

Organic and Biochemistry for Today (4th ed.)
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Biochemistry

- **Biochemistry** is the study of the chemistry of biomolecules and living organisms.
- In organic chemistry, we organized our study of carbon-containing molecules by *functional group* (alcohol, alkene, ketone, carboxylic acid, etc.).
- In the first five chapters, we will take a look at several groups of important biological molecules, many of which have more than one functional group: carbohydrates (Ch. 7), lipids (Ch. 8), proteins and enzymes (Ch. 9 and 10), and nucleic acids (Ch. 11).
- We will also examine the synthesis of proteins (Ch. 11), nutrition (Ch. 12) and metabolism (Ch. 13, 14), and important body fluids (Ch. 15).

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Classification of Carbohydrates

Carbohydrates and Biochemistry

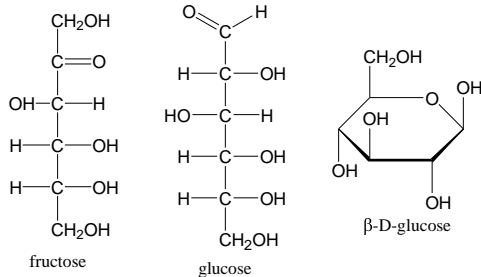
- Carbohydrates are compounds of tremendous biological importance:
 - they provide energy through oxidation
 - they supply carbon for the synthesis of cell components
 - they serve as a form of stored chemical energy
 - they form part of the structures of some cells and tissues
- Carbohydrates, along with lipids, proteins, nucleic acids, and other compounds are known as **biomolecules** because they are closely associated with living organisms.

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Carbohydrates

- **Carbohydrates**, or *saccharides* (*saccharo* is Greek for "sugar") are polyhydroxy aldehydes or ketones, or substances that yield such compounds on hydrolysis.



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Carbohydrates



- Carbohydrates include not only sugar, but also the starches that we find in foods, such as bread, pasta, and rice.



- The term "carbohydrate" comes from the observation that when you heat sugars, you get carbon and water (hence, *hydrate of carbon*).



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Classes of Carbohydrates

- **Monosaccharides** contain a single polyhydroxy aldehyde or ketone unit (e.g., glucose, fructose).



- **Disaccharides** consist of two monosaccharide units linked together by a covalent bond (e.g., sucrose).



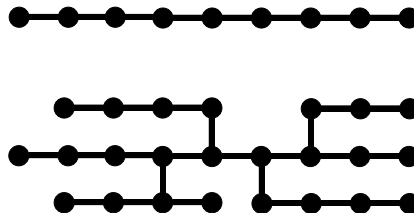
- **Oligosaccharides** contain from 3 to 10 monosaccharide units (e.g., raffinose).



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Classes of Carbohydrates

- **Polysaccharides** contain very long chains of hundreds or thousands of monosaccharide units, which may be either in straight or branched chains (e.g., cellulose, glycogen, starch).

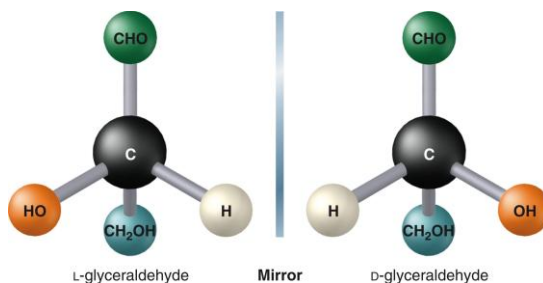


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The Stereochemistry of Carbohydrates

Two Forms of Glyceraldehyde

- Glyceraldehyde, the simplest carbohydrate, exists in two isomeric forms that are mirror images of each other:

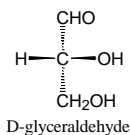
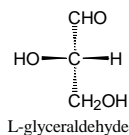


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Stereoisomers

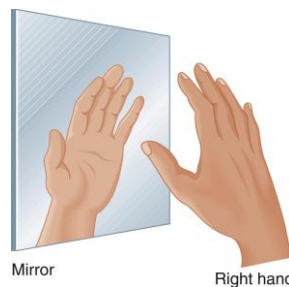
- These forms are **stereoisomers** of each other.
- Glyceraldehyde is a **chiral** molecule — it cannot be superimposed on its mirror image. The two mirror-image forms of glyceraldehyde are **enantiomers** of each other.



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Chirality and Handedness

- Chiral molecules have the same relationship to each other that your left and right hands have when reflected in a mirror.



