RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	6								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9729/03

Paper 3 Free Response

18 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **15** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) (i) Phosphorus reacts with

- F_2 to produce PF_5 as the only product.
- Cl_2 to give both PCl_5 and PCl_3.
- Br_2 and I_2 to give PBr_3 and PI_3 respectively.

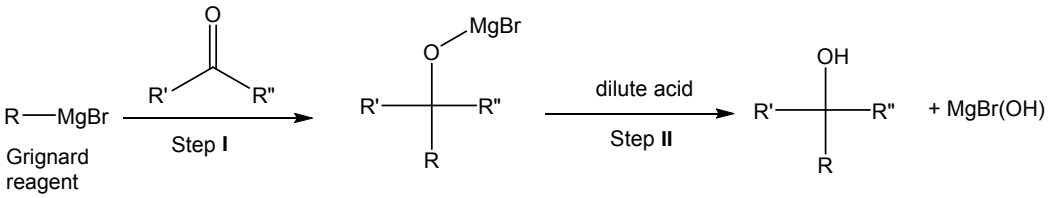
With reference to the *D*ata *B*ooklet, explain the difference in oxidation states of phosphorus in the phosphorus-containing compounds formed. **[3]**

(ii) The table below gives the pK_a values of the hydrogen halides.

hydrogen halide	pK_a
HF	3.17
HC*l*	–7
HBr	–9
HI	–10

Explain the trend in the pK_a values. **[2]**

(b) The following reaction scheme shows the formation of an alcohol via the Grignard reaction.



(i) Suggest the type of reaction undergone in Step **II**. **[1]**

(ii) Suggest the identities of a suitable carbonyl compound and Grignard reagent to form 1-methylcyclohexan-1-ol. **[2]**

(iii) The reaction between the carbonyl compound and the Grignard reagent suggested in **(b)(ii)** is a nucleophilic addition.

Propose the mechanism for this reaction, assuming that the Grignard reagent (R-MgBr) produces the $:R^-$, as the reacting species to form 1-methylcyclohexan-1-ol. **[3]**

(c) Calcium phosphate, $Ca_3(PO_4)_2$, is a sparingly soluble salt. ..

(i) Write the expression for the solubility product of calcium phosphate. **[1]**

(ii) Given that the solubility of calcium phosphate in water is 1.14×10^{-7} mol dm^{-3}, calculate the solubility product of calcium phosphate, stating its units. **[2]**

(iii) Calculate the solubility of calcium phosphate in the presence of 0.150 mol dm^{-3} of potassium phosphate. **[2]**

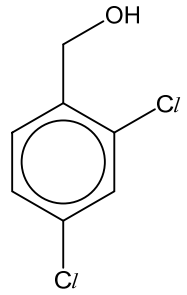
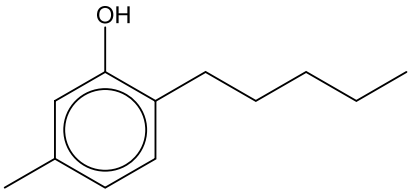
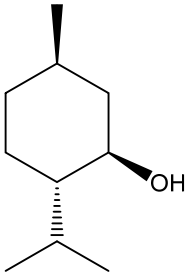
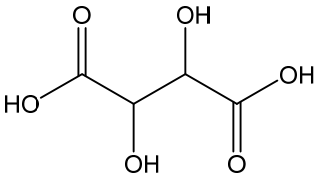
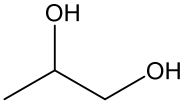
(iv) A saturated solution was prepared by dissolving two sparingly soluble salts, calcium phosphate and calcium sulfate, $CaSO_4$, in tap water. The tap water used was found to be contaminated with trace amounts of SO_4^{2-}.

Explain the impact of the contamination on the solubilities of calcium phosphate and calcium sulfate. **[2]**

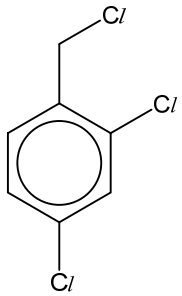
[Total: 18]

2 Strepsils® is a line of throat lozenges used to relieve discomfort caused by mouth and throat infections.

The table below shows the main active and non-active ingredients found in one lozenge.

