THE EFFECTS OF DEUTERATING AN ATTRACTANT OF THE AMERICAN COCKROACH, PERIPLANETA AMERICANA L., AS A TEST FOR THE FREQUENCY THEORY OF OLFACTION

by

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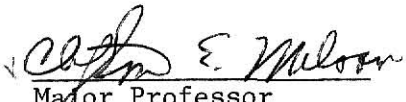

Major Professor

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INTRODUCTION

It is estimated that insects have a total world population of 10^{18} (1). Even though most cockroaches cause no problems for man, approximately 0.1% of insect species are harmful through their destruction of food and property, and through their spreading of diseases.

Among the oldest of these insects is the cockroach, as indicated by fossil remains, dating back 200 million years. Their survival is a result of an excellent adaptability to wide ranges of habitats and living conditions.

Contrary to the bad publicity given the cockroach, largely caused by psychological apprehension, it is generally not an injuriors insect -- although studies have revealed that cockroaches may cause damage to plants or be vectors of diseases. At the same time, cockroaches do contaminate food and kitchen utensils with excrement and salivary secretions, unfortunately produce an unpleasant odor. Some people suffer an asthma allergic reaction to the cockroach, apparently caused by the body of the roach, not an associated odor[2,3].

Controlling the spread of cockroaches demands much money, attention, and planning. Of course, the most effective control will not depend on pesticides but will take advantage of every precaution not to allow the cockroaches to come into the dwelling (general cleanliness, tight seals around all openings, inspecting groceries, etc.). This approach will always procuce better results than attempting to rid the premises, through insecticides, after the cockroaches have established themselves. Once contamination has occurred though, chemicals are generally used to exterminate the roaches. However; some chemicals, like pesticides, have the following disadvantages: (1) they may be toxic not only to the target insects, but also to the harmless,

beneficial insects and other creatures, (2) after much exposure, insect populations may build up resistance, (3) the high cost of production and application, and (4) the persistence of the residues may pollute the environment[4]. As a result of these disadvantages, insecticides are decreasing as a form of pest control and natural chemical alternatives are being sought to combat insect infestations.

Among the more interesting of these attempts is the use of the extremely sensitive olfactory sensations to attract and trap the cockroach. It is known that insects, fish, and many mammals are strongly dependent on odor for communication -- using it for orientation to surroundings, finding foods, avoiding predators, and meeting mates[5]. In the insect world, the chemical senses of taste and smell are essential, and olfaction, the sense of smell, is more sensitive and discriminating than the sense of taste. "As a rule of thumb, the olfactory sense is roughly 10,000 times more sensitive than the sense of taste"[6].

Using these facts, much research is being conducted to discover those chemical and physical properties of compounds which are natural attractants or repellents for different insects. The expectation is that the insects can be attracted to a trap, a destructive toxicant, or a sterilizing compound -- naturally, a chemical repellent could also be used to eliminate the worry of infestation.

Up to date, much work has been done to control stored products insects and to prevent food from infestation. This includes the use of inert gases, radiation, pathogens, growth regulators (such as the juvenile hormone), pheromones, pesticides, sanitation, inspection, good packing and providing good storage facilities[7]. Among them, some research is being conducted to correlate specific molecular attributes with their unique odors.

R. M. Hainer (1954)[8] was the first person to apply this kind of approach to understanding olfaction. He pictured a board with twenty or more lamps which could be individually turned on or left off in 2^{20} or more different ways. He compared the board of lights with the olfactory anatomy apparatus of animals because the receptors are nerve cells which make direct contact with the outside world at one end and at the other have a direct axonal connection with a body called an olfactory glomerulus.

As a pioneering attempt, the theory overlooked certain necessary requirements of an information handling system. The first of these is redundancy. The second factor omitted was economy of equipment. The "odor specialist" and "odor generalist" receptors found on the antennae of several kinds of insects could well be Nature's manifestation of this principle[9].

Broadly speaking, there have been two theories of the molecular specificity - molecular shape and molecular vibration. Of the two competing theories, the stereochemical or "molecular shape" theory of J. E. Amoore[10] considers that the overall shape or "picture" of the molecule is the determining attribute. He supposed that when these molecules engender a sensation, they have to settle themselves into "nests" of matching shape in the sensitive area of the nose and then in some way induce the series of nerve impulses which are received and registered by the brain.

This theory runs into several difficulties. For one, it seems to suggest that an organism should be able to smell only substances for which Nature has endowed it with the appropriately shaped receptor sites. In the past hundred years chemists have synthesized thousands of chemicals which have never existed in Nature but which nevertheless have distinctive odors to which our noses are often highly sensitive[11].

The alternative theory of R. H. Wright regards the molecule as a mechanical structure which can be elastically deformed and will spring back and vibrate in as many ways as there are ways to deform it. Due to this springiness, the molecule has many modes of vibration, each with a specific frequency. The various modes can be set into shaking separately or simultaneously, and altogether they make up a pattern which is not likely to be matched in all its details by the pattern of any other molecule. Individual frequencies, like individual letters of the alphabet, can contribute to many different patterns[11].

The suggestion that odorous character is related to vibrational specificity is at least a hundred years old[12], which did not become capable of detailed experimental investigation until the application of thermodynamic considerations appeared. In the early 1950s, R. H. Wright concluded that, on quantum grounds, the only vibrations likely to be excited at ordinary temperature would be the low-frequency ones. He set an upper limit to the frequencies likely to be significant at approximately 500 cm^{-1}. It now appears that the upper limit of effective frequencies may be as high as 1,100 cm^{-1}. Whether there is a low frequency limitation is still undetermined.

Originally what was sought was an association of particular bands or combination of bands in the far infrared absorption spectra of molecules. More recently, as a larger body of spectroscopic data has become available, it appears that a particular olfactory response may depend upon the absence of some frequencies as well as upon the presence of others[13].

Schafer & Sanchez (1973) pointed out from their morphological work on the antennae of adult American cockroach that male antenna have nearly twice as many olfactory trichoid sensilla as do females. They also found that more than half of the olfactory trichoid sensilla appear in the adult stage, and

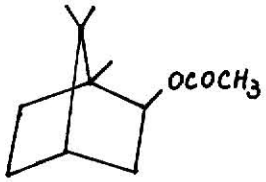
the sexual dimorphism apparent in the adult antennae is due to merely an extra complement of thin walled sensilla trichodea which contain sex pheromone receptors[14]. These morphological findings mean that both adult male and female antennae have common olfactory sensilla, but only the male possesses a sex specific olfactory sensillum containing sex pheromone receptors.

In describing olfactory stimulating odors, there are two kinds of categories proposed in correspondence to the morphological findings. "General odor" was assumed to interact with the general odor receptors on the antennae of males and females. On the other hand, "Special odor" was thought to stimulate the specialized receptors on the male antenna. Food odors which consist of more volatile compounds with low molecular weights (monoterpenoids, linear chained alcohols, etc.) are typical examples of general odors. They give no significant behavioral response. The sex pheromone and its mimics, which induce the typical sexual behavior, belong to special odors.

Since general odors give no significant behavioral response to either sex, D. Schneider (1957)[15] first recorded the electroantennogram (EAG) response in the male silkworm moth, Bombyx mori L.. It was applied in antennal sensory studies of Lepidoptera[16], Coleoptera[17], and Diptera[18]. The results confirmed that the EAG technique was a valuable technique for non-behavioral responses in antennal sensory studies.

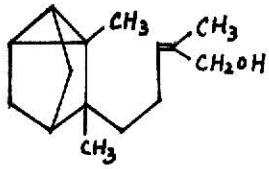
The first sex pheromone mimics of the American cockroach were discovered by Bowers and Bodenstein in 1971[19], who found that the plant derived terpenoids, bornyl acetate (I), α- and β-Santalol (II, III), and a sesquiterpene hydrocarbon ($C_{15}H_{24}$), in addition to being attractants, induced the typical sexual behavior characterized by wing flutter, extension of the abdomen and attempted copulation among male cockroaches. Later germacrene D ($C_{15}H_{24}$) (IV) was identified as one of the sex mimicing hydrocarbons in

plants[20]. In 1975, a sesquiterpenoid T-cadinol (V), which is biogenetically related to germacrene D, was found to stimulate this insect[21]. L. M. Roth & E. R. Willis reported as early as 1952, that the virgin female American cockroach, Periplaneta americana, emits a powerful attractant which elicits intense excitement and characteristic wing-raising in the males of this species[22]. It was not until 1979 that W. C. Still et al. provided the structural proof for the female American cockroach sex attractant, Periplanone B (VI)[23,24].



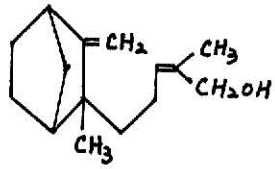
Bornyl acetate

I



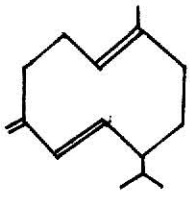
α-Santalol

II



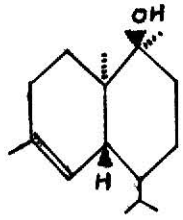
β-Santalol

III



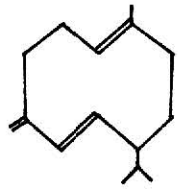
Germacrene D

IV



T-cadinol

V



Periplanone B

VI

From a survey of the literature, it is apparent that the behaviorally active compounds are also structurally complicated molecules. There is no readily available information regarding the relationship between the molecular attributes and these compounds. The research described in this paper considered this relationship.

OBJECTIVE

Up to date, there have been two theories to correlate specific molecular attributes with their unique odors. One of the two theories is the stereochemical or "molecular shape" theory, which considers that the overall shape or "picture" of the molecule is the determining attribute. The alternative, frequency theory, which regrads the molecule as a mechanical structure, suggests that odorous character is related to vibrational specificity.

The objective of this research is to shift the molecular vibrational frequency pattern of an attractant molecule by deuterating portions of it and correlating insect response to the specific and overall frequency changes. By using a small atom such as deuterium the molecular shape of the molecule will not be altered significantly.

The frequency theory hypothesizes that olfactory response is dependent on frequency patterns in a stimulus. If this theory is valid, isotopic substitution ought to affect the odors of compounds. Qualitatively, the argument is this : inasmuch as the frequency of the masses of the moving parts, substituting a heavier or lighter isotope should have little effect on the forces but should affect the frequency and hence the odor because of the change in mass.

Quantitatively for a simple harmonic oscillator the frequency ν is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}$$

where k is the restoring force constant and μ is the "reduced mass" of the system, that is,

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of the relatively moving parts.

Since general odor compounds give no significant behavioral response, the objective of this research is to find a special odor compound and make several deuterated derivatives to alter the frequency pattern, then test them with the American cockroach to see:

(1) the effects of deuteration on the attractiveness,

(2) the molecular frequency dependence of the attractiveness.

For this reason, bornyl acetate, a structurally simple sex attractant, which induced a noticeable behavioral response, was chosen in this experiment. Eight compounds (p. 13) were prepared, seven were deuterated with 1, 2, 3, 3, 4, 5, and 6 atoms to alter the frequency pattern, and one was used as a control.

EXPERIMENTAL

A. Synthesis and identification of bornyl acetate and its deuterated derivatives.

1. Equipment

a. IR: Perkin-Elmer model 180 Infrared Spectrophotometer. The range was 4,000 cm^{-1}-200 cm^{-1}. The cell used was a gas-type, as shown in Figures 1-3. The window was made of polyethylene.

b. NMR: Varian T-60 NMR Spectrophotometer.

c. GC: Tracor-560 Gas Chromatograph equipped with a flame ionization detector.

Column: a 1/8 inch by 6 foot stainless steel column.

Packing materials: after considering the possible impurities in the products, 10% OV-225 on chromosorb w (80/100 mesh) was chosen.

Temperature: Programmed from 90°C to 150°C at a rate of 5°C/min.

2. Compounds

By combination of deuterated and undeuterated chemicals at different positions, the following eight compounds were obtained (Figure 4).

The above eight compounds were identified by IR and NMR, and then confirmed by a standard addition GC method. The purity was evaluated by GC. The deuterium content was determined with NMR.

Figure 1; Side-view of a gas-type cell

A - 14/25 standard taper inner joint

B - Valve with Teflon stem and O-ring seals

C - O-rings

D - Teflon ring

E - Polyethylene film

F - 15 mm I.D. spherical O-ring joint

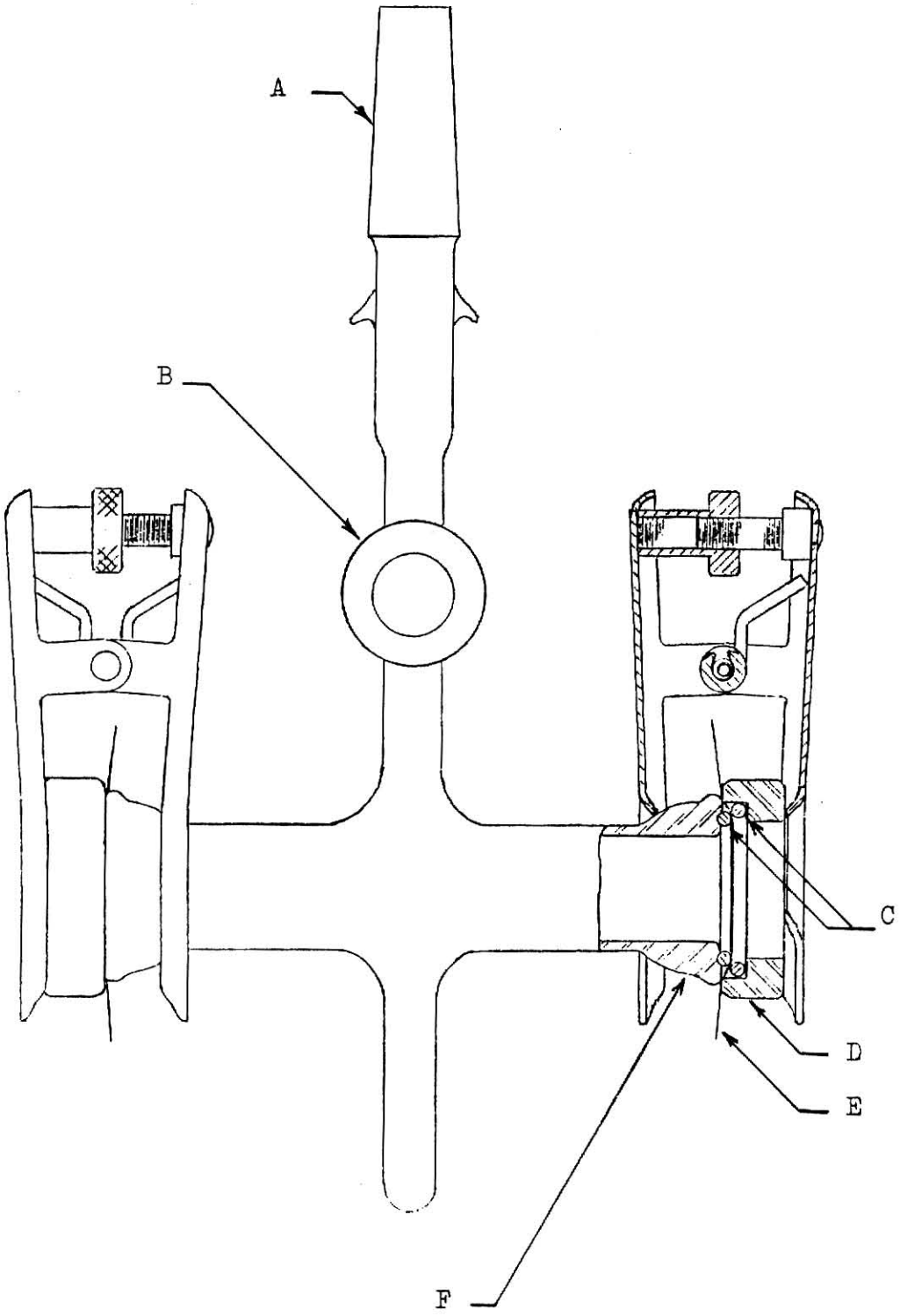

A
B
C
D
E
F

Figure 2; A gas-type cell

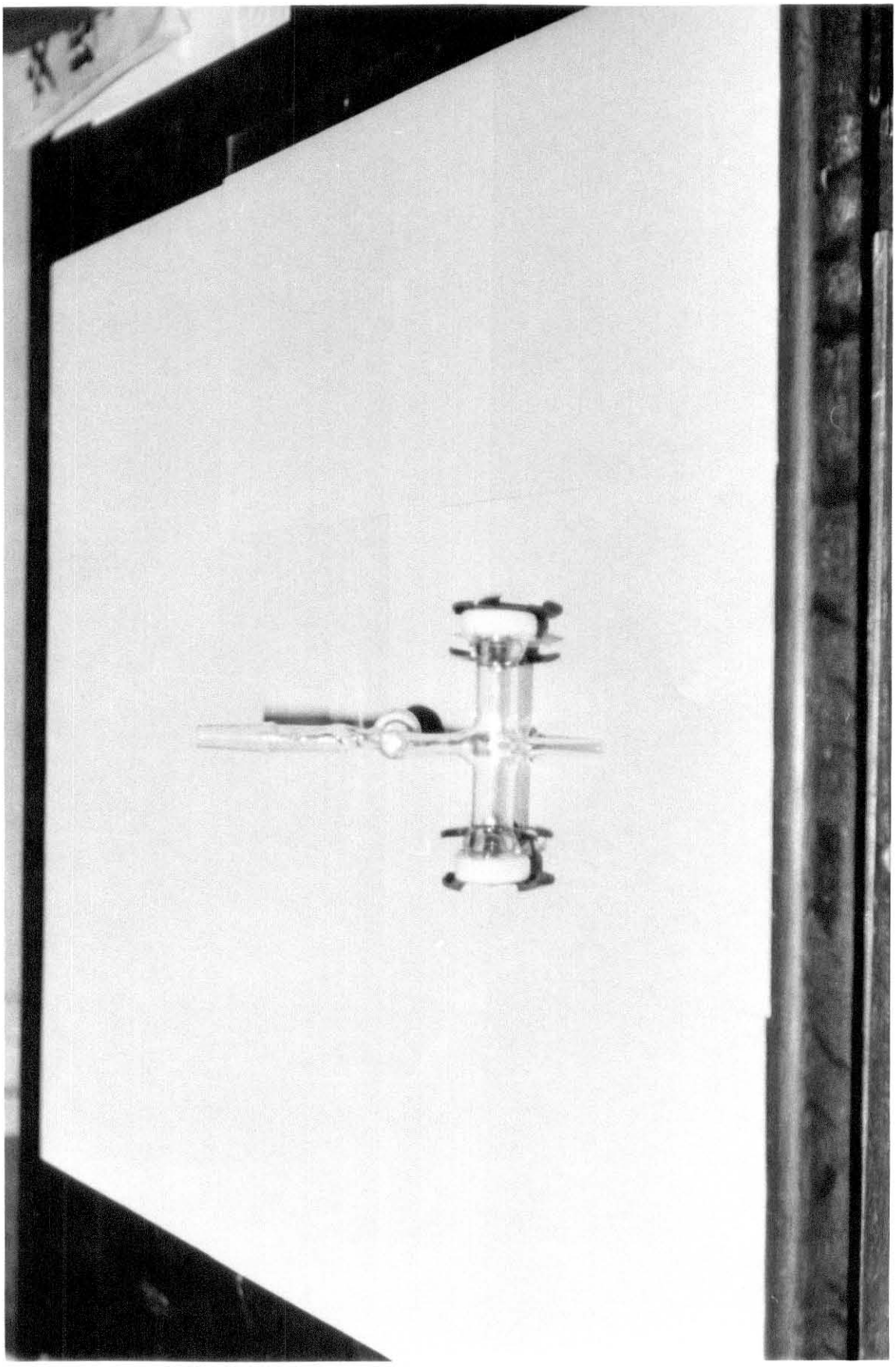


Figure 3; Apparatus to transfer sample vapor into a gas-type cell

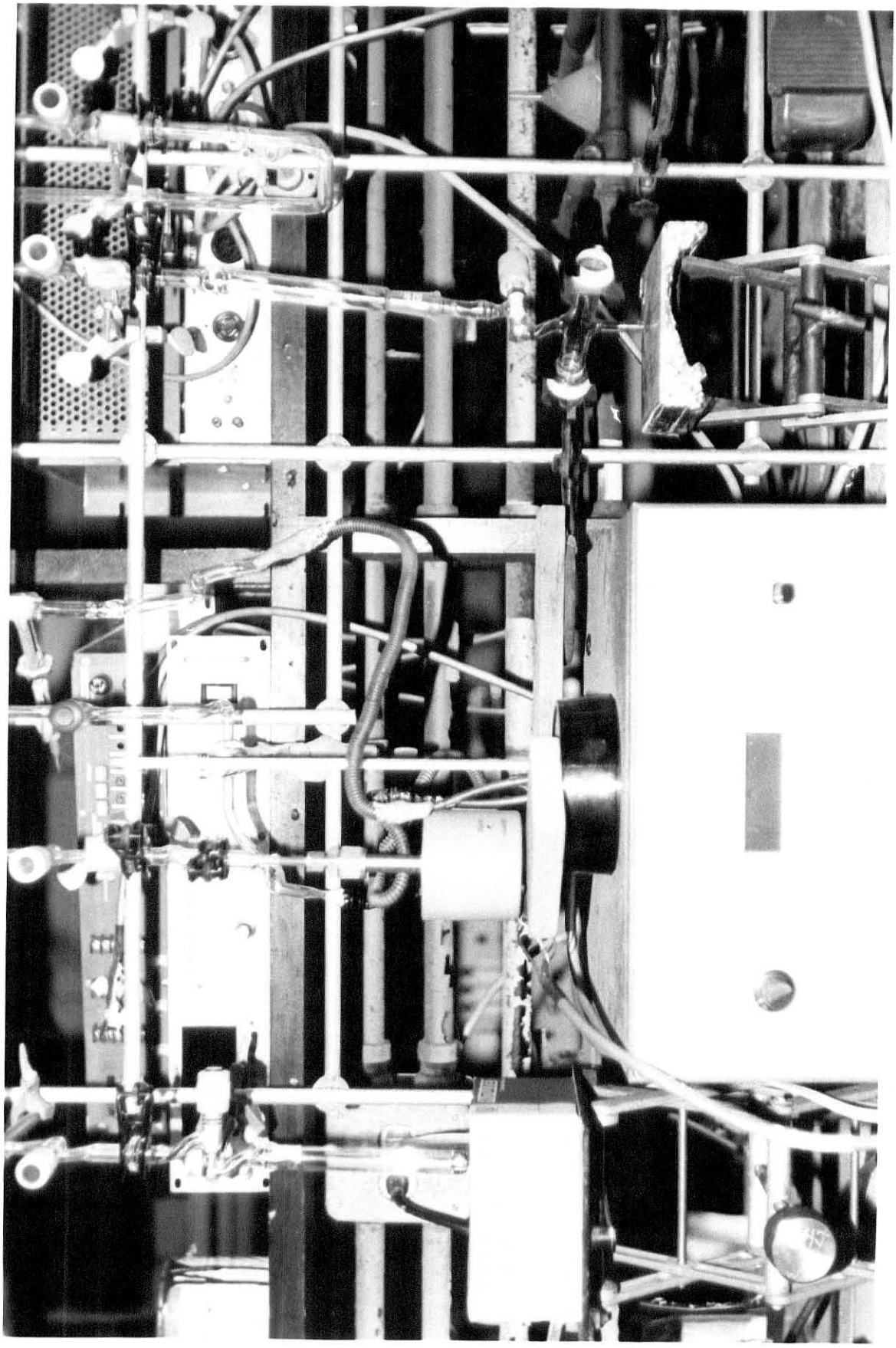


Figure 4; The eight synthetic compounds used in the bioassay tests

I. Bicyclo [2,2,1] heptane-2-ol-1,7,7-trimethyl-acetate

II. Bicyclo [2,2,1] heptane-2-ol-3,3-d_2-1,7,7-trimethyl-acetate

III. Bicyclo [2,2,1] heptane-2-ol-2-d_1-1,7,7-trimethyl-acetate

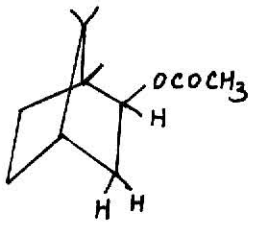
IV. Bicyclo [2,2,1] heptane-2-ol-1,7,7-trimethyl-acetate-d_3

V. Bicyclo [2,2,1] heptane-2-ol-2,3,3-d_3-1,7,7-trimethyl-acetate

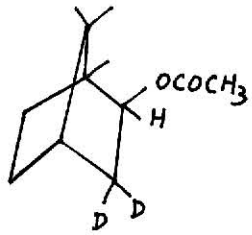
VI. Bicyclo [2,2,1] heptane-2-ol-3,3-d_2-1,7,7-trimethyl-acetate-d_3

VII. Bicyclo [2,2,1] heptane-2-ol-2-d_1-1,7,7-trimethyl-acetate-d_3

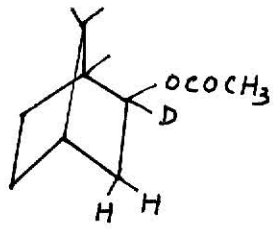
VIII. Bicyclo [2,2,1] heptane-2-ol-2,3,3-d_3-trimethyl-acetate-d_3



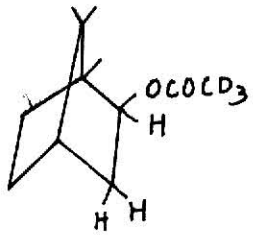
I



II



III



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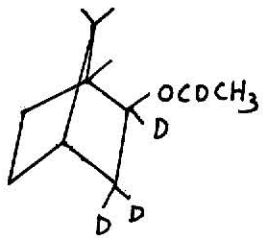
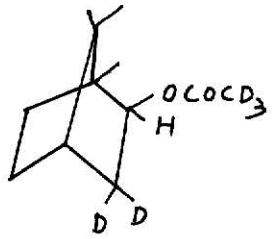
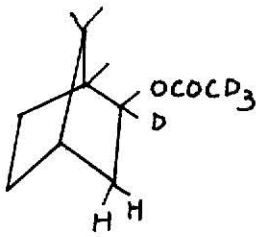


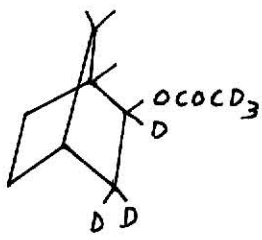
V



VI



VII



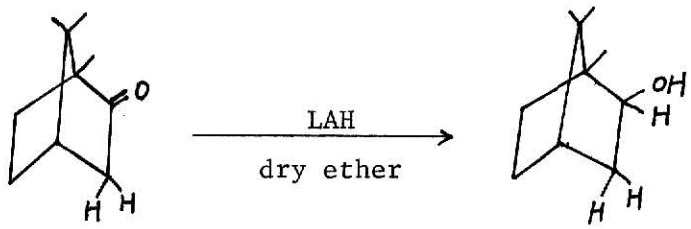
VIII

a. Compound I:

Bicyclo [2,2,1] heptane-2-ol-1,7,7-trimethyl-acetate

1) Synthesis:

