

# **Carbohydrates**

5<sup>th</sup> Sem

Lecture – 3

Paper – CC12

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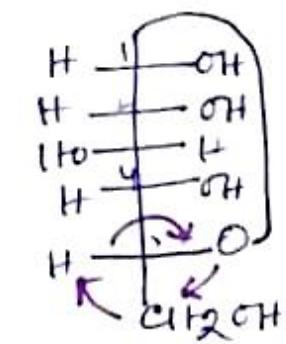
Department of Chemistry

Kharagpur College

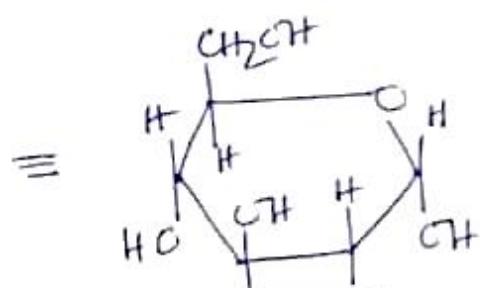
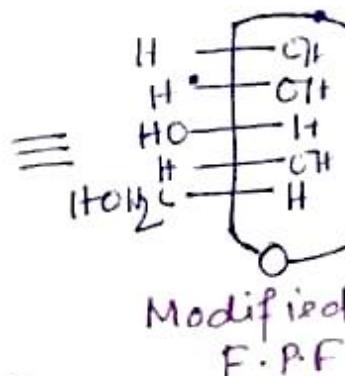
# Carbohydrates

Conformational representation of cyclic structures of monosaccharides

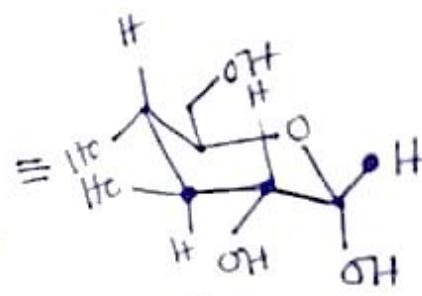
The conventions used to draw Haworth structures can be extended to conformation diagram. In the chair conformation the ring oxygen atom is located at the upper right and groups to the left in F.P.F are drawn upward from the ring. Axial and equitorial positions will logically follow.



