Carbohydrates

↳ Carbohydrates are the most abundant class of compounds in the biological world, making up more than 50% of the dry weight of the Earth's biomass.

↳ Carbohydrates are important constituents of all living organisms and have a variety of different functions. For example, some are important structural components of cells and some act as recognition sites on cell surfaces. Others serve as a major source of metabolic energy.

↳ Carbohydrates are generally hydrates of carbon and the general formula for most of the carbohydrates is $C_x(H_2O)_y$.

↳ Carbohydrates are usually defined as poly-hydroxy aldehydes such as D-glucose and polyhydroxy ketones such as D-fructose or substances such as sucrose that can be hydrolyzed to yield polyhydroxy aldehydes or polyhydroxy ketones.

↳ The aldehyde and ketone groups in carbohydrates don't occure as free aldehyde

one keto groups but usually exist in the form of hemiacetal one hemiketal groups, respectively.

↳ In nature, carbohydrates are produced by green plants by a process called photosynthesis.

$$CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{h\delta} C_6(H_2O)_6 + 6O_2$$

$$C_6(H_2O)_6 + 6O_2 \xrightarrow{\text{metabolism}} 6CO_2 + 6H_2O + \text{energy}$$

Nomenclature —

↳ The name-ending of simple carbohydrates is 'ose'.

↳ Simple carbohydrates are also known as sugar one saccharides (Greek: sakcharon means sugar).

↳ A single polyhydroxy aldehyde unit is called an aldose and the similar unit of ketone is said to be a ketose.

↳ The number of C-atoms present in the main chain is indicated by prefixing tri, tetr, pent, hex etc. before the name-ending.

↳ Some examples of carbohydrates —

Sucrose for ordinary table sugar, glucose for the principal sugar in blood, fructose for a sugar in fruits and honey and

maltose for malt-sugar.

Classification —

↳ Carbohydrates are first classified as —

1) Sugars and 2) Polysaccharides.

1) Sugars —

↳ Sugars have sweet tastes and they are soluble in water. Eg:- D-glucose, D-fructose etc.

↳ Sugars are further classified as —

a) Monosaccharides,

b) Disaccharides and

c) Oligosaccharides.

a) Monosaccharides — Consist of a single polyhydroxy aldehyde or ketone unit which cannot be further hydrolyzed to a still smaller carbohydrate unit. It is the basic building unit of the most abundant polysaccharides. Eg:- D-glucose, a D- aldohexose.

These are also classified according to the number of carbon atoms and nature of carbonyl group present —

No. of C-atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose

⇒ Disaccharides — Hydrolysis of these carbohydrates give two monosaccharide units. eg:- Sucrose —

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

⇒ Oligosaccharides — carbohydrates that hydrolyze to yield three to ten monosaccharides units are called oligosaccharides. eg:- Raffinose —

$$C_{18}H_{32}O_{16} + 2H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6} + \underset{\text{(galactose)}}{C_6H_{12}O_6}$$

⇒ Polysaccharides —

↳ These are very big molecules with high molecular weight.

↳ They have general formula of $(C_6H_{10}O_5)_n$, where, $n = 300 - 1000$.

↳ These are usually non-crystalline substances insoluble in water and donot taste sweet.

↳ Polysaccharides give many monosaccharides on hydrolysis. For example — Starch, cellulose etc.

$$(C_6H_{10}O_5)_n \xrightarrow{n(H_2O)} n\,C_6H_{12}O_6$$

(Starch) (glucose)

↳ Alternatively sugars are further classified as —

i) Reducing sugars and

ii) Non-reducing sugars.

↳ i) Reducing sugars — The sugars which reduce Fehling solution (alkaline cupric tartrate solution) and Tollen's reagent (ammonical silver nitrate solution) are called reducing sugars. All the monosaccharides are reducing sugars. eg:- D-glucose, D-fructose, D-maltose, D-lactose etc.

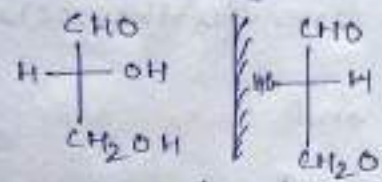
↳ ii) Non-reducing sugars — The sugars that cannot reduce Tollen's reagent and Fehling solution are called non-reducing sugars. eg:- Sucrose (Cane-sugar).

Configurations of monosaccharides (D and L- configuration)

↳ If the OH group attached to the bottom-most chirality center (the second from the bottom carbon) is on the right, the compound is described D-sugars. If the OH group is on the left, the compound is an L-sugar.

↳ Fischer Projection

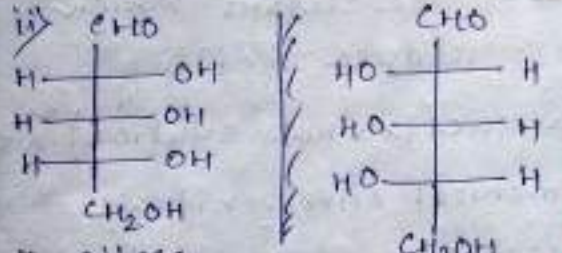
i)



D-glyceraldehyde L-glyceraldehyde

In Fischer Projection of monosaccharides, the carbonyl group is always placed on top (in case of aldoses) OH as close to the top as possible (in case of ketoses)

ii)

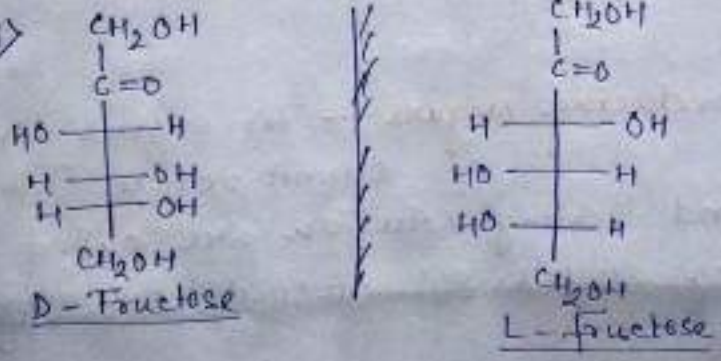


D-ribose L-ribose

Both D- and L-sugars are enantiomers → non-superimposable mirror-image

↳ Mirror image of a D-sugar is an L-sugar.

iii)



