Introduction to Carbohydrates

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Carbohydrates are polyhydroxy ketone or aldehyde, or compounds that can be hydrolysed to them, regarded as hydrates of carbon. H and O are in the same ratio as in H_2O. General formula $C_n (H_2O)_n$. Depending on the number of products formed during hydrolysis, carbohydrates are been classified into:

1. Monosaccharides - Simple sugar; cannot be hydrolyzed/broken further.
2. Oligosaccharides - polymer (made up of 2-10 monosaccharides); joined by glycosidic linkages. The most abundant forms are disaccharides.
3. Polysaccharides - polymers (made up of 100- 1000 monosaccharides).

Monosaccharides

- They are simple sugars (glucose. fructose and galactose), which cannot be hydrolyzed further. It consists of single polyhydroxy aldehyde or ketones units. These are sweet-tasting, crystalline and soluble in water.
- General formula: $C_nH_{2n}O_n$

It can be further classified on the basis of:

i. Number of the carbon atoms present

Composed of 3-7 carbon atoms and are classified according to the number of C atoms as trioses (3C), tetroses (4C), pentoses (5C), hexoses (6C) and heptoses (7C).

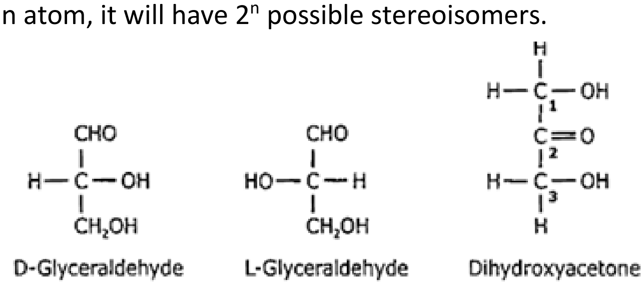
Trioses (3C)	Glyceraldehyde and Dihydroxyacetone
Tetroses (4C) - Rare	Erythrose
Pentoses (5C)- Most Common	Ribose, ribulose, xylulose, and arabinoses.
Hexoses (6C)- Most Common	Glucose), fructose, mannose, galactose.
Heptoses (7C)	Sedoheptulose

ii. Presence of aldehyde or ketone group

If a monosaccharide contains an aldehyde group [–CHO], it is known as an aldose (reducing centre always lies at C1) and if it contains a keto group [=C=O], it is known as a ketose (reducing centre always lies at C2).

Optical activity of monosaccharides

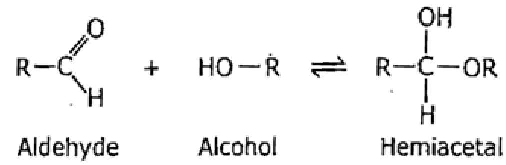
All monosaccharides contain one or more chiral carbon atoms (except Dihydroxyacetone), therefore exist in optically active isomeric forms (enantiomers). If a molecule has one chiral carbon, it will have two different optical isomers (enantiomers). As the number of chiral carbon increases, the number of possible isomers also increases. Therefore, if a compound has 'n' asymmetric carbon atom, it will have 2^n possible stereoisomers.



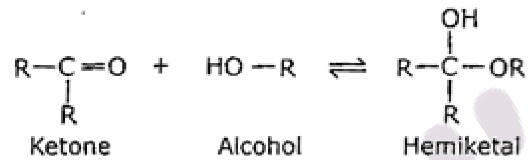
Cyclic Forms of Monosaccharides

Many monosaccharides such as glucose, ribose, fructose etc. exist both in open straight-chain and ring form. Sugar with a 5-membered ring is called furanose sugar. Sugar with a 6-membered ring is called pyranose sugar. They are formed via internal hemiacetal (aldehyde react with alcohol) or hemiketal formation (ketone reacts with alcohol).

