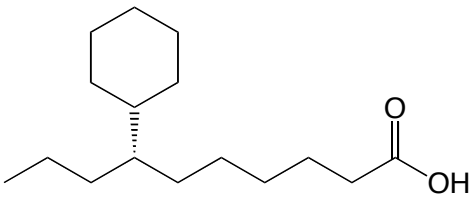
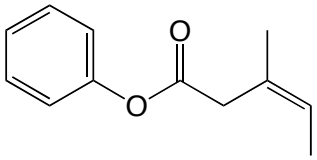
1. Provide an unambiguous name (IUPAC or common) for each of the following molecules. (8 points)

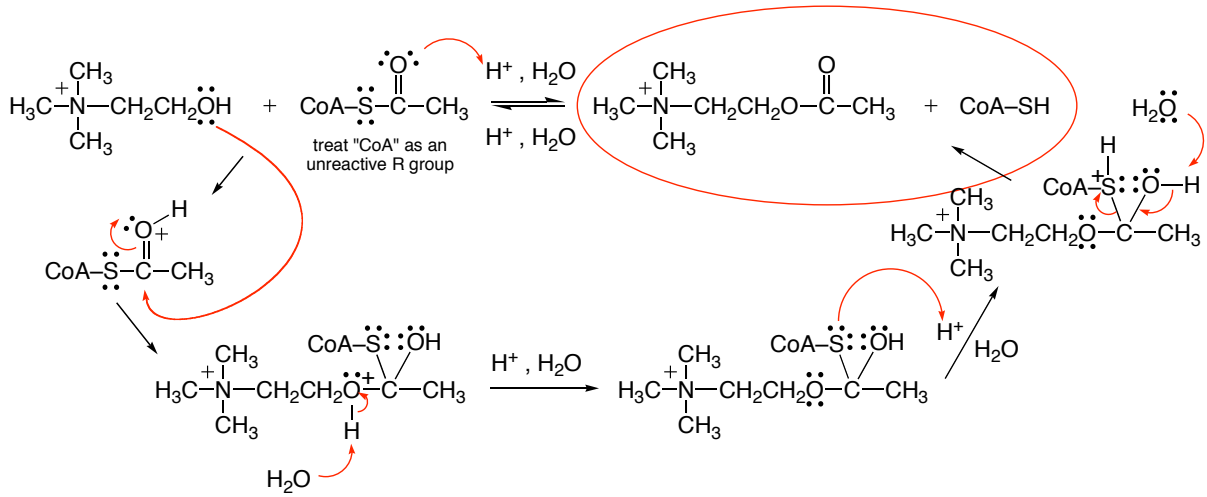


(*S*)-7-cyclohexyldecanoic acid



(*Z*)-phenyl 3-methylpent-3-enoate
or
(*Z*)-phenyl 3-methyl-3-pentenoate

2. The reaction shown below is important in the transmission of nerve impulses. In biological systems, enzymes catalyze this reaction in both directions. Suppose the reaction were to take place outside of the body (in H^+, H_2O). Which side of the equilibrium would be favored (circle the compounds that indicate your choice)? Provide a mechanism for the reaction that proceeds in the selected direction. (10 points)



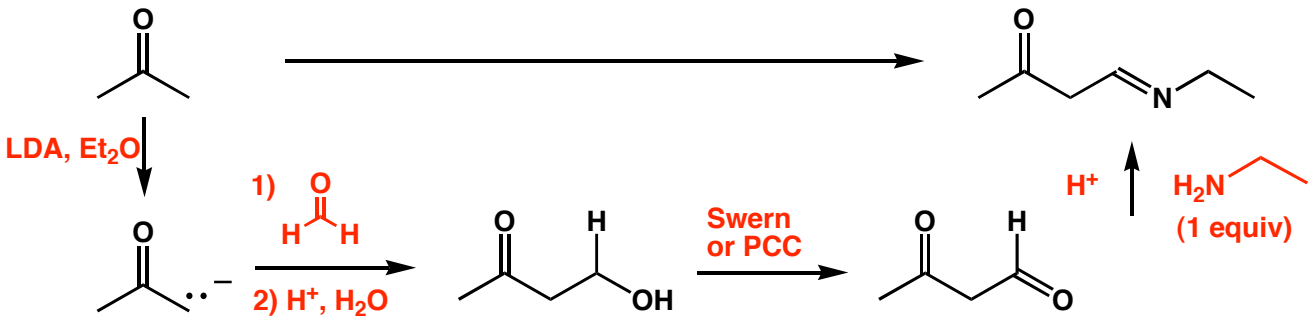
Why is the direction of equilibrium that you chose favored over the other (explain in the space provided)?

