1983

Synthesis and Reactions of Aromatic Ethers as Model Compounds for Coal

James Nicolas Ong Sy
Eastern Illinois University

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SYNTHESIS AND REACTIONS OF AROMATIC ETHERS AS MODEL COMPOUNDS FOR COAL

(TITLE)

BY

JAMES NICOLAS ONG SY

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1983
YEAR

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SYNTHESIS AND REACTIONS OF AROMATIC ETHERS AS MODEL COMPOUNDS FOR COAL

Thesis Approved

Dr. D. H. Buchanan

Dr. D. W. Ebdon

Dr. J. W. Ellis

Dr. G. L. Henderson

SYNTHESIS AND REACTIONS OF AROMATIC ETHERS AS MODEL COMPOUNDS FOR COAL

James Nicolas Ong Sy, Master of Science, August 1983

Thesis directed by : Dr. David H. Buchanan

ACKNOWLEDGEMENT

My sincerest appreciation is hereby extended to my Research Advisor, Dr. David H. Buchanan, whose assistance and guidance during the entire project have been invaluable.

DEDICATION

This piece of work is lovingly dedicated to my family, specially to my parents, whose love, support, encouragement and care made this project possible.

This work is also dedicated to our Almighty God:
Thy word is a lamp unto my feet and a light unto my path.

-Psalm 119 : 105

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ABSTRACT

o-Anisic acid and o-ethoxybenzoic acid were reacted with pyridine hydriodide in pyridine at 115° for 3 days to yield 81% and 18% salicylic acid respectively. o-Anisic acid with KI in pyridine at 115° for 3 days gave 58% salicylic acid while o-anisic acid with $LiI \cdot 3H_2O$ in pyridine at 85° for 3 days gave 54% salicylic acid. p-Anisic acid and o-phenoxybenzoic acid did not undergo cleavage reactions with pyridine hydriodide under similar conditions.

Beta-methylnaphthyl beta-naphthyl ether(I) or alpha-methylnaphthyl alpha-naphthyl ether(II) with pyridine hydriodide in pyridine at 100-115° for 3 days showed no cleavage. Ether I with pyridine hydriodide in the presence of pyridine insoluble Illinois No.6 coal fraction at 115° for 7 days or with added iron salts, such as $FeCl_2$, FeS and FeS_2 also showed no cleavage. Recovered ether averaged 98 ± 3%.

Since pyridine hydriodide or lithium iodide in pyridine increases the free phenolic content and reduces the apparent molecular weight of pre-asphaltene fraction of Illinois No.6 coal, presumably by ether cleavage, the coal structures reacting are not well-modeled by ethers I and II. It is proposed that oxygen atoms of the reacting ether linkages in the coal fraction are hydrogen bonded by phenol groups either on the same or adjacent aromatic cluster which activates them toward S_N2 cleavage by iodide ion under mild conditions.

INTRODUCTION

Studies suggest that coal is composed of macromolecular units linked together by oxygen bonds. Ruberto[1] deduced from solvation studies of coal that it appears to consist primarily of 2- and 3- ring condensed aromatic structures linked mainly by oxygen atoms. Takegami[2] concluded that the formation of asphaltenes from mild hydrogenation of bituminous coal is due to cleavage of ether linkages. Wachowska[3] noted that while the extent of ether linkages varies widely with coal rank, ether groups represent the main linkages between aromatic clusters. It is believed that the single bonds in coal most likely to be broken and assist its liquefaction under mild conditions are[4]:

$Ar\text{-}CH_2\text{-}Ar$ $\quad$ $Ar\text{-}O\text{-}Ar$ $\quad$ $Ar\text{-}CH_2\text{-}O\text{-}Ar$

$Ar\text{-}(CH_2)_n\text{-}Ar$ $\quad$ $R\text{-}O\text{-}Ar$ $\quad$ $R\text{-}O\text{-}R$

and sulfur analogs

where: Ar = aryl groups R = aliphatic groups

The connecting ether linkages in coal have been the subject of several studies. Different cleaving agents and reaction conditions were used to break these bonds in coal and in model compounds.

A model compound is one whose atomic configuration is responsible for coal-like behavior and might be a component of the hypothetical coal molecule[5]. Studies on model compounds are conducted to give a better insight of the structure inside the coal and the connecting linkages responsible for this

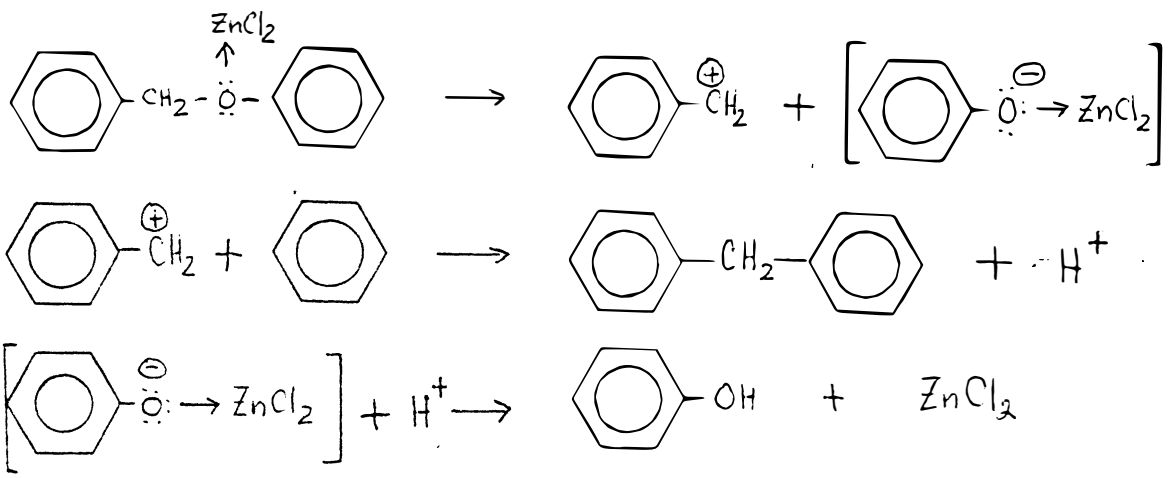
structure. Hydrogenolysis of coal-related model compounds by a $CO-H_2O$ mixture at 300° were conducted and cleavage was found to occur readily[6].

Model Compounds	Products
Benzyl phenyl ether	Benzene, toluene
Phenyl ether	Benzene
Benzyl ether	Benzene, toluene

$ZnCl_2$ has also been used to effect cleavage on model compounds[7]:

Model Compounds	Products
Benzyl ether	Diphenyl methane
Phenyl ether	No reaction
Benzyl phenyl ether	Diphenyl methane
Benzyl naphthyl ether	Diphenyl methane, Beta-naphthol

The postulated mechanism:



When coal itself was treated with K/THF in the presence of naphthalene followed by quenching with dilute HCl, it was found that there was a substantial increase in the hydroxyl content and fluidity of coal[8]. These results were consistent with the cleavage of ether bonds.

The mechanism of the reaction may be:

$K^{o} + C_{10}H_{8} \rightarrow (C_{10}H_{8})^{\bullet -} + K^{+}$

$Ar\text{-}O\text{-}Ar + (C_{10}H_{8})^{\bullet -} \rightarrow (Ar\text{-}O\text{-}Ar)^{\bullet -} + C_{10}H_{8}$

$(Ar\text{-}O\text{-}Ar)^{\bullet -} \rightarrow ArO^{-} + Ar\cdot$

$Ar\cdot + (C_{10}H_{8})^{\bullet -} \rightarrow Ar^{-} + C_{10}H_{8}$

$Ar^{-} + HOH \rightarrow ArH + OH^{-}$

$ArO^{-} + HOH \rightarrow ArOH + OH^{-}$

where Ar-OAr represents diaryl ether linkages.

Sodium in liquid ammonia acts in a similar manner when cleaving ether linkages in coal, resulting in smaller, more soluble fragments[9]:

$$Ar\text{-}O\text{-}Ar \xrightarrow[\text{liq. } NH_3]{Na} (Ar\text{-}O\text{-}Ar)^{\bullet -} \rightarrow ArO^{-} + Ar\cdot$$

$$Ar\cdot \xrightarrow{Na} Ar^{-} \xrightarrow[solv]{H} ArH$$

$$ArO^{-} \xrightarrow[solv]{H} ArOH$$

Coal consists of several fractions which exhibit contrasting solubilities in different solvents:

	Soluble in	Insoluble in
Extracted coal	None	All
Pre-asphaltene(Asphaltol)	Pyridine	Toluene
Asphaltene	Toluene	Hexane
Oil	Hexane	Protic solvents

When Mayo et al[10] reacted an asphaltol fraction of Illinois No.6 Coal with Na/liq. NH_3 followed by quenching with NH_4Cl, there was observed a decrease in molecular weight and increase in the phenolic -OH content of the coal fraction. Similar observations were noted by reacting the asphaltol fraction with pyridine hydriodide at 20°. When they conducted the reaction at 50°, they found that the molecular weight of the coal fraction was reduced to the same extent as with Na/liq. NH_3. Cleavage of ether linkages would explain these results.

Pyridine hydriodide has been well-studied. Odinokov[11] concluded from his infrared and NMR studies of pyridinium salts, that for strong acids like HI(pK_a = -11), proton transfer with pyridine takes place and the "ionic pair" is the predominant species. A hydrogen bonding enthalpy of -6.7 kcal/mole results from the salt formation. This "ionic pair" is confirmed by the presence of N-H stretching frequency maxima at 2833 cm^{-1} in the infrared spectra.

Royer et al[12] has used pyridinium halide salts in ether cleavage reactions. They found that pyridine hydrogen bromide cleaved alkyl naphthyl ethers at 230°. Chen[13] found that when phenyl alkyl ethers and esters were reacted with pyridine hydriodide at 60-80°, no significant ether or ester cleavage

was observed. At 210°, she found that pyridine hydriodide cleaves phenyl ethers and ester. The lower temperature results with models contrast with the coal reactions.

Cleavage Reactions with Pyridine Hydriodide at High Temperature(reaction time: 45 hours, reaction temp.: 210°)

Ether or Ester	Products
Anisole	Phenol
Benzyl phenyl ether	Phenol, toluene
Cyclohexyl phenyl ether	Phenol
Methyl benzoate	Benzoic acid
Phenyl phen(ethyl) ether	Ethylbenzene, phenol

Larsen[14] conducted a reaction which selectively labeled the -OH groups in coal with tri-n-butyltin and used Mössbauer spectroscopy to deduce information about the heteroatom population near the hydroxyl group. He reacted Illinois No.6 Coal with bis(tributyl)tin oxide in refluxing toluene. The tin Mössbauer spectrum of the coal derivative showed that almost all of the tin is in trigonal bipyramid form. No evidence was found for the presence of tetrahedral tin. This can only be true if a nearby atom with an unshared pair of electrons can enter into the coordination shell of tin. This heteroatom must be sufficiently close for it to serve as an acceptor for a hydrogen bond from the now derivatized hydroxyl. In other words, almost all of the -OH in Illinois No.6 Coal may be hydrogen bonded to another heteroatom within the solid.

If this is the case, the first step in ether cleavage, that is, the protonation of the ether oxygen, may not require an external proton source inside the coal because the ether oxygen is already in hydrogen bonded form. In coal, attack by the iodide ion on the carbon adjacent to the ether oxygen maybe sufficient for cleavage and thus the observed reduction in the molecular weight of coal. This internal protonation could well explain the reaction of the asphaltol fraction of coal with lithium iodide. Mayo et al[10] observed that LiI, a reagent that does not have a proton source, is equally effective as pyridine hydriodide in reducing the molecular weight and increasing the phenolic -OH content of coal.

This thesis covers the following areas:

1. An extention of Chen's work with model compounds. That is, synthesis of various naphthyl ethers and the study of their reactions with pyridine hydriodide and other agents.
2. In line with Larsen's results, a study of cleavage reactions of o-anisic acid and p-anisic acid with pyridine hydriodide, $LiI \cdot 3H_2O$ and other cleaving agents. The former acid has its ether in hydrogen bonded form while the latter doesn't.
3. A study of naphthyl ether reaction with pyridine hydriodide using coal as catalyst. The reasoning is that, the environment inside the coal might promote ether cleavage.

EXPERIMENTAL SECTION

General

NMR spectra were obtained on a Varian T-60 nuclear magnetic resonance spectrometer using tetramethylsilane(TMS) as an internal standard. Infrared spectra were recorded by a Perkin-Elmer 337 grating infrared spectrophotometer(calibration peaks at 1601 and 1028 cm^{-1}). Mass spectral analyses were conducted on a Du Pont 21-490 mass spectrometer. HPLC analyses were done on a Beckman Model 342 Gradient Liquid Chromatograph system, retention times and area measurements were recorded by a Shimadzu Chromatopac C-R1B. The column used for the HPLC was 4.6 mm x 15 cm C_{18} reversed phase. Identities of the desired peaks were based on comparison of retention times. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. Pre-injection clean-up of HPLC samples was centrifuging on a Beckman Microfuge™ 11 at 11,000 rpm. Sep-pak used for analytical clean-up of coal-catalyzed reactions is a C_{18} cartridge purchased from Waters Associates. Carbon and hydrogen analyses were done either at the University of Illinois or Mic Anal Organic Microanalysis Laboratory.

Pyridine hydriodide used was previously prepared by Chen[13](m.p. 211-214°, Chen's reported m.p. 212-214°, lit., 214°)[15]. The coal used was the extracted coal portion(pyridine insoluble fraction) of Coal PSOC 252(Penn State Coal Data Bank) prepared by Ballard[16] and has the following DAF elemental analysis: C,74.01%; H, 5.23%; N, 2.03%; O + S, 18.73%(by diff-

erence).

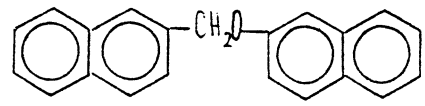
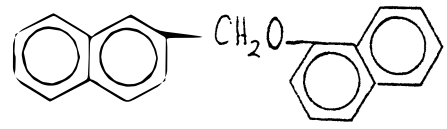
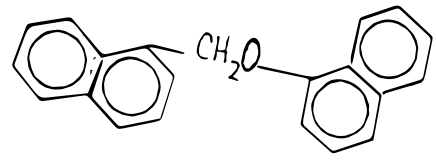
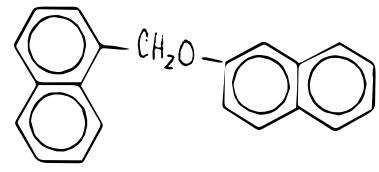
Pyridine was purchased from Fisher Scientific Company and was distilled over BaO, then kept in a round bottom flask capped with a rubber septum to keep it anhydrous. The HPLC water used was distilled deionized water that was passed through 45 micron filter purchased from Millipore Corporation. Methanol and acetonitrile were HPLC grade solvents purchased from J.T. Baker Chemical Co.. o-Anisic acid, o-phenoxybenzoic acid, o-ethoxybenzoic acid, bibenzyl, hydrocinnamic acid, tetrabutyl phosphonium bromide, alpha- and beta- methylnaphthalene were purchased from Aldrich Chemical Company. p-Anisic acid, hydroiodic acid, phthalic acid and p-hydroxybenzoic acid were purchased from Eastman Organic Chemicals. Alpha-naphthol, beta-naphthol were purchased from Fischer Scientific Company. $LiI \cdot 3H_2O$ was purchased from Alfa Division. All were reagent grade chemicals and used without further purification.

Preparation of Alpha and Beta Bromomethylnaphthalene via Photobromination:

The method of Chapman and Williams was used[17]. Beta-methylnaphthalene(100.00 g, 0.70 moles) in CCl_4(300 mL) was put in a 1-L, 3-neck round bottom flask equipped with a magnetic stirrer, condenser and gas trap. Bromine(27.00 g, 0.17 moles) in CCl_4(300 mL) was added dropwise during a 6-hr period to the stirred solution of beta-methylnaphthalene in refluxing CCl_4 and irradiated with a 500-w tungsten bulb 2 inches from the flask. After the evolution of HBr gas had ceased, the reaction mixture was stirred at reflux for another 2 hours. CCl_4 was removed by simple distillation and the residue was fractionated at 5 mm Hg to remove the unreacted beta-methylnaphthalene(b.p. 98-102°/5 mm) to give 75.80 g(75.80% recovery). The crude beta-bromomethylnaphthalene was obtained by continuing the vacuum distillation and collecting a fraction at 118-123°/1.2 mm. The crude product was purified by recrystallization from hot ethanol to give 30.38 g(81% yield). (M.P. 52.5-54.0°, lit., 54°)[17]. NMR($CDCl_3$) Chemical shifts, ppm: 7.8-7.2(m,7); 4.5(s,2). IR(KBr): 3050, 2950, 1600, 1500,1400, 1208, 818, 740 cm^{-1}.

Alpha-bromomethylnaphthalene was prepared in the same way except the starting reagent was alpha-methylnaphthalene. Alpha-bromomethylnaphthalene(m.p. 53.5-55.0°, lit., 56°)[18]. NMR ($CDCl_3$) Chemical shifts, ppm: 8.2-7.2 (m,7); 4.9 (s,2). IR (KBr) : 3050, 2960, 1590, 1500, 1400, 1196, 760 cm^{-1}.

Preparation of Aromatic Naphthyl Ethers I to IV.