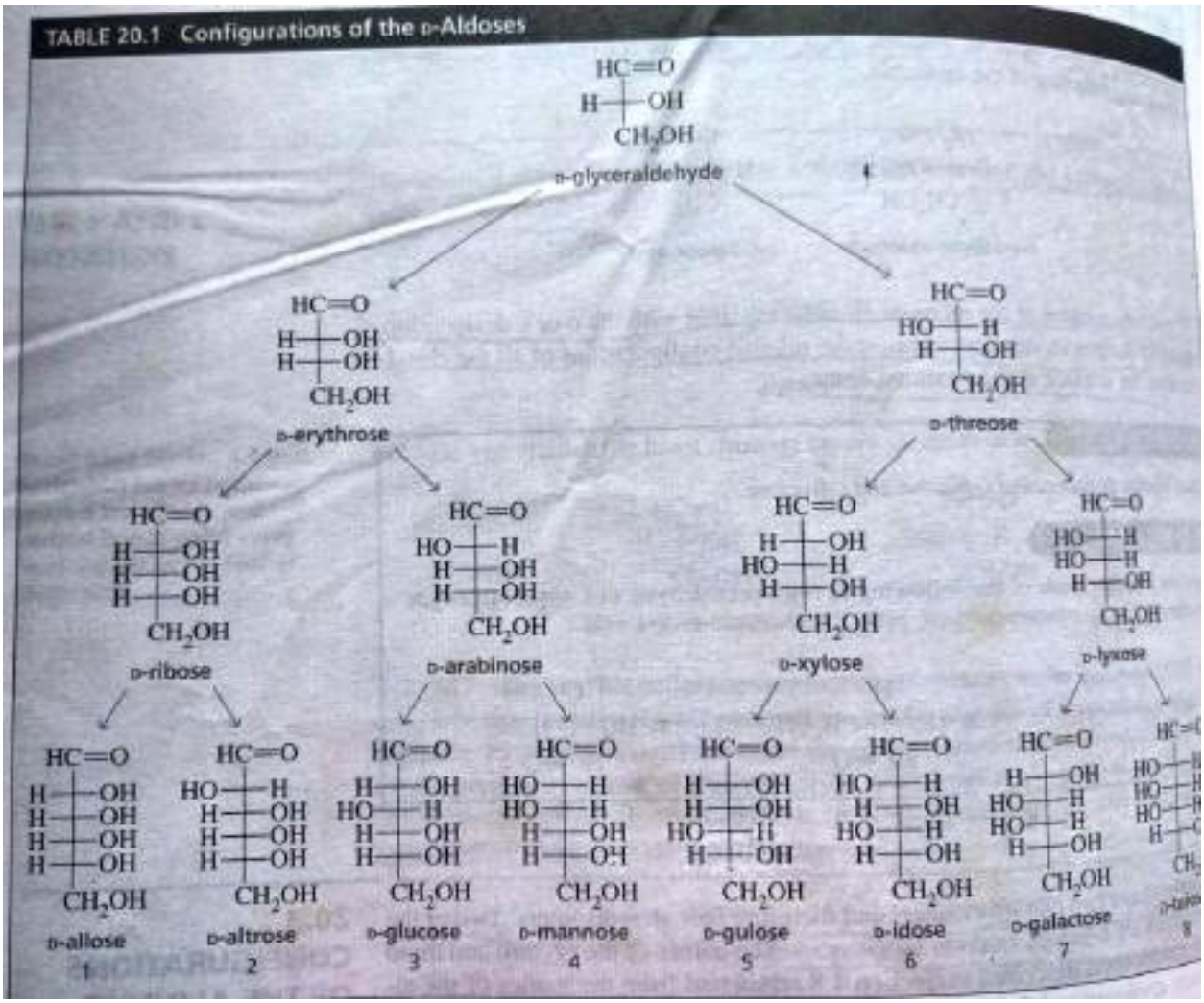
D-Fructose L-Fructose

Configurations of the aldoses —

↳ A monosaccharide can be polyhydroxy aldehyde or polyhydroxy ketone and polyhydroxy aldehydes are called aldoses.

↳ Depending on the number of carbons they contain are classified as trioses (3 carbons), tetroses (4 carbons), pentoses (5 carbons) etc.

↳



↳ A compound can have maximum of 2^n stereoisomers, where 'n' equals to the number of chirality centres.

↳ Note -

Isomers

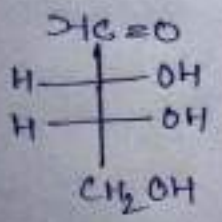
(Compounds that have the same molecular formula but are not identical are called isomers)

1) Constitutional isomers

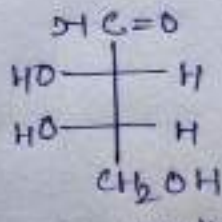
2) Stereoisomers

(Stereoisomers differ in the way their atoms are arranged in space)

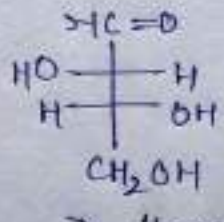
↳ Hence, aldotetroses have two chirality centres and therefore have $\Sigma^2 = 4$ $(n=2)$ Stereoisomers. Two of them are D-sugars and while the other two are L-sugars.



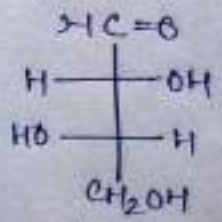
D-erythrose



L-erythrose



D-threose

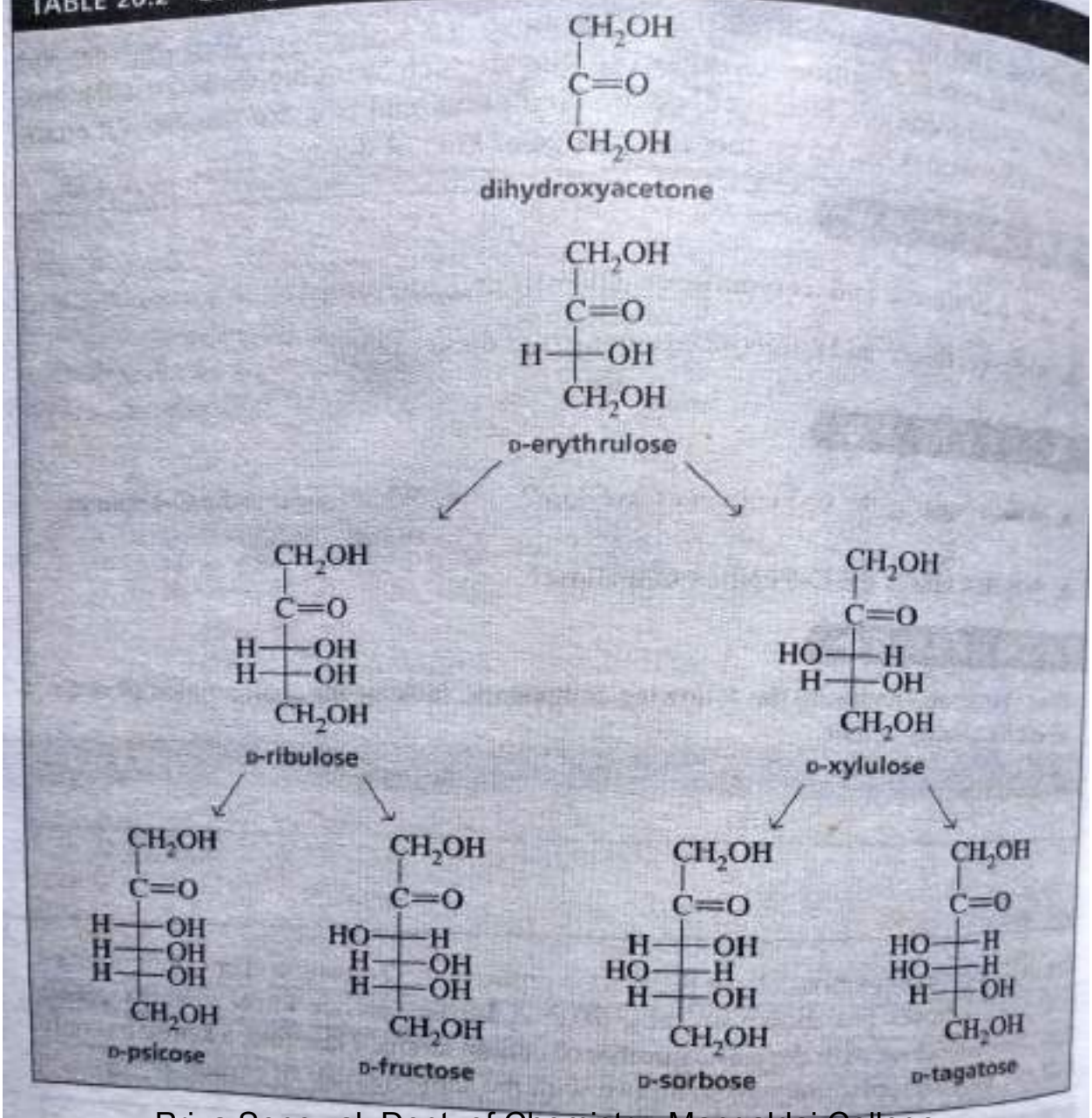


L-threose

Configurations of the ketoses —

- Polyhydroxy ketones are called ketoses.
- Naturally occuring ketoses have the ketone group in the 2- position.