There are two arguments one can use:

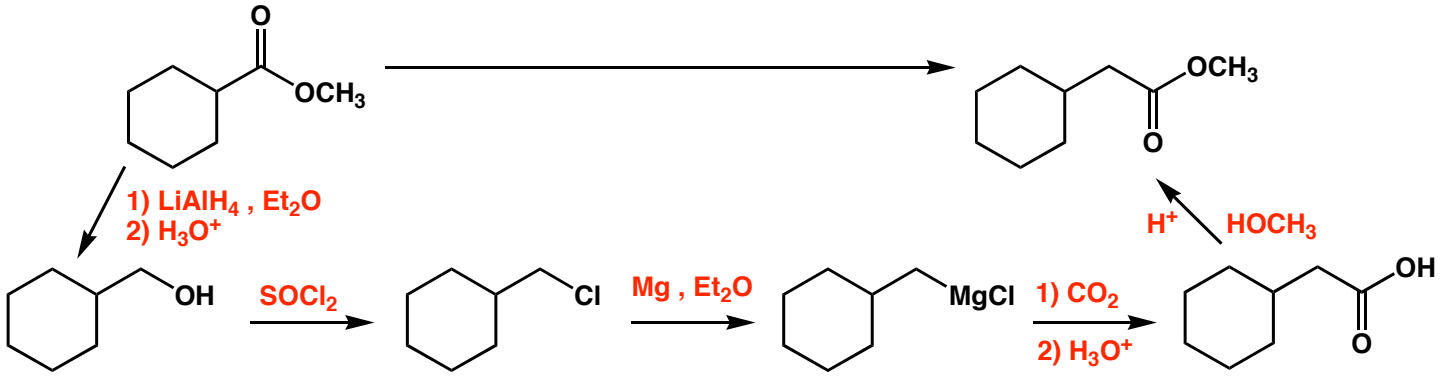
1) S has a larger electron cloud through which to disperse the negative charge. $CoA–S:^-$ is thus more stable than $H_3C–N^+(CH_3)_2–CH_2CH_2O:^-$ and therefore a better leaving group; making the thioester a more reactive carbonyl than the carboxylic ester.

2) the carbonyl carbon of the thioester is more partially positive (making it more reactive) because the C-S bond is longer, making it harder for resonance stabilization by sulfur.