Ether	Name	Structure
I	Beta-methylnaphthyl-beta-naphthyl ether	
II	Beta-methylnaphthyl-alpha-naphthyl ether	
III	Alpha-methylnaphthyl-alpha-naphthyl ether	
IV	Alpha-methylnaphthyl-beta-naphthyl ether	

The method of D'Incan and Viout[19] was used. Beta-naphthol(12.78 g, 0.089 moles) in methylene chloride(200 mL) was put in a 500-mL, 3-neck, round bottom flask equipped with a magnetic stirrer and condenser. NaOH(3.55 g, 0.089 moles) in 40 mL H_2O was added to the flask. The reaction mixture was stirred at room temperature for 30 min.. Beta-bromomethylnaphthalene(14.00 g, 0.063 moles) was added to the flask followed by tetrabutyl phosphonium bromide as phase transfer catalyst. The reaction mixture was stirred at room temperature for 24 hours. The final solution was acidified to pH = 3 with 20% HCl, the layers separated and the water layer extract-

ed with 3 x 10 ml CH_2Cl_2. The organic layers were combined and washed with 20 mL of 5% NaCH and 1 x 10 mL H_2O. The solution was dried with anhydrous Na_2SO_4, passed through a plug of glass wool and the solvent removed on the rotary evaporator. The crude product was purified by recrystallization from hot ethanol. NMR, IR and mass spectra of ethers I to IV are shown in Figures I to XII.

	Ether			
	I	II	III	IV
Yield(%)	21	9	18	6
NMR Chem. Shift(ppm)				
(m,14 H)	8.0-7.0	8.4-6.7	8.3-6.8	8.0-7.0
(s, 2 H)	5.5	5.4	5.6	5.5
Mass Spectrum(m/e)				
Parent peak	284	284	284	284
Base peak	141	141	141	141
IR Spectrum(cm^{-1})	3080	3040	3040	3040
	2930	2920	2930	2950
	1585	1570	1580	1600
	1450	1370	1360	1470
	1258	1260	1263	1250
	1218	1230	1238	1208
	1003	1060	1069	993
Elemental Analysis				
Theoretical				
C	88.70	88.70	88.70	88.70
H	5.67	5.67	5.67	5.67
O	5.63	5.63	5.63	5.63
Actual				
C	88.36	88.64	87.92	88.28
H	5.37	5.42	5.77	5.77
O(difference)	6.27	5.94	6.31	5.95

Standardization of Naphthyl Ether I and Beta-naphthol with Bibenzyl for Quantitative Analysis of Reaction Mixtures.

Naphthyl ether I(10.0 mg) and beta-naphthol(10.0 mg) were weighed into a 25-mL volumetric flask and diluted to volume with acetonitrile to give a stock concentration of 0.400 mg/mL. In a separate 100-ml volumetric flask, bibenzyl(2.0000 g) was weighed and diluted to volume with acetonitrile to give a stock concentration of 20.00 mg/mL. For standard 1, 2 ml of naphthyl ether I + beta-naphthol stock solution was mixed with 1 mL of the bibenzyl stock solution. For standard 2, 1 mL of naphthyl ether I + beta-naphthol stock was mixed with 1 mL of the bibenzyl stock solution. The bibenzyl is an internal standard while beta-naphthol is one of the expected cleavage products.

The two standards were centrifuged, injected into the HPLC and the relative areas recorded. Duplicate runs of each standard were done and the relative areas averaged. From the relative areas and known amount of materials used in calibrating, the detector response factors were determined.

Naphthyl ether III was calibrated in a similar way.

Standardization of Naphthyl Ether I and Beta-naphthol with Naphthalene for Quantitative Analysis of Phenyl Sulfide-Catalyzed Reaction.

Naphthyl ether I(20.0 mg) and beta-naphthol(20.0 mg) were weighed into a 25-mL volumetric flask and diluted to volume with acetonitrile to give a stock concentration of 0.800 mg/ml.

In a separate 10-mL volumetric flask, naphthalene(10.0 mg) was weighed and diluted to volume with acetonitrile to give a stock concentration of 1.00 mg/mL. Standard 1 was prepared by mixing 1 mL of beta-naphthol + naphthyl ether I stock solution with 1 mL of naphthalene stock, while standard 2 was prepared by mixing 2 mL of naphthyl ether I + beta-naphthol stock with 1 mL of naphthalene stock. These 2 standards were centrifuged and calibrated on the HPLC.

Standardization of o-Anisic Acid and Salicylic Acid with Hydrocinnamic Acid for Quantitative Analysis of Cleavage Reactions.

o-Anisic acid(25.0 mg) and salicylic acid(25.0 mg) were weighed into a 25-mL volumetric flask and diluted to volume with 1,2-dichloroethane to give a stock concentration of 1.00 mg/mL. In another 50-mL volumetric flask, hydrocinnamic acid (300.0 mg) was weighed and diluted to volume with 1,2-dichloroethane to give a stock concentration of 6.00 mg/mL. For standard 1, 1 mL of o-anisic acid + salicylic acid stock solution was mixed with 1 mL of hydrocinnamic acid stock solution, while 2 mL of o-anisic acid + salicylic acid stock was mixed with 1 mL of hydrocinnamic acid stock to make standard 2. These 2 standards were centrifuged and used to calibrate the HPLC.

In a second calibration, o-anisic acid(10.0 mg) and salicylic acid(10.0 mg) were weighed into a 25-mL volumetric flask and diluted to volume with 1,2-dichloroethane to give a stock concentration of 0.400 mg/mL. Hydrocinnamic acid (350.0 mg) was weighed into a 50-mL volumetric flask and

diluted to volume with 1,2-dichloroethane to give a stock concentration of 7.00 mg/mL. Two mL of o-anisic acid + salicylic acid stock was mixed with 2 mL of hydrocinnamic acid stock to make standard 1, while 5 mL of o-anisic acid + salicylic acid stock solution was mixed with 2 mL of hydrocinnamic acid stock to make standard 2. These standards were centrifuged and used to calibrate the HPLC.

Standardization of p-Anisic Acid and p-Hydroxybenzoic Acid with Hydrocinnamic Acid for Quantitative Analysis of Reactions.

p-Anisic acid(25.0 mg) and p-hydroxybenzoic acid(25.0 mg) were weighed into a 50-mL volumetric flask and diluted to volume with 1,2-dichloroethane to give a stock concentration of 0.500 mg/mL. In another 50-mL volumetric flask, hydrocinnamic acid(300.0 mg) was weighed and diluted to volume with 1,2-dichloroethane to give a stock concentration of 6.000 mg/mL. For standard 1, 1 mL of p-anisic acid + p-hydroxybenzoic acid stock solution was mixed with 10 mL of hydrocinnamic acid stock solution, while 2 mL of p-anisic acid + p-hydroxybenzoic acid stock was mixed with 10 mL of hydrocinnamic acid stock to make standard 2. These standards were centrifuged and used to calibrate the HPLC.

Standardization of o-Ethoxybenzoic Acid and Salicylic Acid with Phthalic Acid for Quantitative Analysis of Cleavage Reactions.

o-Ethoxybenzoic acid(44.4 mg) and salicylic acid(40.0 mg) were weighed into a 10-mL volumetric flask and diluted to volume with 1,2-dichloroethane to give a stock concentration of 4.44 and 4.00 mg/mL respectively. Iodoethane(160.2 mg) was weighed into a separate 10-mL volumetric flask and diluted

to volume with 1,2-dichloroethane to give a stock concentration of 16.02 mg/mL. In another 100-mL volumetric flask, phthalic acid(200.0 mg) was weighed and diluted to volume with methanol to give a stock concentration of 2.000 mg/mL. For standard 1, 1 mL of o-ethoxybenzoic acid + salicylic acid stock solution was mixed with 2 mL of iodoethane stock and 1 mL of phthalic acid stock solution, while for standard 2, 2 mL of o-ethoxybenzoic acid + salicylic acid stock, 4 mL of iodoethane stock and 1 mL of phthalic acid stock was mixed. These 2 standards were centrifuged and used to calibrate the HPLC.

Standardization of o-Phenoxybenzoic Acid and Salicylic Acid with Phthalic Acid for Quantitative Analysis of Reactions.

o-Phenoxybenzoic acid(50.2 mg) and salicylic acid(50.2 mg) were weighed into a 25-mL volumetric flask and diluted to volume with ethyl ether to give stock concentration of 2.01 mg/mL. The phthalic acid used was prepared above and has a stock concentration of 2.000 mg/mL. For standard 1, 2 mL of o-phenoxybenzoic acid + salicylic acid was mixed with 2 mL of phthalic acid stock, while 5 mL of o-phenoxybenzoic acid + salicylic acid stock was mixed with 2 mL of phthalic acid stock to make standard 2. These 2 standards were centrifuged and used to calibrate the HPLC.

Attempted Cleavage of Naphthyl Ethers I and III with Pyridine Hydriodide and Other Cleaving Agents at Low Temperature.

The procedure for all ether reactions at low temperature are similar. Variations in the cleaving agent employed, reaction time, reaction temperature and concentration of the cleav-

ing agent are noted in the discussion section. A representative reaction is described here:

Naphthyl ether I(50.0 mg,0.176 mmol), pyridine hydriodide (62.1 mg, 0.30 mmol) in 8 mL pyridine were placed in a 25-ml round bottom flask equipped with a nitrogen atmosphere, reflux condenser and magnetic stirrer. The reaction was run at 100° for 3 days. At this point, a yellowish solution was observed. The cooled reaction mixture was then poured into 70 mL of 1M H_2SO_4 until the pH = 2 and no pyridine odor was detected. It was extracted with 3 x 10 mL of ethyl ether and the combined organic extracts washed with 1 x 10 mL brine solution and filtered. Bibenzyl(200.0 mg) was weighed and added to the solution as internal standard. The mixture was shaken and a 1-mL aliquot was taken, centrifuged and HPLC analysis done.

The eluting solvent for the HPLC was 85% acetonitrile/ 9.5% H_2O/0.5% acetic acid. The flow rate was 0.8 mL/min. Injections of 20-microliter or 10-microliter(to keep the peaks onscale) sample was used per run. The detector was a Beckman Model 153 Analytical UV Detector.

For the phenyl sulfide-catalyzed cleavage reaction, the eluting solvent for the HPLC was 60% acetonitrile/38% H_2O/ 2% acetic acid.

Naphthyl Ether I Reactions in the Presence of a Coal Fraction.

Naphthyl ether I(50.0 mg,0.176 mmol) and pyridine hydriodide(62.1 mg, 0.30 mmol) in 10 ml pyridine were placed in a 25-mL round bottom flask equipped with a reflux condenser, magnetic stirrer and connected via a three-way stopcock to a nitrogen line and an aspirator vacuum. Extracted coal[19]

(500.0 mg) was added slowly to the surface of the pyridine. Aspirator vacuum was gently applied and then slowly released to nitrogen atmosphere. This process was repeated 5 times, to insure the coal was thoroughly wetted by the solvent. The temperature was then brought to 110° and the reaction allowed to run for 7 days under nitrogen atmosphere.

After the reaction time, the reaction mixture was allowed to cool under nitrogen to room temperature. It was then poured into 70 mL of 1M HCl and extracted with 4 x 12 mL of ethyl ether. The organic extract was allowed to pass through a plug of glass wool. The combined extract was transferred to a separatory funnel and washed with 2 x 10 mL of 1M HCl, then with 1 x 10 mL brine solution and then diluted to volume in a 50-mL volumetric flask. A 1-mL aliquot was pipetted and passed through a C_{18} Sep-pak and 3 mL acetonitrile used to wash the Sep-pak, all 4 mL was collected. Bibenzyl(10.0 mg) was weighed and added to the aliqout as internal standard. The sample was centrifuged and HPLC analysis conducted. The total weight of the material in the reaction mixture is found by multiplying the weight found in the aliquot by a factor of 50.

Reactions of o-Anisic Acid, p-Anisic Acid, o-Ethoxybenzoic Acid and o-Phenoxybenzoic Acid with Pyridine Hydriodide or Other Cleaving Agents.

The procedure for these cleavage reactions is similar to the one employed for the naphthyl ether reactions, however the following changes should be noted. The extracting solvent was 1,2-dichloroethane or ethyl ether, the internal standard was either hydrocinnamic or phthalic acid, the HPLC eluting

solvent for o-, p-anisic acid was 40% methanol/57% water/2.5% acetic acid. For o-phenoxybenzoic acid, it was 50% methanol/47.5% water/2.5% acetic acid while it was 35% methanol/61.8% water/3.2% acetic acid for o-ethoxybenzoic acid.

o-Anisic acid(26.6 mg, 0.175 mmol), pyridine hydriodide (62.1 mg, 0.300 mmol) in 10 mL pyridine were placed in a 25-mL round bottom flask, the flask being under nitrogen atmosphere and equipped with reflux condenser. The mixture was heated at 85° for 3 days. The work-up follows that of the naphthyl ether I reaction. Hydrocinnamic acid(300.0 mg) was used as internal standard.

In some of the experiments, a modification of the work-up was carried out, The combined organic extract was diluted to volume with 1,2-dichloroethane in a 50-mL volumetric flask. A 10-mL aliquot was pipetted out, hydrocinnamic acid(32.0 mg) was weighed and added to the aliquot. The total weight of the material to be analyzed was found by multiplying the weight of the material in the aliquot by a factor of 5.

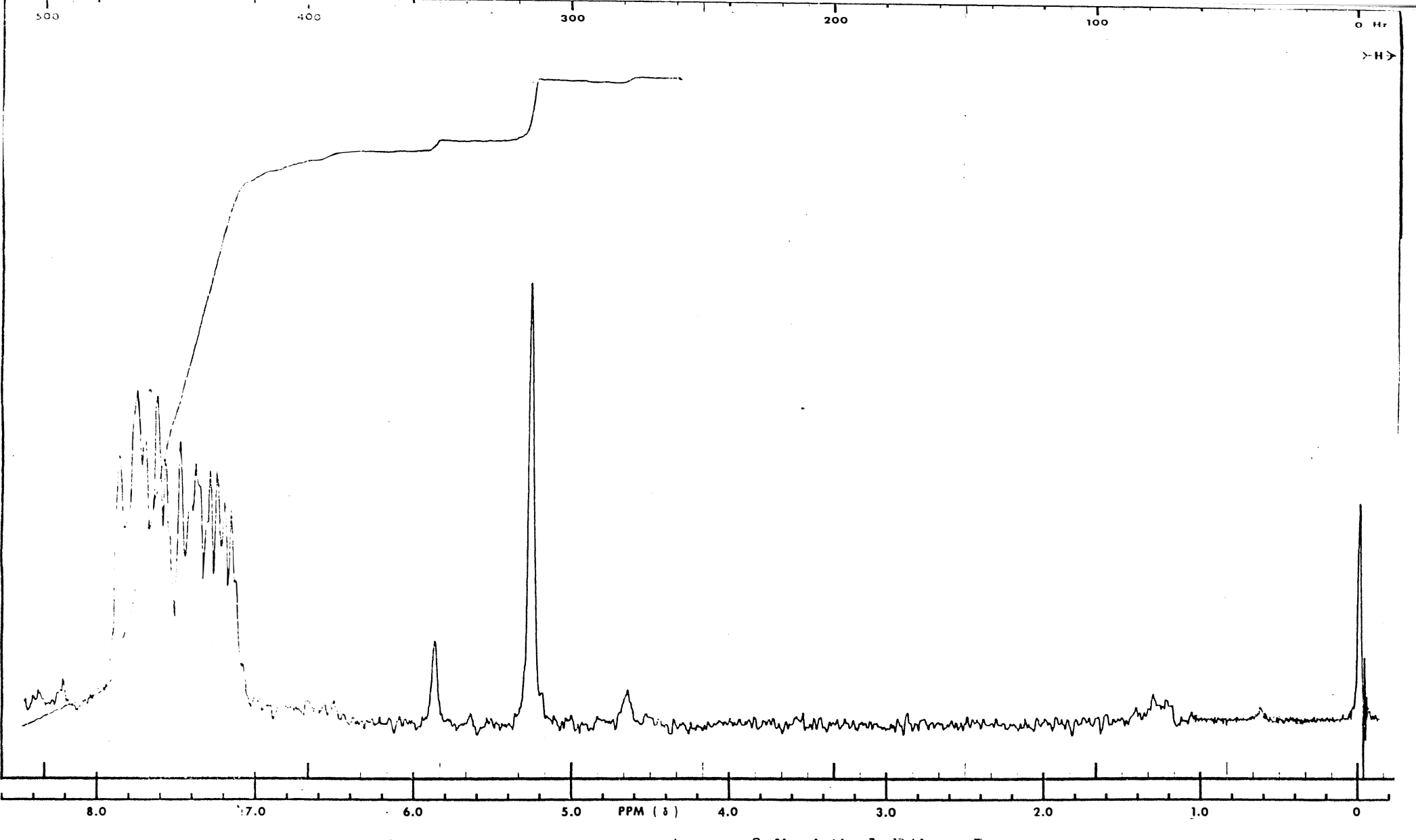


Figure I : nmr spectrum of Naphthyl Ether I

(Beta-methylnaphthyl beta-naphthyl ether)

