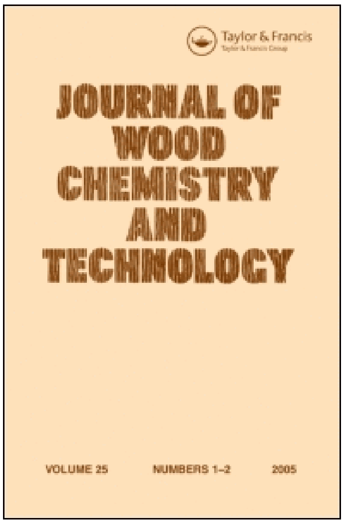

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THE FORMATION OF CONIFERYL ALCOHOL DURING ALKALINE DELIGNIFICATION WITH ANTHRAQUINONE

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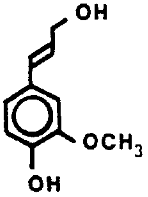
ABSTRACT

Coniferyl alcohol is the major building block of softwood lignin. Although its formation in the cooking liquor during kraft pulping is predicted by the proposed mechanism, it has not been previously found at any appreciable concentration during alkaline delignification. The reason for this is its instability in hot caustic liquors. I have observed the formation of coniferyl alcohol at suprisingly high concentrations as a transient product of delignification of softwood chips in soda, soda-anthraquinone (AQ), kraft and kraft-AQ pulping under normal conditions. Higher yields were obtained with woodmeal than with chips. The maximum concentration is reached at the end of the initial delignification phase during the rise-to-temperature and is particularly dependent on the nature and quantity of additives such as Na_2S, AQ and anthraquinone mono-sulphonate. This observation supports the proposed mechanism of alkaline delignification and is, in fact, the first evidence of this mechanism based on wood rather than model compounds.

INTRODUCTION

Coniferyl alcohol (CA) is the major building block of softwood lignin (1). Although enzymic oxidation of the phenolic alcohol leads to polymer formation even *in vitro*, depolymerisation of lignin has yielded only minimal amounts of the monomer, in spite of the fact that its formation is predicted by the



Coniferyl Alcohol

mechanism of kraft pulping (2). Indeed, rather special conditions are needed to produce any coniferyl alcohol at all. For example, hydrolysis of spruce woodmeal for 1h with 50% dioxane-water at 140-180°C gave a maximum yield of coniferyl alcohol of 1.7% based on Klason lignin (3). Raisanen (4) generated CA under mild alkaline conditions by treating spruce woodmeal with 0.2 M Na_2S in methanol at 100°C. The author claimed that the yield of coniferyl alcohol amounted to 0.5-3% of the lignin depending on the reaction time, temperature and sample of wood. Ashorn (5) treated spruce sawdust with buffered, aqueous Na_2S (pH 8.5) for 72h at 100°C and detected CA in unspecified amount by paper chromatography.

Under normal pulping conditions, however, CA may be entirely absent from spent pulping liquor. A recent, comprehensive analysis of the monomeric phenolics in kraft black liquor by GC and GC/MS did not reveal coniferyl alcohol among the identified monomers (6). On the other hand, Gierer and Lindeberg (30) have reported CA as a minor, phenolic component of kraft spent liquor, although no structural proof was presented.

Nevertheless, coniferyl alcohol and coniferyl alcohol-like structures are considered important intermediates in the degradation of the p-hydroxyl arylglycerol-β-aryl ether units of lig-

