BIOS 452/CHEM 452
Third Exam
Fall, 2010
12:00-12:55pm, Monday, November 22, 2010

Name: Answer Key

UIN: ____________________________

Circle Discussion Section:
Mon 8
Tue 9:30
Wed 9
Thu 9:30
Fri 9
Fri 11

General Instruction
* Do not turn the page until you are told to do so.
* You may take the exam with you only after 12:35pm.
* No calculators allowed. For calculations and graphing, show all your work!!!
* The exam is total 9 pages (including cover page), ~30 questions grouped into 15 for 55 minutes.
* Read the question carefully to the end.
* Pay attention to units.
1. (4 pts) Draw the Fisher projection of the sugar shown below.

\[
\text{Fisher projection of sugar}
\]

2. (1-3) Choose from following:

<table>
<thead>
<tr>
<th>(a) Glucose</th>
<th>(b) Galactose</th>
<th>(c) Ribose</th>
<th>(d) Sucrose</th>
<th>(e) Fructose</th>
</tr>
</thead>
</table>

(1) (2 pts) Which one is enriched in nerve tissues and thus called “brain sugar”? (b)

(2) (2 pts) Which has the highest molecular weight? (d)

(3) (2 pts) Which ones are diastereomers of one another? Choose all that apply. (a) and (b)

3. Shown on the right is a disaccharide called Trehalose.

(1) (3 pts) Circle all the anomeric carbons.

(2) (3 pts) Trehalose as shown on the right is an acetal, ketal, hemiacetal, hemiketal –Circle one

4. (5 pts) Shown on the right is Amylose. The repeating DISACCHARIDE unit of this sugar is [Maltose], which has (+1); Choose either \(\alpha\) or \(\beta\) anomers linked via (+1) -->
Write in numbers) glycosidic bond.

*Make sure you filled out ALL of the 4 BLANKS.

5. (1) (2 pts) Write the name of an amino acid that can form N-linked glycosidic bonds with carbohydrates.

Asparagine - Choose from the 20 amino acids.

(2) (6 pts) Show the structure of the amino acid you chose (1) covalently attached to the monosaccharide on the right in its β-conformation, as it may appear in a glycoprotein.

6. (1) (8 pts + 2 Bonus pts with correct stereochemistry.) Mild hydrolysis of a naturally occurring lipid with dilute NaOH generated L-glycerol 3-phosphoserine and the sodium salts of a hexadecanoate and a Δ⁹-octadecenoate. Draw a chemical structure of the parent lipid.

(2) (4 pts) What are the common names of the constituent fatty acids indicated in (1)?

Palmitate AND Oleate

Palmitic acid

-1 for typo

Oleic acid

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(3) (3 pts) What is the net charge of the parent lipid in (a) at a neutral pH?
(Positive, (Negative, Neutral –Circle one)

7. (3 pts) Which of the following INCREASE(S) during the hydrogenation process used in making traditional margarine?
Circle all that apply.
(a) Number of saturated bonds   (b) Trans-fat content   (c) Food calories per molecule   (d) Melting point of the fat

8. (3 pts) Indicate TRUE (T) or FALSE (F) for each of the following statements about the plasma membrane of a cell.

(1) The lateral diffusion of molecules is much easier than the transverse diffusion. ___

(2) Free fatty acids are a major component. ___

(3) Glycoproteins and glycolipids expose their carbohydrate groups on the outer leaflet of the bilayer. ___

9. (3 pts) Arrange the following compounds (a)-(e) in an increasing order of permeability across a pure synthetic lipid bilayer.

(a) Cl'   (b) O2   (c) Water   (d) Glycerol   (e) Glucose

(a) < (e) < (d) < (c) < (b)

+3 -> all correct
+1 --> 3 are correct.
10. (3 pts) A spontaneous conversion of a compound $S$ to another compound $P$ has a forward reaction rate constant, $k_f$ of 100 hour$^{-1}$ and a reverse reaction rate constant, $k_r$ of 1 hour$^{-1}$. In an enzyme-catalyzed reaction, the same conversion takes place with a different $k_f$ ($k_f\text{, catalyzed}$) that is 2 sec$^{-1}$, what would be the $k_r\text{, catalyzed}$ of this reaction? Make sure to write a unit to your answer.

$$S \xrightleftharpoons[k_r]{k_f} P$$

$$\frac{k_f}{k_r} = \frac{100 \text{ h}^{-1}}{1 \text{ h}^{-1}} = \frac{k_f\text{, catalyzed}}{k_r\text{, catalyzed}} = \frac{2 \text{ sec}^{-1}}{}$$

$$k_r\text{, catalyzed} = 0.02 \text{ sec}$$

11. (6 pts) An enzyme ($E$) catalyzes the conversion of substrate $X$ to product $Y$. The plot on the right shows the concentrations of $Y ([Y])$ versus time of reactions. Can the following change in the reaction condition shift the curve from (i) to (ii)? Answer Yes(Y) or No(N).

