

INTRODUCTION TO BIOCHEMISTRY

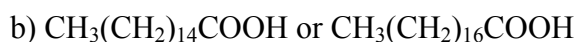
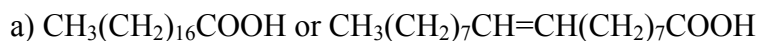
A STUDENT SHOULD BE ABLE TO:

1. With respect to lipids, know:
 - The characteristic common to members of the class: solubility in nonpolar solvents
 - The functional groups most important in triglycerides (triacylglycerols): esters, and in unsaturated fats, alkenes
 - The characteristic common to most naturally occurring fatty acids: even numbers of carbon atoms; *cis* configuration for unsaturated compounds; lack of branching
 - Saturated, unsaturated, and polyunsaturated fats; *cis* and *trans* fatty acids
 - Characteristics that lead to higher melting points for fatty acids: saturation and higher molecular weight; *trans* over *cis*
 - The products (soap and glycerol) of saponification reactions given the triglyceride starting material, or *vice versa*
 - Structural features common to terpenes, steroids, and prostaglandins
2. With respect to carbohydrates, know:
 - The approximate empirical formula characteristic of members of the class: CH_2O
 - The functional groups present in carbohydrate molecules: alcohols (usually several are present); aldehydes and ketones; hemiacetals and acetals
 - Carbohydrates belonging to these classes: ketoses and aldoses; D and L sugars; monosaccharide classes (trioses, tetroses, pentoses, hexoses, etc.); α and β pyranoses; reducing and nonreducing sugars
 - The products of oxidation and reduction reactions of carbohydrates (reducing sugars are those that can be oxidized. They contain hemiacetals (in the cyclic form) and aldehydes or ketones (in the straight chain form))
 - The number of chirality centers in a carbohydrate, given a Fisher projection
 - How to draw the cyclic form given the acyclic structure, and acyclic given the cyclic
3. With respect to amino acids, polypeptides, and proteins, know:
 - The functional groups most important in these compounds. Proteins and polypeptides contain amides made from amino acid monomers; there are carboxylic acid and amine groups on the ends.
 - The degree and site of protonation of amino acids as a function of pH
 - Relative isoelectric points, pI
 - Polypeptide structures from N-terminal analysis, C-terminal analysis, and total and partial hydrolysis results
 - How to link amino acids together to make polypeptides
 - Synthesis of amino acids *via* α -haloacids and Strecker synthesis

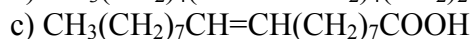
To best prepare for this module, please work suitable Chapters 24-26 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

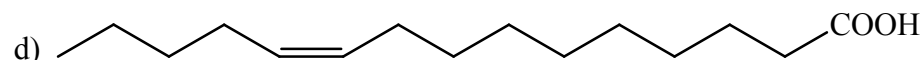
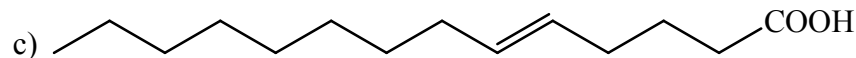
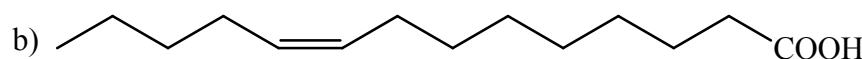
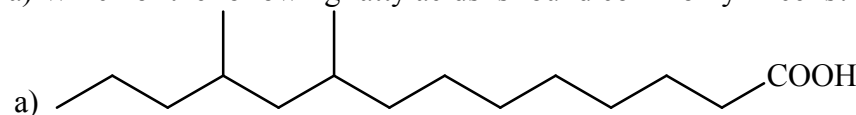
1.1 In each of these pairs, which of the compounds has the higher melting point?



