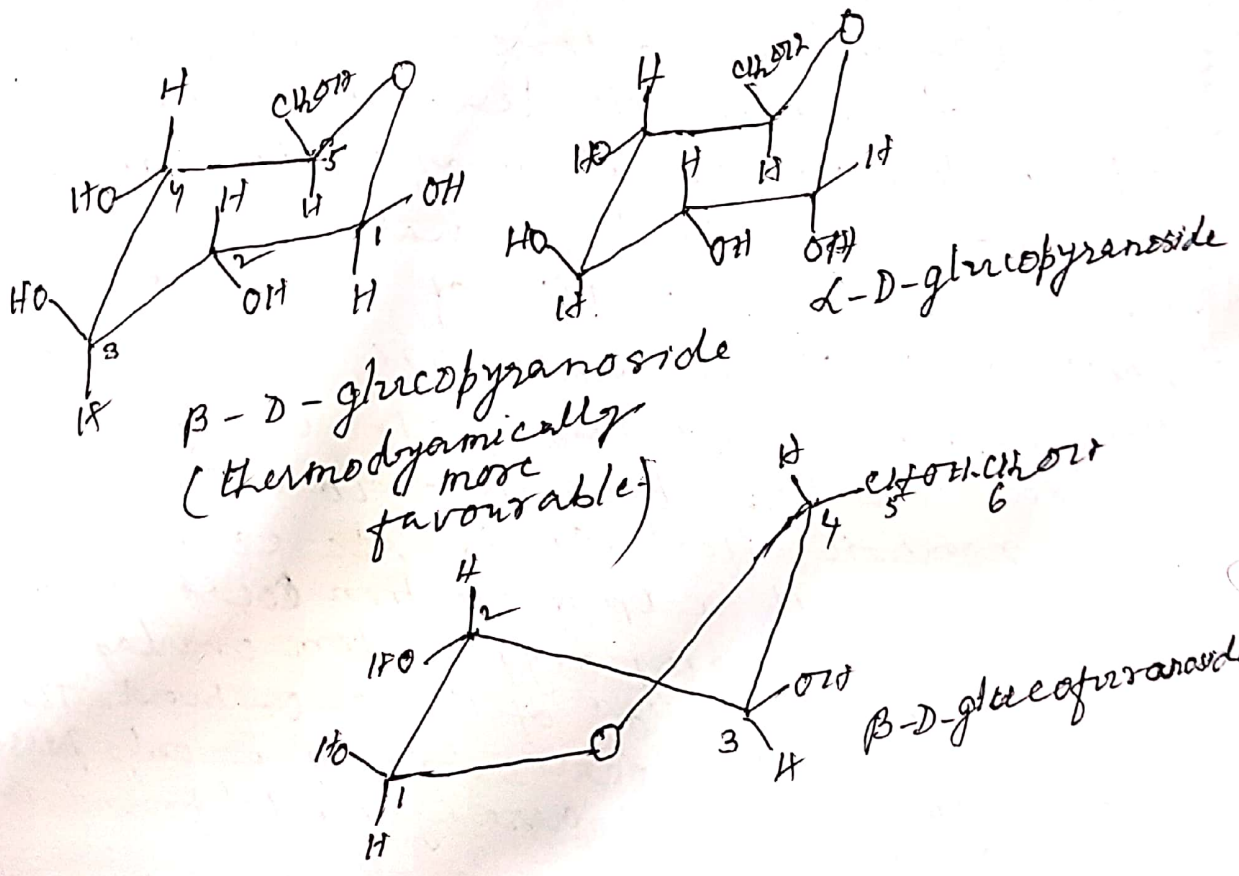


Conclusions:

