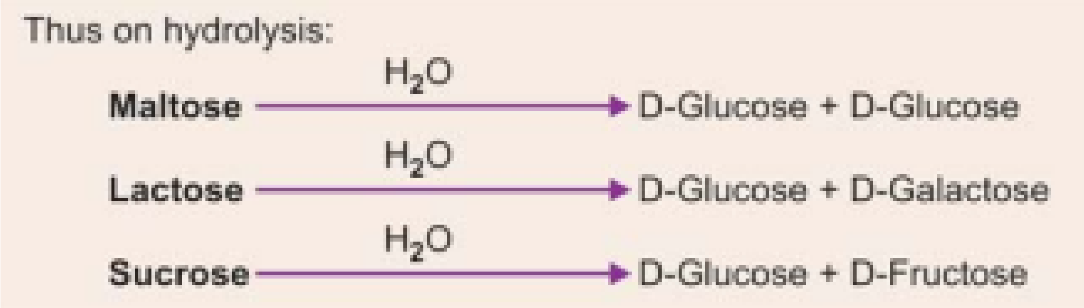
DISACCHARIDES

- A disaccharide consists of two sugars joined by an O-glycosidic bond.
- Three abundant disaccharides are sucrose, lactose, and maltose.
- Sucrose (common table sugar) is obtained commercially from cane or beet.
- The anomeric carbon atoms of a glucose unit and a fructose unit are joined in this disaccharide; the configuration of this glycosidic linkage is a for glucose and β for fructose.
- Sucrose can be cleaved into its component monosaccharides by the enzyme sucrase
- Three most common disaccharides of biological importance are: Maltose, Lactose and Sucrose.
- Their general molecular formula is $C_{12}H_{22}O_{11}$ and they are hydrolysed by hot acids or corresponding enzymes as follows:
- $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$



Thus on hydrolysis:

$$\text{Maltose} \xrightarrow{H_2O} \text{D-Glucose} + \text{D-Glucose}$$

$$\text{Lactose} \xrightarrow{H_2O} \text{D-Glucose} + \text{D-Galactose}$$

$$\text{Sucrose} \xrightarrow{H_2O} \text{D-Glucose} + \text{D-Fructose}$$

- disaccharides are formed by the union of two constituent monosaccharides with the elimination of one molecule of water.
- Lactose, the disaccharide of milk, consists of galactose joined to glucose by a β-1,4-glycosidic linkage.
- Lactose is hydrolyzed to these monosaccharides by lactase in human beings and by b-galactosidase in bacteria.
- In maltose, two glucose units are joined by an a -1,4 glycosidic linkage, as stated earlier.
- Maltose comes from the hydrolysis of starch and is in turn hydrolyzed to glucose by maltase.
- Sucrase, lactase, and maltase are located on the outer surfaces of epithelial cells lining the small intestine

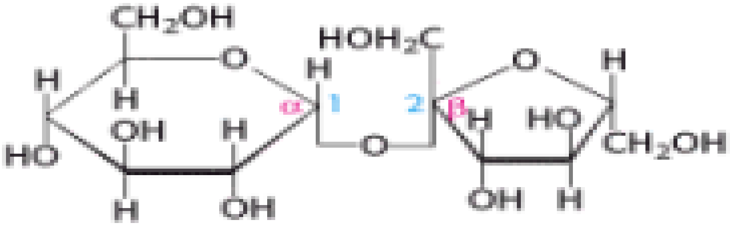
PROPERTIES OF DISACCHARIDES

- **1. Maltose:** Maltose or malt sugar is an intermediary in acid hydrolysis of starch and can also be obtained by enzyme hydrolysis of starch.
- In the body, dietary starch digestion by Amylase in gut yields maltose, which requires a specific enzyme maltase to form glucose.
- It is a rather sweet sugar and is very soluble in water.
- Since it has one aldehyde ‘free’ or potentially free it has reducing properties, and forms characteristic osazones, which has characteristic appearance ‘Sunflower’ like.
- As anomeric carbon of one glucose is free, can form α and β forms and exhibit mutarotation.
- On hydrolysis Maltose yields two molecules of glucose.