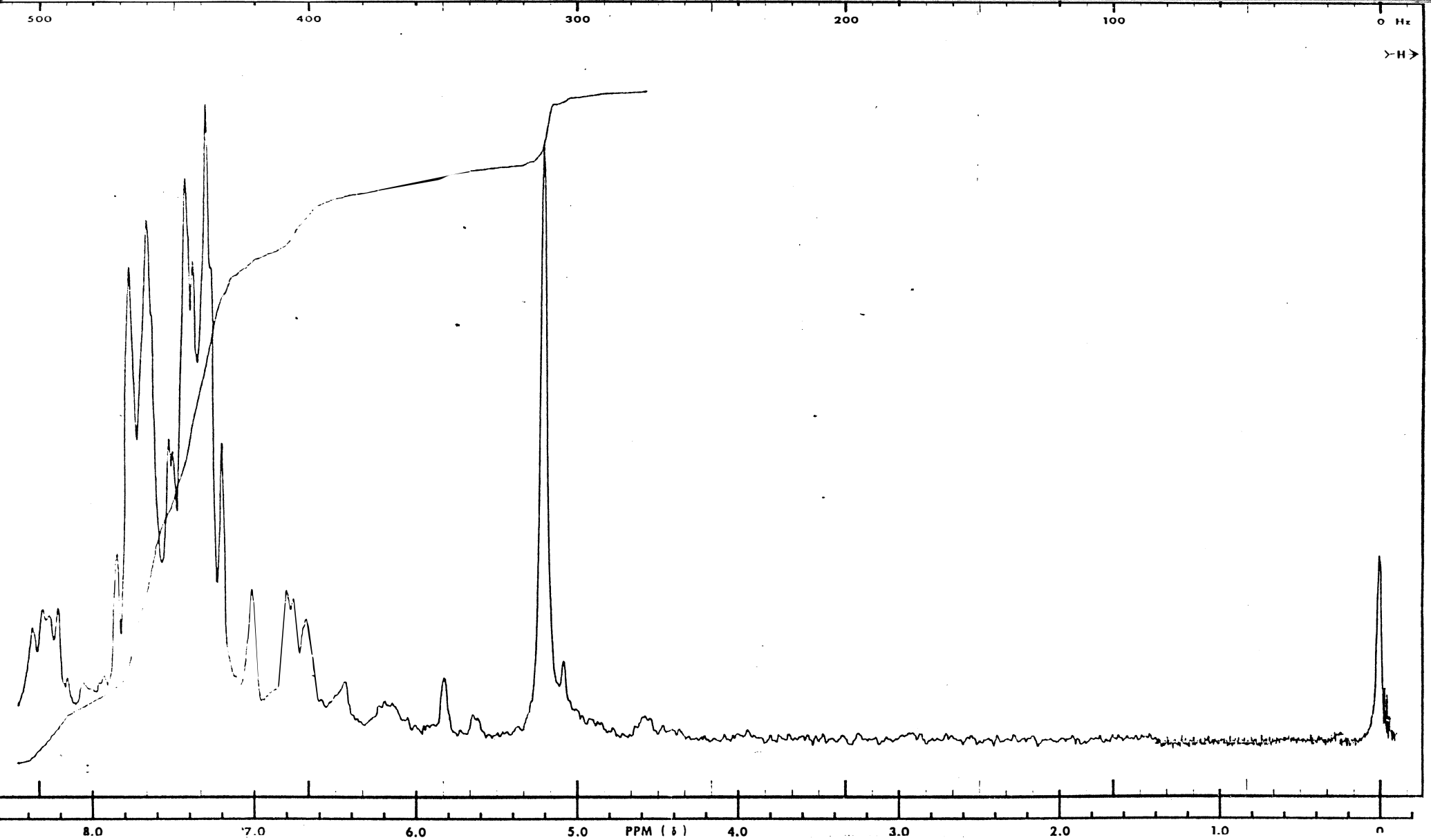


Figure II : nmr spectrum of Naphthyl Ether II

(Beta-methylnaphthyl alpha-naphthyl ether)

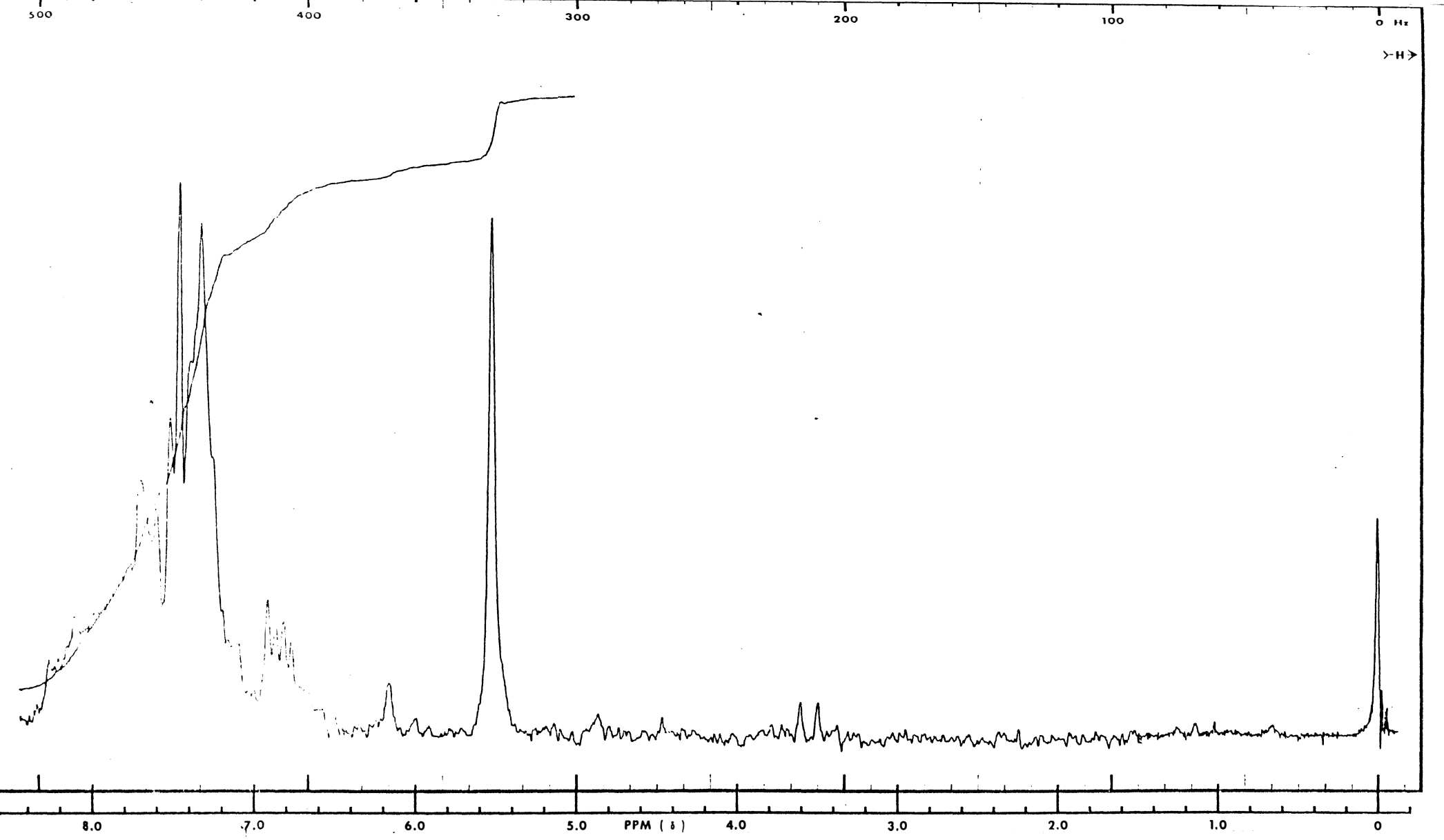


Figure III : nmr spectrum of Naphthyl Ether III

(Alpha-methylnaphthyl alpha-naphthyl ether)

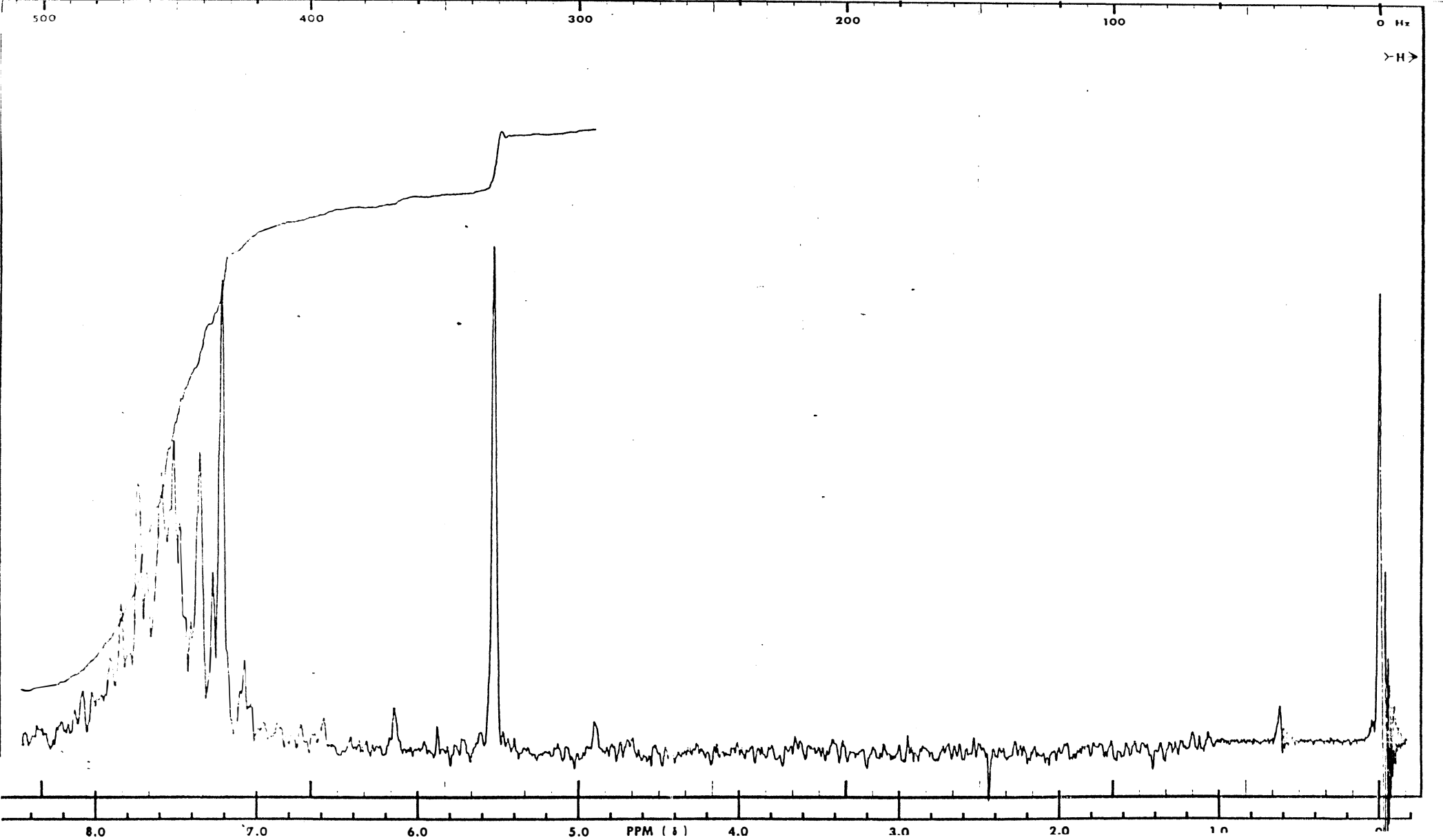


Figure IV : nmr spectrum of Naphthyl Ether IV

(Alpha-methylnaphthyl beta-naphthyl ether)

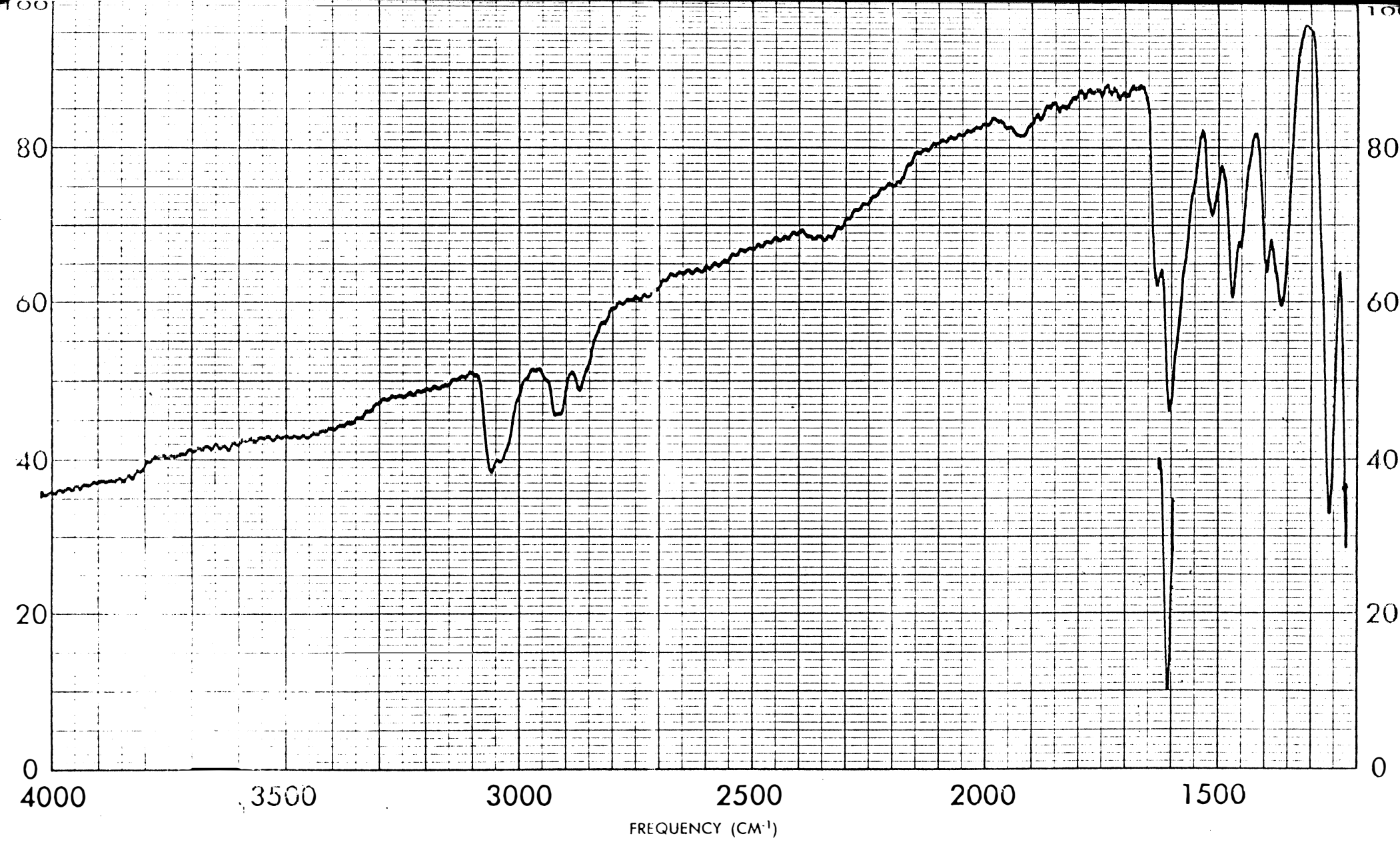


Figure V : ir spectrum of Naphthyl Ether I

(Beta-methylnaphthyl beta-naphthyl ether)

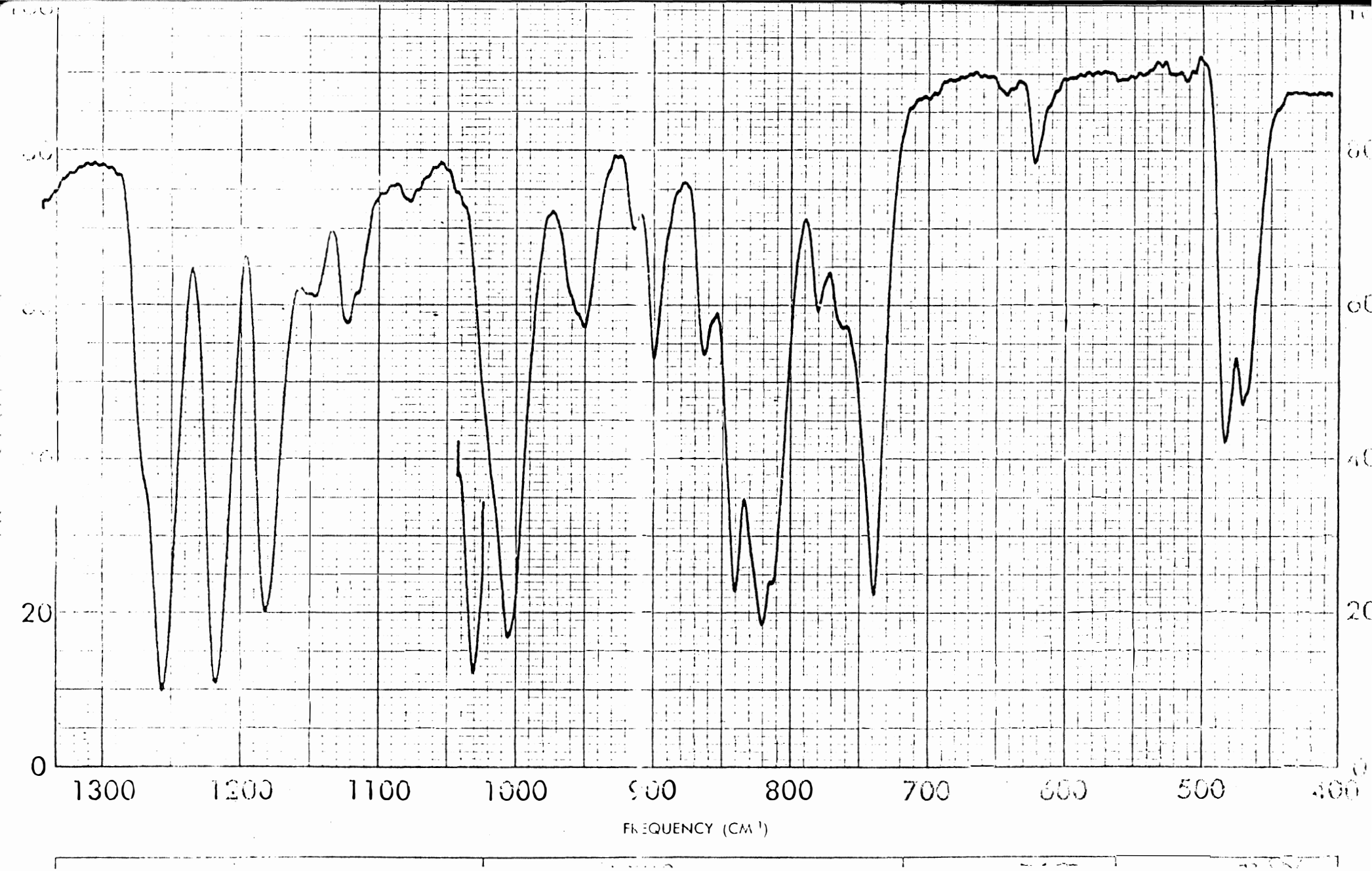


Figure V : ir spectrum of Naphthyl Ether I

(Beta-methylnaphthyl beta-naphthyl ether)

