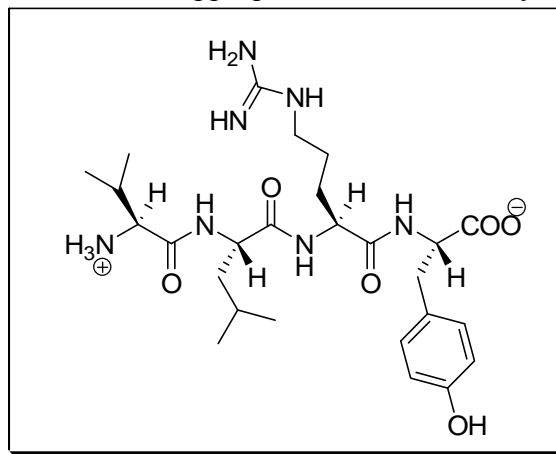


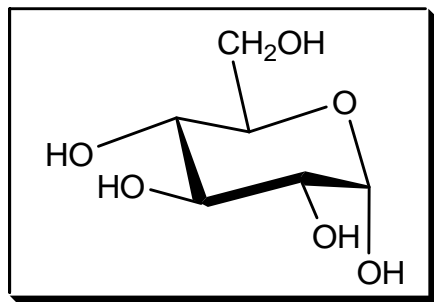
Chemistry 11 Spring 2008
Examination #5 ANSWER KEY

1. (40 pts. total) **BIOCHEMICAL STRUCTURES!** *Important note: use the space provided along with the back pages of this examination for any scratch work; all final structures should be drawn in the boxes provided to receive any credit.*

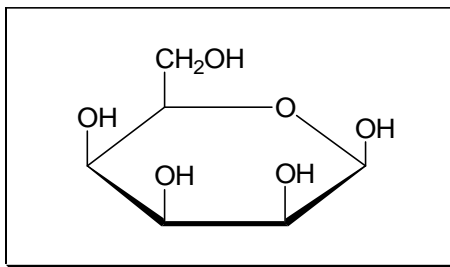
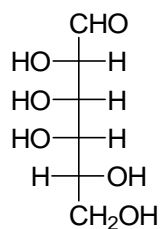
- A. (8 pts.) Draw the tetrapeptide **VLRY** under natural conditions. Make certain to include the appropriate stereochemistry.



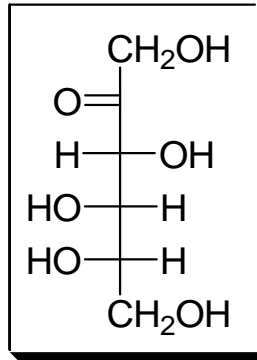
- B. (6 pts.) Draw the most stable CHAIR conformation of α -D-Glucose (no credit for ambiguous ax/eq).



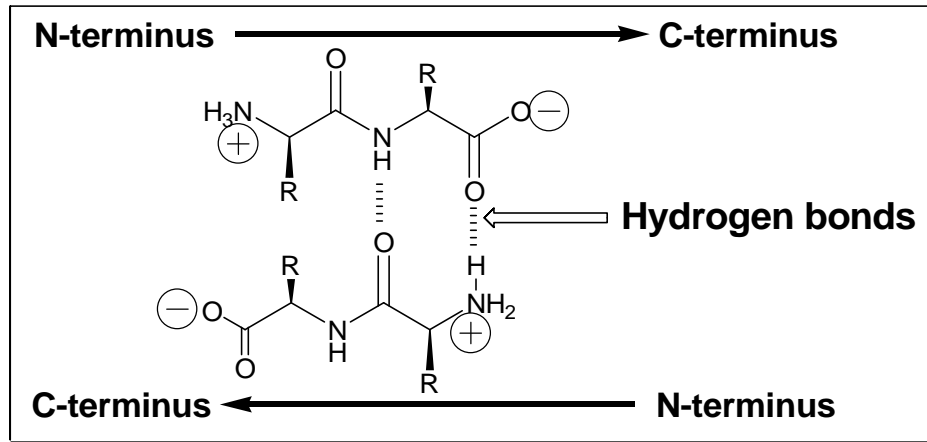
- C. (6 pts.) Draw the Haworth projection of the following hexose (talose) in a β -pyranose form.



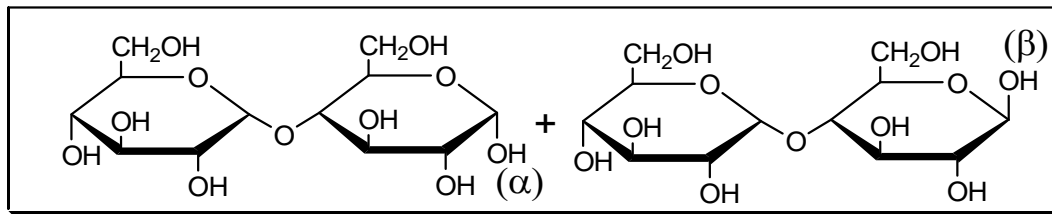
D. (2 pts.) Draw the Fischer projection of L-fructose.



