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Space-filling model of **aspartame**, a noncaloric sweetener, widely used in the drink and food industry.

CHAPTER

7

Carbohydrates-III

Oligosaccharides

The oligosaccharides yield 2 to 10 monosaccharide molecules on hydrolysis. *Disaccharides are the most common oligosaccharides found in nature.* Most of the naturally-occurring representatives occur in plant rather than in animal sources. The three most important disaccharides found free in appreciable quantities are sucrose, lactose and maltose ; a few others are cellobiose and trehalose.

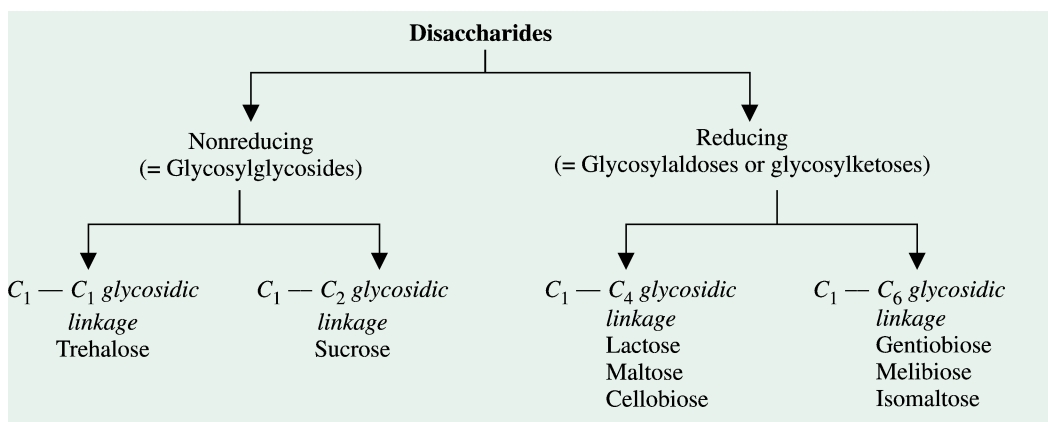
CONFORMATIONS OF PYRANOSE AND FURANOSE RINGS

To name disaccharides, certain rules are followed. First, the compound is written with its nonreducing end to the left. An *O* precedes the name of the first (left) monosaccharide unit, as a reminder that the sugar-sugar linkage is through an oxygen atom. The configuration at the anomeric carbon joining the first (left) monosaccharide unit to the second is then given (α or β). To distinguish 5- and 6-membered ring structures, "furanosyl" or "pyranosyl" is inserted in the name of each monosaccharide unit. The two carbon atoms joined by the glycosidic bond are then shown in parentheses, with an arrow connecting the two numbers; for example, (1 \rightarrow 4) shows that C-1 of first sugar residue is joined to C-4 of the second. If there is a third residue, the second glycosidic bond is described next, by the same conventions. To shorten the description of a complex **polysaccharide**, 3-letter abbreviations for each monosaccharide are often used.

Following this convention for naming oligosaccharides, sucrose is therefore named *O*- α -D- glucopyranosyl-

(1→2)-β-D-fructofuranoside. Because most sugars are the D-enantiomers, and the pyranose form predominates, a shorthand version of the formal name of such compounds is used, giving the configuration of the anomeric carbon and naming the carbons joined by the glycosidic bond. In this abbreviated nomenclature, sucrose is Glc (α1→2) Fru.

Based on the type of linkage present in their molecule, the disaccharides may be classified as follows :



SUCROSE OR SACCHAROSE (Table sugar, Cane sugar, Beet sugar)

Occurrence. Sucrose is the common sugar of commerce and kitchen (hence, also called 'household' sugar) and is widely distributed in all photosynthetic plants. It is the chief constituent of sugarcane (*Saccharum officinarum*), beet (*Beta vulgaris*) and maple (*Acer saccharina*) and is also present in pineapple (*Ananas sativus*) and carrot (*Daucus carota*). Sucrose occurs in varying amounts in different plant organs such as fruits, seeds, flowers and roots. Nectar of flowers is particularly rich in sucrose. It is the raw material for honey. *Sucrose is probably the only foodstuff used in the crystalline form.*

Sucrose is something of a riddle in plant biochemistry. Although D-glucose is the major building block of both starch and cellulose, sucrose is a major intermediate product of photosynthesis. It is the predominant form in which sugar is transported in most plants from the leaves to other organs of plants *via* their vascular system.

Chemistry. It is derived commercially from either sugarcane or beet. Refinement removes the yellow-brown pigments of unrefined sugar to produce the white crystal form of table sugar, while leaving a syrup which does not crystallize. This syrup, known as *molasses*, is also a commercial product and is the least refined form of sucrose. In plants, sucrose is formed by elimination of a molecule of water from glycosidic hydroxyl groups (marked by an asterisk) or α-D-glucose and β-D-fructose (Fig. 7-1.)

It is noteworthy that fructose possesses the furanose ring structure in the sucrose molecule, although the pyranose ring is the dominant and more stable form in the free ketohexose. The linkage between the two disaccharide moieties (= units) of sucrose is a glycosidic one between C₁ of glucose and C₂ of fructose.

Properties. Sucrose is a white crystalline solid, soluble in water and with a melting point 180°C. When heated above its melting point, it forms a brown substance known as *caramel*. Concentrated sulfuric acid chars sucrose, the product being almost pure carbon. It is dextrorotatory and has a

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specific rotation of $+66.7^\circ$. It is by far the sweetest of the 3 common disaccharides (sucrose, lactose, maltose). It is also sweeter than glucose (refer Table 7-1). It crystallizes in colourless crystals.