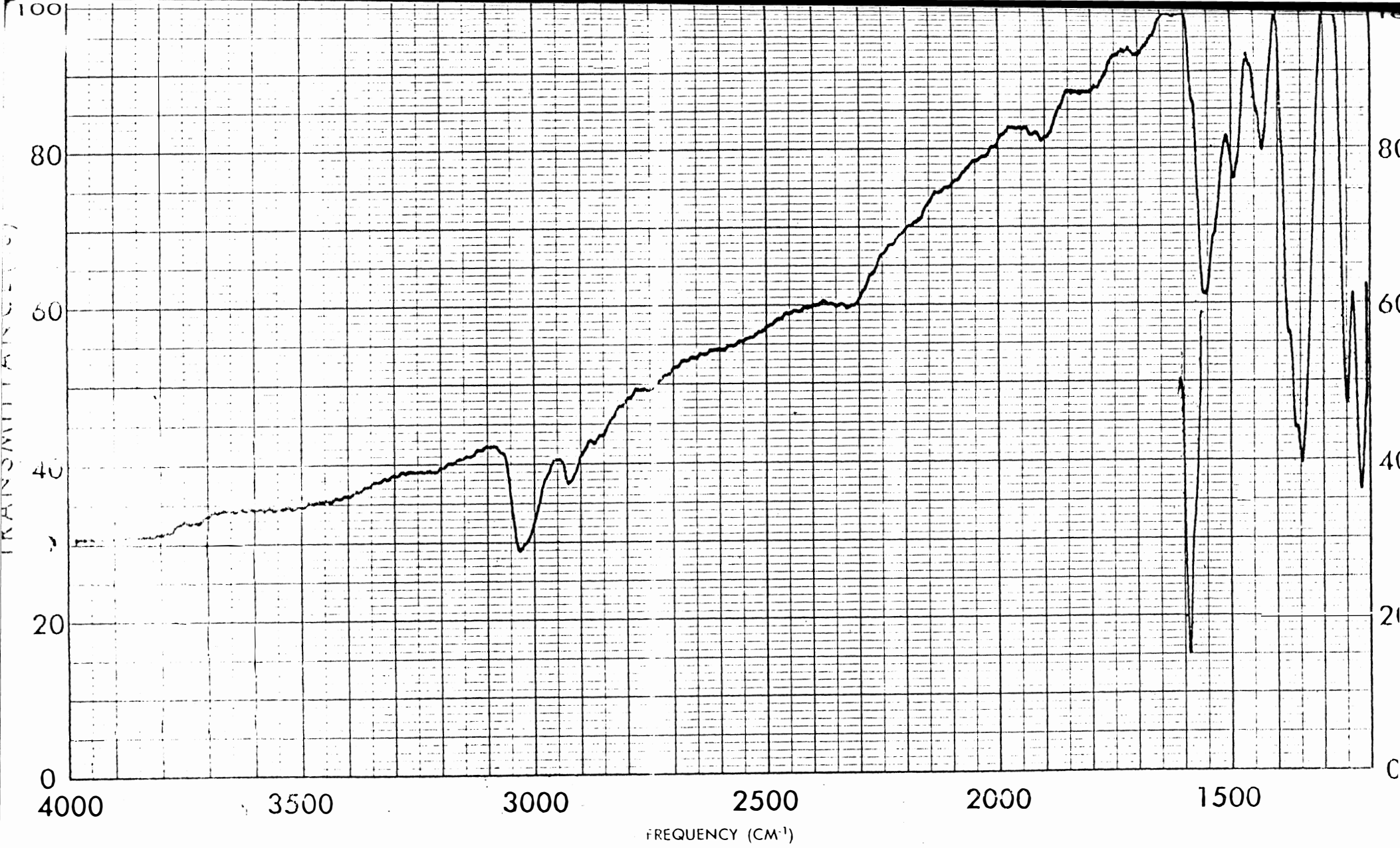


Figure VI : ir spectrum of Naphthyl Ether II

(Beta-methylnaphthyl alpha-naphthyl ether)

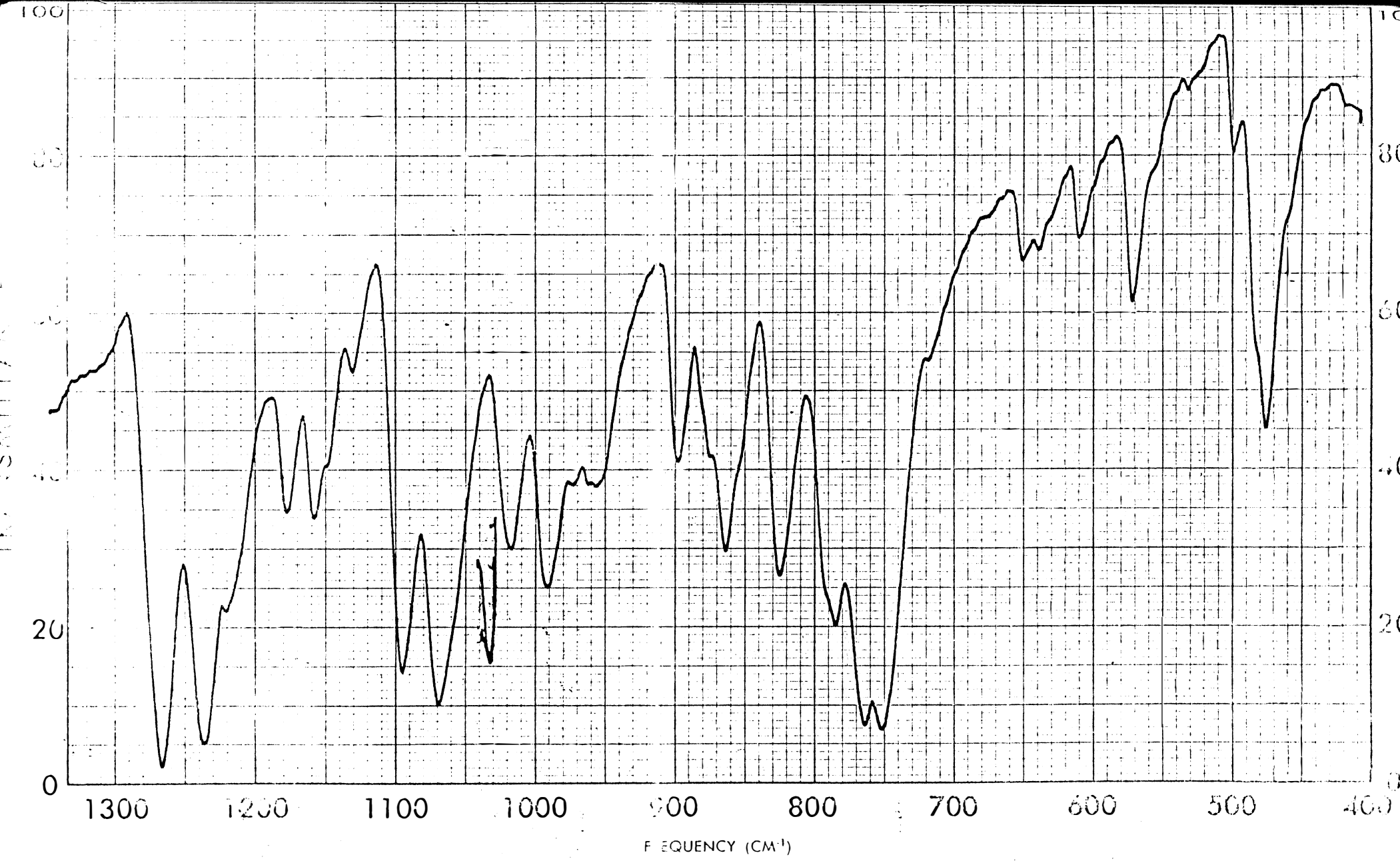


Figure VI : ir spectrum of Naphthyl Ether II

(Beta-methylnaphthyl alpha-naphthyl ether)

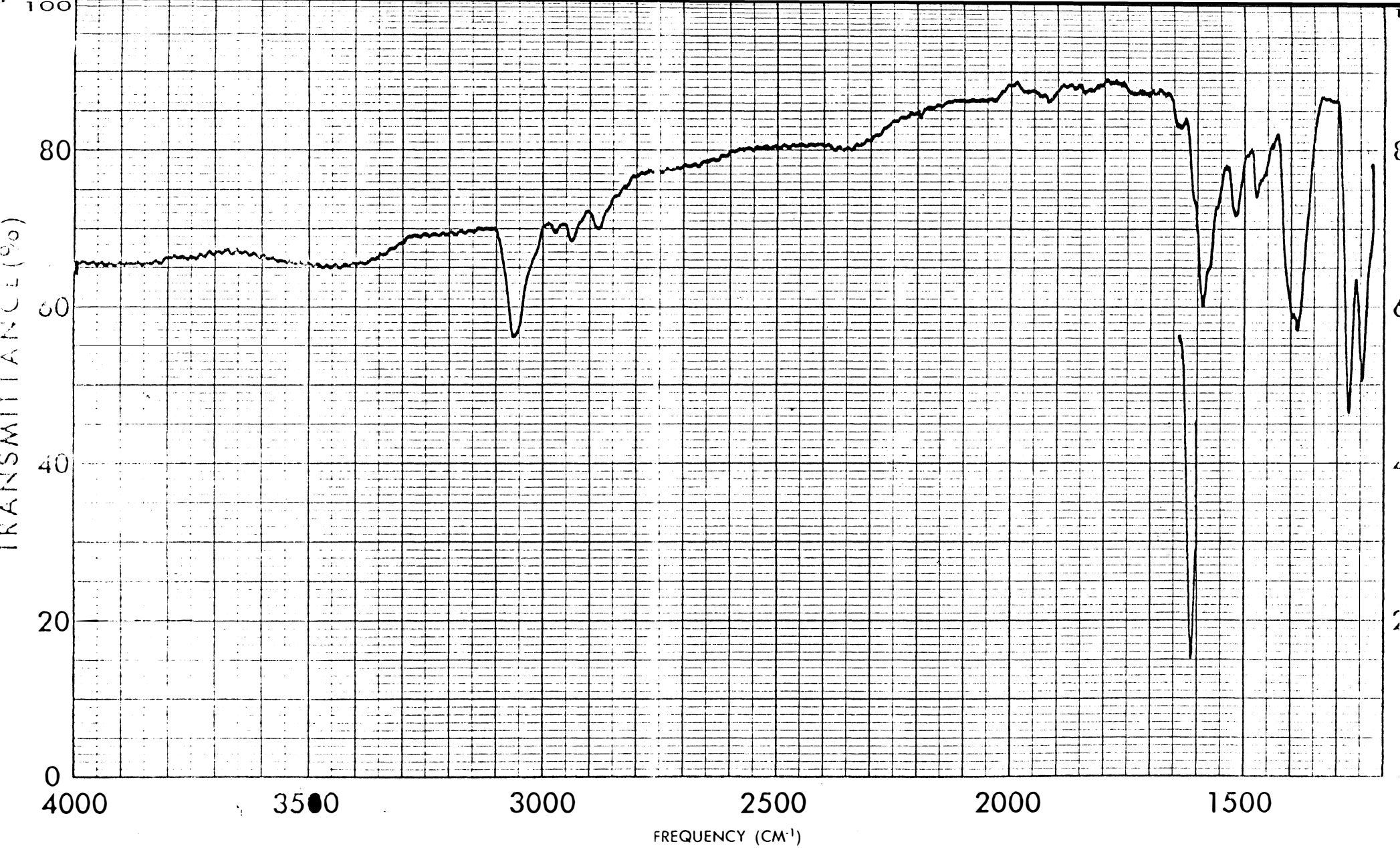


Figure VII : ir spectrum of Naphthyl Ether III

(Alpha-methylnaphthyl alpha-naphthyl ether)

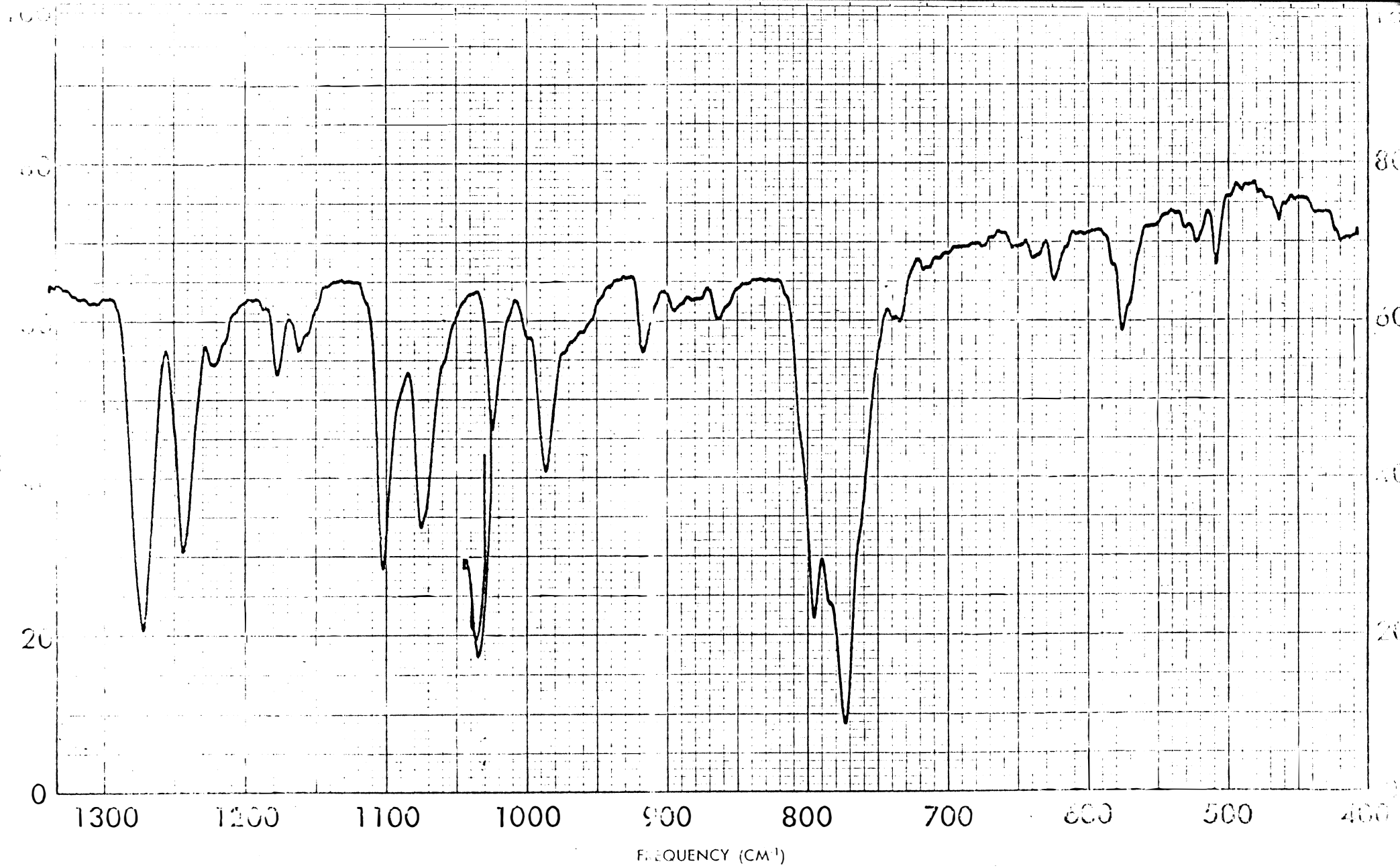


Figure VII : ir spectrum of Naphthyl Ether III

(Alpha-methylnaphthyl alpha-naphthyl ether)

