AN ABSTRACT OF THE THESIS OF

Vahid Ghodoussi for the degree of Doctor of Philosophy in Forest Products presented on August 21, 1992

Title: Structural Determination of a New Carbohydrate-Phenolic Based Resin Coupled with Urea.

Signature redacted for privacy.

Abstract approved: Joseph J. Karchesy

A resin was synthesized by reacting glucose with urea and phenol under acidic conditions. To better understand the structure of this polymer and the mechanism of its formation, this study was undertaken. It was observed that although the polymer backbone is comprised of a carbohydrate, glucose is not incorporated in this resin in its unaltered state.

By isolating key intermediate products, it was hypothesized that glucose reacts with urea to form an imine which deoxygenates to form a keto-imine moeity. The latter can then undergo degradation to form 2-deoxy-D-ribonopyranolactone. The structure of this lactone was established by one and two dimensional proton as well as carbon NMR spectroscopy. Two dimensional heteronuclear correlation and depth experiments also supported this structure as well as the positive-FAB mass spectroscopy. This lactone, or the imine itself, can then undergo homopolymerization as well as heteropolymerization with phenol to form the polymer of this study.

Structural Determination of a New Carbohydrate-Phenolic Based Resin Coupled With Urea

by

Vahid Ghodoussi

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Signature redacted for privacy.

Head of Department of Forest Products

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Dean of Graduate School

Date thesis is presented August 21, 1992

Typed by researcher for Vahid Ghodoussi

Aknowledgement

To my Father and Mother, thank you for being so giving and all that you have done for me through out the years.

To my loving wife Atossa, your coming into my life has given it a true meaning which I shall cherish forever.

To my brother Modjtaba, thank you for all the years of support and the help you gave me in writing parts of this thesis.

To my three sisters, Nahid, Porun, and Homa, you have done so much for me and I shall be there when the time comes for your young ones.

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To my friend Reuben Gonzalez, may the doors always be open to you as you opened them for me.

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INTRODUCTION

Although synthetic polymers are part of everyday life today, the polymer industry is less than 100 years old with phenolic resins being among the first polymers to be made by A. von Baeyer as early as 1872(1). However, Leo Hendrik Baekland is usually credited for developing a commercially valuable resin in his 1907 patent that uses heat and pressure to harden molded parts.

Phenol-formaldehyde resins are still among the most widely used in the world and they are certainly dominant among the adhesives used in the exterior grade plywood manufacturing industries. Their lower cost compared to their alternatives, water solubility, and minimal pollution has caused their usage to increase continuously over the years. When cured, the glue-line is very durable and impregnable to water. Because of the major role that phenol-formaldehyde resins have always played in the polymer industry from its early days, and are foreseen to play for years to come, continuous research has been done to better understand the reaction mechanisms and to improve the formulation of these resins. Numerous research articles, books, and reviews have been published as a result of these studies(1-4).

In general phenol formaldehyde resins are obtained by step-growth polymerization in two steps, addition and condensation reactions(4). The conditions of temperature and pH can have profound effects on the reaction mechanism and products as shown in Figure 1. While the rate of the reaction is dependent on the concentration of the hydrogen ions below pH of 5, the rate becomes dependent on the concentration of hydroxyl ions above pH of 5 with the overall polymerization reaction being slowest at this pH. Under acidic conditions phenol-formaldehyde condensation is ten times faster than addition reactions(4). This results in methylol-phenols being transient intermediates and the condensation following quickly. As the polymer grows, the reactive sites of the inner groups become less available due to steric hindrance which yields a relatively linear polymer referred to as a novolak(5). The methylolation reaction under strong acid conditions is an electrophilic substitution reaction where the hydroxymethylene carbonium ion which forms from methylene glycol initially acts as the hydroxyalkylating agent according to Equations 1-3 with the addition of the hydroxymethylene carbonium ion to phenol being the rate determining step(1).

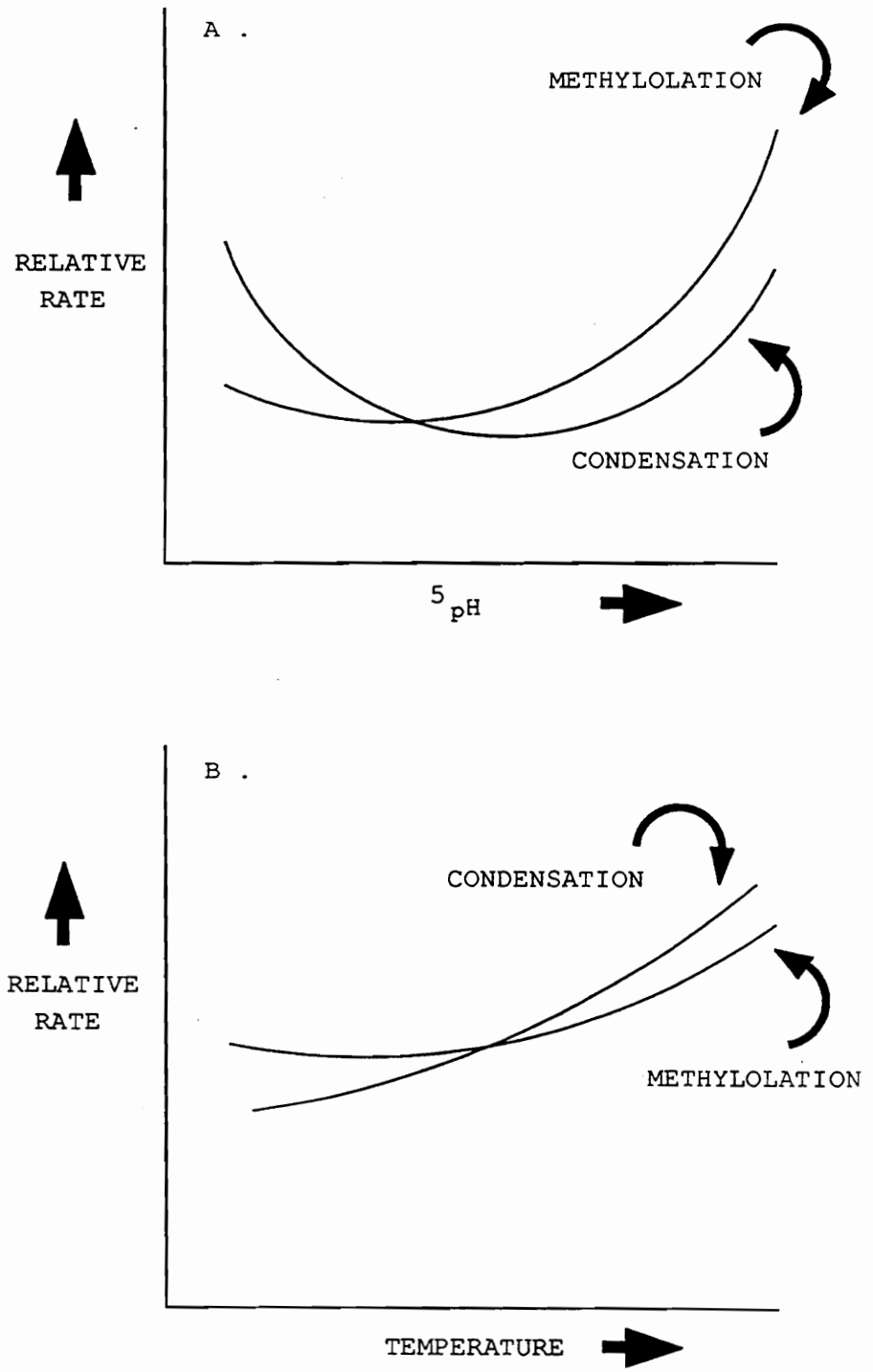
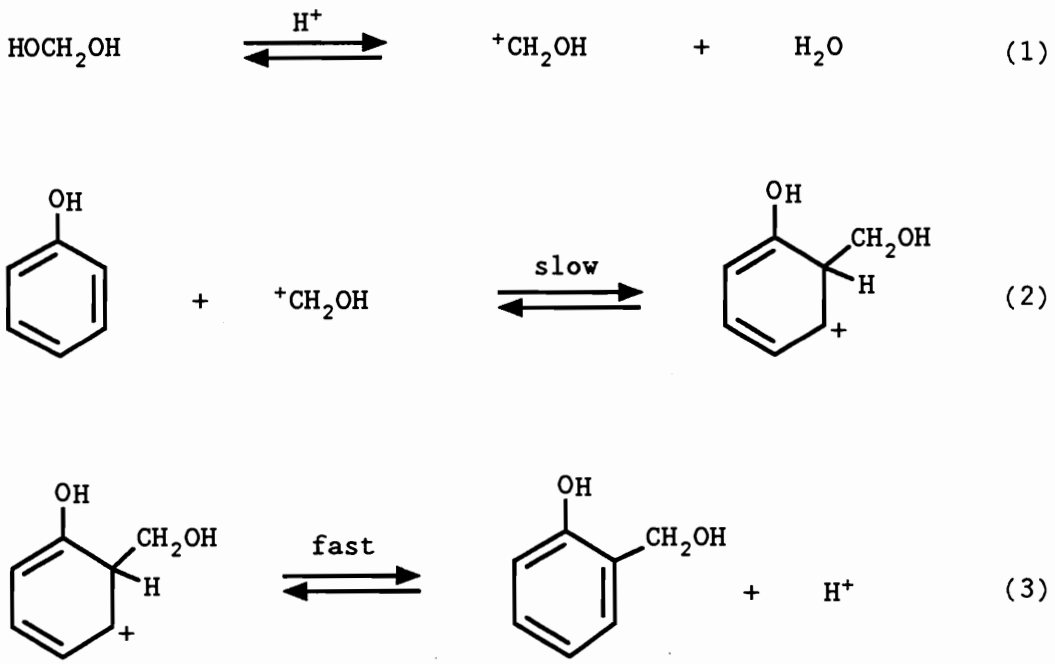
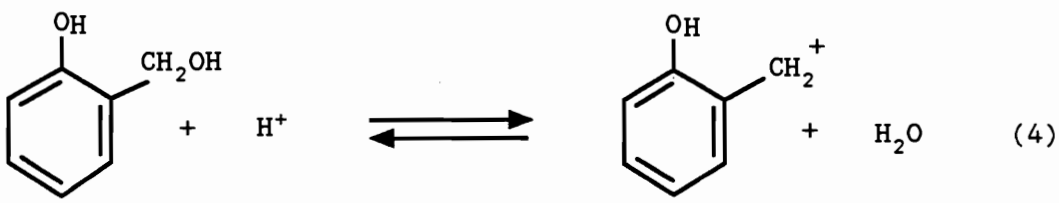


Figure 1. Relative Rates of Methylolation and Condensation as a Function of pH and Temperature, After Drumm and Leblanc (4).

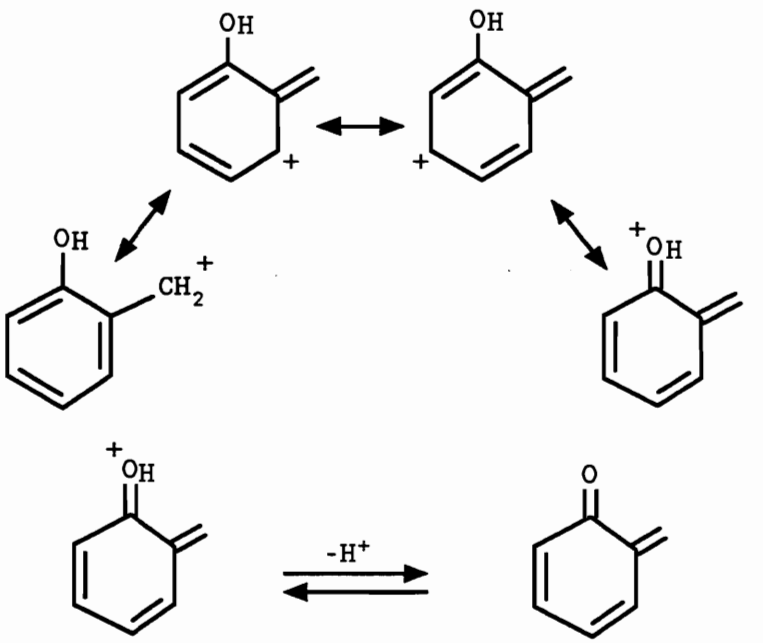


Because of the electronic factors no meta-substitution products are observed.

The methylol group is a transient intermediate under acidic conditions and results in the formation of benzylic carbonium ion as shown in Equation 4.

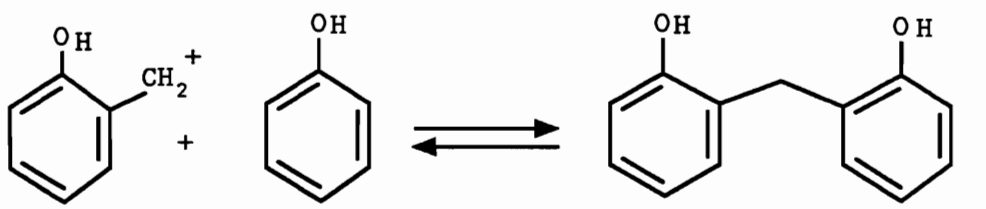


The benzylic carbonium ion is stabilized by several resonance structures which are shown in Scheme I:



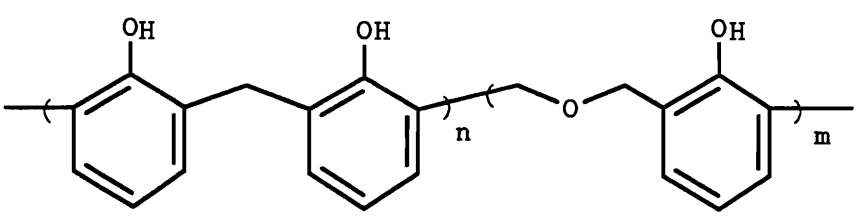
Scheme I

The equilibrium reaction to form the quinone methide moiety is also presented in this scheme. The methylol group subsequently reacts with phenol to form dihydroxydiphenylmethane according to Equation 5(2).



(5)

Because they are highly reactive intermediates under acid conditions, phenol alcohols have not been isolated from the mixture. However, Kopf et al. have proven their existence based on their NMR studies(6). Although the ortho-methylol substitution and methylene bridge formation reactions are shown as the examples above, by adjusting the conditions both reactions can take place preferentially at the para position. Reactions at the ortho site are reduced by increasing the acidity and use of other aldehydes rather than formaldehyde, or using solvent mixtures of alcohol and water. While the ortho-substitution is enhanced with the addition of divalent metal catalysts or use of weak acids as well as using excess phenol(7). Higginbottom et al.(8) has proposed the following structure for ortho-ortho' novolaks using the ^{13}C-NMR data.

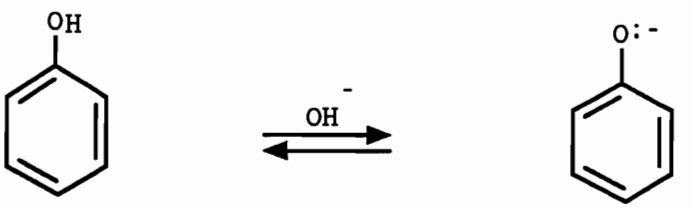


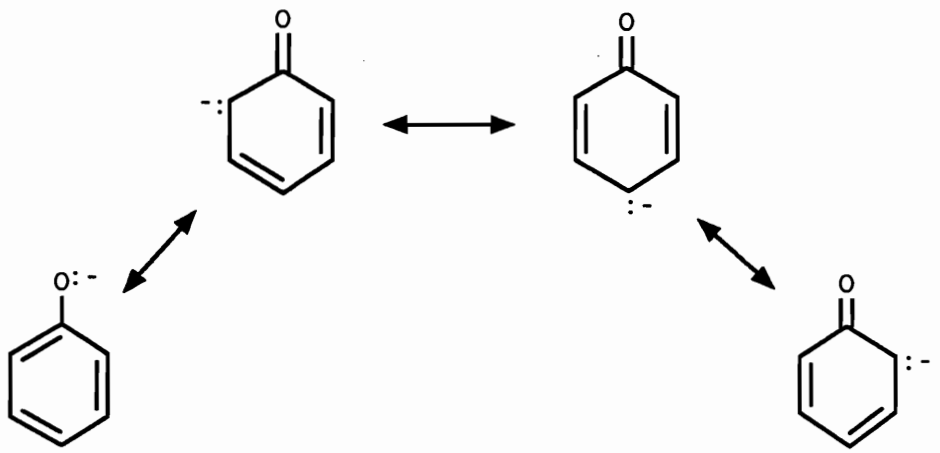
1

While the use of ^{13}C-NMR initially was to complement

^{1}H-NMR spectra, the former is the preferred method of analysis for resins(1). This is due to the fact that ^{13}C-NMR has much greater resolution, all nonequivalent carbons are identifiable, and derivatization is not required. Therefore many researchers have done microstructure characterization of these resins using the carbon resonances(9,10,11).

