PLYWOOD ADHESIVES FROM PYROLYTIC OILS?

by

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ABSTRACT

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A major component of a wood pyrolysis oil,i.e., 4-methyl guaiacol was substituted for phenol in a standard phenol-formaldehyde methylolation reaction. The purpose was to prepare an adhesive resin from the reaction products. These products, however, were not suitable for this purpose. Subsequent gas chromatographic analysis indicated the presence of at least three products. One of these was isolated, but mass spectral and proton magnetic resonance analyses suggested that this was not a single product but a mixture of mono- and di-methylolated isomers. This isomeric mixture complicated interpretation of the mass and p.m.r. spectra; however, it was possible to confirm the presence and identities of the various substituents on the 4-methyl guaiacol ring utilizing these analytical tools. These isomers need to be isolated before valid structural analyses may be made. Conclusions were drawn which indicate the direction of future research on this problem.

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This thesis follows the format and style of Wood Science.

INTRODUCTION

"Plywood adhesive" is a term which applies to a variety of substances which are used to bond thin sheets of wood together to form the common construction material known as plywood. Depending on the application of the plywood, different types of adhesives may be used. One type is the reaction product of phenol and formaldehyde. Phenolic resin glues are more expensive than other adhesives and are required for exterior grade plywood where good moisture resistance is essential (Keutgen, 1969).

The first commerical phenolic resin was produced by L. H. Baekeland in 1909. His product, Bakelite, was the first plastic; within a year of the introduction of this substance, adhesives made from phenol and formaldehyde were also put on the market (Gwynne, 1982). Since their introduction, phenolic adhesives have been used most extensively in the manufacture of plywood, a process which also generates much residual material in the form of plywood trim. Trim is usually burned to provide part of a plant's energy requirements, but there are better uses for this material.

Plywood trim as well as other types of wood residue can be physically and chemically altered to yield various organic compounds. One important way this can be done is through a process known as pyrolysis. Pyrolysis involves the thermal degradation of plant tissue in the presence of little or no air. The oil which results from this treatment contains many different organic species. The phenolic constituents comprise about thirteen percent of the whole oil on a gravimetric basis (Elder, 1979). The phenolic fraction of pyrolytic

oils represents a significant and viable alternate source of phenol for the preparation of phenolic based adhesives. Why is such an alternative necessary? From an industrial point of view, the economics of such a recycling scheme are very attractive. Plywood manufacturers are the largest consumers of phenolic adhesives, and they have to purchase their adhesives from chemical manufacturers. Such dependence is not desirable from the standpoint of the forest products industry. Another problem this industry faces is the dwindling supply of wood. As the land base on which to grow trees shrinks each year, and the demand for forest products increases, the industry will have to phase out the wasteful practices of the past and orient itself toward highly efficient utilization schemes. In order for the forest products industry to match growing demand, it will have to grow more trees on less land and insure the complete conversion of the whole tree to useful goods.

Pyrolysis is one of the keys to solving these two problems. When plywood trim (and other residues) can be pyrolyzed commercially and the phenolic fraction effectively isolated and processed, not only will plywood plants be able to supply a large fraction of their energy needs, but they will be self-sufficient with respect to their phenol needs as well.

How then can plywood adhesives be prepared using the phenolics found in pyrolytic oils? Two general alternatives may be presented. It is the purpose of this paper to describe one of these possibilities, but I will briefly mention the second choice also.

The phenolic components of pyrolytic oils are variously substituted aromatic structures. The component with which I am primarily concerned,

4-methyl guaiacol (4MG), is a tri-substituted single ring structure. The major goal of my research was to substitute 4MG for phenol in the basic reaction with formaldehyde and overcome the interference of the ring substituents, thus adding the hydroxymethyl group ($-CH_2OH$) to all open ring positions.

Two approaches to the problem were considered. First, the reaction conditions could be changed to force the desired substitution. The second approach involved a structural change of the starting material (4MG) to make it more receptive to the methylol ($-CH_2OH$) group. The first approach was adopted in the present research. Before detailing this research, a review of the pertinent literature will be made.

LITERATURE REVIEW

The general reaction of phenol and an aldehyde under acidic conditions was first reported by Baeyer in 1872. He found that phenol and acetaldehyde combined in the presence of an acid catalyst to yield and unmanageable resinous mass. Michael (1883-84) reported that alkalies would also catalyze the reaction. In 1891, Kleberg used formaldehyde in the reaction with phenol. Working independently, Lederer and Manasse (1894) reported that they had been able to synthesize a mono-substituted hydroxymethylated phenol known as saligenin, by a low temperature alkaline phenol-formaldehyde reaction. Smith (1899) was granted the first patent for a phenolic resin product when he described a method for a cast cured resin substitute for hard rubber (Keutgen, 1969).

L. H. Baekeland began working with phenol and formaldehyde in 1905, and by 1907 he had defined the differences between acidic and alkaline catalysis and between the use of more than and less than one mole of aldehyde per mole of phenol well enough to be able to manufacture reproducibly a thermosetting resin. He also conceived the use of counterpressure during hot cure to prevent bubbling and foaming from heat that had plagued all previous attempts to make a stable, solid, strong, cured resinous substance. Baekeland showed that with an excess of formaldehye in the reaction mixture the end product was heat reactive with either acid or alkaline catalyst but that it was controllable only with the alkaline catalyst. He defined three stages of the reaction as follows: (1) the initial or A stage in which the polymer was either liquid or dehydrated to a solid but soluble in simple organic solvents and fusible; (2) the second or B stage in which the resin was solid,

insoluble but swelled by solvents and infusible but softened by heat; and (3) the C stage in which the resin was infusible, insoluble, and not softened with heat or swollen with solvent, i.e., the resin was cured. Baekeland proposed a chemical formula for his resin, but it was not until the efforts of Kienle (1930) that a correct structure was elucidated for the cross-linked polymer (Keutgen, 1969).

Kienle (1930) developed three postulates which describe the reaction of phenol and formaldehyde: (a) high-molecular-weight organic compounds are formed only when the interacting molecules have more than one reactive site; (b) the interlinking of the molecules proceeds according to chance contact of any two individual reactive points; and (c) the relative size and shape of the reacting molecules and the position of the reactive points largely determine the physical properties of the resulting polymer, e.g., hardness, flexibility, or heat convertibility. Formaldehyde has a functionality of two (two reactive sites) and phenol has a functionality of three. Phenol will react at the position para to the hydroxyl group and the two positions ortho to the hydroxyl. The two meta positions will react only under severe conditions not generally found in resin reactions and can be considered inactive. Thus phenol and formaldehyde can react to a three-dimensional cross-linked polymer (Keutgen, 1969). The general reaction of phenol and formaldehyde is shown in Figure 1. The cross-linking of the phenol alcohols is shown in Figure 2.

The reaction shown in Fig. 1 involves the addition of formaldehyde (CH_2O) to introduce the hydroxymethyl group ($-CH_2OH$) and is known as hydroxymethylation or methylolation. The synthesis is carried out with

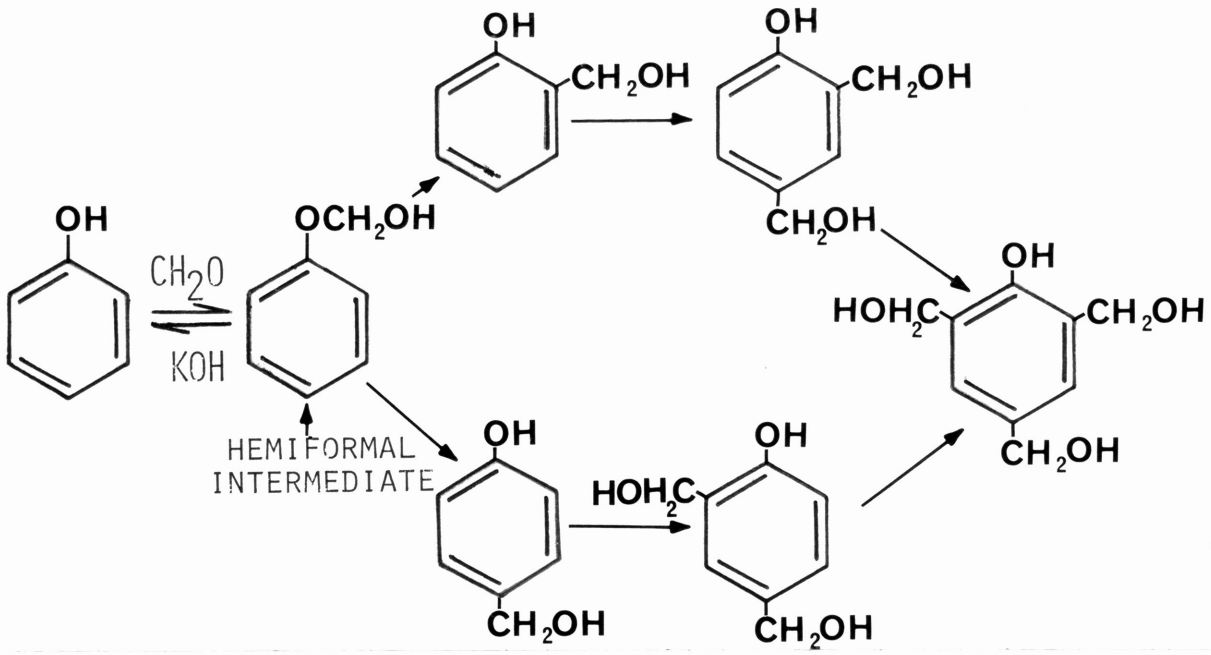


FIG. 1. GENERAL FORMATION OF PHENOL ALCOHOLS INVOLVING THE UNSTABLE HEMIFORMAL INTERMEDIATE (MARTIN, 1956).