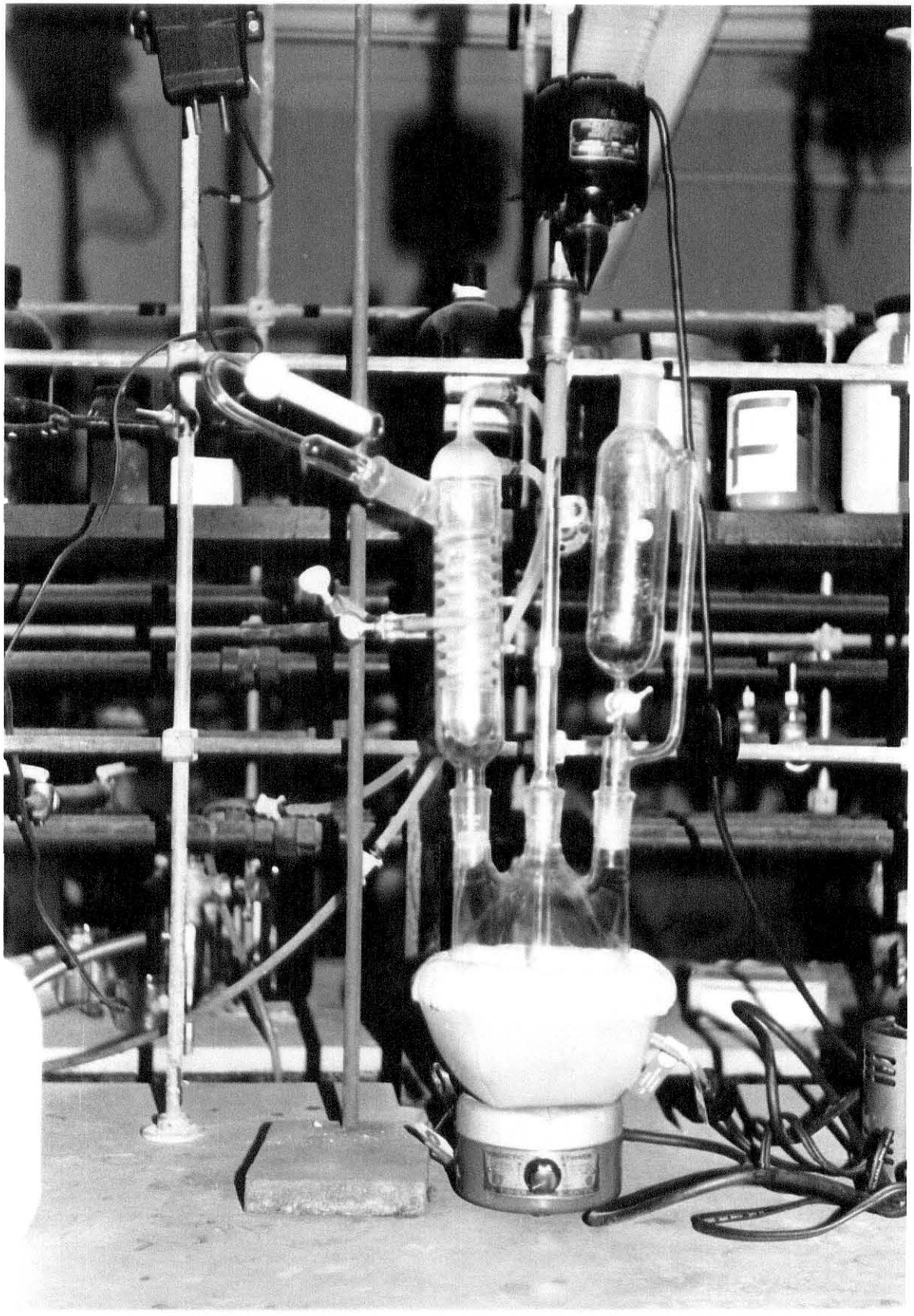
a) 25



(1) (2)

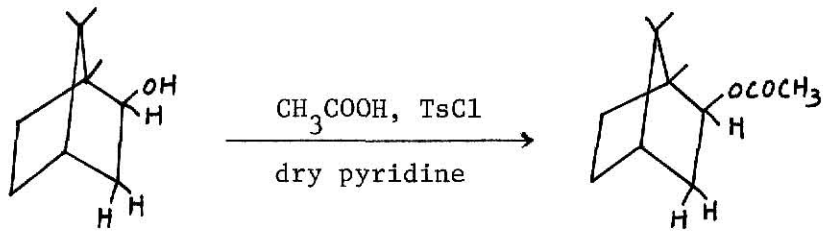
To a 1,000 mL, three necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel, as shown in Figure 5, were added 500 mL of anhydrous ether and 8.4 g (0.21 mole) of $LiAlH_4$. To this stirred mixture was added a solution of 35.0 g (0.23 mole) of compound (1) in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed (about 30 min.), the reaction mixture was then cooled and worked up by adding, dropwise, the following reagents: 9 mL of H_2O, then 9 mL of 15% aqueous NaOH, and then 12 mL of H_2O. This gave a precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H_2O, the layers were separated and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo until all of the solvent was removed. The residue was dissolved in a minimum amount of benzene, recrystallized, giving 21.9 g (67%) of compound (2):

Figure 5; Apparatus for the use of a three-necked round-bottomed flask



m.p. 206-208°C (lit.[28] 207-208°C), IR and NMR spectra as shown in Figures 6 and 7.

b) 26



(2) I

To a 500 mL Erlenmeyer flask, 3.8 mL (0.063 mole) CH_3COOH was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 9.7 g (0.063 mole) of compound (2) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL protions of 5% aqueous potassium bisulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (83%), purity (96%), d-content (0%), b.p. 225-227°C (lit.[29] 223-224°C).

Figure 6; IR spectrum of compound (2)

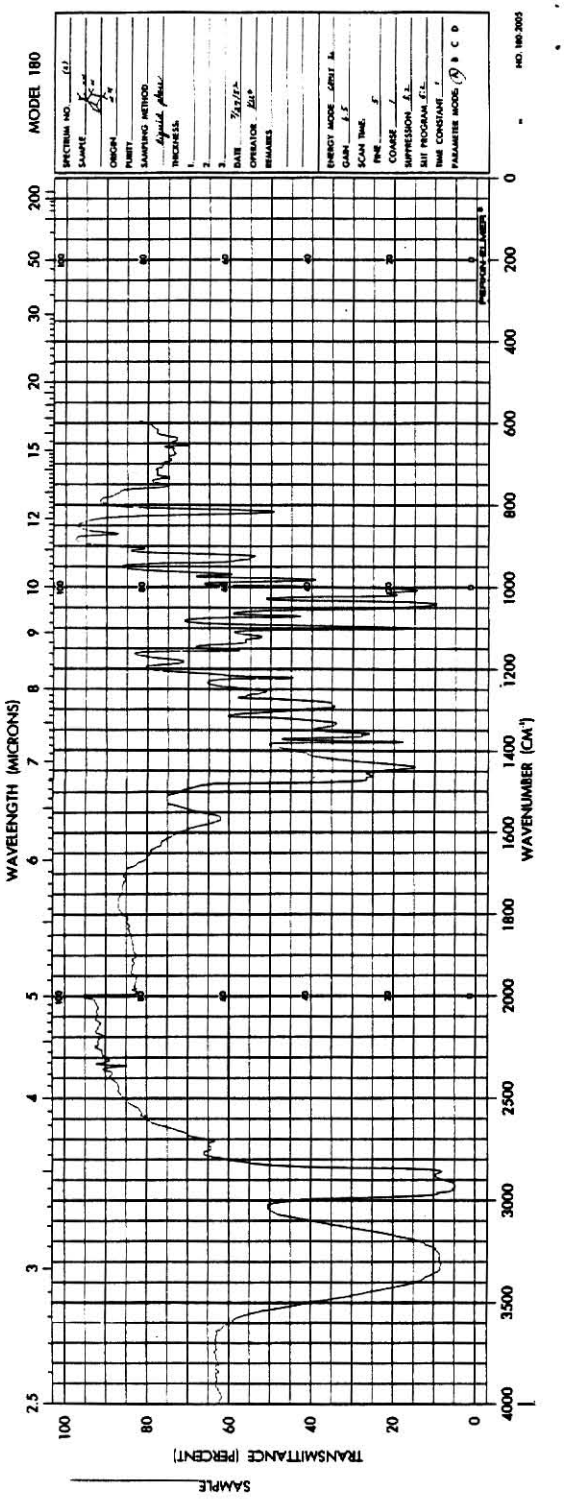
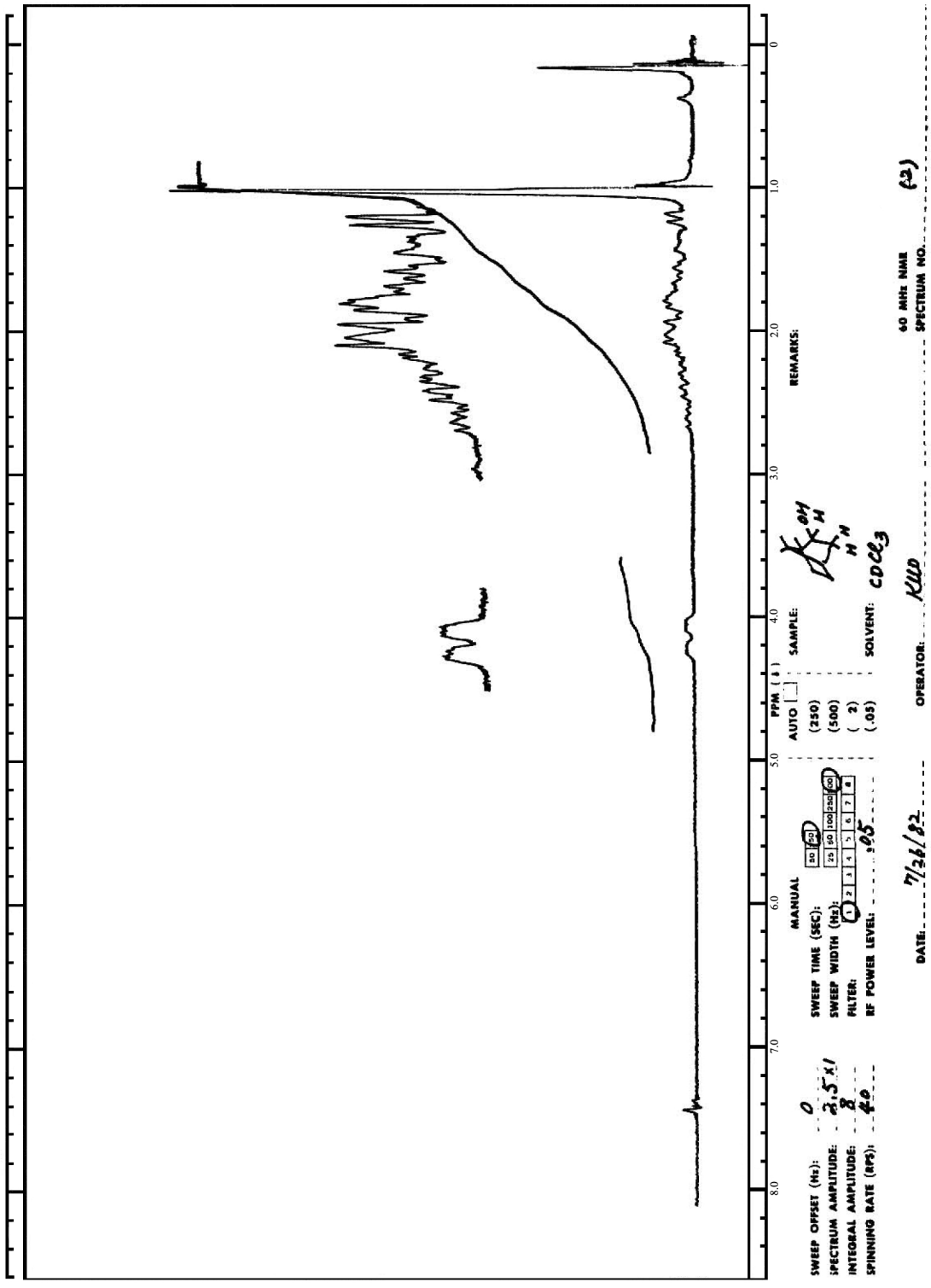

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 7; NMR spectrum of compound (2)


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.5 x 1
INTEGRAL AMPLITUDE: 8
SPINNING RATE (RPS): 40
MANUAL
SWEEP TIME (SEC): 50 60
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: 05
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT: CDCl3
REMARKS:
DATE: 7/26/82
OPERATOR: KWD
60 MHz NMR
SPECTRUM NO. (2)

2) Identification:

a) IR: as shown in Figures 8 and 9.

b) NMR: as shown in Figure 10.

^{1}H-NMR($CDCl_3$) δ 0.8 ppm(s,3H)*, 1.05 ppm(d,6H)**, 1.2-2.7 ppm(m,7H)***, 2.0 ppm(s,3H), 4.5-4.7 ppm(d,1H).

* singlet for three hydrogens.

** doublet for six hydrogens.

*** multiple peaks for seven hydrogens.

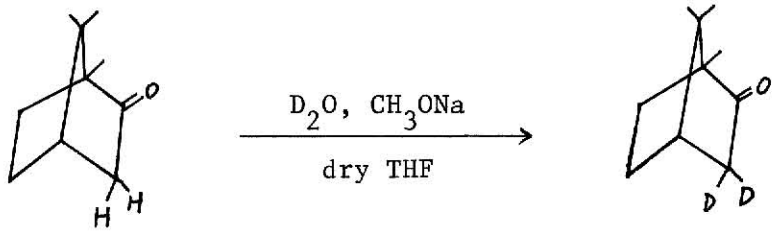
c) GC: the retention time was 9 min. 16 sec., which was matched with commercial product and the peak area was increased on the GC chromatogram.

b. Compound II:

Bicyclo [2,2,1] heptane-2-ol-3,3-d_2-1,7,7-trimethyl-acetate

1) Synthesis

a) 27



(1) (3)

To a 500 mL round-bottomed flask, 45.7 g (0.3 mole) of compound (1) dissolved in an adequate amount of dry THF and 6 mL (0.3 mole) of D_2O (Bio-Rad Lab.) were added. This mixture was refluxed in the presence of CH_3ONa for six hours. The reaction mixture was then cooled and extracted with chloroform. The

Figure 8; IR spectrum of polyethylene as backgound

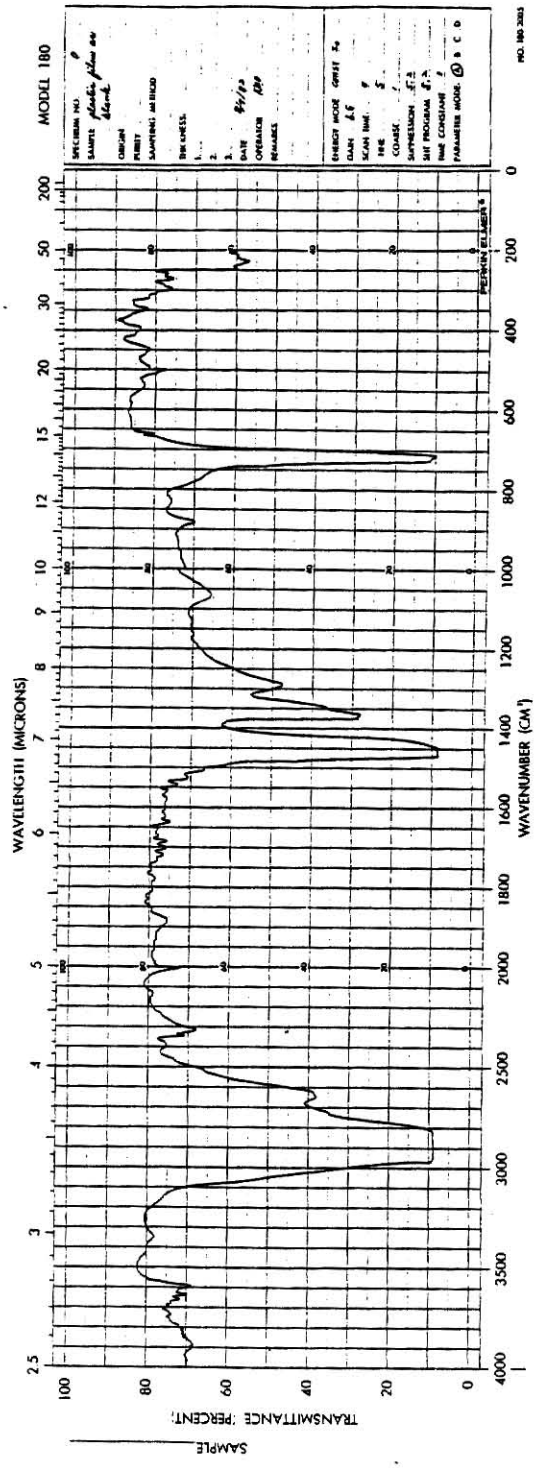

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 9; IR spectrum of compound I

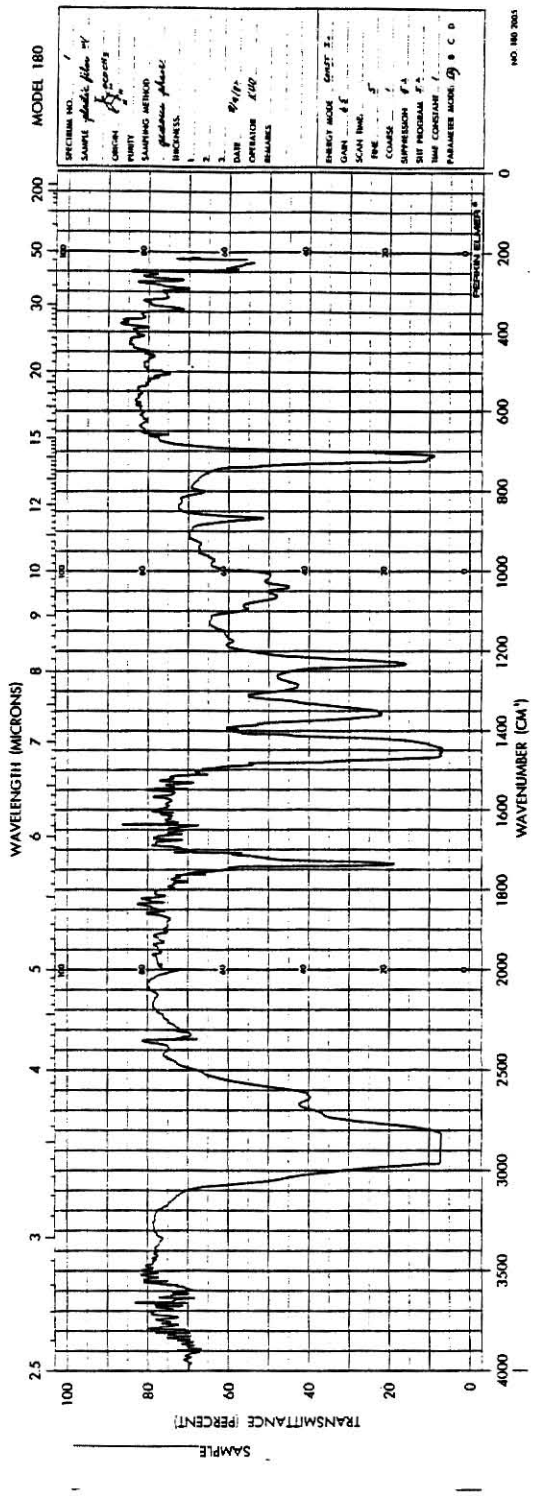
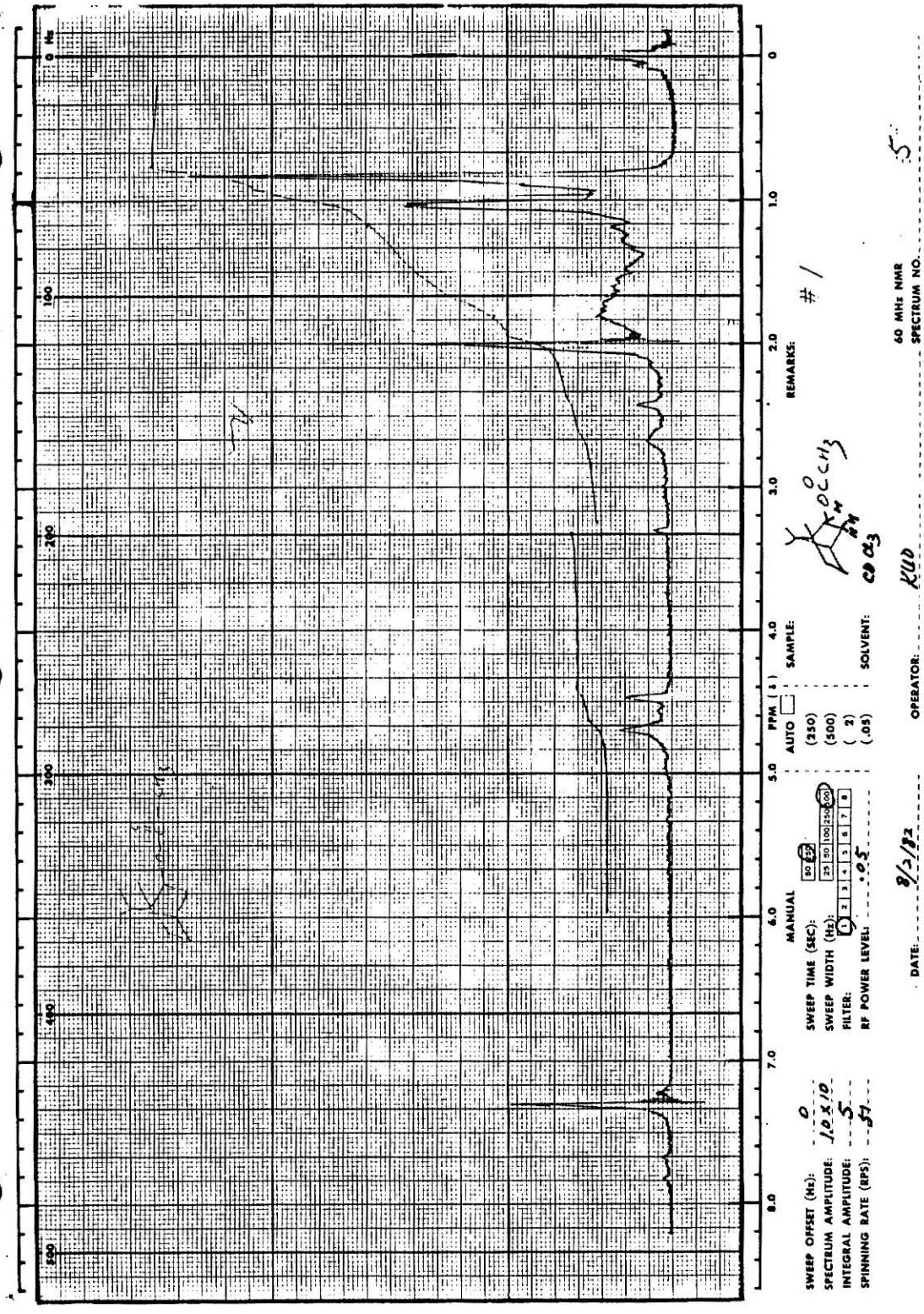
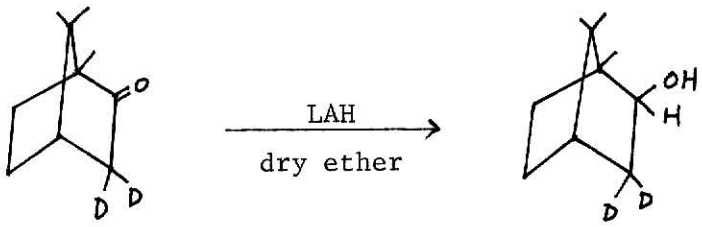

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 10; NMR spectrum of compound I


0 Hz
100
200
300
400
500
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0
MANUAL
AUTO
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 10 X 10
INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): 51
SWEEP TIME (SEC): 50 25
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: .05
SAMPLE: (250) (500) (2) (.05)
SOLVENT: CDCl3
DATE: 8/3/82
OPERATOR: KUO
REMARKS: # 1
60 MHz NMR
SPECTRUM NO. 5

layers were separated and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to remove all of the solvent. The deuterium exchange process was performed for 21 successive times to enhance the concentration. Finally, the residue was dissolved in a minimum amount of benzene, recrystallized to give a pure compound: yield (72%), m.p. 176-178°C (lit.[30] 176-178°C), IR and NMR spectra as shown in Figures 11 and 12.

b) 25



(3) (4)

To a 1,000 mL, three necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel, were added 500 mL of anhydrous ether and 8.4 g (0.21 mole) of $LiAlH_4$. To this stirred mixture was added a solution of 35.5 g (0.23 mole) of compound (3) in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed (about 30 min.), the reaction mixture was then cooled and worked up by adding, dropwise, of the following reagents: 9 mL of H_2O, then 9 mL of 15% aqueous NaOH, and then 12 mL of H_2O. This gave a

Figure 11; IR spectrum of compound (3)

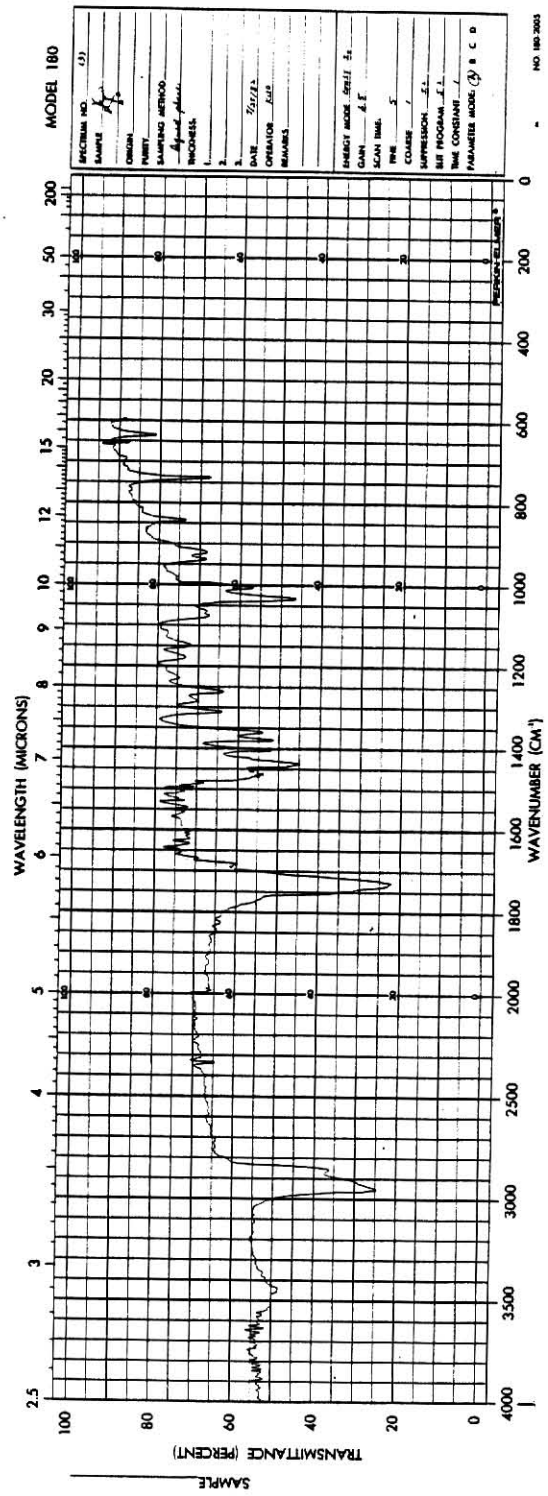
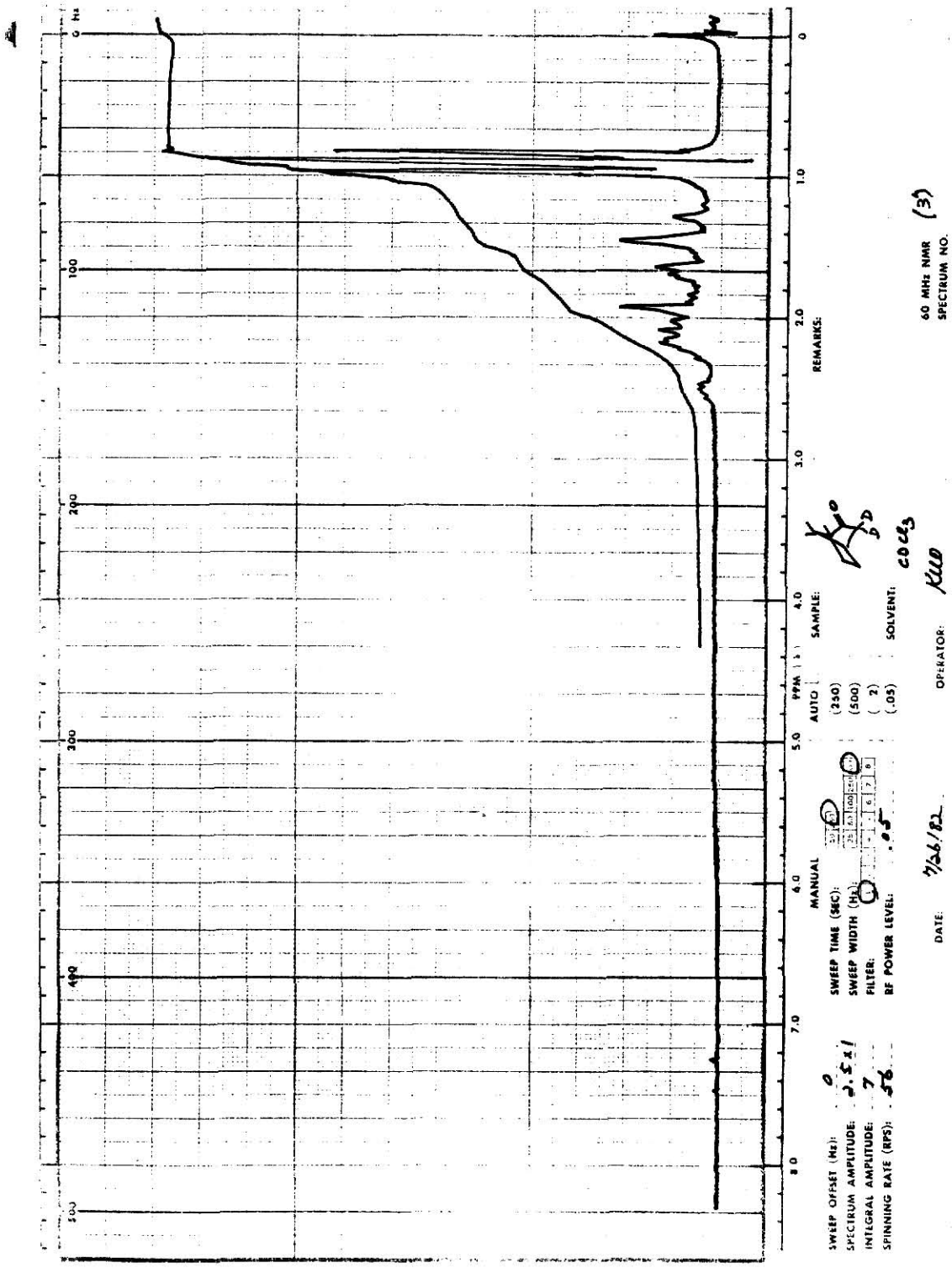