The use of ^{13}C-NMR is not just limited to the acid catalyzed polymerization, but to the base catalyzed reactions as well. The base catalyzed reaction between formaldehyde and phenol is sometimes referred to as Lederer-Manasse reaction since these two first looked at this reaction in 1894(12,13). As it is apparent from Figure 1, the pathway changes as the pH of the reaction is increased. Phenol acting as a weak acid, forms phenoxide ion which is shown in Scheme II along with its resonance configurations:

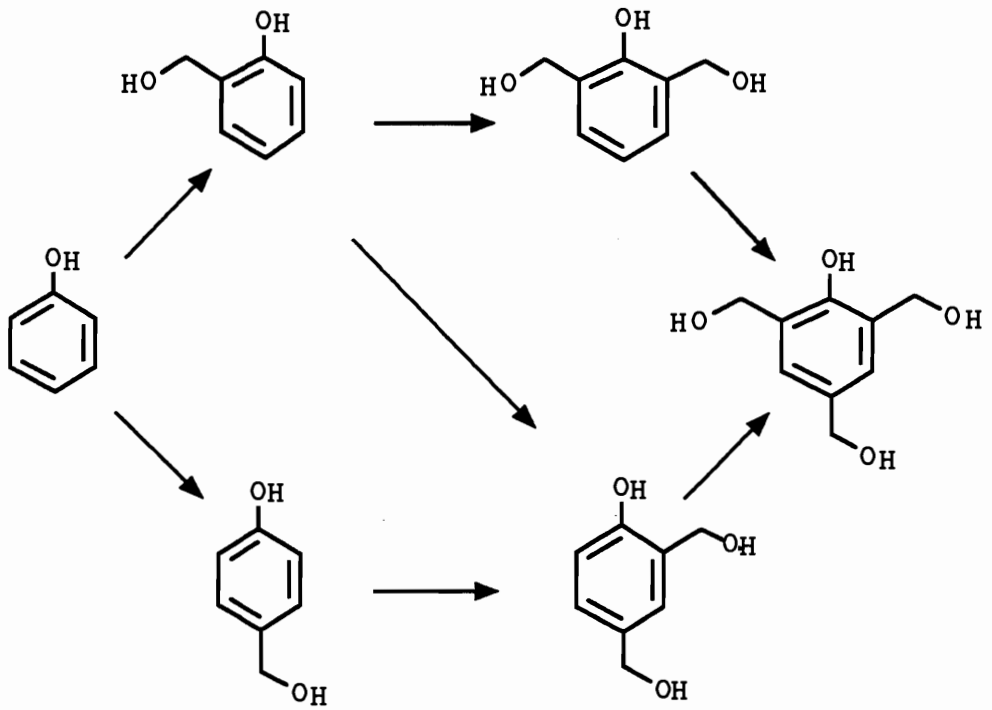




Scheme II

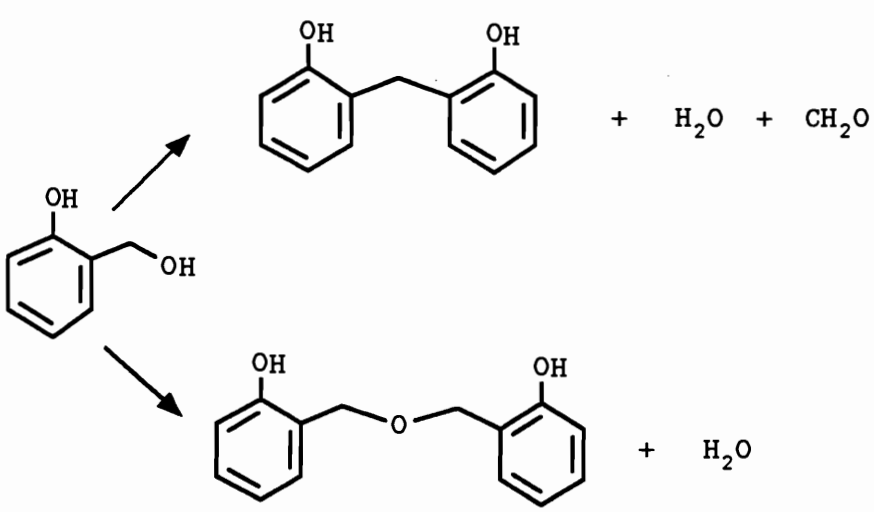
It is due to these resonance hybrids that the negatively charged phenoxide ion is very stable and is formed rapidly once the pH is raised above 5.

Because of the electronic factors hydroxymethylation occurs only at ortho and para positions of the phenol with no meta substitution products being observed. The hydroxyl group is an inductive electron withdrawing group and at the same time it is a conjugatively electron releasing group. The latter of these strongly favors ortho and para substitution. Because of accessibility of para it is probably the more favored reaction site. Even after primary and secondary hydroxymethylation of the phenol ring occurs, it can still react further to form tri-hydroxymethyl substituted phenol. The mono-, di-, and tri-hydroxy substituted products have all been isolated and are solids at room temperature.



Scheme III

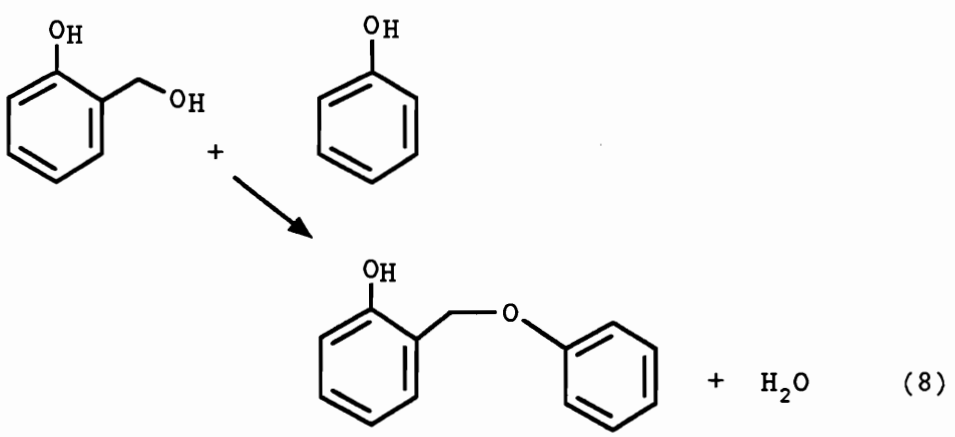
Although there is not a complete agreement in the studies done by various authors as to the mechanism of the condensation reaction, in general two prime reactions have been proposed(2,14):



(6)

(7)

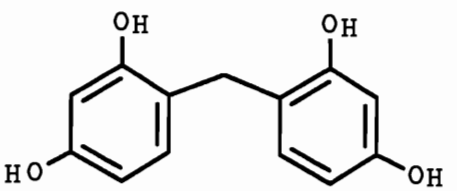
Later studies concluded that when strong alkaline conditions are used diphenylmethane forms according to Equation 6 as the most important reaction, while under weak base or neutral conditions Equation 7 takes precedence. The base catalyzed pre-polymers, generally referred to as resol, are mostly cured at temperatures of 130 to 200C. The reaction mechanism of this polycondensation reaction is different from those of the pre-polymer formation. Based on ^{13}C-NMR results, Maciel et al.(15) have proposed that the thermal curing of the resoles directly involves the hydroxyl group of the phenol ring:



(8)

Other phenolics are also polymerized with formaldehyde

for various applications. Among these resorcinol is the most widely used phenolic compound. Sabenik et al.(16) have used proton and carbon NMR results to deduce that five addition products are formed. According to these researchers the resorcinol-formaldehyde resins form in three steps. First formaldehyde adds to resorcinol and forms hydroxymethyl resorcinol which will then form condensation products with another resorcinol molecule to make methylene 2 and 3, and methylene ether bridges 4. The methylene ether bridges then disproportionate to form methylene bridged resorcinol and formaldehyde.



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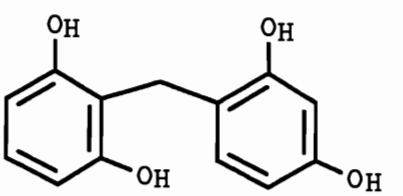

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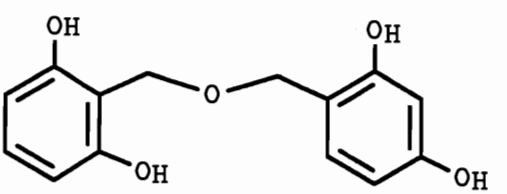
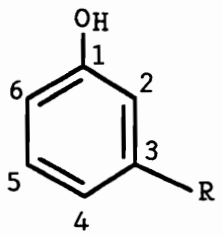


4

Mukoyama et al.(17) correlated the reactivity of the different sites in resorcinol to their chemical shifts

and compared it with those of phenol as shown in Table 1.

Table 1. ^{13}C Chemical Shifts of Phenol and Resorcinol, After Mukoyoma et al. (44).



1) R = H
2) R = OH

	C1	C2	C3	C4	C5	C6
1)	-27.1	+12.3	-1.9	+6.8	-1.9	+12.3
2)	-31.4	+23.4	-31.4	+19.8	-2.9	+19.8

parts per million

Based on the reactivities of these two compounds toward formaldehyde these researchers have concluded that the order of chemical shifts coincides very well with the reactivities. Thus the chemical shifts of the phenolic compound obtained under similar conditions, as those of the resin, can be used to assign the phenolic resin spectra. According to deBreet, although for resorcinol the ortho-ortho position is electronically favored as

compared to the ortho-para positions by a difference of 5.8ppm, but because of steric inaccessibility it is less favored for the reaction with formaldehyde(18). According to these researchers no ortho-ortho substituted products were observed in the spectrum of the resorcinol novolaks. Table 1 also indicates that the much greater reactivity of resorcinol toward formaldehyde, as compared to the reactivity of phenol. Resorcinol reacts with formaldehyde at room temperature even without the addition of any catalyst, however, alkaline catalysts are often used. In general pre-polymers are made with the molar ratio of formaldehyde being less than that of resorcinol and to cure enough formaldehyde is added to make a total molar ratio of 1.1 relative to the resorcinol. Since no acid is used during cure the wood stays undamaged. The glue-line formed is also highly resistant even when the moisture content of the wood is as high as fifteen percent. The high cost of resorcinol has been the major disadvantage of its much greater use.

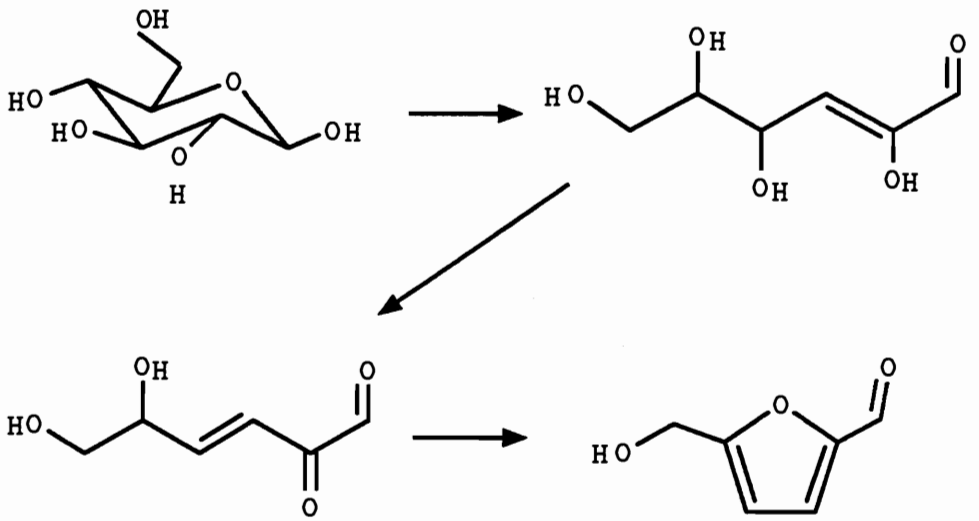
Since resorcinol, phenol, and formaldehyde are all derived from petroleum products, they are unpredictable in terms of their price and availability. Many researchers have looked into replacing these materials to some extent with renewable resources(19). Carbohydrates have received much attention as a source to partly

replace phenol and formaldehyde in their resins. Carbohydrates are readily available in the form of gums, polysaccharide, oligomers, and monomeric sugars in large quantities from renewable resources. While numerous studies for their utilization as modifiers especially as thickeners, colloidal stabilizers, and flow controllers exists(20-23), however as modifiers the carbohydrate is not incorporated in the polymer backbone.

Other researchers have looked to adhesives which result from the reaction of a phenolic compound and a carbohydrate(24-27). In many of these studies the reaction may be with a rearrangement product of the carbohydrate rather than the carbohydrate itself. Meigs holds one of the first patents for a method to synthesize phenol-carbohydrate polymers(24). Later on Chang and Kononenko developed a plywood adhesive which replaced a third of phenol with sucrose(28). Their studies showed these adhesives to have good mechanical properties with wet shear strengths equal to or greater than the dry strengths.

Under strongly acidic conditions carbohydrates in general and dextrose in particular have been shown by various studies to yield hydroxymethylfurfural(29-31). Although there are some disagreement to the mechanism for the

formation of hydroxymethyl furfural, the following has been suggested by Moye using glucose as the representative carbohydrate(29):



Scheme IV

Other researchers have looked to incorporate other compounds, e.g. nitrogenous ones, to make carbohydrate adhesives where the adduct of the carbohydrate or its derivatives are more resistant to degradation by acids(32-35). In 1980 Gibbons and Wondolowski patented a method of using aldose saccharides to replace as much as 50% of phenol in PF resins(35). These researchers used urea or other diamines to couple the carbohydrate derivative to phenol. Their study shows that the preferred carbohydrate is dextrose, although a number of other hexoses and pentoses can be used as well.

A number of studies have focused on the reaction products of carbohydrates with amines, under acidic conditions(36-38). In one such study, Olsson et al. examined the products of the reaction between D-glucose and methylamine under acidic conditions(38). After 24 hours of reaction, 49% of glucose was consumed, 7% of which had rearranged to D-fructose. A wide range of products were isolated by these researchers which are shown in Figure 2. Although hydroxymethylfurfural is formed, however, combination of all the products in Figure 2 accounted for less than 3% of the glucose consumption. A dark-brown precipitate, which was hygroscopic and amorphous, accounted for 3.7% of the glucose, and 5.7% of the methylamine. It is reported by these researchers that this reaction product was composed of 60.5% C, 5.5% H, 5.1% N, and 28.6% O. The empirical formula of this was reported to be $C_{13.0}H_{14.2}NO_{4.6}$. The following net reaction was suggested by Olsson et al. for this product formation:

$$2.0\ C_6H_{12}O_6 + CH_3NH_2 \longrightarrow C_{13.0}H_{14.2}NO_{4.6} + 7.4\ H_2O \quad (11)$$

This isolated fraction also showed a considerable amount of aromatic character according to these researchers. Olsson et al. concluded that the isolated pyrroles shown

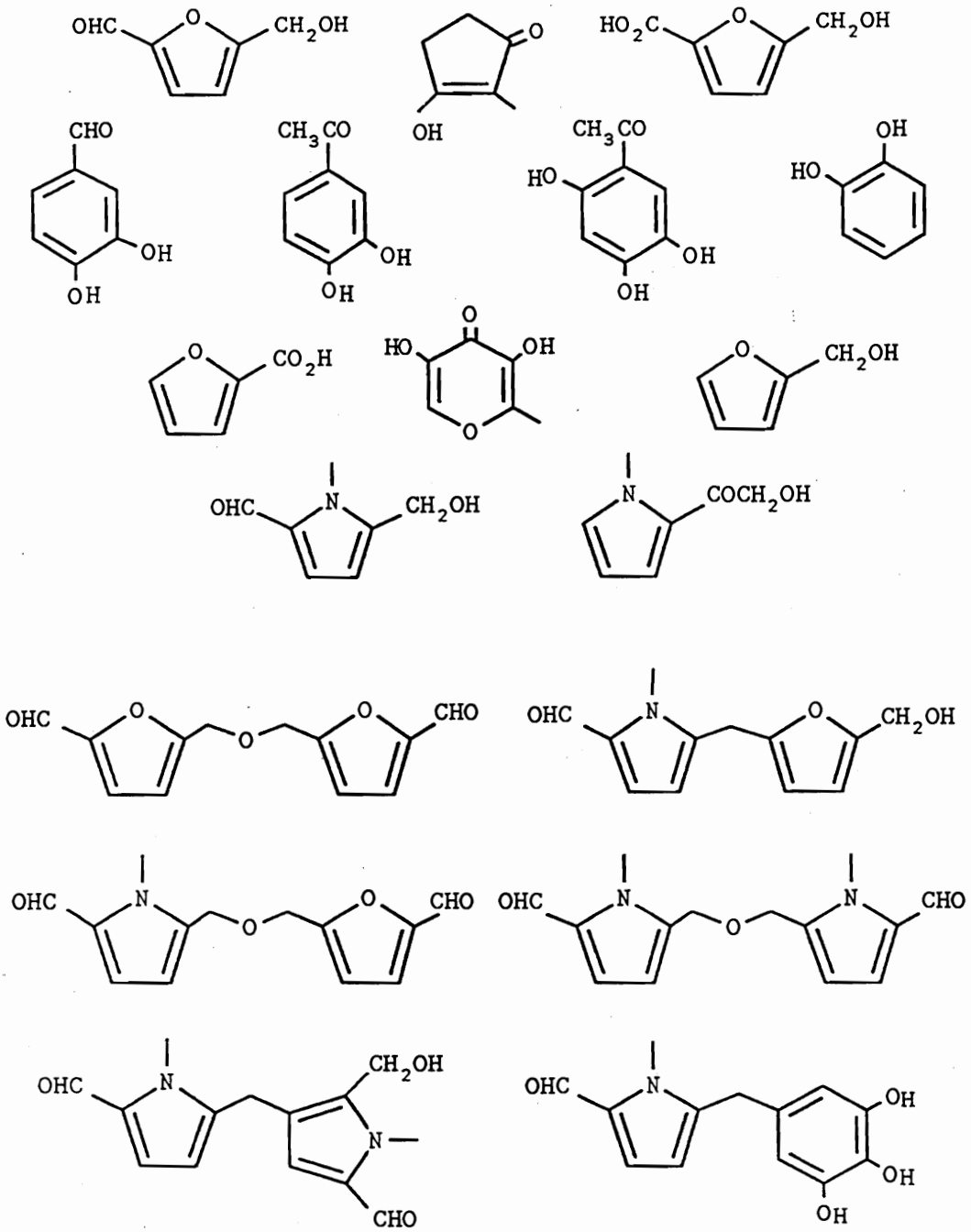
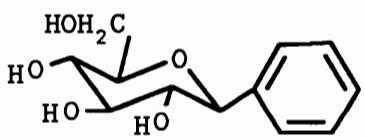


Figure 2: Products of the reaction of D-glucose with methylamine in slightly acidic, aqueous solution, after Olsson et at.(38).

in Figure 2, being fairly stable, are probably not the intermediates in the formation of this fraction.