TABLE 20.2 Configurations of the D-Ketoses

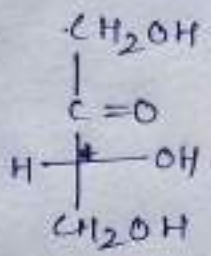


↳ A ketose has one fewer chirality center than does an aldose with the same number of carbon atoms. Therefore, a ketose has only half as many stereoisomers as an aldose with the same number of carbon atoms—

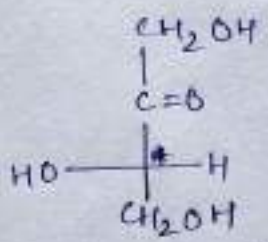
eg: An aldotetrose have two chirality center and therefore four isomers — (2^n, $n=2$, $2^2=4$)

D-erythrose, L-erythrose, D-threose and L-threose.

But an ketotetrose have one chirality centres and therefore two isomers — (2^n, $n=1$, $2^1=2$)



D-erythrulose



L-erythrulose

↳ All the naturally occuring monosaccharides have D-configuration.

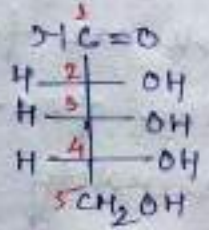
Epimers —

↳ Diastereomers that differ in configuration at only one chirality center are called epimers.

↳ (Diastereomers are stereoisomers but are not related to each other as mirror image one are not enantiomers)

↳ For example ——

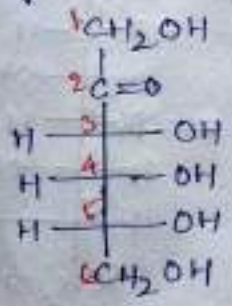
D-ribose and D-arabinose are C-2 epimers (they differ in configuration only at C-2)



D-ribose

D-arabinose

Similarly, D-psicose and D-fructose are C-3 epimers (they differ in configuration only at C-3).



D-psicose

D-fructose

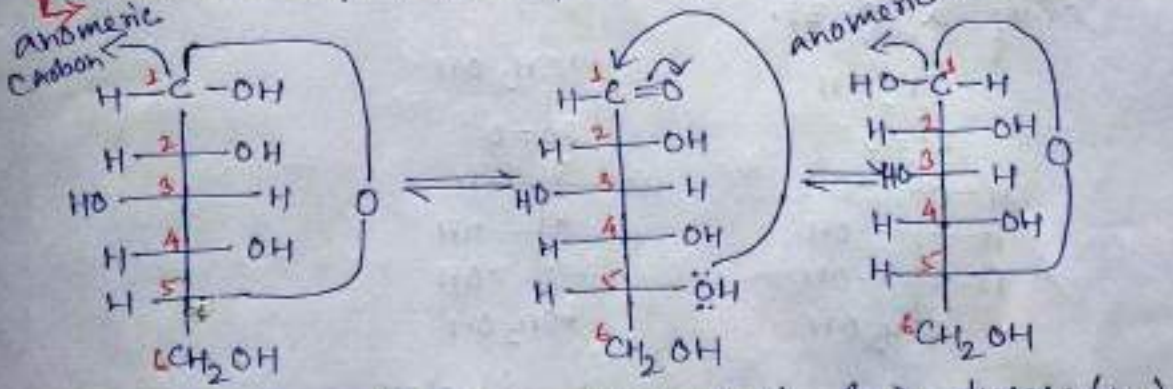
Open-chain and cyclic structure of Glucose ——

↳ D glucose exists in three different forms. There is an open-chain form and two

cyclic forms (α-D-glucose and β-D-glucose).

↳ D-glucose has an aldehyde group and several alcohol groups. The alcohol group bonded to C-5 of D-glucose reacts intra-molecularly with the aldehyde group, forming a six membered ring hemiacetal.

↳ The two different hemiacetals are formed because the carbonyl carbon of the open-chain sugar becomes a new chirality center in the hemiacetal. If the OH-group bonded to the new chirality-centere is on the right-, it is α-D-glucose; if the OH-group is on the left-, it is β-D-glucose.



α-D-glucose (36%) | open-chain (0.02%) form | β-D-glucose (64%)

m.pt = 146°C

$[\alpha]_D$ = +112.2°

(α-D-glucopyranose)

m.pt. = 150°C

$[\alpha]_D$ = +18.7°

(β-D-glucopyranose)

↳ α-D-glucose and β-D-glucose are called anomers.

↳ Anomers are two sugars that differ in configuration only at the carbon that was the carbonyl carbon in the open-chain form. This is called the anomeric carbon.

↳ Thus anomers differ in configuration at the uppermost chirality centre. The anomeric carbon is the only carbon in the molecule bonded to two oxygens.

↳ Anomers like epimers, are a particular kind of diastereomers.

↳ In an aqueous solution, the open-chain compound is in equilibrium with the two cyclic hemiacetals. At equilibrium, there is almost twice as much β-D-glucose (64%) as α-D-glucose (36%).

Open-chain and cyclic structure of Fructose—

↳ Ketoses also exist predominantly in cyclic forms.

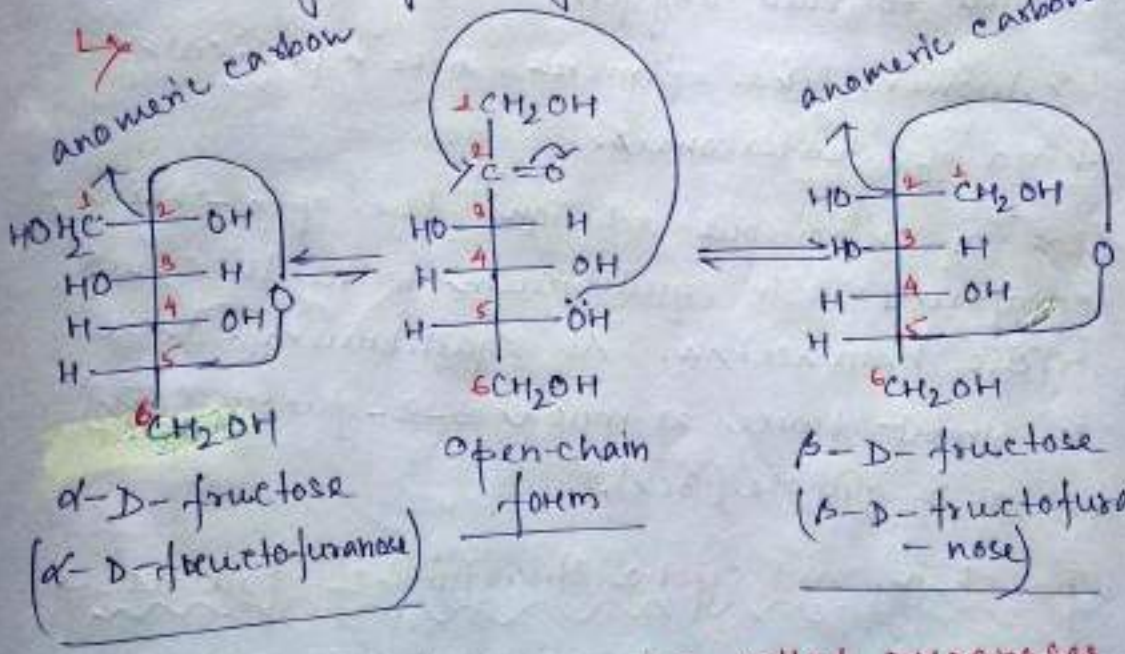
↳ D-Fructose forms a five-membered ring hemiketal as a consequence of the C-5 OH