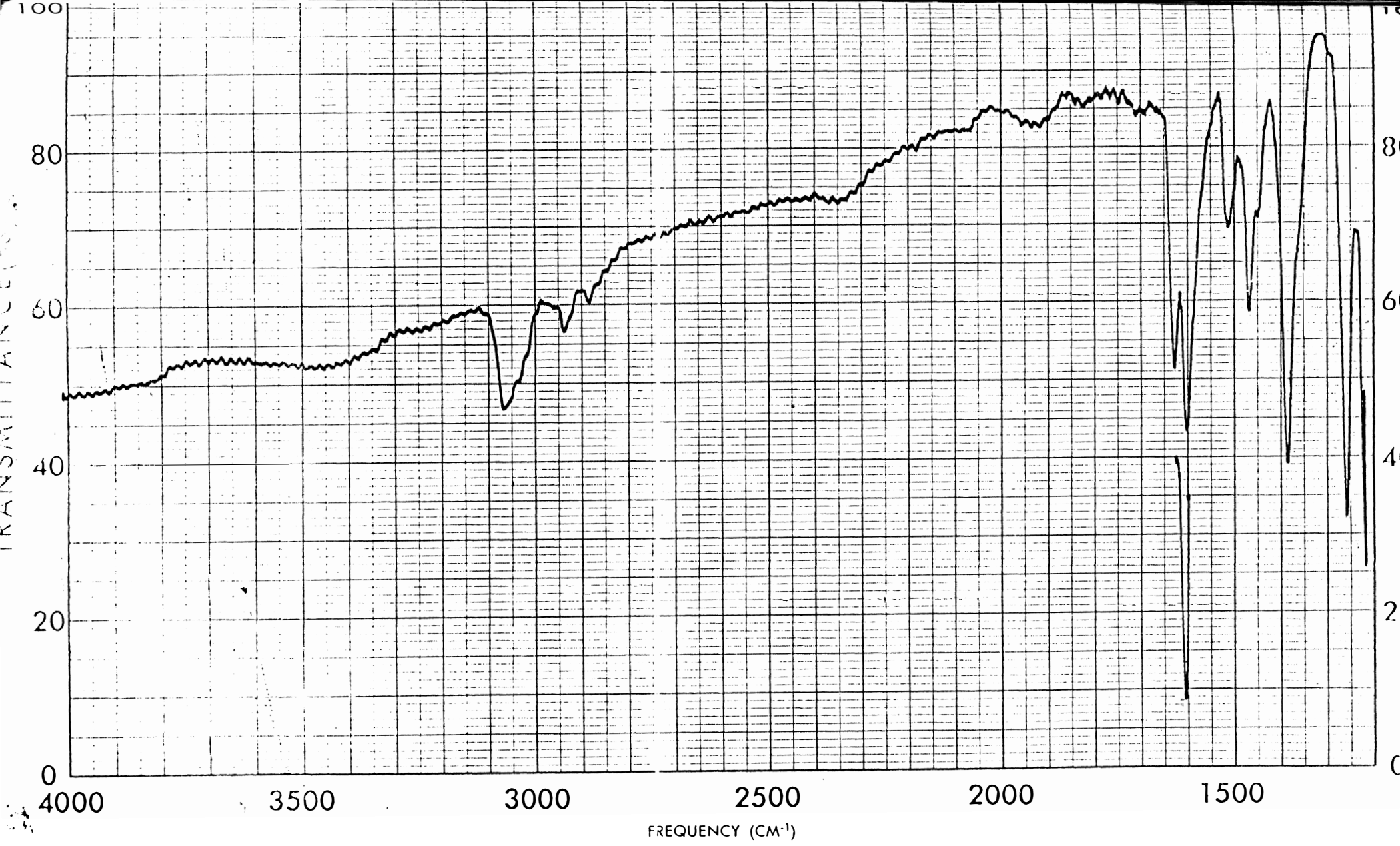


Figure VIII : ir spectrum of Naphthyl Ether IV
(Alpha-methylnaphthyl beta-naphthyl ether)

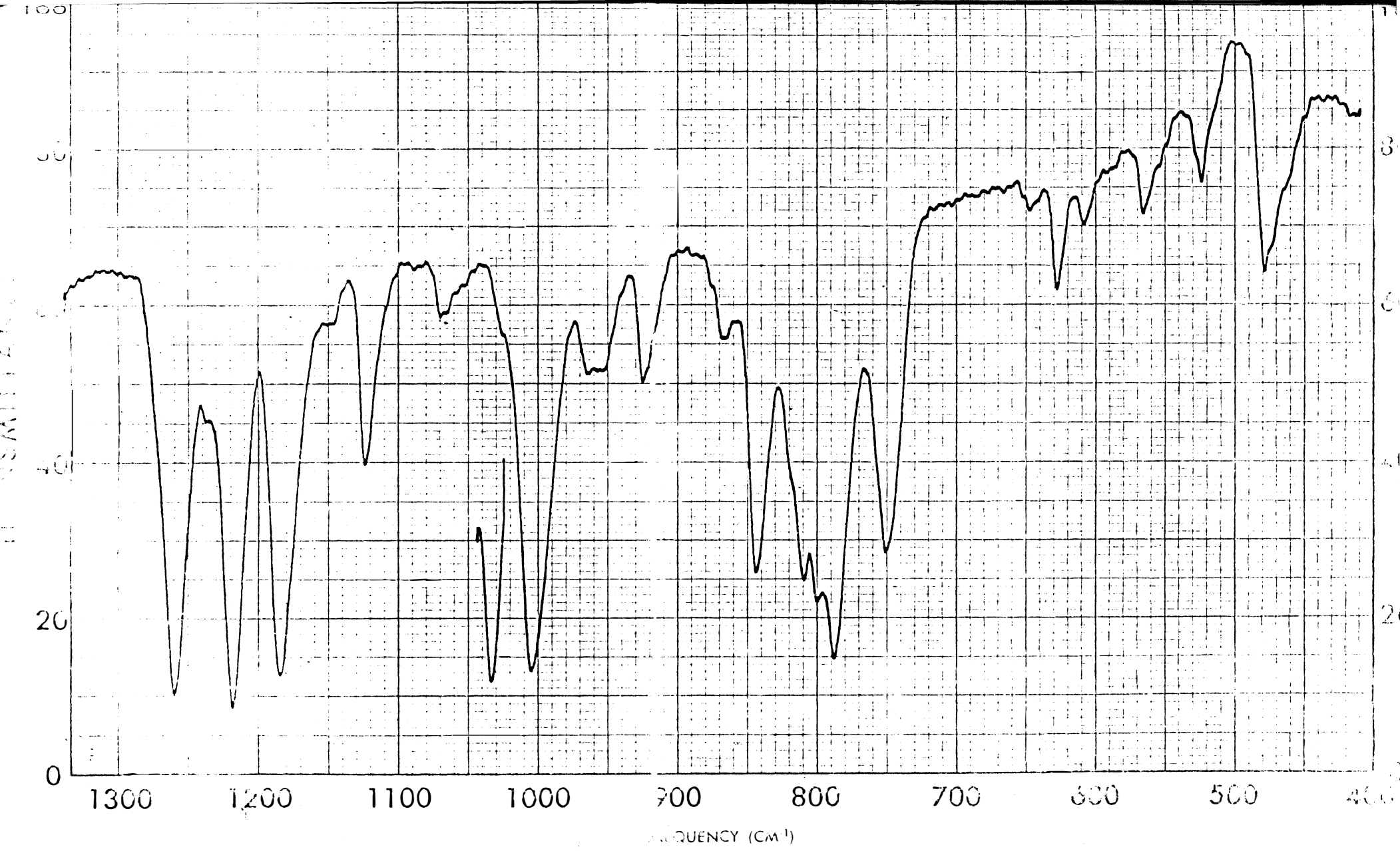


Figure VIII : ir spectrum of Naphthyl Ether IV

(Alpha-methylnaphthyl beta-naphthyl ether)

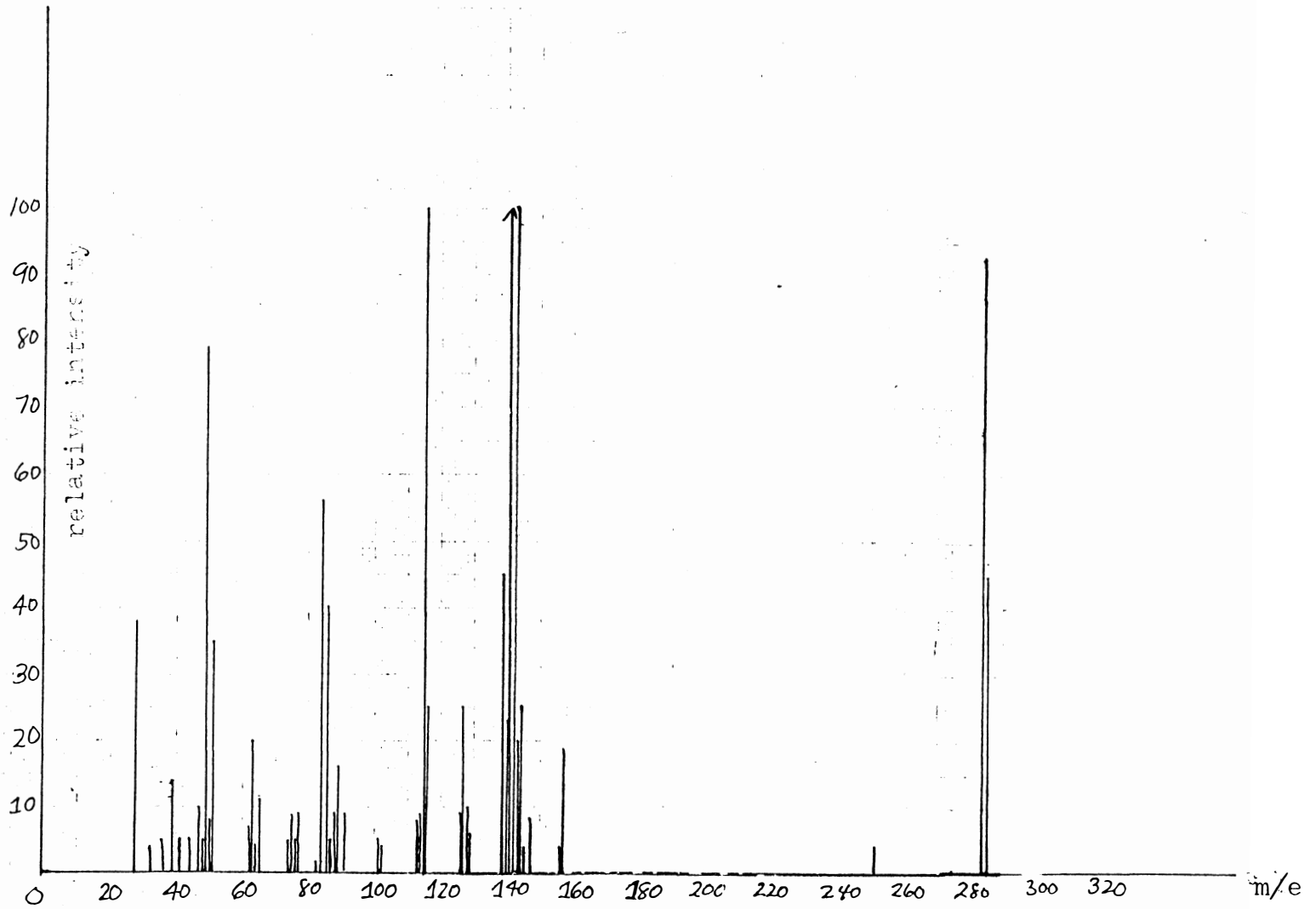


Figure IX : mass spectrum of Naphthyl Ether I
(Beta-methylnaphthyl beta-naphthyl ether)

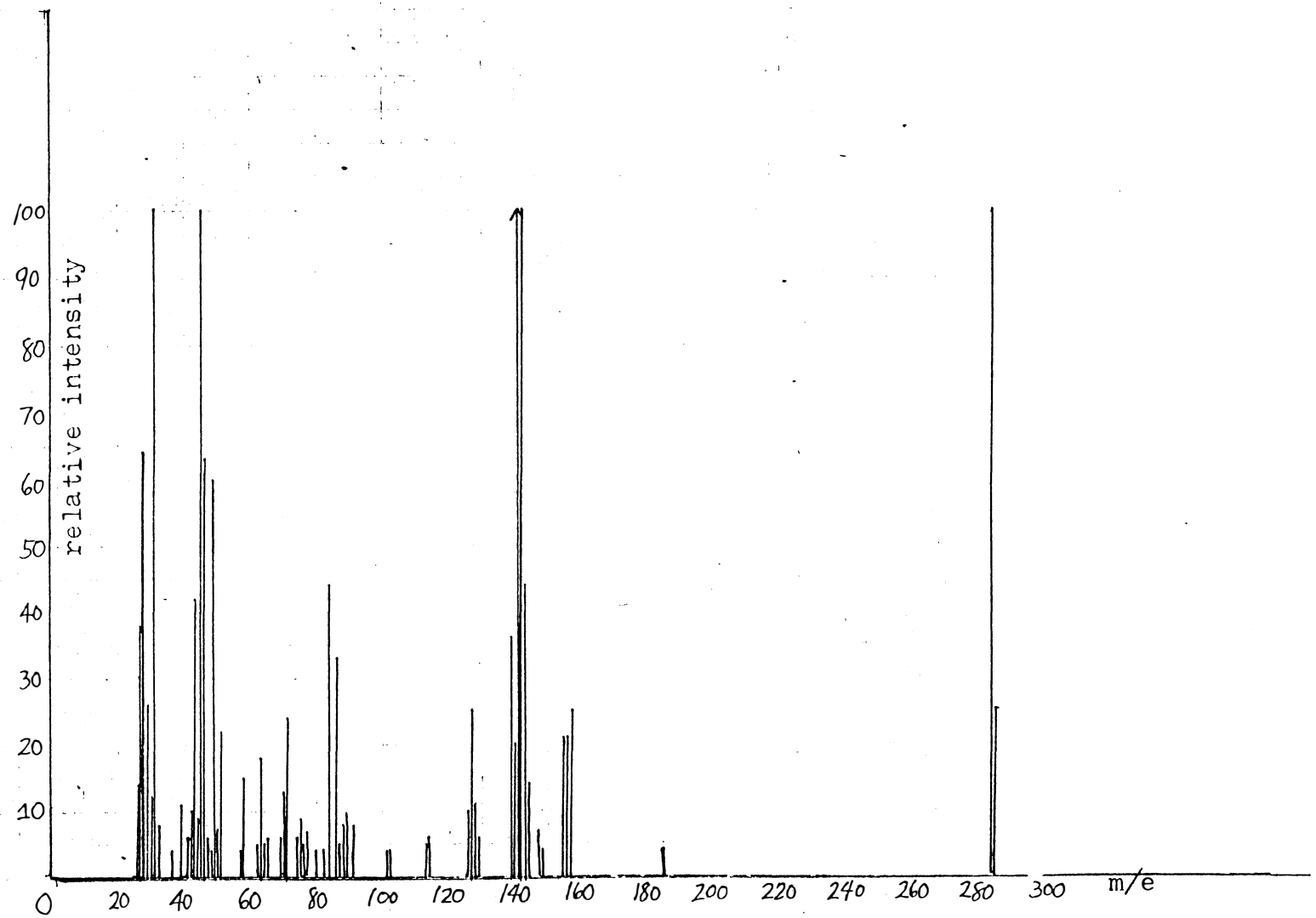


Figure X : mass spectrum of Naphthyl Ether II
(Beta-methylnaphthyl alpha-naphthyl ether)

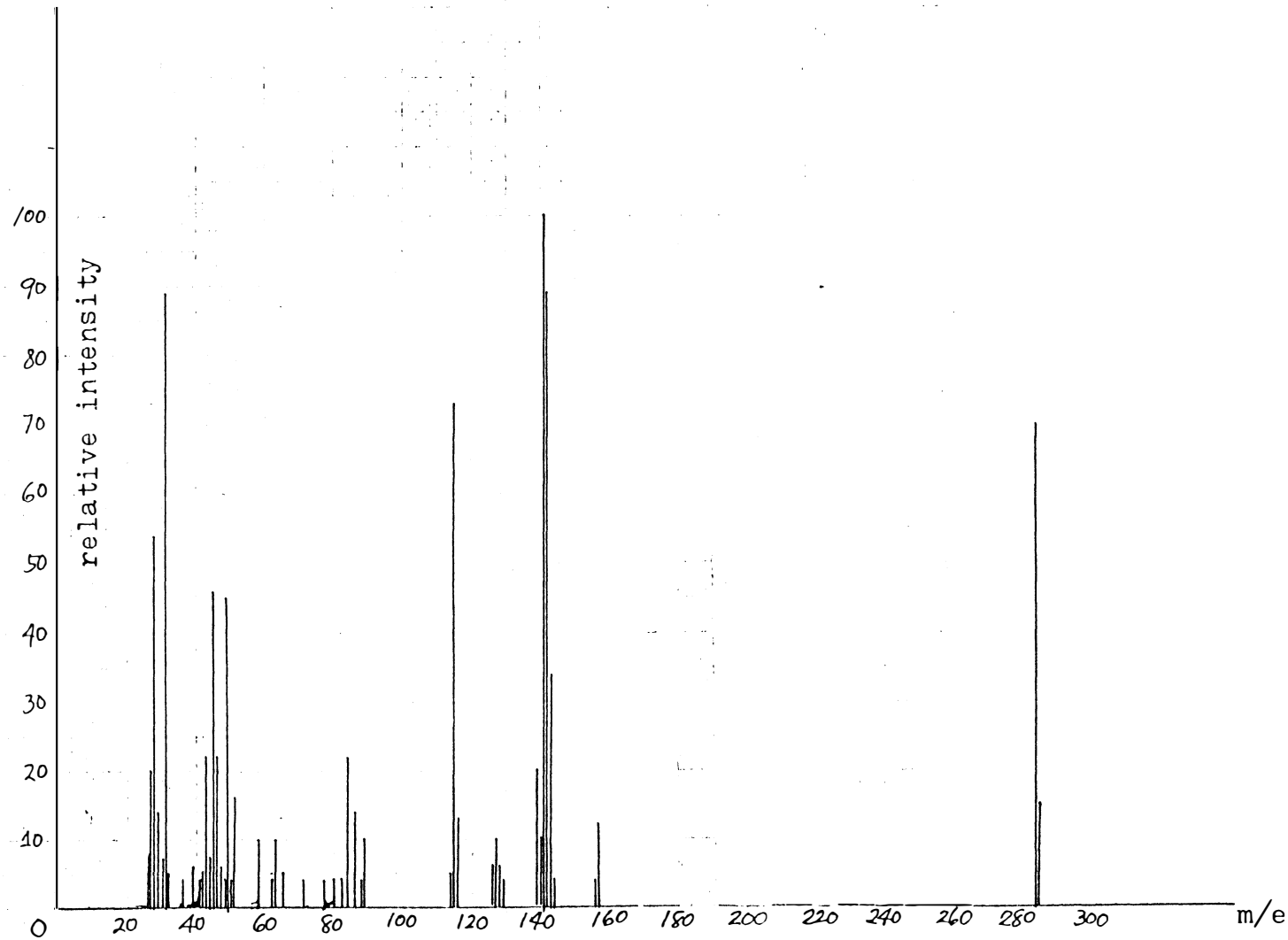


Figure XI : mass spectrum of Naphthyl Ether III
(Alpha-methylnaphthyl alpha-naphthyl ether)

