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Equal molar amounts of (+)-catechin and N-Hydroxymethylacetamide were reacted under acidic conditions. Thin-layer chromatography (TLC) was used to monitor the reaction. The reaction products were isolated by column chromatography using Sephadex LH-20 and elution with 95 percent ethanol.

Three reaction products isolated included one disubstituted and two monosubstituted compounds. The structures of these compounds were determined by using ^1H and ^{13}C nuclear magnetic spectroscopy (NMR), and verified by utilizing both positive and negative ion fast atom bombardment mass spectrometry (FAB-MS). The pattern of substitution on the two monosubstituted products was determined using a two-dimensional NMR technique called a HET-COSY, which showed long distance C-H coupling interactions.

This reaction can be used as a model to cross-link polyvinyl acetate resins (PVA) with condensed tannin derivatives. Such cross-linked resins could possibly make PVA adhesives more suitable for structural applications.

The Reaction of (+)-Catechin with N-Hydroxymethylacetamide:
A Model for Cross-Linking PVA Resins with Tannins

by

Kathryn Anne Wallace

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APPROVED:

Signature redacted for privacy.

Assistant Professor of Forest Products
in charge of major

Signature redacted for privacy.

Head of the Department of Forest Products

Signature redacted for privacy.

Dean of Graduate School

Date thesis is presented April 20, 1989

Typed by Kathryn Anne Wallace

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THE REACTION OF (+)-CATECHIN WITH N-HYDROXYMETHYLACETAMIDE:
A MODEL FOR CROSS-LINKING PVA RESINS WITH TANNINS

Chapter I

Introduction

Polyvinyl acetate (PVA) polymers are currently being used by the forest products industry in several adhesive formulations, including emulsions and cross-linked PVA's. Polyvinyl resin emulsion adhesives are thermoplastic and therefore are restricted in use to packaging and nonstructural interior applications, such as furniture joints and pencils. As a thermoplastic adhesive, the limitations which dictate application of PVA's include lack of resistance to both heat and moisture, and exhibiting the property of creep (Selbo, 1975 and Goulding, 1983).

In an effort to eliminate or reduce these negative properties, the adhesive industry has developed modified PVA's known as thermosetting polyvinyl acetate emulsions, catalyzed PVA emulsions or cross-linked PVA's. Typical monomers used to copolymerize with vinyl acetate are N-Hydroxymethylacrylamide and hydroxymethylated diacetone acrylamide. These contribute hydroxymethyl functional groups to the copolymer which serve as cross-linking agents and provide increased resistance to moisture and heat, and reduce creep. However, these cross-linked PVA's are still not suitable for structural applications nor exterior use. One possibility would be to utilize tannins in the polyvinyl

acetate resins as a means to make these adhesive more suitable for structural applications.

Tannins are polyphenolic compounds widely distributed among the higher plants. Most tannins are classified as either hydrolyzable or condensed. Those of interest in this research are condensed tannins found in bark, specifically those found in Douglas-fir (Pseudotsuga menziesii [Mirb.] Franco). These polyflavonoid compounds could potentially provide additional cross-linking and thereby make a waterproof and heat resistant adhesive with minimal creep.

One method of using tannins in PVA adhesives would be to react the condensed tannin or a condensed tannin derivative with the hydroxymethyl groups, the active functional group of the cross-linking agent already incorporated into the polymer chain as a copolymer. Since PVA adhesives, like any other adhesive contains other additives, such as solvent, fillers, stabilizers, etc., and in the case of PVA cross-links, often a catalyst, it is necessary to reduce the initial reaction to model compounds.

Specifically, this study was to establish a model reaction utilizing (+)-catechin, a monomer of the condensed tannin polymer found in Douglas-fir bark, and N-Hydroxymethylacetamide, representing the cross-linking agent. The reaction was run under acidic conditions and the resulting products were isolated and identified by several methods.

There is an interest in the adhesive industry in making polyvinyl acetate resins suitable for structural applications. And Kreibich (1981) included the development of structural PVA adhesives and the replacement of phenolic compounds with bark tannins in his suggested approaches for chemists to take in achieving the reduction of dependence on petroleum-based chemicals. The research presented here is a preliminary step toward reaching this goal.

Objectives

1. To develop a model for reacting the cross-linking type of polyvinyl acetate resins (PVA) with the condensed tannins found in Douglas-fir bark.
2. To establish the optimum reaction conditions, (+)-catechin was reacted with N-Hydroxymethylacetamide under acidic conditions to obtain the desired products.
3. To isolate and identify these products, using several analytical methods, including nuclear magnetic resonance spectroscopy and mass spectrometry.

Chapter II

Literature Review

A. Vinyl Acetate Monomer and Polymers

1. Vinyl Acetate Monomer

Vinyl acetate is a vinyl ester, first made in the early part of this century. There are two ways of manufacturing vinyl acetate commercially (Llewellyn and Williams, 1972). The first one is the classical method which is a catalyzed reaction of acetylene with acetic acid. A more recent commercial method uses ethylene and acetic acid with a catalyst. The vinyl acetate monomer is very reactive and may polymerize even in moderate heat and light. Therefore, at the time of manufacture, polymerization inhibitors are added which can be easily removed for polymerization purposes (Corey, et. al., 1977).

2. Polymerization of Vinyl Acetate Monomer

For industrial application the polymerization of vinyl acetate is by the use of free radical method (Llewellyn and Williams, 1972). The free radical forming initiators used depend on the type of reaction medium and the reaction temperature. The four polymerization techniques used commercially are bulk, solution, suspension, and emulsion. The method used depends on the form of the polymer desired for the end use. The majority of polyvinyl acetate is produced by the emulsion polymerization technique. Peroxides are frequently used as the free radical catalyst.

The emulsion polyvinyl acetates are the preferred form as the base polymer when used in the formulation of wood adhesives (Corey, et.al., 1977 and Goulding, 1983) The reaction and resulting polymer repeating unit are outlined in Figure 1.

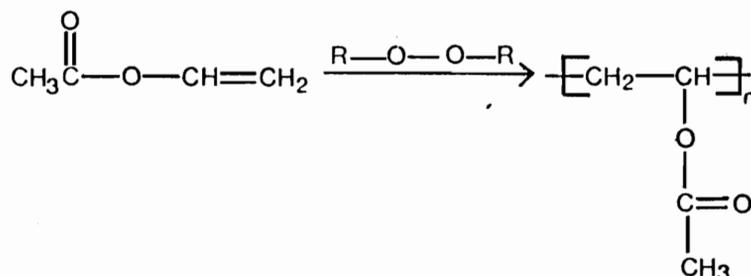


Figure 1. Polymerization of vinyl acetate

A typical polyvinyl acetate emulsion adhesive (Goulding, 1983) consists of the polymer with minor compounding with a plasticizer, such as dibutyl phthalate, a solvent, often one of the lower alcohols, and a filler. Often other binders are added, the most common being polyvinyl alcohol or starches. If needed, a viscosity modifier is also added. These are usually cellulose derivatives, such as carboxymethyl cellulose.

In order to improve the water resistance of PVA emulsion adhesives, a trivalent metal salt such as aluminum nitrate, aluminum chloride, or chromium nitrate may be added

if polyvinyl alcohol is part of the adhesive (Wake, 1982 and Goulding, 1983). Another method is fortifying the resin with a thermosetting formaldehyde resin, such as urea-formaldehyde (UF), melamine-formaldehyde (MF), or phenol-formaldehyde (PF), (Goulding, 1983). Resorcinol-formaldehyde (RF) has also been used (Liu and Chen, 1981). Both of these methods usually result in making the application procedure that of a two component system.

PVA emulsion adhesives have a variety of uses including white glue for home use, and wood glue for finger joints, pencils, and edge glued materials.

3. Copolymerization of Vinyl Acetate

Copolymerization is utilized to produce a polymer with modified properties. The choice of monomer to combine with vinyl acetate depends on the final product. Vinyl acetate copolymerizes with a variety of vinyl monomers. Those commercially important include copolymers with acrylate esters, vinyl chloride, vinylidene chloride, dibutyl and other dialkyl maleates and fumarates (Corey, et. al.). Others included crotonic, acrylic, methacrylic and itaconic acids, vinyl pyrrolidone and ethylene.

Historically the copolymer has been used in a variety of ways such as the vinyl acetate-crotonic copolymer for stiffening of felt hats (Schildknecht, 1952). Copolymers of vinyl acetate are also used for sizing in the textile industry, the bonding of non-woven fabrics, and in coatings, such as paints.

Copolymers soon became of interest to the adhesive industry, especially in the area of packaging (Butts, 1959). Probably the most important of the copolymers is the vinyl acetate-ethylene copolymer which is used as a hot-melt adhesive (Llewellyn and Williams, 1972).

Curable copolymer emulsions have been incorporated into wood adhesives which have been available commercially for more than twenty years (Armour, et.al, 1971 and Selbo, 1975). Often referred to by the adhesive industry as thermosetting PVA's or PVA cross-links, these adhesives incorporate a monomer with vinyl acetate which provides cross-linking capability. The most common monomers used for this application are N-Hydroxymethylacrylamide and hydroxymethylated diacetone acrylamide (Corey, et.al., 1977). When used as a comonomer with vinyl acetate, the amount of N-Hydroxymethylacrylamide usually ranges from one to sixteen percent by weight. Figure 2 shows the reaction of the vinyl acetate and N-Hydroxymethylacrylamide monomers with the resulting copolymer structure.

formulations, as a two-part adhesive where the acidic metal curing agent is added just before utilization (Goldberg and Jasinski, 1967). Some patented formulations also exist with a premixed catalyst (Woo, 1981).

The purpose of developing cross-linking polyvinyl acetate adhesives is to provide chemical resistance, water resistance and increased strength properties, especially a reduction in the creep property of the adhesive bond. Although these goals are accomplished to a certain extent, the curable PVA emulsion adhesives are still not suitable as structural adhesives. Additional attempts have been made to improve the cross-links, providing greater water resistance and minimal creep characteristics. Armour (March, 1969) patented a system utilizing the addition of B stage phenolic resins to PVA's, and another (May, 1969) using sulfonated B stage resins. Both of these methods achieved the degree of water resistance needed to meet and/or exceed standards.

Cross-linking PVA's are used in edge gluing, finger jointing, high pressure laminating and panel to frame gluing. There are some formulations which can be used on wood with higher moisture contents. They are also combined with other adhesives, such as urea-formaldehyde and used to bond some types of interior decorative plywood.

B. Tannins

Interest in utilizing bark began primarily as a means to use what was originally considered to be a waste product of the forest products industry. With the increased demand for petroleum and the oil shortages of the 1970's, it became more common to use bark as a hog fuel in mills (Anderson, 1976 and Ayla, 1983). From these same oil shortages stemmed the need to use natural products as substitutes for the petrochemicals used in adhesives, such as resorcinol and phenol. There was also increased interest in using bark to derive the chemicals themselves (Hemingway, 1981). This need became even more crucial for other nations that depended almost exclusively on imported oil and petrochemicals, making these already expensive petroleum products even more so. In some of these countries however, such as South Africa, New Zealand and others, research in this area had already been established, resulting in the decrease in the dependence on the oil-based chemicals used in wood adhesives (Porter and Hemingway, 1986).

Despite the increased interest and research utilizing both bark powders and extracts in existing adhesive formulations as partial substitutes, and the tannins themselves as the main ingredient of new formulations, the only large commercial today use is of wattle tannin (Ayla, 1983). There are several reasons for this. First of all, wattle tannins are more readily adaptable to adhesive formulation due to relatively low molecular weights and the

resorcinol functionality which is exhibited especially in the reaction with formaldehyde. Another reason is the ability of the industry to provide consistently standardized tannins. Factors which contribute to the uniform tannin products include forestation techniques, harvesting on a fixed rotation to insure a continuous supply, a moderate growth climate, and standardized extraction techniques and concentration procedures (Steiner, 1981). Also, it is probable that the commitment to research in this area motivated by high imported oil prices has provided a major impetus in the development of wattle tannin adhesives on a commercial scale.

Pizzi (1983) summarizes many types of wattle tannin adhesive formulations. For exterior grade plywood several formulations suitable for industrial application include many that are fortified with other resins, such as phenol-formaldehyde, phenol-resorcinol-formaldehyde, and urea-formaldehyde. There are also some formulations that utilize metal ion catalysts. Exterior grade particleboard adhesives use modified condensed wattle tannins. This modification is a series of acid and alkali treatments of the tannin extract. This coupled with the development of gluing and pressing techniques for specific use with wattle tannin adhesives result in shorter press times.

Fortified tannin adhesives as previously described are also used for interior grade particleboard (Pizzi, 1979). Others included are tannin extracts fortified with 4,4'-

diphenylmethane diisocyanate, known commercially as MDI. Laminating adhesives include cold-setting, fast-setting and radio-frequency cured resins. Five systems are described (Pizzi, 1983) including the "Honeymoon" or "separate application" system. These utilize resorcinol formaldehyde, resorcinol terminated phenol-formaldehyde, or resorcinol terminated urea formaldehyde resins along with some type of wattle tannin resin. One other system consists of acid hydrolysis of the tannin etherocyclic ring combined with simultaneous grafting of resorcinol without formaldehyde. And finally, wattle tannin extract combined with urea formaldehyde, formaldehyde and starch yields an adhesive used for corrugated cardboard (Saayman and Brown, 1977).

Conifer tannins have not enjoyed such commercial success. Porter and Hemingway (1986) note that much of the early published work concerning particleboard tannin adhesives focused on radiata pine tannins, with the use of the concentrated extracts and paraformaldehyde for cross-linking. These were applicable for interior particleboard only. They go on to summarize other conifer tannin formulations. These include using white fir, ponderosa pine, Douglas-fir, and western hemlock tannins in other adhesive formulations for composite boards. Most of these also did not achieve the amount of water-resistance necessary to be classified as exterior grade. Tannaphen, marketed by New Zealand Forest Products, Ltd. is a radiata pine tannin extract, to be used for both particleboard and

plywood (Woo, 1982), but again, most formulations were only suitable for interior use. The most successful formulations have been the combination of MDI and conifer tannins, including Tannaphen. Some success has also be achieved in the area of particleboard adhesives by combining tannin extracts with melamine and wattle-formaldehyde resins. And as in the case of wattle tannin, conifer tannins have been successfully used as a partial substitute for phenol in PF resins.

