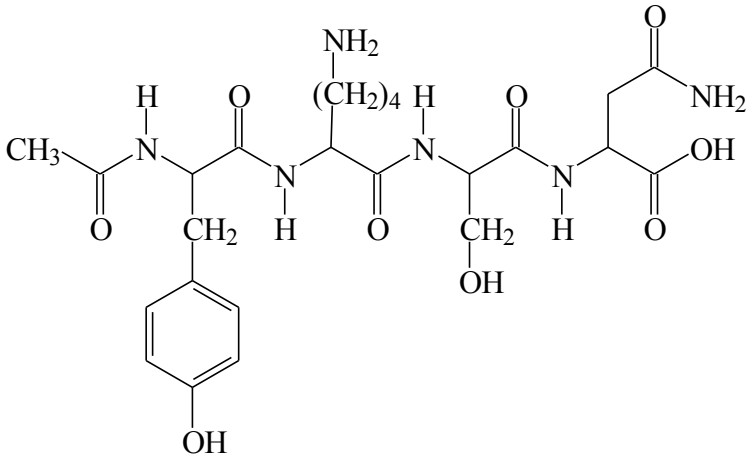
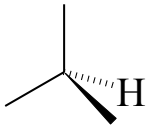
Marks
10

- The constitutional formula of a derivative of the naturally occurring tetrapeptide, Tyr-Lys-Ser-Asn is shown below.

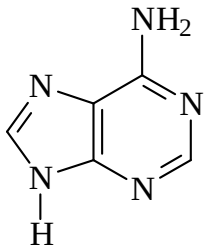


Give the Fischer projection of L-Ser as the zwitterion.	Complete the stereoformula of (*R*)-Lys.
	

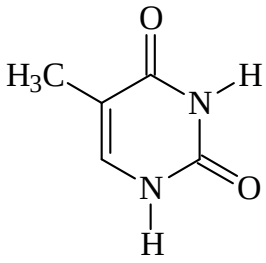
Give the constitutional formulas in the correct ionic states of the products obtained from the vigorous basic hydrolysis (5 M KOH) of the tetrapeptide.

Marks 4

- Adenine and thymine have the structures shown below.



adenine



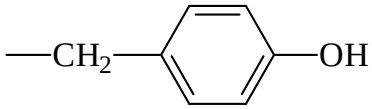
thymine

Draw a tautomer of the shown structure of adenine.

In DNA, adenine forms a “base pair” with thymine. Explain what is meant by “base pair” and indicate the point(s) of interaction between adenine and thymine.

Marks 6

- L-Tyrosine is a naturally occurring amino acid with the following side-chain.



The pK_a values of tyrosine are 2.20 (α-COOH), 9.19 (α-$NH_3^{\oplus}$) and 10.47 (sidechain). Draw the Fischer projection of L-tyrosine indicating the correct charge state at physiological pH.

What is the absolute stereochemistry of L-tyrosine? Write (*R*) or (*S*).

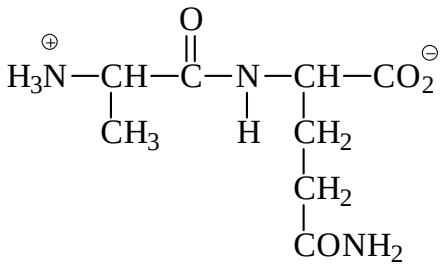
What is the value of the pI of L-tyrosine?

What does pI represent?

Account for the difference in acidity of the carboxylic acid group and the phenol.

Marks 3

- Draw the products of acid hydrolysis of the following peptide, indicating the correct charge state under these conditions.



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Marks 7

- Glycine, NH_2CH_2COOH, is the simplest of all naturally occurring amino acids. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4.

Use your structure to illustrate the concept of resonance.

What are the hybridisation states and geometries of the two carbon atoms and the nitrogen atom in glycine?

Propionic acid, CH_3CH_2COOH, has a melting point of –20.7 °C while glycine has a melting point of 292 °C. Suggest a reason why these two molecules have such different melting points.

