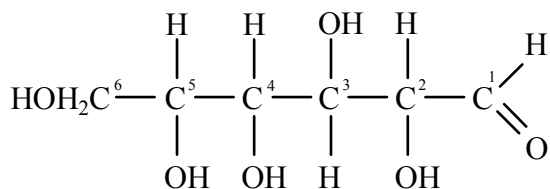


Some Carbohydrate Chemistry

Introduction

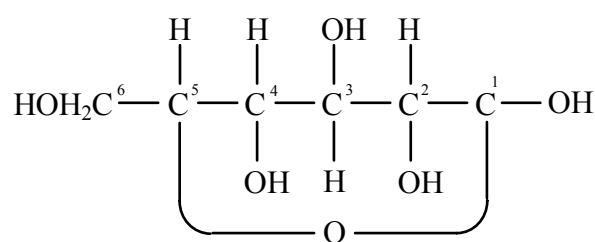
We are usually concerned with **hexoses**, i.e. monosaccharides (such as glucose) with the general formula $(\text{CH}_2\text{O})_6$, and disaccharides and polysaccharides composed of these residues.



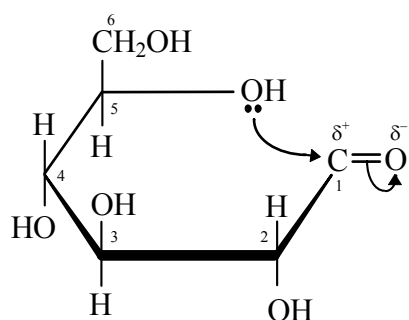
Fischer projection of D-glucose

The structure of glucose can be represented by a **Fischer projection** such as that shown on the left for glucose. There is a carbonyl (aldehyde) group on C₁, making glucose an **aldohexose**. The presence of this group allows glucose to reduce Cu(II) in **Fehling's reagent** and so it is also a **reducing sugar**.

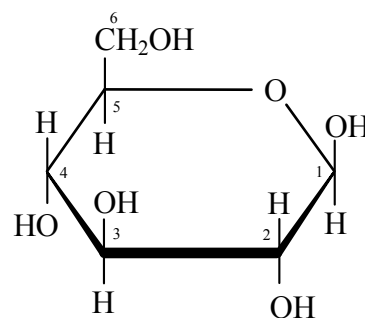
However, only a very small proportion of glucose exists in this open-chain configuration because the hydroxyl group on C₅ is able to react with the carbonyl group on C₁ to produce a closed **pyranose** ring. This is a six-membered ring comprising five carbon atoms and one oxygen atom. The Fischer projection of this structure is shown on the right. However, monosaccharides are best represented by **Haworth projections** (see below right), and you will be expected to recognise and draw these.



Fischer projection of D-glucopyranose



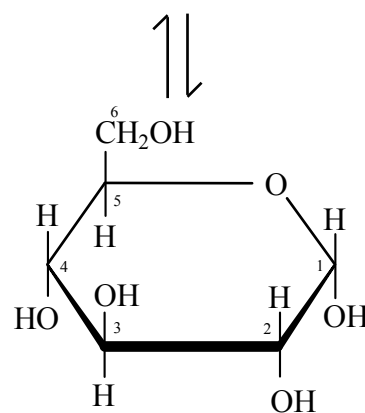
Formation of the pyranose ring



Haworth projection of β-D-glucopyranose

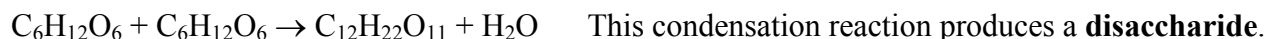
Isomers

C₂, C₃, C₄ and C₅ of aldohexoses are chiral. This is seen most easily in the Fischer projection of glucose at the top of the page (remember, look at the whole of each group attached to these carbon atoms). There are eight different aldohexoses depending on the locations of the hydroxyl groups, and each can exist as a D- or L- enantiomer (D-glucose is most common aldohexose). However, the formation of the pyranose ring causes C₁ to become chiral too. This creates two **anomers** depending upon whether the hydroxyl group on C₁ lies above or below the plane of the ring. C₁ is called the **anomeric carbon atom**. The α and β anomers are interconvertible in aqueous solution (probably via the open-chain configuration), and at equilibrium about 64% of glucose is in the form of the β anomer.

