STRUCTURAL ELUCIDATION OF UNKNOWN ORGANIC COMPOUND 'A' USING PHYSICAL, CHEMICAL AND SPECTROSCOPIC METHODS

BY

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A project carried out as part of 4th year B. Pharm of course 1985/86 in partial fulfilment for the degree of Bachelor of Pharmacy, University of Nairobi

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1985/86

DEDICATION

This work is dedicated to my parents Mr & Mrs Onesmus Kamau Mahiu.

> " Those who aspire not to guess and devine, but to discover and know, who propose not to devise mimic and fabulous worlds of their own, but to examine and dissect the nature of this very world itself, must to go facts themselbes for everything."

Source?

ACKNOWLEDGEMENTS

I am very much indebted to Mr. J. O. Ogeto, Lecturer in Pharmaceutical Chemistry, Department of pharmacy, for his tireless suggestions, encouragements and supervision both outside and outside the Laboratory. I am also thankful for his suggestions concerning the ammendment of the original manuscript.

My thanks also extend to the ~~tecterical~~ technical staff, Mr. I. G. Mureithi and Mr. Joe Thuranira who never got tired in helping me. Special thank also go to Mr. Mwalughu who made sure that I received all the chemicals that I needed in my work. I cannot forget my colleagues for the conclusive atmosphere that facilitated working.

CONTENTS

Page

ABSTRACT

The compound has been subjected to investigations by chemical, physical and spectroscopic reactions and its structure suggested.

Physical investigations shows the compound to be contains carbon, Hydrogen and Oxygen with a molecular Formula of $C_8H_8O_3$.

After spectroscopic analysis and derivative preparation, the compound was found to be methyl p-hydroxy benzoate. It is commonly known as methylparaben.

Methylparaben is used as a preservative in foods, beverages and cosmetics.

INTRODUCTION

In structural elucidation of an organic compound, the compound to be studied can ~~w~~ either be;

(a) An already known compound as is described in the chemical literature.

(b) A new compound discovered for the first time in the former(a) the investigator is required to identify the compound by showing that its chemical, physical and spectroscopic behavioour agree in all respecteds as those reported in literature.

In the later case (b) the task is to establish the structure of the compound and describe its properties and behaviour, so that later on, it can be identified and recognused by others.

Structural elucidation usually involves a systematic examination of the compound under two main techniques

(a) Physical and chemical tests
(b) Spectroscopic methods

The physical and chemical tests are designed to elicit a fairly comprehensive picture of the chemical behaviour of the unknown compound. These will give the functional groups in the compound and the reactivity of the functional groups.

The spectroscopic methods elicits the behaviour of the compound when subjected to structure and functional group determining waxelengths of the electromagnetic spectrum. Both chemical and spectroscopic information about an unknown compound are sought in an integrated way and each technique more often than not qualifies and supplements the other.

Depending on the chemical state of the sample provided, and analysis starts with purification of the compoodd. This may require separation of compounds o if a mixture, by use of chromutographic, fractional precipitation and fractional distillation techniques whichever would be applicable. If the sample is a mixture of compounds it will show different spots in thin layer chromatography under high resolving solbents.

...

Element analysis by use of the sodium fusion technique, preliminary tests of physical properties ~~loose~~ like melting or boiling points and solubility in various solbents; can give a clue on direction to be taken in subsequent tests. The sodium fusion test gues the elements present in the compound. Generally audic compounds will show solubility in aqueous basic medic. However very weak acids eg olic acids are insoluble in basic aqueous media. Solubility in dilute acid implies that the compound is basic. The absence of say nitrogen in the sodium fusion list eliminates all nitrogen containing organic compounds eg. omines, nitro compounds etc.

Element analysis is followed by spectroscopic methods for confarmation of functional groups present in the compound. Spectroscopic methods which are used are ultraviolet, infrared, Nuclear magnetic resonance and mass spectroscopy. Ultraviolet spe spectroscopy. will show presence of various groups in the compound functional groups Infrared, spectroscopy will indicate presence of various functional groups depending on their absorption frequency. Nuclear magnetic resonance will indicate presence of protons and their positions in the compound. Mass spectroscopy is useful in determining the molecular weight of the compound and its fragmentation patterns.

However final identification of the compound ties on preparing one or more derivatives whose physical properties match those recorded in literature. The change in absorption the in the electromagnetic spectrum of the various derivatives also studied as a confirmatory aid especially if the derivatives are not recorded in literature.

OBJECTIVE

The objective of this work is to try to elucidate the structure of the unknown white powdered compound 'A' using Physical, Chemical and spectroscopic methods.

CHEMICALS AND REAGENTS

CHEMICAL NAME	SUPPLIER	GRADE
Acetic acid, glacial	May and Baker	Laboratory reagent Analar
Acetone	British Drug House	
Acetyl chloride	"	"
Acetic anhydride	May and Baker	Laboratory
Benzoyl chloride	Merk-schuchardt	Chemical for synthesis
Bromine	British Drug House	Laboratory reagent AnalaR
Carbon tetrachloride	"	
Chloroform	Koch-light ltd	AnalaR
Diethyl ether	House and Mc george	Lab. Chemicals
2,4 Dumtropherydhydrazine	British Drug House	AnalaR
Ethanol	House and Mc george	Lab. Chemicals
Ferrous sulphate	"	"
Ferric chloride	May and Baker	"
Conc. Hydrochloric acid	May and Baker	Lab. reagent
Iodine, resublimed	E.T. Monks	"
Lead acetate	May and Baker	Lab. chemicals
Methanol	Koch-light ltd	"
Molybdic acid	British Drug House	Lab. reagent
Conc. Nitric acid	Nepkim and Williams	AnalaR
Potassium bromide	British Drug House	Lab. reagent
Potassium hydroxide pellets	May and Baker	"
Potassium permagnate	House and Mc george	Lab. chemicals
Sodium bicarbonate	E.t. Monks	"
Sodium hydroxide pellets	House and Mc george	"
Sodium metal	Sarabhai. M. Chemicals	Lab. reagent
Conc. suphuric acid	Koch-light Ltd	General purpose reagent.

INSTRUMENTS	MANUFACTURER
Infrared sp 1000 spectrophotometer	Pye Unicam
Ultra-violet Sp 8000 spectrophotometer	Pye Unicam
Melting point apparatus	Gallenkamp.
Test tubes, flasks, measuring cylinders etc.	

REPARATIONS OF TEST SOLUTIONS

1. Ferric chlorule test solution - A 5% w/v solution of Ferric chlorule in water made according to B.p 1973 page A.25.
2. Dilute sodium hydroxide-made according to B.P 1973 page A.46
3. Sulphuric acid, Dilute made according to B.p 1973 page A.50.
4. 0.1N Hydrochloric acid made according to B.P 1973 page A.56.
5. Sodium hydrogen carbonate solution - 5% w/v solution of sodium hydrogen carbonate in water.
6. Bromine solution. A freshly prepared saturated solution of bromine in water.
7. Hydroxylamine hydrochloride - prepared according to BP 1973 page A.28.

8. Ammonium molybdate - prepared according to USP xlx (1975) page 763 but filtered through common filter paper instead of filtering through asbestos filters.
9. Potassium bromide dried in an oven at 60°c for three days.

EXPERIMENTAL DETAILS

Physical Examination of Compound 'A'

TEST	OBSERVATION	INFERENCE
Appearance, smell and taste.	A white crystalline powder with pleasant arematic smell ?	Unknown compound is likely to be Nitro, azo compou dicarbonyls, nitr compounds which a coloured are unlikely to be present.
SOLUBILITY (i) Cold water 0.1 gms of the compound was put into a flask and water added gradually with straking until complete dissolution (ii) Hot water	0.1 gms of the unknown compound dissolved in 200mls of cold water to give a clear solution of neutral pH 0.1 gms of unknown dissolved in 100mls of hot water to give a neutral solution.	The compound is sparingly soluble in water. Neutera of solutions indi te absence of strong acidic an groups in the compound.
Action of dilute acid (hydrochloric acid)	0.1 gms of the unknown was not soluble even on addition of 300mls of dilute hydrocloric acid.	Unknown compound is less soluble dilute acid than in cold water This indicates absence of stron basic. groups eg. most armes
Action of dilute alkali (dilute sodium hydroxide)	0.1 gms of the unknown compound assolved completely in 2mls of dilute sodium hydroxide no gas was evolved. On heating, a white solid material remained.	The unknown is m soluble in dilut alkali than in c water. therefor it is most likel to be acidic-carboxylic acid or phenols and dervatives It cannot be a polyhdric pheno since it did no turn dark on heating.