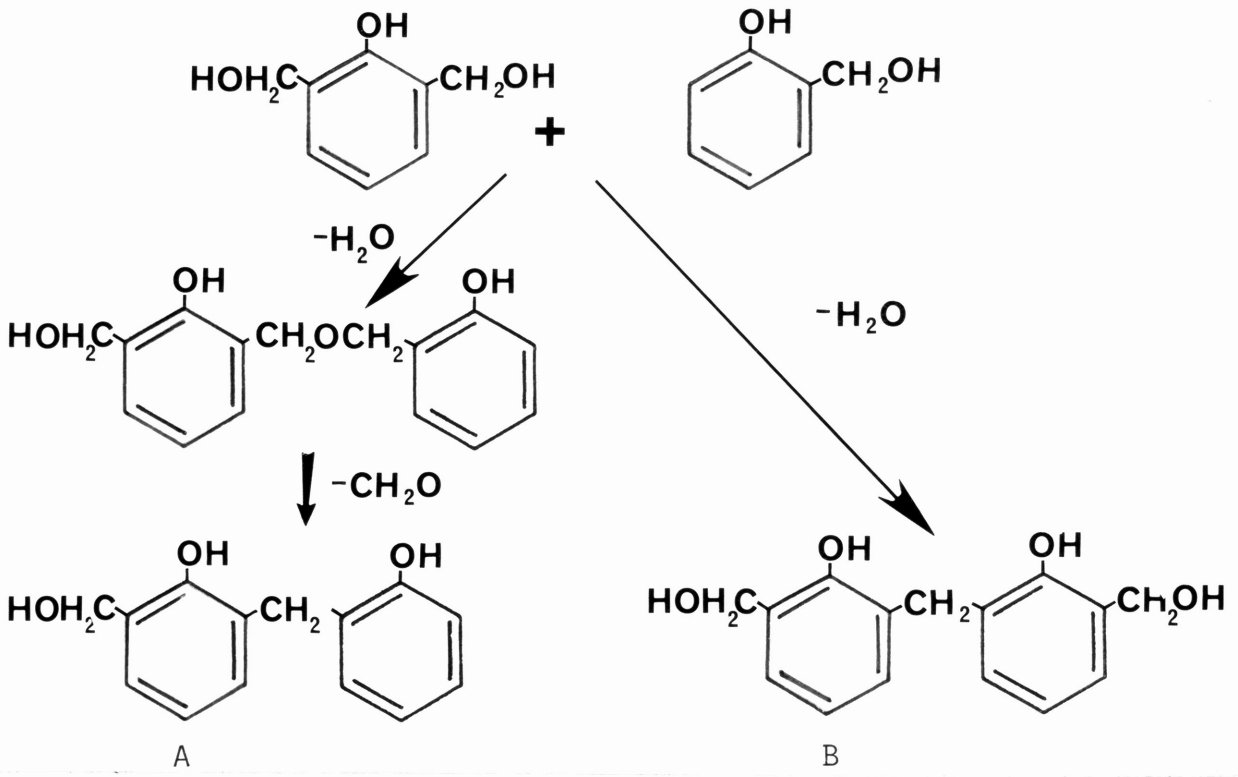


FIG. 2. (A) CONDENSATION OF ETHER LINKAGES RELEASING FORMALDEHYDE. (B) METHYLENE BRIDGE FORMATION LIBERATING WATER. (ELDER AND SOLTES, 1979)

an excess of formaldehyde in the presence of an alkaline catalyst. The complexity of the reaction is demonstrated by the fact that there are at least fifteen unique reaction pathways and the extent of these is determined by the structure of the original phenol, the temperature at which the reactants are heated, and the time of heating (Carswell, 1947). Megson and Hollingdale (1955) reported that for the average polymer of eight phenol rings there exist 1,485 unbranched isomers and approximately 12,000 isomers when branching is possible (Keutgen, 1969).

An accepted mechanism for the reaction shown in Fig. 1 involves the addition of formaldehyde to the hydroxyl group of phenol with the subsequent tautomeric rearrangement of the unstable hemiformal yielding a mono, di, or tri-substituted phenol alcohol (Carswell, Keutgen, Martin, and Updegraff and Suen). The phenol alcohols (methylol derivatives) condense through ether linkages with the liberation of formaldehyde or through methylene bridges with the release of water (Fig. 2) (Elder and Soltes, 1979). The monomers and dimers formed will continue to react with further heating and the average molecular weight of the resin will increase. The reaction can be stopped at any point by cooling (Keutgen, 1969).

At this point, a distinction should be made between conducting the reaction with molar ratios of phenol to formaldehyde of less than 1:1 and greater than 1:1. With an acid catalyst, one mole of phenol, and one or more moles of formaldehyde, an uncontrollable reaction occurs. If less than one mole of formaldehyde is used a controllable reaction ensues. With an alkaline catalyst, one mole of phenol, and one or more moles of formaldehyde a controllable one-step resin results. If less

than a mole of formaldehyde is used, the reaction is controllable but the degree of substitution is not adequate. This distinction is made clear in Table 1.

Table 1. General Types of Phenolic Resin*

Catalyst type	One mole phenol, one or more moles formaldehyde	One mole phenol, less than one mole formaldehyde
acid	uncontrollable	controllable novolac
alkaline	controllable one-step resin	highly ortho-substituted novolac

* (Keutgen, 1969)

My research deals only with the case in which the catalyst is alkaline and the molar ratio of phenol (or model) to formaldehyde is greater than 1:1. Subsequent discussions will treat only this specific situation.

The general reaction shown in Fig. 1 occurs at pH 8 and above. That these single-ring phenol alcohols are the simplest of the initial products has been shown repeatedly, from the work of Lederer and Manasse to the pioneering paper chromatographic techniques of Freeman (1952) and the isolation from more recent experiments by Zavitsas (1966-67) using the gas chromatographic techniques of Higgenbottom, Culbertson, and Woodbrey (1965). Evidence to support the formation of the unstable hemiformal intermediate (Fig. 1) was provided by Woodbrey, Higgenbottom, and Culbertson who utilized proton magentic resonance spectroscopy (p.m.r.) to detect the benzyl hemiformal during the early stages of

resinification (Keutgen, 1969).

The phenol-formaldehyde reaction and its commercial significance are well established; however, phenol is not the only compound that will react with formaldehyde to yield a resin. Various poly-substituted phenolic structures such as 3,5-dimethylphenol, 2,4-dimethylphenol, and m-cresol are more reactive than phenol and readily react with formaldehyde (Keutgen, 1969). Other less reactive compounds include 3, 4-dimethylphenol, 2,5-dimethylphenol, p-cresol, and o-cresol. The relative reactivities are determined by the type of substitution and the nature of the substituents on the phenolic ring. Substitution at the ortho or para positions tends to deactivate the ring to about one third of its original reactivity. Activating substituents at both meta positions (3,5-dimethylphenol) reinforce the reactivity of the ortho and para positions (Keutgen, 1969).

Another substantially less reactive compound than phenol is 4-methyl guaiacol (4MG); it is a major component of pyrolytic oils (Elder, 1979 and Elder and Soltes, 1979). The structure is shown in Figure 3. The substituents at carbons two and four block the addition of any groups ($-CH_2OH$) to these ring positions. The methyl group ($-CH_3$) directs substitution at ring positions ortho and para to itself, but the hydroxyl group (-OH), which is also an ortho-para director, overrides the direction of the methyl group because the -OH is a much stronger ring activating group. Therefore, substitution of 4MG may occur at any of the open positions, but the most reactive site is carbon six.

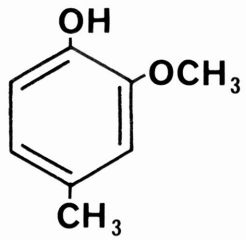


FIG. 3. STRUCTURAL FORMULA OF 4-METHYLGUAIACOL

In order to produce an adhesive resin from 4MG, the $-CH_2OH$ group must be added to all available ring positions. Without tri-substitution, the methylol derivatives of 4MG cannot cross-link to form a three-dimensional polymer. With di- and mono-substitution, condensation will occur but the products will only be dimers and linear polymers. Again, these types of products are not suitable for producing an acceptable adhesive resin, but because of the nature and the degree of substitution of 4MG, the potential for forming the tri-substituted methylol derivative justifies the use of 4MG as a model in my research.