Since phenol has been shown to be a reaction product of the D-glucose rearrangement in the absence of amines, Pernemalm has suggested that amines catalyze the further reaction of phenol with carbohydrates and this accounts for the absence of phenol in the isolated products. In another study Pernemalm has examined the reaction of D-glucose with phenol under acidic conditions(39). He isolated three fractions; A. An aqueous-soluble fraction containing 5 through 8, B. A polymeric fraction which was not investigated, C. An organic soluble fraction which was pure leucoaurin 9.



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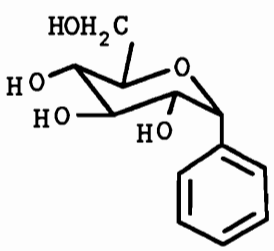

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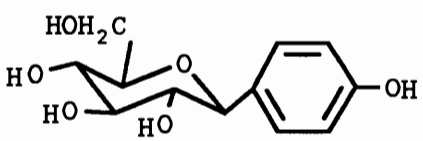

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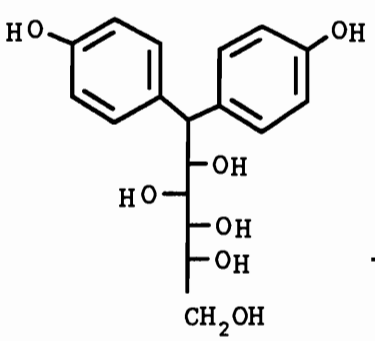

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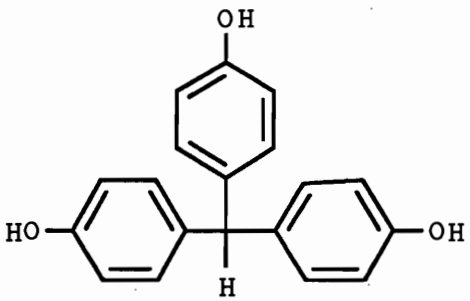

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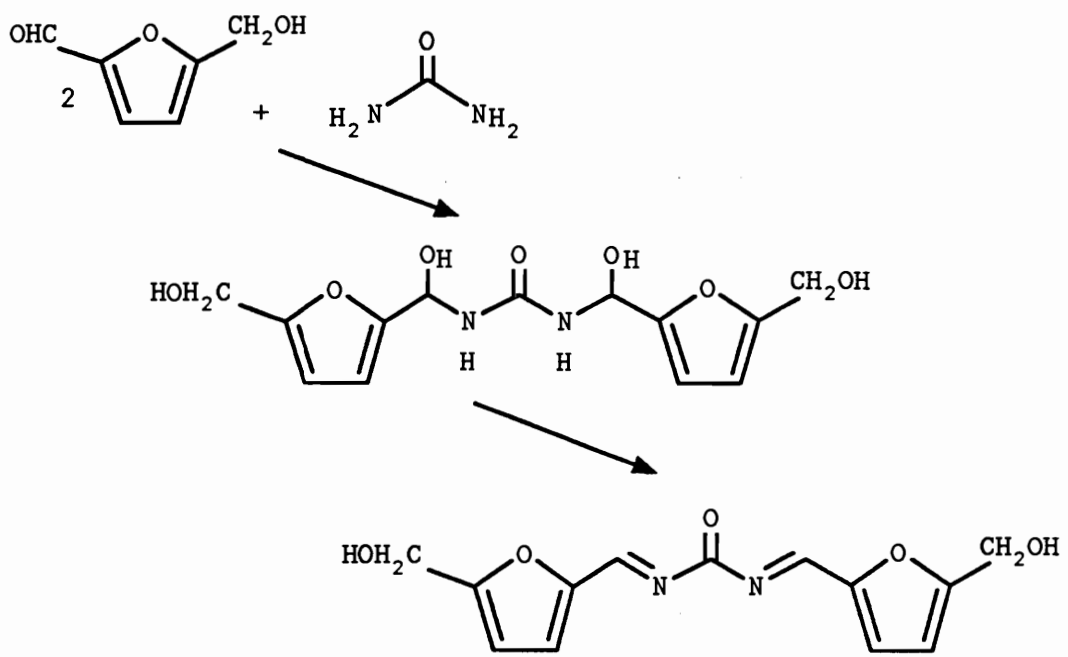
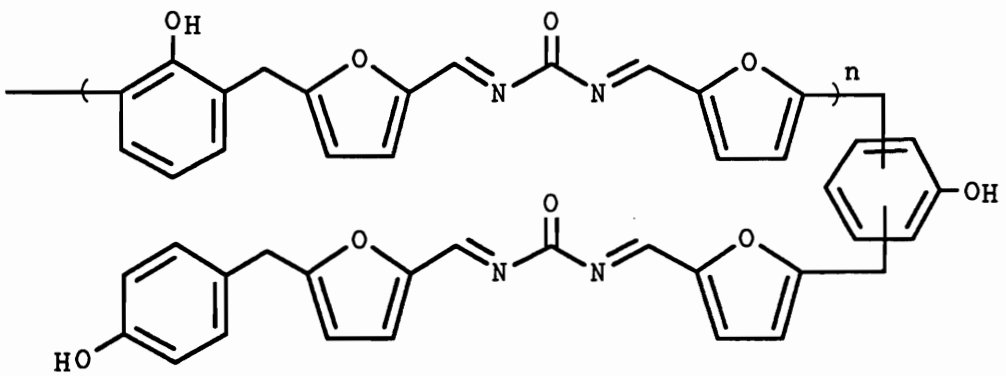
Gibbons and Wondolowski, however, suggested that under these conditions, nearly all the glucose is consumed to form hydroxymethylfurfural. They further suggest that once the hydroxymethylfurfural is formed, it can react with urea to form a diureide as shown in Scheme V.



Scheme V

The resulting diureide can then react with phenol to form a polymeric backbone structure as shown here:



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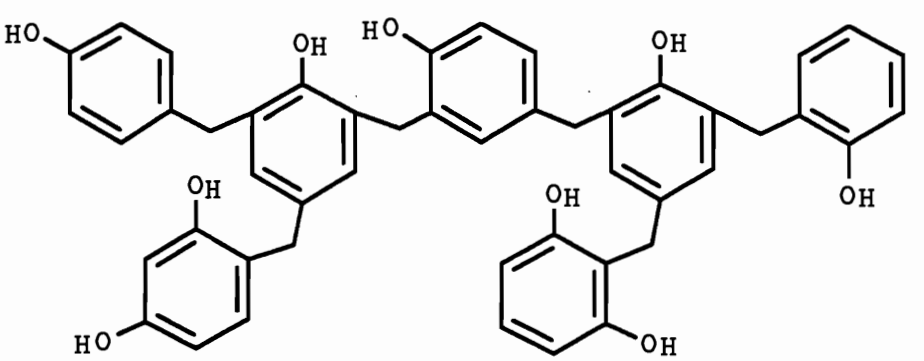
Although good physical properties were obtained by these researchers for the above carbohydrate-based resins, no proof of the existence of any furan rings in these resins was set forward.

Studies of Christansen et al. of these carbohydrate-phenolic based adhesives concluded that the most water-resistant bonds were formed when the phenol to carbohydrate mole ratio was at least 1:1(40). Based on their ^{13}C-NMR studies during the course of the reaction, they reported that no signals attributable to furan rings exist. Furthermore they reported only 45g weight

reduction, per mole of glucose, in the reaction of glucose and urea. This is significantly less than the 72g per mole of glucose that is expected by the hydroxymethylfurfural formation. They have also reported that there is significant amounts of nitrogen lost in this reaction as well.

More recently Clark et al. developed a fast curing adhesive by grafting resorcinol onto a glucose-urea-phenol based resole(41). By grafting resorcinol onto this polymer, these researchers have taken advantage of the greater reactivity of resorcinol, as compared to phenol, toward formaldehyde in the curing stage without excessive cost overruns. A phenol-formaldehyde resin capped with resorcinol would have the following general structure:



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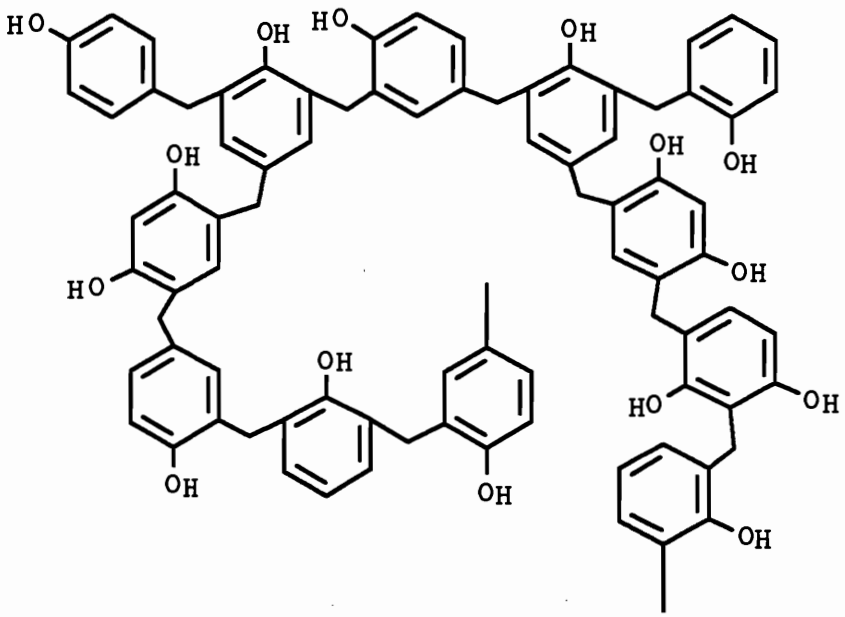
Once this pre-polymer is cured with the addition of formaldehyde and the application of heat, the cross-linked resin would have the following general structure:



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This enhanced reactivity was obtained when the carbohydrate-based adhesive was capped with resorcinol as well.

The different formulations of the adhesives used by these researchers is shown in Table 2 and the conditions of the reactions is shown in Table 3. The wood failure results obtained by these researchers shows excellent values for the cold-setting adhesives as shown in Table 4.

Table 2. Resin Ingredients as Percent of Total Weight, After Clark et al. (41).

Ingredients	Resin						
	1	2	3	4	5	6	7
Glucose	28.5	25.0	24.9	28.3	30.3	24.6	27.6
Urea	4.7	4.2	4.2	4.7	5.0	4.1	4.7
90% phenol[a]	16.5	14.4	14.4	16.3	17.5	14.2	15.9
5N sulfuric acid	1.4	1.2	1.2	1.4	1.5	1.2	1.4
Calcium hydroxide	1.3	1.2	1.4	1.4	1.5	1.2	1.3
Water	0	0	0	0	0	10.9	5.1
Isopropanol	0	0	0	0	0	0.9	1.0
50% sodium hydroxide[a]	0	0	0	0.4	0.4	0.7	1.5
35% formaldehyde[a]	47.5	41.6	41.6	33.5	28.8	23.4	26.2
82.5% resorcinol[a]	0	12.3	12.3	13.9	14.9	18.6	15.3

[a] Aqueous solution w/w.

Table 3. Time and Temperature of Resin Cooks, After Clark et al. (41).

Reaction stage and parameter	Resin						
	1	2[a]	3[a]	4[b]	5	6	7
Stage 1							
Temperature (°C)	133	135	135	135	138	145	140
Time (min.)	240	270	240	240	240	240	240
Stage 2							
Temperature (°C)	80	80	80	80	80	80	82
Time (min.)	60	195	240	160	170	210	195
Stage 3							
Temperature (°C)	--	80	80	80	80	70	65
Time (min.)	--	--	--	60	60	60	60

[a] Solidified while resorcinol was being added.

[b] Solidified 1 hour after resorcinol was added.

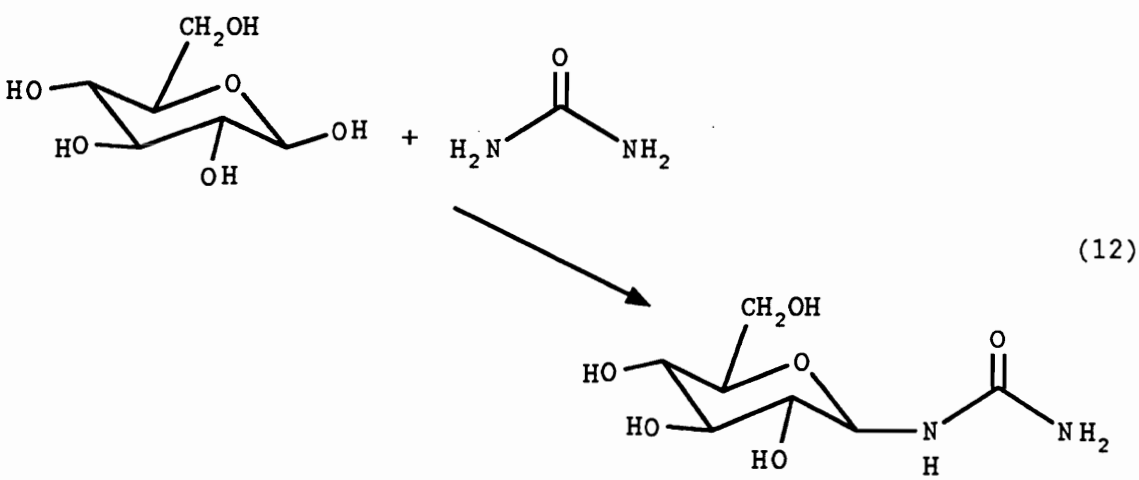
Table 4. **Average Percent Wood Failure of 2-Ply Douglas-fir Laminates Made With Cold-setting Adhesive, After Clark et al. (41).**

Shear test	Average wood failure
Dry shear[a]	94
Vacuum-pressure[b]	91
2-hour boil[b]	95

[a] Average of four specimens.

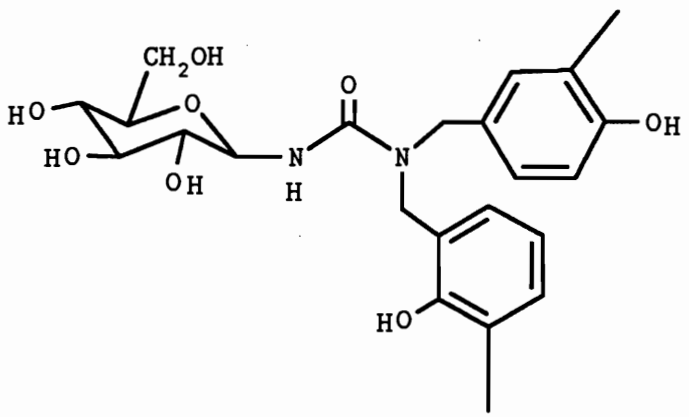
[b] Average of three specimens.

Clark et al. did not observe any evidence of furan rings formation also. According to these researchers, the ^{13}C-NMR analysis of this resin, as its peracetate derivative, does not show the characteristic furan absorptions of about 110 ppm. Clark et al. have suggested that the resonances in the 60ppm to 80ppm region of the ^{13}C-NMR of the peracetylated resin is due to the Glucosyl ring carbons. The disappearance of the glucose has been attributed to the condensation reaction of glucose with urea to form glucosylureas as shown here:



(12)

According to these researchers these glucosylurea moieties can then bind to the methylolated phenol groups, which are formed after the addition of formaldehyde, to form the following general structure for the polymer



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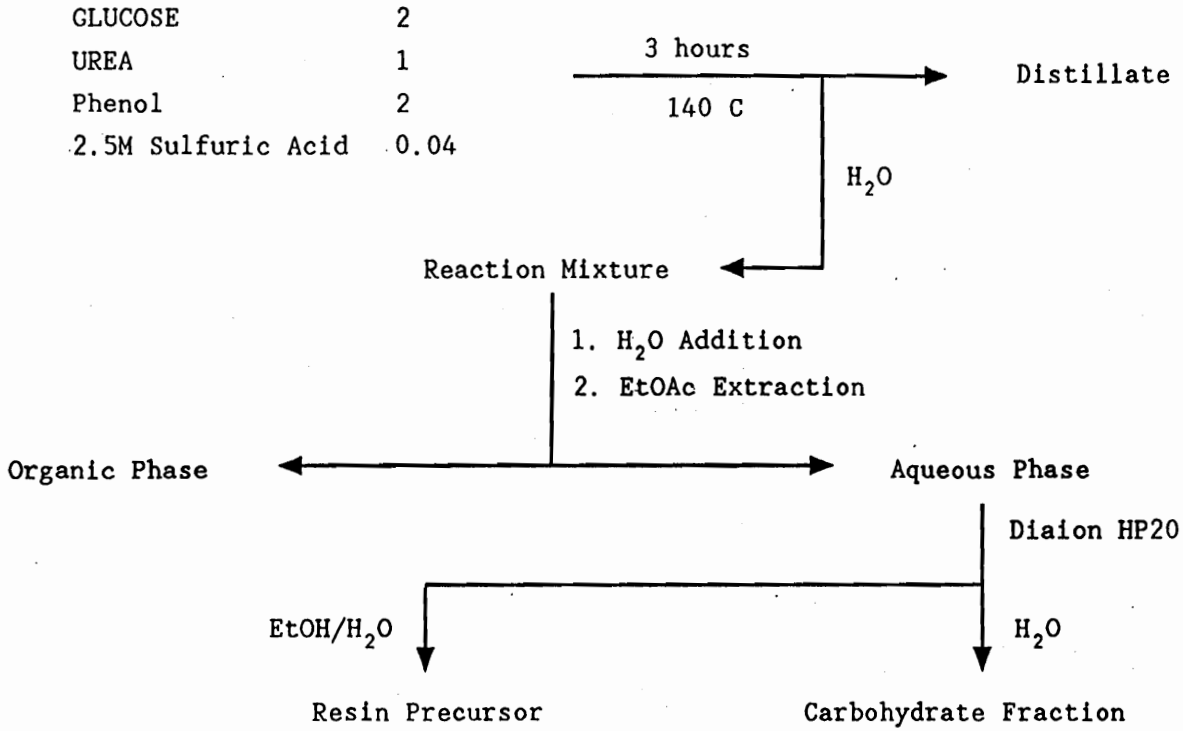
Further investigations by Karchesy et al. proved existence of the glucopyranosylurea moieties in these resins in the initial stages of the reaction(42).

