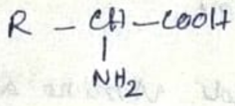
Amino Acids, carbohydrates, fats and oils

Amino acids are the organic compounds which contains both amino ($-NH_2$) and carbonyl group ($-COOH$) groups. Among all amino acids α-amino acids are special, ~~cont~~ because these are the main constituents of cell.

structure of α-amino acid.



$$R-\underset{\underset{NH_2}{|}}{CH}-COOH$$

α-amino acid.

→ α-amino acid contains an amino group and a carboxyl group attach to the same carbon atom.

→ There are 20 α-amino acids obtained from the hydrolysis of proteins.

classification of Amino Acids :→

Amino acids are classified as
→ acidic
— Basic &
→ Neutral, on the basis of the number of $-NH_2$ and $-COOH$ groups in the molecule.

(i) **Acidic amino acids**:→ If an amino acid contains an additional carboxylic group such amino acids are called acidic amino acid.

(ii) **Basic Amino acid**:→ If an amino acid contains additional ($-NH_2$) group in the molecule such amino acid are called Basic amino acid.

(iii) **Neutral amino acid**:→ If an amino acid contains only one ($-NH_2$) group in the molecule which is attached to an α-carbon atom with respect to the $-COOH$ group.

Amino acids also can be classified into two categories — ① Essential amino acid.

② Non-essential amino acids.

① Essential amino acids:- Amino acids which cannot be synthesized by the body must be supplied through diet for growth. For eg: Leucine, Valine, Arginine.

② Non-essential amino acid: Amino acids which are synthesised within our body are called non-essential amino acids. For eg: Glycine, Alanine, Proline.

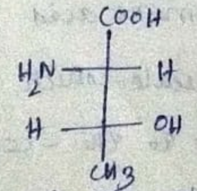
Optical Activity of Amino Acids:

The optical isomer which rotates the plane of ~~polarization~~ polarized light to right i.e. clockwise known as dextrorotatory indicated by (+) sign.

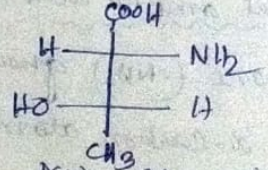
While the isomer that rotates the light to the left i.e. anticlockwise, is termed as laevorotatory indicated by (-) sign.

Most of the natural amino acids have L-configurati

The symbol D and L are used for the configuratio of the α-carbon atom. When two asymmetric centr are present in an α-amino acid, then D, and L refer t the α-carbon atom and naturally occurring acids is known as L-amino acid. eg: L(-)-threonine, and D-(+)-threonine.



L(-)- threonine

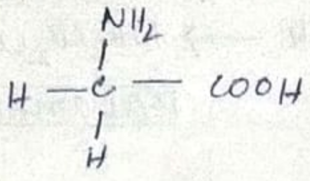


D(+)- threonine.

Glycine:

Glycine is an amino acid which contains only two carbon atoms and doesnot passess any ~~asymm~~ assymetric carbon atom.

Structure

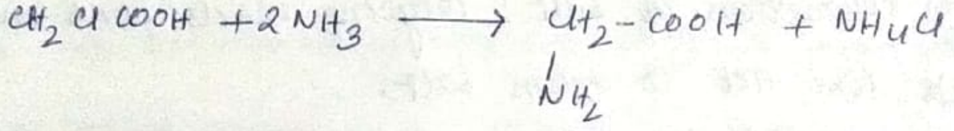


$$H-\overset{NH_2}{\underset{H}{C}}-COOH$$

Gly, G

Syntheses of Glycine

① When α-chloro or α-bromo ethanoic acid is treated with concentrated ammonia sol^n, glycine is produced.

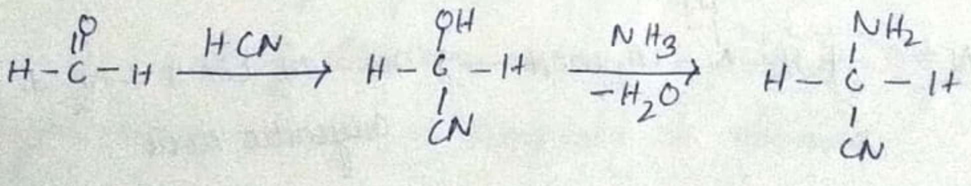


$$CH_2ClCOOH + 2NH_3 \longrightarrow \underset{NH_2}{CH_2}-COOH + NH_4Cl$$

$\boxed{\text{Glycine}}$

(II) Strecker synthesis:

When methanal is treated with a mixture of HCN and NH_3, α-amino nitrile is produced, On acid hydrolysis of α-amin nitrile glycine can be produced.