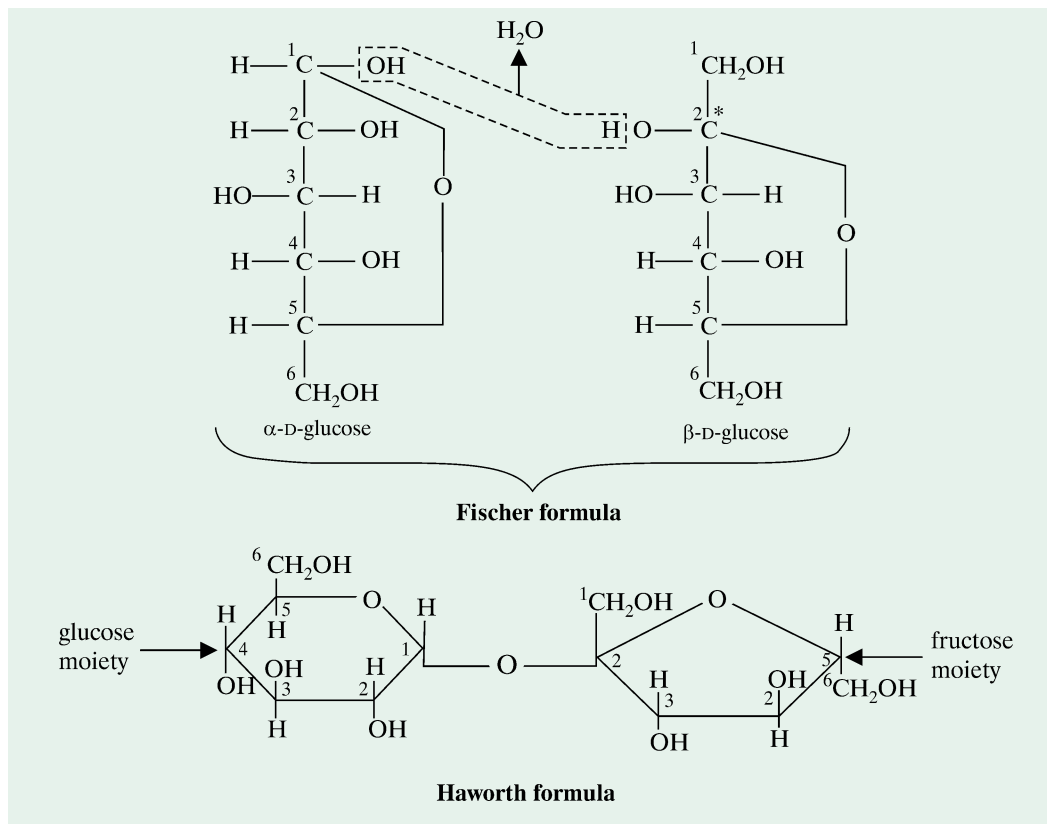


Fig. 7-1. Structure of sucrose

O- α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranoside or Glc (α 1 \rightarrow 2) Fru

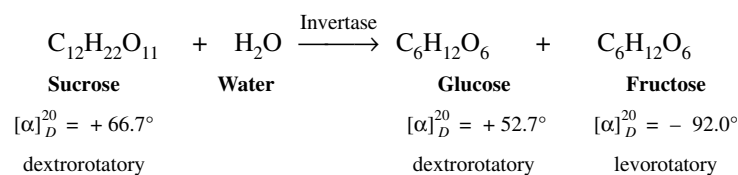
It can be seen from the formula of sucrose that both the carbonyl groups (marked by an asterisk) are involved in the formation of glycosidic bond. Consequently, sucrose contains no active group and, therefore, does not exhibit those properties which depend upon the presence of this group. Obviously, sucrose does not exhibit mutarotation and is *not* a reducing sugar. It also does not form an osazone or an oxime.

Hydrolysis. Upon hydrolysis, sucrose yields equimolar mixture of glucose and fructose which is often called *invert sugar*. This mixture readily reduces Fehling's solution and other alike reagents. The name 'invert sugar' is given to this mixture because the levorotatory fructose, thus produced, changes (or inverts) the previous dextrorotatory action of the sucrose. In fact, sucrose (which is dextrorotatory with a specific rotation, $[\alpha]_D^{20}$ of $+66.7^\circ$), upon hydrolysis, gives a mixture of equimolar quantities of D(+) glucose (dextrorotatory; $[\alpha]_D^{20}$ of $+52.7^\circ$) and D(-) fructose (levorotatory; $[\alpha]_D^{20}$ of -92.0°). And as the levorotation of fructose is greater than the dextrorotation of glucose, the mixture so obtained is levorotatory, contrary to the initial dextrorotatory sucrose.

Table 7-1. Sweetness index* of some sugars and noncaloric sweeteners

| Sugar / Sweetener | Relative sweetness |
|--------------------------------|--------------------|
| Sugars | |
| Lactose | 0.16 |
| Raffinose | 0.20 |
| D-galactose | 0.32 |
| Maltose | 0.32 |
| D-xylose | 0.40 |
| Glycol | 0.50 |
| D-glucose | 0.74 |
| Sucrose | 1.00 |
| Invert sugar | 1.23 |
| D-fructose | 1.73 |
| Sweeteners | |
| Sucaryl sodium | 30 |
| Aspartame | 180 |
| Acesulfame-K | 200 |
| Stevia extract | 300 |
| Saccharin | 400 |
| Neohesperidine dihydrochalcone | 1,000 |
| Monellin | 2,000 |

* Sweetness index is ascertained with respect to sucrose whose sweetness level is arbitrarily taken as one.



Mixture of glucose and fructose is levorotatory with $[\alpha]_D^{20}$ value of $(92.0 - 52.7) = -39.3^\circ$.

This reaction which is called “inversion of sucrose” is catalyzed by the enzyme invertase and also by H^+ ions. Animals cannot absorb sucrose as such, but it is made available for absorption by the enzyme sucrase present in the intestinal mucosal cells. As already pointed out, this enzyme catalyzes the hydrolysis of sucrose to D-glucose and D-fructose, which are readily absorbed in the bloodstream.

It is interesting to note that the invert sugar is more sweeter than the sucrose itself owing to the presence of fructose in invert sugar which is sweetest of all the sugars. This also explains why honey which contains a large proportion of invert sugar is sweeter than sucrose. The invert sugar is used in candy both because of its sweetness and also because the monosaccharides do not crystallize.

Invertase is also called *sucrase*, *saccharase* or *6-D-fructosidase* the first name being the most preferred one. This enzyme has been found to occur in green leaves, fruits, grains, stems, potato tubers, some roots, pollen and such lower plants as fungi and bacteria. It is especially abundant in yeast. Salts of heavy metals (Ag, Cu, Hg) inhibit its action. Maximum activity is obtained with low concentrations of sucrose (5–10%). Sucrase also hydrolyzes the sugars gentianose, raffinose, stachyose and, to some extent, inulin.