Helm and Karchesy developed a method that allowed them to separate the carbohydrate fraction from the more complex polymeric fraction of the resin mixture in the beginning stages of the resin formation(43). Scheme VI illustrates this separation procedure. These researchers were able to isolate the glucopyranosylurea moieties in their perbenzoylated form. According to these researchers during the course of the first stage of the reaction the concentration of glucosylureas reach a maximum, then they level off, and as the reaction is continued the glucosylureas disappear as shown in Figure 3. This can be due to polymerization reactions or degradation.



Scheme IV. A Separation Procedure for the Isolation of Carbohydrates From the Resin Precursor, After Helm and Karchesy (43).

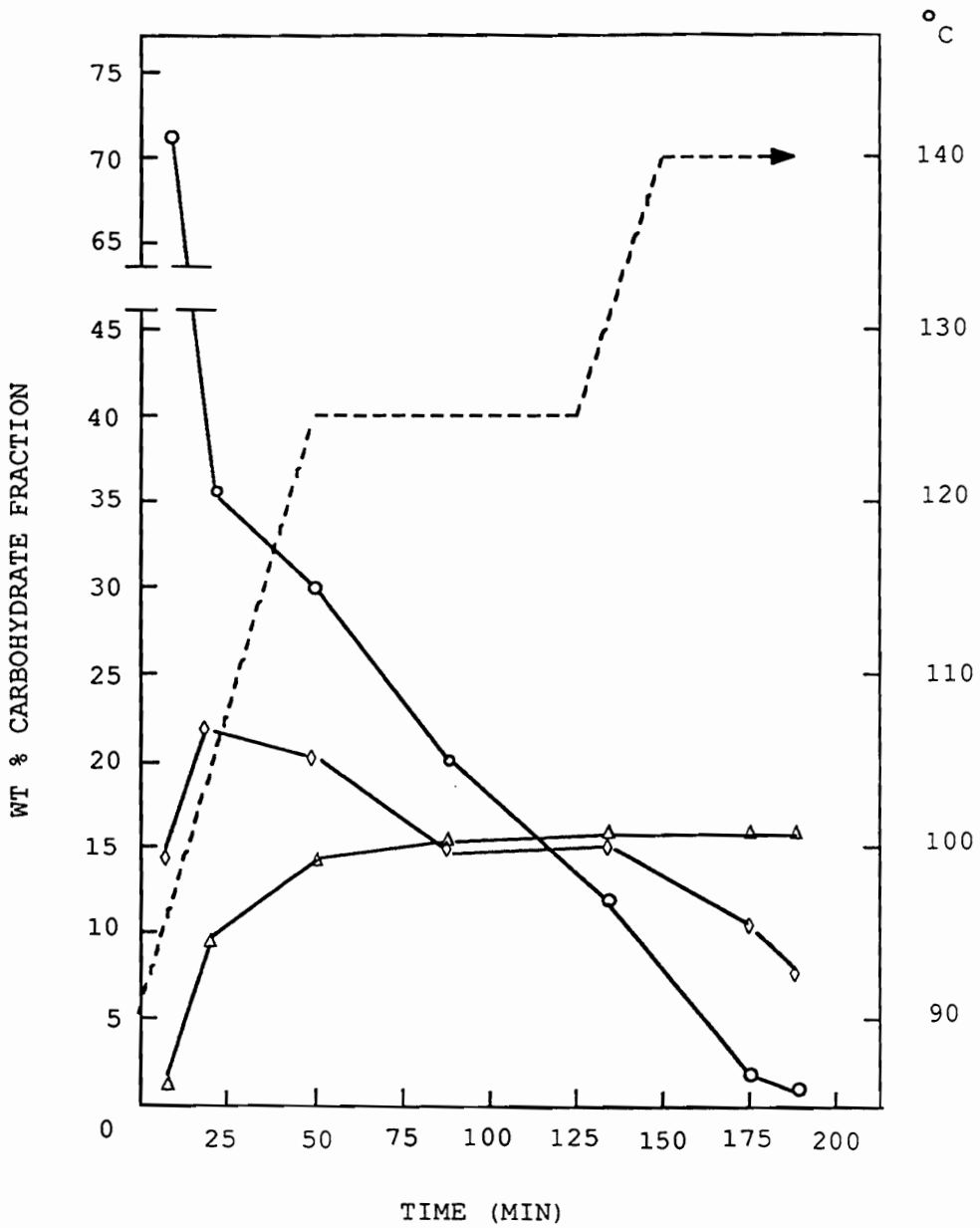


Figure 3: Percent by Weight of Glucose (o), Monoglucosylurea (◊), and Diglucosylurea (Δ), Present in the Carbohydrate Fraction as a Function of Time and Temperature (--), After Helm and Karchesy (43).

However, this study did not show whether the glucopyranosylurea moieties were involved in the polymerization reaction. Furthermore, due to its complexity, these researchers did not characterize the structure of the resin precursor which was formed.

OBJECTIVES AND GOALS

A new carbohydrate phenolic resin was synthesized in our labs by grafting resorcinol on a known glucose-urea-phenol based resole(41). This resin was used to formulate fast curing adhesives which were used to glue veneers having as much as 18% moisture content as well as formulating cold setting glu-lam adhesives with generally good physical properties under various lab test conditions. This carbohydrate phenolic resin has shown promise to replace up to half of phenol and formaldehyde in exterior plywood adhesives. We therefore decided to undertake a study to determine the role glucose or its derivatives play in these resins. By realizing the reactions of glucose, we can elucidate a general structure for the pre-polymers. Furthermore we can get much better insight as to the short-term and the long-term behavior of the resins as well as improving the reaction conditions to result in the formation of the desirable products and reduce the undesirable ones.

The resin was prepared in the same manner as that reported by Clark et. al.(41). We did not try to vary the reaction concentrations or conditions instead we chose resin #7 in the series reported by these researchers since it had the best properties of the series tested. For our purposes and to determine the

structure of the glucose derivatives and polymers, we decided to continue the reaction to the point that the acid stage of the reaction is neutralized, and before any formaldehyde is added. We believe that after the addition of formaldehyde the major reaction is addition and condensation ones to form methylene bridges. We felt that the addition of formaldehyde would add to the complexity of the mixture and overshadow our stated goals.

The reaction mixture was isolated into three separate fractions based on the solubility and the absorption properties of the reaction components. These fractions were studied independently and the results were combined to deduce a general structure for these resins.

EXPERIMENTAL

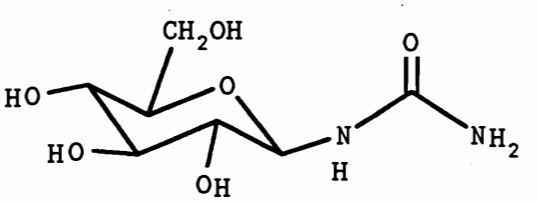
The resin to be used in this study was first prepared by the following reaction procedure: A 500 ml three-necked round-bottomed flask was charged with 70g crystalline phenol, and 7.75ml water. The flask was equipped with a condenser head and a thermometer and a mechanical stirrer. The mixture was heated to 90C and then 22.5g urea (99.9% Chemical Dynamics, South Plainfields, NJ) and 125g D-glucose were added. The mixture was stirred until it became homogeneous(30 minutes). which resulted in an orange colored solution. Then 7ml of a 2.5M H_2SO_4 solution was added and the temperature was increased to 140C and the condenser was replaced by a short-path distillation head and receiver. The reaction was continued for three hours and 44ml of distillate was collected. The reaction was then quenched by adjusting the pH to neutral by the addition of base.

1). Analysis of the Resin for the Existence of Glucosylureas:

It is well known that under aqueous acidic conditions D-glucose reacts with urea to produce glucopyranosylurea moieties. The resin mixture was therefore examined by analytical means for the existence of monoglucopyranosylurea as well as diglucopyranosylurea. Benn and Jones method was used to prepare authentic

samples of glucopyranosylurea and diglucopyranosyl-urea(44).

A. Preparation of Monoglucopyranosylurea: 20g D-glucose and 20g urea were reacted in 10ml of 5% aqueous sulfuric acid which was stirred at 70C for 18 hours. An additional 10ml of sulfuric acid was added at this time and the reaction was continued for a further 24 hours. The mixture was then cooled and the crystals were then triturated with methanol to give glucopyranosylurea as the major component which was purified by subjecting it to liquid chromatography using silica with amine end groups as the stationary phase and $CH_3CN:H_2O$ in the volumetric ratio of 75:25 as the eluent.



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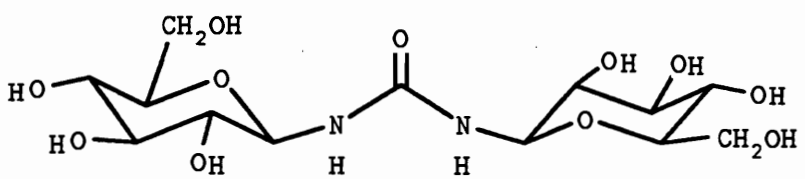
Pure N-B-D-glucopyranosylurea needles were obtained by crystallization from ethanol-water mixture. NMR data for the β anomer has been published by Karchesy et al. previously and is shown in Table 5(43).

B. Preparation of Diglucopyranosylurea: 35g D-glucose and 5g urea were reacted in 20ml of 5% aqueous sulfuric acid

Table 5. NMR Chemical Shifts for Mono- and Di-D-glucopyranosylurea.

Compound	Chemical Shifts (p.p.m)						
	C1	C2	C3	C4	C5	C6	C=O
14	81.45	72.43	77.01	69.84	77.58	61.12	161.2
15	81.31	72.35	76.94	69.81	77.65	61.08	159.04
	Chemical Shifts (p.p.m)						
	H1	H2	H3	H4	H5	H6a	H6b
14	4.61d	3.17t	3.35t	3.21t	3.32m	3.53q	3.70q
15	4.70d	3.20t	3.36t	3.22t	3.34m	3.53q	3.70q
	Coupling constants						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
14	9.3	9.0	9.3	9.4	5.6	2.1	-12.4
15	9.2	9.1	9.2	9.4	5.3	2.0	-12.3

solution. The solution was kept at 70C for 18 hours. The mixture was then cooled and diluted with 20ml water. The solution was then neutralized by addition of 2.2g barium carbonate. Charcoal was added and the mixture was stirred for 15 minutes before it was filtered. Diglucopyranosylurea was then purified by liquid chromatography using the same system as that used for monoglucopyranosylurea. This was then crystallized from methanol-water solution. NMR data for the β,β anomer has been published by Karchesy et al. previously and is shown in Table 5(43).



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C. HPLC Analysis of the Carbohydrate Fraction: The carbohydrate fraction of the resin was analyzed by means of a partisil 10A HPLC column using $CH_3CN:H_2O$ in 75:25 ratio as eluent. The analysis of the resin sample against authentic samples of monoglucopyranosyurea and diglucopyranosylurea proved the existence of these substrates in the resin precursor. These findings have been reported by Karchesy et al. previously(42).

2). Analysis of the Polymeric Fraction in the Resin:

Then the polymeric mixture was analyzed to establish whether glucosylurea moieties play any role as building blocks or not. The procedure that was outlined in Scheme VI was used to isolate the polymeric fraction out.

A. Isolation of the Polymeric Fraction: First the resin mixture was suspended in one liter of water. The water solution was then extracted with four 500ml aliquots of ethyl acetate till the organic phase was pale yellow. The extracts were combined and rotary evaporated to 125ml. This consisted the organic soluble phase.

The aqueous layer was rotary evaporated to remove traces of ethyl acetate and reduce the volume to 300ml. This was then subjected to a polystyrene divinylbenzene column(donated by Mitsubishi Chemical Industry Ltd. Tokyo). Prior to use, 400g of the beads were cleaned with three aliquots of hot ethanol, to remove any ethanol soluble impurities, and then they were dried. The beads were then made into a water slurry, and were packed into a column. The column was then washed with water at a flow rate of 100ml/hr for 48hrs to remove traces of ethanol. The water fraction was then charged onto the

column and the column was eluted with three liters of water till the solution was nearly colorless.

The dark residue that was left on the column was then recovered by eluting the column with a mixture of 50:50 water and 95% ethanol solution. This fraction was rotary evaporated and freeze dried from water to result in 21g of a brown colored, fluffy, hygroscopic material which was polymeric in nature and will be referred to as the polymer fraction.

A1. Elemental Analysis of the Polymer: Elemental Analysis of the dark-brown, hygroscopic, and amorphous polymeric fraction was done by Galbraith Laboratories Inc.. The sample was freeze-dried prior to the analysis to remove any hydration water. The polymer comprised of 51.46% carbon, 5.71% hydrogen, 9.37% nitrogen, and 31.84% oxygen. The calculated empirical formula based on these results would be $C_{12.8}H_{17.0}N_{2.0}O_{6.0}$.

A2. HPSEC Studies of the Polymer: Next we decided to analyze this reaction product for its molecular weight distribution. This analysis was done utilizing a Waters Associates model 6000A chromatograph operating at 254 nm interfaced with a Spectra Physics model 4200 computer to record the chromatograph, weight average, number average,

Z, and Z+1 molecular weights. Four μ-styragel columns (100,500,1000,10000 A) were used in series to analyze the resin, with tetrahydrofuran as the eluting solvent at 2.0ml/min. The system was calibrated by using monodispersed polystyrene strands with molecular weights ranging from 580 to 7600 (Figure 4). The resin was peracetylated using acetic anhydride in pyridine and this was then run through the HPSEC system and the molecular weights were calculated by the computer based on the retention time of the resin elution pattern as shown in Figure 5. The distribution curve of Log MW vs. %Area shows a nice guassian curve with the maximum at about 1000 mass units.

A3. NMR Studies of the Polymer: For the NMR studies, the polymer samples were freeze-dried from D_2O several times to replace the exchangeable hydrogens with deuterium. 200mg of the deuterated resin was dissolved in 0.7ml of D_2O and acetone was used as the reference peak. As is shown in Figure 6 an aggregate of resonances are seen in the δ 3.5-5.0ppm region which are attributed to carbohydrate type hydrogens, while the major ones in the δ 6.5-8.7ppm region are due to the aromatics. The down field shift of the aromatic protons of phenol can only result from substitution of phenol with electron withdrawing groups like carbonyls.

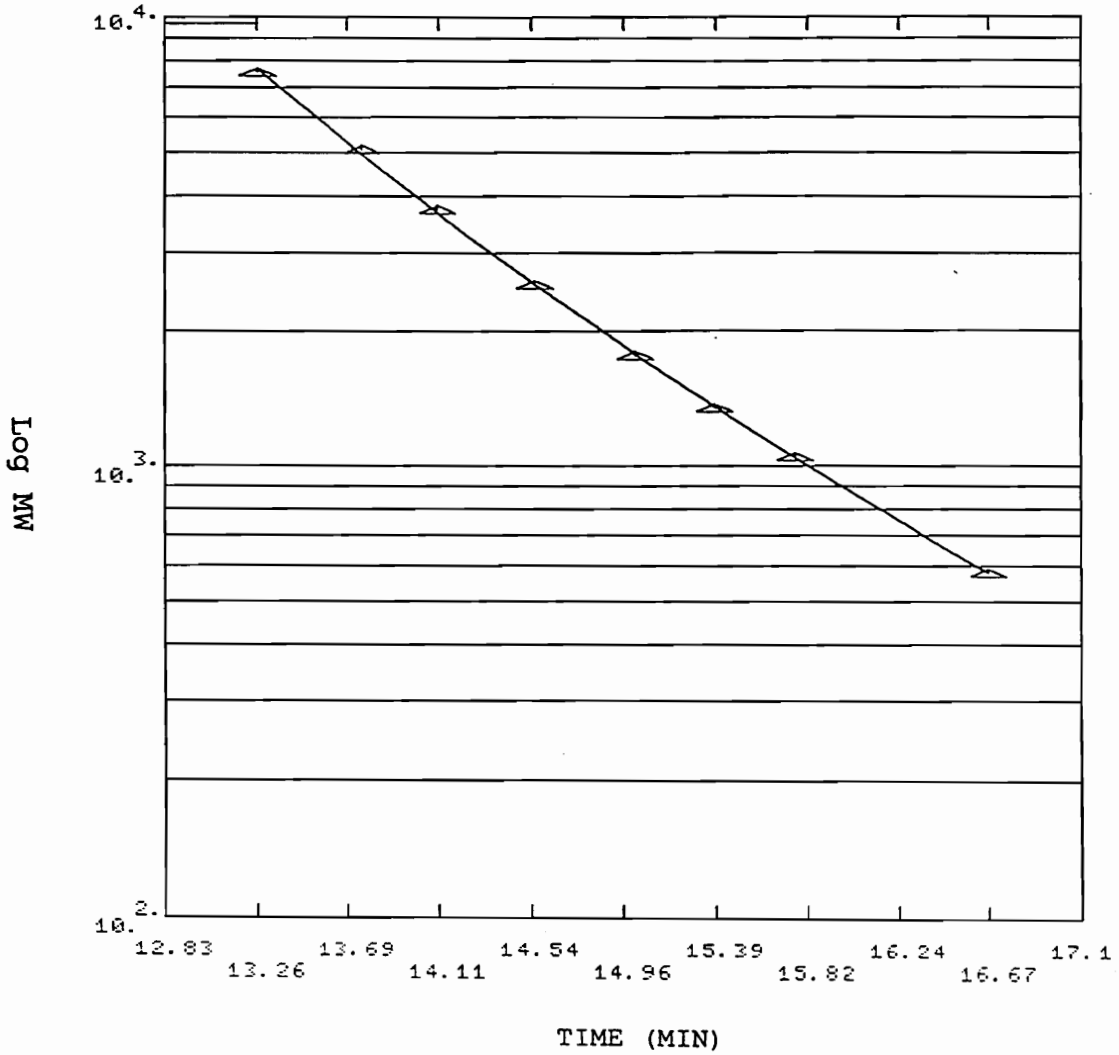


Figure 4: The HPSEC Caliberation Curve for Polystyrene Strands with a Range of Molecular Weights from 580 to 7600.