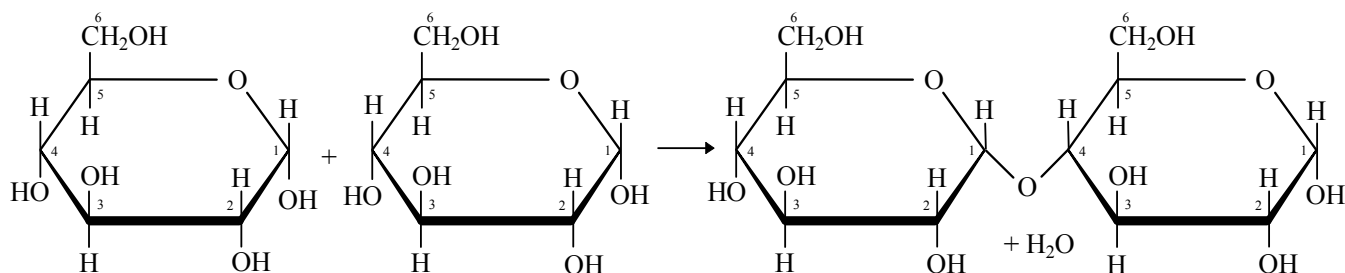


Disaccharides

Two monosaccharides can react together via two hydroxyl groups with the elimination of water:



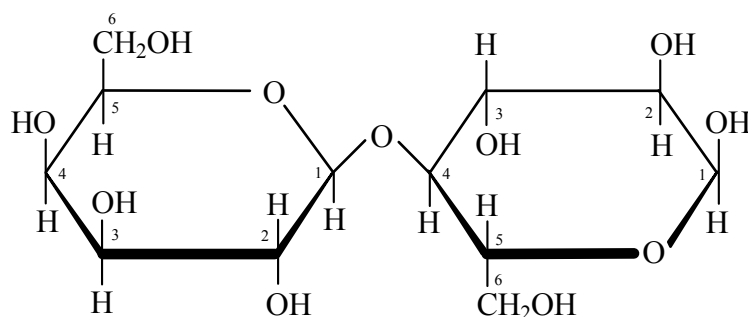
1. Maltose



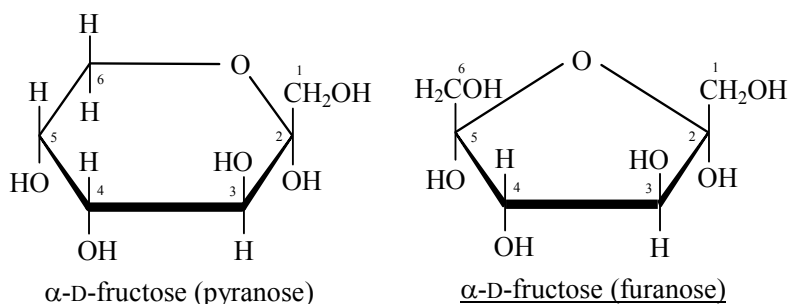
Maltose comprises two glucose molecules joined by an α -1,4-glycosidic bond. C₁ on the second pyranose ring is not involved in the formation of maltose; it is still anomeric and it can form the aldehyde group in an open-chain structure. As a result, like glucose, maltose is a reducing sugar.

2. Lactose

Lactose comprises a galactose molecule joined to a glucose molecule by a β -1,4-glycosidic bond. It has a free anomeric carbon atom and so is a reducing sugar. Note the difference between galactose and glucose at C₄, and that glucose appears “upside down”.



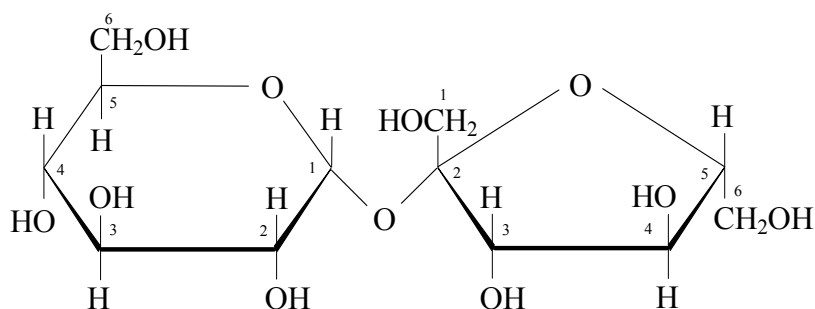
3. Sucrose



Sucrose (“cane sugar”) comprises a glucose molecule joined to a β -fructose molecule by an α -1,2-glycosidic bond. Fructose is rather unusual: as a monosaccharide it exists in the pyranose form, but in disaccharides and polysaccharides it exists in the **furanose** (five-membered ring) form (see left).

