Disaccharides

All the disaccharides are crystalline solids, soluble in water, and fall into two classes, the *reducing* sugars and the *non-reducing* sugars.

Just as methanol forms methyl glycosides with the monosaccharides, so can other hydroxy-compounds form similar unions with the monosaccharides. Since the latter are themselves hydroxy-compounds, it is possible that they can link up with themselves to form acetals, *i.e.*, glycosides in which the aglycon is another sugar molecule. A number of such compounds occur in nature, *e.g.*, *sucrose*, *maltose* and *lactose*.

Sucrose, cane-sugar, $C_{12}H_{22}O_{11}$, is one of the most important compounds commercially, and is obtained from the sugar-cane and sugar-beet. In addition to crystalline sucrose, a syrup is always obtained which will not crystallise. This syrup, known as *molasses*, is also a commercial product.

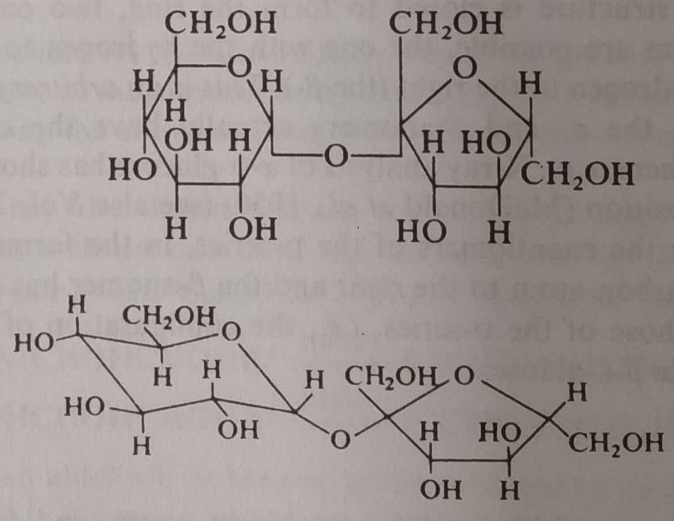
Sucrose is a white crystalline solid, m.p. 180°C, soluble in water. When heated above its melting point, it forms a brown substance known as caramel. Concentrated sulphuric acid chars sucrose, the product being almost pure carbon. Sucrose is dextrorotatory, its specific rotation being +66·5°. On hydrolysis with dilute acids sucrose yields an equimolecular mixture of D(+)-glucose and D(−)-fructose:

$$C_{12}H_{22}O_{11}+H_2O \xrightarrow{HCl} \underset{\text{glucose}}{C_6H_{12}O_6}+\underset{\text{fructose}}{C_6H_{12}O_6}$$

Since D(−)-fructose has a greater specific rotation than D(+)-glucose, the resulting mixture is lævorotatory. Because of this, the hydrolysis of cane-sugar is known as *the inversion of cane-sugar* (this is not to be confused with the *Walden inversion*), and the mixture is known as *invert sugar*. The inversion (*i.e.*, hydrolysis) of cane-sugar may also be effected by the enzyme *invertase* which is found in yeast.

Controlled oxidation of sucrose in alkaline solution with air gives D-arabonic acid. Oxidation of sucrose with nitric acid under different conditions gives either oxalic acid (80%), tartaric acid (40%), or glucaric acid (30%). Hydrogenation of sucrose under controlled conditions gives a mixture of mannitol and sorbitol (these may be separated by fractional crystallisation).

Sucrose is *not* a reducing sugar, *e.g.*, it will not reduce Fehling's solution; it does not form an oxime or an osazone, and does not undergo mutarotation. This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose. Thus a tentative structure of sucrose is one in which two molecules, glucose and fructose, are linked by the aldehyde group of the former and ketonic group of the latter. This has been amply confirmed by further work, and sucrose has been shown to be α-D-glucopyranosyl-β-D-fructofuranoside (*i.e.*, α-glucose is linked to β-fructose).



