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INTRODUCTION TO BIOCHEMISTRY

A STUDENT SHOULD BE ABLE TO:

1. With respect to lipids, know:
   - The characteristic common to the class: solubility in nonpolar solvents
   - The functional groups most important in triglycerides (triacylglycerols): esters, and in unsaturated fats: alkenes
   - The characteristics 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 mechanism and 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: CH₂O
   - 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 furanoses and 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 structures and the mechanisms to convert the cyclic form given the acyclic structure, and acyclic form given the cyclic structure

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 carboxylate and ammonium groups on the ends
   - The extent 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 the Strecker synthesis
To best prepare for this module, please work appropriate 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?

   a) CH₃(CH₂)₁₆COOH or CH₃(CH₂)₇CH=CH(CH₂)₇COOH
   b) CH₃(CH₂)₁₄COOH or CH₃(CH₂)₁₆COOH

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

   a) CH₃(CH₂)₁₄COOH
   b) CH₃(CH₂)₄(CH=CHCH₂)₄(CH₂)₂COOH
   c) CH₃(CH₂)₇CH=CH(CH₂)₇COOH

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

   a)
   b)
   c)
   d)

   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:

   a) prostaglandin  b) triglyceride  c) terpene  d) steroid
1.5 Draw the saponification (hydrolysis) mechanism of the monoglyceride below. Show all arrows, intermediates, lone pairs, and charges, where appropriate.

\[
\begin{align*}
\text{OH} & \quad \text{O} & \quad \text{O} & \quad \text{NaOH} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{NaO} \\
\text{excess} & \quad \text{excess} & \quad & \quad \\
\text{HO} & \quad \text{Na} & \quad \text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Structure</th>
<th>Family</th>
<th>Backbone</th>
<th>Configuration</th>
<th># of Chirality Centers</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>ketose</td>
<td>tetrose</td>
<td>D</td>
<td>1</td>
</tr>
<tr>
<td>b)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>c)</td>
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<td>d)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 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)?

![Sucrose and lactose structures](image)

2.3 a) Draw the β-pyranose form of talose:

![Talose structure](image)

b) Draw the mechanism for the above reaction using an H$_3$O$^+$ catalyst.
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.

![Ribulose structure]

3.1 Based on the pKₐ 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: pKₐ values of 2.3 (for the α-COOH) and 9.6 (for the α-⁻NH₃).

![Glycine structure]

b) Glutamic acid, pKₐ values of 2.2, 9.7 (for the ⁻NH₃), and 4.3 (for the COOH group at the bottom).

![Glutamic acid structure]

c) Histidine, pKₐ values of 1.8, 9.2 (for the ⁻NH₃), and 6.0 (for the conjugate acid of the N designated with a *).

![Histidine structure]
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 Edman 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:

a) \[
\begin{align*}
\text{O} & \quad 1. \text{Br}_2, \text{PBr}_3 \\
\text{OH} & \quad 2. \text{H}_2\text{O} \\
\text{xs NH}_3
\end{align*}
\]

b) \[
\begin{align*}
\text{S} & \quad \text{NH}_4\text{Cl}, \text{NaCN} \\
\text{H} & \quad \text{H}_3\text{O}^+ \quad \text{heat}
\end{align*}
\]
3.6 Synthesize alanine ($\text{CH}_3\text{CH(}^{\text{NH}_3}\text{)CO}_2^- \text{)}$) 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)

1.5

2.1 Structure  
Family  
Backbone  
Configuration  
Number

<p>| | | | | |</p>
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</tr>
<tr>
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<td>ketose</td>
<td>hexose</td>
<td>D</td>
<td>3</td>
</tr>
<tr>
<td>c)</td>
<td>aldose</td>
<td>hexose</td>
<td>L</td>
<td>4</td>
</tr>
<tr>
<td>d)</td>
<td>ketose</td>
<td>triose</td>
<td>none</td>
<td>0</td>
</tr>
<tr>
<td>e)</td>
<td>aldose</td>
<td>pentose</td>
<td>D</td>
<td>3</td>
</tr>
</tbody>
</table>
2.2 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.

2.3

a)

β-form: OH on anomeric carbon is up, cis to CH₂OH

pyranose = 6 membered ring

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

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

```
  CH₂OH
  /   \
 O   O
 /    \
H—OH  H—OH
  |    |   |
  CH₂OH  CH₂OH
```

Ribulose D

```
  CH₂OH
  /   \
 O   O
 /    \
H—OH  H—OH
  |    |   |
  CH₂OH  CH₂OH
```

Ribulose L

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

```
glycine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 3

```
glycine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 7

```
glycine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 13

b) Glutamic acid: pI = average of pKa values for two acidic groups = 3.3

```
glutamine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 3

```
glutamine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 7

```
glutamine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       (CH₂)₂    (CH₂)₂    (CH₂)₂    (CH₂)₂
       COOH      COOH      COOH      COOH
```

pH = 13

c) Histidine: pI = average of pKa values for two basic groups = 7.6