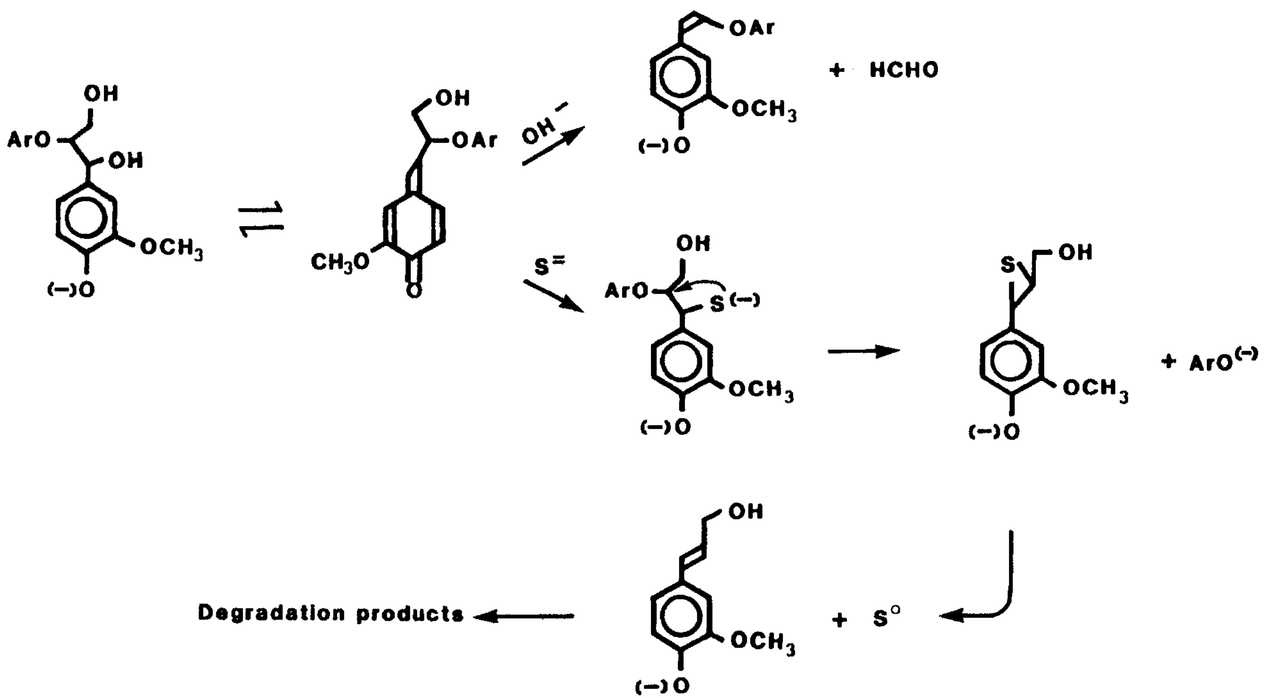


Figure I. Degradation of phenolic β-aryl ether structures during soda and kraft pulping.

nin (7, 8). Figure 1 presents the scheme developed by Gierer (31, 32) and by Brunow and Miksche (33-35) to explain the role of sulphide in accelerating delignification. According to this hypothesis, coniferyl alcohol would be readily formed from a phenolic precursor during kraft pulping. Brunow and Miksche (9) pointed out, however, that coniferyl alcohol would be present only at low, steady-state concentrations in the liquor of a kraft cook because it is only moderately stable in alkaline media at pulping temperature.

A few years ago, anthraquinone (AQ) was demonstrated to accelerate delignification (10). Shortly thereafter, Landucci (11), then Gierer (12), showed that the reduced form of AQ (AQ_2^-) combined with quinone methides to form a thermally unstable intermediate. Collapse of this adduct resulted in β-aryl ether cleavage and formation of the original AQ. Based on these observations, the mechanism of soda-AQ pulping is thought (11,12) to resemble that of kraft pulping, illustrated in Fig. 1, with the exception that reduced AQ takes the place of sulphide ion. This leads to the same result: accelerated β-aryl ether cleavage and formation of coniferyl alcohol. I wish to report that CA does in fact occur in kraft, kraft-AQ and soda-AQ liquors at surprisingly high concentrations depending on the additive and its charge but only during the rise-to-temperature of the cooks (110-170°C).

RESULTS AND DISCUSSION

To determine the profile of the anthraquinone concentration during soda-AQ pulping of black spruce, samples were withdrawn from a 20L digester at regular intervals for HPLC analysis (13). The CH_3CN extracts of these samples contained not only AQ but also a number of other liquor components. One such compound, now identified as coniferyl alcohol, was found to increase markedly

