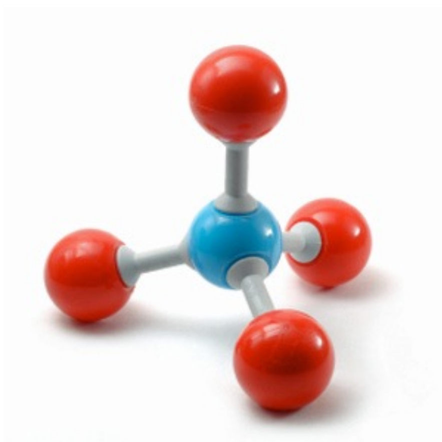
Ch13

Chirality

Carbohydrates and more complex structures.

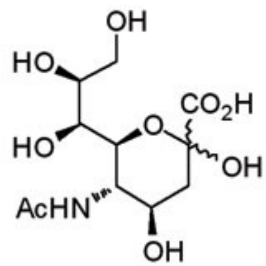
Understanding their nature and chiral shapes.



version 1.0

Chirality

- Carbohydrates
  - Definition & Examples
  - Place in the Food Chain
    - Photosynthesis & Respiration
  - Classification
    - Monosaccharides
      - Aldose and Ketose; 3-8 Carbons



- Chirality
  - Molecular Identity
    - Composition (1D), Connectivity (2D)
    - Shape (3D) can contain chirality
      - chiral vs achiral
  - Isomers:
    - Structural isomers
    - Stereo-isomers
      - Chiral Carbons
      - Enantiomeric Molecules
  - Showing Chirality
    - Drawing Chiral Shapes
    - Enantiomer Specific Receptor Sites

- Chirality in carbohydrates
  - Fischer Projections
    - Showing many chiral carbons
  - Classifying Carbohydrates (D/L)
    - Chiral center farthest from the carbonyl group
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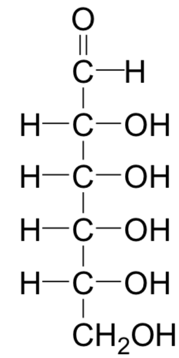
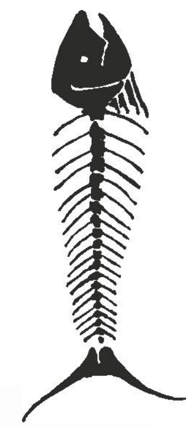
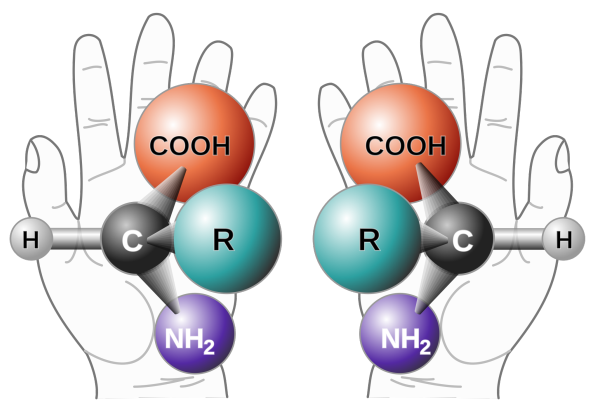
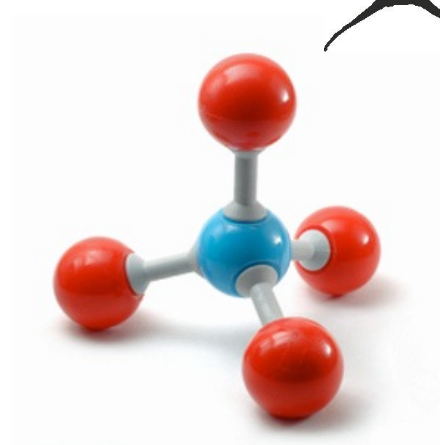
    - D-Glucose, D-Galactose, D-Fructose



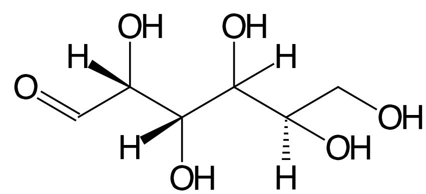


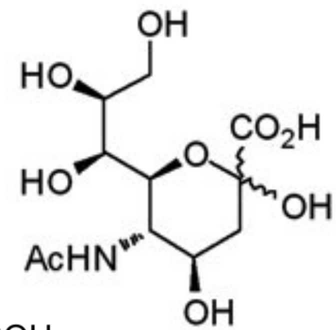


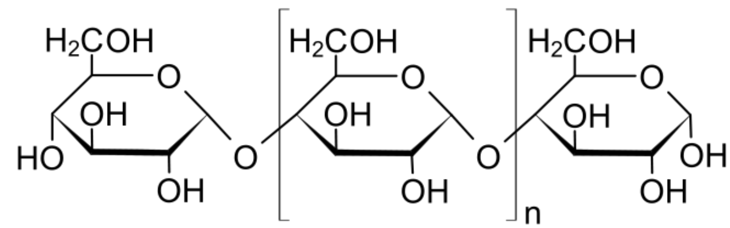


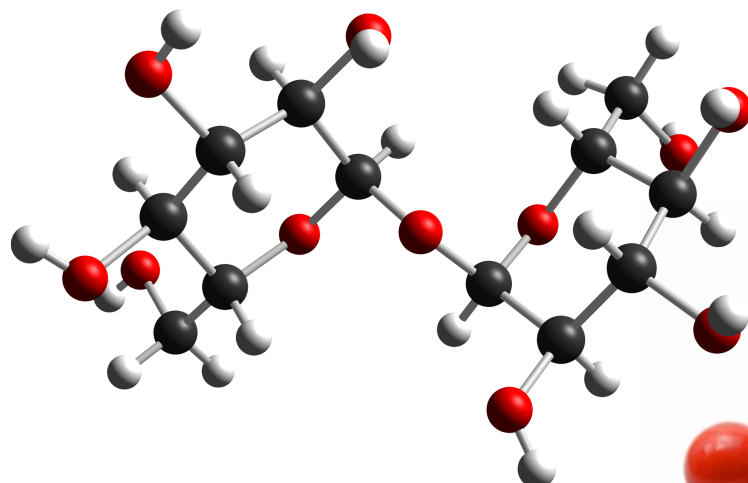
Carbohydrates

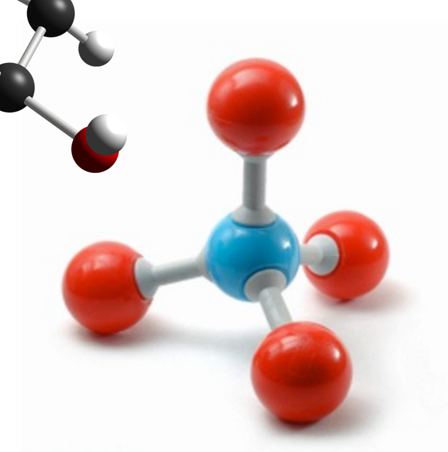
- We went from…
  - stone knives and clubs
    - logs burn, sticks provide structure
    - alkanes, alkenes, alkynes…
  - bronze spear heads and steel plows
    - functionalized substances
    - alcohols, thiols, ketones…
  - machines with pulleys and gears
    - complex/interconnected functionality
    - carboxylic acids, amides, esters…
- Now we want to talk about bigger molecules, even more involved and ambitious systems
- We'll start with carbohydrates.





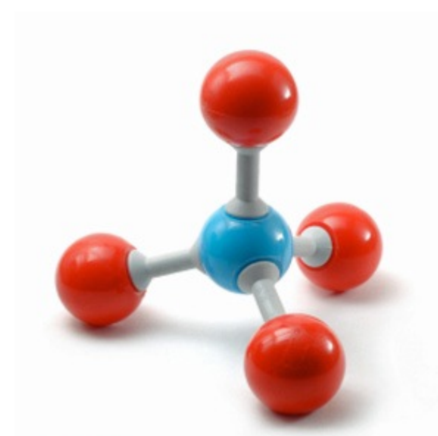






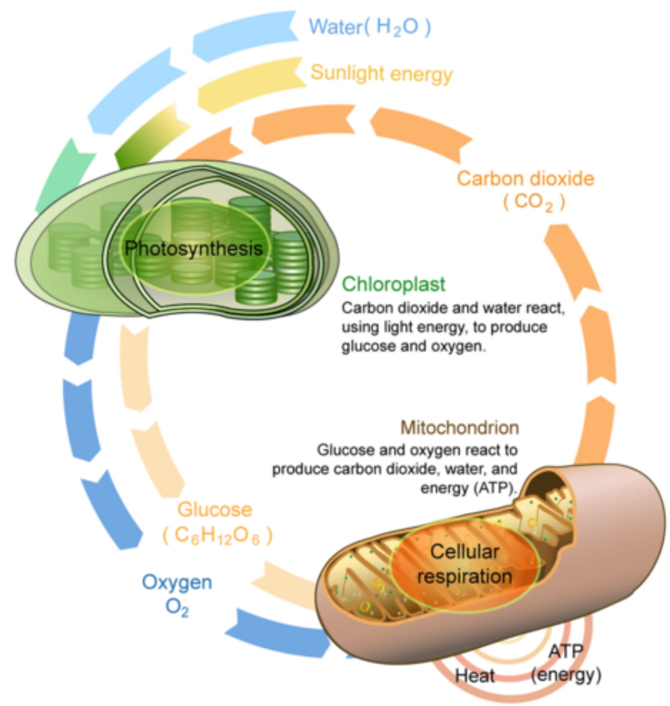
Carbohydrates

- We'll start with carbohydrates.
- Carbohydrates are
  - a major source of energy from our diet
  - made from the elements carbon, hydrogen, and oxygen
  - also called saccharides, which means "sugars"



Carbohydrates

- We'll start with carbohydrates.
- Carbohydrates are
  - a major source of energy from our diet
  - made from the elements carbon, hydrogen, and oxygen
  - also called saccharides, which means "sugars"
- Carbohydrates are produced by photosynthesis
  - Sunlight drives the reduction of carbon dioxide and water to form higher energy structures (carbohydrates).
- Carbohydrates are consumed through cellular respiration
  - Animals perform controlled oxidation of carbohydrates to release that chemical energy and power biological processes



$$6CO_2 + 6H_2O + \text{energy} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} C_6H_{12}O_6 + 6O_2$$

Chirality

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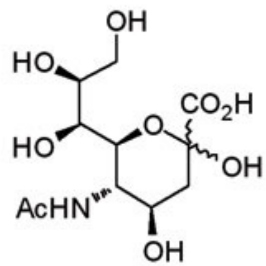

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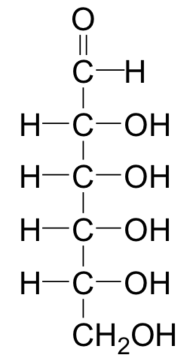
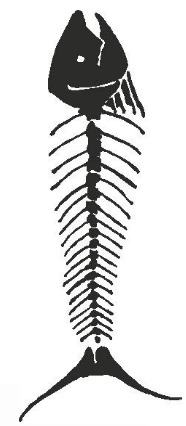
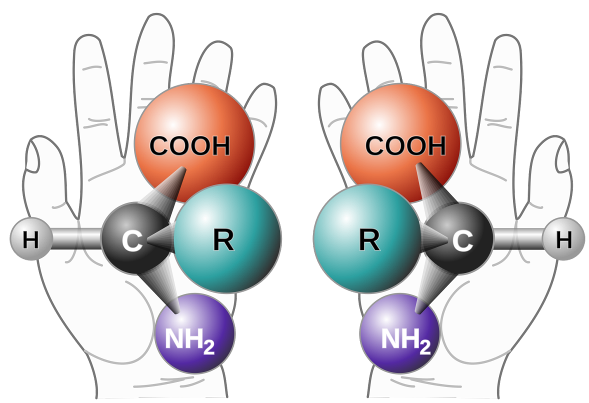
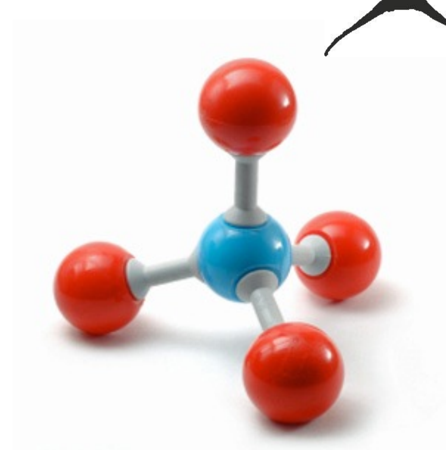


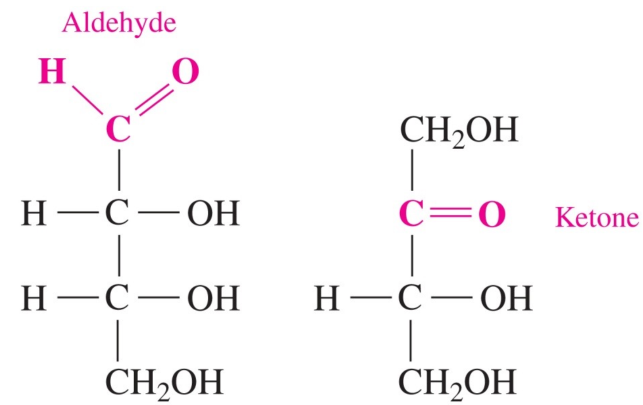






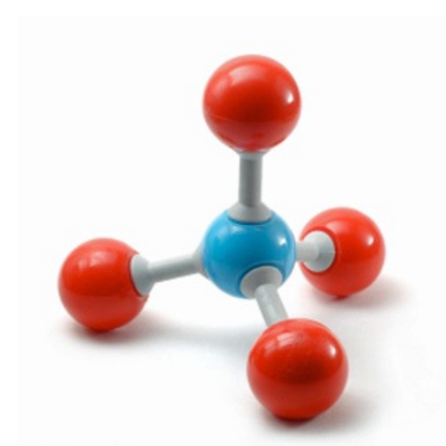
Monosaccharides

- The simplest carbohydrates are monosaccharides.
- Monosaccharides are carbon chains of:
  - three to eight carbons
  - with one carbonyl group
  - and hydroxyl groups attached to each of the other carbons.
- We classify monosaccharides by the location of the carbonyl.
  - Aldose are monosaccharides where the carbonyl group is on the last carbon in the chain (an aldehyde).
  - Ketose are monosaccharides where the carbonyl group is on the second to last carbon in the chain (ketones).



