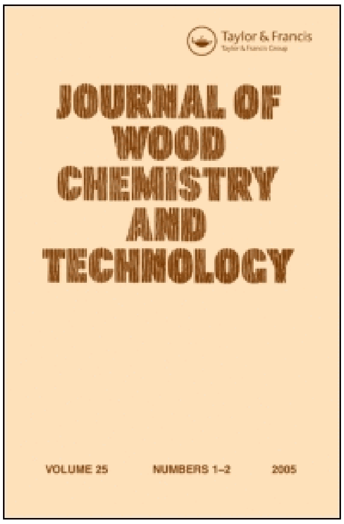

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THE FORMATION OF MONOMERIC PRODUCTS FROM LIGNIN BY THE ACTION OF AMMONIUM SULFIDE

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ABSTRACT

Acetoguaiacone and propioguaiacone were found to be the dominant lignin monomeric products (molar ratio 1.3 to 1) from the spent liquor of hemlock pulped with ammonium sulfide/methanol/water. The combined amounts of the ketones were as high as 3.5% based on wood. This is higher than reported monomer quantities from any other pulping process.

The model compounds, guaiacyl glycerol β-(2-methoxyphenyl) ether and coniferyl alcohol, also produced aceto- and propioguaiacone, upon ammonium sulfide treatment at 180°C. The molar conversion to these two ketones was more than 50% in both cases. It was, therefore, concluded that uncondensed β-O-4 lignol structures were the primary lignin precursors of the ketones, and coniferyl alcohol was an intermediate in this conversion.

Studies using coniferyl alcohol and wood meal were also conducted at 140°C. An alpha carbonyl intermediate was found which primarily formed propioguaiacone.

INTRODUCTION

The significant feature of ammonium sulfide/organosolv pulping was recently shown to be exceptionally high yields - a 14% increase on wood over kraft(1). Preliminary sephadex fractionation of the spent liquor lignin indicated an unusually low average molecular weight. In addition, large amounts of water soluble lignin from the

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spent liquor were isolated as an oily material by chloroform extraction. This paper describes the major monomeric products of the water-soluble fraction, and the probable pathway of their formation. The quantities of monomers found may increase the attraction of the ammonium sulfide pulping process.

RESULTS AND DISCUSSION

Identification and Quantification of Monomeric Products in Soluble Lignin

The UV spectrum of the water soluble lignin, shown in Figure 1, contains a shoulder at 310 nm in neutral solution and a peak at 345 nm in alkali, indicating the presence of a conjugated carbonyl structure. An HPLC chromatogram of the soluble lignin fraction extracted into chloroform is shown in Figure 2A. The striking feature of both HPLC and GC(2) chromatograms was the dominance of only two peaks, quite unlike the multiplicity of peaks that appear in chromatograms of kraft lignin(3). The first and second peaks were determined to be acetoguaiacone (Ac, 1) and propioguaiacone (Pr, 2), respectively, on the basis of IR, NMR, UV and TLC analyses, and retention times in GC and HPLC(2) in comparison with authentic compounds.

Yields of the two dominant monomers in the soluble lignin were obtained by HPLC analysis, using the synthetic compounds as standards. Table 1 contains the results of the Ac and Pr analyses and the soluble and insoluble lignin quantities under a variety of chemical pulping charges. In general, there appears to be a decrease in Ac and Pr formation when both methanol and ammonium sulfide were increased. The molar ratio of Ac to Pr however, was found to be approximately 1.3 to 1, regardless of the chemical charge. The highest quantity of these ketones found, was equivalent to 10.7% based on the weight of lignin. Assuming a methoxyl content of 16%(4) based on Klason lignin, it can be

