Tour and quick review of the major compounds important to the human body.

[Study guide covering chapter 5]

Last edited: 08.04.2019

Important functional groups: those with oxygen, nitrogen, phosphorus, sulfur.

- Acyl group: the part of the structure that provides the --C=O carbonyl group in an ester/amide linkage. "-yl" ending.
- Aliphatic: open chains (non-ring).
- Aromatics/Benzene rings. "Phenyl" if ring is a substituent.

Carbohydrates (sugars).

- Formula: CnH2nOn. Glucose is C6H12O6.
- Classified by: carbonyl group (aldose/ketose); # of carbons; positions of the -OH group on the anomeric carbon (D=right/L=left OH position, stereoisomers, epimers); any additional substituents; number of saccharides; how the components are linked (e.g. glycosidic bonds).
- For n asym centers  $>> 2^n$  stereoisomers generally speaking.
- Humans use D-sugars. "D for Delightful sugars!"
- Epimer: a pair of stereoisomers that differ only in one position of the OH at a chiral carbon.
- Epimerases: enzymes that make epimer conversions.
- Glycoproteins: proteins + sugars.
- Proteoglycans: proteins that are heavily glycosylated. Many long unbranched polysaccharide chains attached to a protein core. VIP to extracellular matrix, aqueous humor, cells that make mucous secretions, & cartilage.
- Glycosaminoglycans: polypeptide chains with repeating disaccharide units w/oxidized acid sugars, sulfated sugars, and N-acetylated amino sugars. Structure looks like a bottle brush.
- <u>https://themedicalbiochemistrypage.org/glycans.php</u>
- <u>https://www.mdpi.com/1424-8247/11/1/27/pdf</u>
- Glycosylation: a reaction where a carbohydrate is attached to a hydroxyl or other functional group.
- Glycolipids: lipids + sugars.
- In solution, OH on anomeric carbon spontaneously changes (mutarotation) from alpha to beta and back to change from open to ring forms such as chair/boat etc. Chair/boat etc are usually more stable so there's a greater chance that a compound will be in those configurations.
- If the anomeric carbon forms a bond with another molecule, those mutarotations cannot happen due to the bond which limits configurational possibilities.
- Common substituted groups: phosphate, amino, sulfate or N-acetyl.
- Most free monosaccharides in the body are phosphorylated at the terminal carbons preventing transport out of cell.

- Galactosamine & glucosamine are examples of an amino group replacing one of the OH groups. Usu. the amino group gets acetylated forming an N-acetylated sugar.
- Acetylation: adding an acetyl functional group to a compound.
- Acyl group. <u>http://www.chem.ucla.edu/~harding/IGOC/A/acetyl\_group.html</u>
- <u>https://www.oit.edu/docs/default-source/library-documents/library-publishing/che102-intro-organic-chemistry/chapter-1-7.pdf</u>
- Sugars can get oxidized at the aldehyde carbon to form "-onic acid" or "-onate".
- Uronic ("-uronic acid") acid forms when the the terminal OH group gets oxidized.
- Polyol sugar: a sugar where the aldehyde gets reduced where all the carbon atoms have OH. Eg. Sorbitol.
- Deoxy sugar: a sugar that has reduced such that 1+ carbons contains only H's. Carbon 2 of deoxyribose.
- The OH of the anomeric carbon can react with an OH (O glycosidic bonds found in sugar-sugar, sugar-hydroxyl bonds) or NH (N glycosidic bonds found in nucleosides and nucleotides) group to form an alpha/beta glycosidic bond.
- Alpha glycosidic bond. The Greek alpha looks like a fish which is DOWN in the sea.
- Beta glycosidic bond. The Greek beta looks like a bird UP in the air.
- Disaccharide: 2 monosaccharides joined by O-glycosidic bond.
- Oligosaccharide: 3-12 linked monosaccharides via N or O glycosidic bonds.
- Polysaccharides: thousands of monosaccharides joined to make chains and/or branches.

