Carbohydrates

Defination, Introduction and Classification.

Monsaccharides-Interconversion of Glucose and Fructose, chain lengthening, chain shortening of aldoses. Conversion of Glucose in to mannose. Determination of openchain structure of glucose & pyranose ring structure of glucose . Mechanism of Mutarotation and Introduction to disaccharides (maltose, sucrose and lactose) and

Polysaccharides (Starch and cellulose) without involving structure determination.

Introduction :-

The carbohydrates are an important class of naturally occuring organic compounds. They are all composed of C, H & [O]. Generally carbohydrates represented by the formula $C_m(H_2O)_n$. carbohydrates are synthesised by nearly all plants & animals. A French chemist gave them the class name carbohydrates (carbon-Hydrates)

Plants synthesize the carbohydrates by a process called as photosynthesis in which carbon-dioxide & water in presence of sunlight & chlorophyll as catalyst are converted into a carbohydrates

e.g.

$$x\,CO_2 + y\,H_2O \xrightarrow[\text{chlorophyll}]{\text{Solar energy, sunlight}} C_x(H_2O)_y + xO_2$$

Carbohydrates

e.g. glucose (grape sugar), fructose (Honey), sucrose (cane - sugar), Starch (potatoes), & cellulose (wood) etc.

Generally hydrates means it contains water molecules but carbohydrates do not contains any water molecule carbohydrates are often referred as Saccharides (Latin, Saccharum - sugar) because of the sweet taste of the simple members of the class the sugar.

In common name system the carbohydrates ending by - ose

e.g. 1) fruct-ose 2) gluc-ose
3) sucr-ose 4) cellul-ose etc.

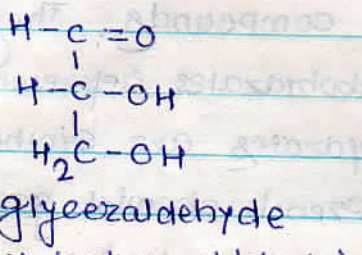
What are carbohydrates :-

Carbohydrates are polyfunctional compounds, they contains the following functional group.

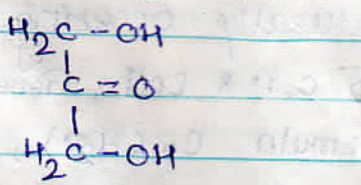
1) Hydroxy gr (alcoholic) $-OH$
2) Aldehyde gr $-\overset{O}{\overset{\|}{C}}-H$
3) Ketone gr $-\overset{O}{\overset{\|}{C}}-$ etc.

The precise defination of carbohydrate is " polyhydroxy-aldehyde or polyhydroxyketone & large molecules that produce these compounds on hydrolysis " are called carbohydrates

Simple example of carbohydrate is given below & it contain three carbon with diffnt functional group.



glyceraldehyde
(Polyhydroxy aldehyde)



Dihydroxy acetone
(Polyhydroxyl ketone)

Classification of carbohydrates :-

The carbohydrates are divided into three major classes, depending on the number of simple sugar units present in their molecules. (In other words on hydrolysis how many no. of sugar molecules same or different produced) which is given below;

1) Monosaccharides - e.g. glucose $C_6H_{12}O_6$.
2) oligosaccharides → Disaccharides e.g. sucrose $C_{12}H_{22}O_{11} + H_2O$
   → Trisaccharides e.g. Raffinose $C_{18}H_{32}O_{16} + 2H_2O$
3) poly saccharides - e.g. starch or cellulose $(C_6H_{10}O_5)_n$.

Monosaccharides :-

These are single unit carbohydrates (polyhydroxy ketones or polyhydroxyaldehydes) or it is simple sugar, that cannot be broken into simpler carbohydrates upon hydrolysis.

e.g.

$$C_6H_{12}O_6 + H_2O \xrightarrow{H^\oplus} \text{No reaction}$$

glucose or fructose

~~Disaccharides~~ Classification of Monosaccharides

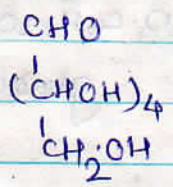
The monosaccharides are again classified on the two basis or factors;

1) By the carbonyl function : &
2) By the No. of carbon atoms.

1) In first method those containing the aldehyde funtn $-CHO$ are called as Aldoses, & those containing the keto group $-\overset{O}{\overset{\|}{C}}-$ are called as Ketoses.

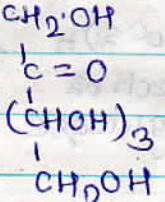
e.g. glucose (Aldohexose) fructose (Ketohexose)

e.g. (A)



Aldohexose (glucose)

(B)



Ketohexose (fructose).

Monosaccharides are nonhydrolysable so that they are considered as basic units of carbohydrates.

Oligosaccharides :-

Oligosaccharides are made of 2 to 10 units of monosaccharides or simple sugers. Generally oligosaccharides containing two monosaccharide units called as Disaccharides & those containing three monosaccharide units are called as Trisaccharides. oligosaccharides on hydrolysis gives the two or more simple suger molecules

e.g. given below,

(A) Disaccharide example.

1) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose → glucose + fructose.

(B) Trisaccharide example.