THE ARTIFICIAL OR SYNTHETIC SWEETENERS

Sweeteners are customarily grouped into two categories, based on the difference in the amount of energy provided by them. These two groupings are :

A. Nutritive or Caloric Sweeteners. These contain calories, hence have nutritive value. These include sugar sweeteners (*e.g.*, refined sugars, high fructose corn syrup, crystalline fructose, glucose, dextrose, corn sweeteners, honey, lactose, maltose, invert sugars, concentrated fruit juice) and sugar alcohols.

B. Nonnutritive or Noncaloric Sweeteners. These contain no calories, hence have no nutritive value. These have been developed artificially, hence also called as **artificial sweeteners**. As they sweeten with little volume, they may also be referred to as **high-intensity sweeteners**. They have been developed especially for obese or diabetics, for whom sugar consumption is harmful. Artificial sweeteners stimulate the taste buds of the tongue that are stimulated by sugars but, unlike sugars, they are of no food value and may have harmful effects, if used to excess. Some sweeteners are considered 'Generally Recognized As safe' (GRAS) ingredients and others are considered food additives. The safety limit of food additives or conditions of use is expressed as the acceptable daily intake (ADI), that is, the estimated amount per kilogram body weight that a person can safely consume every day over a lifetime without risk. ADI is a conservative level – it usually reflects an amount 100 times less than the maximum level at which no observed adverse effects occur in animals.

A description of some important artificial sweeteners (Fig. 7.2) follows :

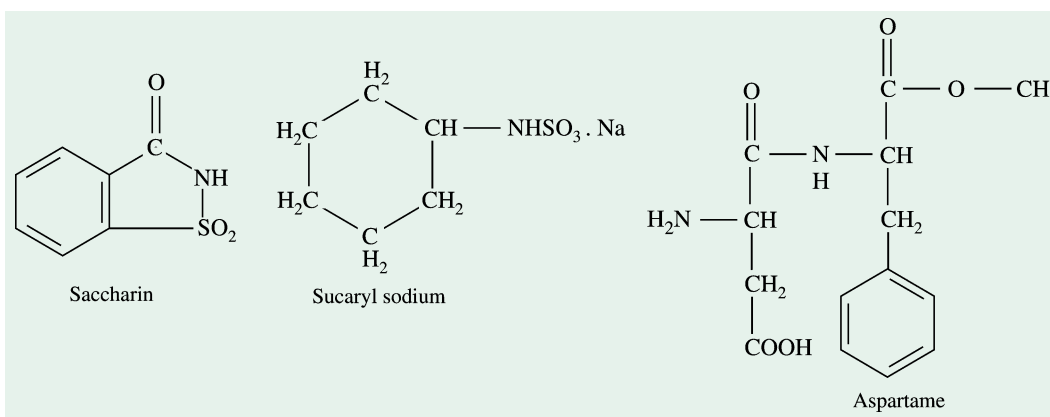


Fig. 7-2. Some artificial sweeteners

1. Saccharin. Saccharin is the first artificial sweetener which was discovered accidentally by Constantine Fahlberg in 1879. *It is the most-widely used artificial sweeteners.* In fact, saccharin was not used extensively as a sweetener until the advent of World War I when the use of sugar was strictly rationed. When World War II hit, sugar rationing started again, leading to another significant rise in saccharin use. Saccharin is sold under the tradename Sweetex™. It has a molecular formula $C_6H_4SO_2CONH$, and its chemical structure is different from that of a carbohydrate. It possesses no OH group but rather a sulfonamide. It is manufactured from toluene, $C_6H_5CH_3$. Saccharin is a white, crystalline, sparingly soluble solid with a m.p. 227 °C. It is heat-stable and is 400 times sweeter than sucrose by weight in aqueous solutions (Table 7-1). It is advised that pregnant women

While working on new food preservatives, Fahlberg accidentally spilled a compound he had synthesized. When he ate his dinner that night, he noticed that the intense residual sweetness of the chemical still lingered on his hands. He named the compound saccharin after the Latin *saccharum* which means sugar, referring sweetness in this context.

avoid saccharin.

2. Sucaryl sodium. It is also a sulfonamide and is 30 times sweeter than sucrose.

3. Monellin. This protein sweetener is present in the sap of serendipity berries, fruit of a western African plant, *Dioscoreophyllum cumminsii*. This sweet protein is composed of two noncovalently-associated polypeptide chains (one having 42 amino acid residues and the other 50 residues) and is 2,000 times as sweet as sucrose. Monellin's sweetness requires the undissociated protein since neither protomer has a sweet taste. Presently, monellin is being studied as a nonfattening, nontoxic food sweetener for human use. In case of the African plant *Katemfe*, its intense sweetness is attributed to two proteins, which together are 1,600 times sweeter than sucrose.

4. Aspartame. This is an essentially noncaloric, sugar-free sweetener being commercially used (Technically, aspartame is nutritive as it contains 4 calories per gram, but since it is added in such tiny doses that it really makes little, if any, contribution to the total calorific intake). Aspartame is a synthesized dipeptide, containing aspartic acid (Asp) and the methyl ester of phenylalanine (Phe).

Aspartame is marketed under the tradenames Nutrasweet™ (when included in food) and Equal™ (when sold as a powder). It is about 180 times sweeter than sucrose by weight (*i.e.*, about half as sweet than saccharin) and does not have the bitter aftertaste, often associated with saccharin. It, thus, has a better taste profile than saccharin. Interestingly, (S–S)-aspartame is a sweetener whereas its enantiomer, (S–R)-aspartame is bitter in taste. However, aspartame has a shelf life of about 6 months, after which it breaks down into its components and loses its sweetening power. Also, it splits at high temperatures (which means that it cannot be used in hot or baked items). Intestinal enzymes hydrolyze aspartame to phenylalanine, aspartic acid and methanol in the ratio 5 : 4 : 1.

It is now widely used in the drink and food industry, *e.g.*, soft drinks, cold cereals, beverages, gelatin desserts, puddings, toppings and fillings for baked goods, and cookies. Aspartame has an additional advantage as it does not promote tooth decay, hence also used in gum and candies. Some users have reported suffered from adverse reactions to aspartame such as headache, dizziness, seizure and nausea. Such persons must abstain from using it. Because aspartame is made from phenylalanine, people with phenylketonuria (who cannot metabolize Phe) should avoid aspartame. Also, the pregnant women are advised to refrain from aspartame. Aspartame is approved for use in more than 100 nations.

