1. An unknown hydrocarbon, X, is composed of four carbons. A known mass of this hydrocarbon X is placed in a 250 mL volumetric flask and made to the mark with ethanol to form a 0.0500 M solution.

   4 X 20.00 mL aliquots were taken from the volumetric flask placed in four separate c100 mL conical flasks and titrated against a 0.100 M Br_2 solution. The solution in the conical flask remained clear until the end point was reached at which point the solution turned brown. An average titre of 10.01 mL was achieved.

a. Is the hydrocarbon saturated or unsaturated? Justify your answer with a calculation. All working out must be clearly shown in the space below. *3 marks*

Unsaturated ---- 1 mark

The brown Br_2 solution turned clear as it reacted with the hydrocarbon solution.

$n_{\text{hydrocarbon in the conical flask}}$ = C X V = 0.0500 mol/L X 0.0200 L = 0.001
Find the mol of Br_2 that reacted with the hydrocarbon in the conical flask
n_{bromine} = C X V = 0.100 X 0.01001 = 0.001

------ 1 mark for calculations of mol

Simplest ratio of Hydrocarbon to Br_2 => 1 : 1 ----- 1 mark
The hydrocarbon has one carbon-to-carbon double bond (C=C)

b. Below is an organic pathway, fig. 1, starting with hydrocarbon X and the spectra of some of the compounds.

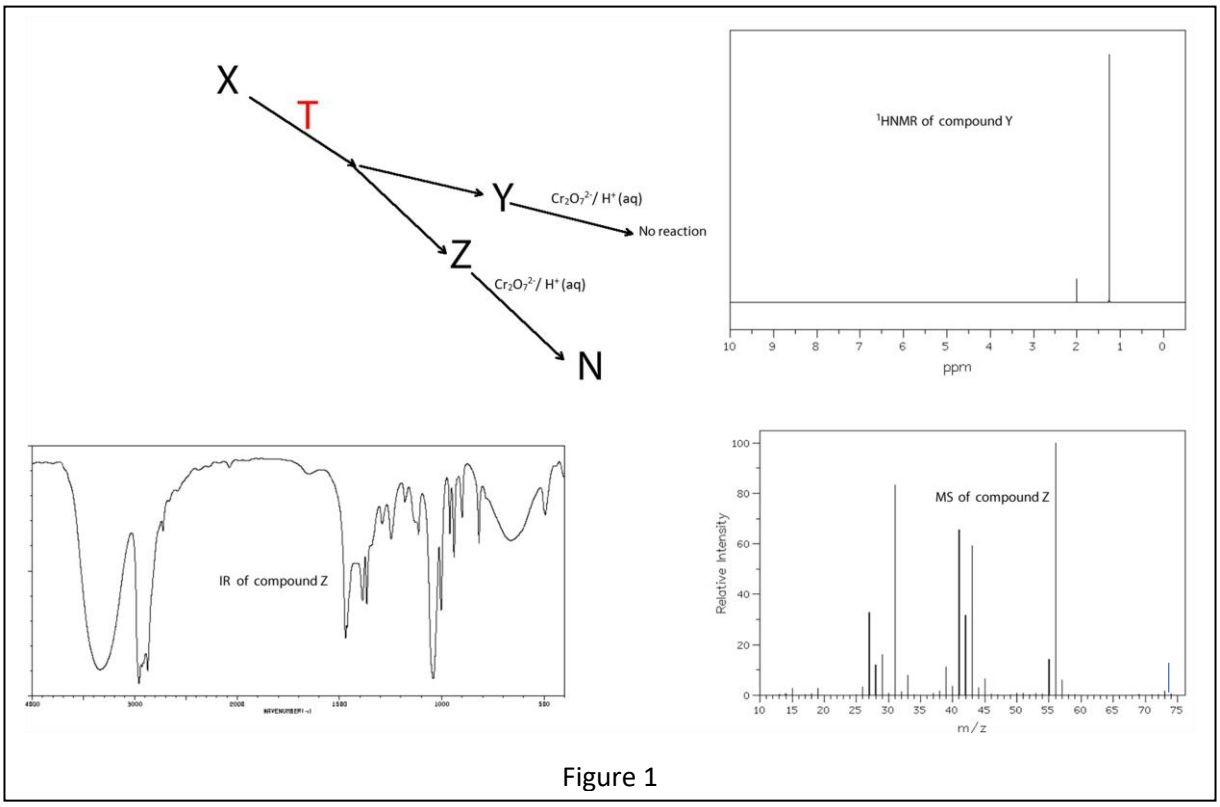
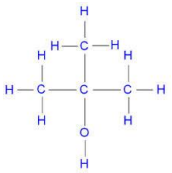