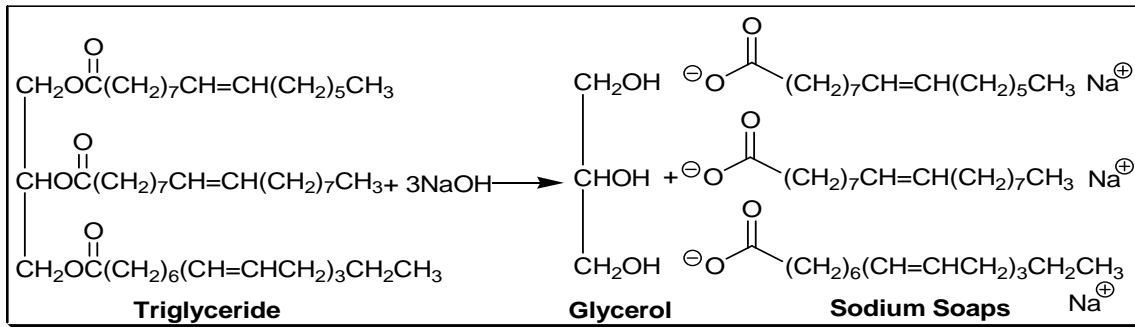
E. (6 pts.) Draw an antiparallel β -sheet containing FOUR total cysteines. Make sure to denote any important hydrogen bonding. (**Note: R = cysteine below!**)



F. (8 pts.) Label and draw both anomers of the disaccharide maltose



G. (4 pts.) Determine the products of the saponification of the triglyceride:



2. (40 pts. total) **CONCEPTUAL!** Respond to each of the following:

A. (6 pts.) Do all α and β anomers necessarily exhibit mutarotation? Thoroughly explain why or why not.

Mutarotation is the change in specific rotation that accompanies the equilibration of α and β anomers in aqueous solution. Mutarotation occurs between the open-chain form and closed-chain (hemiacetal) form of a sugar. Once the closed-chain form of the carbohydrate reacts with an alcohol, a glycoside is formed, a carbohydrate in which the $-\text{OH}$ group on its anomeric carbon is replaced by an $-\text{OR}$ group. Mutarotation is NOT possible in this formed glycoside because an acetal is no longer in equilibrium with the open-chain carbonyl-containing compound.

B. (4 pts.) Define what is meant by the “reducing end” of a polysaccharide.

A reducing sugar consists of a cyclic hemiacetal that is in equilibrium with its open-chain form (i.e. aldose or ketose) and hence can be oxidized to a carboxyl group. Structurally, the anomeric carbon contains an adjacent $-\text{OH}$ group.

C. (12 pts.) Completely describe the primary, secondary, and tertiary levels of protein structure. Your answer must be thorough and reflect significant detail. Does denaturation of a protein affect all three levels of protein structure? Briefly explain.

The linear sequence of amino acids is the primary structure of a protein. This primary structure is largely responsible for the eventual higher-order structures of proteins. The repeating short-range conformations (i.e. α -helix, β -pleated sheet, random coil) are the secondary structure of a protein. This level of protein structure refers to those repetitive structures that are held together via hydrogen bonds between groups on the peptide backbone only. The tertiary

structure of a protein is the three-dimensional conformation of the protein molecule. These structures result from various interactions between the R side chains of the amino acid residues. Denaturation only affects secondary and tertiary protein structure; the protein's primary structure remains intact.

- D. (4 pts.) How is a disulfide bridge formed? Describe its role and appearance in protein structure as well as identify the specific amino acid involved.

The amino acid cysteine is unique in that it can be dimerized by mild oxidizing agents to form a disulfide bond (bridge). The formation of this disulfide bond provides a covalent linkage that binds together two separate residues or two parts of the same chain.

- E. (4 pts.) Why is starch easily digestible by humans but cellulose is not?

Humans and other animals cannot use cellulose as food because our digestive systems do NOT contain the necessary enzymes to catalyze the hydrolysis of polysaccharides that contain β -1,4-glycosidic bonds. Instead, we only possess α -glucosidases, which can hydrolyze polysaccharides such as starch which contain α -glycosidic bonds.

- F. (4 pts.) What structural features account for the fact that all lipids are insoluble in water but slightly soluble in solvents of low polarity such as dichloromethane or diethyl ether?