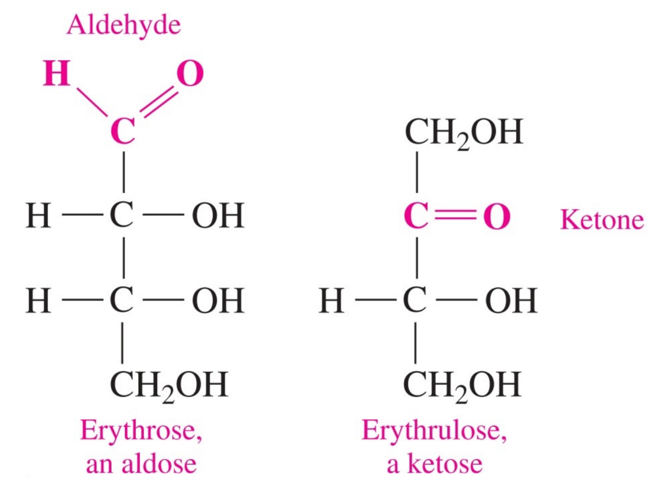
Erythrose, an aldose

Erythrulose, a ketose

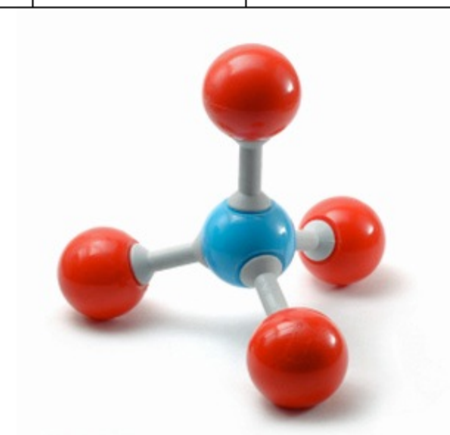


Monosaccharides

- The simplest carbohydrates are monosaccharides.
- Monosaccharides are carbon chains of:
  - three to eight carbons
  - with one carbonyl group
  - and hydroxyl groups attached to each of the other carbons.
- We further classify monosaccharides by the number of carbons in the chain.
  - Triose are monosaccharides of 3 carbons
  - Tetrose are monosaccharides of 4 carbons
  - Pentose are monosaccharides of 5 carbons
  - Hexose are monosaccharides of 6 carbons
  - Heptose are monosaccharides of 7 carbons
  - Octose are monosaccharides of 8 carbons

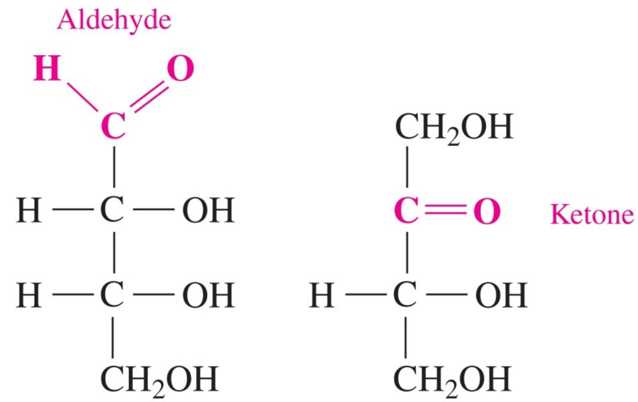


Carbon Atoms	General terms	Aldehydes	Ketones
3	Triose	Aldotriose	Keto triose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose



Monosaccharides

- The simplest carbohydrates are monosaccharides.
- Monosaccharides are carbon chains of:
  - three to eight carbons
  - with one carbonyl group
  - and hydroxyl groups attached to each of the other carbons.
- Examples:
  - An aldopentose is a five-carbon saccharide with an aldehyde group.
  - A ketohexose is a six-carbon saccharide with a ketone group.



Erythrose, an aldose — Erythrulose, a ketose

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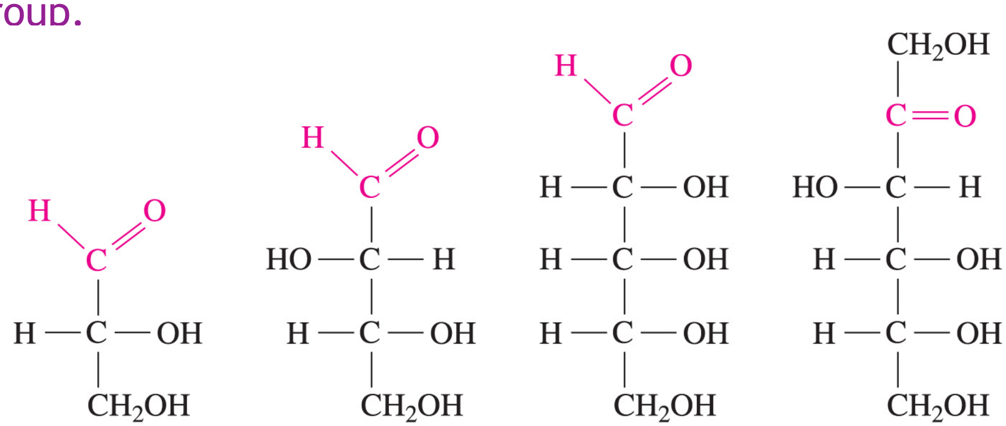
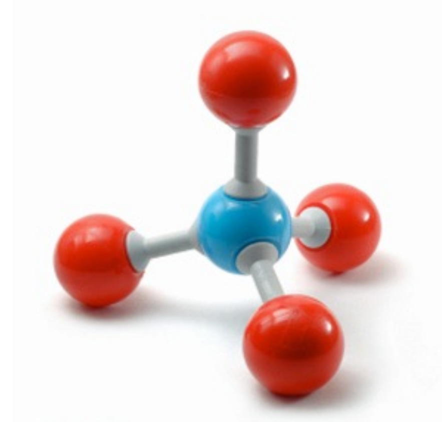
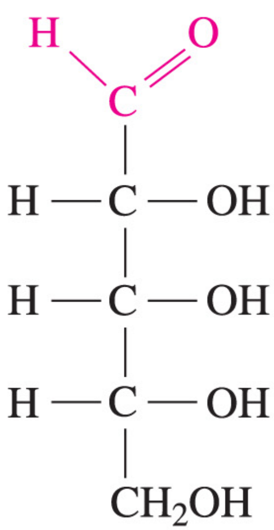


Glyceraldehyde (aldotriose) — Threose (aldotetrose) — Ribose (aldopentose) — Fructose (ketohexose)

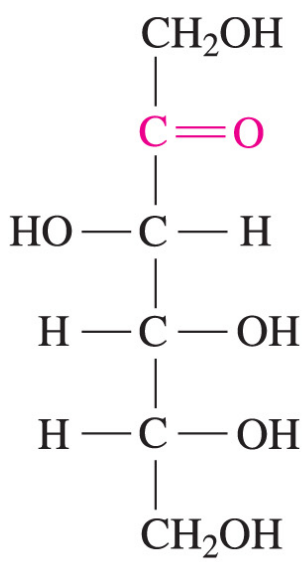


Monosaccharides

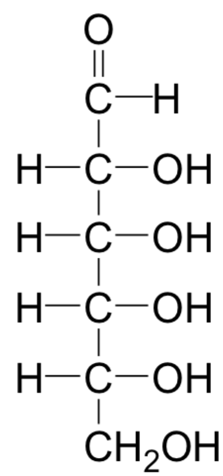
- Classify each monosaccharide below:



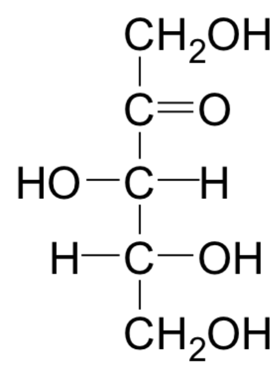
aldopentose



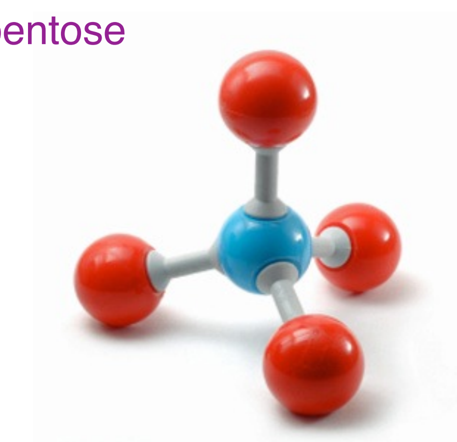
ketohexose



aldohexose



ketopentose



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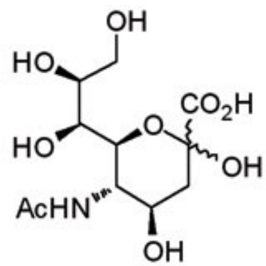

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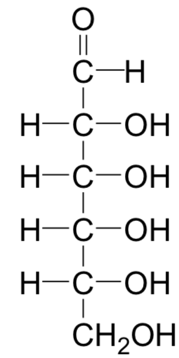
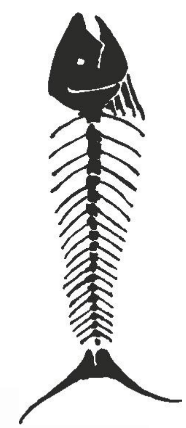
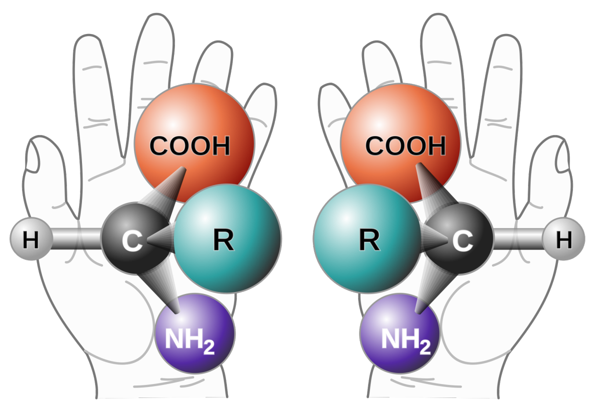
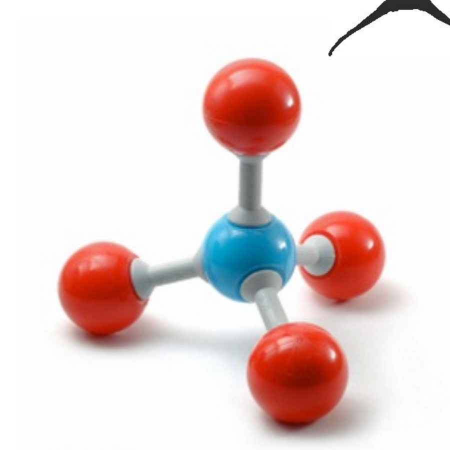








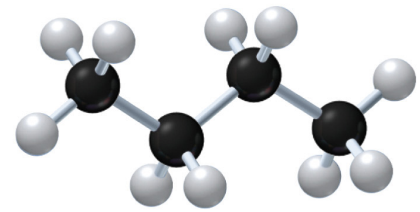
Structural Isomers

Reminder!

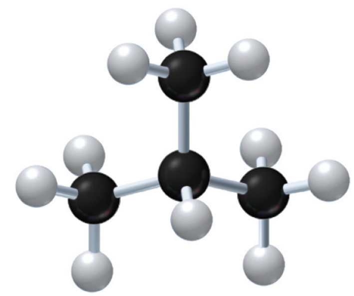
- Isomers are substances that have the same molecular formula but other differences.
- Structural isomers have…
  - the same composition (formula)
  - different connectivity (structure)
- Structural isomers are different substances.
  - A chemical change is required to convert between structural isomers – you have to break and make bonds.
  - This is not the same as conformational changes where you just rotate along bonds.
  - Structural isomers may have different properties:
    - Different boiling point.
    - Different density.
    - Different melting point.
  - Structural isomers have the same composition, so they do have some things in common.
    - The same chemical formula.
    - The same molar mass.