METHODS AND MATERIALS

Synthesis of Methylol Derivatives

The synthetic procedure utilized in the research was taken from Sorenson and Campbell (1961) and modified as necessary. The original procedure called for reacting 94 grams distilled phenol (1 mole) with 123 grams of formalin (1.5 moles formaldehyde) solution and 4.7 g barium hydroxide octahydrate as the alkaline catalyst. The reaction time was specified as 2 hours, and the reaction mixture was maintained at 70°C. in a three-necked round bottom flask fitted with a reflux condenser, stirring bar, and thermometer. The heat source was an oil bath placed on top of a stirrer-hot plate. After the 2-hour reflux the pH was adjusted to 6-7 with 10% sulfuric acid. Ten percent hydrochloric acid was also used to lower the pH and reduce precipitation of barium salts (barium chloride is more soluble than barium sulphate). With the pH at 6-7 the reaction mixture was dehydrated under a vacuum of 30-50 mm Hg and at a temperature of not greater than 70°C. One to two milliliter samples were withdrawn every 15 minutes and tested for gel time; by working with a spatula on a hot plate at 160°C., gel time was taken as the time required for the resin to set up to a rubbery infusible solid. The dehydration was stopped when the gel time was less than 10 seconds. The phenol source was reagent grade crystals obtained from MCB Manufacturing Chemists, Inc. The formaldehyde was in the form of the aqueous formalin solution which is 36% formaldehyde by weight. The formalin and barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) were also obtained from MCB.

The original reaction of phenol and formaldehyde was repeated so that a general synthetic framework could be established. In effect this reaction served as a control. The changes made during the course of the research involved increasing the molar ratio of phenol to formaldehyde (greater than 1:1.5), increasing the pH of the system (using more or stronger base), lengthening the reaction time, and increasing the reaction temperature.

In following the original procedure to the letter, some problems were encountered in obtaining a resin that would set up properly. The problems were never clearly defined, but the consensus was that the barium hydroxide was not sufficiently alkaline for our needs; therefore, a stronger base (potassium hydroxide, KOH) was used in place of the $Ba(OH)_2$. This solution seemed adequate because a suitable resin with an acceptable set up time was produced. The original molar ratio of phenol to formaldehyde was maintained at 1:1.5, but rather than using 4.7 g of $Ba(OH)_2$, six times the molar equivalent of KOH to this quantity of $Ba(OH)_2$ was used. This quantity was determined by trial and error. The gel time of the resin prepared with this amount of base was 18 seconds--not quite the desired set up time, but it was the best attainable under the given circumstances. One problem with using that much KOH was the precipitation of potassium chloride (KCl) salt during the dehydration step. This problem was a constant annoyance, but the presence of the KCl did not appear to adversely affect the set up of the resin.

Another modification of the original procedure was the application of quantity reduction ratios designed to maintain original molar proportions but reduce the quantities of the reactants so that smaller

samples could be prepared with minimum waste of materials. These reduction ratios were quite necessary when the reaction was carried out with 4MG because only limited quantities of this reagent were available.

The 4MG used as the substitute for phenol in the basic reaction was purchased from Pfaltz and Bauer, Inc. The molecular weight of 4MG is 138. One sixteenth of this weight in grams (8.62g) was reacted with 7.82 g of formalin; the reaction was catalyzed with 5 ml of saturated KOH. The reaction time ranged from 2.5- 3.0 hours, and the reaction temperature was maintained at about 70°C. These reaction conditions were the most extreme.

Analysis of Methylol Derivatives

Sample Preparation for GC Analysis

The methylol derivatives of phenolic compounds are not sufficiently volatile or stable to be analyzed with gas chromatography (g.c.). To enhance separation of the various reaction products on the g.c., these products (methylol derivatives) must be derivatized again. In the present research, two derivatizing schemes have been employed.

An acetylation procedure is one of these. The method was borrowed from Higgenbottom et al. (1965) and involves the freeze-drying of aqueous samples under neutral conditions and the subsequent acetylation with acetic anhydride and pyridine as the catalyst. For details of this and the the alternate scheme the reader is referred to the Appendix.

The other derivatizing method is adapted from one proposed by Cooper and Wheatstone (1973). This procedure involves the extraction of the aqueous methylol derivatives from the reaction mixture with methyl

iso-butyl ketone and then silylating these with bis-trimethyl silyl trifluoroacetamide (BSTFA). See the Appendix.

The acetylation procedure involves more work than the silylation method, but the latter is not as well established in the literature as the former. Both methods were valuable depending on the type of analysis made. If retention times (on g.c.) could be easily established for reactants and products using standard compounds, then the silylating procedure was adequate. If the analysis had to be done without reference compounds, the acetylation scheme was appropriate because the retention times of the participating species and their reaction products were well established in the literature. In other words, the silylating scheme was used for preparing the methylols derived from 4MG, and the acetylation procedure was used for derivatizing the methylols obtained from phenol.

Another difference between the two methods which may prove to be important is the extraction sequence. In the acetylation procedure the acetate derivatives are formed first and then the extraction is made. The silylation procedure involves first an extraction of the crude methylols and then the derivatization. The acetates of the higher molecular weight methylols may be more extractable with ether than are the corresponding crude methylols when MiBK is the extraction solvent. Therefore, derivatization prior to extraction might yield more of the "heavier" methylols than extraction prior to derivatization. This possibility should be considered and studied further.

Analysis of Methylols on the G.C.

The gas chromatograph used for the analysis of the methylolation reactions was a Tracor 560 fitted with a flame ionization detector. The

column utilized was an SE-54 glass capillary column. The inside coating of the column (stationary phase) was 94-5-1 methyl phenyl (vinyl) silicone. Helium was used as the carrier gas at a pressure of 20 p.s.i. Oven temperature was programmed to range from 60°C. to 280°C. at a rate of 5°C. per minute with a three minute initial hold.

Preliminary separations made on the g.c. were qualitative in nature and entailed the noting and recording of retention times of the various components of the reaction mixture. When the standard recorder was used, the retention times were determined from the chart speed (0.5 cm/min.) and the calibration marks on the chart paper. When the computing integrator was employed (Spectra Physics 4100 Computing Integrator), the retention times were displayed next to corresponding peaks and also in tabular form in the report at the end of the run. Retention times were used to identify component peaks.

Along with the retention times were listed the areas and area percents of the component peaks. These areas were used in various computations (both by machine and operator) to determine the relative and absolute concentrations of the various components. One type of computation was the internal standard method. This method was tried by the researcher but was not really needed because comparison of relative peak areas was all that was necessary for the type of preliminary quantitative analyses being performed. Disappearance of reactants and appearance of products could easily be followed by noting the decrease or increase in area of the corresponding peaks.

Data for the quantitative analyses was worked up in the following manner. The reactant peaks were identified by running

derivatized samples of the reactants on the g.c. and noting the retention times. Peaks corresponding to major products were also identified by the process of elimination. Internal standard peaks were identified and calculations were made relative to these peaks. The relative proportions of reactants and products to the total was determined by adding the areas of all peaks and dividing into peak area(s) of interest. The percent conversion of 4MG to products was determined by the equation:

$$\% \text{ conversion} = \frac{\text{Sum of product peaks x 100}}{\text{Sum of all peaks}}$$

The reaction products were redissolved in the extraction solvent (MiBK) and "recrystallized" by evaporating off the solvent. Actually, the recrystallization resulted in a semi-solid residue. This residue was again dissolved in the solvent and derivatized with BSTFA reagent. The sample was analyzed on the g.c. to determine its purity. Some of the semi-solid residue was submitted to the Center for Trace Characterization (courtsey of John Efimenko) for a mass analysis. The instrument utilized was a Hewlett-Packard 5980A mass spectrometer interfaced with the H-P 5933A Data System. The product was also analyzed by proton magnetic resonance spectroscopy and the instrument used was the Varian XL 200 Superconducting NMR spectroscope (courtesy of Trish Klahn and Dr. Silbur, Chemistry Department). The operating frequency of the XL 200 was 200 MHz. A structural determination of the product and a confirmation of the mass spectral (m.s.) analysis was the purpose of this study.

RESULTS AND DISCUSSION

Results of G.C. Analysis

Separation of the crude aqueous products of the reaction of phenol and formaldehyde was hampered by the nature of these compounds. A typical chromatogram is shown in Figure 4. Because of low volatility and general polarity, the variously substituted methylols tended to elute from the column in groups. The two peaks shown in Fig. 4 represent two such groups. This clustering necessitated derivatization as described earlier. Initially it was hoped to be able to separate the products with minimum modification of the reaction mixture, but this was not possible.

After extraction of the crude methylols with MiBK separation was a little better but still not satisfactory. The improved separation is shown in Figure 5. Here three major peaks are present. The derivatized MiBK extracts are shown in Figure 6. This figure shows that six products were resolved as compared to only two shown in Figure 4.

