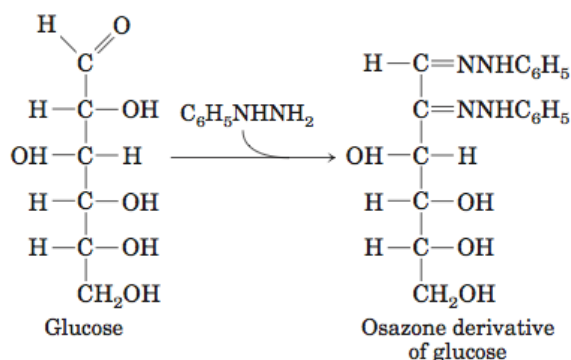


**CHEM 331 Problem Set #6- Lehninger 5e, Chapter 7**  
**Due Wednesday, November 14, 2012**  
**ANSWER KEY (56 total pts.)**

1. In the monosaccharide derivatives known as sugar alcohols, the carbonyl oxygen is reduced to a hydroxyl group. For example, D-glyceraldehyde can be reduced to glycerol. However, this sugar alcohol is no longer designated D or L. Why?

(2 pts.) With reduction of the carbonyl oxygen to a hydroxyl group, the stereochemistry at C-1 and C-3 is the same; the glycerol molecule is not chiral.

2. Many carbohydrates react with phenyl-hydrazine ( $\text{C}_6\text{H}_5\text{NHNH}_2$ ) to form bright yellow crystalline derivatives known as osazones:



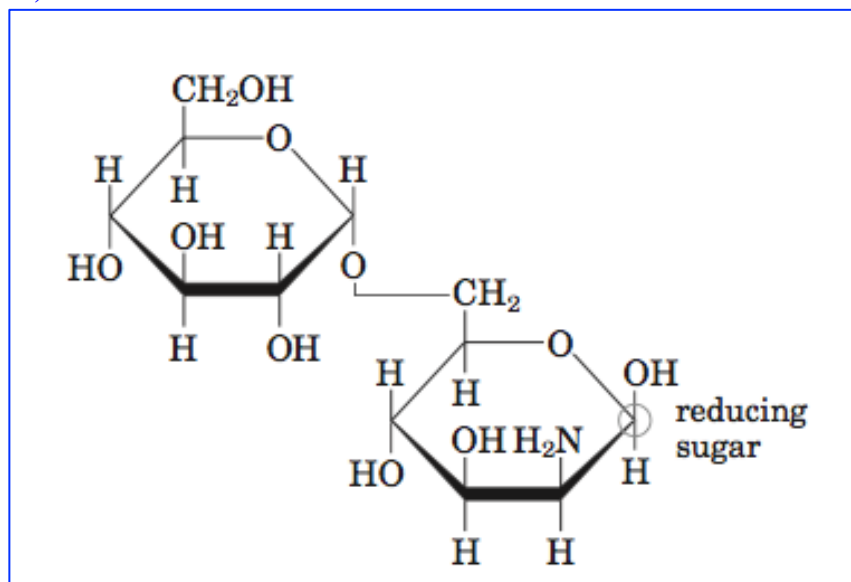
The melting temperatures of these derivatives are easily determined and are characteristic for each osazone. This information was used to help identify monosaccharides before the development of HPLC or gas-liquid chromatography. Listed below are the melting points (MPs) of some aldose-osazone derivatives:

Monosaccharide	MP of anhydrous monosaccharide (°C)	MP of osazone derivative (°C)
Glucose	146	205
Mannose	132	205
Galactose	165–168	201
Talose	128–130	201

As the table shows, certain pairs of derivatives have the same melting points, although the underivatized monosaccharides do not. Why do glucose and mannose, and similarly galactose and talose, form osazone derivatives with the same melting points?

(3 pts.) The configuration at C-2 of an aldose is lost in its osazone derivative, so aldoses differing only at the C-2 configuration (C-2 epimers) give the same derivative, with the same melting point. Glucose and mannose are C-2 epimers and thus form the same osazone; the same is true for galactose and talose (see Fig. 7-3).