A Haworth projection of sucrose is shown on the right. Notice that there are no free anomeric carbon atoms, so sucrose is not a reducing sugar. However, it is optically active producing a clockwise (+) rotation of plane-polarised light. When sucrose is hydrolysed, the mixture produces an anticlockwise (–) rotation of

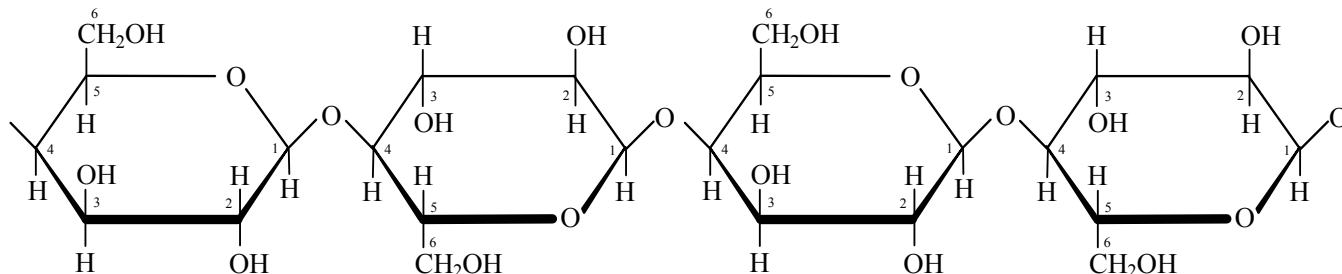
polarised light because glucose is only weakly (+)-rotatory, but fructose is strongly (–)-rotatory. This change is called **inversion**, and the mixture is called **invert sugar**.



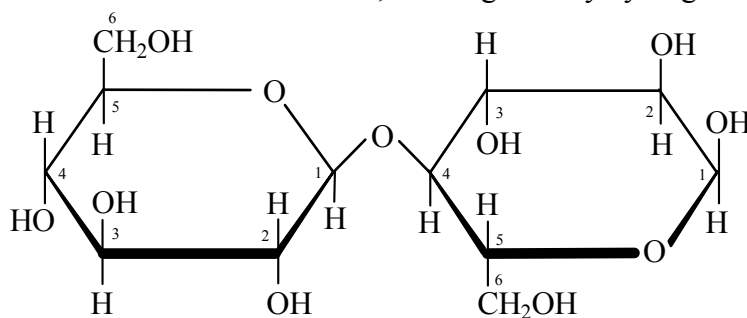
Polysaccharides

A huge variety of polysaccharides exist in nature, being used mainly for storage or as structural components. The polysaccharides covered in Ch09 are all **homopolysaccharides** of glucose – the differences between them come from the different glycosidic bonds. Make sure that you know which bonds occur in these polysaccharides, and the likely physical and chemical properties which result.

1. Cellulose



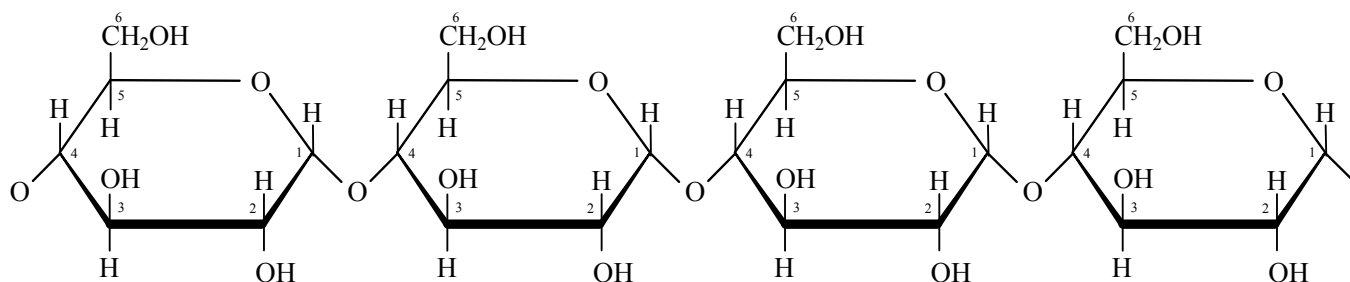
Cellulose comprises a linear molecule in which glucose molecules are joined by β -1,4-glycosidic bonds (see diagram above). Bundles of parallel cellulose chains can form, held together by hydrogen bonds. As a result, cellulose is very tough, and it is the major component of wood (and so paper). Cotton is nearly pure cellulose. If cellulose is completely hydrolysed using strong acids, only D-glucose is formed. However, if it is partially hydrolysed, the disaccharide cellobiose is formed. Note that cellobiose is a reducing sugar.