1.2 Which of the following fatty acids is a) saturated, b) monounsaturated, and c) polyunsaturated?

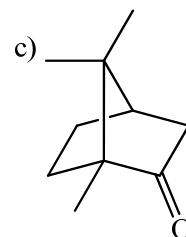
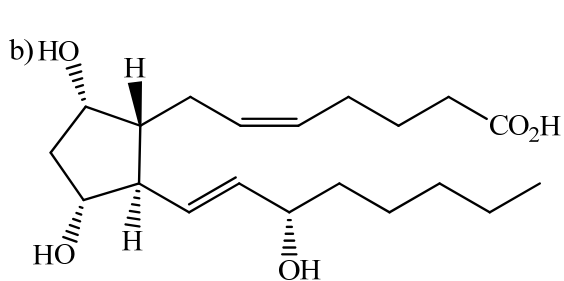
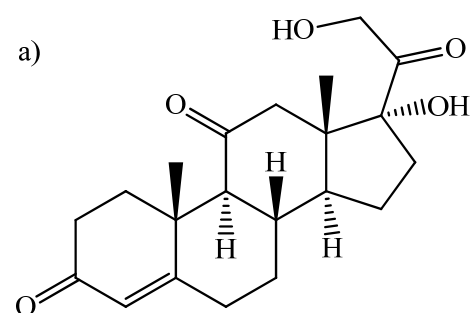


1.3 a) Which of the following fatty acids is found commonly in cells?



b) Identify each of the compounds in part (a) as *cis*, *trans*, or neither.

1.4 Match the structures shown below to the appropriate type of lipid:



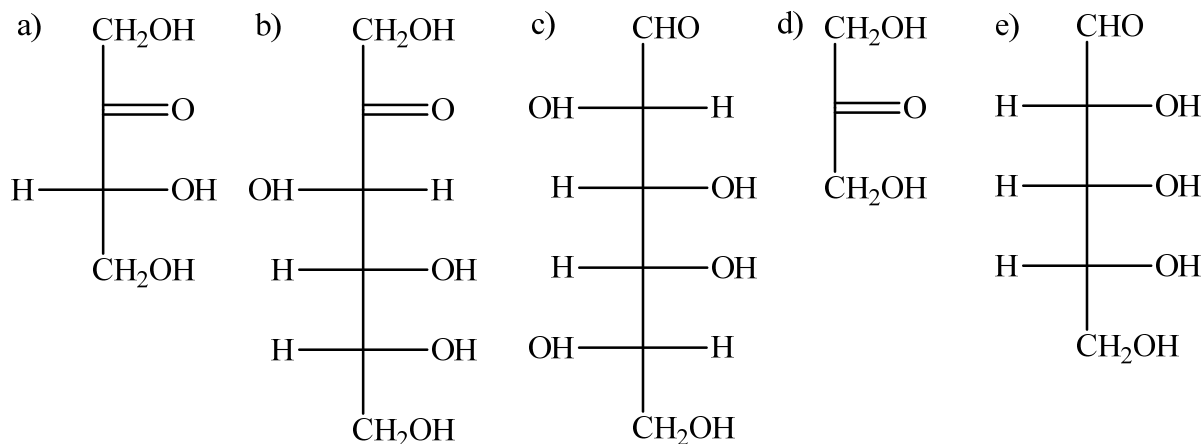
prostaglandin

triglyceride

terpene

steroid

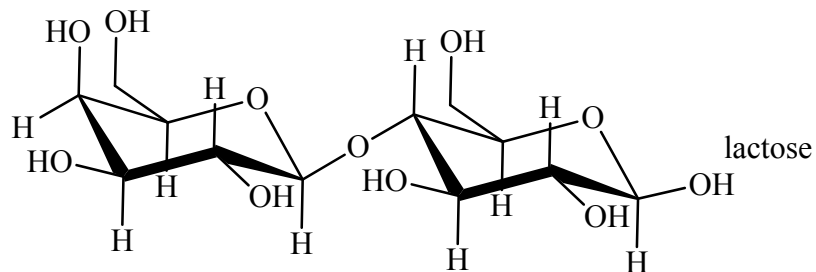
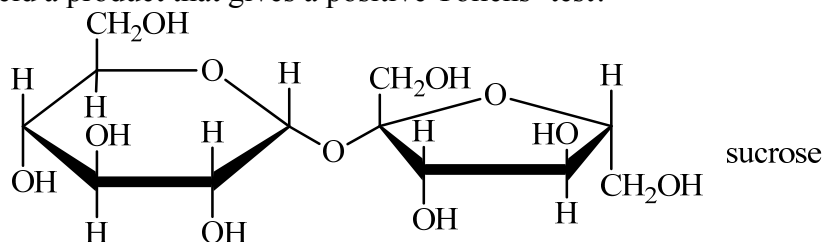
2.1 For each of the structures below, provide the information needed to complete the table.