$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HCN} H-\overset{OH}{\underset{CN}{C}}-H \xrightarrow[-H_2O]{NH_3} H-\overset{NH_2}{\underset{CN}{C}}-H$$

α-Amino nitrile.

$$\underset{NH_2}{CH_2}-CN \xrightarrow{H_2O/H^-} \underset{NH_2}{CH_2}COOH$$

$\boxed{\text{α-aminonitril}}$ $\boxed{\text{Glycine}}$

Some reactions of Glycine

Ⓐ Reactions of carbonyl group:

ⓐ Formation of salt:

Glycine reacts with alkali solution to form

$$NH_2CH_2COOH + NaOH \longrightarrow NH_2CH_2COONa + H_2O$$

$\boxed{\text{Sod aminoethanoate}}$

ⓑ Reaction with $LiAlH_4$:

Glycine is reduced to 2-aminoethanol by $LiAlH_4$

$$NH_2CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[LiAlH_4]{[H]} NH_2CH_2CH_2OH$$

$\boxed{\text{2-Aminoethanol}}$.

Ⓑ Reactions of amine groups

ⓒ Formation of salt: Glycine reacts with mineral acid like HCl to form salt.

$$NH_2CH_2COOH + HCl \longrightarrow \overset{-}{Cl}\,\overset{+}{N}H_3CH_2COOH$$

Glycine hydrogen chloride.

ⓓ Reaction with nitrous acid ($NaNO_2 + HCl$)

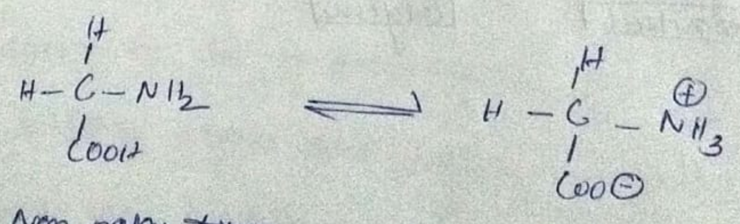
Glycine reacts with nitrous acid to form glycolli

acid.

$$HO-N=O + H-\overset{H}{N}-CH_2COOH \longrightarrow HO-CH_2COOH + N_2 + H_2O$$

Glycollic acid

Q. Write down the structures of both non-polar and dipolar form of glycine.



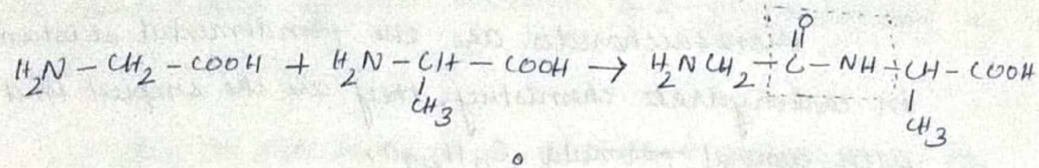
$$H-\overset{H}{\underset{COOH}{C}}-NH_2 \rightleftharpoons H-\overset{H}{\underset{COO^{\ominus}}{C}}-\overset{\oplus}{N}H_3$$

Non-polar form

Dipolar or Zwitterionic form.

Peptides:

Amino acids undergo intermolecular condensation reaction, where $-NH_2$ group of one amino acid condenses with the $-COOH$ group of the other molecule by eliminating a ~~mole~~ water molecule.



$$H_2N-CH_2-COOH + H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH \rightarrow H_2NCH_2-\overset{O}{\overset{\|}{C}}-NH-\underset{CH_3}{\underset{|}{CH}}-COOH$$

The resulting compound $[-\overset{O}{\overset{\|}{C}}-NH-]$ linkage is called peptide linkage.

→ If the resulting molecule is form from the condensation of two amino acids, ~~are~~ called dipeptide.

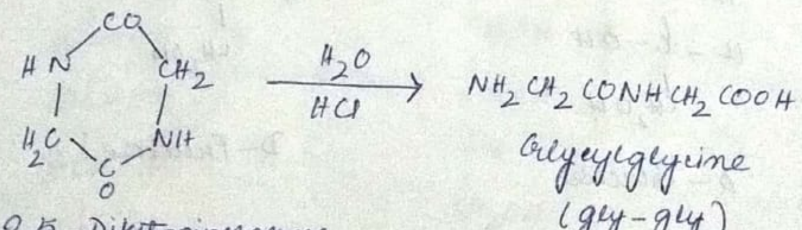
→ If the resulting molecule is form from the condensation of three amino acids, called tripeptide.

→ When a large number of amino acids are combine the resulting compound is called polypeptide.

Preparation of Dipeptides:

ⓐ By partial hydrolysis of diketopiperazine:

When diketopiperazine is partially hydrolysed with hydrochloric acid, a dipeptide is formed.



2,5-Diketopiperazine.

Glycylglycine
(gly-gly).