2) $C_{18}H_{32}O_{16} + 2H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{12}O_6$

Raffinose → glucose + fructose + galactose.

(C) Tetrasaccharide example.

3) $C_{24}H_{42}O_{21} + 3H_2O \xrightarrow{H^+} 4 \cdot C_6H_{12}O_6$

Stachyose → four glucose molecules.

Polysaccharides :-

Polysaccharides contain more than ~~the~~ ten monosaccharide units in the molecule. e.g. one molecule of starch or cellulose upon hydrolysis yields a very large no. (n) of the glucose units.

e.g.

$$(C_6H_{10}O_5)_n + H_2O \xrightarrow{H^+} n\cdot C_6H_{12}O_6$$

Starch or glucose → glucose.

Sugars & Non-Sugars :-

The monosaccharide & oligosaccharides are soluble in water; they are crystalline substance having sweet taste. They are collectively known as sugar.

Polysaccharides are insoluble in water, & amorphous substances are called as non-sugars, generally they are sweetless e.g. starch; cellulose etc.

Monosaccharides:- These are simple unit of carbo-hydrates (Polyhydroxy ketone or polyhydroxy aldehydes) or it is simple sugar that cannot be broken into simpler carbohydrates upon hydrolysis.

e.g.

$C_6H_{12}O_6 + H_2O \xrightarrow{H^+}$ No reaction.

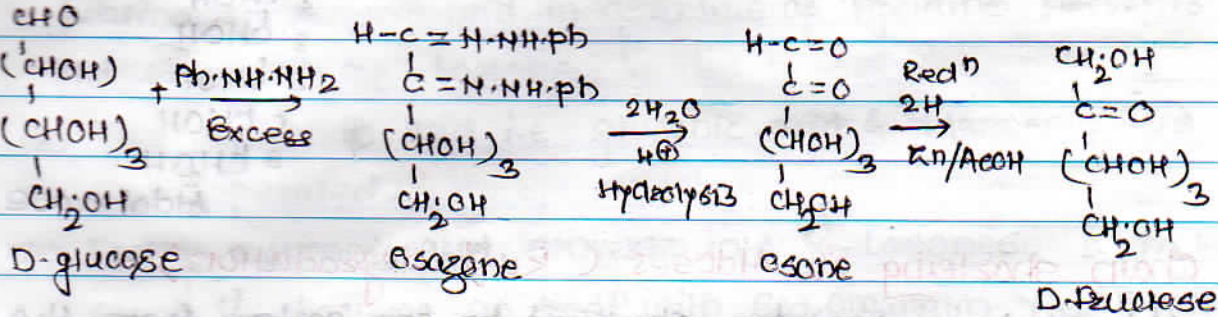
glucose or fructose

Interconvesion of glucose & fructose or (Aldoses & Ketose)

a) Conversion of D-glucose to D-fructose -

An aldoses or D-glucose converted into D-fructose by heating D-glucose with excess phenyl hydrazine gives osazone. Then on hydrolysis of osazone to osone with dil- HCl. Lastly reduction of osone to D-fructose or ketose with zinc & acetic acid.

e.g.

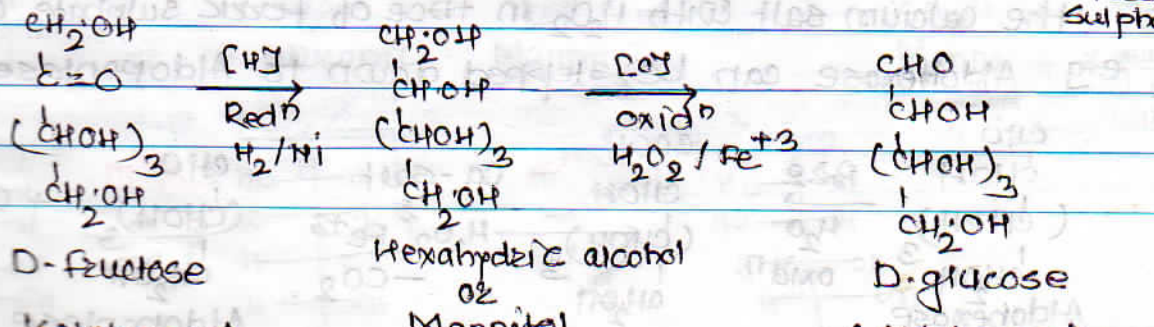


b) Conversion of D-fructose to D-glucose -

D-fructose or ketohexose may be converted into D-glucose or isomeric aldoses by following steps i) Redn of $-\overset{|}{C}=O$ to CHOH with nickel

ii) oxidn of CH_2OH to CHO with H_2O_2 + ferric sulphate

e.g.