The alternate (actually original) acetylation procedure provided for a fine separation of products as can be seen in Fig. 7a. The reference chromatogram found in the literature (Higginbottom et al., 1965) is shown in Fig. 7b. The assignments made for the peaks in Fig. 7a should be considered tentative because there was not an exact matching of analysis conditions or equipment with the original research. The utility of the two chromatograms stems from a comparison of relative retention times within an analysis and a general contrasting of trends

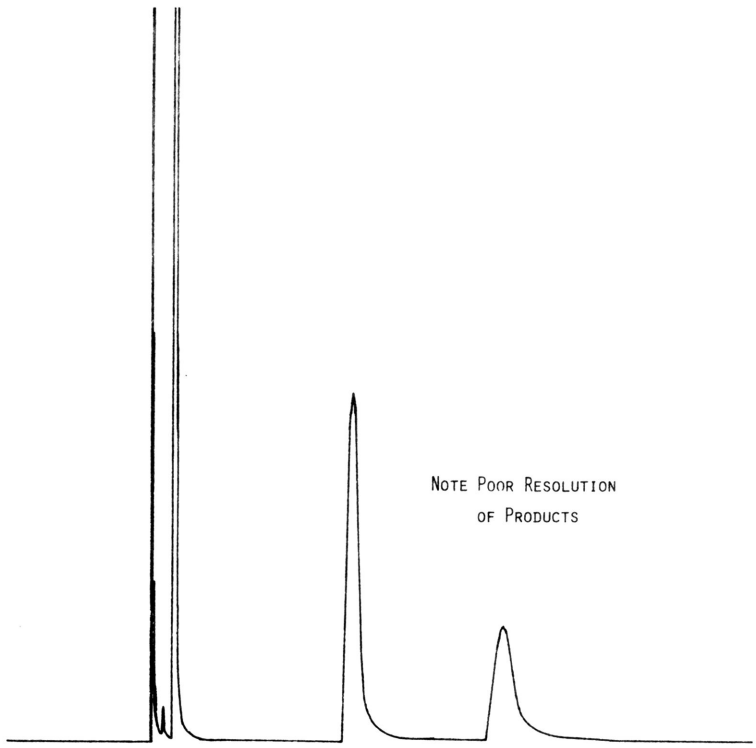


FIG. 4. Crude Aqueous Methylol Derivatives

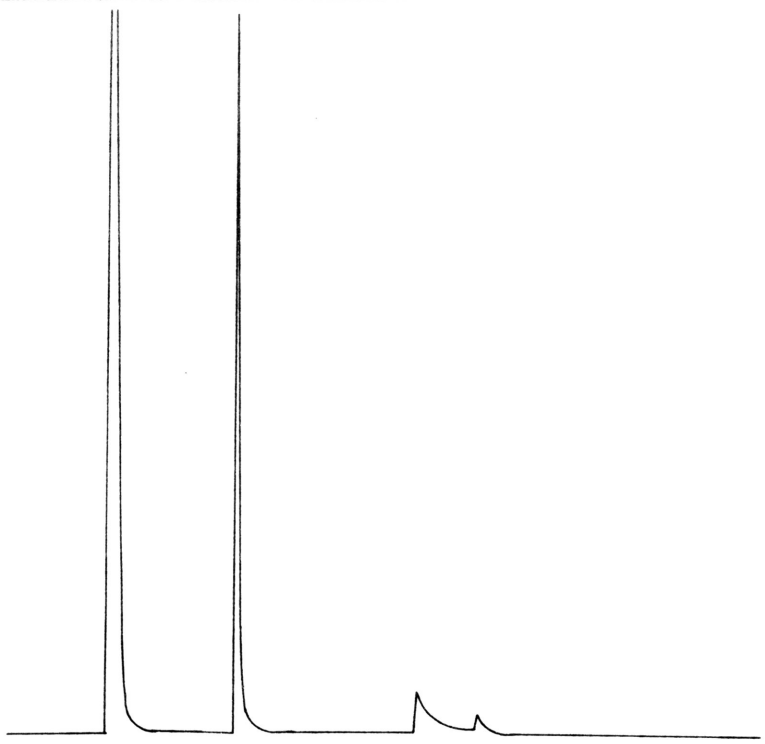


FIG. 5. Crude Methylol Derivatives Extracted with Methyl-iso-butyl Ketone

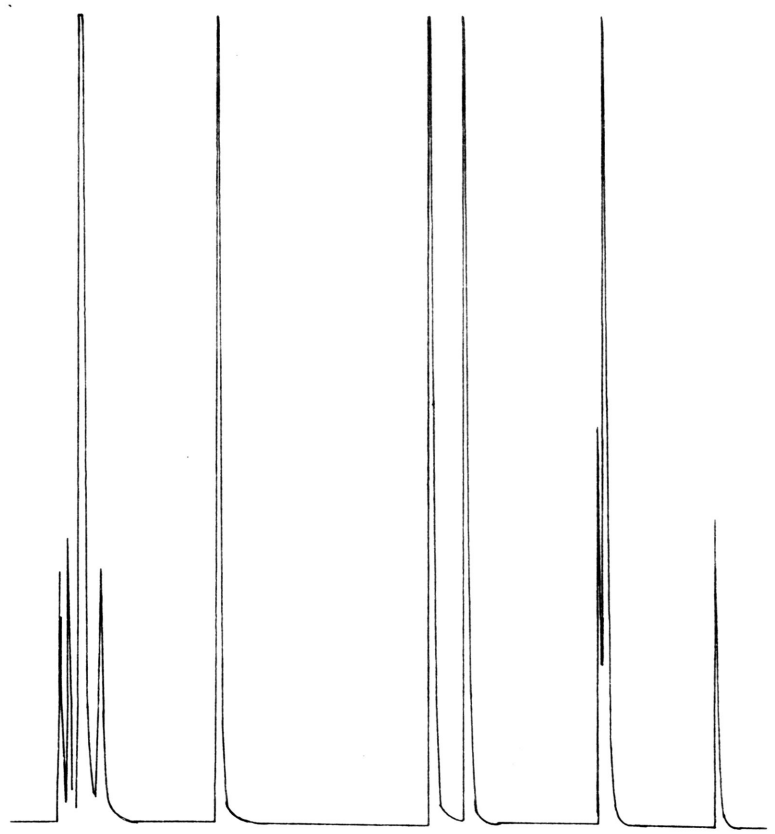


FIG. 6. BSTFA DERIVATIVES OF MIBK EXTRACTED METHYLOLS

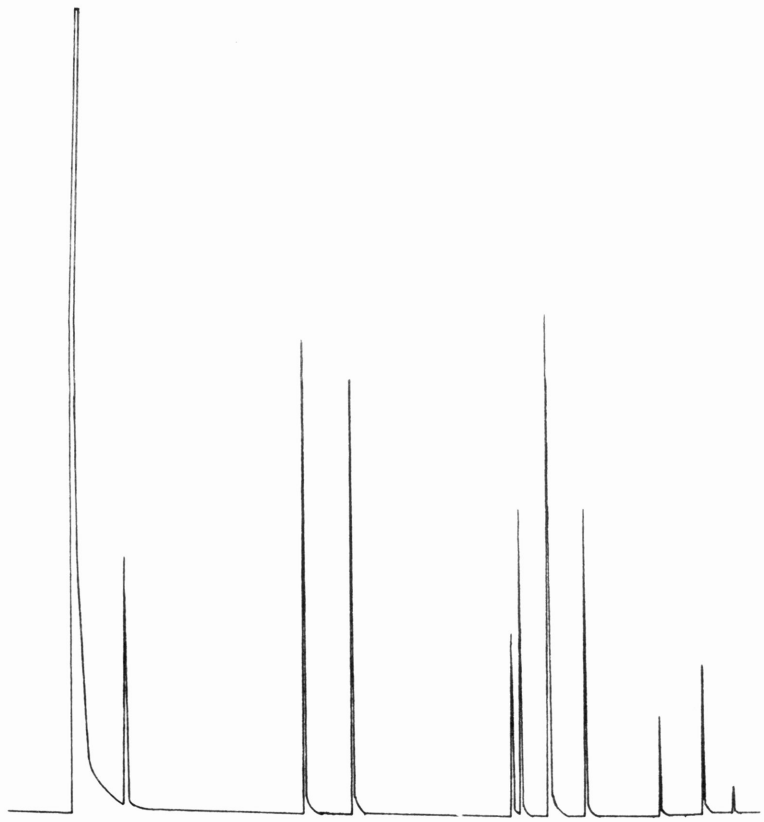


FIG. 7A. ACETATE DERIVATIVES OF AQUEOUS METHYLOLS IN ETHER

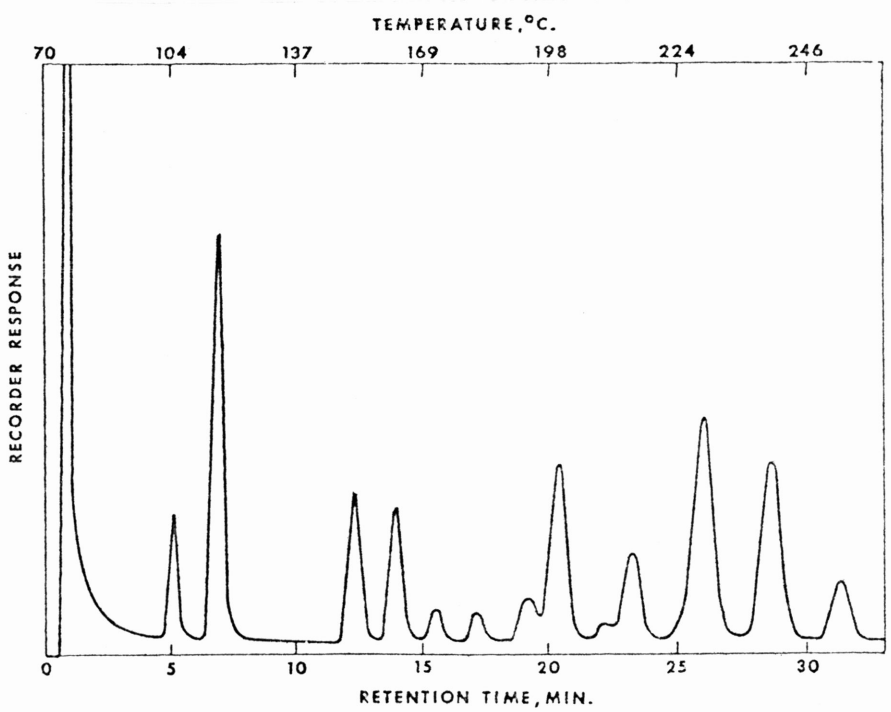


FIG. 7B. Analysis of resole prepolymer system

between analyses. A one-to-one correspondence between the peaks in the two figures cannot be tenably established without a more meticulous study; therefore, the original chromatogram can serve only as a general guide.

Peak number one in Fig. 7a. corresponds to the starting material phenol. Apparently all the phenol is not consumed in the foramtion of methylol derivatives. The degree of substitution of phenol increases from left to right. The least substituted product elutes first whereas the most substituted product elutes last.

When 4MG was reacted with formaldehyde with saturated KOH as the catalyst, the starting material was apparently completely converted to products. The chromatogram shown in Fig. 8 demonstrates this fact because there are three product peaks and no reactant peak. The retention time of derivatized 4MG was determined to be 19.3 minutes. There is no peak corresponding to this retention time in the figure. The retention times of the products are: 28 min. (major peak), 32.3 min. and 43.2 min. Rearrangement of 4MG was a possibility that was considered but this was eliminated by "reacting" 4MG with the catlayst and no formaldehyde. The retention time of the extracted and derivatized mixture was very similar (18.7) to that of the derivatized 4MG; therefore, no rearrangement of 4MG occurs under the given reaction conditions.