ⓑ By Schwyzer method:

When amino ester with react with chloroacetonitrile, dipeptide molecule results.

$$NH_2CHRCOONa + CH_2ClCN \longrightarrow NaCl + NH_2CHRCOOCH_2CN$$

$$\downarrow NH_2CHR'COOH$$

$$NH_2CHRCONHCHR'COOH$$

$\boxed{\text{Dipeptide}}$.

Monosaccharides :

Carbohydrates are palydroxyaldehyde, Carbohydrates are naturaly occuring substances known as saccharides because of the sweet taste of the simpler members of the carbohydrate.

Monosaccharides are the fundemental substances in carbohydrate chemistry, they are the simplest unit with general formula $C_nH_{2n}O$,

Monosaccharides are divided into two types –

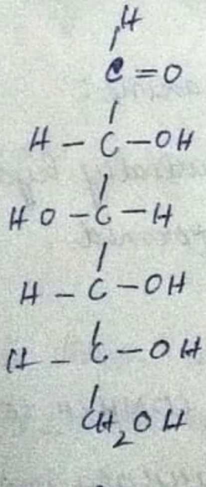
① Aldoses.

② Ketoses.

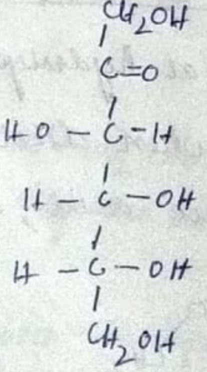
Two important monosaccharides are glucose which is an aldohexase and fructose which is a ketohexose.

Glucose is the most common monosaccharide found in sweet fruit, grapes and honey.

Fructose is found in the juices of ripe fruits and in honey.



D – Glucose



D– Fructose.

Mutarotation and Enomers:

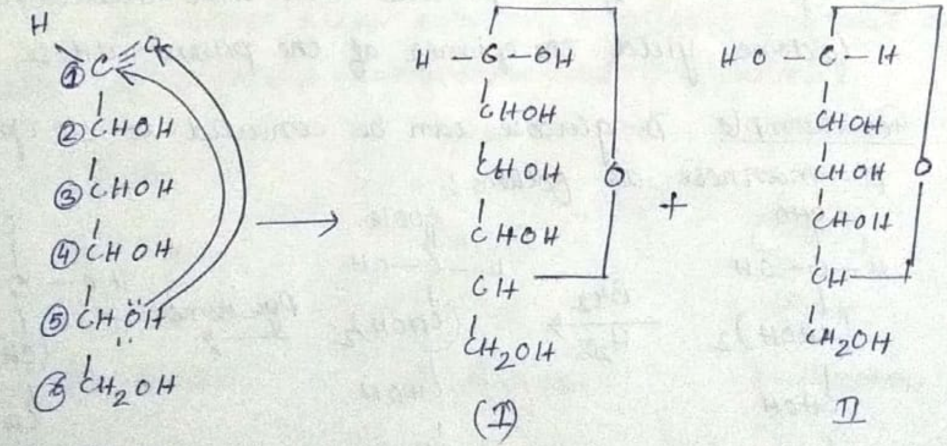
D-glucose can be found in two isolated forms α-D-glucose and β-D-glucose.

α-D-glucose is obtained by the crystallization from a concentrated aqueous solution of D-glucose, it has a specific rotation of +112°.

On the otherhand β-D-glucose is obtained by the crystallization from hot glacial acetic acid solution of D-glucose, it has a specific rotation of +19°.

When either α-D-glucose or β-D-glucose is dissolved in water, the specific rotation of α-form falls and that of β-form rises to a constant value 53°. This change in optical rotation of a solution of D-glucose is called mutarotation.

D-glucose form a cyclic hemiacetal between the -CHO and the -OH group, on the C-5 carbon atom. In this process C-1 carbon becomes assymetric resulting two isomers I and II.



D-glucose α-D-Glucose β-D-glucose.

The isomer I and II are called enomers and the assymetric carbon of these isomers is known as enomeric carbon. The enomer I with -OH to the right is designated as α-D-Glucose and others with -OH to the to the left is designated as β-D-glucose. the α- and β-forms of D-glucose are not enantiomers as they are not mirror images, but they are disterisomers.

Epimerisation and Epimers

When a molecule contains two or more assymetric carbon atoms and the configuration of only one of these is inverted by some reaction, this process is called epimerisation, Epimerisation produces an epimer of the original configuration.