In plywood formulations, the major problem in the utilization of conifer tannins has been the rapid polymerization and subsequent control of viscosity. Again, the early work centered around radiata pine tannins, mixed with paraformaldehyde and formalin (Herzberg, 1960). Similar types of adhesives were made with western hemlock tannins (Steiner and Chow, 1975). The use of alkaline tannin extracts, which are heated and then acidified, washed and purified provided higher bond quality and better adhesive properties. These alkaline extracts were used as a partial substitute for phenol in PF resins, but failed to achieve exterior grade status (Hemingway and McGraw, 1977). Several formulations have been tried using finely ground conifer bark powders as a partial replacement for phenol (Hemingway, 1977).

Recently, sulfonated tannin extracts have been fortified with phenol-formaldehyde to make adhesives suitable for exterior grade plywood (Kreibich, 1988). As

with wattle tannins, laminating adhesives have been formulated using conifer tannins. These include the combination with PF resin after reacting the tannins with sodium bisulfite, the acid catalyzed cleavage of the interflavonoid bond in combination with resorcinol to make resorcinol adducts, and as resorcinol replacements in the "honeymoon" system similar to that used for wattle tannins (Kreibich and Hemingway, 1987). Sodium sulfite extractions of southern pine bark combined with PRF resins have also been used in this "Honeymoon" method.

C. Tannins and Polyvinyl Acetate

There is no evidence in the literature that tannins have been reacted with or combined in any manner with polyvinyl acetate resins. Nor has any evidence been found of reacting tannins with either N-Hydroxymethylacrylamide or N-Hydroxymethylacetamide. However, work has been done in the area of modifying alkali bark extracts with an amide of a dicarboxylic acid, such as a dimethylolamide of a dibasic acid. This modified bark extract, a combination of western bark species, mainly Douglas-fir and white fir, was developed and patented by Hsu (1972) with the intention of use in plywood adhesives. Specifically, the extract can be used to up to a 65 percent direct replacement of phenol in a typical PF resin.

Research has been done with reacting another phenolic compound, resorcinol, and formaldehyde with N-

Hydroxymethylacrylamide (Siimer and Krist'yanson, 1978).
However nothing was found in the literature about the
reaction of (+)-catechin with either N-
Hydroxymethylacrylamide or N-Hydroxymethylacetamide.

Chapter III

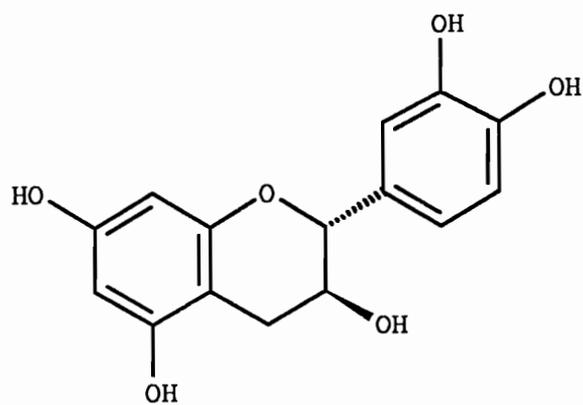
Experimental Procedure

Douglas-fir is the most important commercial timber species of the Pacific Northwest and as a result, a large quantity of bark is generated every year. Although there are already many low value uses for this bark, there is an excess available to provide an adequate source for tannin production. For this reason, Douglas-fir condensed tannins were the ones chosen to be represented by a model compound in this experiment. The other model compound used represents N-Hydroxymethylacrylamide. This particular acrylamide is used extensively to provide cross-linking capability in commercial PVA resins. It is also a relatively simple compound.

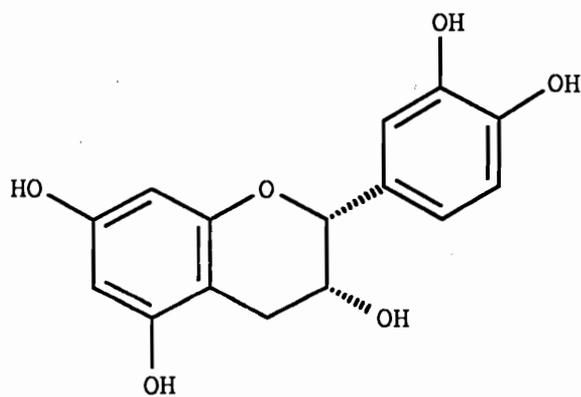
Model compounds were used in this experiment in order to establish the best reaction conditions and to simplify the procedure. The resulting reaction products were isolated and then analyzed to determine their structures.

A. Design of the Experiment

The condensed tannin polymers of Douglas-fir bark consist of (+)-catechin and (-)-epicatechin monomers (Karchesy, et.al., 1976). The structures of these condensed tannin monomers are give in Figure 3.



(+)-Catechin



(-)-Epicatechin

Figure 3. Condensed tannin monomers of Douglas-fir bark.

One of these monomers, (+)-catechin was chosen to represent the Douglas-fir tannins in this reaction. Two systems are commonly used to number the (+)-catechin structure (Foo and Porter, 1980, Markham, et. al., 1982). The one used in this discussion is illustrated in Figure 4.

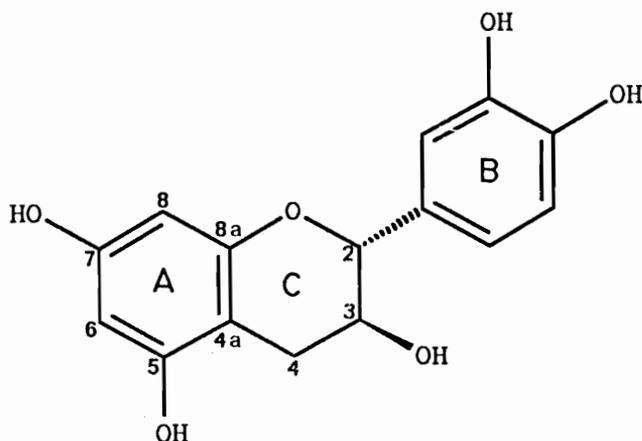


Figure 4. Numbering system used for (+)-catechin.

The hydroxylation pattern on the A ring of (+)-catechin is considered to be a phloroglucinol type and behaves as such. It is known that electrophilic substitution readily occurs at the C-6 and C-8 positions of the A ring and that these reactions can be acid or base catalyzed. In contrast, the B ring with o-dihydroxyl functional groups has been shown to be unreactive to electrophilic substitution by formaldehyde and similar compounds (Hillis, 1981 and Steiner, 1981). The reaction studied here was designed to take advantage of the high reactivity of the phloroglucinol A ring towards electrophilic substitution. N-Hydroxymethylacetamide, the

other compound used in the reaction was chosen to provide the hydroxymethyl groups such as those found in cross-linking PVA's which use N-Hydroxymethylacrylamide to copolymerize with the vinyl acetate.

When these two compounds were combined under acidic conditions, the reaction was expected to produce three products which included one disubstituted (C-6 and C-8) and two monosubstituted products (C-6 or C-8), because it was expected that the C-6 and C-8 positions would have similar reactivity. The reaction and the proposed structures of the expected products are shown in Figure 5.

The proportions of the starting materials, solvent and acid were suggested from a similar procedure of synthesizing 2-(Aminomethyl)phenols (Stokker, et. al., 1980). In preliminary reaction studies, the addition of heat (80° C) produced a rigid gel in thirty minutes, so the decision was made to run the reaction at room temperature. Detailed descriptions of the reaction and isolation procedures are outlined in the sections that follow.

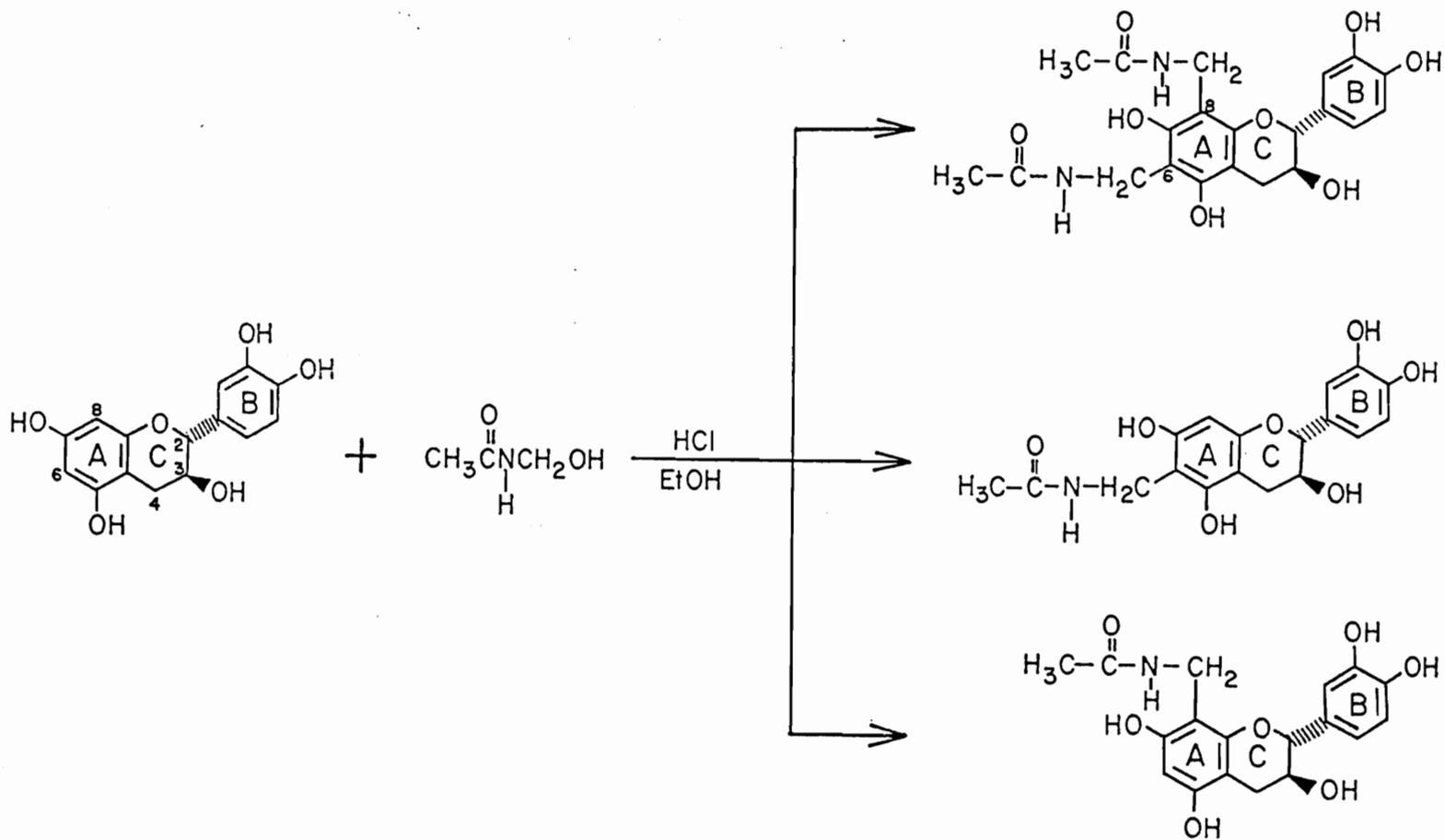


Figure 5. Reaction and expected products.

B. Reaction Procedure

The starting materials for the reaction were N-Hydroxymethylacetamide (Lancaster Synthesis, Ltd., Windham, NH) and (+)-catechin (Sigma Chemical Co., St. Louis, MO). Anhydrous ethanol (USI Chemicals Co.) was used as the reaction medium and concentrated hydrochloric acid (J. T. Baker, reagent grade) was used as the acid catalyst.

Thin-layer chromatography (TLC) was used to monitor both the reaction and isolation procedures. Cellulose plates (Schleicher and Schuell F1440/LS254, 10 x 10 cm) were used for both one- and two-dimensional TLC. Six percent acetic acid was the solvent system used to develop the one-dimensional chromatogram. The two-dimensional TLC was developed with (BAW) t-butyl alcohol-acetic acid-water (3:1:1 v/v/v) in the first dimension and six percent acetic acid in the second. Plates were sprayed with vanillin-HCl reagent (600 mg. vanillin, 1.5 ml. conc. HCl, 60 ml. ethanol).

Equal molar amounts of (+)-catechin and N-Hydroxymethylacetamide were dissolved in anhydrous ethanol, a minimum amount of concentrated HCl was added and the solution was stirred thoroughly. Two typical reaction mixtures are given in Table 1.

Table 1. Typical Reaction Mixtures

Reaction Mixture #1

1.0000 gram (+)-catechin
.2670 grams N-Hydroxymethylacetamide
2.0 mls anhydrous ethanol
.1 ml conc. HCl

Reaction Mixture #2

2.0000 grams (+)-catechin
.5340 grams N-Hydroxymethylacetamide
4.0 mls anhydrous ethanol
.2 ml conc. HCl

The mixture was allowed to react at room temperature for several days. During this time, the reaction was monitored by TLC at periodic intervals to follow the formation of the reaction products. Each plate was spotted with the reaction mixture and a second spot of unreacted (+)-catechin for the purposes of comparison. Following application of the vanillin-HCl spray reagent the unreacted (+)-catechin was dark pink with an Rf of .53, the product with an Rf of .77 was a light purple, and the two remaining products were brownish-pink in color had Rf's of .67 and .62 respectively. The separation pattern is illustrated in Figure 6. A two-dimensional TLC of the reaction mixture was also run. A distinct separation of the three reaction products as well as unreacted (+)-catechin were observed (Figure 7).

