5.) Reaction with phenyl hydraxine :(i) Glucose reacts with one equivalent of phenyl hydrazine to form glucose phenyl hydrazone.

$$CH_2OH-(CHOH)_4-CH=O + H_2N\cdot NHC_6H_5 \longrightarrow CH_2OH-(CHOH)_4-CH=N\cdot NHC_6H_5 - H_2O$$

(ii) However if excess of phenyl hydrazine is used; one mole of glucose reacts with three moles of the reagent to give one mole of glucosazone (i.e. osa zone). This reaction is given by all α-hydroxy Carbonyl Compound.

$$\underset{\text{Glucose}}{\begin{matrix}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix}} + \underset{\text{phenylhydrazine}}{3C_6H_5NH-NH_2} \longrightarrow \underset{\text{Glucosazone}}{\begin{matrix}CH=N.NC_6H_5\\|\\C=N.NHC_6H_5\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}} + C_6H_5NH_2 + NH_3$$

(B) Reactions of hydroxyl groups

1. Acetylation : on acetylation with acetic anhydride in presence of Sodium acetate or pyridine glucose yields glucose penta-acetate.

$$\begin{matrix}CH_2-(CH-)_4-CHO\\|\quad\quad\quad|\\OH\quad\quad OH\end{matrix} \xrightarrow[Py]{(CH_3CO)_2O} \begin{matrix}CH_2-(CH-)_4-CHO\\|\quad\quad\quad|\\OCOCH_3\quad\quad OCOCH_3\end{matrix}$$

Glucose penta acetate.

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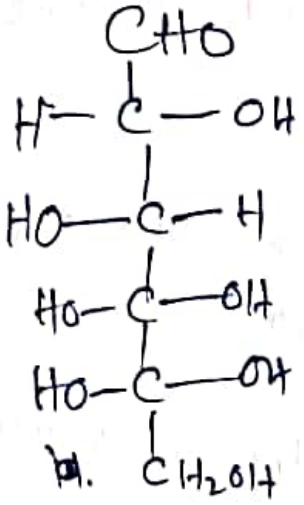
Open chain structure of glucose

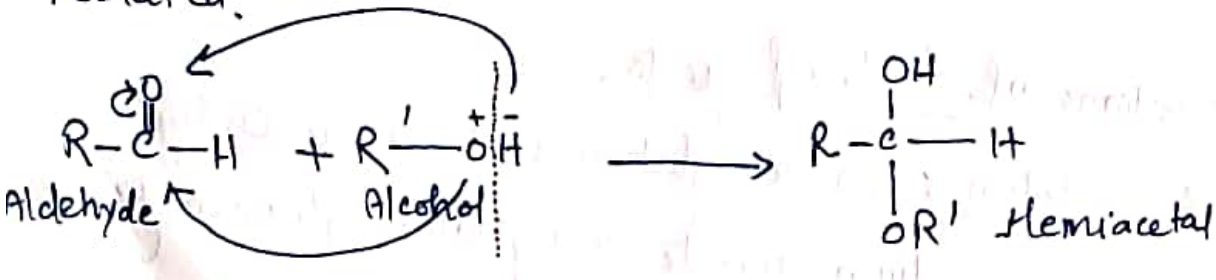


D - (+) - glucose

Cyclic structure of glucose

: Aldehyde

Reacts with one molecule of an alcohol to give a hemiacetal. The hemiacetal is not stable and most hemiacetals decompose spontaneously to the aldehyde and alcohol. So, hemiacetals are rarely isolated.



If aldehyde group and hydroxyl groups are part of same molecules, then a cyclic hemiacetal results. These cyclic hemiacetals are stable if they result in five or six-membered rings. These are more stable