group reacting with the ketone carbonyl group.

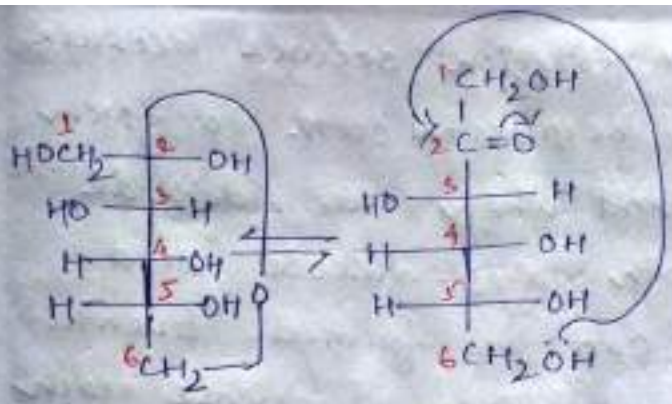
↳ If the new chirality center has the OH-group on the right in a Fischer projection, the compound is α-D-fructose; if the OH-group is on the left, the compound is β-D-fructose.

↳ D-fructose can also form a six-membered ring by using the C-6 OH group.

↳

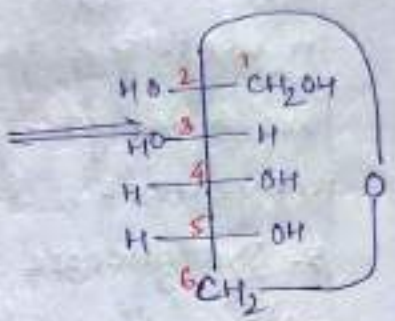


(Six-membered sugars are called pyranoses and five-membered sugars are called furanoses, eg:- α-D-glucose is also called α-D-glucopyranose, 5-membered α-D-fructose is called α-D-fructofuranose etc)



α-D-fructose (α-D-fructopyranose)

Open-chain form



β-D-fructose (β-D-fructopyranose)

Mutarotation —

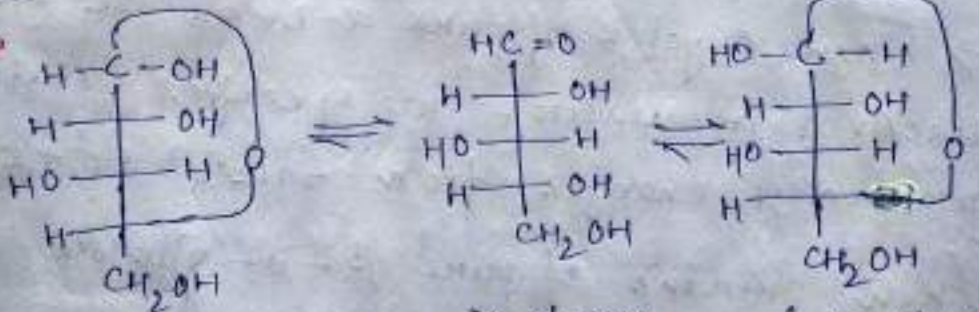
↳ Mutarotation is a change in the optical rotation of a solution due to a change in the equilibrium between alpha (α) and beta (β) anomers, upon dissolution in the aqueous solution.

↳ When crystals of pure α-D-glucose are dissolved in water, the specific rotation gradually changes from +112.2° to +52.7°. When crystals of pure β-D-glucose are dissolved in water, the specific rotation gradually changes from +18.7° to +52.7°.

This change in rotation occurs because in water, the hemiacetal opens to form the aldehyde and when the aldehyde recyclizes, both α-D-glucose and β-D-glucose can be formed. Eventually, the three forms of glucose reach equilibrium concentration. The specific rotation of the equilibrium mixture is +52.7°, which is why the same specific rotation results whether the crystals originally dissolved in water are α-D-glucose or β-D-glucose.

↳ Therefore a slow change in optical rotation to an equilibrium value is known as mutarotation.

↳



α-D-glucose

$[\alpha] = +112.2°$

D-glucose

$[\alpha] = +52.7°$

β-D-glucose

$[\alpha] = +18.7°$

Specific rotation, $[\alpha]$ → The specific rotation is the number of degrees of rotation caused by a solution of 1.0 g of compound per mL of solution in a sample tube 1.0 dm long at a specified temperature and wavelength.