(+)-sucrose

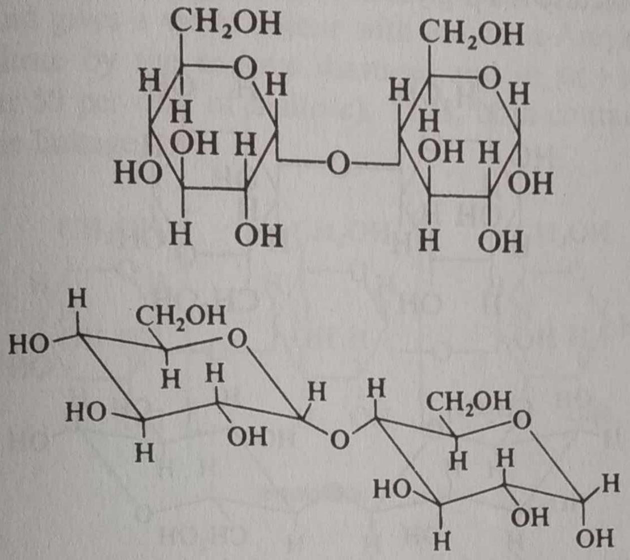
It should be noted that the fructose molecule in sucrose exists as the furanose form, and that when sucrose is hydrolysed, it is the pyranose form of fructose which is isolated.

Maltose (*malt sugar*), $C_{12}H_{22}O_{11}$, is produced by the action of malt (which contains the enzyme *diastase*) on starch:

$$(C_6H_{10}O_6)_n+\frac{n}{2}H_2O \xrightarrow{\text{diastase}} \frac{n}{2}C_{12}H_{22}O_{11}$$

Maltose is a white crystalline solid, m.p. 160–165°C, soluble in water, and is dextrorotatory.

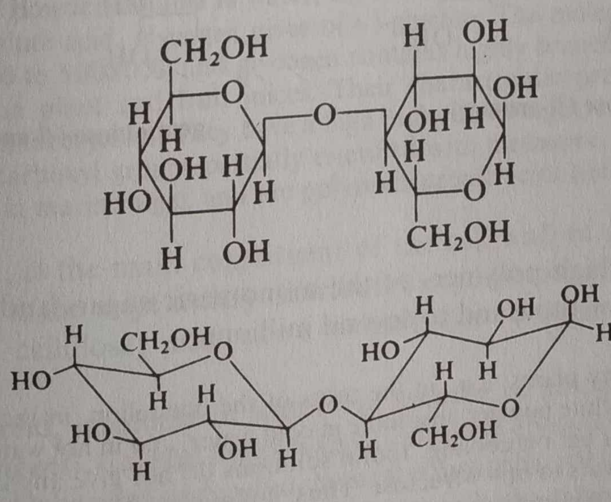
When it is hydrolysed with dilute acids or by the enzyme *maltase*, maltose yields two molecules of D(+)-glucose. Maltose is a reducing sugar, *e.g.*, it reduces Fehling's solution; it forms an oxime and an osazone, and undergoes mutarotation. This indicates that at least one aldehyde group (of the two glucose molecules) is free in maltose. Further work has shown that maltose is 4-*O*-α-D-glucopyranosyl-D-glucopyranose (*i.e.*, the reducing half is linked to the non-reducing half by an α-link). It should also be noted that the enzyme maltase splits only α-glycosidic links, and hence is used to ascertain the presence of this bond in disaccharides and polysaccharides.



(+)-**maltose**; **α-anomer**

Cellobiose, $C_{12}H_{22}O_{11}$, may be obtained from cellulose by acetylating good filter paper (which is almost pure cellulose) with acetic anhydride in the presence of concentrated sulphuric acid. The octa-acetate of cellobiose so obtained is hydrolysed with potassium hydroxide or with sodium ethoxide, whereupon cellobiose is produced.