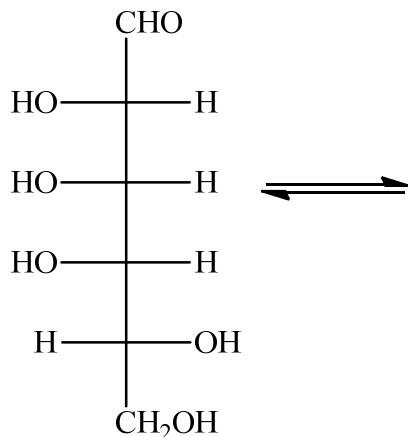
Structure	Family	Backbone	Configuration	# of Chirality Centers
a)	ketose	tetrose	D	1
b)				
c)				
d)				
e)				

2.2 a) Which of these disaccharides, shown here in different drawing conventions, gives a negative Tollens' test (that is, does not give a silver mirror when treated with a solution of silver nitrate in aqueous ammonia)?

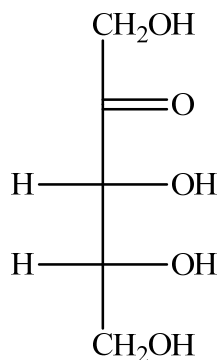
b) Why would heating the compound that is the answer to part (a) with dilute aqueous acid yield a product that gives a positive Tollens' test?



2.3 Draw the β -pyranose form of talose:

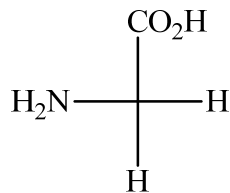


2.4 The structure of an important plant ketopentose, ribulose, is shown below. How many chirality centers does this molecule contain? Draw the structures of the other stereoisomers, and identify each as D or L.

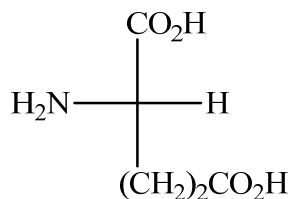


3.1 Based on the pK_a values given, draw the dominant form of each of the following amino acids at pH 3, at pH 7, and at pH 13. Also, calculate the pI for each.

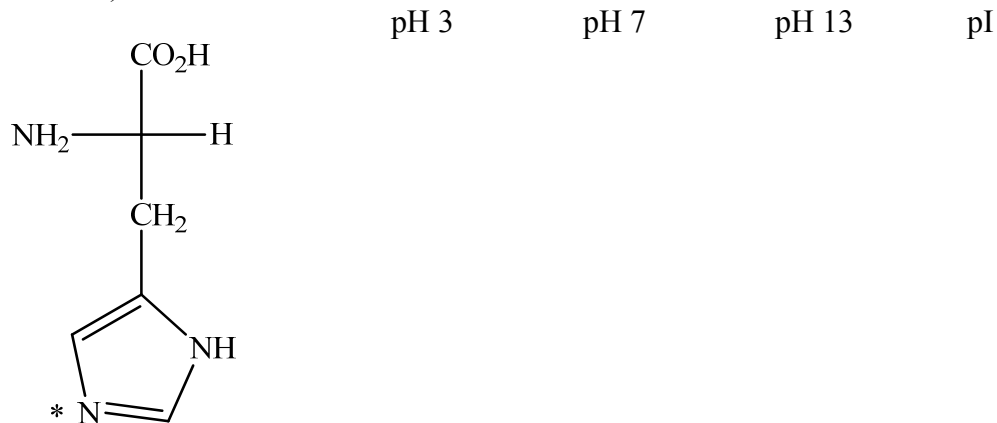
a) Glycine: pK_a values of 2.3 (for the α -COOH) and 9.6 (for the α - NH_3^+).



b) Glutamic acid, pK_a values of 2.2, 9.7, and 4.3 (for the COOH group at the bottom).



- 3.1 c) Histidine, pK_a values of 1.8, 9.2, and 6.0 (for the conjugate acid of the N designated with a *).



- 3.2. A pentapeptide was completely hydrolyzed and found to contain aspartic acid (Asp), lysine (Lys), proline (Pro), and methionine (Met). After partial hydrolysis the dipeptides Lys-Asp, Met-Pro, Lys-Met, and Pro-Lys were identified in the product. What is the sequence of amino acids in this pentapeptide?