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times c}$$

Where,

T = Temperature in °C

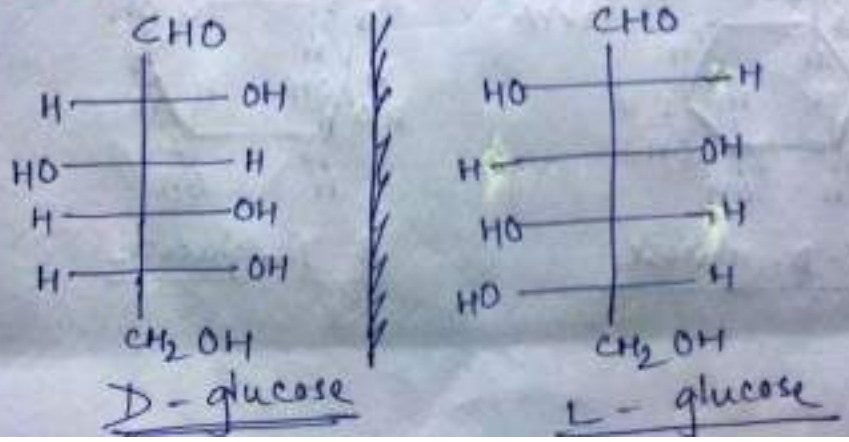
λ = Wavelength of the incident light

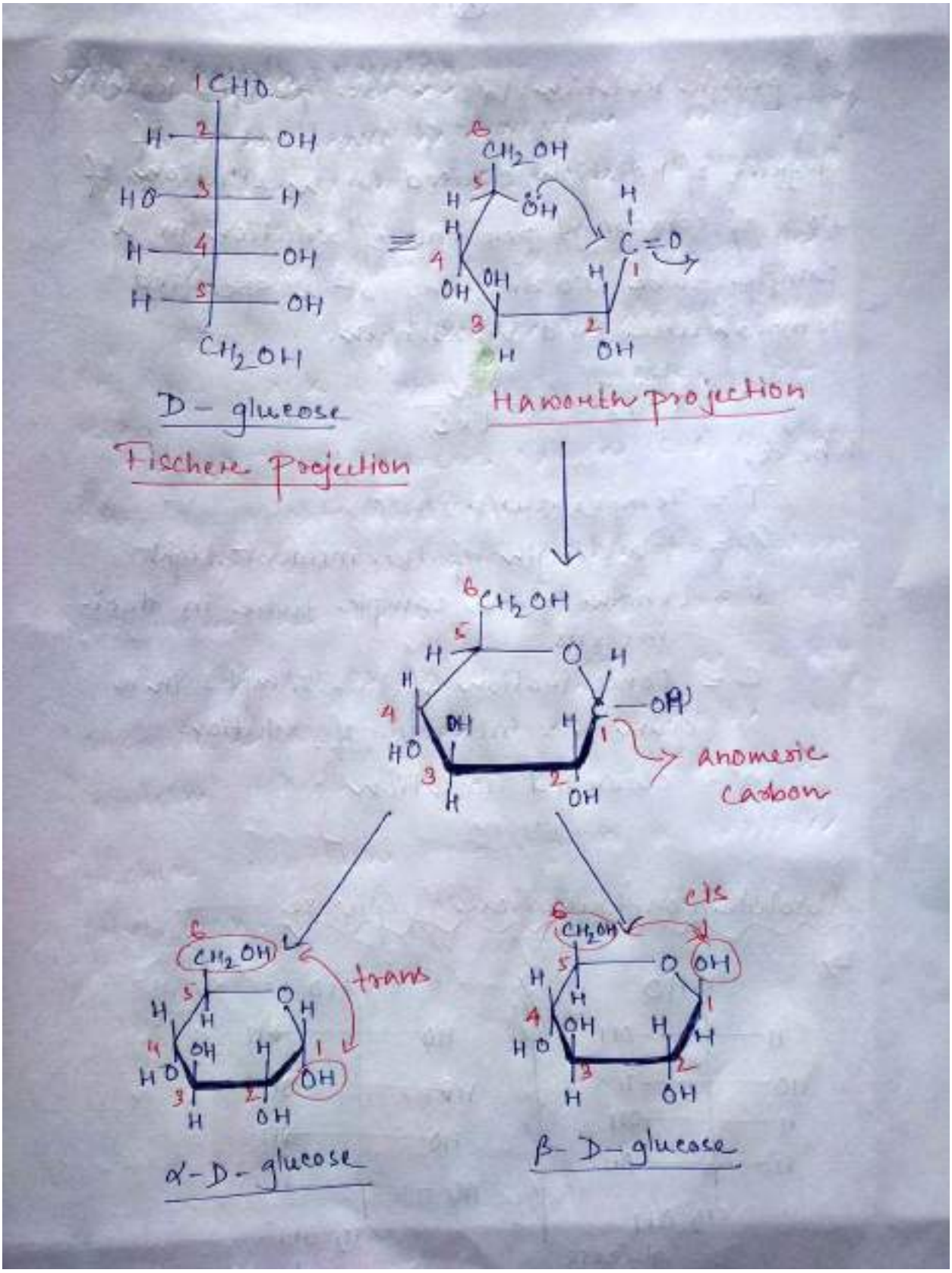
l = Length of the sample tube in decimeters

c = Concentration of the sample in gram per millilitre of solution

α = observed rotation

Absolute configuration of Glucose




D – glucose
Fischer Projection
Haworth projection
anomeric carbon
trans
cis
α-D-glucose
β-D-glucose

Haworth Projection —

In a Haworth projection of a D-pyranose, the six-membered ring is represented as —