Boiling point: -1.0 °C
Density: 0.579 g/mL
Melting point: -140 °C

C_4H_{10}
Molar mass: 58.12 g/mol



$CH_3—CH_2—CH_2—CH_3$

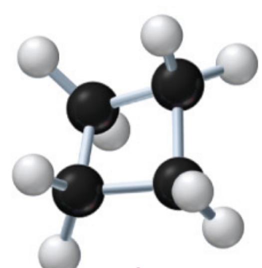


$CH_3—CH(CH_3)—CH_3$

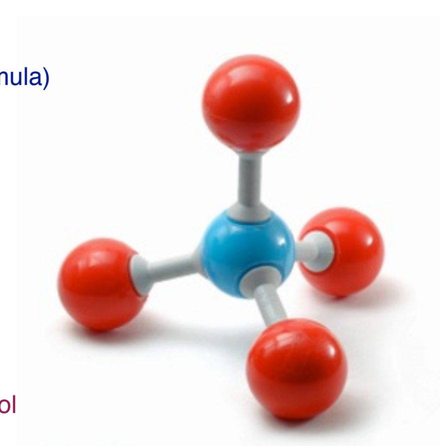
Boiling point: -11.7 °C
Density: 2.064 g/mL
Melting point: -159.6 °C

C_4H_{10}
Molar mass: 58.12 g/mol

Note: cyclobutane is **not** a structural isomer of butane! (it has a different molecular formula)

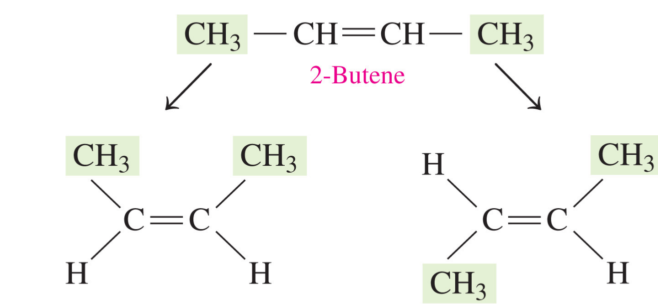


C_4H_8
Molar mass: 56.11 g/mol



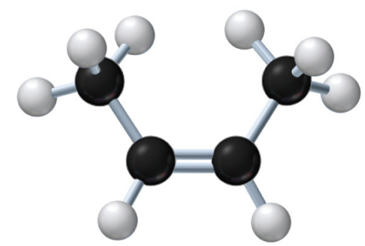
Stereo Isomers

- Isomers are substances that have the same molecular formula but other differences.
- Structural isomers have…
  - the same composition (formula)
  - different connectivity (structure)
- Stereo isomers have…
  - the same composition (formula)
  - the same connectivity (structure)
  - different shape (sketch)
- Stereo isomers <u>are different substances</u>.
  - This is not the same as conformational changes where you just rotate along bonds.
  - Stereo isomers may have different properties:
    - Different boiling point.
    - Different density.
    - Different chemical reactivity.
  - Structural isomers have the same composition and connectivity so they do have some things in common.
    - The same chemical formula.
    - The same molar mass.
    - The same bond orders.

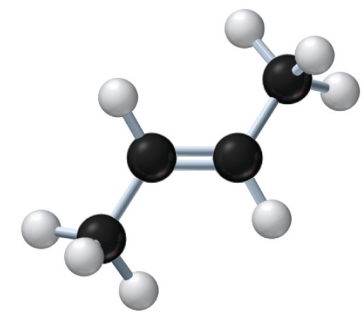


cis-2-Butene (mp −139 °C; bp 3.7 °C)

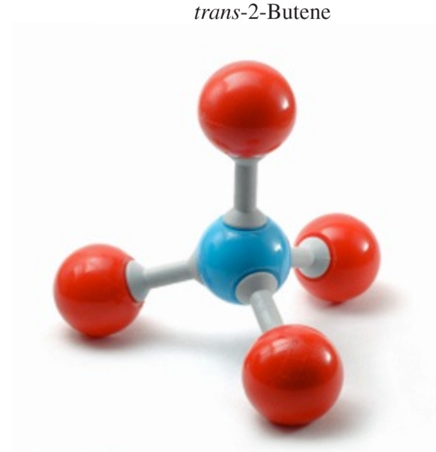
trans-2-Butene (mp −106 °C; bp 0.3 °C)



cis-2-Butene

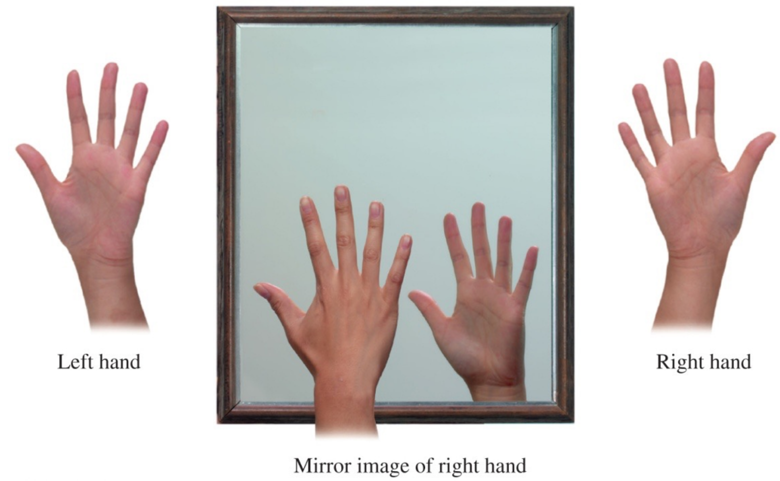


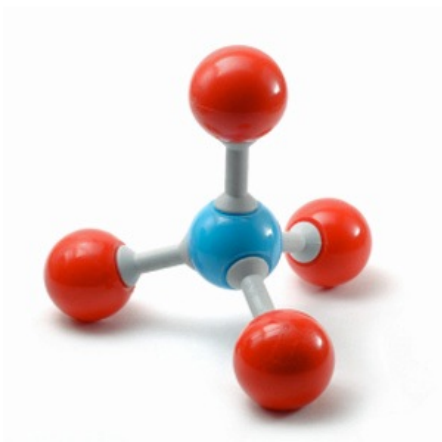
trans-2-Butene



Chirality

- Shapes may have the property of chirality.
- Chiral shapes are not superimposable on their mirror image.
- Not all shapes have this property.
- Achiral shapes are superimposable on their mirror image.





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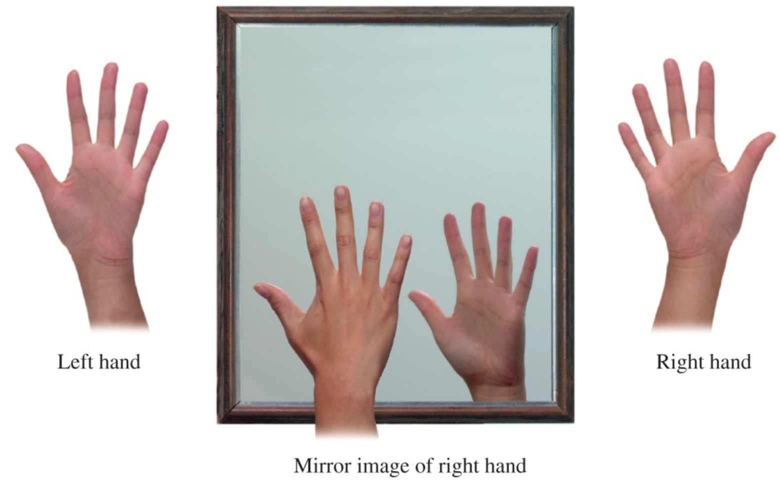
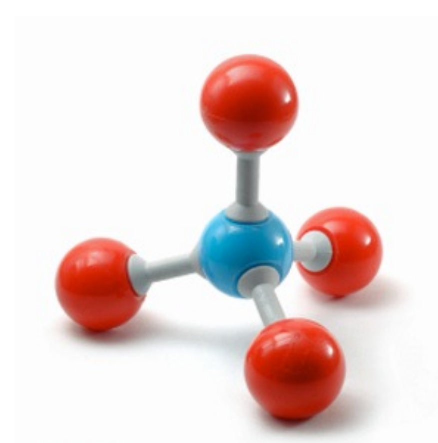


Chiral

Achiral



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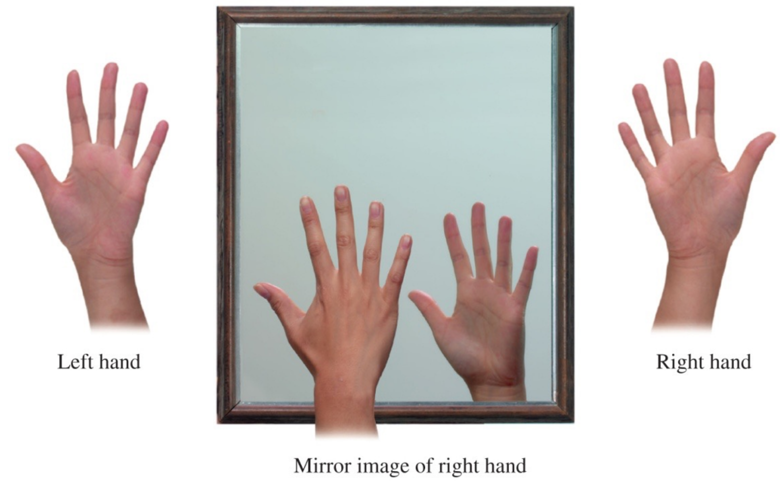

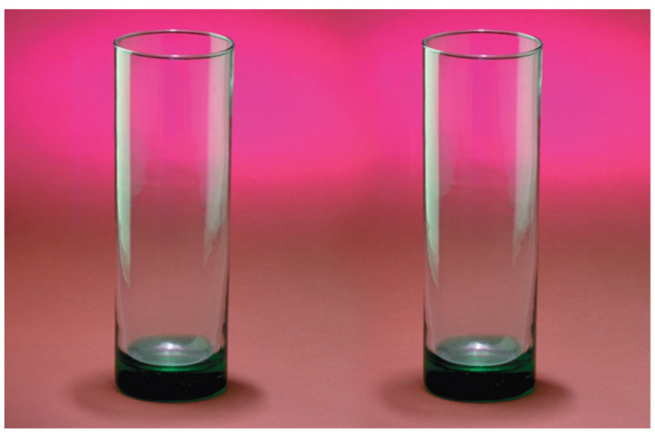

Achiral

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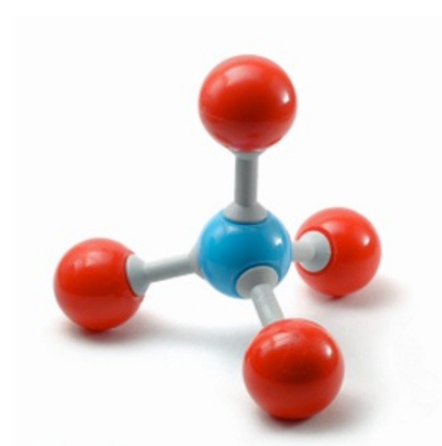

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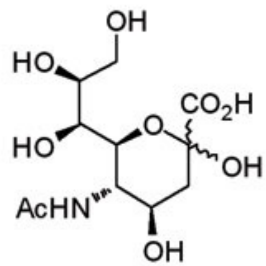

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    - Structural isomers
    - Stereo-isomers
      - Chiral Carbons
      - Enantiomeric Molecules
  - Showing Chirality
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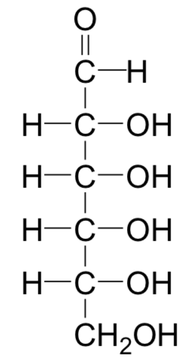
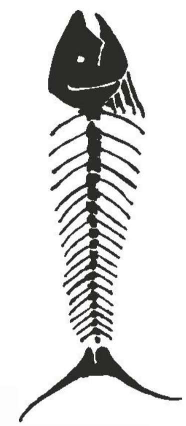
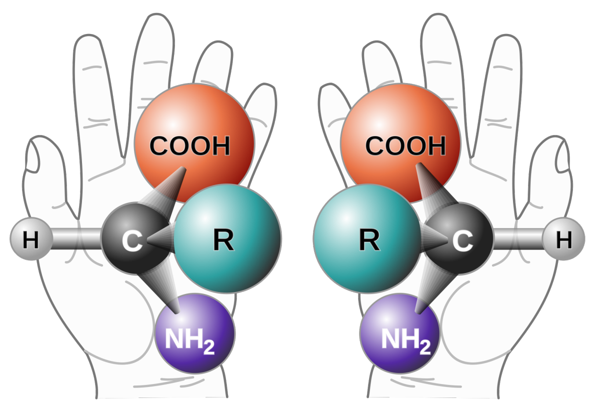
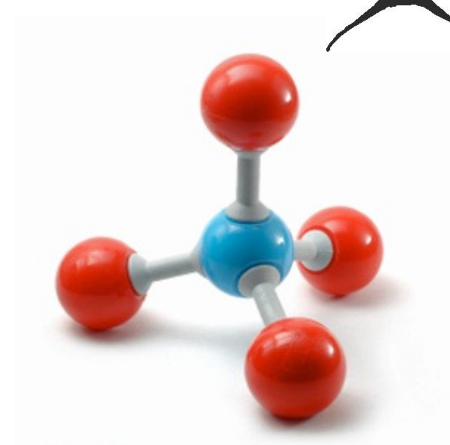


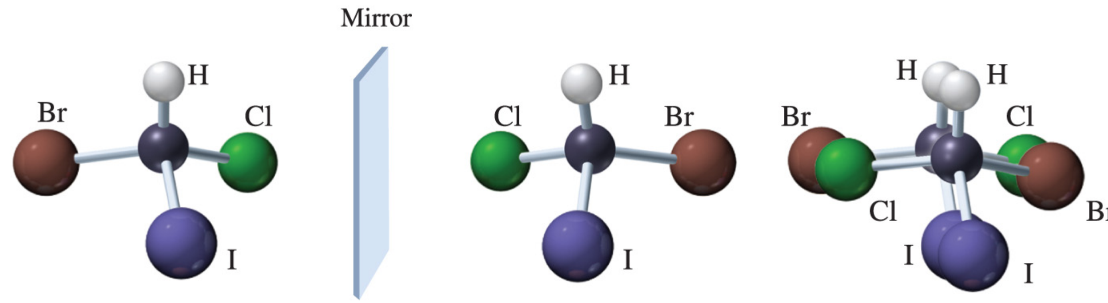


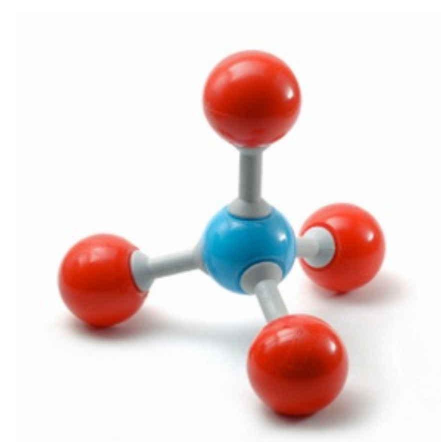




Chirality

- Molecules may have a chiral shape.
- When molecules have a chiral shape, this chirality can produce stereoisomers.
- Stereo isomers have...
  - the same composition (formula)
  - the same connectivity (structure)
  - different shape (sketch)
- Molecules are chiral when they have
  - at least one or more chiral carbon atoms
    - a carbon atom, bonded to four different groups
  - nonsuperimposable mirror images
- These types of isomers are called enantiomers.