Figure 1

i. Identify the conditions and reagents at T. *$H_3PO_4(s)$, H_2O, 300°C* *1 mark*

ii. A further reaction of compound Y with $Cr_2O_7^{2-}$ in an acidic solution is not possible. In the space below, draw the structural formula and name compound Y *2 marks*

Compound Y __*2-methylpropan-2-ol*_____



It has to be a tertiary alcohol because tertiary alcohols do not undergo oxidation with oxidants such as $Cr_2O_7^{2-}$ and MnO_4^- in acidified solutions.
The ^{1}HNMR indicates only two hydrogen environments which is consistent with the structure of 2-methylpropan-2-ol

iii. To what class of organic compounds does compound Y belong to. *1 mark*

Y _____*Tertiary alcohol*_____

iv. An excess amount of $Cr_2O_7^{2-}$ is reacted with compound Z to form compound N. Give the IUPAC name for compound N and identify the class of organic compounds that N belongs to. *2 marks*

IUPCAC name_____*2-methylpropanoic acid*_____-

Class of organic compounds_____*carboxylic acids*_____

v. After completing a purifying technique to isolate compound N, a student suggested that N might not be a pure substance as it may be contaminated with compound Z . Provide a test that can be conducted to determine the presence of Z and clearly outline the outcomes of the test that shows the presence of Z. *2 marks*

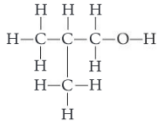
Add $Cr_2O_7^{2-}$ ions in an acidified solution ---- 1 mark
Addition of orange acidified $Cr_2O_7^{2-}$ ions should turn the solution green ----- 1 mark as the alcohol reduces the orange CrO_7^{2-} to green Cr^{3+}
N (carboxylic acid) should not react with with CrO_7^2 /H^{+-}

vi. Give the structural formula of the fragment responsible for the peak at 31 m/z in the mass spectrum of compound Z? *1 mark*

_____*$[CH_2OH]^+$*_____

vii. Give the IUPAC name and structure for compound Z in the space provided below.

Compound Z

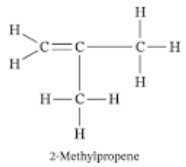


2-methylpropan-1-ol

2 *marks*

viii. Give the IUPAC name and structural formula of compound X in the space below.

Compound X



2-Methylpropene

2 marks

ix. In the ^{1}HNMR spectrum of compound Z, identify the number and type of signals observed. For instance, specify the presence of signals such as 2 triplets, 1 singlet, etc.

Correct number of each signal split ----- 1 mark
Correct type of splitting ---- 1 mark
2 X doublets, 1 X nonet, 1 X singlet.

2. Cyclooxygenase is an enzyme responsible for producing prostaglandins, which trigger inflammation and increase pain sensitivity. Figure 2 illustrates how two different drugs interact with cyclooxygenase. Aspirin chemically modifies the enzyme by reacting with its active site to form a permanent covalent bond, while ibuprofen blocks the entry of arachidonic acid into the active site by forming temporary, reversible bonds with the acitve site.