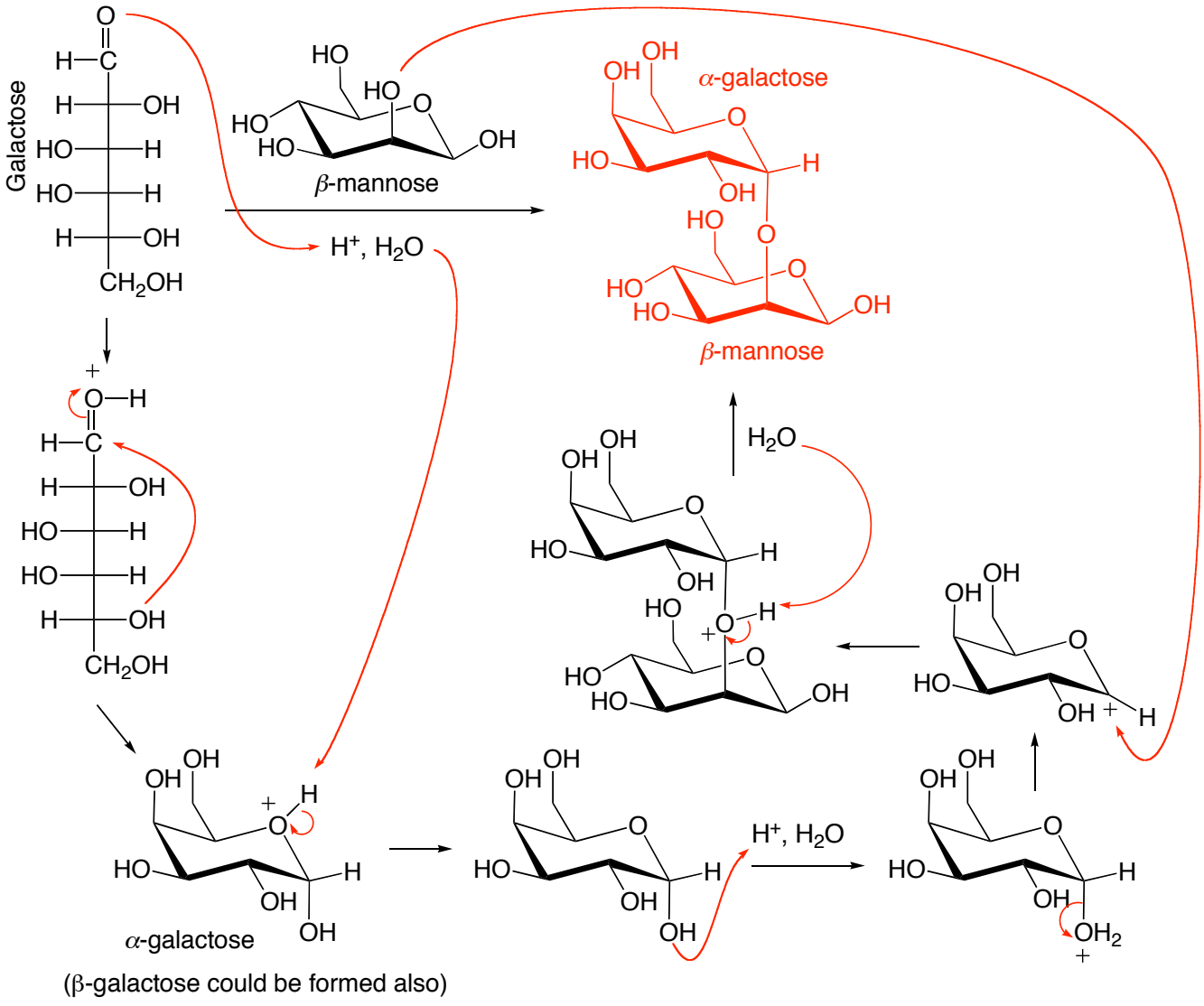
3. Provide a synthesis for the following transformation (include the products of each major step). (8 pts)



4. Provide a synthesis for the following transformation (include the products of each major step). (10 pts)

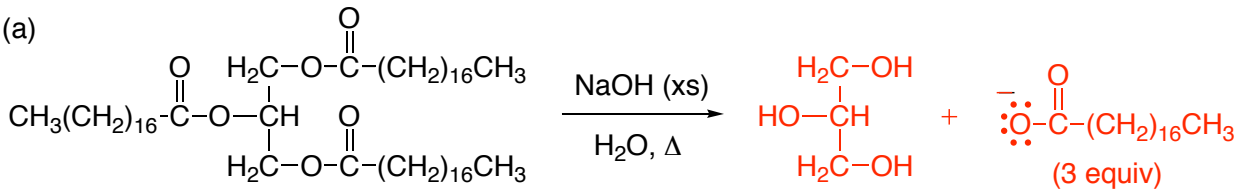


5. Draw the structure of the α-1,2-disaccharide of galactose and β-mannose. Provide a mechanism that shows how this dissacharide could be formed from the starting materials provided. Show the products of each step for full credit. (10 points)