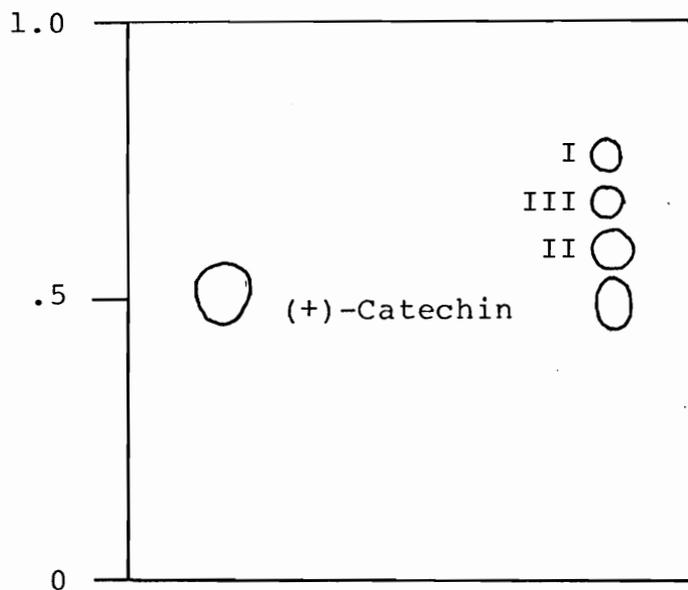


Figure 6. One-dimensional TLC.

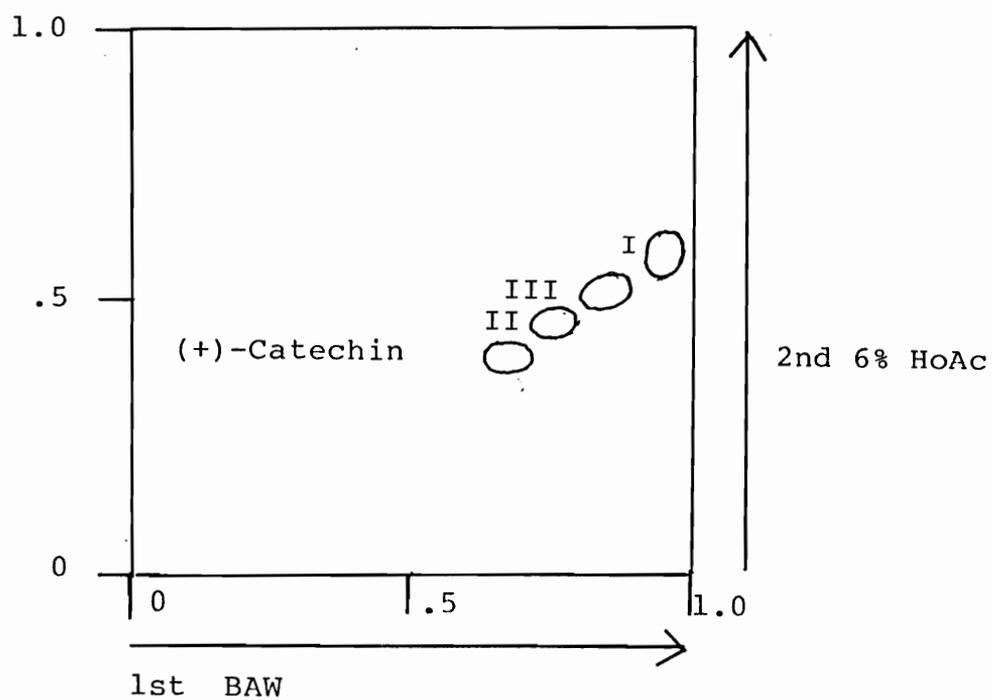


Figure 7. Two-dimensional TLC.

Once the reaction was judged to have reached maximum formation of the reaction products, the mixture was neutralized with two percent sodium hydroxide solution to a pH of approximately 7.6, determined by using indicator paper (pHydrion Microfine). The neutralized solution was extracted three times with ethyl acetate. Sodium sulfate was added to the extract in order to remove any trace amount of water. The extract was then filtered, and evaporated to dryness on a Buchi Rotavapor. The dried combined reaction product was placed in a desiccator with Drierite for several days.

C. Isolation Procedure

The reaction product (2.33 grams) was redissolved in a minimum amount of anhydrous ethanol and the solution was applied to a column (39.0 cm x 1.1 cm) of Sephadex LH-20. The column was eluted with 95 percent ethanol using gravity flow. The fractions were collected on a Gilson fraction collector at an approximate rate of one milliliter per minute. These fractions were monitored by the one-dimensional TLC system outlined previously in the Reaction Procedure section. The fractions were then combined to give the isolated products. The isolated products were evaporated to dryness on the rotary evaporator, placed in a desiccator for several days and then freeze-dried. The products were weighed and yields were determined.

The dried products of reaction mixtures #1 and #2 (Table 1) were combined before redissolving and placing on

the Sephadex LH-20 column for separation. The total dry weight of the crude reaction product placed on the column was 2.33 grams. The three products of interest were the first to be eluted from the column, followed by unreacted (+)-catechin and other products thought to be polymeric material.

The first product to be eluted from the column was product I, composed of 10 fractions, 7.5 mls each, and had an Rf of .77. The yield was .3709 grams. The second product eluted, product II, consisted of 10 fractions and an Rf of .67. This product proved to be more difficult to isolate and had to be run through the column a second time, with a final yield of .2928 grams. The final product of interest, product III was the third to be eluted and had 14 fractions. The Rf value for this product was .62 and the yield was .2599 grams. All three reaction products were dried easily into powders.

D. Analysis of Reaction Products

Analysis of the isolated reaction products was accomplished primarily with the use of nuclear magnetic resonance spectroscopy (NMR). In order to determine the structures, the NMR spectra were obtained at the Oregon State University Department of Chemistry's NMR facility on a Bruker AM 400 Spectrometer at 400 MHz for the proton NMR and 100.6 MHz for the Carbon-13 NMR. A series of NMR's were performed on every isolated product. Each sample weighed

50.0 - 75.0 mg. was dissolved in CD₃OD and placed in Norell 508 UP NMR tubes. All NMR's were run reference to the solvent. The types used were 1-H and 13-C one-dimensional NMR's, two dimensional 1-H COSY and HET-COSY NMR's. The one-dimensional spectra were compared to those of unreacted (+)-catechin.

The second method used to determine and confirm the structures of the three products was fast atom bombardment mass spectrometry (FAB-MS). These FAB-MS spectra were obtained from the Oregon State University Department of Agricultural Chemistry on a Krotos MS-50TC mass spectrometer. Both positive and negative FAB-MS were run with the samples dissolved in a glycerol liquid matrix.

Chapter IV

Results and Discussion

The results of this research were both positive and significant. Of primary importance was that the reaction did work. The hydroxymethyl groups were reactive under acidic conditions, with electrophilic substitution occurring at both the six and eight position of the (+)-catechin A ring. This reaction produced the three expected compounds. These consist of one disubstituted product, 6,8-dimethylacetamido-catechin (I), and two monosubstituted products, 8-methylacetamido-catechin (II) and 6-methylacetamido-catechin (III). These three compounds are most likely intermediate products, with the final reaction products being the additional products that were isolated, thought to be polymeric material. This would account for the low yields of the three reaction products of interest. The 6,8-diacetamidomethyl-catechin (I) yield was 13.6 percent based on (+)-catechin, with yields of 10.76 percent for 8-acetamidomethyl-catechin (II) and 9.55 percent for 6-acetamidomethyl-catechin (III). Another reason for the low yields was the presence of unreacted (+)-catechin, most likely indicating that the reaction was not optimized.

It should also be noted that this reaction is relatively simple to perform. No complex equipment or extreme conditions are necessary. The products are easily separated by column chromatography and monitored by TLC.

The most significant result of this research experiment is that the three products produced by this reaction are new compounds. Moreover, a model has been established and theoretically this same model can be used to react condensed tannins of Douglas-fir bark with cross-linking PVA resins.

The structure determination of these three products was very important, considering that these are new compounds. One method used to identify the structures of these compounds was nuclear magnetic resonance spectroscopy (NMR). The ^1H and ^{13}C spectra of each compound were compared with those for unreacted (+)-catechin. The second method of analysis used was fast atom bombardment spectrometry (FAB-MS). The FAB-MS samples were run with a glycerol liquid matrix. In this chapter the structure analyses of the three products of interest are discussed separately in detail. The remainder of this chapter discusses the determination of the substitution pattern on the two monosubstituted products. Also included is a brief general characterization of the additional reaction products which were of secondary importance to this research project.

A. Structure Identification

1. 6,8-Diacetamidomethyl-catechin (I)

This product was the first to be eluted from the Sephadex LH-20 column and also had the highest R_f on the one-dimensional TLC of .77 as compared to unreacted (+)-catechin of .53. The structure is given in Figure 8.

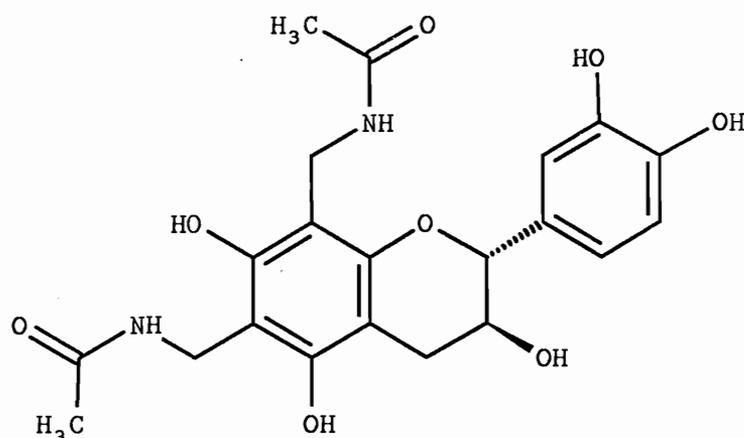


Figure 8. 6,8-Diacetamidomethyl-catechin (I).

The ¹H NMR spectrum of product I (Fig. 9) showed significant differences when compared to the (+)-catechin standard NMR. No significant peaks appeared in the region around δ 6, indicating that the hydrogens at the six and eight positions on the A ring have been substituted. By comparison to a spectrum of unreacted (+)-catechin, two singlets appear at δ 5.94 (H-6) and δ 5.93 (H-8). At δ 4.24 and δ 4.22, two singlets (which integrate for two hydrogens each) appear on the spectrum of product I representing the two CH₂ groups bonded to the A ring at the six and eight

positions. In addition, two more singlets (three hydrogens each) appear at δ 1.91 and δ 1.88 respectively, representing the two CH_3 groups which are also part of the substituent groups on the A ring. Neither of these two sets of signals appear on the spectrum of standard (+)-catechin. A complete list of proton assignments can be found in Table 2. The ^1H two-dimensional COSY (Appendix) confirmed the coupling patterns shown in the one-dimensional proton NMR.

The carbon-13 NMR spectrum of I (Fig. 10) showed peaks representing C-6 and C-8 of the A ring at 107.8 ppm and 105.8 ppm. On a spectrum of (+)-catechin, these two peaks appear at 96.3 ppm (C-6) and 95.5 ppm (C-8). The C-4a peak on the spectrum of product I appears at 101.98 ppm, which is approximately the same location as the C-4a on standard (+)-catechin. Two additional peaks appear on the ^{13}C spectrum of product I which are not present on that of standard (+)-catechin. These are peaks at 34.5 ppm and 34.2 ppm representing the carbon of the CH_2 groups of the substituents and a peak at 21.8 ppm, representing the carbons of the CH_3 groups on the same substituents. On both the spectra of the product I and (+)-catechin standard, the C-4 peak appears at 28 ppm. A listing of all of the ^{13}C NMR assignments can be found in Table 3.

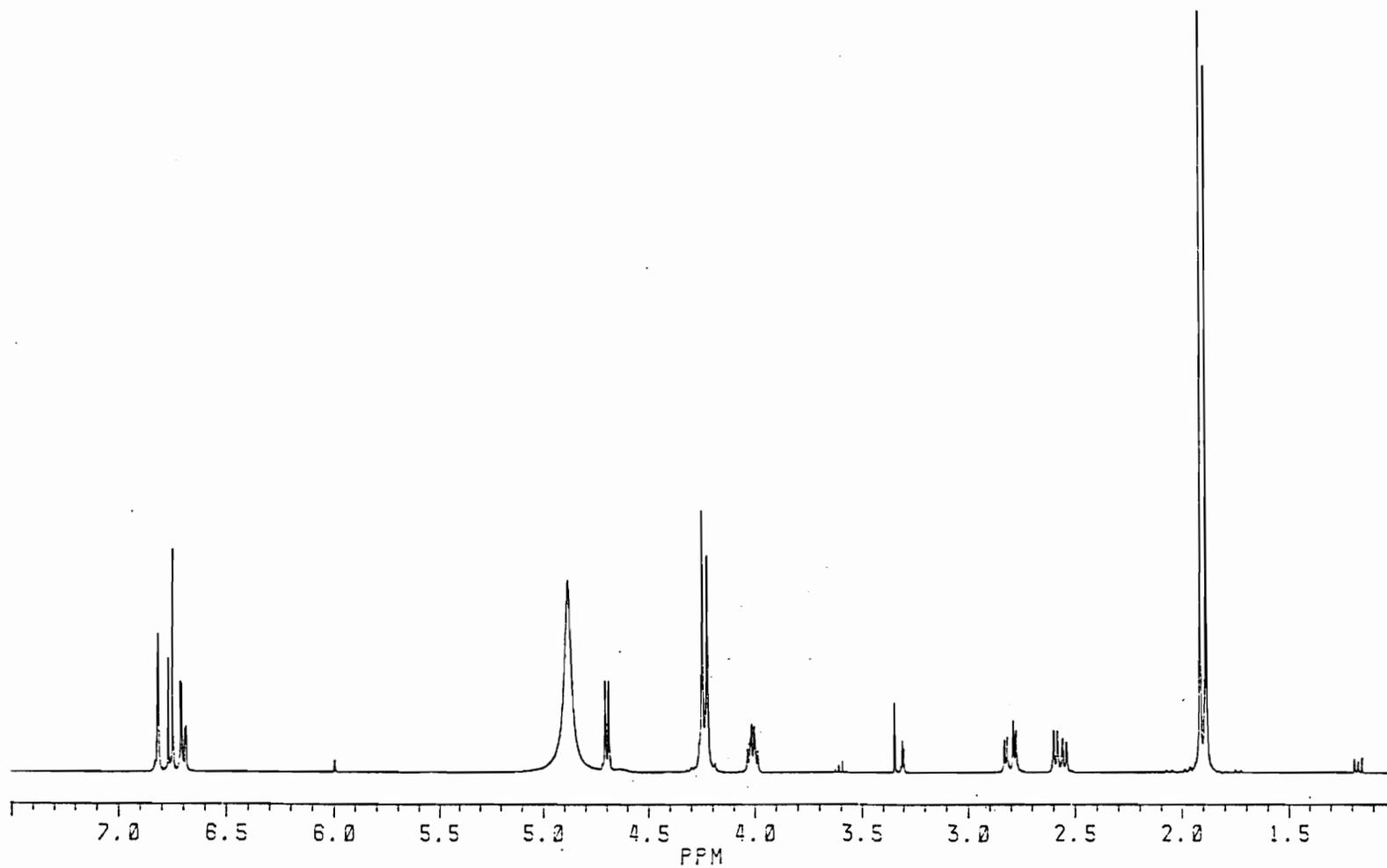


Figure 9. Proton NMR spectrum of Product I.

