Stereochemistry
2 – Optical Activity

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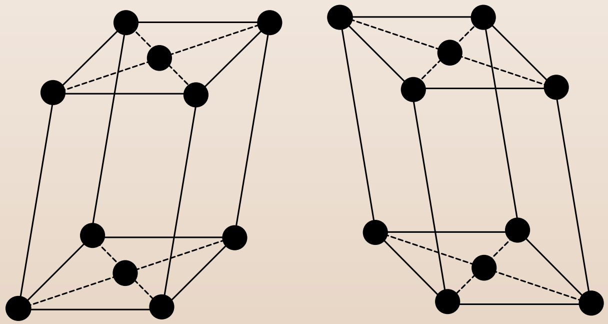
Pasteur's Discovery of Enantiomers

Louis Pasteur discovered that sodium ammonium salts of tartaric acid crystallize into right handed and left handed forms, for example the crystals below are mirror images.



- The optical rotations of equal concentrations of these forms had opposite optical rotations.
- The solutions contain mirror image isomers, called **enantiomers** and they crystallized in mirror image shapes.

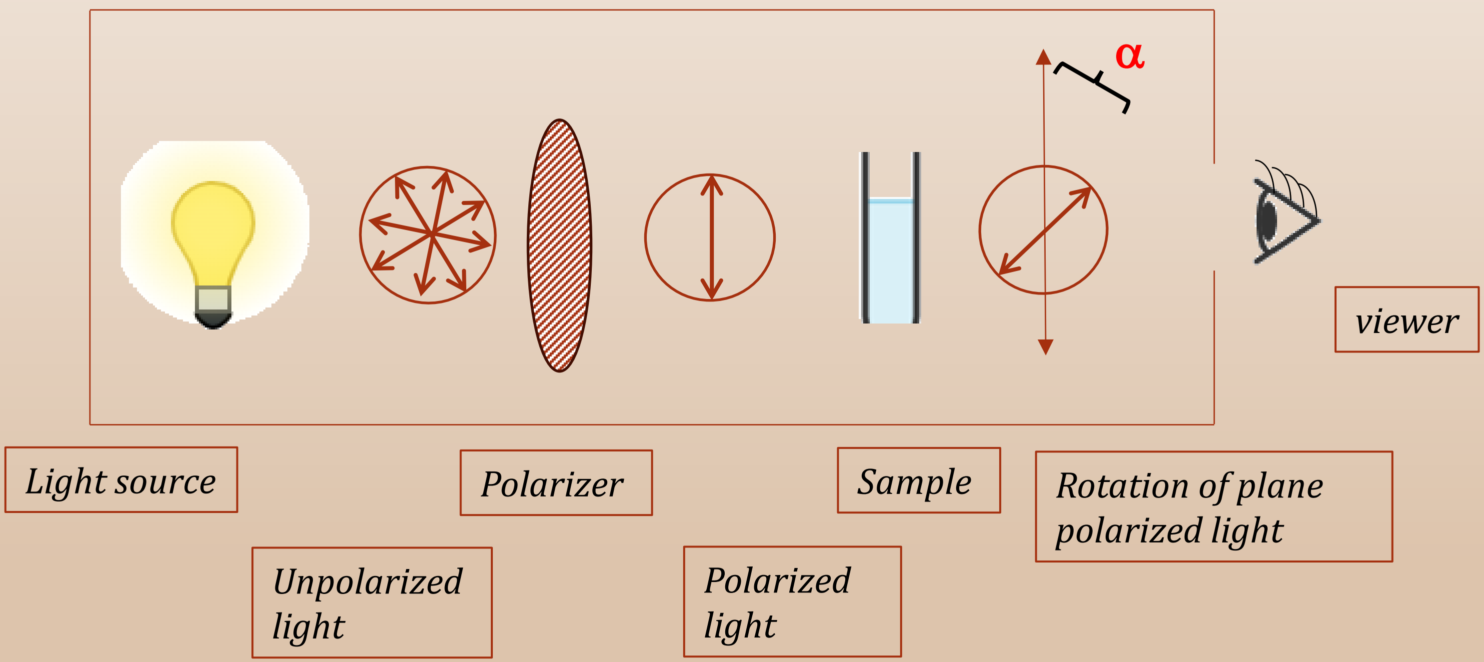
Optical Activity

In early 19th century it was discovered by Jean-Baptiste Biot that light restricted to pass through a plane is *plane-polarized.*

- Plane-polarized light that passes through a solution of compounds that **don't** have a chiral center stays in its original plane of polarization. These compounds are *optically inactive*.
- Solutions of chiral compounds rotate plane-polarized light and the molecules are said to be *optically active.*
- The instrument that measures this light rotation is called a polarimeter. The rotation is measured in degrees, is [α].
- Clockwise rotation is called **dextrorotatory (d)**.
- Anti-clockwise is **levorotatory (l)**.

The Polarimeter - Schematic

Below is a schematic of a polarimeter. The light source passes through a **polarizer** and then is detected at a second polarizer which shows the angle between the entrance and exit planes is the optical rotation. Rotation to the right is + (dextrorotatory) and left is – (levorotatory).

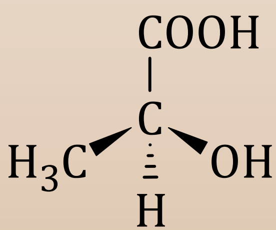


Specific Rotation

Specific rotation is that observed for 1 g/mL in solution in cell with a 10 cm path using light from sodium metal vapor (589 nm).

