

## Carbohydrates: Biochemical Examples

- Primary energy producing metabolism
- Can form polymer like polypeptide
  - Repeating units through covalent interactions
  - Long polymers and the individual components: residue
  - Different lengths
- How they can linked to protein molecule
  - Commonly found in mammalian cells
  - Communication in cells
- Carbohydrate
  - Contain carbon skeleton
  - Multiple different hydroxyl groups
  - If it contain aldehyde is aldose
  - Ketose contain ketone groups
  - Glyceraldehyde aldose
    - 3 carbons aldotriose
  - Increase number of carbon
  - hexoses/ aldoses/ 6 carbons
  - Individual sugar subunit → long polymer
- S
- Monosaccharides are designed L or D isomers.
  - Which one is the hydroxyl
  - Assign stereochemistry of the sugar.
  - Further away from
- D is the most common conformation.
- Internal carbon is a stereoisomer
- Many have different names
  - Sugars that differ around one carbon are epimers
  - D mannose is epimer of glucose
- S
- Monosaccharides adopt cyclic structure
  - C5 alcohol attack C1 carbon of glucose → Cyclic structure is produce a reaction if aldehyde
  - React ketone with alcohol, you get hemiacetal
  - Hemiketal group
- C5 can attack from the back or the front different stereoisomer anomeric emanomers. Alpha or beta.
  - These forms are exchange in solution rapidly.
  - Different cyclic rings.
- Monosaccharides adopt cyclic structure
  - 6 carbon rings- pyranoses
  - 5 carbon rings- furanoses
  - They don't form flat rings, they form half chairs

- Take cyclic form of glucose
  - 2 possible chair conformation 46 kJ/mol to switch between chair forms.
  - Alpha or beta alternative pyrunose
  - Cyclization - generate series of cyclic rings
- Added to hydroxyl groups
- S
- Organisms contain a variety of hexose derivatives
- S
- Disaccharides contain a glycosidic bond
- Each carbonyl group in monosaccharide able to make
- Anomoeric carbon hemiacetal interact with alcohol in a second glucose
- When it does so, it forms a covalent bond it turns it into a full acetal. Link them together 2 monosaccharide→ polymers that linked by glycosidic bonds
  - Sugar residues that are linked through glycosidic bonds.
  - It doesn't matter how many you link together there will be a nonreducing group
  - Available to react with something. You can react with another sugar residue. Can be react with copper sulfate.
  - Available hemiacetal reducing the cooper
  - Reducing end. End that contains nonreducing is reducing end.
  - They can form disaccharides and
  - Linked together by glycosidic bonds
- S
- Polysaccharides are polymers of many sugar units
  - Extremely common
  - Move away from carbohydrates
  - You can separate polysaccharide
  - Polysaccharides and heteropolysaccharides
  - Poly- different combination and put them together
    - Homopolysaccharides- long string of identical sugar molecule
      - Glucose glucose .....
    - Heteropolysaccharides-different combination of monosaccharide to produce polysaccharide combination
  - Linear or branched
    - Branch 2 glycosidic bonds from one molecule
    - One glycosidic bond from link to 2 glycosidic bonds.
  - Very variable in sequence and length.
  - Not produced using a template
    - Formation of very heterogenous sequence varying length.
  - Homopolysaccharides: starch glycogen
  - Heteropolysaccharides: peptidoglycan and glucosaminglycans
- S
- Homopolysaccharides can be fuel storage
- Starch

- Store it for later use
- Amylose and amylopectin
  - Amylose glucose glucose glucose (unbranch)
  - Amylopectin- branch points where instead of branched (1,4) (1,6) through 2nd glycosidic bond.
  - Branch point gives a helical structure wrapping around helical arrangement.
- Polysaccharides fold into 3D structure same
  - Sound proteinatious
  - Protein tertiary structure
  - Greater diversity than polysaccharides
  - But they still do
  - Peptide rigid peptide bond
  - Certain allowable angle
    - Phi and psi- certain are allowed and some not
  - The pyranous ring for glucose residue - rigid
  - Like peptide
  - All have to relate to one another through certain angles
  - Derive psi and phi values
  - Given certain value
  - Lead to steric clashes
  - Additional interaction- favorable
  - Formation of bond or not
  - Certain conformational
  - Graph of all possible psi and phi - thereotical value high value in peak highly unfavorable
  - Low -energetically favorable.
  - Amylose most prefer helical structure satisfy certain allow values. 1 residue amylose chain relate to one another 6 residue rotation 6 residues per turn. Tightly constrain helical structure
- Plant starch/ animal glycogen → energy storage
  - glucose high effect in osmolarity high concentration negative effects
- S
- Proteoglycan and Glycoproteins are found on the cell surface.
  - Carbohydrate covalently linked to protein molecules protein carbohydrate complex
  - Outside surface of cells
  - By conjugates with carbohydrate more functions
  - Furry is carbohydrate chain project outer membrane of the eukaryotic cell.
  - Glycocalyx- in order to get to cell membrane other cells make out of cell
  - Separate two type of cells
    - Proteoglycan: proteins covalently linked to glucosaminoglycan
    - glycoprotein : proteins covalently linked oligosaccharide (any sequence of structure)

