Carbohydrates

Chapter 22

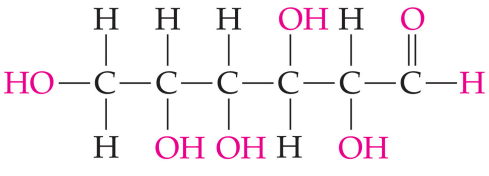
Carbohydrates

Carbohydrates are a class of molecules that includes

- Simple sugars
- Starch
- Cellulose (Insoluble Fiber)
- Glycogen (animal starch)
- Chitin (Lobster Shells)
- Heparin (Anti coagulate)
- Glycoproteins
- Others?

Atoms in Carbohydrates

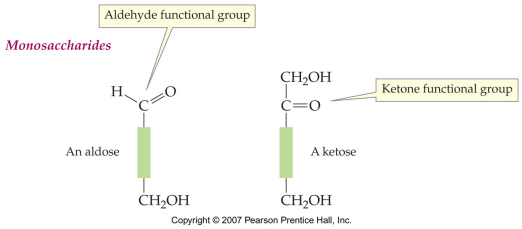
- Carbohydrates have the general formula $C_nH_{(2xn)}O_n$



Glucose

Functional Groups in Carbohydrates

- Carbohydrates are polyhydroxy aldehydes and ketones. Polyhydroxy refers to the numerous –OH.



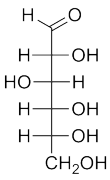
General Classes of Carbohydrates

Carbohydrates can be:

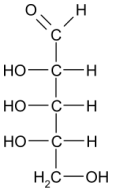
- Monosaccharide - One single sugar molecule. (glucose, fructose)
- Disaccharides –Two sugar molecules (table sugar)
- Polysaccharides – Many Sugar Molecules (starch, fiber, pectin)

Some Monosaccharides

- Simple sugars
- 3 to 7 carbon atoms
- Similarities and differences?
- Aldose or Ketose?



Glucose

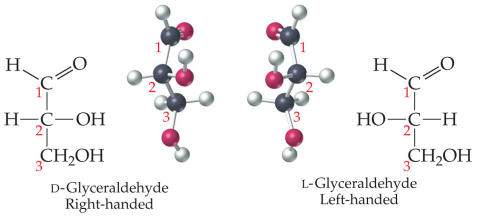


Ribose

Glyceraldehyde

Chirality of Simple Sugars

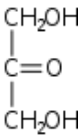
Which carbon, or carbons, are chiral?



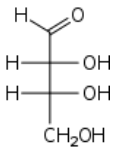
D-Glyceraldehyde
Right-handed

L-Glyceraldehyde
Left-handed

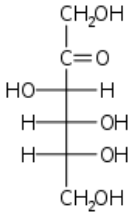
How Many Chiral Centers?



Ketotriose

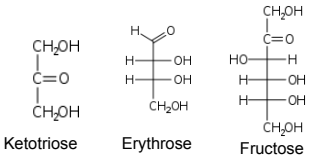


Erythrose



Fructose

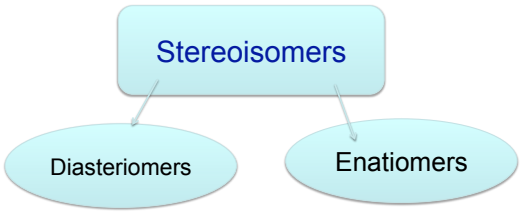
How Many Stereo Isomers?



Sterioisomers Isomers that depend on the arrangement of the atoms in space, not just their connections.

# of Stereoisomers = 2N, where N= # of chiral centers

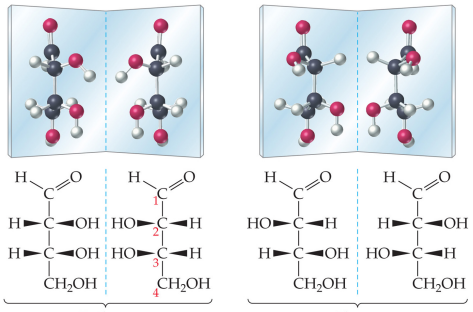
Types of Stereoisomers



Stereoisomers that are not mirror images of each other

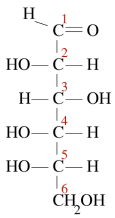
Stereoisomers that are mirror images of each other.