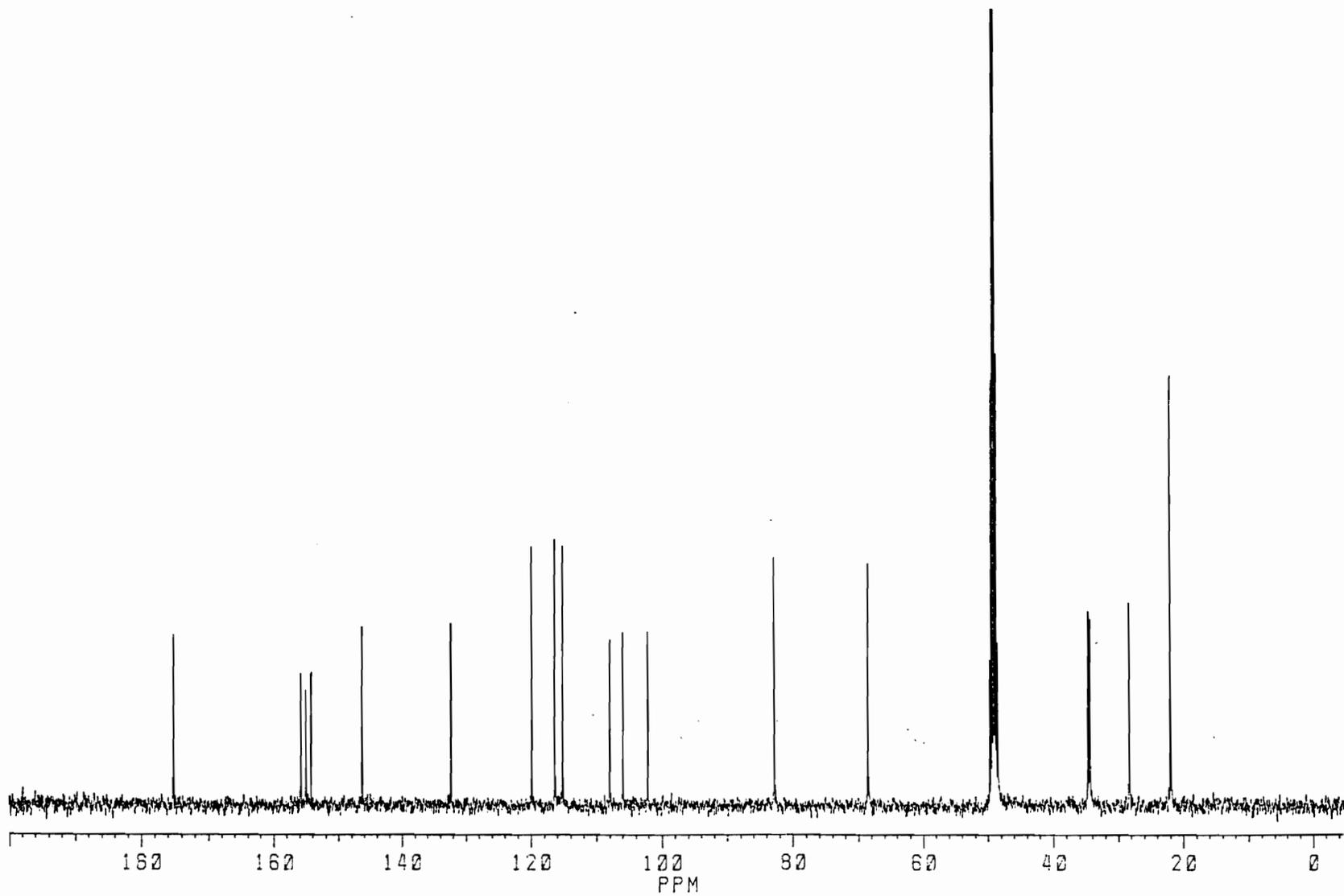


Figure 10. Carbon-13 NMR spectrum of Product I.

Table 2. Proton NMR assignments

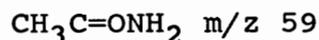
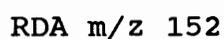
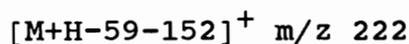
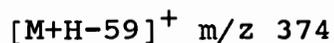
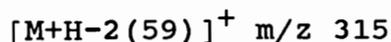
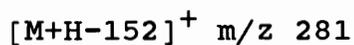
Compound	Proton Number							
	2	3	4a	4b	6	8	CH ₂	CH ₃
I	4.69 d J=6.8Hz	4.00-4.02 m	2.77-2.83 m	2.53-2.59 m	_____	_____	4.22 s 4.24 s	1.88 s 1.91 s
II	4.72 d J=6.7Hz	3.99-4.04 m	2.74-2.79 m	2.51-2.57 m	5.99 s	_____	4.25 dd J=14Hz	1.88 s
III	4.58 d	3.95-4.01 m	2.82-2.87 m	2.50-2.56 m	_____	5.93 s	4.24 s	1.93 s
Catechin	4.58 d	3.96-4.01 m	2.82-2.87 m	2.48-2.55 m	5.94 s	5.93 s		

Table 3. Carbon-13 NMR Assignments

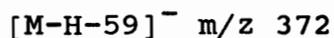
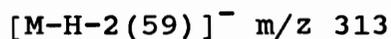
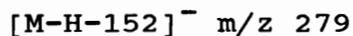
Compound	Carbon Number					
	2	3	4	4a	6	8
I	82.7	68.4	28.2	102.0	107.8	105.8
II	82.6	68.4	27.8	100.9	96.9	104.8
III	82.7	68.7	28.6	101.7	106.7	95.6
Catechin	82.7	68.7	28.3	101.8	96.3	95.5

Compound	Carbon Number				
	5	7	8a	CH ₂	CH ₃
I	155.7	154.9	154.2	34.2 34.5	21.8
II	157.1	156.3	154.8	34.0	22.0
III	156.0	156.4	156.2	34.1	21.9
Catechin	157.6	157.4	156.8		

On FAB-MS, both positive and negative ion, the fragmentation schemes involved retro-Diels-Alder (RDA) pattern, which is typical for the flavonoid compounds (Karchesy, et. al., 1986, Mabry and Markham, 1982). The fragmentation patterns for product I are illustrated in Figure 11 (positive ion) and Figure 12 (negative ion). The molecular weight of compound I is 432. For the positive ion the parent peak is present as $[M+H]^+$ at m/z 433. Other significant peaks are as follows:



The negative ion FAB-MS has a similar fragmentation scheme to that of the positive ion. The parent peak is $[M-H]^-$ at 431. Other important peaks are as follows:



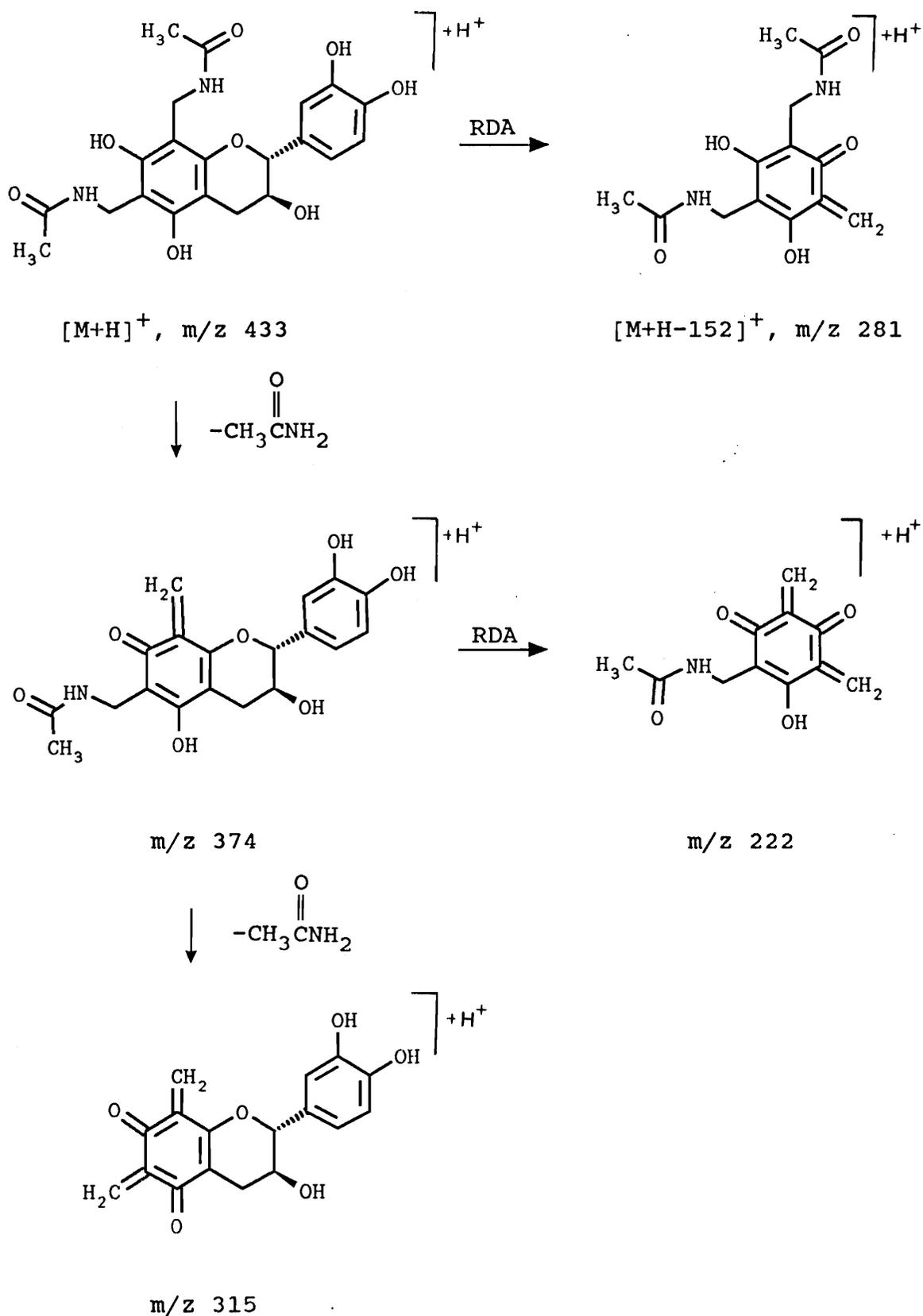


Figure 11. Fragmentation scheme for Product I (pos. ion).

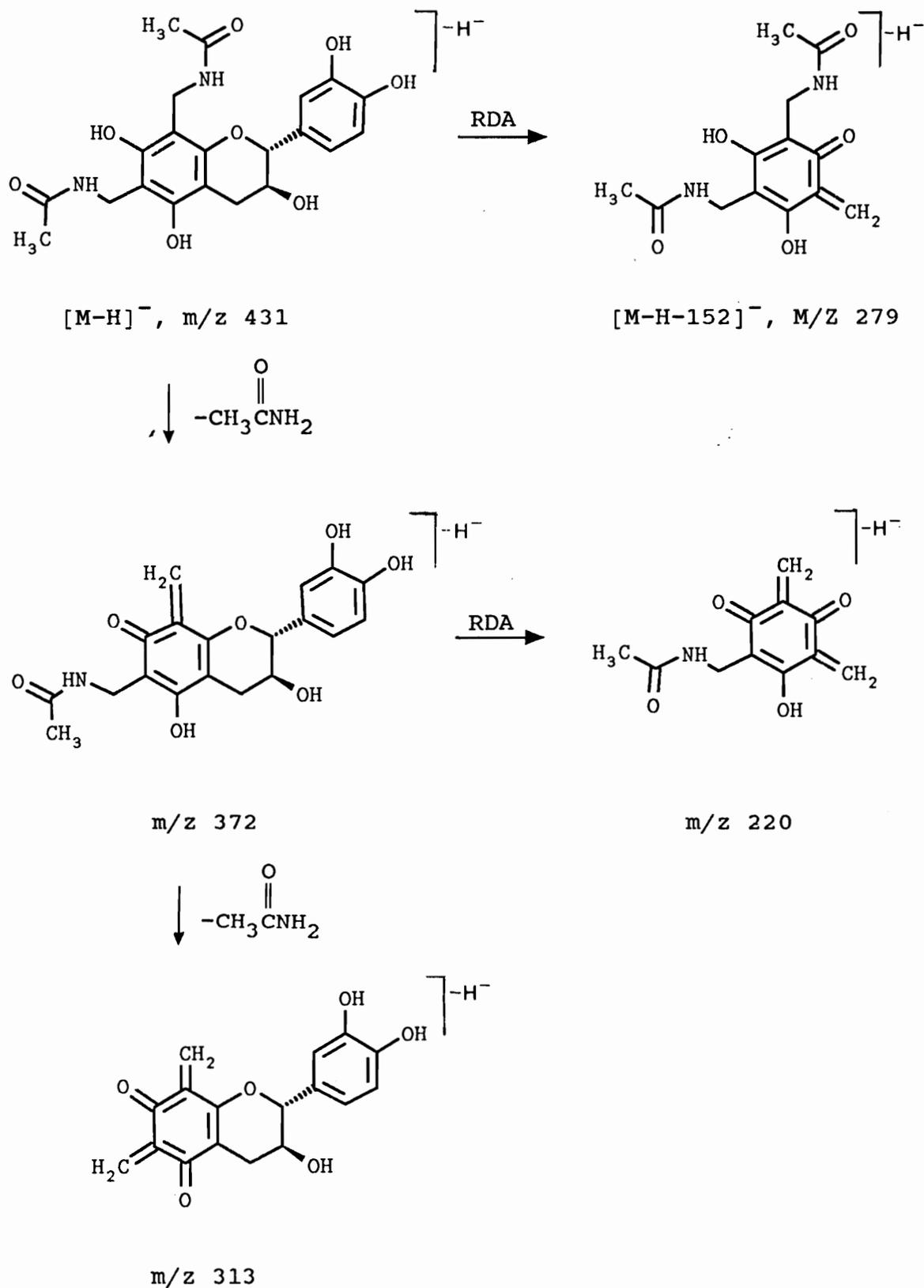


Figure 12. Fragmentation scheme for Product I (neg. ion).