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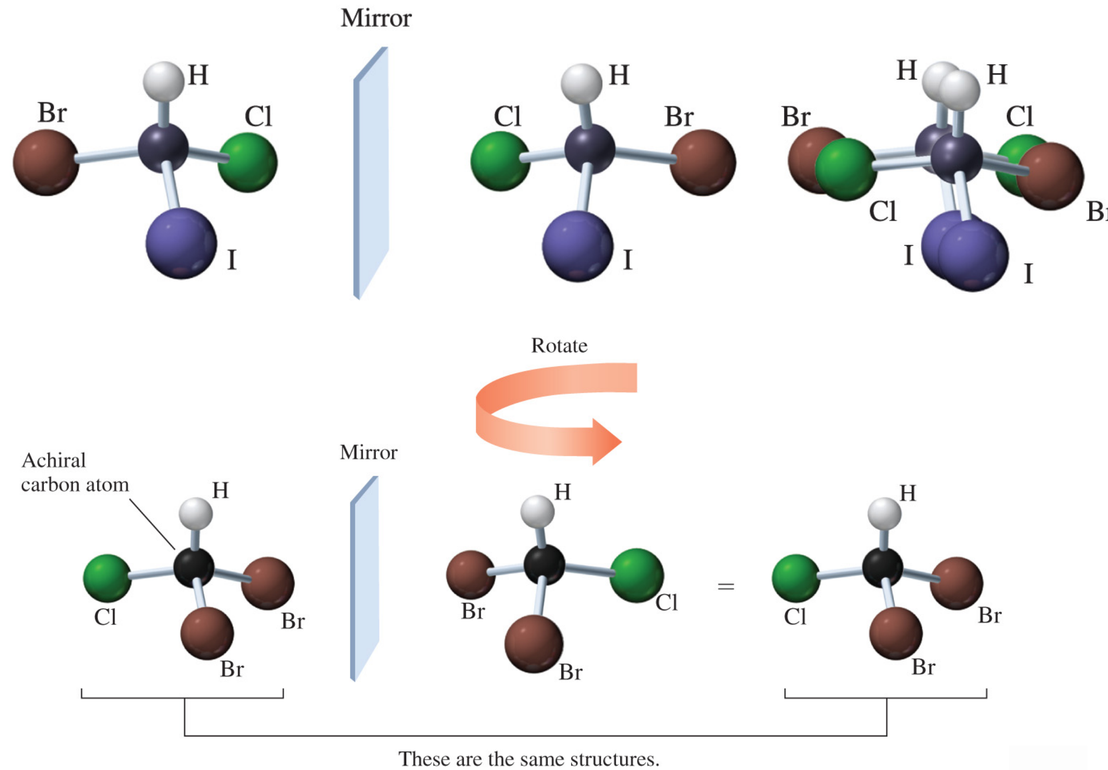

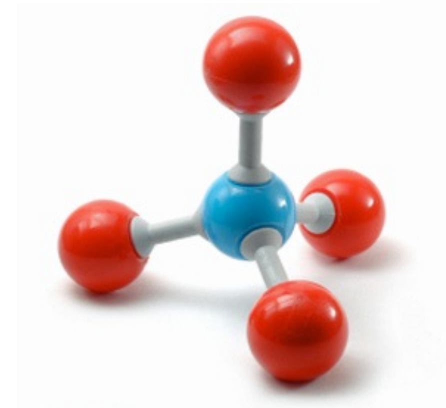

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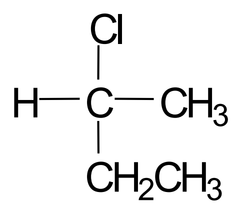
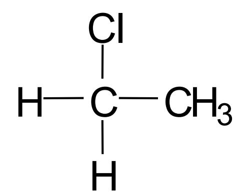


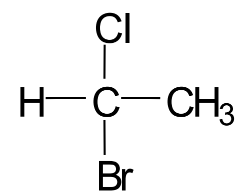
A

chiral



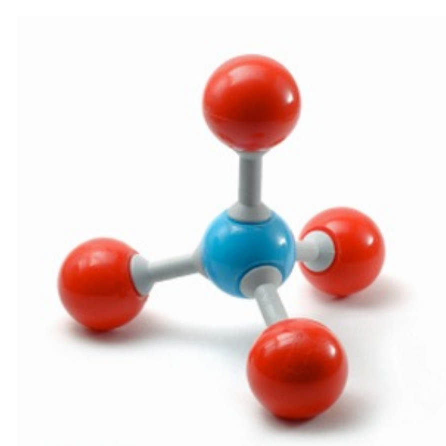
B

achiral



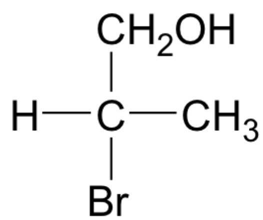
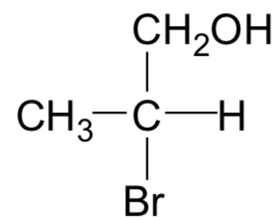
C

chiral

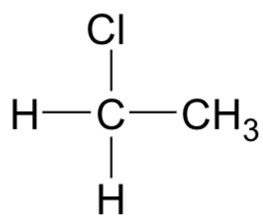
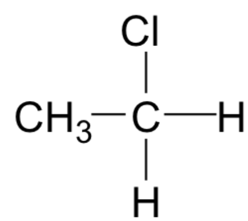


Enantiomers

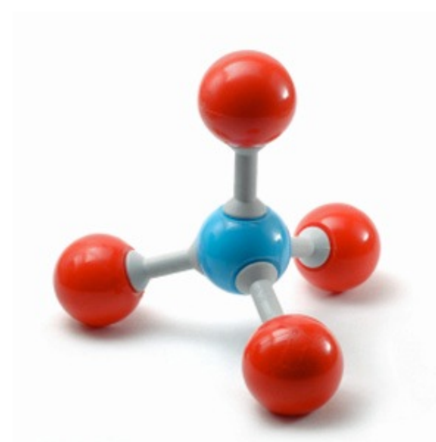
- Indicate whether each pair is a mirror image that cannot be superimposed (enantiomers).

A.  and 

YES

B.  and 

NO



Chirality

- Carbohydrates
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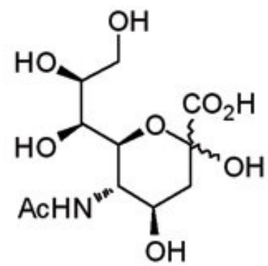
  - Place in the Food Chain
    - Photosynthesis & Respiration
  - Classification
    - Monosaccharides
      - Aldose and Ketose; 3-8 Carbons



- Chirality
  - Molecular Identity
    - Composition (1D), Connectivity (2D)
    - Shape (3D) can contain chirality
      - chiral vs achiral
  - Isomers:
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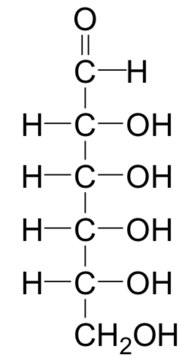
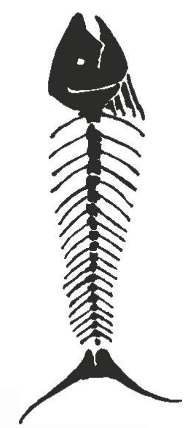
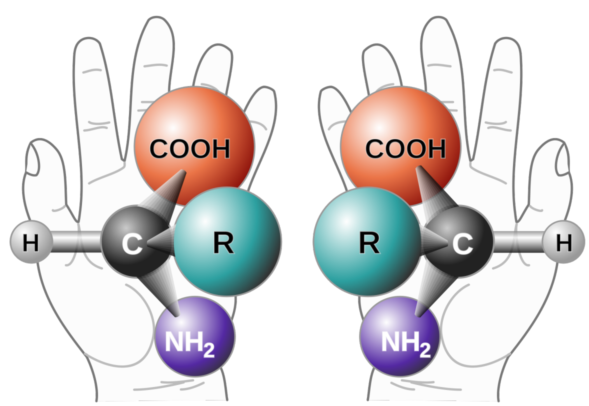
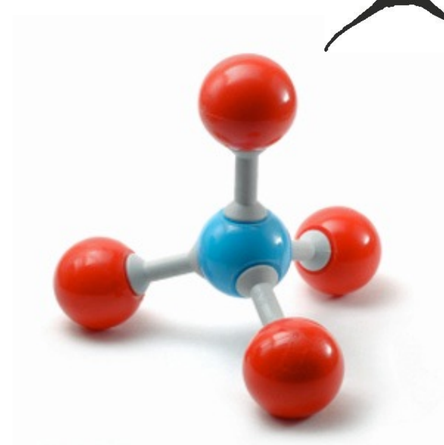




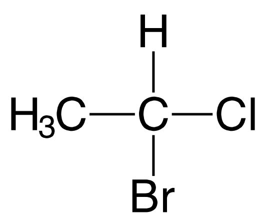


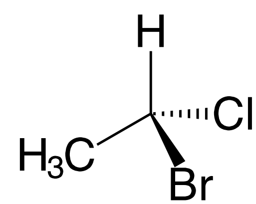


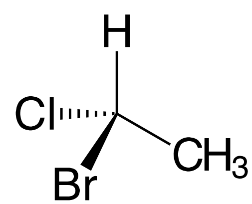
Showing Chirality

- If there are two different stereoisomers that share a single chemical formula and a single structure, we need to draw a sketch (or model) to distinguish them.

$CH_3CHBrCl$



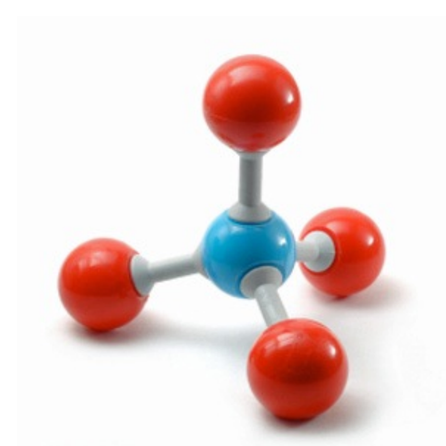




We sometimes embed connectivity information in formulas.

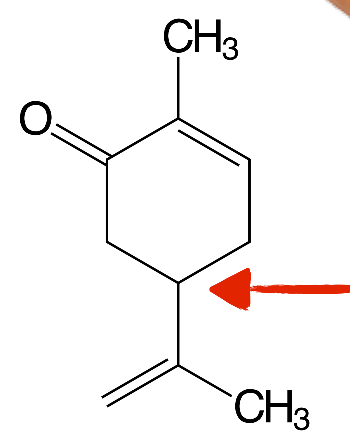
Notice we didn't write this C_2H_4BrCl

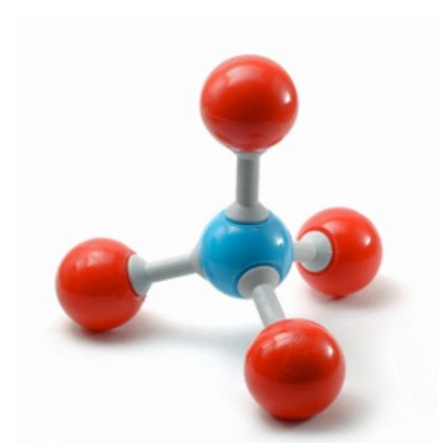
Similarly, we sometimes embed shape information in structures.



Showing Chirality

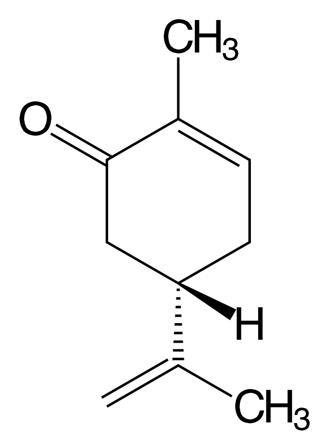
- Carvone has the following structure. It's found in caraway seeds and gives rye bread it's taste.
- Is this molecule chiral?
- Can you identify a chiral carbon in this molecule?

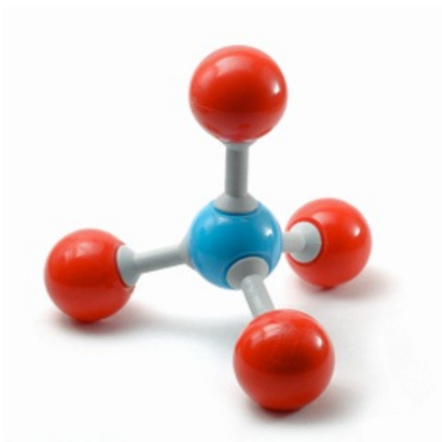




Showing Chirality

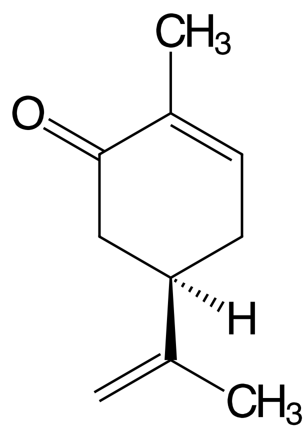
- Carvone has the following structure. It's found in caraway seeds and gives rye bread it's taste.
- Is this molecule chiral?
- Can you identify a chiral carbon in this molecule?
- Instead of sketching the whole molecule, we can just indicate the stereochemistry at that one carbon.