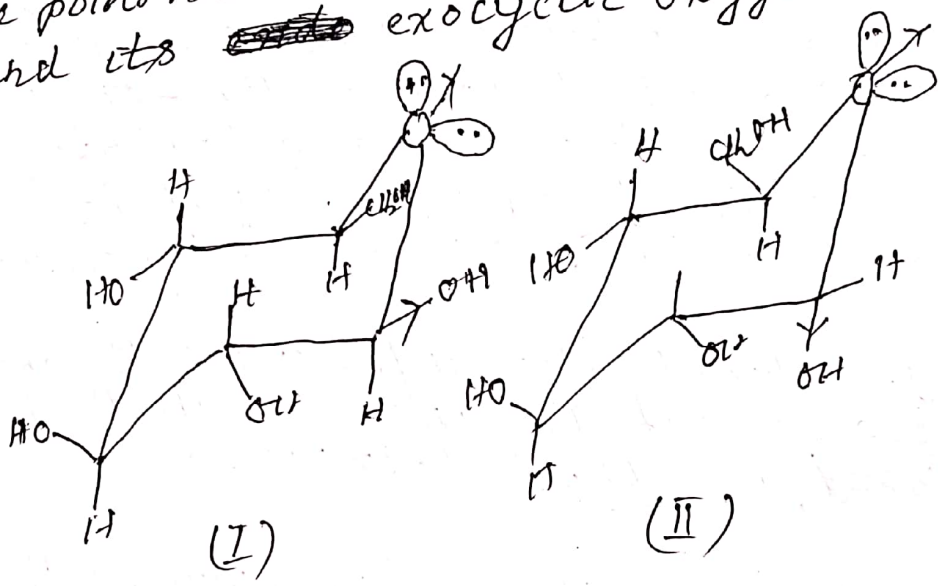
1. Hence the monosaccharides or their derivatives having the pyranose ring will have chair form in their stable state
2. The monosaccharides having the furanose ring will maintain either its twist form or its envelope form.
3. Many other factors like hydrogen bonding, Vander Waal's interaction can be encountered with the change in the factors (situations) are considered for the stability for a given form.

The size of the cyclic hemiacetal ring adopted by a given monosaccharide is not constant, but may vary with substituents and other structural features. Aldohexoses usually form pyranose rings and their pentose homologs tend to prefer the furanose form, but there are many counter examples. It was found that the pyranose is more common than the furanose form, especially in polysaccharides. In some monosaccharides, both forms exist in equilibrium.

In the pyranose form, the molecule have always preferred chair conformation. According to convention, we can imagine the group at equatorial position on each ring carbon in order to avoid possible 1,3-diaxial interaction.

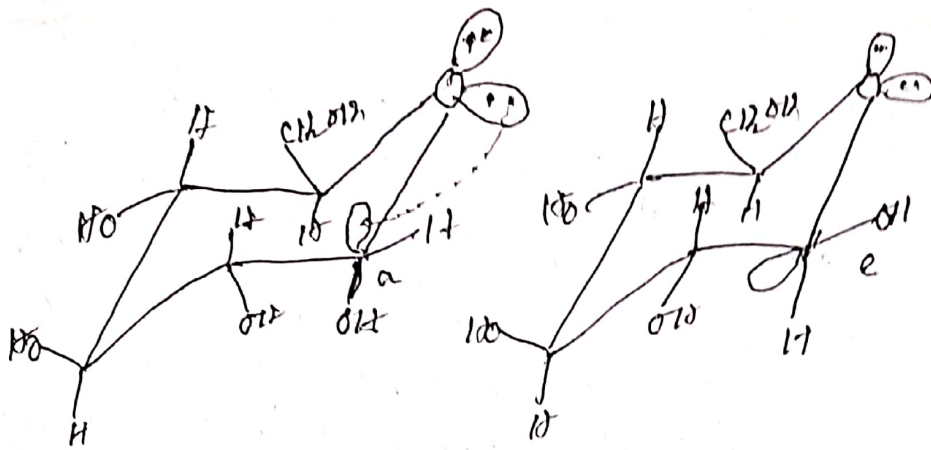


In order to ^{explain} the configuration at C₁ in the chair form, we must have to consider the anomeric effect in monosaccharides. It partly involves a dipole-dipole effect based on intramolecular electrostatic interaction of two dipoles next to the anomeric center. One of the two dipoles arises from the two lone pairs of the ring oxygen and the other dipole points along the polarised bond between the anomeric carbon and its ~~axial~~ exocyclic oxygen atom.



The anomeric configuration where the two dipoles partially neutralize each other are favored over the other.