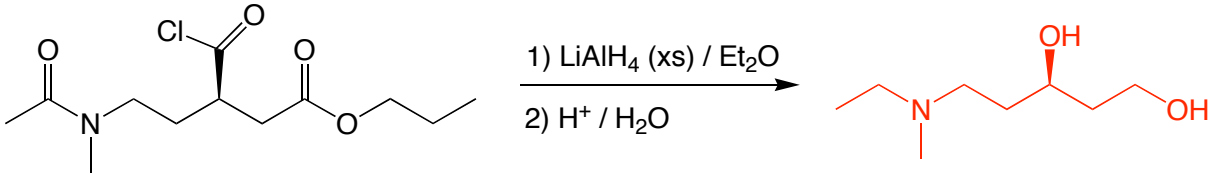


6. Draw the **major product(s)** of each of the following reactions. (20 pts)

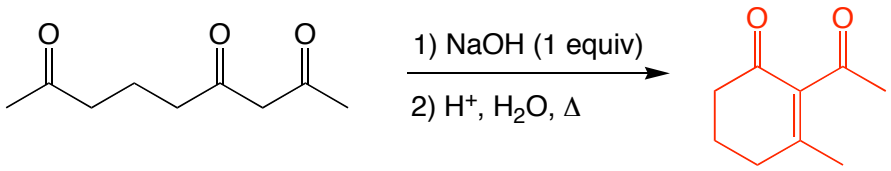
(a)



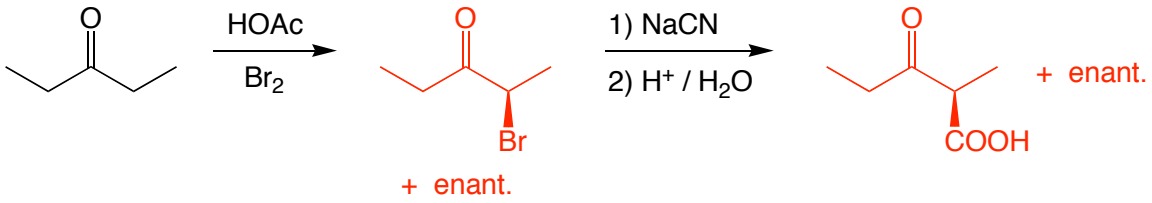
(b)



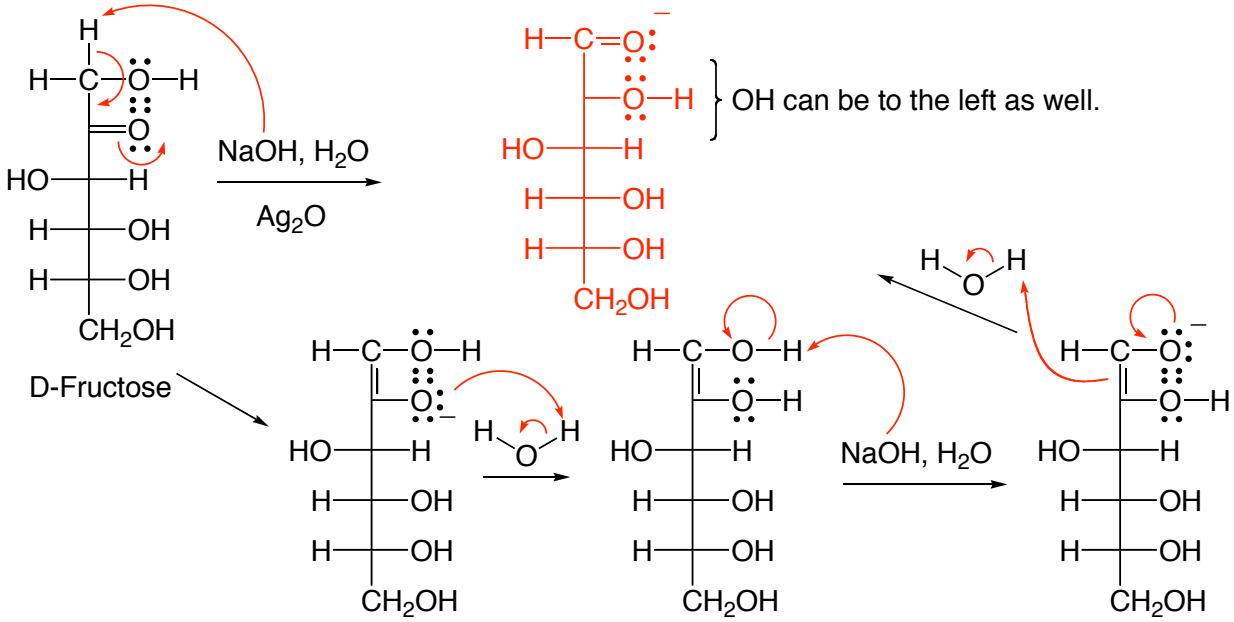
(c)



