1 A peptide is hydrolysed to form a solution containing a mixture of amino acids. This mixture is then analysed by silica gel thin-layer chromatography (TLC) using a toxic solvent. The individual amino acids are identified from their R_f values.

Part of the practical procedure is given below.

1. **Wearing plastic gloves to hold a TLC plate**, draw a pencil line 1.5 cm from the bottom of the plate.
2. Use a capillary tube to apply a very small drop of the solution of amino acids to the mid-point of the pencil line.
3. Allow the spot to dry completely.
4. In the developing tank, add the developing solvent to **a depth of not more than 1 cm**.
5. Place your TLC plate in the developing tank.
6. Allow the developing solvent to rise up the plate **to the top**.
7. Remove the plate and quickly mark the position of the solvent front with a pencil.
8. Allow the plate to dry **in a fume cupboard**.

(a) Parts of the procedure are in bold text.

For each of these parts, consider whether it is essential and justify your answer.

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(4)

(b) Outline the steps needed to locate the positions of the amino acids on the TLC plate and to determine their R_f values.

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(4)

(c) Explain why different amino acids have different R_f values.

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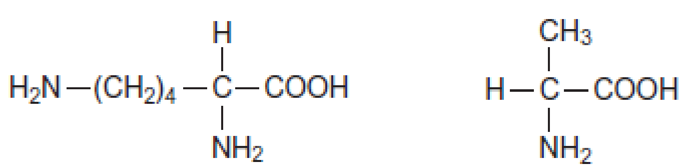
(2)
(Total 10 marks)

2 Lysine and alanine are two amino acids.



lysine alanine

(a) Give the IUPAC name of lysine.

....

(1)

(b) Draw structures to show the product formed in each case when lysine reacts with

(i) an excess of aqueous HCl

(1)

(ii) an excess of aqueous NaOH

(1)

(iii) methanol in the presence of a small amount of concentrated H_2SO_4

(1)

(c) The mass spectrum of alanine gives a major peak at $m / z = 44$

Write an equation for the fragmentation of the molecular ion of alanine to give an ion that produces this peak.
In your answer, draw the displayed formula for this fragment ion.

(2)

(d) Draw a dipeptide formed from one molecule of lysine and one molecule of alanine.

(1)

(e) The dipeptide in part (d) is hydrolysed in acid conditions and the mixture produced is analysed by column chromatography. The column is packed with a resin which acts as a polar stationary phase.

Suggest why lysine leaves the column after alanine.

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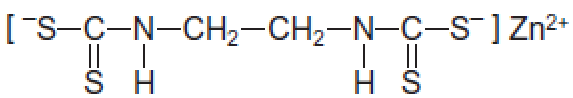
(2)
(Total 9 marks)

3 (a) Because of the toxic nature of the copper(II) ion, a wide range of alternative anti-fungal drugs has been developed for use in agriculture. One example is Zineb.



Zineb

(i) The negative ion in Zineb could act as a bidentate ligand.

On the structure above, draw a ring around each of **two** atoms that could provide the lone pairs of electrons when this ion acts as a bidentate ligand.

(1)

(ii) Calculate the M_r of Zineb. Give your answer to the appropriate precision.

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(1)

(iii) Name the functional group formed at each end of the negative ion when all the sulfur atoms in the structure of Zineb are replaced by oxygen atoms.

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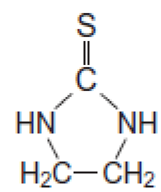
(1)

(b) Zineb has been investigated for harmful effects. Generally, Zineb has been found to be safe to use in agriculture. It is only slightly soluble in water and is sprayed onto plants. A breakdown product of Zineb is ethylene thiourea (ETU), which is very soluble in water. The structure of ETU is shown below.



Determine the percentage, by mass, of sulfur in ETU (M_r = 102.1).

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(1)

(c) Chromatography is a technique used to show the presence of a small amount of ETU in Zineb.

Outline how this technique is used to separate and identify ETU from a sample of Zineb powder.

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(4)
(Total 8 marks)

4 (a) A chemist discovered four unlabelled bottles of liquid, each of which contained a different pure organic compound. The compounds were known to be propan-1-ol, propanal, propanoic acid and 1-chloropropane.

Describe four **different** test-tube reactions, one for each compound, that could be used to identify the four organic compounds.
Your answer should include the name of the organic compound, the reagent(s) used and the expected observation for each test.

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(Extra space) ....

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(8)

(b) A fifth bottle was discovered labelled propan-2-ol. The chemist showed, using infrared spectroscopy, that the propan-2-ol was contaminated with propanone.

