Name of the course — DIFAT IInd Year
Topic — DISACCHARIDE
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Pages — 1 to 8

What are carbohydrates?

Polyhydroxyaldehyde or Polyhydroxyketone, and large molecule that produce these compounds on hydrolysis.

OR

A polyhydroxy compound that has an aldehyde or a ketone function present, either free or as hemiacetal or acetal.

Carbohydrates are classified into three groups:

1. Monosaccharides! These are single unit carbohydrate [polyhydroxyaldehyde or polyhydroxyketones) that cannot be broken into simpler carbohydrates upon hydrolysis. e.g Glucose, fructose, Galactose etc.

2. Oligosaccharides: - These are made of two to ten units of monosaccharides or simple sugars. Oligosaccharides are further classified into disaccharides, trisaccharides, tetrasaccharides etc.

DISACCHARIDES : On hydrolysis gives two monosaccharides units.

The common disaccharides are dihexoses, having molecular formula $C_{12}H_{22}O_{11}$.

Formation of Glycosides:

When monosaccharides reacts with methanol forms methyl glycosides. So can other hydroxy compounds also forms glycosides. The monosaccharides are also hydroxy compounds. When one monosaccharide molecules unite with other monosaccharide molecules to forms glycosides links.

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Classification of disaccharides [occurs in natural compounds]

1. The two monosaccharide molecules are linked through their reducing groups, e.g Sucrose.
2. C-1 of one molecule is linked to C-4 of the other, e.g, Maltose, cellobiose etc.
3. C-1 of one molecule is linked to C-6 of the other, e.g., Melibiose

Other types of combinations [In natural and/or Synthetic dihexoses) are C_1-C_2, C_1-C_3 and C_1-C_5.

Since the glycosidic link may be α or β, their different stereoisomeric forms become possible for a given pair of hexoses.

In group[1]

Four forms possible theoretically: $\alpha_1-\alpha_2$, $\alpha_1-\beta_2$, $\beta_1-\alpha_2$ and $\beta_1-\beta_2$,

~~In g~~ Since both reducing groups are involved in glycosidic formation, the resultant disaccharide will be non-reducing.

In group (2) and (3), since one reducing group is free, the resultant disaccharide will be reducing, and can exist in two forms, the α- and β-

General procedure for the separation of disaccharide and structural determination:

Separation of disaccharide

1. Prepare a column of activated carbon and celite [1:1].
2. Adsorption of the mixture on column.
3. The column then eluted with water.
4. If elution is carried out with aqueous ethanol, then disaccharides are removed.

Structure determination

1. Disaccharides is first hydrolysed with dilute acids.
2. Methylation of the disaccharide by Haworth's method [to ascertain the involment of glycosidic link.]
3. Hydrolysed the methylated disaccharide.

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4. Methylated monosaccharide obtained are investigated by oxidation methods. [see pg. 288 (7a), 289 (7b), and 292 (7c) of I.L FINAR, Volume II]

5. Another method for ~~determination~~ determining the position of the glycosidic linkage is the periodate oxidation method.

6. To decide ~~weth~~ whether the glycosidic link is α- or β-, This is done by means of enzymes, maltase hydrolysing α-glycosides and emulsin β-glycosides.

Nomenclature :

Since disaccharides are monosaccharide glycosides, non-reducing disaccharides are glycosyl glycosides. and reducing disaccharides [in which one glycosidic hydroxyl group is still present) are o-glycosyl-glycoses. For eg Maltose (Reducing disaccharide) It has two monosaccharide units. The name of the reducing disaccharide ~~is~~ Maltose is

4-O-α-D-glucopyranosyl-D-glucopyranose

OR

O-α-D-glucopyranosyl-(1→4)-D-glucopyranose

Structure determination of Maltose.

Occurence → Present in germinated seeds, essentially in cereals, rice, corn, etc.