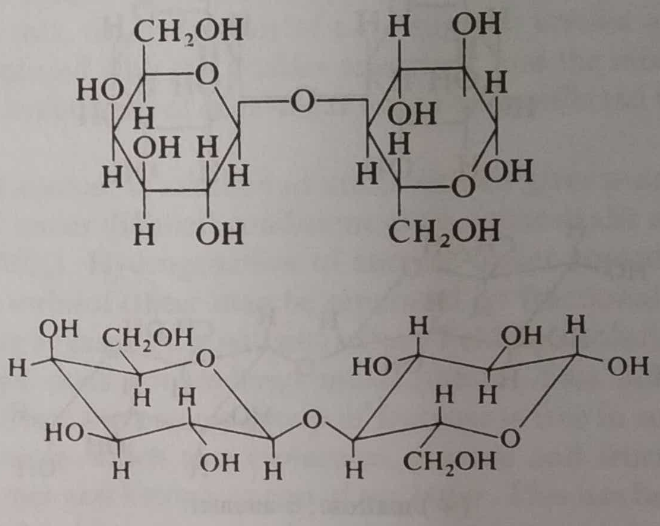
Cellobiose is a white crystalline solid, m.p. 225°C, soluble in water, and dextrorotatory. When hydrolysed with dilute acids or by the enzyme *emulsin*, it yields two molecules of D(+)-glucose. It is a reducing sugar, forms an oxime and osazone, and undergoes mutarotation. Cellobiose is 4-*O*-*β*-D-glucopyranosyl-D-glucopyranose. Thus, the only difference between cellobiose and maltose is that in the former the glycosidic link is *β*, whereas in the latter it is α. Furthermore, the enzyme emulsin splits only *β*-glycosidic links (*cf.* maltase).



(+)-**cellobiose**; **α-anomer**

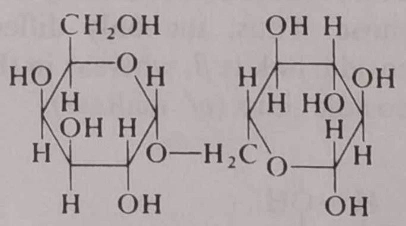
Lactose (*milk-sugar*), $C_{12}H_{22}O_{11}$, occurs in the milk of all animals, and is prepared commercially from whey by evaporation to crystallisation; whey is obtained as a by-product in the manufacture of cheese.

Lactose is a white crystalline solid, m.p. 203°C (with decomposition), soluble in water, and is dextrorotatory. It is hydrolysed by dilute acids or by the enzyme *lactase*, to an equimolecular mixture of D(+)-glucose and D(+)-galactose. Lactose is a reducing sugar, forms an oxime and osazone and undergoes mutarotation. It is 4-*O*-*β*-D-galactopyranosyl-D-glucopyranose. It should also be noted that lactase is a *β*-glycosidase, *i.e.*, splits *β*-glycosides (it has been shown to be identical with emulsin).

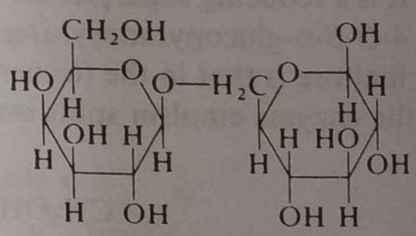


(+)-lactose; *β*-anomer

Sucrose, maltose and lactose are three disaccharides which occur naturally. Cellobiose may be prepared from cellulose. Two other disaccharides which have been prepared are **melibiose** (from the trisaccharide *raffinose*), and **gentiobiose** (from the trisaccharide *gentianose*). These differ from the other disaccharides in that the two monosaccharide molecules are linked by the *sixth* carbon atom (the aldehyde carbon atom being number one) of the reducing monosaccharide (see also Vol. 2, Ch. 7):



melibiose (*β*-anomer)



gentiobiose (*β*-anomer)

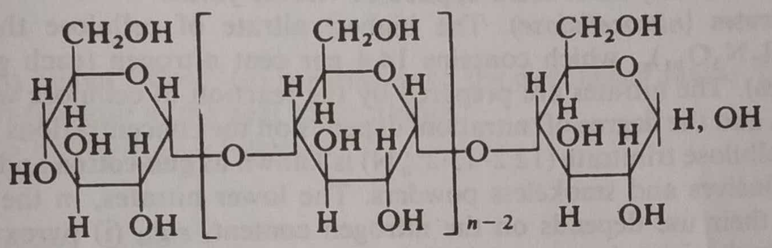
Polysaccharides

The polysaccharides are high polymers of the monomeric sugars and have molecular weights that may range from a few thousand to several millions.

Inulin occurs in many plants, *e.g.*, in the roots of the dandelion, in the tubers of the dahlia and in certain lichens. It is a white powder, insoluble in cold water, and in hot water forms a colloidal solution which does not form a gel on cooling. Inulin solutions do not give any colour with iodine. Inulin is hydrolysed by dilute acids to D(−)-fructose. Thus, inulin is $(C_6H_{10}O_5)_n$, and n has a value of about 30 (obtained by chemical methods).