# Lipids.

- Hydrophobic.
- Usu. straight chains, methyl group at one end (w-carbon) and carboxyl at the other end.
- Most FA in humans have even number of carbons betw. 16-20.
- Most common FA in cells are stearic and palmitic FAs.
- \*Special notation for FA's pg. 69-70.
- http://rogersal.people.cofc.edu/Lipids.pdf
- https://www.cs.mcgill.ca/~rwest/wikispeedia/wpcd/wp/f/Fatty\_acid.htm
- <u>https://courses.lumenlearning.com/suny-nutrition/chapter/2-33-fatty-acid-naming-food-sources/</u>
- https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3646453/
- <u>https://www.uio.no/studier/emner/matnat/farmasi/nedlagte-emner/FRM2041/v06/undervisningsmateriale/fatty\_acids.pdf</u>
- FA also classified by distance from w-carbon to the double bond.
- Fatty acids. Esterified to glycerol >> triacylglycerols (triglycerides) or phosphoacylglycerols (phosphoglycerols).
- Tri acyl glyderols: 3 acyl FA groups attached to glycerol; fat stores in the body.
- Sphingolipids: FA + sphingosine (serine + palmitate FA). No glycerol backbone.
- Ceramides (type of amides) = sphingosine + FA attached at the amino group.
- More sphingolipids formed from attaching substituents onto the OH of the ceramide.
- Cerebrosides + gangliosides = sugars glycosidically bonded to OH of ceramides.
- Sphingomyelin = phosphorylcholine + ceramide; vip part of cell membranes and myelin sheath.
- Glycolipids: lipids + sugar hydroxyl group.

- Polyunsaturated FA: building blocks of eicosanoids.
- Eicosanoids: signalling molecules via enZ or non-enZ oxidation of arachidonic acid or other polyunsat. FA. Hormone-like compounds. Polyunsat FA with 20 carbons (eicosa) and have 3-4-or-5 double bonds (e.g. prostaglandins, thromboxanes, leukotrienes).
- Naturally occurring FA typically cis.
- There are also trans.
- Cholesterol: formed from isoprene units.
- Bile salts.
- Steroid hormones.
- Isoprenyl unit: combined in long chains to make structures such as side chains of Coenzyme Q in humans and Vit A in plants.
- Geranyl groups = 10 carbons & polymers of isoprenyl units.
- Farnesyl groups = 15 carbons + isoprenyl units.
- Geranyl and farnesyl groups often get attached to proteins so that proteins can interact w/other cellular structures.
- Acylglycerols: glycerol with 1+ FAs (acyls via ester linkages). Mono- di- and triacylglycerols contain 1, 2, and 3 FA esterified to glycerol. Triacylglycerols don't usu. have the same FA at all 3 positions (usu. mixed).
- Phosphoacylglycerols: FA at positions 1 and 2; phosphate group (or substituent attached to phosphate group) at position 3. If it's only the phosphate group and NO other substituents at position 3, then it's a phosphatidic acid.
- Phosphatidylcholine (lecithin) found in membranes. Has polar and nonpolar duality.
- Lysolipid = phosphoacylglycerols fatty acyl group
- Steroids: 4-ring steroid nucleus; cholesterol precursor; diff species made by modifying ring or C20-side chains.
- Cholesterol hydrophobic can convert to hydrophilic bile salt (eg. cholic acid). Branched 5-carbon units w/1 double bond (isoprenyl unit)
- Bile salts are on micelles survaces in the intestinal lumen.

Nitrogen Compounds.

- Amino groups.
- Heterocyclic ring.
- Amino acids: carboxyl group; amino group; 1+carbons.
- Purines: has heterocyclic N ring.
- Pyrimidines: has heterocyclic N ring.
- Pyridines: has heterocyclic N ring.
- Nucleosides: N ring + sugar (usu. ribose or deoxyribose) via N-glycosidic bond.
- Nucleotide: nucleoside + phosphate.
- In proteins, amino acids (AA) are L-alpha-AA.
- While it is rare that beta or gamma AAs get formed, only L-alpha-AAs get incorporated into proteins.
- D-aminos are used by bacterial in their cell walls.
- N as a component in heterocyclic rings or N-bases.
- Common rings: purines, pyrimidines, pyridines.