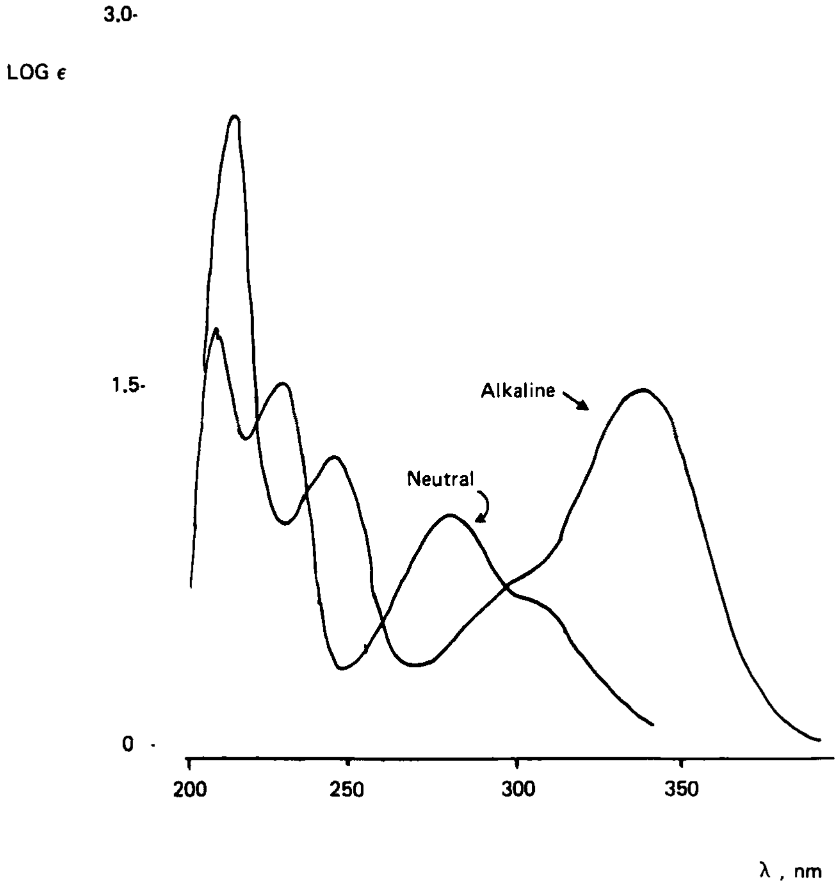

FIGURE 1. Ultra-violet spectra of ammonium sulfide soluble lignin. (~2 x 10^{-5}g/liter).

calculated that 12.5% of all lignin monomeric units were converted to Ac and Pr under ammonium sulfide reaction.

Propioguaiacone and especially, acetoguaiacone are frequently reported monomers in the spent liquor of sodium sulfide, hydrosulfide and kraft-type processes. They have been found in these liquors in various, although usually low total yields (2% or less based on lignin(5)). Table 2 shows a few of these values. The only results that can compare with those of ammonium sulfide

FIGURE 2. HPLC chromatograms of ammonium sulfide reaction products obtained at 180°C. (HPLC solvent - 2:1 MeOH:water). Part A: Soluble spent liquor lignin. Part B: Guaiacyl glycerol-beta-(2-methoxyphenyl) ether. Peak symbols: 1. Acetoguaiacone. 2. Propioguaiacone. G. Guaiacol. X. Internal Standard.

TABLE 1

Yields of Ac and Pr from Ammonium Sulfide Pulping of Hemlock

	MeOH		L-free	L Isolated		%Ac	%Pr	Mol Ratio
(AS)	(%)	Kappa	Yield%	%Insol.	%Sol.	on L		Ac/Pr
0.46M	30	80	60.6	8.2	11.0	5.7	5.0	1.2
0.46M*	30	100	60.4	16.9	5.3	4.6	3.7	1.3
0.93M	30	49	60.5	15.4	7.6	4.4	3.5	1.4
0.46M	50	72	62.2	16.3	6.5	5.3	4.2	1.4
0.93M	50	55	62.6	15.0	10.1	3.7	3.3	1.2
1.54M	50	45	60.5	25.1	3.2	0.9	0.7	1.4

COOKING CONDITIONS: Western Hemlock T max = 180°C
Time to Temp = 30 min, Time at Temp = 4 hrs
(except * = 2 hrs) Liquor:Wood = 6:1