When the methylolation of 4MG was catalyzed with saturated KOH, 4MG was apparently converted quantitatively to at least three products as shown in Fig. 8. In order to determine whether or not sufficient addition of $-CH_2OH$ occurred without a complicated analysis, some of the MiBK extract was concentrated and worked on a hot plate with a spatula.

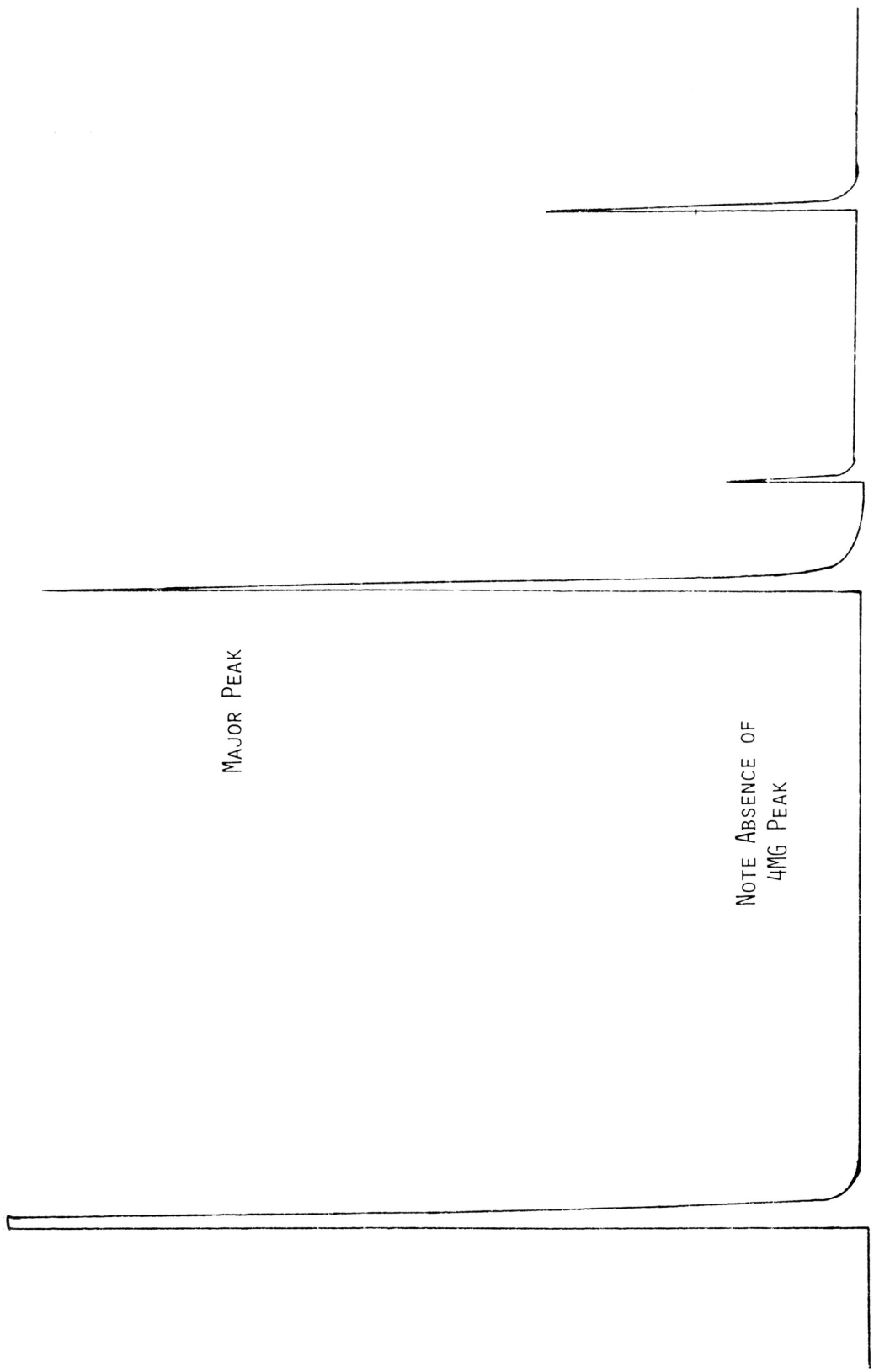


Fig. 8. Chromatogram of the Derivatized Reaction Products of 4MG and Formaldehyde.

The concentrate did not set up on the plate. This was a preliminary indication that insufficient hydroxymethylation occurred--a fact which was supported by subsequent analyses.

Originally, the researcher intended to study or characterize the reaction parameters favoring the methylolation of a major constituent of a pyrolysis oil, namely, 4MG. This type of research would have involved extensive reaction kinetics studies. Because of time constraints, however, this goal was changed. Instead it was decided to focus on identifying the products of the reaction of 4MG and formaldehyde. The remainder of this section will address the identification and structural determination of the products formed in the reaction of 4MG and formaldehyde.

M.S. and P.M.R. Results

A mass spectral analysis was made of both the starting material and the products. The mass spectrum of 4MG is shown in Fig. 9a, and that of the products is shown in Fig. 9b. The mass of 4MG (138) is indicated by the peak of 100% abundance at a mass/charge ratio (M/E) of 138. The peaks shown to the left of this major peak are those which result from the fragmentation of 4MG when bombarded with 70 eV of energy. The relative abundance of each molecular fragment reflects its stability. Unstable pieces of the original molecule rapidly break down into simpler structures and are not detected in large quantities, whereas more of the stable fragments reach the detector intact and contribute more mass relative to the other fragments.

In Fig. 9b, the peak of 100% abundance is located at an M/E of 150.