- "-ines" denotes nitrogen in the structure. Uracil (pyrimidine) is an exception to the naming.
- Tautomers: in N rings, hydrogen can shift positions with the double bonds and this is called tautomers or tautomerization.
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Book%3A\_Organic\_Chemistry/Book%3A\_Organic\_Chemistry\_With\_a\_Biological\_Emphasis\_(Soderberg)/13%3A\_Reactions\_with\_stabilized\_carba\_nion\_intermediates\_I/13.1%3A\_Tautomers\_</u>
- http://www.chem.ox.ac.uk/vrchemistry/nor/notes/tautomers.htm
- <u>https://www.khanacademy.org/science/organic-chemistry/ochem-alpha-carbon-chemistry/formation-of-enolate-anions/v/keto-enol-tautomerization</u>

### Free Radicals.

- Compounds w/single electron in outer shell.
- Extremely reactive and unstable.
- Usually formed as intermediates.
- Usu. negative effects.

#### Oxidation/Reduction.

- Carbon-carbon or carbon-oxygen bonds said to be oxidized or reduced depending on # of electrons around the carbon.
- LEO: lose electrons (lose H atoms) oxidation.
- GER: gain (gain H or lose O) electrons reduction.
- More oxidized from alcohol to aldehyde/ketone to carboxyl.

#### Acid/Base.

- Cations are catfabulous (+)! Anions (onions) make you cry (-).
- Common anionic groups: carboxylate; phosphates (P); sulfates.
- Common cationic groups: N, amines.

## Bond Polarity & Partial Charges.

- Carboxylate.
- Phosphate.
- Sulfate.
- Ester = carboxylic acid + alcohol water
- Thioester = acid + sulfhydryl
- Amide = acid + amine
- Phosphoester = phosphoric acid + alcohol
- Anhydride = acid1 + acid2

Resources.

- <u>https://www.researchgate.net/publication/268224079\_A\_New\_and\_Simple\_Method\_for\_Drawing\_of\_the\_Monosaccharide\_Fischer\_Projection\_Based\_on\_New\_Monosaccharide's\_Barcodes</u>
- Isoprene unit.
   <u>https://chem.libretexts.org/Ancillary\_Materials/Reference/Organic\_Chemistry\_Glossary/I</u>
   <u>soprene\_Rule</u>
- Drawing sugars. <u>http://www.chtf.stuba.sk/~szolcsanyi/education/files/Chemia%20heterocyklickych%20zl</u> <u>ucenin/Prednaska%206/Odporucane%20studijne%20materialy/Drawing%20sugar%20str</u> <u>uctures.pdf</u>
- Aldose configurations. <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemist</u> <u>ry\_(McMurry)/Chapter\_25%3A\_Biomolecules%3A\_Carbohydrates/25.04\_Configuration</u> <u>s\_of\_Aldoses</u>
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry</u>
- https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry\_(McMurry)/Chapter\_25%3A\_Biomolecules%3A\_Carbohydrates/25.02\_Depicting\_Carbohydrate\_Stereochemistry%3A\_Fischer\_Projections
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry</u>
- https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemist ry\_(McMurry)/Chapter\_25%3A\_Biomolecules%3A\_Carbohydrates/25.05\_Cyclic\_Struct ures\_of\_Monosaccharides%3A\_Anomers
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry</u>
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry</u>
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry</u>
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry (McMurry)/Chapter\_25%3A\_Biomolecules%3A\_Carbohydrates/25.10\_Other\_Import\_ant\_Carbohydrates</u>
- <u>https://chem.libretexts.org/Bookshelves/Organic\_Chemistry/Map%3A\_Organic\_Chemistry\_(McMurry)/Chapter\_26%3A\_Biomolecules%3A\_Amino\_Acids%2C\_Peptides%2C\_a\_nd\_Proteins</u>

References.

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