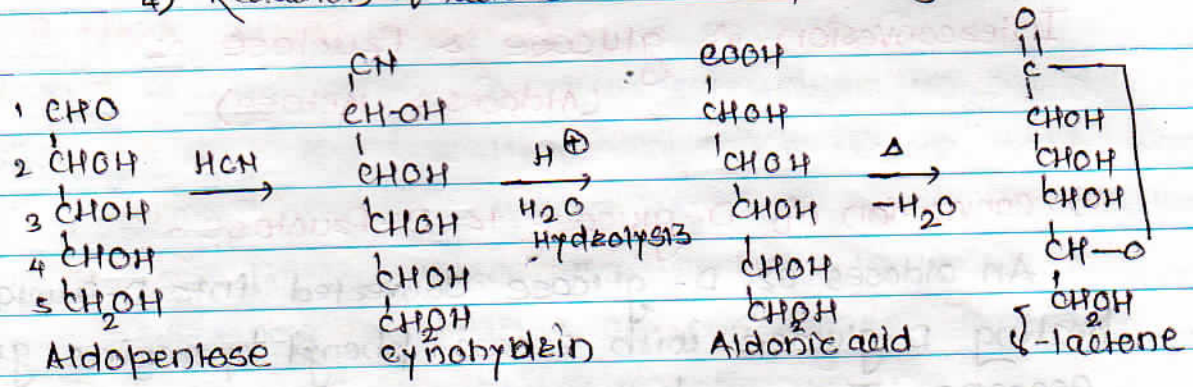
Chain lengthening of aldoses (Killiani-Fischer synthesis) –

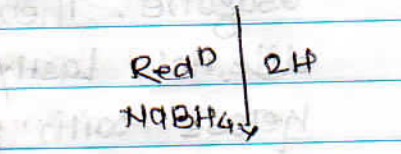
The aldoses chain may be lengthened by one carbon by known procedure "Killiani-Fischer synthesis".

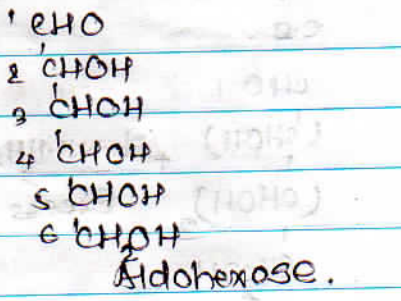
e.g. Aldopentose convert in to Aldohexoses by following steps

1) Reaction with HCN gives cynohydrin.
2) Hydrolysis of -CN to -COOH gives aldonic acid.
3) conversion of aldonic acid to δ-lactone by heating
4) Reduction of lactone with $NaBH_4$ to higher aldoses.

e.g.





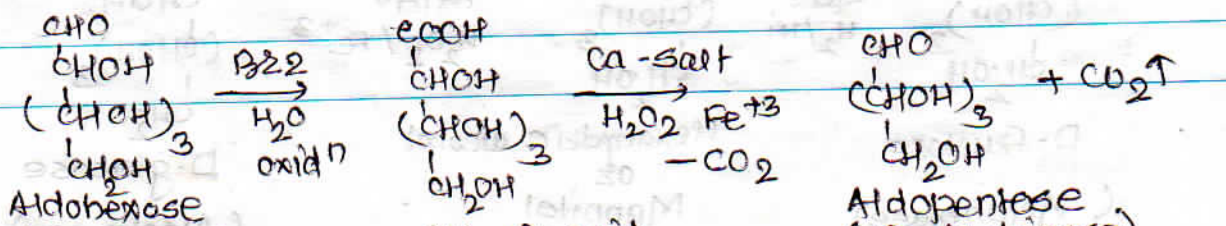


Chain shortening of Aldoses (Ruff degradation) –

Aldose chain may be shortened by one carbon from the aldehyde end by the reaction sequence known as Ruff Degradation method, by following steps;

1) oxid^n of aldose to aldonic acid by using Br_2 water,
2) oxidative decarboxylation of aldonic acid by treating the calcium salt with H_2O_2 in the of ferric sulphate catalyst,