5. Alitame. Alitame, also a peptide, is composed of *l*-aspartic acid, *d*-alanine and a novel C-terminal amide moiety. It is 2,000 times sweeter than sucrose without the bitter and metallic qualities of noncaloric sweeteners. Curiously, although alitame tastes sweet to most people, it tastes bitter to a miniscule part of population. This may be due to a genetic difference in taste perception. Alitame blends with other artificial sweeteners to maximize the quality of sweetness.

6. Neohesperidine dihydrochalcone. It is a carboxylic derivative product from bitter components of the grape fruit's skin. It is about 1,500–1,800 times sweeter than sucrose at threshold limit concentration but the intensity depends on many factors such as pH and the product to which it is added. It takes some time to reach maximum sweetness perception and a very light sweet methanol-like aftertaste. It has a synergistic sweetening effect when combined with sugar alcohols, and with aspartame, saccharin, acesulfame-K and cyclamate. This characteristic has many advantages :

- (a) reduction in cost.
- (b) reduction in the daily intake of any particular sweetener
- (c) a more satisfying sucrose-like taste.

It may be used in beverages, juices, dairy products and alcoholic drinks such as beer. It is also used to sweeten diet and low-calorie food.

7. Sugar alcohols. Polyalcohols (or polyols) are part of a group of compounds called sugar alcohols. These include sorbitol, manitol and xylitol. Polyols can also be categorized as '*sugar*

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replacers' because they can replace sugar sweeteners, usually on a one-to-one basis. They offer less energy and offer potential health benefits (*e.g.*, reduced glycemic response, reduced dental caries risk, etc). Commercially, these sweeteners are synthesized and not extracted from natural sources. Sugar alcohols contain 2-3 calories per gram but are only slowly metabolized to glucose. These are found in sugar-free candy, gum, cake mix and syrup, as well as some medications. Like aspartame, they also do not promote tooth decay. However, sugar alcohols can cause gastrointestinal symptoms ranging from mild stomach discomfort to severe diarrhea. Hence, those products likely to cause ingestion of 50 g or more of sorbitol are required to carry a level reading,

“Excess consumption may have a laxative effect”.

8. Acesulfame potassium (=Acesulfame-K). It is the newest alternative sweetener approved in the US and is marketed under the tradenames Sunette™ and SweetOne™. It was formulated in the late 1960s and was evaluated for safety in 1983. Food and Drugs Administration (FDA) approved acesulfame-K in 1988. Acesulfame-K is about 200 times sweeter than sucrose. Blends of acesulfame-K with other nutritive and nonnutritive sweeteners can synergize the sweetness potential and the bitter taste. It has a shelf life of about 3-4 years as it is heat-stable (hence can be used for baked items). It does not provide any energy as it is not metabolized by the body and is excreted in the urine unchanged. Acesulfame-K finds applications in gum, powdered drink mixes, gelatins, puddings, candy, throat lozenges, tabletop sweeteners, yogurt and nondairy creamers. It is also used as a sweetener in soft drinks, chewing gum, coffee, tea, flavouring, salted food and dairy items.

9. Stevia extract. The plant sweet honey leaf (*Stevia rebaudiana*) is a herbaceous perennial. It is native to Brazil, Venezuela, Columbia and Paraguay where the native Guarani have used it for over 1,500 years to sweeten otherwise unpalatable medicinal drinks. It is a natural herbal sweetener. The sweetness of *Stevia* is attributed to 2 compounds, *stevioside* and *rebaudioside*, which can be up to 300 times sweeter than sucrose. *Stevia* has an advantage over artificial sweeteners in that it is stable at high temperatures and a pH range of 3 to 9. *Stevia* extract is used as sweetener or flavour enhancer in many countries such as China, Japan, Korea, Israel, Brazil and Paraguay. It is also used in soft drinks, ice creams, cookies, pickles, chewing gum, tea and skin care products. *Stevia* plant and its extract both are used in weight-loss programmes because of their ability to reduce the cravings for sweet and fatty foods. Sweet honey leaf is, however, banned in food products in the US because a derivative of stevioside may be harmful to humans.

Thus, mankind's search for the ultimate sweetener goes on. In fact, sweetness is rather subjective measure of taste. The sensation of sweetness is believed to be due to the interaction between molecules of the sweetening agent and receptor sites of the tongue. Furthermore, perception of sweet taste can be influenced by genetic behaviour, health status and aging. Robert Margolskee of the Mount Sinai of Medicine in New York hopes to have definite proof that gene TIR3 is truly the “sweet tooth” receptor gene. He feels that the present artificial sweeteners were developed at random and by chance. However, by having the receptor protein that normally binds sugars and sweeteners, one should be able to target more specifically better-designed molecules that will bind and activate the receptor.

LACTOSE

(Milk sugar)