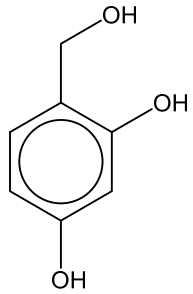
primary active ingredients	2,4-dichlorobenzyl alcohol	
	amylmetacresol	
non-active ingredients	(–)-menthol	
	tartaric acid	
	propylene glycol	

(a) 2,4-dichlorobenzyl alcohol can be prepared from 2,4-dichlorobenzyl chloride (shown below) via a one-step synthesis.



(i) State the reagent and condition for the reaction. **[1]**

(ii) Explain why the molecule below will not be obtained as a by-product.



[1]

(iii) A student carries out the synthesis using the reagent in **(a)(i)** that has been contaminated with sodium ethoxide.

Draw the structure of the possible by-product that may result. **[1]**

(iv) Describe a simple chemical test that can distinguish between 2,4-dichlorobenzyl alcohol and amylmetacresol.

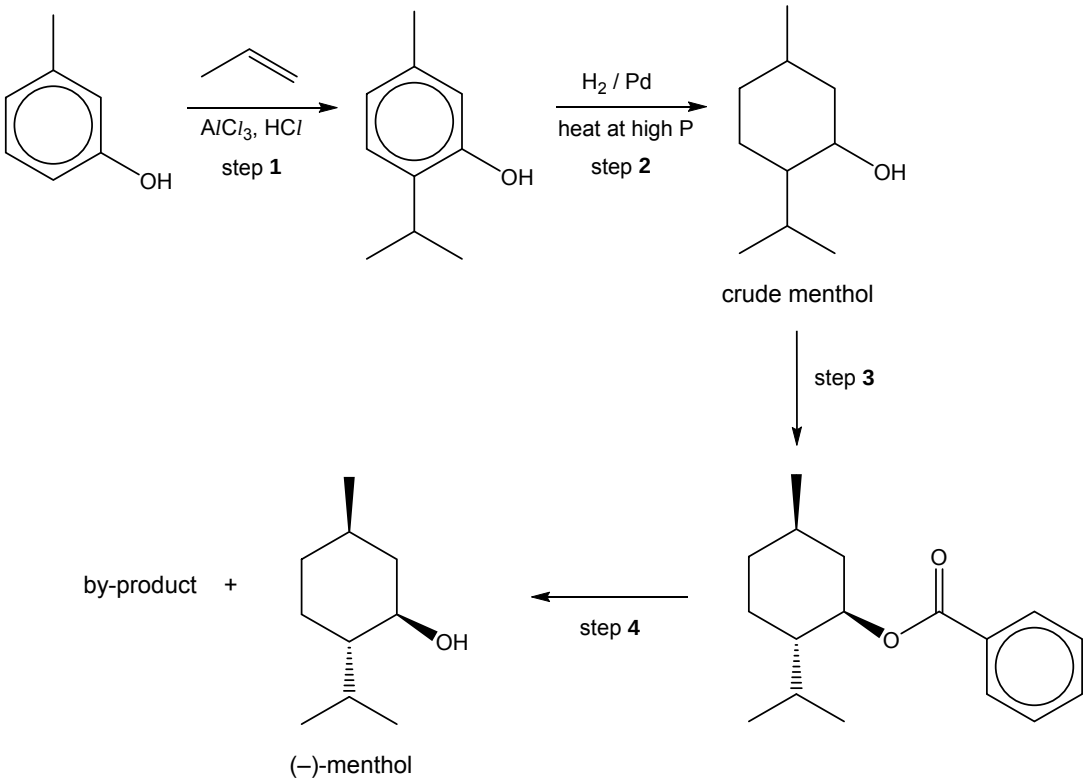
State the expected observations for each compound. **[2]**

(b) Arrange amylmetacresol, menthol and tartaric acid in increasing order of acidity.

Explain your answer.