e.g. Aldohexose can be stepped down to Aldopentose,



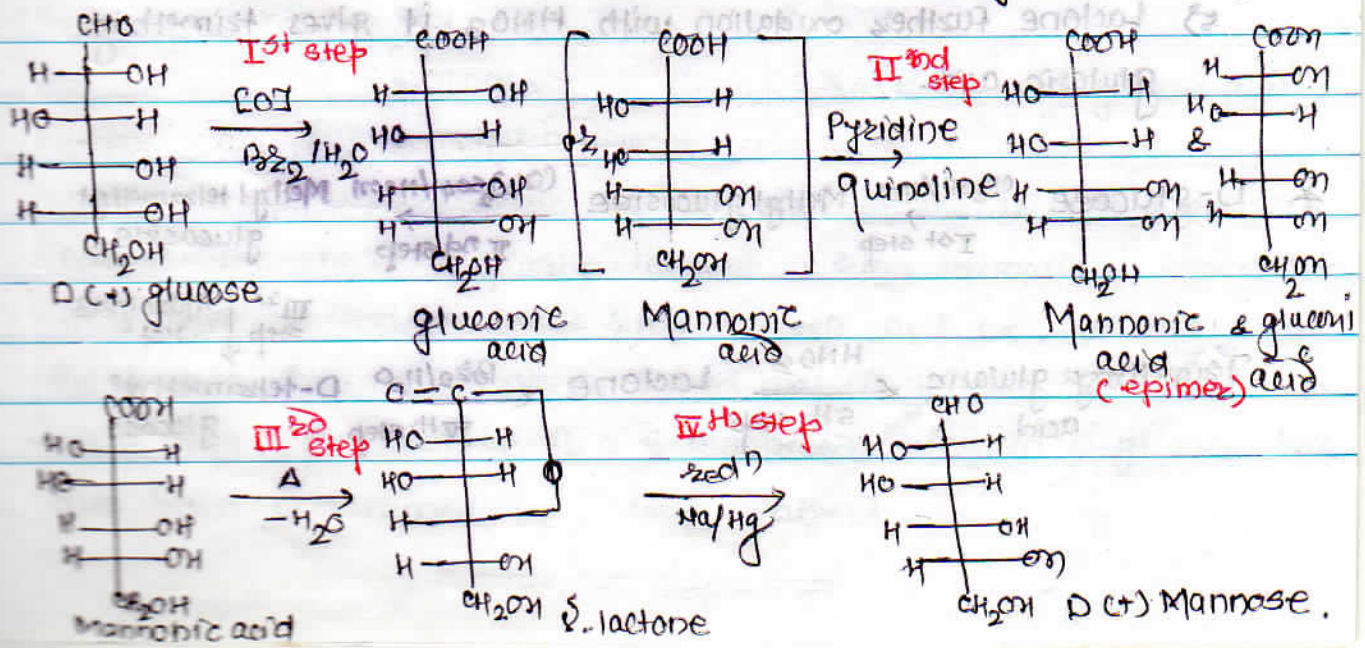
Conversion of glucose into Manose :-

Stereoisomers which differs in the configuration at only one asymmetric carbon atom (generally at α-carbon or carbon-2) are called as epimers.

D-glucose & D-Mannose differs in the configuration of CHOH group at Carbon-2. Hence they are epimers. The process of converting one epimer into other i.e inversion of configuration at one stereogenic centre (asymmetric centre, generally at α-carbon in a molecule containing several stereo-genic centres is known as epimerisation.

D-glucose converts in D-mannose by following steps

1) D(+) glucose is oxidised by bromine in water to gluconic acid
2) gluconic acid heated at 150°C in aq. quinoline or pyridine to obtain original gluconic acid & its epimer mannonic acid in equilibrium mixture. By heating of gluconic acid in quinoline or pyridine prevents the formation of lactone.
3) Two epimeric acid i.e gluconic acid & Mannonic acid are separated.
4) Lastly mannonic acid converts into δ-Lactones. & in last step δ-lactone on redn with Sod. amalgum yield D-Mannose (+)

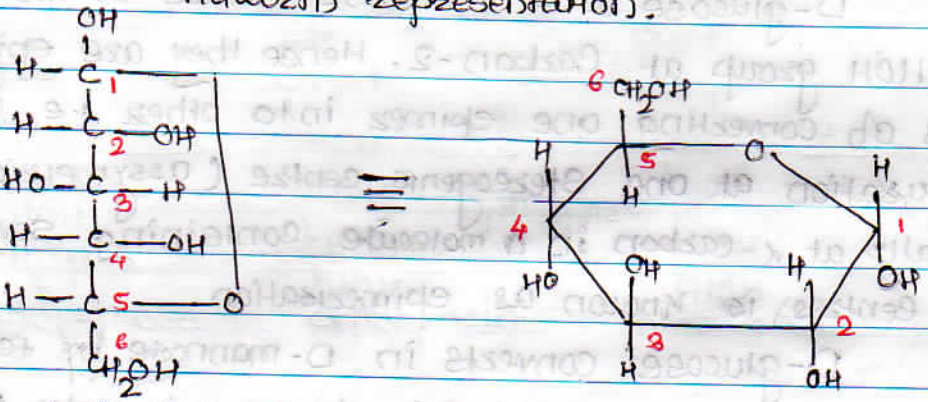


Determination of ring size of Monosaccharide :-

The size of the ring in sugars (Monosaccharide) can be determined by the methylation method;

Fischer suggested a five membered ring structure for glucose in which oxide ring is present between C_1 & C_4 but later on Haworth & coworker in 1926 established the presence of a six membered oxide ring between C_1 & C_5 carbon atoms. The structure generally referred as pyranose,

Haworth representation.



α-D-glucose (Fischer) ≡ α-D-glucopyranose (Haworth)

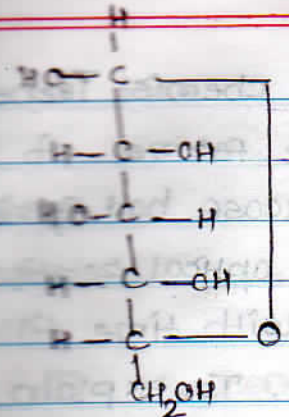
Lastly it is provided by the following series of reaction;

1) Methylation of glucose by heating with methanolic HCl.
2) Methylated product further treated with dimethyl sulphate in ince of NaOH.
3) Tetramethyl D-glucose hydrolysis by HCl
4) Again, tetramethyl D-glucose oxidise by bromine water gives Lactone
5) Lactone further oxidation with HNO_3 it gives trimethoxy glutaric acid.