The chemist separated the two compounds using column chromatography. The column contained silica gel, a polar stationary phase.

The contaminated propan-2-ol was dissolved in hexane and poured into the column. Pure hexane was added slowly to the top of the column. Samples of the eluent (the solution leaving the bottom of the column) were collected.

- Suggest the chemical process that would cause a sample of propan-2-ol to become contaminated with propanone.
- State how the infrared spectrum showed the presence of propanone.
- Suggest why propanone was present in samples of the eluent collected first (those with shorter retention times), whereas samples containing propan-2-ol were collected later.

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(Extra space) ....

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(4)
(Total 12 marks)

5 (a) Name compound **Y**, $HOCH_2CH_2COOH$

....

(1)

(b) Under suitable conditions, molecules of **Y** can react with each other to form a polymer.

(i) Draw a section of the polymer showing **two** repeating units.

(1)

(ii) Name the type of polymerisation involved.

....

(1)

(c) When **Y** is heated, an elimination reaction occurs in which one molecule of **Y** loses one molecule of water. The organic product formed by this reaction has an absorption at 1637 cm^{-1} in its infrared spectrum.

(i) Identify the bond that causes the absorption at 1637 cm^{-1} in its infrared spectrum.

....

(1)

(ii) Write the displayed formula for the organic product of this elimination reaction.

(1)

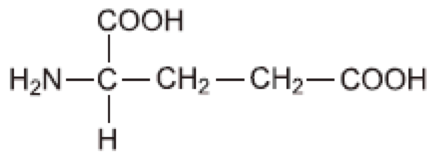
(iii) The organic product from part (ii) can also be polymerised.
Draw the repeating unit of the polymer formed from this organic product.

(1)

(d) At room temperature, 2-aminobutanoic acid exists as a solid.
Draw the structure of the species present in the solid form.

(1)

(e) The amino acid, glutamic acid, is shown below.



Draw the structure of the organic species formed when glutamic acid reacts with each of the following.

(i) an excess of sodium hydroxide

(1)

(ii) an excess of methanol in the presence of concentrated sulfuric acid

(1)

(iii) ethanoyl chloride

(1)

(f) A tripeptide was heated with hydrochloric acid and a mixture of amino acids was formed.
This mixture was separated by column chromatography.
Outline briefly why chromatography is able to separate a mixture of compounds.
Practical details are **not** required.

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(3)
(Total 13 marks)

Mark schemes

1 (a) **Wear plastic gloves:**

Essential – to prevent contamination from the hands to the plate

1

Add developing solvent to a depth of not more than 1 cm^3:

Essential – if the solvent is too deep it will dissolve the mixture from the plate

1

Allow the solvent to rise up the plate to the top:

Not essential – the R_f value can be calculated if the solvent front does not reach the top of the plate

1

Allow the plate to dry in a fume cupboard:

Essential – the solvent is toxic

Allow hazardous

1

(b) Spray with developing agent or use UV

1

Measure distances from initial pencil line to the spots (x)

1

Measure distance from initial pencil line to solvent front line (y)

1

R_f value = x / y

1

(c) Amino acids have different polarities

1

Therefore, have different retention on the stationary phase or different solubility in the developing solvent

1

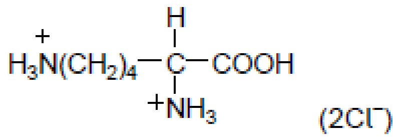
[10]

2 (a) <u>2,6-diaminohexanoic acid</u>

Ignore additional , or – or spaces.

1

(b) (i)



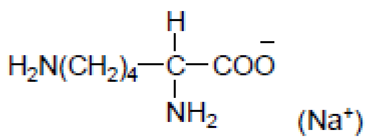
NB both N must be protonated.

Allow $-NH_3^+$ *allow* CO_2H *Allow* $-^+H_3N$.

Penalise – C_4H_8 – *here.*

1

(ii)



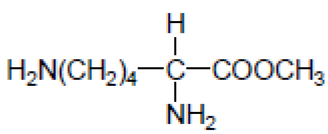
Allow CO_2^-.

Allow $-H_2N$.

Allow –COONa but penalise O–Na bond shown.

1

(iii)

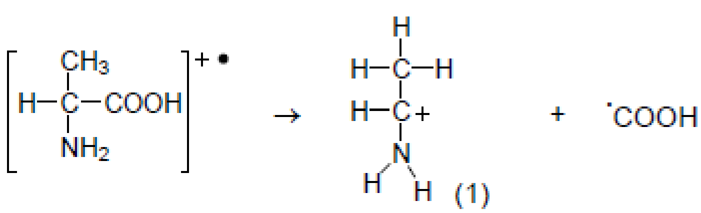


Allow CO_2CH_3.

