Unit-I-[A] - Carbohydrate

Q. Determine structure of Maltose.

* Answer :-

1) Molecular formula of Maltose is $C_{12}H_{22}O_{11}$.
2) Maltose on enzymatic hydrolysis or hydrolysis by aq. acid (dilute acid) gives two moles of glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{dil. HCl}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

3) (a) (+) Maltose reduces Tollen's and Fehling's reagents. Hence, it is a reducing sugar.

(b) Maltose on reaction with Hydroxylamine (NH_2OH) gives Oxime. Maltose on reaction with phenyl hydrazine gives Osazone.

(c) Maltose on oxidation with Br_2 (bromine) water gives Maltobionic acid.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{C_6H_5NHNH_2} \underset{\text{Osazone}}{C_{12}H_{20}O_9(=NNHC_6H_5)_2}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[{[O]}]{Br_2\ \text{water}} \underset{\text{Maltobionic acid}}{(C_{11}H_{21}O_{10})COOH}$$

∴ Maltose is a reducing sugar in which one aldehyde (-CHO) group of ~~one of~~ the two glucose units is free and the other group should ~~have~~ be~~en~~ engaged in bonding (linking).

(3) Two anomers of Maltose, viz. α-anomer and β-anomer are known which show Mutarotation (in solution)

α-anomer : Specific rotation $[\alpha]_D$: 168°

β-anomer : specific rotation $[\alpha]_D$: 112°

Specific rotation ~~at~~ of both the anomers at equilibrium $[\alpha]_D$ = 136°

∴ free -CHO (aldehyde) group should be in hemiacetal form similar to monosaccharide.

4) Hydrolysis of maltose is achieved (performed) by maltase enzyme.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Maltase}} 2\,C_6H_{12}O_6$$

Glucose.

∴ Two glucose units of maltose are joined by α-glycosidic linkage. [i.e. Anomeric carbon (C_1) of one glucose unit is attached with non-anomeric carbon of other unit by α-linkage]

* To determine the complete structure of maltose, two questions need to be answered :

(i) Which -OH group from one D(+)-Glucose unit is linked with the anomeric -OH group of other α-D(+)-glucose?

(ii) What are the sizes of rings present in both monosaccharides?

6) The answers of above questions can be found

from the study of oxidation, methylation & hydrolysis.

(a) Maltose on complete methylation gives Octa-O-methyl maltose.

∴ There are 8 free -OH groups in (+) maltose.

(b) Maltose $\xrightarrow{\text{Methylation}}$ Octa-O-methyl maltose $\xrightarrow[\text{Hydrolysis}]{HCl}$ Hepta-O-methyl maltose

$\downarrow$ H_3O^+ Hydrolysis

2,3,4,6-tetra-O-methyl glucose + 2,3,6-tri-O-methyl glucose

→ This proves the following :

(i) Formation of hepta-O-methyl maltose suggests that there is one free reducing group present.

(ii) Structure of 2,3,4,6-tetra-O-methyl glucose is known in which -OH group on C_1 is free. Thus, this free -OH group on C_1 must be attached to -OH group of 2,3,6-tri-O-methyl glucose other than C_1 -OH group.

(iii) Formation of & structure determination of 2,3,6-tri-O-methyl glucose suggests that C_1-carbon of non-reducing glucose unit should be linked with C_4- or C_5- carbon of reducing glucose unit.

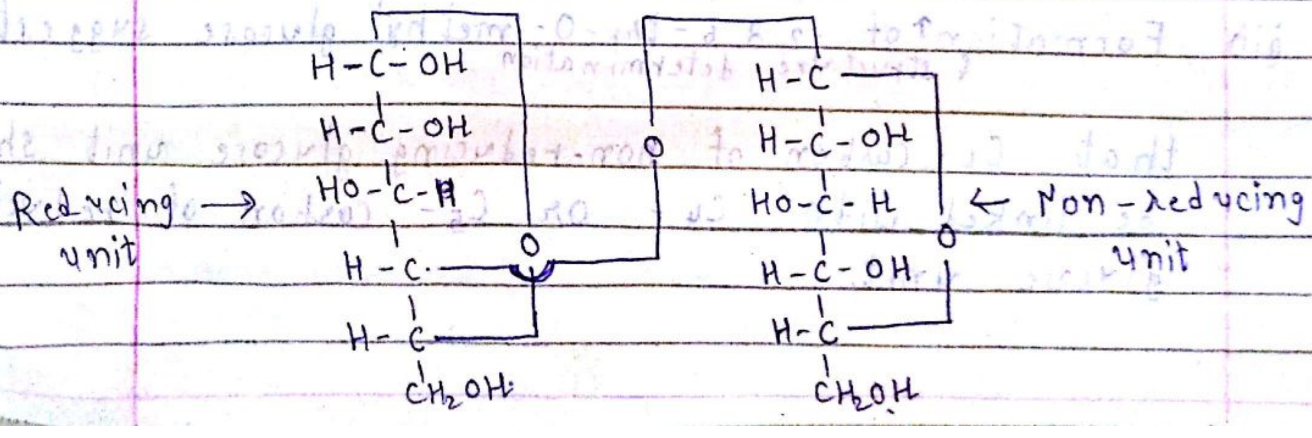
Dr. Dipti K. Dodiya.