+2 (1) Add an uncompetitive inhibitor. **Y**

+2 (2) Replace the substrate $X$ with $X'$ that has a lower $K_m$ but the same $V_{max}$. **N**

+2 (3) Decrease the total reaction volume without changing the concentrations of reaction components. **N**
12. Below is a kinetic scheme of a simple enzyme-catalyzed reaction.

\[
E + S \xleftrightarrow{k_1} ES \xrightarrow{k_2} E + P
\]

Michaelis & Menten used a steady state assumption to express the reaction velocity \( (\frac{d[P]}{dt}) \) as a function of quantities that can be easily measured such as \([E]_{\text{total}}\) and \([S]_{\text{total}}\): \( V = k_2 [E]_{\text{total}} [S] / (K_m + [S]) \) (eq. 1)

(1) (4 pts) Write a rate equation, i.e., a differential equation, that describes the steady state assumption.

\[
\begin{align*}
\frac{d[ES]}{dt} &= -k_1 [E][S] - k_2 [ES] + k_4 [ES] + k_3 [ES] \\
\frac{d[ES]}{dt} &= 0 \quad \text{or} \quad [ES] = \text{constant}
\end{align*}
\]

(2) (3 pts) In the eq. 1, [S] is the concentration of free S, NOT total S ([S]_{\text{total}}). Nevertheless, we often take the value of [S] as that of [S]_{\text{total}}. Why?

\[
[S]_{\text{total}} \gg [E]_{\text{total}}
\]

(3) (3 pts) Which describes the condition under which \( K_m \) can be regarded as the dissociation constant of the binding equilibrium between E and S to form ES complex?

\[
( k_1 \gg k_1, \quad k_1 \gg k_2, \quad \text{ } \text{ } \text{ } \text{ } k_4 \gg k_2 )
\]

\[
k_1 < k_1, \quad k_1 < k_2, \quad k_1 < k_2 \quad - \text{Circle one.}
\]
13. An enzyme called “happyase” catalyzes the following reaction with a $k_{\text{cat}}$ of 100 sec$^{-1}$: \[ \text{SAD} \rightleftharpoons \text{HAPPY} \]

Below is a plot of the initial velocity versus the substrate concentration for happyase. The initial velocity at 1 mM [SAD] was measured to be 40 nM/sec.

![Plot of initial velocity versus substrate concentration](image)

(1) (3 pts) What is the total happyase concentration used above? Indicate unit.

\[
[E]_T = \frac{V_{\text{max}}}{k_{\text{cat}}} = \frac{40 \text{ nM/sec}}{100 \text{ sec}^{-1}} = 0.4 \text{ nM}
\]

-1 for using $V_{\text{max}}$ 35-39 nM/sec

(2) (4 pts) What is the $K_m$ of happyase for SAD? Indicate unit.

\[ K_m = [S] \text{ when } V_o = \frac{V_{\text{max}}}{2} \text{ on graph (or calculation?)} \]

+2 for showing $K_m = [S]$ when $V_o = \frac{V_{\text{max}}}{2}$ on graph (or calculation?)

(3) (4 pts) What is the SAD concentration at time = 0 when 480 pmole of HAPPPY is formed during the first minute in a 1-mL reaction?

\[
V_o = \frac{480 \text{ pmole}}{1 \text{ mL}} \cdot \frac{1}{60 \text{ sec}} = 8 \text{ nM/sec} \\
\frac{40 \text{ nM/sec} \cdot [S]}{12 \mu M + [S]} \\
8(12 + [S]) = 40[S] \\
[S] = \frac{12}{4} \mu M = 3 \mu M
\]

* If formula ok then +3.
(4) (3 pts) Considering the diffusion-limited bimolecular rate constant is \(1 \times 10^8 \text{ M}^{-1} \text{s}^{-1}\), how much slower is the reaction catalyzed by happyase than a diffusion-limited reaction? (1, 10, 100, 1000, 10,000 – Circle one) – times.

\[
\frac{k_{\text{cat}}}{K_m} = \frac{100 \text{ sec}^{-1}}{10 \text{ mM}} \approx 10^7 \text{ M}^{-1} \text{ sec}^{-1}
\]

(5) (Bonus 3 pts) In a separate experiment, the total enzyme concentration was decreased by 2-fold. How does the \(V_{\text{max}}\) and \(K_m\) change?

\[
\begin{align*}
V_{\text{max}} & \text{ decreases by 2-fold} \quad +1 \\
K_m & \text{ doesn't change} \quad +1
\end{align*}
\]

(6) (Bonus 2 pts) Thus the effect of reducing total enzyme concentration is similar to the effect of adding a (Competitive, Uncompetitive, Noncompetitive – Circle one) inhibitor.

14. (1) (3 pts) STRESS is a competitive inhibitor of happyase described in 16. Draw a kinetic scheme for competitive inhibition.

\[
E + S \rightleftharpoons ES \rightarrow E + P
\]

(2) (4 pts) \(K_i\) of STRESS is 10 nM. Calculate the apparent \(K_m\) and the apparent \(k_{\text{cat}}\) when 10 nM STRESS is added to a happyase-catalyzed reaction which shows \(K_m\) of 9 uM and \(k_{\text{cat}}\) of 120 sec\(^{-1}\) in the absence of any inhibitor.

\[
\alpha = 1 + \frac{10 \text{ nM}}{10 \text{ nM}} = 2
\]

Competitive

\[V_{\text{max, app}} = \alpha \cdot K_m = 2 \times 9 \text{ uM} = 18 \text{ uM}\]

\[k_{\text{cat, app}} = k_{\text{cat}} = 120 \text{ sec}^{-1}\]
15. The experimental curve of initial reaction velocity versus [S] with and without inhibitor (I) is shown for an enzyme and a substrate.

(1) (4 pts) What is a possible mechanism of inhibition?
(Competitive, Uncompetitive, Noncompetitive - Circle one.)

+2 for showing curved $V_{m, app} = \frac{V_m}{\alpha}$, $K_{m, app} = \frac{K_m}{\alpha}$
where $\alpha = 3$.

(2) (3 pts) Which best describes the Lineweaver-Burke plot of the enzyme with the inhibitor (I) at [I]=K_i. Circle one among (i) to (vi)

+1 for matching graph w/ (1)