(AS) = Ammonium Sulfide concentration (mol/liter)
Ac = Acetoguaiacone, Pr = Propioguaiacone, L = Lignin

TABLE 2
Reported Yields of Aceto- and Propioguaiacones from Softwood Lignins

Starting Material	Treatment	Wt. % Isolated Aceto-guaiacone	Wt. % Isolated Propio-guaiacone	Total	Ref.
Spruce MWL	Sulfate pulping	0.5	0.2	0.7	5
Spruce Chips	NaSH, 170^{o}C, 3 hrs	3.3	+	~ 3.5	6
Spruce Wood	NaSH, at pH 8.5, 24 days at 110^{o}C	6.5	1.3	7.8	7
Hemlock Chips	0.5 M $(NH_4)_2S$ in MeOH-H_2O, 4 hrs at 180^{o}C	5.7	5.0	10.7	Present Work

delignification, are those by Ashorn(7) using sodium hydrosulfide and 24 days reaction time. The sum of Ac and Pr is greater, however, for ammonium sulfide pulping than for any other process.

The Origin of Acetoguaiacone and Propioguaiacone

Ashorn, Enkvist and Hastbacka(7,8) suggested that the uncondensed aryl glycerol β aryl ether structure, which constitutes almost half (46%) of lignin(9,10,11), was a likely precursor of Ac and Pr under sodium hydrosulfide reaction. They reacted the model compound, guaiacyl glycerol β (2-methoxyphenyl) ether (3) ("β ether"), with sodium hydrosulfide and found acetoguaiacone (15.8%) and propioguaiacone (2.4%), as well as some coniferaldehyde.

Reaction of the β ether model compound with ammonium sulfide in methanol/water under pulping conditions produced Ac and Pr (together with guaiacol) in 57% total yield (Figure 2B). The ratio of Ac to Pr was approximately the same as that found from wood (i.e., 1.3).

Ashorn(8) found only 18.2% Ac and Pr in sodium hydrosulfide cooking of the β ether, despite his relatively high yield from wood (Table 2). Assuming that lignin is a random polymer, then almost half of the estimated 38% uncondensed lignin units(11) will be uncondensed β ether structures (18%). Acetoguaiacone and propioguaiacone found in this study (10.7%), would represent approximately 60% yield based on these β ether precursor structures in lignin. The 57% yield, therefore, indicates not only a high degree of conversion of the β ether units to Ac and Pr, but is also approximately the same as the calculated percent of conversion of the guaiacyl glycerol β guaiacyl ether structures in wood.

The indication is, then, that the β ether structure was the primary precursor of the Ac and Pr produced in the ammonium sulfide pulping of wood.

The Role of Coniferyl Alcohol As an Intermediate

If the β ether was the structural precursor, then, what is the mechanistic pathway by which Ac and Pr were formed?

That coniferyl alcohol 3 was a degradation product of the β ether, was already suspected by Brunow and Miksche in 1969(12), and it was found by Gierer and Lindeberg(3) in 1980 after the kraft cooking of wood. The highest yields of coniferyl alcohol obtained thus far from the kraft process, however, have been only 0.5% based on lignin(13). The most recent results(14) indicate that although the low coniferyl alcohol yield is mainly due to condensation with other components of dissolved lignin, only a fraction of cleaved phenolic β ether structures are converted to this compound in the kraft process.

Coniferyl alcohol formation, and subsequent ketone production, might also be expected during ammonium sulfide reaction. When coniferyl alcohol was subjected to ammonium sulfide, under the same conditions as the wood chips - including 180°C - almost two thirds of the coniferyl alcohol reacted to form Ac (33%) and Pr (30%), again at a molar ratio of 1.3. No other monomers were detected. Coniferyl alcohol was also reacted with ammonium sulfide in a purely aqueous medium, and with ammonium hydrosulfide (initially polysulfide-free) in separate experiments. The results were all identical. This strongly supports the idea that all of the Ac and Pr formed, passed through the intermediate - coniferyl alcohol - which, in turn, was formed from the β ether.