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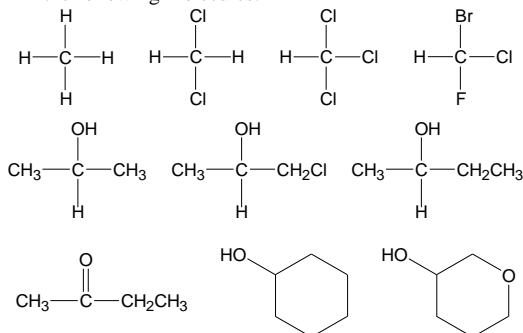
Chiral Carbons

- *Chiral* objects cannot be superimposed on their mirror images — e.g., hands, gloves, and shoes.
- *Achiral* objects *can* be superimposed on the mirror images — e.g., drinking glasses, spheres, and cubes.
- Any carbon atom which is connected to *four different groups* will be chiral, and will have two nonsuperimposable mirror images; it is a **chiral carbon** or a **center of chirality**.
 - If *any* of the two groups on the carbon are the same, the carbon atom *cannot be chiral*.
- Many organic compounds, including carbohydrates, contain more than one chiral carbon.

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Examples: Chiral Carbon Atoms

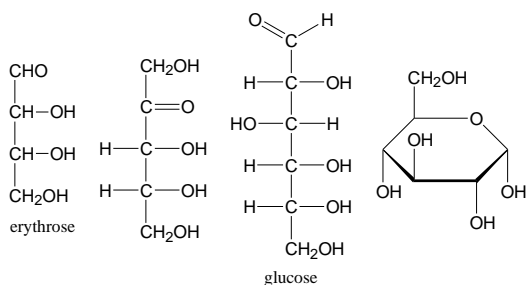
- Identify the chiral carbon atoms (if any) in each of the following molecules:



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Examples: Chiral Carbons in Carbohydrates

- Identify the chiral carbons (if any) in the following carbohydrates:

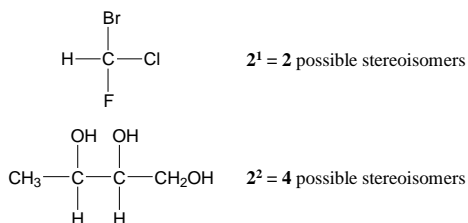


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2ⁿ Rule

- When a molecule has more than one chiral carbon, each carbon can possibly be arranged in either the right-hand or left-hand form, thus if there are *n* chiral carbons, there are 2ⁿ possible stereoisomers.

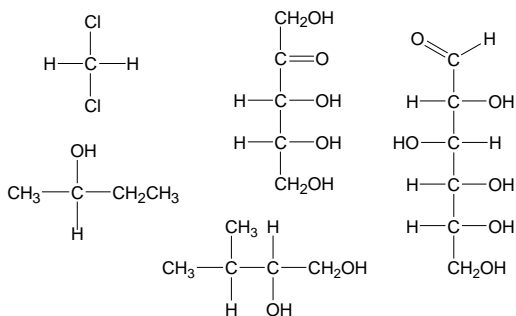
Maximum number of possible stereoisomers = 2ⁿ



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Examples: Number of Stereoisomers

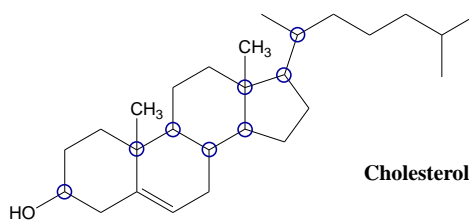
- What is the maximum number of possible stereoisomers of the following compounds?



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Examples: Number of Stereoisomers

- What is the maximum number of possible stereoisomers of the following compound?

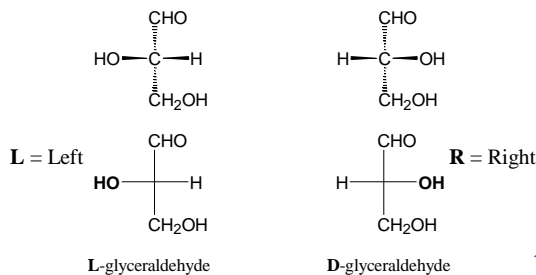


2⁸ = 256 possible stereoisomers.
(But Nature makes only one!)

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Fischer Projections

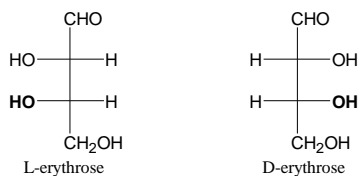
- Fischer projections are a convenient way to represent mirror images in two dimensions.
- Place the carbonyl group at or near the top and the last achiral CH_2OH at the bottom.



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Naming Stereoisomers

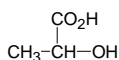
- When there is more than one chiral center in a carbohydrate, look at the chiral carbon farthest from the carbonyl group: if the hydroxy group points to the right when the carbonyl is "up" it is the D-isomer, and when the hydroxy group points to the left, it is the L-isomer.