~~An Aldose with Br_2 water to produce~~

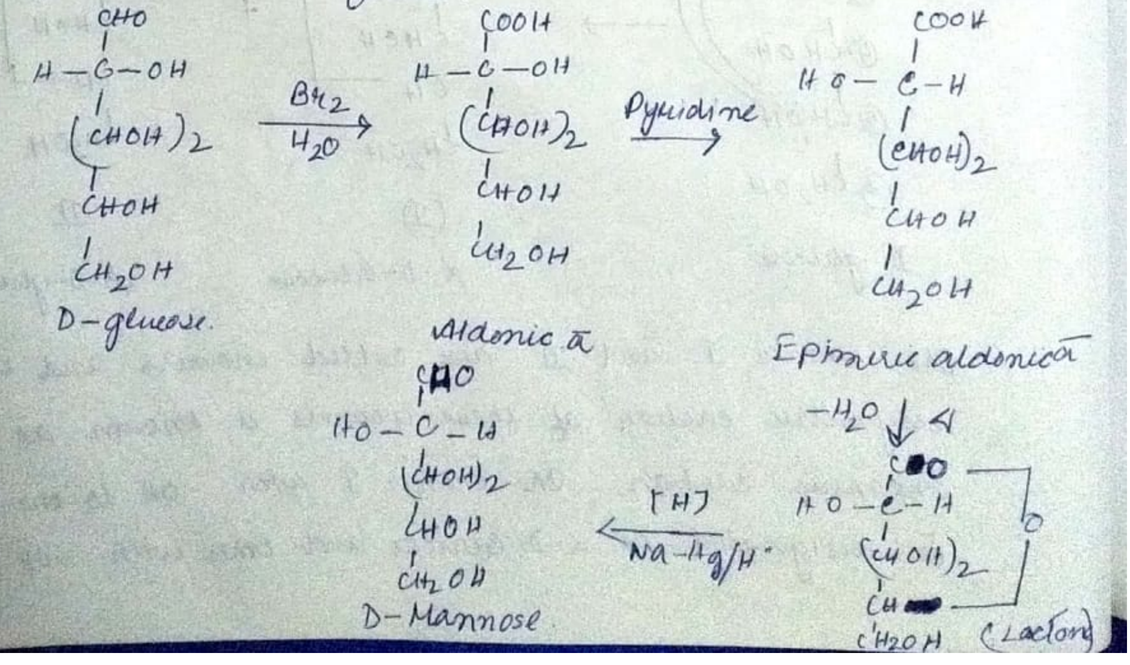
Aldose having two or more assymetric carbon atoms converted to its epimer with opposite configuration at C-2 carbon; such conversion can be done by involving the following steps →

ⓐ Oxidation of aldose with Br_2 water produce aldonic ā acid.

ⓑ Heating the aldonic ā with pyridine, C_6H_5N produce an equilibrium mixture of the original acid and its epimeric form.

ⓒ Seperation of the epimeric acid and reduction of its lactone yield the epimer of the parent aldose.

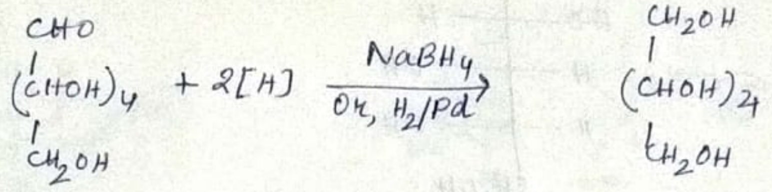
For example: D-glucose can be converted to its epimer D-mannose as follows:



Reactions of Glucose

(i) Reduction reaction:

D- Glucose on reduction with sodium borohydride NaBH$_4$, or catalytic reduction (H_2/Pd), produces corresponding alcohol D-glucitol (sorbitol).

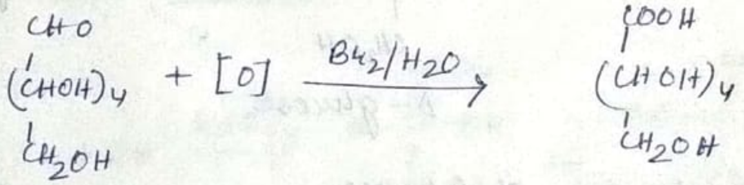


$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} + 2[H] \xrightarrow[\text{Or, } H_2/Pd]{NaBH_4} \begin{matrix} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$$

D-Glucose D- Glucitol (Sorbitol).

(ii) Oxidation reaction:

When D-Glucose is treated with weak oxidising agent such as Br_2 water, –CHO group of D-glucose is oxidized to –COOH group to form gluconic acid.