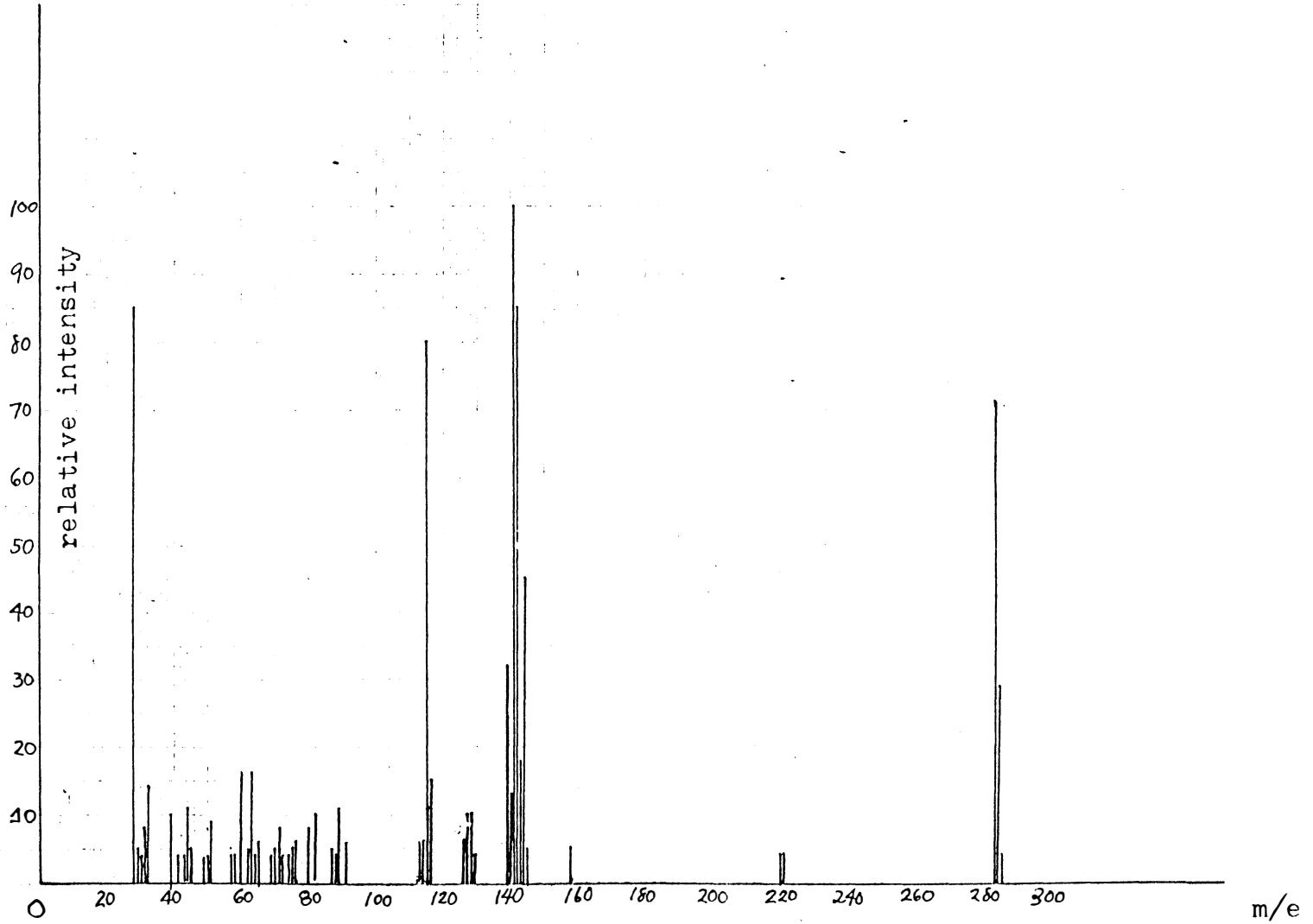


Figure XII: mass spectrum of Naphthyl Ether IV
(Alpha-methylnaphthyl beta-naphthyl ether)

Standardization of Naphthyl Ether I and Beta-naphthol Using Bibenzyl as Internal Standard

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Bibenzyl	3.2	6.67 10.0	80290 80917	1 0
Naphthyl Ether I	4.1	0.267 0.200	43877 21375	0.0708 0.0013
Beta-Naphthol	2.1	0.267 0.200	29478 14149	0.104 0.0018

Standardization of Naphthyl Ether I and Beta-naphthol Using Naphthalene as Internal Standard

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Naphthalene	4.6	0.500 0.333	164585 79841	1 0
Beta-Naphthol	2.7	0.400 0.533	119811 113879	1.146 -0.034
Naphthyl Ether I	14.5	0.400 0.533	199608 203240	0.600 0.072

* For bibenzyl and naphthalene, $C_1;C_2$ is $C_{is}1;C_{is}2$.

** For bibenzyl and naphthalene, $A_1;A_2$ is $A_{is}1;A_{is}2$; Integrated areas are average of duplicate runs.

Standardization of o-Phenoxybenzoic Acid and Salicylic Acid Using Phthalic Acid as Internal Standard.

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Phthalic Acid	2.3	1.00 0.571	139518 118691	1 0
o-Phenoxybenzoic Acid	7.3	1.01 1.44	135895 249523	1.348 -0.2988
Salicylic Acid	3.9	1.01 1.44	74428 151934	2.037 -0.0725

Standardization of Naphthyl Ether III and Alpha-naphthol Using Bibenzyl as Internal Standard

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Bibenzyl	3.0	6.67 3.33	123419 87450	1 0
Naphthyl Ether III	3.8	0.533 0.667	52147 85854	0.3635 -0.0051
Alpha-Naphthol	2.1	0.533 0.667	28881 49372	0.2149 -0.0109

* For phthalic acid and bibenzyl, $C_1;C_2$ is $C_{is}1;C_{is}2$.

** For phthalic acid and bibenzyl, $A_1;A_2$ is $A_{is}1;A_{is}2$
Integrated areas are average of duplicate runs.

Standardization of o-Anisic Acid and Salicylic Acid Using Phthalic Acid as Internal Standard

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Phthalic Acid	2.7	0.667 0.333	71429 58556	1 0
o-Anisic Acid	4.2	0.667 0.833	45509 90230	1.661 -0.059
Salicylic Acid	5.6	0.667 0.833	27766 60554	2.327 0.010

Standardization of o-Anisic Acid and Salicylic Acid Using Hydrocinnamic Acid as Internal Standard***

Compound	Retention Time(min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Hydrocinnamic Acid	7.8	3.00 2.00	75630 59404	1 0
o-Anisic Acid	4.1	0.500 0.667	74192 161797	0.1693 0.0006
Hydrocinnamic Acid	7.8	3.50 2.00	317804 198112	1 0
Salicylic Acid	4.8	0.200 0.286	67544 98612	0.3005 -0.0067

* For phthalic and hydrocinnamic acid, $C_1;C_2$ is $C_{is}1;C_{is}2$.

** For phthalic anf hydrocinnamic acid, $A_1;A_2$ is $A_{is}1;A_{is}2$ Integrated areas are average of duplicate runs

*** This calibration was done at 2 different concentrations of the standards.

Standardization of p-Anisic and p-Hydroxybenzoic Acid Using Hydrocinnamic Acid as Internal Standard

Compound	Retention Time (min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Hydrocinnamic Acid	8.1	5.45 5.00	155946 70103	1 0
p-Anisic Acid	6.1	0.0454 0.0833	125697 121572	0.009 0.0011
p-Hydroxybenzoic Acid	3.0	0.0454 0.0833	120639 104275	0.0117 -0.0007

Standardization of o-Ethoxybenzoic Acid and Salicylic Acid Using Phthalic Acid as Internal Standard

Compound	Retention Time (min.)	$C_1;C_2$* (mg/mL)	$A_1;A_2$**	$F_1;F_2$
Phthalic Acid	3.1	0.500 0.286	118510 48258	1 0
o-Ethoxybenzoic Acid	8.7	1.11 1.27	194494 158209	1.354 -0.0025
Salicylic Acid	7.1	1.00 1.14	126107 105924	1.765 0.121

* For phthalic and hydrocinnamic acid, $C_1;C_2$ is $C_{is}1;C_{is}2$

** For phthalic and hydrocinnamic acid, $A_1;A_2$ is $A_{is}1;A_{is}2$

Integrated areas are average of duplicate runs.

RESULTS

Table I : Cleaving agents, solvent, temperature, reaction time and ether recovery for naphthyl ether reactions **

Exp No.	Ether	Cleaving Agent	Solvent	Temp. (°C)	Time (days)	% Ether Recovery
1	I	----	Pyridine	90°	3	96
2	I	Py·HI	Pyridine	85°	6	103
3	I	Py·HI	Pyridine	100°	3	101
4	I	Py·HI	95% Pyridine 5% H_2O	110°	7	96
5	I	Py·HI	CH_3CN	78°	5	94
6	I	HI gas	Pyridine	59°	3	94
7	I	57% HI	aq. HI	135°	0.13	69*
8	I	Py·HI $FeCl_2 \cdot 4H_2O$	Pyridine	95°	6	95
9	I	Py·HI FeS_2	Pyridine	95°	4	99
10	I	FeS	Pyridine	90°	5	102
11	I	Py·HI FeS	Pyridine	90°	5	102
12	I	$LiI \cdot 3H_2O$	Pyridine	90°	5	98
13	III	Py·HI	Pyridine	115°	3	102
14	I	Py·HI $(Ph)_2S$	Pyridine	115°	3	94
15	I	Py·HI coal	Pyridine	115°	7	94
16	I	coal	Pyridine	115°	7	93

* 0.023 mmol of beta-naphthol was also detected(13% cleavage).

** The average for ether recovery is 98 ± 3%.

Table II : Quantitative Analysis of Naphthyl Ether Product Mixture by HPLC

Exp. No.	Ether	Amount Ether (mmol)	Cleaving Agent	Amount C.A. (mmol)	Area of Standard	Area of Ether	Wt. of Standard (mg)	Recovered Ether (mmol)
1	I	0.176	----	-----	131707	198575	450	0.169
2	I	0.176	Py·HI	0.300	8707	31431	200	0.181
3	I	0.176	Py·HI	0.300	50288	88941	400	0.178
4	I	0.176	Py·HI	0.600	36468	122868	200	0.169
5	I	0.176	Py·HI	0.600	60153	98701	400	0.165
6	I	0.176	HI gas	3-hr bubbling	39667	131718	200	0.166
7	I	0.176	57% HI	7.60	166458	402807	200	0.122
8	I	0.176	Py·HI $FeCl_2 \cdot 4H_2O$	0.300	83382	278793	200	0.168
9	I	0.176	Py·HI FeS_2	0.300 0.040	57066	198847	200	0.175
10	I	0.176	FeS	0.090	153217	241540	450	0.179
11	I	0.176	Py·HI FeS	0.300 0.090	93319	146959	450	0.179
12	I	0.176	$LiI \cdot 3H_2O$	0.300	127207	193071	450	0.172

Table II : Quantitative Analysis of Naphthyl Ether Product Mixture by HPLC(cont'd)

Exp. No.	Ether	Amount Ether (mmol)	Cleaving Agent	Amount C.A. (mmol)	Area of Standard	Area of Ether	Wt. of Standard (mg)	Recovered Ether (mmol)
13	III	0.176	Py·HI	0.300	126232	105822	60.0*	0.179
14	I	0.176	Py.HI $(Ph)_2S$	0.300 0.130	199618	601287	5.0**	0.165
15	I	0.176	Py·HI ext. coal	0.300 0.50 g	174278	112075	20.0***	0.165
16	I	0.176	ext. coal	0.50 g	161360	102860	20.0***	0.163

* 1/5 aliquot was analyzed

** 1/5 aliquot was analyzed, naphthalene used as internal standard

*** 1/50 aliquot was analyzed.

Table III : Cleaving agents, solvent, temperature, reaction time and ether recovery for cleavage reactions involving o-anisic acid and related ethers**

Exp No.	Ether	Cleaving Agent	Solvent	Time (days)	Temp (°C)	% Ether Recovery	% Clvg* Product
A	o-anisic acid	Py·HI	Pyridine	3	85°	80	10
B	o-anisic acid	Py·HI	Pyridine	3	115°	10	86
C	o-anisic acid	Py·HI	Pyridine	3	115°	18	76
D	o-anisic acid	KI	Pyridine	3	115°	33	58
E	o-anisic acid	$LiI \cdot 3H_2O$	Pyridine	3	85°	44	54
F	o-anisic acid	Py·HI	CH_3CN	4	75°	99	--
G	o-anisic acid	KI in 18-c-6 ether	CH_3CN	4	75°	94	--
H	o-anisic acid	Py·HI	DMSO	4	75°	94	--
I	o-ethoxy-benzoic acid	Py·HI	Pyridine	3	115°	84	18
J	p-anisic acid	Py·HI	Pyridine	3	115°	96	--
K	o-phenoxy-benzoic acid	$LiI \cdot 3H_2O$	Pyridine	5	90°	94	--
L	o-phenoxy-benzoic acid	Py·HI	Pyridine	3	115°	101	--

* The cleavage product detected was salicylic acid.

** The average for mass balance is 96 ± 3%.

Table IV : Quantitative Analysis of o-Anisic Acid and Related Ether Reactions by HPLC

Exp. No.	Ether	Amount Ether (mmol)	Cleaving Agent	Amount C.A. (mmol)	Area of Standard	Area of Ether	Wt. of*** Standard (mg)	Ether Recovered (mmol)
A	o-anisic acid	0.175	Py·HI	0.333	279172	218080	32.0**	0.140
B	o-anisic acid	0.175	Py·HI	0.310	258858	24448	32.0**	0.017
C	o-anisic acid	0.175	Py·HI	0.300	256336	43107	32.0**	0.032
D	o-anisic acid	0.173	KI	0.333	264846	83147	32.0**	0.057
E	o-anisic acid	0.175	$LiI \cdot 3H_2O$	0.370	185936	43662	300.0	0.077
F	o-anisic acid	0.175	Py·HI	0.300	134532	111508	20.0*	0.174
G	o-anisic acid	0.175	KI in 18-c-6 ether	0.300 0.060	120386	94214	20.0*	0.164
H	o-anisic acid	0.175	Py·HI	0.300	137035	108246	20.0*	0.165
I	o-ethoxy-benzoic acid	0.162	Py·HI	0.300	62304	208488	1.0**	0.136
J	p-anisic acid	0.179	Py·HI	0.300	328846	278910	300.0****	0.172
K	o-phenoxybenzoic acid	0.175	$LiI \cdot 3H_2O$	0.300	102974	149800	20.0*	0.165
L	o-phenoxybenzoic acid	0.175	Py·HI	0.300	154497	202020	5.0**	0.176

* The internal standard was phthalic acid.