- a) Lys-Met-Pro-Lys-Asp
- b) Asp-Lys-Pro-Met-Lys
- c) Lys-Asp-Met-Pro-Lys
- d) Pro-Met-Lys-Pro-Asp

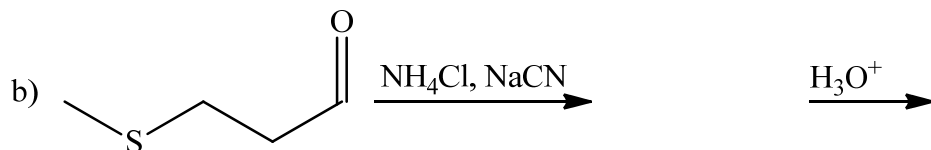
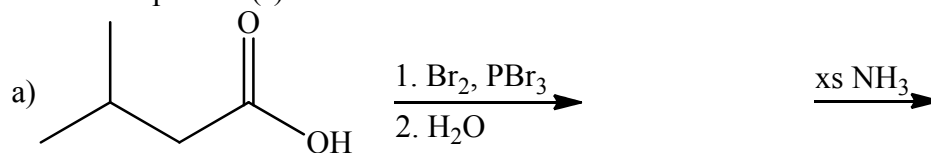
- 3.3 A tridecapeptide (an oligopeptide with 13 amino acid residues) has the following amino acid composition: Ala, Arg, Asp(2), Glu(2), Gly(3), Leu, and Val(3). After partial acid hydrolysis of the tridecapeptide, the following peptides were isolated, and their sequences were determined by Erdman degradation. What is the sequence of the original tridecapeptide?

The peptides are:

Asp-Glu-Val-Gly-Gly-Glu-Ala
 Val-Asp-Val-Asp-Glu
 Val-Asp-Val
 Glu-Ala-Leu-Gly-Arg
 Val-Gly-Gly-Glu-Ala-Leu-Gly-Arg
 Leu-Gly-Arg

- 3.4 Draw the structure that results when Asp, Gly, Glu and Ala are joined together to form this peptide: Asp-Gly-Glu-Ala. The structures of the amino acids are in your book.

3.5 Predict the product(s) of these reactions:



3.6 Synthesize alanine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$) starting from:

a) propanoic acid

b) acetaldehyde

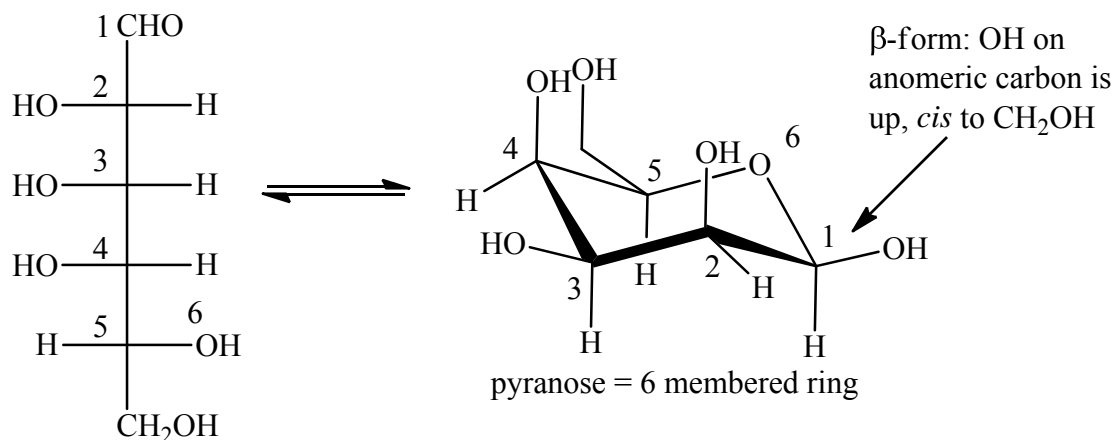
SOLUTIONS TO SAMPLE PROBLEMS:

- 1.1 a) $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ b) $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
 1.2 a) a b) c c) b
 1.3 a) b b) b and d are *cis*, c is *trans*, and a is neither *cis* nor *trans*.
 1.4 a) steroid (cortisone) b) prostaglandin c) terpene (camphor)