Naming Stereoisomers

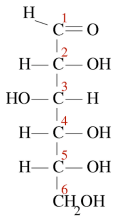


Pairs of Enantiomers are Named D or L

- The position of the –OH on the chiral carbon atom furthest from the –CHO or -CO group determines the "**D**" or "**L**" nature.



L-Glucose



D-Glucose*

Cyclic Stuctures

Most of the time sugars are not in straight chains. Instead the atoms in each simple sugar are arranged to form a ring.

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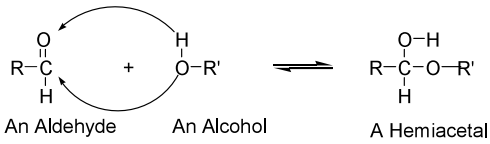
When an aldehyde or ketone reacts with alcohol – hemiacetals are formed.



The key to recognizing the hemiacetals is the presence of a carbon atom bound to both an -OH and a -OR group.

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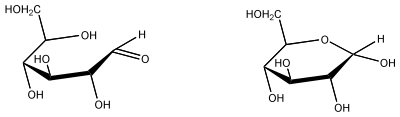
Sugars contain an aldehyde or ketone and an alcoholic group on the same molecule and they form an internal hemiacetal



- Such cyclic structures are called Hayworth projections.
- In these structures the OH groups on the left of the open chain structure always point up and the OH group on the right point down.
- The carbon that had the C=O bond, is called the anomeric carbon.

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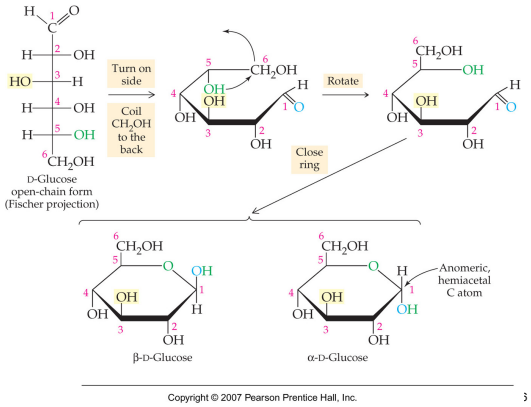
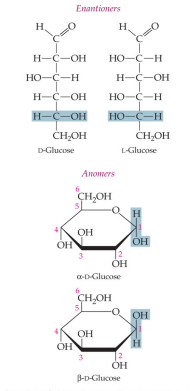
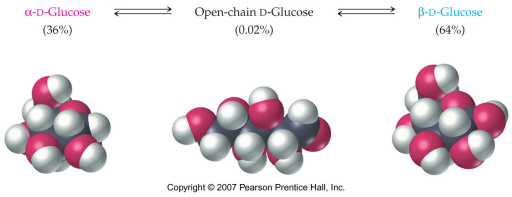


The cyclic form of the simple sugars adds another level of complexity to naming the sugars. When the –OH is on the side opposite of the -CH_2OH, it is labeled an α-sugar, and when it is on the same side as the –CH2OH it is labeled β-sugar.





The crystaline form of D-Glucose is entirely in its alpha form. Once crystalline D-Glucose is dissolved in water beta-D-glucose is seen. This shift is gradual. In the end the glucose maintains the same % of each type. (What determines the relative amounts, and why is the interconversion slow?

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Some important monosaccharides:

- Glucose
- Galactose
- Fructose
- Ribose and deoxyribose

D-Glucose

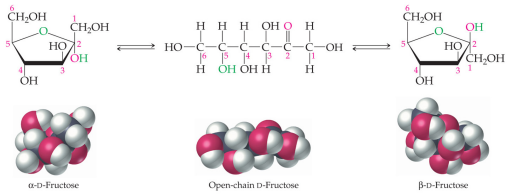
- D-Glucose, sometimes called dextrose or blood sugar, is the most widely occurring of all monosaccharides.
- In nearly all living organisms, D-glucose serves as a source of energy for all biochemical reactions.
- It is the final stage in carbohydrate digestion and is easily converted to acetyl-SCoA.
- D-glucose is stored in polymeric form as starch in plants and as glycogen in animals.
- .