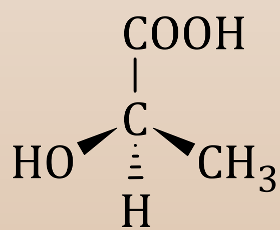
$$[\alpha] = \frac{\alpha}{c - l}$$

$[\alpha]$ = specific rotation
α = observed rotation
c = concentration of solution in g/mL
l = length of tube in dm (1 dm = 10 cm)



(S) – (+) Lactic acid

$[\alpha]^{21}_{D} = +2.6^{o}$



(R) – (-) Lactic acid

$[\alpha]^{21}_{D} = -2.6^{o}$

Specific Rotation and Molecules

A compound must be chiral for it to be optically active.

Enantiomers rotate plane polarized light in equal number but opposite in sign.

- There is **no correlation** between the ***R/S*** designation of an enantiomer and the direction **[(+) or (-)]** or the degree to which it rotates plane polarized light.
  - dextrorotatory (d) is + (positive degree number)
  - levorotatory (l) is – (negative degree number)
- Racemic mixture is equal mixture of enantiomers which shows no optical rotation and designated (±).

Chirality in the Biological World

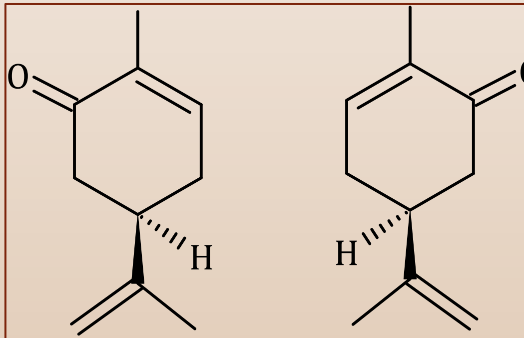
Majority of molecules of living systems are chiral except for inorganic salts and a few low-molecular-weight organic substances. Although these molecules can exist as a number of stereoisomers, generally only one is produced and used in a given biological system.

- For example, chymotrypsin, a protein-digesting enzyme in the digestive system of animals has 251 chiral centers so the maximum number of stereoisomers possible is 2^{251}. There are only 2^{38} stars in our galaxy!
- Enzymes like chymotrypsin, is like hands in a handshake.
    - The substrate fits into the enzyme binding site on the enzyme surface.
    - A left-handed molecule, like hands in gloves, will only fit into a left-handed binding site and a right-handed molecule will only fit into a right-handed binding site.
    - The differences in their interactions with other chiral molecules in living systems cause enantiomers to have different physiological properties.

Some More Examples

There are several chiral molecules with each enantiomer having specific properties. Here are a two naturally occurring enantiomers with distinct properties.

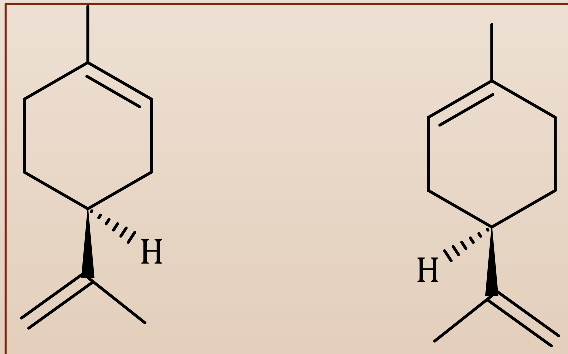
Carvone (spearmint vs. caraway)



R (-)
spearmint
mosquito repellant

S (+)
araway/cumin seeds
preservative

Limonene (orange vs. lemon)



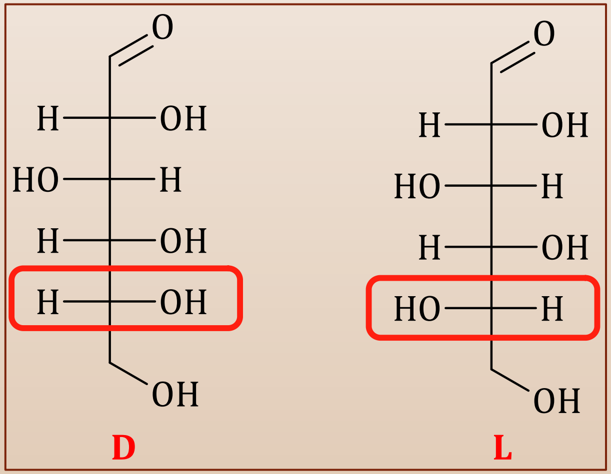
R (+)
orange flavor

S (-)
turpentine odor

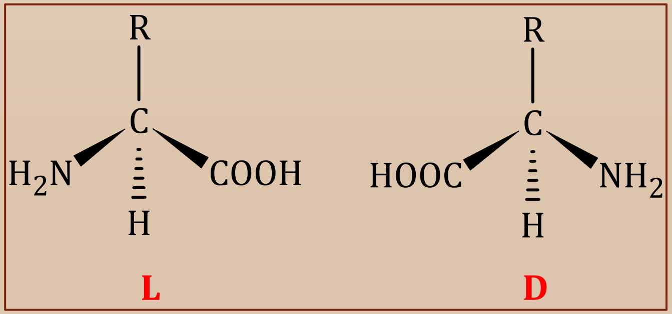
One More Classification D/L

In the biological world, there can be different classifications of family of compounds depending on the orientation/stereochemistry of one group. This classification is D and L (not the same as d and l).

In **carbohydrate** chemistry, the D is when the second carbon OH is on the right, and L is when OH is on the left side. D carbohydrates are the naturally occurring and the one we consume. The structure on the right is of D and L glucose. They are enantiomers.



In **amino acids** the D and L isomers are enantiomers. Instead of using R and S, D and L are more commonly used. L enantiomer is the naturally occurring amino acid in our bodies.



Key Words/Concepts

- Understand polarimeter.
- Dextrorotatory
- Levorotatory
- Optical rotations (d + and l -)