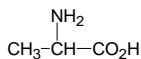
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Examples: Fischer Projections

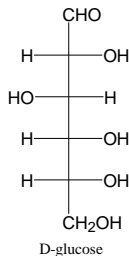
- Draw Fischer projections of D and L lactic acid:



- Draw Fischer projections of D and L alanine:



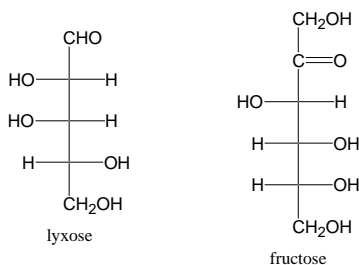
- Given the structure for D-glucose, draw the structure of L-glucose:



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Examples: Fischer Projections

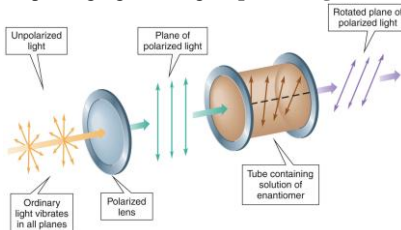
- Identify the following compounds as D or L isomers, and draw their mirror images.



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What's So Great About Chiral Molecules?

- Molecules which are enantiomers of each other have exactly the **same** physical properties (melting point, boiling point, index of refraction, etc.) but not their interaction with **polarized light**.
- Polarized light vibrates only in one plane; it results from passing light through a **polarizing filter**.



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Optical Activity

- A **levorotatory** (–) substance rotates polarized light to the left [e.g., *l*-glucose; (–)-glucose].
- A **dextrorotatory** (+) substance rotates polarized light to the right [e.g., *d*-glucose; (+)-glucose].
- Molecules which rotate the plane of polarized light are **optically active**.
- Many biologically important molecules are chiral and optically active. Often, living systems contain only one of the possible stereochemical forms of a compound, or they are found in separate systems.
 - D-lactic acid is found in living muscles; D-lactic acid is present in sour milk.
 - In some cases, one form of a molecule is beneficial, and the enantiomer is a poison (e.g., thalidomide).
 - Humans can metabolize D-monosaccharides but not L-isomers; only L-amino acids are used in protein synthesis.

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Monosaccharides

Classification of Monosaccharides

- The monosaccharides are the simplest of the carbohydrates, since they contain only one polyhydroxy aldehyde or ketone unit.
- Monosaccharides are classified according to the number of carbon atoms they contain:

| No. of carbons | Class of Monosaccharide |
|----------------|-------------------------|
| 3 | triose |
| 4 | tetrose |
| 5 | pentose |
| 6 | hexose |

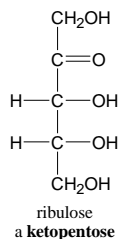
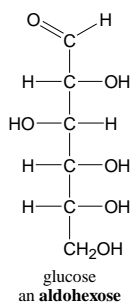
- The presence of an aldehyde is indicated by the prefix **aldo-** and a ketone by the prefix **keto-**.

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Classification of Monosaccharides

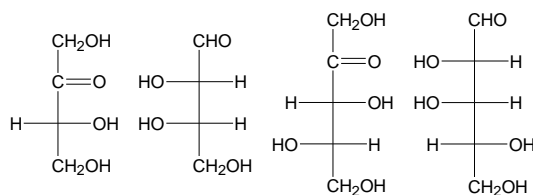
- Thus, glucose is an **aldohexose** (aldehyde + 6 Cs) and ribulose is a **ketopentose** (ketone + 5 Cs)



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Examples: Classifying Monosaccharides

- Classify the following monosaccharides:



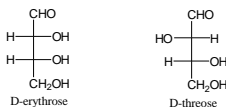
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The Family of D-aldoses

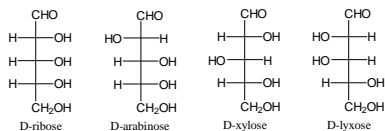
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Aldotriose
 $2^1 = 2$



Aldotetroses
 $2^2 = 4$

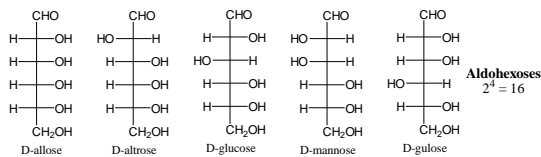


Aldopentoses
 $2^3 = 8$

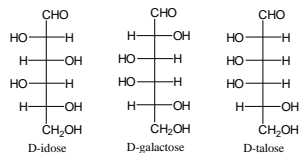
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The Family of D-aldoses

(L-forms not shown)



Aldohexoses
 $2^4 = 16$



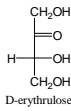
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The Family of D-ketoses

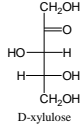
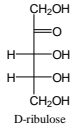
(L-forms not shown)



Ketotriose
 $2^0 = 1$



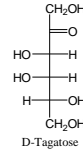
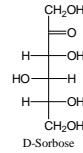
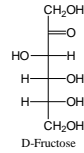
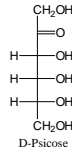
Ketotetroses
 $2^1 = 2$



Ketopentoses
 $2^2 = 4$

The Family of D-ketoses

(L-forms not shown)



Ketohexoses
 $2^3 = 8$

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Physical Properties of Monosaccharides

- Most monosaccharides have a sweet taste (fructose is sweetest; 73% sweeter than sucrose).
- They are solids at room temperature.
- They are *extremely* soluble in water:
 - Despite their high molecular weights, the presence of large numbers of OH groups make the monosaccharides much more water soluble than most molecules of similar MW.
 - Glucose can dissolve in minute amounts of water to make a syrup (1 g / 1 ml H₂O).