2.1	Structure	Family	Backbone	Configuration	Number
a)		ketose	tetrose	D	1
b)		ketose	hexose	D	3
c)		aldose	hexose	L	4
d)		ketose	triose	none	0
e)		aldose	pentose	D	3

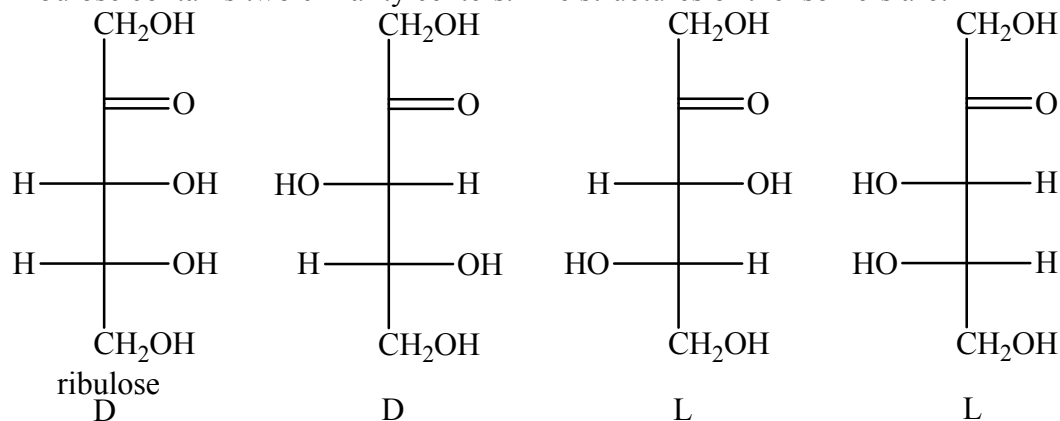
- 2.2 a) Sucrose would give a negative Tollens' test. This indicates that sucrose is not a reducing sugar because sucrose does not contain a hemiacetal. Lactose would give a positive Tollens' test due to the hemiacetal functional group contained in the structure. The cyclic hemiacetal ring can open to the carbonyl, which undergoes oxidation.
 b) Warming with dilute aqueous acid hydrolyzes sucrose into two monosaccharides by cleaving the acetal linkage. These monosaccharides could then cyclize to produce hemiacetal groups, and thus they become reducing sugars.

2.3

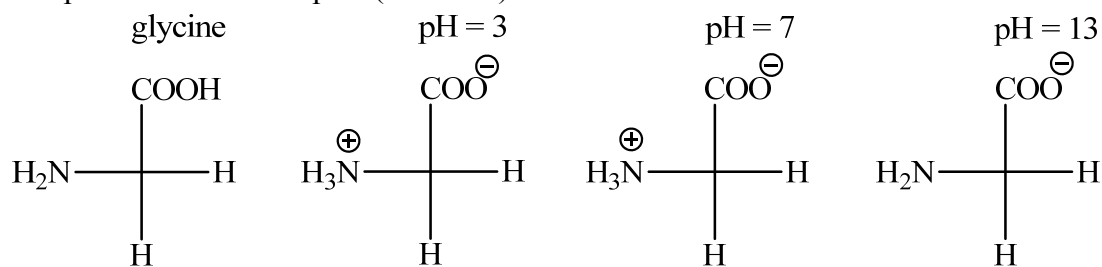


groups on the left of the Fisher projection are up in the cyclic form

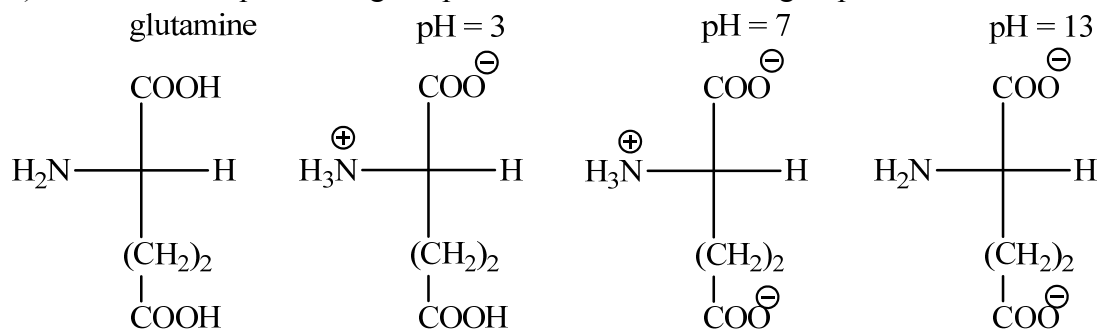
2.4 Ribulose contains two chirality centers. The structures of the isomers are:



