

Points

1. The stimulation of glycogen breakdown by hormones was the first experimental system in which a "second messenger" signaling pathway was demonstrated for the ultimate activation of the enzyme **phosphorylase**. This pathway acts as a "cascade" in that the product in each step is a catalyst for the next step, resulting in an amplification of the signal.

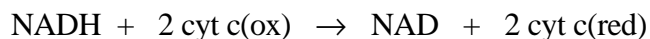
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- (8) (a) Diagram this signaling pathway for **liver**, indicating all the intermediate steps and intermediates from the first interaction of the hormone with the cell to the covalent modification of phosphorylase.

- (4) (b) What is the identity of the "second messenger" in this scheme (draw its structure), identify the protein it activates, and describe how it interacts with that protein.

- (6) (c) Name three other enzymes in liver whose activities are affected by covalent modification stimulated directly or indirectly by this second messenger. For each, indicate whether each enzyme is **activated** or **inhibited**.

2. In the presence of cyanide and excess cytochrome c, mitochondria can carry out the following reaction (where the NADH is generated from oxidation of substrates via the TCA cycle):



- (6) (a) Calculate  $\Delta G^{\circ'}$  for this reaction.  
( $E'_{\circ}$  for NAD/NADH is  $-0.32$  volts and for cyt c(ox)/cyt c(red) is  $+0.25$  volts;  
 $F = 96.5 \text{ kJ mol}^{-1} \text{ volt}^{-1}$ )
- (6) (b) Identify all the intermediate electron carriers involved in this reaction, indicating which are organized in multiprotein complexes.
- (4) (c) If these mitochondria are tightly coupled to ATP synthesis, what molar ratio of ATP made to NADH oxidized would you expect? Explain your answer
- (2) (d) Why is it necessary to add cyanide to observe this reaction?
- (6) 3. **Oligomycin** would block the reduction of cytochrome c described in question 2 if the mitochondria are tightly coupled to ATP synthesis, but **dinitrophenol** would relieve this inhibition allowing cytochrome c reduction to resume. Explain how these two inhibitors would be interacting with the system to show these effects.

- (15) 4. A number of components are involved in the light reaction of plant photosynthesis. Match a component in the list at the right with each statement below by placing the appropriate letter in the blank. Only one component per blank. (P700 is **photosystem I**, P680 is **photosystem II**).

_____ reduced directly by P680*	a. Z, a tyrosine residue
_____ reduced directly by P700*	b. phycoyanin
_____ oxidized directly by P680 <sup>+</sup>	c. plastocyanin
_____ oxidized directly by P700 <sup>+</sup>	d. Ao, a chlorophyll molecule
_____ an accessory pigment	e. pheophytin
_____ chlorophyll a without Mg <sup>2+</sup>	f. cytochrome a <sub>3</sub>
_____ reduced by cytochrome b/f complex	g. ferredoxin
_____ removes electrons from the Mn cluster	
_____ a Cu containing protein	
_____ an Fe/S protein	

- (6) 5. **Rubisco** is the most abundant protein in the biosphere. In addition to catalyzing the fixation of CO<sub>2</sub> into organic form, it also catalyzes a competing reaction with O<sub>2</sub>, a reaction responsible for **photorespiration**. Give the structure of the reactants and products of this reaction with O<sub>2</sub>.

- (6) 6. This side reaction can be partly overcome by increasing the concentration of CO<sub>2</sub>. Some plants, called C<sub>4</sub> plants, trap CO<sub>2</sub> with another reaction for the purpose of concentrating it. Give the structure of the reactants and products, and the name of the enzyme, that is involved in this "trapping" CO<sub>2</sub> fixation reaction.

- (6) 7. Because of the side reaction with oxygen described in question 5, regulatory mechanisms have evolved that prevent Rubisco from being active in the dark when photosynthesis cannot occur. Describe these regulatory mechanisms and how they stimulate Rubisco in the light but not in the dark.

- (10) 8. For the four plasma lipoproteins -- chylomicrons, VLDL, LDL, and HDL -- identify which is referred to in each of the following statements (more than one lipoprotein may be identified by a statement).

Carries triglyceride from dietary fat.

Scavenges cholesterol from tissues.

Contains the lowest % content of protein

Does not contain apo C

Contains the highest % content of protein

Contains apo B-100

Contains the highest % content of cholesterol

Elevated in **familial hypercholesterolemia**

Supplies cholesterol to peripheral tissues

Carries triglyceride from the liver

- (15) 9. Fatty acids are released from triglycerides by the action of **lipoprotein lipase** at the surface of cells. They cross the plasma membrane and are immediately activated to a coenzyme A derivative as the first step in their ultimate oxidation in the mitochondria. Give the structures of all the intermediates in this process from the first activation step through the first cycle of oxidation in the mitochondria which leads to a fatty acyl CoA derivative that is two carbons shorter (i.e. only one "turn" of the oxidation spiral). Give a name for the enzyme catalyzing each step of the process.