CARBOHYDRATE

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Short Notes

- Mucopolysaccharide (Glycosamino glycans)
- Digestion & absorption of carbohydrate
- Lactose intolerance

DM- Shortnotes

- Diagnosis of Diabetes Mellitus
- Metabolic alteration in Diabetes Mellitus
- Acute and Chronic complication of Diabetes Mellitus
- Biochemical explanation of Diabetic Ketoacidosis
- Define and significant of Glycate haemoglobin

Comments

- Structure of proteoglycan is well suited for its function.
- Lactase enzyme deficiency cause diarrheal after milk ingestion.
- Human can not digest cellulose.
- Sucrose is non- reducing.
- Sucrose is called "invert sugar".
- Oral rehydration solution is made up of glucose and sodium both.
- Carbohydrate are essential for the metabolism of fat.

Comments-DM

- Insulin is use to correct hyperkalemia.
- Patient of IDDM have more risk of diabetic ketocidosis than NIDDM.
- Cataract is more common in diabetes mellitus.
- Estimation of C-Peptide is better parameter to differentiate IDDM & NIDDM.

Sucrose

- It is sweetening agent known as cane sugar.
- It contains Glucose & Fructose
- The linkage involves first carbon of glucose & second carbon of Fructose. & No free reducing groups available.
- So, sucrose is Non-reducing Sugar.

Sucrose

- Hydolysis of Sucrose (Optical Rotation +66.5) will produce one molecule of glucose(+52.5) and one molecule of fructose(-92).
- Therefore, the products will change the dextro rotation to levorotation, means the plane of rotation is inverted,
- So, Invert Sugar.

MUTAROTATION

D-Glucose is crystallized at Room Temperature & ROTATION OF α- ANOMER +112.2° & OF β-ANOMER +18.7°. IN SOLUTION, INTERCONVERSION OF α & β-ANOMERS OCCURS. After 12-18 Hrs, AT EQUILIBRIUM, OPTICAL ROTATION STABILISES AT +52.7°. AT EQUILIBRIUM 63 % ARE β-ANOMERS, 36% ARE α- ANOMERS WHILE 1% ARE IN STRAIGHT CHAIN.



REACTIONS OF MONOSACCHARIDES

1. ENEDIOL FORMATION

In mildly alkaline solns, carbohydrates containing free aldehyde or keto group will tautomerise to form **enediols** (compounds where 2 –OH grp containing C-atoms are linked by double bonds).

SUGARS CAN BE INTERCONVERTED BY FORMATION OF A COMMON ENEDIOL

H - C - OHс — он он**—** Ċ **—** Н **н**— Ç — ОН н**−**С́ − он CH2OH ENEDIOL

Enediols are highly reactive and capable of reducing ions. Eg., Cupric ions to cuprous ions.

This is the basis of reduction tests done to detect the presence of reducing sugars like Glucose in urine. Eg., Benedict's test, Fehling's test, Barfoed's test.

REACTIONS OF MONOSACCHARIDES

2. OXIDATION

Depending on the oxidising agent used, the aldehyde / keto group or the terminal alcohol group or both may be oxidised to carboxyl group to produce the corresponding acid. Under mild oxidative conditions, aldehyde grp is oxidised to carboxyl grp tp form aldonic acid.

Eg., glucose-gluconic acid galactose- galactonic acid mannose- mannonic acid.

COOH

$$H - C - OH$$

 $OH - C - H$
 $H - C - OH$
 $H - C - OH$
 $H - C - OH$
 CH_2OH
GLUCONIC ACID

When primary alcohol group is oxidised to –COOH grp, uronic acid is formed. CH₂OH Eg., glucose- glucuronic acid H - C - OHон — <u>с</u> — н galactose-galacturonic acid H - C - OHн-с-он mannose-mannuronic acid. COOH GLUCORONIC ACID

Under strong oxidative conditions

The first and last C-atoms are simultaneously oxidised to form dicarboxylic acids (saccharic acids)

eg., glucose- glucosaccharic acid, mannose- mannosaccharic acid galactose- mucic acid. COOH H-C-OH OH-C-H H-C-OH H-C-OH

REACTIONS OF MONOSACCHARIDES

3. <u>REDUCTION</u>

When treated with reducing agents, the aldehyde or keto group of monosaccharides is reduced to its corresponding alcohol.

