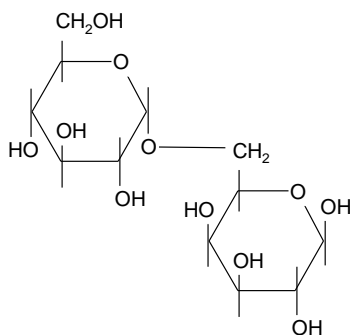


Problem Set 2 Answers
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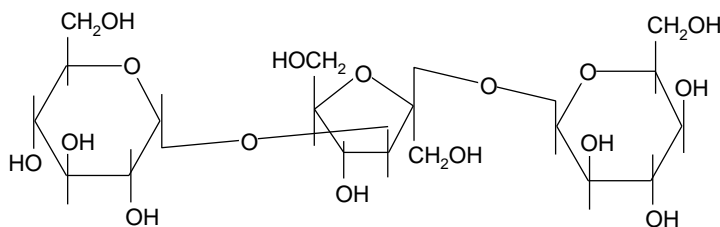
1a.



b.i. Only C2 and C3 are free to be methylated at a branch point glucose. C1,4,6 are linked to other glucosyl residues. C5 is linked to C1, as always. Question: What would be the methylated products corresponding to non-branch point glucosyl residues? How 'bout the single glucosyl residue at the reducing end of glycogen?

b.ii. 10% of glucosyl residues are at branch points.

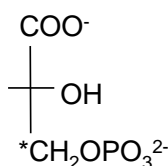
2.



This structure will not reduce Tollen's reagent.

3. The liver glucose transporter has a high K_m (≥ 20 mM), while that of brain has a low K_m (< 1 mM). This allows the velocity of glucose uptake by liver to respond nearly proportionally to blood glucose concentrations over the physiological range (5-20 mM). Thus the liver acts as an effective glucose "buffer". In contrast, the velocity of the brain glucose transporter will be near maximal at all glucose concentrations above ~ 5 mM.

4.



5a. False; b. True

6a. $F \rightarrow G \rightarrow D \rightarrow A \rightarrow E \rightarrow C$; b. $F \rightarrow G$; c. $F \rightarrow G$; d. $E \rightarrow C$; e. $F \rightarrow G$ or $G \rightarrow D$

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7a-c. Discuss in section

d. P_i – no effect, ADP – no effect, NAD^+ - increased CO_2 production, pyruvate - increased CO_2 production.

8. See lectures on regulation of PFK.

9. See lectures on mechanism of phosphorylation of glyceraldehyde-3P by oxidation. In the reaction in water, aldehydes are spontaneously converted to their covalent hydrates (gem-diols). The gem-diol undergoes 2e⁻ oxidation by NAD^+ to a carboxylic acid (know the mechanism). This reaction is highly favorable ($\Delta G = -12$ kcal/mol) and drives the very unfavorable ($\Delta G = +11.8$ kcal/mol) phosphorylation of the carboxylic acid to form the acylphosphate. In the enzyme-catalyzed reaction, the same reactions occur but instead of water, it is a sulfhydryl group in the active site that attacks the aldehyde to form a thiohemiacetal, which is then oxidized to a thioester which in turn reacts with phosphate. The enzyme-catalyzed reaction is faster because the energy of the thioester intermediate is significantly higher than that of the carboxylic acid, and therefore the energy well, out of which the phosphorylation reaction must climb, is not nearly as deep.

10. step 1: oxidize primary alcohol at C2 to a ketone by an NAD^+ -dependent enzyme (see lectures on biological oxidations involving $NAD^+/NADH$). Step 2: cleavage - see lectures on chemical mechanism of aldolase.