Allow $-NH_3^+$ *or* $-H_2N$.

1

(c)



1 for <u>displayed formula</u> of fragment ion.

1 for molecular ion of alanine AND radical.

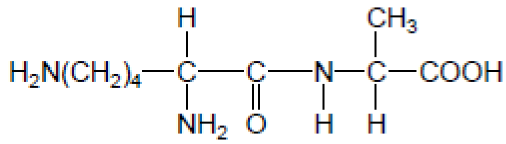
Allow molecular ion without brackets and fragment ion in brackets with outside +.

Allow dot anywhere on radical.

Allow $[C_3H_7NO_2]^{+\bullet}$ *for molecular ion.*

2

(d)



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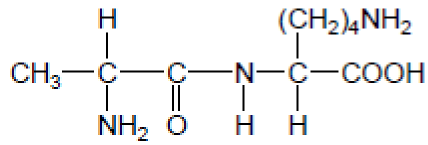

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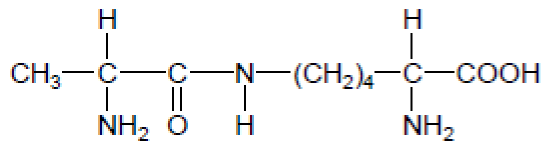


Dipeptide, not repeating unit /.

Allow CO_2H Allow $–H_2N$.

Allow –CONH–.

1

(e) M1 In acid lysine has double positive or more positive charge

1

M2 (Lysine ion) has greater affinity / greater attraction / adheres better / sticks better to polar / stationary phase

M2 only scores after a correct M1.

Ignore greater retention time.

1

[9]

3 (a) (i) Two rings only around nitrogen or sulfur

Lose this mark if more than 2 atoms are ringed.

Do not allow two atoms at the same end of the ion.

1

(ii) 275.8

Accept this answer only. Do not allow 276

1

(iii) Carboxylate / $COO^–$

Allow salt of carboxylic acid or just carboxylic acid.

1

(b) (32.1 / 102.1) = 31.4%

Do not penalise precision but do not allow 1 significant figure.

1

(c) Zineb is mixed with a <u>solvent / water</u>

Max=2 if M1 missed

1

Use of column / paper / TLC

Lose M1 and M2 for GLC

1

Appropriate collection of the ETU fraction
OR Appropriate method of detecting ETU

Allow ETU is an early fraction in a column or collecting a range of samples over time, lowest retention time / travels furthest on paper or TLC (allow 1 mark for having the longest retention time in GLC).

1

Method of identification of ETU (by <u>comparison</u> with standard using chromatography)

If method completely inappropriate, only M1 is accessible

1

[8]

4 (a) **If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br_2 test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg $AgClr_2$**

propan-1-ol

acidified
potassium
dichromate

sodium

Named acid + conc H_2SO_4

named acyl chloride

PCl_5

M1

1

(orange) turns green

effervescence

Sweet smell

Sweet smell /misty fumes

Misty fumes

M2

1

propanal

add Tollens or Fehlings / Benedicts

acidified
potassium
dichromate

Bradys or 2,4-dnph

if dichromate used for alcohol cannot be used for aldehyde

M3

1

Tollens: silver mirror or Fehlings/ Benedicts: red ppt

(orange) turns green

Yellow or orange ppt

M4

1

propanoic acid

Named carbonate/ hydrogencarbonate

water and UI (paper)

Named alcohol + conc H_2SO_4

sodium or magnesium

PCl_5

if sodium used for alcohol cannot be used for acid

M5

1

effervescence

orange/red

Sweet smell

effervescence

Misty fumes

if PCl_5 used for alcohol cannot be used for acid

M6

1

1-chloro propane

NaOH then acidified $AgNO_3$

$AgNO_3$

If acidification missed after NaOH,
no mark here but allow mark for observation

M7 **1**

white ppt

white ppt

M8 **1**

(b) oxidation (of alcohol by oxygen in air)

M1 **1**

absorption at <u>1680 -1750</u> (due to C=O)

Must refer to the spectrum

M2 **1**

comparison of polarity of molecules or correct imf statement:
propanone is less polar OR propan-2-ol is more polar
OR propanone has dipole-dipole forces
OR propan-2-ol has hydrogen bonding

M3 **1**

about attraction to stationary phase or solubility in moving phase
Propan-2-ol has greater affinity for stationary phase or vice versa
OR propanone is more soluble in solvent/moving phase or vice versa