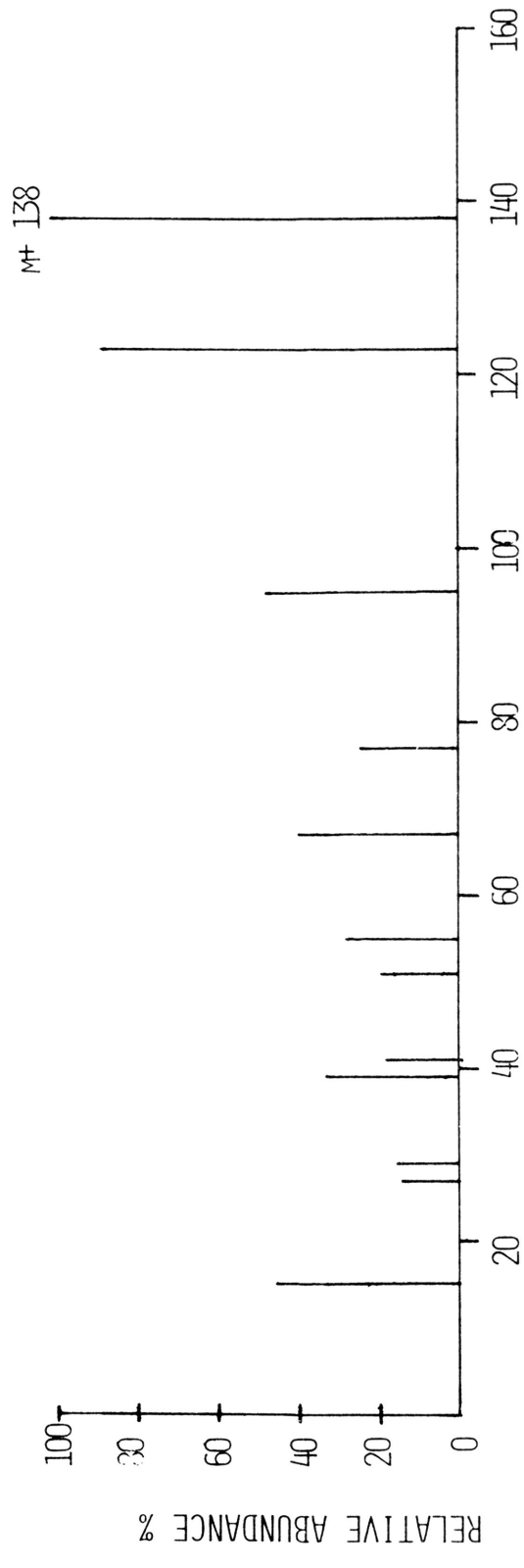


FIG. 9A. MASS SPECTRUM OF 4-METHYLGUAIACOL

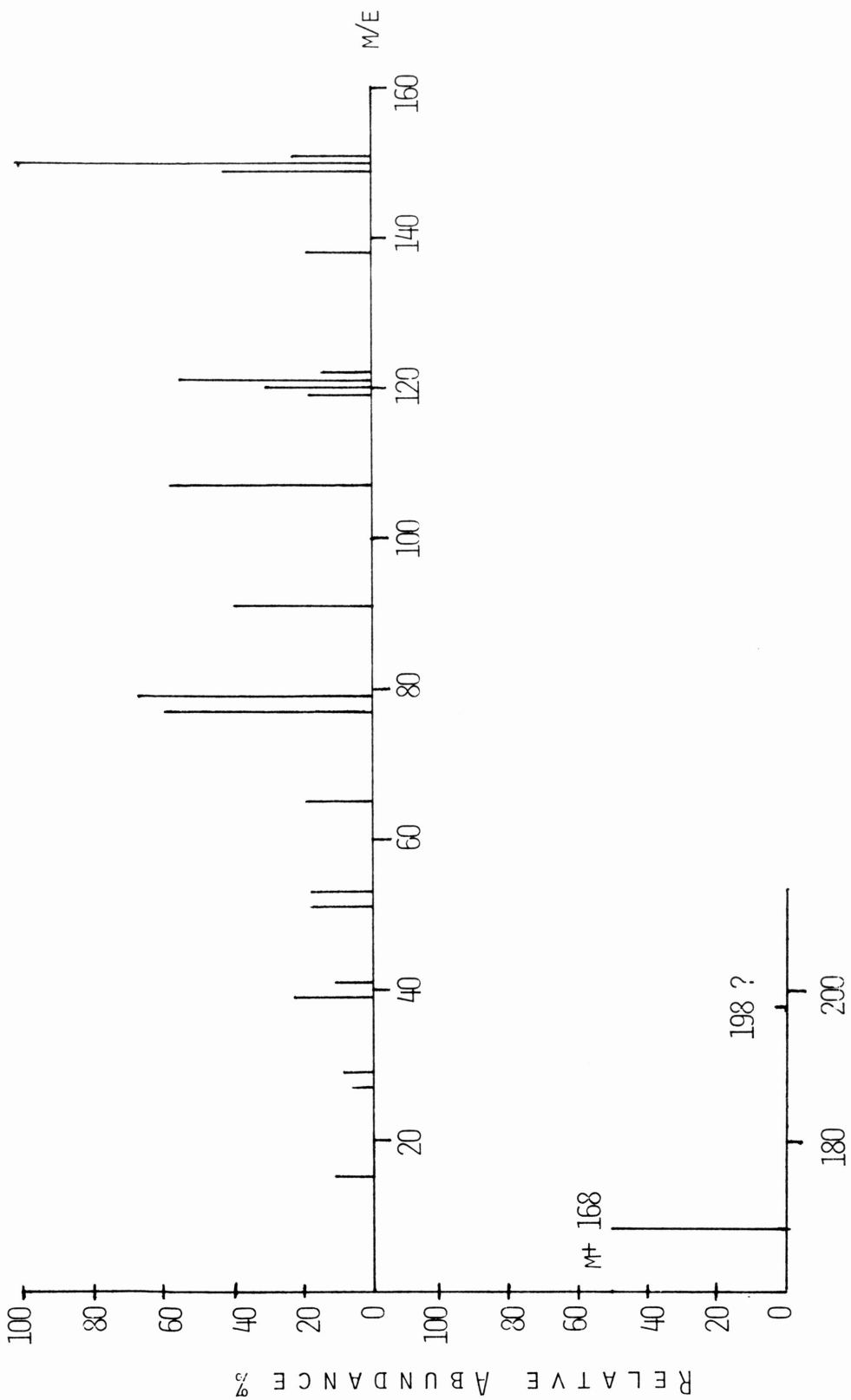


FIG. 9B. MASS SPECTRUM OF METHYLOLATED 4-METHYLGUAIACOL

This fragment represents the loss of a molecule of water from the parent ion shown at an M/E of 168. The relative abundance of this ion (about 50%) indicates not only the addition of a $-CH_2OH$ (30 mass units) group, but also that the resulting species is relatively stable. Thus, the existence of at least a mono-methylol derivative of 4MG is strongly suggested. It is not possible, however, to determine the location of the substituent on the ring from the m.s. analysis because of insufficient structural information and the presence of conflicting data. The p.m.r. analysis was to supply some of the missing structural clues and help clarify the nature of the conflicting information. One more point should be made here. In addition to the mono-substituted product there was also some evidence to suggest that some di-substitution had occurred. This possibility is indicated in Fig. 9b by the trace amount of product located at an M/E of 198 (two $-CH_2OH$ groups). The relative abundance is slightly exaggerated and is actually 1-2%. The presence of this species contributed to general confusion when an interpretation of a single structure was attempted. The p.m.r. analysis helped to clarify matters a bit.

At first the value of the p.m.r. analysis was overestimated. This was due in part to the ignorance of the researcher and to the inherent limitations of the technique.

The g.c. analysis of the product indicated that it was pure. If the tri-substituted structure was formed no position isomers would be possible because all the ring positions would be occupied. With mono- and di-substitution, however, three sturctures are possible--the difference among them being only the order of attachment of the $-CH_2OH$

groups. Evidently the g.c. column used (SE-54) did not separate the isomers detected by the mass spectrometer. This leads to the limitations of both the m.s. and p.m.r. analyses.

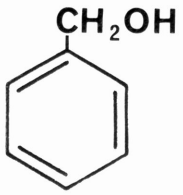
In order for valid structural determinations to be made with either (or both) of the mentioned techniques, the sample analyzed must be pure. The presence of more than one structure will generate conflicting information rendering the analysis at best difficult and at worst useless. This was the problem encountered in my analysis of the product of the reaction of 4MG and formaldehyde.

Both the m.s. and p.m.r. studies suggested the presence of an isomeric mixture of products. The most that could be derived from the m.s. analysis was the masses of the different products. The p.m.r. study confirmed the existence and identities of the different substituents but did not yield much tenable structural information, thus making definite product identification virtually impossible.

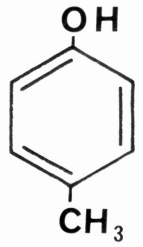
The evidence to support the assignments made to the ring substituents is presented in Table 2 and is a comparison of the chemical shifts of the product substituents and those of standard compounds found in the literature. The chemical shift of a substituent is characteristic of the specific group and can be used to reliably identify the structure. The standard compounds were found in the Sadtler Handbook of Proton N.M.R. Spectra (1978). Although the compounds shown (Fig. 10) are not quite the same as my products, the substituents which the references possess are identical to those attached to my products. The similarity of the chemical shifts strongly supports the existence and identify of my products' substituents.