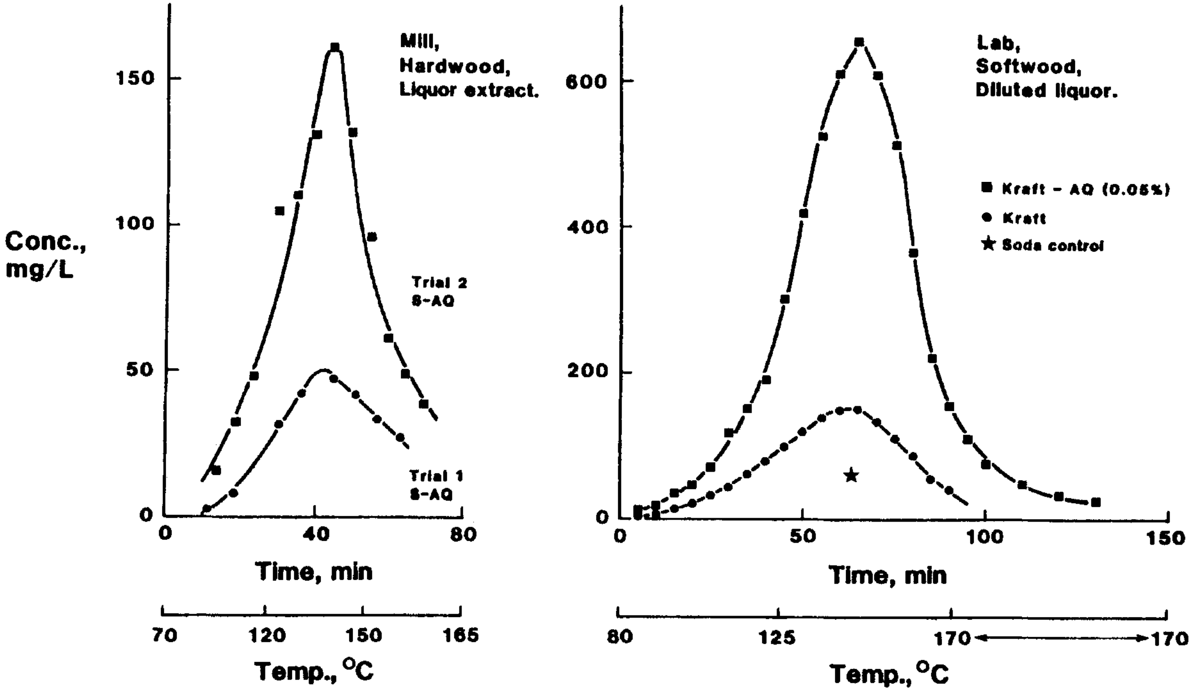


Figure II. Profiles of coniferyl alcohol concentrations during the rise-to-temperature of alkaline pulping. Hardwood liquor samples were extracted (CH_3CN), and the extracts were analyzed by HPLC; softwood liquor samples were diluted then analyzed directly by HPLC.

during the rise-to-temperature and then to disappear. At subsequent mill trials of soda-AQ pulping of mixed hardwoods, the same phenomenon was again observed. Figure 2 shows the profiles of the coniferyl alcohol concentrations from two, hardwood, mill trials and from two laboratory cooks of softwood. During the mill trials, the maximum AQ concentrations measured were 42.4 and 233 mg/L for trials 1 and 2, respectively. This was the first indication that the AQ charge could affect the maximum coniferyl alcohol concentration.

Identification of Coniferyl Alcohol

That the unknown was coniferyl alcohol was first suggested by comparison of the UV spectra and HPLC retention times of vinyl guaiacol and isoeugenol with those of the unknown peak. Figure 3 shows that the UV spectra are essentially identical. The order of elution (6.6, 9.9 and 11.4 min. for the unknown, vinyl guaiacol and isoeugenol respectively) indicated that the unknown was a more polar compound than vinyl guaiacol or isoeugenol.

The unknown was then isolated from a CH_2Cl_2 extract of a neutralized cooking liquor from a soda-AQ, softwood cook which was stopped at 140°C during the rise-to-temperature. Comparison of the mass spectrum, melting point, UV spectrum and HPLC retention time of the isolated solid with those of a commercial sample of coniferyl alcohol confirmed the structural assignment.

Analysis of coniferyl alcohol in pulping liquor

Whereas HPLC analysis of the CH_3CN extract of the pulping liquor might have provided a convenient means of determining the coniferyl alcohol concentration, the extraction efficiency was low (15-25%) when equal volumes of acetonitrile and liquor were used. Furthermore, the dependence of extraction efficiency on