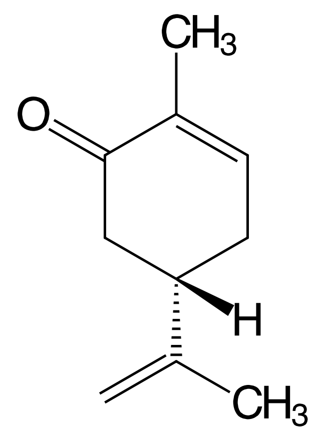


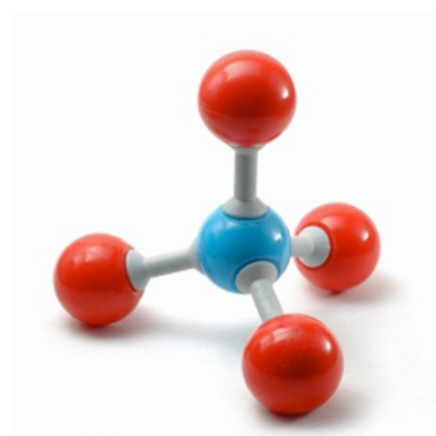


Showing Chirality

- Knowing that stereochemistry is important to knowing that substance.
- One enantiomer of carvone tastes like rye bread, the other tastes like spearmint.
- They are different substances with different physical and chemical properties.

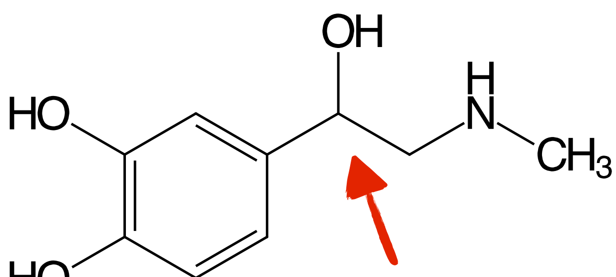




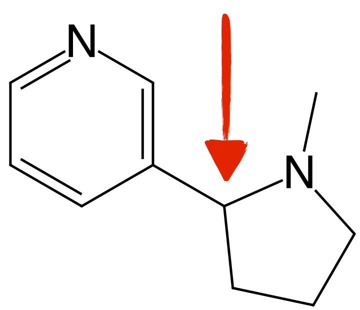


Showing Chirality

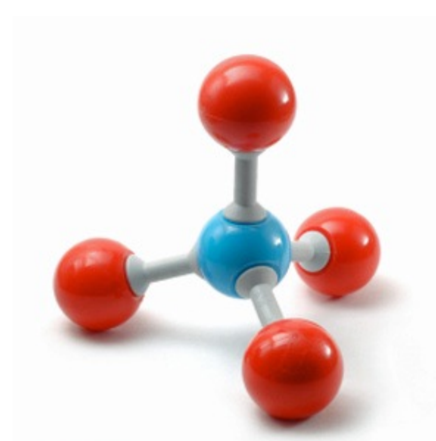
- Biologically active molecules are often chiral.
- Are nicotine or adrenaline chiral?
- Can you find the chiral carbon?



adrenaline



nicotine



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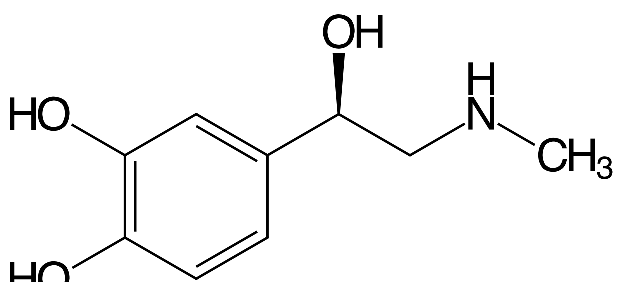
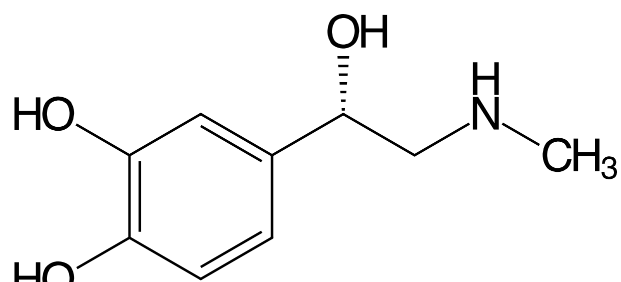
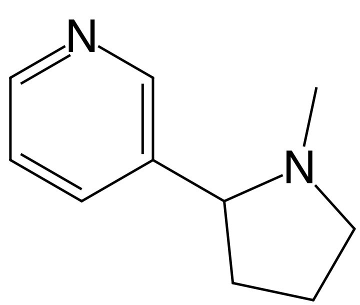


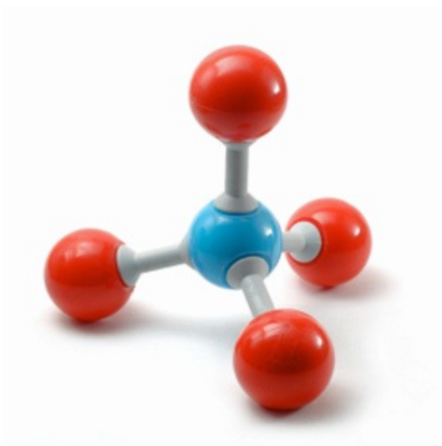
adrenaline



something else



nicotine



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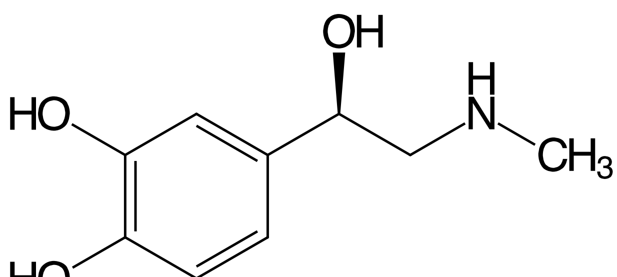

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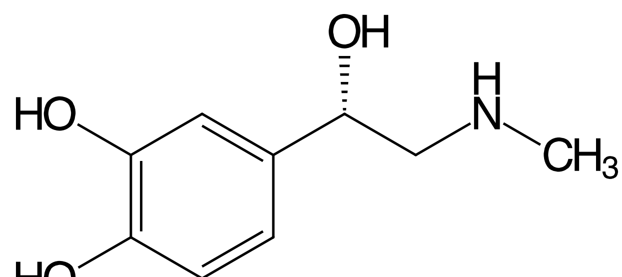

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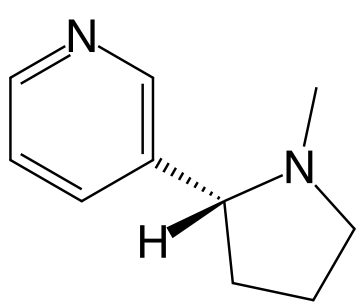
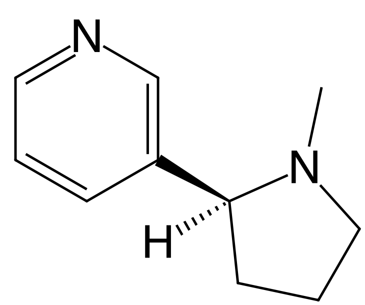
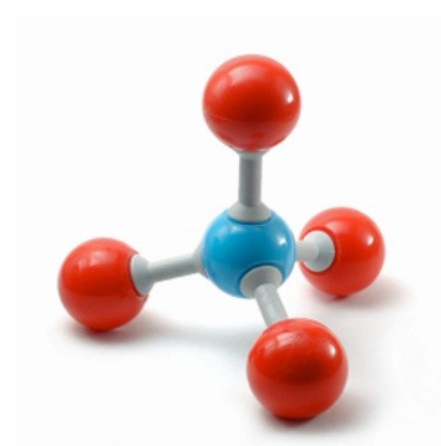


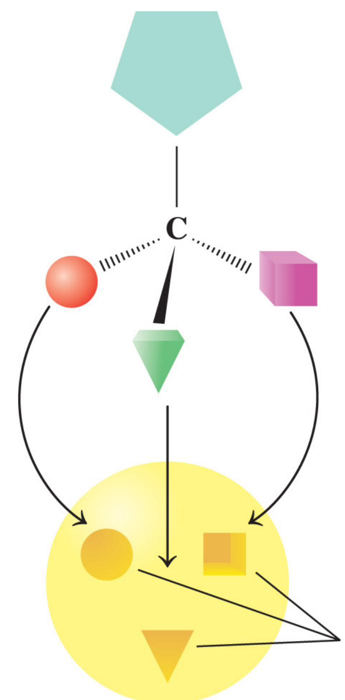
nicotine

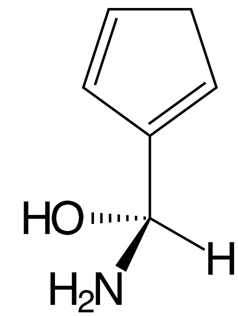


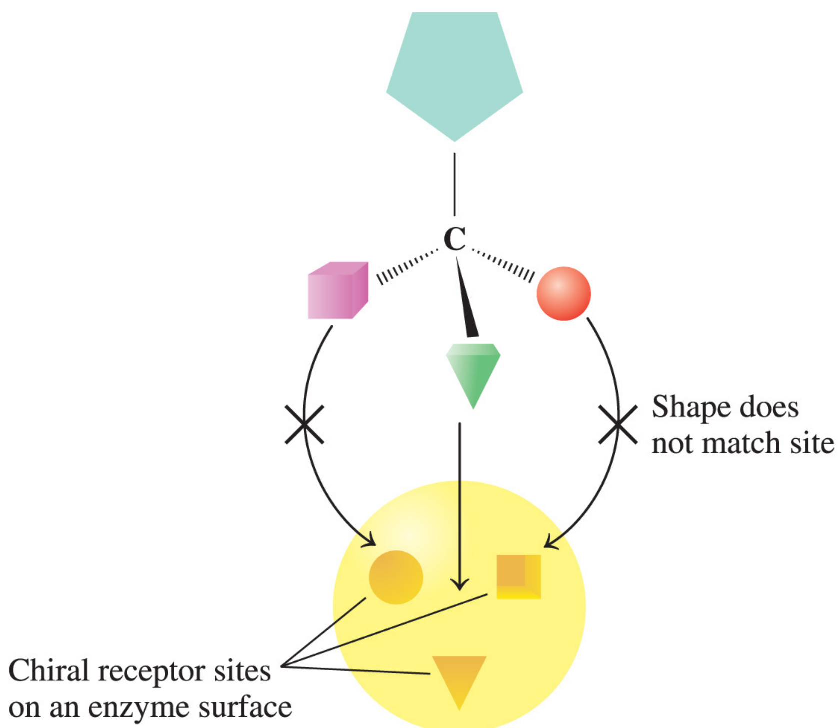
not nicotine

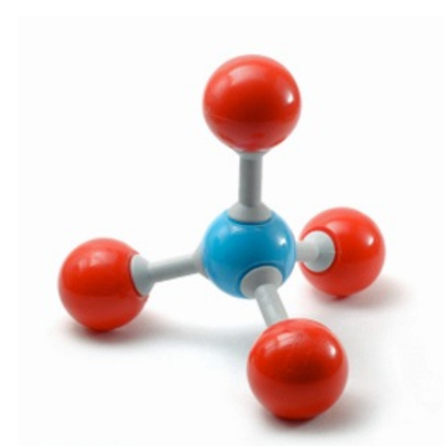


- The biological activity of these molecules often results from how they fit into receptor sites in the body.
- The chirality of the drug must match the chirality of the site it's binding to, to work properly.
- The wrong enantiomer may be inactive, or may have unexpected (even dangerous) activity.