* D-glucose $\xrightarrow[\text{I}^{st}\text{ step}]{CH_3OH/HCl}$ Methyl glucoside $\xrightarrow[\text{II}^{nd}\text{ step}]{(CH_3)_2SO_4/NaOH}$ Methyl tetramethyl glucoside

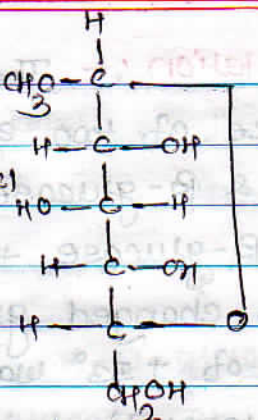
Methyl tetramethyl glucoside $\xrightarrow[\text{III}^{rd}\text{ step}]{\text{Hydrolysis HCl}}$ D-tetramethyl glucose

D-tetramethyl glucose $\xrightarrow[\text{IV}^{th}\text{ step}]{Br_2/H_2O}$ Lactone $\xrightarrow[\text{5th step}]{HNO_3}$ Trimethoxy glutaric acid.



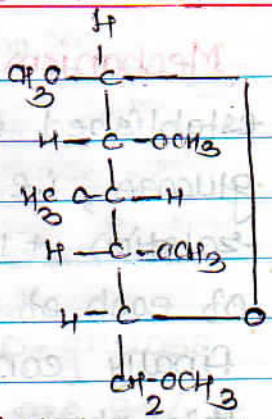
D-glucose

1st step: CH_3OH/HCl, Reflux



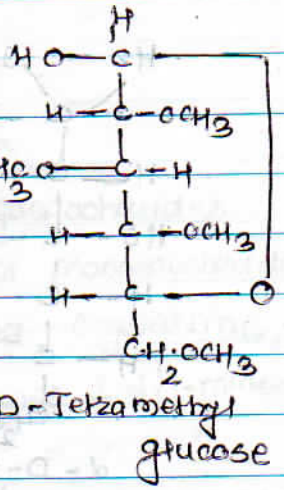
Methyl glucoside

2nd step: $(CH_3)_2SO_4/NaOH$



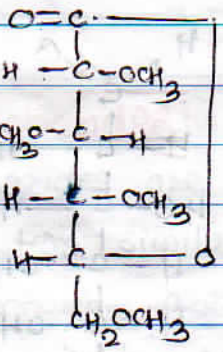
Methyl tetramethyl glucoside

3rd step: HCl, Hydrolysis



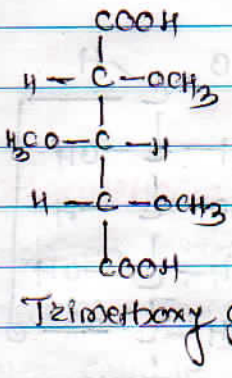
D-Tetramethyl glucose

4th step: Br_2/H_2O, 90°C

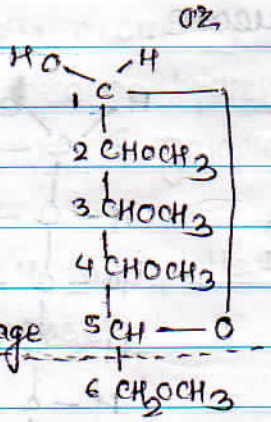


Lactone

5th step: HNO_3, [O]

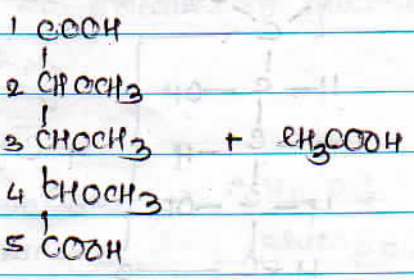


Trimethoxy glutaric acid.



Tetra-O-methyl-D-glucose

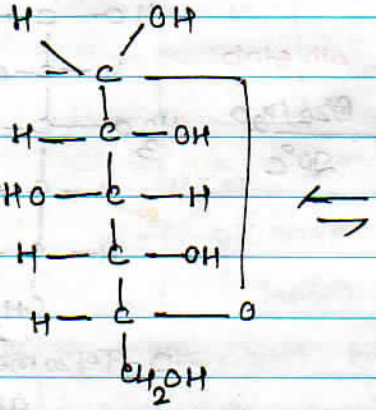
HNO_3, [O]



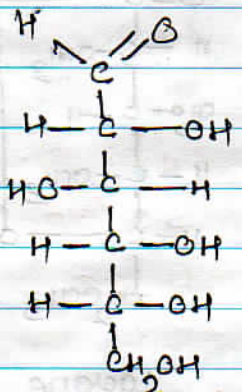
2,3,4-trimethoxyl glutaric acid

Obviously the two carboxylic carbon (C1,5) of the trimethoxy glutaric acid are the one's originally involved in ring formation. Hence there must have existed an oxide ring between C_1 & C_5. Tracing back the reaction sequence it stands proved that D-glucose has a six-membered ring. The presence of a 6-membered ring in D-glucose has also been confirmed by X-ray analysis