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Physical Properties of Monosaccharides

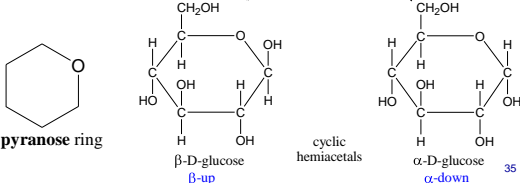
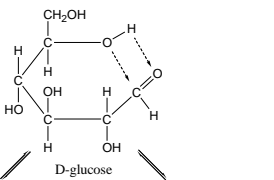
Table 7.2 The relative sweetness of sugars (sucrose = 1.00)

| Sugar | Relative Sweetness | Type |
|--------------|--------------------|---------------------------------|
| Lactose | 0.16 | Disaccharide |
| Galactose | 0.22 | Monosaccharide |
| Maltose | 0.32 | Disaccharide |
| Xylose | 0.40 | Monosaccharide |
| Glucose | 0.74 | Monosaccharide |
| Sucrose | 1.00 | Disaccharide |
| Invert sugar | 1.30 | Mixture of glucose and fructose |
| Fructose | 1.73 | Monosaccharide |

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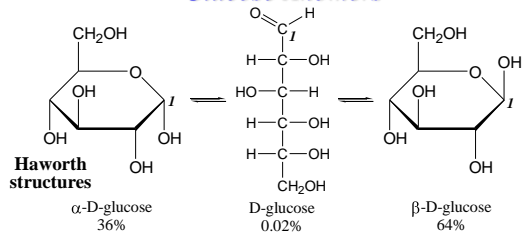
Chemical Properties of Monosaccharides

- Monosaccharides do not usually exist in solution in their “open-chain” forms: an alcohol group can add into the carbonyl group in the same molecule to form a **pyranose ring** containing a stable cyclic hemiacetal or hemiketal.



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Glucose Anomers

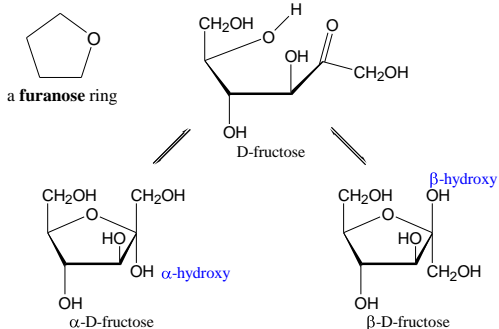


- In the pyranose form of glucose, carbon-1 is chiral, and thus two stereoisomers are possible: one in which the OH group points down (α -hydroxy group) and one in which the OH group points up (β -hydroxy group). These forms are **anomers** of each other, and carbon-1 is called the **anomeric carbon**.

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Fructose Anomers

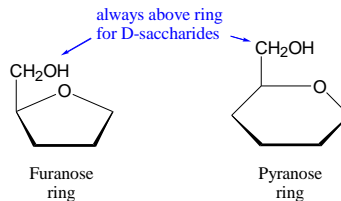
- Fructose closes on itself to form a **furanose ring**:



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Drawing Furanose and Pyranose Rings

- Monosaccharides are often represented using the Haworth structures shown below for furanose and pyranose rings.
- The remaining OH groups on the ring point up or down depending on the identity of the sugar.

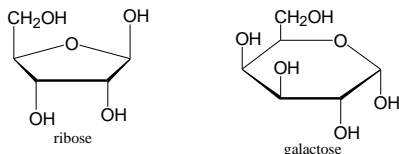


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Examples: Anomers

With Friends Like These, Who Needs Anomers?

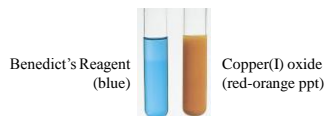
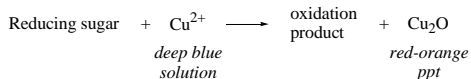
- Identify the structures below as being the α - or β -forms, and draw the structure of their anomers:



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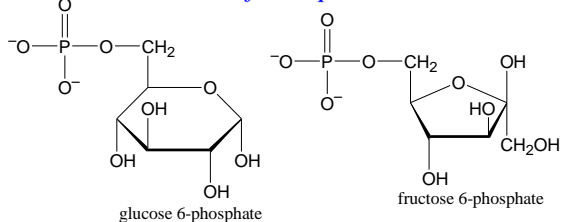
Oxidation of Monosaccharides

- Aldehydes and ketones that have an OH group on the carbon next to the carbonyl group react with a basic solution of Cu^{2+} (**Benedict's reagent**) to form a red-orange precipitate of copper(I) oxide (Cu_2O).
- Sugars that undergo this reaction are called **reducing sugars**. (All of the monosaccharides are reducing sugars.)