Chirality

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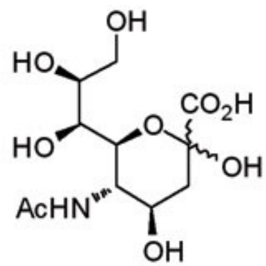

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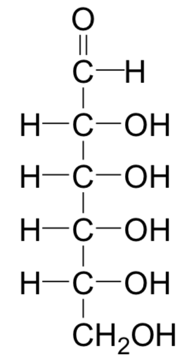
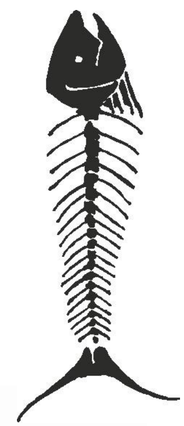
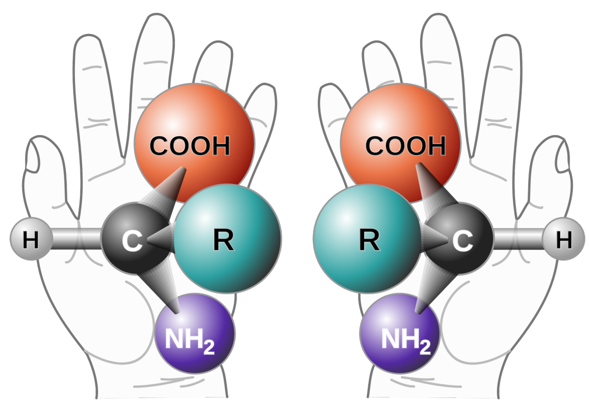
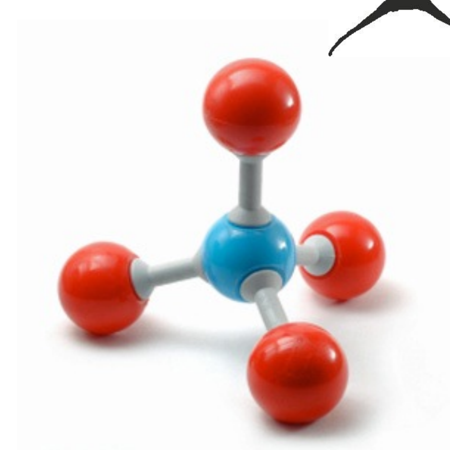


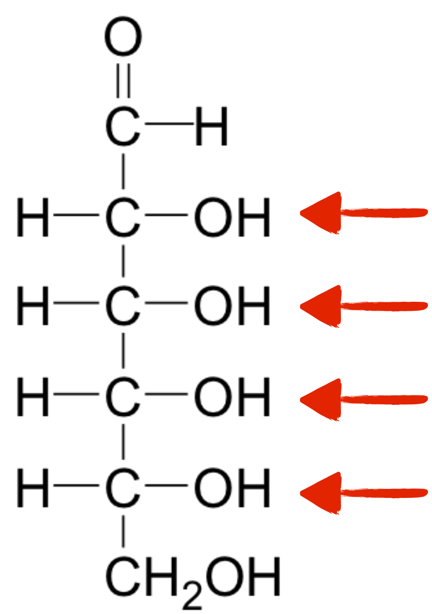


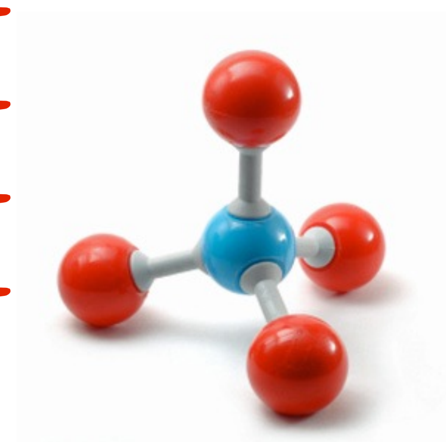




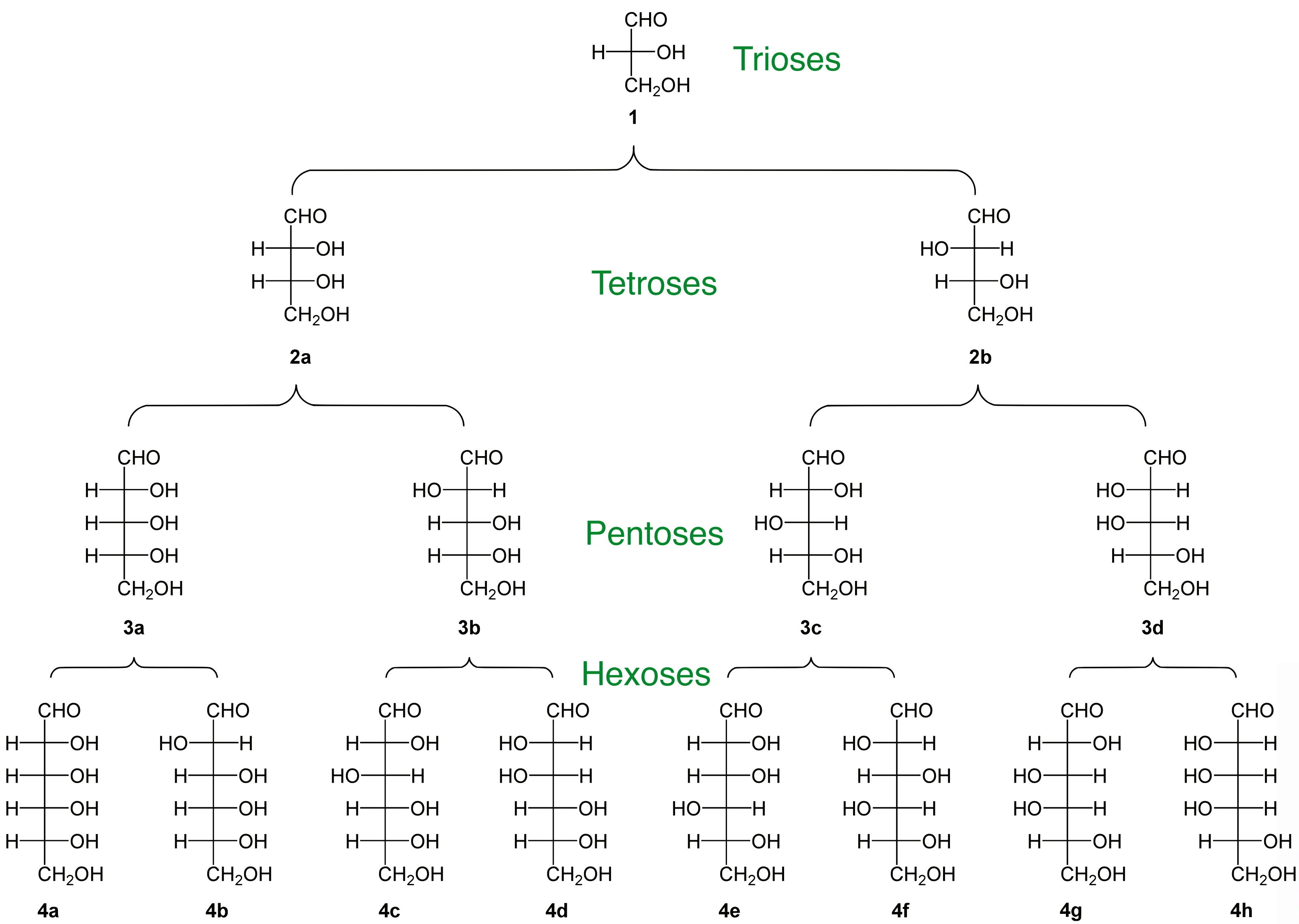
Fischer Projections

- Monosaccharides have many chiral carbons.
- Each non-terminal carbon in the backbone that has an alcohol attached to it is chiral.
- That means each carbon we add to the backbone doubles the number of stereo isomers possible for that chemical formula.





Their are many sugars… *plus their enantiomers*.

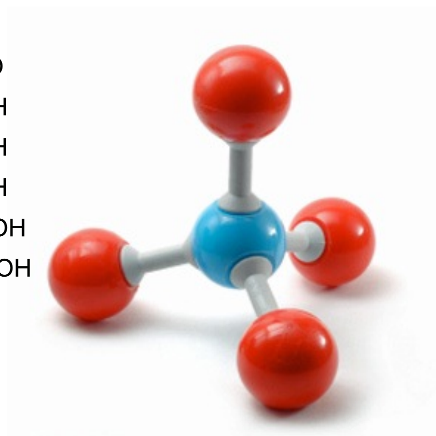


(1) D-(+)-glyceraldehyde

(2a) D-(–)-erythrose
(2b) D-(–)-threose

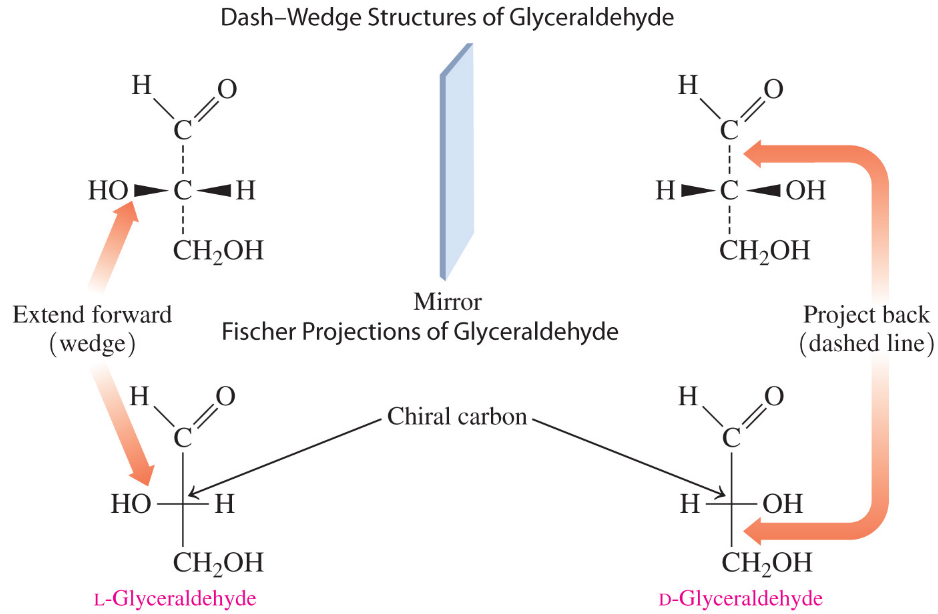
(3a) D-(–)-ribose
(3b) D-(–)-arabinose
(3c) D-(+)-xylose
(3d) D-(–)-lyxose

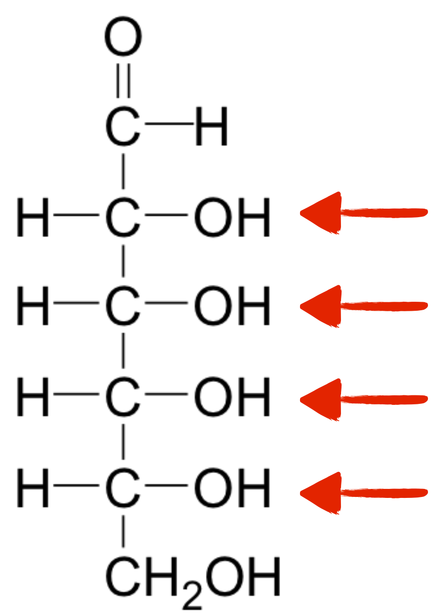
(4a) D-(+)-allose
(4b) D-(+)-altrose
(4c) D-(+)-glucose
(4d) D-(+)-mannose
(4e) D-(–)-gulose
(4f) D-(–)-idose
(4g) D-(+)-galactose
(4h) D-(+)-talose

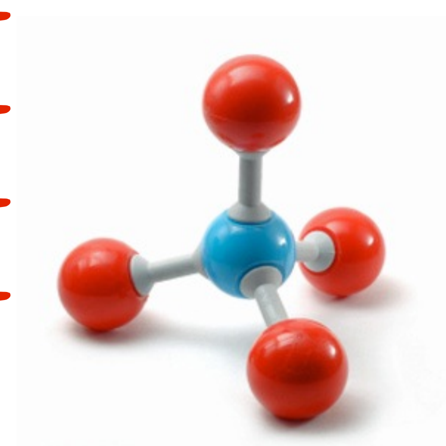


Fischer Projections

- Monosaccharides have many chiral carbons.
- We draw them using a standard called a Fisher projection to simplify communicating their chirality.
- A Fischer projection
  - is a two-dimensional representation of a three-dimensional molecule
  - places the most highly oxidized carbon group at the top
  - orients the backbone bending away from the viewer
  - uses vertical lines in place of dashes for bonds that go back
  - uses horizontal lines in place of wedges for bonds that come forward

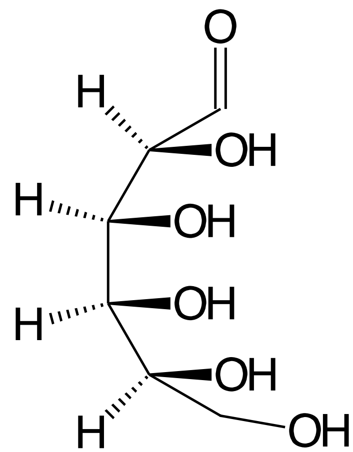


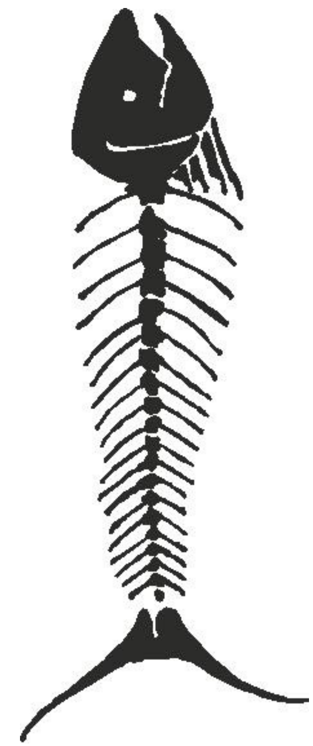


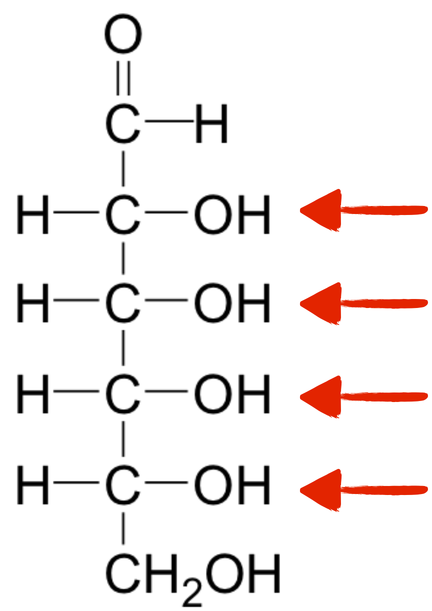


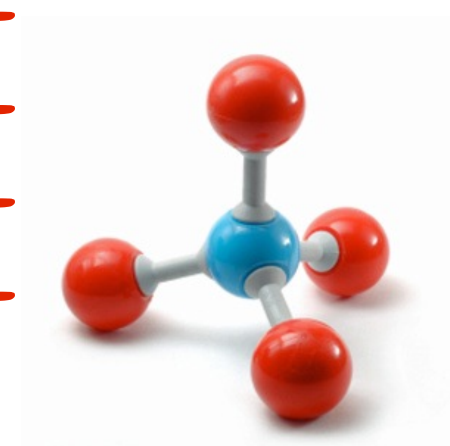
Fischer Projections

- Monosaccharides have many chiral carbons.
- We draw them using a standard called a Fisher projection to simplify communicating their chirality.
- A Fischer projection
  - is a two-dimensional representation of a three-dimensional molecule
  - places the most highly oxidized carbon group at the top
  - orients the backbone bending away from the viewer
  - uses vertical lines in place of dashes for bonds that go back
  - uses horizontal lines in place of wedges for bonds that come forward