The lone pair-lone pair interaction have been also used to explain the anomeric effect. It is actually stereoelectronic effect, in which a lone pair located in n-M.O. of the ring oxygen atom overlaps with the antibonding σ^* of the anomeric C-O bond. This favourable $n \rightarrow \sigma^*$ delocalisation is only possible when anti-periplanar arrangement occurs.



6.

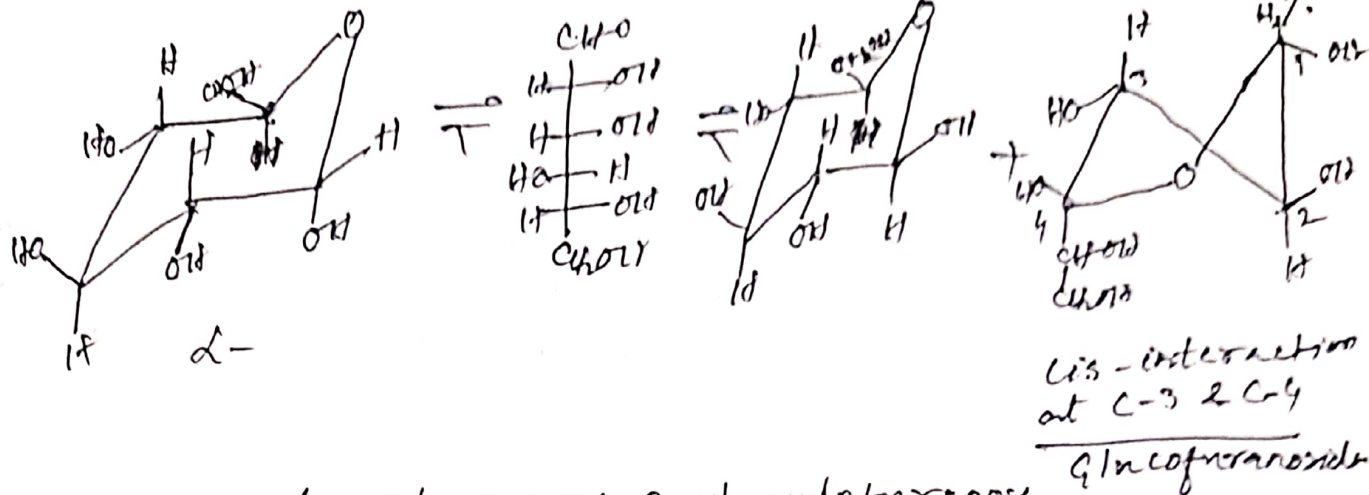
The anomeric effect is of different extent in different cases. It is strongly influenced by the substituent at C-2. When it has equatorial orientation of the -OH group, as in the case of glucose and galactose, the effect is weak and the effect is enhanced when the -OH is axially oriented (mannose)

The solvent also influences the anomeric effect, because with the increase in the polarity of the solvent, the effect decreases.

Rationalisation of the composition of the reducing sugars in their aqueous solution:-

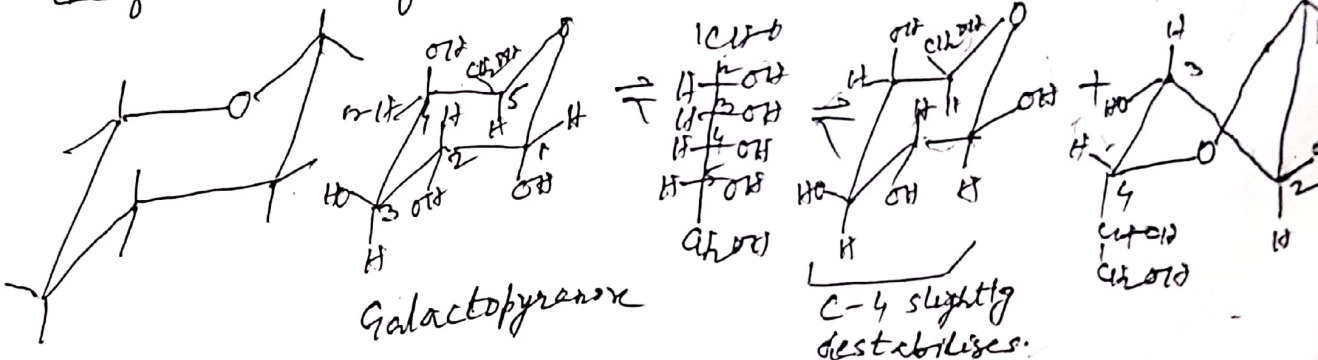
When a reducing sugar is dissolved in excess water, one anomeric form of the sugar is converted into its another anomeric form until the equilibrium is attained (Mutarotation). This interconversion passes through their open chain form and so the equilibrium in the solution always possesses traces of this form.