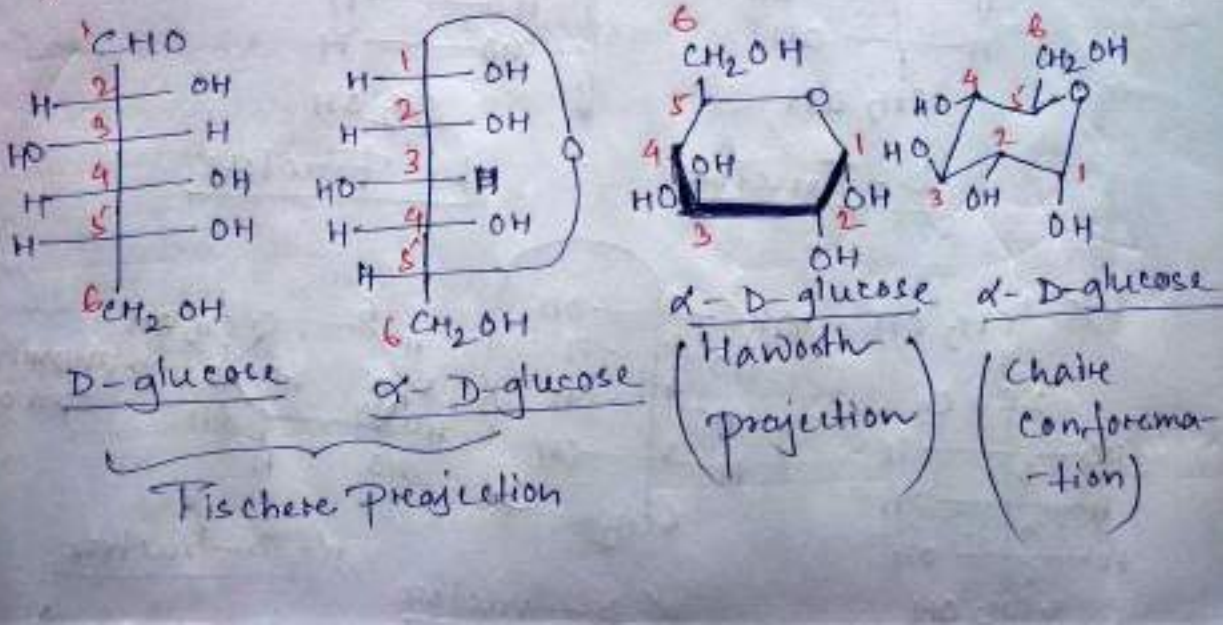
i) Flat and is viewed edge on

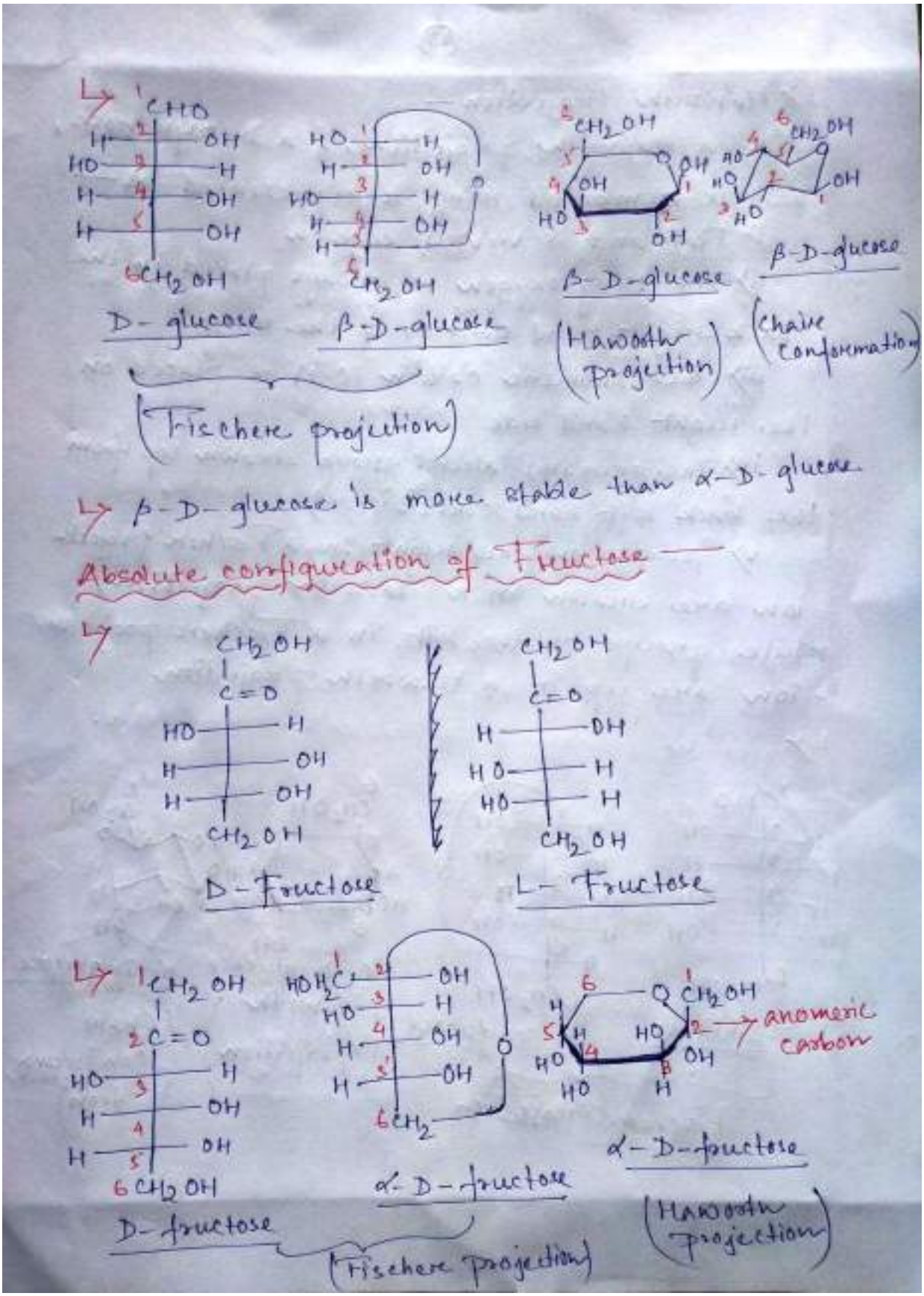
ii) The ring oxygen is always placed in the back right-hand corner of the ring.

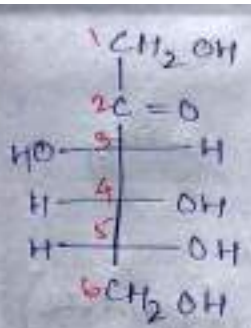
iii) The anomeric carbon (C-1) is placed on the right hand side

iv) The primary alcohol group drawn up from the back left-hand corner (C-5).

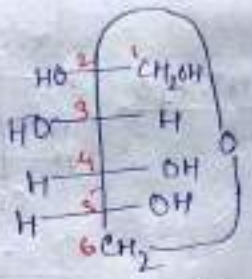
v) Groups on the right in a Fischer projection are drawn in a Haworth projection, while groups on the left in a Fischer projection are up in a Haworth projection.




D- glucose
β-D-glucose
(Fischere projection)
β-D-glucose
(Haworth projection)
β-D-glucose
(chair conformation)
β-D-glucose is more stable than α-D-glucose
Absolute configuration of Fructose
D-Fructose
L-Fructose
D-fructose
α-D-fructose
(Fischere projection)
anomeric carbon
α-D-fructose
(Haworth projection)

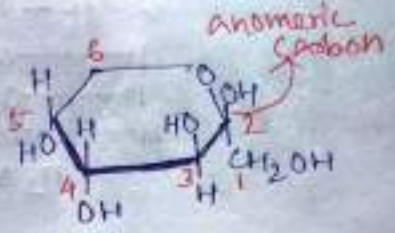


D-fructose



β-D-fructose

(Fischer projection)



β-D-fructose

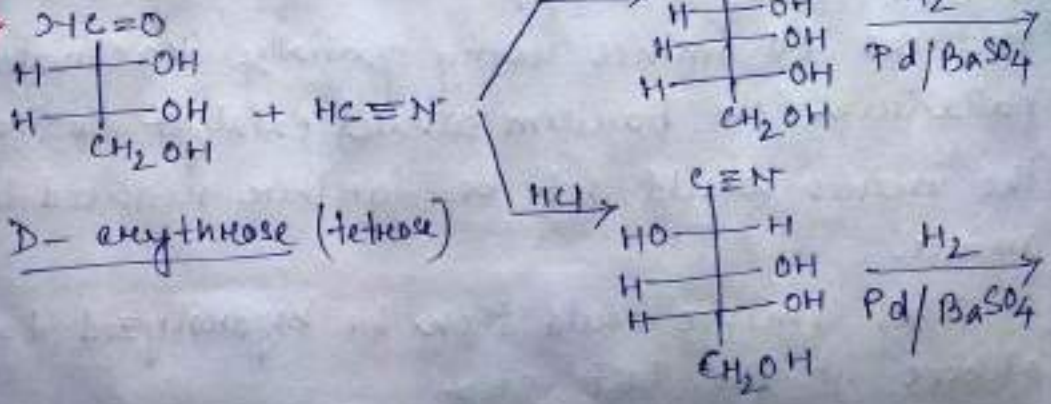
(Haworth projection)

Ascending and descending in monosaccharides—

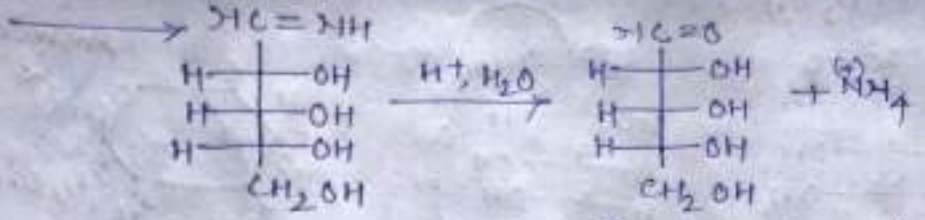
Ascending/chain elongation — (Kiliani-Fischer synthesis)

↳ The carbon chain of an aldose can be increased by one carbon by the Kiliani-Fischer synthesis. In these words, tetroses can be converted into pentoses, and pentoses can be converted into hexoses ~~etc~~. etc.

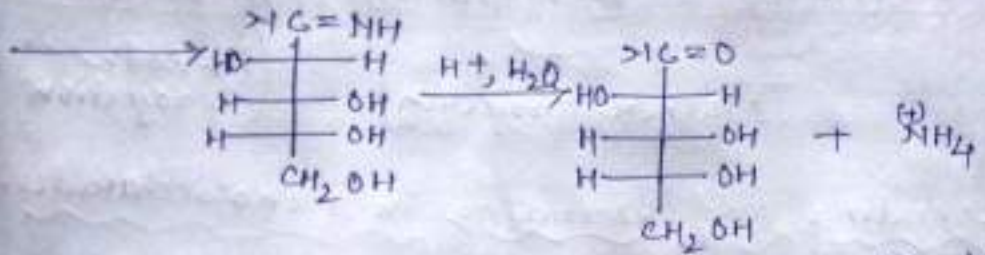
↳



D-erythrose (tetrose)



D-ribose (pentose)



D-arabinose (pentose)

↳ In the first step of the reaction, HCN is added to the aldose and addition of cyanide ion ($:\ddot{C}N$) to the carbonyl group creates a new chirality center. Consequently, two cyanohydrins that differ only in configuration at C-2 are formed.