Marks 6

- Alanine ($R = CH_3$) and lysine ($R = CH_2CH_2CH_2CH_2NH_2$) are two common amino acids. Using *ala* and *lys* to represent the two amino acids, represent all constitutional isomers of the tripeptide formed from one *ala* and two *lys* units.

Comment, giving your reason, on whether the tripeptide(s) will be acidic, neutral or basic in character.

Draw the constitutional formulas, indicating the correct ionic state, of the products formed from acid hydrolysis of one of your tripeptides.

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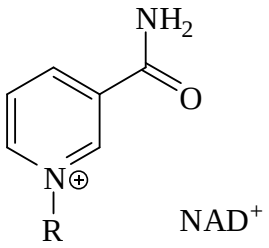
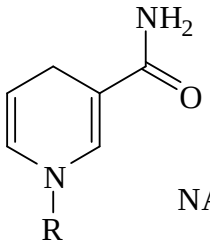
• In the spaces provided, explain the meanings of the following terms.	**Marks 3**
(a) enzyme	
(b) cofactor	
(c) peptide	

Marks 7

- NAD^+/NADH is a biological redox system. The two species may be represented by the structures below.



NAD^+



NADH

What are the requirements for a compound to be aromatic? Indicate which of NAD^+ and/or NADH fulfil these requirements.

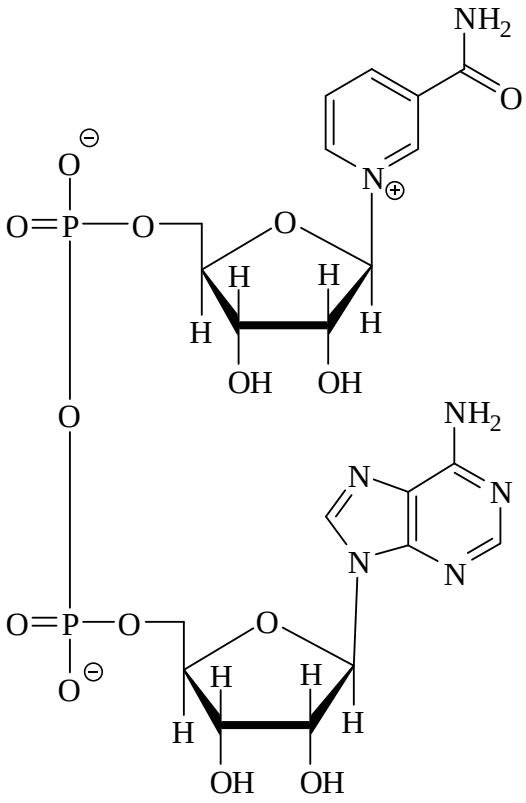
Which of NAD^+ and/or NADH will react with cold dilute H^+ in an acid/base reaction? Using the structures above, give the chemical equation for the reaction and a brief explanation for your choice.

Draw the structure of a tautomer of NADH.

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks 4

The full structure of NAD^+ contains ribose, two phosphate groups and adenine.

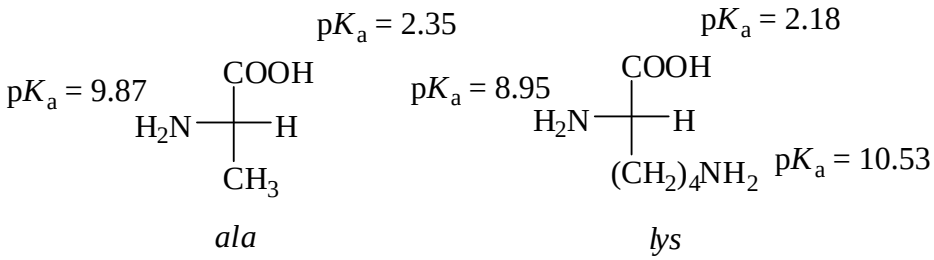


Draw ribose as a Fischer projection.

Adenine is also a component of DNA used in forming complementary strands by hydrogen bonding. Indicate the sites of hydrogen bonding on adenine that are used in forming complementary strands in DNA and differentiate between those sites that are hydrogen bond donors and those that are hydrogen bond acceptors.