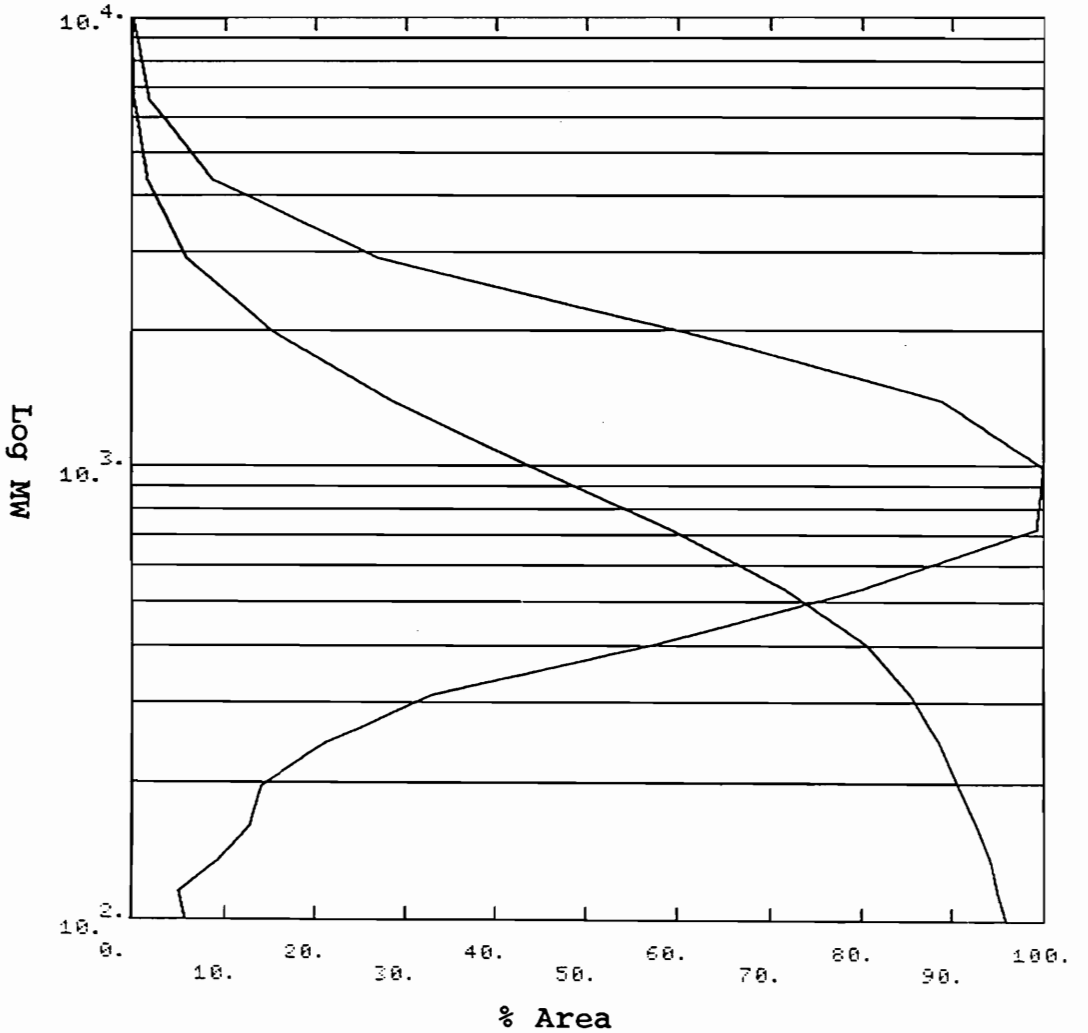


Figure 5: The Molecular Weight Distribution for the Peracetylated Resin Obtained by HPSEC analysis.

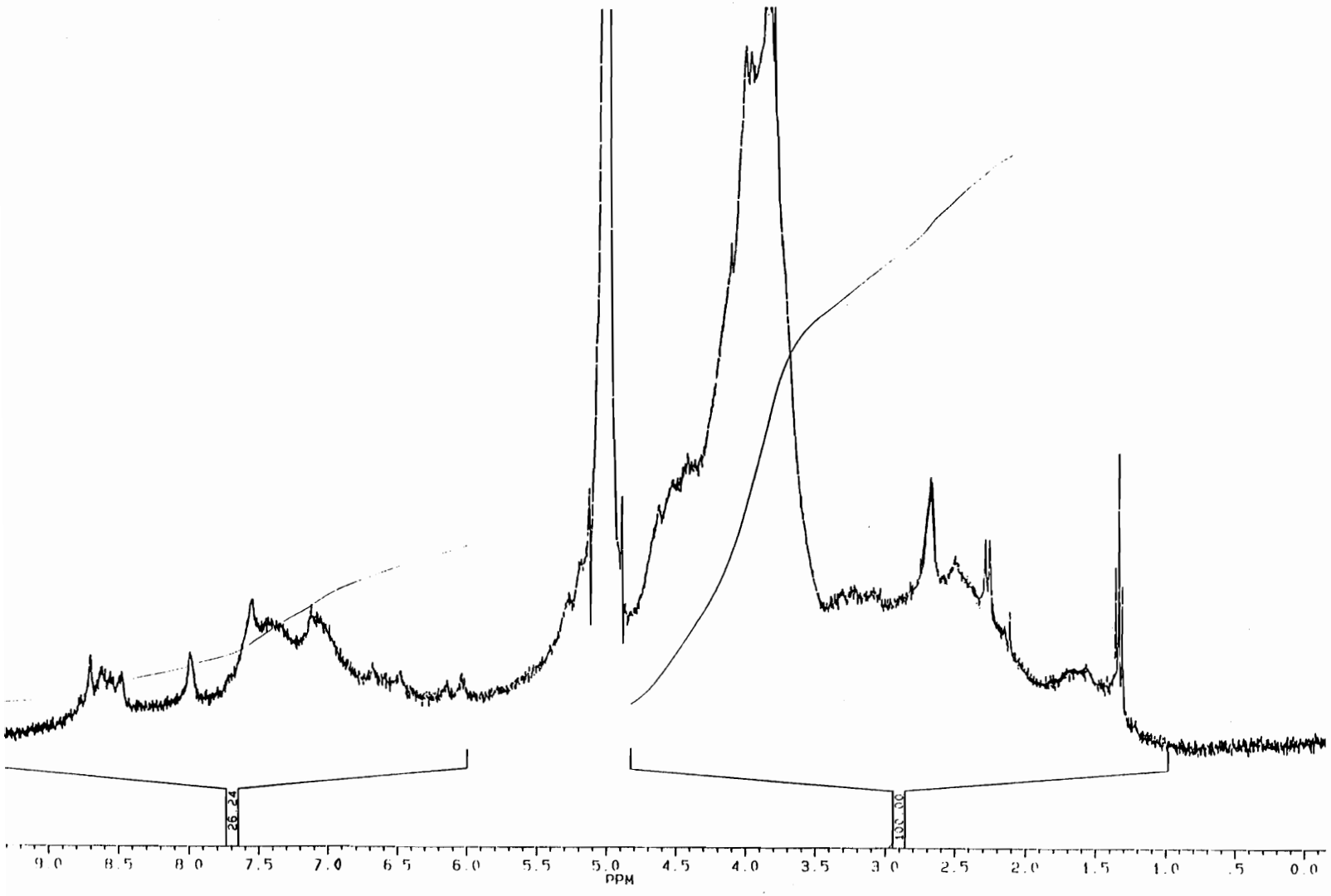


Figure 6: Proton NMR Spectrum of the Polymer Precursor.

Some of the resonances above δ 8.2ppm can be due to formamide type protons. The ratio of the carbohydrate resonances to the aromatic ones was estimated to be about 3:1. The ^{1}H-NMR of the acetylated resin was also examined to obtain as much data as possible about the resin. As is shown in Figure 7, the carbohydrate-type proton resonances break up into two groups, those from δ 3.5-4.7ppm region, and those from δ 4.7-5.7ppm region. This downfield shift in the resonances of the latter protons is simply due to the deshielding effect of acetyl groups on the substituted sites. The ratio of the areas under the absorbance peaks for the acetyl methyl protons at δ 1.3-2.3ppm, carbohydrate protons at δ 3.5-4.7ppm and δ 4.7-5.7ppm, and aromatic protons from δ6.5-8.5 is roughly 12:3:3:2.

The ^{13}C NMR, as shown in Figure 8, was much more helpful in deducing structural characteristics of the polymeric fraction. The furthest upfield of major resonances which appears at δ 21ppm can arise from carbons alpha to an imine. The next major resonance of δ 40ppm is most likely due to a carbon adjacent to a carbonyl group or a similar deshielding group. The series of resonances in the δ 60-76ppm region are carbohydrate type carbons but they differ greatly from those resonances which exist in

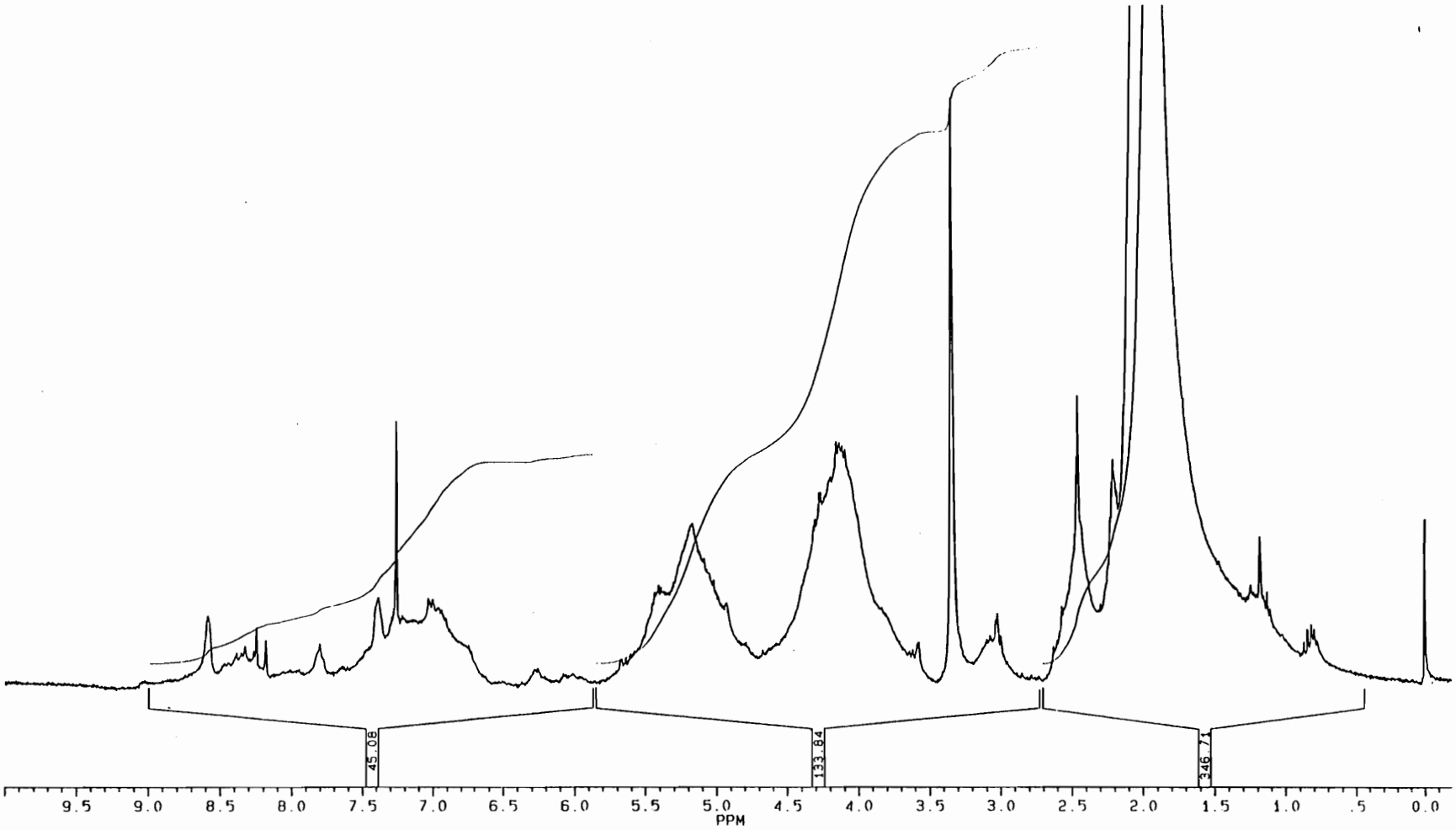


Figure 7: Proton NMR Spectrum of the Polymer Precursor in its Peracetylated Form.

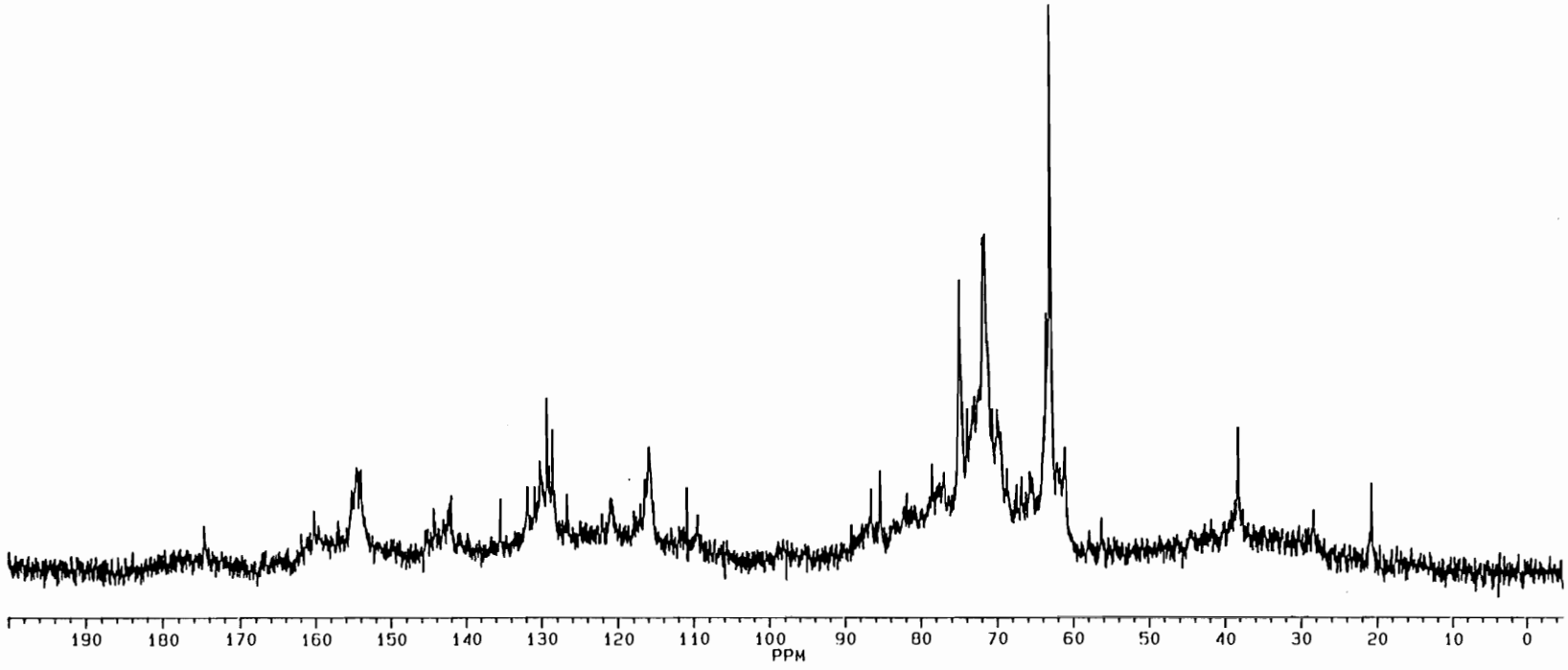


Figure 8: Carbon NMR Spectrum of the Polymer Precursor.

the ^{13}C-NMR of glucose. The latter has resonances C1 at δ 96.7ppm, C2 at δ 74.9ppm, C3 at δ 76.9ppm, C4 at δ 70.4 ppm, C5 at δ 76.5ppm, and C6 at δ 61.6ppm. However, in the resin ^{13}C NMR we see three major resonances in this region, δ 64ppm, δ 72ppm, and δ 76ppm.

Examining the ^{13}C-NMR data for glucosylureas which are included in Table 5, we see that these resonances are very similar to those of D-glucose and therefore they do not resemble the resonances of the resin. The only major difference of the resonances of glucose and those of glucosylureas are in the anomeric carbon being shifted to δ 81.6ppm for the glucosylureas due to the substitution reaction. Therefore neither glucose, nor glucosylureas were comprising the polymer in their unaltered state.

The polymer precursor shows a number of absorptions in the aromatic region. Much of these resonances are due to the incorporation of the starting phenol. Our examination of the recovered phenol showed a ten percent loss due to the reaction as well.