Unit-4-[A]-Carbohydrate

(c) (4) maltose $\xrightarrow[\text{water [O]}]{Br_2}$ Maltobionic acid $\xrightarrow[NaOH]{(CH_3)_2SO_4}$ Octa-O-methyl maltobionic acid $\xrightarrow[\text{Hydrolysis}]{H_3O^+}$ 2,3,4,6-tetra-O-methyl glucose + 2,3,5,6-tetra-O-methyl D-gluconic acid (II)

→ The product (II) is easily convertible to γ-lactone. Therefore, the two glucose units of maltose contain pyranose (1:5) cycle. Hence, the C_1 carbon of non-reducing glucose unit of maltose is linked with C_4 - carbon of reducing glucose unit.

7) Hence, two glucose units of maltose contain pyranose cycle & both these units are linked by α-glycosidic linkage between C_1 and C_4. Therefore, maltose is 4-O-(α-D-glucopyranosyl)-D-glucopyranose. The structure of maltose can be shown as under:



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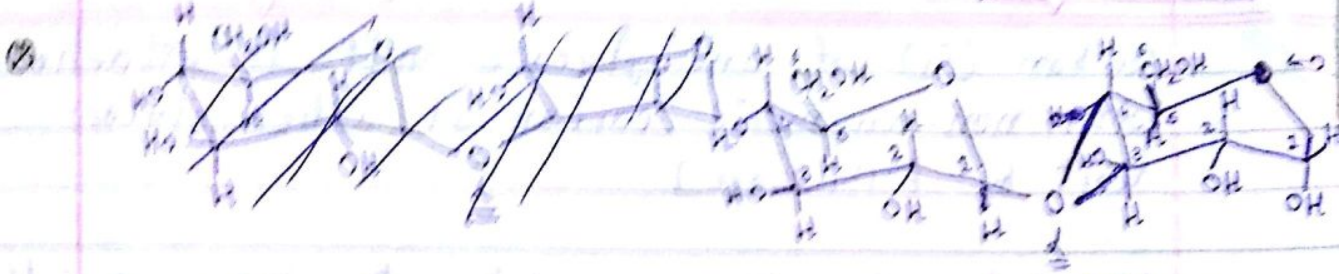


Maltose (α-anomer)

Q. Determine structure of Cellobiose.

* Answer :

1) ~~1)~~

→ See 1), 2), 3(a)-3(c) of maltose. Replace maltose with Cellobiose. All reactions/formulas ~~will be so~~ remains same.

3 (d) Two anomers of Cellobiose, viz. α-anomer and β-anomer are known which show Mutarotation in solution.

α-anomer : specific rotation $[\alpha]_D$: $+72^\circ$

β-anomer : specific rotation $[\alpha]_D$: $+35^\circ$

∴ free -CHO (aldehyde) group should be in hemiacetal form similar to monosaccharide.

4) Hydrolysis of Cellobiose is achieved by the enzyme emulsin

$$C_{12}H_{22}O_{11} \xrightarrow{Emulsin} 2C_6H_{12}O_6$$

Glucose

∴ Two glucose units of Cellobiose are joined by β-glycosidic linkage [i.e anomeric carbon (C_1) of one glucose unit is attached with non-anomeric carbon of other glucose unit by β-linkage]

* To determine the complete structure of Cellobiose, two questions need to be ~~determined~~ answered :-

(i) Which -OH group from one D(+)- Glucose unit is linked with the anomeric -OH group of other α-(D)(+)-glucose ?

(ii) What are the size of rings present in both monosaccharides ?

6) The answers of above questions can be found from the study of oxidation, methylation & hydrolysis

(a) Cellobiose on complete methylation gives Octa-O-methyl cellobiose.

∴ There are 8 free -OH groups in (+)-Cellobiose.