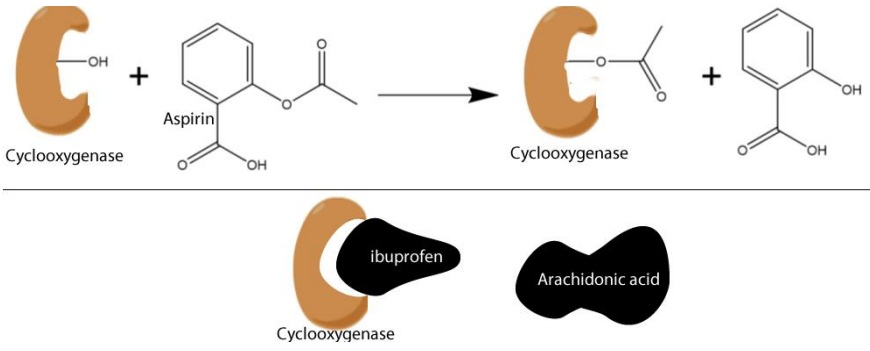


Figure 2 – aspiring and ibuprofen interactions with cyclooxygenase

a. On the set of axes shown in fig 3 draw a clearly labelled graph of a reaction catalysed by: *3 marks*

i. cyclooxygenase. *----- 1 mark*
As the concentration of substrate (arachidonic acid) increases the rate plateaus at level "A" as the active site is swamped with susbstrate.

ii. cyclooxygenase with aspirin *----- 1 mark*
Aspirin initially competes for the active site but once attached to the active site it irreversibly disables the active site.

iii. cyclooxygenase with ibuprofen. *----- 1 mark*
Ibuprofen will slow the rate down initially as it competes with arachidonic acid for the active site but is outcompeted as the concentration of substrate increases.

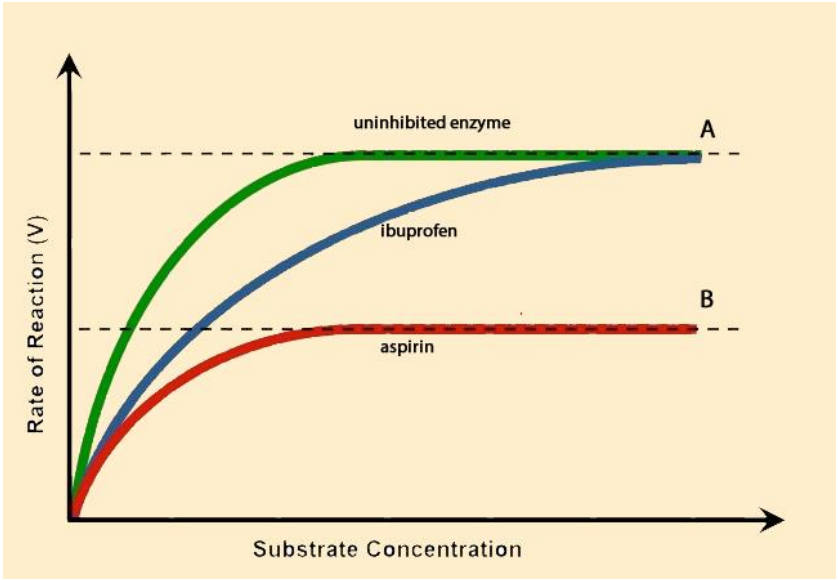


Figure 3

b. Clearly define the term "competitive inhibitor" and explain why aspirin and ibuprofen are classified as competitive inhibitors. *3 marks*

Competitive inhibitors compete for the active site of an enzyme
This type of inhibition can generally be overcome with an increase in substrate concentration ----1 mark
Ibuprofen is considered a competitive inhibitor because it compete for the active site of the cyclooxygenase enzyme, which is also the binding site for the enzyme's natural substrate, arachidonic acid. Increasin the concentration of substrate cause the ibuprofen to be out competed and thus overcoming the inhibition ----- 1 mark

Aspirin even though it initially competes with the substrate for the active site it irreversibly disables the active site and hence the inhibition can not be overcome by an increase in substrate concentration. ------ 1 mark