There are two groups of resonances in the regions around δ 120-122ppm, and δ 142-146ppm. An aggregate of resonances appear around δ 115-118ppm, δ 128-132ppm, and δ 153-157ppm regions. The resonances of δ 115-118ppm

region are characteristic of positions 2 and 2′ of phenol in their unsubstituted form. From the intensity of the resonances in this region it is observed that the phenolic groups in the resin are generally not substituted in both the ortho and the ortho′ positions. The less intense resonances of δ 120-122ppm are for the position para to the hydroxyl group in its unsubstituted form. Its much lower intensity cannot be just due to its statistical differences with the ortho position, but rather due to its greater substitution in the polymer chain. It is deduced that most of the aromatic groups in the polymer are o,p substituted phenols rather than o,o′-substituted ones. However, this does not rule out existence of o,o′ substitution patterns. The aggregate of resonances in the δ 128-134ppm region should be due to the position 3,3′ of phenol as well as the resonances of substituted 2,2′ or 4 positions.

Because of the electronic factors we do not expect any substitution at the 3,3′ positions. The resonances at δ 142-144ppm can also arise from 2,2′ or 4 positions when they are substituted. The resonances of δ 153-156ppm can arise from the C1 position of substituted phenols. The resonance of δ 160ppm can arise from imine resonances while those resonances at δ 174.5ppm are most likely due to carboxylate type carbonyl carbons. These were

indicative of a general structure for the resin which would have a carbohydrate moiety, possibly a derivative of glucose or glucosylureas, as well as an aromatic moiety which could be a substituted form of phenol.

B. Liquid Chromatography of the Polymer: Many attempts were made to isolate, by means of liquid chromatography, any polymeric chains that were ordered enough to have resolved spectroscopical characteristics which would have resulted to structural determination. However, finding a separation system for the oligomers proved to be impossible. This was attributed to the fact that the oligomers were a highly complex mixture. With the possibility of formation of a wide range of glucose derivatives, under reaction conditions of this study, as well as the many different possible reaction pathways and substitution patterns, the mixture showed no dominant structure which could have been isolated. The choice of chromatography was also limited since the mixture was fully soluble in water alone.

This polymer was partially soluble in methanol. By dissolving away the methanol soluble fraction of the polymer by washing the mixture with several aliquots of hot methanol, a very polar residue was left which was insoluble in alcohols. We refer to this as the aqueous

soluble polymer. The choices of chromatographic systems were limited to reverse phase ones with water as one of the main eluents in the system. Our efforts were further hindered by difficulties in using refractive index as the detector of choice. The variation in the water concentration gave rise to false absorptions which added to the complexity of this work. After exhausting all possible chromatographic systems, certain polymeric structures which had no aromatic character were isolated, on a Toyopearl HW-40 liquid chromatography system using a volumetric ratio of 85:15 methanol/water as the solvent mixture. The aqueous polymer was dissolved in a volumetric mixture of 75:25 methanol/water solution. The solubility was only 2mg/10ml of this solution which required a total of 50 chromatographic runs of 10 milliliters of this solution at each time to charge a 100mg of this sample onto the column. Upon rechromatography and HPLC analysis, the sample consistently resulted in one peak.

B1. <u>NMR Study of the Chromatographed Polymer</u>: The proton and carbon NMR are shown in Figures 9 and 10 respectively. Since only a few milligrams of this fraction was obtained, but also because of the variation in the chemical regions of the carbon atoms within the

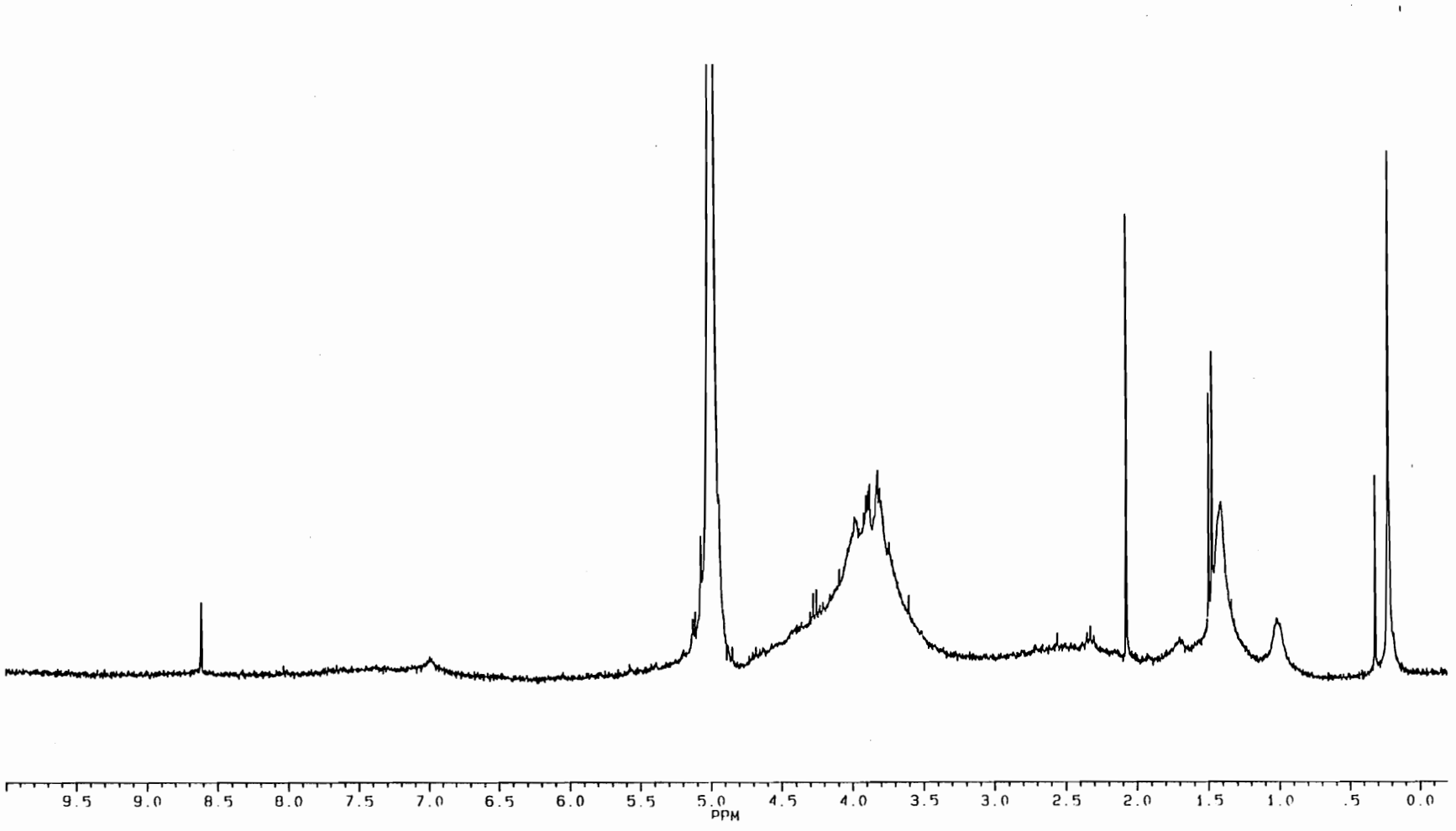


Figure 9: Proton NMR Spectrum of the Chromatographed Polymer.

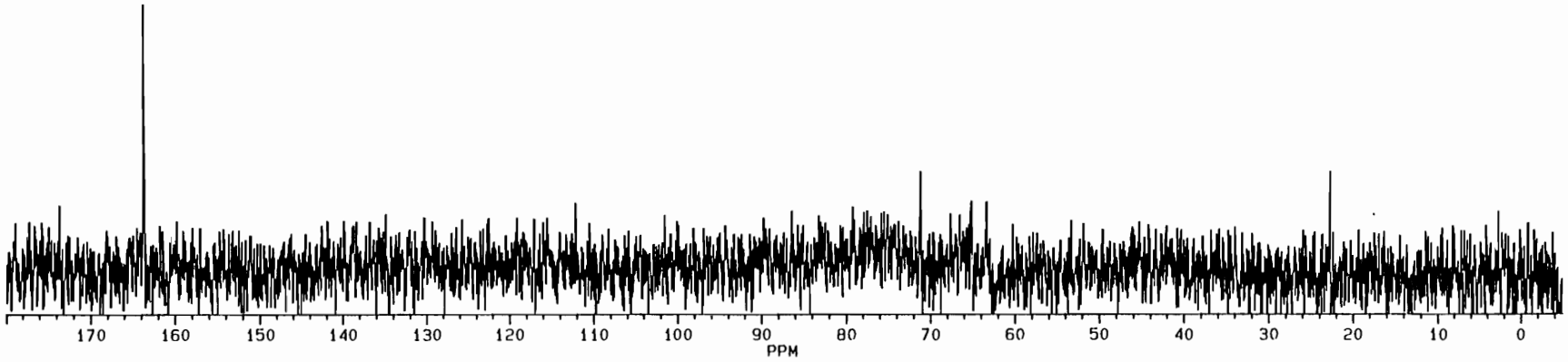


Figure 10: Carbon NMR Spectrum of the Chromatographed Polymer.

polymer, the carbon resonances are hardly detectable. Therefore no fundamental structure for the resin was set forth at this point. The major finding of this analysis was that the isolated fraction did not show any aromatic resonances. The proton NMR indicates existence of a formamide moiety which shows a sharp singlet resonance at δ 8.65ppm. The carbon NMR is also consistent with this finding and the carbonyl resonance of δ 164ppm can only arise from formamide type aldehyde.

3). Analysis of the Ethyl Acetate Fraction:

At this point the ethyl acetate fraction was analyzed to look for possible intermediates in the polymerization process. After removing as much of the ethyl acetate on a rotary evaporator as possible, a dark red viscous solution was left which mainly consisted of phenol. TLC analysis on Kieselgel-60 silica gel, with benzene:acetone:methanol in the volumetric ratio of 6:3:1 respectively, of the ethyl acetate fraction also showed phenol in abundance but also a series of other spots were detected. To remove the phenol, a column was packed with 900g of Silica Kieselgel-60, 70-230 Mesh. The column was flushed with ethyl acetate at a flow rate of 1ml/min for 24 hours. The organic phase, which had a volume of 135ml, was then charged onto the column. Straight ethyl acetate was used as the solvent and phenol eluted from

the column with the solvent front. Monitoring by TLC, the fractions were combined to make a total of five where the first fraction was unreacted phenol. The solvent system was then changed to a volumetric mixture of 75:25 ethyl acetate and methanol solution. This gradient solvent change was continued till 100% methanol was reached. This step-wise gradient solvent manipulation proved to be very helpful in all our separation experiments. A total of fifteen fractions were collected with some being very complex mixtures. This again affirms the complexity of this reaction and the enormousness of the number of products being formed. Fraction #2 was examined on silica Kieselgel-60 TLC plates utilizing different solvent systems. Under these conditions relatively good separation was observed with chloroform as the solvent. A 100g of silica kieselgel-60 was packed into a column and flushed with chloroform for 24 hours. Fraction #2 was then charged onto this column using chloroform as eluent. By means of TLC monitoring of the system three fractions were obtained with no fraction being more than 3mg. Studies of proton NMR showed no pure product but still mixtures of several components in each fraction. The NMR results were very complex and they differed from the spectra of the resin precursor completely. These were therefore not studied further. Fraction #3 was also subjected to a silica

column with chloroform as the eluent. The fractions were monitored by using the above TLC system and they were combined to six portions. Again none of the fractions were more than a few milligrams and NMR analysis of these fractions warranted complex mixtures to exist. Since these NMR spectra proved these components to be different from those incorporated in the polymer precursor, these sub-fractions were not investigated further. This held true for all other fractions but fraction #4.

Fraction #4 showed best separation on silica plates with benzene, acetone, and methanol as solvent mixture in the volumetric ratios of 6:3:1 respectively. Preparative plate chromatography of this mixture resulted in four distinct bands. This fraction which weighed 100mg was charged onto eight 20x20cm silica Kieselgel-60 plates. These plates were then chromatographed twice and the four sub-fractions were recovered afterwards. Sub-fractions 1, 2, and 4, all were mixtures of several compounds with different spectral characteristics in relation to the polymeric fraction. Sub-fractions 3, however, seemed to be a mixture of a major component 14, and several minor ones, where 14 had sound spectral resemblance to the non-aromatic region of the polymer precursor. To our surprise, only 14 was soluble in acetone. This solubility difference was used to yield pure 14(8mg).

The various spectroscopic techniques were utilized for structural identification of this product. F.a.b.-m.s. indicated a molecular weight of 132 (m/z 133 (M + H)+) for this compound. The proton NMR, as shown in Figure 11, shows two resonances H2a and H2b, centered at δ 2.33ppm and δ 2.52ppm respectively. From the cosy spectra of Figure 12 we observe that protons H2a and H2b are coupled to each other and to the proton H3 which is centered at δ 3.86ppm. These protons show a distinct ABX pattern with $J_{2a,2b} = J_{2b,2a} = 15.5Hz$, $J_{2a,3} = 8.1Hz$ and $J_{2b,3} = 4.2Hz$. Therefore H2a and H2b are vicinal protons on a carbon which is fixed in a rigid structure. The chemical shifts suggest that H2a and H2b are alpha to a carbonyl moiety while H3 is a carbohydrate type proton. The splitting constants as well as the chemical shifts suggest that H2a is in the axial position while H2b is equitorial. H3 should also be in the axial position due to its relatively large coupling constants. The cosy spectra shows that H3 is also coupled to H4 which is centered at δ 3.51ppm. The latter proton is coupled to H5a and H5b which are centered at δ 3.57ppm and δ 3.71ppm respectively. The splitting pattern of H5a, H5b, and H4 is also of ABX type. The coupling constants are $J_{5a,5b} = J_{5b,5a} = 11.1Hz$, $J_{5a,4} = 6.5Hz$, and $J_{5b,4} = 3.9Hz$. We can

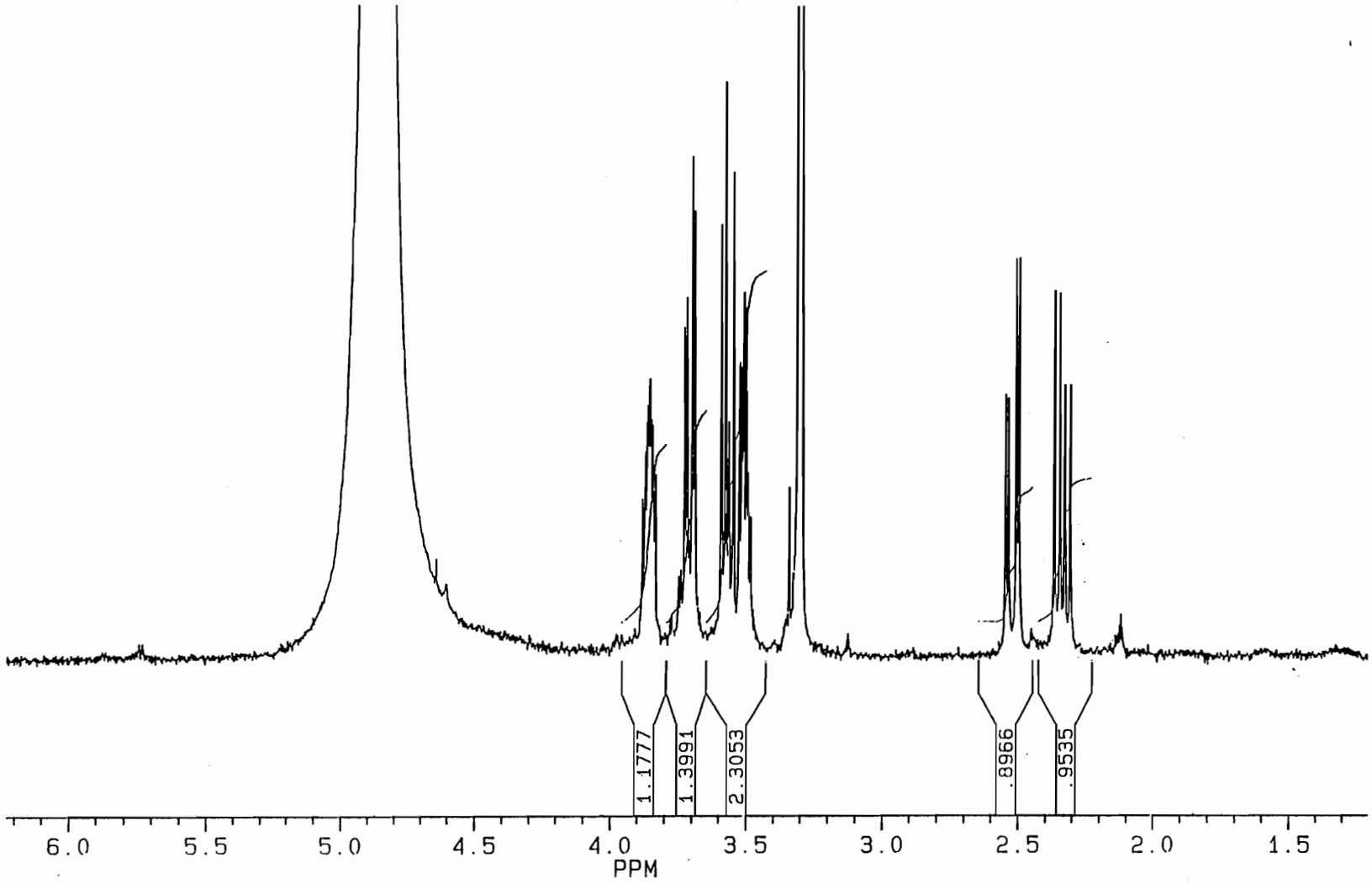


Figure 11: Proton NMR Spectrum of the Isolated Product.