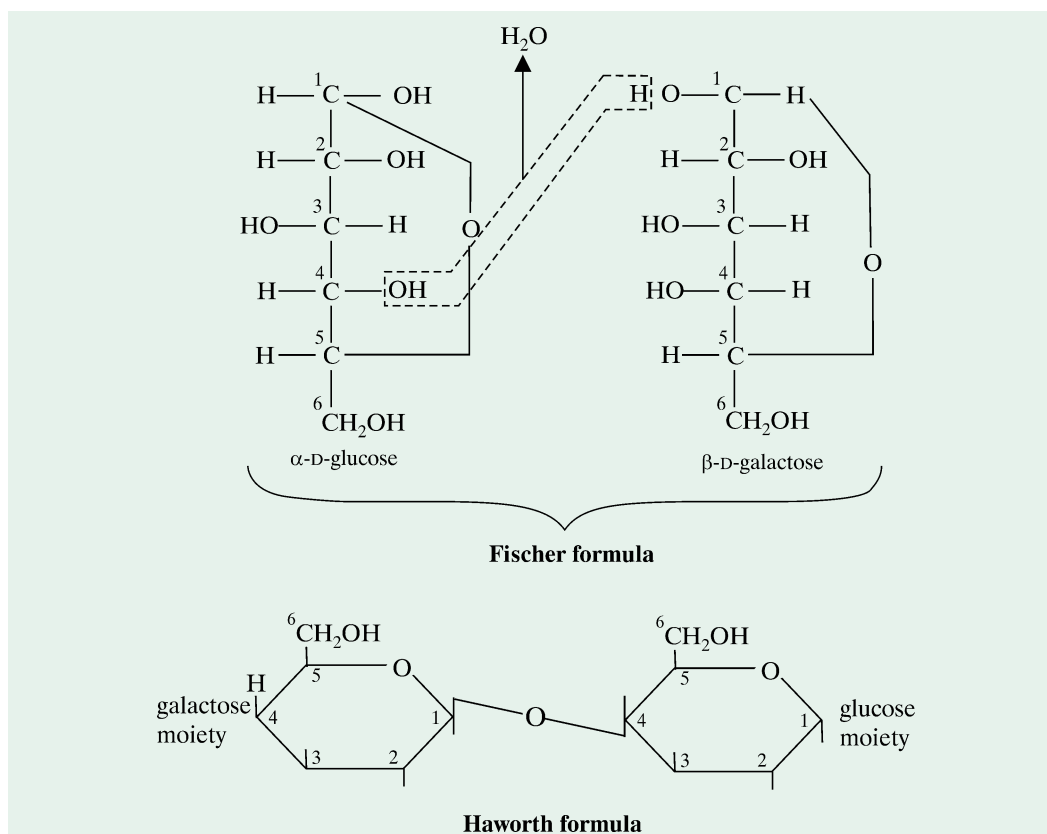
Occurrence. Lactose is solely of animal origin and is found in the milk of mammals. Human milk contains about 6-8 % (and 0.3% of higher oligosaccharides) ; cows' milk, about 4.8% (refer Table 7-2); hence, mother's milk is about 1.5 times sweeter than cow's milk. It is an unique product of mammary glands and is not found in other parts of the animal body. A minute quantity of lactose is also present in the milk as neuramin lactose. However, during pregnancy, it may be found in urine. Interestingly and curiously enough, there is no lactose in the milk of seals and other close relatives.

Kuhn (1949) has, however, found lactose to be present in the pollen of *Forsythia* plant.

Table 7-2. Percentage composition of milk

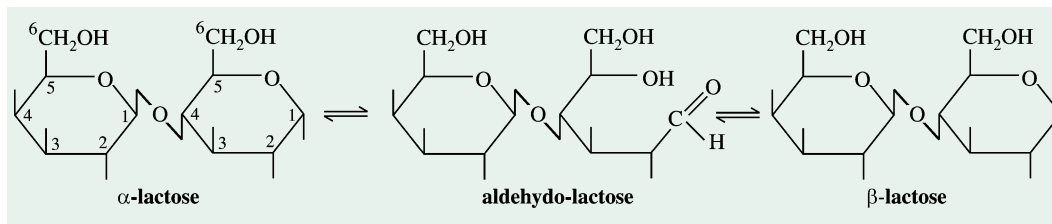
| Contents | Human milk | Cow's milk |
|---------------------------------|------------|------------|
| Water | 88.5 | 87.0 |
| Fat | 3.3 | 3.5 |
| Lactose | 6.8 | 4.8 |
| Casein | 0.9 | 2.7 |
| Lactalbumin + other proteins | 0.4 | 0.7 |
| Ash (containing minerals) | 0.2 | 0.7 |

Chemistry. Lactose is prepared commercially from whey by evaporation to crystallization. Whey is obtained as a by-product in the manufacture of cheese. Lactose may be formed by elimination of a molecule of water from the glycosidic OH group of β -D-galactose and the alcoholic OH group on carbon atom 4 of D-glucose (Fig. 7-3). As D-glucose exists in 3 forms (α , *aldehydo* and β), it is obvious to have 3 forms of lactose viz., α form, *aldehydo* form and β -form. The *aldehydo* form is present in traces only. The formula shown in Fig. 7-3 is that of α -lactose.

Fig. 7-3. Structure of α -lactose

Lactose, in solution, consists of an equilibrium mixture of all the 3 forms. Using the simplified scheme of representing the Haworth formula, the 3 forms may be shown as below :

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It may be emphasized that the α - and β -forms of lactose differ from each other only in hemiacetal configuration ; the linkage in both the forms being β -1, 4-galactoside.

Properties. Lactose is a white, crystalline solid with a melting point 203°C (with decomposition) and is also dextrorotatory. The α - and β -forms have a specific rotation of $+90^{\circ}$ and $+35^{\circ}$ respectively. The equilibrium mixture has a specific rotation $+52.5^{\circ}$. It is less soluble in water and much less sweet than sucrose. The α -diastereoisomer is less soluble than the β -form. Sometimes, the α -isomer crystallizes in ice-cream, making the product seem sandy in texture. The more soluble β isomer is used in diets for infants. Since lactose has a free carbonyl group on carbon atom 1 of glucose unit, it is a reducing sugar. Hence, it exhibits mutarotation, reduces Cu^{++} ions to Cu^{+} ions and forms osazone and oxime. It crystallizes in rhombic prisms with a mole of water.

Hydrolysis. Upon hydrolysis with the enzyme, *lactase*, it yields an equimolar mixture of glucose and galactose. It should be noted that lactase is a β -glycosidase, *i.e.*, splits β -glycosides (hence, it is identical with emulsin). Lactose itself cannot be absorbed from the intestine into the bloodstream unless it is first hydrolyzed into monosaccharide units. The enzyme lactase is actively secreted by the intestinal mucosal cells in suckling infants and therefore the lactose, in the form of milk suckled by them, is easily hydrolyzed to the component monosaccharide units, thus effecting absorption by the intestinal tract. Although milk is the universal food of newborn mammals and one of the most complete human foods, many adult humans cannot digest milk because they are deficient in intestinal lactase, the enzyme that hydrolyzes the milk sugar, lactose. Such individuals may, therefore, show **lactose intolerance**, which is genetically determined. It is characterized by abdominal bloating, cramps, flatulence, colic pains, abnormal intestinal flow, nausea and watery diarrhea. All these symptoms appear within 30 to 90 minutes after ingesting milk or its unfermented by-products (fermented dairy products such as yogurt and cheese create no intolerance problems). North Europeans and their descendants, which include the majority of North American whites, are most tolerant of milk. Many other ethnic groups are generally intolerant to milk, including the Japanese, Chinese, Jews in Israel, Eskimos, South American Indians and most African blacks. Only about 30% of North American blacks are tolerant; those who are tolerant are mostly descendants of slaves brought from east and central Africa, where dairying is traditional and tolerance to lactose is high. Lactase deficiency appears to be inherited as an autosomal recessive trait and is usually first expressed in adolescence or young adulthood. The prevalence of lactase deficiency in human populations varies greatly. For example, 3% of Danes are deficient in lactase, compared with 97% of Thais.