Marks 7

- Alanine (*ala*) and lysine (*lys*) are two amino acids with the structures given below as Fischer projections. The pK_a values of the conjugate acid forms of the different functional groups are indicated.



ala *lys*

Draw the structure of the dipeptide *ala-lys* in its zwitterionic form.

Would you expect the dipeptide to be soluble in water? Give a brief reason for your choice.

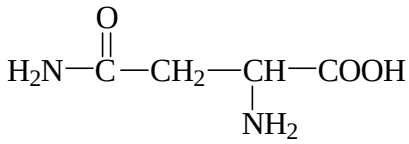
Would you expect the dipeptide to be acidic, neutral or basic? Give a brief reason for your choice.

Estimate the isoelectric point of the dipeptide.

Marks 4

- The amino acid, asparagine, was isolated from asparagus juice in 1806. The uncharged form, **Y**, is given below.

Y

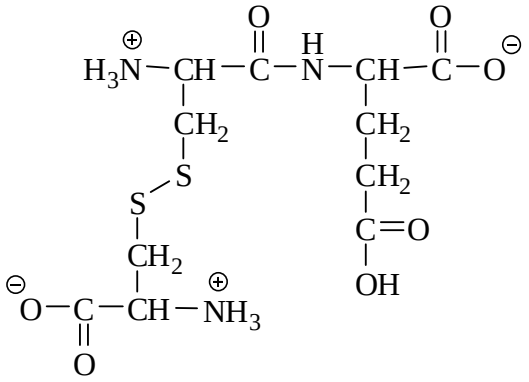


Draw the constitutional formula of the product(s) formed in the reaction of **Y** with the following reagents.

Cold, dilute hydrochloric acid	Cold, dilute sodium hydroxide
Hot, 6 M hydrochloric acid	Hot, 6 M sodium hydroxide

Marks
7

- A peptide has the following structure.

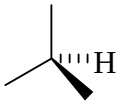


Would you expect this peptide to be soluble in water? Explain your answer.

Give the products formed after treatment of the peptide with Zn/H^+.

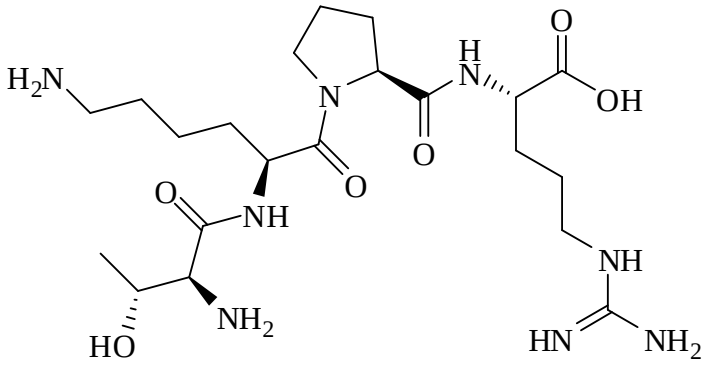
These products are then heated with excess aqueous OH^-. Draw the constitutional formulas of the different amino acids formed. Ensure you represent the amino acids in the correct charge state for the conditions.

Choose one of the amino acids produced on hydrolysis and draw the (*S*) configuration.



Marks 6

- Tuftsin is a tetrapeptide (Thr-Lys-Pro-Arg) produced by enzymatic cleavage of the Fc-domain of the heavy chain of immunoglobulin G. It is mainly produced in the spleen and its activity is related primarily to immune system function.



tuftsin

Draw the Fischer projections of the four L-amino acids that result from the acid hydrolysis of tuftsin.

What is the major species present when lysine (Lys) is dissolved in water at pH 12 and pH 5.6. The pK_a values of lysine are 1.82 (α-COOH), 8.95 (α-$NH_3^{\oplus}$) and 10.53 (side chain).

Marks 4

pH 12	pH 5.6

Give the constitutional formulas for the following dipeptides in their zwitterionic states. The pK_a values of proline are 1.95 and 10.64.