TEST	OBSERVATION	INFERENCE
Action of bicarbonate	0lgms of the compound dissolved in about 100 mls of delute sodium bicarbonate and no carbenondioxide gas was produced.	Carboxylic auds (excep the higher members) sulphenic acids, and many nitrophenols give positive test and therefore are unlikely to be present. However other acidec compounds eg phenols and h lower carboxylic acids are likely to be present
Action of <u>Heat</u> A small amount of the compound was burned on a crucible.	The compound melted on heating and then burned with a smoky flame. A brown residue remained.	Compounds with high C:H ratios, principally simple aromatic and unsaturated compounds likely to be present.
<u>MELTING POINT</u> using the melting point apparatus	The melting point range was 129-131^{o}c.	The unknown compound is aromatic with melting point range of 129-131^{o}c.

Can you tell what [illegible] from M P ? Nothing

CHEMICAL INVESTIGATION OF UNKNOWN COMPOUND 'A'

THE SODIUM FUSION TEST

METHOD: Fleshly cut sodium metal (rice grain size) was placed in the bottom of a small test-tube. The test-tube was held with a test-tube holder and the sodium was melted over a small flame. 20mg of the unknown was them added. The mixture was heated strongly for 3 minutes and the re-hot tube was plunged into distilled water in a beaker. The resulting solution was then filtered. The resulting filtrate fusion solution was used to test the following:

TEST	OBSERVATION	INFERENCE
(a) Test for Nitrogen About 0.1g of ferrous sulphate was added to 1ml of fusion solution and boiled for 1 min. then acidified with dil. Sulphuric acid	On addition of sulphuric acid, a yellow solution was positive.	Unknown Comp. does not conta Nitrogen. The fore this con rms the absen of an azo com an amine, a n o group and other Nitroge containing compounds A blue-green solution is positive. N--CN--FE(CN) --Fe(Fecn)$_4$ blue
Test for Sulphur (1) Nitroprusside test A small amount of sodium nitroprusside was dissolved in 1ml of cold distilled water and 1ml fusion solution was added	On addition of fusion solution, a reddish brown coloured solution was formed.	Unknown Compo does not cont sulphur. In presence of s hur, a purple colour should have develope (for nitropru ide test) For the lead sulphide test if sulphur wa present

TEST	OBSERVATION	INFERENCE
(i) Lead Sulphide Test About 1ml fusion solution, was acidified with glacial acetic and 1ml lead acetate solution was added	On acidification and addition of lead acetate -ate solution, there was no observable reaction A colourless solution was formed.	In the compound, a black precipitate of lead sulphide should be observed. S--S^{2-}--Pbs black. This confirms the absence of sulphunic acid and other sulphu containing compounds
Test for Halogens About 1ml of fusion solution (test) and 1ml of distilled water (blank) were acidified will 1ml of aqueous nitric acid. 1ml of aqueous Silver nitrate was then added.	On addition of silver nitrate solution, no precipitate was formed. The solutions remained clear. There was no observable difference between test and blank	Unknown compound does not contain halogen otherwise a precipita should have formed.
Test for Phosphorous About 2ml of fusion solution was boiled with 1ml conc. nitric acid and then cooled. Aqueous ammonium mohybdate was then added and test-tube kept in boiling water for 4 minites	There was no precipitate formed. A yellow coloured solution was formed.	The yellow colour could have beere due to decomposing nitric acid. lack of yellow precipitate indicates absence of phosphorou in the unknown compound.
OTHER CHEMICAL TESTS		
Test	Observation	Inference
Action of Bromine Test for unsaturation or easy substitution	The unknown compound dissolved in chloroform decolourised bromine water when a few drops were added. A white precipitate was formed.	Decolournisation of the bromine indicates addition of bromine to a double or triple bond or substitution in an activated aromatic nucleus.
		A white precipitate indicates that a brom dervatone of a phenol may be present. Thus the compound is most likely a phenol with an activated nucleus

TEST	OBSERVATION	INFERENCE
Ferric Chloride Test (test for phenols) The unknown was suspended in aqueous methanol and 2 drops of ferric chloride solution was added.	A dark green coloured solution was formed.	This confirms that the compound is a phenol with activate aromatic nucleus.
Action of Permanganate Test for unsaturation or easy oxidation	The colour of potassium permanganate was not discharged on addition of 2 drops of potassium permanganate.	Unsaturated compounds and other easily oxidized groups are unlikely to be presen Therefore unknown is a phenol with an activated aromatic nucleus.
Action of 2.4 dimiltro phenylhydrazine test for aldehydes or ketones	A clear solution was formed. No precipitate was formed.	unknown does not contain aldehyde or ketone or their derivatives.
Hydrexmic acid Acid test The 5mls of dilute sodium hydroxide 0.01g of hydroxylamine hydrochloride and 0.01g of unknown were added. The mixture was boiled for 2 minites; acidified and a few drops of ferric chloride added.	A violet coloured solution was formed.	Red or violet colour indicates formation o hydroxlamic acid whic complexes with Fe(ii ions to give the viol coloured complex therefore unknown compound contains an ester group.

From the above physical and chemical tests, the following inferences can be made;

(i) The unknown compound conatins carbon, hydrogen and oxygen.

(ii) The compound is aromatic

(iii) It is acidic in character

(iv) It is a phenol with an activated aromatic nucleus

(v) It contains an ester grouping.

NUMBER OF DOUBLE BOND EQUIVALENTS IN THE COMPOUND.

For a compound $C_aH_bO_c$, containing C,H and O only the mumber of double bond equivalent is given by the equation; $1 + (x-y/_2)$

Where x = Number of carbon atoms

y = Number of hydrogen atoms

Thus for the compound with molecule formula $C_8H_8O_3$;

number of Double bond equivalents (DBE) = $1+(8-\frac{8}{2}) = 5$

An aromatic benzene ring system and its three double bonds would take up 4 double bond equivalents

(since the compound is aromatic)

The fifth double bond equivalent is due to C = O

bond. It cannot be C = C bond since the compound

did not discolourise potassium permanganate solution.

ELEMENT ANALYSIS

Presence of oxygen in the unknown compound was confirmed by element analysis. The percentages of C, H and O were found to be as follows:

C = 63.15%

H = 5.3%

O = 31.55%

Molecular weight = 152.15

EMPIRICAL FORMULA DETERMINATION

C	H	O
$\frac{63.15}{12}$	$\frac{5.3}{1}$	$\frac{31.55}{16}$
5.26	5.30	1.97
2.67	2.69	1