(b) Cellobiose $\xrightarrow{\text{Methylation}}$ Octa-O-methyl Cellobiose $\xrightarrow[\text{Hydrolysis}]{HCl}$ Hepta-O-methyl cellobiose

$\downarrow$ H_3O^+ Hydrolysis

2:3:4:6-tetra-O-methyl glucose + 2:3:6-tri-O-methyl glucose

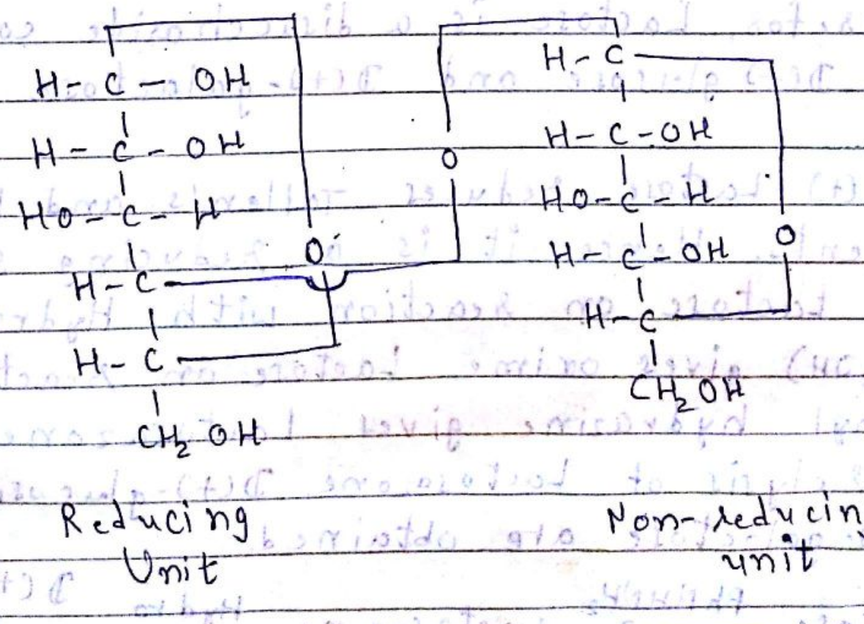
→ This proves the following :

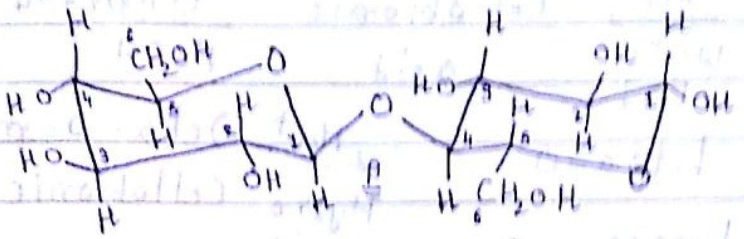
— Description as per answer for Maltose —

(c) Cellobiose $\xrightarrow[\text{Water [O]}]{Br_2}$ Cellobionic acid $\xrightarrow[NaOH]{(CH_3)_2SO_4}$ Octa-O-methyl Cellobionic acid $\xrightarrow[\text{Hydrolysis}]{H_3O^+}$ 2,3,4,6-tetra-O-methyl glucose + 2,3,5,6-tetra-O-methyl-D-gluconic acid

→ - Description as per answer for Maltose ←

7) Hence, two glucose units of cellobiose contain pyranose cycle & both these units are linked by β-glycosidic linkage between C_1 and C_4. Therefor, cellobiose is 4-O-(β-D-glucopyranosyl)-D-glucopyranose. The structure of Cellobiose can be shown as under :





Cellobiose (β-anomer)

Q. Determine structure of Lactose.

* Answer :-

1) Molecular formula of Lactose is $C_{12}H_{22}O_{11}$.
2) Lactose on enzymatic Hydrolysis or hydrolysis by aq. acid (dilute acid) gives one mole of D (+)-glucose and one mole of D-(+)-galactose.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{Hydrolysis}]{\text{dil. HCl}} C_6H_{12}O_6 + C_6H_{12}O_6$$

D(+)-glucose D(+)-galactose

Therefor, Lactose is a disaccharide consisting of D(+) glucose and D(+)-galactose units.

3) (a) - (+) - Lactose reduces Tollen's and Fehling's reagents. Hence, it is a reducing sugar.
(b) - Lactose on reaction with Hydroxylamine (NH_2OH) gives oxime. Lactose on reaction with phenyl hydrazine gives Lactosazone. Upon hydrolysis of Lactosazone, D(+)-glucosazone and D(+)-galactose are obtained.