3. Describe the common structural features and the differences for each pair: (a) cellulose and glycogen; (b) D-glucose and D-fructose; (c) maltose and sucrose. (3 pts.)
- Both are polymers of D-glucose, but they differ in the glycosidic linkage: ( $\beta 1 \rightarrow 4$ ) for cellulose, ( $\alpha 1 \rightarrow 4$ ) for glycogen.
  - Both are hexoses, but glucose is an aldohexose, fructose is a ketohexose.
  - Both are disaccharides, but maltose has two ( $\alpha 1 \rightarrow 4$ )-linked D-glucose units; sucrose has ( $\alpha 1 \rightarrow 2\beta$ )-linked D-glucose and D-fructose.
4. Define "reducing sugar." Sucrose is a disaccharide composed of glucose and fructose (Glc( $\alpha 1 \rightarrow 2$ )Fru). Explain why sucrose is not a reducing sugar, even though both glucose and fructose are. (2 pts.)
- A reducing sugar is one with a free carbonyl carbon that can be oxidized by  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$ .
  - The carbonyl carbon is C-1 of glucose and C-2 of fructose. When the carbonyl carbon is involved in a glycosidic linkage, it is no longer accessible to oxidizing agents. In sucrose (Glc( $\alpha 1 \rightarrow 2$ )Fru), both oxidizable carbons are involved in the glycosidic linkage.
5. Draw the structural formula for  $\alpha$ -D-glucosyl-(1 $\rightarrow$ 6)-D-mannosamine and circle the part of this structure that makes the compound a reducing sugar. (4 pts.)



6. The enzyme glucose oxidase isolated from the mold *Penicillium notatum* catalyzes the oxidation of  $\beta$ -D-glucose to D-glucono- $\delta$ -lactone. This enzyme is highly specific for the  $\beta$  anomer of glucose and does not affect the  $\alpha$  anomer. In spite of this specificity, the reaction catalyzed by glucose oxidase is commonly used in a clinical assay for total blood glucose—that is, for solutions consisting of a mixture of  $\beta$ - and  $\alpha$ -D-glucose. What are the circumstances required to make this possible? Aside from allowing the detection of smaller quantities of glucose, what advantage does glucose oxidase offer over Fehling's reagent for the determination of blood glucose?

(3 pts.)

The rate of mutarotation (interconversion of the  $\alpha$  and  $\beta$  anomers) is sufficiently high that, as the enzyme consumes  $\beta$ -D-glucose, more  $\alpha$ -D-glucose is converted to the  $\beta$  form, and, eventually, all the glucose is oxidized. Glucose oxidase is specific for glucose and does not detect other reducing sugars (such as galactose). Fehling's reagent reacts with any reducing sugar.

7. Describe one biological advantage of storing glucose units in branched polymers (glycogen, amylopectin) rather than in linear polymers.

(2 pts.)

The enzymes that act on these polymers to mobilize glucose for metabolism act only on their nonreducing ends. With extensive branching, there are more such ends for enzymatic attack than would be present in the same quantity of glucose stored in a linear polymer. In effect, branched polymers increase the substrate concentration for these enzymes.

8. The almost pure cellulose obtained from the seed threads of *Gossypium* (cotton) is tough, fibrous, and completely insoluble in water. In contrast, glycogen obtained from muscle or liver disperses readily in hot water to make a turbid solution. Despite their markedly different physical properties, both substances are (1 $\rightarrow$ 4)-linked D-glucose polymers of comparable molecular weight. What structural features of these two polysaccharides underlie their different physical properties? Explain the biological advantages of their respective properties.

(4 pts.)

Native cellulose consists of glucose units linked by ( $\beta$ 1 $\rightarrow$ 4) glycosidic bonds. The  $\beta$  linkages force the polymer chain into an extended conformation. Parallel series of these extended chains can form *intermolecular* hydrogen bonds, thus aggregating into long, tough, insoluble fibers. Glycogen consists of glucose units linked by ( $\alpha$ 1 $\rightarrow$ 4) glycosidic bonds. The  $\alpha$  linkages cause bends in the chain, and glycogen forms helical structures with *intramolecular* hydrogen bonding; it cannot form long fibers. In addition, glycogen is highly branched and, because many of its hydroxyl groups are exposed to water, is highly hydrated and therefore very water-soluble. It can be extracted as a dispersion in hot water.

The physical properties of the two polymers are well suited to their biological roles. Cellulose serves as a structural material in plants,

consistent with the side-by-side aggregation of long molecules into tough, insoluble fibers. Glycogen is a storage fuel in animals. The highly hydrated glycogen granules, with their abundance of free, nonreducing ends, can be rapidly hydrolyzed by glycogen phosphorylase to release glucose 1-phosphate, available for oxidation and energy production.