Therefore Empirical Formula = $C_{2.67}H_{2.69}O$

MOLECULAR FORMULA

From the molecule weight of 152.15

$(C_{2.67}H_{2.69}O)_x = 152.15$

$(12 \times 2.67 + 1 \times 2.69 + 16 \times 1)_x = 152.15$

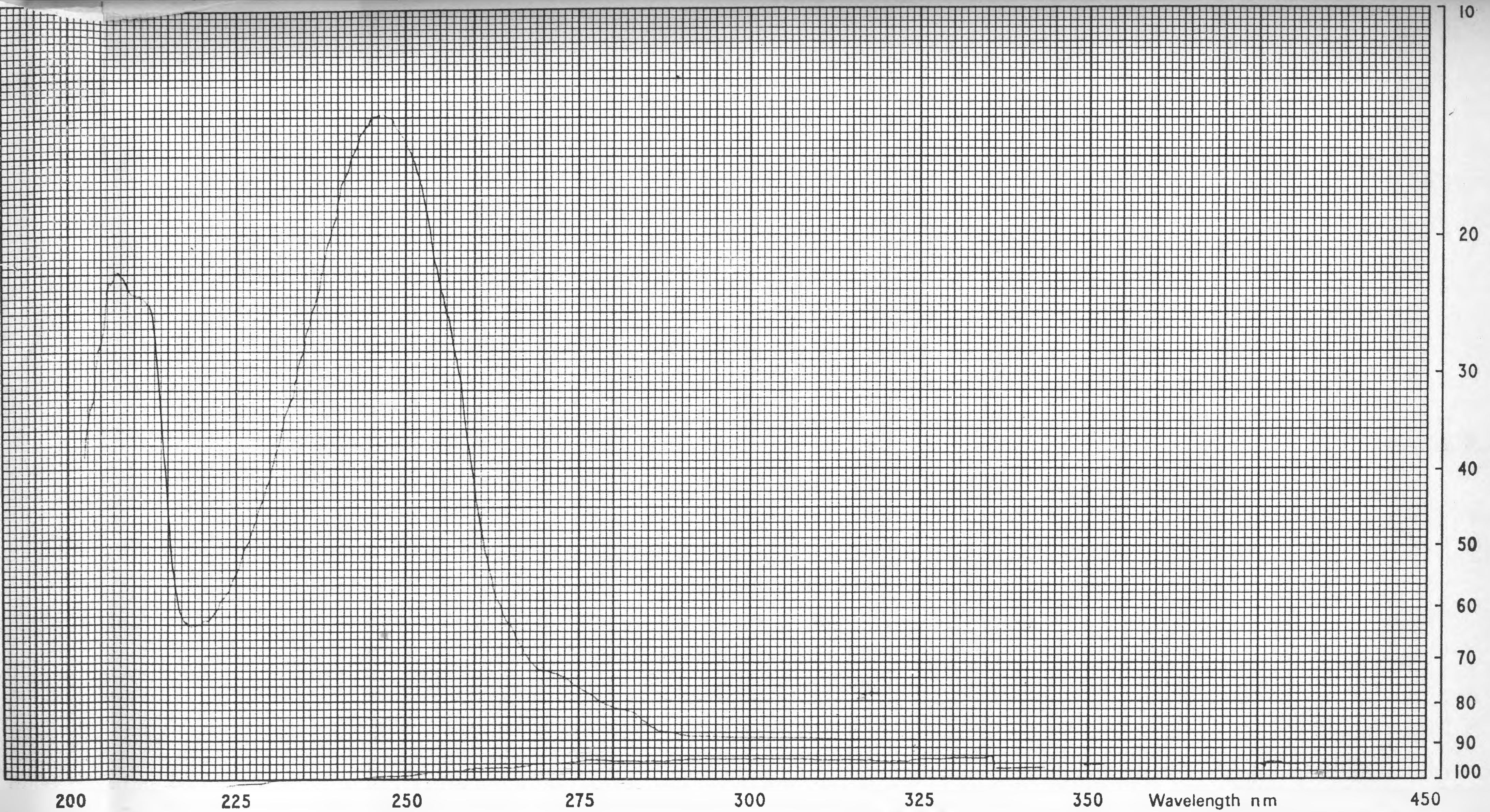
$(32.04 + 2.69 + 16)_x = 152.15$

$50.73\,x = 152.15$

$x = 2.999 = 3.0$

Molecular Formula = $(C_{2.67}H_{2.69}O)3.0$

$= C_8H_8O_3$



nd Formula A

FIGURE 1

Concentration 0.05%

Reference n Hexane

Path Length mm

Scan Speed fast ☐ slow ☐

Absorbance Range 0–0·2A ☐ 0–1·0A ☐

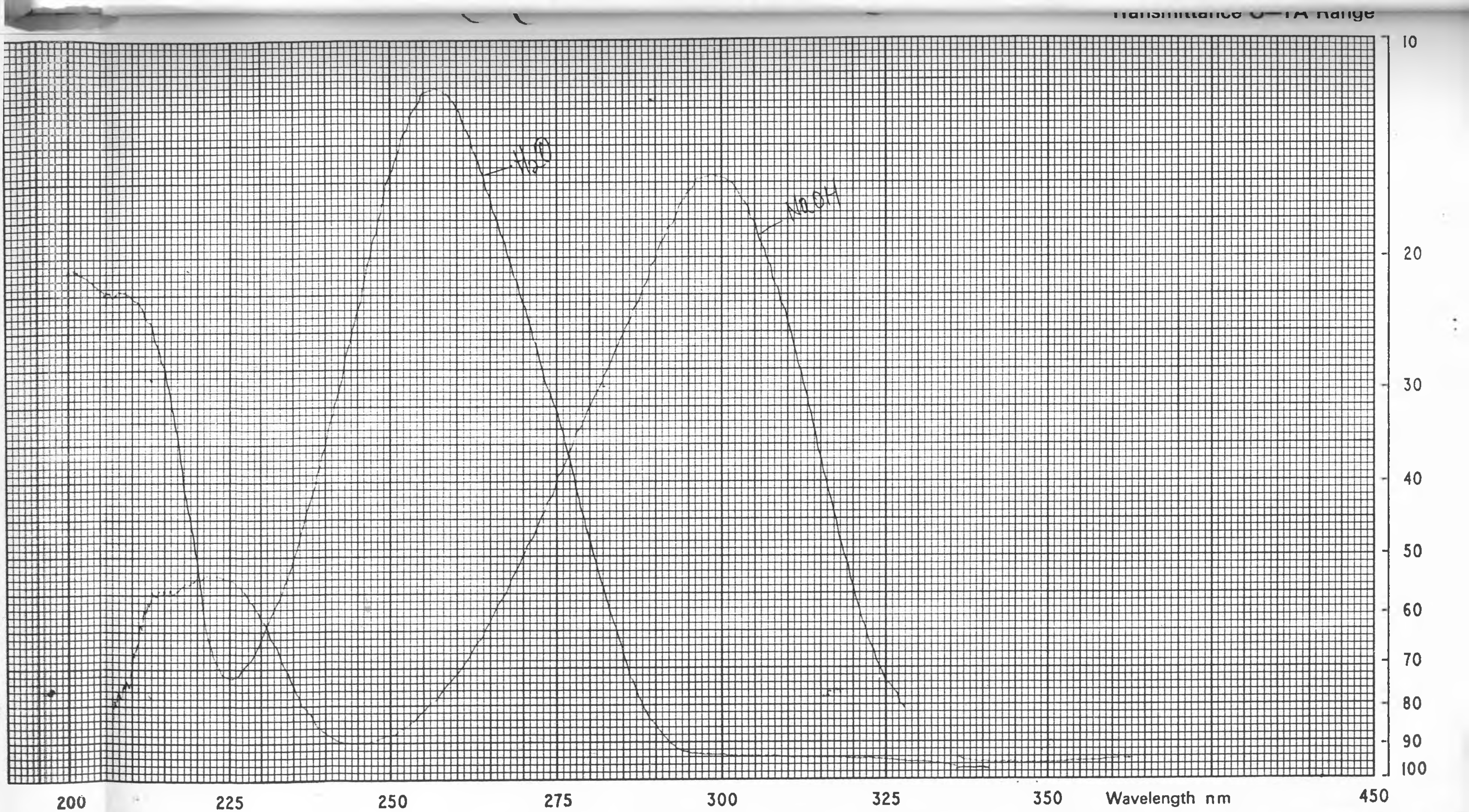
Operator

Date

Align with index on recorder

PYE UNICAM LTD CAMBRIDGE ENGLAND

Catalogue Number 608850



and Formula A

Figure 2

Concentration

Reference

Path Length mm

Scan Speed fast ☐ slow ☐

Absorbance Range 0–0·2A ☐ 0–1·0A ☐

Operator Date

Align with index on recorder

PYE UNICAM LTD CAMBRIDGE ENGLAND

Catalogue Number 60885

ULTRAVIOLET SPECTROSCOPY

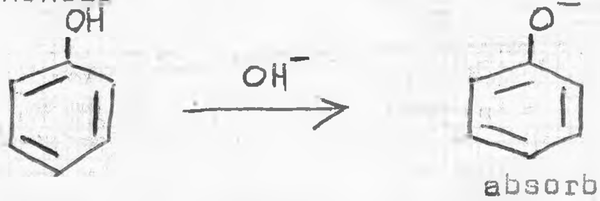
Results - from the spectra

SOLVENT	λMAX	
N-Hexane (figurel)	246	212
Water (fig2)	257	214
Sodium hydroxide (fig2)	298	213

INFERENCES

(1) Two series of absorption bands are shown indicating the presence of an aromatic ring.

(2) When sodium hydroxide is added to the aqueous solution, the absorption is at a longer wavelength this indicates the presence of a phenate formed from a phenol.



absorbs at a longer wavelength

This further confirms the presence of a phenol.

(3) Phenol itself absorbs at λmax 270mm and 210.5mm the unknown compound absorbs at shorter wavelengths indicating that an electron withdrawing group as attached to the benzene ring.