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

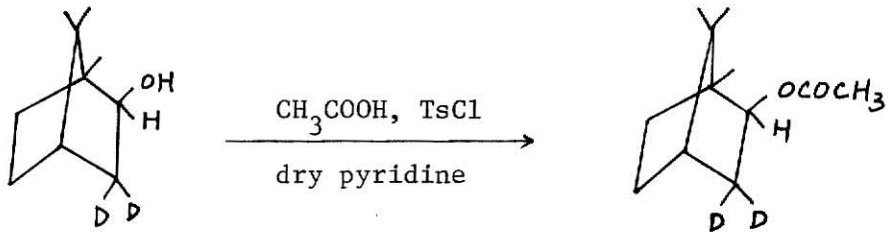
Figure 12; NMR spectrum of compound (3)


Hz
0
100
200
300
400
500
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
MANUAL
AUTO
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.5x1
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 56
SWEEP TIME (SEC): (250)
SWEEP WIDTH (Hz): (500)
FILTER: (2)
RF POWER LEVEL: .05
SOLVENT: CDCl3
SAMPLE:
REMARKS:
DATE: 7/26/82
OPERATOR: KWO
60 MHz NMR SPECTRUM NO. (3)

precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H_2O, the layers were separated and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo until all of the solvent was removed. The residue was dissolved in a minimum amount of benzene, recrystallized, giving 21.0 g (64%) of compound (4): m.p. 206-208°C (lit.[28] 207-208°C), IR and NMR spectra as shown in Figures 13 and 14.

c)

26



(4) II

To a 500 mL Erlenmeyer flask, 3.8 mL (0.063 mole) CH_3COOH was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 9.8 g (0.063 mole) of compound (4) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium hydrogen sulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and

Figure 13; IR spectrum of compound (4)

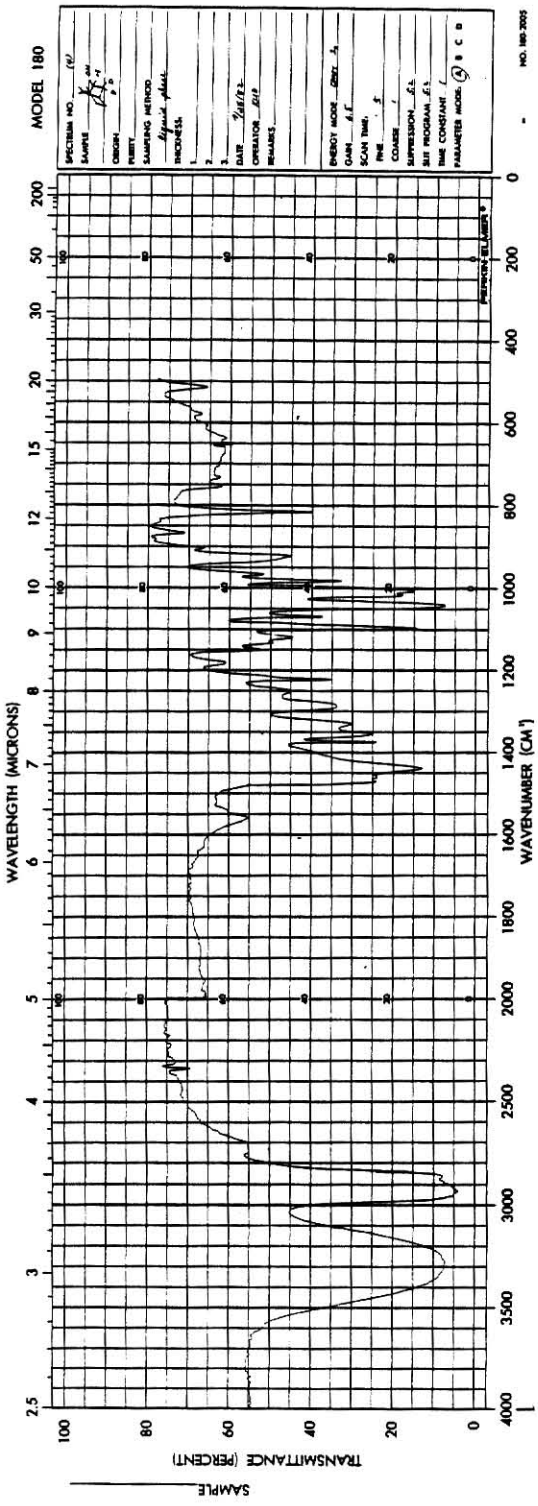
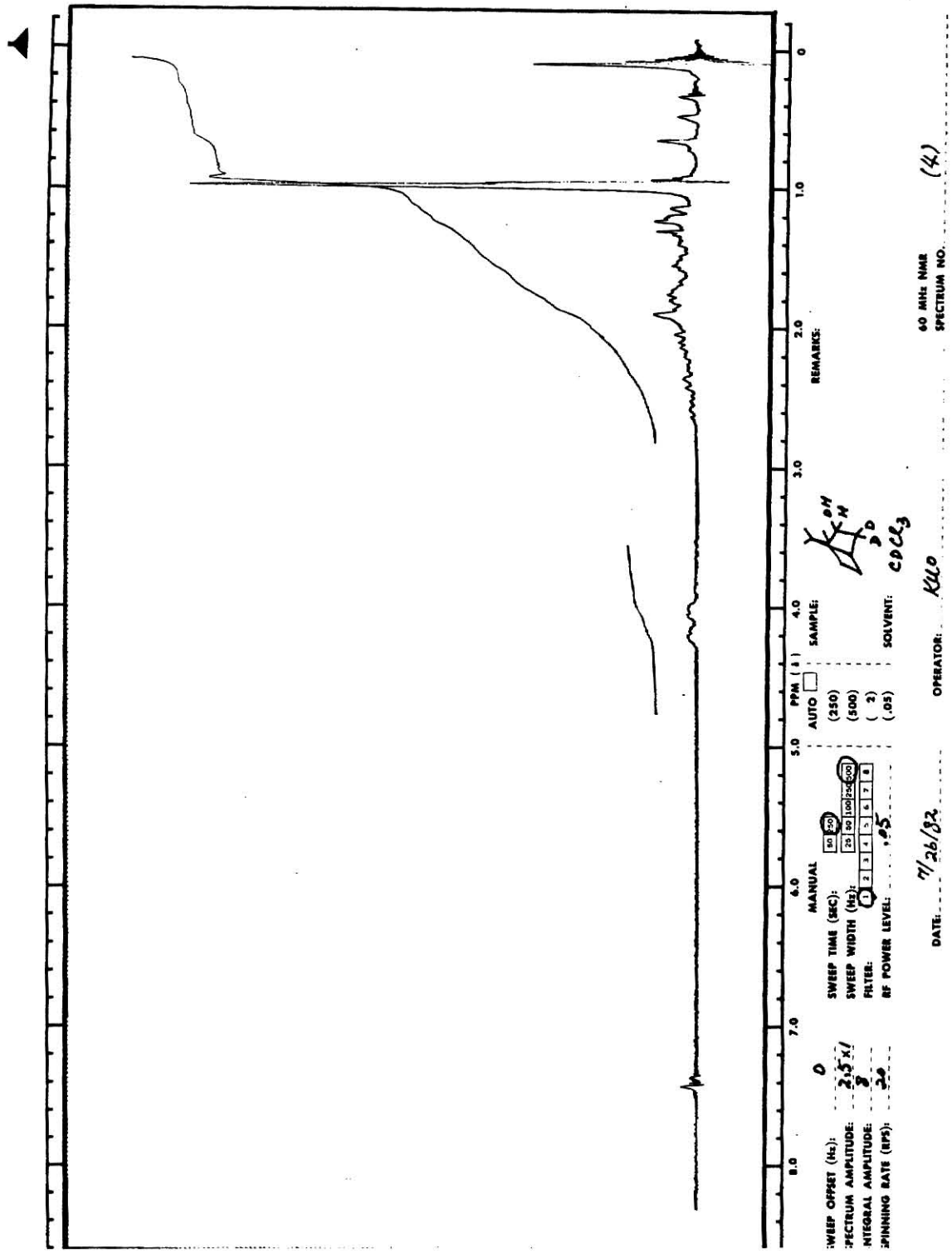

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 14; NMR spectrum of compound (4)


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
MANUAL
AUTO
SAMPLE:
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.5 x1
INTEGRAL AMPLITUDE: 3
SPINNING RATE (RPS): 20
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 0 2 3 4 5 6 7 8
RF POWER LEVEL: .05
(250)
(500)
(2)
(.05)
SOLVENT: CDCl3
REMARKS:
DATE: 7/26/82
OPERATOR: KLO
60 MHz NMR
SPECTRUM NO. (4)

then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (81%), purity (94%), d-content (95%), b.p. 225-227°C (lit.[29] 223-224°C).

2) Identification:

a) IR: as shown in Figure 15.

b) NMR: as shown in Figure 16.

^{1}H-NMR($CDCl_3$) δ 0.82 ppm(s,3H), 1.0 ppm(d,6H), 1.17-2.82 ppm(m,5H), 2.0 ppm(s,3H), 4.47-4.66 ppm(d,1H).

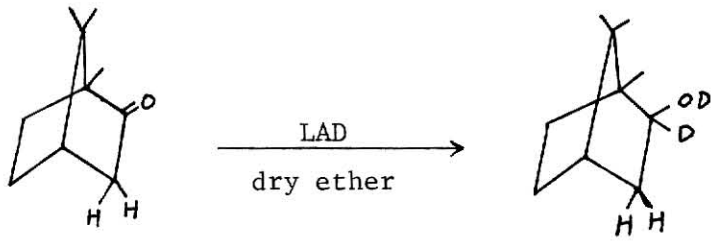
c) GC: the retention time was 9 min. 24 sec., and matched the hydrogenated standard.

c. Compound III:

Bicyclo [2,2,1] heptane-2-ol-2-d_1-1,7,7-trimethyl-acetate

1) Synthesis:

a) 25



(1) (5)

To a 1,000 mL, three necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel, were added 500 mL of anhydrous ether and 8.8 g (0.21

Figure 15; IR spectrum of compound II

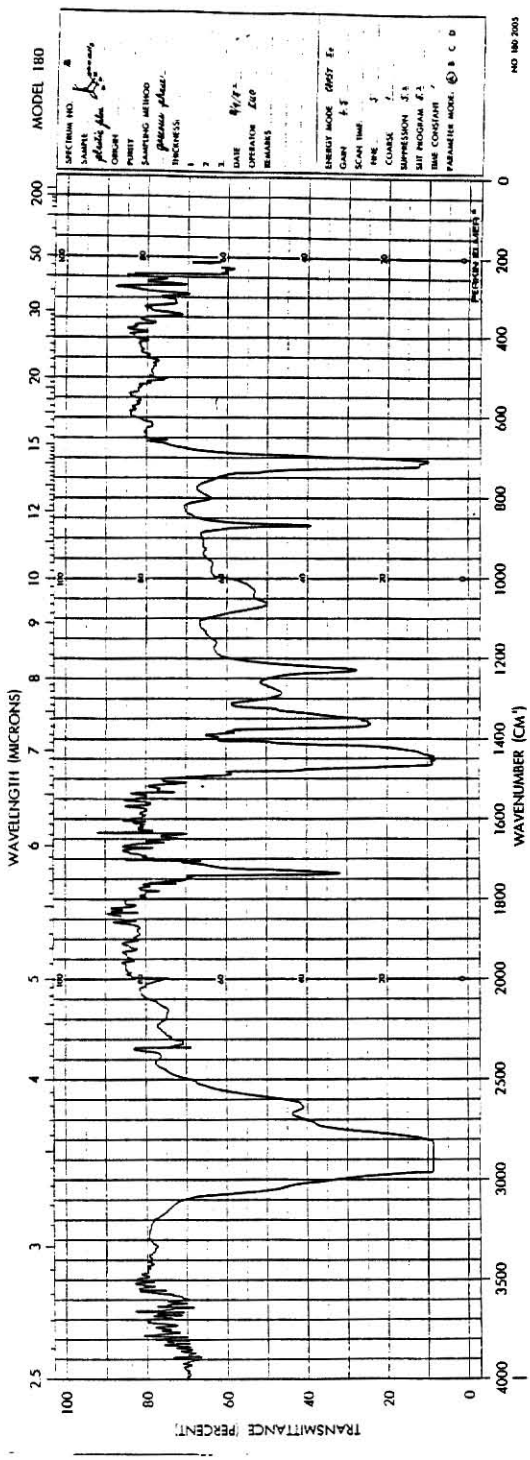
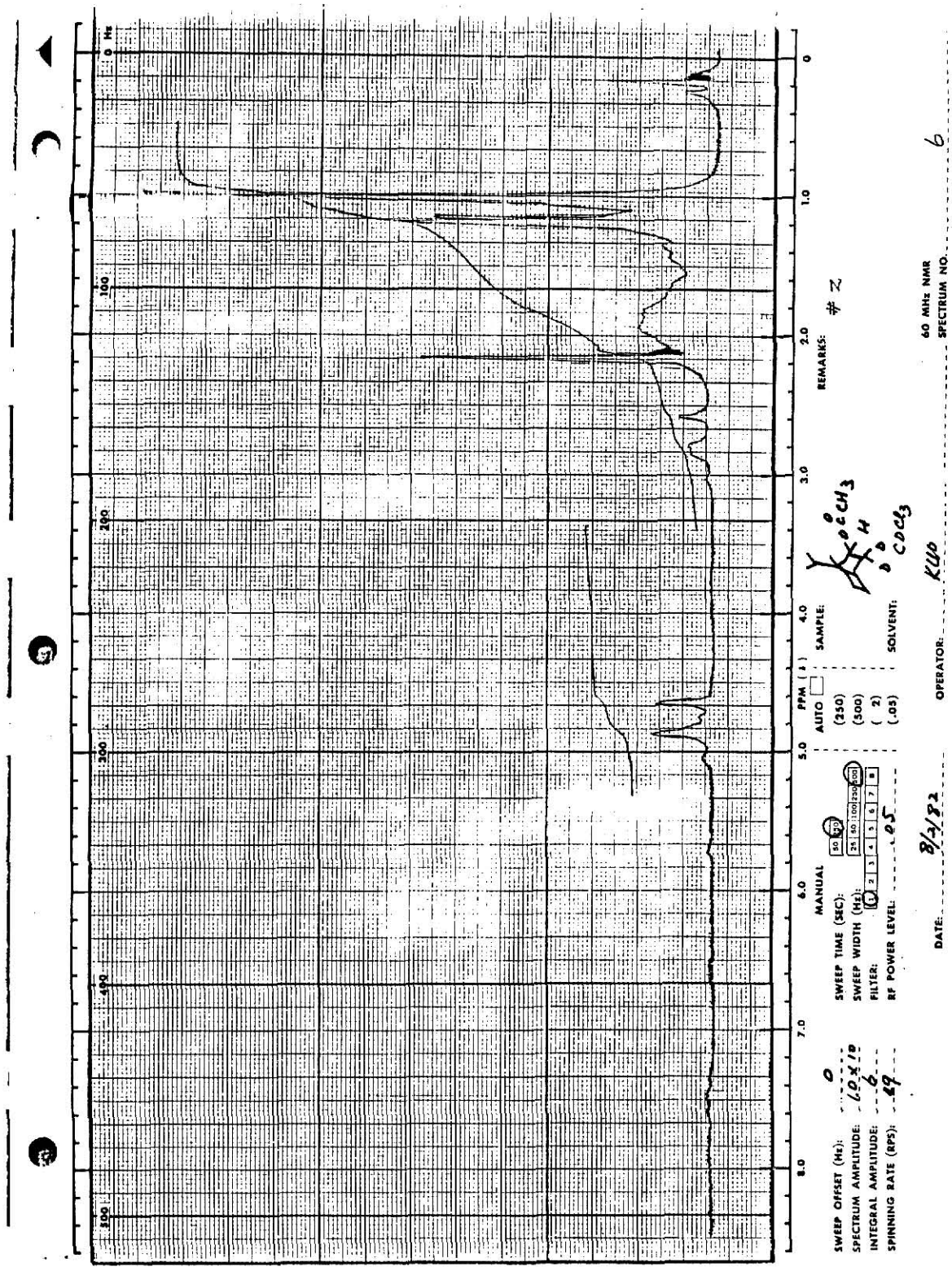

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)

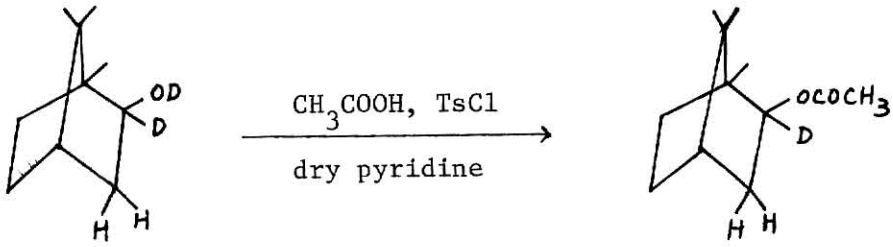
Figure 16; NMR spectrum of compound II


0 Hz
100
200
300
400
500
8.0
7.0
6.0
MANUAL
5.0
PPM (δ)
AUTO
4.0
3.0
2.0
1.0
0
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 10 x 10
INTEGRAL AMPLITUDE: 6
SPINNING RATE (RPS): 49
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: .05
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT: CDCl3
REMARKS: # 2
DATE: 8/3/82
OPERATOR: KWO
60 MHz NMR
SPECTRUM NO. 6

mole) of $LiAlD_4$ (Aldrich). To this stirred mixture was added a solution of 35.0 g (0.23 mole) of compound (1) in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed (about 30 min.), the reaction mixture was then cooled and worked up by adding, dropwise, of the following reagents: 9 mL of H_2O, then 9 mL of 15% aqueous NaOH, and then 12 mL of H_2O. This gave a precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H_2O, the layers were separated and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo until all of the solvent was removed. The residue was dissolved in a minimum amount of benzene, recrystallized, giving 22.3 g (68%) of compound (5): m.p. 206-208°C (lit.[28] 207-208°C), IR and NMR spectra as shown in Figures 17 and 18.

b)

26



(5) III

To a 500 mL Erlenmeyer flask, 3.8 mL (0.063 mole) CH_3COOH was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled

Figure 17; IR spectrum of compound (5)

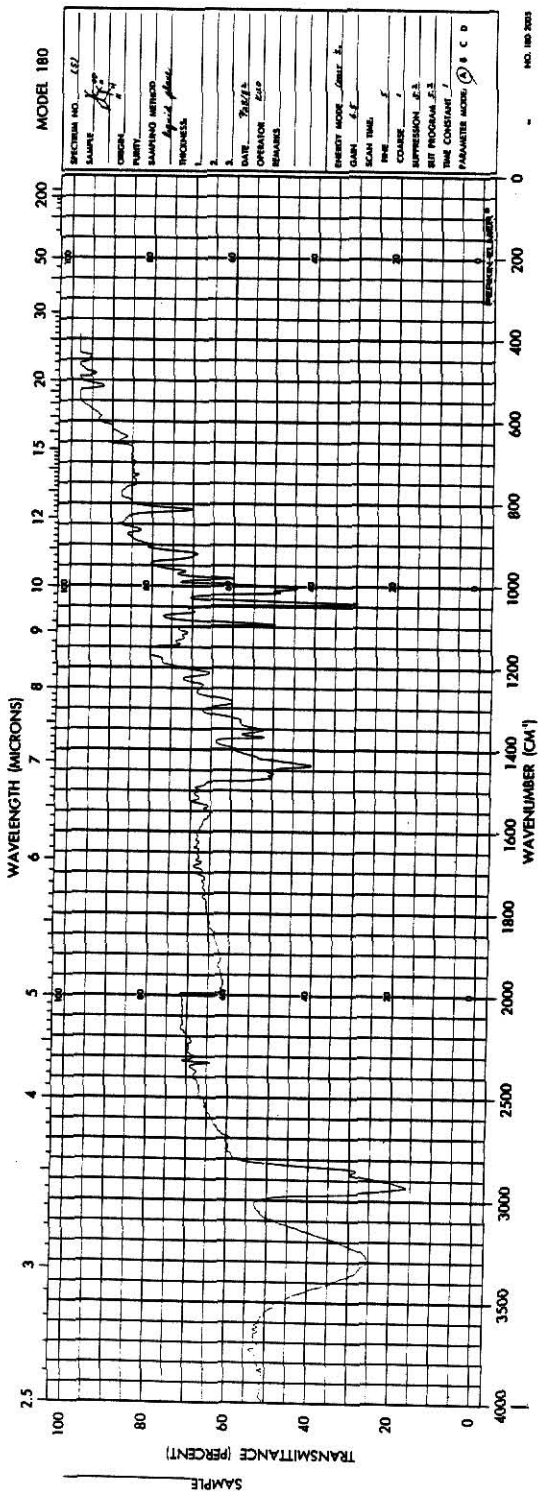
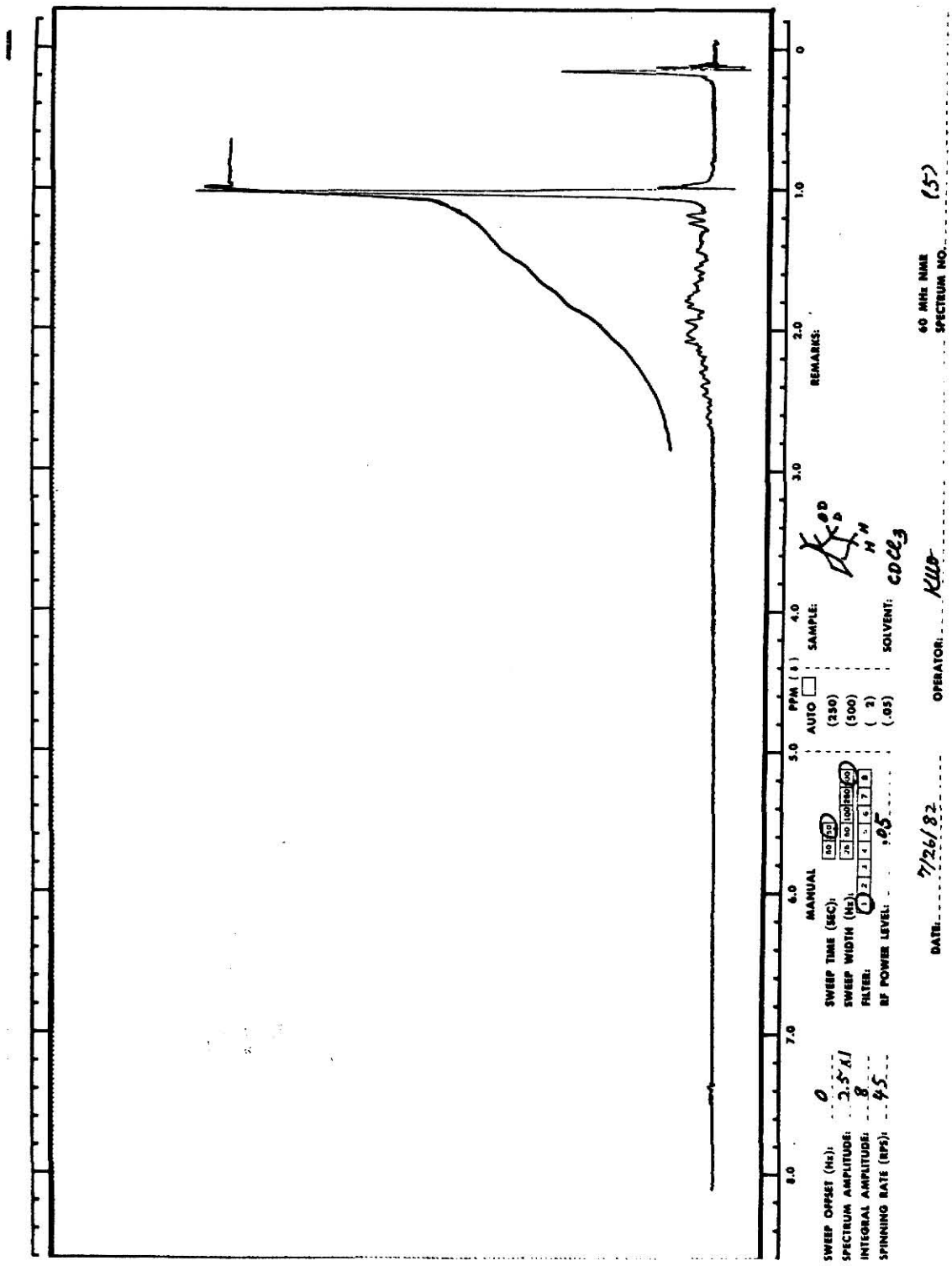

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 18; NMR spectrum of compound (5)


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.5x1
INTEGRAL AMPLITUDE: 8
SPINNING RATE (RPS): 45
MANUAL
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: .95
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT: CDCl3
REMARKS:
DATE: 7/26/82
OPERATOR: KWD
60 MHz NMR
SPECTRUM NO. (5)

in ice and 9.8 g (0.063 mole) of compound (5) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium bisulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (84%), purity (94%), d-content (99%), b.p. 226-227°C (lit.[29] 223-224°C).

2) *Identification:*

a) IR: as shown in Figure 19.

b) NMR: as shown in Figure 20.

^{1}H-NMR($CDCl_3$) δ 0.81 ppm(s,6H), 1.0 ppm(s,3H), 1.1-2.4 ppm(m,7H), 2.0 ppm(s,3H).

c) GC: The retention time was 9 min. 12 sec., and matched the hydrogenated standard.