Lactose $\xrightarrow{PhNHNH_2}$ Lactosazone $\xrightarrow{\text{Hydrolysis}}$ D(+)-glucosazone + D(+)-galactose

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(c) - Lactose on oxidation with Br_2 (bromine) water gives Lactobionic acid.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{[O]}]{Br_2,\ \text{water}} (C_{11}H_{21}O_{10})COOH$$

Lactobionic acid

(d) Two anomers of Lactose viz. α-anomer & β-anomer are known which show Mutarotation in solution.

Therefor, Lactose is a reducing sugar in which one anomeric group is present, i.e one aldehyde (-CHO) group is free.

Further formation of D(+)-galactose and D(+)-glucosazone upon hydrolysis of Lactosazone suggests that D(+) glucose should be present as reducing unit & D(+) galactose unit should be present as non-reducing unit

∴ C_1 carbon of D(+)-galactose should be attached (linked/bonded) with the D(+)-glucose unit at the carbon other than the C_1 carbon.

4) Hydrolysis of Lactose is achieved by the enzyme Lactase.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{Hydrolysis}]{\text{Lactase}} \text{D-(+)-Glucose} + \text{D-(+)-Galactose}$$

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→ C_1 anomeric carbon of D(+) galactose should be bonded with the carbon of D(+)-glucose unit by β-glycosidic linkage.

* To determine the complete structure of Lactose, two questions need to be answered:

~~(i) Which carbon of D(+)-glucose Which -OH group from D(+)-glucose -OH~~

(i) -OH group from which carbon of glucose is linked with the -OH of anomeric carbon of β D(+) galactose?

(ii) What are the sizes of rings present in both monosaccharides?

6) The answers of above questions can be found from the study of oxidation, methylation & hydrolysis.

(a) Lactose $\xrightarrow[NaOH]{(CH_3)_2SO_4}$ Octa-O-methyl lactose $\xrightarrow[Hydrolysis]{HCl}$ Hepta-O-methyl Lactose

$\downarrow H_3O^+$ Hydrolysis

2:3:4:6-tetra-O-methyl D(+) galactose + 2:3:6-tri-O-methyl D(+) glucose

→ This proves the following:

(i) Formation of hepta-O-methyl lactose suggests that there is one free reducing group present.

(ii) Formation & structure of 2:3:4:6-tetra-O-methyl-D(+)-galactose suggests that it contains pyranose cycle and -OH group on anomeric (C_1) carbon must be attached to -OH group of D(+) glucose other than C_1-OH group of D(+) galactose.

(iii) Formation & structure determination of 2,3,6-tri-O-methyl glucose suggests that C_1 carbon of non-reducing D(+) galactose unit should be linked with C_4 or C_5 carbon of reducing D(+)-glucose unit.

(b) Lactose $\xrightarrow[\text{[O]}]{Br_2 \text{ water}}$ Lactobionic acid $\xrightarrow{(CH_3)_2SO_4 + NaOH}$ Octa-O-methyl lactobionic acid $\xrightarrow{H_3O^+ \text{ Hydrolysis}}$ 2:3:4:6-tetra-O-methyl D(+)-galactose + 2:3:5:6-tetra-O-methyl-D-gluconic acid (II)

→ The product (II) is easily convertible to γ-lactone. ~~Therefor, the two glucose units of La~~ Therefore, D(+) glucose and D(+) galactose units of Lactose contain pyranose cycle. ~~and C_1 carbon of D(+) galactose unit is linked with C_4 carbon of reducing D(+) glucose unit by β-glycosidic linkage.~~