In the second step the cyanohydrins are reduced to imines using partially deactivated palladium (on barium sulfate) catalyst so that the imines would not be further reduced to amines.

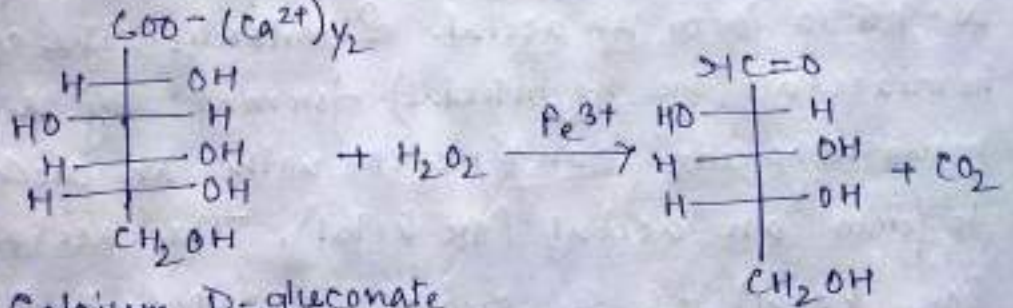
The imines could then be hydrolyzed to aldoses at the last step.

ii) Descending / Chain shortening: (Chain The Ruff Degradation)

↳ The Ruff degradation is the opposite of the Kiliani-Fischere synthesis. Thus the Ruff degradation shortens an aldose chain by one carbon, for example hexoses are converted into pentoses and pentoses are converted into tetroses etc.

↳ In Ruff degradation, the calcium salt of an aldonic acid is oxidized with hydrogen peroxide. Ferric ion catalyzes the reaction. The oxidation reaction cleaves the bond between C-1 and C-2 forming CO_2 and an aldehyde. It is known that the reaction involves the formation of radicals.

↳

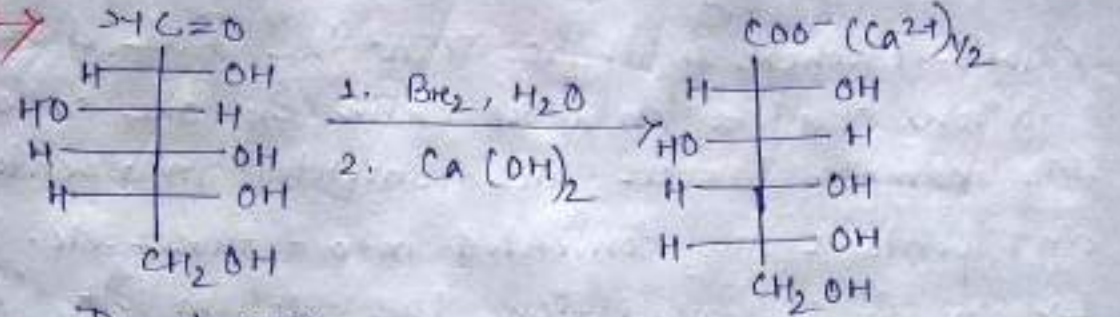


Calcium D-gluconate

D-arabinose (pentose)

↳ The calcium salt of the aldonic acid is easily obtained by oxidizing an aldose with

an aqueous solution of bromine and then adding calcium hydroxide to the reaction mixture.

↳ 

D-glucose (hexose)

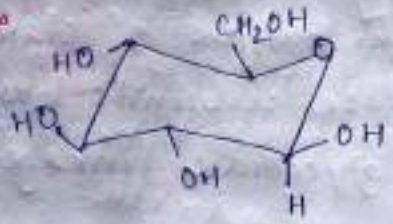
Calcium D-gluconate

Formation of Glycosides—

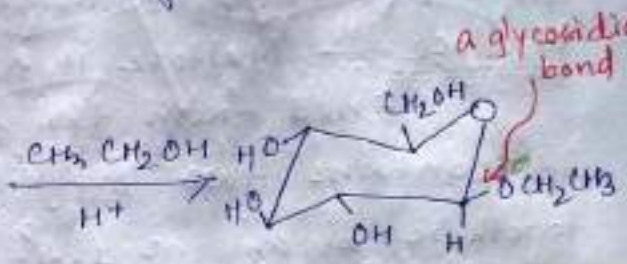
↳ An aldehyde reacts with an equivalent of an alcohol to form a hemiacetal, the hemiacetal reacts with a second equivalent of alcohol to form an acetal. Similarly, the cyclic hemiacetal (or hemiketal) formed by a monosaccharide can react with an alcohol to form an acetal (or ketal). The acetal (or ketal) of a sugar is called a glycoside and the bond between the anomeric carbon and the alkoxy oxygen is called a glycosidic bond.

↳ If a pyranose or furanose name is used the acetal is called a pyranoside or a furanoside.

↳

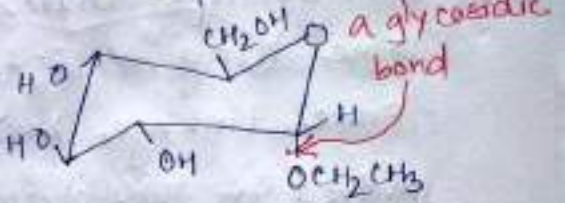


β-D-glucose
or
β-D glucopyranose



ethyl β-D-glucoside
or
ethyl β-D-glucopyranoside

+



ethyl α-D-glucoside
or
ethyl α-D-glucopyranoside

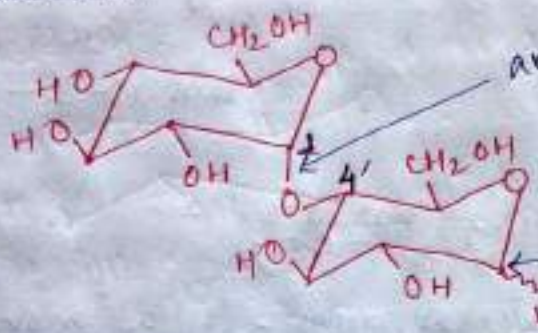
Structure of Disaccharides —

↳ If the hemiacetal group of a monosaccharide forms an acetal by reacting with an alcohol group of another monosaccharide, the glycoside that is formed is a disaccharide.

↳ Disaccharides are compounds with two

monosaccharide subunits are hooked together by an acetal linkage.

Maltose — Maltose is a disaccharide obtained from the hydrolysis of starch. It contains two D-glucose subunits hooked together by an α-1,4'-glycosidic linkage. The linkage is between C-1 of one sugar subunit and C-4 of the other. The 'prime' superscript indicates that C-4 is not in the same ring as C-1. It is an α-1,4'-glycosidic linkage because the oxygen atom involved in the glycosidic linkage is in the α- position.