Figure 19; IR spectrum of compound III

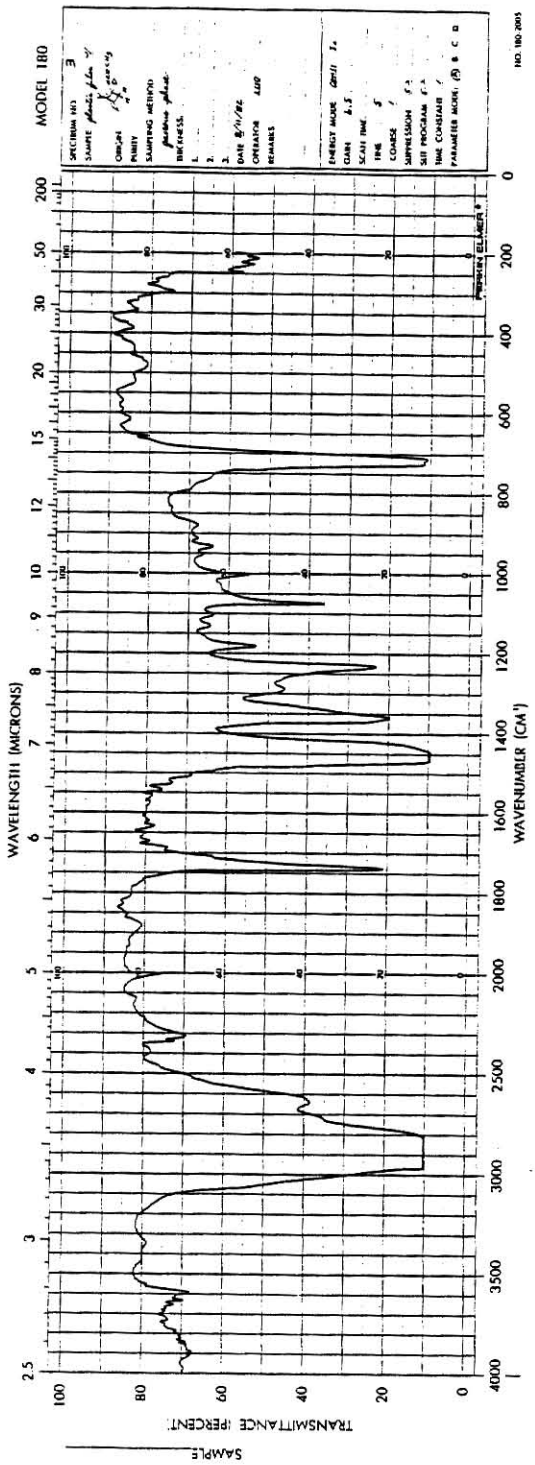
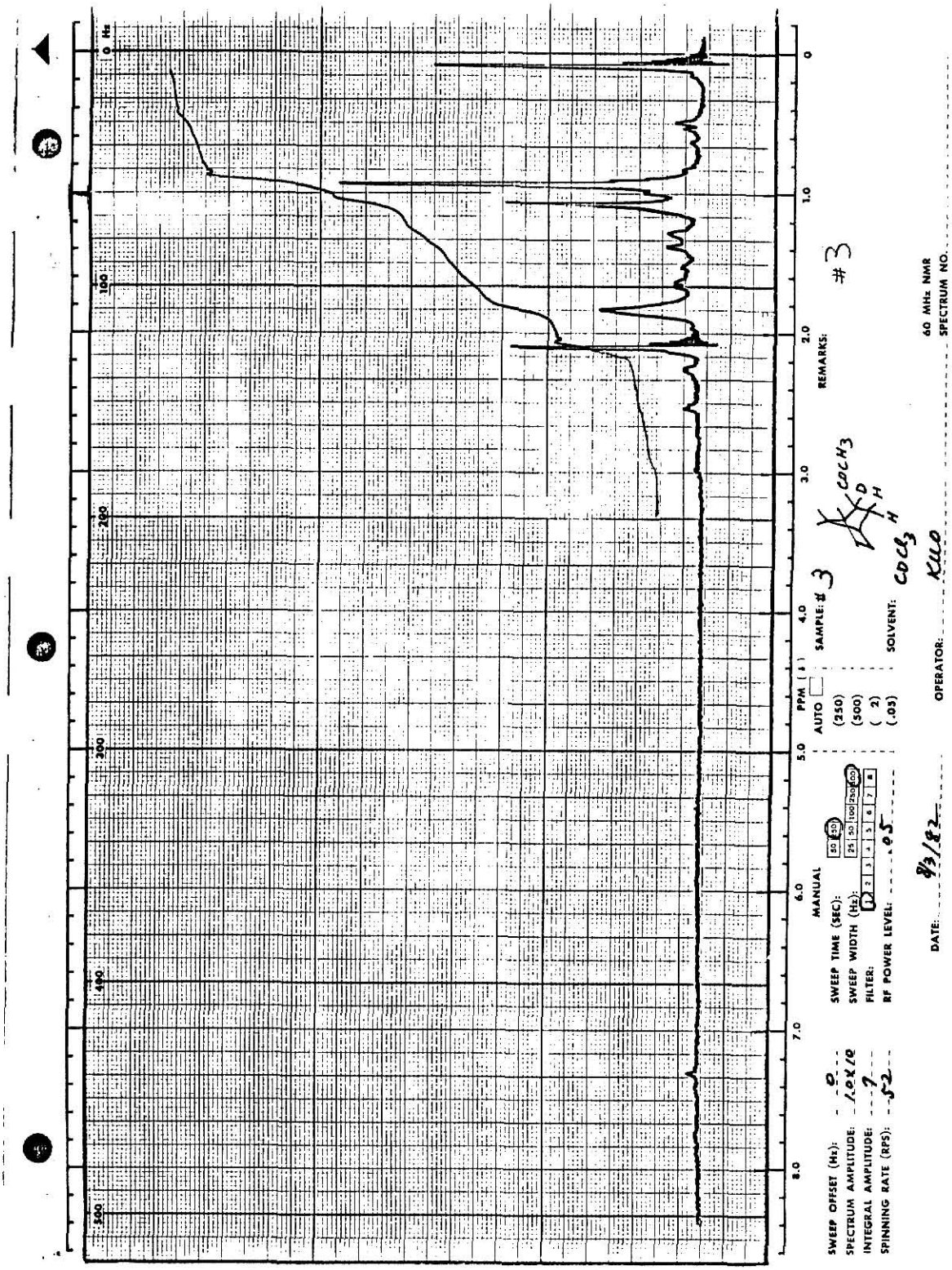

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 20; NMR spectrum of compound III

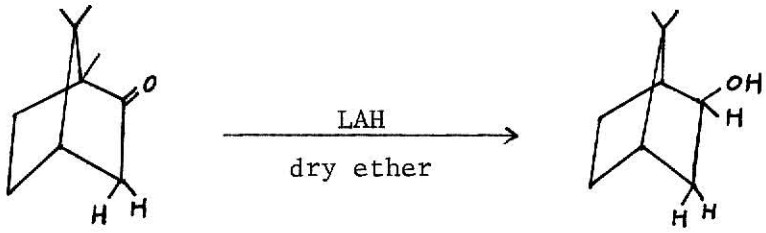

500
400
300
200
100
0 Hz
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
MANUAL
AUTO
SWEEP OFFSET (Hz): -0-
SPECTRUM AMPLITUDE: 1.0X10
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 52
SWEEP TIME (SEC): 50 (250)
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: Ω 2 3 4 5 6 7 8
RF POWER LEVEL: .05
SAMPLE: #3
SOLVENT: CDCl3
REMARKS: #3
DATE: 8/3/82
OPERATOR: Kuo
60 MHz NMR
SPECTRUM NO.

d. Compound IV:

Bicyclo [2,2,1] heptane-2-ol-1,7,7-trimethyl-acetate-d_3

1) Synthesis:

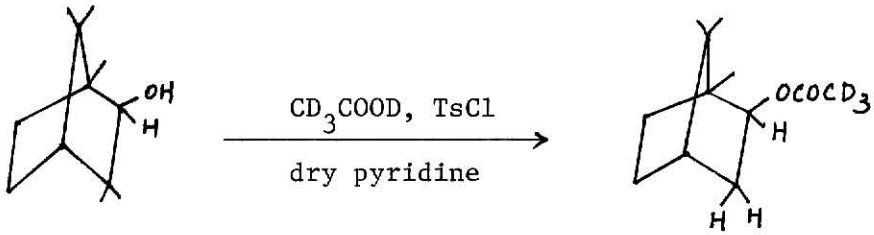
a) 25



(1) (2)

Procedure same as a, 1), a), on page 14.

b) 26



(2) IV

To a 500 mL Erlenmeyer flask, 4.1 mL (0.063 mole) CD_3COOD (Aldrich) was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 9.7 g (0.063 mole) of compound (2) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous

solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium bisulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (86%), purity (95%), d-content (92%), b.p. 226-227°C (lit.[29] 223-224°C).

2) Identification:

a) IR: as shown in Figure 21.

b) NMR: as shown in Figure 22.

^{1}H-NMR($CDCl_3$) δ 0.85 ppm(s,3H), 1.05 ppm(d,6H), 1.15-2.75 ppm(m,7H), 4.45-4.75 ppm(d,1H).

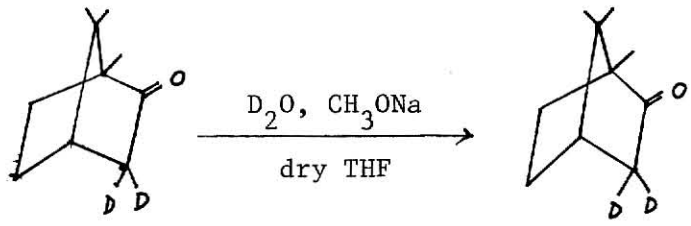
c) GC: The retention time was 9 min. 26 sec., and matched the hydrogenated standard.

e. Compound V:

Bicyclo [2,2,1] heptane-2-ol-2,3,3-d_3-1,7,7-trimethyl-acetate

1) Synthesis

a) 27



(1) (3)

Figure 21; IR spectrum of compound IV

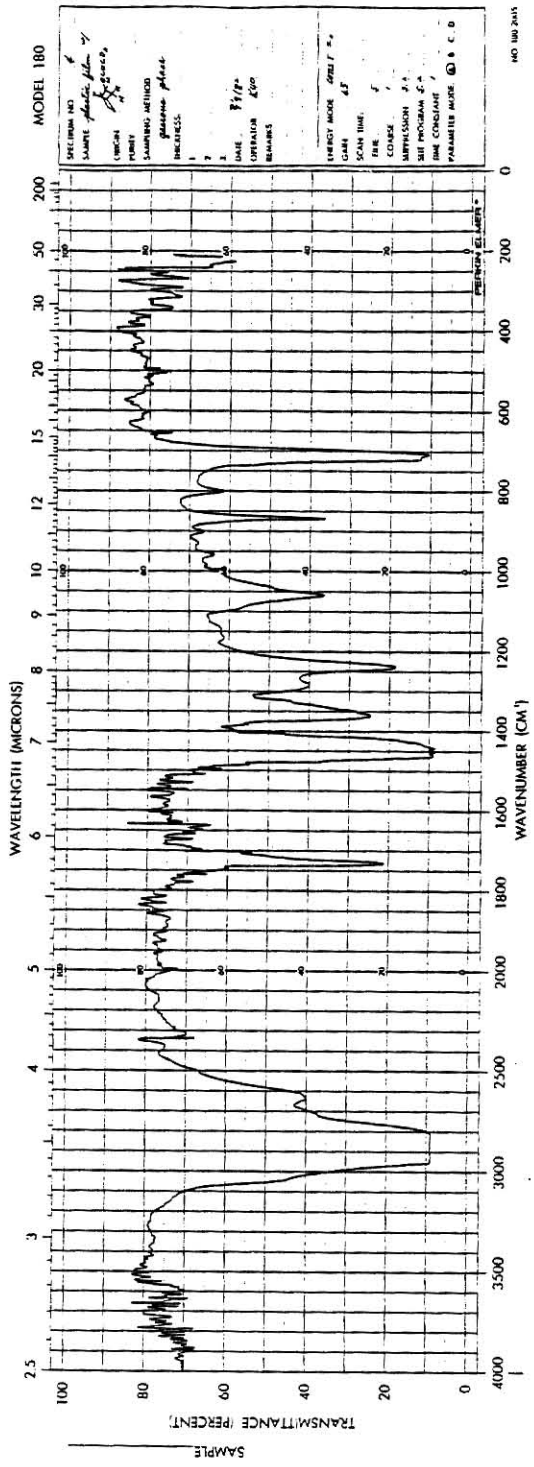

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 22; NMR spectrum of compound IV

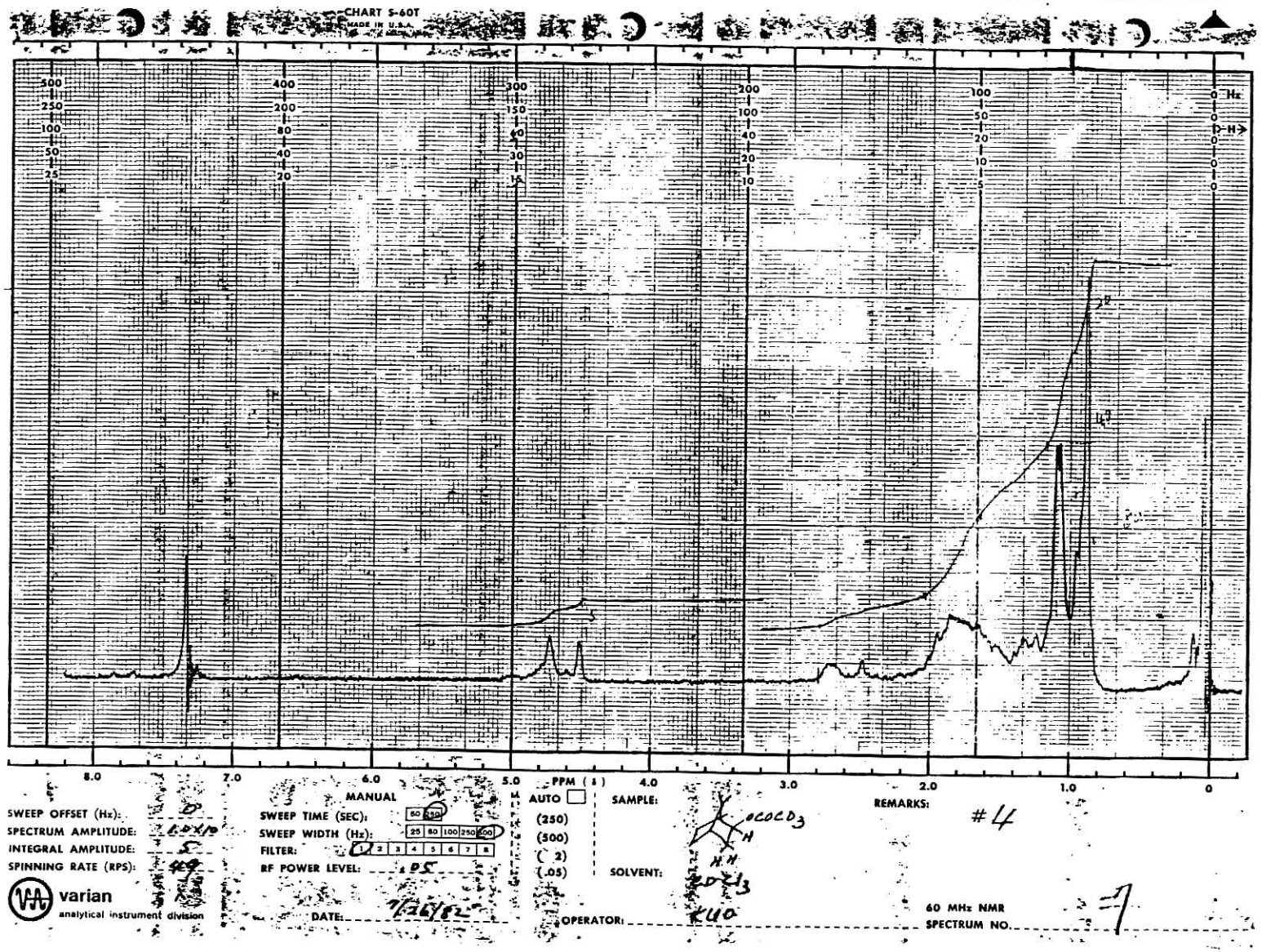
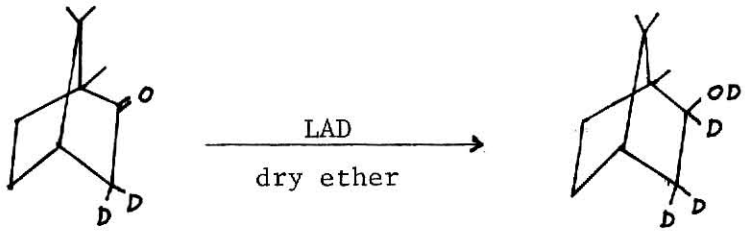


CHART 5-60T
MADE IN U.S.A.
500
250
100
50
25
400
200
80
40
20
300
150
60
30
15
200
100
40
20
10
100
50
20
10
5
0 Hz
0 P-H
0
0
0
0
0
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0
MANUAL
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.0x10
INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): 49
SWEEP TIME (SEC): 60 120
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: .25
DATE: 7-16-82
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
OCOCD3
H
H H
SOLVENT: CDCl3
OPERATOR: KUO
REMARKS: #4
60 MHz NMR
SPECTRUM NO. 1
varian
analytical instrument division

Procedure same as b, 1), a), on page 19.

b) 25

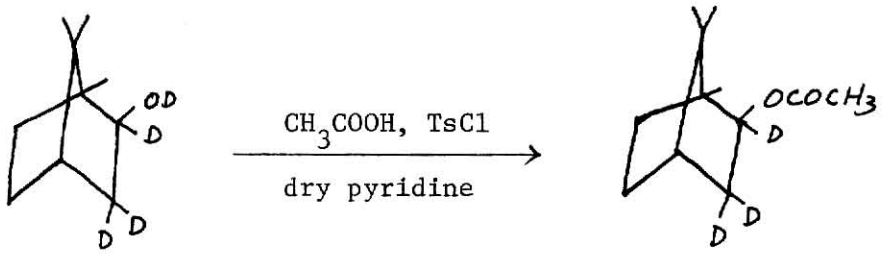


(3) (6)

To a 1,000 mL, three necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel, were added 500 mL of anhydrous ether and 8.8 g (0.21 mole) of $LiAlD_4$ (Aldrich). To this stirred mexture was added a solution of 35.5 g (0.23 mole) of compound (3) in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed (about 30 min.), the reaction mixture was then cooled and worked up by adding, dropwise, of the following reagents: 9 mL of H_2O, then 9 mL of 15% aqueous NaOH, and then 12 mL of H_2O. This gave a precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H_2O, the layers were separated and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo until all of the solvent was removed. The residue was dissolved in a minimum amount of benzene, recrystallized, giving 20.1 g (62%) of compound (6):

m.p. 206-208°C (lit.[28] 207-208°C), IR and NMR spectra as shown in Figures 23 and 24.

c) 26



(6) V

To a 500 mL Erlenmeyer flask, 3.8 mL (0.063 mole) CH_3COOH was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 10.0 g (0.063 mole) of compound (6) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium hydrogen sulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (80%), purity (93%), d-content (98%), b.p. 226-227°C (lit.[29] 223-224°C).

Figure 23; IR spectrum of compound (6)

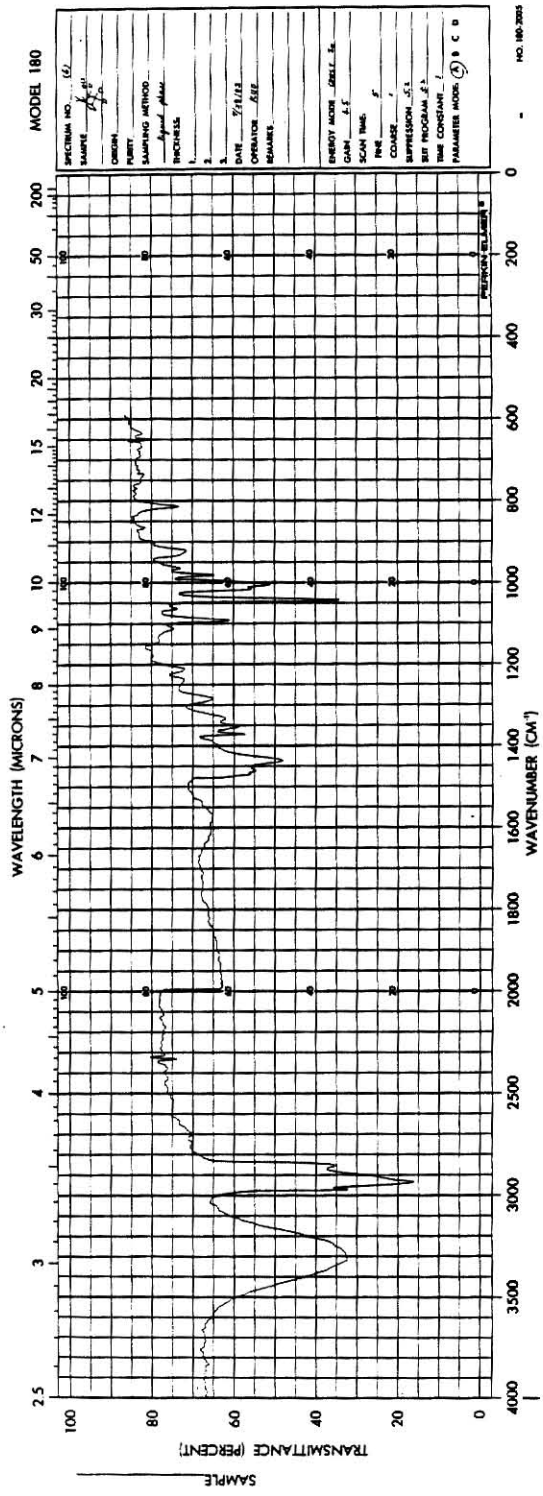
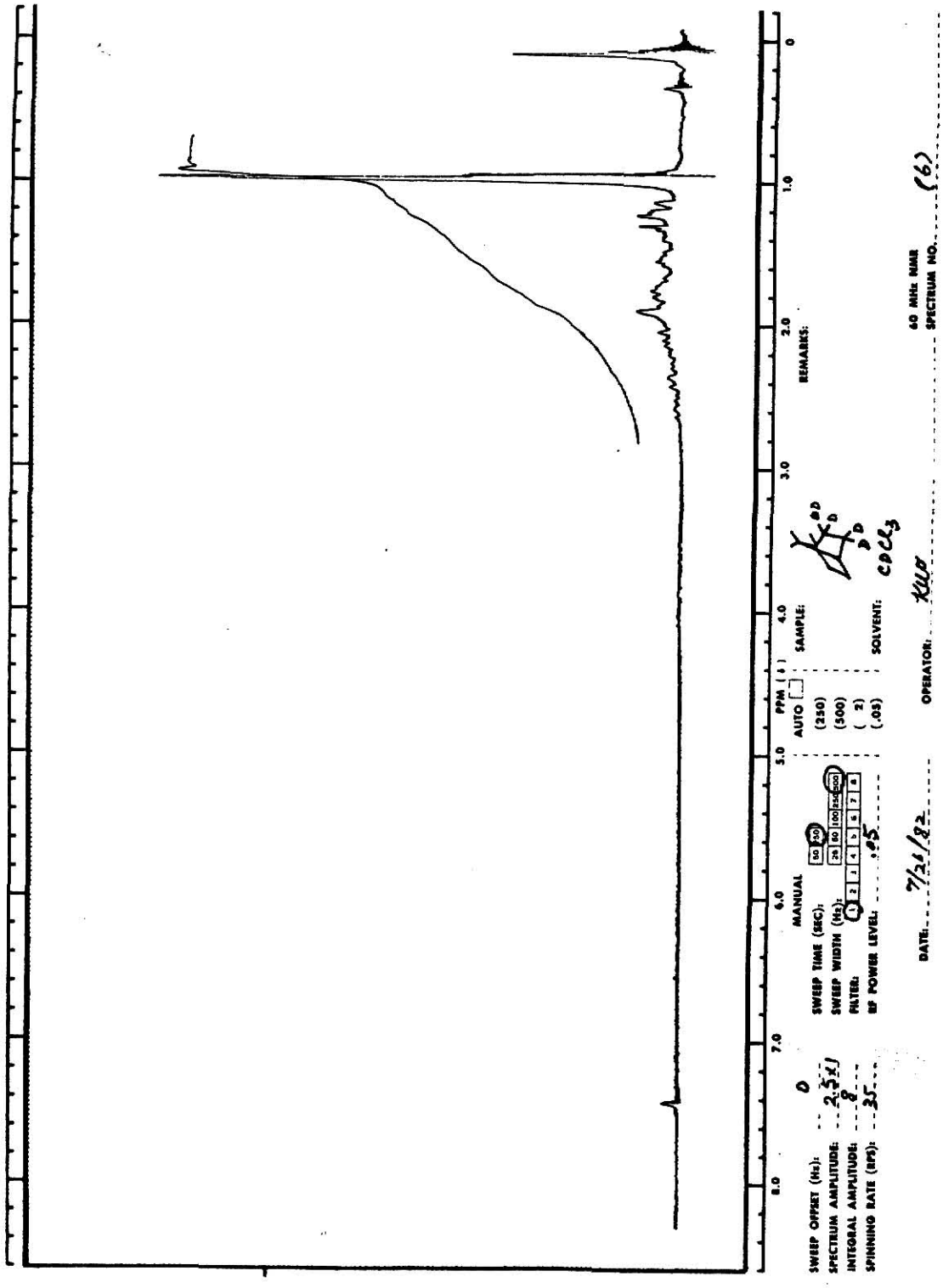

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 24; NMR spectrum of compound (6)


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 2.5x1
INTEGRAL AMPLITUDE: 8
SPINNING RATE (RPS): 35
MANUAL
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: .05
AUTO
(250)
(300)
(2)
(.03)
SAMPLE:
SOLVENT: CDCl3
REMARKS:
DATE: 7/21/82
OPERATOR: KWO
60 MHz NMR
SPECTRUM NO. (6)

2) Identification:

a) IR: as shown in Figure 25.

b) NMR: as shown in Figure 26.

^{1}H-NMR($CDCl_3$) δ 0.8 ppm(s,3H), 0.9 ppm(s,3H), 1.05 ppm(s,3H), 1.05-1.18 ppm(m,5H).

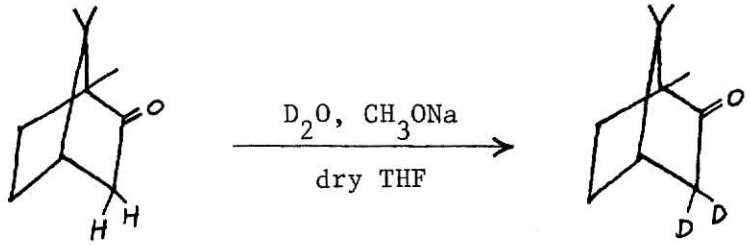
c) GC: The retention time was 9 min. 18 sec., and matched the hydrogenated standard.

f. Compound VI:

Bicyclo [2,2,1] heptane-2-ol-3,3-d_2-1,7,7-trimethyl-acetate-d_3

1) Synthesis

a) 27



(1) (3)

Procedure same as b, 1), a), on page 19.