Common F.P.F  
of  $\alpha$ -D-glucopyranose

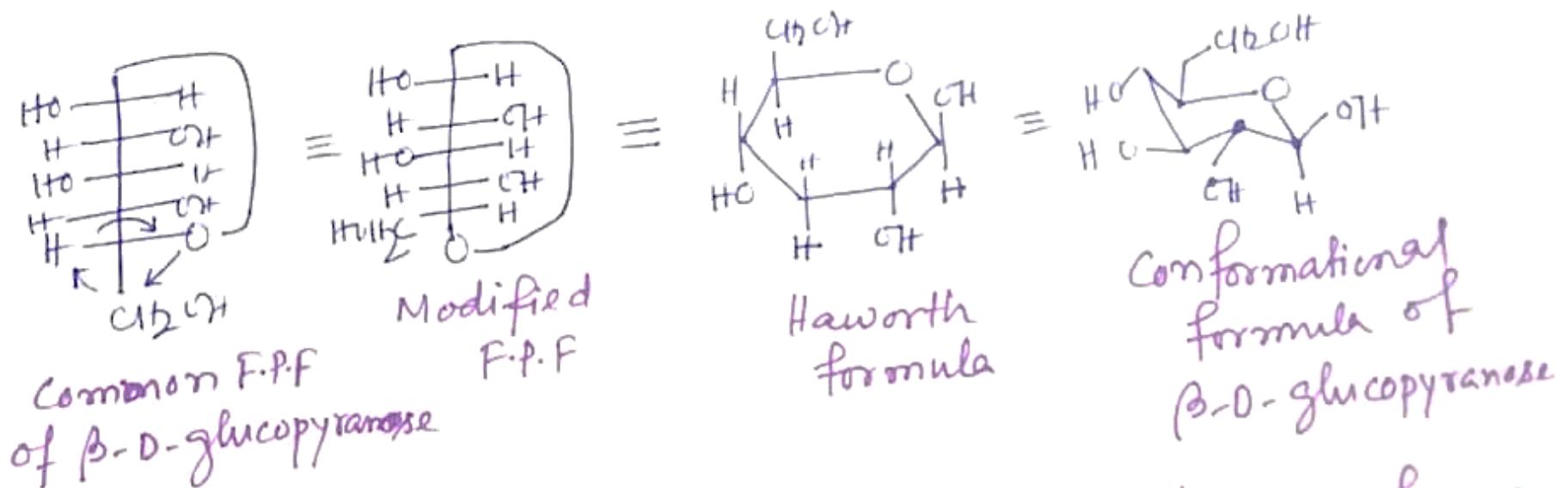


Haworth formula



Conformational formula of  
 $\alpha$ -D-glucopyranose

# Carbohydrates



F.P.F

Right groups  $\rightarrow$  Downwards  
Left side groups  $\rightarrow$  Upward

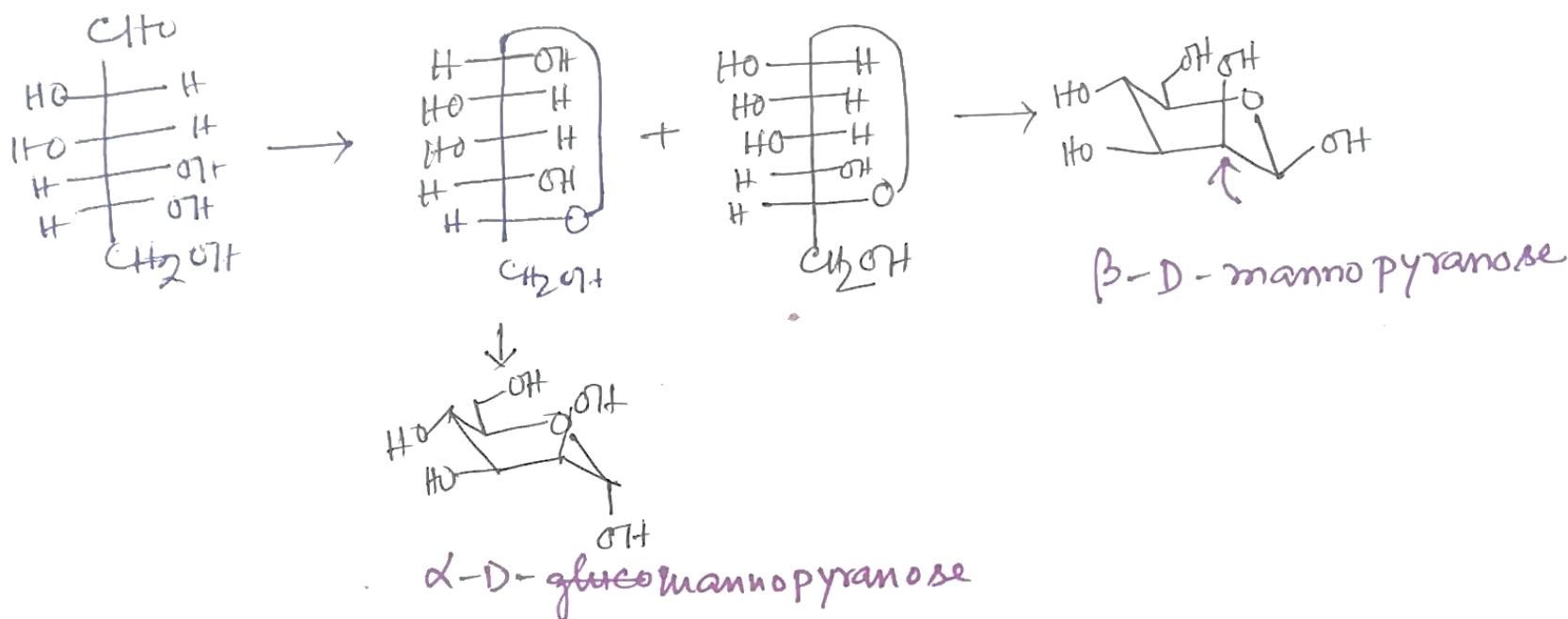
# Carbohydrates

Two chair conformation of  $\beta$ -D-glucose are given below



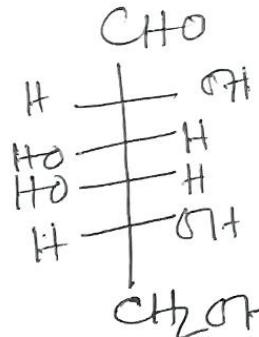
Between structure (I) & (II)  
Structure (I) is more stable as all large groups are in equatorial position.