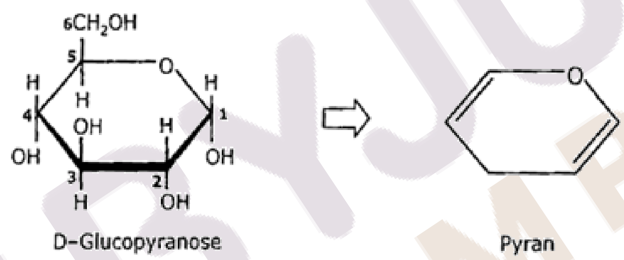
Hemiacetal:

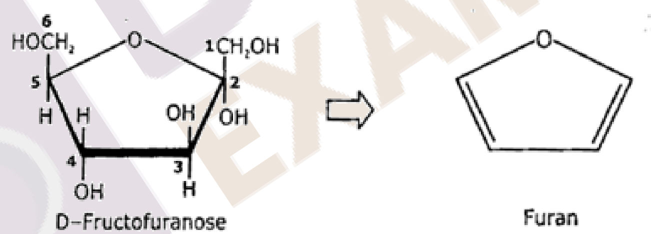


Hemiketal:

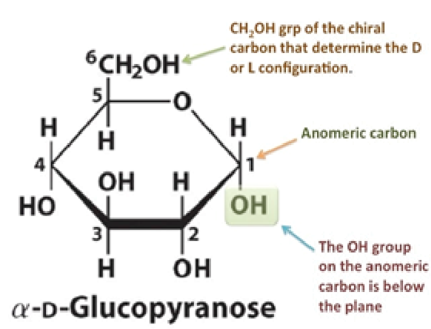


The cyclic form of glucose is a six-membered ring; such sugars are called pyranose because they resemble the cyclic form of pyran. Similarly in fructose (5 membered rings) called furanose because they resemble furan.





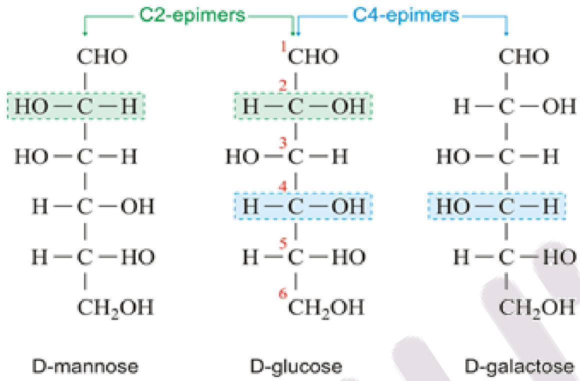
The hemiacetal or hemiketal bond formation creates a new asymmetric centre at C_1 in aldose sugar and C_2 in ketose sugar which is now called an anomeric carbon atom. The—OH group at the reducing centre (i.e., C No. 1 in aldose sugars and C No. 2 in ketose sugars) is present below the plane of the ring, the sugar is said to be in α-form. And if it is present above the plane of the ring, the sugar is said to be β-form. Thus α-form and β-forms are called anomers. The two anomers have different physical and chemical properties**.**



In an aqueous solution, interconversion of α and β-forms via the open-chain structure gives rise to an equilibrium mixture. This phenomenon is called **mutarotation.**

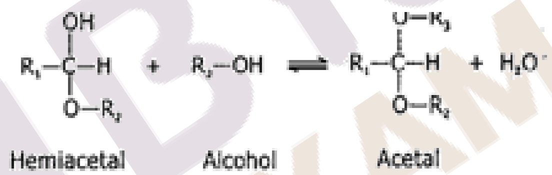
Epimers

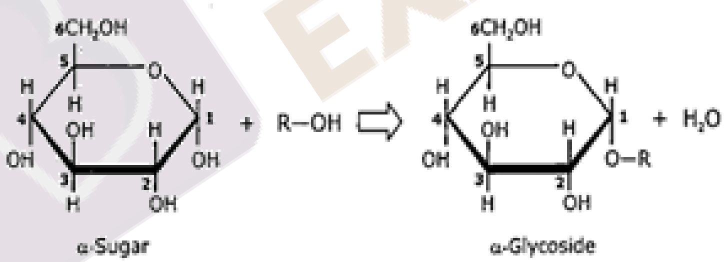
If sugars are closely related but differ only by stereochemistry at a single carbon atom (other than anomeric carbon), they are called epimers. D- Glucose and D- mannose are epimers because they differ in C2. Similarly, D- Glucose, and D-galactose are epimers because they differ in C4. However, D- Mannose, and D- Galactose are not epimers because their configuration differs at more than one carbon.