The difference in monomeric products between sodium and ammonium based reactions was demonstrated by performing a sodium hydrosulfide reaction (0.7 M, 170°C) likewise on coniferyl alcohol. The results, indicated the presence of Ac (16.5%), but the amount of Pr was insignificant (0.8%). Instead, vanillin (5%) appeared, quite unlike the ammonium sulfide results. Furthermore, the total yield of these carbonyl compounds was less than half the yield given by ammonium sulfide under similar reaction conditions. Participation of ammonia as a Schiff's base(15) might be a contributing factor in the unusually large Pr quantities. Although acetoguaiacone is a commonly found monomer from kraft-type reactions (Table 2), Pr is never found in the quantities indicated from ammonium sulfide.

In order to investigate the mechanistic formation of Ac and Pr, coniferyl alcohol experiments were conducted at 140°C. Figures 3A and 3B show two of the chromatograms with reaction times of 15 minutes and 2 hours. A new peak, which was shown to contain an alpha-carbonyl by UV (345 nm maximum in alkaline solution), is evident in significant amount. Since the peak reached a maximum at about 30 minutes and then declined, it probably represents an intermediate. The results of these experiments are plotted in Figure 4.

It can be seen from the figure that when the intermediate peak had dropped to zero, the Pr peak was still increasing. This indicates the temporary formation of another intermediate immediately preceding Pr that was not chromatographable. The Ac peak reached its maximum more rapidly than the Pr peak indicating a slower rate of formation for Pr. By three hours reaction time, however, Pr had caught up with Ac to produce the usual molar ratio of Ac to Pr, i.e., 1.3: 1.

The Mechanistic Proposal

Synthesizing the ammonium sulfide experimental results and information collected from the literature, a scheme is proposed in Figure 5 to explain the conversion of coniferyl alcohol to the ketones.

Coniferyl alcohol is first converted to its quinone methide 4 in this scheme, which may react with hydro(poly)sulfide to produce omega hydroxypropioguaiacone (ketone 5). This structure can give Ac directly, or pass through a further alpha-carbonyl intermediate 6 to yield Pr and elemental sulfur.

Support is available from the literature for the idea of ketone 5 being a degradative intermediate. Gierer(15) reacted ketone 5 in alkali and found only Ac and Pr as products, although no