Chirality

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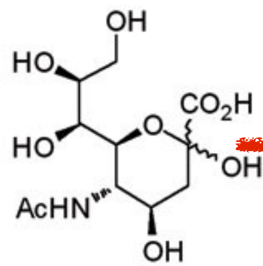
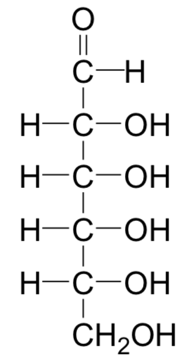
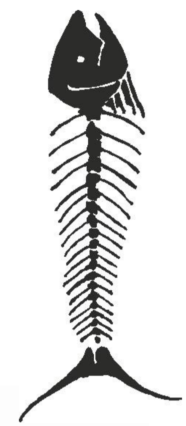
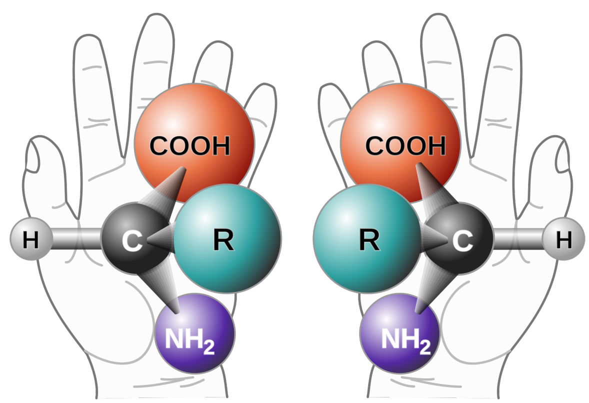


- Chirality in carbohydrates
  - Fischer Projections
    - Showing many chiral carbons
  - Classifying Carbohydrates (D/L)
    - Chiral center farthest from the carbonyl group
  - Properties and Uses
    - D-Glucose, D-Galactose, D-Fructose

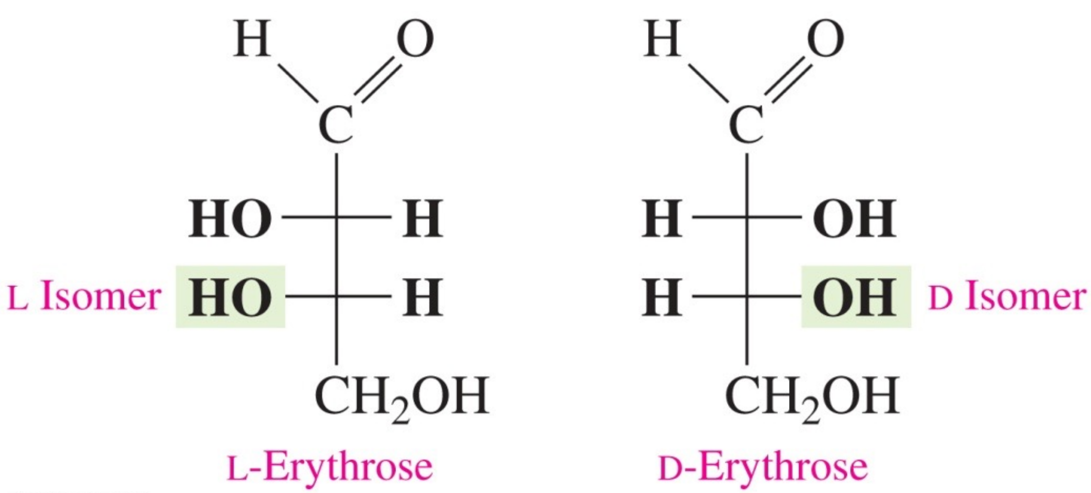


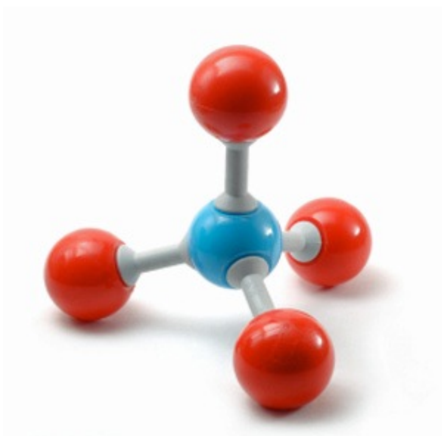




D/L Designations

- Carbohydrate stereoisomers are assigned D or L designations according to the position of the — OH group on the chiral carbon farthest from the carbonyl carbon.
  - The letter L is assigned to the structure with the — OH on the left.
  - The letter D is assigned to the structure with the — OH on the right.





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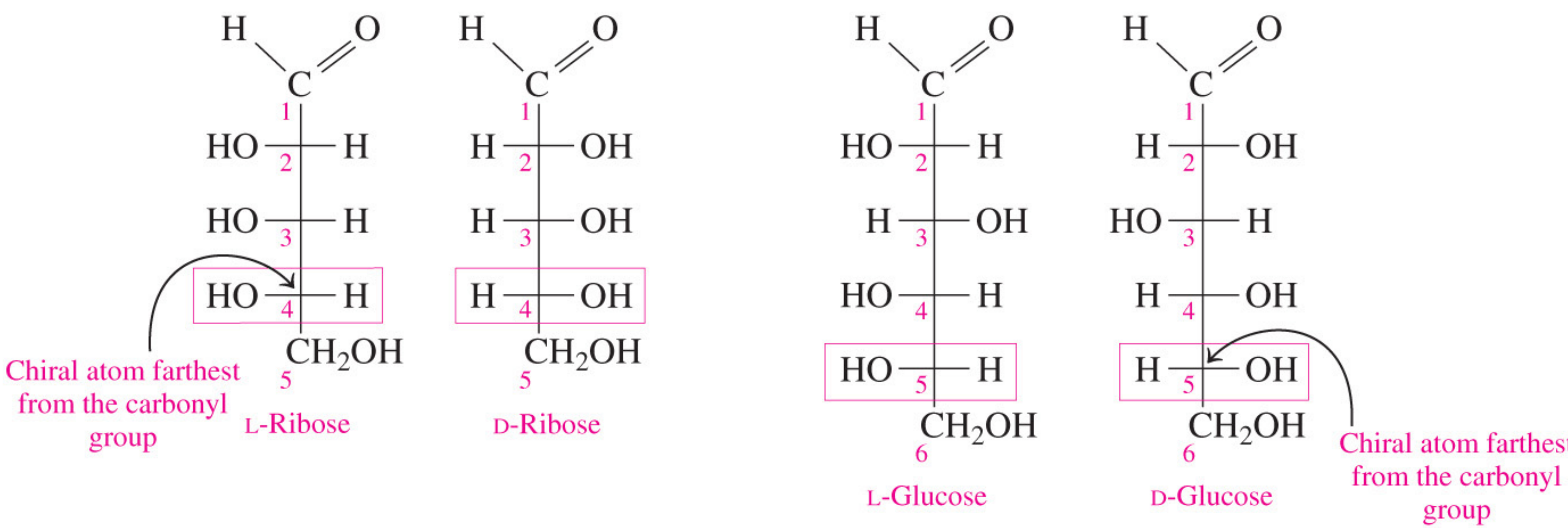
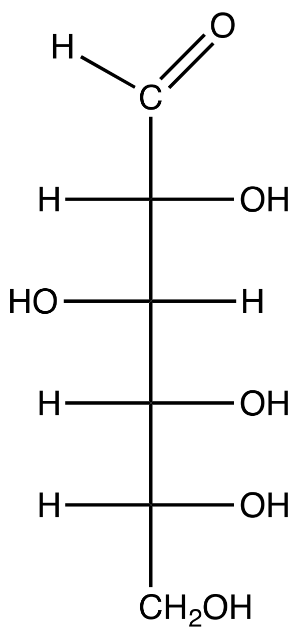


D/L Designations

- Below are two different sugars (both aldoses). Identify the following Fischer projections of each as the L or D isomers of each sugar:

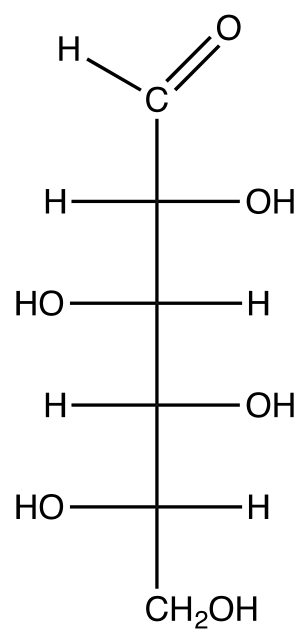
A.



A (D) Isomer;
— OH is on the right

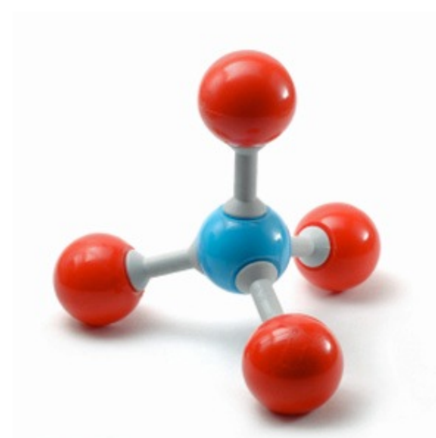
(this is D-Glucose)

B



An (L) Isomer;
— OH is on the left

(this is L-Idose)



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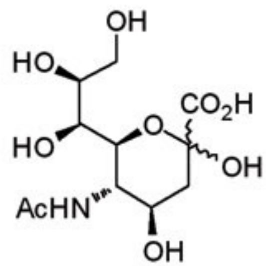

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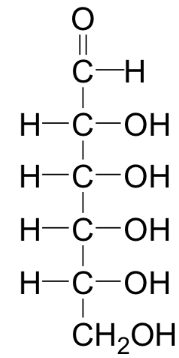
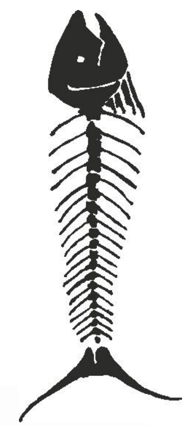
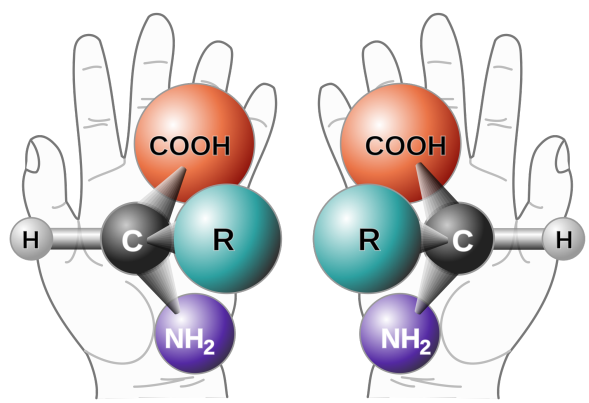
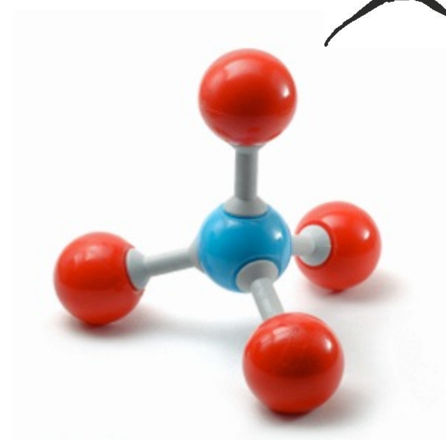


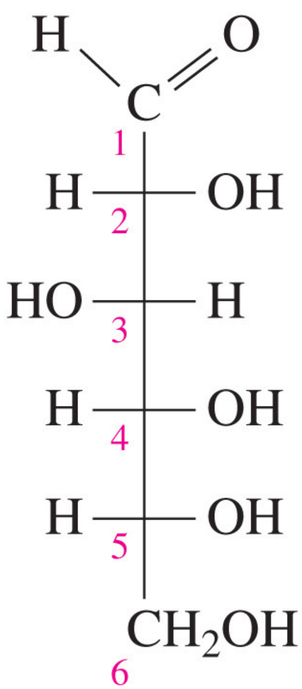




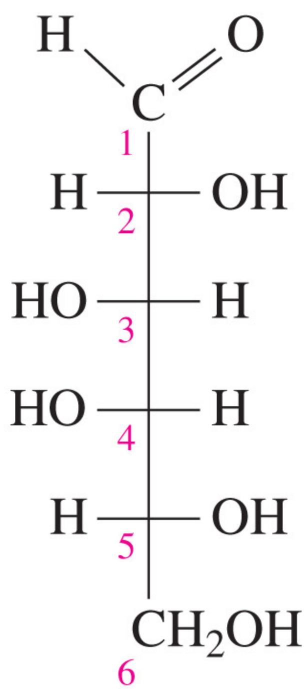


Most Important Monosaccharides

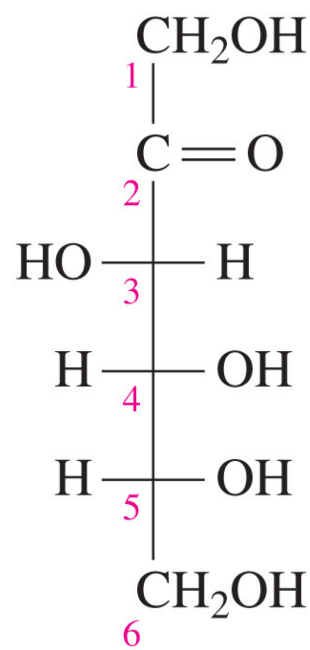
- The most important monosaccharides are Glucose, Galactose, and Fructose.