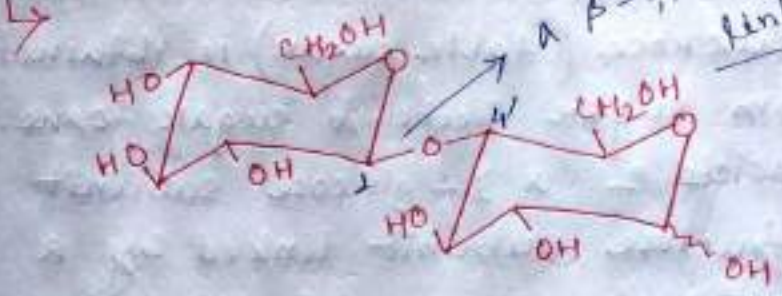
an α-1,4'-glycosidic linkage

the configuration of this carbon is not specified

Maltose

Cellobiose — Cellobiose is a disaccharide obtained from the hydrolysis of

Cellulose, also contains two D-glucose subunits. It differes from maltose in that the two glucose subunits are hooked together by a β-1,4'-glycosidic linkage. Thus, the only difference in the structures of maltose and cellobiose is the configuration of the glycosidic linkage.



Cellobiose

Lactose — Lactose is a disaccharide found in milk. One of the subunit of lactose is D-glucose and the other is D-galactose. The D-glucose subunit is a hemiacetal and the D-galactose subunit is an acetal. The subunits are joined through a β-1,4'-glycosidic linkage.

Structure of Polysaccharides —

↳ Polysaccharides contain 10 - several thousand monosaccharide units joined together by glycosidic linkages.

↳ The most common polysaccharides are starch and cellulose.

Starch — Starch is the major component of flour, potatoes, rice, beans, corn and peas. It is a mixture of two different polysaccharides — Amylose (about 20%) and amylopectin (about 80%)

Amylose is composed of unbranched chains of D-glucose units joined by α-1,4'-glycosidic linkages.

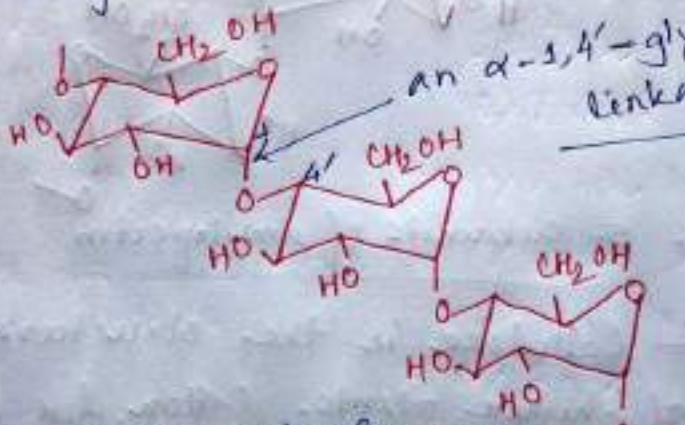


fig:- 3 - subunits of amylose

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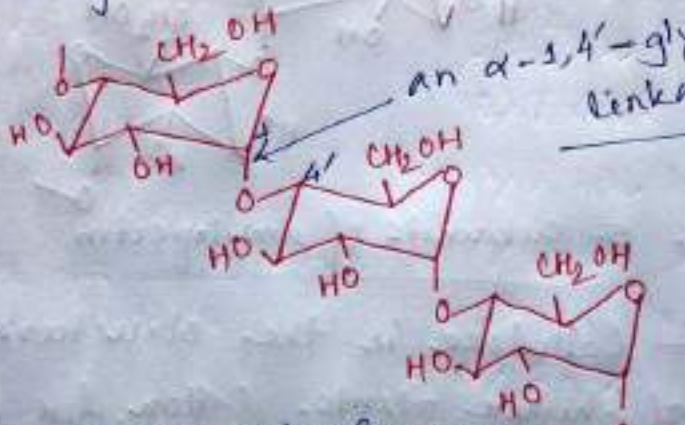

fig:- 3 - subunits of amylose

Amylopectin is a branched polysaccharide. Like amylose, it is composed of chains of D-glucose units joined by α-1,4'-glycosidic linkages. Unlike amylose, however amylopectin also contains α-1,6'-glycosidic linkages. These linkages create the branches in the polysaccharide.

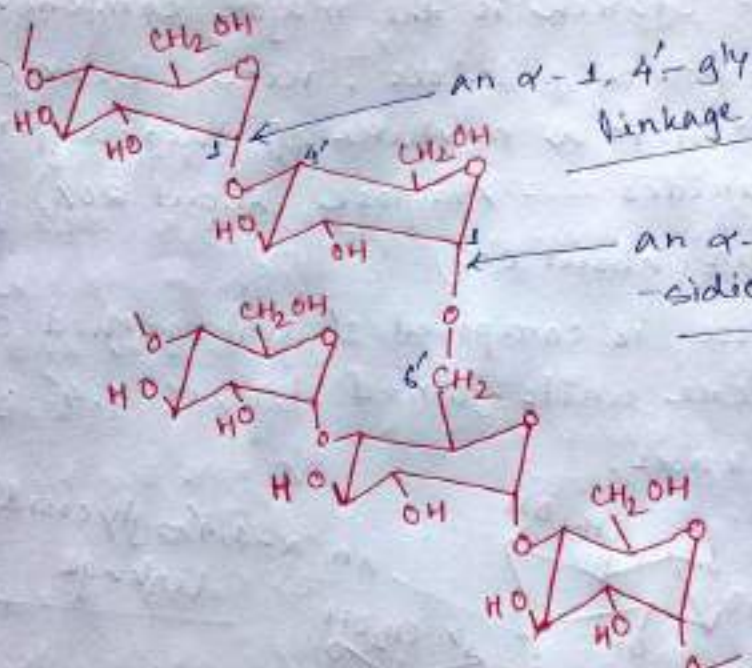

fig:- 5- subunits of amylopectin

Cellulose — Cellulose is the structural material of higher plants. Cotton, for example composed of about 90% cellulose, and wood is about 50% cellulose. Like amylose, cellulose

is composed of unbranched chains of D-glu-cose units. Unlike amylose, however, the glucose units in cellulose are joined by β-1,4'-glycosidic linkages, not α-1,4'-glyco-si dic linkages.

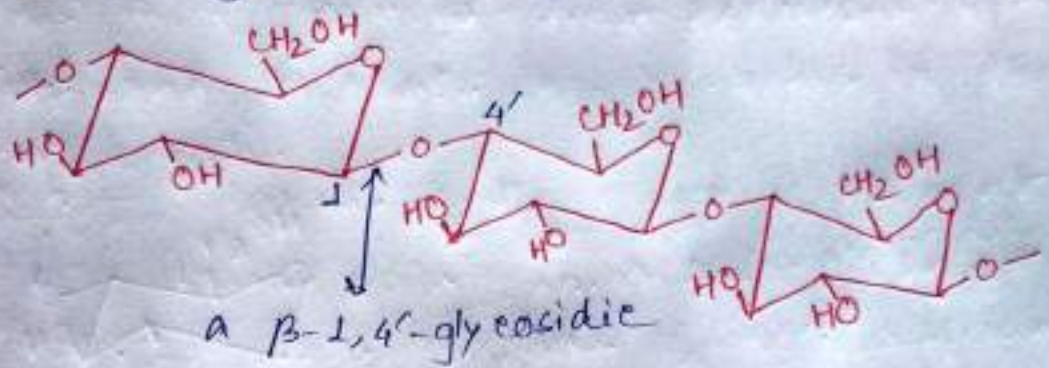

Fig:- 8-subunits of cellulose