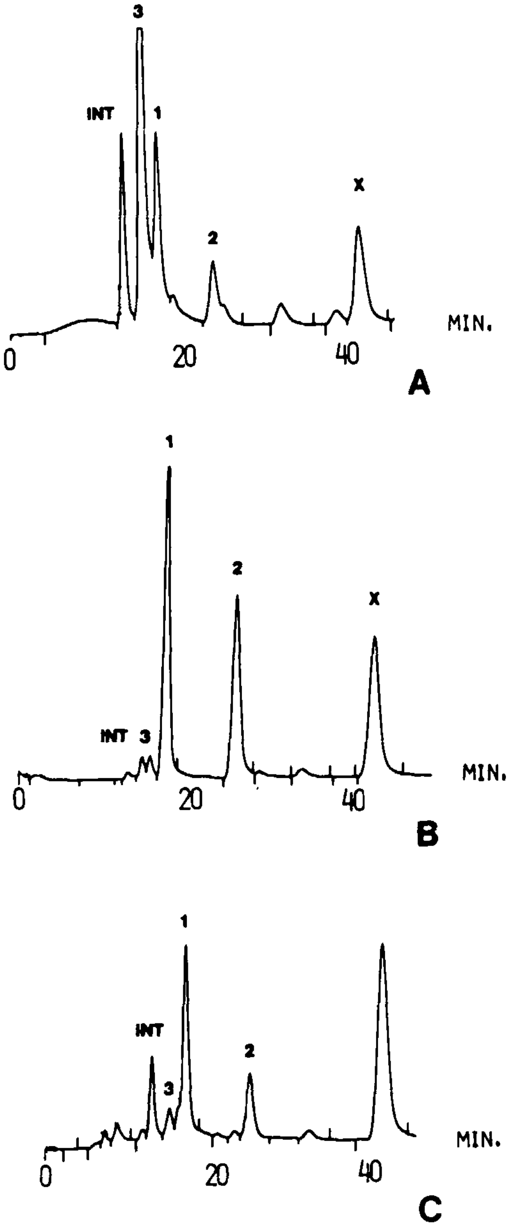

FIGURE 3. HPLC chromatograms of ammonium sulfide reaction products obtained at 140°C. (HPLC solvent - 1:1 MeOH:water). Parts A and B. Coniferyl alcohol reacted for 15 min., and 2 hours, respectively. Part C. Hemlock wood meal pulped for 75 min., 30% MeOH. Peak symbols: 1. Acetoguaiacone. 2. Propioguaiacone. 3. Coniferyl Alcohol. INT. Intermediate. X. Internal Standard.

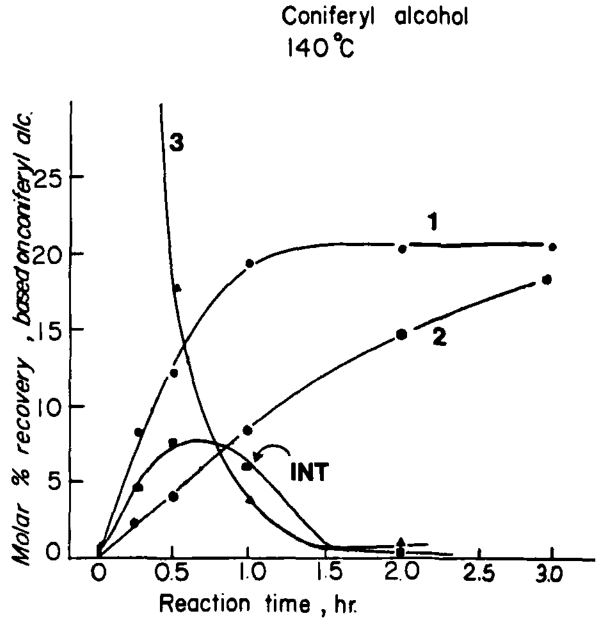

FIGURE 4. Formation of Reaction Products from coniferyl alcohol treated with ammonium sulfide at 140°C. Peak symbols: 1. Acetoguaiacone. 2. Propioguaiacone. 3. Coniferyl Alcohol. INT. Intermediate.

amounts were given. This compound was also suspected by Ashorn et al(8) to be an intermediate, although they didn't recognize the importance of coniferyl alcohol. When they reacted ketone 5 with sodium hydrosulfide (actually hydro(poly)sulfide according to Brunow and Miksche(17)), they obtained Ac, Pr and a dimeric monosulfide which gave these two ketones on further digestion. These results support the intermediacy of ketone 5. Its facile reaction by reversed aldol also helps explain the more rapid formation of acetoguaiacone (Figure 5).

Since the literature indicates that both ketones are formed from ketone 5, it is not a likely candidate for the alpha carbonyl intermediate detected after reaction at 140°C. This intermediate