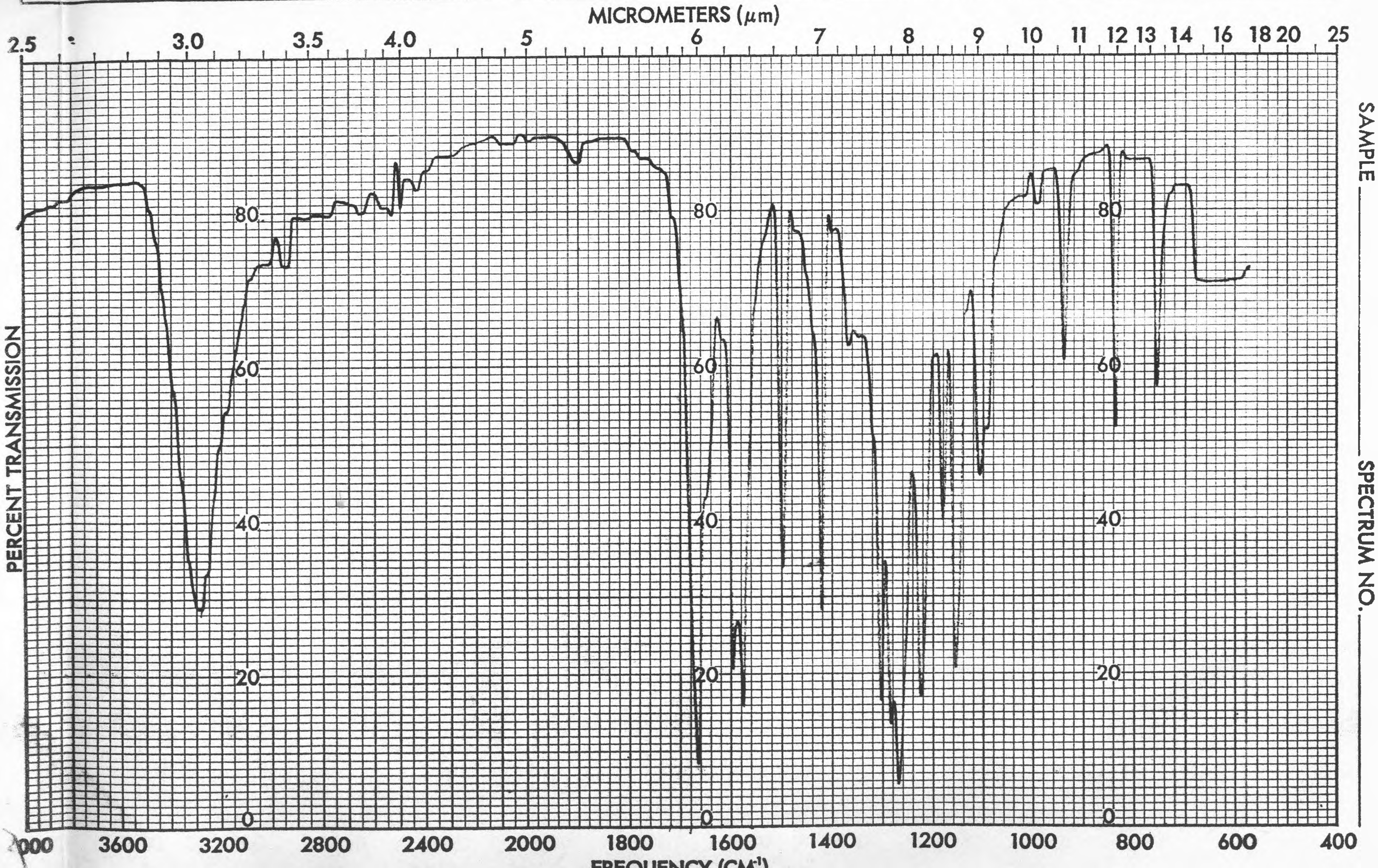
CONCENTRATION
THICKNESS
PHASE KBR
REMARKS

SCAN MODE ACCY. ☐ SURVEY ☑
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR KAMAU J.N DATE 10/1/86

SPECTRUM NO.
SAMPLE A

ORIGIN

FIGURE 3



CONCENTRATION

THICKNESS

PHASE

REMARKS

SCAN MODE ACCY. ☐ SURVEY ☑

HI ENERGY ☐ CAL. ☐

RESOLUTION ☐

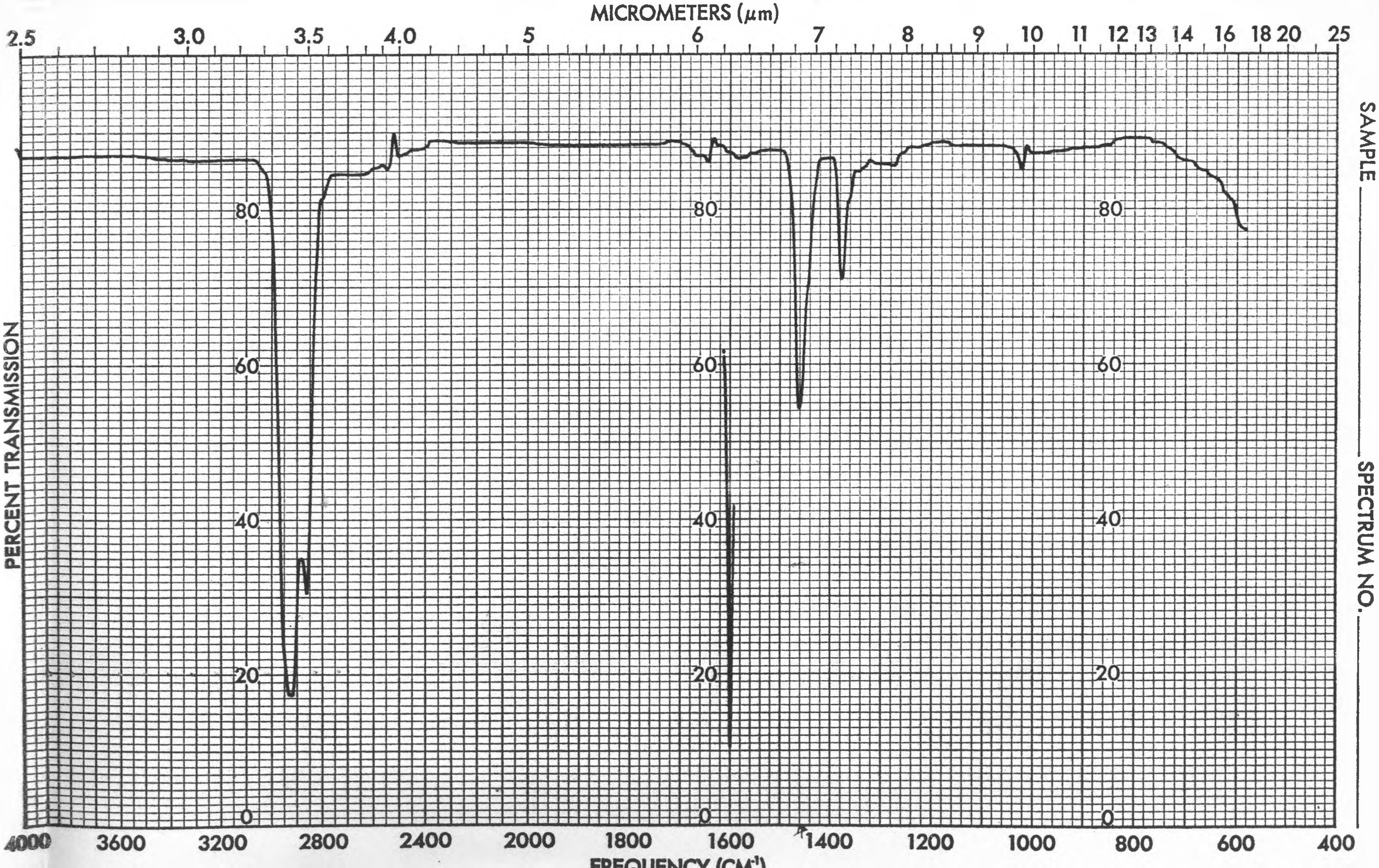
OPERATOR DATE 21/1/85

SPECTRUM NO.