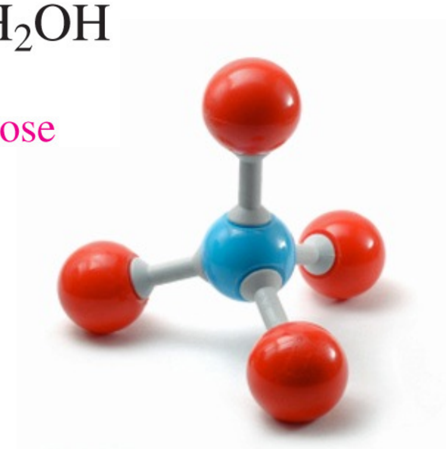
D-Glucose



D-Galactose



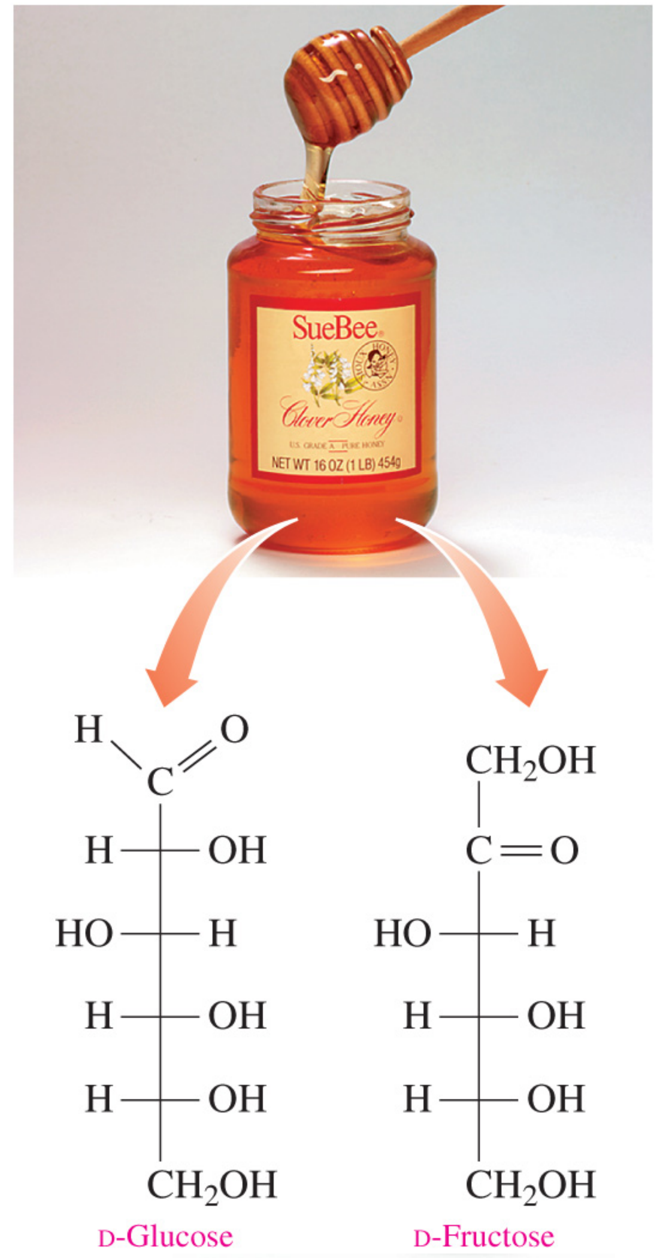
D-Fructose



Common Monosaccharides

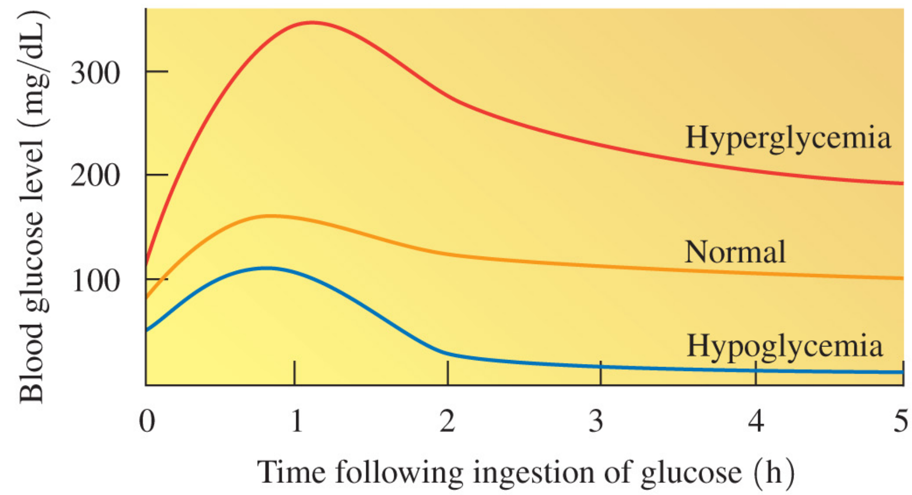
- D-Glucose is
  - found in fruits, corn syrup, and honey
  - an aldohexose with the formula $C_6H_{12}O_6$
  - known as dextrose and blood sugar in the body
  - a building block in sucrose, lactose, maltose, and in polysaccharides such as cellulose and glycogen

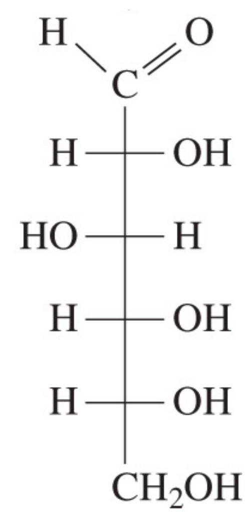
- D-Fructose, obtained from sucrose, is
  - a ketohexose with the formula $C_6H_{12}O_6$
  - the sweetest of the carbohydrates, twice as sweet as sucrose



Hyperglycemia and Hypoglycemia

- In the body,
  - glucose has a normal blood level of 70–90 mg/dL
  - a glucose tolerance test measures blood glucose for several hours after ingesting glucose





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Hyperglycemia and Hypoglycemia

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  - glucose has a normal blood level of 70–90 mg/dL
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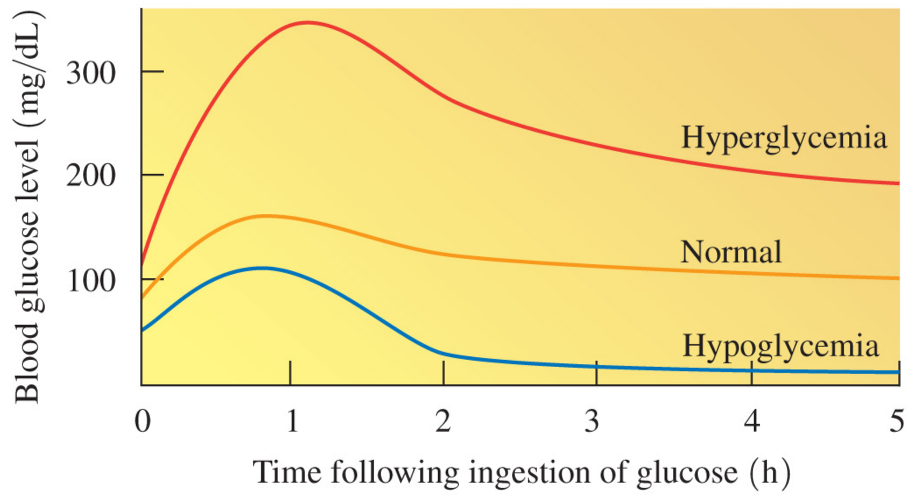
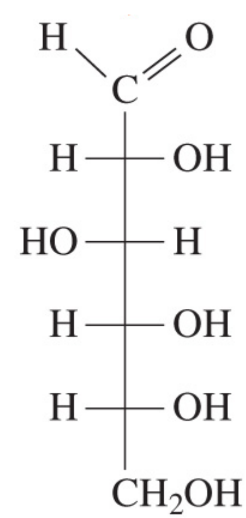
- Diabetes mellitus can cause hyperglycemia, which
  - occurs when the pancreas is unable to produce sufficient quantities of insulin
  - allows glucose levels in the body fluids to rise as high as 350 mg/dL of plasma
- Symptoms of diabetes include
  - thirst and excessive urination
  - increased appetite and weight loss
- In older adults, diabetes is sometimes a consequence of excessive weight gain.





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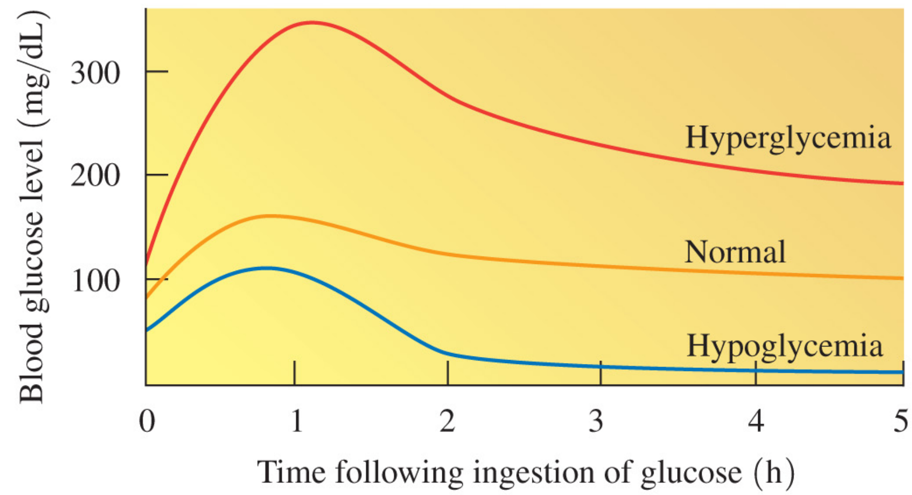
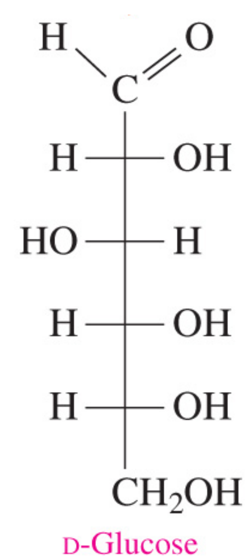
- When a person is hypoglycemic,
  - the blood glucose level rises and then decreases rapidly to levels as low as 40 mg/dL
  - low blood sugar may occur as a result of an overproduction of insulin by the pancreas
  - symptoms may appear, such as dizziness, general weakness, and muscle tremors
  - a diet may be prescribed that consists of several small meals high in protein and low in carbohydrates





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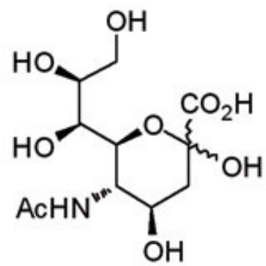

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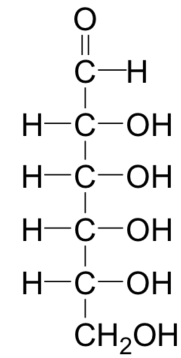

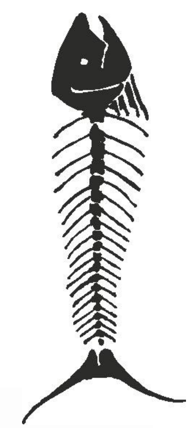

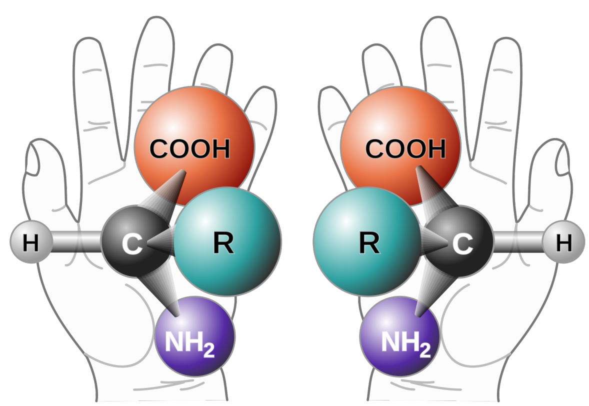

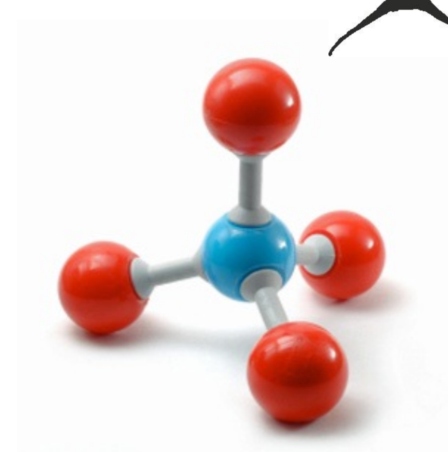

Questions?