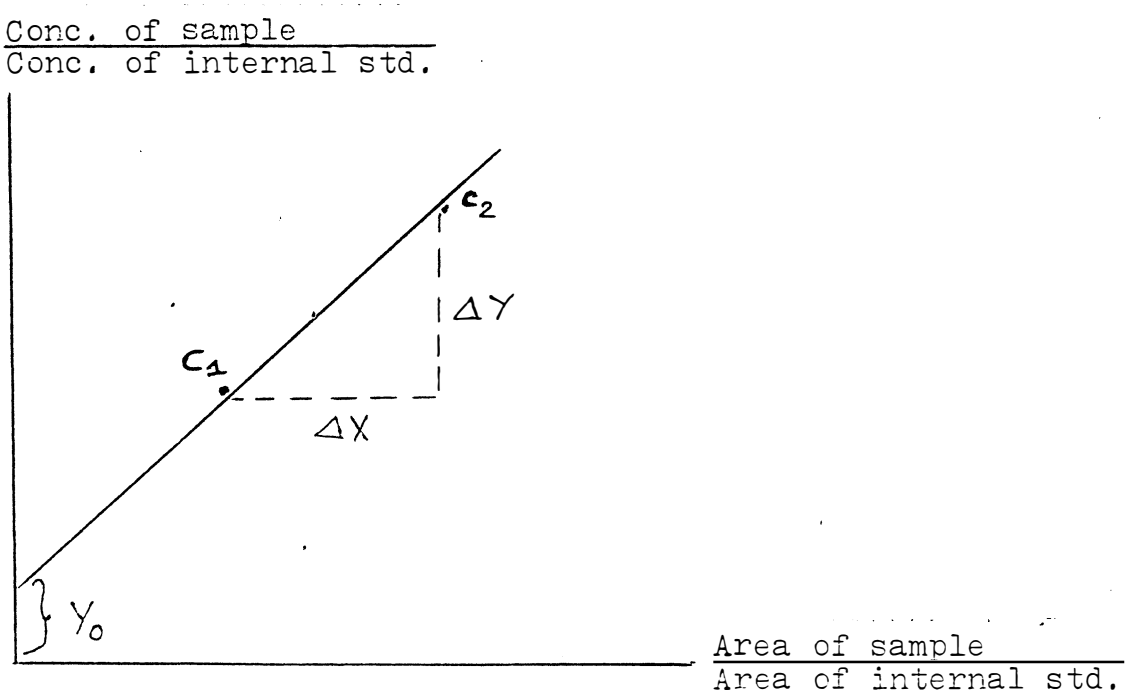
** 1/5 aliquot was analyzed.

*** Unless specified otherwise, the internal standard used was hydrocinnamic acid.

**** 1/10 aliquot was analyzed.

DISCUSSION

The analytical procedure for the HPLC quantitative analysis was done in the following way: A method called 2-point calibration was used. Duplicate determination of two solutions containing different concentrations of standard compounds and internal standard were injected into the HPLC. Since the 2 solutions contain known amounts of each component and the areas under the peaks are integrated, a response factor can be calculated. In calibrating against an internal standard, a plot of the concentration of sample/concentration of internal standard vs. area of sample/area of internal standard would yield the slope($\Delta Y/\Delta X$) called F_1 and the Y-intercept (Y_o) called F_2.



$$F_1 = \frac{C_2 \times C_{is}^1 - C_1 \times C_{is}^2}{C_{is}^1 \times C_{is}^2 (A_2/A_{is}^2 - A_1/A_{is}^1)} \quad ; \quad F_2 = \frac{C_2}{C_{is}^2} - F_1 \times \frac{A_2}{A_{is}^2}$$

C_1 : concentration of standard sample 1

C_2 : concentration of standard sample 2

C_{is}^1 : concentration of internal standard in standard sample 1

C_{is}^2 : concentration of internal standard in standard sample 2

A_1 : peak area of standard sample 1

A_2 : peak area of standard sample 2

A_{is}^1 : peak area of internal standard in standard sample 1

A_{is}^2 : peak area of internal standard in standard sample 2

With the response factor for the compound of interest determined, if a known amount of internal standard is now added to a reaction mixture, the content of the mixture can be calculated:

$$W_{spl} = (F1_i \times A_i/A_{is} + F2_i) \times W_{is}$$

Where:

A_i = area of sample

A_{is} = area of internal standard

$F1_i$ = response factor for slope

$F2_i$ = response factor for intercept

W_{is} = weight of internal standard

W_{spl} = weight of material in the sample

It should be noted that the absolute weight of the material in the sample can be calculated directly even though

the calibration was done in terms of concentration because both the compound of interest and the internal standard were in the same volume of reaction mixture and thus the factor for volume cancels out in the computation.

Attempted Cleavage of Naphthyl Ethers I and III with Pyridine Hydriodide and Other Cleaving Agents

Reactions of naphthyl ethers were conducted to understand the results of Mayo *et al*[10] who had shown that pyridine hydriodide in pyridine at room temperature decreased the molecular weight and increased the phenolic -OH content of an Illinois No.6 asphaltol fraction. Pyridine hydriodide in pyridine at 50° reduced the molecular weight of an Illinois No.6 asphaltol fraction to the same extent as sodium in liquid ammonia. In both cases it is believed that the ether linkages in coal are being cleaved.

Experiment No.1 served as a control experiment where no cleaving agent was added. With ether I in pyridine for 5 days at 90°, recovered ether after work-up was 96%.

In experiment 2, ether I was reacted with pyridine hydriodide in pyridine at 85° for 6 days. In experiment 3, the temperature was raised to 100° but the reaction time shortened to 3 days. No ether cleavage was detected in both runs, ether recovery being 103% and 101% respectively.

In experiment 4 and 5, cleavage with pyridine hydriodide was attempted in other solvents such as 95% pyridine/5% water or acetonitrile. In these solvents, no cleavage products were

found and ether recoveries were 96% and 94% respectively.

In experiment 6, HI gas was bled into a pyridine solution of ether I for 3 hours, then the reaction was allowed to proceed at 59° for 3 days. Ether recovery was 94%.

Hydroiodic acid is known as a standard cleaving agent of alkyl ethers[20]. In experiment 7, aqueous HI is tested in cleaving ether I, the reaction was carried out at 135° for 3 hours, ether recovered was 69% and 13% beta-naphthol was detected. This run showed ether I undergoes cleavage under standard ether cleaving conditions.

It is reported that Illinois No.6 coal contains about 0.9% Fe[21]. Experiment 8 was done to find out if the iron present in coal may aid pyridine hydriodide in cleaving ether linkages. Ether I was reacted with Py·HI and $FeCl_2.4H_2O$ in pyridine at 95° for 6 days, recovered ether was 95% and no cleavage product detected. Sulfur is another element present in significant amounts in coal, a typical Illinois No.6 coal contains about 3.5% S[21]. FeS_2 was tested as a possible catalyst for ether cleavage with Py·HI. FeS_2 with Py·HI was reacted with ether I in pyridine at 95° for 4 days in run 9, no ether cleavage was observed and ether recovery was 99%.

Kamiya et al [22] reported that coal ash, specifically silica-alumina and iron sulfide, enhances the decomposition of model ethers at 400°. Experiment 10 was done to check if iron sulfide maybe acting as an ether cleaving agent. No cleavage was observed when this reagent was reacted with ether I at 90° for 5 days and ether recovery was 102%. In experiment 11, its possible function in aiding Py·HI in ether cleavage was also

tested. When ether I was reacted with Py·HI and FeS in pyridine at 90° for 5 days, no cleavage resulted and ether recovery was 102%.

In experiment 12, $LiI \cdot 3H_2O$ was used as a cleaving agent. Lithium iodide cleaved 2-methoxynaphthalene in collidine at 172° [23]. At 90° for 5 days in pyridine however, ether I does not undergo cleavage with this reagent, ether recovery being 98%. In experiment 13, naphthyl ether III was subjected to cleavage reaction with pyridine hydriodide in pyridine at 115° for 3 days. No cleavage was observed and recovery was 102%. In experiment 14, phenyl sulfide was tested for its catalytic activity with Py·HI in cleaving ether I. The reaction was run in pyridine at 115° for 3 days, no cleavage was observed and ether recovery was 94%.

These reactions are interpreted to mean the general inertness of benzylic naphthyl ethers to mild cleaving agents such as Py.HI. It should be recalled that Py·HI in pyridine at room temperature decreases the molecular weight and increases the phenolic -OH content of an asphaltol fraction, however, this same reagent in pyridine does not cleave benzylic naphthyl ethers at 115°, therefore, one can safely conclude that these simple ether linkages are not responsible for the changes observed by Mayo *et al* [10].

The environment inside the coal matrix may be conducive for ether cleavage. In experiment 15 and 16, the effect of coal on ether cleavage reactions were tested. In experiment 16, extracted coal [16] (pyridine insoluble fraction) was reacted with ether I in pyridine at 115° for 7 days, no cleavage was

observed and ether recovery was 93%. In experiment 15, ether I was reacted with Py·HI and extracted coal at 115° for 7 days, no cleavage resulted and ether recovered was 94%. There are several things to mention about this observed result of ether reaction of Py·HI in coal. First, there is always the possibility that ether I and Py·HI were not drawn inside the coal matrix even after repeatedly wetting the coal with the ether solution, hence the reaction didn't really occur inside the coal. Second, once ether I gets inside the coal matrix, it may intercalate within the coal structure and thus rendering cleavage reaction with Py·HI even harder to occur. Third, Py·HI does not cleave ether I even inside the coal matrix.

Cleavage Reactions of o-Anisic Acid and Related Acids with Pyridine Hydriodide and Other Cleaving Agents

The standardization of o-anisic acid and salicylic acid against hydrocinnamic acid was done twice. It was observed that the first calibration was more accurate in quantitating o-anisic acid recovery while the second calibration was more sensitive to salicylic acid. Thus, a combination of the 2 calibrations was used. Also, it is hard to get rid of the last traces of pyridine even after the work-up, which showed up as a small peak at or near the internal standard peak. Hence, a correction of the internal standard peak has been done to correct for the pyridine background. Typically, the internal standard has an area of 300,000 units while the pyridine peak registers an area of 30,000 units.

A literature search on cleavage reactions of o-anisic acid and related acids was conducted. Royer et al[24] showed that p-anisic acid is cleaved by pyridine hydrochloride at 220° to p-hydroxybenzoic acid in 70% yield. McCarthy et al[25] reported that NaCN in DMSO cleaves the following:

Compound	Product	Time (hrs.)	Temp. (°C)	Yield (%)
2-methoxynaphthalene	2-naphthol	24	180	77
1-methoxynaphthalene	1-naphthol	5	180	77
o-anisic acid	salicylic acid	8	180	89

McOmie and Press[26,27] reported that boron tribromide cleaves these following ethers at room temperature:

Compound	Product	Yield (%)
1-methoxynaphthalene	1-naphthol	14
2-methoxynaphthalene	2-naphthol	67
o-anisic acid	salicylic acid	94
p-anisic acid	p-hydroxybenzoic acid	92
p-ethoxybenzoic acid	p-hydroxybenzoic acid	94

As yet, no ether cleavage with pyridine hydriodide has been reported. Also, the results of ether cleavage with pyridine hydriodide in pyridine will help us gain a better understanding of Mayo's work on coal with pyridine hydriodide.

In experiment A, o-anisic acid was reacted with pyridine hydriodide in pyridine at 85° for 3 days, 10% salicylic acid

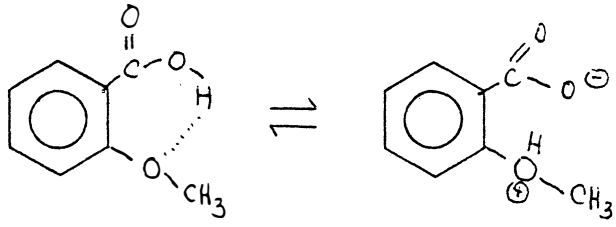
was detected and 80% ether was recovered. In experiments B and C, o-anisic acid was reacted with pyridine hydriodide in pyridine at 115° for 3 days, average of the 2 runs showed 81% cleavage and 14% ether recovery.

Reacting KI with o-anisic acid in pyridine at 115° for 3 days in experiment D, resulted in 58% cleavage and 33% recovered ether. Lithium iodide is known to cleave 2-methoxynaphthalene in collidine at 172° [23]. This reagent was tested in cleaving o-anisic acid in pyridine at 85° for 3 days in experiment E, 54% cleavage and 44% recovery was observed. In experiment F, o-anisic acid was reacted with Py·HI in acetonitrile for 4 days at 75°, no cleavage was observed and recovery of o-anisic acid was 99%. In experiment G, o-anisic acid was reacted with KI and 18-crown-6 ether in CH_3CN at 75° for 4 days, no cleavage resulted and ether recovered was 94%. In experiment H, o-anisic acid was reacted with Py·HI in DMSO at 75° for 4 days, ether recovery was 94% and no cleavage was observed. In experiment I, o-ethoxybenzoic acid was reacted with pyridine hydriodide in pyridine at 115° for 3 days, 18% cleavage was observed and ether recovered was 84%. In experiment J, p-anisic acid was reacted with Py·HI in pyridine at 115° for 3 days, no cleavage resulted and p-anisic acid recovered was 96%.

In experiment K and J, o-phenoxybenzoic acid was tested for cleavage with lithium iodide or Py·HI. With $LiI \cdot 3H_2O$ in pyridine at 90° for 5 days, no cleavage occurred and 94% ether was recovered. In pyridine with Py·HI at 115° for 3 days, 101% ether was recovered and no cleavage was observed.

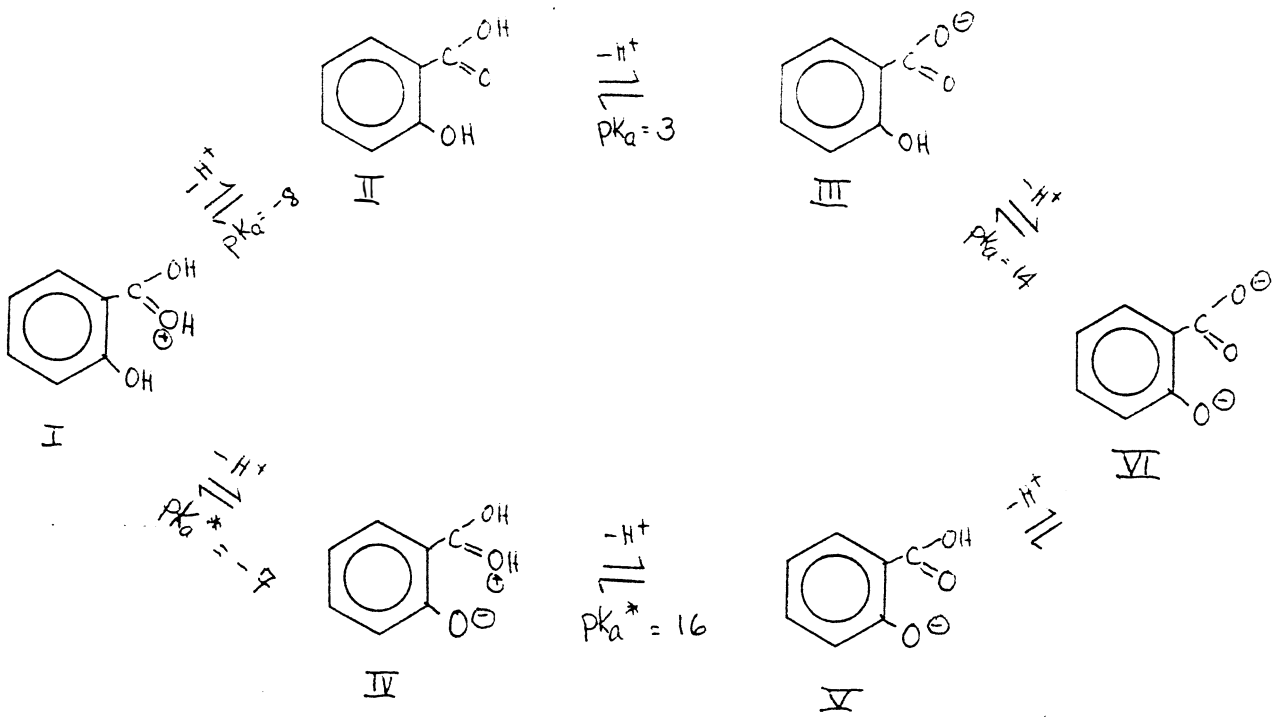
Based on these results, the followimg are noted: o-Anisic acid undergoes more extensive cleavage(81%) than o-ethoxybenzoic acid(18%) with Py·HI under similar conditions, while o-phenoxybenzoic acid is not cleaved at all. This is suggestive of an S_N2 mechanism: the ethyl group is relatively hindered compared to the methyl group for a backside attack by an iodide ion. Streitwieser[29] reported that the methyl group undergoes S_N2 reaction faster than the ethyl group by a relative rate of 30 : 1 in simple systems. The phenyl group does not undergo S_N2 reaction, hence the inertness of o-phenoxybenzoic acid to Py·HI.

Can internal protonation of the ether oxygen of o-anisic acid occur? Will iodide ion be equally effective in cleaving ether A as well as ether B?

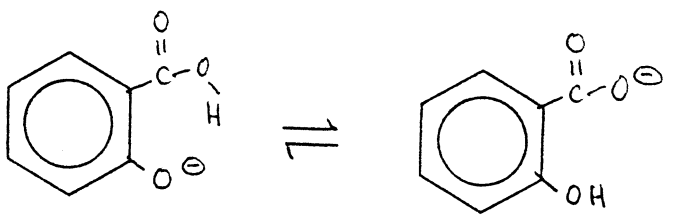


A ⇌ B

Kovi et al[30] measured the successive pK_as of salicylic acid on going from concentrated acid to concentrated base solutions, both in the ground and excited states:

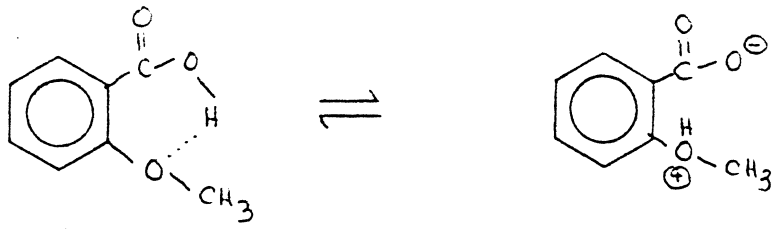


They concluded that the path going from I→II→III→VI occurs in the ground state while the path from I→IV→V→VI occurs in the excited state.