2. 8-Acetamidomethyl-catechin (II)

This product was the second to be eluted from the column of Sephadex LH-20, and was the most difficult to purify. It had to be run through the column a second time to obtain a relatively clean sample. The R_f on the one-dimensional TLC was .62. The structure is given in Figure 13.

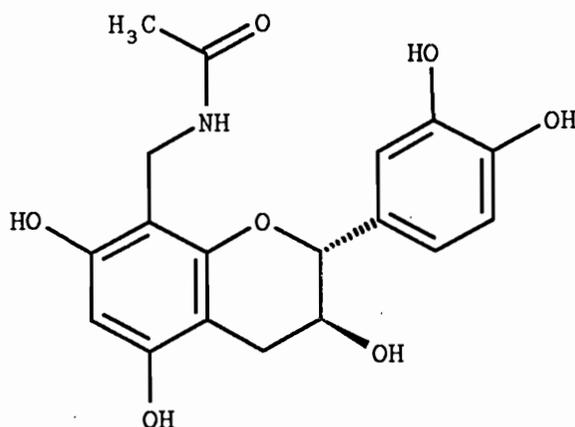


Figure 13. 8-Acetamidomethyl-catechin (II).

The ^1H NMR spectrum (Fig. 14) shows a singlet for one hydrogen at δ 5.99 which can be attributed to the hydrogen at either the six or eight position on the A ring, and indicates substitution at the remaining position. By comparison, the ^1H NMR spectrum of standard (+)-catechin shows two peaks at δ 5.94 (H-6) and δ 5.93 (H-8), respectively. This spectrum does not provide enough information to determine the exact location of the substitution. An additional singlet which does not appear with standard (+)-catechin is at δ 1.88 (three hydrogens)

and can be attributed to the hydrogens of the CH₃ group. The other indication of the substitution on the A ring appears as a doublet of a doublet (two hydrogens) in a range from δ 4.30 to 4.22. This group of peaks represents the hydrogens on the CH₂ group of the substituent. A complete assignment for the protons is given in Table 2. The ¹H two-dimensional COSY (Appendix) confirmed the coupling patterns found in the ¹H NMR spectrum.

The carbon-13 NMR spectrum of II (Figure 14) showed peaks at 104.8 and 96.9 ppm, whereas on the (+)-catechin spectrum the two peaks are at 96.3 ppm (C-6) and 95.5 ppm (C-8). This downfield shift of one peak on the spectrum of product II indicates that there is substitution at either the six or eight position on the A ring. On the (+)-catechin ¹³C spectrum the C-4a appears at 100.8 ppm, and for product II, at a similar shift (100.9 ppm). Two additional peaks appear on the product II spectrum which do not appear on standard (+)-catechin. One at 34.0 ppm, which is the carbon of the CH₂ group and one at 22.0 ppm, which is the carbon of the CH₃ group. On both the (+)-catechin and II spectra, C-4 peaks are present at approximately 28 ppm. All of the assignments for the ¹³C NMR of product II are given in Table 3.

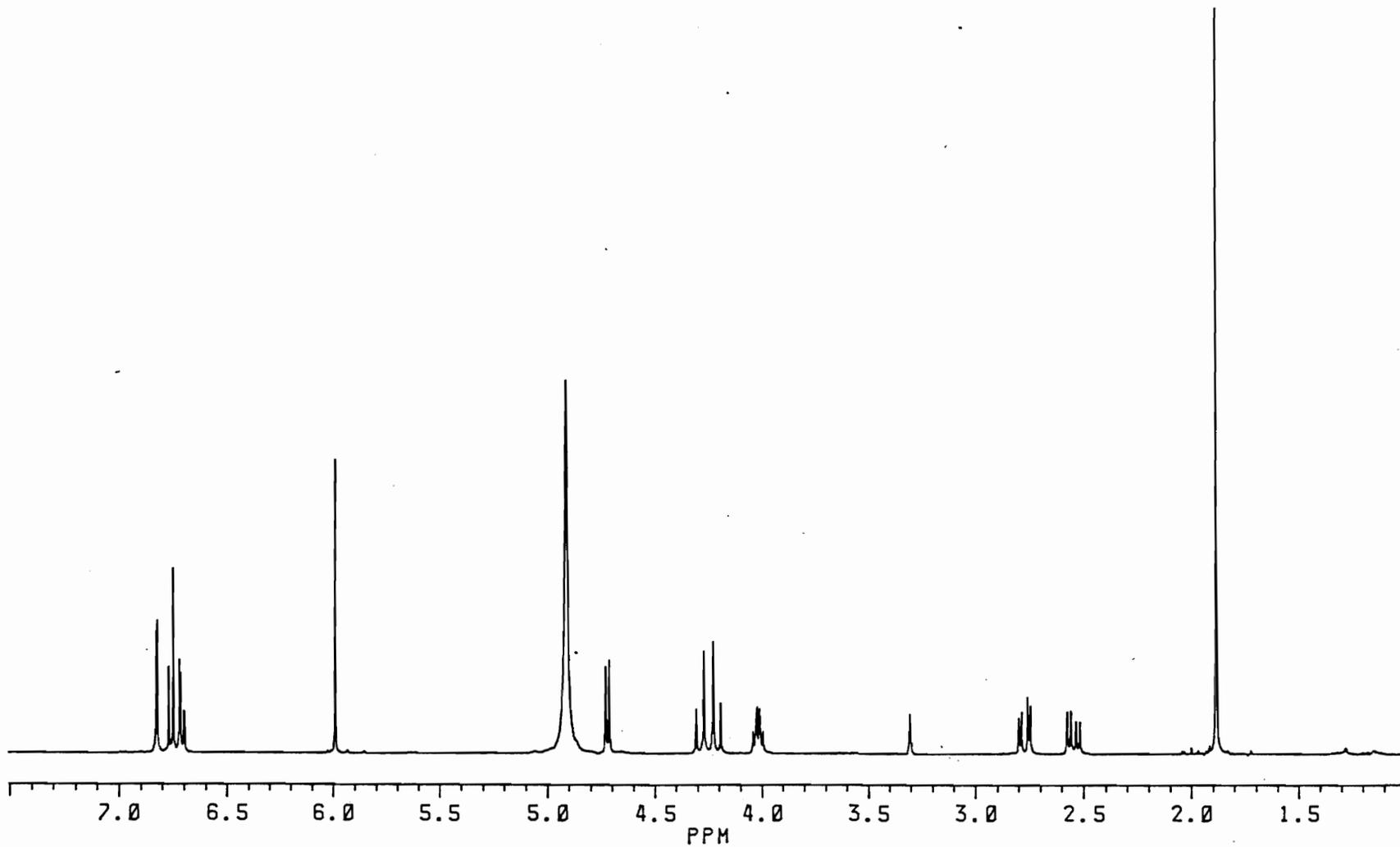


Figure 14. Proton NMR spectrum of Product II.

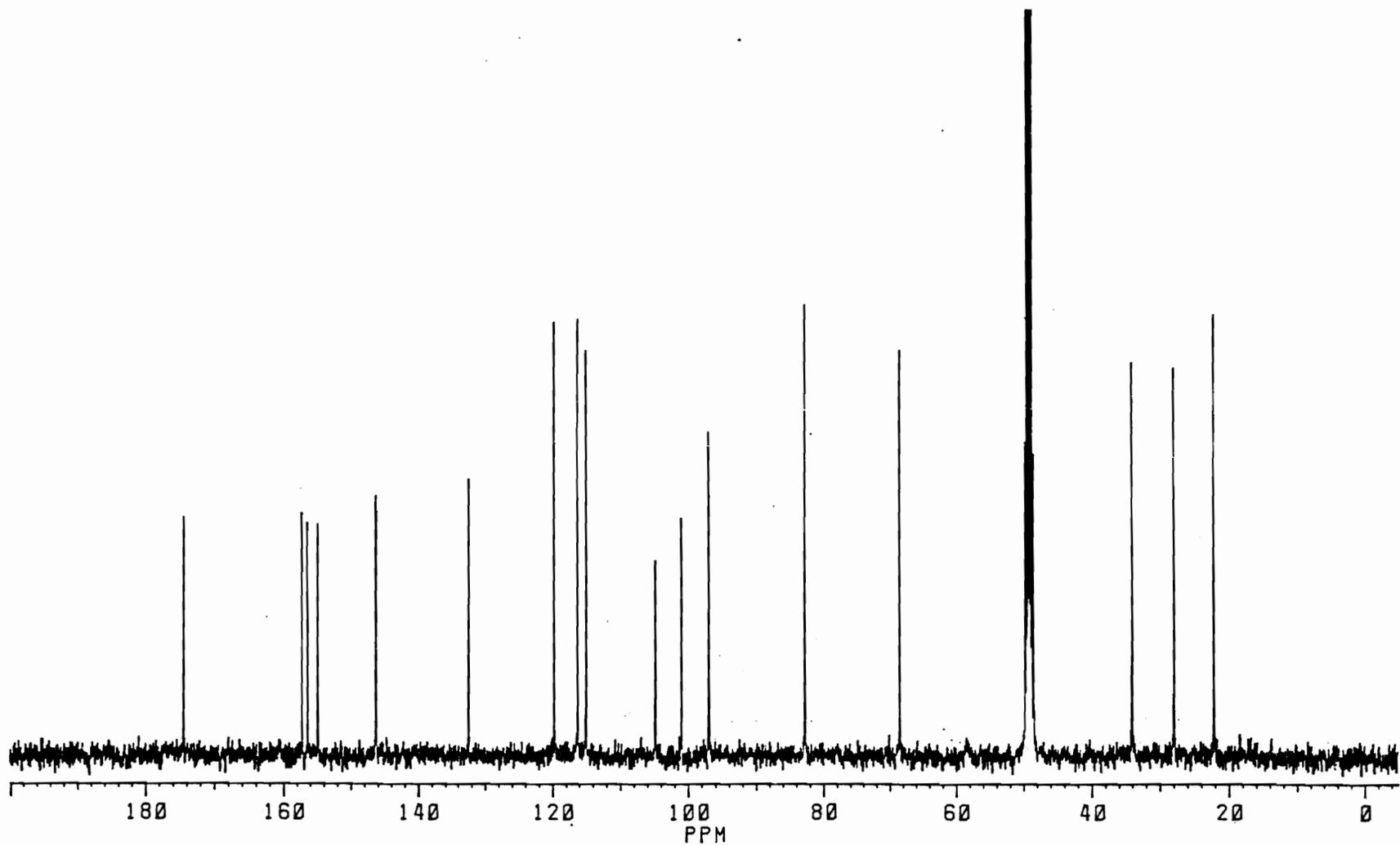
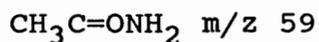
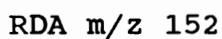
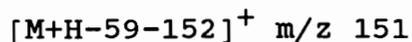
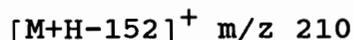
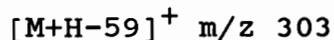


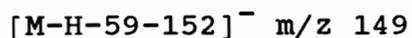
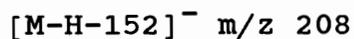
Figure 15. Carbon-13 NMR spectrum of Product II.

The molecular weight of the compound II is 361. The fragmentation schemes for both the negative and positive ion FAB-MS are based on retro-Diels-Alder fission.

In the positive ion FAB-MS, the parent peak is $[M+H]^+$ m/z 362. Others which illustrate the fragmentation scheme are as follows:



The negative ion FAB-MS had a similar fragmentation pattern. The parent peak $[M-H]^-$ is observed at m/z 360. Others in the fragmentation scheme are as follows:



3. 6-Acetamidomethyl-catechin (III)

The second monosubstituted product was the third to be eluted on the Sephadex LH-20 column, with a one-dimensional TLC Rf of .67. The structure is given in Figure 16.