Cellobiose

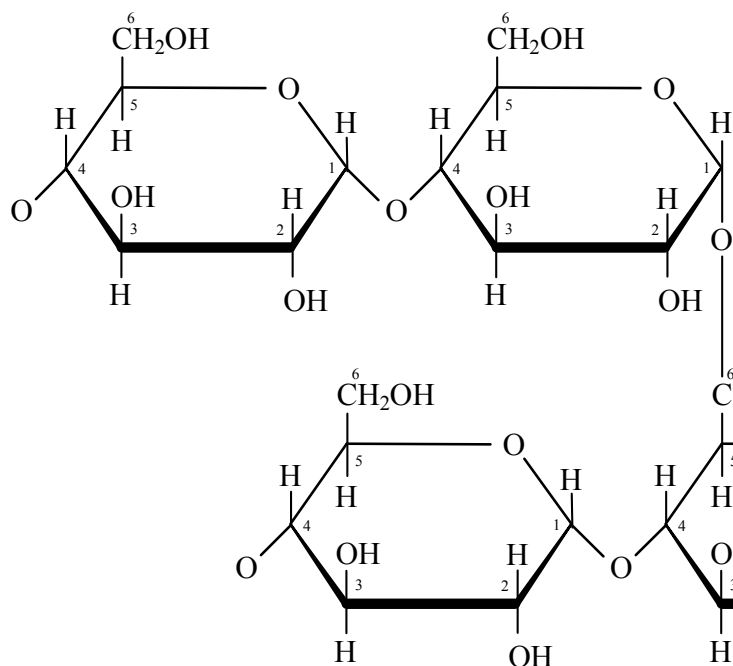
2. Starch

Starch occurs in two forms, α -amylose and amylopectin. Like cellulose, α -amylose is unbranched, but its D-glucose residues are joined by α -1,4-glycosidic bonds. α -amylose is not truly soluble in water, but forms a colloidal suspension of hydrated micelles in which the polysaccharide chains twist into helical coils. Its M_r varies from about 5 000 to 500 000. It gives a blue colour with iodine.



α -amylose

Amylopectin has a highly branched structure (see diagram overleaf). α -1,4-glycosidic bonds form a main chain similar to α -amylose, but every 24 to 30 glucose residues there is an α -1,6-glycosidic bond which creates a branch. Like α -amylose, amylopectin forms colloidal or micellar suspensions, but its M_r can be as high as 100 million, and it gives a red-violet colour with iodine.



Amylopectin

Make sure that you can identify the α -1,4-glycosidic bonds and the β -1,6-glycosidic bonds here.

3. Glycogen

Glycogen is very similar to amylopectin in that α -1,4-glycosidic bonds form a main chain with α -1,6-glycosidic bonds creating branches. It also forms a red-violet colour with iodine. However, it is more branched (branches occur every 8 to 12 glucose residues), and it can be much larger.

Hydrolysis of polysaccharides by enzymes

Polysaccharides can hydrolysed enzymically in various ways depending on the enzyme used:

1. α -amylase is found in saliva and pancreatic juice. It can hydrolyse α -1,4-glycosidic bonds at random in polysaccharides, but it will not hydrolyse the α -1,4-glycosidic bond in a maltose unit.
2. β -amylase is found in malt. It can hydrolyse the α -1,4-glycosidic bonds between successive maltose units, starting from the non-reducing end.
3. α -1,6-glucosidase can hydrolyse α -1,6-glycosidic bonds, i.e. it will attack branches.

Enzymes which will hydrolyse cellulose are rare. Some bacteria and fungi produce these **cellulases**, but most animals do not and so are unable to digest cellulose. Ruminants such as cows use bacteria in part of their gut to digest the cellulose for them. However, although we cannot use cellulose as a source of energy, it is an important food component as it provides roughage which helps food pass through the gut.

In starch, α -amylase is hydrolysed by α -amylase to produce a mixture of glucose and free maltose. It is also hydrolysed by β -amylase, which nibbles away from the non-reducing end to produce maltose quantitatively. Amylopectin is also hydrolysed by both amylases to produce **dextrins**, which are polysaccharides of various sizes from the branches. Continued hydrolysis by β -amylase produces a highly branched core called a **limit dextrin** (see diagram on the right). The combined action of β -amylase and α -1,6-glucosidase will completely degrade starch. A similar situation exists for glycogen.