SAMPLE Nujol

ORIGIN

FIGURE

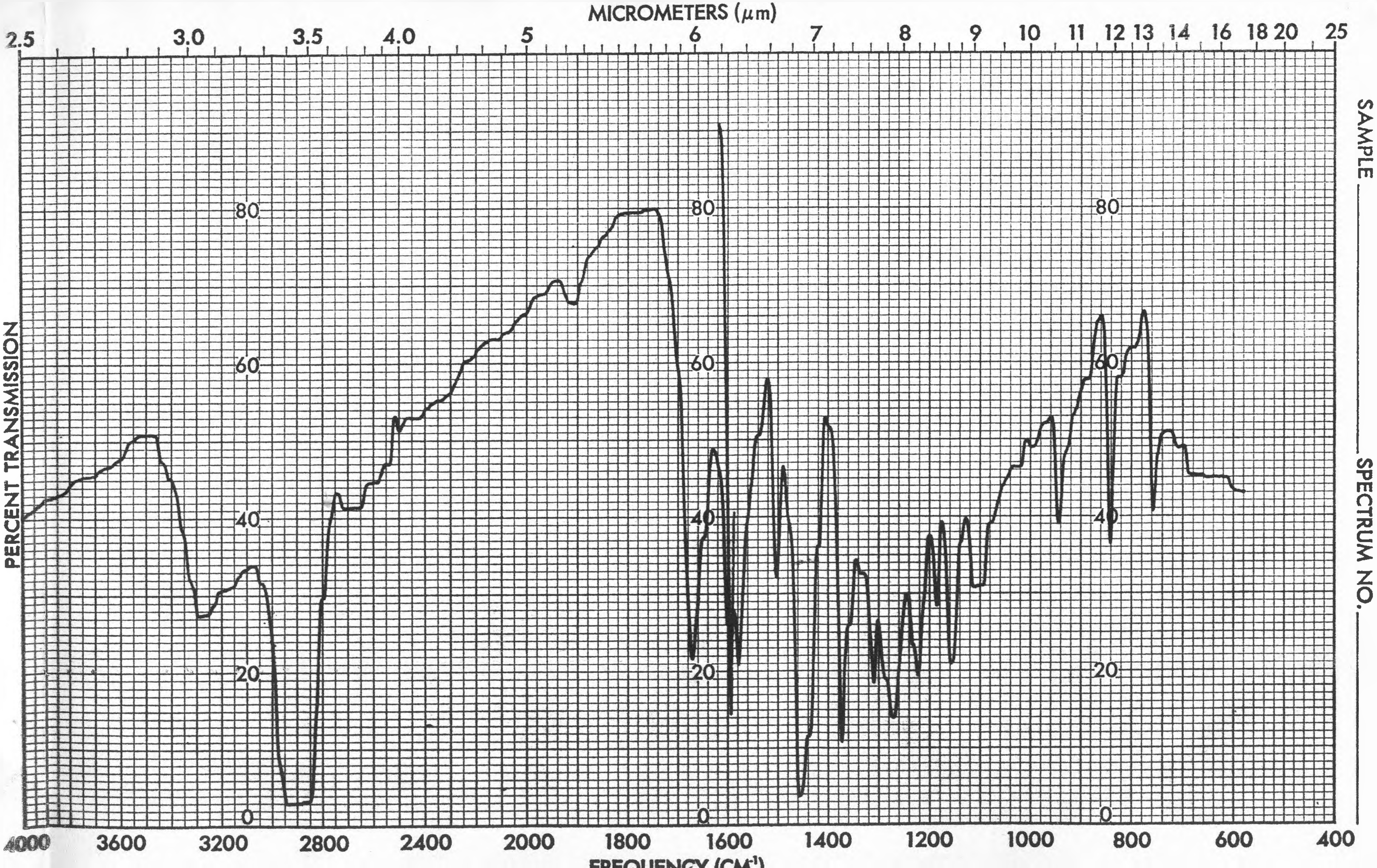


CONCENTRATION ______
THICKNESS ______
PHASE Nujoll
REMARKS ______

SCAN MODE ACCY. ☐ SURVEY ☑
HI ENERGY ☐ CAL. ☐
RESOLUTION ☐
OPERATOR KARIU J.K. DATE 21/1/85

SPECTRUM NO. ______
SAMPLE A
______
ORIGIN ______

FIGURE



INFRARED SPECTROSCOPY

The spectrum of the compound was run both innuyoll mull and in potassium bromide discs (KBR discs)

(KBR discs (fig 3)About 0.05-0.1 of the compound and about 100mg of dry powdered potassium bromide were fruturated thoroughly in an agate metor. A sufficent amount was transfered into a nut and belt and pressed under pressure of 10,000 kg force in vacuo to form a transparent disc. The obtained transparent disc. was then screened to give the spectrum.

(NUJOLL SPECTRA (FIGS 4 and 5) A small amount of the sample was triturated thoroughly with two drops of the mulling agent. A small portion of the resulting solution was put on a plate and the spectrum recorded (Fig5) An infrared spectrum for the mulling agent itself was also recorded (Fig4).

INTERPRETATION OF THE SPECTRA. (for both nujoll and KBR disc)

Peak at 3300cm^{-1} (strong) - O-H stretching vibration of phenol; intermolecularly hydrogen bonded; polymeric association. Intermolecular hydrogen bonds are formed by para substituted compounds. Ortho substituted compounds will form intermolecular hydrogen bonds.

PEAK AT 2850-2950cm^{-1} - very strong m nujoll and am almost insignificant in KBR. This is due to C-H stretching of alkane - saturated due to nujoll. The slight peak in KBR Shows that it can als be due to C-H of alkane of molecule and also C-H aromatic.

1660-1680 cm^{-1} Peak is characteristic of carbonyl absorption From the chemical tests, this carbonyl cannot be of an amide, ketone or an aldehyde. It can only be due to an ester (compound gives a positive hydroxamic acid test)

1580-1600cm^{-1}and 1500cm^{-1} C---C stretching of aromatic ring.

1460cm^{-1} - C-H bending due to CH_2 of nujoll

1420cm^{-1} - C---C stretching of aromatic bonds

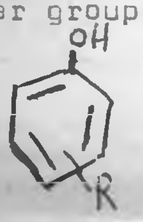
1380cm^{-1} - C-H bending of CH_3 of compound

1310cm^{-1} - O-H bending of phenol

All peaks 1100-1300cm^{-1} - C-O stretch of ester

760-790 cm^{-1} - C-H out of plune bending of aromatic ring.

From the above infrared evidence, the unknown compound is a phenol which is substituted (either P,M or O to OH of phenol) by an ester grouping.



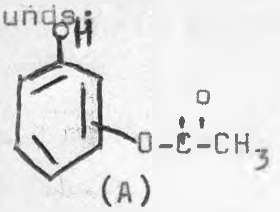
R = ester group

phenol = C_6H_5O

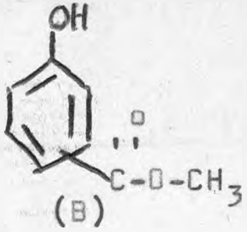
therefore R= $C_2H_3O_3$

~~R being an ester it can wither~~ be

R being an ester it can either be $-O-\overset{O}{\overset{\shortparallel}{C}}-CH_3$ or $-\overset{O}{\overset{\shortparallel}{C}}-O-CH_3$ to give the compounds:



(A)



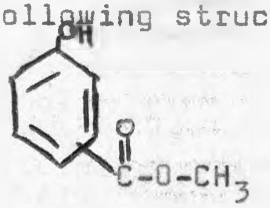
(B)

It cannot be compound (A), since on heating it did not give pungent smelling acetic acid (which would be expected from compound (A)). Therefore it can only be compound (B).

Infrared evidence cannot give conclusive evidence whether the ester group is ortho, meta or para substituted. Conclusive evidence is given by derivature preparation.

DERIVATIVE PREPARATION

From the above physical, chemical and spectroscopic analysis, the compound has the following structure.



Whether ortho, meta or para substituted can be determined by preparation of a derivative. However, the ortho compound (methylsalicy late) is ruled out since it is a liquid. Information on the meta compound was not found in the available literature.

PREPARATION OF PHENOL DERIVATIVE

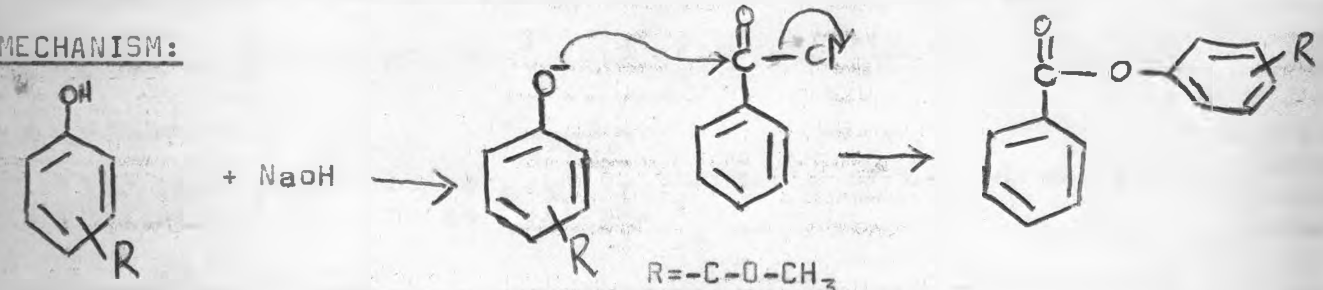
THE BENZOATE DERIVATIVE WAS PREPARED AS FOLLOWS:

In a 50ml flask, 20ml of 2N sodium hydroxide solution and 1g of the unknown compound (a phenol) were placed. 2ml of benzoyl chloride was added, corked firmly, and the flask shaken for 10 minutes (the cork was released occasionary).