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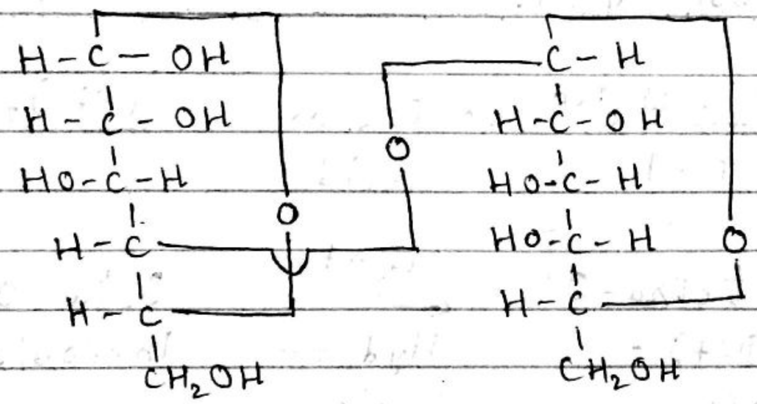
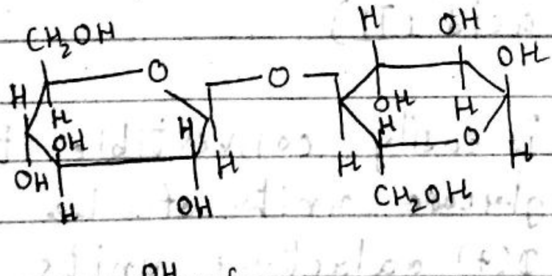
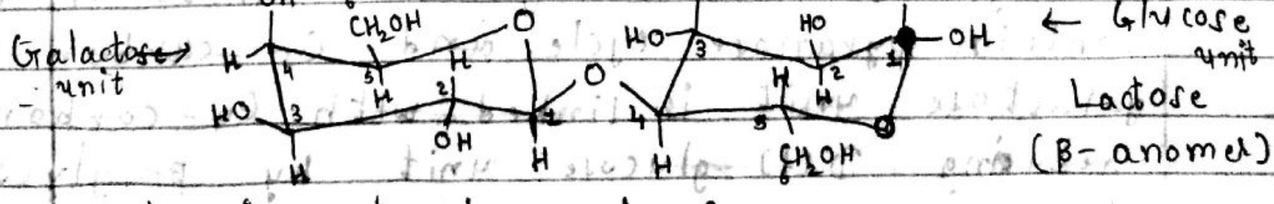
7) Hence, D(+) glucose and D(+) galactose contain pyranose cycle and C_1 carbon of D(+) galactose unit is linked with C_4 carbon of reducing D(+) glucose unit by β-glycosidic linkage.

∴ Lactose is 4-O-(β-D(+)-galactopyranosyl)-D(+)-glucopyranose. The structure of Lactose can be shown as under :



Reducing Glucose unit   Non-reducing galactose unit





Q. Determine structure of Sucrose.

* Answer :-

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→ 1) Molecular formula of Sucrose is $C_{12}H_{22}O_{11}$.
2) Sucrose on hydrolysis gives D(+)-glucose & D(-) Fructose.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{Hydrolysis}]{H_3O^+} \underset{\text{D(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D(-)-Fructose}}{C_6H_{12}O_6}$$

Therefore, Sucrose is a disaccharide made up of D(+)-glucose and D(-)-Fructose.

3) a) - Sucrose does not reduce Tollen's reagent and Fehling's solution.
-(b) - Sucrose does not give oxime on reaction with Hydroxyl amine (NH_2OH). Sucrose does not give Osazone on reaction with phenyl hydrazine.
→ Therefore, Sucrose is a non-reducing sugar. There is no free "Carbonyl" group. Both monosaccharides should be joined by their anomeric carbons, i.e C_1 carbon of D(+)-glucose unit should be linked with C_2 carbon of D(+)-fructose unit.

4 (a) - Sucrose upon acetylation gives octa-acetyl derivative.
(b) - Sucrose upon methylation gives octa-O-methyl derivative.
∴ Sucrose contains 8 free -OH groups.

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5) Sucrose upon hydrolysis by aq. dilute acid or by the enzyme "invertase" gives the equimolar mixture of D(+)-glucose and D(-)-fructose.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{dil. HCl}]{\text{Invertase or}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(+)-Sucrose Hydrolysis D(+)-Glucose D(-)-Fructose

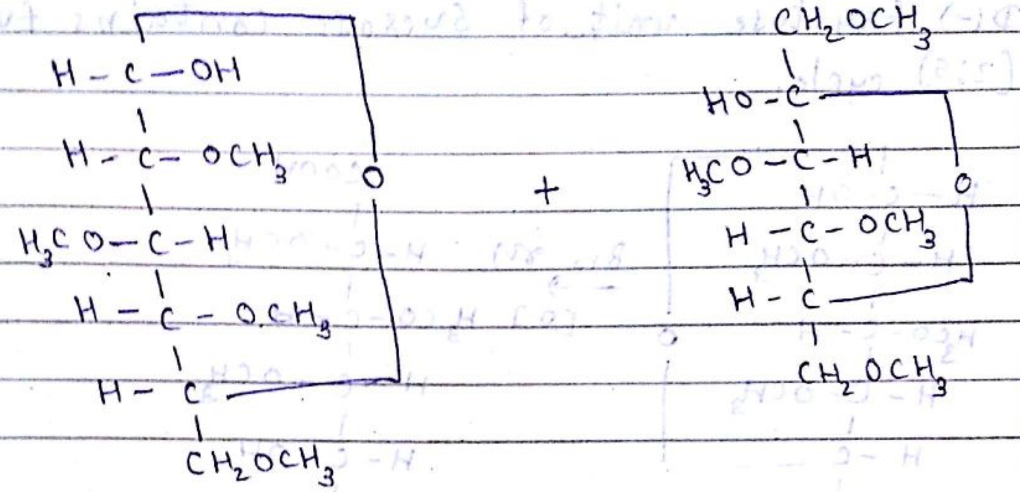
$[\alpha]_D = 66.5°$ $[\alpha]_D = 52.7°$ $[\alpha]_D = -92.4°$