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Formation of Phosphate Esters

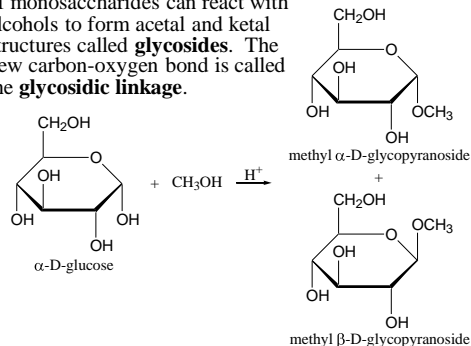


- Phosphate esters can form at the 6-carbon of aldohexoses and aldoketoses.
- Phosphate esters of monosaccharides are found in the sugar-phosphate backbone of DNA and RNA, in ATP, and as intermediates in the metabolism of carbohydrates in the body.

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Glycoside Formation

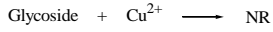
- The hemiacetal and hemiketal forms of monosaccharides can react with alcohols to form acetal and ketal structures called **glycosides**. The new carbon-oxygen bond is called the **glycosidic linkage**.



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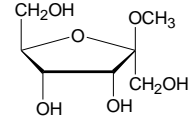
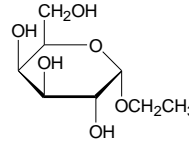
Glycoside Formation

- Once the glycoside is formed, the ring can no longer open up to the open-chain form. Glycosides, therefore, are **not** reducing sugars.



Examples: Glycoside Formation

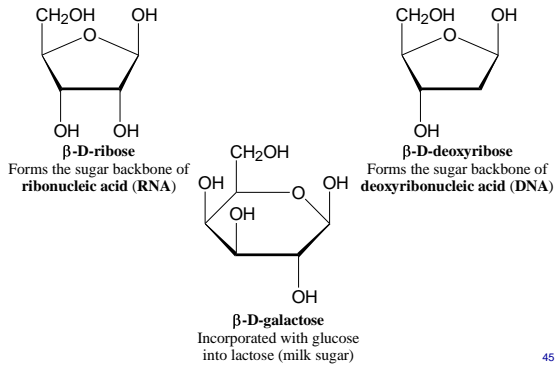
- Identify the glycosidic linkage in each of the following molecules:



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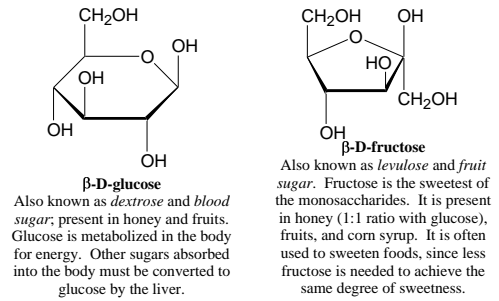
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Important Monosaccharides



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Important Monosaccharides

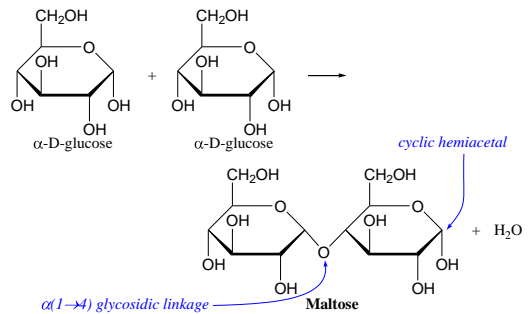


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Disaccharides and Oligosaccharides

Disaccharides

- Two monosaccharides can be linked together through a glycosidic linkage to form a **disaccharide**.

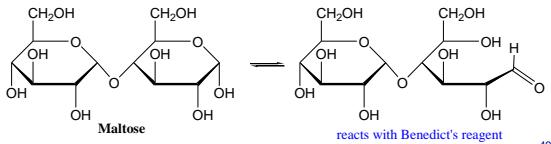
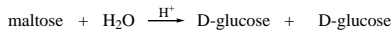


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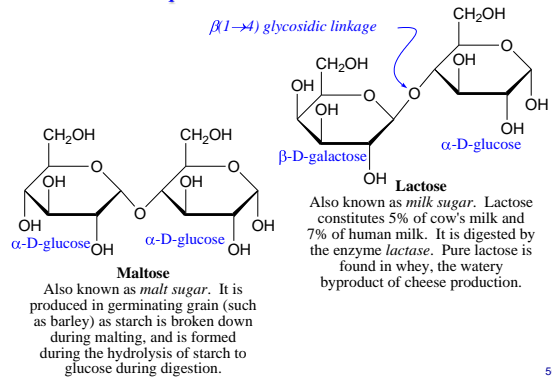
Disaccharides

- Disaccharides can be hydrolyzed into their monosaccharide building blocks by boiling them with dilute acids or reacting them with the appropriate enzymes.
- Disaccharides that contain hemiacetal groups are reducing sugars.