You only need to consider the first acid dissociation of tartaric acid. **[3]**

(c) Menthol is produced commercially via the Haarmann-Reimer process. A modified version of the process is shown below.



(i) Suggest the types of reactions occurring in steps **1** and **2**. **[2]**

(ii) Given that crude menthol does not exhibit optical activity, determine the number of enantiomers crude menthol has.

Hence, calculate the proportion of each enantiomer formed. **[2]**

(iii) Draw the structure of the by-product formed. **[1]**

(d) (i) A 25.0 cm^3 solution of 0.0100 mol dm^{-3} tartaric acid in a conical flask is titrated with 0.0100 mol dm^{-3} NaOH(aq) from a burette.

Given that pK_{a1} = 2.89 and pK_{a2} = 4.40, and ignoring the auto-ionisation of water, determine the pH of the solution when the following volumes of NaOH(aq) are added:

- 0.00 cm^3
- 12.50 cm^3
- 50.00 cm^3

[4]

(ii) When the second equivalence point is reached, the solution is heated to dryness. The residue left is a white solid.

Explain, using structure and bonding, why the boiling point of the solid residue is higher than that of tartaric acid. **[2]**

(e) Propylene glycol can be produced from gaseous propene.

(i) State the reagent and condition required for propene to form propylene glycol. **[1]**

(ii) When propene is reacted with the reagent in **(e)(i)** under a different set of condition, an organic liquid and an inorganic gas are formed.

Draw the displayed formula of the organic liquid. **[1]**

(iii) The inorganic gas is collected in an evacuated glass bulb at 30 °C. It is found that the mass of the 500 cm^3 glass bulb increased by 0.36 g.

Identify the inorganic gas and determine the pressure of the gas collected. **[2]**

[Total:23]

3 Transition elements and their compounds have found many applications in industries as both homogeneous and heterogeneous catalysts.

For example, nickel is used as a catalyst for hydrogenation of alkenes and vanadium pentoxide (V_2O_5) is used in the manufacture of sulfuric acid.

(a) Explain what is meant by the term *heterogeneous catalyst*. **[2]**

(b) The following table list the colours of various vanadium ions in aqueous solution:

ion	oxidation state	colour
V^{2+}	+2	violet
V^{3+}	+3	green
VO^{2+}	+4	blue
VO_3^-	+5	yellow

When a sample of yellow VO_3^- solution is mixed with an excess of zinc powder, the solution undergo a series of colour changes over time.

Using relevant $E^{\ominus}$ values from the *Data Booklet*, account for all the observed colour changes. There is no need to write any balanced chemical equation. **[3]**

(c) A similar process as **(b)** was carried out as follows:

100 cm^3 of 0.0500 mol dm^{-3} of $NaVO_3$ is reacted completely with zinc powder. The final colour of the solution is blue-green.

25.0 cm^3 of this blue-green solution requires 20.63 cm^3 of 0.0200 mol dm^{-3} of $KMnO_4$ for complete reaction under acidic conditions.

(i) There are 2 different vanadium containing ions in this blue-green solution, of which one of them is VO^{2+}.

State the identity of the other ion. **[1]**

(ii) Write a balanced chemical equation between VO^{2+} and MnO_4^- under acidic conditions. **[1]**

(iii) Calculate the amount of $KMnO_4$ that has undergone reaction. **[1]**

(iv) Given that:

- 5 mol of the ion identified in **(c)(i)** reacts exactly with 2 mol of $KMnO_4$
- x mol of VO^{2+} is present in 25.0 cm^3 of the blue-green solution

Show that the total amount of $KMnO_4$ reacted = $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x$.

Hence, calculate the mass of zinc powder added to the original mixture. **[4]**

(d) Vanadium pentoxide can be used as a catalyst in a reaction known as oxidative esterification. In this reaction, an aldehyde can react with an alcohol or phenol to form an ester:

$$R_1{-}CHO + HO{-}R_2 \rightarrow R_1{-}COO{-}R_2 + 2[H]$$

Compound **A**, $C_8H_8O_2$ undergoes oxidative esterification in the presence of V_2O_5 catalyst to form a neutral compound **B**, $C_8H_6O_2$. On heating **B** under reflux with NaOH(aq), the sodium salt of compound **C**, $C_8H_8O_3$, was formed. Compounds **A**, **B** and **C** reacts with $LiAlH_4$ in dry ether to form compound **D**, $C_8H_{10}O_2$, while compounds **A**, **C** and **D** are able to decolourise aqueous bromine.