(d)

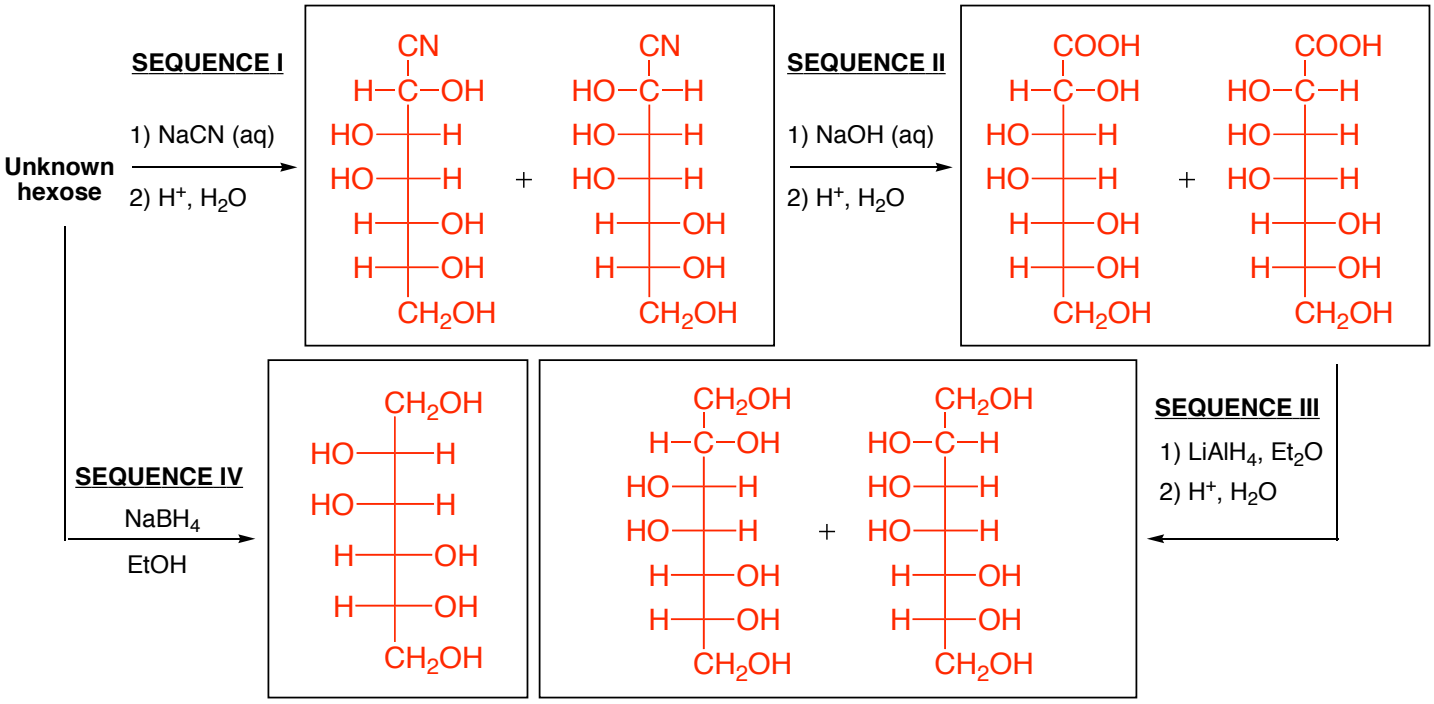


7. Provide a mechanism that explains why D-fructose gives a positive Tollens test (i.e. acts as a reducing sugar) even though it doesn't contain an aldehyde group. Recall that the Tollens test is done under aqueous, basic conditions (NaOH, H_2O). Note: you are *not* being asked to provide the mechanism of the Tollens rxn.



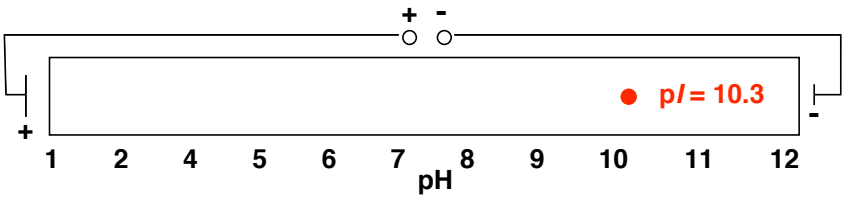
Through base-catalyzed keto-enol tautomerization, the carbonyl can end up on the first carbon. Once an aldehyde is formed, it can react with (reduce) Ag_2O.