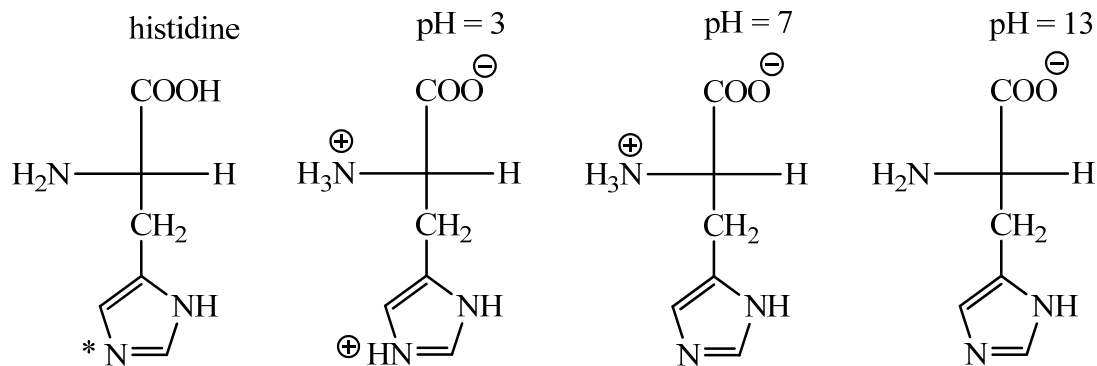
3.1 a) Glycine pK_a values: 2.4 and 9.8. If the pK_a value for a given proton is less than the pH, that proton is removed. $pI = (2.4 + 9.8)/2 = 6.1$



b) Glutamic acid: $pI = \text{average of } pK_a \text{ values for two acidic groups} = 3.25$



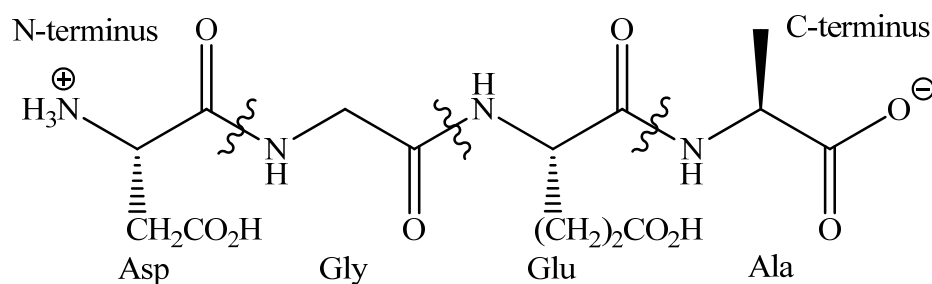
3.1 c) Histidine: $pI = \text{average of } pK_a \text{ values for two basic groups} = 7.6$



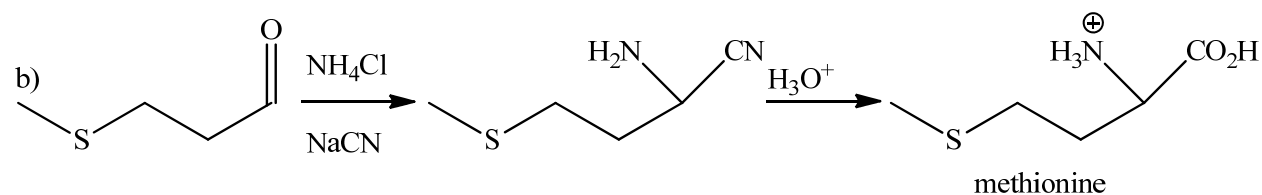
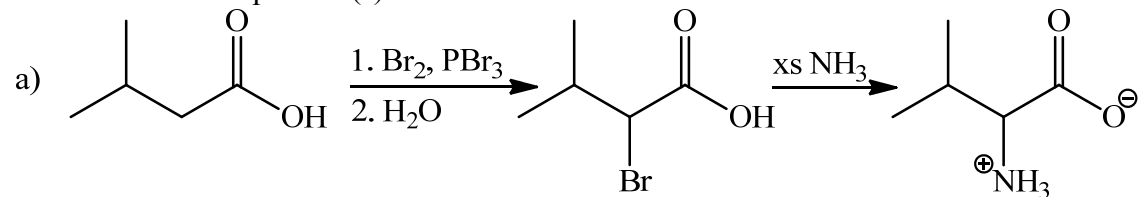
3.2 a