Lactose intolerance should not be confused with the genetic galactosemia.

MALTOSE

(Malt sugar)

Occurrence. Maltose does not occur abundantly in nature. However, its occurrence has been occasionally reported. It is the major product of enzymic hydrolysis of starch. Sprouting cereal grains

are rich in *amylases* which split the starch present to dextrins and maltose. Malt, prepared from sprouting barely, is an excellent source of maltose.

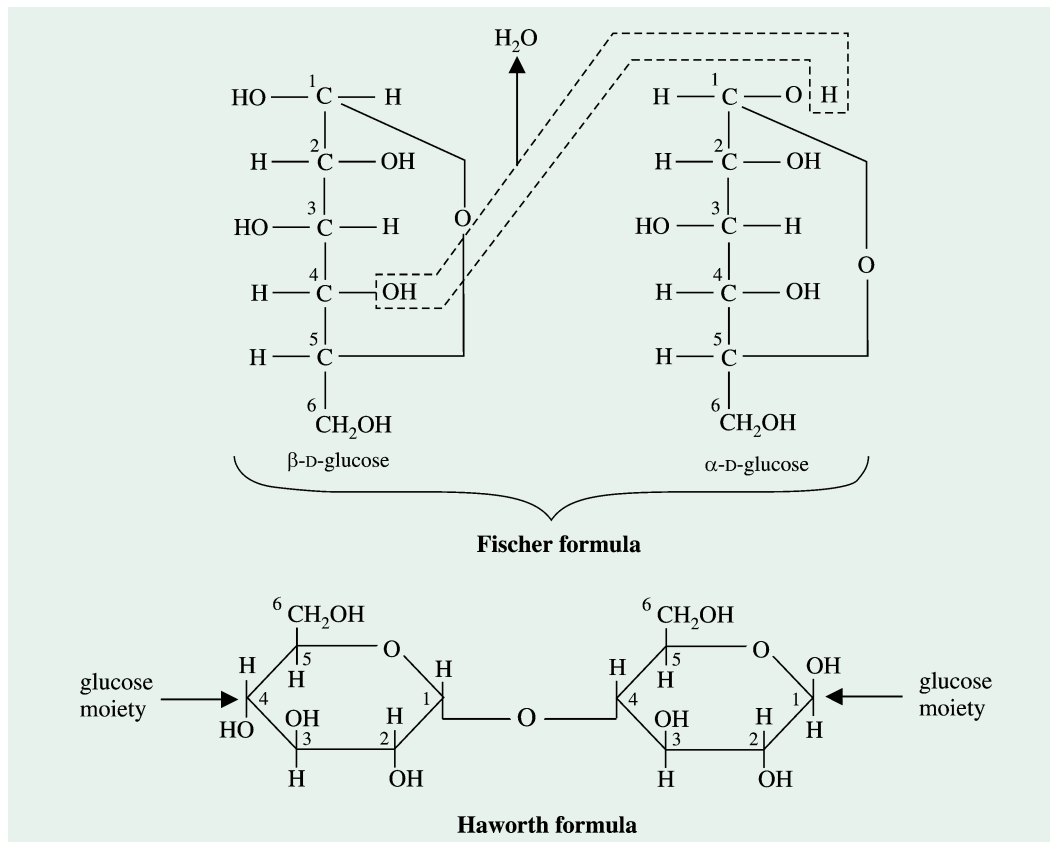
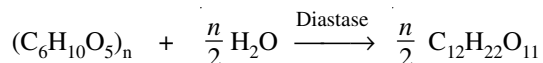


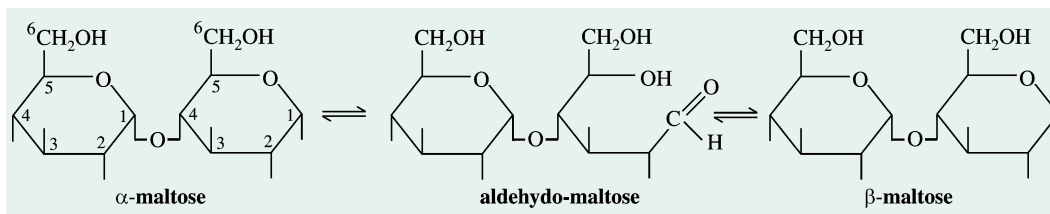
Fig. 7-4. Structure of β -maltose
O- α -D-glucopyranosyl-(1 \rightarrow 4)- β -D-glucopyranose or Glc (α 1 \rightarrow β 4)Glc

Chemistry. Maltose is the simplest of the disaccharides and is produced by the action of malt (which contains the enzyme *diastase*) on starch :



Maltose may be considered as originating by splitting out a molecule of water from the glycosidic OH group of α -D-glucose and the alcoholic OH group on carbon atom 4 of D-glucose (Fig. 7-4). Maltose, like lactose, has one free hemiacetal group. Consequently, it too exists in 3 forms ; α , β and *aldehydo*. Maltose is usually found in β -form. Maltose, in solution, also exists as an equilibrium mixture of all the 3 forms.

It may be noted that the linkage in both α - and β -forms of maltose is always an α -1, 4-glucoside.



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Properties. Maltose is a white crystalline solid, with a melting point 160–165 °C. It is soluble in water and is dextrorotatory. Because of the free aldehyde group, maltose is also a reducing sugar and forms osazone with phenyl hydrazine. It is also capable of exhibiting mutarotation.

Hydrolysis. Maltose is easily hydrolyzed into 2 identical units of glucose by dilute acids or by the enzyme, *maltase*, found in the intestine. It should also be noted that the enzyme maltase hydrolyzes or splits only α -glycoside linkages and has no action upon β -glycosides. It has, hence, been used to ascertain the presence of this bond in disaccharides and polysaccharides. Hydrolysis may also be brought about by the enzyme, *diastase* (= *amylase*), found in sprouting barley.

CELLOBIOSE

Occurrence. It is probably present in only traces in nature. However, it is apparently released during the digestion of a polysaccharide, cellulose by the *cellulases* of microorganisms.