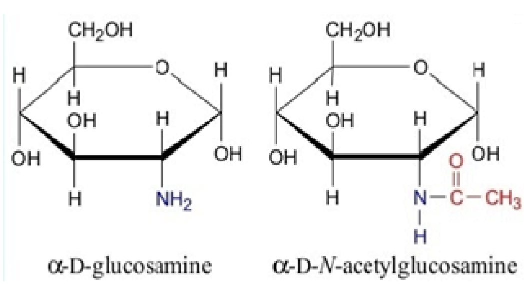
Derived Monosaccharides

i. Glycosides - When hemiacetals react with alcohol, they form acetals and if hemiacetal of sugar reacts with an alcohol to form acetyl, it is known as a glycoside. It is formed by condensation between the hydroxyl groups of anomeric Carbon of monosaccharides whereas the second compound mayor may not be another monosaccharide. For example, ouabain that inhibits the enzyme action that pumps Na^+ and K^+ across the cell membrane.





ii. Amino sugar - Hydroxyl group is replaced by an amino or acetylamino group. For example glucosamine and galactosamine.

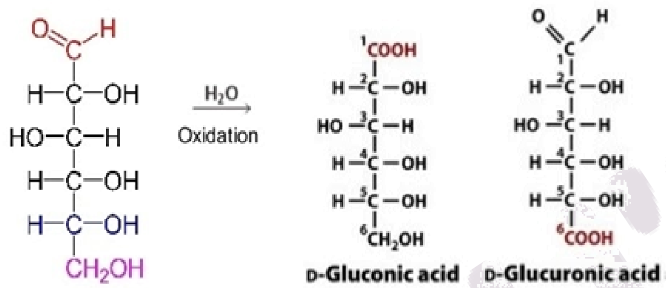


iii. Sugar-acid - Aldehyde group at C1 or the hydroxyl group at C6 is oxidized to produce sugar acid. For example, ascorbic acid, glucuronic acid (oxidation of glucose), and galacturonic acid (oxidation of galactose)

iv. Sugar alcohol - Carbonyl group reduced to the hydroxyl group to form sugar alcohols. For example, glycerol and mannitol (present in brown algae).

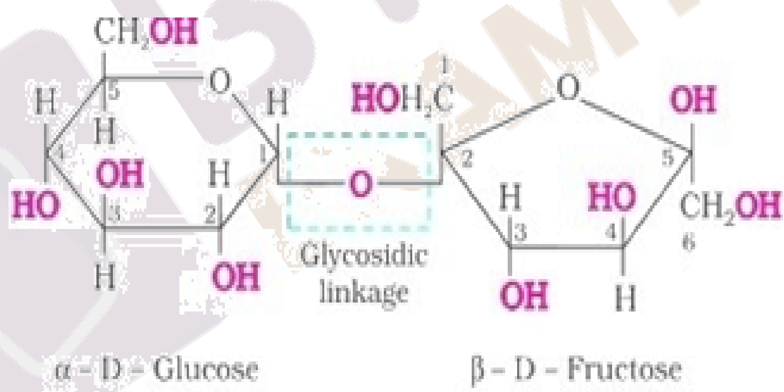
Oligosaccharides

Carbohydrates that produce 10 monosaccharide units at max are known as oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides and so on



Disaccharides

Disaccharides consist of two sugar joined by o-glycosidic bonds**.** The two monosaccharides are linked by oxide linkage and such linkage is known as glycosidic linkage. If the reducing groups (aldehyde or ketone) possess bonds, the sugar is a non-reducing sugar**.** Sucrose is a non-reducing sugar formed as an end product of photosynthesis. In sucrose's structure, the glycosidic linkage is seen at the C1 terminal of α-D-glucose and C2 of β-D-fructose. Maltose is prepared by the breakdown of amylase into starch. Maltose is composed of α-D-glucose in which C1 is of glucose and is linked to C4 of another glucose unit.