The derivative was cooled in ice and continous shaking was done. Filteration and recrystalligation from aqueous ethanol was then carried out.

The melting point of the derivative was them determined.

MECHANISM:



R=-C-O-CH$_3$

~~R$_1$ = C-OH~~

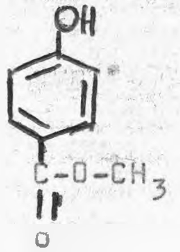
RESULTS: The melting point of the derivative was 222-225^{o}C.

INFERENCE: From tables of physical constants, the following melting points are obtained for methylo-hydroxy benzoate (methyl salicylate), methyl-m-hydroxy benzoate and methyl p-hydroxy benzoate and their benzoate derivatives.

COMPOUND	M.P OF COMPOUND	M.P OF BENZOATE DERIVAT
Methyl-O-hydroxy benzoate (methylsalicylate)	Liquid	159°C
Methyl-m-hydroxy benzoate	Not available in literature	201°C
Methyl p-hydroxy benzoate	131°C	224°C

NB: The compounds are first hydrolysed to hydroxybenzoic acid by sodium hydroxide before they form the benzoate derivature of phenol.

From the above literature values and the determined melting points of the compound (129°C-131°C) and that of the benzoate derivative (222-224°C), the unkmown compound is methyl p-hydroxy benzoate.



Hydrolysis of ester to acid and alcohol

The surest identification of an ester lies in identifying the constituent acid and alcohol. Since the compound is an aromatic ester, it requires a 1 hour reflux with 10% ethanolic potassium hydroxide to effect hydrolysis. In this case, since ethanol is used as a solvent, it is not practicuble to try and isolate the aliphatic alcohols from the ester and identification must test an characterisation of the acid.

RESULTS: Melting point of acid after purification 212-214°C.

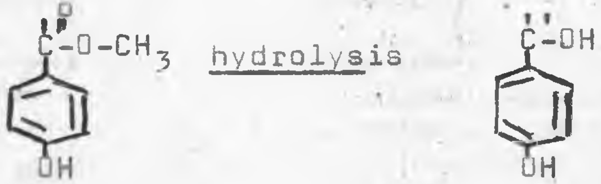
INFERENCE

From tables of melting points, the m.p's of O-,m-, and p-substituted acids are as follows.

ACID	M.P.
O-Hydroxybenzoic acid (salicylic acid)	159°C

ACID	M.P.
M-Hydroxybenzoic acid	201°C
P-Hydroxybenzoic acid	214°C

The M.P obtained 212-214°C amd this corresponds to that of P-hydroxybenzoic acid This further confirms that the compound is methyl-p-hydroxybenzoate.



Methyl
P-hydroxybenzoate
M.p = 131°C

P-hydroxybenzoic
acid
M.P. = 214°C

ENTRATION

THICKNESS

PHASE KBr

REMARKS

SCAN MODE

ACCY. ☐ SURVEY ☐

HI ENERGY ☐ CAL. ☐

RESOLUTION ☐

OPERATOR DATE

SPECTRUM NO.

SAMPLE Methyl paraben

ORIGIN

~~Fig6~~

Fig6

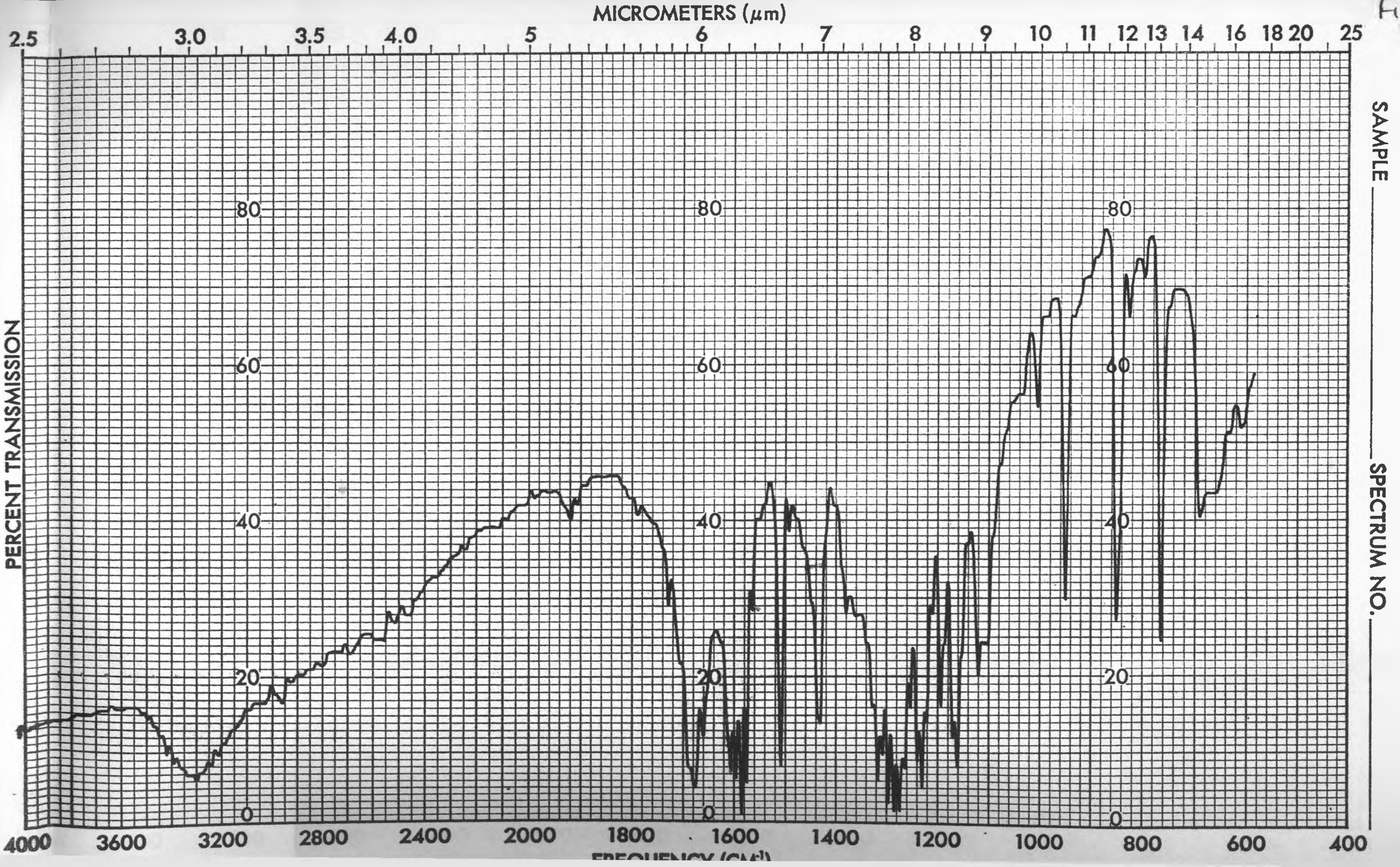
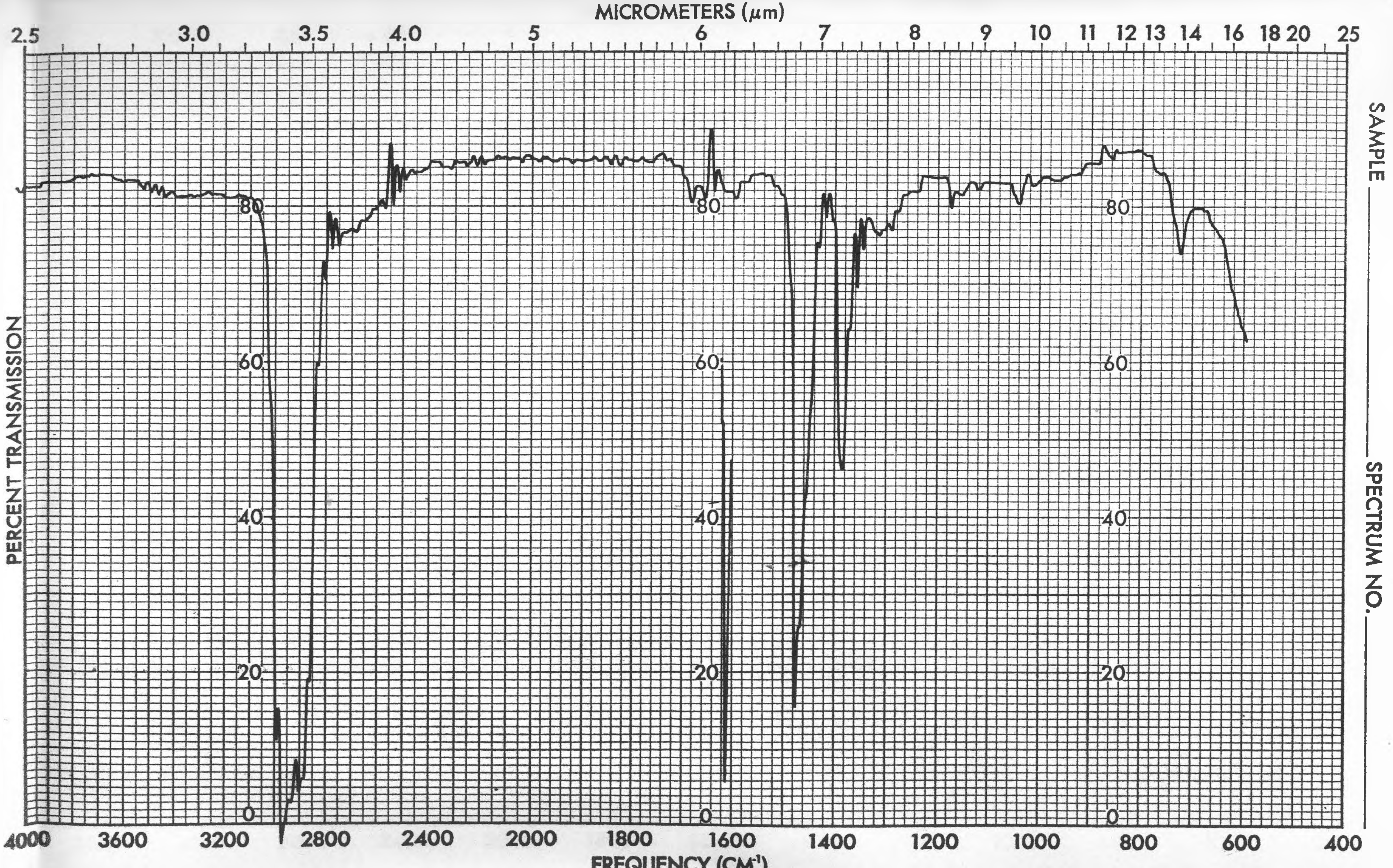