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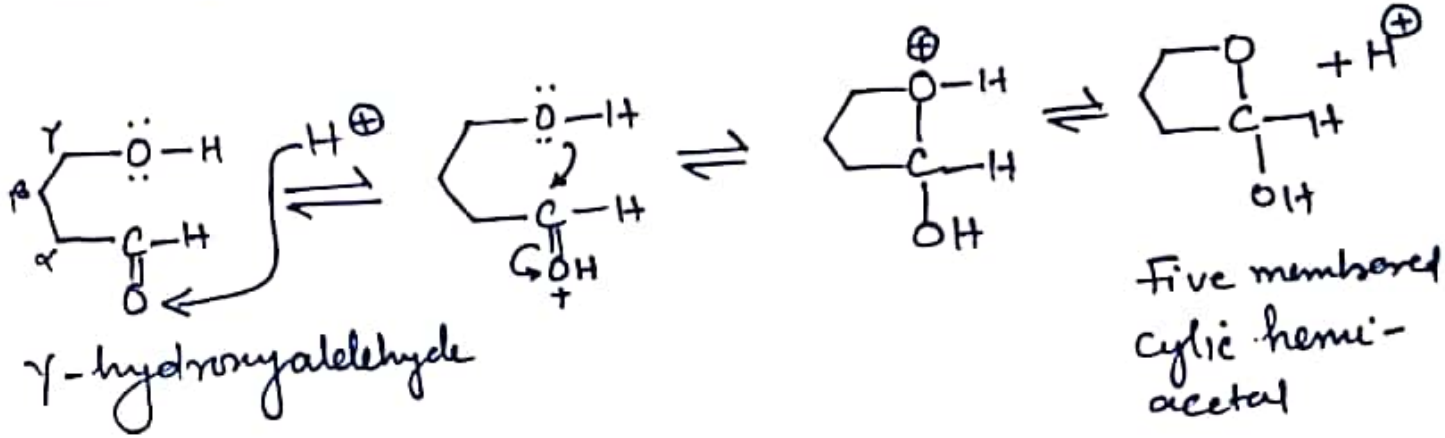
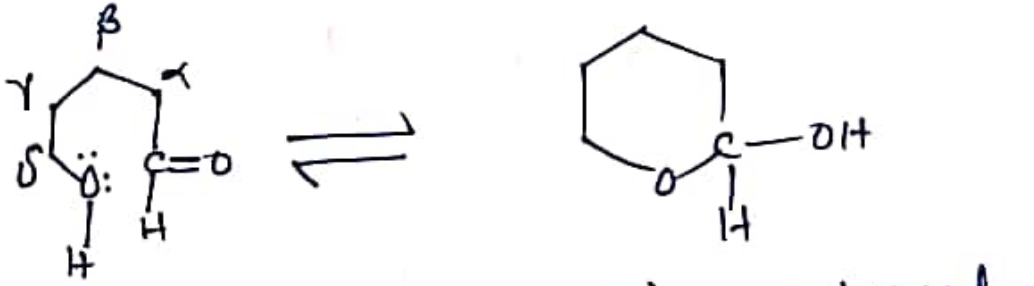
than open chain forms. Thus γ and δ-hydroxy aldehydes exist predominantly as cylic hemiacetals.



γ-hydroxyaldehyde

Five membered cylic hemi-acetal



δ-hydroxyaldehyde

Six membered cylic hemiacetal

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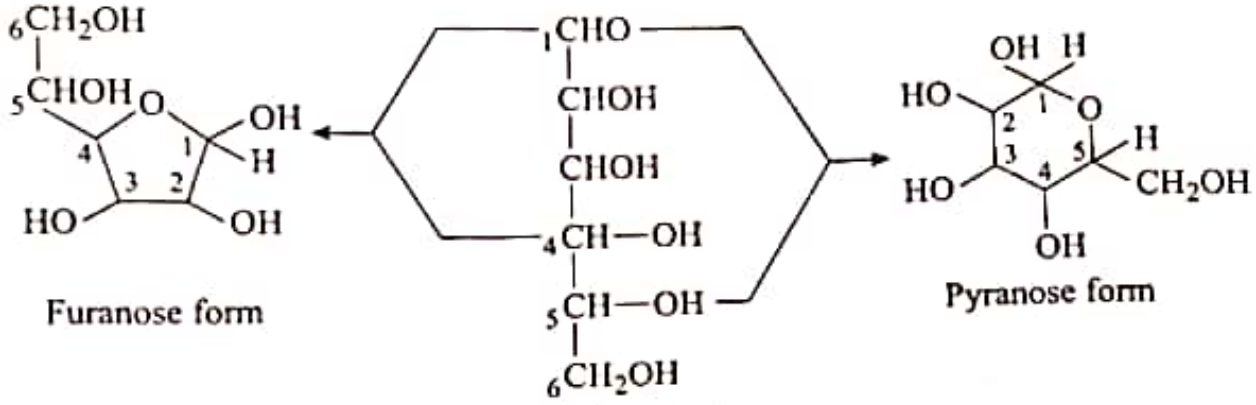
The same is true of sugars. **Although sugars are often written by convention as acyclic carbonyl compounds, they exist predominatly as cyclic hemiacetals.** An aldohexose, for example, can exist as either a five-membered or six-membered cyclic hemiacetal depending on which hydroxyl group undergoes cyclisation.



