

The D and L families of sugars....Fischer Projections!

Fischer projections show the molecule in its non-cyclic form and indicates whether it is D or L. Bonds that point up and out of the page are shown as horizontal lines, and bonds that point behind the page are shown as vertical lines. If you look at the OH group the furthest from the carbonyl carbon, the direction it faces indicates if the sugar is D or L. D point to the right and L point to the left.

D-Glyceraldehyde

L-Glyceraldehyde

Nature LOVES carbohydrates that are in the D family, and remember that the body preferred amino acids that were in the L family. Try not to mix those up! Note that D and L do not denote which direction the molecule rotates polarized light. The direction of rotation cannot be predicted, but it is TRUE that the D will rotate one direction to a certain degree, and the L will rotate to the opposite direction to the same degree.

L = levo (left)
D = dextro (right)

Structure of Glucose and other Monosaccharides

In most living organisms, D-glucose serves as a source of energy to fuel biochemical reactions. It is stored in polymeric form as starch in plants and as glycogen in animals. Though we CAN write monosaccharides such as glucose in their Fischer-projection form, they actually exist in cyclic form. Note that glucose written in its Fischer form has an alcohol hydroxyl group AND an aldehyde carbonyl group, so it can do internal hemiacetal formation...meaning it can cyclize! Monosaccharides with 5 or 6 carbons form rings in the same way.

- OH groups shown on the left of a Fischer projection point UP in the cyclic structure.
- OH groups shown on the right in a Fischer projection point DOWN in the cyclic form.
- CH₂O₂ group is always ABOVE the plane of the ring.

B-D-Glucose

A-D Glucose

What is an anomeric carbon?

When cyclic monosaccharides differ only in the position of the subs at Carbon 1, this is known as an anomer, and Carbon 1 is an anomeric carbon. Note that the alpha and beta anomers of a given sugar are NOT optical isomers because they are not mirror images of one another. Anomers account for the vast differences in the digestibility of starch and cellulose.

What is maturotation?

Maturotation is the change in rotation of plane-polarized light resulting from the equilibrium between cyclic anomers and the open-chain form of a sugar. In water, equilibrium is established among the open chain form of a sugar and the anomers.

A-D-Glucose

Open-Chain

B-D-Glucose

Some important monosaccharides

Monosaccharides have many opportunities for hydrogen bonding so they are generally high-melting, soluble in water and insoluble in polar solvents. They are mostly white crystalline solids. Most are sweet tasting, digestible and non-toxic.

All monos are aldohexoses and aldopentoses except for glyceraldehydes and fructose.

Glucose is the most important simple CHO in human metabolism. It is the final product of CHO digestion and provides acetyl groups for the citric acid cycle (acetyl-SCoA).

D-Galactose is widely distributed in plant gums and pectins. It also makes up lactose along with glucose and is produced from lactose during digestion.

Galactose differs from glucose only in the spatial orientation of the –OH at Carbon 4. In the body galactose is converted to glucose to provide energy!

Fructose occurs in honey and many fruits. It makes up sucrose along with glucose. It is a six-carbon sugar but is a ketohexose! As a phosphate, fructose is an intermediate in glucose metabolism.

Ribose and 2-Deoxyribose are both five-carbon aldehyde sugars. They are important parts of coenzyme A, ATP, 2nd messenger cyclic AMP and RNA/DNA.

Reactions of Monosaccharides

Oxidation

Recall that aldehydes can be oxidized up to Carboxylic Acids...this happens to aldose monosaccharides when they are in the open chain form. The really interesting thing here is that ketoses can also oxidize! But wait! Ketones don't oxidize! How does this happen?

In BASE, a hydroxyketone (basically a sugar) will undergo some rearrangement that results in an intermediary called an ENEDIOL (basically a compound with two hydroxy groups and a double bond), which then undergoes more rearrangement to become an aldose. Once it is in the aldose form it can oxidize up to the carboxylic acid anion.

Ketose

Enediol

Aldose

Aldonic acid anion

So, the end result is that IN BASIC SOLUTIONS, all monosaccharides are reducing sugars. This ability to act as a reducing agent is the basis for most laboratory tests for the presence of monosaccharides.