3. The three substances ibuprofen, paracetamol and aspirin are shown below in fig.4.

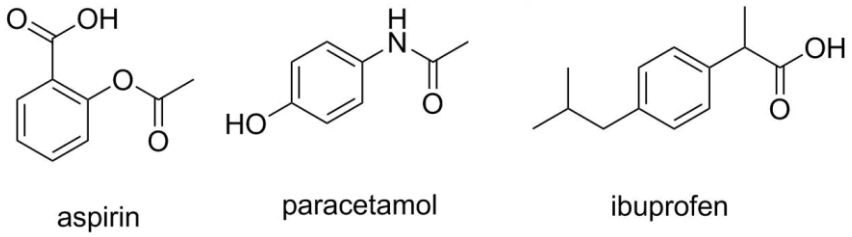


Figure 4

A solution containing the three substances was placed in a reverse phase HPLC column, where the stationary phase is non-polar and the mobile phase is polar.

The chromatogram shown in fig. 5 was obtained.

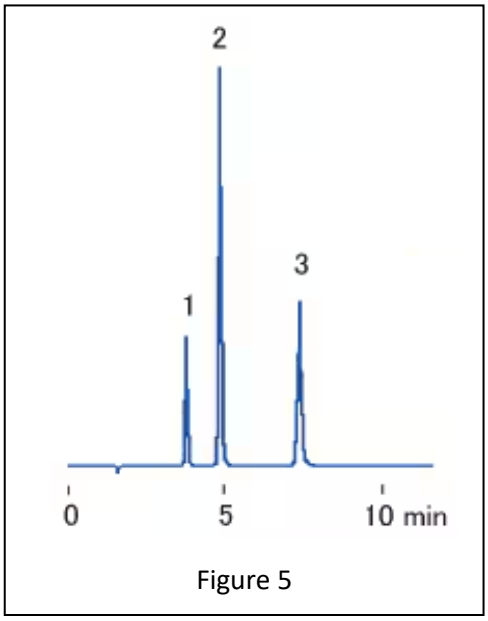


Figure 5

a. Identify the compound that belongs to each peak . *3 marks*

1. *paracetamol (most polar)*
2. *_aspirin_____*
3. *ibuprofen (least polar)*

b. Which substance is present in the highest concentration? *1 mark*

_____2 or aspirin ___

c. Explain how each of the following changes to the column would alter the chromatogram in Fig. 5, and provide a justification for your answer.

i. Smaller beads used as the stationary phase.

Smaller beads increase the surface area with which the molecules interact with the stationary phase, thus slowing the progress of the non-polar molecules through the column to a greater extent ------- 1 mark
We should expect to see the peak for ibuprofen, being the least polar, to move further to the right then the peaks of aspiring and paracetamol. ---- 1 mark

ii. Pressure driving the solution through the column was doubled.

Increasing the pressure speeds the passage of the particles through the column.

------ 1 mark
This may have any of the following impacts. ---- 1 mark only one needs to be mentioned

- It may increase the width and therefore the resolution of each peak as particles have less time to interacts with the stationary phase and separate out.

- It will reduce the retention times of all particles as they have less time to interact with the stationary phase.

iii. Temperature of the mobile phase was decreased.

Lower temperatures decrease the kinetic energy of the molecules in the mobile phase, leading to stronger interactions between the analytes and the stationary phase. ---- 1 mark
This results in longer retention times, as analytes take more time to pass through the column ---- 1 mark

or

This also results in better separation between particles with similar chemical properties. This can lead to better separation and increased resolution between peaks, as particless interact more strongly with the stationary phase.

iv. Normal phase HPLC was used where the mobile phase is non-polar and the stationary phase is polar.

Since the mobile phase is now non-polar the non-polar molecules will interact less with the stationary phase and therefore have lower retention times. ----- 1 mark
The peaks will be reversed the ibuprofen will now have the lowest retention time whilst the paracetamol will have the longest retention time. ----- 1 mark

d. The chromatogram shown in fig 6 was conducted on a different HPLC column under totally different conditions.

i. Substance 2, from the chromatogram shown in fig 5, had a retention time of 5 minutes. Can we be sure it is present in this mixture? Justify your answer.