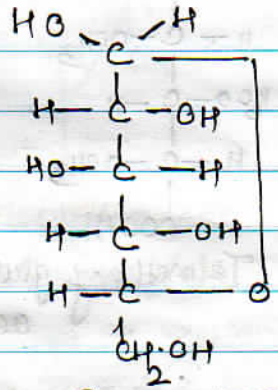
Mechanism of Mutarotation :- The French chemist Tarnet established the existence of two crystalline forms of glucose, i.e α-glucose & β-glucose. α-glucose had specific rotation +112°, while β-glucose +19°. The optical rotation of each of these forms changed gradually with time till finally constant value of +53° was reached. To explain this phenomenon of mutarotation, it was visualised that the α & β-glucose were in reality the cyclic hemiacetal form of glucose which were interconvertible via the open chain forms. The constant value of +19° represented the state of equilibrium between α-D-glucose & β-D-glucose



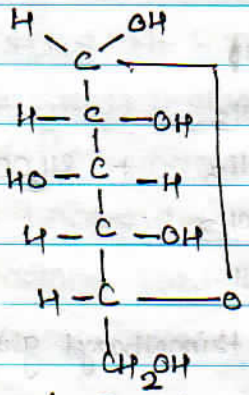
α-D-glucose



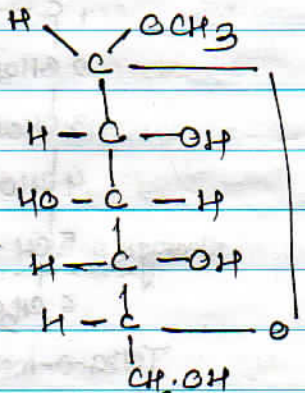
open chain glucose.



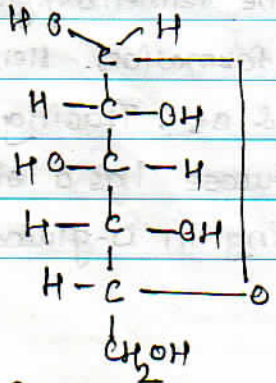
β-D-glucose.

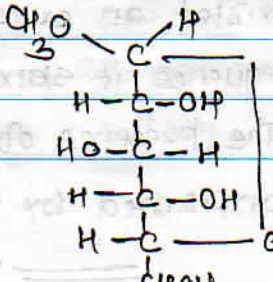


α-D-glucose



Ethyl α-D-glucose
(No aldehyde reaction)





Methyl β-D-glucose
(No aldehyde

The concentration of α-D-glucose & β-D-glucose & the open chain glucose at equilibrium are 36%, & 64% & less than 0.01%, respectively. This explains why D-glucose can react both as an aldehyde & a cyclic hemiacetal in which -CHO is absent.

Disaccharides

Introduction :- Disaccharides are type of oligosaccharides which on hydrolysis yields two similar or different monosaccharides molecules. In general disaccharides are sweet tasting, crystalline, water soluble substances, easily hydrolysed by enzymes & dil-mineral acids to two monosaccharide units.

Naturally occuring disaccharides are e.g. Maltose, sucrose & lactose, these on hydrolysis yields two molecules of glucose, glucose & fructose, glucose & galactose respectively.

e.g.

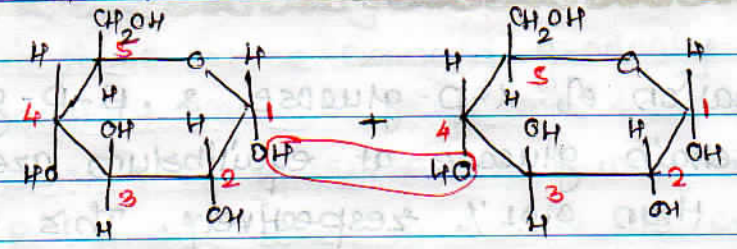
a) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Maltose — glucose — glucose.

b) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Sucrose — glucose — Fructose.

c) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Lactose — glucose — galactose.

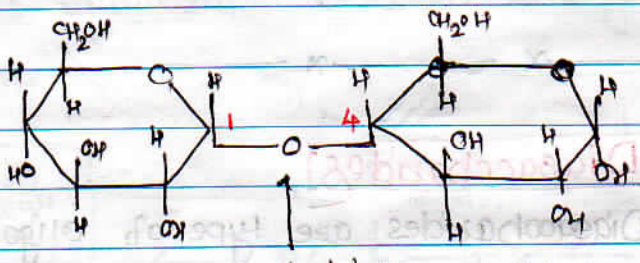
@ Maltose

It is obtained from starch. It is composed of two α-D-glucose units joined by an α-glycosidic linkage between C_1 of one unit & C-4 of the other unit as follows,



α-D-glucose + α-D-glucose

$\downarrow -H_2O$



α-Linkage Maltose structure.