Those sugars which have all substituents (except the anomeric -OH) are equatorially placed in the pyranose form (glucose, xylose), a very little amount of the furanose form is found at the equilibrium.

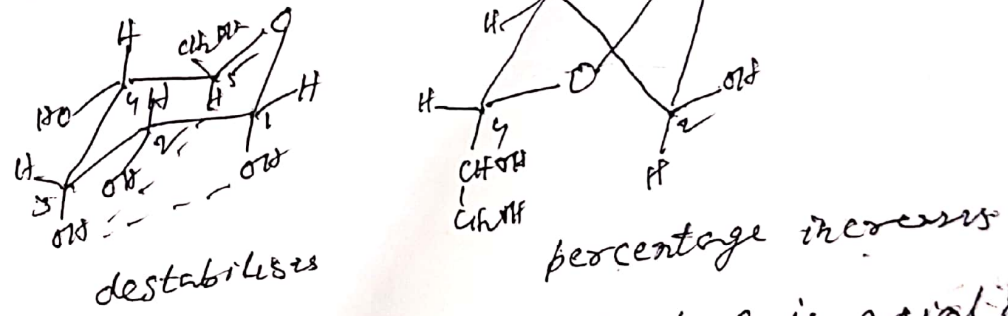


In the glucopyranose and xylofuranose, a cis-interaction at C-3 & C-4 destabilizes the ring.

When the pyranose form of galactose and arabinose are considered, an axial -OH at C-4 destabilises the ring slightly and this increases the furanose form in the solution.



There is a single axial -OH at C-3 in the ribopyranose and allopyranose.



In the mannopyranose, the -OH at C₂ is axial but the substituents at C₂, C₃ and C₄ are cis in the furanose form and hence the furanose form in the solution are found in traces.

D-Fructose can be compared with D-arabinose with the anomeric hydrogen replaced by a hydroxyl methyl group and therefore the furanose form of this compound exists like D-arabinose in the solution.

General configuration of Monosaccharides in the pyranose form

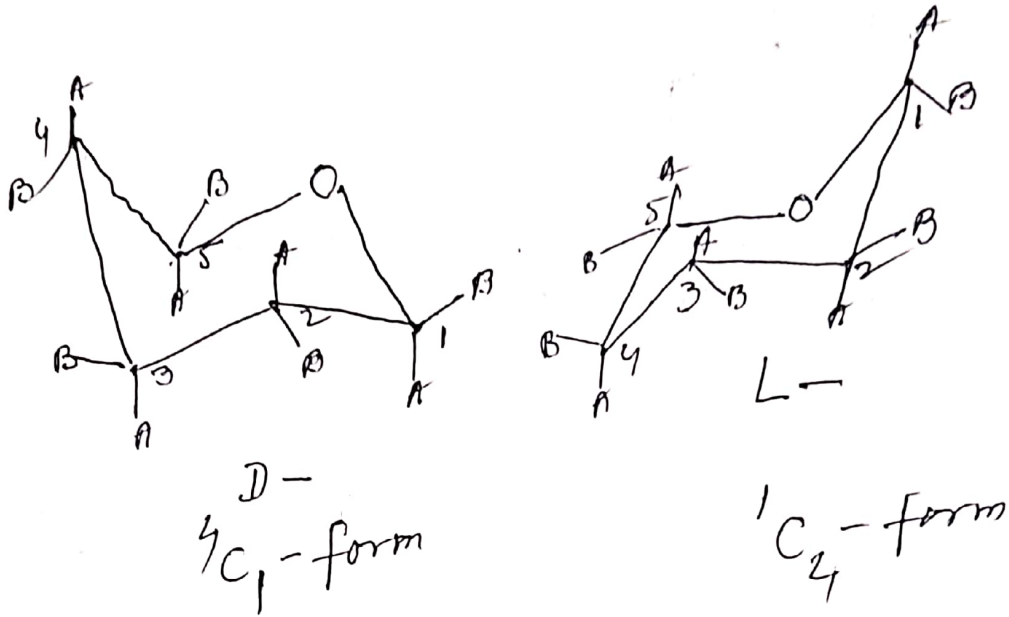
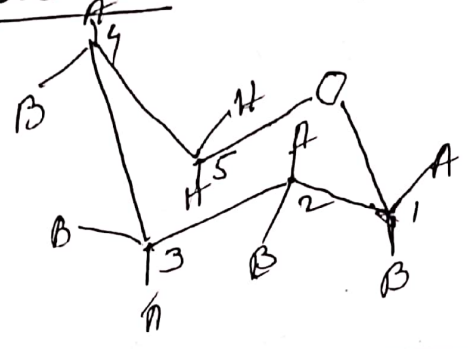