→ Sucrose is levorotatory. Before hydrolysis, sucrose has the specific rotation of 66.5°. The mixture of D(+)-Glucose and D(-)-Fructose obtained after hydrolysis has the specific rotation -20°. The change in specific rotation from + (plus) to minus (-) is known as inversion and sucrose is known as invest sugar.

→ The α- and β-anomers of Sucrose are ~~un~~ not known and sucrose does not show mutarotation.

6) Sucrose on complete methylation gives Octa-O-methyl sucrose which on hydrolysis gives 2:3:4:6-tetra-O-methyl D-(+)-glucose and 1:3:4:6-tetra-O-methyl-D(-)-fructose.

$$\text{Sucrose} \xrightarrow[\text{+ NaOH, Methylation}]{(CH_3)_2SO_4} \text{Octa-O-methyl Sucrose} \xrightarrow[\text{Hydrolysis}]{\text{dil. acid}}$$



2:3:4:6 - tetra-O-methyl- D(+)- glucose (I)   1:3:4:6 - tetra-O-methyl -D(-)-fructose (II)

7) The products (I) and (II) obtained as per above reactions were separated, their structures were determined & and sizes of cycles present in monosaccharides were deterimed as follows:

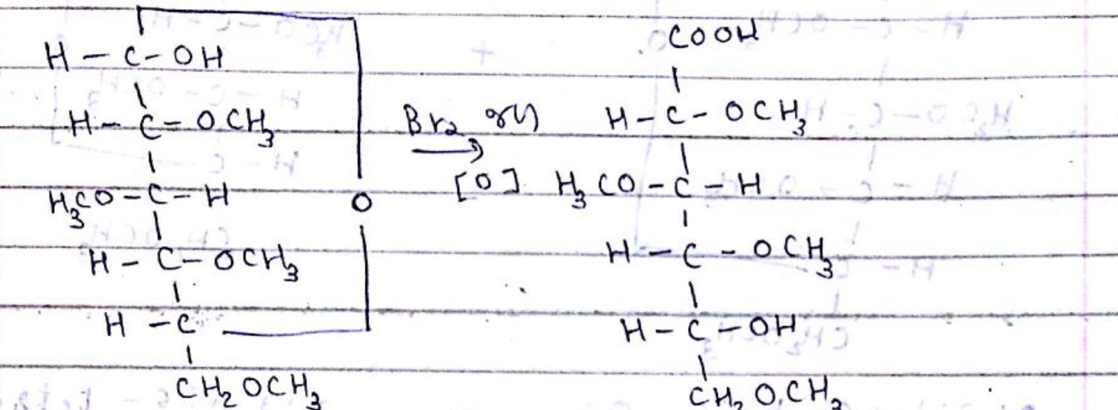
(a) product (I) upon oxidation with Br_2 water gives 2:3:4:6:- tetra- O- methyl D(+) gluconic acid which on oxidation with HNO_3 gives xylo-trimethoxy glutaric acid (IV). Formation of (IV) suggests that D(+)- glucose unit of sucrose ~~gives~~ contains pyranose (1:5) cycle.

→ See equation on next page.

(b) Product (II) upon oxidation with dil. HNO_3 give tri- O- methyl- fructonic acid which on oxidation with $KMnO_4$ and H_2SO_4 gives dimethyl tartaric acid (VI). Formation of (VI) suggests that

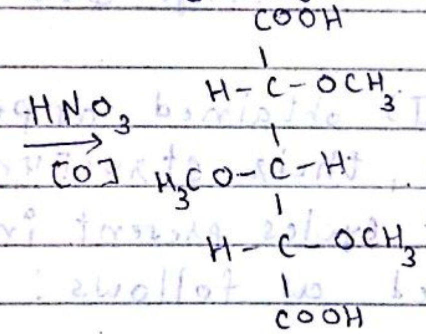
D(-) fructose unit of sucrose contains furanose (2:5) cycle.