Figure 25; IR spectrum of compound V

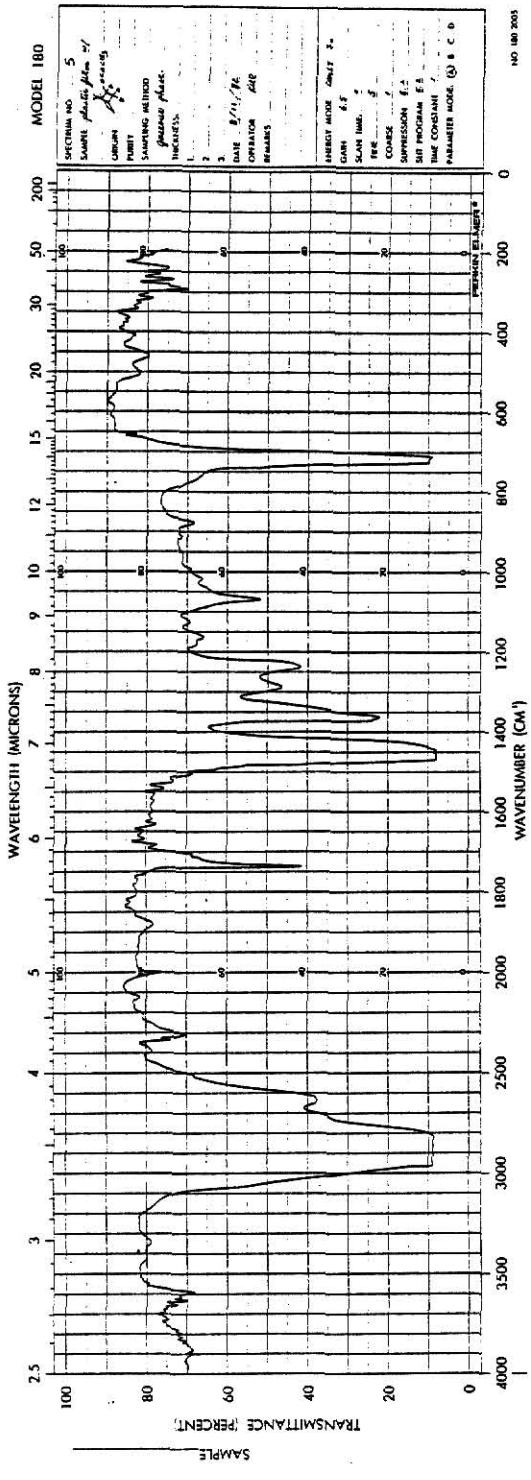
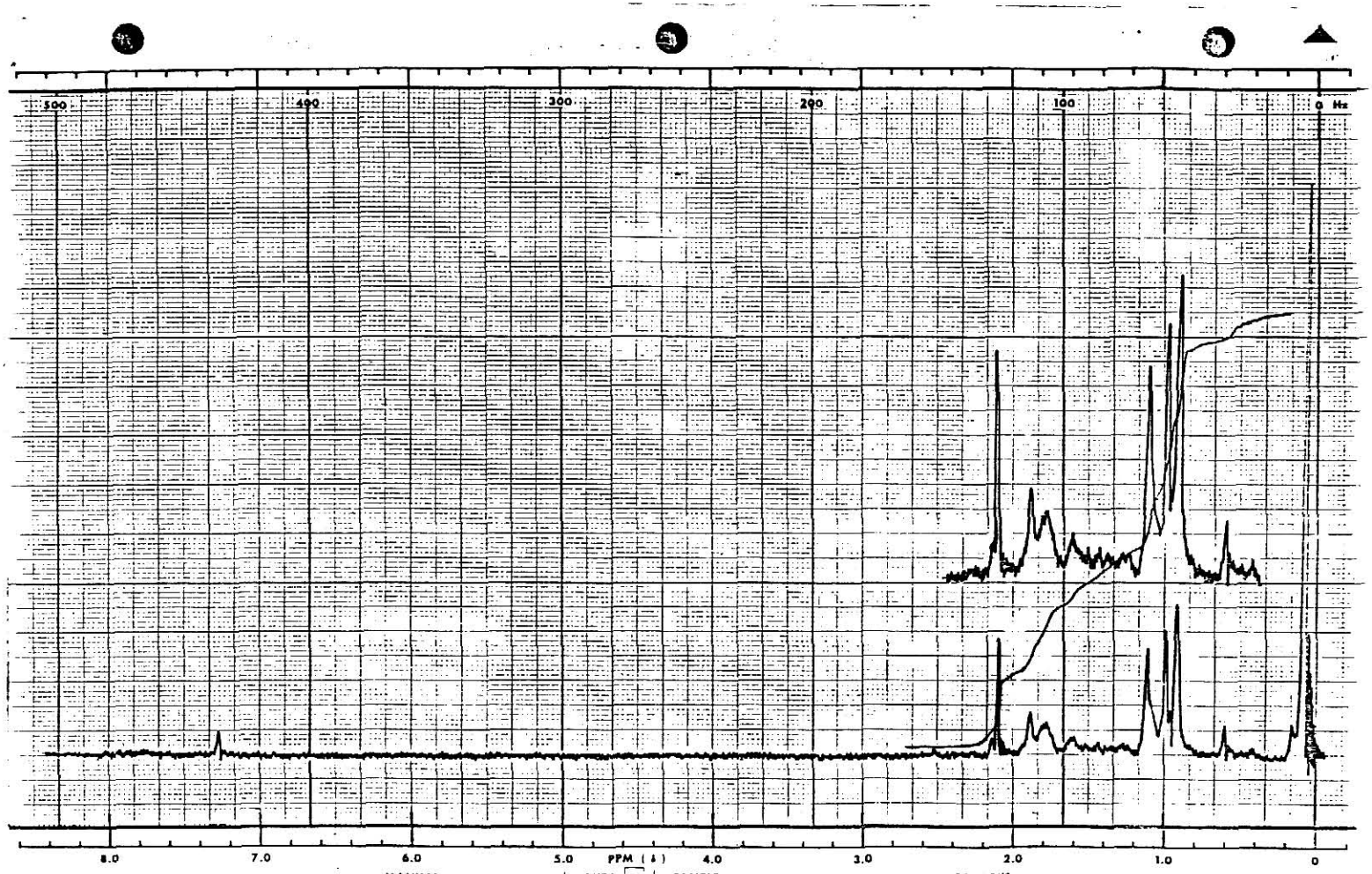

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 26; NMR spectrum of compound V

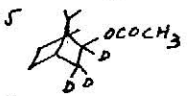


MANUAL AUTO

SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 1.4 X 10
INTEGRAL AMPLITUDE: 7
SPINNING RATE (RPS): 52

SWEEP TIME (SEC): 50 (25)
SWEEP WIDTH (Hz): 25 50 100 250 (500)
FILTER: (1) 2 3 4 5 6 7 8 (250) (500) (2)
RF POWER LEVEL: .05 (.05)

SAMPLE: #5



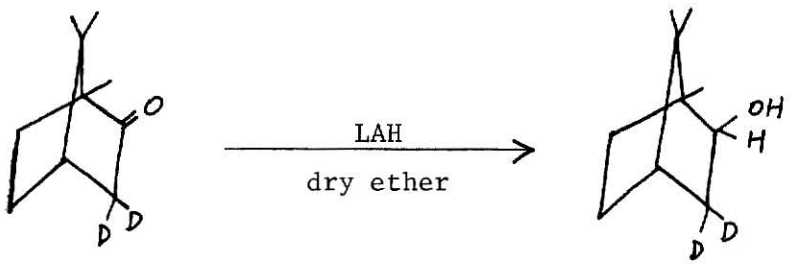
SOLVENT: $CDCl_3$

REMARKS: #5

DATE: 9/27/82 OPERATOR: KUO

60 MHz NMR
SPECTRUM NO.

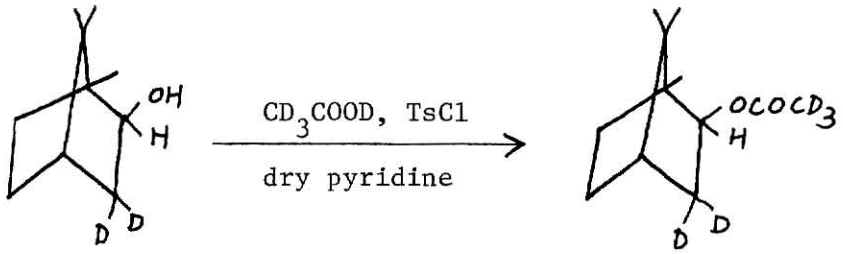
b) 25



(3) (4)

Procedure same as b, 1), b), on page 23.

c) 26



(4) VI

To a 500 mL Erlenmeyer flask, 4.1 mL (0.063 mole) CD_3COOD (Aldrich) was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 9.8 g (0.063 mole) of compound (4) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice an water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium hydrogen sulfate and once with 35 mL of water. The chloroform solution was dried over

anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (87%), purity (95%), d-content (98%), b.p. 226-227°C (lit.[29] 223-224°C).

2) Identification:

a) IR: as shown in Figure 27.

b) NMR: as shown in Figure 28.

^{1}H-NMR($CDCl_3$) δ 0.8 ppm(s,3H), 0.9 ppm(s,3H), 1.0 ppm(s,3H), 1.1-2.4 ppm(m,5H), 4.3 ppm(s,1H).

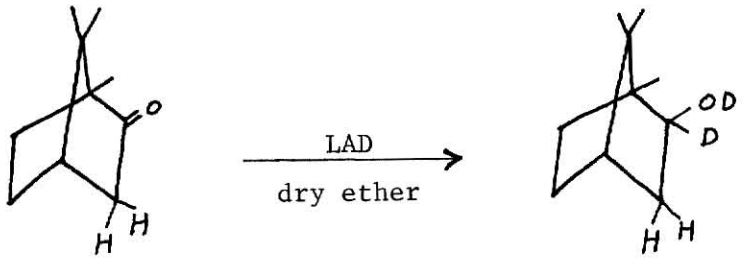
c) GC: The retention time was 9 min. 20 sec., and matched the hydrogenated standard.

g. Compound VII:

Bicyclo [2,2,1] heptane-2-ol-2-d_1-1,7,7-trimethyl-acetate-d_3

1) Synthesis

a) 25



(1) (5)

Procedure same as c, 1), a), on page 29.

Figure 27; IR spectrum of compound VI

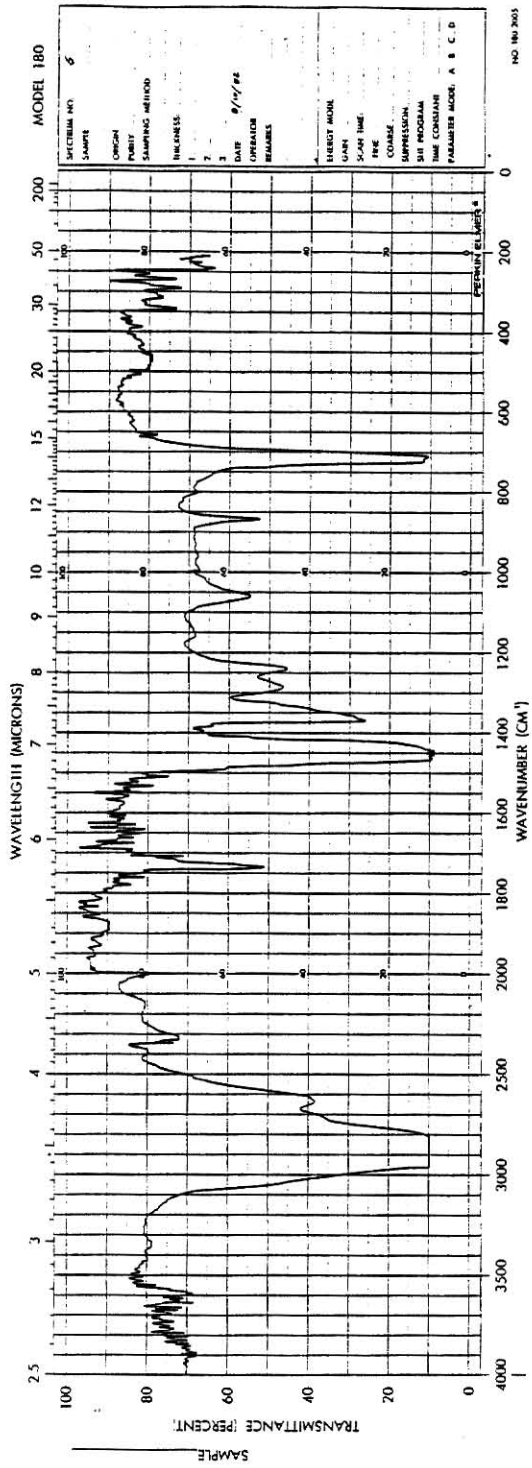
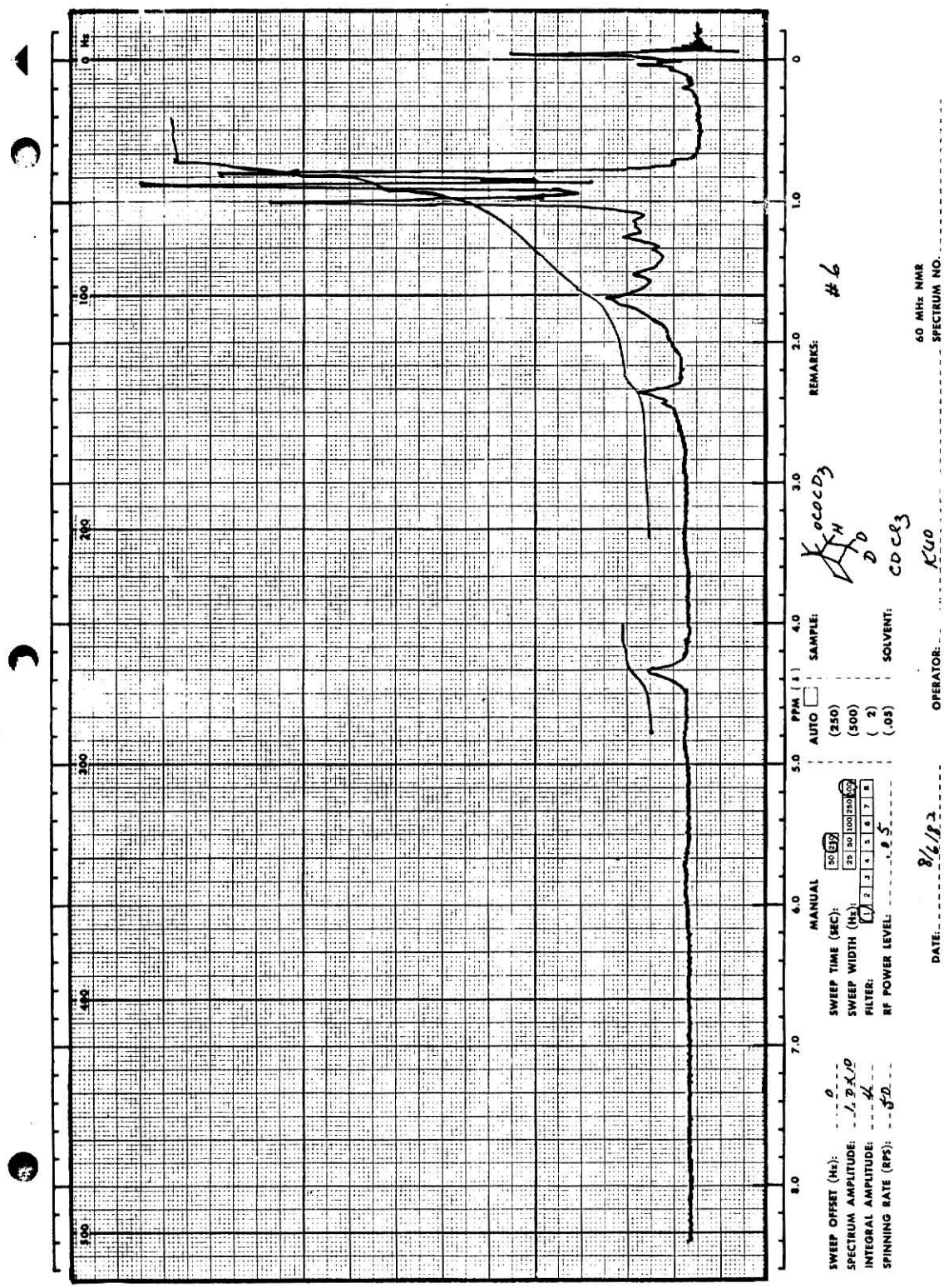
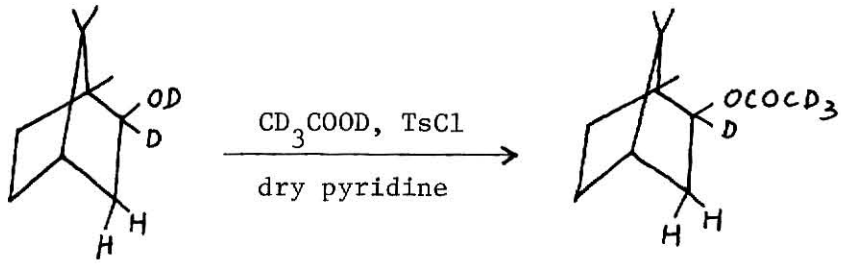

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE

Figure 28; NMR spectrum of compound VI


0 Hz
100
200
300
400
500
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 1.2x10
INTEGRAL AMPLITUDE: 44
SPINNING RATE (RPS): 50
MANUAL
SWEEP TIME (SEC): 50 25
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: .85
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT: CDCl3
REMARKS: #6
DATE: 8/12
OPERATOR: KUO
60 MHz NMR
SPECTRUM NO.

b) 26



(5) VII

To a 500 mL Erlenmeyer flask, 4.1 mL (0.063 mole) CD_3COOD (Aldrich) was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl chloride was added. The solution was chilled in ice and 9.8 g (0.063 mole) of compound (5) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium hydrogen sulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (82%), purity (93%), d-content (98%), b.p. 226-227°C (lit.[29] 223-224°C).

2) Identification:

a) IR: as shown in Figure 29.

b) NMR: as shown in Figure 30.

Figure 29; IR spectrum of compound VII

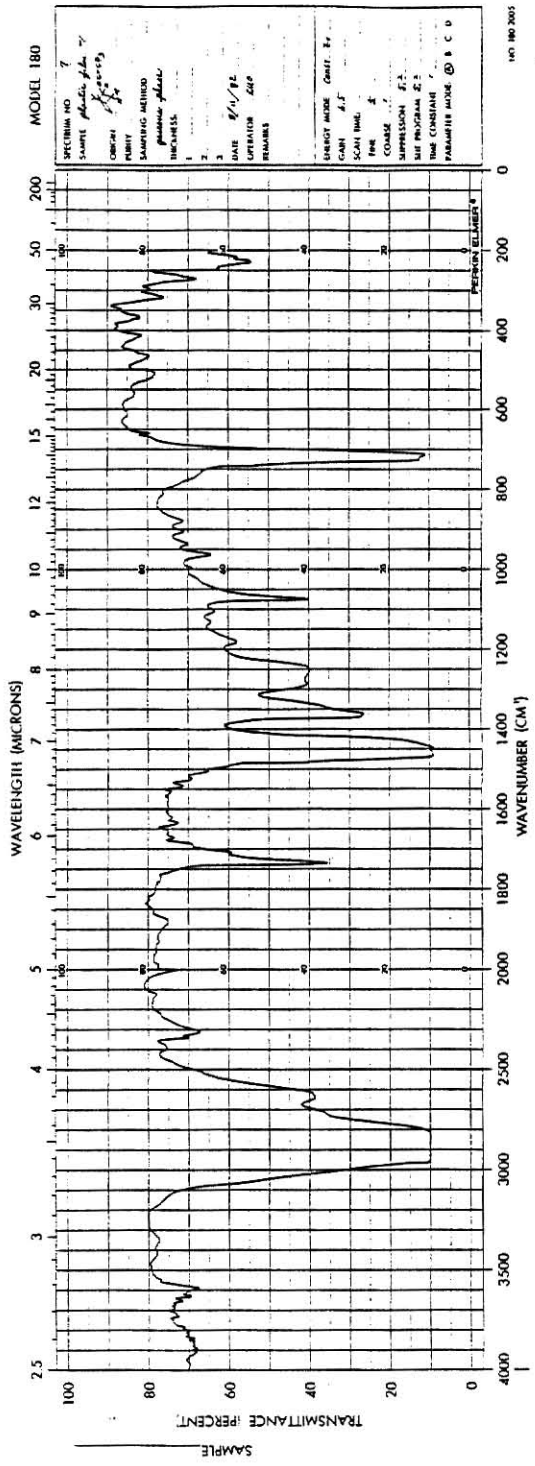
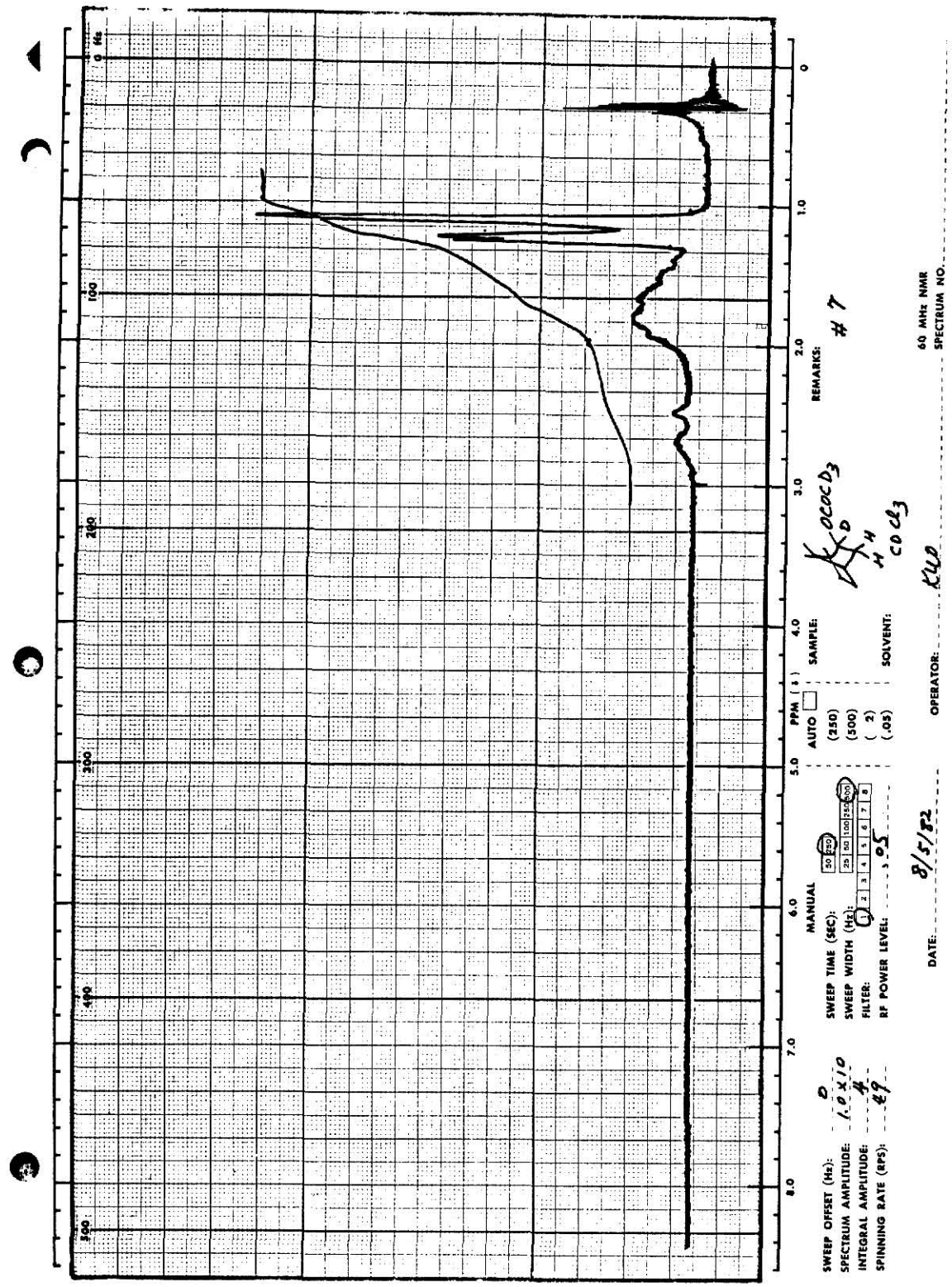

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE
PERKIN ELMER

Figure 30; NMR spectrum of compound VII


SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 1.0 x 10
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 49
MANUAL
SWEEP TIME (SEC):
SWEEP WIDTH (Hz):
FILTER:
RF POWER LEVEL: .05
PPM (δ)
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT:
DATE: 8/5/82
OPERATOR: KLD
REMARKS: # 7
60 MHz NMR
SPECTRUM NO.

^{1}H-NMR($CDCl_3$) δ 0.8 ppm(s,3H), 1.0 ppm(d,6H), 1.0-2.6 ppm(m,7H).

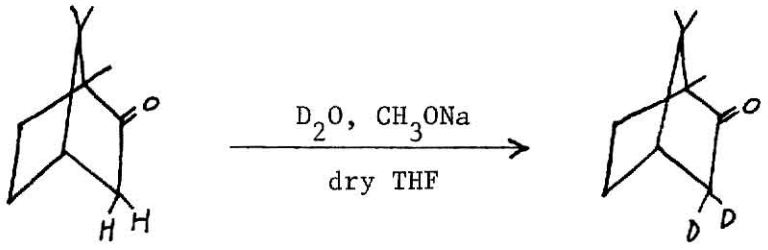
c) GC: The retention time was 9 min. 19 sec., and matched the hydrogenated standard.

h. Compound VIII:

Bicyclo [2,2,1] heptane-2-ol-2,3,3-d_3-trimethyl-acetate-d_3

1) Synthesis

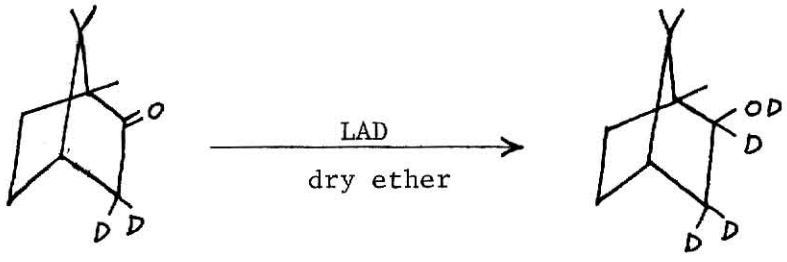
a) 27



(1) (3)

Procedure same as b, 1), a), on page 19.

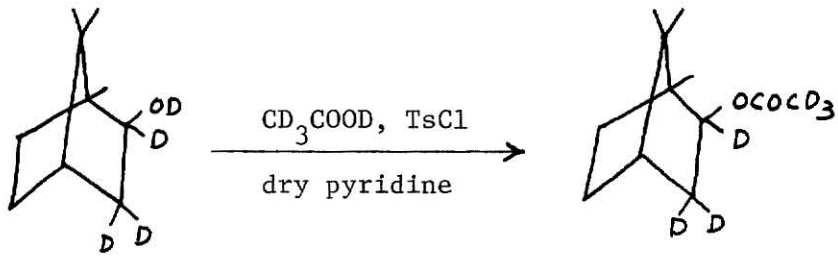
b) 25



(3) (6)

Procedure same as e, 1), b), on page 42.

c) 26



(6) VIII

To a 500 mL Erlenmeyer flask, 4.1 mL (0.063 mole) CD_3COOD (Aldrich) was dissolved in 100 mL of dry pyridine and 24.0 g (0.126 mole) toluene sulfonyl cholride was added. The solution was chilled in ice and 10.0 g (0.063 mole) of compound (6) was added. The solution was kept cold for about one hour and then poured into 350 mL of an ice and water mixture. The aqueous solution was extracted with two 100 mL portions of chloroform. The chloroform extract was then washed with eight 35 mL portions of 5% aqueous potassium hydrogen sulfate and once with 35 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The residue was distilled in vacuum and the fraction at 50-52°C/1 mmHg was collected to give the final product: yield (80%), purity (91%), d-content (95%), b.p. 226-227°C (lit.[29] 223-224°C).

2) Identification:

a) IR: as shown in Figure 31.

b) NMR: as shown in Figure 32.

^{1}H-NMR($CDCl_3$) δ 0.85 ppm(s,3H), 0.89 ppm(s,3H), 0.99 ppm(s,3H), 1.1-2.4 ppm(m,5H).

c) GC: The retention time was 9 min. 14 sec., and matched the hydrogenated standard.

B. Bioassay Tests

Adult male American cockroaches, Periplaneta americana (Linnaeus), were used as the test insects and three different bioassay choice tests were performed. Twenty replicates of five insects each were used for each bioassay with each of the eight compounds. In addition, a bioassay was devised to attempt to determine if radiation alone was responsible for the insect behavior.

1. Description of Periplaneta americana (Linnaeus)

From commercial trading, the American cockroach now exists in the lower latitudes and in the majority of temperate regions of the world. Its presence is hardest felt in tropical and subtropical areas[31].

Comparatively, it is a large cockroach (28-44 mm. long). It generally is of a red-brown color and is pale yellow around the edge of the pronotum. Its distinctive pronotal pattern and terminal abdominal segments make it easily distinguishable from other Periplaneta[31].