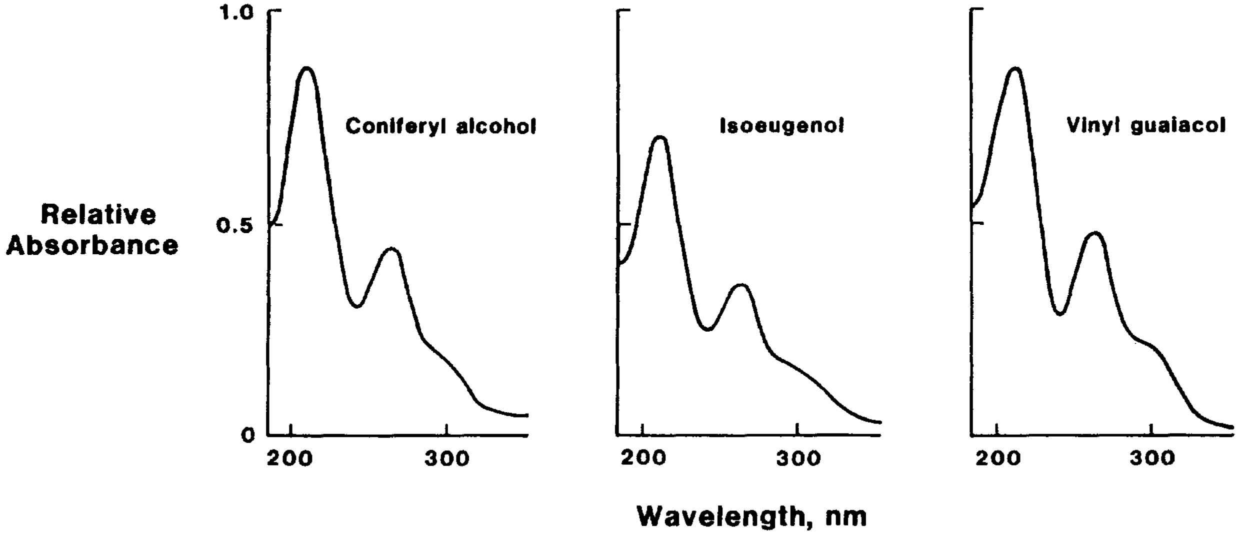


Figure III. UV spectra of coniferyl alcohol and related monomers.

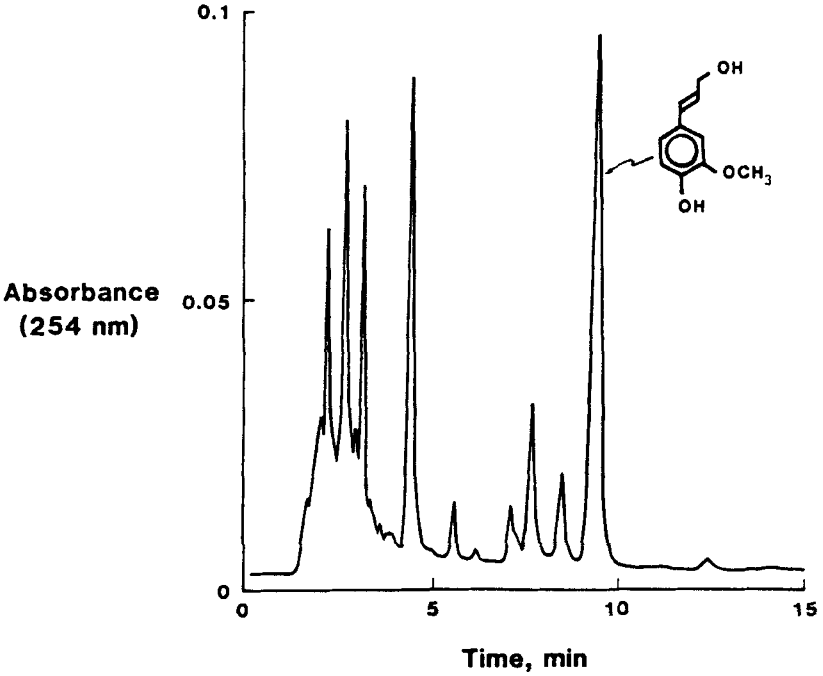


Figure IV. Isochratic portion of the HPLC analysis of coniferyl alcohol in alkaline pulping liquor.

coniferyl alcohol concentration was unknown. To circumvent this potential problem an analysis was developed based on the liquor itself (see Experimental). Figure 4 represents the isochratic portion of a typical HPLC chromatogram. The UV spectrum of the coniferyl alcohol peak (the HP 1084B liquid chromatograph has a stop flow-UV scan capability) suggested that it was a single component. The small peak at 8.5 minutes is vanillin, while the other peaks are thought to arise from carbohydrate degradation.

In order to measure the coniferyl alcohol concentration accurately, aliquots (10 µL) of standard solutions (10-200 mg/L) of both isolated and purchased material were injected into the

TABLE I. Summary of Data from Repeatedly Sampled Cooks

Wood Type	Sulphidity, %	Active Alkali, %	AQ, %	Time to Temp., min[1]	Maximum temp., °C	CA max.,[2] mg/L	Temp. at CA max., °C	CA yield,[5] %
Softwood	30	18	0	90	170	152	143	0.22
Softwood	30	18	0.1	93	170	655	145	0.94
Hardwoods	0	16	0.1	62	175	400[3]	147	0.73
Hardwoods	0	16	0	60	175	60[3]	147	0.11
Hardwoods	0	16	n.a.[4]	100	170	200[3]	143	0.36
Softwood	30	18	0.1	90	170	400[3]	145	0.57
Hardwoods	0	16	0.1	100	170	640[3]	143	1.16

[1] Initial temperature 70–80°.