Reactions with Alcohols

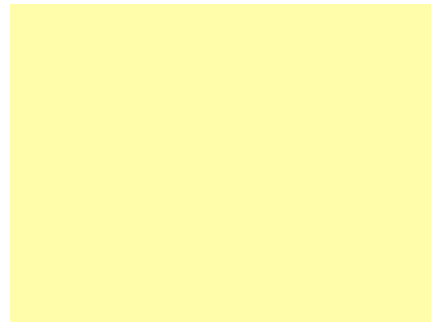
Recall that hemiacetals react with alcohols to form acetals...and recall that glucose and other monosaccharides are cyclic hemiacetals so they form acetals when reacting with alcohol also. These acetals are called GLYCOSIDES...the -OH group on the anomeric carbon is replaced by an -OR group. The bond between the anomeric carbon and the -OR group is a GLYCOSIDIC BOND. If your glycoside does not contain hemiacetal groups then your sugar is NOT a reducing sugar...we'll see this later on with sucrose.

Glycosidic bonds also connect monosaccharides together to form disaccharides and polysaccharides. We'll see lots of this coming up soon. When this link is broken it is a hydrolysis reaction. Hydrolysis takes place during the digestion of carbohydrates.

Formation of Phosphate Esters of Alcohols

Phosphate esters contain a phosphoryl group bonded to the oxygen atom of an -OH group. The -OH groups of sugars can add phosphoryl groups to form phosphate esters in the same manner. The resulting phosphate esters appear as reactants and products throughout the metabolism of CHOs.

The first phosphate ester to be formed is glucose phosphate...it sets the stage for subsequent reactions. It is produced by the transfer of a phosphoryl group from ATP to glucose in the first step of glycolysis.



Disaccharides

Structure: Two monosaccharides connected by a glycosidic bond
Bond can be alpha, beta or anomeric
Alpha goes down, beta goes up!

	Components	Link	Reducing	Misc
Maltose	a-D-Glucose + a-D-Glucose	a-1,4	Yes	Present in fermenting grains Can be prepared by enzyme-catalyzed degradation of starch Produced during starch digestion by a-amylase, then hydrolyzed to glucose by a second enzyme.
Lactose	b-D-Galactose + b-D-Glucose	b-1, 4	Yes	Lactose intolerance is the norm Milk sugar
Sucrose	a-D-Glucose + b-D-Fructose	1, 2 anomeric	No	Sugar beets and sugarcane Hydrolysis yields 50:50 mixture Invert sugar

Draw them here:

Variations on the Carbohydrate Theme

Monosaccharides can have distinctive functional groups, making them a component of a wide variety of biomolecules. You can also have short chains of monosaccharides (called oligosaccharides) that enhance the functions of proteins and lipids.

For example, Glucose with a carboxylate anion group is b-D-Glucuronate...and Glucose with an amine group is b-D-Glucosamine.

Chitin

- This is the second-most common polysaccharide in the world (cellulose is most common.)
- Composed of N-acetyl-d-glucosamine (otherwise identical to cellulose which is made up of glucose)

Connective Tissue and Polysaccharides

- Composed of protein fibers embedded in syrupy matrix
- Serve as lubricants and shock absorbers around joints and in extracellular spaces
- Hyaluronate molecules make up synovial fluid
- Chondroitin 6-sulfate is present in tendons and cartilage, where it is linked to proteins...it has been used in artificial skin!

Heparin

- Associated with connective tissue
- Anticoagulant
- Lot of negative charges
- Many of the monosaccharides of heparin contain sulfate groups

Glycoproteins

- Contain short carbohydrate chains (oligosaccharide chains)
- CHO is connected via glycosidic bond between anomeric carbon and a side chain of the protein...it is either a C-O bond, or a C-N bond (depending on what side chain of the protein is connected)
- Functions include acting as receptors and in blood typing

Important Polysaccharides

Cellulose

- Fiber
- Made up of b-D-glucose units joined by b-1,4 links
- Tetrahedral bonding at each carbon, the CHO rings are in chair conformation
- Each glucose ring is reversed relative to the next
- Humans can't hydrolyze b-1,4 links...but cows and termites can!

Starch

- Also a polymer of glucose
- Joined by α -1,4 links
- Humans can hydrolyze α -1,4 links so it is fully digestible
- Two forms...amylose and amylopectin
 - Amylose coils into helices
 - Amylose accounts for about 20% of starch
 - Amylose is somewhat soluble in hot water
 - Amylopectin accounts for about 80% of starch
 - Amylopectin has α -1,6 branches about every 25th glucose
 - Amylopectin is not water soluble
- Starch molecules are digested mainly in the small intestine by α -amylase

Same kind of links that are in maltose and lactose.

Glycogen

- Sometimes called animal starch
- Polymer of α -D-glucose
- Serves energy storage role in animals
- Largest amounts are stored in liver and muscles
- In muscles, glycogen is converted to glucose 6-phosphate for the synthesis of ATP
- Similar to amylopectin, but with more branches and more glucose units.