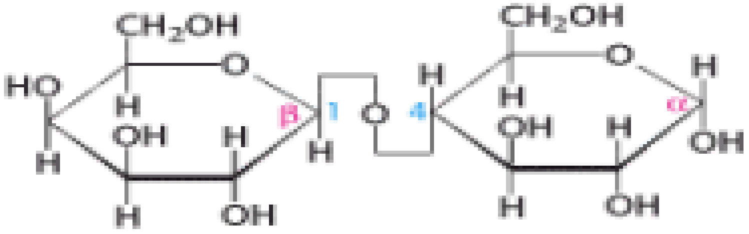
- **2. Lactose:** Lactose is milk sugar and found in appreciable quantities in milk to the extent of about 5 per cent and occurs at body temperature as an equilibrium mixture of the α and β forms in 2:3 ratio.
- It is not very soluble and is not so sweet. It is dextrorotatory. Specific enzyme which hydrolyses is lactase present in intestinal juice.
- On hydrolysis it yields one molecule of D-Glucose and one molecule of D-Galactose.
- Because it contains galactose as one of its constituents, it yields mucic acid on being treated with Conc HNO3 after hydrolysis.
- As one of the aldehyde group is free or potentially free, it has reducing properties and can form osazones.
- Lactosazone crystals have typical hedgehog shape or powder puff appearance.
- As anomeric carbon of glucose is free, can form α and β forms and exhibits mutarotation.

- **3. Sucrose:** Ordinary table sugar is sucrose.
- It is also called as ‘Cane sugar’, as it can be obtained from sugarcane.
- Also obtained from sugar beet, and sugar maple. Also occurs free in most fruits and vegetables, e. g. pineapples, and carrots.
- It is very soluble and very sweet and on hydrolysis yields one molecule of D-Glucose and one molecule of D-Fructose.
- The specific enzyme which hydrolyses sucrose is sucrase present in intestinal juice.
- As both aldehyde and ketone groups are linked together (α 1 → 2), it does not have reducing properties, and cannot form osazones.
- As both anomeric carbons are involved in ‘linkage’, it does not exhibit mutarotation

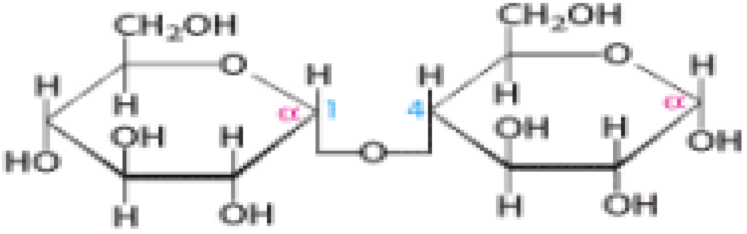
- Common Disaccharides. Sucrose, lactose, and maltose are common dietary components.