Table: 1 - for 4C₁ form

Sugar	Configurations of -OH					
	C ₁ (α)	C ₁ (β)	C ₂	C ₃	C ₄	C ₅
(A) Hexoses						
(i) Allose	a	e	e	a	e	e
(ii) Altrose	a	e	a	a	e	e
(iii) Glucose	a	e	e	e	e	e
(iv) Mannose	a	e	a	e	e	e
(v) Gulose	a	e	e	a	a	e
(vi) Idose	a	e	a	a	a	e
(vii) Galactose	a	e	e	e	a	e
(viii) Talose	a	e	a	e	a	e

It must be noted that all equatorial -OH of 4C₁ conformation became axial in the 1C₄ conformation.

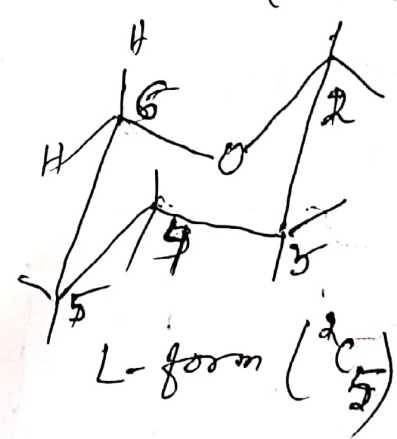
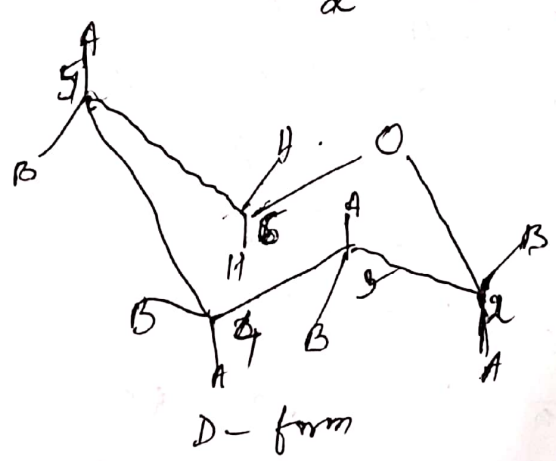
Table - 2 - $4C_1$ conformation of Pentoses



A or B may be -OH/-H

Sugars	configuration of -OH				
	C ₁ (α)	C ₂ (β)	C ₃	C ₄	C ₅
Ribose	a	e	e	a	e
Arabinose	a	e	a	a	e
Xylose	a	e	e	e	e
Lyxose	a	e	a	e	e

Table - 3 - $5C_2$ conformation of ketoses (hexoses)



Sugars	configuration of -OH				
	C ₂ (α)	C ₃ (β)	C ₄	C ₅	C ₆
Psicose	a	e	e	a	e
Fructose	a	e	a	a	e
Sorbose	a	e	e	e	e
Tagatose	a	e	a	e	e

In the D-form of ketohexose, if
 A = -OH
 B = -CH₂OH
 at C₂.

10/ Although the monosaccharides generally exist in their pyranose form, the furanose form is also found in nature for some monosaccharides. For example, the aldopentoses, ribose and its deoxy-derivative, are found in their furanose form in RNA and DNA respectively.

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