Draw the conformational isomer of  $\beta$ -D-manno pyranose

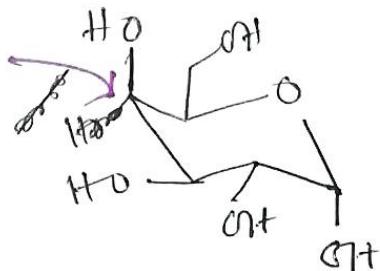


# Carbohydrates

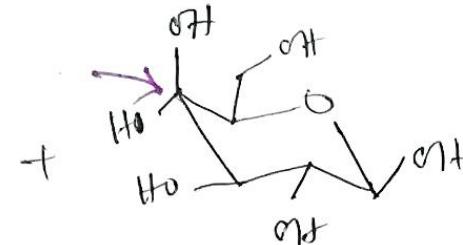
Similarly for  $\beta$ -D-galactopyranose



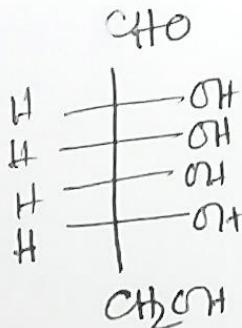
D- galactose  
galactose



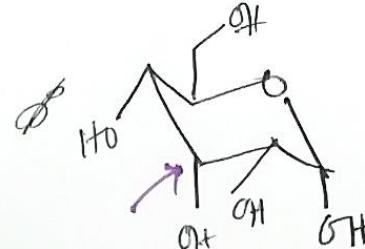
$\alpha$ -D-galactopyranose



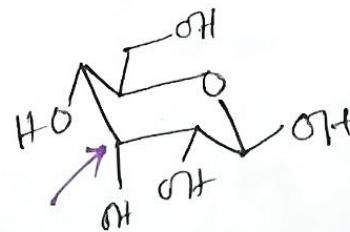
$\beta$ -D-galactopyra-  
nose



D- Allose



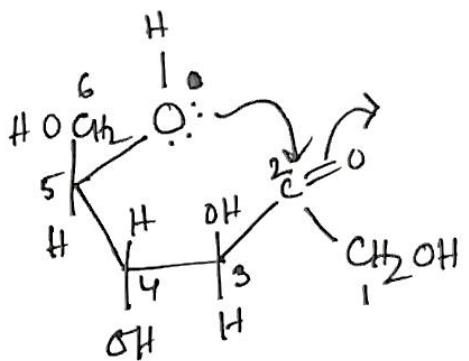
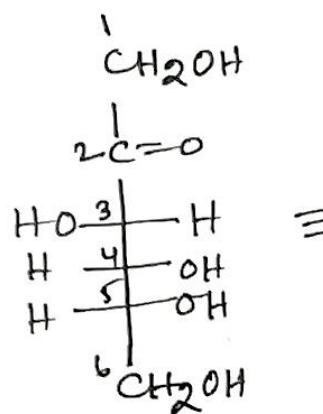
$\alpha$ -D-Allopyranose