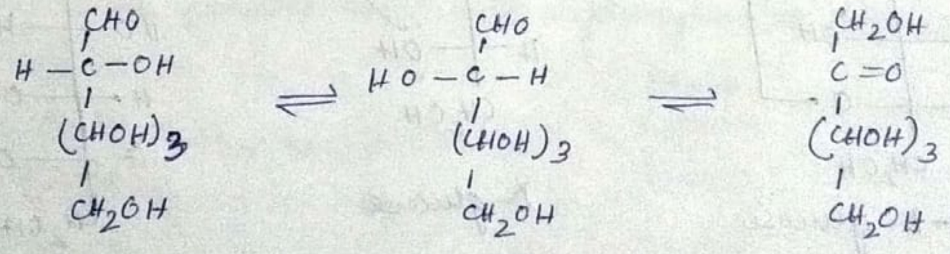


$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} + [O] \xrightarrow{Br_2/H_2O} \begin{matrix} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix}$$

D- Glucose Gluconic acid.

(iii) Action of alkali:

In dilute alkali solution D-glucose produces a mixture of D-glucose, D-mannose and D-fructose.



$$\begin{matrix} CHO \\ | \\ H-C-OH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} \rightleftharpoons \begin{matrix} CHO \\ | \\ HO-C-H \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} \rightleftharpoons \begin{matrix} CH_2OH \\ | \\ C=O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix}$$

D-Glucose D-Mannose D-Fructose.

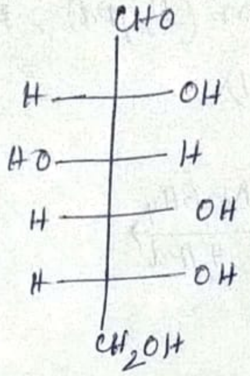
(iv) Fermentation:

Glucose in presence of enzyme zymase present in yeast, undergoes alcoholic fermentation to produce ethanol.

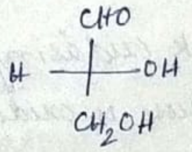
$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

Structure of Glucose

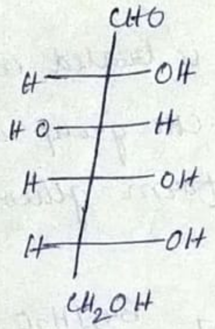
The exact spatial arrangement, i.e. the configura of glucose is determined by Emil Fisher



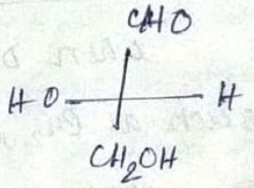
Since the structure of glucose corresponds to D-glyceraldehyde, glucose is called D-glucose.



D-glyceraldehyde



D-glucose



L-glyceraldehyde.

Cyclic structure of Glucose

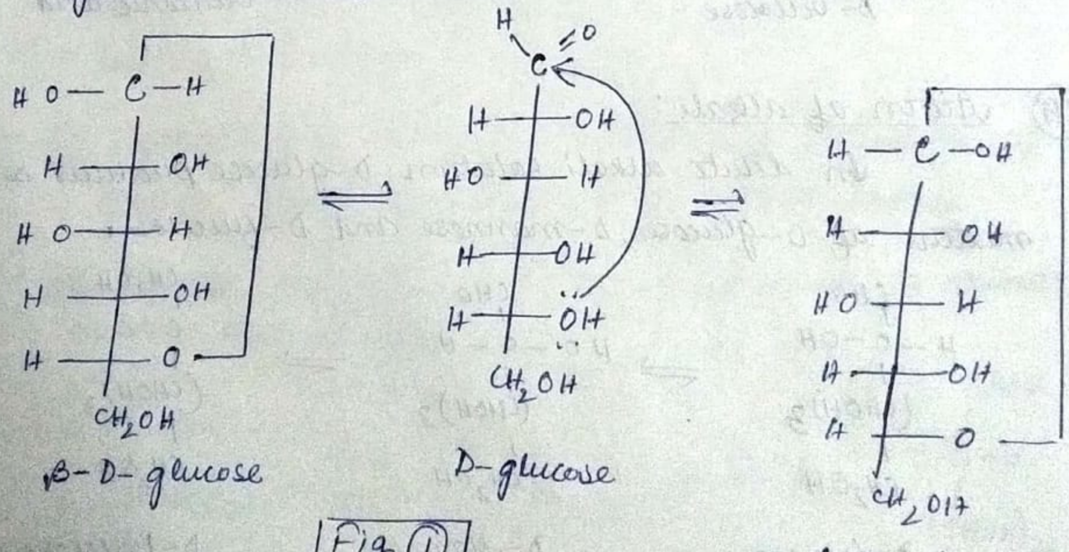
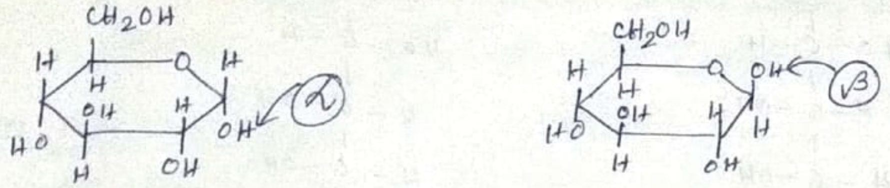


Fig ①

The α- and β- forms of glucose are not enantiomers since they are not mirror images but are diastereomers.