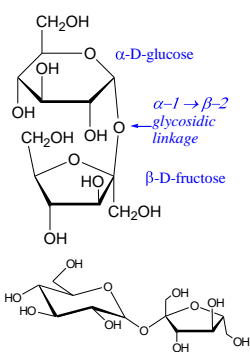
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Important Disaccharides



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Important Disaccharides

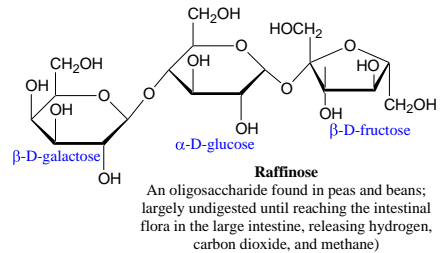


Sucrose
Also known as *table sugar*. Both anomeric carbons of glucose and fructose are tied together in the glycosidic linkage; thus neither ring can open, and sucrose is *not* a reducing sugar. Sucrose is found in fruits, nectar, sugar cane, and sugar beets; maple syrup contains about 65% sucrose, with glucose and fructose present as well. *Caramel* is the solid residue formed from heating sucrose. A flavoring agent called *invert sugar* is produced by the hydrolysis of sucrose under acidic conditions, which breaks it apart into glucose and fructose; invert sugar is sweeter than sucrose because of the fructose. Some of the sugar found in honey is formed in this fashion; invert sugar is also produced in jams and jellies prepared from acid-containing fruits.

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Oligosaccharides

- Oligosaccharides contain from 3 to 10 monosaccharide units.



Raffinose
An oligosaccharide found in peas and beans; largely undigested until reaching the intestinal flora in the large intestine, releasing hydrogen, carbon dioxide, and methane)

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Polysaccharides

Polysaccharides

- Polysaccharides** contain hundreds or thousands of carbohydrate units.
- Polysaccharides are *not* reducing sugars, since the anomeric carbons are connected through glycosidic linkages.
- We will consider three kinds of polysaccharides, all of which are polymers of glucose: *starch*, *glycogen*, and *cellulose*.

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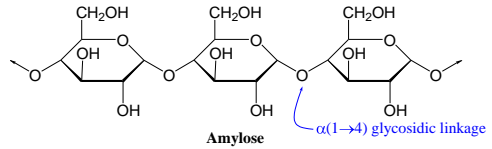
Starch

- **Starch** is a polymer consisting of D-glucose units.
- Starches (and other glucose polymers) are usually insoluble in water because of the high molecular weight.
 - Because they contain large numbers of OH groups, some starches can form thick colloidal dispersions when heated in water (e.g., flour or starch used as a thickening agent in gravies or sauces).
- There are two forms of starch: **amylose** and **amylopectin**.

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Starch — Amylose

- **Amylose** consists of long, *unbranched* chains of glucose (from 1000 to 2000 molecules) connected by $\alpha(1\rightarrow4)$ glycosidic linkages.

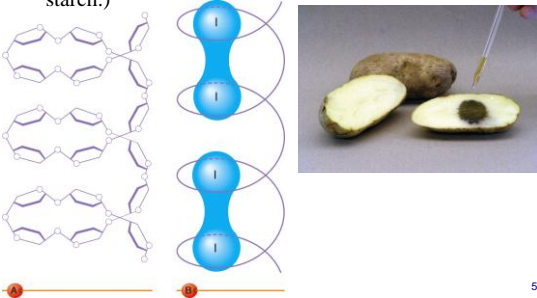


- 10% -20% of the starch in plants is in this form.
- The amylose chain is flexible enough to allow the molecules to twist into the shape of a helix. Because it packs more tightly, it is slower to digest than other starches.

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Starch — Amylose

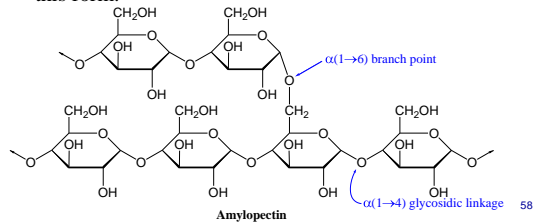
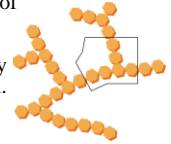
- Amylose helices can trap molecules of iodine, forming a characteristic deep blue-purple color. (Iodine is often used as a test for the presence of starch.)



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Starch — Amylopectin

- **Amylopectin** consists of long chains of glucose (up to 10^5 molecules) connected by $\alpha(1\rightarrow4)$ glycosidic linkages, with $\alpha(1\rightarrow6)$ branches every 24 to 30 glucose units along the chain.
- 80% -90% of the starch in plants is in this form.



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Glycogen

- **Glycogen**, also known as *animal starch*, is structurally similar to amylopectin, containing both $\alpha(1\rightarrow4)$ glycosidic linkages and $\alpha(1\rightarrow6)$ branch points. Glycogen is even more highly branched, with branches occurring every 8 to 12 glucose units.
- Glycogen is abundant in the liver and muscles; on hydrolysis it forms D-glucose, which maintains normal blood sugar level and provides energy.