Sucrose
(α-D-Glucopyranosyl-(1 → 2)-β-D-fructofuranose



Lactose
(β-D-Galactopyranosyl-(1 → 4)-α-D-glucopyranose



Maltose
(α-D-Glucopyranosyl-(1 → 4)-α-D-glucopyranose

Differences between Sucrose and Lactose

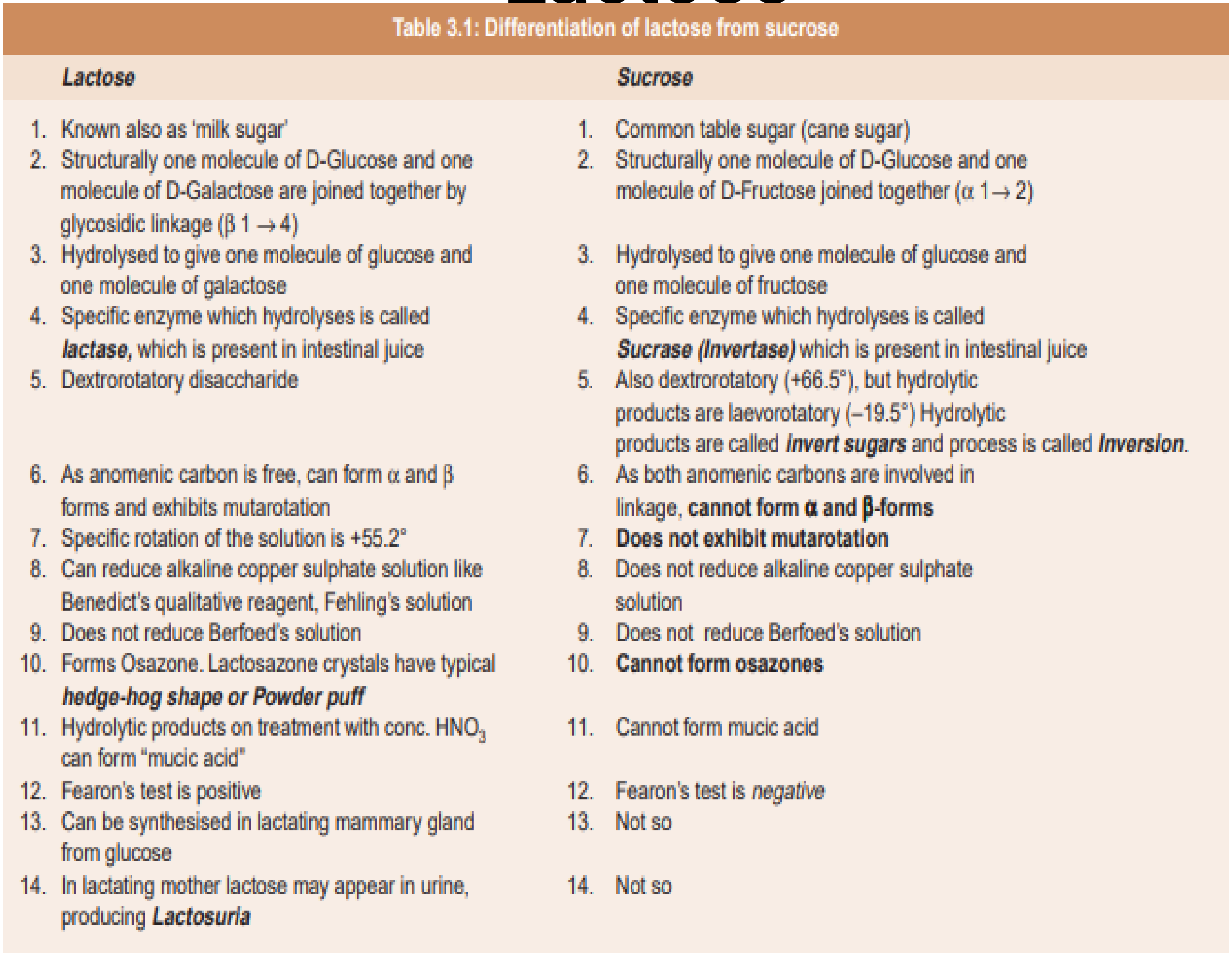


Table 3.1: Differentiation of lactose from sucrose

Lactose	***Sucrose***
1. Known also as 'milk sugar'	1. Common table sugar (cane sugar)
2. Structurally one molecule of D-Glucose and one molecule of D-Galactose are joined together by glycosidic linkage (β 1 $\rightarrow$ 4)	2. Structurally one molecule of D-Glucose and one molecule of D-Fructose joined together (α 1 $\rightarrow$ 2)
3. Hydrolysed to give one molecule of glucose and one molecule of galactose	3. Hydrolysed to give one molecule of glucose and one molecule of fructose
4. Specific enzyme which hydrolyses is called ***lactase***, which is present in intestinal juice	4. Specific enzyme which hydrolyses is called ***Sucrase (Invertase)*** which is present in intestinal juice
5. Dextrorotatory disaccharide	5. Also dextrorotatory (+66.5°), but hydrolytic products are laevorotatory (–19.5°) Hydrolytic products are called ***Invert sugars*** and process is called ***Inversion***.
6. As anomenic carbon is free, can form α and β forms and exhibits mutarotation	6. As both anomenic carbons are involved in linkage, **cannot form α and β-forms**
7. Specific rotation of the solution is +55.2°	7. **Does not exhibit mutarotation**
8. Can reduce alkaline copper sulphate solution like Benedict's qualitative reagent, Fehling's solution	8. Does not reduce alkaline copper sulphate solution
9. Does not reduce Berfoed's solution	9. Does not reduce Berfoed's solution
10. Forms Osazone. Lactosazone crystals have typical ***hedge-hog shape or Powder puff***	10. **Cannot form osazones**
11. Hydrolytic products on treatment with conc. HNO_3 can form "mucic acid"	11. Cannot form mucic acid
12. Fearon's test is positive	12. Fearon's test is *negative*