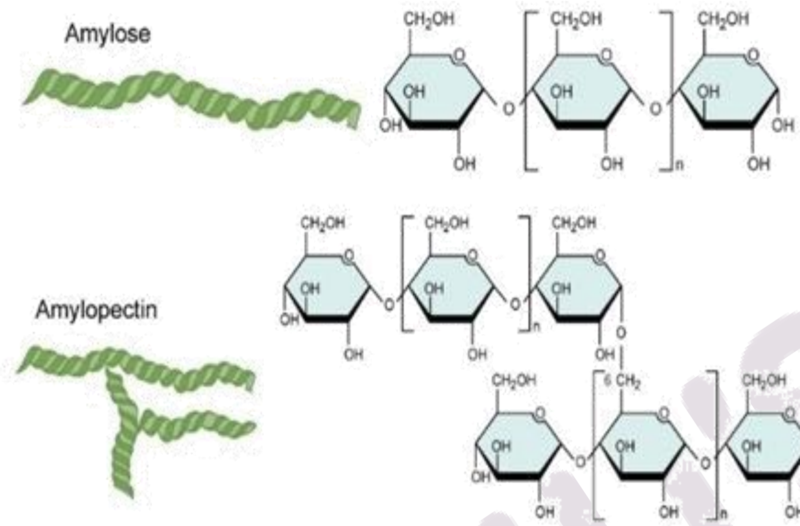


Structure of Sucrose

Polysaccharides

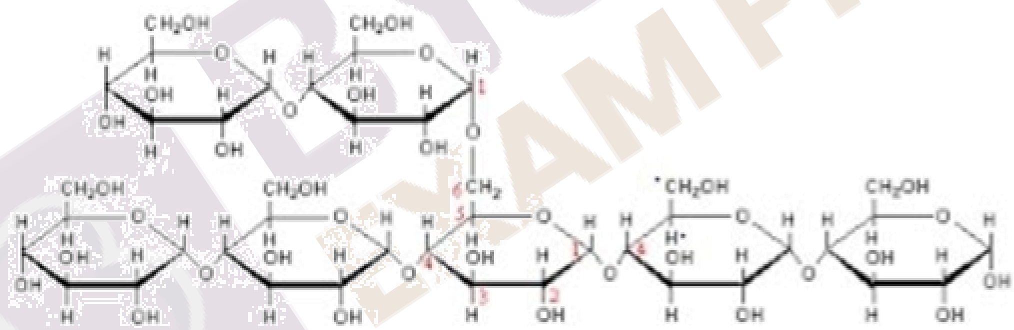
They are the large units of monosaccharides joined together by glycosidic linkages. These molecules mainly are food storage or structural materials. Polysaccharides are broadly classified as homopolysaccharides and heteropolysaccharides.

Homopolysaccharides are the type of polysaccharides that are formed from only one monosaccharide unit. Starch, Glycogen and Cellulose are examples of homopolysaccharides. Starch is used as the glucose storage form of carbohydrates in plants. It contains a mixture of amylase and amylopectin. Amylose is linear unbranched polymer whereas amylopectin is a branched polymer of glucose.



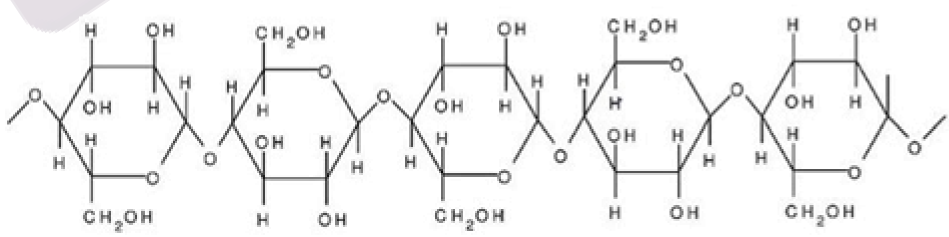
Structure of Amylose and Amylopectin

Glycogen is used as the glucose storage form of carbohydrates in animals, mostly found in the liver and muscle. It is also made up of glycogen and glucose. It is composed of α-1,4-glycosidic bonds with an α-1,6 bond present which is seen at every tenth monomeric unit.



Structure of Glycogen

Cellulose is another example of polymers of glucose is a linear, branched homopolysaccharide of D- glucose units of beta-1, 4-glycosidic linkage. It strengthens the cell wall. Some common forms of cellulose known to each one of us are paper and wood.



Structure of cellulose

ii. Heteropolysaccharides are types of polysaccharides that are made up of different monosaccharide units. Peptidoglycan and hyaluronic acid are some examples of heteropolysaccharides. Peptidoglycan or murein is responsible for the formation of the bacterial cell's cell wall and chitin is responsible for the formation of the exoskeleton of arthropods whereas hyaluronic acid can work as a lubricant in joint's synovial fluids.

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