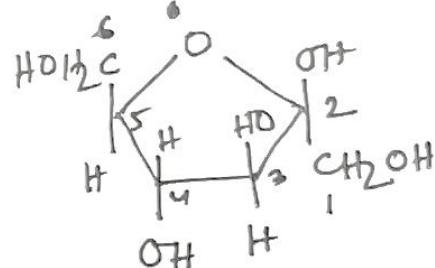
$\beta$ -D-Allopyranose

# Carbohydrates

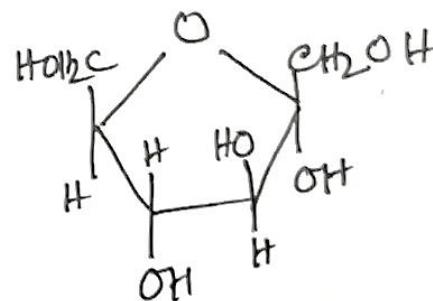
Five membered cyclic structure of fructose:



$\equiv$



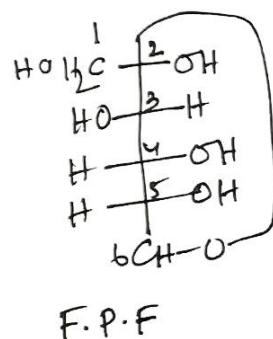
$\beta$ -D-fructofuranose



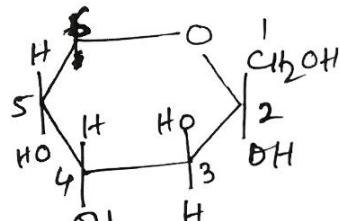
$\alpha$ -D-fructofuranose

# Carbohydrates

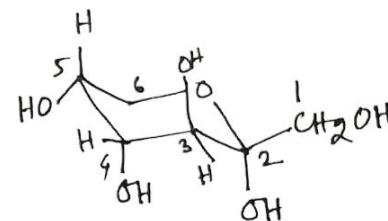
$\alpha$ -D-Fructopyranose:



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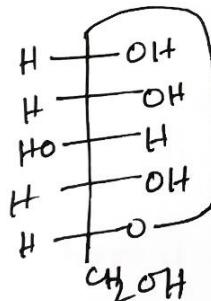


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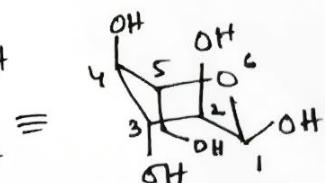
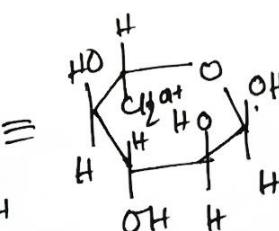
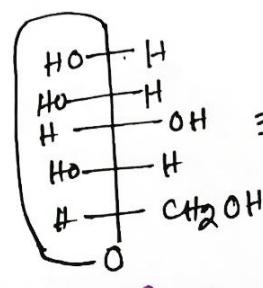
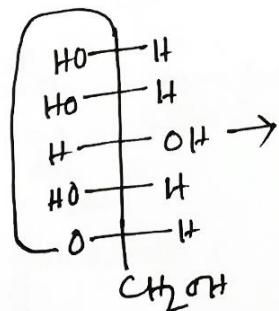


chair conformation of  
 $\alpha$ -D-fructopyranose.