3.3 Val-Asp-Val-Asp-Glu-Val-Gly-Gly-Glu-Ala-Leu-Gly-Arg

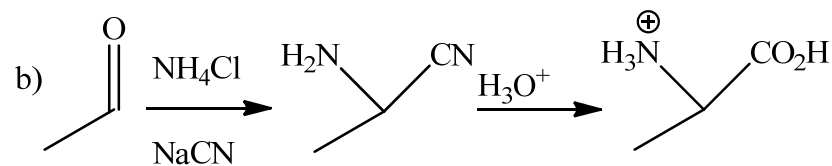
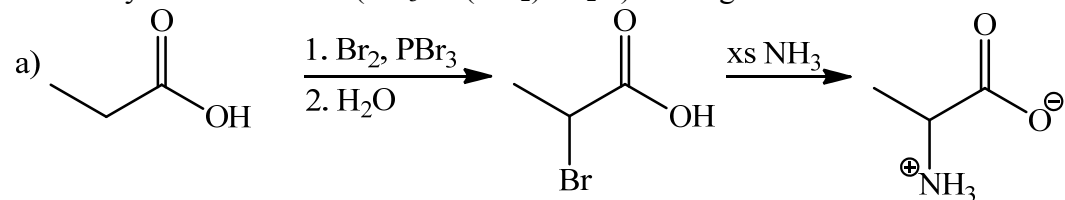
3.4



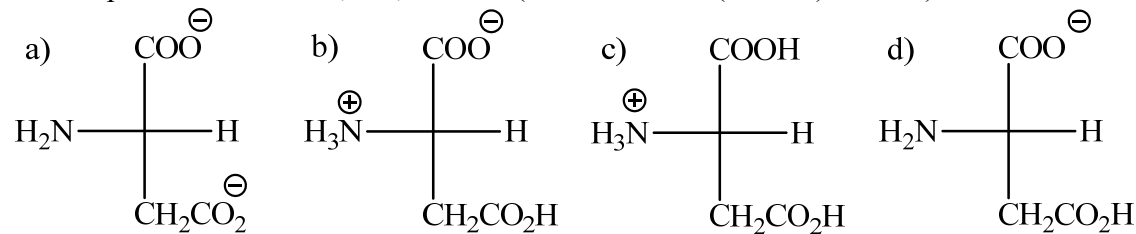
3.5 Predict the product(s) of these reactions:



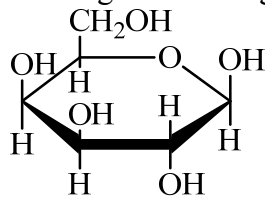
3.6 Synthesize alanine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$) starting from:



1. What is the structure of the amino acid $\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ at a pH of 2.5? The pK_a values are 2.2, 9.7, and 4.3 (for the second (bottom) COOH).



2. Which of the following functional groups is NOT present in the molecule shown?

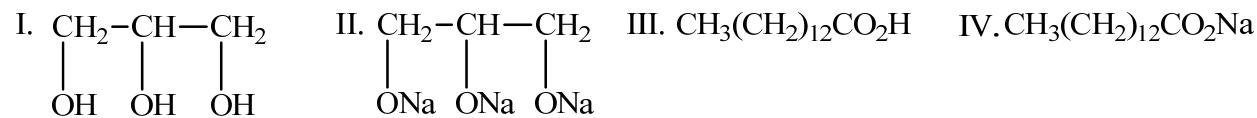
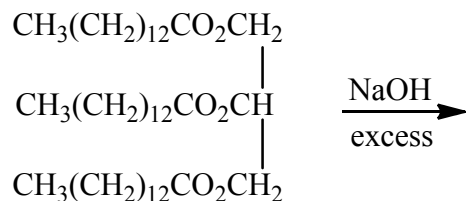