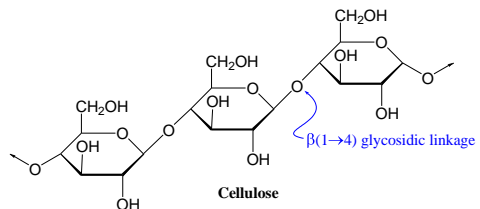


Starches (plants)
 Amylose – unbranched
 Amylopectin – branched
Glycogen (animals) – highly branched

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Cellulose

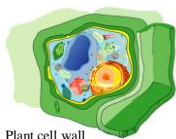
- **Cellulose** is a polymer consisting of long, *unbranched* chains of D-glucose connected by $\beta(1\rightarrow4)$ glycosidic linkages; it may contain from 300 to 3000 glucose units in one molecule.



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Cellulose

- Because of the β -linkages, cellulose has a different overall shape from amylose, forming extended straight chains which hydrogen bond to each other, resulting in a very rigid structure.
- Cellulose is the most important structural polysaccharide, and is the single most abundant organic compound on earth. It is the material in plant cell walls that provides strength and rigidity; wood is 50% cellulose.



Plant cell wall

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Cellulose

- Most animals lack the enzymes needed to digest cellulose, but it does provide roughage (dietary fiber) to stimulate contraction of the intestines and help pass food through the digestive system.
- Some animals, such as cows, sheep, and horses (ruminants), can process cellulose through the use of colonies of bacteria in the digestive system which are capable of breaking cellulose down to glucose; ruminants use a series of stomachs to allow cellulose a longer time to digest. Some other animals such as rabbits reprocess digested food to allow more time for the breakdown of cellulose to occur.
- Cellulose is also important industrially, from its presence in wood, paper, cotton, cellophane, rayon, linen, nitrocellulose (gun cotton), photographic films (cellulose acetate), etc.

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Nitrocellulose, Celluloid, and Rayon

- *Gun cotton* (German, *schießbaumwolle*) is cotton which has been treated with a mixture of nitric and sulfuric acids. It was discovered by Christian Friedrich Schönbein in 1845, when he used his wife's cotton apron to wipe up a mixture of nitric and sulfuric acids in his kitchen, which vanished in a flash of flame when it dried out over a fire. Schönbein attempted to market it as a smokeless powder, but it combusted so readily it was dangerous to handle. Eventually its use was replaced by *cordite* (James Dewar and Frederick Abel, 1891), a mixture of nitrocellulose, nitroglycerine, and petroleum jelly, which could be extruded into cords.
- *Celluloid* (John Hyatt, 1869) was the first synthetic plastic, made by combining partially nitrated cellulose with alcohol and ether and adding camphor to make it softer and more malleable. It was used in manufacturing synthetic billiard balls (as a replacement for ivory), photographic film, etc.; it was eventually replaced by less flammable plastics.
- *Rayon* (Louis Marie Chardonnet, 1884) consists of partially nitrated cellulose mixed with solvents and extruded through small holes, allowing the solvent to evaporate; rayon was a sensation when introduced since it was a good substitute for silk, but it was still highly flammable.

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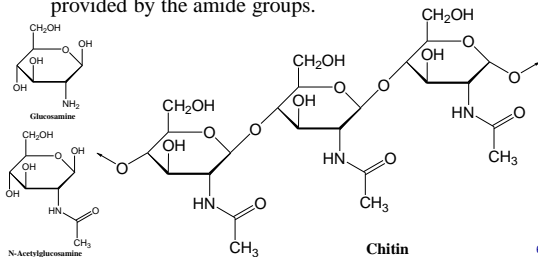
Dietary Fiber

- Dietary fiber consists of complex carbohydrates, such as cellulose, and other substances that make up the cell walls and structural parts of plants.
- Good sources of dietary fiber include cereal grains, oatmeal, fresh fruits and vegetables, and grain products.
- Soluble fiber, such as pectin, has a lower molecular weight, and is more water soluble. Soluble fiber traps carbohydrates and slows their digestion and absorption, thereby leveling out blood sugar levels during the day. Soluble fiber also helps to lower cholesterol levels by binding dietary cholesterol.
- Insoluble fiber, such as cellulose, provides bulk to the stool, which helps the body to eliminate solid wastes.

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Chitin

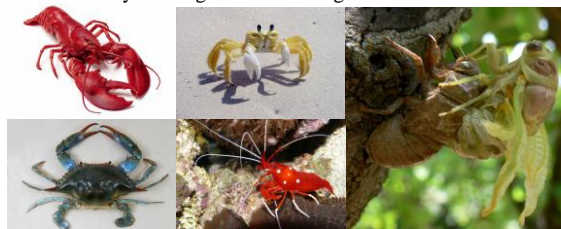
- **Chitin** is a polymer of N-acetylglucosamine, an amide derivative of the *amino sugar* glucosamine, in which one of the OH groups is converted to an amine (NH_2) group. The polymer is extremely strong because of the increased hydrogen bonding provided by the amide groups.