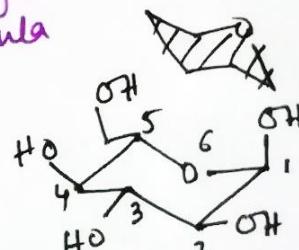
$\alpha$ -L-Glucopyranose :-



1



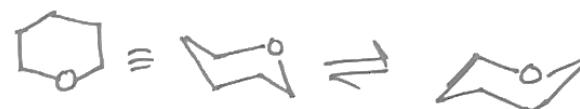
formula



more stable

## Anomeric effect

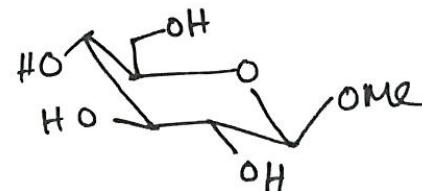
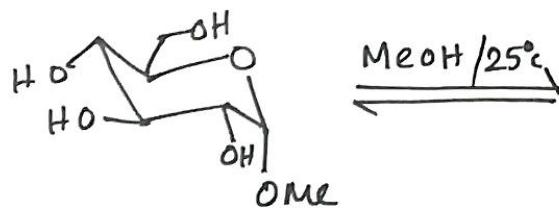
Tetrahydropyran is more stable in chair conformation as in cyclohexane.



However, compounds of pyran series do not always obey the conformational rule (due to 1,3-diaxial interaction a bulky substituent in the equatorial position is more stable than axial position). There are large number of examples in the carbohydrate chemistry where pyranose sugars with a strong electronegative substituents, such as halogens, alkoxy, acyloxy etc at C-1 are often more stable when the substituent has an axial orientation rather than equatorial orientation, though the axial orientation of C-1 polar groups involve 1,3-diaxial strain.

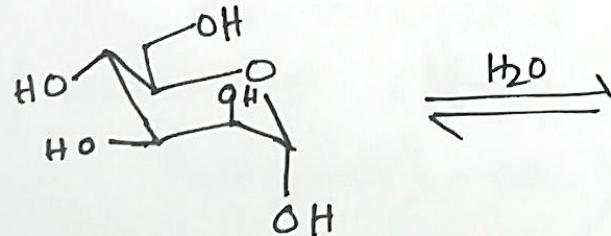
# Carbohydrates

The phenomenon of extra-preference for an axial orientation over the equatorial orientation of an electro-negative substituent at the anomeric carbon of a pyranose derivative in solution is known as the anomeric effect. A few examples are given below:



Methyl- $\alpha$ -D-glucoside  
67%.

Methyl- $\beta$ -D-glucoside  
33%.



$\alpha$ -D-Mannopyranose  
69%.

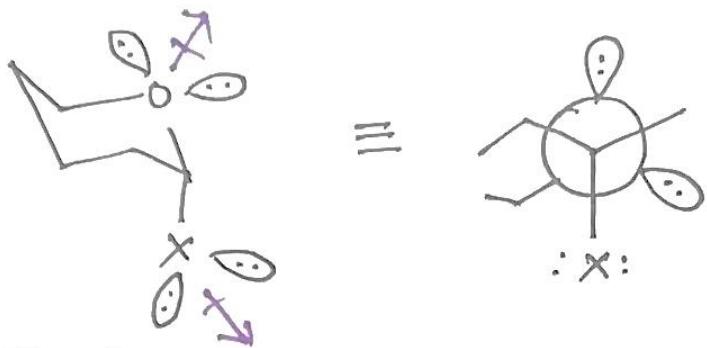


$\beta$ -D-Mannopyranose  
31%.

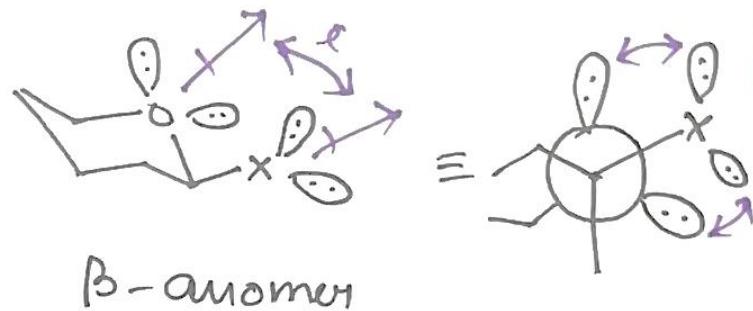
# Carbohydrates

Explanation:- The anomeric effect is attributed due to

- i) Repulsion bet'n the dipoles associated with the nonbonding electrons of electronegative substituents ( $X$ ) on the anomeric carbon and the nonbonding electrons on the ring oxygen. This repulsion is unfavourable for equatorial or  $\beta$ -anomer and favourable for  $\alpha$ -anomer.