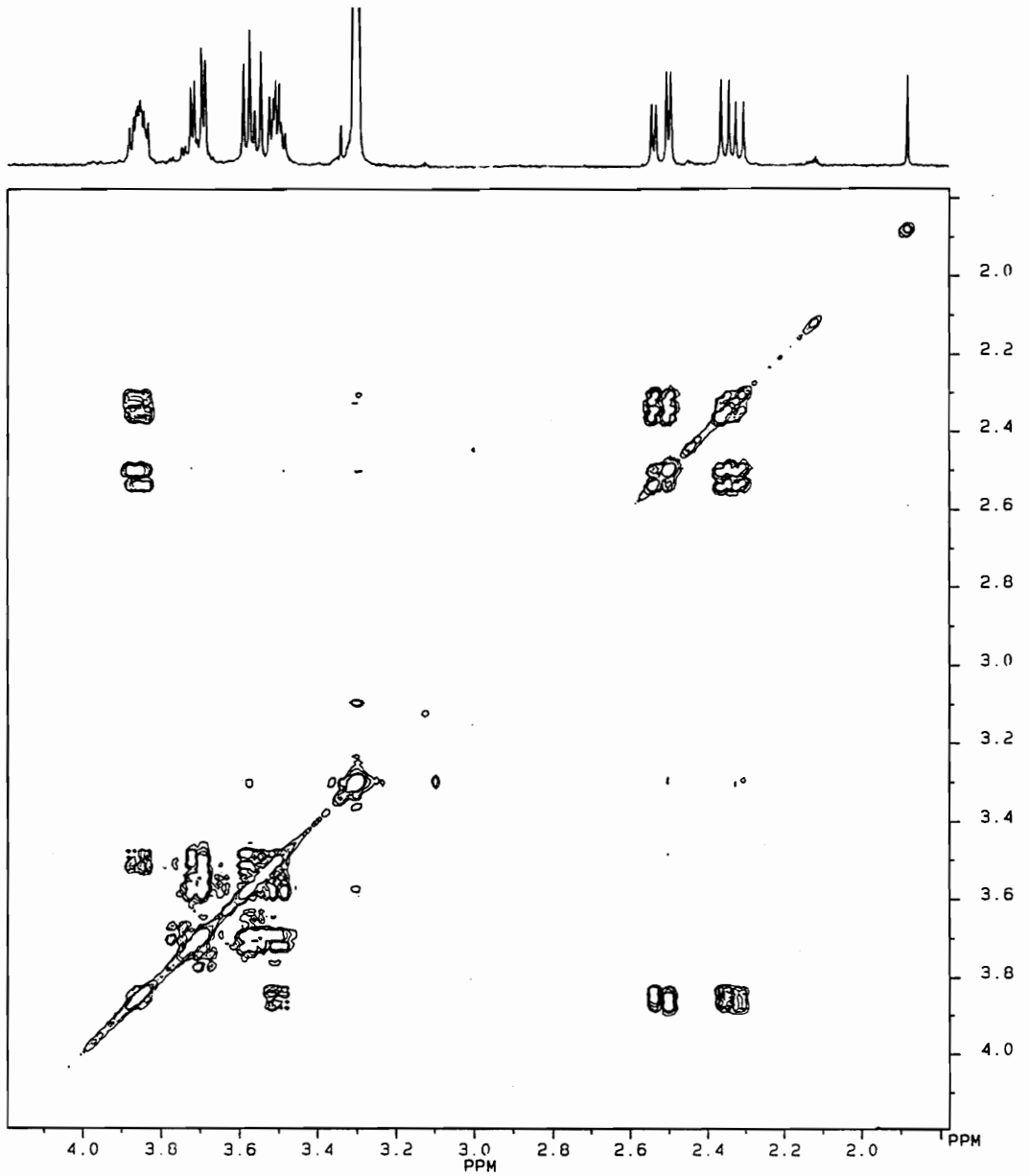


Figure 12: Cosy NMR Spectrum of the Isolated Product.

conclude that H5a and H5b are also vicinal hydrogens on a carbon fixed in a rigid structure and have chemical shifts of carbohydrate type protons. Based on the chemical shifts and the coupling constants H5a must be the axial and H5b must be the equitorial one.

The ^{13}C-NMR which is shown in Figure 13 indicates a resonance C2 at δ 41.23ppm due to a carbon likely to be adjacent to the carbonyl group C1 of δ 180.82ppm. The three carbon resonances of δ 64.66ppm, δ 71.10ppm, and δ 76.02ppm for C5, C3, and C4 respectively, are for carbohydrate type carbons. The results of the depth experiment, as shown in Figure 14, indicate that while C2 and C5 bear two protons each, C3 and C4 bear one proton each. The ^{1}H-^{13}C correlated NMR spectroscopy, for directly-bonded interactions, is shown in Figure 15. This spectra indicates that protons H2a and H2b are coupled to C2. We also observe that C5, which is also a methylene type carbon, bears protons H5a and H5b. Finally, the carbons C3 and C4 are bonded to protons H3 and H4 respectively.

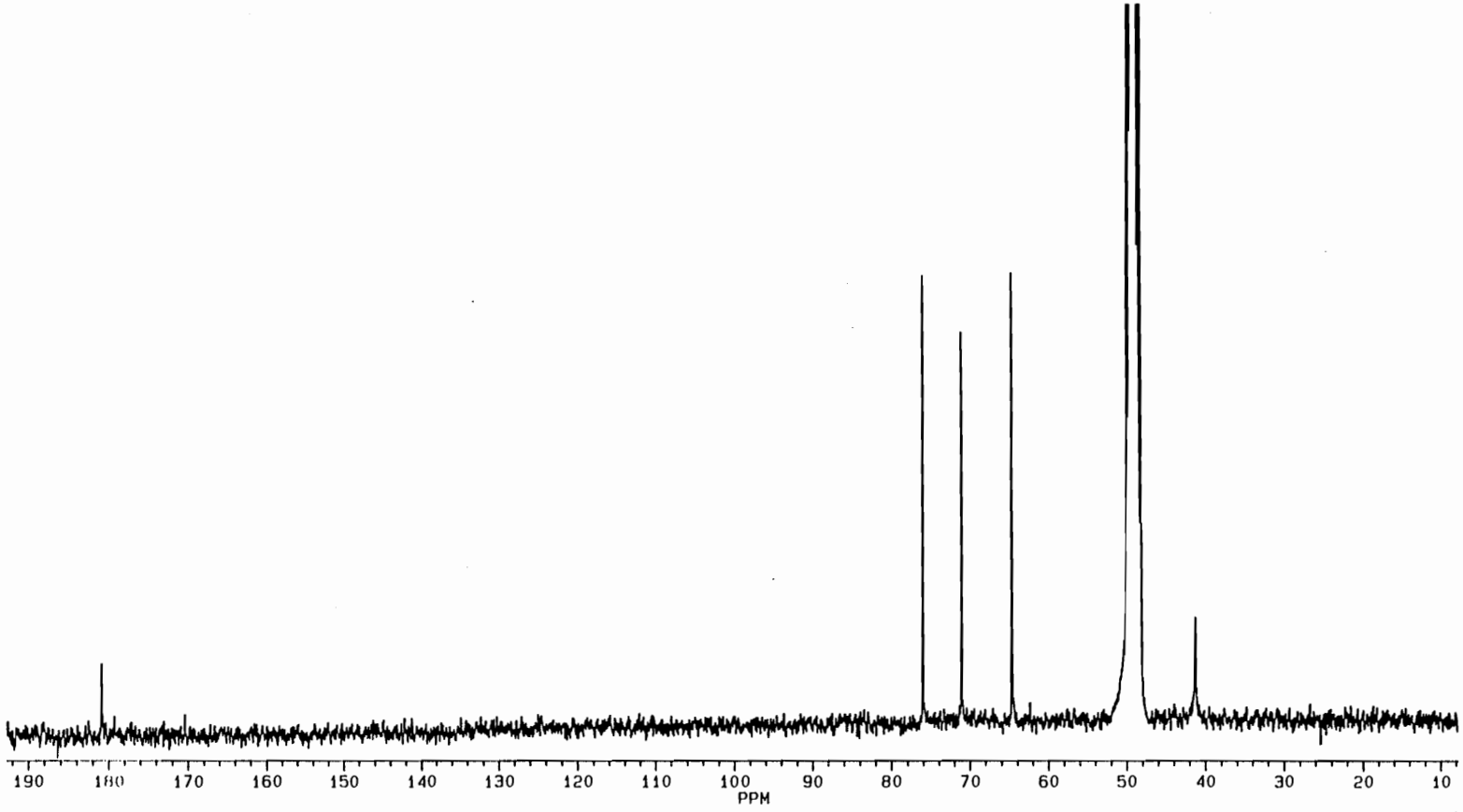


Figure 13: Carbon NMR Spectrum of the Isolated Product.

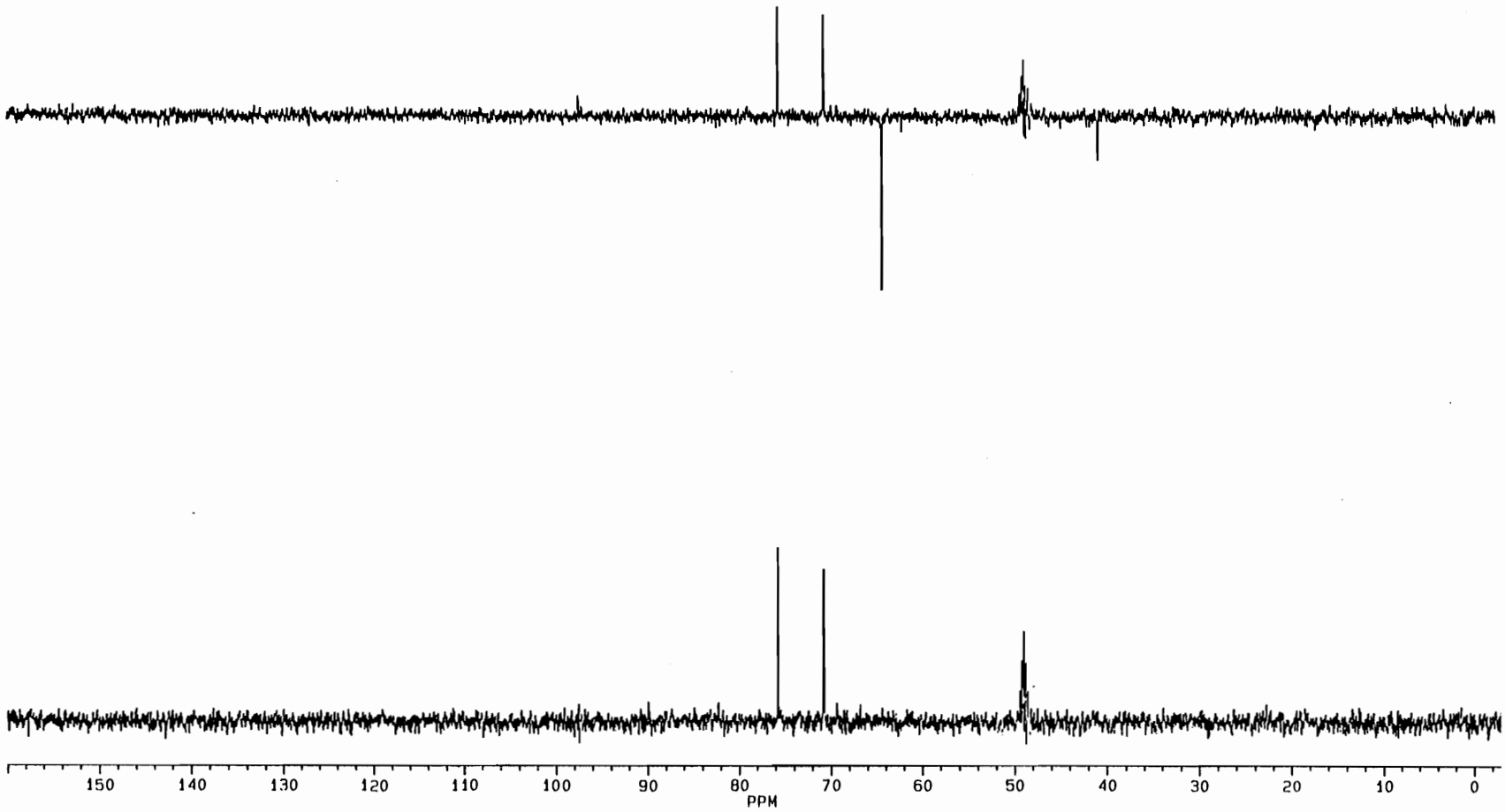


Figure 14: Results of the Depth Experiment for the Isolated Product.

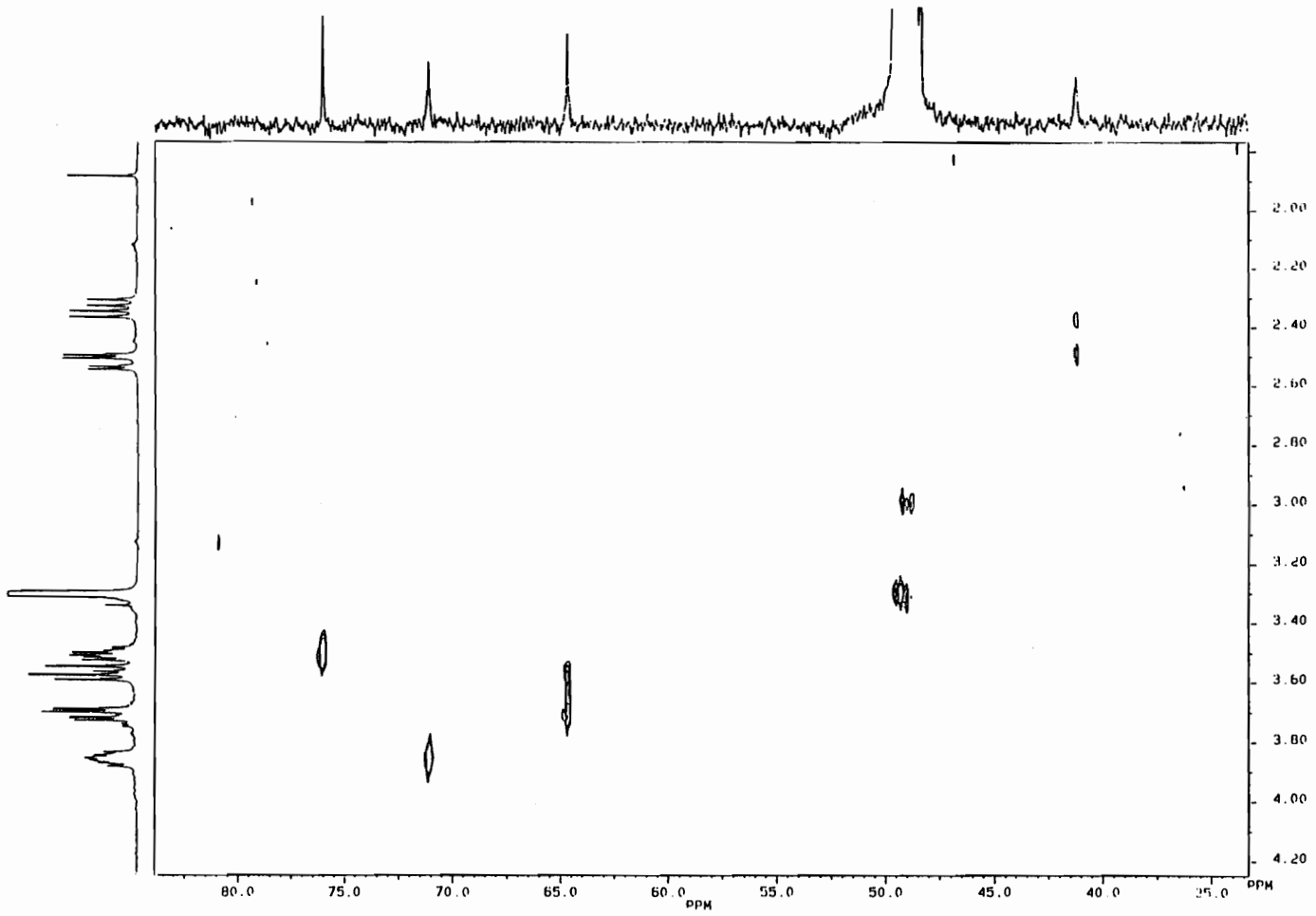
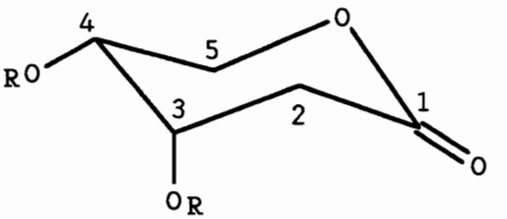


Figure 15: Het-Cor NMR Spectrum of the Isolated Product.

DISCUSSION OF RESULTS

The structure of 16 was identified to be 2-deoxy-D-ribonopyranolactone which is shown below. A review of the pertinent literature indicates that 2-deoxy-D-ribonolactone has been synthesized from 3-deoxy-D-erythro-hexosulose, which was made by NaOH conversion and lactonization of 3-O-benzyl-D-glucose (45). Though spectral evidence was not provided to decide whether this material is a pyrano- or a furanolactone, it is most probable that it is the same compound as 16. To our knowledge this is the first reporting of 2-deoxy-D-ribopyranolactone formation from D-glucose, through a glucopyranosylurea intermediate.



16 R = H

16a R = Ac

The only spectral data available in literature are those of the 2-deoxy-L-ribonopyranolactone in its acetylated form 16a(46). These NMR data are shown in Table 6 along with those of compound 16.

TABLE 6. - NMR Chemical Shifts for 2-Deoxy-D-Ribonopyranolactone (16), and acetylated 2-Deoxy-L-Ribopyranolactone (16a).

Compound	Chemical Shifts (p.p.m)				
	C1	C2	C3	C4	C5
16	180.82	41.23	71.10	76.02	64.66
16a	173.74	34.83	71.12	82.05	63.33

	Chemical Shifts (p.p.m)					
	H2a	H2b	H3	H4	H5a	H5b
16	2.33dd	2.52dd	3.86m	3.51m	3.57dd	3.71dd
16a	2.62dd	2.99dd	5.27dt	4.67td	4.28dd	4.38dd

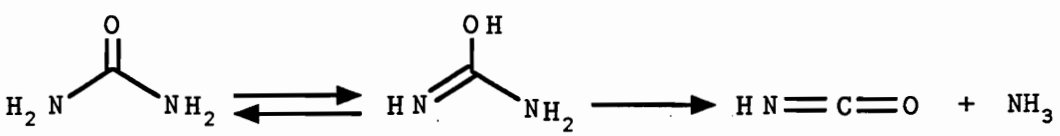
	Coupling constants (Hz)					
	$J_{2a,2b}$	$J_{2a,3}$	$J_{2b,3}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$
16	15.5	8.1	4.2	6.5	3.9	11.1
16a	18.9	7.3	2.8	3.5	3.5	12.1

16 was analyzed in CD_3OD

16a was analyzed in $CDCl_3$, after Numata et al. (46).

