# Lipids and membranes

BIOS 1006

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## Objectives

- Know all definitions.
- Describe the roles played by lipids.
- Describe micelle and bilayer structures.
- Describe the forces that stabilize lipid structures.
- Predict the relative melting points of fatty acids and the lipids in which they are found.
- Draw a fatty acid given a name or designation: (e.g. trans-18:1$^{\Delta 9}$ or 18:1$\omega$9) and name fatty acids if given a structure.
- Describe the essential and non-essential designations.
- Recognize a triacylglycerol or phospholipid given the names, structures or designations of the components.
- Describe the relationship between lipid fluidity and melting point.
- If given a list of fatty acids or lipids, rank the melting points.
- Describe the biological roles, the chemical reactions and the physical and structural properties of each lipid class.
- Determine the class of a lipid if given a structure.
- Determine the class of isoprenoids, and locate isoprene units in molecules.

# Lipids

Are water-insoluble molecules that are highly soluble in organic solvents. They are defined by their solubility (in organic solvents, not water)

## Roles of lipids

- Structure (membranes)
- Energy storage (fats, oils)
- Protection (antioxidants, water-proofing)
- Pigments (carotenoids)
- Coenzymes (vitamins, heme)
- Signaling (hormones, growth factors)

### Lipids do not form covalent polymers!

Recall:

- proteins are covalent polymers of amino acids
- nucleic acids are covalent polymers of nucleotides
- polysaccharides are covalent polymers of sugars

Lipids also form higher order structures, but the esubunits are not covalently attached. These structures are micelles and bilayers (membranes) that are maintained by IMFs such as LDFs (non-polar parts), hydrogen bonds, dipole-dipole forces, and ion-dipole forces (between lipids and $H_2O$).

## Classes and nomenclature of lipids

- Free fatty acids
- Triacylglycerols
- Phospholipids
- Glycolipids
- Isoprenoids

### Fatty acids

Monocarboxylic acids composed of a long hydrocarbon chain with a carboxyl group at the end

- Even number of carbon atoms

- Generally unbranched chain (straight chain)
- Hydrophilic and hydrophobic ends (amphipathic)
- Varying degrees of saturation
- Produced by organisms and synthesized from Acetyl-CoA
- Plants make all the fatty acids they need
- We only produce some fatty acids, the rest must be obtained from our diet (essential fatty acids)
- Essential: in your diet
- Non-essential: can be synthesized by your body (doesn't mean not important!)
- We need to consume **essential fatty acids** (omega-6, omega-3)
- Think of the numbering scheme from the $\omega$-carbon
- Saturated fatty acids are flexible (free rotation aroudn C-C bonds)
- Linear conformation ist he most stable due to steric constraints
- Chains pack tightly against each other and form more rigid, organized aggregates (i.e. membranes)
- London Force Strength is proportional to surface area, depends on length and proximity

**saturated fatty acids** 0 double bonds

**monounsaturated fatty acids** 1 double bond

**polyunsaturated fatty acids** 2 or more double bonds

Double bonds can result in one of two orientations. (cis (favored)/trans)

**Saturated fatty acid nomenclature**

- 18 carbon saturated fatty acid: 18:0 (carbons:double bonds)
- IUPAC: Octadecanoate (protonated: octadecanoic acid)
- Common: Stearate (protonated: stearic acid)

14:0 **tetra**<u>deca</u>noic acid (tetra = 4, deca = 10)
16:0 hexadecanoic acid
18:0 octadecanoic acid
20:0 **eicosanoic** acid
22:0 **do**<u>cos</u>anoic acid (do = 2, cos = 22)
24:0 tetracosanoic acid
26:0 hexacosanoic acid

**Monounsaturated fatty acid nomenclature**

18 carbon cis monounsaturated fatty acid with a double bond **starting** at position 11

- Full IUPAC name: cis $\Delta^{11}$-octadecene/-oic acid
- IUPAC shorthand: $18{:}1^{\Delta 11}$
- 18:1 $\omega$ 7 (counting backwards)

**Polyunsaturated fatty acid nomenclature**

18 carbon cis monounsaturated fatty acid with 2 double bonds **starting** at positions 9 and 12

- Full IUPAC name: cis-cis- $\Delta^{9}$, $\Delta^{12}$-octadecadienoic acid (dien = 2 double bonds)
- IUPAC shorthand: $18{:}1^{\Delta 9,\Delta 12}$
- 18:2 $\omega$ 6 (from the first double bond counting backwards. assuming all are cis and any other double bond is 3 carbons away)

## Lipid fluidity

The higher the melting point, the lower the fluidity (this is why butter is solid and olive oil is liquid)

Also depends on chain length. Longer chains have...