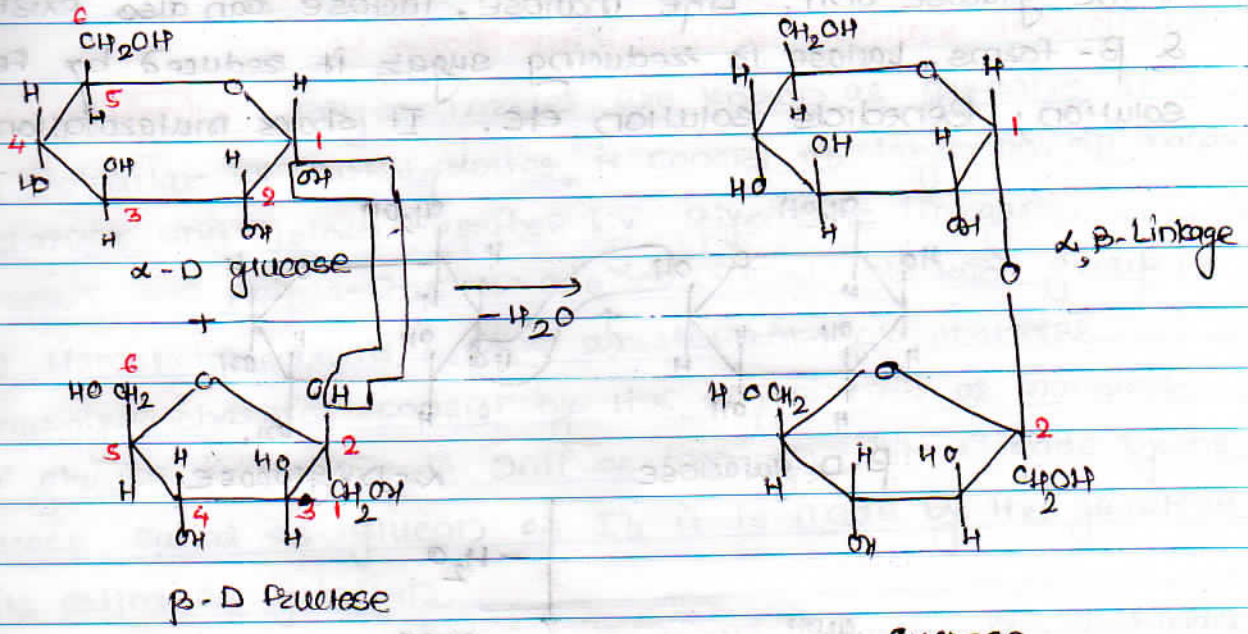
$C_1 - C_4^{O_2}$ α-glycosidic linkage.

Molecular formula of Maltose is $C_{12}H_{22}O_{11}$ it is also known as malt sugar. It is soluble in water, maltose is white crystalline solids. Maltose is reducing sugar it reduces by the Fehling's solution, Benedicts & Tollen's solutions.

Maltose exist in two anomeric forms i.e α-(+) maltose $[\alpha]_D^{25} = +168^\circ$ & β-(+) maltose $[\alpha]_D^{25} = +112^\circ$ maltose undergoes mutarotation. it oxidized by bromine water, & yields a monocarboxylic acid, maltonic acid.

(b) Sucrose (cane sugar)

Sucrose is ordinary table sugar. It is obtained from cane sugar. Sucrose is composed of α-D glucose unit & β-D fructose unit. These units are joined by α, β-glycosidic linkage between C-1 of the glucose unit & C-2 of the fructose unit as follows,

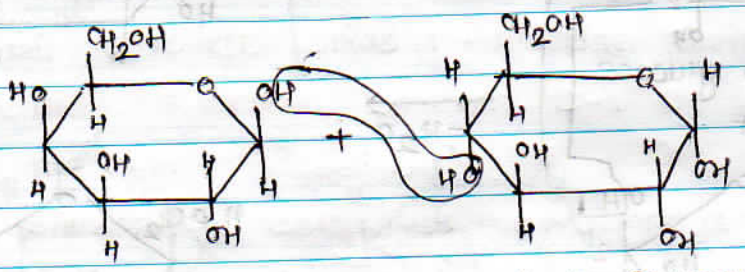


It is the most widely occuring disaccharide & is found in all photosynthetic plants. Molecular formula of sucrose is $C_{12}H_{22}O_{11}$. Hydrolysis by (acid) or enzyme (invertase) sucrose yields 1 mole of D-glucose & 1 mole of D-fructose.

Sucrose is non-reducing sugar. It does not reduce by Benedicts, Febling & Tollen's reagents. Sucrose does not undergoes mutarotation.

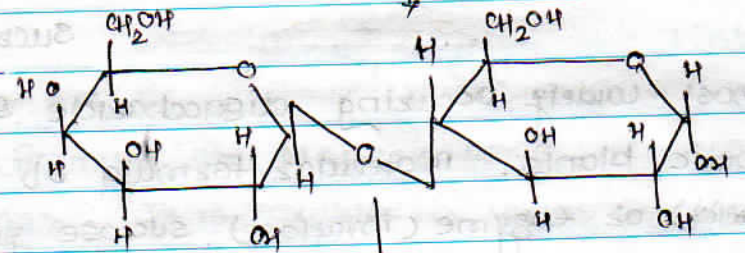
© Lactose (milk sugar)

It is found in the milk of all animals. cow's milk contains 4-5% & human milk contains 6-7% Lactose. Lactose is composed of β-D-galactose unit & α-D-glucose unit joined by β-D-glycosidic linkage between C-1 of the galactose & C-4 of the glucose unit. Like maltose, lactose can also exist in α- & β- forms. Lactose is reducing sugar, it reduced by Febling solution, Benedicts solution etc. It shows mutarotations.