13. Can be synthesised in lactating mammary gland from glucose	13. Not so
14. In lactating mother lactose may appear in urine, producing ***Lactosuria***	14. Not so

OLIGOSACCHARIDES

- Integral membrane proteins contain covalently attached carbohydrate units, oligosaccharides, on their extracellular face.
- Many secreted proteins, such as antibodies and coagulation factors also contain oligosaccharide units.
- These carbohydrates are attached to either the side-chain O2 atom of serine or threonine residues by O-glycosidic linkages or to the side chain nitrogen of Asparagine residues by N-glycosidic linkages.
- N-linked oligosaccharides contain a common pentasaccharide core consisting of three mannose and two N-acetyl glycosamine residues.
- Additional sugars are attached to this common core in many different ways to form the great variety of oligosaccharide patterns found in glycoproteins.

POLYSACCHARIDES

- Polysaccharides are more complex single substances. Some are polymers of a single monosaccharide and are termed as Homopolysaccharides (Homoglycans), e.g. starch, glycogen, etc.
- • Some contain other groups other than carbohydrates such as hexuronic acid and are called as Heteropolysaccharides (heteroglycans), e.g. Mucopolysaccharides.

HOMOPOLYSACCHARIDES (HOMOGLYCANS)

- **1. Starch**
- Starch is a polymer of glucose, and occurs in many plants as storage foods.
- It may be found in the leaves, and stem, as well as in roots, fruits and seeds where it is usually present in greater concentration.
- • **Starch granules:** Appear under microscope as particles made up of concentric layers of material.
- They differ in shape, size and markings according to the source (Fig. 3.18). Starchy foods are mainstay of our diet.
- • **Composition of starch granule:** It consists of two polymeric units of glucose called

i Amylose and

ii Amylopectin, but they differ in molecular architecture and in certain properties.