D-Galactose

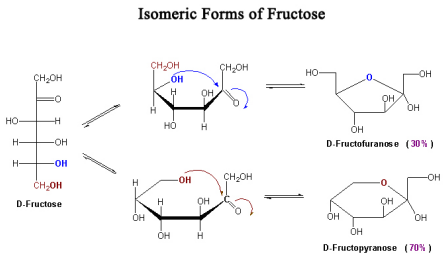
- It is found in plant gums and pectins and is one of the sugars in lactose.
- Galactose is easily converted to Glucose. They differ only is the orientation of the atoms at one of the carbons in the carbon chain.
- In some people conversion of galactose to glucose is impaired. In these cases patients must eat a diet low in galactose. (No dairy, caution with vitamins and medicines, no organ meets or garbanzo beans.)

D-Fructose

- A 6 carbon sugar, that forms a 6 member as well as a 5 member ring.

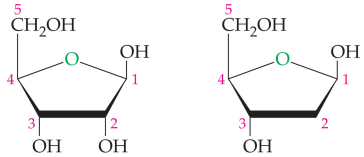


Cyclic Forms of D-Fructose



D-Ribose

- 5 Carbon sugar that forms a 5 member ring.
- Ribose is part of many other important molecules (Coenzyme A and ATP, oxidizing and reducing coenzymes.)
- Ribose is found in its Oxy and Deoxy forms

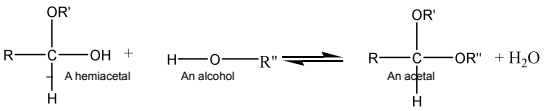


Reducing Sugars

- Aldehydes can reduce other substances and themselves be oxidized to form a carbocylic acid.
- In basic solution ketoses can also reduce other substances and be oxidized to a carbocylic acid
- The fact that these can reduce other substances is used as a common way to test for monosacharides

Disacchrides

Reactions with alcohols (glycoside and disaccharide formation)



- Hemiacteal : An alcohol and an -OR l group attached to a carbon atom. (The R stands a carbon atom with 3 other things attached to it.
- Acetal : Two –OR groups attached to a carbon atom.
- (acetyl group : CH_3CO-).
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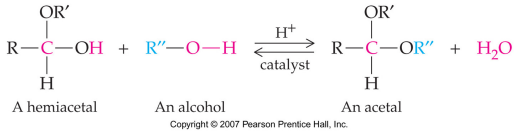
Hemiacetals and Alcohols



- Hemiacteal : An alcohol and an –OR group attached to a carbon atom. (The R stands a carbon atom with 3 other things attached to it.
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- *Monosaccharides* react with alcohols to form acetals, which are called *glycosides*.

Glycosides

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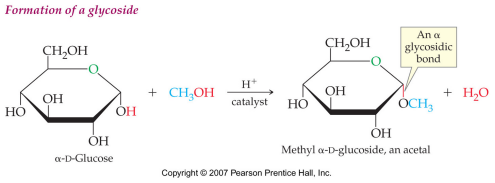

Glycoside Bonds

- The type of bond formed between and alcohol and monosaccharide can occur between to monosaccharides.
- The bond between the anomeric carbon atom and the oxygen atom of the –OR group is known as glycosidic bond.
- The bonds between to monosaccharides are glycosidic bonds.

In polysaccharides the monosaccharides are connected to each other by **glycosidic bond**.

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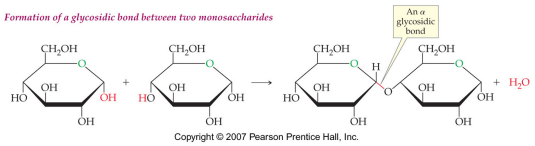
Linking Monosaccharides

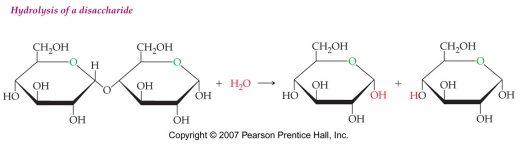


- The anomeric carbon (C1) is reacting with the C4 to for a glycosidic bond.
- In this case the bond is between two D-Glusose sugar molecules.
- The anomeric carbon is in the α form and this link would be called a α-1,4 link

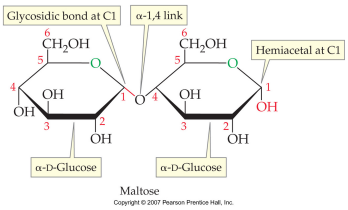
- Since the glycosides no longer contain the hemiacetal group that is established equilibria with open chain form they are not reducing sugars.

