

Lecture 5

Chemical properties of carbohydrates

Monosaccharides

Reactions of monosaccharides are due to the presence of hydroxyl (-OH) and the potentially free aldehyde (-CHO) or keto ($>C=O$) groups.

Reaction with alkali

Dilute alkali

- Sugars in weak alkaline solutions undergo isomerization to form **1,2-enediol** followed by the formation of a mixture of sugars.

Strong alkali

Under strong alkaline conditions sugar undergo **caramelization reactions**.

Reducing property of sugars

- Sugars are classified as either reducing or non-reducing depending upon **the presence of potentially free aldehyde or keto groups**.
- The reducing property is mainly due to the ability of these sugars to **reduce metal ions such as copper or silver to form insoluble cuprous oxide, under alkaline condition**.
- The aldehyde group of aldoses is oxidized to carboxylic acid.
- This reducing property is the basis for qualitative (Fehling's, Benedict's, Barfoed's and Nylander's tests) and quantitative reactions.
- All monosaccharides are reducing. In the case of oligosaccharides, if the molecule possesses a free aldehyde or ketone group it belongs to reducing sugar (maltose and lactose).
- If the reducing groups are **involved in the formation of glycosidic linkage**., the sugar belongs to the non-reducing group (trehalose, sucrose, raffinose and stachyose).

Reaction with phenylhydrazine

- When reducing sugars are heated with **phenylhydrazine** at pH 4.7 a yellow precipitate is obtained.

- The precipitated compound is called as **osazone**.
- One molecule of reducing sugar reacts with three molecules of phenylhydrazine.
- D-mannose and D-fructose form same type of osazone as that of D-glucose since the configuration of C-3, C-4, C-5 and C-6 is same for all the three sugars.
- This reaction serves to distinguish between aldose and ketose sugars.

Reaction with acids

- Heating a solution of hexoses in a strong non-oxidising acidic conditions, **hydroxyl methyl furfural** is formed.
- The hydroxymethyl furfural from hexose is usually oxidized further to other products. When **phenolic compounds such as resorcinol, β -naphthol or anthrone** are added, mixture of coloured compounds are formed.
- The **molisch test** used for detecting carbohydrate in solution is based on this principle.
- When conc. H_2SO_4 is added slowly to a carbohydrate solution containing β -naphthol, a pink color is produced at the juncture.
- The heat generated during the reaction **hydrolyse and dehydrate** it to produce **furfural or hydroxymethyl furfural** which then react with β -naphthol to produce the pink color.