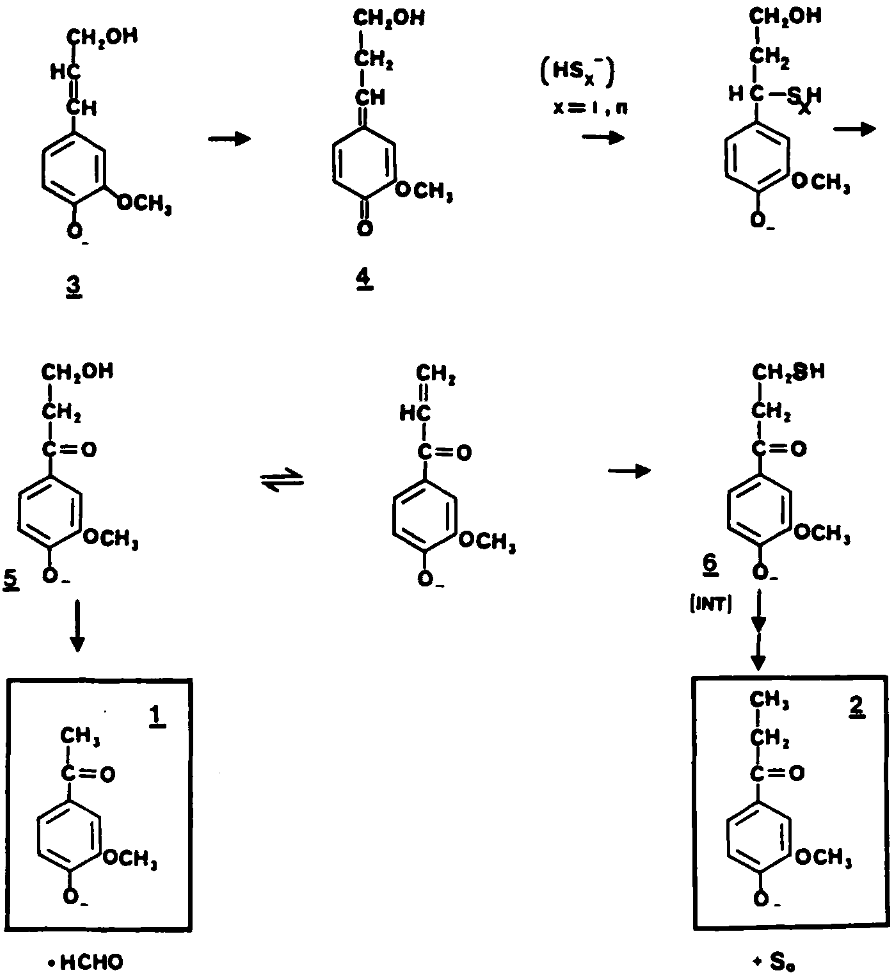

FIGURE 5. Proposed reaction pathway from coniferyl alcohol to acetoguaiacone and propioguaiacone.

apparently did not contribute to acetoguaiacone formation (Figure 4). It was, therefore, speculated that the chromatographed intermediate had structure 6 in the scheme, and contained a gamma SH group.

The proposal of the coniferyl alcohol mechanism was based on model compound studies. The question still remains - whether or not the proposed intermediates and suggested mechanism will actually apply to wood. Wood meal, reacted at 140°C in precisely the same manner as coniferyl alcohol, gave the HPLC chromatogram shown in Figure 3C. The presence of the same alpha carbonyl intermediate <u>6</u>, in addition to the same ratios of Ac and Pr found in the coniferyl alcohol model experiments, is evident. This confirms the proposition that the β ether in lignin reacts to form coniferyl alcohol which, in turn, produces the ketones as depicted in the scheme of Figure 5.

EXPERIMENTAL

Isolation of Lignin from Pulping Liquors

Industrial western hemlock chips (25 g) were extracted with acetone in a soxhlet for 48 hours and air-dried before pulping in a 310 ml Parr reactor (452 HC). Cooking liquors were prepared from 22% aqueous ammonium sulfide (Mallinckrodt) and diluted to the correct molarity with reagent grade methanol and distilled water (chip moisture not included). Molarities and methanol percentages by volume actually used are shown in Table 1. Air was not excluded from the digestion vessel because of the facile loss of ammonia.

Ammonium sulfide pulpings were performed with various chemical charges, and the lignin was isolated from each cook as described in Figure 6. The procedure for lignin isolation involved evaporation of the methanol from the spent liquor followed by acidification. After centrifugation, the supernatant liquor was extracted with chloroform and this extract ("soluble lignin") was further analyzed instrumentally. The HPLC peaks were confirmed to be a mixture of Ac and Pr by NMR analysis.