Chemistry. Cellobiose is identical with maltose except that the former has a β -1, 4-glucosidic linkage (Fig. 7-5) in contrast to the α -1, 4-glucosidic of the latter. It also exists in an equilibrium mixture of 3 forms : α , β and *aldehydo*. On hydrolysis, cellobiose yields glucose units only.

Properties. Cellobiose is a white crystalline solid with a melting point 225 °C. It is soluble in water and is dextrorotatory. Since cellobiose contains a free hemiacetal group, it is also a reducing sugar and undergoes mutarotation in aqueous solution and forms an oxime or osazone. In fact, all the disaccharides with a free hemiacetal group (lactose, maltose, cellobiose, etc.) are reducing sugars and

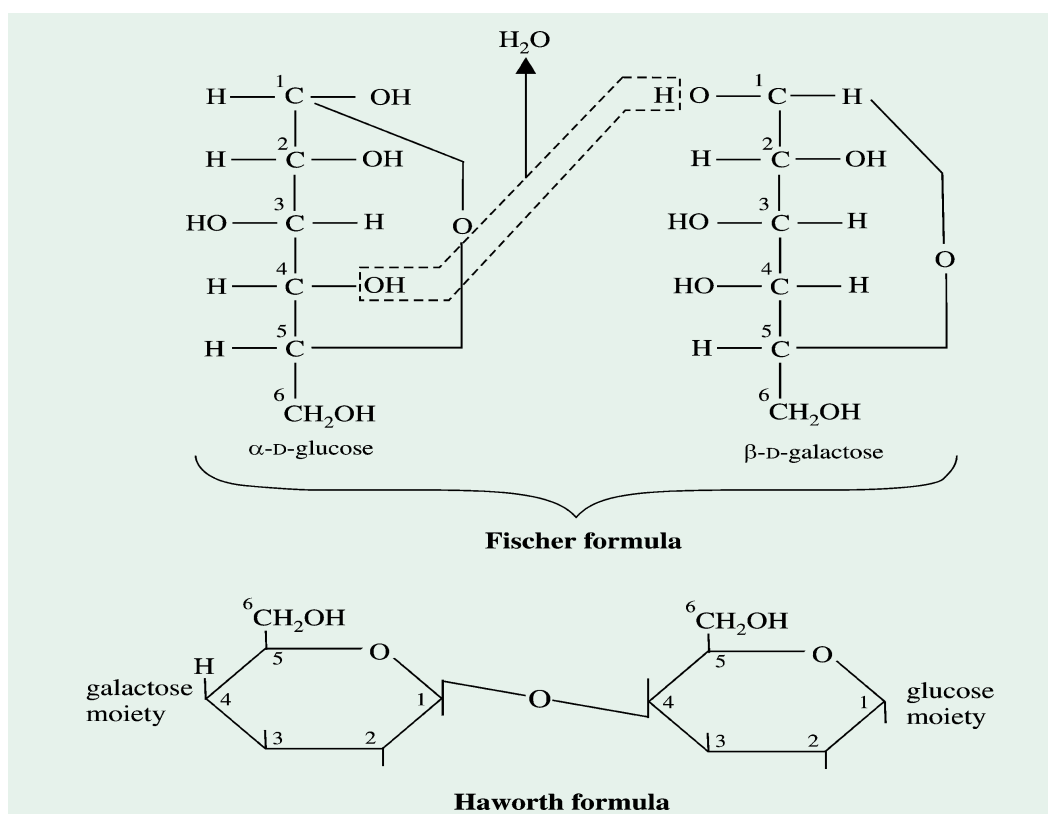


Fig. 7-5. Structure of α -cellobiose

O- β -D-glucopyranosyl-(1 \rightarrow 4)- α -D-glucopyranose or Glc (β 1 \rightarrow α 4)Glc

as such reduce cupric copper to cuprous oxide in the Fehling test and the silver ion to metallic silver in the silver mirror reaction. However, they are not as powerful reducing agents as are the

monosaccharides glucose, galactose and fructose, and do not readily reduce Barfoed's reagent to cuprous copper. The reason for this difference is that while C-1 of one of the two glucose residues is free to revert back to the carbonyl (= reducing) form, that on the second residue is stabilized in the cyclic form by the existence of the glycosidic linkage.

Hydrolysis. When hydrolyzed with dilute acids or by the enzyme *emulsin*, cellobiose yields identical units of D (+)-glucose. It may be noted that the enzyme *emulsin* splits only β -glycosidic linkages (*cf* maltase).

ISOMALTOSE

It is similar to maltose except that it has an α -1, 6-glucoside linkage (Fig. 7-6).

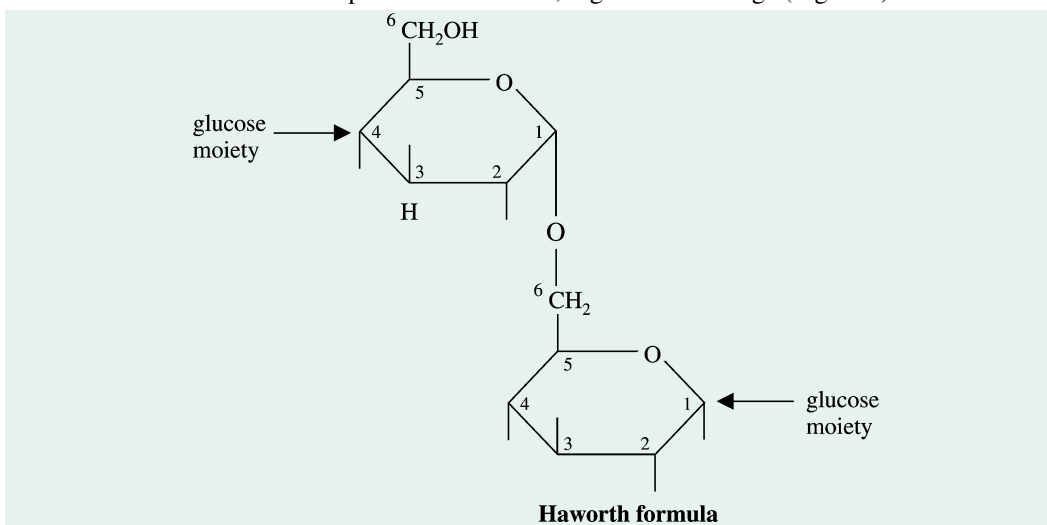


Fig. 7-6. Structure of isomaltose

O - α -D-glucopyranosyl-(1 \rightarrow 6)- α -D-glucopyranose or Glc (α 1 \rightarrow α 6)Glc

TREHALOSE

Trehalose is a major constituent of the circulating fluid (hemolymph) of insects, in which it serves as an energy storage compound. It is also found in yeasts and other fungi. Here, the two anomeric carbon atoms of the two α -D-glucose moieties connect each other (Fig. 7-7). Consequently, it resembles sucrose in being a nonreducing sugar as it has no free aldehyde group. Trehalose does not form an osazone. On hydrolysis, it yields glucose. It is hydrolyzed by HCl to 2 moles of D-glucose.