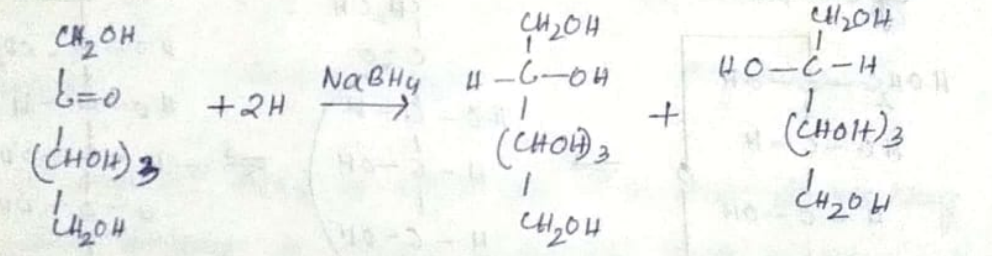
The Fisher projection formula in fig① donot give the exact shape of the hemiacetal ring of glucose. The cyclic structure of glucose also called pyranose structure, because of its similiarty with pyran, and is better represented by the Haworth projection formula.



Fig② Orientation of –OH group in (α) and (β).

Reactions of Fructose

① **Reduction reaction**: Fructose on reduction with $NaBH_4$, produces two epimeric hexahydroxy alcohols as C-2 becomes assymetric after reduction.

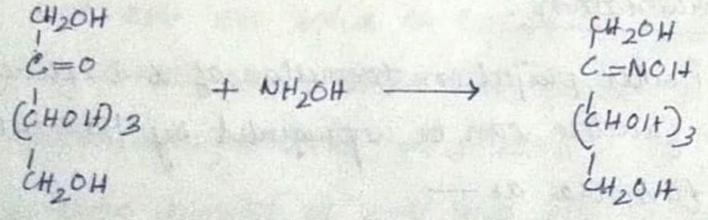


$$\begin{matrix} CH_2OH \\ | \\ C{=}O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} + 2H \xrightarrow{NaBH_4} \begin{matrix} CH_2OH \\ | \\ H-C-OH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} + \begin{matrix} CH_2OH \\ | \\ HO-C-H \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix}$$

D-Fructose D-Glucitol D-Mannitol

(ii) **Reaction with hydroxylamine**:

When fructose react with hydroxylamine forms oxime.



$$\begin{matrix} CH_2OH \\ | \\ C{=}O \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix} + NH_2OH \longrightarrow \begin{matrix} CH_2OH \\ C{=}NOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{matrix}$$

D-Fructose Fructose oxime.

(iii) **Fermentation reaction**:

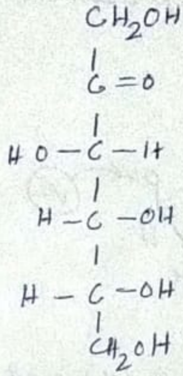
D-fructose undergoes alcoholic fermentation in the presence of zymase to form ethanol.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

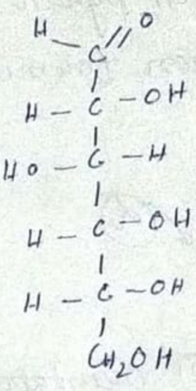
Fructose Ethanol

Structure of Fructose

The open chain structure of fructose is comparable to the open-chain structure of glucose.



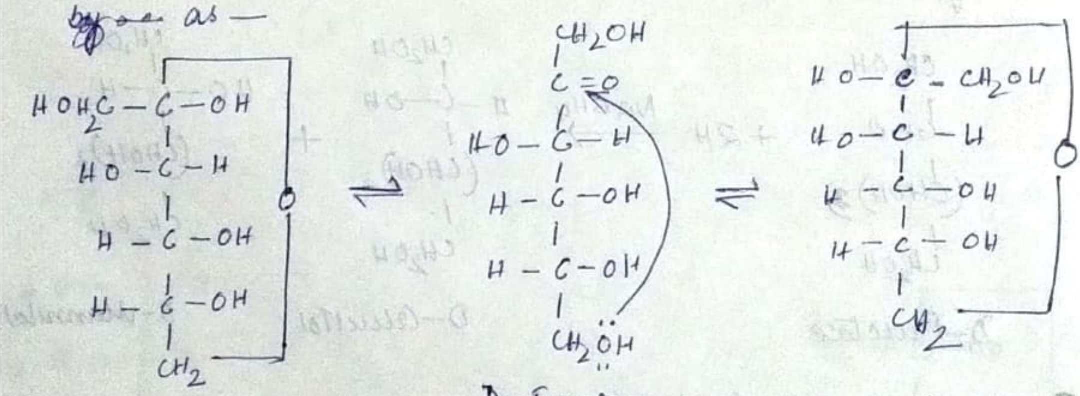
D-fructose



D-Glucose

Cyclic structure of fructose

D-Fructose exhibits mutarotation similar to D-glucose. Due to mutarotation α- and β-form of D-Fructose are in equilibrium via open chain, which ~~max~~ is represented ~~by a~~ as —