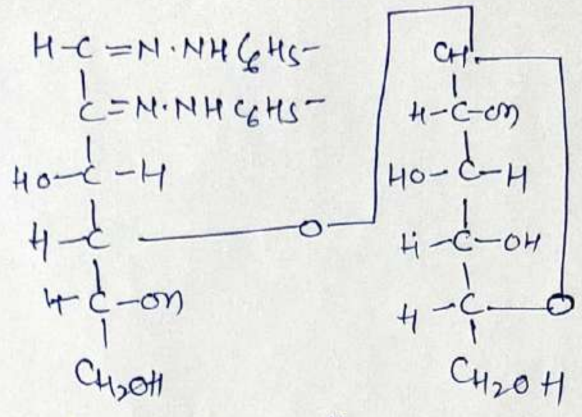
Isolation → $\text{Starch} \xrightarrow[\text{Partial}]{\text{hydrolysis}} \text{D-Maltose} \xrightarrow{\text{hydrolysis}} \text{D-Glucose}$

Let us look some of the facts from which structure of maltose has been deduced.

1. D-Maltose has the molecular formula $C_{12}H_{22}O_{11}$.
2. M.P : — 102-103°C
3. It reduces Tollen's and Fehling solution and hence it is a reducing sugar [means one reducing group is free which exist in hemiacetal form]

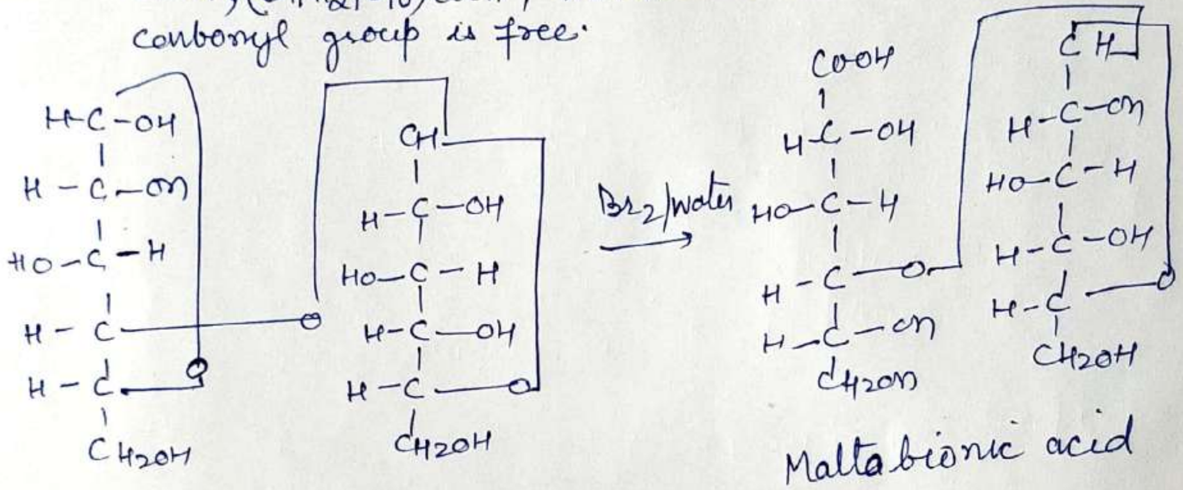
contn — ④

4. It reacts with phenyl hydrazine give or yield osazone $C_{12}H_{20}O_9(=N\,NHC_6H_5)_2$. means carbonyl group is free.



Structure of Maltasazone

5. It is oxidized by bromine water to monocarboxylic acid, $(C_{11}H_{21}O_{10})COOH$, maltobionic acid. It also means carbonyl group is free.



Maltabionic acid

D(+) Maltose

6. D(+) Maltose ~~those~~ undergo mutarotation in solution [equilibrium
[α] = +136°]
alpha [α] = + [168°] , Beta β [[α] = +112°]

All these facts indicate that maltose contains a carbonyl group that exists in the reactive hemiacetal form as in the monosaccharide we have studied.