Lignin was isolated from wood meal (Wiley mill - 1 mm round hole) pulpings in the same manner, except that after evaporation of the wash methanol (pH 7), extraction with chloroform was performed without further acidification. Wood meal (1 gram) was cooked at

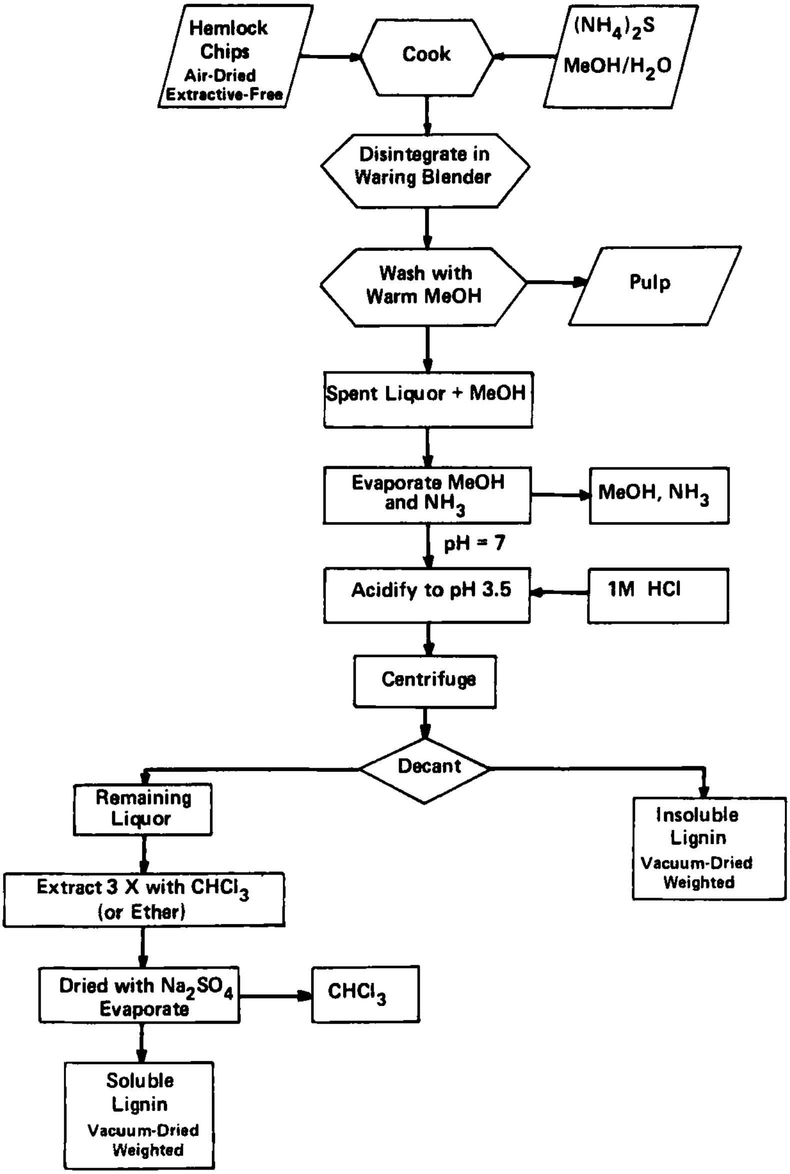

FIGURE 6. Scheme for lignin isolation from ammonium sulfide spent liquor.

both 140°C and 180°C, and total immersion time of the 8 ml capacity bombs in the oil bath was the reported cooking time. Yields based on O.D. wood for the wood meal pulping at 140°C, 0.5 M ammonium sulfide, 30% MeOH, were Ac - 0.2%; Pr - 0.1%; coniferyl alcohol - 0.5%; and "intermediate" - 0.7%.

Instrumental Analysis

Soluble lignin samples and model compounds were analyzed and checked for purity by the following instruments:

The ultraviolet-visible spectrophotometer (UV) used was a Perkin-Elmer Coleman model 571. Lignin and model compounds were run in methanol or methanol-water (2:1) with the same solvent in the reference cell. The infrared spectrophotometer (IR) used was a Perkin-Elmer model 727B. Lignin and model compounds were run in chloroform between sodium chloride plates with chloroform in the reference beam. The nuclear (proton) magnetic resonance (NMR) spectra were recorded on a Varian T-60 with trimethylsilane as the internal standard and deuterated chloroform as the solvent. The gas chromatograph (GC) used was a dual column Hewlett Packard F and M scientific model 5750, equipped with a hydrogen flame ionization detector. Oxygen-free nitrogen was used both as a carrier (20 ml per minute) and an auxiliary gas (30 ml per minute). The column used was an 8 ft x 18 in stainless steel SE-52% (100120 Chromosorb, Supelco). The injection port temperature was 230°C and the flame detector was 220°C. The usual temperature programming used was four minutes at 130°C (post-injection interval) and eight degrees per minute until 220°C was reached. GC retention times were 12.9 min for AC and 14.9 min for Pr. The high performance liquid chromatograph (HPLC) employed was a Waters Associates product including a 3000 psi pump, Chromatronix Model 220 absorbance detector (wavelength - 280 nm), and optic unit. The preparative reversed phase micro-Bondapak C18 Waters column was flushed with methanol after each analysis. At a flow rate of 1.5 ml per minute, Ac retention time was 12.5 min, Pr was 14.7 min, Guaiacol was 13.6 min and the internal standard was 19.8 min.

Retention times and peak areas for both the HPLC and GC analyses were determined by a Hewlett Packard integrator - model 3390A.

"Spiking" on the GC and HPLC by simultaneous injection of a known compound and unknown sample, was used to determine if the two were identical.

Individual compounds were collected as they eluted off the HPLC preparative column until there was enough material to obtain an NMR spectrum (15 mg). UV spectra were also determined on the collected peaks.

Solvents were removed under an aspirator vacuum using a rotary-evaporator at 30-35°C.

Thin layer chromatography (TLC) was performed using pre-coated TLC plates of silica gel 60 F254 with a layer thickness of 2 mm (MCB Manufacturing). The developing solvent was chloroform or ether. The spots were visualized with a Universal UV lamp at 350 or 254 nm.

Synthesis of Propioguaiacone

A procedure(18) for the synthesis of propioguaiacone (Pr) consisting of the condensation between guaiacol and propionic acid, was followed. Nakazawa obtained Pr, however, as a colorless oil, and was unable to crystallize it. If guaiacol crystals (mp 28-30°C and crystallized in ethyl acetate:hexane 1:1), were used as the starting material, Pr crystals (mp 58-60°C) could be obtained from ethanol:ethyl acetate (1:1) mixtures. Spectra and chromatograms (NMR, IR, UV, HPLC, GC) from these crystals consistent with the structure of Pr were obtained.

Quantitative Determination of the Monomers in Ammonium Sulfide Lignin

Synthetic preparations of acetoguaiacone (Ac, acetovanillone) and propioguaiacone (Pr, propiovanillone) in methanol were combined with known amounts of ethyl guaiacol (internal standard). Once it was determined that the HPLC and GC instruments gave similar results, the HPLC was relied upon for the quantitative values. The alpha-carbonyl intermediate <u>6</u> - found at 140°C - was determined quantitatively by using the calibration curve of acetoguaiacone.

Model Compound Reactions

Coniferyl alcohol (Aldrich Co.) and the β ether, erthyro-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (89-91°C), were reacted in 8 - 30 mg portions with 3.0 ml of ammonium sulfide (0.54M, 50% methanol), except where otherwise noted. The reaction vessel was an 8 ml capacity bomb which was placed in an oil bath at 180 or 140°C (within 3°C) for various reaction times. The long, slender bombs came to temperature within about three minutes, but the total immersion time was the time reported in this study.

At the completion of the reaction, the bombs were immediately quenched in cold water. After opening, the usual procedure was the addition of 10 ml of water. Carbon dioxide was slowly bubbled in the solution until pH 7 was reached. If the pH was not below 8, a substantial portion of the acetoguaiacone was not recovered because of its relatively low ionization constant. The reaction product mixture was extracted four times with chloroform and the chloroform extracts were washed twice with water. The chloroform was dried with sodium sulfate and evaporated. The solid residue was dissolved in methanol:water (7:3). Internal standard was added and the sample was subjected to HPLC analysis.

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