8. One of the 8 naturally occurring hexoses (shown below) is subjected to the reactions shown. The product of SEQUENCE IV is chiral. as are the two products that result after SEQUENCE III. The β-pyranose of the unknown contains only 1 axial hydroxyl group. Determine the identity of the unknown hexose (provide its name) and provide products for each sequence of reactions (use Fisher projections). (12 pts)

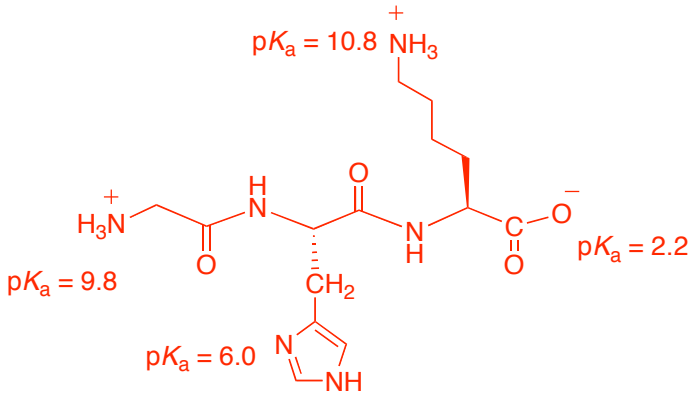


Name of unknown hexose: Mannose

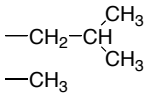
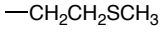
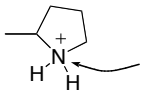
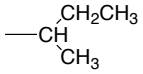
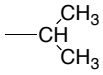
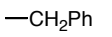
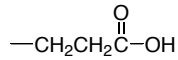
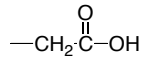
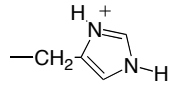
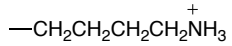
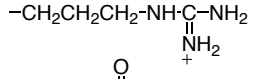
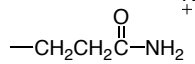
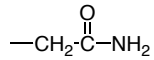
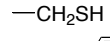
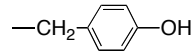
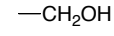
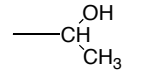
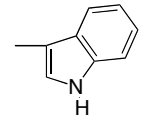
9. Draw (showing the correct stereochemistry for each stereocenter) the predominant form of Gly-His-Lys at pH 8.5. Then indicate where it would show up on the p*H* gradient electrophoresis gel below. (12 points)



Structure of Gly-His-Lys:



The side chains of the 20 common amino acids and their acidities.

Name	3-letter Abbr.	1-letter Abbr.	Side Chain (protonated form)	pK_a α-COOH	pK_a α-NH_3^+	pK_a side chain
leucine	Leu	L		2.4	9.6	---
alanine	Ala	A		2.3	9.9	---
methionine	Met	M		2.3	9.2	---
proline	Pro	P		2.0	10.6	---
glycine	Gly	G		2.4	9.8	---
isoleucine	Ile	I		2.4	9.7	---
valine	Val	V		2.3	9.6	---
phenylalanine	Phe	F		1.8	9.1	---
glutamic acid	Glu	E		2.2	9.7	4.3
aspartic acid	Asp	D		2.0	10.0	3.9
histidine	His	H		1.8	9.2	6.0
lysine	Lys	K		2.2	9.2	10.8
arginine	Arg	R		1.8	9.0	12.5
glutamine	Gln	Q		2.2	9.1	---
asparagine	Asn	N		2.0	8.8	---
cysteine	Cys	C		1.8	10.8	8.3
tyrosine	Tyr	Y		2.2	9.1	10.9
serine	Ser	S		2.1	9.2	---
threonine	Thr	T		2.6	10.4	---
tryptophan	Trp	W		2.4	9.4	---

The naturally occurring hexoses