

Name: \_\_\_\_\_

## Chem 462 - Biochemistry Hour Exam II

1. (10 points) Compare and contrast the structure of  $\alpha$ -keratin, collagen, and silk Fiberoin.

$\alpha$ - keratin

right handed  $\alpha$ -helical 2<sup>nd</sup> structure

2 parallel coils coiled around each other in left handed manner to make higher order structure

Coils held together via hydrophobic amino acids and disulfides on matching surfaces

Coils bound together in protofilaments and protofibrils  
can stretch as  $\alpha$  helix pulled into extended

Collagen

helix structure with 3 residues/turn in a left handed helix

3 strand super-twisted around each other in right handed sense

35% glycine 11% Ala and 21% Pro or Hpro

G needed as inner most residue

Pro need for extended structure

Collagen fibers then assembled in higher order structures

little stretch because already mostly extended, and 3d interaction does not allow to extend further

silk fiberoin

$\beta$  sheet structure

antiparallel  $\beta$ -sheets

rich in Ala and Gly

Ala on one side of sheet

Gly on other side of sheet

Sheets bonded together by Ala-Ala or Gly-gly interactions

does not stretch because already extended.

2. (10 points) Compare and contrast the two major theories of protein folding and how do these theories relate to the idea of a free-energy funnel.

Molten globule

hydrophobic interaction make disorganized hydrophobic core appear first  
secondary structure forms within core and structure begins to solidify

Hierarchical folding

regular secondary structure ( $\alpha$ ,  $\beta$ , etc) forms first  
these fold against each other to form higher order structure  
higher order structure combines to form domains  
domains fold together to make completed protein

Both models start with a large number of possible intermediates

as the folding process continues the number of possible structures get smaller as the energy of the structures gets more favorable

As the E of the protein state gets lower and lower the number of possible structure that can have this lower E gets smaller and smaller, until there is only 1 structure with the lowest possible E

3. (10 points) A Hill plot is a plot of  $\log\left(\frac{q}{1-q}\right)$  vs  $\log [L]$ . What is a Hill plot, why is it used, and what does it tell us about the binding of  $O_2$  to hemoglobin?

Hill plot is used to detect cooperativity

the slope of line determines amount of cooperativity

slope = 1 no cooperativity

slope  $\neq$  1 slope tells # of cooperative units

if slope < 1 have negative cooperativity

In hemoglobin slope is about 3 at physiological  $O_2$  concentrations saying that there are at least 3 monomers in the cooperative unit

sketch similar to 7-13 is nice

4. (10 points) In class you learned about specific acid-base catalysis, general acid-base catalysis, covalent catalysis, and metal ion catalysis. Describe each of these types of catalysis

Specific acid-base:  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is part of the reaction mechanism

General acid-base: Functional groups on the protein act as acids or bases in the catalytic mechanism. Can be in Bronstead-Lowry sense (proton donors or acceptors) or in Lewis sense (electron donors or acceptors)

Covalent catalysis: A temporary covalent bond is formed between the enzyme and the substrate that is broken in subsequent steps of the mechanism.

Metal ion catalysis: A metal ion is used at some point in the reaction mechanism. Many different uses are observed. Can be used simply to stabilize a single conformation, or can be used as part of a general acid or base, or can be used as part of a covalent catalysis

5. (10 points) D-Ribose is a 5 C sugar, and its structure as given on page 296 of your text show in figure A. This is the sugar that is used to make RNA. When you see its structure in RNA it looks like figure B. Propose a name for this ring structure of ribose. Why are these structures different. Could there be another form of ribose, that the books aren't showing us? Could these forms of the free sugar interconvert? Could these forms interconvert in the RNA structure?

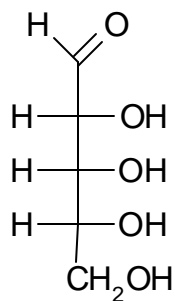


Figure A

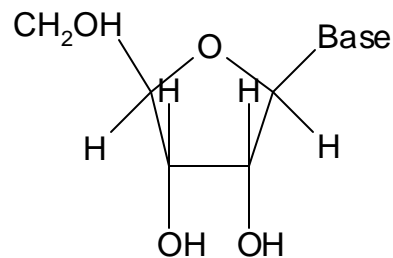


Figure B

(Please don't feel like you have to fill this page with writing.)

$\beta$ -D-ribofuranose is figure B

There could be an  $\alpha$ -D-ribofuranose that is not shown.

The three forms interconvert because the OH in the 4 position likes to react with aldehyde in 1 position to make a hemiacetal. Free interconversion will take place in the base sugar, but once the anomeric C is tied up in the RNA structure no further interconversion can occur

I suspect that there may be a 6 member ring conformer as well, where the #6 C attacks the anomeric C, but it must not be very stable because I have never seen it mentioned in biochemistry

6. (10 points) Compare and contrast the structure of chitin and cellulose and glycogen. Include in this comparison the different sources of these substances, where they are found, what do the monomer units look like, how are the monomer units connected and any other structurally pertinent facts.

Chitin Source arthropod exoskeleton

N-acetyl-D-Glucosamine in  $\beta$ 1-4 linkages

Linear, lots of H-bonds between saccharides, low water solubility

Cellulose found in Extracellular matrix of plants

Glucose in  $\beta$  1-4 linkages

Linear, lots of H-bonds between saccharides, low water solubility

Glycogen storage sugar in mammalian systems

Glucose in  $\alpha$  1-4 linkages additional  $\alpha$ 1-6 linkages about every 10 sugars

some H-bonds between saccharides make into a coiled structure, lots of additional H-bonds to water make very water soluble

7. (10 points) The carbohydrate portion of some glycoproteins may serve as a cellular recognition site. In order to perform this function the oligosaccharide portion of the protein must have the potential to exist in a large variety of forms. Which can produce a greater variety of structures: oligopeptides composed of 5 different residues, or oligosaccharides composed of 5 different monosaccharides?

If you have 5 residues then you have 4  $\phi$  and  $\chi$  angles and between residues to make a total of  $2 \times 2 \times 2 \times 2$  16 different angles each of which can vary over a range

You can make same argument for a linear array of sugars; there will be 4 joins between sugars, and in each join you can vary the angle of one sugar or the other to get roughly the same number of conformations

The real difference comes in the fact that sugars don't have to be in linear 1-4 linkages, many other linkages like 1-6 can occur and you can have one sugar with multiple linkages so branched structures are also possible. This greatly enlarges the number of different conformation states. There is also the choice between  $\alpha$ - and  $\beta$ - conformers at the anomeric C position. Further, while there are only 20 amino acids, there are probably 2 to 3 times this number of different sugars, especially when you start modifying the sugars with all the different derivative that are available. The net result is that there is a much richer range of structures available to 5 carbohydrates than to 5 amino acids.