```
histidine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       CH₂       CH₂       CH₂       CH₂
       *N═N      *N═N      *N═N      *N═N
       H          H          H          H
```

pH = 3

```
histidine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       CH₂       CH₂       CH₂       CH₂
       *N═N      *N═N      *N═N      *N═N
       H          H          H          H
```

pH = 7

```
histidine
H₂N         H₂N         H₂N         H₂N
       COOH      COOH      COOH      COOH
       H         H         H         H
       CH₂       CH₂       CH₂       CH₂
       *N═N      *N═N      *N═N      *N═N
       H          H          H          H
```

pH = 13
3.2 a

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

3.4

N-terminus
\[ \text{Val-Asp-Val-Asp-Glu-Val-Gly-Gly-Glu-Ala-Leu-Gly-Arg} \]
C-terminus

3.5 Predict the product(s) of these reactions:

a) \[
\begin{align*}
\text{CH}_3\text{CH(OH)CO}_2^-(\text{Br})\text{OH} & \xrightarrow{1.\text{Br}_2,\text{PBr}_3} \text{CH}_3\text{CH(OH)CO}_2^-(\text{Br})\text{OH} \\
& \xrightarrow{2.\text{H}_2\text{O}} \text{CH}_3\text{CH(OH)CO}_2^-(\text{Br})\text{OH} \\
& \xrightarrow{\text{x}\text{sNH}_3} \text{CH}_3\text{CH(OH)CO}_2^-(\text{NH}_3)_\text{NH}_3^+
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_3\text{CH\(\text{NH}_2\)CN} & \xrightarrow{\text{NH}_4\text{Cl, NaCN}} \text{CH}_3\text{CH\(\text{NH}_2\)CN} \\
& \xrightarrow{\text{H}_3\text{O}^+\text{heat}} \text{CH}_3\text{CH\(\text{NH}_2\)CO}_2\text{H}
\end{align*}
\]

methionine

3.6 Synthesize alanine (CH\(\text{3CH}(^\text{\(\text{NH}_3\)}\text{CO}_2\text{)}\text{)} starting from:

a) \[
\begin{align*}
\text{CH}_3\text{CH(OH)CO}_2^- & \xrightarrow{1.\text{Br}_2,\text{PBr}_3} \text{CH}_3\text{CH(OH)CO}_2^- \text{Br} \\
& \xrightarrow{2.\text{H}_2\text{O}} \text{CH}_3\text{CH(OH)CO}_2^- \text{Br} \\
& \xrightarrow{\text{x}\text{sNH}_3} \text{CH}_3\text{CH(OH)CO}_2^- \text{NH}_3
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_3\text{CH\(\text{NH}_2\)CN} & \xrightarrow{\text{NH}_4\text{Cl}} \text{CH}_3\text{CH\(\text{NH}_2\)CN} \\
& \xrightarrow{\text{H}_3\text{O}^+\text{heat}} \text{CH}_3\text{CH\(\text{NH}_2\)CO}_2\text{H}
\end{align*}
\]
1. What is the structure of the amino acid $\text{HO}_2\text{CCH}_2\text{CH(NH}_2\text{)}\text{COOH}$ at a pH of 2.5? The $pK_a$ values are 2.2, 9.7, and 4.3 (for the second (bottom) COOH).
   a) $\text{HO}_2\text{CCH}_2\text{CH(NH}_2\text{)}\text{COO}^-$  
   b) $\text{HO}_2\text{CCH}_2\text{CH(NH}_2\text{)}\text{COO}^-$  
   c) $\text{H}_3\text{N}^-\text{CH}_2\text{COOH}$  
   d) $\text{H}_2\text{N}^-\text{CH}_2\text{COO}^-$

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

   ![Molecule Diagram]
   a) Acetal  
   b) Hemiacetal  
   c) $1^\circ$ Alcohol  
   d) $2^\circ$ 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?

$$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2 \xrightarrow{\text{NaOH excess}} \text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH} \xrightarrow{} \text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2$$

   I. $\text{CH}_2\text{CHCH}_2$  
   II. $\text{CH}_2\text{O}^-\text{Na}^+$  
   III. $\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$  
   IV. $\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{Na}$

   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):

   ![Ribose Diagram]
   a) Aldopentose  
   b) Aldohexose  
   c) Ketopentose  
   d) Ketohexose
1. Complete the following equation.

\[
\text{HO} \quad \text{O} \quad \text{NH}_4\text{Cl} \quad \text{NaCN} \quad \text{H}_3\text{O}^+ \\
\]

2. Which of these compounds does NOT give a silver mirror with Tollens’ reagent?

a) ![Chemical Structure a)](image)
b) ![Chemical Structure b)](image)
c) ![Chemical Structure c)](image)
d) ![Chemical Structure d)](image)

3. What is the structure of the amino acid shown at a pH of 2? The pKa values are 2.2 (COOH), 9.0 (conj. acid of NH\(_2\)), and 10.5 (conj. acid of side chain NH\(_2\)). What is the pI?

\[
\text{CO}_2\text{H} \\
\text{H}_2\text{N} \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2
\]

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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