[2] CA_{max} is the maximum concentration of coniferyl alcohol measured.

[3] Analysis of CH_3CN extract; assuming 25% extraction efficiency.

[4] Mill trial; estimated as 0.02% based on AQ analysis of liquor.

[5] Based on lignin; 28% for black spruce and 22% for mixed hardwood, predominantly maple (16).

HPLC. A plot of peak area versus concentration provided a calibration curve for subsequent liquor analyses. Since liquor samples were diluted 5-10 times, the range of standard concentrations was sufficient for our purposes. The standard curve was necessary, however, since the absorbance-concentration relationship was linear only below 50 mg/L (500 ng) of coniferyl alcohol. The reproducibility of the analysis would be improved if an internal standard were added to the samples (13).

The Coniferyl Alcohol Concentration Profile

Coniferyl alcohol production is much affected by the presence of AQ or sulphide and increases in the order, soda < kraft << soda-AQ ~ kraft-AQ. Figure 2 shows concentration profiles for coniferyl alcohol produced during kraft and kraft-AQ cooks of black spruce (20L digester) and during soda-AQ cooks of mixed hardwoods (mill trials). For reference, the maximum concentration of coniferyl alcohol found in a softwood soda cook has also been included. This value, 63.7 ± 3.5 mg/L, was derived from three separate 1L bomb cooks (see Experimental). All the profile maxima illustrated in Figure 2 occur at the same temperature, 145 ± 2°C, regardless of the time-to-temperature profile, wood type or nature of the cooking liquor (see Table I).

Factors Affecting the Yield of Coniferyl Alcohol

1. The Additive Charge

Analyses of mill liquors and liquors from lab. cooks had indicated that the maximum coniferyl alcohol concentration was related to the additive charge and, possibly, to the type of additive. In order to define these relationships, a series of bomb cooks of black spruce chips were done at various anthraquinone and anthraquinone monosulfonate (AMS) charges. In all

TABLE II. Coniferyl Alcohol Produced in Alkaline Cooking with Various Additive Charges

Charge of Additive, % on o.d. wood	CA in Liquor at 140°C, mg/L[1] [2]		
	Additives		
	AQ	AQ (Duplicate)	AMS[3]
0	66.8	60	n.a.
0.012	n.a.	163	n.a.
0.048	n.a.	323	n.a.
0.10	405	480	n.a.
0.20	533	640	155
0.40	635	760	210
0.80	675	n.a.	300
1.6	733	n.a.	425

[1] The deviation in duplicate CA analyses was ± 0.5%.
[2] Liquor-to-wood = 4 L/kg, EA = 45 g/L as Na_2O, 25-140°C in 72 min.
[3] Sodium anthraquinone monosulphonate monohydrate.

cases, the bombs were heated from 25°C to 140°C at 1.6°C/min then quickly chilled. The results are listed in Table II and plotted in Figure 5.

The apparent gap between the two AQ series is probably due to the use of different batches of chips. At 140°C the larger chips (thickness, >4 mm) were incompletely penetrated. Small differences in the chip size distribution would account for the observed variation of the coniferyl alcohol yield. The chips used for the first AQ series and for the AMS series were from the same batch; therefore, the higher yield of CA from AQ is consistent with the greater activity of AQ as a delignification catalyst compared to AMS (10).