Glycoside Hydrolysis

- The reverse reaction is the **hydrolysis** of the glycosidic bond. This takes place during digestion of all carbohydrates.



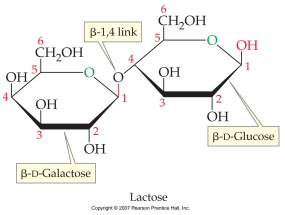
Maltose



Made from 2 α-D-glucose molecules
Joined by a α 1,4 link
2 D-Glucose molecules can join in many ways they do not all give maltose.

- Present in fermenting grains, it is produced when the enzyme amylase breaks down starches. (What type of enzyme is amylase?)
- It is hydolyzed to glucose by another enzyme.

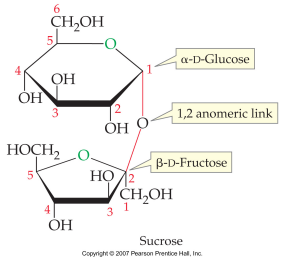
Lactose



Made from β-D-glucose and β-D galactose
Joined by a β 1,4 link
This glycoside link requires *lactase* in order to by hydrolyzed

- If it is not broken down it can draw water into the intestines and cause bloating.
- If not broken down it can be fermented by bacteria in the gut to CO_2, CH_4, and lactate and H_2.
- The result is pretty miserable.

Sucrose



- Made from D-glucose and D-fructose
- Joined by a 1,2 anomeric link
- This involves the 5 carbon ring form of fructose

- The enzyme invertase breaks the glycoside bond and forms a D-glucose D-fructose solution
- Sucrose is table sugar.

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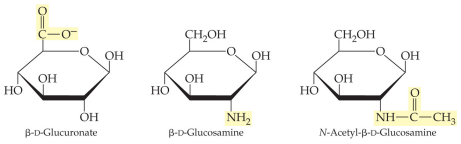
Derivatives of Monosaccharides



The –OH groups provide many opportunities to form derivatives of simple sugars. These derivatives are important in the function of many polysaccharides as well as in glucose metabolism.

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Variations on Carbohydrates:

- Many carbohydrates have additional functional groups. These groups can be carboxylic, amino and acetyl groups.
- Chitin: is a polysaccharide composed of N acetyl –D- glucosamine.
- Connective Tissue:
  Blood vessels, cartilage and tendons are made of protein fibers that are embedded in a syrupy unbranched polysaccharide – **mucopolysaccharide**.This jell like substance works as a shock absorber in the joints and extra-cellular space.

Chitin

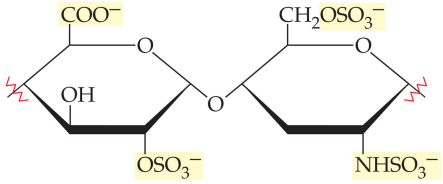
- Chitin: is a polysaccharide composed of N acetyl –D- glucosamine.
- It is tough and somewhat rigid.
- It forms the outside of lobsters, shrimps,and many bugs.
- It is the 2nd most abundant polysaccharide.

Connective Tissue

- Connective Tissue: Carbohydrates form a syrupy unbranched polysaccharide – **mucopolysaccharide**.This jell like substance works as a shock absorber in the joints and extra-cellular space
- **Hyaluronate** Along polysaccharide composed of 25,000 disaccharide units. It is a very rigid polysaccharide that makes a viscous solution with H_2O. -It is made with sugar derivatives that have carboxyl groups ($–CO2^-$). Water is held next to the charged group so this rigid molecule can act as a lubricant for joints
- **Chondroitin 6–sulfate** is present in tendons and cartilage where it is linked to proteins. Glucosamine-sulfate, as well as chondroitin-6-sulfate is sold to help with joint conditions.

Heparin

- Heparin: This is a polysaccharide associated with connective tissue. It is an anticoagulant.
- It is composed of variety of monosaccharides many of which contain sulfate groups.



Example of repeating unit in heparin

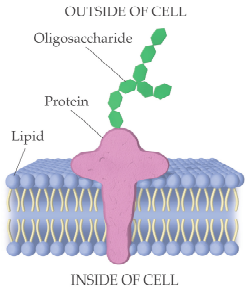
Heparin

- Highest negative charge density of any known biological molecule
- It large density of negative charge causes it to binds strongly to blood clotting factors and this prevents clot formation.
- Its natural utility in animals is not known. It seems to have a role in healing from an injury.
- It is obtained from slaughtered pigs and cows.