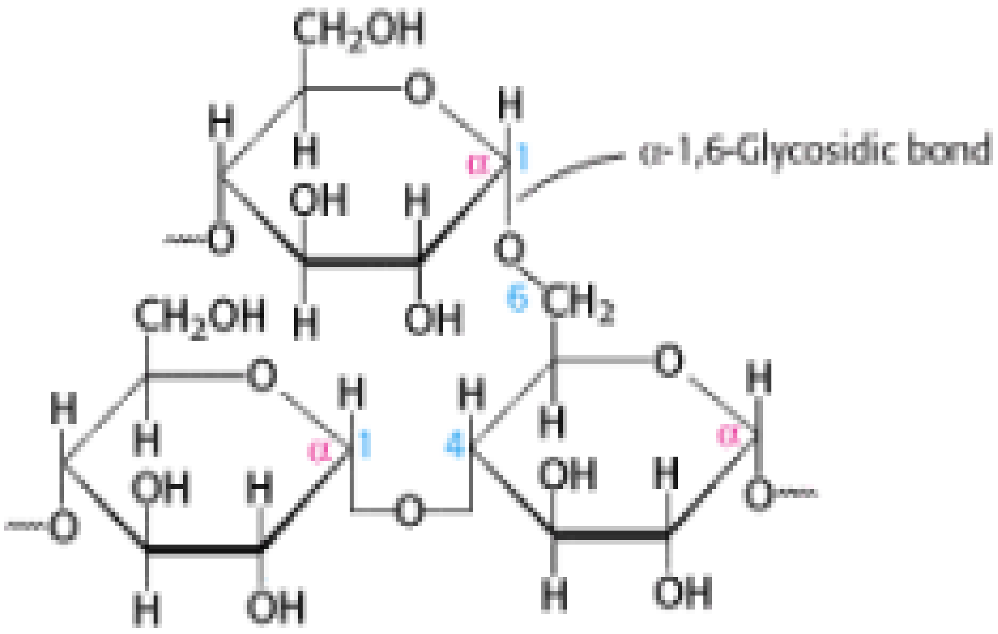
- • **Solubility:** Starch granules are insoluble in cold water, but when their suspension is heated, water is taken up and swelling occurs, viscosity increases and starch gels or pastes are formed.
- • **Reaction with I_2:** Both the granules and the colloidal solutions react with Iodine to give a blue colour.
- This is chiefly due to amylose, which forms a deep-blue complex, which dissociates on heating.
- Amylopectin solutions are coloured blue-violet or purple.
- • **Ester Formation:** Starches are capable of forming esters with either organic or inorganic acids.
- • **Hydrolysis of starch:** It yields succession of polysaccharides of gradually diminishing molecular size

- **Course of Hydrolysis   Reaction with Iodine**
- Starch   Blue
- ↓
- Soluble starch   Blue
- ↓
- Amylodextrin   Purple
- ↓
- Erythrodextrin   Red
- ↓
- Achroodextrin   Colourless
- ↓
- Maltose

- Enzyme (amylase) hydrolysis ends at maltose.
- It is not quantitative conversion; traces of dextrins are also formed. For formation of glucose, it requires the enzyme maltose.
- But if the hydrolysis is accomplished by acids much of the starch will be converted into glucose.
- • **Types of amylases:** Two broad classes of amylases exist as:
- – α-amylase is present in saliva and pancreatic juice,
- – β-amylase is present in sprouted grains and malts.
-
- Large polymeric oligosaccharides, formed by the linkage of multiple monosaccharides, are called polysaccharides.
- Polysaccharides play vital roles in energy storage and in maintaining the structural integrity of an organism.

- If all of the monosaccharides are the same, these polymers are called homopolymers. The most common homopolymer in animal cells is glycogen, the storage form of glucose.
- Glycogen is a very large, branched polymer of glucose residues.
- Most of the glucose units in glycogen are linked by α -1,4-glycosidic bonds.
- The branches are formed by α -1,6-glycosidic bonds, present about once in 10 units.

- Branch Point in Glycogen. Two chains of glucose molecules joined by a -1,4-glycosidic bonds are linked by an a -1,6-glycosidic bond to create a branch point. Such an a -1,6-glycosidic bond forms at approximately every 10 glucose units, making glycogen a highly branched molecule



- The nutritional reservoir in plants is starch, of which there are two forms.
- Amylose, the unbranched type of starch, consists of glucose residues in α -1,4 linkage.
- Amylopectin, the branched form, has about 1 α -1,6 linkage per 30 α -1,4 linkages, in similar fashion to glycogen except for its lower degree of branching.
- More than half the carbohydrate ingested by human beings is starch.
- Both amylopectin and amylose are rapidly hydrolyzed by α-amylase, an enzyme secreted by the salivary glands and the pancreas.
- Cellulose, the other major polysaccharide of glucose found in plants, serves a structural rather than a nutritional role.
- Cellulose is one of the most abundant organic compounds in the biosphere.