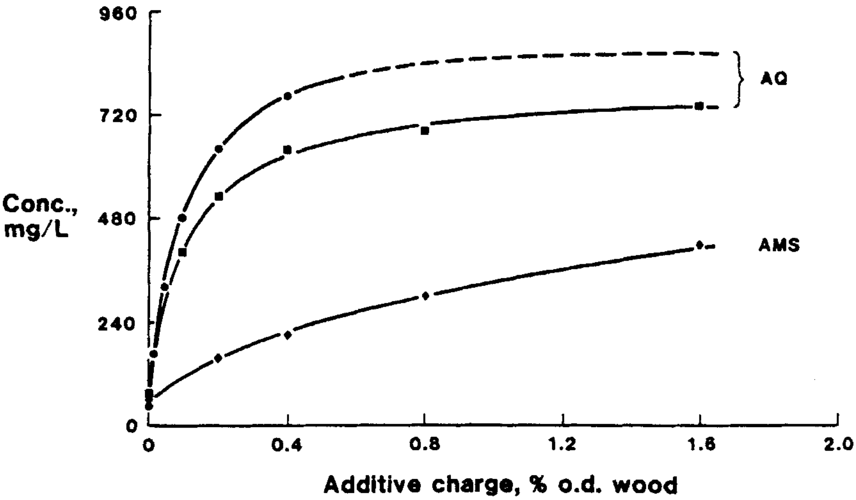


Figure V. The formation of coniferyl alcohol from black spruce chips as a function of additive charge.

Because of the incomplete penetration of wood chips at 140°C and below, many of the subsequent experiments were done with woodmeal. CA yields were invariably higher (20-60%) when using meal rather than chips.

Werthemann and Pekkala (14) recently observed a linear relationship between the reciprocal of the Kappa number of the pulp and the square root of the AQ charge up to an AQ dose of ~0.3%. For AMS, the plot was linear for all charges tested, up to 3% AMS on o.d. wood. Likewise, when the coniferyl alcohol concentrations were plotted against the square root of their respective charges, the relationship was linear (Figure 6) for AQ up to an AQ dose between 0.2 and 0.4% and for AMS throughout the range tested (<1.6%). The curvature of the AQ plots in Figure 6 above an AQ charge of ~0.2% may be due to incomplete solubility of the anthraquinone. Fine, yellow crystals of AQ were observed in the spent liquors at the higher AQ charges. This was especially noticeable when the experiments were done at 125°C (see later).

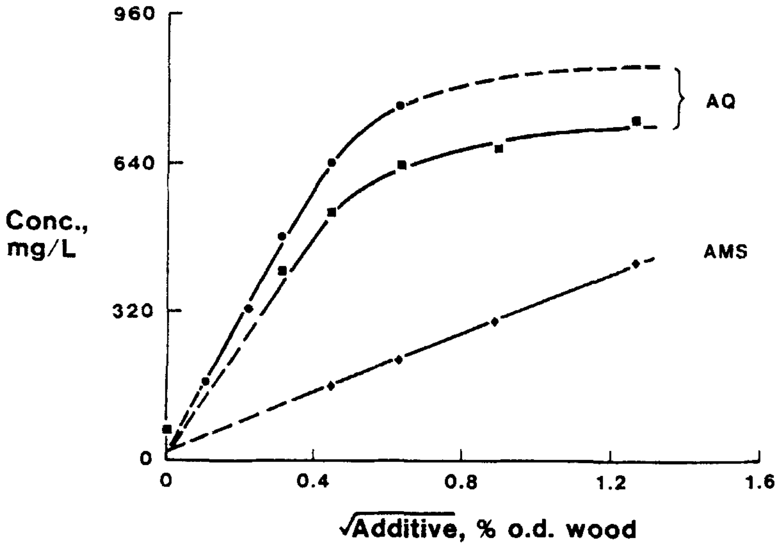


Figure VI. The linear relationship of coniferyl alcohol concentration and the square root of the additive charge.

2. Effect of Temperature

Examination of the CA concentration profiles in Figure 2 shows that CA formation is a function of time. Because this part of the cooking cycle is the rise-to-temperature, CA formation is also a function of temperature. During the rise to $[CA]_{max}$ at 145°C, the curve passes through an inflection point at 125°C which is the point of optimum CA formation, i.e., rate of formation is highest relative to rate of degradation. Figure 7 shows the formation of CA at three different temperatures: 110°C, 125° and 140°C. In each case, the cooks were started at 80°C and heated to the required temperature at 1°C/min and held there. At 110°C, the rate of CA formation was slow and the CA concentration remained low. At 140°C, the rate of degradation rapidly became dominant and the coniferyl alcohol maximum concentration was passed within a few minutes at temperature. At 125°C, a plateau