(a)



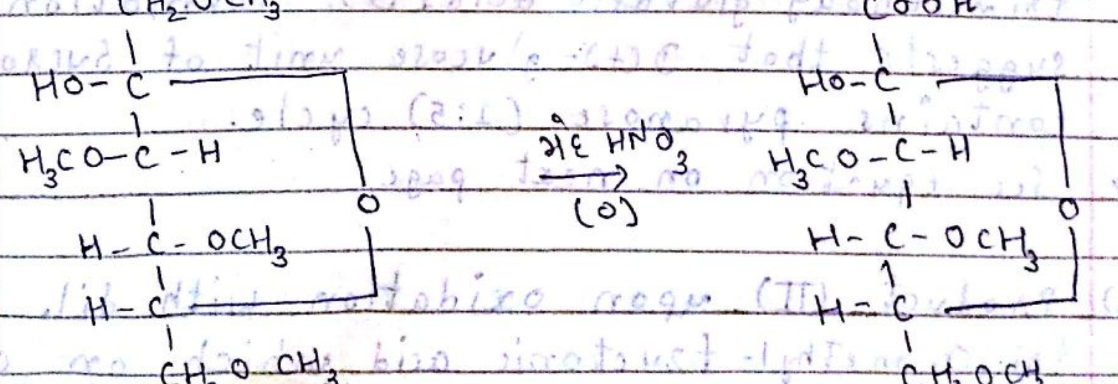
2:3:4:6-tetra-O-methyl D(+)-glucose (I)

2:3:4:6-tetra-O-methyl D(+) gluconic acid (III)



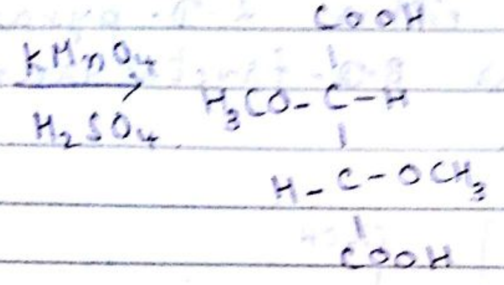
Xylo dimethoxy glutaric acid (IV)

(b)



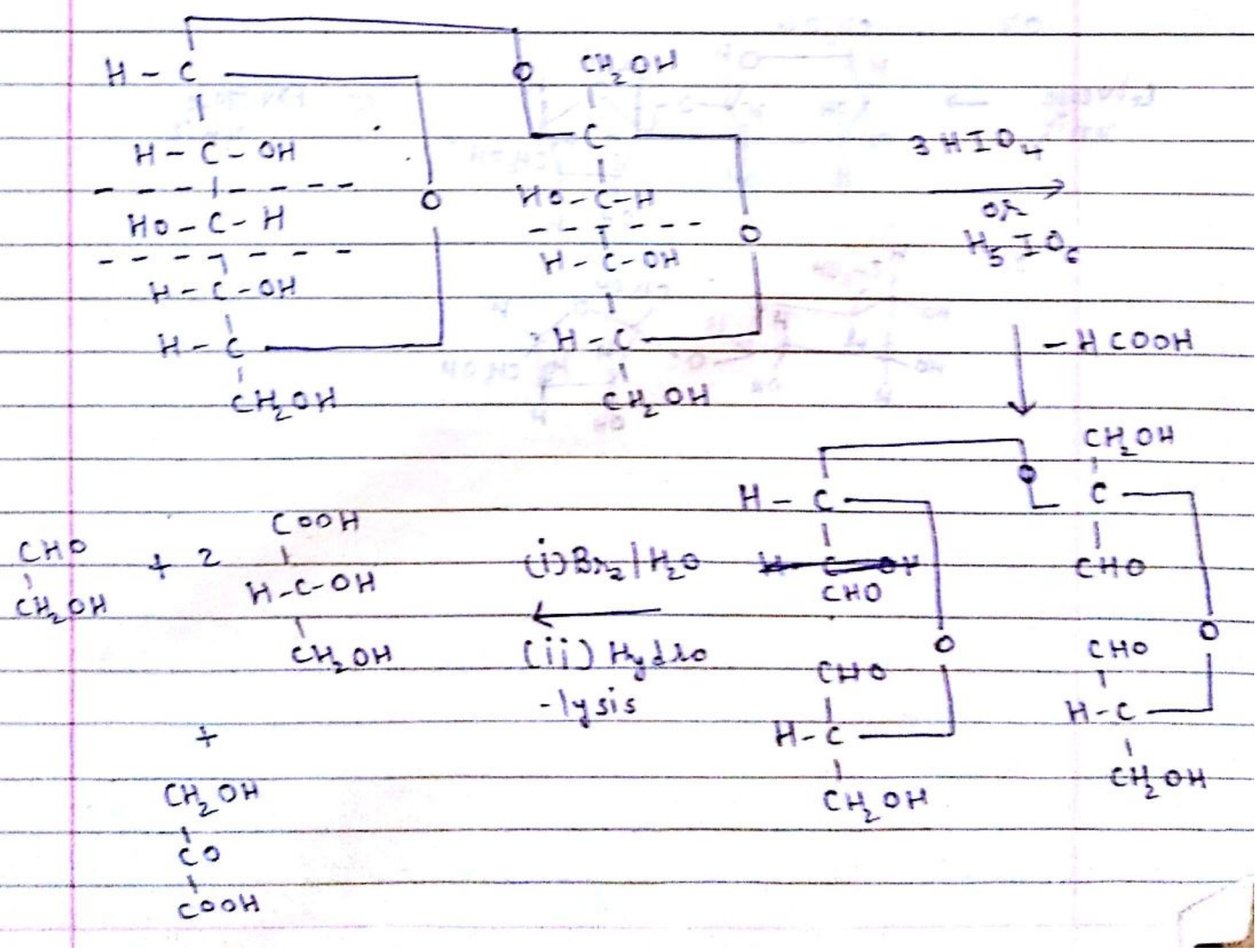
1:3:4:6-tetra-O-methyl D(-) fructose (II)