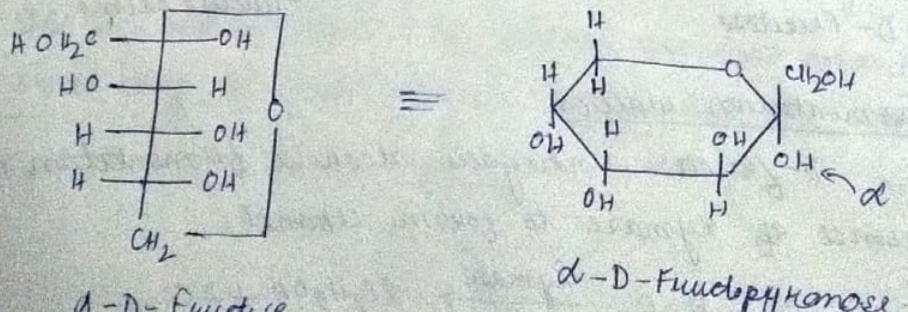
α-D-Fructose

D-Fructose (open-chain)

β-D-Fructose

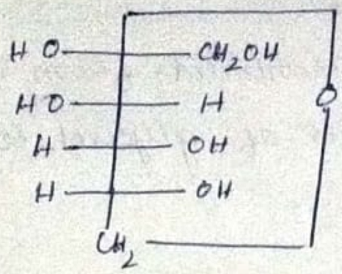
Haworth representation:

The fischer projection formula of α-D-fructose and β-D-fructose can be represented by Haworth projection formula as —

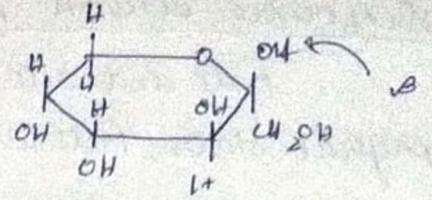


α-D-Fructose (Fisher)

α-D-Fructopyranose (Haworth).



β-D-Fructose
(Fischer)

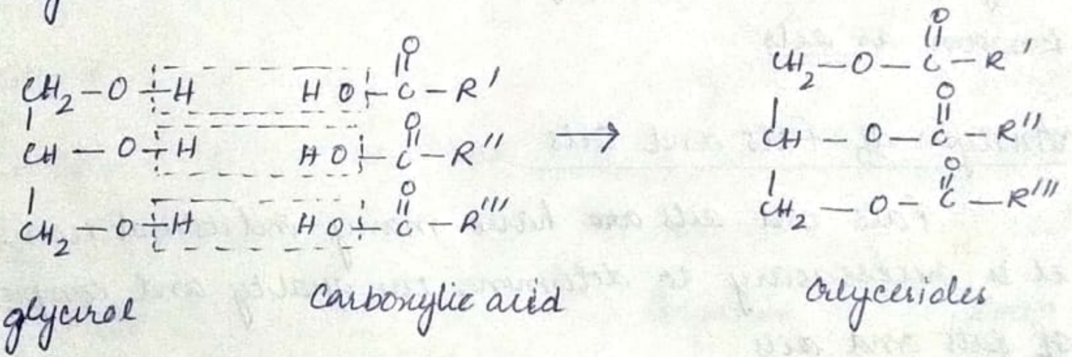


β-D-Fructopyranose.
(Haworth).

Fats, oils and Soaps :

Fats and oils are the most important natural esters, belong to naturally occurring group of compound called lipid.

Fats and oils are triesters of glycerol with long chain carbonylic acids —



R′, R″ and R‴ may be same or different. If ~~so~~ they are same known as simple glycerides, and if different they are known as mixed glycerides.

Physical properties of fats and oils

(i) Fats and oils are solid or liquid are greasy in nature.

(ii) They are insoluble in water but soluble in organic solvent like chloroform, benzene, ether etc.

(iii) The specific gravity of fats and oils is lower than that of water, so when they mixed they floats over water.

Difference between fats and oils

Fats and oils can be differentiated from their physical states, fats are solid esters of glycerol whereas oils are liquid esters of glycerol.

They are natural triesters of glycerol known as glycerides. Long chain fatty acids are involved in the formation of glycerides.

If the proportion of saturated fatty acids is more, the glyceride exists in solid state, known as fats.