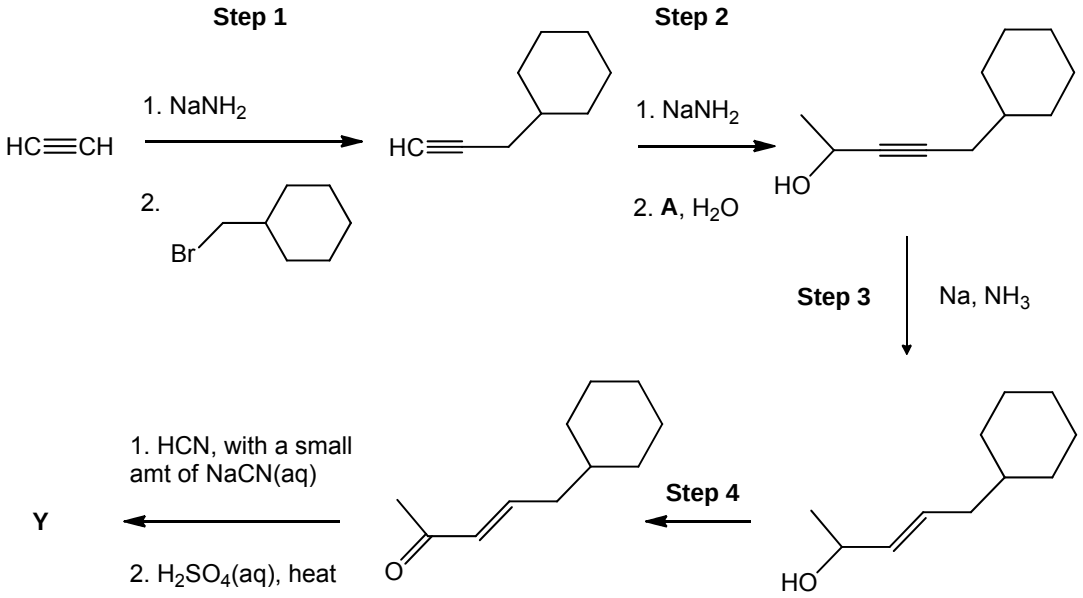
Draw the structures of **A**, **B**, **C** and **D**, and explain your reasoning. **[7]**

[Total: 19]

Section B

Answer **one** question from this section.

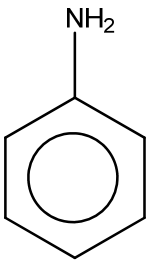
4 **(a)** Compound **Y** can be obtained from ethyne using the following synthesis pathway:



(i) Given that $HC{\equiv}C^-$ is formed, state the role of $NaNH_2$ in Step **1**. **[1]**

(ii) Name and outline the mechanism for the reaction in Step **1** Part **2**. Show relevant lone pairs and dipoles, using curly arrows to indicate the movement of electron pairs. **[3]**

(iii)



phenylamine

Suggest why phenylamine is unable to carry out the role of sodium amide, $NaNH_2$, in Step **1**. **[1]**

(iv) Suggest the reagent **A** in Step **2**, and reagents and conditions for Step **4**. **[2]**

(v) Draw the structure of Compound **Y**.

Explain why HCN reacts with C=O but not with C=C in the same compound. **[3]**

(b) Sodium borohydride, $NaBH_4$, is another inorganic sodium compound that is often used in organic synthesis. It is also used to make the prototypes of direct borohydride fuel cell. Aqueous sodium borohydride undergoes catalytic decomposition to produce the hydrogen needed for the fuel cell.

$$NaBH_4(s) + 2H_2O(l) \rightarrow NaBO_2(s) + 4H_2(g) \qquad \Delta H^{\ominus} = -210 \text{ kJ mol}^{-1}$$

Boron is similar to carbon in its ability to form stable covalently bonded molecular network.