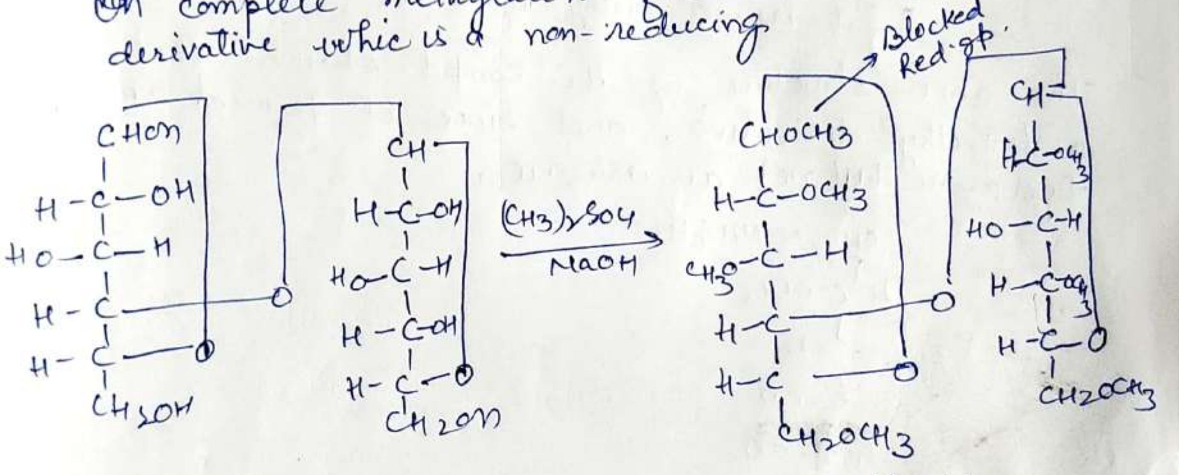
7. Maltose is hydrolysed or heated in aqueous acid, or treated with enzyme maltase (from yeast), , Maltose is completly converted into D-(+)-glucose. This indicates that maltose($C_{12}H_{22}O_{11}$) is made up of two glucose units joined together with the loss of one molecule of water

→ contn ⑤

8. Hydrolysis by acid to give a new reducing group [two reducing D-(+)-glucose molecules in place of one (+) maltose molecule) is characteristic of glycosides ; hydrolyses by enzyme maltase is a characterstic of alpha glucosides. A glycoside is an acetal formed by interaction of an alcohol with a carbonyl group of a carbohydrate ; in this case the alcohol concerned can only be a second molecule of D-(+)-glucose. So (+) Maltose contains two D(+)-glucose units, joined by an alpha-glucoside linkage between the carbonyl group of one D-(+)glucose unit and an -OH group of the other.

So two questions may arise which -OH group is involved, and what are the sizes of the rings in the two D-(+) glucose units?. Answers of these two questions are given by the sequence of oxidation, methylation and hydrolysis.

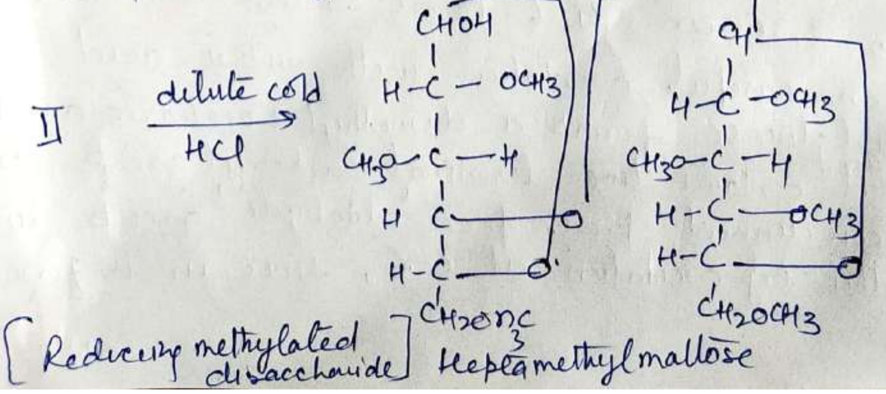
On complete methylation of D(+)maltose gives octamethyl derivative whic is a non-reducing



Maltose I

Maltoside II

and this compound (maltoside) on hydolysis with very dilute cold hydrochloric acid, is converted into hepta-methylmaltose, which has a reducing properties [due to the presence of reducing group]



[Reducing methylated disaccharide] Heptamethylmaltose

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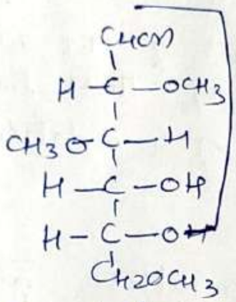
So, the octamethyl derivative must be methyl hepta–O –O–methyl–D–maltoside; This is further evidence that only one free reducing group is present in maltose.