Although retention time is a useful metric for identifying an analyte in HPLC, it is most reliable when pure samples of the analyte have been run through the same column under identical conditions. ------- 1 mark

When using a different column or different experimental conditions, the retention times can vary. Consequently, if a substance has a similar retention time to another known compound under different conditions, it is not sufficient to confirm its identity without further verification. ---- 1 mark

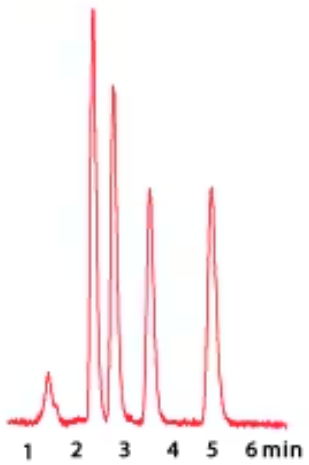


Figure 6

Therefore, if substance "2" shows a similar retention time but was run under different conditions or a different column, it cannot be conclusively identified as the same substance based solely on retention time. ---- 1 mark

4. Consider the molecule of ibuprofen pictured in fig 7.

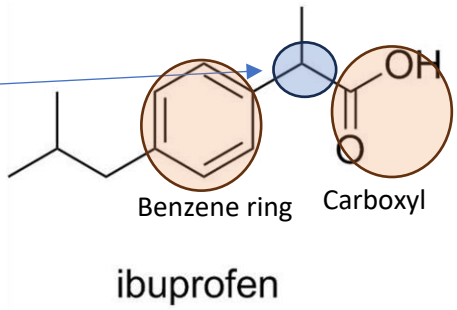


Figure 7

a. How many chiral carbons are present in ibuprofen?
_____*1*_____

b. How many optical isomers must the manufacturer of this product test for harmful side effects in Humans? *1 mark*
_____*2*_____

c. Define an optical isomer.

An optical isomer is one of a pair of stereoisomers that are non-superimposable mirror images of each other. These isomers have identical physical properties but differ in their interaction with plane-polarised light.
Must mention non-superimposable and rotate plane-polarised light.

d. Circle and label two functional groups in fig. 7 above.
Benzene ring properly circled ----- 1 mark
Carboxyl group properly circled ---- 1 mark

e. A chiral molecule has two different optical isomers (enantiomers). Complete the table below by identifying if the enantiomers behave in similar or different ways to the following . Circle the appropriate response. *7 marks*

Condition	Enantiomer A	Enantiomer B
Interaction with a strong acid	Different reaction Identical reaction	Different reaction Identical reaction
Reaction with a strong base	Different reaction Identical reaction	Different reaction Identical reaction
Interaction with a chiral enzyme	Different reaction Identical reaction	Different reaction Identical reaction
Rotation of plane-polarized light	Rotates polarized light clockwise Identical rotation of polarized light	Rotate polarized light anticlockwise Identical rotation of polarized light
Reaction in a chiral solvent	Different reaction Identical reaction	Different reaction Identical reaction
Melting point in an achiral environment	Different MP Identical MP	Different MP Identical MP
Taste or smell perception	Different / Identical	Different / Identical

5. A student is tasked with determining the concentration of acetic acid in a vinegar solution. A 25.0 mL sample of the vinegar (acetic acid) was placed in a 250.0 mL volumetric flask and made to the mark using distilled water. Four 25.0 mL aliquots of the diluted acid solution were transferred into four conical flasks with 2 drops of an appropriate indicator. The solution in each conical flask was titrated against a standard solution of sodium hydroxide (NaOH) of concentration 0.100 M.