On the otherhand high proportion of unsaturated fatty acids make the glycerides exists in liquid state, known as oils.

Analysis of Fats and Oils

Fats and oils ~~are~~ have many industrial uses, so it is necessasary to determine the quality and composition of fats and oils.

There are many useful method are developed to analyse a sample of fats and oils, some are →

(I) saponification number:

$$\text{saponification value} = \frac{(b-a) \times 0.02805 \times 1000}{\text{Massing of the sample}}$$

a, b are titre value of test and blank solutions.

(II) Iodine number

$$\text{Iodine number} = \frac{(b-a) \times 0.0127 \times 100 \times N}{\text{Mass of sampling} \times 0.1}$$

a → volume of sol^n required to test sol^n.

b → volume of the sol^n required to blank sol^n

N → Normalety.

(III) Reichert – Meissl (RM) number

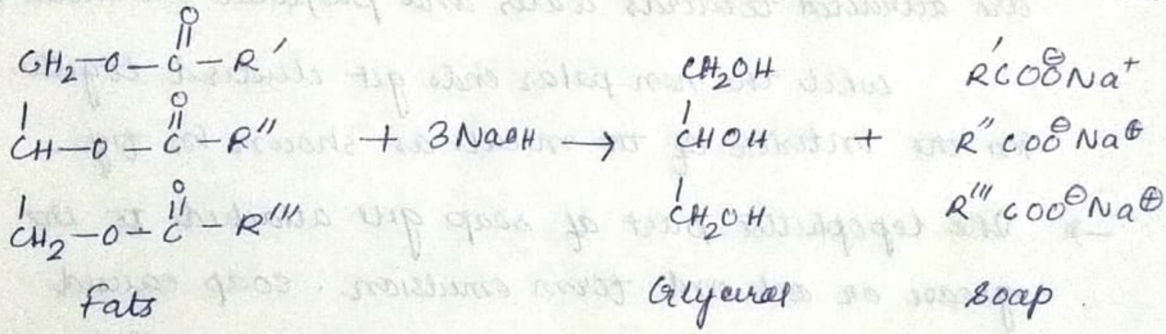
(IV) Acid value:

$$\text{Acid value} = \frac{a \times 0.0056 \times 100}{\text{Mass of sampleing} \times 0.1}$$

$a \rightarrow$ Titre value.

Soaps:

Soaps are sodium or potassium salts of long chain fatty acids. Potassium soaps are softer and more soluble in water in comparison to sodium soap. Soaps are ~~produced~~ the products of hydrolysis of fats or oils with 'NaOH'. (saponification).



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R'' \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R''' \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R'COO^{\ominus}Na^{+} \\ R''COO^{\ominus}Na^{\oplus} \\ R'''COO^{\ominus}Na^{\oplus} \end{array}$$

→ Soap with higher proportion of saturated acids like palmitic acid or stearic acid are hard, soap with higher proportion of unsatured acids like oleic acid produced soft.

→ Soap are soluble in water and form lather; soap does not form lather with hard water because Ca^{2+} and Mg^{2+} ions are present in hard water form insoluble calcium and magnesium salts.

→ Soap are surface active agents. They are used to form lather with water for cleaning purpase, shaving purpose etc.

cleasing action of soap

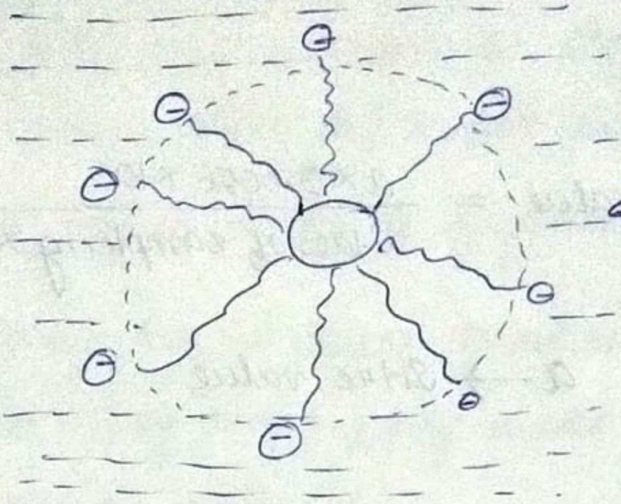


Fig: Soap micelles

→ Soap has a hydrophillic polar group $(-COO^{-})$ and a hydrophobic or lopophillic non-polar $(-R)$ group.

→ When added to water it forms micelles, polar ends are attracted towards water and projected outwards, while the non-polar ends get clustered together in the interior of the micells as shown in fig.

→ The lopophillic part of soap gets attached to the grease or oil and form emulsion. Soap caused ~~emulsion~~ emulsification of dirt particles, which is further removed from fibre by washing with water.