- Proteoglycan contain glycosaminoglycan chains
  - By containing different repeating units by 2
  - Heavily sulfated → sulfate covalent linked at position occupied by hydroxyl groups.
  - Addition of sulfate ions negative charges
  - Glycoaminoglycan coated with negative charge create platform for small positive charge protein.
  - Consensus sequence covalent bond serine glycine X glycine
  - Attachment point for protein to be protein 5 defined sugar
    - Invariant with each other tetrasaccharide bridge.
    - Emerge from the sides
  - S
- Proteoglycans can organize the outer membrane
- 4 different example of function
  - Glucosaminary chain green heavily sulfated NS site antithrombin when thrombin bind conformational bind
  - Regulate blood clotting.
- Glycoproteins have covalently attached oligosaccharides
  - 2 types N linked
  - O linked consensus- no consensus but rich in G, v, P

## Metabolism

- Reposition
- Group transfer high
- Catabolism-breakdown metabolic steps
- Highly order into smaller molecule extract energy to ATP
- All reaction have negative delta G.
- Pathway are irreversibly not doing both things at the same time.
- Large free energy at least one step of reverse reaction difficult
- Keep substrate low when substrate available is low
  - Cell keep substrate level low when substrate concentration is low it is sensitive to changes
- Lots of allosteric regulation
- Make or break c-c bond
- Internal rearrangements, isomerization, and elimination
  - Involve redistribution of electrons without changing overall oxidation state of the molecule
- Free radicals
  - Rare changes
- Group transfer
  - Activation of metabolite
  - Presence of high energy group make it a good LG
  - Much good LG - common phosphoryl group
  - Future reactions are more favorable because of the phosphoryl group being released
  - Taking phosphoryl and transferring to glucose and generate g6p
  - Catalyzed by kinase bind to atp and catalyze the transfer of one of the phosphates
  - Kinases add phosphate group and Phosphatases remove phosphate groups.
- Oxidation-reduction
  - Most reduced alkanes to most oxidized co2
  - Dehydrogenation is most common oxidation reduction reaction
  - Lactate to pyruvate lost of 2 protons 2 electrons
  - Highly reduced → more oxidized lost are transferred to electron carrier.
    - Terminal - molecule high affinity for electron
- Complex molecules break down
- Power early steps or anabolic relation→ complex
- ATP is
  - Hydrolysis has a large delta G break the bond that yields free energy
  - High negative delta G
  - Relieve of charge repulsion.
  - Close proximity of negative

- Remove the phosphate large negative delta G.
  - Electro
  - Atp value of low adp is lower excess of ATP over ADP
  - Cell wants to keep the number of ATP over ADP because it wants that potent free energy to release large negative delta G.
  - As ATP decreases, the potency of ATP as a fuel to decrease.
    - It is important to maintain the concentration to be high.
  - ATP typically provides energy y group transfer
  - Glu→ Gln ATP was phosphoryl transfer to glu good LG take oxygen with it and nucleophilic attack on carbon of glu sidechain via amine covalent intermediate phosphate departing taking oxygen with it amine bound to it yielding glutamine.
  - Not random ATP transfer.
  - Almost always phosphoryl intermediate
- Transfer of different sections of ATP
    - All are available for nuc attack all electrophilic
    - Can perform on any of the phosphosphate you can if you get alpha nuc you get rib and adenine all attached to
    - Atp negative transfer lots of
- Lot of oxidation reduction examples
    - NADH and NADPH cosubstrate they are cofactors
    - Cosubstrate come and go prosthetic group come and go
    - Heme as a prosthetic group NADH and NADPH are good at electron transport good at redox reaction NADPH is phosphite + NADH the benzene ring come be reduced.
    - **Overall reaction liberation of 2 electrons and 2 protons 2 electrons and 1 protons go to NAD+**
    - Oxidized is more than reduced form NAD+ participates in oxidation reduction.
    - Keeping NAD higher
    - Reduced form NADPH higher they conduct reverse reaction
    - Transfers to substrate keeping concentration of electron accepts we can get them to participate in different reaction
  - Tertiary structure rossmann fold protein motif good at binding NAD and NADP this is part of the fold bind to electron acceptor or shuttle.
    - There are other electron carrier
    - Electron flavin nucleotide bind to protein when they bind they make flavoproteins.
    - 2 flavoprotein 1) flavin adenine dinucleotide FAD→ 2) flavin mononucleotide
    - They are related to each other side of reduction is at nitrogen.