- a) Acetal b) Hemiacetal c) 1° Alcohol d) 2° Alcohol

3. What functional group is most abundant in proteins?

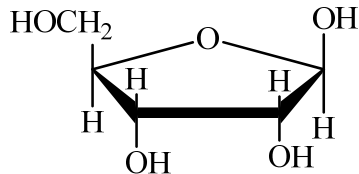
- a) Amide b) Amine c) Carboxylic acid d) Alcohol

4. What are the major products of the reaction shown?



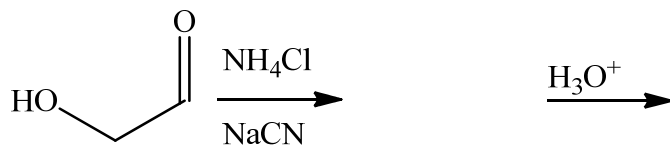
- a) I and III b) I and IV c) II and III d) II and IV

5. The structure of ribose is shown. Ribose is a (an):

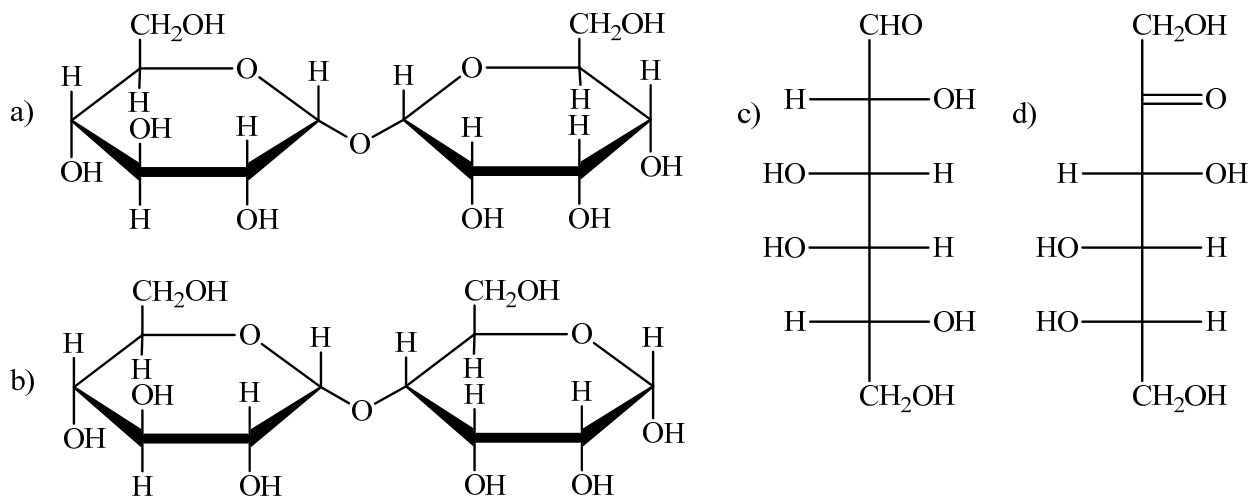


- a) Aldopentose b) Aldohexose c) Ketopentose d) Ketohehexose

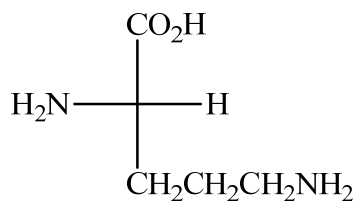
1. Complete the following equation.



2. Which of these compounds does NOT give a red precipitate with Benedict's reagent?



3. What is the structure of the amino acid shown at a pH of 2? The pKa values are 2.2 (COOH), 9.0 (NH₂), and 10.5 (side chain NH₂). What is the pI?



4. An oligopeptide was analyzed and found to contain the amino acids Phe, Cys, Ala, Ile, Asp, Trp, Thr, and Arg. N-terminal analysis identified Phe, and C-terminal analysis gave Ile. The fragments Arg-Ala-Ile, Cys-Asp-Arg, and Trp-Thr-Cys were identified after partial hydrolysis. What is the amino acid sequence of this peptide?

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