Three gradual metamorphosis of life stages characterize the cockroach: egg, nymph, and adult. The adult female, after maturation produces a small, bean-like egg capsule, or oothecae, which is usually

Figure 31; IR spectrum of compound VIII

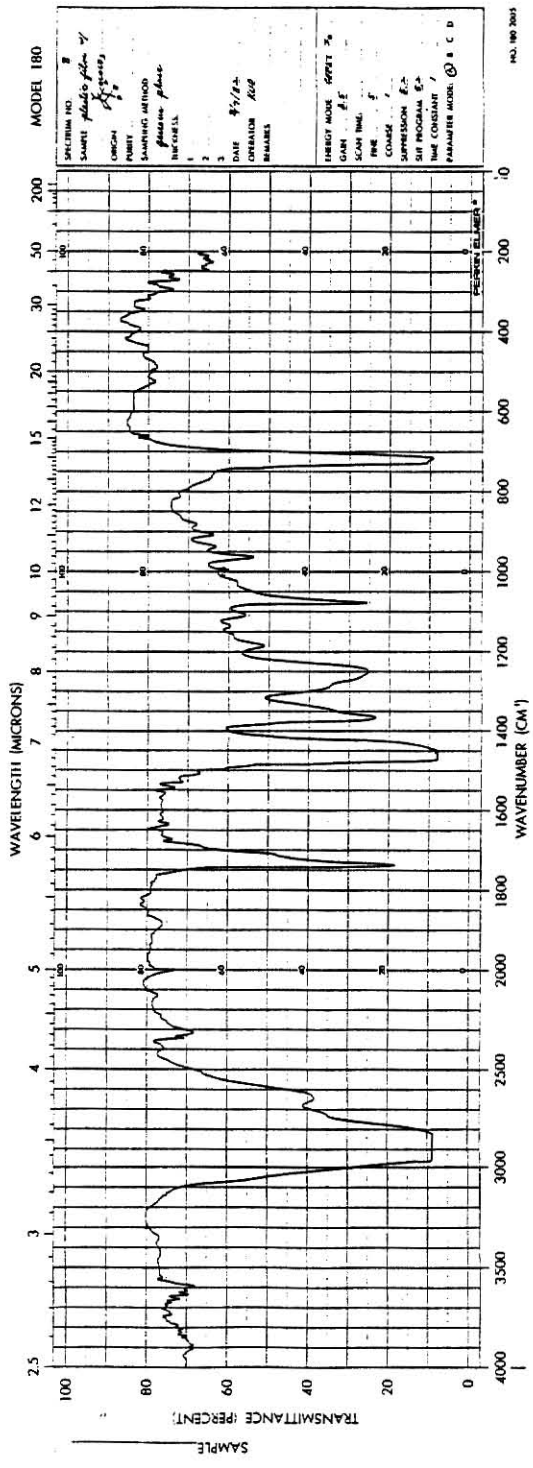
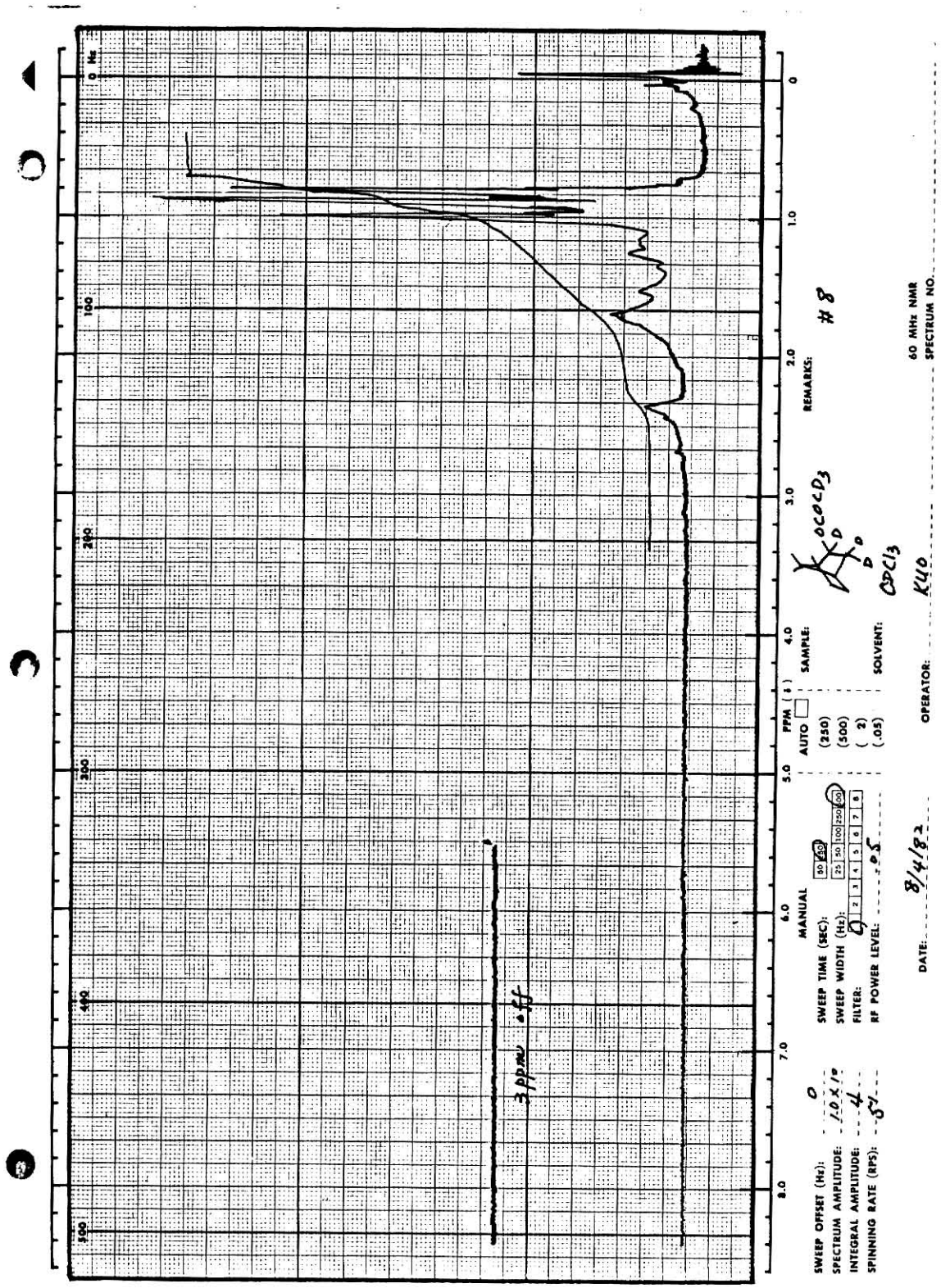

MODEL 180
WAVELENGTH (MICRONS)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (PERCENT)
SAMPLE
PERKIN ELMER

Figure 32; NMR spectrum of compound VIII


0 Hz
500
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
3ppm off
SWEEP OFFSET (Hz): 0
SPECTRUM AMPLITUDE: 10x10
INTEGRAL AMPLITUDE: 4
SPINNING RATE (RPS): 37
MANUAL
SWEEP TIME (SEC): 50 250
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 2 3 4 5 6 7 8
RF POWER LEVEL: .5
AUTO
(250)
(500)
(2)
(.05)
SAMPLE:
SOLVENT: CDCl3
REMARKS: # 8
DATE: 8/4/82
OPERATOR: KUO
60 MHz NMR
SPECTRUM NO.

dropped within a day after its formation. These capsules are usually dropped in an area with an available food source and miscellaneous debris that is used to cover them. After hatching, a nymph emerges which closely resembles its parent, but it is smaller and does not have fully developed wings. Several periods of molting precede maturation.

Distinguishing the sex of the early instars is possible by noting the posterior margin of the ninth sternite. While the female has a sharp median notch, the male is smooth and only slightly indented (Figure 33)[31].

For the adult American cockroach, the female has a ventral keel with a slit running along the tip of the abdomen. While both sexes have a pair of well-developed cerci, the adult male has only a pair of ventral styles on the last abdominal sternite. The male has fully developed wings which extend past the tip of the abdomen, but on the female they just overlap the abdomen (Figure 34). When needed, these wings can propel the cockroach for short distances, even though these flights occur rarely and are sluggish in appearance [31].

Because the cockroach is very sensitive to changes in nutrition and temperature, great differences are possible between different studies, each conducted with unique conditions and in varied geographical locations. Earlier research concluded that the time required for the development from egg to adult required four to five years[32]. However, this likely would only occur under very adverse conditions. Later research reveals that actual life expectancy may vary from as little as 630 days to as high as 1,243 days, with a controlled environment simulating a building heated at 29°C and observing the cockroach from the egg stage to its natural death[31].

Figure 33; Ventral view of the terminal abdominal sternites of second instar nymphs of P. americana (Courtesy-Cornwell[31])

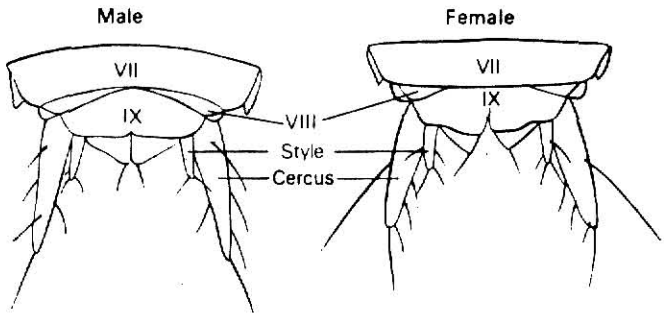
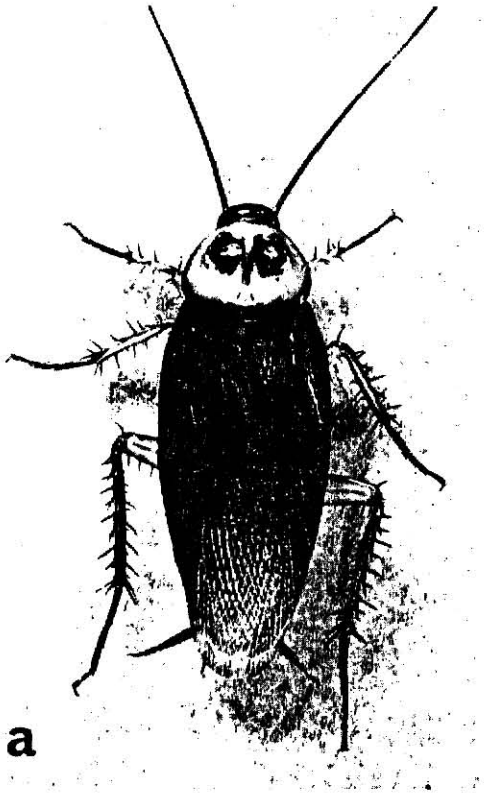
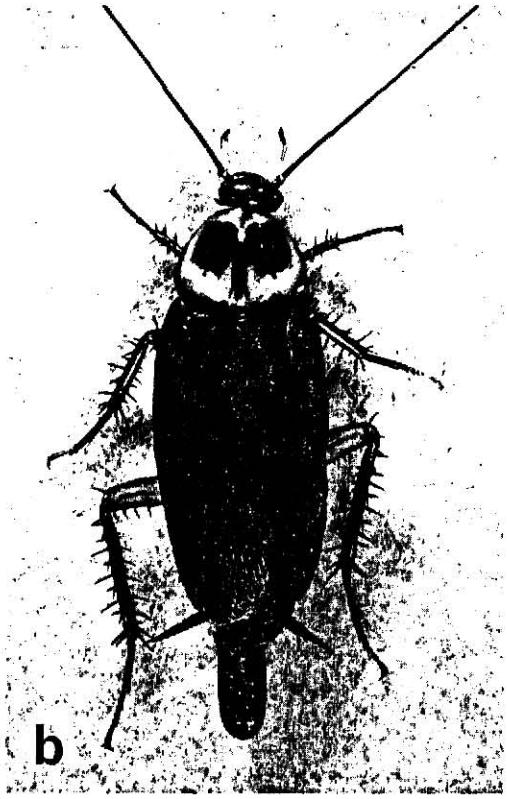

Male
Female
VII
IX
VIII
Style
Cercus
VII
IX

Figure 34; Adult P. americana, above (a) male; below (b) female with ootheca (x2) (Courtesy-Cornwell[31])


a


b

2. Insect Rearing and Handling

The cockroaches used in the tests were obtained from a laboratory colony. The adult males were isolated from the females for more than 6 weeks before being subjected to the bioassay. They were housed in an open, greased, plastic laundry box, and reared in a room with a temperature of 25±1°C. The relative humidity was not controlled. The photo period was a 10 hr day followed by a 14 hr night. The container was equipped with dog food and water soaked into absorbent cotton in a Petri-dish. The bioassay was performed in the night cycle under a dimly lighted condition in the rearing room.

3. The Bioassay Methods

a. Bay olfactometer test

The Bay olfactometer shown in Figure 35 was used in this part of the test. Five cockroaches were placed in the chamber at the end of the olfactometer, which separates into two smaller tubes to allow the cockroaches a choice between untreated air and the chemically altered odor. An air pump forced the air through the system at approximately 200 mL per minute. Then, every 30 minutes for two hours, the response of the cockroaches was recorded.

b. Y-tube test

In this experiment (the equipment is shown in Figure 36) the natural drift of odorous air was the only impetus to attract the cockroach, as one chamber contained a test compound, while the other

Figure 35; Bay olfactometer

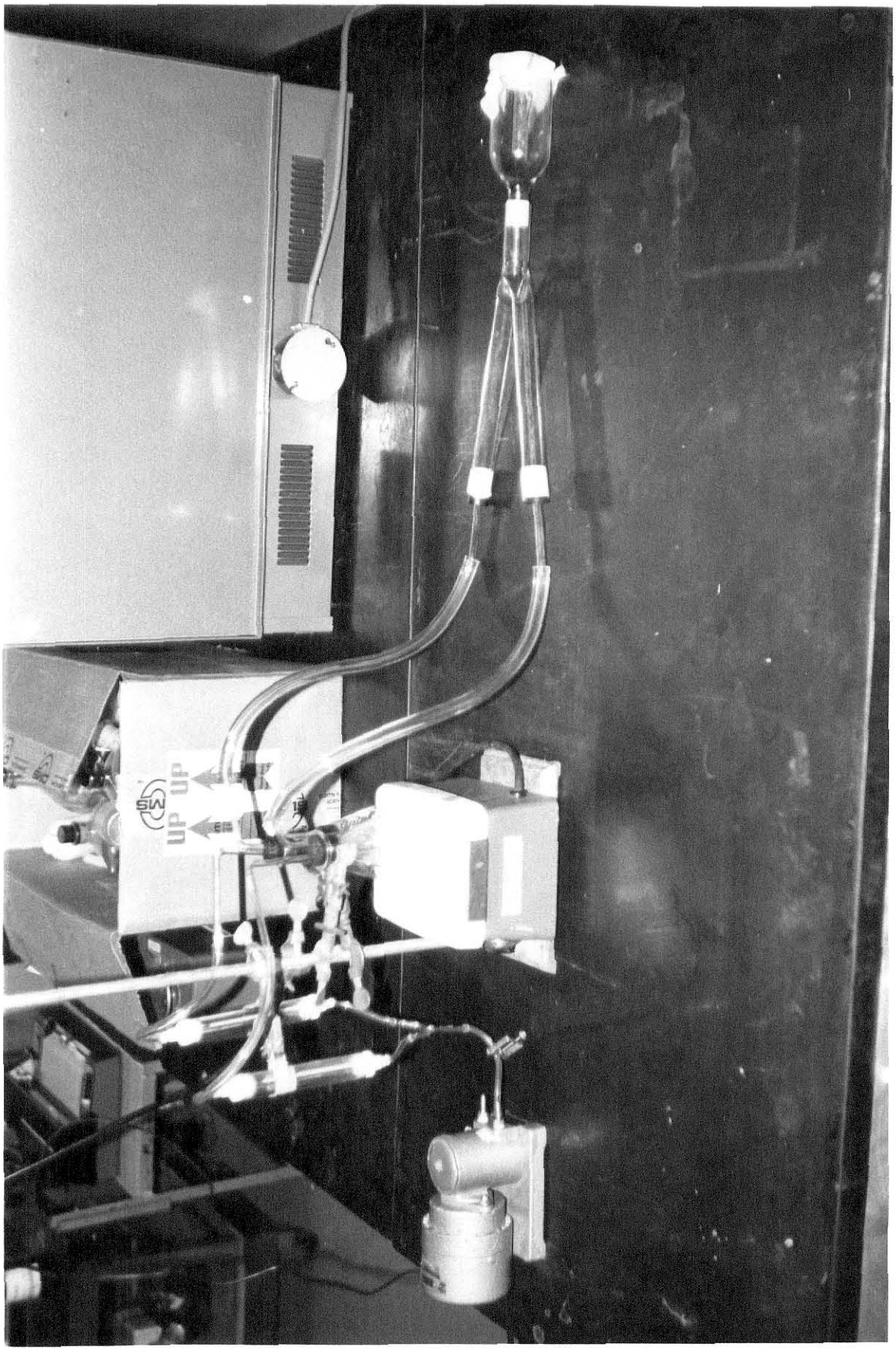
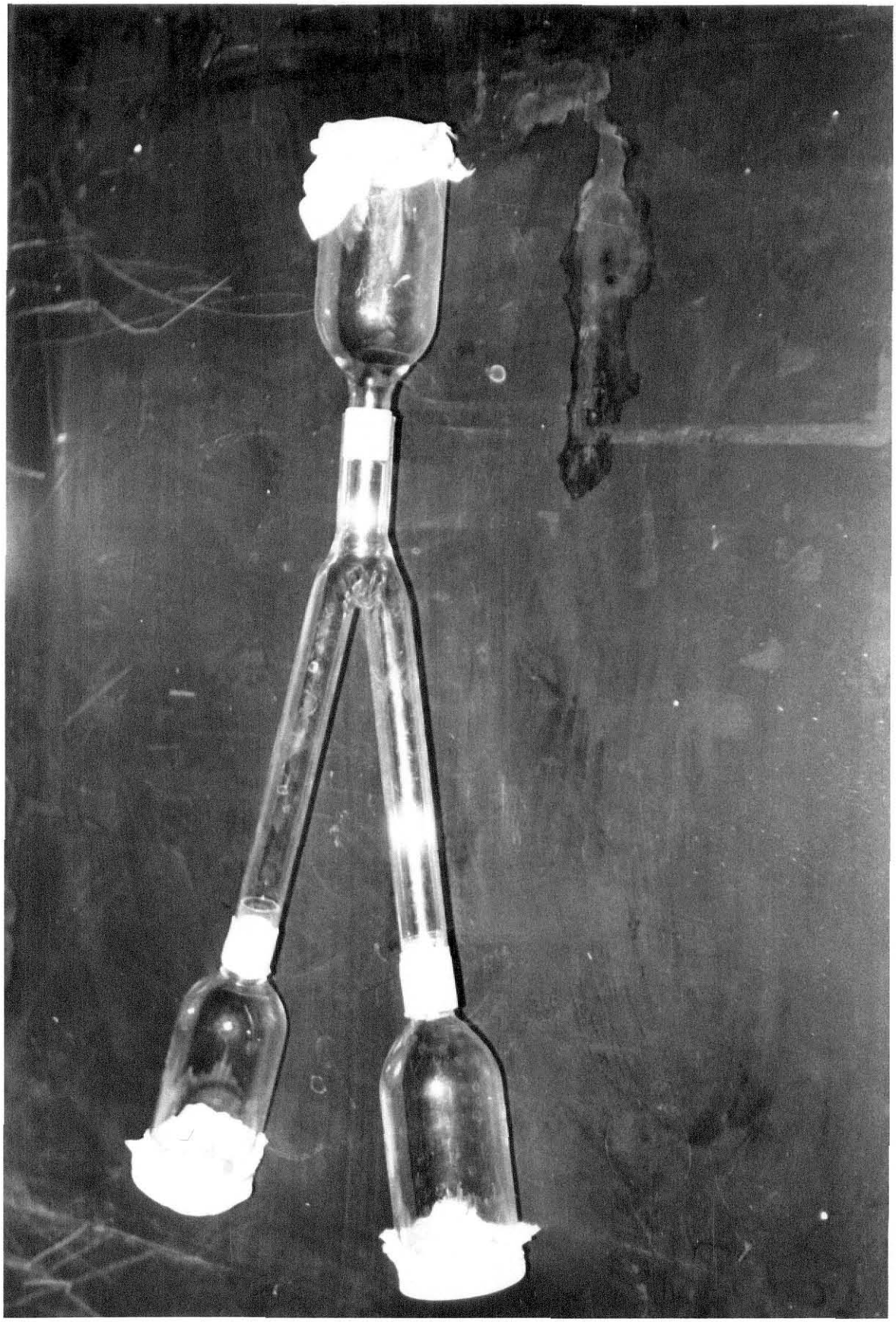

UP
UP

Figure 36; Apparatus for the Y-tube choice test



was empty. The only difference of these two tests was the absence of the air pump.

c. Simple choice test

The apparatus is shown in Figure 37. Five males were placed in a 37 x 27 x 16 cm plastic container. The cockroaches were offered a choice of two cups in the container, one of which contained a test compound. The type of cups used were 1 pint polyethylene cups obtained from a local store. Two shallow V-openings were cut into the open end of all of the cups so that the cockroaches could enter easily when the cups were inverted in the container. The tests were conducted for a period of two hours and a count of the cockroaches in each cup was made every 30 minutes. After each test, the cockroaches were removed from the cups and the position of the cups was also reversed.

d. Cylindrical chamber test

It was suggested that insect antennae could receive and respond to some specific patterns of frequencies emitted by chemicals without direct contact with the chemical itself[33,34,35]. This part of the experiment was designed to test this proposal. A cylinder built out of polyethylene with dimension of 47 cm x 17 cm ID is shown in Figures 38 and 39. This cylinder was divided into three sections, with a volume ratio of 1:5:1.

To rule out the possibility of the diffusion of the compound into the middle section through a hole in the plastic, it was assumed that any holes in the plastic would be random so a double layer was

Figure 37; Apparatus for a simple choice test

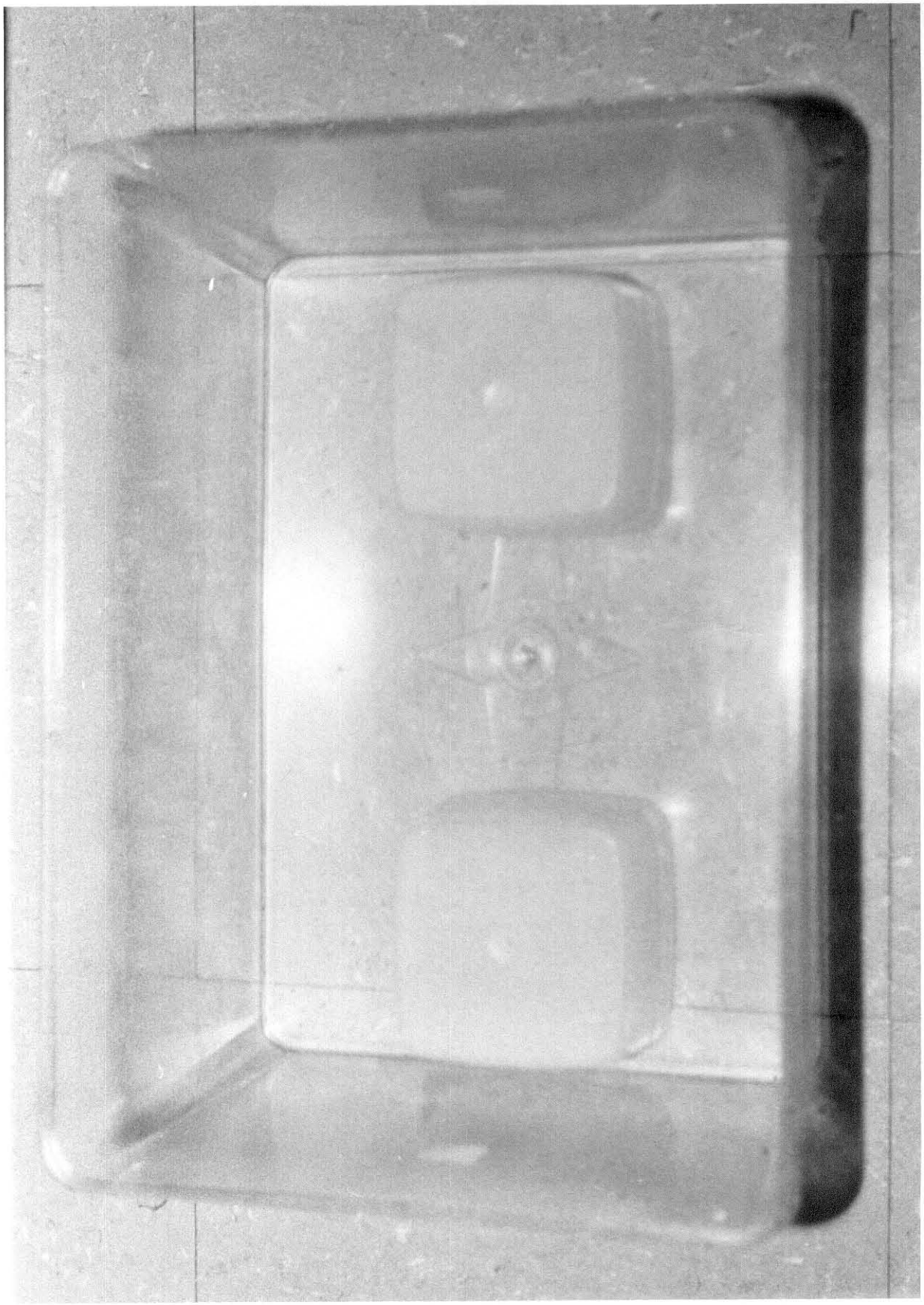


Figure 38; Side-view of a cylindrical chamber

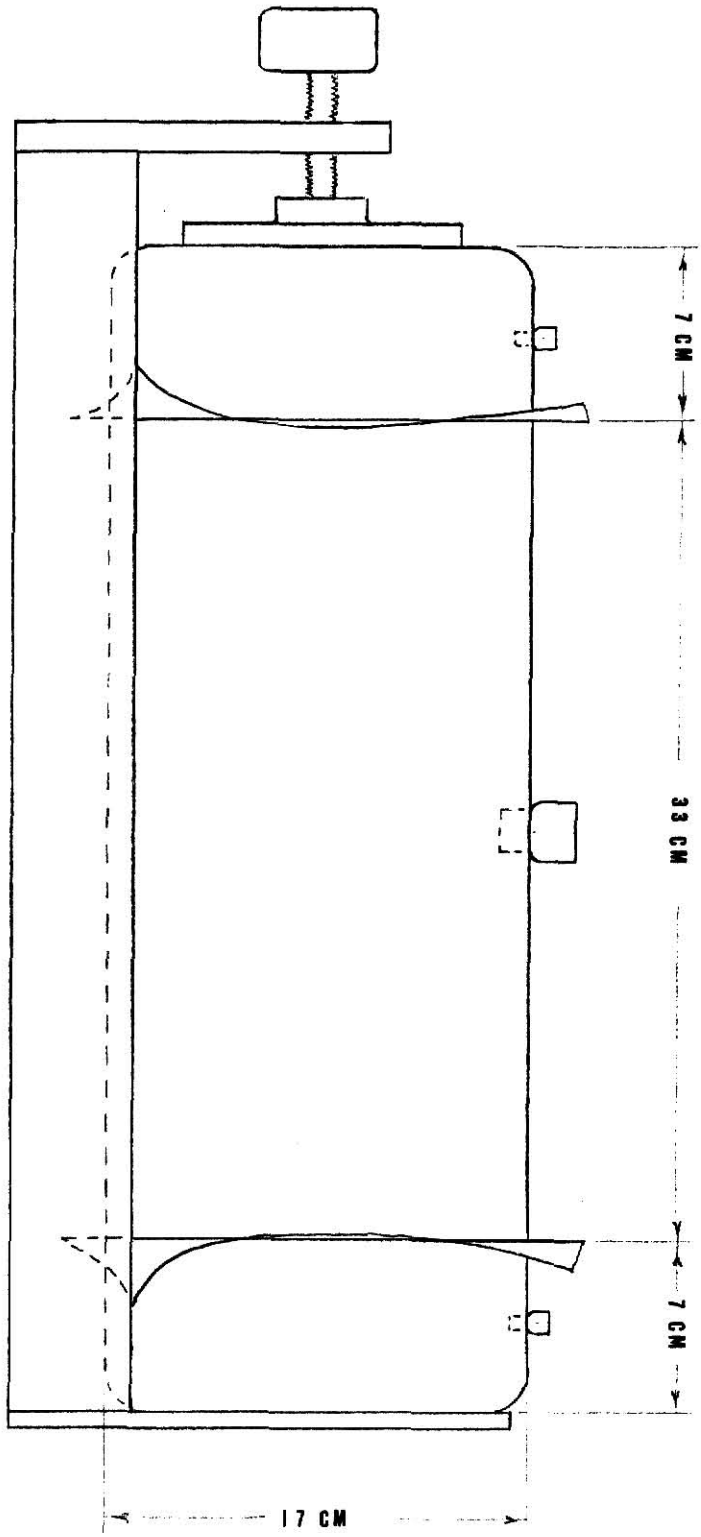
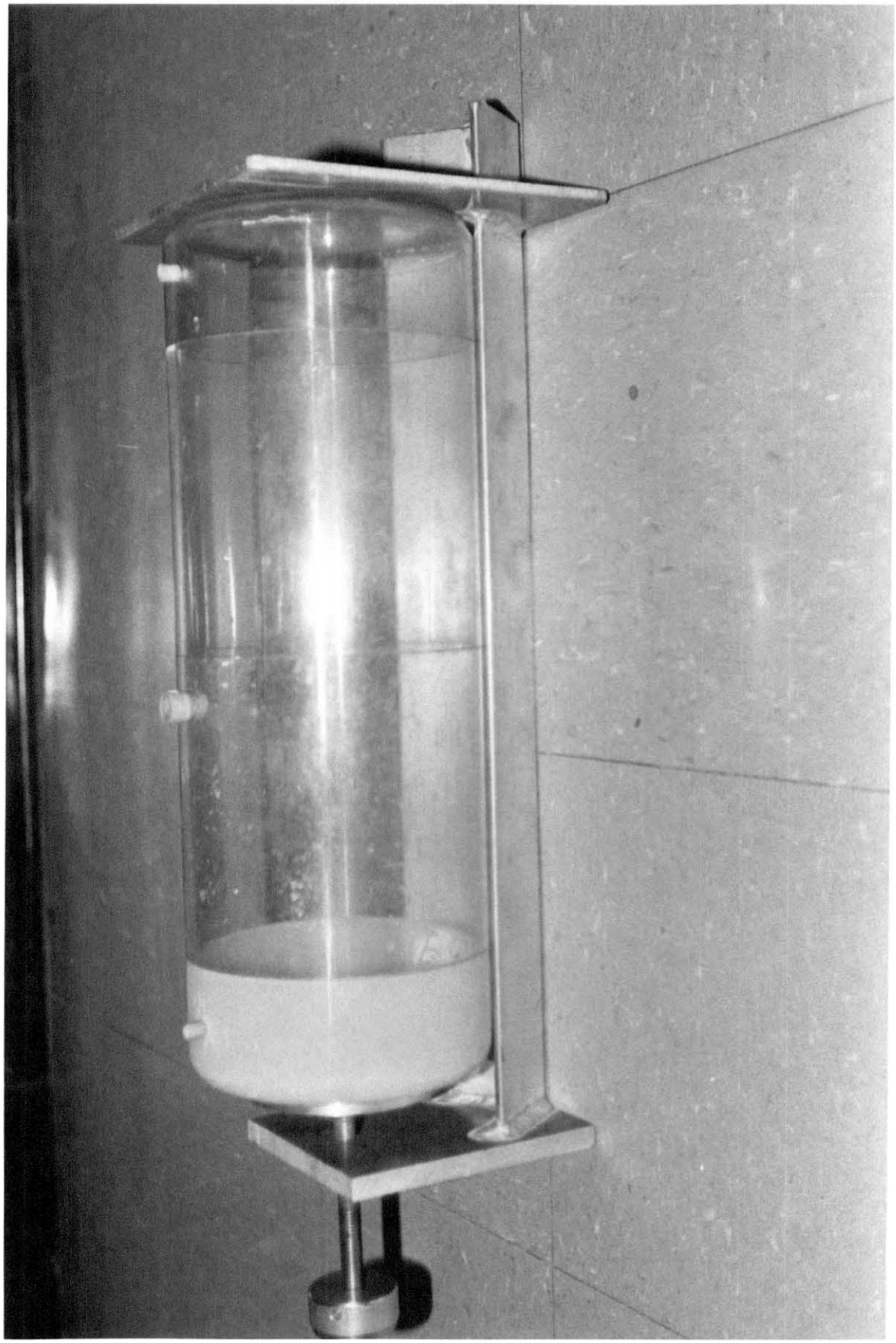

7 CM
33 CM
7 CM
17 CM

Figure 39; Apparatus for the cylindrical chamber test



used. The sections were sandwiched with doubly-layered polyethylene film (0.1 mm thick), then, tightened with a vise.