The five-membered cyclic hemiacetal form of a sugar is called the furanose form (after furan); the six-membered cyclic hemiacetal form of a sugar is called the pyranose form (after pyran).



Glucose and other aldohexoses exist predominantly in the pyranose form but the furanose form of some sugars (specially fructose) are important.

Hemiacetal formation creates a new chiral centre usually called the **anomeric carbon or anomeric centre.** In turn, this results in two diastereomeric products differing in configuration only at anomeric carbon (C–1 carbon in aldoses and C–2 carbon in ketoses). These diastereomeric products are known as anomeric products. These anomers are deginated as α or β depending upon the relative configuration at anomeric carbon and at the carbon used to establish the sugar as *D* or *L*. In the Fischer representation of α-D-glucopyranose, the C1–OH group (the hemiacetal hydroxy group) is on the same side of the carbon skeleton as is the oxygen bonded to

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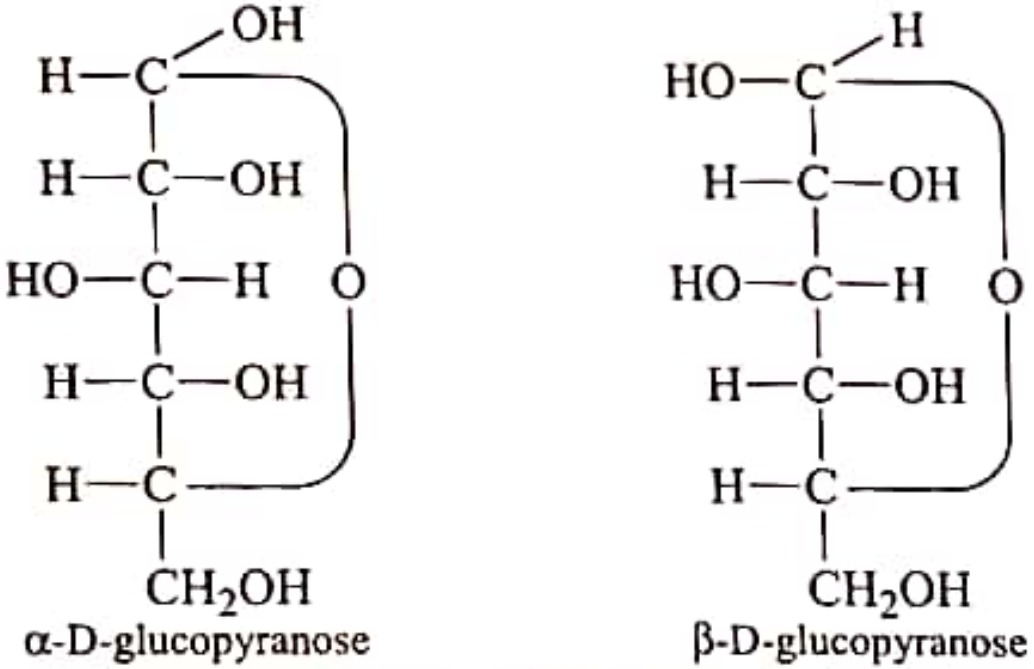
the carbon that labels the sugar as *D* or *L* (in glucose, this carbon is C–5). In β-D-glucopyranose, there are two hydroxyl groups are opposite sides of the skeleton.



Fisher structure of glucose anomers

Thus α-*D*-glucose and β-*D*-glucose are anomers. **Anomers** are two sugars that differ in configuration only at the carbon that is the carbonyl carbon in the open chain form.

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