Triglycerides are triesters of glycerol and long-chain carboxylic acids called fatty acids. The hydrophobic character of triglycerides is caused by the long hydrocarbon chains present. The ester groups, although polar themselves, are buried in a surrounding nonpolar environment, which makes the triglycerides virtually insoluble in water.

- G. (6 pts.) Briefly define and explain the various types of chemical bonding exhibited by the hemoglobin molecule. How is this particular protein unique? Do all proteins exhibit this level of protein structure? Briefly explain.

Hemoglobin exhibits quaternary protein structure and consists of four subunits: two identical chains (called alpha) containing 141 amino acid residues each and two other identical chains (beta) containing 146 residues each. These four hemoglobin subunits contain a heme group or a planar ring structure centered around an iron atom located near the exterior of the molecule. The bond between the heme group and the Fe^{+2} ion is formed via a coordinate

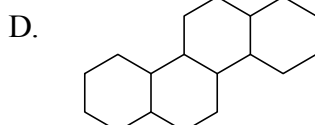
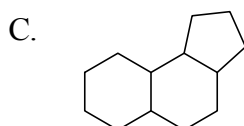
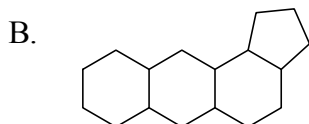
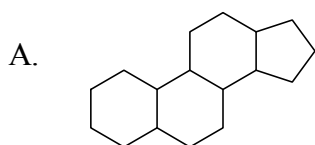
covalent bond, where any direct attachment to the metal is due to the contribution of the surrounding ligands. The ligands themselves are held together by covalent bonds.

3. (10 pts. total; 2 pts. each) **MULTIPLE CHOICE!** The next five questions involve selecting the *best* answer choice. Write your final response on the blank beside each number.

 E 1) Which of the following is the biological precursor for all other steroids?

- A. testosterone
- B. estrone (an estrogen)
- C. cortisone
- D. aldosterone
- E. cholesterol

 A 2) The steroid nucleus is represented by which of the following?



E. None of the above

 E 3) Determine which of the following is NOT *expected* to increase the level of HDL.

- A. exercise
- B. weight loss
- C. pregnancy
- D. Both A and B
- E. None; they all result in an increase in HDL.

B 4) The complete hydrolysis of lactose results in which of the following?

- A. glucose and fructose
- B. galactose and glucose
- C. galactose and fructose
- D. two glucose constituents
- E. two fructose constituents

 D 5) The configuration at which carbon of a ketopentose determines if the pentose has the D or L configuration?

- A. carbon-1
- B. carbon-2
- C. carbon-3
- D. carbon-4
- E. carbon-5

4. (10 pts. total) **APPLICATION!** The last set of questions on this examination involve reading (scanning) the enclosed article from *The Journal of Chemical Education* entitled “Introduction to Protein Structure through Genetic Diseases” (Vol. 85 No. 5 May 2008). In order to minimize the time spent on unnecessary details, students are urged to first read the questions below, scan the article, and finally focus on specific excerpts for analyses.

- 1) (4 pts.) The article argues that the awareness of how individual amino acids may be responsible for a variety of medical conditions is crucial to understanding genetic diseases. Which particular genetic disease is discussed and what specific amino acids are involved? If left untreated, how could this genetic disease affect a patient?

The specific genetic disease discussed in this single case study involve phenylketonuria, an autosomal recessive metabolic disorder affecting amino acid processing owing to mutations in the enzyme phenylalanine hydroxylase (PAH). PAH catalyzes the conversion of L-phenylalanine to L-tyrosine and is the main catabolic mechanism for phenylalanine removal. Mutations in PAH result in reduced or complete inability to process phenylalanine, leading to a toxic buildup of phenylalanine and ultimately varying degrees of mental retardation in untreated patients.

- 2) (3 pts.) Approximately how many mutations can ultimately lead to this particular genetic disease? Which mutation is most prevalent in Caucasians?

There are over 500 known mutations that lead to phenylketonuria. Many of these mutations can lead to a severe form of this disease. The

most prevalent splicing mutation in Caucasians results in expression of a protein lacking the C-terminal 52 amino acids. This deletion eliminates PAH activity in the cell owing to protein instability.

- 3) (3 pts.) According to the article, what are some possible treatments that could counter the effects of this particular genetic disease?

Existing molecular treatment of phenylketonuria relies on dietary manipulation. Adherence to an L-phenylalanine-restricted diet is one possible treatment, limiting the buildup of phenylalanine to sub-toxic levels. Moreover, an increased intake of the tetrahydrobiopterin cofactor can lead to a normalization of phenylalanine concentrations that may aid patients with certain PKU genotypes.