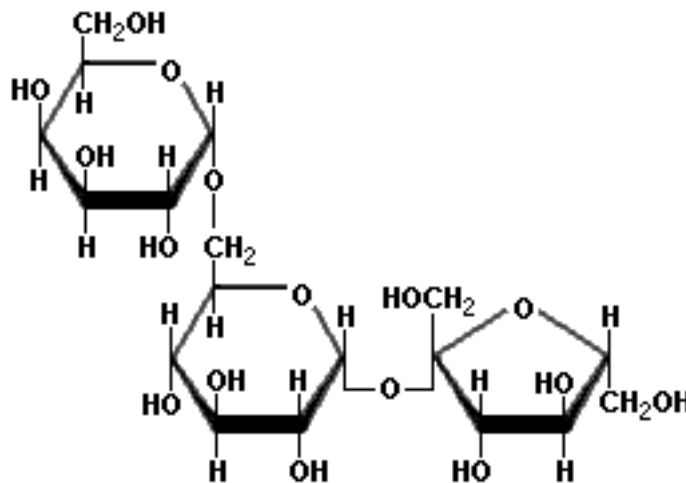
9. Sketch the principal components of a typical proteoglycan, showing their relationships and connections to one another.  
(3 pts.)

A typical proteoglycan consists of a core protein with covalently attached glycosaminoglycan polysaccharides, such as chondroitin sulfate and keratin sulfate. The polysaccharides generally attach to a serine residue in the protein via a trisaccharide (gal–gal–xyl). (See Fig. 7-24, p. 253.)

10. What are lectins? What are some biological processes which involve lectins?  
(3 pts.)

Lectins are proteins that bind to specific oligosaccharides. They interact with specific cell-surface glycoproteins thus mediating cell-cell recognition and adhesion. Several microbial toxins and viral capsid proteins, which interact with cell surface receptors, are lectins.

11. The trisaccharide drawn below is named **raffinose**. What is its systematic name?



(4 pts.)

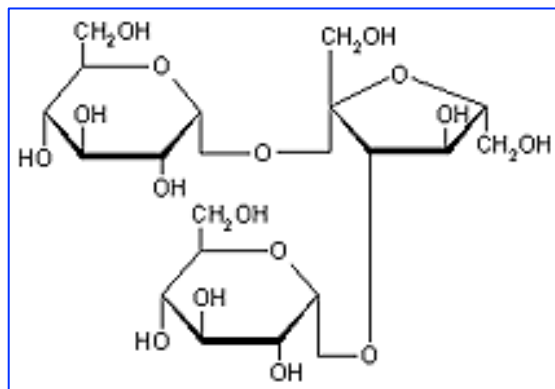
$\alpha$ -D-galactopyranosyl-(1 $\rightarrow$ 6)- $\alpha$ -D-glucopyranosyl  $\beta$ -D-fructofuranoside  
(sequential method)

or

[ $\alpha$ -D-Galp-(1 $\rightarrow$ 6)- $\alpha$ -D-Glcp-(1 $\rightarrow$ 2) $\beta$ -D-Fruf]

12. The systematic name of a sugar is *O*- $\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 3)-*O*- $\beta$ -D-fructofuranosyl-(2 $\rightarrow$ 1)- $\alpha$ -D-glucopyranoside. Draw its molecular formula. Is it a reducing sugar?

(6 pts.)



This sugar, whose common name is melezitose, is NOT a reducing sugar because all three anomeric carbons are involved in glycosidic bonds.

13. Most paper is made by removing the lignin from wood pulp and forming the resulting mass of largely unoriented cellulose fibers into a sheet. Untreated paper loses most of its strength when wet with water but maintains its strength when wet with oil. Explain.

(2 pts.)

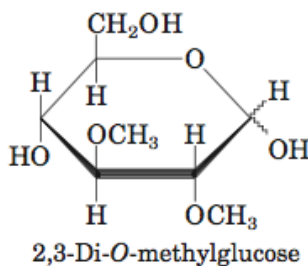
Water disrupts the intrafiber hydrogen bonds that hold the cellulose fibers together; oil has no effect on hydrogen bonds.

14. A molecule of amylopectin consists of 1000 glucose residues and is branched every 25 residues. How many reducing ends does it have? How many non-reducing ends?

(3 pts.)

There will only be one reducing end. The number of reducing ends will depend on the degree of branching and the length of the branches. For a 1000-residue polysaccharide, the maximum number of branch points would be obtained assuming that each branch is only one residue long. If there is a branch point every 25<sup>th</sup> residue you would have  $1,000/26 = 38$  branch points (using 988 residues) and would have 12 residues left over, so the main chain would be 962 residues long and there would be 38 branches. The number of non-reducing ends would be  $38 + 1 = 39$ .

15. The amount of branching (number of ( $\alpha 1 \rightarrow 6$ ) glycosidic bonds) in amylopectin can be determined by the following procedure. A sample of amylopectin is exhaustively methylated—treated with a methylating agent (methyl iodide) that replaces the hydrogen of every sugar hydroxyl with a methyl group, converting  $-OH$  to  $-OCH_3$ . All the glycosidic bonds in the treated sample are then hydrolyzed in aqueous acid, and the amount of 2,3-di-*O*-methylglucose so formed is determined.