M4 **1**

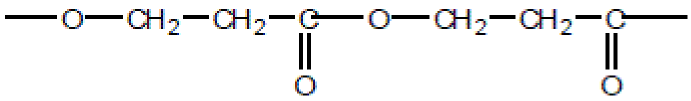
[12]

5 (a) 3-hydroxypropanoic acid

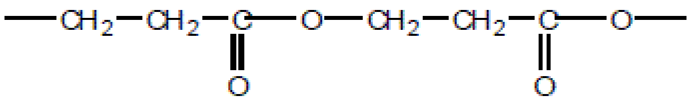
allow 3-hydroxypropionic acid
must be correct spelling

1

(b) (i) must show trailing bonds



or can start at any point in the sequence, e.g.



not allow dimer

allow –O–$CH_2CH_2COOCH_2CH_2CO$–

or –$CH_2CH_2COOCH_2CH_2COO$–

ignore ( ) or n

NB answer has a total of 6 carbons and 4 oxygens

1

(ii) condensation (polymerisation)

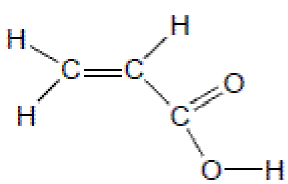
Allow close spelling

1

(c) (i) C=C or carbon-carbon <u>double</u> bond

1

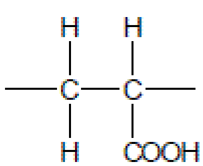
(ii)



*must show **ALL** bonds including O–H*

1

(iii) must show trailing bonds

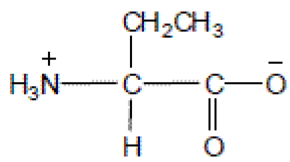


allow polyalkene conseq on their c(ii)

ignore n

1

(d)

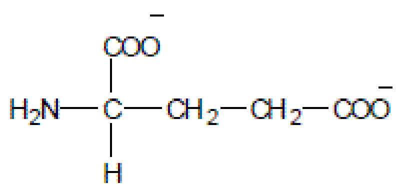


allow NH_3^+ —

allow COO^-

1

(e) (i)



In (e), do not penalise a slip in the number of carbons in the -CH_2CH_2- chain, but all must be bonded correctly

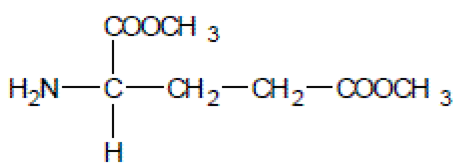
NB two carboxylate groups

Allow COONa or COO^- Na^+ but not covalent bond to Na

allow NH_2–

1

(ii)



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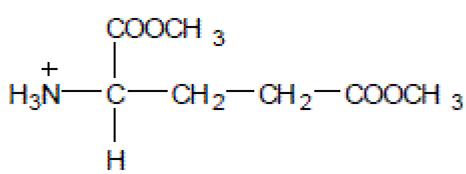


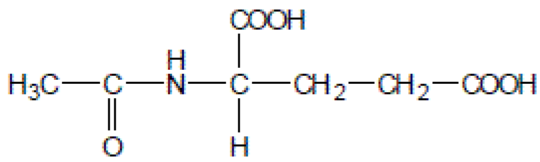
In (e), do not penalise a slip in the number of carbons in the -CH_2CH_2- chain, but all must be bonded correctly

NB two ester groups

allow NH_2– or $^+NH_3$–

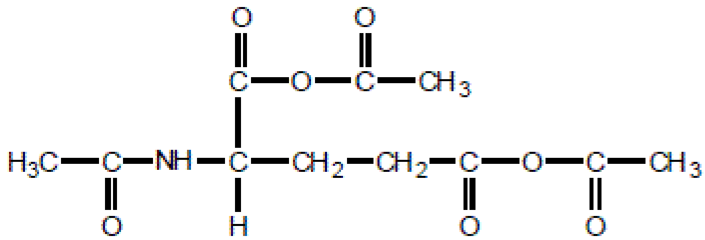
1

(iii)



In 4(e), do not penalise a slip in the number of carbons in the -CH_2CH_2- chain, but all must be bonded correctly

allow anhydride formation on either or both COOH groups (see below) with or without amide group formation



1

(f) **M1** phase or eluent or solvent (or named solvent) is <u>moving or mobile</u>

1

M2 stationary phase or solid or alumina/silica/resin

1

M3 separation depends on balance between solubility or affinity (of compounds) in each phase

OR

different adsorption or retention

OR

(amino acids have) different R_f values

OR

(amino acids) travel at different speeds or take different times

1

[13]