Table 2. Chemical Shifts of Standard Reference Compounds and Reaction Products.

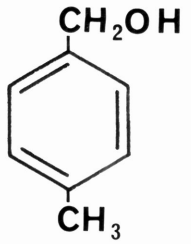
Compounds	Substituent				
	ø-OH	R-OH	ø-CH_3	ø-OCH_3	ø-CH_2-
benzyl alcohol	-	3.10	-	-	4.41
p-cresol	6.45	-	2.20	-	-
p-methyl benzyl alcohol	-	2.94	2.28	-	4.37
m-methoxy phenol	6.67	-	-	3.61	-
o-hydroxy benzyl alcohol	9.22	4.69	-	-	4.55
o-methoxy benzyl alcohol	-	3.11	-	3.69	4.60
p-methoxy benzyl alcohol	-	3.09	-	3.69	4.40
p-xylene-a,a'-diol	-	5.10	-	-	4.51
4-methyl guaiacol	7.13	-	2.30	3.76	-
my products	6.68	2.94	2.14	3.79	4.62



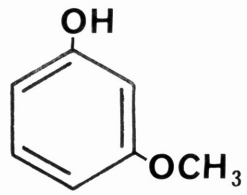
BENZYL ALCOHOL



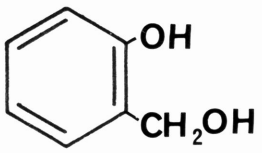
PARA-CRESOL



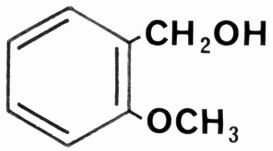
P-METHYL BENZYL ALCOHOL



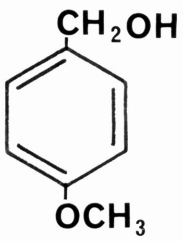
M-METHOXY PHENOL



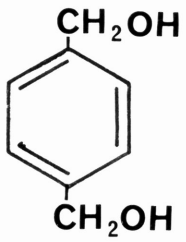
O-HYDROXY BENZYL ALCOHOL



O-METHOXY BENZYL ALCOHOL



P-METHOXY BENZYL ALCOHOL



P-XYLENE-A,A'-DIOL

FIG. 10. STANDARD REFERENCE COMPOUNDS FOR P.M.R. ANALYSIS

The p.m.r. spectrum of the starting material 4MG is shown in Fig. 11, and that of the products is shown in Fig. 12. Structural assignments have been made to each peak in both figures. The most important aspects of these spectra are the area under each peak and the positioning relative to other peaks. Peak area indicates the number of protons contained within a particular structure. The relative position of a peak as indicated by its chemical shift (δ scale, 0-10 p.p.m.) provides additional clues about the structure of a substituent and the location of the group in the molecule.

In the case of 4MG, the structural clues furnished by the spectrum are obvious and easily interpreted. The spectrum of the isomeric product mixture is not easily understood because the presence of more than one species provides conflicting evidence which makes the elucidation of a single structure difficult. The most important aspect of this spectrum is the confirmation of the existence of the substituent ($-CH_2OH$) which the m.s. analysis indicated was added to 4MG (mol. wt. 138 to 168 and 198). The spectrum cannot be used by itself to make a valid structural determination. If, however, the isomers could be isolated by using a different g.c. column then they could be analyzed separately (g.c., m.s., p.m.r.) and this spectrum could serve as a general guide to interpreting the individual spectra of the isomers.