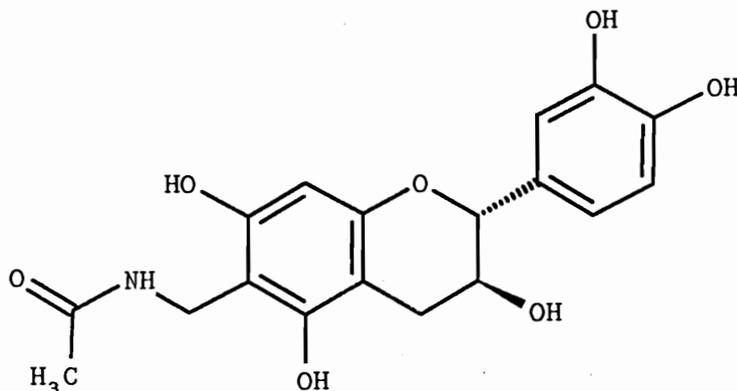


Figure 16. 6-Acetamidomethyl-catechin (III).

The proton NMR of compound III (Figure 17) shows a one proton singlet at δ 5.93, whereas the (+)-catechin standard ^1H NMR shows two peaks at δ 5.94 (H-6) and δ 5.93 (H-8). Again, this indicates that substitution has occurred at either the six or eight position of the A ring of compound III. One peak which appears on the product III ^1H NMR spectrum, but not on the standard (+)-catechin spectrum is a three proton singlet at δ 1.93, which is indicative of the the CH_3 group. At δ 4.24, a single peak can be attributed to the hydrogens of the CH_2 in the substituent. This peak cannot be found on a ^1H NMR spectrum of unreacted (+)-catechin. A listing of assignments is given in Table 2, and a spectrum of the two-dimensional ^1H COSY in the Appendix.

Carbon-13 NMR spectrum for product III (Fig. 18) show peaks at 106.9, 101.7, and 95.6 ppm. The peak at 101.7 can be attributed to C-4a, as it is similar to the shift for (+)-catechin (100.8). The peak at 106.8 ppm is shifted downfield and is an indication of substitution at either the C-8 or C-6. The other peak (95.5 ppm) indicated no substitution. For (+)-catechin, the C-6 and C-8 are at 96.3 ppm and 95.5 ppm, respectively. Additional peaks that are seen on the spectrum of product III but not for (+)-catechin are at 34 ppm (carbon of CH₂) and 21.9 ppm (carbon of CH₃). On both the spectra of product III and (+)-catechin, the peak for C-4 appears at approximately 28 ppm. Additional carbon assignments are listed in Table 3.

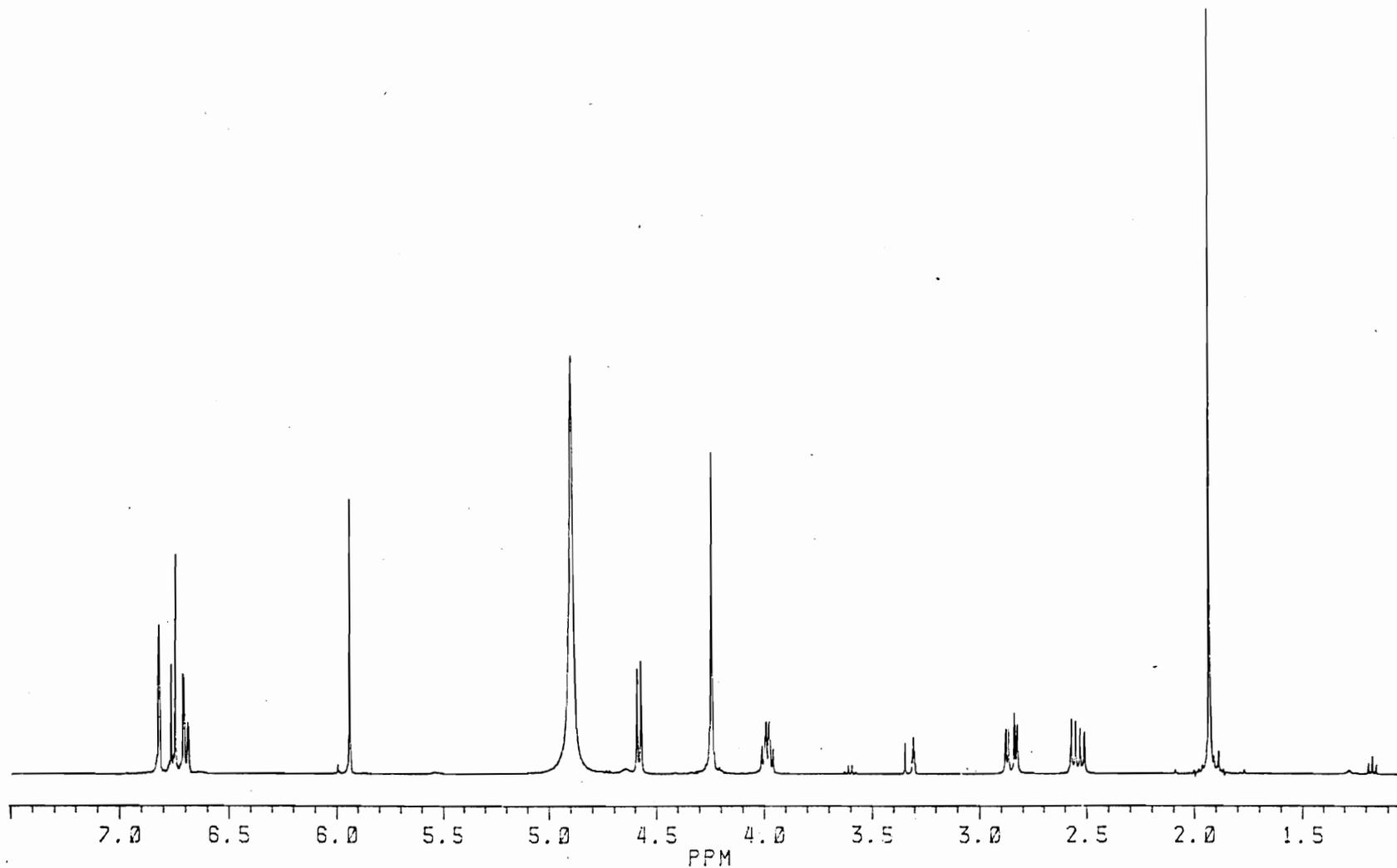


Figure 17. Proton NMR spectrum of Product III.

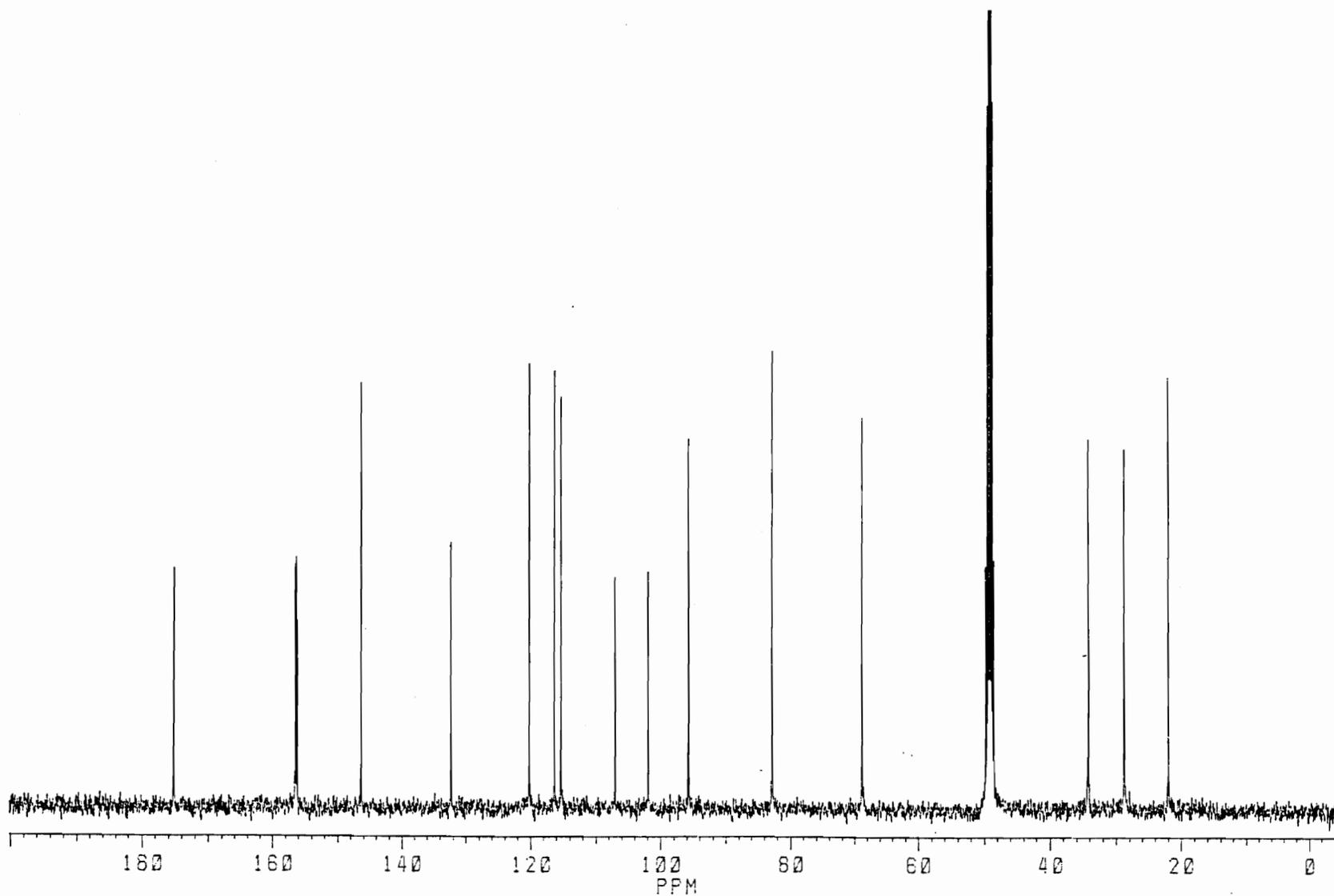


Figure 18. Carbon-13 NMR spectrum of Product III.

The molecular weight of this monosubstituted product is also 361. In the FAB-MS of this compound both $[M+H]^+$ and $[M-H]^-$ ions were observed. As was the case for the other monosubstituted product, the fragmentation schemes for the positive and negative ion FAB-MS are based on retro-Diels-Alder pattern. Both fragmentation patterns are numerically the same as for the other monosubstituted product. Therefore, the only difference is in the structure of each product based on the substitution pattern on the A ring.

B. Pattern of Substitution

In the process of verifying the final structures of the two monosubstituted products (II and III), it was necessary to try to determine the substitution pattern for each. Preliminary indications were obtained from the carbon-13 NMR spectra. On unreacted (+)-catechin, the C-6 is shifted just slightly further downfield at 96.3 ppm than the C-8 at 95.5 ppm. In the product III, the substituted carbon at 106.8 ppm is shifted further downfield than the substituted carbon of product II at 104.8 ppm. The assumption made initially was that product II had been substituted at the C-8 position and that product III had been substituted at the C-6 position.

To obtain more conclusive evidence of the substitution patterns, a type of two-dimensional NMR, called a HET-COSY was performed on both monosubstituted products. This particular NMR utilizes two and three bond C-H coupling interactions.

The spectrum for product II (Figure 19) indicates strong C-H coupling of the protons (4a and 4b) on C-4 with the adjacent carbon (C-4a) as expected. Also there is long distance coupling (two bond) of the axial proton on the C-4 (4a) with the carbon at the two position. The equatorial proton on C-4 (4b) correlates with the adjacent C-3. Both C-4 protons are correlated through long distance coupling with either the C-5 or C-7, but most probably the C-5, since it is two bond coupling. The axial proton on C-4 is also

coupled with the 8a carbon (two bond). This identification is reinforced by the long distance coupling of the 8a carbon through the C ring oxygen of the proton on C-2. The protons on the CH₂-N substituent are coupled with C-8a (154.8 ppm) and C-7 (156.3 ppm). This means that the proton at δ 5.99 is coupled to the C-5 (157.1 ppm) and C-7, and confirms that substitution has occurred at the C-8 position. Figure 20 shows an expanded view in this region. The structure of product II is as previously identified (Fig. 13).

The HET-COSY NMR for reaction product III (Figure 21) had similar final results. However, the spectrum had to be expanded (Figure 22) in the region of the oxygen bearing A ring carbons to establish connectivities. The 8a carbon is the only carbon that can correlate with both the protons at the C-2 and C-4 positions. The 8a carbon was thus established due to the signal at 156.2 ppm, by its dual connectivity to the protons at C-2 (δ 4.58) and C-4 (δ 2.67-2.81). The C-8a signal also shows a connectivity to the proton singlet at δ 5.93, thus establishing that this proton resides on C-8. In confirmation, the CH₂ group protons (δ 4.24) show coupling to the other two oxygen bearing carbons at 156.0 ppm and 156.4 ppm. The carbon at position seven is also established by its long range coupling to the C-8 proton. Thus the signal at 156.0 ppm is due to C-5.

One other characteristic concerning the one-dimensional ¹H NMR's of the monosubstituted products (II and III) merits a brief discussion. For product II, the protons of the CH₂

are magnetically non-equivalent and appear at δ 4.25, ($J=14$) as a doublet of doublets. However, for product III, these protons appear as a singlet and are thus magnetically equivalent. It is not entirely clear at this time why the CH_2 group protons at the C-8 position should be equivalent in the disubstituted product I and non-equivalent in the monosubstituted product II.