- a. Explain the basis of this procedure for determining the number of ( $\alpha 1 \rightarrow 6$ ) branch points in amylopectin. What happens to the unbranched glucose residues in amylopectin during the methylation and hydrolysis procedure?

(2 pts.)

In glucose residues at branch points, the hydroxyl of C-6 is protected from methylation because it is involved in a glycosidic linkage. During complete methylation and subsequent hydrolysis, the branch-point residues yield 2,3-di-*O*-methylglucose and the unbranched residues yield 2,3,6-tri-*O*-methylglucose.

- b. A 258 mg sample of amylopectin treated as described above yielded 12.4 mg of 2,3-di-*O*-methyl- glucose. Determine what percentage of the glucose residues in amylopectin contain an ( $\alpha 1 \rightarrow 6$ ) branch. (Assume the average molecular weight of a glucose residue in amylopectin is 162 g/mol.)

(3 pts.)

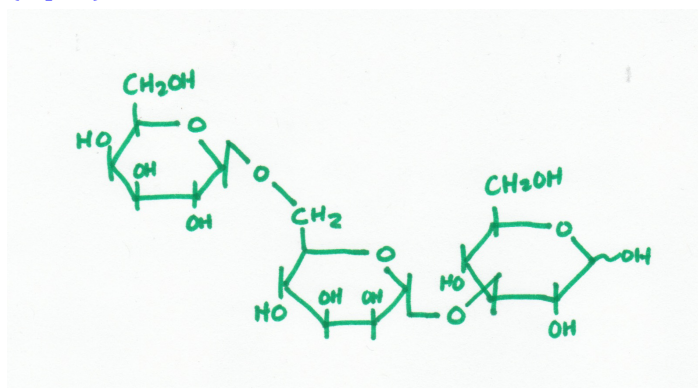
Using the average molecular weight of a glucose residue, 258 mg of amylopectin contains  $\frac{258 \times 10^{-3} \text{ g}}{162 \text{ g/mol}} = 1.59 \times 10^{-3} \text{ mol of glucose}$

The 12.4 mg yield of 2,3-di-*O*-methylglucose (MW=208) is equivalent to  $\frac{12.4 \times 10^{-3} \text{ g}}{208 \text{ g/mol}} = 5.96 \times 10^{-5} \text{ mol of glucose}$

Thus, the percentage of glucose residues in amylopectin that yield 2,3-di-*O*-methylglucose is  $\frac{(5.96 \times 10^{-5} \text{ mol})(100\%)}{1.59 \times 10^{-3} \text{ mol}} = 3.75\%$

16. Exhaustive methylation of a trisaccharide followed by acid hydrolysis yields equimolar quantities of 2,3,4,6-tetra-*O*-methyl-D-galactose, 2,3,4-tri-*O*-methyl-D-mannose, and 2,4,6-tri-*O*-methyl-D-glucose. Treatment of the trisaccharide with  $\beta$ -galactosidase yields D-galactose and a disaccharide. Treatment of this disaccharide with  $\alpha$ -mannosidase yields D-mannose and D-glucose. Draw the structure of the trisaccharide and state its systematic name.

(5 pts.)



D-Galactopyranosyl - $\beta$  -(1 $\rightarrow$ 6)-D-mannopyranosyl- $\alpha$ -(1 $\rightarrow$ 3)-D-glucopyranose

Note that the reducing sugar (D-glucose, at the reducing end) is not methylated on the anomeric carbon because although a methyl group was added to that position in the exhaustive methylation, a methyl ESTER was produced (because glucose is an aldose instead of an ether. It would be removed by hydrolysis.

17. The carbohydrate portion of some glycoproteins may serve as a cellular recognition site. In order to perform this function, the oligosaccharide moiety of glycoproteins must have the potential to exist in a large variety of forms. Which can produce a greater variety of structures: oligopeptides composed of five different amino acid residues or oligosaccharides composed of five different monosaccharide residues? Explain.

(2 pts.)

Oligosaccharides; their monosaccharide residues can be combined in more ways than the amino acid residues of oligopeptides. Each of the several hydroxyl groups of each monosaccharide can participate in glycosidic bonds, and the configuration of each glycosidic bond can be either  $\alpha$  or  $\beta$ . Furthermore, the polymer can be linear or branched. Oligopeptides are unbranched polymers, with all amino acid residues linked through identical peptide bonds.