Starch, $(C_6H_{10}O_5)_n$, occurs in all green plants; the commercial sources of starch are maize wheat, barley, rice, potatoes and sorghum.

Starch consists of two fractions, one being known as **α-amylose** (the 'A' fraction), and the other as **β-amylose** or **amylopectin** (the 'B' fraction); the former comprises 10–20 per cent of starch, and the latter 80-90 per cent. α-Amylose is insoluble in water, and the solution gives a blue colour with iodine. This blue colour is believed to be due to the formation of an inclusion complex. An aqueous solution of α-amylose slowly forms a precipitate, since α-amylose has a strong tendency to 'revert' to the insoluble state in solution. Amylopectin is soluble in water, is stable in contact with water, and gives a violet colour with iodine. α-Amylose and amylopectin are both hydrolysed to maltose by the enzyme diastase, and to D(+)-glucose by dilute acids (amylopectin gives about 50 per cent of maltose). Thus, both contain D-glucopyranose units joined by the α-glucosidic linkage.



α-amylose

α-Amylose consists of an *unbranched chain*, with a molecular weight varying between 10 000 ($n = \sim 60$) and 1 000 000 ($n = \sim 6000$). The value of n depends on the source and treatment of α-amylose. Amylopectin differs from α-amylose in that it contains *branched chains*, the branching occurring through 1,6-linkages (and other linkages) and the length of the unbranched sections being about 24–30 glucose units. The molecular weights recorded for amylopectin vary between 50 000 and 10 000 000.

The **dextrins**, $(C_6H_{10}O_5)_n$, are produced by the partial hydrolysis of starch by boiling with water under pressure at about 250°. They are white powders, and are used for making adhesives and confectionery, for sizing paper, etc.

Glycogen, $(C_6H_{10}O_5)_n$, is found in nearly all animal cells, occurring mainly in the liver; it is the reserve carbohydrate of animals, and so is often known as '*animal starch*'. It has also been isolated from plant sources.

Glycogen is a white powder, soluble in water, the solution giving a purplish-red colour with iodine. On hydrolysis with dilute acid, glycogen gives D(+)-glucose. The molecular weight of glycogen has been given as 1 000 000 to 5 000 000, and glycogen contains highly branched chains.

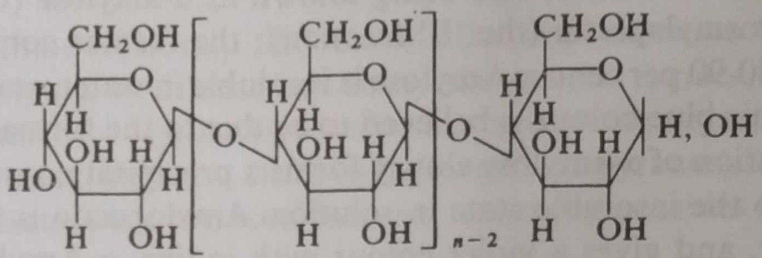
Pectins are found in plant and fruit juices. Their characteristic property is the ability of their solutions to gelate, *i.e.*, form jellies. They have a high molecular weight, and are polygalacturonic acids (linked 1,4) with the carboxyl groups partially esterified with methanol.

Alginic acids occur in marine algæ, and are polymannuronic acids (linked 1,4).

Cellulose, $(C_6H_{10}O_5)_n$, is the main constituent of the cell-wall of plants, and also occurs in certain animal tissues. It is the most widely distributed organic compound, and its main source is cotton (almost pure cellulose) and wood (which also contains *lignin*, which is not a polysaccharide).

Cellulose is a white solid, insoluble in water but soluble in ammoniacal copper hydroxide solution (*Schweitzer's reagent*). Careful hydrolysis of cellulose gives cellobiose; it is also possible to isolate *cellotriose* (trisaccharide) and *cellotetrose* (tetrasaccharide). All of these saccharides, on further hydrolysis, yield only D(+)-glucose which exists in the β-form in cellulose (*cf.* starch).

The molecular weight of cellulose varies between 20 000 and 500 000, and the compound consists of an unbranched chain.



cellulose