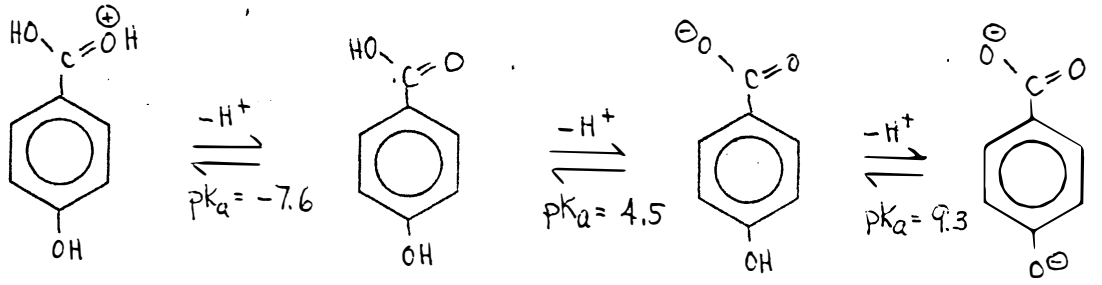
V III

A theoretical calculation of the tautomerism of V ⇌ III (since both don't co-exist in the ground state) based on the given pK_as showed III as the predominant tautomer, with a relative pK_a = -6.5, or 3.2 x 10^6 tautomeric form III per molecule of V. In consideration of this theoretical basis, this type of internal protonation appears likely in the ground state:

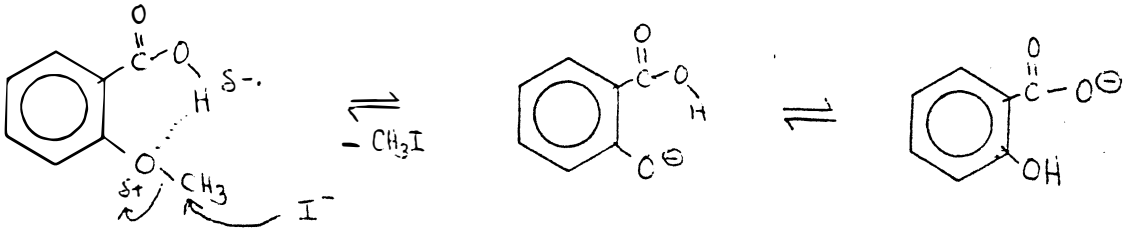


C ⇌ D

On the other hand, Paul and Schulman[28] observed that no such intramolecular or intermolecular phototautomerism occurs with p-hydroxybenzoic acid. They measured the successive pK_as of p-hydroxybenzoic acid in the ground state:



o-Anisic acid may be more susceptible to S_N2-type displacement by an iodide ion. Whether in the tautomer C (where the methoxy group is hydrogen bonded by the carboxylic hydrogen) or in the tautomer D (where intramolecular hydrogen transfer took place), the etheric oxygen is rendered electropositive and thereby facilitating an S_N2 attack by the iodide ion.



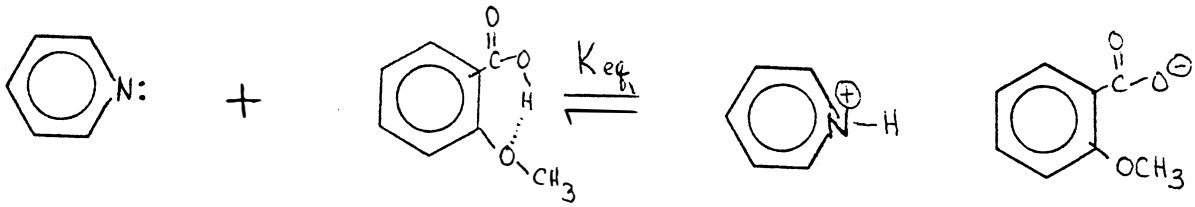
No intramolecular hydrogen bonding is possible in p-anisic acid, hence an S_N2 attack is not facilitated. In view of

these arguments, it is apparent why o-anisic acid is cleaved by Py·HI but p-anisic acid is not.

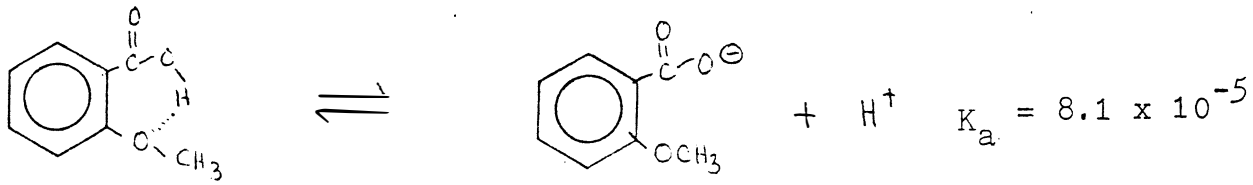
Why does the reaction occur only in pyridine and not in acetonitrile or dimethyl sulfoxide?

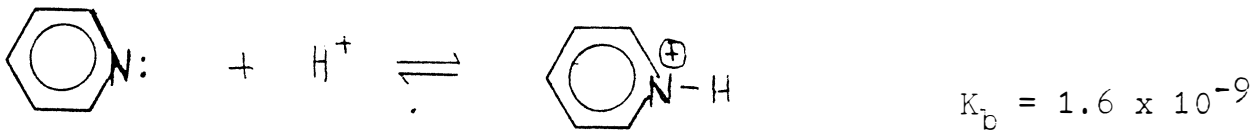
There are several possible explanations: Bos and Dahmen[31] reported that while benzoic acid has a $pK_a = 4.0$ in water at 25°, it has a $pK_a = 11$ in pyridine, which means that normally weak acids are even weaker in pyridine. o-Anisic acid, with $pK_a = 4.2$ in water at 25°, is estimated to show a $pK_a \sim 11$ in pyridine. In other words, the carboxyl hydrogen of o-anisic acid is not transferred in pyridine and thus can participate in hydrogen bonding with the methoxy group.

A more substantial argument would be to find the equilibrium constant of this reaction :

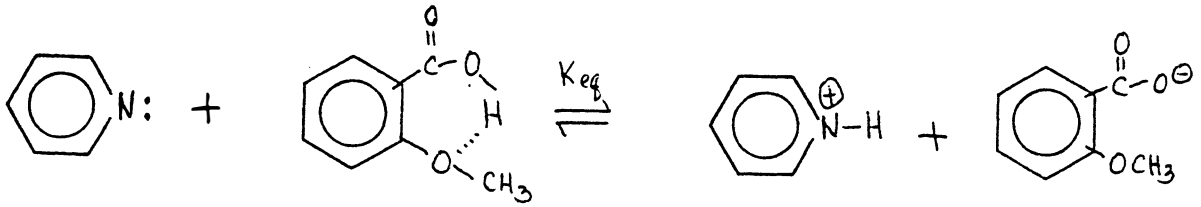


This expression can be broken down into 2 equations, the values of which are readily available in literature[32,33].





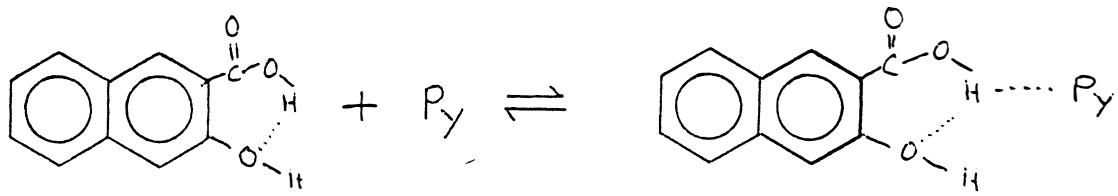
The equilibruim constant of this reaction in water at 25° can thus be calculated. The calculated K_{eq} however, is for equilibruim occuring in water solution and hence its value may be too small for the actual K_{eq} in pyridine, hence the value is to be taken only as a rough estimation of the actual K_{eq}.



$$K_{eq} = K_a \times K_b = (8.1 \times 10^{-5})(1.6 \times 10^{-9}) = 1.3 \times 10^{-13}$$

The smallness of the value of K_{eq} suggest that intermolecular proton transfer between o-anisic acid and pyridine does not takes place to any appreciable extent in water at 25°. Which means that in the presence of pyridine, the carboxylic hydrogen of o-anisic acid is available for internal hydrogen bonding or protonation with the adjacent methoxy group.

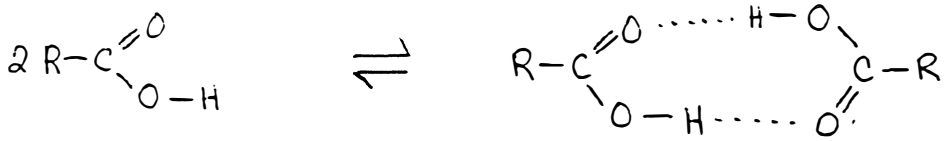
Ware et al[34], in their work with hydroxynaphthoic acid and pyridine, believed that pyridine forms a complex with the acidic proton of the carboxyl group:



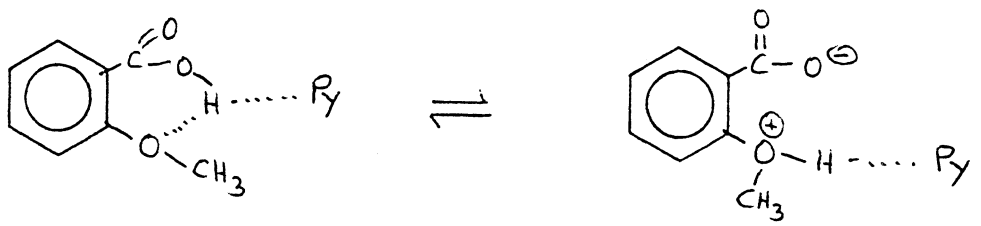
In the process, pyridine might be weakening the carboxyl O—H bond, acting as proton transfer agent and facilitating intramolecular hydrogen transfer. This effect is absent in either DMSO or acetonitrile because neither of these 2 solvents is

involved in complex formation.

It is known that carboxylic acids dimerize in solutions[35].



Because of this dimerization, there is competition for the carboxyl hydrogen available for internal hydrogen bonding or internal protonation of the adjacent methoxy group, hence the number of molecules present as internally hydrogen bonded form is diminished. But if pyridine is available to complex the carboxyl hydrogen, dimerization is reduced and most of the o-anisic acid is present in the reactive form, i.e.,



with this complex available, cleavage reaction may be more facile.

In the order of increasing cleavage reaction, the following series in pyridine was observed:

$KI < Py \cdot HI < LiI \cdot 3H_2O$

The capacity of KI as a cleaving agent is limited by its solubility in pyridine. Whereas lithium iodide is completely soluble in pyridine at 85°, KI is not completely soluble in pyridine even at 115°.

Mayo et al[10] reported that pyridine hydriodide decreased the molecular weight and increased the phenolic -OH content of an Illinois coal fraction at room temperature. Furthermore,

they reported that lithium iodide is equally effective as pyridine hydriodide in reproducing the above results with the coal fraction.

Naphthyl ethers, specifically beta-methylnaphthyl beta-naphthyl ether and alpha-methylnaphthyl alpha-naphthyl ether, when reacted with either Py·HI or $LiI \cdot 3H_2O$ in pyridine at 115° for 3 days, no cleavage was detected and quantitative recoveries of the starting ethers were obtained. On the other hand, when o-anisic acid and o-ethoxybenzoic acid was reacted with Py·HI in pyridine at 115° for 3 days, 81% and 18% cleavage was observed respectively. o-Anisic acid with $LiI \cdot 3H_2O$ in pyridine at 85° for 3 days resulted in 54% cleavage.

These results are consistent with Larsen's[14] Mössbauer study of the tin derivative of Illinois No.6 Coal. He concluded that almost all of the -OH in Illinois No.6 Coal may be in hydrogen bonded form. For o-anisic acid and o-ethoxybenzoic acid, the first step in ether cleavage, that is, protonation of the ether oxygen, does not require an external proton source because their etheric oxygens are already in hydrogen bonded form. For these compounds, attack by an iodide ion on the alkyl group is sufficient to cleave these ethers. In direct contrast, p-anisic acid, in which no such intramolecular hydrogen bonding is possible, showed no cleavage with Py·HI in pyridine at 115° for 3 days.

These results indicate that ethers linked to aromatic rings where the ortho ring substituents are capable of hydrogen bonding with these ethers maybe better models than ethers linked to monosubstituted ring systems for those linkages present in coal.

References:

1. Ruberto, R. G., Cronaner, D. C., Jewell, D. M. and Seshadri, K. S., Fuel, 1977, 56, 25.
2. Takegami, Y., Kajiyama, S., and Yokokawa, C., Fuel, 1963, 42, 291.
3. Wachowaska, H. and Pawlak, W., Fuel, 1977, 56, 422.
4. Larsen, J. W., Ed., "Organic Chemistry of Coal", ACS Symposium Series, Washington, D. C., 1978, p 126.
5. Berkowitz, N., "An Introduction to Coal Technology", Academic Press Inc., New York, 1979, p 115.
6. Takemura, Y., Itoh, H. and Ouchi, K., Fuel, 1981, 60, 379.
7. Mobley, D. P. and Bell, A. T., Fuel, 1979, 58, 661.
8. Wachowska, H., Nandi, B. N. and Montgomery, D. S., Fuel, 1974, 53, 212.
9. Ignasiak, B. S. and Gawlak, M., Fuel, 1977, 56, 216.
10. Mayo, F. R., Buchanan, D. H. and Pavelka, L. A., ACS Div. Fuel Preprints, 1980, 25(2), 182.
11. Odinokov, S. E., Mashkovsky, A. A. and Glazunov, V. P., Spectrochimica Acta, 1976, 32A, 1355.
12. Royer, R., Buisson, J. P. and Dermerseman, P., Bull. Soc. Chim. Fr., 1971, 8, 4362.
13. Chen, M. Y., "Pyridine Hydrogen Iodide as an Ether Cleaving Agent in Coal Chemistry", M. S. Thesis, Eastern Illinois University, 1981, p 23.
14. Larsen, J. W., Nadar, P. A., Mohammadi, M. and Montano, P. A., Fuel, 1982, 61, 889.
15. Cook, O.,Can. J. Chem., 1961, 39, 2009.

16. Ballard, M. L., "Analysis of Coal Fractions Using Dibromotriphenylphosphorane", M. S. Thesis, Eastern Illinois University, 1981, p 59.

17. Chapman, N. B. and Williams, J. F. A., J. Am. Chem. Soc., 1952, 54, 5045.

18. King, F. E. and Henshell, T., J. Chem. Soc., 1945, 417.

19. D'Incan, E. and Viout, P., Tetrahedron, 1975, 31, 159.

20. Vogel, A. I., "Practical Organic Chemistry", Lowe and Brydone Ltd., London, 1956, p 316.

21. Karr, Clarence Jr., Ed., "Analytical Methods for Coal and Coal Products", Academic Press Inc., New York, 1979, p 363.

22. Kamiya, Y., Nagea, S. and Oikawa, S., Fuel, 1983, 62, 31.

23. Harrison, I. T., Chem. Comm., 1969, 616.

24. Royer, R., Bachelet, J. P., and Demerseman, P., Bull. Soc. Chim. Fr., 1974, 11(2), 2631.

25. McCarthy, J. R., Moore, J. L. and Cregge, R. J., Tett. Lett., 1978, 52, 5183.

26. Press, J. B., Synth. Comm., 1979, 9(5), 407.

27. McOmie, J. F. W., Watts, M. L., and West, D. E., Tetrahedron, 1968, 24, 2289.

28. Paul, W. L. and Schulman, S. G., Anal. Chim. Acta, 1974 69, 195.

29. Streitweiser, A. Jr., "Solvolytic Displacement Reactions", New York, McGraw-Hill Book Company Inc., 1962, p 13.

30. Kovi, P. J., Miller, C. L. and Schulman, S. G., Anal. Chim. Acta., 1972, 61, 7.

31. Bos, M., Dahmen, E. A., Anal. Chim. Acta, 1971, 55, 285.

32. Olmstead, W. N., Tetrahedron, 1971, 27(13), 2713.

33. Fischer, A., Galloway, W. J. and Vaughan, J., J. Chem. Soc., 1964, 3591.

34. Ware, W. R., Shukla, P. R., Sullivan, P. J. and Bremphis, R. V., J. Chem. Phys., 1971, 55, 4048.

35. Patai, S., Ed., "The Chemistry of Carboxylic Acids and Esters", London, John Wiley and Sons, 1969, p 238.

VITA

Name : James Nicolas Ong Sy.

Permanent Address : 516 Nicodemus St., Tondo, Manila, Phil.

Degree and date to be conferred : M.S. Chemistry, August 1983

Date of Birth : July 24, 1960

Place of Birth : Laoag City, Philippines

Secondary Education : St. Stephen's High School.

Collegiate Institutions Attended	Date	Degree
University of Santo Tomas(Phil.)	6/77-3/81	B.S. Chemistry
Eastern Illinois University	6/82-8/83	M.S. Chemistry

Major : Organic Chemistry

Positions Held	Date	Institution
Research Assistant	6/81-12/81	San Miguel Corporation
Graduate Assistant	8/82-8/83	Eastern Illinois Univ.