$-X = -OR$ , halogen,  $-OCOR$  etc  
 $\alpha$ -anomer

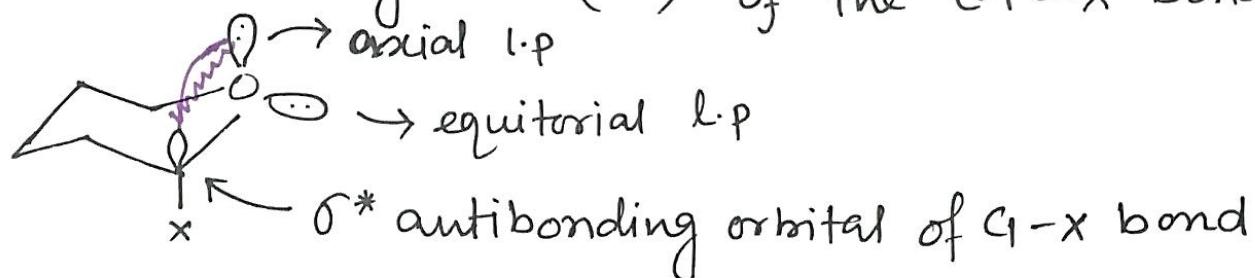


$\beta$ -anomer

$\ell\cdot p - \ell\cdot p$  repulsion or dipole repulsion destabilise the  $\beta$ -anomer.

# Carbohydrates

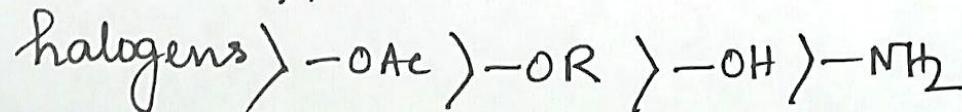
(ii) The most favoured and accepted explanation involves the interaction bet<sup>n</sup> a lone pair of electrons located 'axially' in a molecular orbital ( $\pi$ ) on ring oxygen and an unoccupied, antibonding m.o ( $\sigma^*$ ) of the C-1-X bond.



The 'anti-periplanar' arrangement found in the axial anomers favours this 'backbonding' resulting  $\alpha$ -anomer become stabilised.

\*\*

The anomeric effect depends very much on the nature of the electronegative substituents. The decreasing order of anomeric effect is



# Carbohydrates

\*\* Anomeric effect also depends on the polarity of the solvent and diminishes with increase of the dielectric constant of the solvent. Thus

	<u>Solvent</u>	<u><math>\alpha</math>-D-Glucose</u>	$\rightleftharpoons$	<u><math>\beta</math>-D-glucose</u>
Maximum effect	$\rightarrow \text{C}_6\text{H}_6$	major		minor
	MeOH	50 %.		50 %.
anomeric effect completely disappears or decreases	$\rightarrow \text{H}_2\text{O}$	36 %.		64 %.

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The dielectric constant of  $\text{H}_2\text{O}$  is greater than the MeOH. In  $\text{H}_2\text{O}$  the % of  $\alpha$ -anomer remain their ideal value. It is considered that in water anomeric effect completely disappear. This is due to the decrease of dipole-dipole interaction betn the lone pairs of ring oxygen and the lone pair of an equitorial polar substituent. In this case lone pairs are engaged in favourable solvation with the solvent  $\text{H}_2\text{O}$ , at the less hindered equitorial position. But MeOH is a low polar solvent. Here the anomeric effect of the polar -OH group is greater so the % of axial anomer increases to 50.1.