Five cockroaches were placed in the middle section, while one of the side sections contained 1.0 mL of the chemical compound. The tests were conducted for a duration of one hour and the number of cockroaches on each side was recorded every 15 minutes.

RESULTS AND DISCUSSION

Due to the concern of an impurity content which may affect the biological test, the undeuterated compound was made by the same synthetic procedure.

In order to find an optimal amount of dosage, the male cockroaches were tested with different dose levels of bornyl acetate. The relationship between the dosage and the cockroach response is shown in Figure 40. The percentage response was proportional to the log of the dosage, which agreed with the earlier work of D. R. A. Wharton, et al. [36].

The highest dose level employed was 1.0 μL/test. Because of the confined test area, doses which were higher than this were not practical. In the following bioassay tests the dosage used was 1.0 μL/test. The compound was taken up with a micro syringe, transfered to a filter paper (1 x 1 cm), and placed on a glass plate (2.5 x 2.5 cm).

1. Bay olfactometer test

   During this test, the cockroaches clearly responded but not as well as hoped for. However, the response was much better than the blank, as shown in Table 1. The insects were essentially docile throughout the experiment, possibly an effect of the air flow produced by the olfactometer.

2. Y-tube choice test

   It was believed that the air flow in the Bay olfactometer might influence the insects' response (i.e. - having to travel "upwind"). Therefore the pump was turned off so the only flow rate was that of diffusion. The insects' response was noticeably better, as shown in Table 2.

Figure 40; Relationship between the dosage and the cockroach response

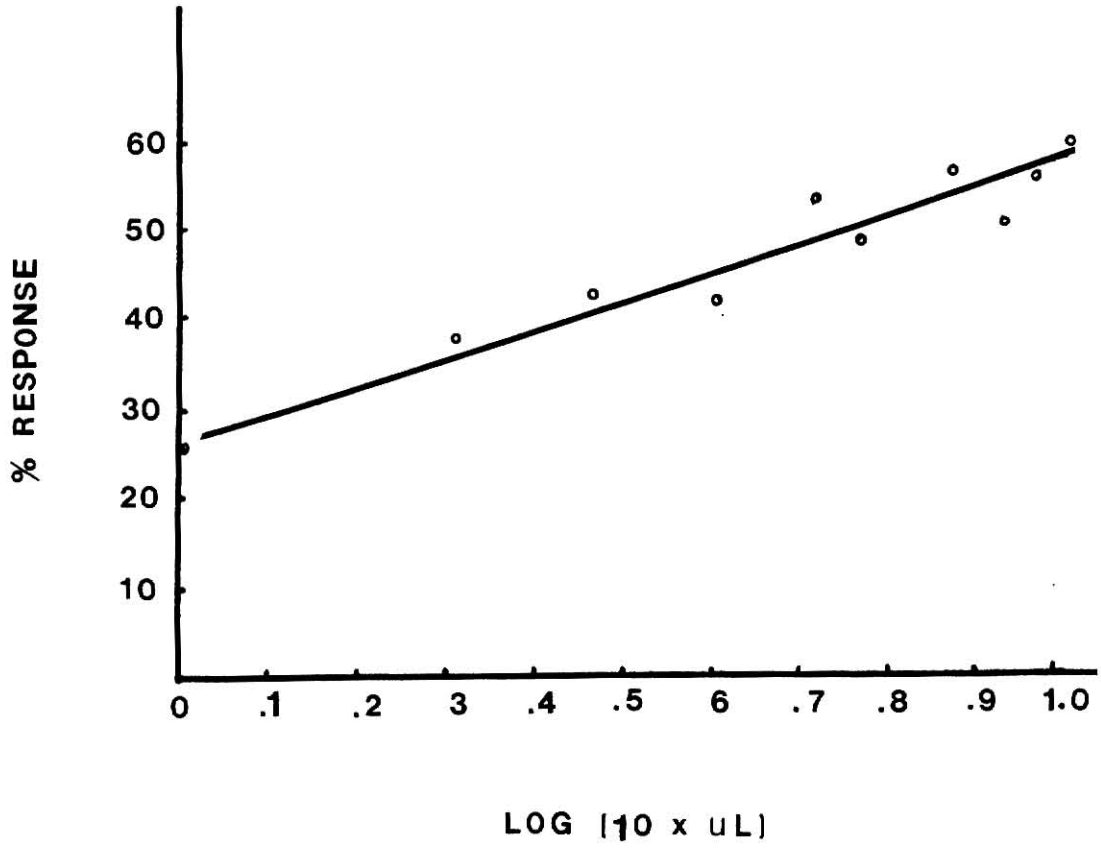

% RESPONSE
60
50
40
30
20
10
0
.1
.2
3
.4
.5
6
.7
.8
.9
1.0
LOG [10 x uL]

Table 1; Results of the Bay olfactometer test

Compound	Sample size*	Response	Blank	Net response
1	100	38	7	31
2	100	33	3	30
3	100	34	5	29
4	100	39	8	31
5	100	32	4	28
6	100	32	3	29
7	100	33	5	28
8	100	30	3	27

* All sample sizes were 20 replicates of 5 each

Table 2; Results of the Y-tube choice test

Compound	Sample size	Response	Blank	Net response
1	100	62	6	56
2	100	64	10	54
3	100	61	8	53
4	100	67	11	56
5	100	63	14	49
6	100	62	9	53
7	100	64	11	53
8	100	55	8	47

3. Simple choice test

The results obtained are shown in Table 3. This apparatus also produced better responses than the Bay olfactometer.

In order to determine if there were significant differences from the above results, these data were subjected to a Statistical Analysis System (SAS): a General Linear Models (GLM) and Duncan's multiple range test for the different variables. Computer programs for doing this are attached as appendixes. The statistical analysis shows:

(1) These three different methods are significantly different at $\alpha = .05$ level.

(2) Based on the response, the Y-tube choice and the simple choice gave better results than the Bay olfactometer, but the first two are equally good, as shown in Table 4.

(3) Based on the net response, the Y-tube choice induced more insects to respond, as shown in Table 5.

(4) When compared to the blank, it can be concluded that, even though the results of the simple choice test were similar to that of the Y-tube choice, this test was not as objective in its design, as shown in Table 6.

(5) The Duncan's multiple range test shows that these eight compounds have significant effects at $\alpha = .05$ level, as shown in Table 7. As the table illustrates, the order of attraction is as follows: compound 1 > 4 > 2 > 3 > 6 > 7 > 5 > 8. When examining the functional groups, the order of attraction is as follows: no D > $-CD_3$ > $-CD_2$ > $-CD$ > $(-CD_3)+(-CD_2)$ > $(-CD_3)+(-CD)$ > $(-CD_2)+(-CD)$ > $(-CD_3)+(-CD_2)+(-CD)$.

Table 3; Results of the simple choice test

Compound	Sample size	Response	Blank	Net response
1	100	67	15	52
2	100	59	11	48
3	100	68	20	48
4	100	65	14	51
5	100	56	12	44
6	100	59	11	48
7	100	65	19	46
8	100	57	16	41

Table 4; Comparison of bioassay methods based on the response

Method	Mean*	Grouping**
Y-tube	62.3	A
Simple choice	62.0	A
Bay olfac.	33.9	B

* Mean is the average response in each method.

** Means with the same letter are not significantly different at $\alpha = .05$ level.

Table 5; Comparison of bioassay methods based on the net response

Method	Mean*	Grouping**
Y-tube	52.6	A
Simple choice	47.3	B
Bay olfac.	29.1	C

* Mean is the average net response in each method.

** Means with the same letter are not significantly different at $\alpha = .05$ level.

Table 6; Comparison of bioassay methods based on the blank

Method	Mean*	Grouping**
Simple choice	14.8	A
Y-tube	9.6	B

* Mean is the average value for blank in each method.

** Means with the same letter are not significantly different at $\alpha = .05$ level.

Table 7; Duncan's multiple range test for the effectiveness of the eight synthetic compounds

Compound	Mean*	Grouping**
1	46.3	a
2	44.0	b c
3	43.3	c
4	46.0	a b
5	40.0	d e
6	43.3	c
7	42.3	c d
8	38.3	e

* Mean is the average net response of each compound for these three methods.

** Means with the same letter are not significantly different at $\alpha = .05$ level.

Since the frequency range from 600 cm^{-1} to 200 cm^{-1} is believed to be responsible for this attribute, the expanded spectra in this range were obtained, as shown in Figures 41-47.

By examining the Far IR spectra and comparing the compounds, the possible reason for that result is shown in Table 8, which could explain the effect of the order of attraction.

4. Cylindrical chamber test

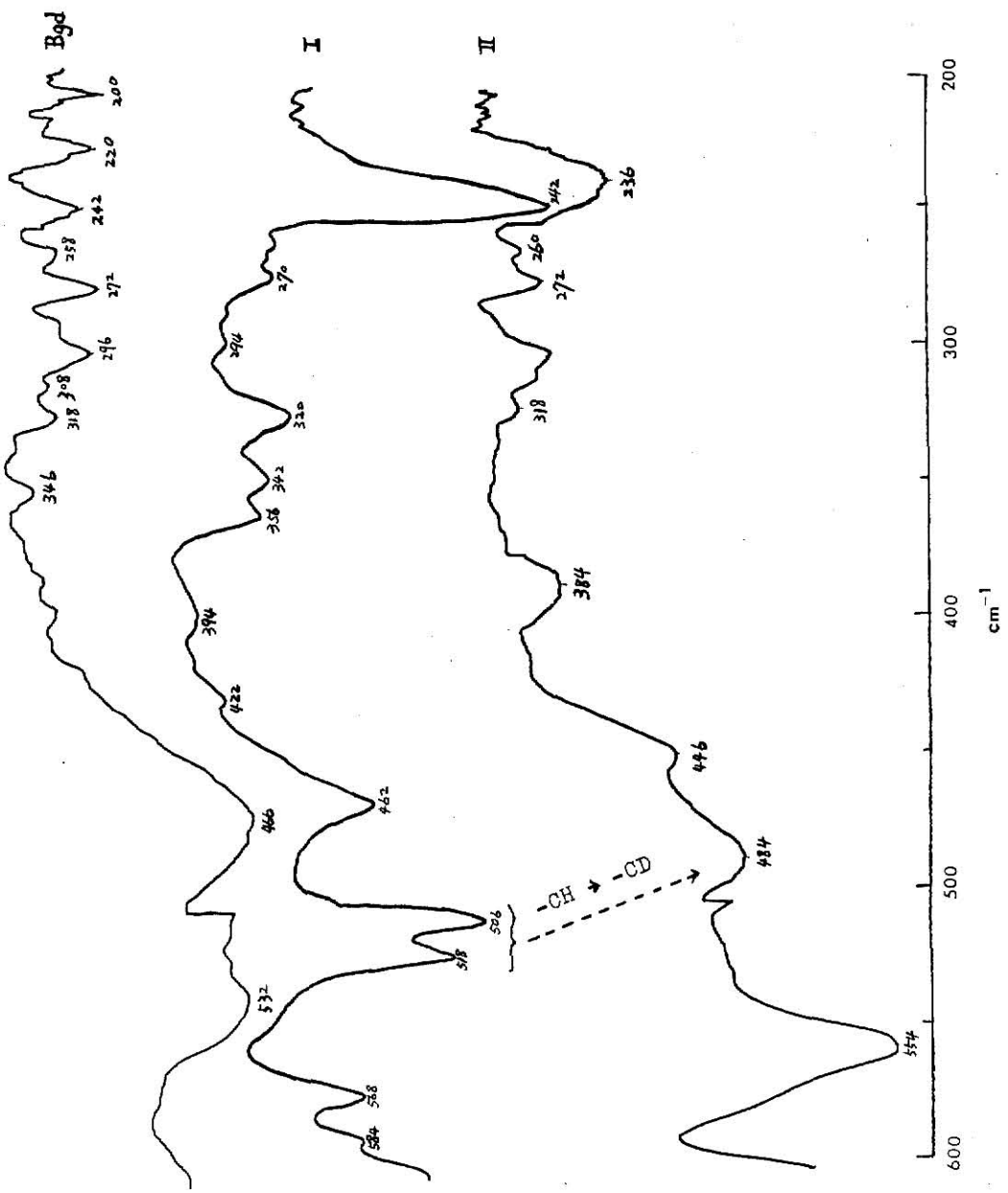
The previous results indicated that by shifting the frequency pattern that the insects responded less. Is it then necessary for the molecule to actually come in contact with the receptor site or will just radiation of the proper frequency suffice to induce a response?

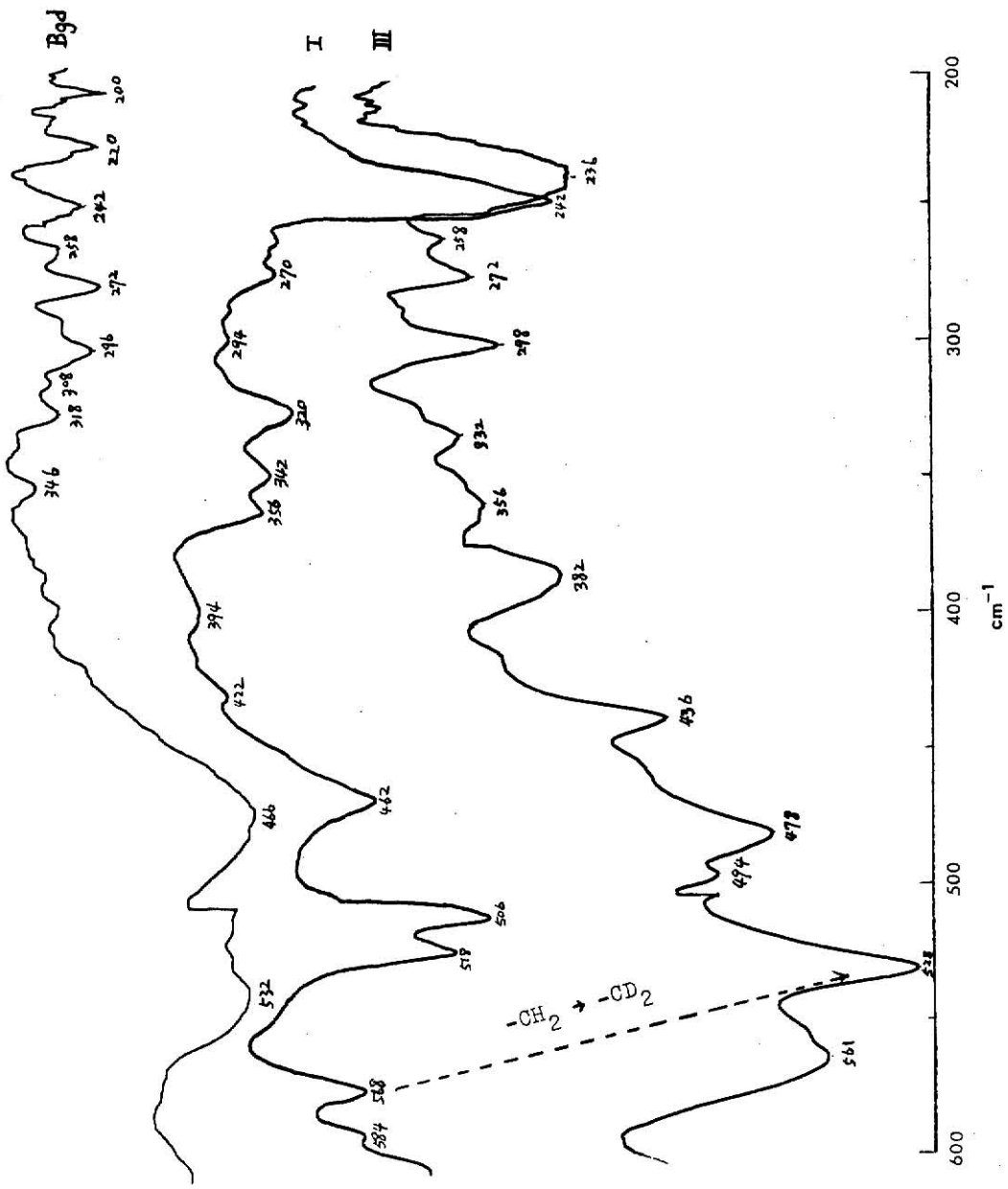
To test this, a three chambered apparatus was prepared (Figures 38 and 39) in which a test compound was placed on one side of a plastic barrier transparent to as much of the radiation as possible but not permitting the molecules to pass through. The insects were placed on the opposite side of the barrier., The third chamber served as the control. The system was tested at room temperature to duplicate natural environmental conditions.

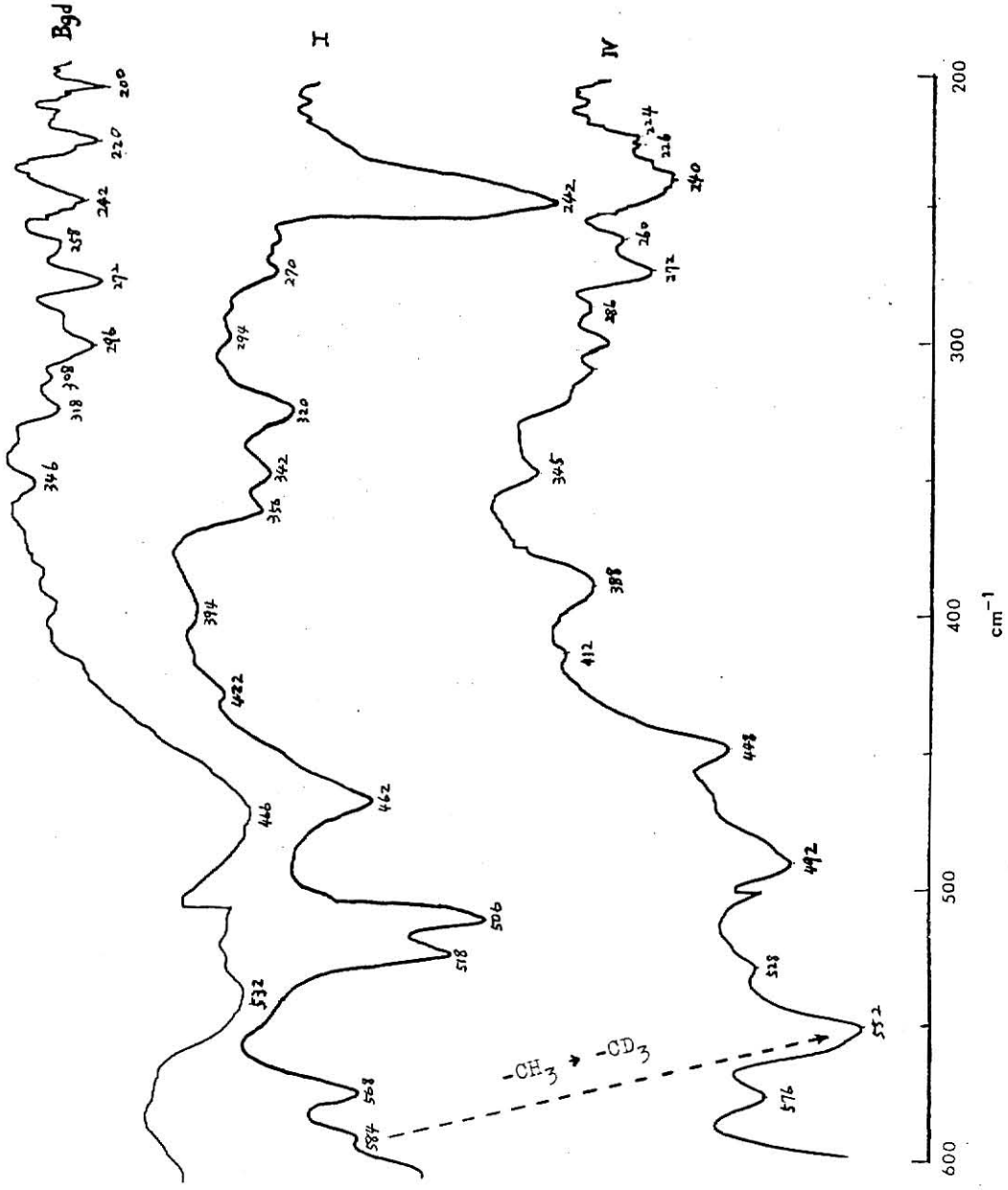
To examine the possibility of the diffusion of the compound into the middle section through a hole, the sections were sandwiched with doubly-layered polyethylene films. The diffusion of the test compound through the film was measured with a GC. The diffusion profile as a function of time is shown on Figure 48.

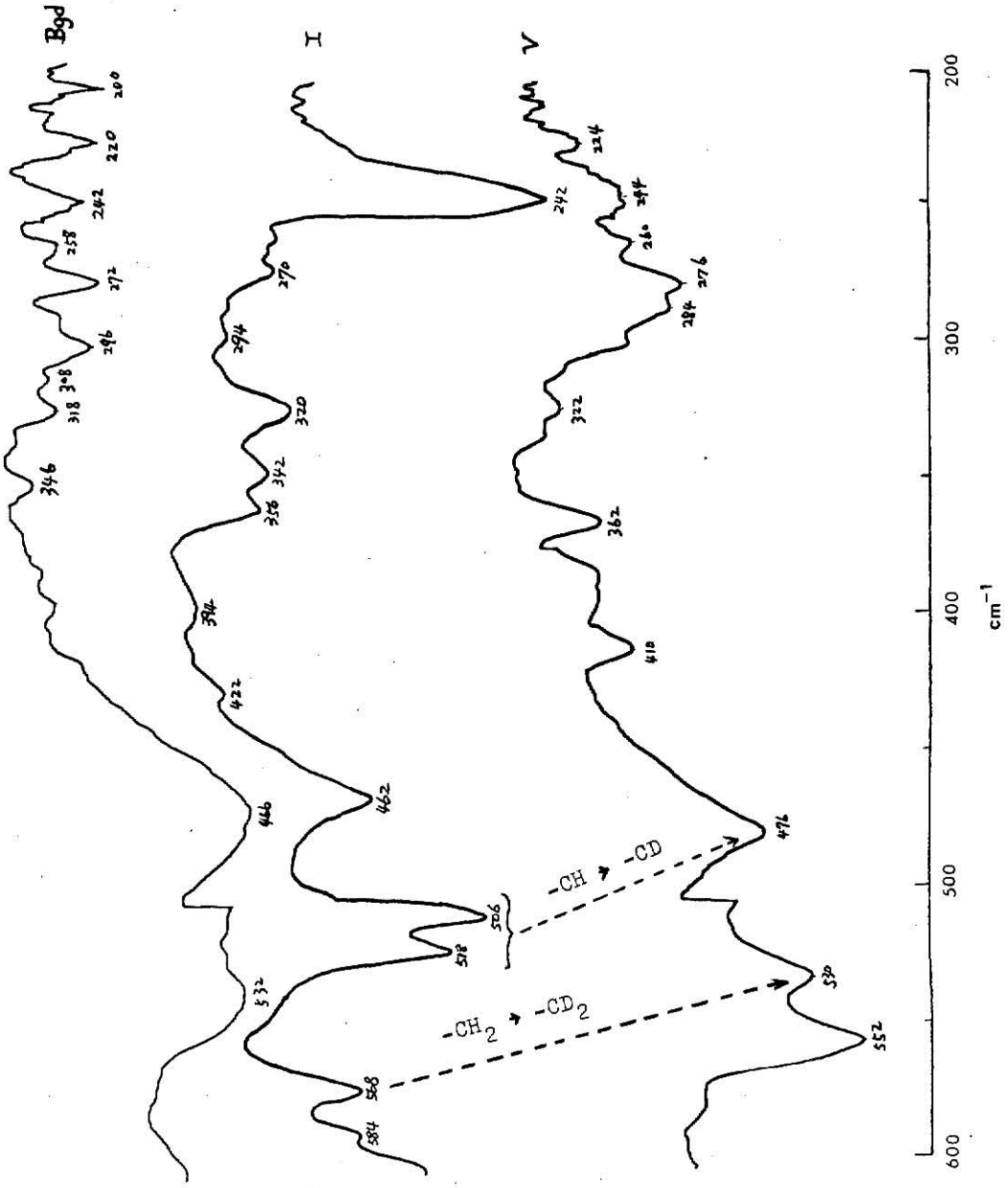
The diffusion was not detectable at a level of 5 ppm for the first five minutes, after that point, detectable diffusion occured. As a consequence of the diffusion profile, this part of the experiment was conducted for a period of one hour, and the results were divided into two