Fig 7

ONCENTRATION
THICKNESS
PHASE Nujol
REMARKS

SCAN MODE
ACCY. ☐
HI ENERGY ☐
RESOLUTION ☐
SURVEY ☐
CAL. ☐
OPERATOR
DATE

SPECTRUM NO.
SAMPLE
ORIGIN



CONCENTRATION

THICKNESS

PHASE Nujol

REMARKS

SCAN MODE

ACCY. ☐

SURVEY ☐

HI ENERGY ☐

CAL. ☐

RESOLUTION ☐

OPERATOR

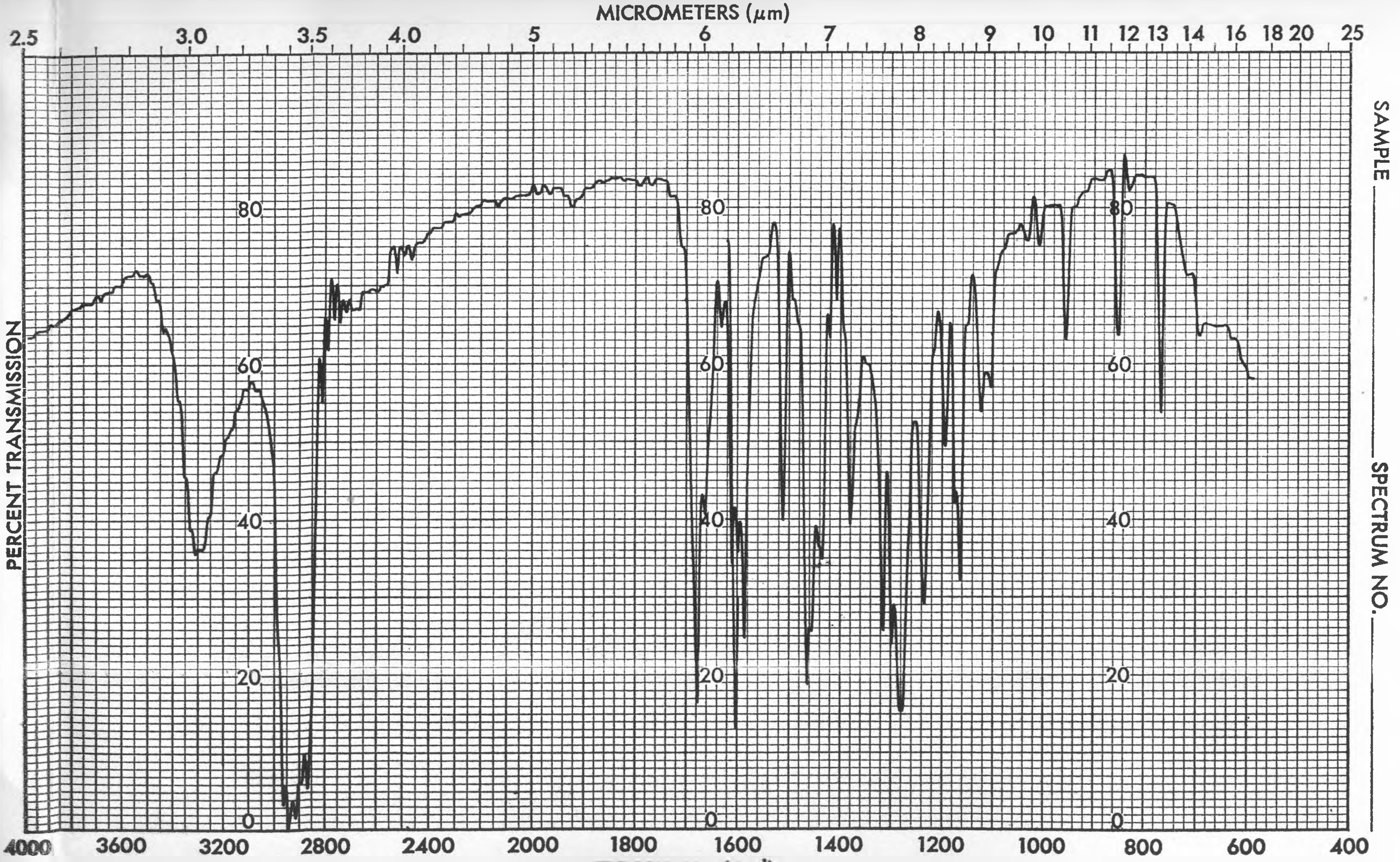
DATE

SPECTRUM NO.

SAMPLE Methyl paraben.

ORIGIN

FIG 8



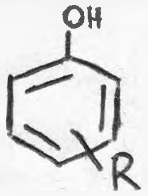
DISCUSSION

The aim of the experiments was to try to elucidate the structure of the unknown organic compound 'A' using physical, chemical and spectroscopic methods. These experimental methods were carried out and tend to suggest and qualify each other as to the possible functional groups and nature of the compound as a whole.

On physical examination, the unknown compound was found to be a white crystalline powder with pleasant aromatic smell. The sparing solubility of the compound in water and the increased solubility in dilute sodium hydroxide as compared to insolubility in dilute hydrochloric acid showed that the unknown compound was weakly acidic. Decolurisation of bromine indicated substitution in an activated aromatic nucleus - a white precipitate which was produced indicacated a bromo derivative of a phenol. The possibility of unsaturated compounds and other easily oxidized groups was eliminated since the unknown did not discharge the colour of potassium permanganate.

From the burning test, the smoky flame showed that the compound was aromatic, and had a melting point of 129-131^{o}C. This narrow range of m.p. also showed that the compound was pure.

From the sodium fusion test and element analysis the compound was found to contain carbon, hydrogen and oxygen. From the calculation , the molecular formular of the compound was $C_8H_8O_3$. From the calculations of double bond equivalents, the compound was found to have. 5 double bond equivalents. Since the compound was found to be aromatic, the benzone ring system takes up 4 double bond equivalents i.e ring + 3 double bonds of the ring. The coumpound eas confirmed to be a phenol by the ferric chloride test.



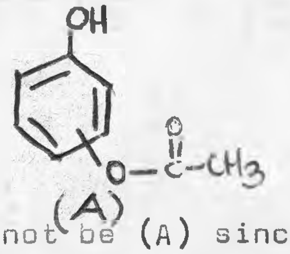
C_6H_5O

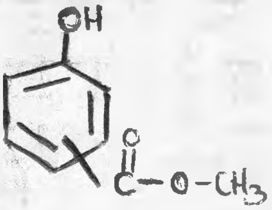
$R=C_2H_3O_2$

By the hydroxamic acid test, the compound was found to be an ester. Thus R is an ester group. Therefore fifth double bond equivalent is due to C = O of an ester.