Hydrolysis of hepta–O–methyl maltose with moderately concentrated hydrochloric acid produces 2,3,6–tri–O–methyl –D–glucose and 2,3,4,6–tetra–O–methyl–D–glucose.

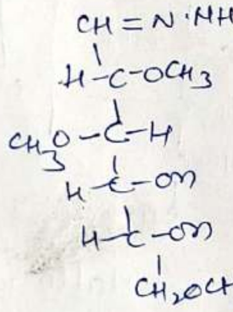
The structure determination of 2,3,4,6–tetra –O–methyl –D–glucose is known. [see page no 288, 7a]

The structure of 2,3,6–tri–O–methyl –D–glucose is elucidated as follows.



2,3,6-tri–O–methyl D glucose.

The above structure of the compd. showed that it has a trimethyl derivative, and since it formed a phenyl hydrazone but not an osazone.



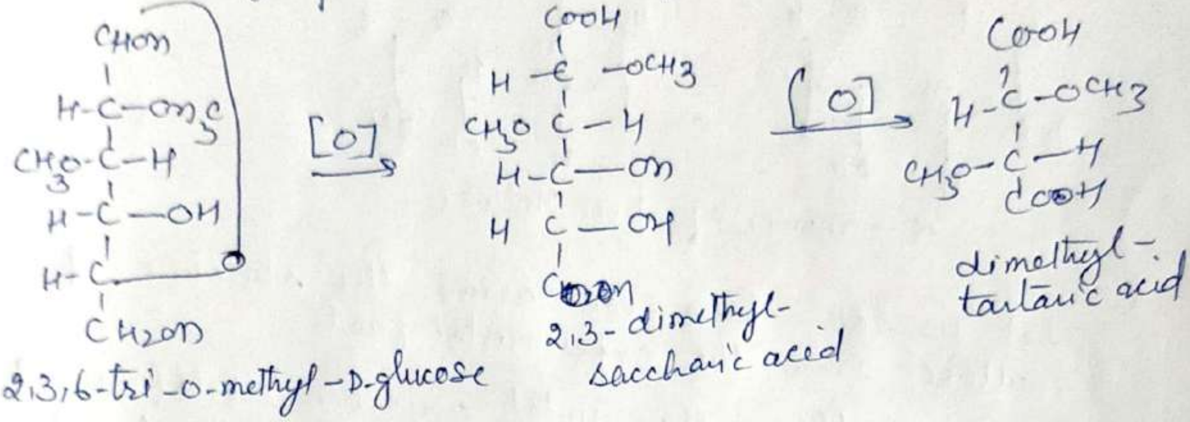
C–2 must therefore be attached to a methoxyl group. On further methylation, 2,3,6-tri-O-methyl-D-glucose gives 2,3,4,6-tetra-O-methyl-D-glucose, and so the trimethyl compound must be one of the following 2,3,4-, 2,3,6-, or 2,4,6-tri-O-methyl-D-glucose.

Now, on careful oxidation with nitric acid, the trimethylglucose forms a dimethyl saccharic acid. This acid contains two terminal carboxyl group, one has been derived from free 'aldehyde' group, and the other by oxidation at C-6, since in its formation

Contn – 7

one methyl group is lost, Thus the trimethyl glucose must be either 2,3,6 or 2,4,6-tri-o-methyl-D-glucose. On further oxidation, the dimethyl saccharic acid forms dimethyl-D-tartaric acid: this can only arise from a precursor with two methoxyl groups on adjacent carbon atoms, and so it follows that the trimethyl glucose must be 2,3,6-tri-O-methyl-D-glucose.