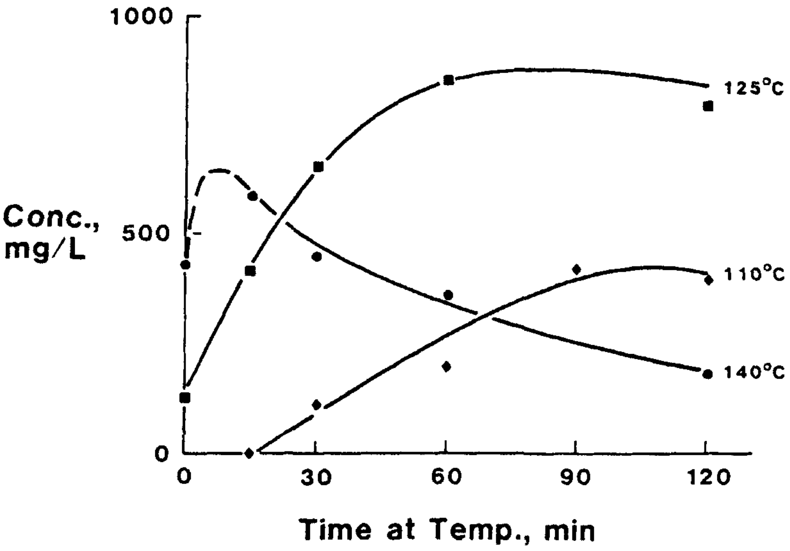


Figure VII. The effect of temperature on formation of coniferyl alcohol from black spruce chips: Liquor-to-wood = 5 L/kg, 1N NaOH, 0.1% AQ on o.d. wood.

was reached after about 60 minutes showing that the rate of degradation was relatively slow at this temperature.

The rise-to-temperature is a critical time in the pulping cycle. Unfortunately, the number of interrelated variables makes it complex. Thus, changing the cooking temperature in soda-AQ pulping alters not only the balance of coniferyl alcohol formation and degradation but also the concentration of dissolved AQ. During attempts to maximize the production of coniferyl alcohol, charges of 0.1 and 0.4% AQ yielded the same CA concentration after 60 min at 125°C. Presumably, the higher charge was not fully dissolved. At 140°C, the higher AQ charge produced more coniferyl alcohol than the lower charge, consistent with the plots in Figures 5 and 6.

3. The Alkali Charge

Black spruce woodmeal was cooked at 125°C for 60 min at various alkali concentrations (L:W = 10, AQ = 0.1%). The final concentrations of coniferyl alcohol in the cooking liquors are presented in Figure 8 (upper curve) as function of initial alkali concentration. The CA level reached a maximum concentration at 0.3N NaOH and then gradually declined. The lower curve in Figure 8 shows the residual alkali levels in the cooking liquor as a function of initial alkali. There was no significant residual until the initial alkali was 0.3N, at which point the CA concentration had reached a plateau. The yield of coniferyl alcohol seems to be independent of the alkali charge provided that there is enough alkali to neutralize all acidic functional groups. Further increases in the alkalinity cause degradation of CA.

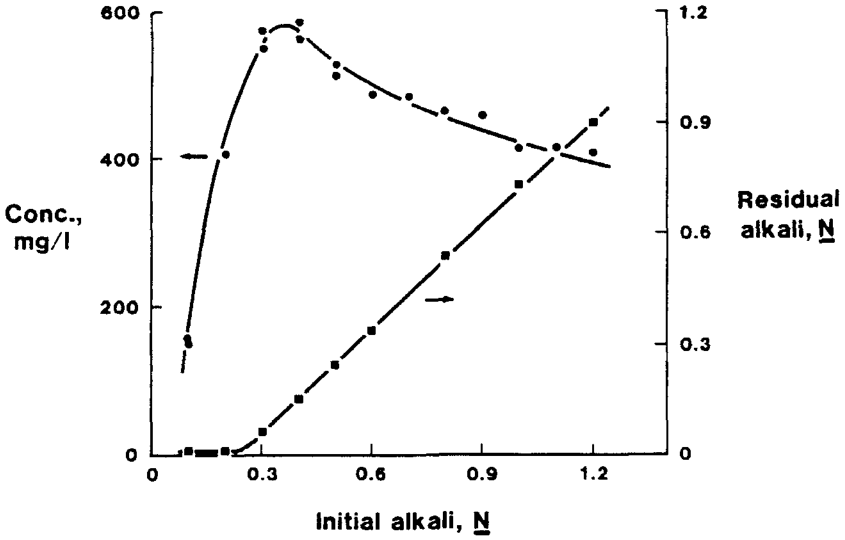


Figure VIII. The effect of alkali concentration on coniferyl alcohol formation from black spruce woodmeal.