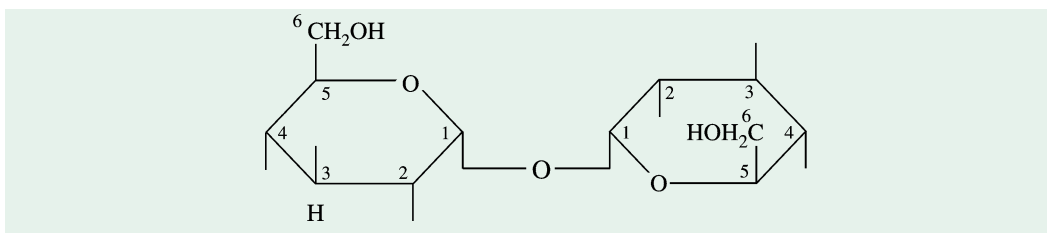


Fig. 7-7. Structure of trehalose

O - β -D-glucopyranosyl-(1 \rightarrow 4)- α -D-glucopyranose or Glc (β 1 \rightarrow α 4)Glc

Two isomeric forms of trehalose are recognized :

- (a) *Isotrehalose* (β -D-glucopyranosyl- β -D-glucopyranoside)
- (b) *Neotrehalose* (α -D-glucopyranosyl- β -D-glucopyranoside)

A summary chart of the important disaccharides is given on the next page.

Table 7-3. Summary of occurrence, structure and properties of some important disaccharides

| Name | Occurrence | Constituent monosaccharides* | Oxide linkage involved | Groups involved in linkage | Properties | Hydrolysis |
|--------------------------------|--|---|--|--|---|--|
| Sucrose (Cane sugar) | Solely of plant origin : found in sugarcane, beet and maple | α -D-glucose and β -D-fructose | glycosidic linkage between C ₁ of glucose and C ₂ of fructose | glycosidic OH on C ₁ glycosidic OH on C ₂ | Dextrorotatory; a non- reducing sugar; does not exhibit mutarotation; does not form osazone; | Yields an equimolar mixture of glucose and fructose on hydrolysis with invertase |
| Lactose (Milk sugar) | Solely of animal origin; found in milk of mammals | β -D-galactose and D-glucose | β -1, 4-galactoside | glycosidic OH on C ₁ alcoholic OH on C ₄ | Dextrorotatory; a reducing sugar; exhibits mutarotation; forms osazone; nonfermentable. | Yields an equimolar mixture of galactose and glucose on hydrolysis with lactase |
| Maltose (Malt sugar) | Does not occur abundantly in nature; malt from sprouting barley an excellent source | α -D-glucose and D-glucose | α -1, 4-glucoside | glycosidic of OH on C ₁ alcoholic OH on C ₄ | A reducing sugar; exhibits mutarotation; forms osazone; fermentable | Yields identical units of glucose on hydrolysis with maltase or diastase |
| Cellobiose | Probably present in only traces in nature | β -D-glucose and D-glucose | β -1, 4-glucoside | glycosidic OH on C ₁ alcoholic OH on C ₄ | A reducing sugar; exhibits mutarotation | Yields identical units of glucose on hydrolysis with β -glycosidases or with dilute acids |
| Trehalose | Major sugar of insect hemolymph; also occurs in fungi and yeasts | α -D-glucose and α -D-glucose | α -1, 1-glucoside | glycosidic OH on C ₁ glycosidic OH on C ₁ | A nonreducing sugar; does not exhibit mutarotation; does not form osazone | Yields glucose units on hydrolysis |

* All the constituent monosaccharides are present in pyranose ring form except β -D-fructose which has a furanose ring structure.

REFERENCES

See list following Chapter 8.

PROBLEMS

1. The hydrolysis of sucrose (specific rotation $+66.5^\circ$) yields an equimolar mixture of D-glucose (specific rotation $+52.5^\circ$) and D-fructose (specific rotation -92°).
 - (a) Suggest a convenient way to determine the rate of hydrolysis of sucrose by an enzyme preparation extracted from the lining of the small intestine.
 - (b) Explain why an equimolar mixture of D-glucose and D-fructose formed by hydrolysis of sucrose is called invert sugar in the food industry.
 - (c) The enzyme invertase (its preferred name is now sucrase) is allowed to act on a solution of sucrose until the optical rotation of the solution becomes zero. What fraction of the sucrose has been hydrolyzed ?
2. The manufacture of chocolates containing a liquid centre is an interesting application of enzyme engineering. The flavored liquid centre consists largely of an aqueous solution of sugars rich in fructose to provide sweetness. The technical dilemma is the following : the chocolate coating must be prepared by pouring hot melted chocolate over a solid (or almost solid) core, yet the final product must have a liquid, fructose-rich centre. Suggest a way to solve this problem. (Hint : The solubility of sucrose is much lower than the solubility of a mixture of glucose and fructose.)
3. Although lactose exists in two anomeric forms, no anomeric forms of sucrose have been reported. Why ?
4. A sample of disaccharide is either lactose or sucrose. No reddish precipitate forms in Fehling's reaction, unless the compound is first warmed in dilute acid. Is it lactose or sucrose ? Explain.
5. The carbohydrate portion of some glycoproteins may serve as a cellular recognition site. In order to perform this function, the oligosaccharide moiety of glycoproteins must have the potential to occur in a large variety of forms. Which can produce a larger variety of structures: oligopeptides composed of five different amino acid residues or oligosaccharides composed of five different monosaccharide residues ? Explain.