The following titres were obtained

- Trial 1: 22.10 mL
- Trial 2: 22.00 mL
- Trial 3: 22.19 mL
- Trial 4: 22.05 mL

a. Write a balanced chemical equation for the reaction taking place in the conical flask.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
----- 1 mark correct formulae
---- 1 mark for states and balanced eqn.

b. Calculate the average titre. Show all working out *2 marks*
_____22.05 mL_____
----- 1 mark for correct average titre
---- 1 mark for using concordant results

c. Calculate the amount, in mol, NaOH in an average titre. Give the answer to the right number of significant figures. 2 marks

$N_{NaOH} = C \times V = 0.100 \times 0.02205 = 2.21 \times 10^{-3}$
----- 1 mark for correct value
---- 1 mark for correct number of significant figures

d. Calculate the mol of acetic acid in the volumetric flask. *2 marks*

$n_{HCl} = 2.21 \times 10^{-3} \times (250/25) = 2.21 \times 10^{-2}$

---- 1 mark for using the appropriate multiplying factor
---- 1 mark for using correct mol of HCl

e. Calculate the concentration, in %w/v, of acetic acid in the vinegar. *3 marks*

Mass of HCl in the conical flask = $2.21 \times 10^{-2} \times 36.5 = 0.807$ g --- 1 mark
mass per mL = 0.807 / 25.0 = 0.0323 g/mL ----- 1 mark
correct value %w/v = 3.23%w/v ---- 1 mark

f. The indicator used by the student during the titration was methyl orange. Explain whether the use of methyl orange is appropriate for this titration, and discuss how the choice of this indicator could affect the validity of the results obtained.

Methyl orange changes colour from red to yellow at pH range 3.1 – 4.4. ---- 1 mark
The colour change will indicate that the end point was reached earlier with a lower titre than the true value. -------- 1 mark
This would make the results invalid ----- 1 mark

g. Sodium hydroxide is not considered a primary standard.

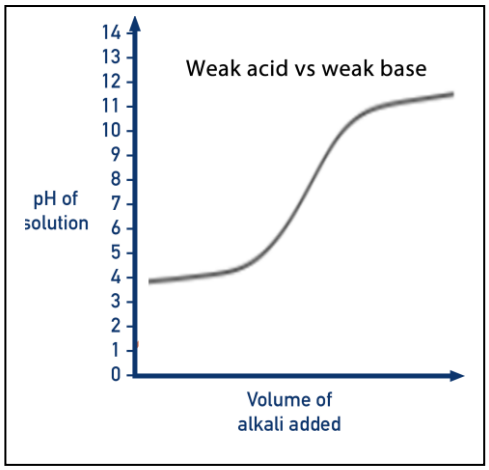
i. Define what is meant by a primary standard and list four essential criteria that a substance must meet to be considered a primary standard.

A primary standard is a chemical substance used to prepare standard solutions in analytical chemistry. ----- 1 mark
Essential criteria for a substance to be considered a primary standard include:
***High Purity**: The substance must be of known and consistent purity. It should be available in a form that is pure enough to ensure accurate and reproducible results.*
***Stability**: The substance should be chemically stable over time and not degrade or change in composition under normal storage conditions. It should remain consistent in quality and concentration during its use.*
***Non-Hygroscopic**: The substance should not absorb moisture from the air or react with gases in the air, which could alter its mass and thus affect the accuracy of measurements.*
***Accurate and Reproducible**: The substance should have a well-defined and known chemical formula, allowing for precise determination of its molar mass and concentration. It should provide consistent results when used in titrations or other quantitative analyses*
------ 1 mark for two correct
------ 2 marks for four correct

ii. Although NaOH is not a primary standard, a solution of NaOH can still be used as a standard solution. Explain how this is achieved and why it is important for ensuring accurate titrations.

NaOH is not a primary standard as it absorbs moisture from the air and becomes impure. Thus weighing a sample of NaOH does not accurately reflect the mol of NaOH present. ---- 1 mark
However if a solution of NaOH is titrated with an acidic standard solution to determine the concentration of NaOH accurately then the NaOH solution can be used as a standard solution. ----- 1 mark

h. A student proposed using sodium bicarbonate ($NaHCO_3$), which is considered a primary standard, to make a standard solution with which to titrate an unknown solution of acetic acid (CH_3COOH). Assess the validity of this suggestion. Discuss whether $NaHCO_3$ is suitable for this titration and address any potential issues that might occur. Use the provided space to draw a pH curve to support your explanation.