3:4:6-tri-O-methyl-Fructonic acid (V)

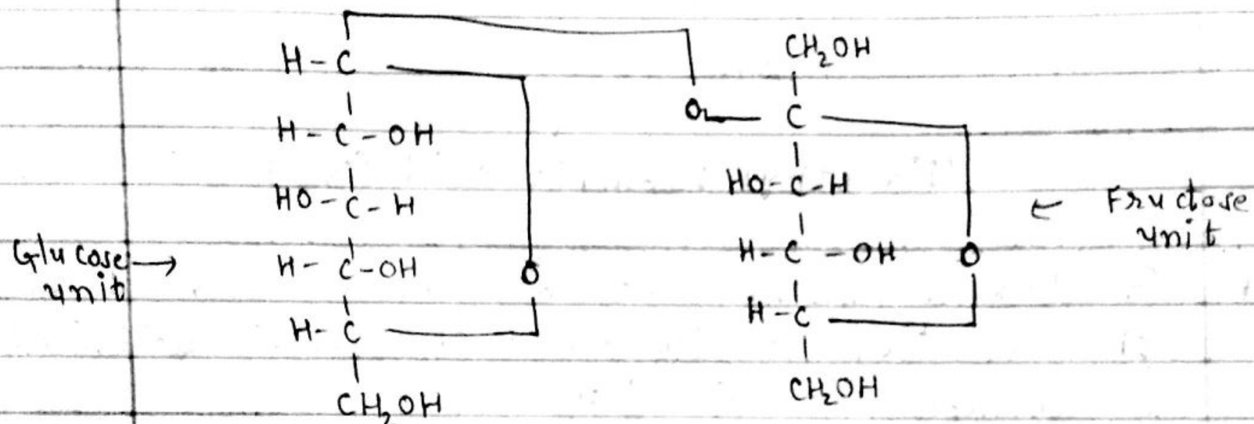


Dimethyl tartaric acid (VI)

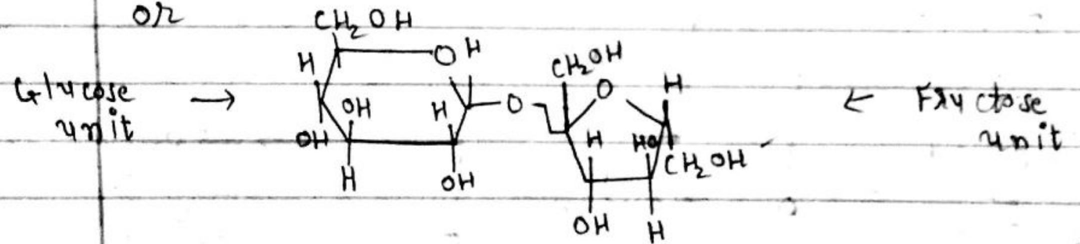
* Structure of Sucrose can also be confirmed from the reaction of Sucrose with periodic acid (HIO_4) or othoperiodic acid (H_5IO_6)



→ Therefore, sucrose is either α-D-pyranosyl-β-D-fructofuranoside or β-D-fructofuranosyl-α-D-glucopyranoside.



or



or