(i) What do you understand by the term *lattice energy*? **[1]**

(ii) With the aid of an energy cycle, use the following data and appropriate data from the *Data Booklet* to calculate the lattice energy of sodium borohydride.

enthalpy change of formation of $H_2O(g)$	-241 kJ mol^{-1}
standard enthalpy change of atomisation of Na	$+107$ kJ mol^{-1}
standard enthalpy change of formation of $BH_4^-(g)$	-78.2 kJ mol^{-1}
standard enthalpy change of vapourisation of $H_2O(l)$	$+40.8$ kJ mol^{-1}
standard enthalpy change of formation of $NaBO_2(s)$	-1059 kJ mol^{-1}

[5]

(c) A breathalyzer does not directly measure blood alcohol content or concentration, which involves the analysis of blood sample. It measures the blood alcohol content by measuring the amount of alcohol in the exhaled breath instead.

Ethanol is a volatile compound. In lungs, the ethanol dissolved in blood can change its state from liquid to gaseous and it is exhaled with air. When a user breathes into the breathlyzer, the ethanol in the exhaled air is passed through a solution of potassium dichromate. The ethanol is oxidised to ethanoic acid.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

The direct oxidation of ethanol by potassium dichromate is carried out in an electrochemical cell and the current generated can be used to estimate the alcohol content of blood.

(i) When a user breathes into the breathlyzer which contains potassium dichromate, a current of 0.12 A is recorded for 1 min.

Determine the mass of ethanol per breath. **[3]**

(ii) A partition ratio of "2100:1" is used to estimate the blood alcohol content in blood from the amount of alcohol in a breath. This partition ratio implies that 2100 cm^3 of breath contains the same amount of ethanol as 1 cm^3 of blood.

Given that the volume of exhaled air in **(c)(i)** is 65 cm^3, calculate the amount of ethanol per cm^3 of blood. **[1]**

[Total: 20]

5 **(a)** Most plants do not thrive in highly acid or highly alkaline soil, though a few have adapted to such extremes. Soil pH may be adjusted using suitable chemicals.

Describe, with the aid of balanced equations, the actions of acid and/or base on the oxides of magnesium and phosphorus, if any.

Hence, suggest why oxides of phosphorus should not be used to adjust soil pH. **[3]**

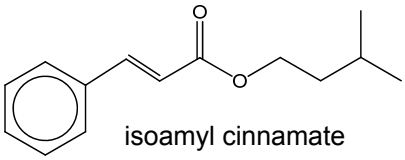
(b) RVCM®Calmag is a solid fertiliser containing calcium nitrate and magnesium nitrate in a fixed mole ratio of 2:1.

Two equal masses of fertiliser samples were heated at 575 K and 949 K respectively until there is no more change to their masses. For both samples, brown fumes were observed and a gas that rekindled a glowing splint was evolved.

(i) Write a balanced equation to represent any one reaction that occurred. **[1]**

(ii) The loss in mass for **sample 1** heated at 949 K is three times that of **sample 2** heated at 575 K. Account for this observation. **[3]**

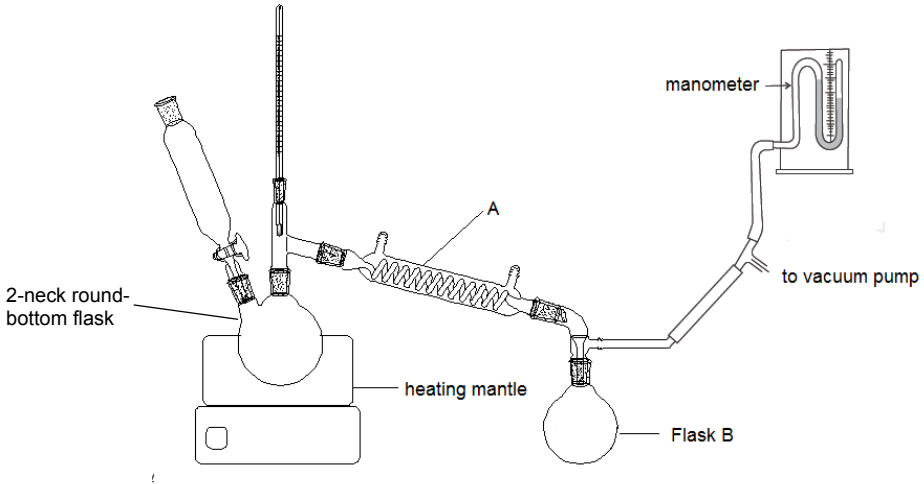
(c) Isoamyl cinnamate extracted from several types of trees from the genus *Cinnamomum* has a balsamic odour, reminiscent of cinnamon with an amber note.