The foregoing reactions may be written as

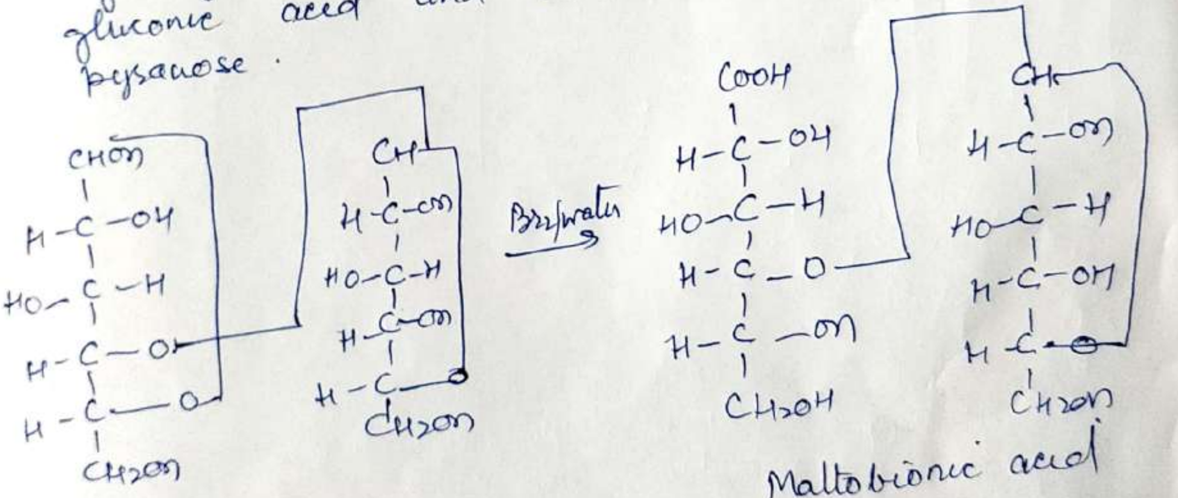


2,3,6-tri-o-methyl-D-glucose

2,3-dimethyl-saccharic acid

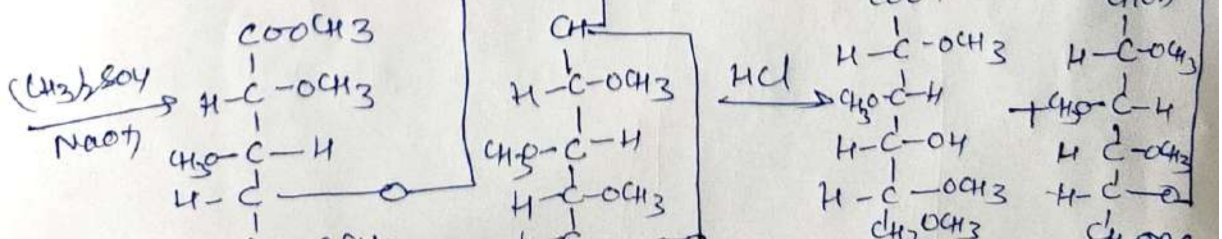
dimethyl-tartaric acid

Oxidation of maltose by bromine water gives maltobionic acid which on methylation yields octa-methyl-D-maltobionic acid (it is non-reducing) followed by hydrolyses gives 2,3,5,6-tetra-O-methyl-D-gluconic acid and 2,3,4,6-tetra-o-methy-D-gluco pyranose.



Maltobionic acid

D(+) Maltose

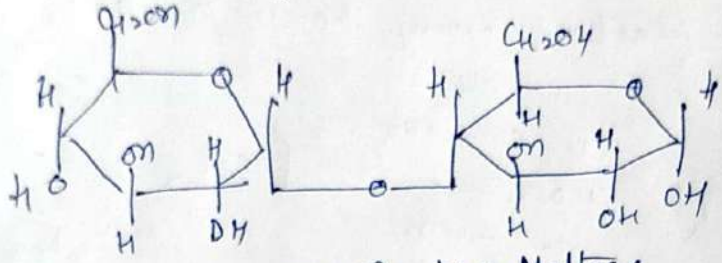


2,3,6-tri-O-methyl-D-gluconic acid

2,3,4,6-tetra-O-methyl-D-gluco pyranose

Contn-8

These facts indicates that (+) maltose has structure which is given the name 4-O-α-D-glucopyranosyl D-glucopyrano. It is the -OH group on C-4 that serves as the alcohol in the glucoside formation; both halves of the molecule contains the six membred ring.



α - anomer of D(+) Maltose.

Let us see how we arrive the structure of maltose from the experimental facts:

First of all, the initial oxidation labels (with a -COOH gp) the D-glucose unit that contains 'free' aldehyde group. Next, methylation labels (as OCH_3) every free -OH group. Finally, upon hydrolysis, the absence of a methoxyl group shows which -OH group were not free.