D-glucose – Sorbitol Galactose – galactitol Mannose - mannitol Fructose – mannitol + sorbitol Ribose - Ribitol





REACTIONS OF MONOSACCHARIDES

4. DEHYDRATION

When treated with conc. H₂SO₄, monosaccharides undergo dehydration with removal of 3 molecules of water to form furfural derivatives which condense with phenolic compounds to form coloured compounds.

Molisch Test (general test for all carbohydrates) is based on this principle.





5. OSAZONE FORMATION

Osazones are insoluble crystals formed when phenylhydrazine in acetic acid is boiled with reducing sugars. **Osazones - characteristic for each sugar** - used to differentiate sugars in biological fluids like urine. In osazone formation, first 2 C-atoms are involved. Sugars which differ in C1 & C2 will produce the same osazone as their differences will be masked by phenylhydrazine

Glucosazone



Broomstick appearance

Lactosazone



Powderpuff appearance

Maltosazone



Sunflower petal appearance

6. ESTER FORMATION

Hydroxyl groups of monosaccharides may be esterified with phosphate/ propionate/ acetate/ benzoate etc. Esterification with phosphate is very common in metabolism. Eg., Glucose-1-PO₄, Glucose-6-PO₄. (ATP is the phosphate group donor)

6. ESTER FORMATION



7. GLYCOSIDE FORMATION

- Formed when the -OH grp. of the anomeric carbon reacts with -OH grp. or -NH of another compound.
- carbohydrate or non-carbohydrate (*aglycone*) eg., phenol, glycerol, nitrogenous base).
- Reducing property may be lost.
- Glycosidic bond may be α or β depending on the anomeric carbon.
- > May be O-glycosidic bond or N-glycosidic bond.

O-GLYCOSIDIC LINKAGE



N-GLYCOSIDIC LINKAGE



GLYCOSIDIC BONDS ARE CLEAVED BY GLYCOSIDASE ENZYMES



PHYSIOLOGICALLY IMPORTANT GLYCOSIDES:-

<u>Glucovanillin(glucose + vanillin</u>): a natural substance which imparts flavour. <u>Cardiac Glycosides(glucose + steroid</u>): used as a drug to stimulate cardiac muscle. Eg., Digoxin&Digitoxin.

<u>DERIVATIVES OF</u> MONOSACCHARIDES

- 1) Phosphoric acid esters
- 2) Sugar acids

- 3) Sugar alcohols
- 4) Amino sugars
- 5) Deoxy sugars
- 6) Neuraminic acid
- 7) Sialic acid

AMINO SUGARS: -

- -OH grp of sugars may be replaced by amino grps to give rise to amino sugars.
 - Eg., glucosamine, galactosamine.
 - They are present as constituents of heteropolysaccharides.
- Further acetylation may take place to produce Nacetylated sugars. Eg., N-acetyl glucosamine(GluNac), N- acetyl galactosamine(GalNac).

They form important constituents of glycoproteins & glycolipids.



DEOXY SUGARS

Oxygen of the –OH groups may be removed to form deoxy sugars.

- CHOH becomes – CH₂

- CH₂OH becomes CH₃
- Eg., Deoxyribose- important constituent of DNA.

Rhamnose, Fucose – found in

polysaccharides.





NEURAMINIC ACID

A nine carbon sugar derived from <u>mannosamine</u> and <u>pyruvate</u>.

SIALIC ACID OR N-ACETYL NEURAMINIC ACID (NANA)

Acetylated derivatives of neuraminic acid.