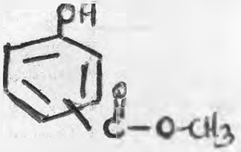
Further confirmation of the benzone ring eas given by the ultraviolet spectrum absorption by the two absorption bonds (fig1). Confirmation of the phenol e was given by a shift to a higher wavelength when sodium hydroxide was added to an aqueous solution of the compound (fig 2). Since the compound absorbs at a shorter wavelength than phenol itself, the compound must be having an electron withdrawing group attached to the ring - from the above chemical tests, this group must be the ester.

From the infrared absorption spectrum, aromatic ring is confirmed by C-=-C stretching vibration of aromatic rings (1580-1600cm^{-1}, 1500cm^{-1} and 1420cm^{-1}) and the c-H out of plane bending of aromatic ring (beteeen 760-940cm^{-1}) Peak at 3300cm^{-1} indicated) O-H stretching of phenol, intermoleculalarly hydrogen bonded, polymeric association. Peak at 1660-1680cm^{-1} is characterised of carhomyl absorption - thus is the carhonyl of unester. there are two possibilities of the ester - either an ester of phenol (A) or an ester of an ester of an alcohol (B)





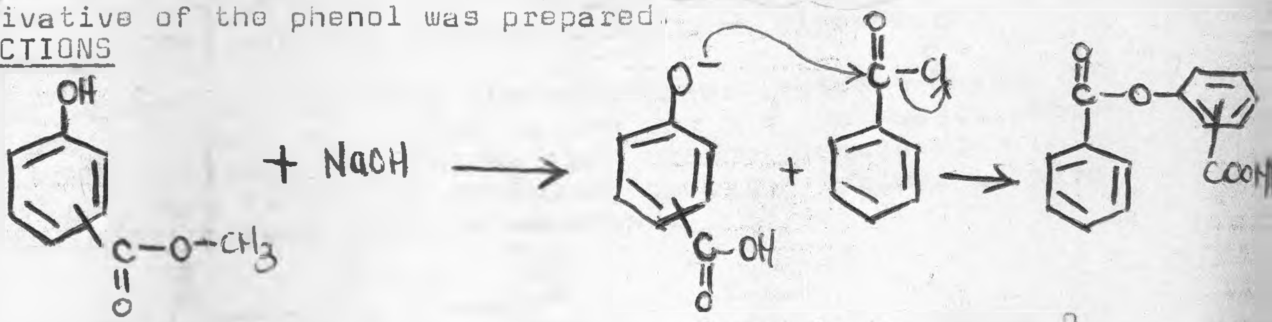
It cannot be (A) since on heating the pumgent samalling aletic acid was not detected. Therefore it can only be (B)



The frequency of the carbonyl absorption for the ester was much lower than expected. This is because the methoxy group is electron withdrawing and thus weakens the C=O bond and thus absorbs at a lower frequency.

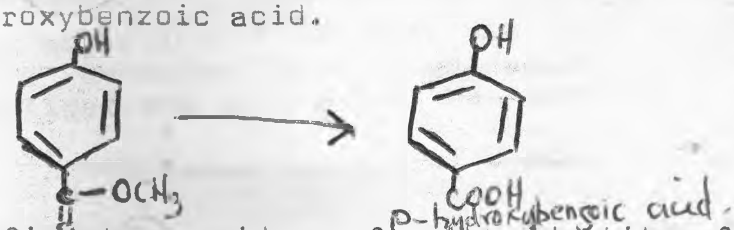
The determine whether the compound eas octhometa para substituted, a derivative of the phenol was prepared.

REACTIONS



The melting point of the dervative was found to be 222-224°c.

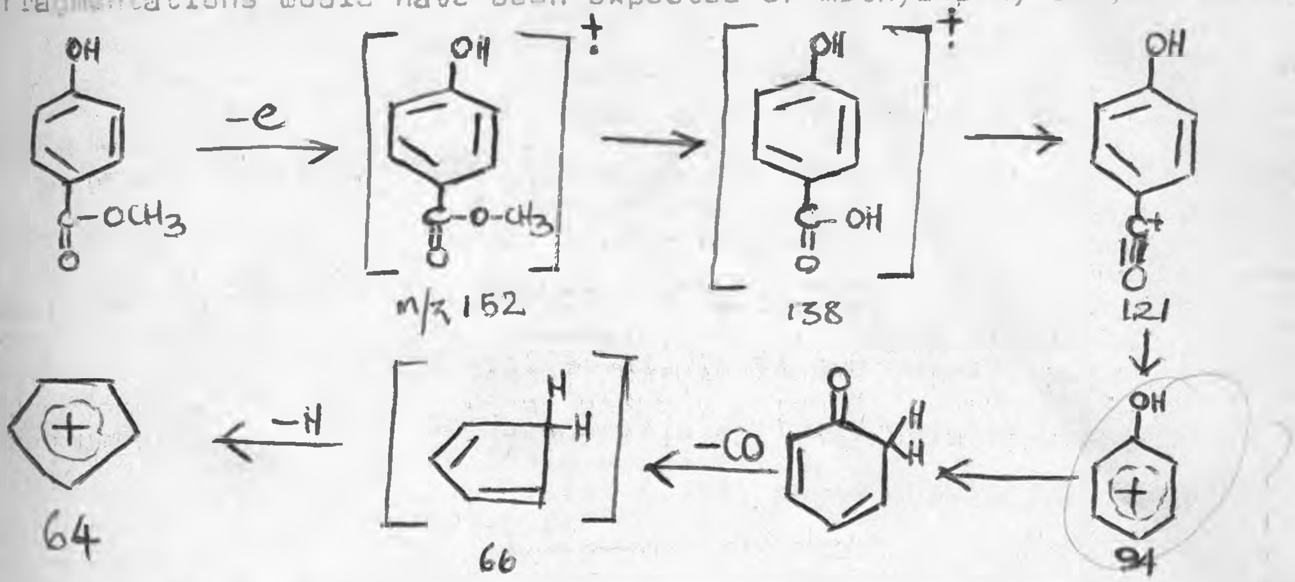
From comparison of the compoinds and their dervatives from literature, the compound was found to be methyl p-hydroxybenzoate Further evidence was given by hydrogens of the ester. The acid formed lead a melting point of 212-214°c and this corresponds to p-hydroxybenzoic acid.



confirmatony evidence for the identity of the unknown compound was obtained by using a known sample of methyl p-hydroxybenzoate. The melting point of unknown was found to be identical to that of the known (129-131°c). A mixed melting point was done and the m.p. was found to correspond to the above two. The infrared spectra of both the unknown and the known methyl p-hydroxybenzoate were also found to be the same (figs 6,7,8).

If mass spectrometer and the nuclear magnetic resonance instruments were available, structural elucidation could have been possible even without preparation of dervatives.

Mass spectrometery would also give the molecular weight and the molecular formula of the compound. From the fragmentation patterns, structural elucidation could have been easier. The following fragmentations would have been expected of methyl p-hydroxybenzoate.



In nuclear magnetic resonance (NMR) spectrum the following would be observed.

A peak around 4.5 due to ON group of phenol. This can be raised up to 10 depending on the extent of hydrogen bonding. If the sampl is shaken with D_2O, and then run on NMR, the peak disappears, this is because deuterium exchanges with the hydrogen of OH and since deuterium does not show any peak, the peak disappears.

The benzene protons will absorb anywhere between 0=6-8. The compou has unsignmetical para substitation and the two substituents have different shelding influences. Each proton couples with the protons ortho and para to it. The following spectrum typical of para substituted benzene would be observed.

A peak at 0 = 3.9 would be observed due to CH_3 protons. Ratio of protons 1: 4: 3 from the integration sizes.

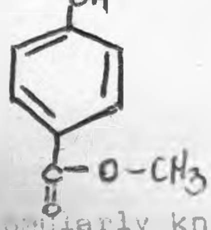
CONCLUSION

The objective of the work was to determine the structure of the unknown compound (A' by physical, chemical and spectroscopic means. Investigations have shown that compound A has:

(i) A molecular formula of $C_8H_8O_3$

(ii) An ester group and is a phenol and that these two groups are para to each other.

The unknown compound 'A' could then be suggested to be p-hydroxym benzoate (or 4 hydroxybenzoic acid methyl ester). It has the structu



It is popularly known as methylparabon.

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