Glycoproteins

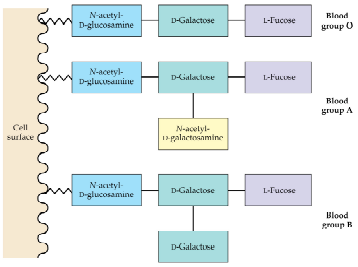
- Glycoproteins: Proteins containing short carbohydrate chains are known as glycoproteins.
- Many uses organism, in some cases they are used to protect a protein from digestion.
- Some glycoproteins are present at the surface of cells. The protein part of the molecule lies embedded in the cell membrane and the hydrophilic carbohydrate portion extends into the surrounding fluid.

Polysaccharides On the Surface of Cells



Polysaccharides on Cell Surfaces

- The oligosaccharide chains function as the receptors for molecular messengers, other cells, pathogens, or drugs. They are also responsible for the A, B and O typing of blood.



Storage Polysaccharides

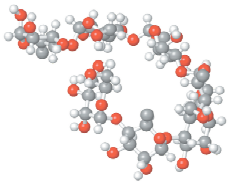
Stach and Glysogen

Starch_

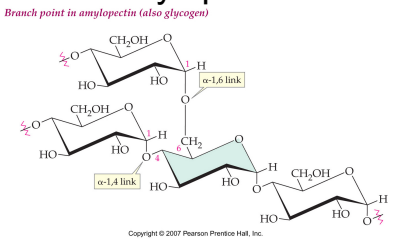
- Starch is a polymer of α D glucose joined by α - 1,4 linkage, not a 1,4 linkage as is cellulose.
- Starch is the way that energy is stored in plants.
- Starch is fully digestible to humans
- Starch digestion begins in the mouth where the enzyme amylase can break the starch down into maltose.
- In the small intestine, amylase is released from the pancreas and finishes off the digestion
- Starch has two forms- Amylose and amylopectin.

Amylose

- Amylose accounts for about 20 % of the starch .
- It is soluble in water..
- The amylose oligosaccharide is a chain, that is often coiled.



Amylopectin



- Very similar to amylose but it is branched, and made up of very long polymers

Glycogen-Structure

- **Glycogen:** Also called animal starch. Glycogen is structurally similar to starch as it is a polymer of α-D-glucose. Glycogen is much more branched than the starch molecule and has a much larger molecular weight up to a million glucose units per molecule.

Glycogen-Uses

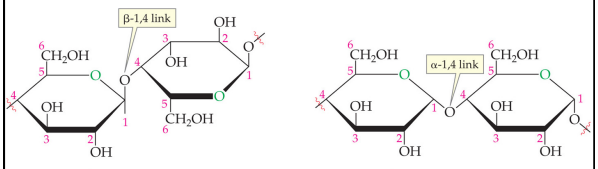
- Glycogen is concentrated in the liver and in muscles.
- In muscles it can be quickly converted to glucose and used to make ATP.
- In the liver it can be converted to glucose when blood sugar becomes low

Cellulose

Cellulose

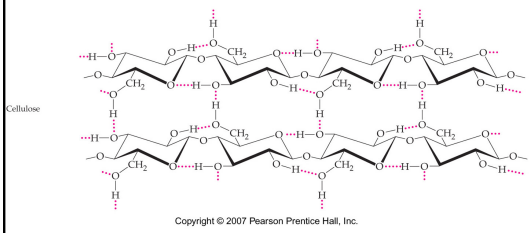
- β-D glucose units joined by β-1.4 linkage.
- The seemingly minor difference between the α and β units of glucose in starch and cellulose accounts for the inability in digestion of cellulose. In grazing animals and termites and moths there are microorganisms that reside in the digestive tracts. These produce enzymes that can hydrolyze the β glycosidic bonds in cellulose. Cellulose is the fiber that we need in our diet, but we can not digest it.
- (What other example have we seen of needing enzymes in bacteria in the gut in order to digest a food.)

Cellulose vs. Starch



- Similar link different anomers.

Cellulose – Overall Structure



- Hydrogen bonds between chains are one of the reasons for cellulose's strength.

Summary

- Overview of the Structure and Function of
  - Monosaccharides
  - Disaccharides
  - Polysaccharides