Constituent of glycoproteins and glycolipids

OLIGOS&CCHARIDES

2 to 10 monosaccharide units joined by glycosidic linkages.
Eg., disaccharides, trisaccharides, tetrasaccharides

DISACCHARIDES - Most common oligosaccharide

Reducing

Maltose-Glu+Glu Lactose-Glu+Gal Isomaltose- Glu+Glu **Non-Reducing**

Sucrose- Glu+Fruc

Trehalose- Glu+Glu
Maltose:-

- Contains 2 glucose molecules linked by α-1,4 glycosidic bond.
- A reducing disaccharide.
- An intermediate in the digestion of starch & glycogen by the action of the enzyme, α-amylase.

Lactose: -

major carbohydrate found in milk.
Contains one molecule of β-D galactose & one molecule of β-D glucose linked by β-1,2 glycosidic linkage.

STRUCTURE OF MALTOSE



STRUCTURE OF LACTOSE



SUCROSE(COMMON TABLE SUGAR):-

- Disaccharide of glucose & fructose.
- α- 1,2 glycosidic bond.
- Non –reducing sugar due to absence of free anomeric carbon atom which are involved in the glycosidic bond.
- Hydrolysed by enzyme sucrase(invertase).

TREHALOSE: -

A non-reducing disaccharide containing two glucose units linked by α-1,1 linkage.
No free anomeric carbon.

STRUCTURE OF SUCROSE



CLINICALLY IMPORTANT CARBOHYDRATES

NAME OF CARBOHYDRATE	ASSOCIATED DISORDER
D-Glucose	Diabetes mellitus
D-Fructose	Hereditary Fructose Intolerance
D-Galactose	Galactosemia & Cataract
D-Lactose	Lactose Intolerance
L-Xylulose	Essential Pentosuria
Sucrose	Sucrase deficiency
Glycogen	Glycogen Storage Disorder

POLYSACCHARIDES (GLYCANS)

Homopolysaccharides (Homoglycans):-

1. Starch

- 2. Glycogen
- 3. Cellulose
- 4. Inulin
- 5. Dextrans

STARCH: -

- Major plant polysaccharide.
- Homopolysaccharide composed of Glucose units linked by α-glycosidic bonds.
- Two types of structural components-Amylose(10-20%):- unbranched, watersoluble, α-1,4 linkages.

Amylopectin(80-90%):- highly branched, water-insoluble, α -1,6 linkages at the branch points.

STARCH FORMS BLUE COLOURED COMPLEX WITH IODINE WHICH DISAPPEARS ON HEATING & REAPPEARS ON COOLING

Amylose:-

α -D Glucose linked by $\alpha 1 \rightarrow 4$ glycosidic bonds in straight chains





<u>GLYCOGEN</u>: -

*** MAJOR ANIMAL POLYSACCHARIDE** HOMOPOLYSACCHARIDE COMPOSED OF GLUCOSE UNITS LINKED BY α -1,4 LINKAGE α -1,6 LINKAGES AT THE BRANCH POINTS STORED IN MUSCLES & LIVER *** 5% OF THE LIVER WEIGHT IS DUETO ITS GLYCOGEN CONTENT GIVES RED-BROWN OR BROWN-VIOLET COLOUR WITH IODINE**

α - Glucose α (1-4) & α (1-6)



GLYCOGEN MOLECULE

<u>CELLULOSE</u>: -

 PLANT POLYSACCHARIDE
 CONTAINS GLUCOSE UNITS LINKED BY B- GLYCOSIDIC LINKAGE

* CANNOT BE DIGESTED IN HUMAN DUE LACK OF ENZYME HYDROLYSING β-GLYCOSIDIC BOND

INULIN:-

* HOMOPOLYSACCHARIDE COMPOSED OF FRUCTOSE UNITS

OCCURS IN GARLIC, ONION & OTHER TUBERS

*WATER SOLUBLE, LOW MOL.WT., USED TO MEASURE GLOMERULAR FILTRATION RATE(TO ASSESS KIDNEY FUNCTION)

DEXTRANS: -

Homopolymer of glucose
Highly branched
Formed by microorganisms
Plasma expander
chromatography

<u>CHITIN:-</u>

 Homopolysaccharide of N-acetyl glucosamine
 Structural polysaccharide occuring in some invertebrates.