isoamyl cinnamate

Isoamyl cinnamate can be oxidised to give different products depending on the choice of oxidising agents and the reaction conditions. A pure sample of isoamyl cinnamate was heated with acidified potassium dichromate using the apparatus setup as shown in **Figure 5.1**.

Figure 5.1



(i) State the function of the apparatus **A**. **[1]**

(ii) Name and write balanced equations for two major reactions that occur in the 2-neck round-bottom flask.

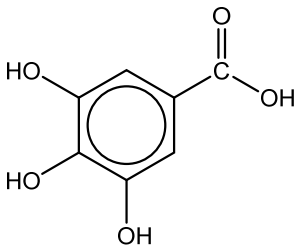
You may use [O] or [H] to balance the equations. **[2]**

(iii) Identify the first organic compound that is likely to be collected in flask **B**. **[1]**

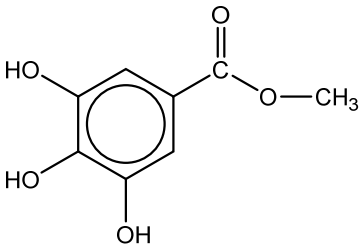
(iv) Draw the skeletal structures of all the organic products formed if acidified potassium manganate(VII) is used instead of acidified potassium dichromate. **[2]**

(d) Pu'erh (Chinese: 普洱) is a variety of fermented tea produced in Yunnan province, China. Black Pu'erh tea is known to contain more gallic acid than green Pu'erh tea. Gallic acid and its derivatives have been reported to elicit antioxidant, anti-cancer and anti-diabetic activities.

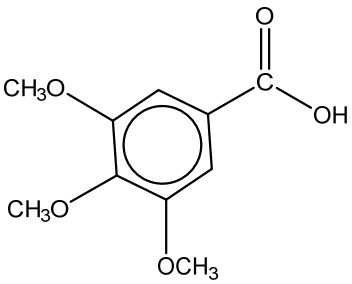
The structures of gallic acid and its derivatives are given below:



gallic acid



methyl gallate



3,4,5-trimethylgallic acid

(i) Gallic acid can dissolve in water and diethyl ether. The partition coefficient for the separation of gallic acid in the two immiscible phases is given below:

$$K_{partition} = \frac{[gallic\ acid]_{aqueous}}{[gallic\ acid]_{diethyl\ ether}}$$

In an experiment, 1.00 g sample of pure gallic acid was dissolved in 100 cm^3 of water. This aqueous solution of gallic acid and 50.0 cm^3 of diethyl ether were placed in a separatory funnel which is shaken to mix well. The mixture was then allowed to stand for 30 minutes before the two immiscible layers were separated.

It was found that 20.0 cm^3 of the aqueous layer required 20.25 cm^3 of 0.180 mol dm^{-3} sodium hydroxide for complete neutralisation.

Calculate the amount of gallic acid in each layer, and hence the partition coefficient. **[3]**

(ii) A sample containing both gallic acid and 3,4,5-trimethylgallic acid are dissolved in 50 cm^3 of diethyl ether.

Describe and explain how would you modify the solvent extraction method in **d(i)** such that mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer. **[2]**

(iii) Suggest a chemical test to distinguish methyl gallate from gallic acid. **[2]**

[Total: 20]

- End of Paper -

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