β-D-galactose + α-D-glucose

$-H_2O$



β-Linkage

Structure of Lactose

Polysaccharides (starch & cellulose)

without involving structure determination.

Introduction:- Polysaccharides are known as glycans. It is high molecular wt carbohydrates, it consist of large no. of monosaccharides unit joined together by glycosidic linkages.

Polysaccharides are classified into two group i.e 1) Homopolysaccharides & 2) Heteropolysaccharides. Homopolysaccharides consist by the single unit or monomer i.e glucose or galactose unit or monomer. If it made by the glucose called as glucan or If it is made by the galactose units called as galactan.

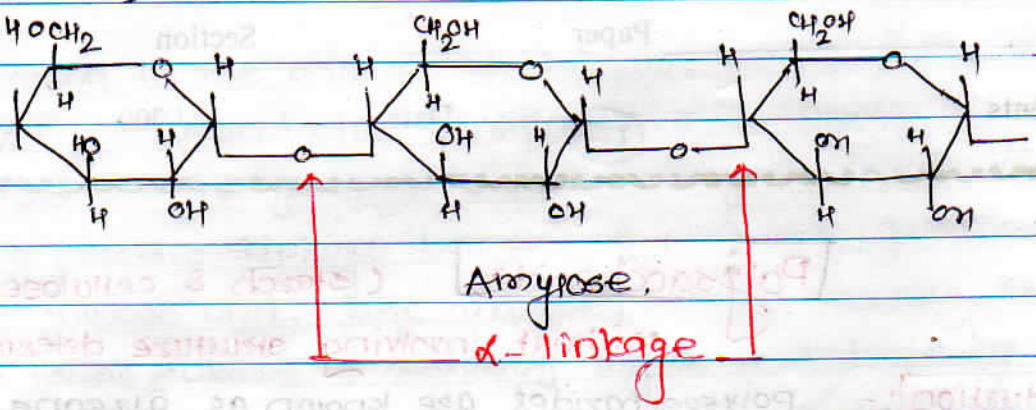
The most important naturally occuring polysaccharides are starch & cellulose.

(a) Starch

Starch is the main contributor of carbohydrates in our diet. It exists exclusively in plants, stored in the seeds, roots & fibres as food reserve. The chief sources of starch are cereals potatoes, corn & rice.

Starch is actually a mixture of two structurally differents polysaccharides. Amylose (20%) & Amylopectin (80%) when starch is heated with hot water it can be separated into these components. The part that is soluble in water is amylose & remaining fraction is amylopectin. Both amylose & amylopectin are composed of D-glucose units. The amylose molecule is made up of D-glucose unit jointed by α- glycosidic linkages between C-1 of one glucose unit & C-4 of next glucose unit

as follows,



Amylopectin has a branched-chain structure. It is composed of chains of 25 to 30 units D-glucose units joined together by α-glycosidic linkages between C-1 of one glucose unit & C-4 of the next glucose unit.

Starch is colourless amorphous powder having no definite melting point. It gives colloidal soln in water.

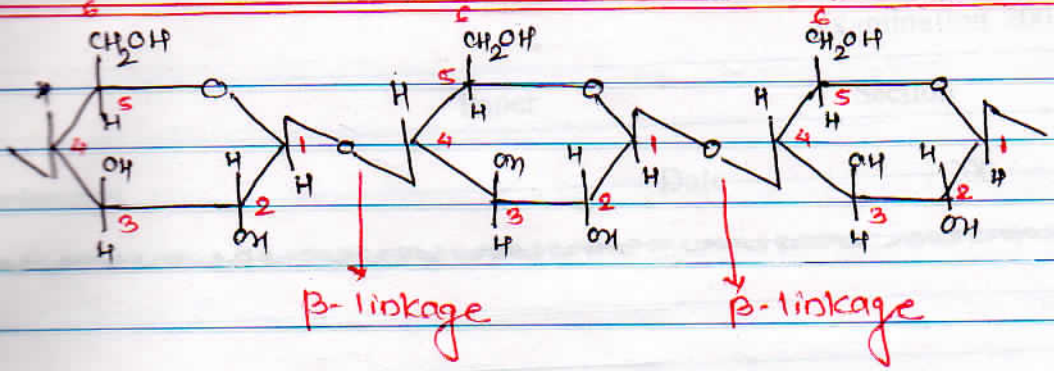
(b) Cellulose

Cellulose is the main structural material of trees & other plants. Wood is 50% cellulose, while cotton wool is almost pure cellulose. other source of cellulose is straw, corncobs, bagasse & similar agricultural wastes.

Cellulose ~~are~~ is a colourless solids, insoluble in water & organic solvents but readily soluble in ammonical cupric hydroxide solution, (schweizer reagent). Cellulose does not having melting point. It decompose on strong heating.

cellulose is a straight-chain polysaccharide comp-ased of D-glucose units. These units are joined together by β-glycosidic linkages between C-1 of one glucose unit & C-4 of the next glucose unit. The no. of D-glucose unit in cellulose ranges from 300 - 2500.

Structure of Cellulose.



Cellulose structure.

End