- Some 10^{15}kg of cellulose is synthesized and degraded on Earth each year.
- It is an unbranched polymer of glucose residues joined by β-1,4 linkages.
- The β configuration allows cellulose to form very long, straight chains.
- Both of them hydrolyse only α-glycosidic linkage. α-amylase produces a random cleavage of glycosidic bonds well inside the starch molecule yielding a mixture of maltose and some fragments larger than maltose (dextrins),
- whereas, β-amylase splits off maltose moietes liberating successive maltose units commencing at the non-reducing end of the starch molecule and ends in Limit dextrin.

- **2. Glycogen**
- Glycogen is the reserve carbohydrate of the animal; hence it is called as animal starch.
- It has been shown to be present in plants which have no chlorophyll systems, e.g. in fungi and yeasts.
- It is also found in large amounts in oysters and other shell fish.
- In higher animals, it is deposited in the liver and muscle as storage material which are readily available as immediate source of energy.
- It is dextrorotatory with an [α] D 20° = +196° to +197°. Formation of glycogen from glucose is called as Glycogenesis and breakdown of glycogen to form glucose is called as glycogenolysis.
- Postmortem glycogenolysis is very rapid but ceases when the pH falls to 5.5 due to lactic acid formed from glucose.

- **Specific Enzymes Are Responsible for Oligosaccharide Assembly**
- Oligosaccharides are synthesized through the action of specific enzymes, glycosyltransferases, which catalyze the formation of glycosidic bonds. Each enzyme must be specific, to a greater or lesser extent, to the sugars being linked.
- Given the diversity of known glycosidic linkages, many different enzymes are required.
- Note that this mode of assembly stands in contrast with those used for the other biological polymers heretofore discussed that is, polypeptides and oligonucleotides.
- As these polymers are assembled, information about monomer sequence is transferred from a template, and a single catalytic apparatus is responsible for all bond formation.
- The general form of the reaction catalyzed by a glycosyltransferase, the sugar to be added comes in the form of an activated sugar nucleotide.
- Sugar nucleotides are important intermediates in many processes

- Note that such reactions can proceed with either retention or inversion of configuration at the glycosidic carbon atom at which the new bond is formed; a given enzyme proceeds by one stereochemical path or the other.
- The human ABO blood groups illustrate the effects of glycosyl- transferases. Carbohydrates are attached to glycoproteins and glycolipids on the surfaces of red blood cells.
- For one type of blood group, one of the three different structures, termed A, B, and O, may be present.
- These structures have in common an oligosaccharide foundation called the O (or sometimes H) antigen.
- The A and B antigens differ from the O antigen by the addition of one extra monosaccharide, either N-acetylgalactosamine (for A) or galactose (for B) through an a -1,3 linkage to a galactose moiety of the O antigen.
- Specific glycosyltransferases add the extra monosaccharide to the O antigen.

- Each person inherits the gene for one glycosyltransferase of this type from each parent.
- The type A transferase specifically adds N-acetylgalactosamine, whereas the type B transferase adds galactose.
- These enzymes are identical in all but 4 of 354 positions.
- The O phenotype is the result of a mutation that leads to premature termination of translation and, hence, to the production of no active glycosyltransferase.
- These structures have important implications for blood transfusions and other transplantation procedures.
- If an antigen not normally present in a person is introduced, the person's immune system recognizes it as foreign.
- Adverse reactions can ensue, initiated by the

- Why are different blood types present in the human population?
- Suppose that a pathogenic organism such as a parasite expresses on its cell surface a carbohydrate antigen similar to one of the blood-group antigens.
- This antigen may not be readily detected as foreign in a person with the blood type that matches the parasite antigen, and the parasite will flourish.
- However, other people with different blood types will be protected.
- Hence, there will be selective pressure on human beings to vary blood type to prevent parasitic mimicry and a corresponding selective pressure on parasites to enhance mimicry.
- The constant "arms race" between pathogenic microorganisms and human beings drives the evolution of diversity of surface antigens within the human population