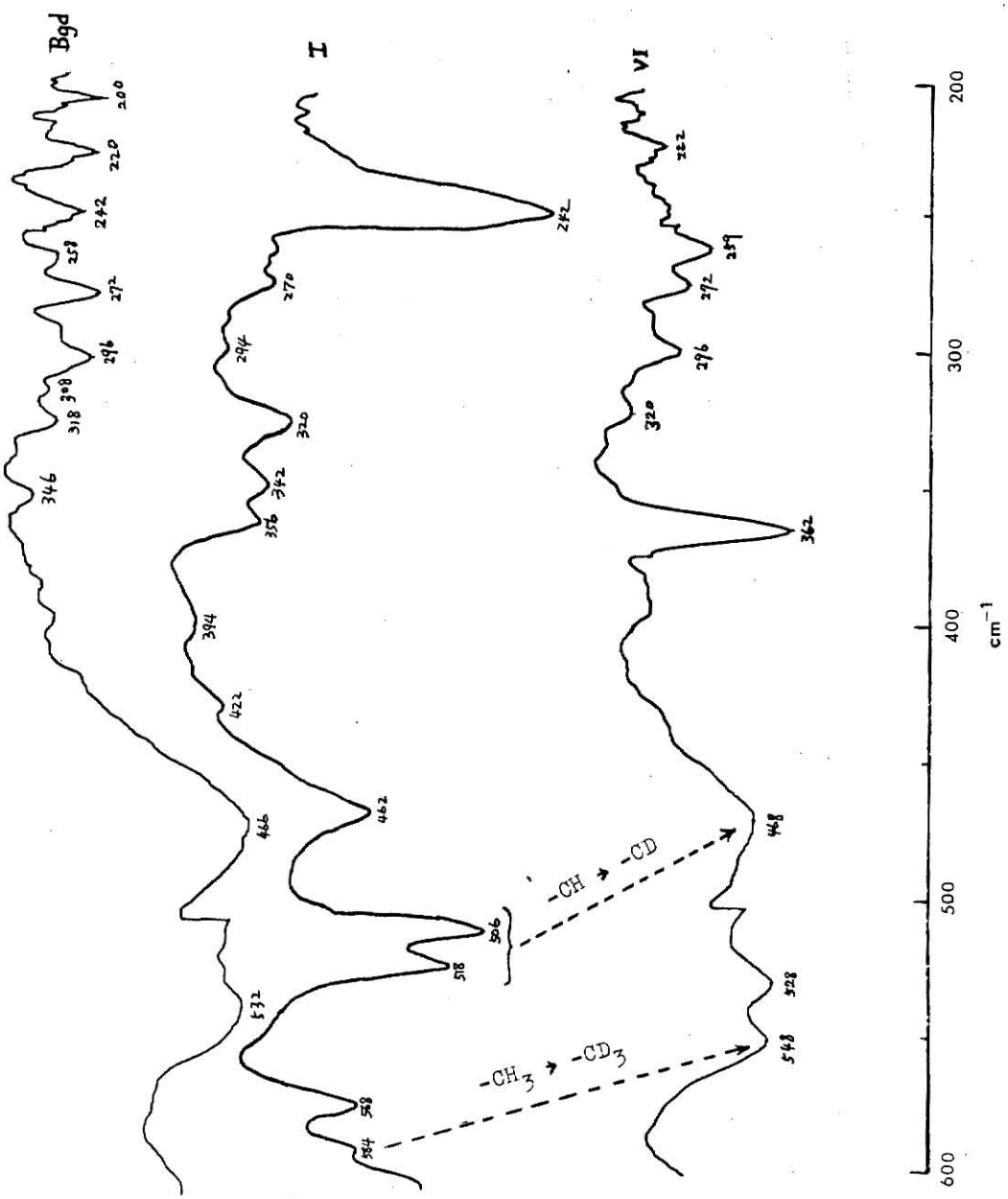
Figures 41-47; Comparisons of the Far IR spectra of compound II-VIII with compound I

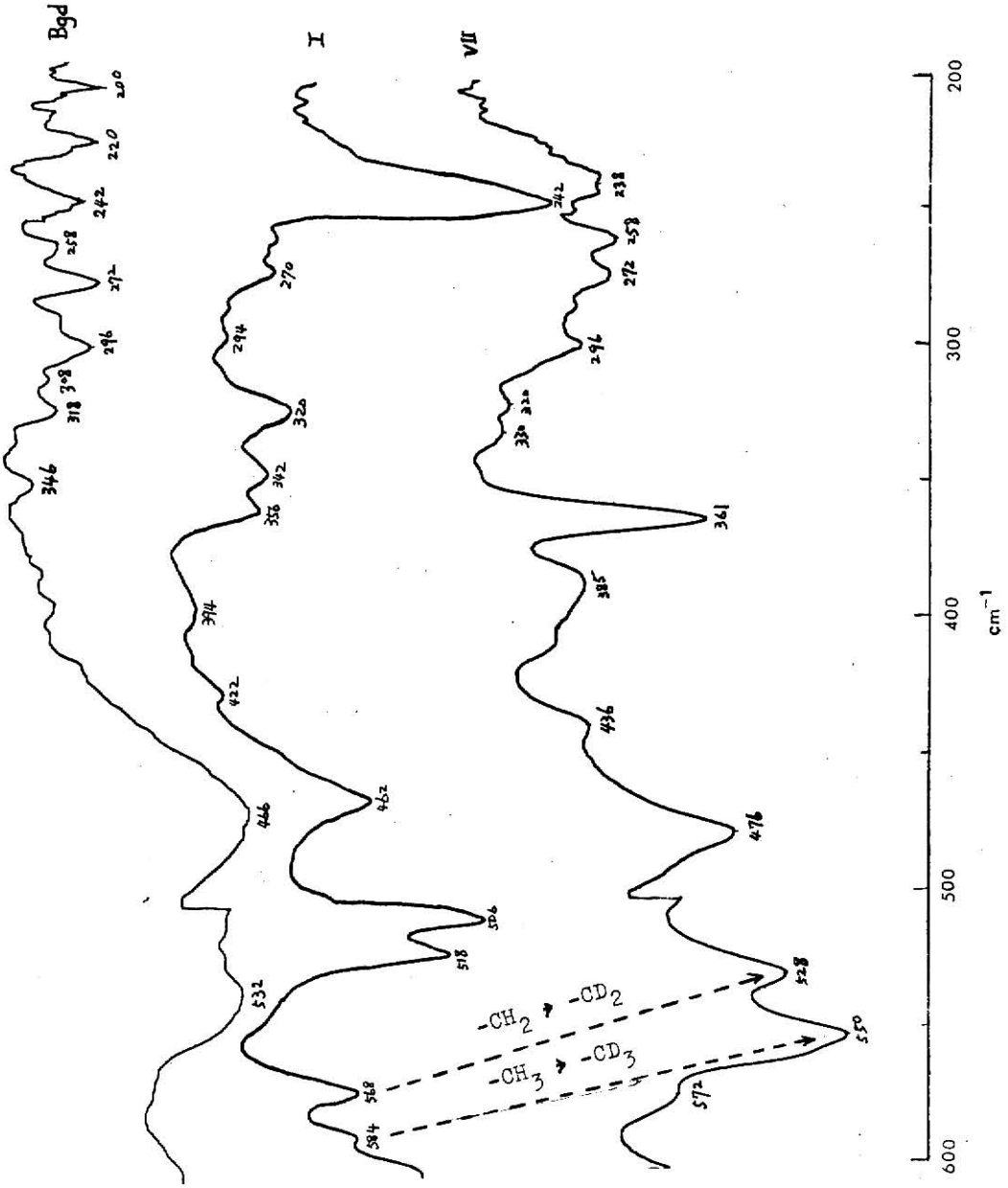

Bgd
I
II
346
318
308
296
272
258
242
220
200
394
422
462
466
532
568
584
518
596
-CH → -CD
384
446
484
554
342
336
260
272
318
370
394
330
362
358
200
300
400
500
600
cm⁻¹

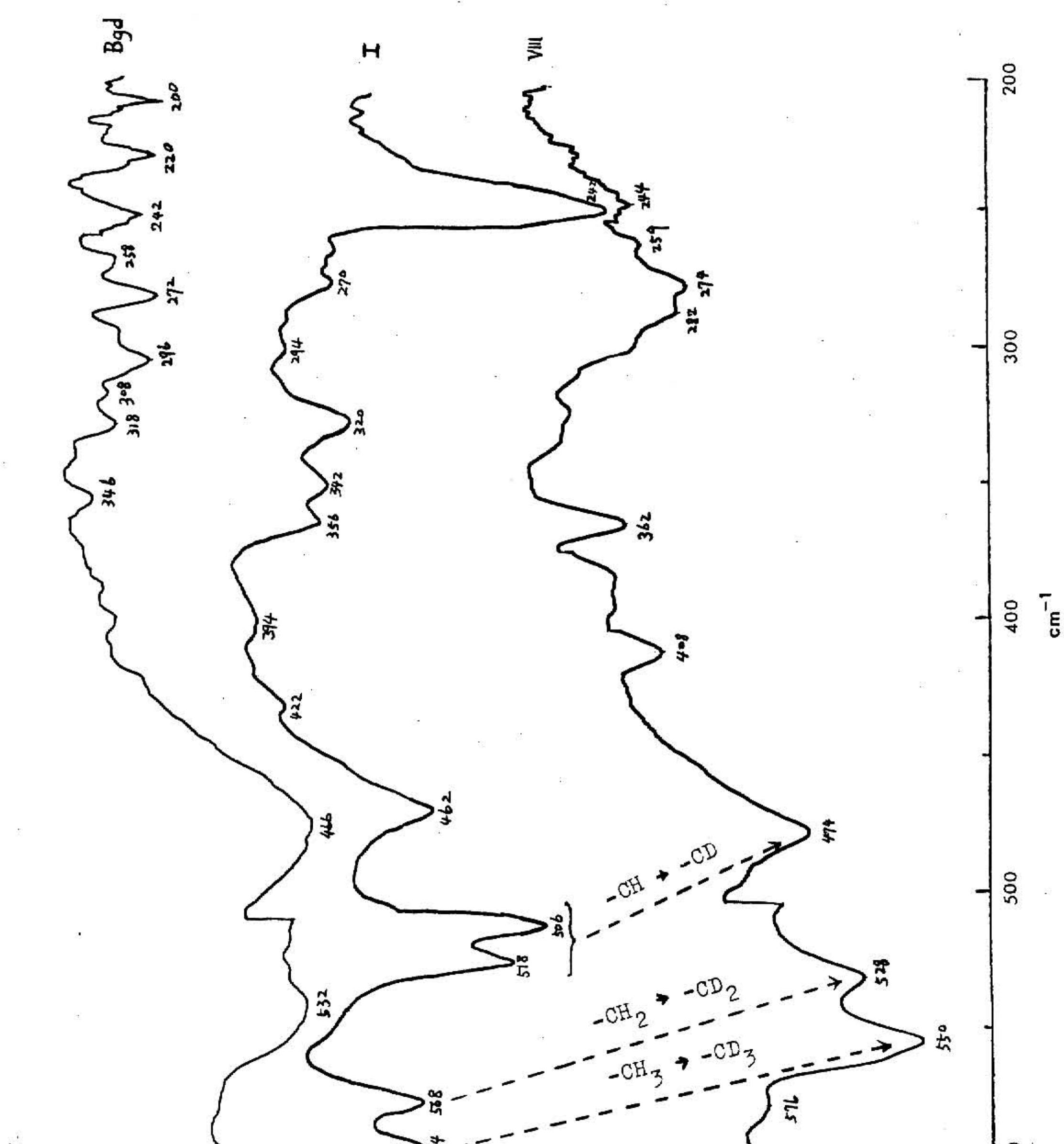

Bgd
I
III
346
318
308
296
272
258
242
220
200
394
422
446
462
506
518
532
548
584
270
294
320
342
358
236
272
298
332
356
332
436
478
494
518
561
$-CH_2 \rightarrow -CD_2$
200
300
400
500
600
cm^{-1}


Bgd
I
IV
346
318
308
296
272
258
242
220
200
394
422
462
446
532
518
506
584
568
270
294
320
342
358
242
345
388
412
468
492
518
552
576
240
260
272
286
224
228
200
300
400
500
600
cm⁻¹
-CH3 → -CD3


Bgd
I
V
346
318
308
296
272
258
242
220
200
370
294
320
342
328
394
422
462
446
532
518
506
568
584
-CH → -CD
-CH2 → -CD2
476
520
552
242
224
244
260
276
284
322
362
418
200
300
400
500
600
cm-1


Bgd
346
318
308
296
272
253
242
220
200
I
292
270
294
320
342
356
394
422
462
506
518
532
558
564
VI
362
320
296
272
259
222
448
528
548
-CH → -CD
-CH3 → -CD3
600
500
400
300
200
cm-1


Bgd
I
VII
346
318
308
296
272
258
242
220
200
270
294
320
342
336
314
422
462
446
506
518
532
568
584
572
528
550
436
476
385
361
330
320
296
272
258
238
242
$-CH_2 \rightarrow -CD_2$
$-CH_3 \rightarrow -CD_3$
200
300
400
500
600
cm^{-1}

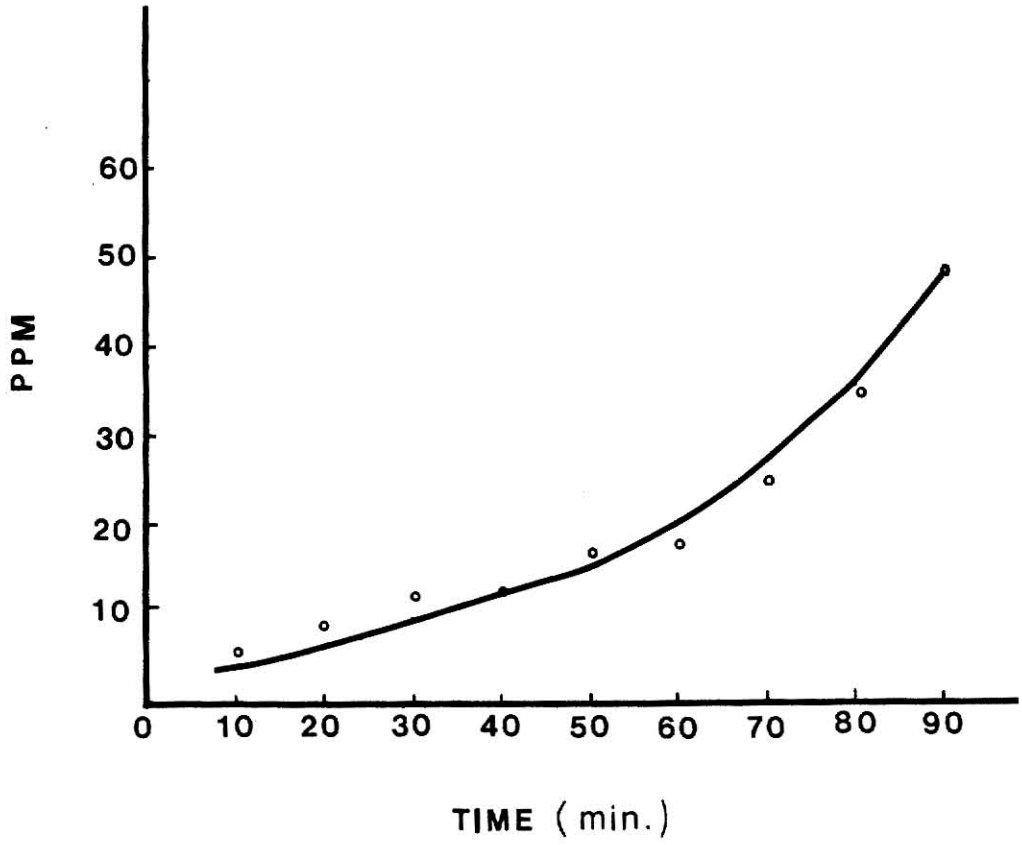


Bgd
I
VIII
-CH → -CD
-CH2 → -CD2
-CH3 → -CD3
200
300
400
500
600
cm-1

Table 8; Relationship between shifted peaks and functional groups

Shifted peaks cm^{-1}	Difference cm^{-1}	% Shift	Functional group
584 → 550	34	5.8	$-CH_3$ → $-CD_3$
568 → 528	40	7.0	$-CH_2$ → $-CD_2$
518 506 → 476	39	7.6	-CH → -CD

Figure 48; Diffusion profile as a function of time


PPM
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
TIME (min.)

parts, one for the first five minutes, the second for the following 55 minutes and recorded every 15 minutes, as shown in Tables 9 and 10.

A response or blank was judged to be positive if the insect either crawled on the plastic or was up next to it. From Table 9, it seemed that the response of the cockroaches was erratic or indifferent to the compounds. It could be that they might need some time to adjust themselves to the new environment.

Observing the net response from Table 10, it seemed to have a similar response order as the foregoing three biological tests. But in view of statistical analysis, there was no significant difference among these eight compounds at $\alpha = .05$ level. This order may simply be a result of direct chemical contact or an expected result of the antennae theory. If the former was the case, then the poor response was probably due to the low concentration. If the latter, then the insect's response to a chemical meant it might be responding to the direct radiation of these same frequencies, though it remains uncertain.

Table 9; Results for the first five minutes of the cylindrical chamber test

Compound	Sample size	Response	Blank	Net response
1	100	17	12	5
2	100	22	15	7
3	100	9	11	-
4	100	19	13	6
5	100	21	17	4
6	100	12	13	-
7	100	7	10	-
8	100	15	12	3

Table 10; Results for the following 55 minutes of the cylindrical chamber test

Compound	Sample size	Response	Blank	Net response
1	100	30	10	20
2	100	32	13	19
3	100	29	11	18
4	100	31	11	20
5	100	24	9	15
6	100	31	12	11
7	100	26	8	18
8	100	25	11	14

CONCLUSION

The deuteration of a chemical will affect its attraction ability on a specific insect. This effect depends on the degree of frequency shift. The information obtained in this paper supports the frequency theory of olfaction.

FUTURE WORK

Though the effect of the deuteration of a chemical on its attraction ability toward a specific insect has been confirmed, the cockroaches' ability to distinguish between frequency shift should be examined to determine the maximum productive frequency change.

The indication obtained is that an insect might respond to the direct radiation of the same frequencies emitted by an attractant, however, the experiment set-up must be designed to rule out any possibility of diffusion. Furthermore, because moist air will heavily absorb the relevant frequencies, the source of the radiation would have to be extremely close to the insect.

Certainly, continued research in this area will produce a wealth of useful knowledge for many fields, related in any way, working toward more efficient insect control and may even be found fruitful for other environmental needs.

REFERENCES

1. J. J. Vollmer and S. A. Gordon, "Chemical Communication, Part I. Nonsocial Insects." Chemistry, 47 (10), 1974.

2. H. S. Bernton and H. Brown, "Insect Allergy-Preliminary Studies of the Cockroach." J. Allergy, 35 (6), 1964.

3. H. S. Bernton and H. Brown, "Cockroach Allergy II: The Relation of Infestation to Sensitization." Southern Medical Journal, 60 (8), 1967.

4. J. J. Vollmer and S. A. Gordon, "Chemical Communication, Part II. Between Plants and Insects and Among Social Insects." Chemistry, 48 (4), 1975.

5. P. G. Seybold, "The Chemical Senses: The Molecule Is the Message Part I. Taste." Chemistry, 48 (3), 1975.

6. P. G. Seybold, "The Chemical Senses: The Molecule Is the Message Part II. Smell." Chemistry, 48 (8), 1975.

7. Chemical Control of Insect Behavior: Theory and Application, pp. 345-351, John Wiley & Sons, Inc., 1977.

8. R. M. Hainer, A. G. Emslie and A. Jacobson, "An Information Theory of Olfaction." Ann. N. Y. Acad. Sci., 58, Art. 2, 158-174, 1954.

9. R. H. Wright, "Understanding Olfaction." Soap, Perfumery & Cosmetics, Vol. XLVI, No. 10, Oct, 1973.

10. J. E. Amoore, 1970., "Computer Correlation of Molecular Shape with Odor: A Model for Structure-Activity Relationships." in: Taste and Smell in Vertebrates, London, J. and A. Churchill.

11. R. H. Wright, "Odorous Comparisons." Chemistry in Canada, Feb., 1977.

12. J. Tyndall, 1868, "Heat, A Mode of Motion." London Longmans, Green. Chapter XI.

13. R. H. Wright and R. E. Brugess, 1970, "Molecular Mechanisms of Olfactory Discrimination and Sensitivity." in: Gustation and Olfaction, Acad. Press, London, New York.

14. R. Schafer and T. V. Sanchez, "Antennal Sensory System of the Cockroach Periplaneta americana, Postembryonic Development and Morphology of the Sense Organs." J. Comp. Neur., 149: 335-354, 1973.

15. D. Schneider, "Electrophysiologishe Untersuchungen von Chem-und Mechanorezeptoren der Antenne des Seiden-Spinners Bombyx mori L.." Z. Vergl. Physiol. 40: 8-41, 1957.

16. W. L. Roelofs and A. Comear, "Sex Pheromone Perception: Electroantennogram Responses of the Red-Banded Leaf Roller Moth." J. Insect Physiol. 17: 1969-1982, 1971.

17. T. L. Payne, "Bark beetle Olfaction. III. Antennal Olfactory Responsiveness of Dendroctonus frontalis Zimmermon and D. brevicomis Le Conte (Coleoptera: Scolytidae) to Aggregation Pheromones and Host Tree Terpene Hydrocarbons." J. Chem. Ecol. 1: 233-242, 1975.

18. V. Lacher, "Electrophysiologishe untersucheingen an einzelnen Geruchs rezeptoren auf den Antennen Weiblicher Moskitos (Aedes aegypti L.)." J. Insect Physiol. 13: 1461-1470, 1967.

19. W. S. Bowers and W. G. Bodenstein, "Sex Pheromone Mimics of the American Cockroach." Nature 232: 259-261, 1971.

20. S. Tahara, "A Sex Stimulant to the American Cockroach in the Compositae Plants." Agri. Biol. Chem., 39 (7), 1975.

21. C. Nishino, et al., "Electroantennogram Responses to a Stimulant, T-Cadinol, in the American Cockroach." Agri. Biol. Chem., 41 (2), 1977.

22. L. M. Roth and E. R. Willis, "A Study of Cockroach Behavior." Am. Midland Naturalist, 47, 471, 1952.

23. W. C. Still, "(±)-Periplanone-B. Total Synthesis and Structure of the Sex Excitant Pheromone of the American Cockroach." J. Am. Chem. Soc., 101, 2493, 1979.

24. M. A. Adams, et al., "Sex Pheromone of the American Cockroach: Absolute Configuration of Periplanone-B." J. Am. Chem. Soc., 101, 2495, 1979.

25. T. J. Marshall and W. N. Cannon, "Alkylation of α-Substituted Acetoacetic Esters." J. Org. Chem., 21, 245, 1956.

26. I. T. Harrison and S. Harrison, Compendium of Organic Synthetic Methods, Wiley-Interscience, New York.

27. F. E. Condon, "Synthesis and Mass Spectra of Some Hexa-, Hepta-, and Octadeuterated Derivatives of Propane." J. Am. Chem. Soc., 73, 4675, 1951.

28. Aldrich Catalog Handbook, p. 136, 1981-1982.

29. Aldrich Catalog Handbook, p. 136, 1981-1982.

30. Aldrich Catalog Handbook, p. 184, 1981-1982.

31. P. B. Cornwell, The Cockroach, Vol. 1, Hutchinson & Co. (publishers) Ltd.

32. L. O. Howard, The Insect Book, Doubleday, Page & Co., New York.

33. P. S. Callahan, "Insect Antennae with Special Reference to the Mechanism of Scent Detection and the Evolution of the Sensilla." Int. J. Insect Morphol. & Embryol. 4 (5): 381-430, 1975.

34. P. S. Callahan, "Far Infrared Stimulation of Insects with the Glagolewa - Arkadiewa "Mass Radiator"." The Florida Entomologist, 54 (2), 1971.

35. P. S. Callahan, "Comments on Mark Diesendorf's Critique of My Review Paper." Int. J. Insect Morphol. & Embryol. 6 (2), 1977.

36. D. R. A. Wharton, et al., "The Odorous Attractant of the American Cockroach, Periplaneta americana (L.). I. Quantitative Aspects of the Response to the Attractant." J. Gen. Physiol., 37, 461, 1954.

APPENDIXES

The data obtained in this paper were subjected to a computer program by using a Statistical Analysis System (SAS): a General Linear Models (GLM) and Duncan's multiple range test. The computer program and the results were as follows:

1. Computer program

```
 1  DATA ALL;
 2  IMPUT METHODS COMP SIZE RESPON BLANK NETRESP;
 3  IF METHODS= 4 THEN DELETE;
 4  CARDS;
37  PROC GLM;
38  CLASSES METHODS COMP;
39  MODEL RESP BLANK NETRESP= METHODS COMP ;
40  MEANS METHODS COMP/DUNCAN;
```

2. Statistical results

GENERAL LINEAR MODELS PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
METHODS	3	1 2 3
COMP	8	1 2 3 4 5 6 7 8

NUMBER OF OBSERVATIONS IN DATA SET = 24

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: RESPON

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	9	4464.87500000	496.09722222	69.40	0.0001	0.978076	5.0727
ERROR	14	100.08333333	7.14880952		STD DEV		RESPON MEAN
CORRECTED TOTAL	23	4564.95833333			2.67372578		52.70833333

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE IV SS	F VALUE	PR > F
METHODS	2	4256.58333333	297.71	0.0001	2	4256.58333333	297.71	0.0001
COMP	7	208.29166667	4.16	0.0112	7	208.29166667	4.16	0.0112

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: BLANK

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	9	445.04166667	49.44907407	6.54	0.0010	0.807759	28.3318
ERROR	14	105.91666667	7.56547619		STD DEV		BLANK MEAN
CORRECTED TOTAL	23	550.95833333			2.75054107		9.70833333

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE IV SS	F VALUE	PR > F
METHODS	2	400.08333333	26.44	0.0001	2	400.08333333	26.44	0.0001
COMP	7	44.95833333	0.85	0.5667	7	44.95833333	0.85	0.5667

GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: NETRESP

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	9	2577.75000000	286.41666667	180.22	0.0001	0.991442	2.9318
ERROR	14	22.25000000	1.58928571		STD DEV		NETRESP MEAN
CORRECTED TOTAL	23	2600.00000000			1.26066876		43.00000000

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE IV SS	F VALUE	PR > F
METHODS	2	2425.75000000	763.16	0.0001	2	2425.75000000	763.16	0.0001
COMP	7	152.00000000	13.66	0.0001	7	152.00000000	13.66	0.0001

GENERAL LINEAR MODELS PROCEDURE

DUNCAN'S MULTIPLE RANGE TEST FOR VARIABLE RESPCN

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

ALPHA LEVEL=.05 DF=14 MS=7.14881

GROUPING	MEAN	N	METHODS
A	62.250000	8	2
A			
A	62.000000	8	3
B	33.875000	8	1

GENERAL LINEAR MODELS PROCEDURE

DUNCAN'S MULTIPLE RANGE TEST FOR VARIABLE BLANK

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

ALPHA LEVEL=.05 DF=14 MS=7.56548

GROUPING	MEAN	N	METHODS
A	14.750000	8	3
B	9.625000	8	2
C	4.750000	8	1

GENERAL LINEAR MODELS PROCEDURE

DUNCAN'S MULTIPLE RANGE TEST FOR VARIABLE NETRESP

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

ALPHA LEVEL=.05 DF=14 MS=1.58929

GROUPING	MEAN	N	METHODS
A	52.625000	8	2
B	47.250000	8	3
C	29.125000	8	1

GENERAL LINEAR MODELS PROCEDURE

DUNCAN'S MULTIPLE RANGE TEST FOR VARIABLE NETRESP

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

ALPHA LEVEL=.05 DF=14 MS=1.58929

GROUPING	MEAN	N	COMP
A	46.333333	3	1
A			
B A	46.000000	3	4
B			
B C	44.000000	3	2
C			
C	43.333333	3	3
C			
C	43.333333	3	6
C			
D C	42.333333	3	7
D			
D E	40.333333	3	5
E			
E	38.333333	3	8

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THE EFFECTS OF DEUTERATING AN ATTRACTANT OF THE AMERICAN COCKROACH, PERIPLANETA AMERICANA L., AS A TEST FOR THE FREQUENCY THEORY OF OLFACTION

by

CHUNG-KUO KUO

B. S., National Taiwan University, 1975

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1982

ABSTRACT

By choosing a relatively simple attractant, bornyl acetate, for the American cockroach, Periplaneta americana L., seven deuterated derivatives were also made.

Bioassays were developed to test the effect of deuteration on the attraction and the attraction dependence on the molecular frequencies.

The results showed that the effect of deuteration was positive and was dependent on the degree of frequency shift, while the test for the antennae theory needs further research.

VITA

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