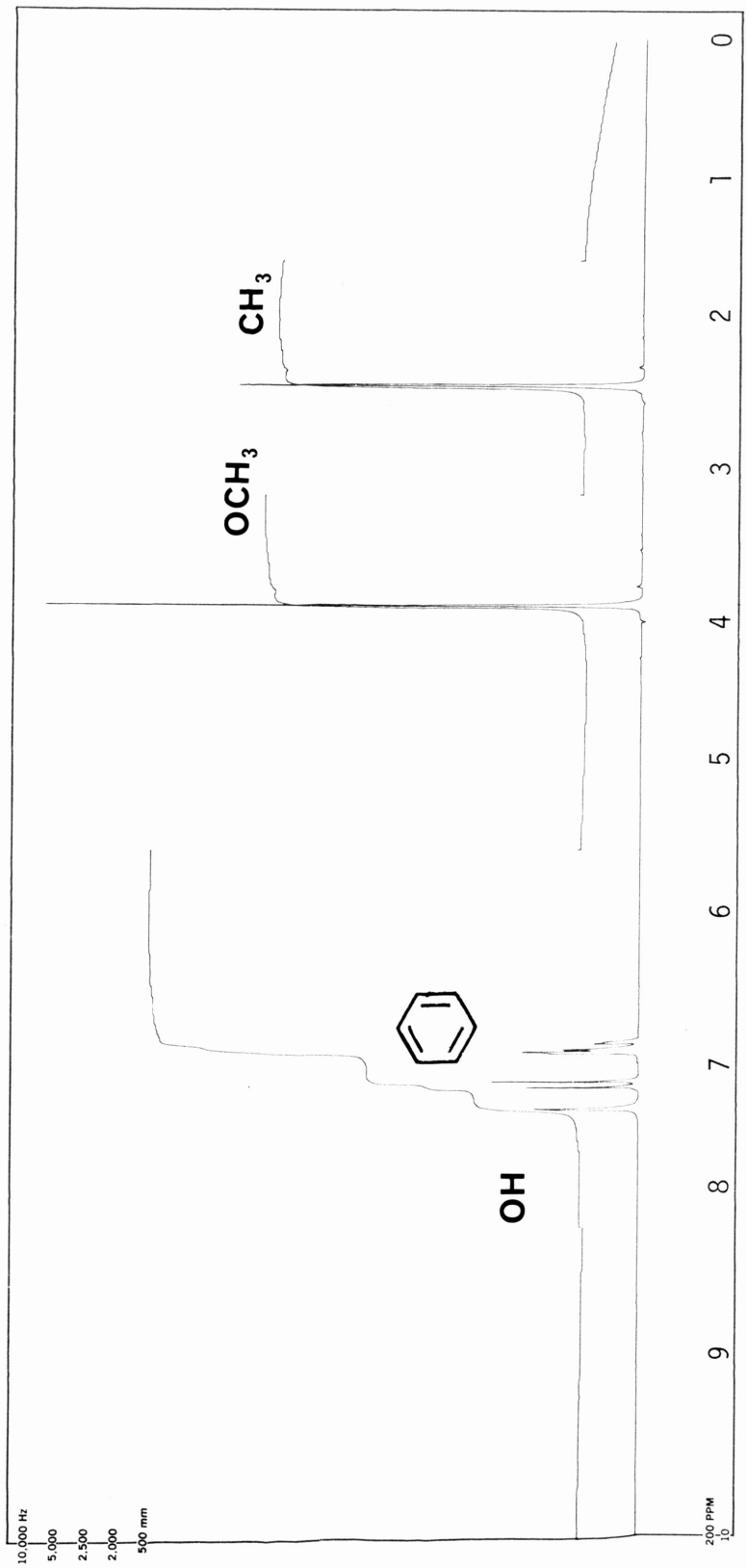


FIG. 11. PMR SPECTRUM OF 4-METHYL GUAIACOL

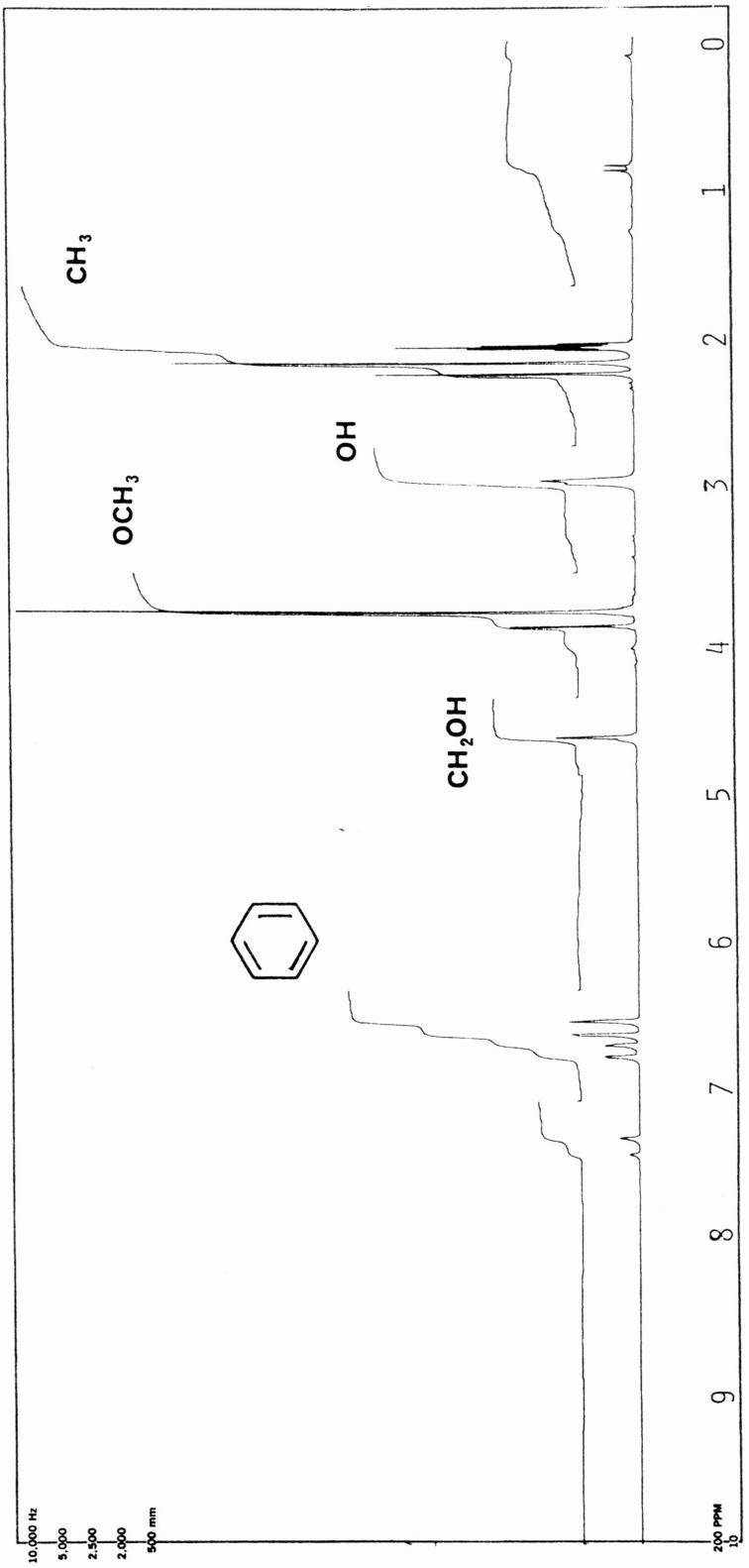


FIG. 12. PMR SPECTRUM OF METHYLOLATED 4-METHYLGUAIACOL

SUMMARY AND CONCLUSIONS

Initially the main objective of the research was to characterize the reaction parameters favoring the hydroxymethylation of the phenolic constituents of a pyrolysis oil. This goal was too general and a more specific goal was established. One phenolic component, namely, 4-methyl guaiacol was chosen as a substitute for phenol in the basic reaction with formaldehyde. The basicity of the reaction medium (water) was increased in an effort to force tri-substitution of the 4MG molecule. An attempt was made to condense an adhesive resin from the reaction products. These three objectives comprise the reformulated goal which was to prepare a suitable plywood adhesive from the products of the reaction of 4MG and formaldehye.

At least three products were formed in the reaction. Except for various isomeric structures these products were separated on the g.c. A semi-solid was isolated from the mixture of reaction products. A g.c. analysis of this isolated semi-solid indicated that it was pure (a single peak); however, m.s. and p.m.r. analysis suggested that it was an isomeric mixture. Because these analyses provided contradictory information a structural determination of the product could not be made. It was possible, though to confirm the presence and identities of the various substitutents which were added to the starting material, 4MG.

Early in the research it was believed that substitution at the positions meta to the hydroxyl group was not very probable because of the overriding ortho-para directing influence of the hydroxyl group. The formation of an isomeric mixture of products hints that addition of

a hydroxymethyl group ($-CH_2OH$) to a meta position is not as improbable as it was first believed to be. Also, formation of a di-substituted product (mol. wt. 198) supports this idea. How then do the meta positions become more reactive?

One hypothesis is that after the first $-CH_2OH$ group is added to the open position ortho to the hydroxyl group (carbon 6) the directing influenece of the -OH group is not important because the two ortho and one para positions are blocked. At this point, the methoxyl group ($-OCH_3$) is the most influential ortho-para director because it is a moderate ring activator whereas the CH_3 and $-CH_2OH$ are weakly activating substituents. All three structures, $-CH_3$, $-CH_2OH$, and $-OCH_3$ reinforce the reactivity of the meta positions (relative to -OH), and so both positions should be equally receptive to the $-CH_2OH$ group. According to this hypothesis tri-substitution of 4MG is possible, but some unknown factor is inhibiting the addition of the second $-CH_2OH$ and preventing the addition of the third. One possibility is that the pi electrons are so dispersed and delocalized over the ring and its substituents that the energy of activation provided by the substituents is not sufficient to overcome the energy barrier to a quantitative formation of the tri-substituted product. If this is the case, complex equilibria may exist between the mono- and di-substituted isomers and between these and the tri-substituted product with the mono-methylol derivatives being most favored.

Two possibilities exist for obtaining the desired tri-methylol derivative of 4MG. Research efforts could be concentrated on identifying the reaction conditions which would produce the desired product. This could be a lengthy and somewhat frustrating process. The other

approach would involve altering the structure of 4MG in some way so that the ortho-para postions were open to the $-CH_2OH$. Success with such an approach seems much more achieveable than with the first especially in view of some recent developments (Soltes, 1982). Whichever approach is taken in the future it will have to yield a tri-substituted product to make an adhesive suitable for plywood from the pure starting material, 4MG. This fact does not necessarily preclude the use of 4MG as an extender in phenol-formaldehyde resins. In such an application, mono- or di-substituted 4MG may participate in the three-dimensional cross-linking to enhance the adhesive properties of the resin. Probably the most important conclusion which may be drawn from the research is that although my efforts were less than successful in some respects, they contributed to a clarification of the direction to take in future endeavors. In this regard, and because much was learned about the research process, my efforts were indeed fruitful.

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APPENDIX

Acetylation Procedure for Aqueous Methylols

The aqueous reaction mixture was diluted to approximately a 5% solids level and neutralized to a pH of 6 to 7. The calculations for obtaining the 5% solids level are as follows:

(1) with phenol as starting material, assumptions:

- weight of phenol completely converted to methylol derivative
- 1.00 g/ml = density of H_2O

$$\frac{\text{grams of phenol}}{\text{weight phenol + weight formalin}} \times 100\% = \% \text{ solids}$$

(a) grams reaction mixture needed = $\frac{\text{g solids desired}}{\% \text{ solids}/100}$

(b) ml H_2O needed = $\frac{\text{g solids desired}}{\% \text{ soilids desired}/100}$

combine a with b to the volume specified in b.

(2) with 4MG as the starting material, substitute the weight of 4 MG for the weight of phenol.

The dilute solution was then freeze-dried to give 2.5 to 3.0 grams of soildi or semi-solid residue. Preferably, the dehydrated resin was immediately acetylated or, during intervening periods, it was maintained at a temperature of 0°C., or below.

Next, the dehydrated sample was treated with a mixture of 20 ml of acetic anhydride and 5 ml of dry pyridine, at a temperature of 0°C. The mixture was stirred, strictly maintaining the temperature below 10°C., until all the resin dissolved and there was a lightening in

solution color.

After the initial reaction the acetylation mixture was allowed to warm to room temperature and stand for 1 hour or more. Approximately 100 ml of water were combined with the acetylation mixture in a 500-ml separatory funnel. Ether was added to give a clean separation of the organic phase from the aqueous phase after equilibration. If a clean separation was accomplished, the aqueous layer was withdrawn and rejected. In a few cases, solubility limitations necessitated the use of dichloromethane in place of ether.

The ether extract was washed with a cold water wash, a dilute acid wash (2% HCl), and two saturated bicarbonate washes. The ether layer was then dried over magnesium sulfate and then filtered. The ether was removed from the organic pahse by evaporation on a rotary-evaporater to yield a viscous resole acetate sample suitable for g.c. analysis.

Tri-methyl Silyl Ether Derivatization Procedure

Five milliliter aliquots of reaction mixture were diluted to 50 ml. The amount of sample used here may be adjusted as desired to alter concentration of derivatized product in the analysis sample. The pH of the mixture was adjusted to between 6 and 7 with 10% HCl. This "neutral" mixture was extracted 3-5 times with 10 ml. portions of methyl iso-butyl ketone (4-methyl-2-pentanone, from MCB). The extracts were combined and washed with distilled water to remove residual HCl. The organic layer was then dried over magnesium sulfate, filtered, and concentrated to 5.00 ml. (or whatever the initial volume of the aliquot

was). If the concentrate was cloudy, it was dried again. One tenth milliliter of extract was diluted to 1.00 ml with 0.9 ml MiBK (methyl iso-butyl ketone), and 10 ml benzynol were added as an internal standard. One milliliter of this solution was derivatized with 0.3 ml of BSTFA silylating reagent which was obtained from Supelco. All samples were stored in bottles with suitably lined caps. In this case aluminum was used, but Teflon may also be used. The lining protects samples from contamination.