Lys-Thr

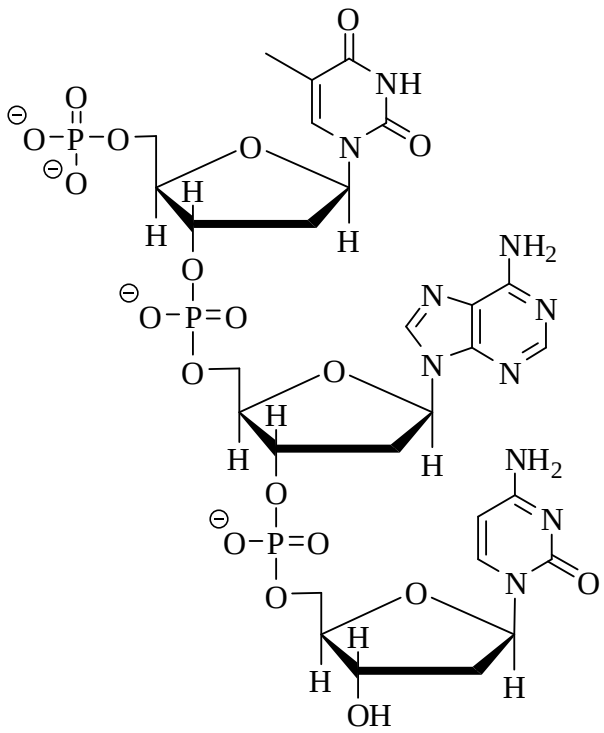
Pro-Lys

- Glycine, NH_2CH_2COOH, is the simplest of the naturally occurring amino acids. It has a melting point of 238 ^oC, while CH_3CH_2COOH has a melting point of –21 ^oC. Give one reason for this difference.

2

- Is the following structure a fragment of DNA or RNA? Give two reasons.

Marks 5



Clearly identify on the above structure one example of each of the following subunits.

nucleic base

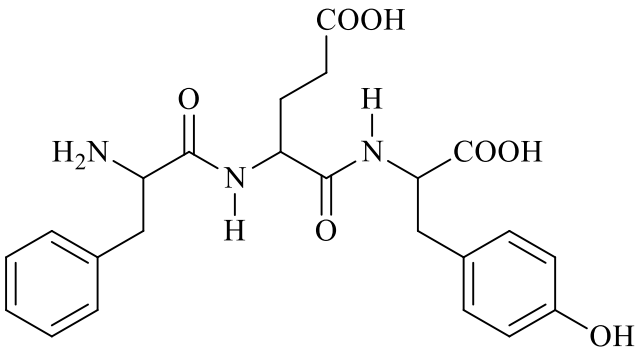
nucleoside

nucleotide

Marks
3

- Consider the tripeptide phenylalanylglutamyltyrosine (Phe-Glu-Tyr) (**F**), whose constitutional formula is shown below.

(**F**)



Draw the constitutional formula(s) of the product(s) obtained when the tripeptide (**F**) is subjected to the following conditions. Make sure you show the products in the appropriate ionic states.

cold 2 M NaOH

5 M HCl / heat

Marks 4

The pK_a values of tyrosine are pK_{a1} = 2.20 (α-COOH), pK_{a2} = 9.11 (α-$NH_3^{\oplus}$) and pK_{a3} = 10.07 (-$CH_2C_6H_4OH$). Draw the structure of the zwitterionic form of tyrosine.

At what pH will this be the predominant species in aqueous solution?

The naturally occurring isomer of phenylalanine is (L)-phenylalanine. Draw the zwitterionic structure of (L)-phenylalanine and indicate the stereogenic centre with an asterisk (*). Determine whether this amino acid has the (*R*) or (*S*) configuration. Show your working.

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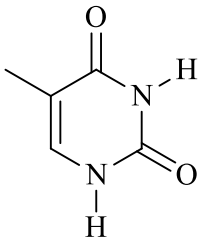
	Marks
• Draw a tautomer of the structure of thymine, shown below.	**1**

thymine



tautomer of thymine