----- 1 mark for an appropriate curve showing no steep rise on the pH scale and starting from a low pH relevant to weak acid and plateauing at a pH relevant to a weak base.
----- 1 mark for suggesting that no indicator can clearly give and end point close to the equvalence point due to the lack of a sudden change in pH producing a steep section to the graph.
----- 1 mark results are therefore invalid.

i. Explain the difference between :

- A burette and pipette

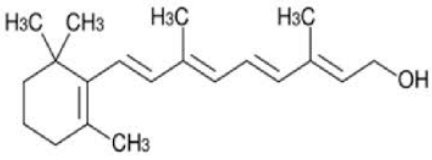
  A pipette is an instrument that dispenses an accurate, fixed volume of liquid
  ------ 1 mark
  A burette is an instrument that dispenses an accurate, variable volume of liquid
  ----- 1 mark

- An aliquot and a titre.

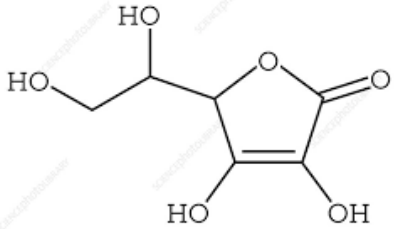
  Titre – minimum volume of a titrant solution required to reach the end point.
  ---- 1 mark

  Aliquot – an accurate volume of sample delivered by a pipette.
  ----- 1 mark

6. A pharmaceutical manufacturer has accidentally mixed a batch of vitamin C with vitamin A. The costly error can be remedied by using a purifying technique called solvent extraction. The structures of both vitamins are shown in fig 7. In the space provided outline a
step-by-step process for the purification of each vitamin from the solid mixture in powder form given that you have a ethanol and hexane at your disposal.



Vitamin A



Vitamin C
$C_6H_8O_6$

Figure 7

Any plausible method is accepted with logical sequential steps that will lead to the purification of both vitamins. Eg
Step1 add the powdered mixture to liquid hexane and mix thoroughly ------ 1 mark

The non-polar vitamin A will dissolve in the hexane whilst the polar vitamin C will remain in solid form ---- 1 mark

Step 2 Filter the solution so that the filtrate passing through the filter paper contains the vitamin A whilst the undissolved vitamin c is trapped in the filter paper. ----- 1 mark

Step 3 Heat the filtrate until all the solvent, hexane, has evaporated and the solid solute, vitamin A , is left. ------ 1 mark
Step 4 collect the residue left in the filter paper, which is vitamin C contaminated now with hexane and undissolved vitamin A. Heat it to evaporate the unwanted hexane and dissolve it in ethanol. ----- 1 mark
Step 5 Any undissolved vitamin A that may have been present from the first extraction should now remain in the solid form and be trapped in the filter paper during filtration. ---- 1 mark

Step 6 Evaporate the ethanol by mild heating so as to leave the pure vitamin C. ---- 1 mark

b. Describe the difference between steam distillation and fractional distillation and suggest one appropriate use for each process.

Steam distillation is a separation process used to distil temperature-sensitive compounds, such as essential oils like lavender oil, or organic compounds, that decompose at high temperatures. The compound is co-distilled with steam, allowing it to vaporize at a lower temperature than its boiling point. The vapour is then condensed to separate the desired product. ---- 2 marks

Fractional distillation is a process used to separate a mixture of liquids with different boiling temperatures such as the components of crude oil. The mixture is heated, and the components are separated based on their boiling points using a fractionating column, which allows for multiple evaporation-condensation cycles. This gives a greater degree of separation of substances with boiling temperatures that are very close. ---- 2 marks