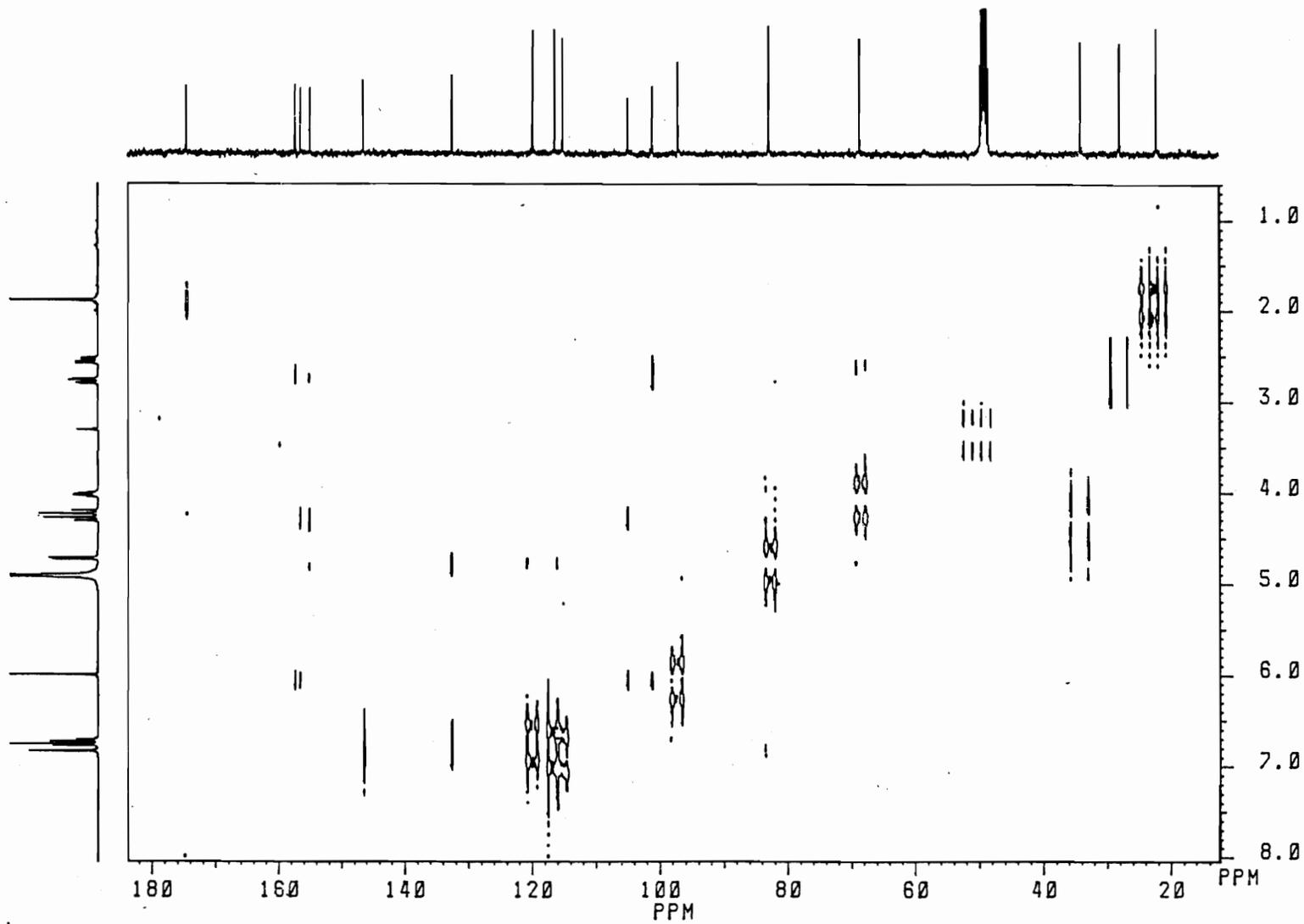


Figure 19. HET-COSY NMR spectrum of Product II.

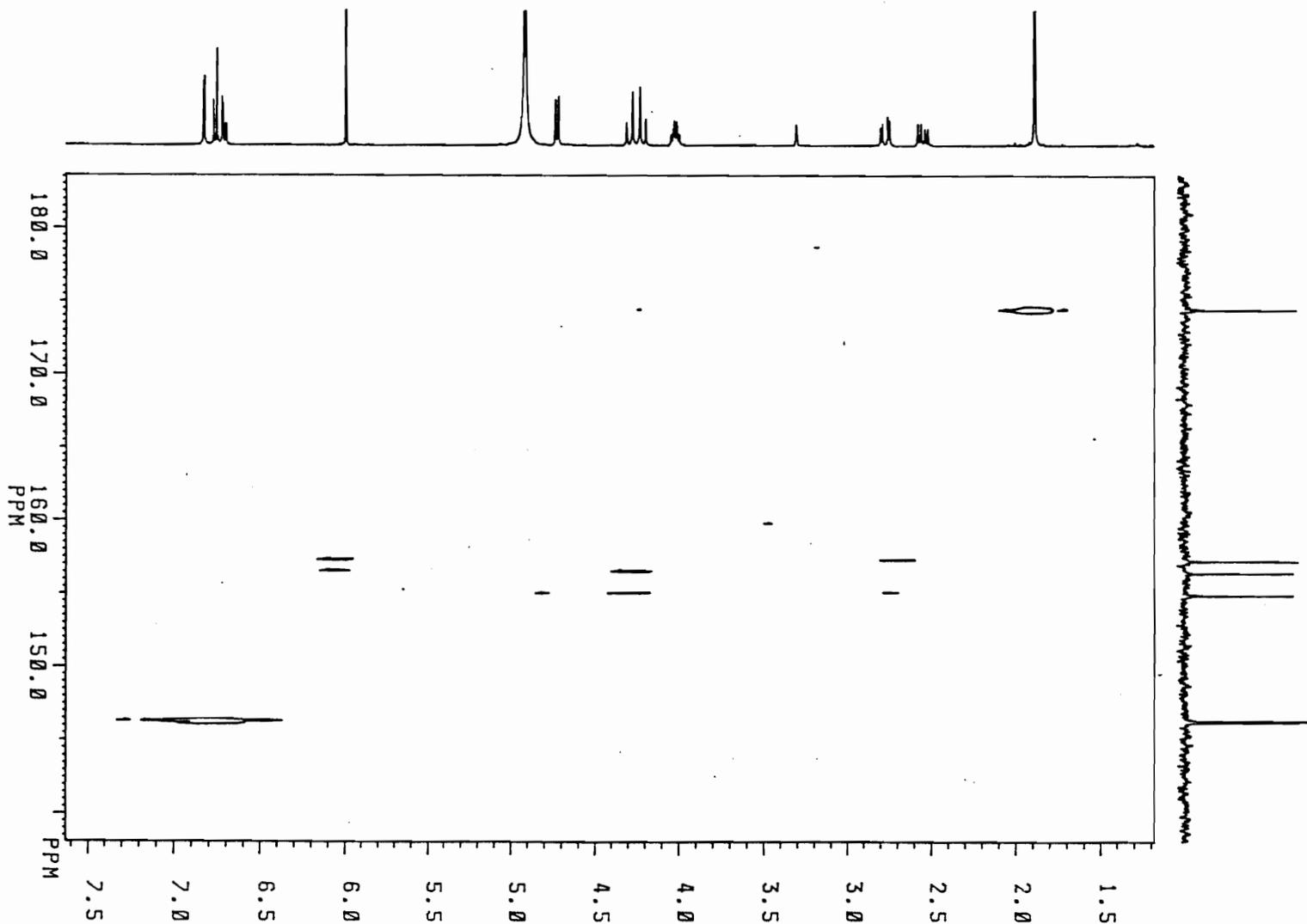


Figure 20. Expanded view of HET-COSY NMR spectrum (Product II).

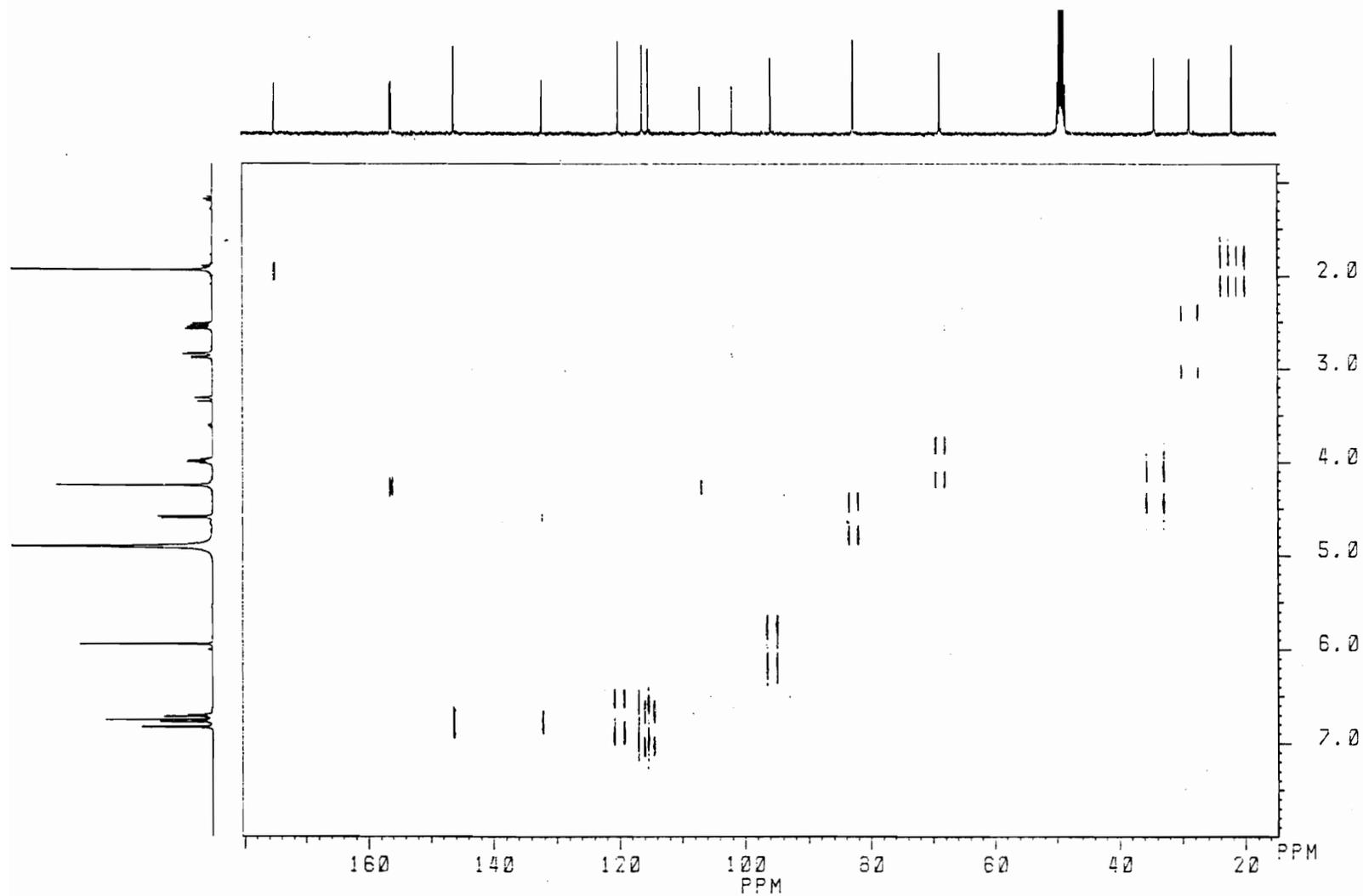


Figure 21. HET-COSY NMR spectrum of Product III.

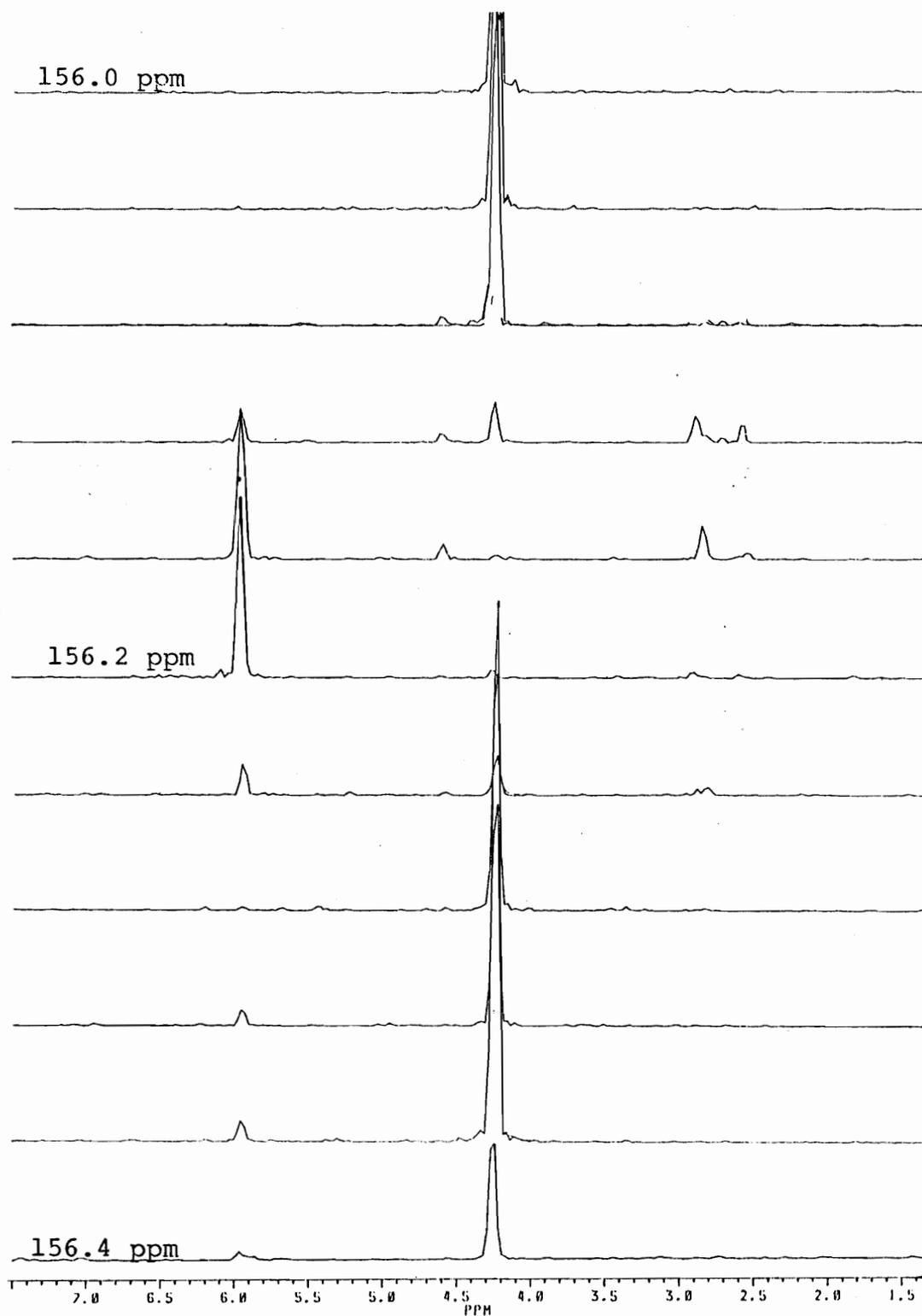


Figure 22. Expanded section of HET-COSY NMR spectrum (Product III).