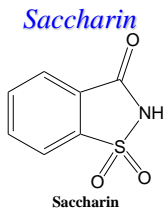
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Chitin

- Chitin is the main component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans and insects, and the beaks of cephalopods. The chitin is often embedded in either a protein matrix, or in calcium carbonate crystals. Since this matrix cannot expand easily, it must be shed by molting as the animal grows.



How Sweet It Is! Sugar Substitutes

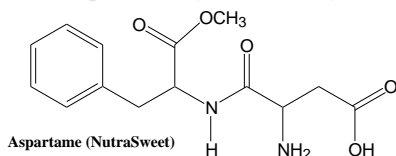


The first of the artificial sweeteners, saccharin is noncaloric and about 500 times sweeter than sugar. It was discovered in 1879 by Constantine Fahlberg, a chemistry student at Johns Hopkins University working for Ira Remsen; he noticed that the bread he was eating was unusually sweet, and went back to his lab bench and tasted all of the compounds he had been working with that day to find the compound responsible. It was marketed commercially as a non-nutritive sweetener very quickly, especially for use by diabetics. It was banned in some areas for some time because it was a suspected carcinogen.

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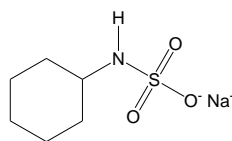
68

Aspartame (NutraSweet)

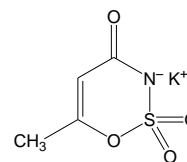


Aspartame (NutraSweet) is about 160 times sweeter than sugar; it is composed of the amino acids aspartic acid and phenylalanine, neither of which has a sweet taste. It was discovered at Searle by James Schlatter in 1965, who was preparing intermediates for the synthesis of a tetrapeptide for an anti-ulcer project. Schlatter had spilled some of the dipeptide intermediate on his hands, and noticed later that there was a strong, sweet taste; he went back to his bench and tasted the dipeptide and found that it indeed was extremely sweet. Aspartame is sensitive to heat, so it cannot be used in cooked foods, and it decomposes slowly in liquids, reducing their shelf life.

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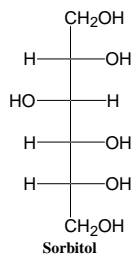


Discovered by Michael Sveda in 1937, who noticed that a cigar that he was smoking in the lab tasted especially sweet. It is about 30-50 times sweeter than sugar, and is often used in combination with other artificial sweeteners. It is heat-stable. Cyclamate was banned by the FDA in 1970, although it is still used in other countries.

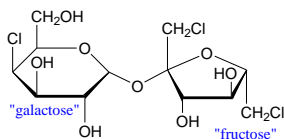


Discovered accidentally at Hoechst AG when a chist accidentally dipped his fingers into the chemicals that he was working with, and later licked his finger to pick up a piece of paper. It is 200 times sweeter than sugar, noncaloric, and is heat-stable and can be used during cooking. It is often used in combination with other artificial sweeteners, so that each one masks the others' aftertaste.

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A sugar alcohol; incompletely absorbed during digestion, and contribute fewer calories than carbohydrates; found naturally in fruits; used commercially in sugar-free candies, cookies, chewing gum, etc.

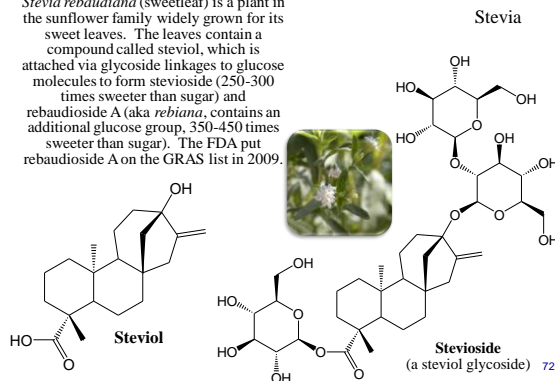


A non-caloric artificial sweetener approved by the FDA in 1998. The glucose in sucrose is replaced by a galactose, and three of the OH groups are replaced by Cl atoms. It is about 600 times sweeter than sucrose, and is non-caloric and heat-stable.

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Steviol (Truvia, PureVia)

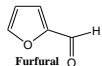
Stevia rebaudiana (sweetleaf) is a plant in the sunflower family widely grown for its sweet leaves. The leaves contain a compound called steviol, which is attached via glycoside linkages to glucose molecules to form steviolosides (250-300 times sweeter than sugar) and rebaudioside A (aka *rebiana*, contains an additional glucose group, 350-450 times sweeter than sugar). The FDA put rebaudioside A on the GRAS list in 2009.



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The Maillard Reaction

- The **Maillard Reaction** occurs between foods containing carbohydrates and proteins under heating; it results in a complex mixture of products and the development of a brown color. It is observed in the grilling or browning of meats, the formation of crust on baked breads, the boiling of maple syrup, the brewing of beer, the roasting of coffee and cocoa beans, the roasting of nuts, and other sources. In addition to the darkened colors, many complex flavors are developed. There are hundreds of compounds produced during these reactions, not many of which are well-characterized.



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The End

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