- Greater surface area
- Stronger London Forces
- Increased melting point

Lipid fluidity also depends on degree of unsaturation. **More double bonds = lower melting points** (kinks in structure preventing close interactions)

Trans fats (human-introduced by hydrogenation, more solid, higher melting point) are more easily packed together than cis fats (more liquid, lower melting point).

## Triacylglycerols

- Glycerol backbone (linear vertical chain of CH-OH)
- Ester linkage containing 3 fatty acid chains and alcohol
- Constituent fatty acid lengths and degrees of unsaturation can vary (fats or oils), depending on number of double bonds/carbons
- Primarily used for energy storage in animal (adipose) and plants
- **Simple** triacylglycerols: All fatty acids are the same
- **Mixed** triacylglycerols: Fatty acids are different

## Phospholipids

- Involved in generation of signaling molecules, anchoring proteins, and membrane formation
- An amphipathic derivative of glycerol (3 OH groups) or sphingosine

### Phosphoglycerides (phospholipids)

- Composed of glycerol, two fatty acids (R groups), phosphate group, and "X" (amino alcohol or hydrogen)
- Simplest form: phosphatidic acid (X=H) and R = fatty acids
- Others classified according to the amino alcohol attached (X)
- Fatty acids attached can be the smae or different
- Example: **lecithin** (phosphatidylcholine), pH insensitive, a phosphoglyceride with choline
- **Cephalins** (phosphoglycerides with ethanolamine or serine) such as phosphatidylserine and phosphatidylethanolamine

### Sphingolipids (includes phospholipids)

- Hydrophobic tail
- Ignored OH group
- Amide with fatty acid
- OH group that can attach a sugar (acetal) or a phosphate-amino alcohol
- Sphingosine + fatty acid = seramide
- General structure: sphingosine (sphingolipid) + fatty acid

### Spingophospholipids

Sphingosine + fatty acid + phosphate + amino alcohol (e.g. A sphingomyelin, brain and nervous system tissue)

**Find the amide bond!**

### Sphingoglycolipids

Sphingosine + fatty acid + carbohydrate

### Properties of phosphoglycerides and sphingolipids

Hydrophilic head and hydrophobic tails

## Isoprenoids

Generated from acetyl-coA, composed of isoprene subunits $(CH2\text{-}C{=}CH\text{-}CH2\text{-})_n$

2 classes: **terpenes** and **steroids**

### Terpenes

Large and diverse class of strong-smelling organic compounds, mostly produced by plants.

Classified by the number of isoprene or terpene units (**1 terpene unit = 2 isoprene units**)

**monoterpenes** 2 isoprene units, used in perfumes

**sesquiterpenes** 3 isoprene units, citronella

**tetraterpenes** 8 isoprene units, carotenoids

**polyterpene** 1000s of isoprene units, rubber

**Mixed terpenoids** - also contain a non-isoprene component (e.g. ubiquinone, vitamin K)

### Steroids

Triterpene derivatives (6 isoprene units, 4 fused rings)

**Cholesterol:**

- Basic structure with multiple rings and alcohol (hydroxyl) group at the end. 4 fused carbon rings, 2 stacked on top of the other 2, mismatched
- Found in all eukaryotes and some bacteria
- A component of plasma membranes
- Precursor for all steroid hormones, Vitamin D and bile salts
- Found as esters with fatty acids and sugars

## Micelles and membranes

### Structures of lipid assemblies

**Conical** lipids such as fatty acids form micelles (spherical, fatty acids, detergents)

**Cylindrical** lipids such as glycerophospholipids form membranes (rectangular, packed closely)

**Inverted conical** lipids such as triacylglycerols also form membranes

### Lipid bilayers

Phospholipids and glycolipids prefer to form bilayer structures in aqueous solutions.

- Structure: Sheet-like

- Thickness: 2 leaflets (outer + inner), 30-40Å
- Stabilized by IMFs (tails: IMFs, heads: with $H_2O$ - ion-dipole, dip-dip, H-bond)
- "Fluid Mosaic Model" (Singer & Nicholson)
- Membranes are dynamic structures composed of proteins and phospholipids
- The bilayer is a fluid matrix (lateral diffusion)
- Lipids and proteins can rotate and freely migrate or diffuse within a leaflet