C. Additional Reaction Products

Other reaction products that were eluted on the Sephadex LH-20 column after the three products of interest and unreacted (+)-catechin are thought to be oligomeric or polymeric in nature. These products were only crudely separated, and as a result, produced more than one spot on the one-dimensional TLC. ^1H and ^{13}C NMR's were run on several of these crudely separated products, but no specific characterizations can be made without further separation. As previously noted, these other reaction products are probably the final products formed by this reaction, and the three that are of primary interest in this research are most likely transient intermediates leading to these polymeric products.

Chapter V

Conclusions

The two model compounds, N-Hydroxyemthylacetamide and (+)-catechin were successfully reacted under acidic conditions. Three reaction products were formed through electrophilic substitution on the (+)-catechin A ring and through to be intermediate in nature. They included one disubstituted and two monosubstituted compounds, and were the ones of primary interest to this research. In addition to these, other products were formed and crudely isolated and thought to be polymeric in nature. Unreacted (+)-catechin was also present.

These products were monitored with TLC and easily separated by column chromatography. Yields were relatively low, mainly due to their transitory nature. However, the low yields also indicated that the reaction was probably not optimized. Identification was readily made by comparing the NMR spectra of the products with those of unreacted (+)-catechin. In addition, the structures were confirmed by using positive and negative FAB-MS in a glycerol matrix, which exhibited characteristic retro-Diels-Alder (RDA) fragmentation patterns.

The most significant results of this research project was that the three reaction products are new compounds, and that the conditions under which they were produced can be used to establish a model reaction. Based on this model

Douglas-fir condensed tannins or their derivatives should react with the cross-linking polyvinyl acetate resins. This would provide a means to form structural polyvinyl acetate adhesives.

Chapter VI

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APPENDIX

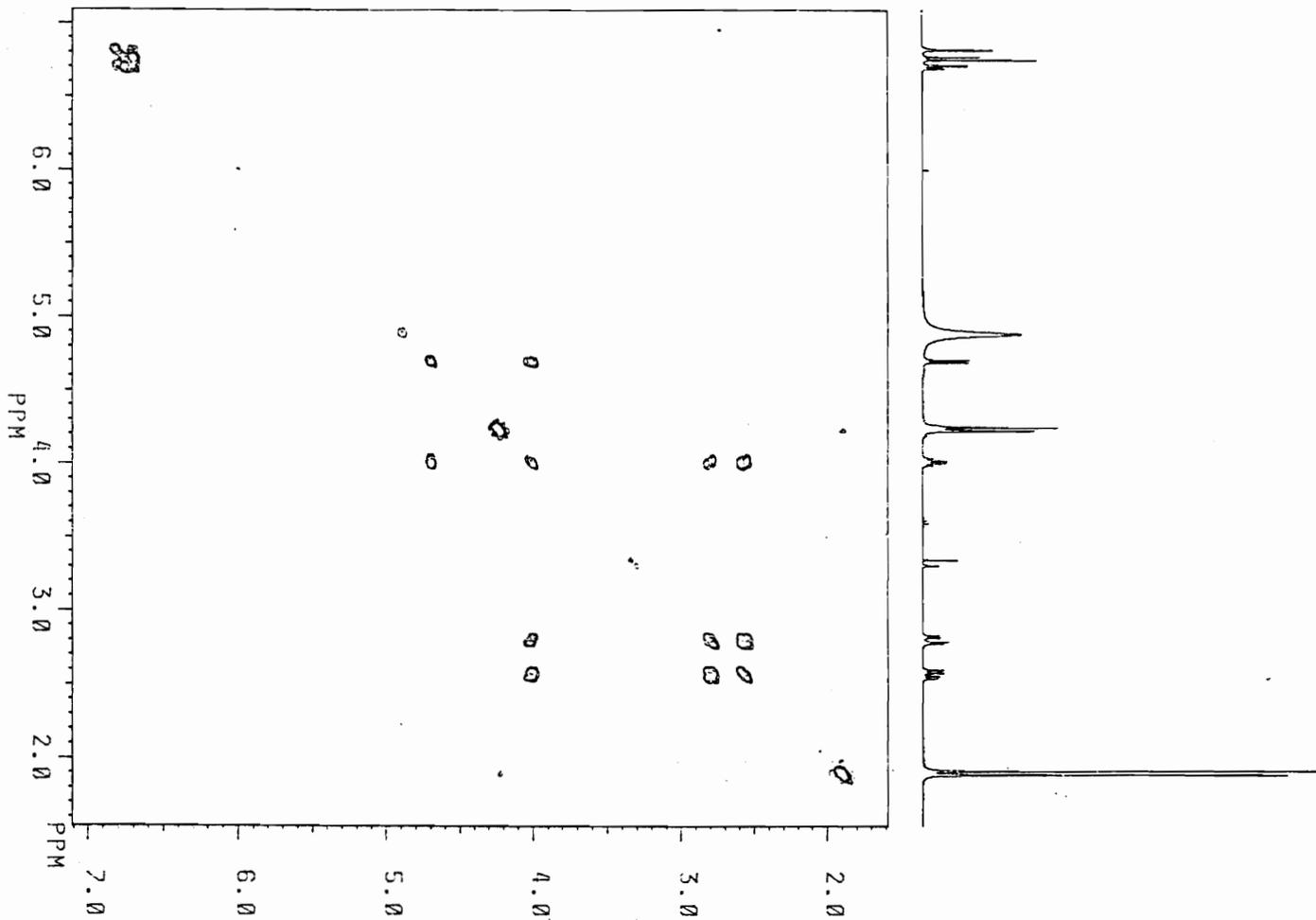


Figure 23. Two-dimensional ^1H COSY NMR spectrum (I).

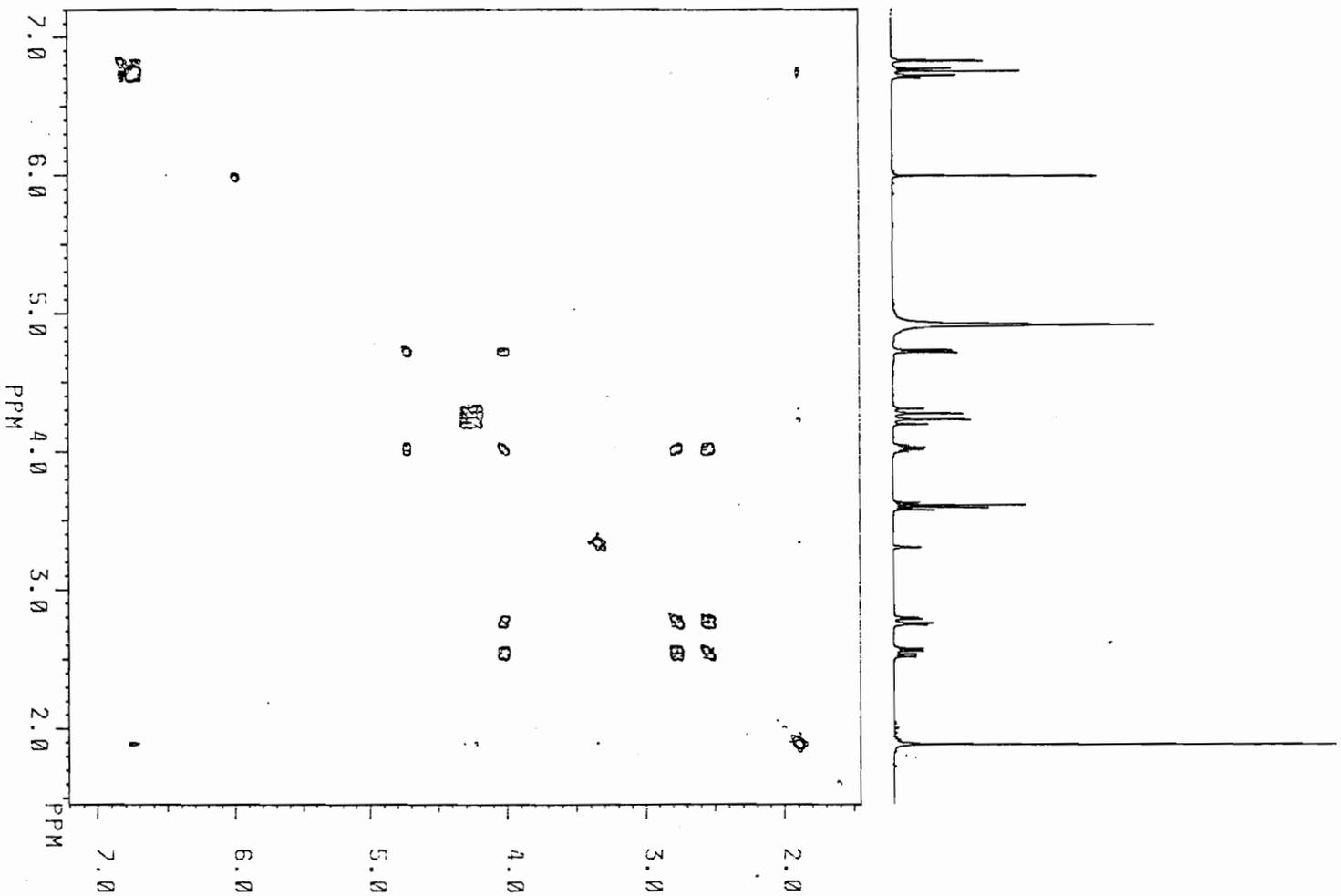


Figure 24. Two-dimensional ¹H COSY NMR spectrum (II).

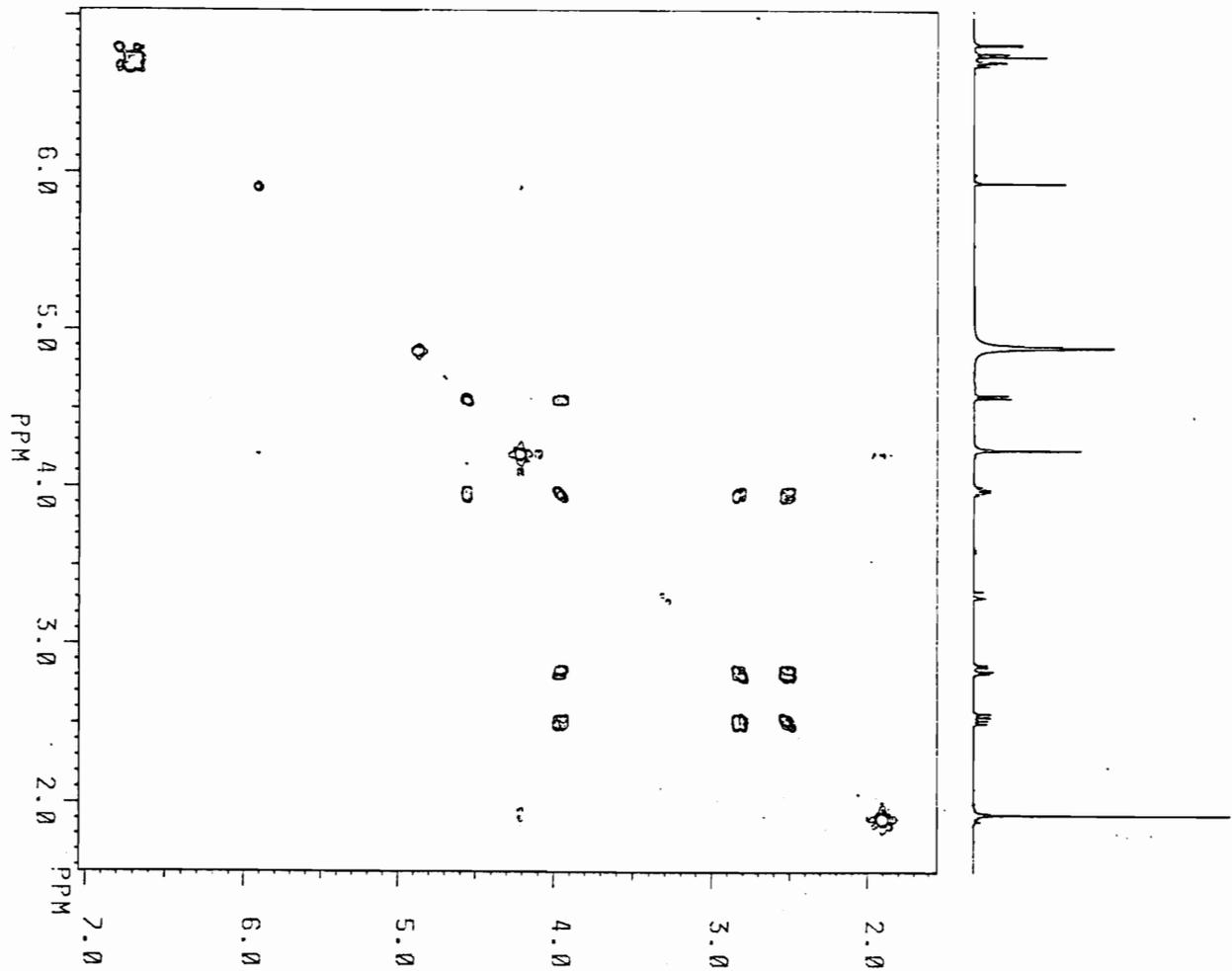


Figure 25. Two-dimensional ^1H COSY NMR spectrum (III).