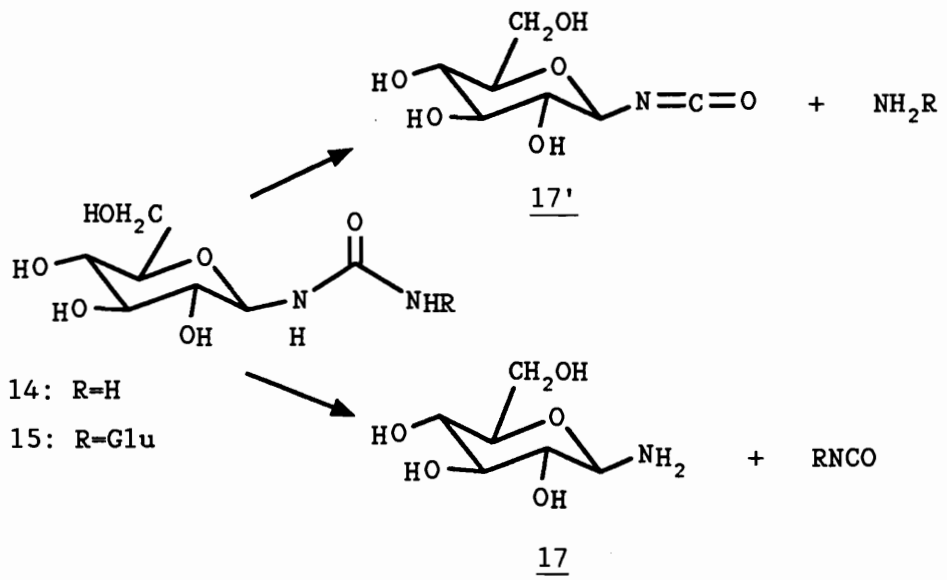
Comparing the NMR data for these two compounds, we see pronounced differences between the proton data due to the acetyl groups in the acetylated isomer. These differences are well within the expected range that is observed among the acetylated and underivitized forms of similar structures. The carbon resonances show much lesser deviations which is due to the lesser deshielding effects of the acetyl groups. These differences are also partly due to these two systems being stereoisomers as well as differing solvent systems. While NMR analysis of 16 was carried out in deuterated methanol, for 16a deuterated chloroform was the solvent of choice.

The disappearance of monoglucosylurea as well as diglucosylurea could result from degradation of the urea moiety in these compounds. Urea has been shown to undergo degradation reaction to form isocyanic acid, and an amine at temperatures above 130C as shown in Scheme VII (47):



Scheme VII

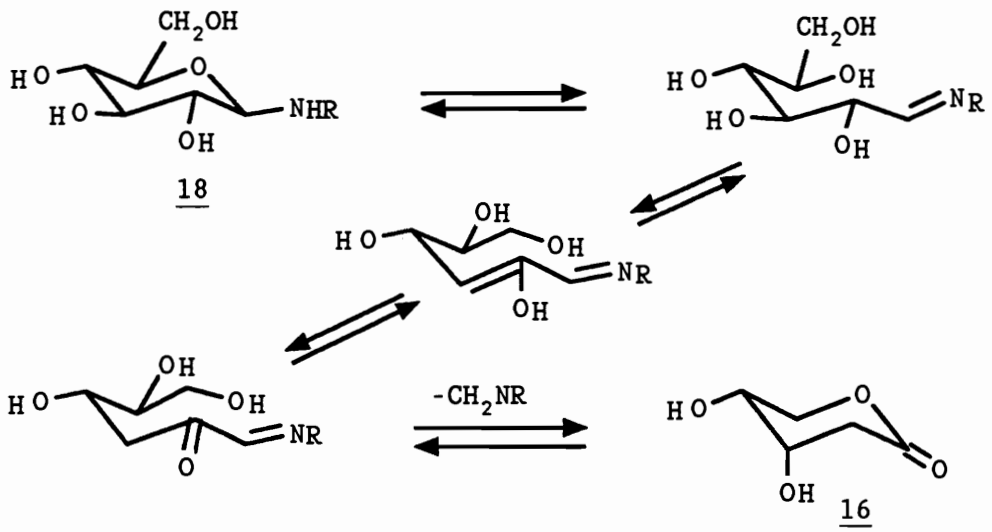
Both monoglucosylurea and diglucosylurea can undergo degradation of the urea moiety to produce two different products, 17 would require the loss of isocyanic moiety, while 17′ would involve the loss of an amine group as shown here in Scheme VIII:



Scheme VIII

Any of the compounds 14, 15, or 17 can rearrange to form 16 as shown in Scheme IX. In the first step of this mechanism abstraction of the proton at the glycosidic nitrogen forms an imine. The existence of this intermediate has been supported by deuterium isotope effect studies(48). The dehydration in the next step of this mechanism is facilitated by the formation of a conjugated system as well as the removal of water. The tautomerization reaction which follows favors the

formation of the ketone and the removal of the enol moiety. The ketone subsequently forms 2-deoxy-D-ribonopyranolactone by rearrangement and the loss of the substituted methyleneamine.



18=14: R=$CONH_2$

18=15: R=CONHGlc

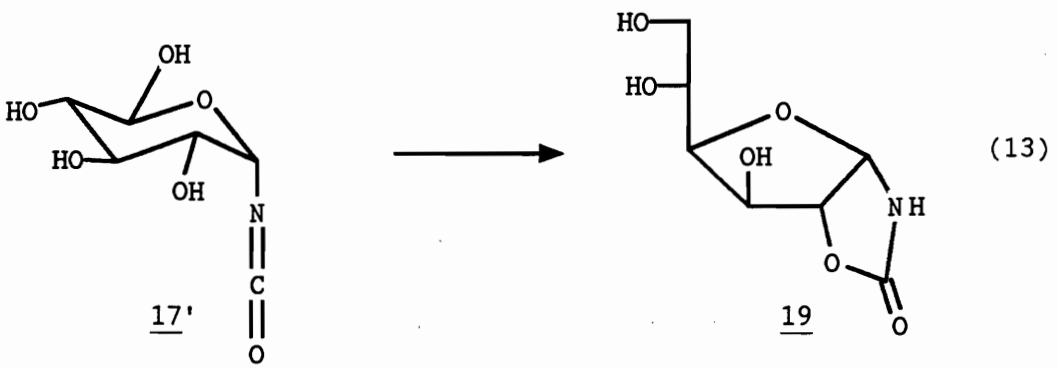
18=17: R=H

Scheme IX

Although we did not observe the furano isomer of 16, we would not rule out its formation in this reaction. The above schemes are drawn for the beta anomer of mono- and diglucosylureas, however, they are equally responsible for the consumption of the alpha anomer as well.

One would expect formation of certain lactams from 17' since the isocyanate moiety is highly reactive toward

hydroxyl groups. The bicyclic Carbamate 19 has been previously reported to be a product of this reaction(49). Its formation can easily be explained by the following intramolecular rearrangement reaction of 17′ as shown here in Equation 13.



(13)

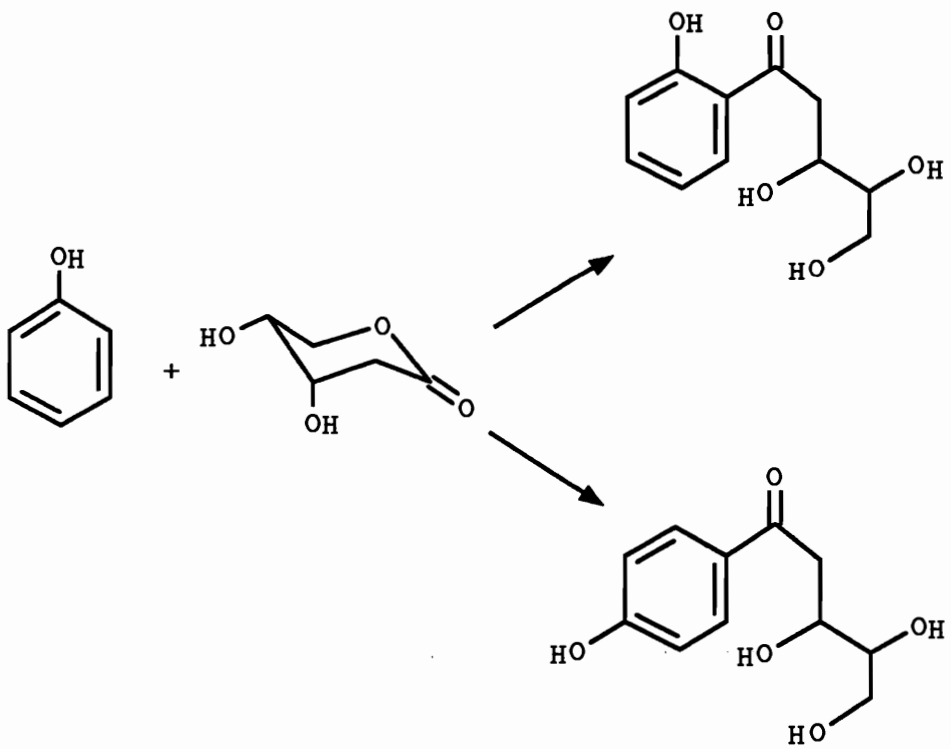
Isolation of the above mentioned compounds is further evidence for the mechanism presented here. The low concentration of the isolated products and the absence of others is attributed to the great reactivity of these intermediate products. It is known that lactones can undergo homopolymerization as well as heteropolymerization reactions(50-52). Although the polymerization of lactones have been of considerable interest, the structure of these polymers have not been yet characterized.

These findings fit very well with those previously reported by us and others. The formation and

disappearance of the mono- and diglucosylureas, as shown in figure 5, as well as formation of the isolated products of the reaction can easily be explained by the above mechanisms. The most significant finding of this study is that deoxy-D-ribopyranolactone moiety, which is the first reporting of it for this reaction, is the major building block of the polymer precursors formed. While the proton NMR of the polymeric fraction indicates that the resonances in the non-aromatic region of the spectra are in the same region as those in the lactone 16, the carbon NMR shows that all of the major resonances in the carbohydrate region of the spectra are homotopic with those of the 2-deoxy-D-ribopyranolactone. The two carbon resonances of C4 and C5 of compound 16 have the exact same chemical shifts as that of the polymer, while the C3 chemical shift is only different by 1ppm from that of the polymer. Furthermore, the C2 resonance of 16 at δ = 41ppm is closely related to the resonance of δ = 39ppm which appears in the NMR of the polymeric fraction. This difference in the shifts is due to the fact that while 16 is a cyclic compound, in the polymerization process the lactone opens up to a linear unit. The intensities of these carbon resonances are exactly as we would expect as well. In the polymer, the resonance that we have assigned to a methylene carbon has twice the intensity of the resonances that are assigned to methine carbons.

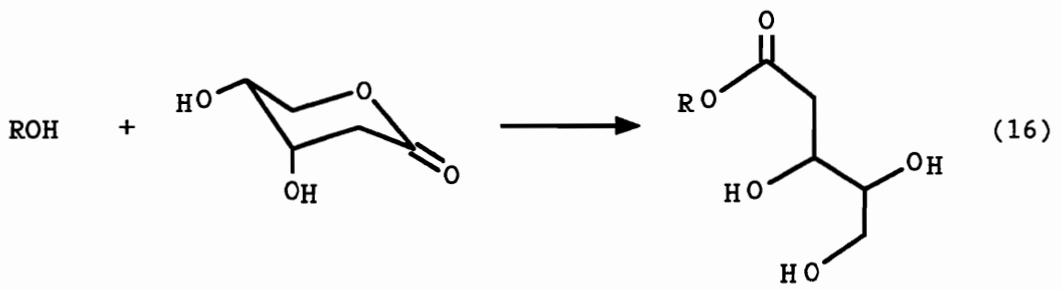
This hypothesis is supported by the proton NMR data. In the same region where H1 and H2 resonances of 16 occur, the polymer shows a doublet. Once the ring structure is opened and the rigidity is lost, the two protons attached to the C2 moiety will be equivalent and they will only be coupled to H3.

The lactone can undergo reaction by nucleophilic attack at the carbonyl group. The nucleophile can be the ortho or para positions of phenol as indicated by Equations 14 and 15, or it can react with the various hydroxyl groups as shown in Equation 16:



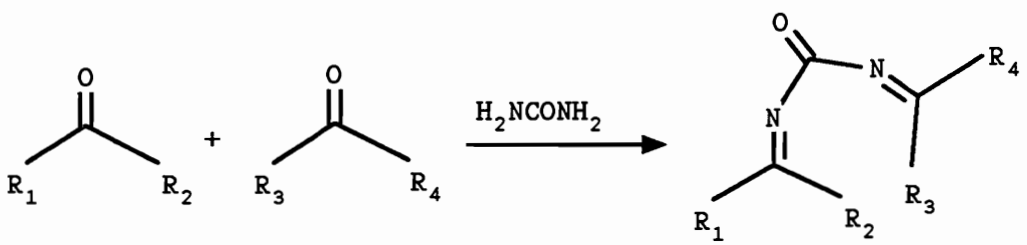
(14)

(15)



(16)

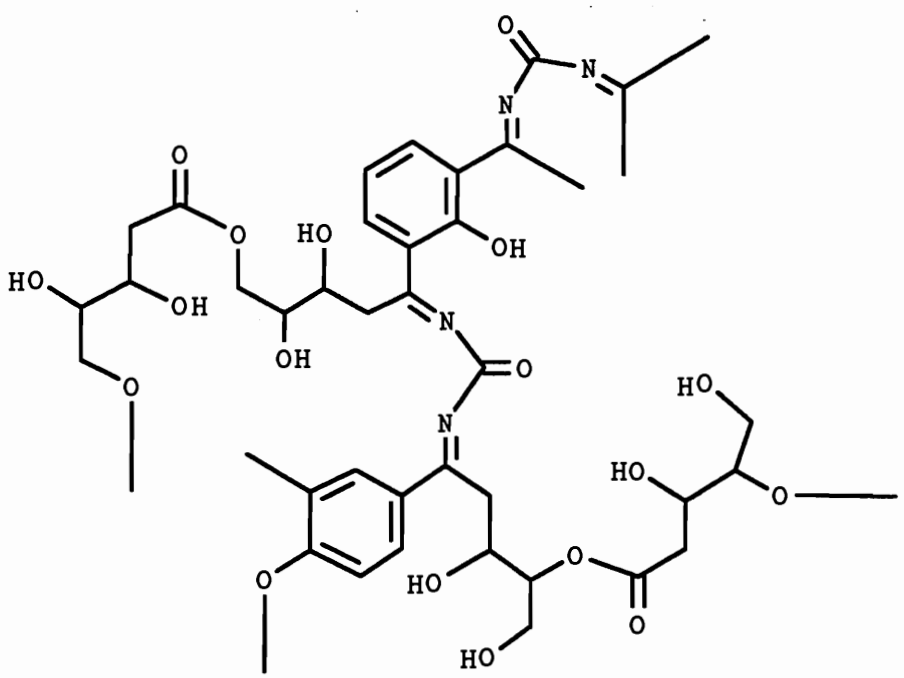
The R group can be a monomeric unit or a polymer. These polymers are then crosslinked by the coupling reaction of the urea nitrogen and the carbonyl groups as shown by Equation 17:



(17)

This reaction causes the formation of imine and the loss of some of the carbonyl groups. This is observed in the ^{13}C-NMR of the resin where the intensity of the carbonyl moieties is reduced and the imine resonance is observed at around δ = 155ppm which overlaps with the resonances of the C1 position of phenol. Also the methylene group which is alpha to the C=N group should be shifted to δ = 21ppm for the syn isomer, and to δ = 28ppm for the anti isomer. As is seen in the ^{13}C-NMR of the polymer precursor, the syn isomer is predominant as compared to

the anti one. This is well justified since when R group is a phenol ring, or other bulky groups, the nitrogen substituent would be anti to this group and syn to the smaller methylene group. The resonance of δ = 160ppm therefore results from the carbonyl group of the urea moiety. Since a resonance at δ = 175ppm appears, therefore not all the carbonyl groups have reacted with nitrogen. In fact comparing the intensities of the carbonyls at one end of the spectrum to each other, and those of the methylenes at the other end to each other, indicates that nearly half the carbonyl groups have reacted with nitrogen, while the other half stayed intact. The three dimensional network which is formed is therefore highly polar and hygroscopic due to the incorporation and formation of high numbers of polar functional groups like hydroxyls, ketones, and imines. Since there are many reactive sites in the many intermediates in this highly complex reaction, the polymer formed is amorphous, therefore we cannot give an exact structure of the polymer. A generalized structure for the polymer precursor should however contain 2-deoxy-D-ribonose and phenol in its backbone structure and incorporate urea in the crosslinking of the structure. One such structure which would have these characteristic is given below:



20

This also fits well with the empirical formula of $C_{12.8}H_{17.0}N_{2.0}O_{6.0}$ we obtained for the polymeric fraction. These results are close parallels of those reported by Olsson et al. in a similar study. Their reported empirical formula of $C_{13.0}H_{14.2}NO_{4.6}$ is mainly different due to the type of the amine used in their study and the aromatic groups in the polymer being the rearrangement products of glucose.

This study not only has characterized the structure of this polymer and the fate of the glucose in this reaction, but also has cleared the path to understanding the structure of the polymers formed in nature or in lab between glucose and amines under acidic conditions.

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