TABLE III. The Effect of L:W Ratio on CA Formation (Chips)

Time at 125°C, min[1]	Coniferyl Alcohol Produced			
	L:W = 5 L/kg, 1 N NaOH		L:W = 10 L/kg, 0.5 N NaOH	
	Conc., mg/L	% on lignin	Conc., mg/L	% on lignin
0	102	0.20	20	0.07
15	408	0.79	135	0.50
30	650	1.26	200	0.74
60	824	1.60	283	1.05
120	796	1.58	316	1.18

[1] Time to temp. (125°C) = 60 min; 0.1% AQ

The same observation was made with black spruce chips under the same conditions (except L:W = 5). The maximum coniferyl alcohol concentration was reached between 0.25 and 0.5 N NaOH.

4. The Effect of the Liquor:Wood Ratio

Table III lists the concentrations of coniferyl alcohol produced by cooking black spruce chips for various periods of time at 125°C at L:W = 5 and L:W = 10. There was a significant reduction in the amount of CA produced when the L:W ratio was increased. This is as expected. When the liquor:wood ratio is increased at a constant AQ charge, a larger fraction of AQ will be in the liquor (15) and less will be present in the wood to boost the CA yield.

A similar observation was made with black spruce woodmeal cooked for 60 min at 125°C (Table IV). As the L:W ratio increased the yield of coniferyl alcohol based on lignin decreased until

TABLE IV. The Effect of L:W Ratio on CA Formation (Woodmeal)

Sample*	L:W Ratio	CA, mg/L	CA Yield, % of lignin
1	10	475	1.70
2	15	291	1.56
3	20	176	1.26
4	25	145	1.29
5	30	123	1.32
6	35	105	1.31

* time to temp. = 45 min (80-125°C); AQ = 0.1%; 1N NaOH

L:W = 20 was reached. Above this ratio, the yield became relatively constant. The reason for this is, as yet, unknown.

5. Effect of Wood Type

Whereas softwood lignin is essentially a polymer of coniferyl alcohol, hardwood lignin is a co-polymer of two phenolic monomers, coniferyl and sinapyl alcohols (16). If they are incorporated into the hardwood lignin in the same manner, with proportionally the same number of free phenolic groups, one might expect both coniferyl and sinapyl alcohols in the liquors of AQ-catalysed cooks. Preliminary results on poplar and white birch indeed show that both monomeric phenols are formed in soda-AQ cooks.

6. Effect of Methylating Wood

Our present knowledge of alkaline delignification indicates that there are two significant pulping stages, the initial and the bulk delignification phases (17-20). In the initial phase which occurs during the rise-to-temperature, the lignin units with free phenolic hydroxyl groups are thought to react in the manner outlined in Fig. 1. The lignin units with etherified phenolic hydroxy groups can not react until the reaction temperature is sufficient (150-170°C) to accelerate hydroxide ion cleavage of the β-aryl ether groups (21). Naturally, any free phenolic hydroxy groups released as a result of this ether cleavage can undergo the reactions characteristic of the initial phase.

Diazomethane reacts rapidly with acidic hydroxyl functions found in phenols and carboxylic acids. Gierer (17) has demonstrated that reaction of woodmeal with diazomethane effectively inhibits the initial delignification phase but not the bulk delignification phase. We have observed a 95% reduction in coniferyl alcohol formation (910 → 50 mg/L) as a result of methylation of spruce woodmeal with excess diazomethane. This observation indicates that coniferyl alcohol is formed from a precursor with a free phenolic hydroxy group.

7. Supplementary Observations

a) Kubes *et al.* (22) have demonstrated the ability of amines, in particular ethylene diamine (EDA), to accelerate alkaline delignification. We have observed no significant increase in the production of coniferyl alcohol, however, by adding either EDA or NH_3 to a soda cook even at charges of 200% on o.d. wood.

b) Once the lignin precursor of coniferyl alcohol has been exposed to alkaline pulping conditions, one might expect it to be destroyed whether it generated coniferyl alcohol or followed other reaction pathways. It was, therefore, not surprising to find that kraft lignin produced no coniferyl alcohol in a soda-AQ cooking liquor after 1h at 125°C. Glucose was added to the reaction mixture to reduce AQ.

In contrast, several industrial lignin sulphonates did form coniferyl alcohol when treated with alkali and AQ at 125°C. With a charge of 0.25% AQ, the yields of coniferyl alcohol were in the range of 0.5-0.75% (based on lignin sulphonate weight). These values are similar to those observed in the case of wood. Those lignin sulphonates containing reducing sugars needed no addition of glucose. In the absence of AQ, however, the yield of coniferyl alcohol dropped by 90%.

The greatest difference between the formation of CA from wood and from lignin sulphonate is the greater reaction rate of

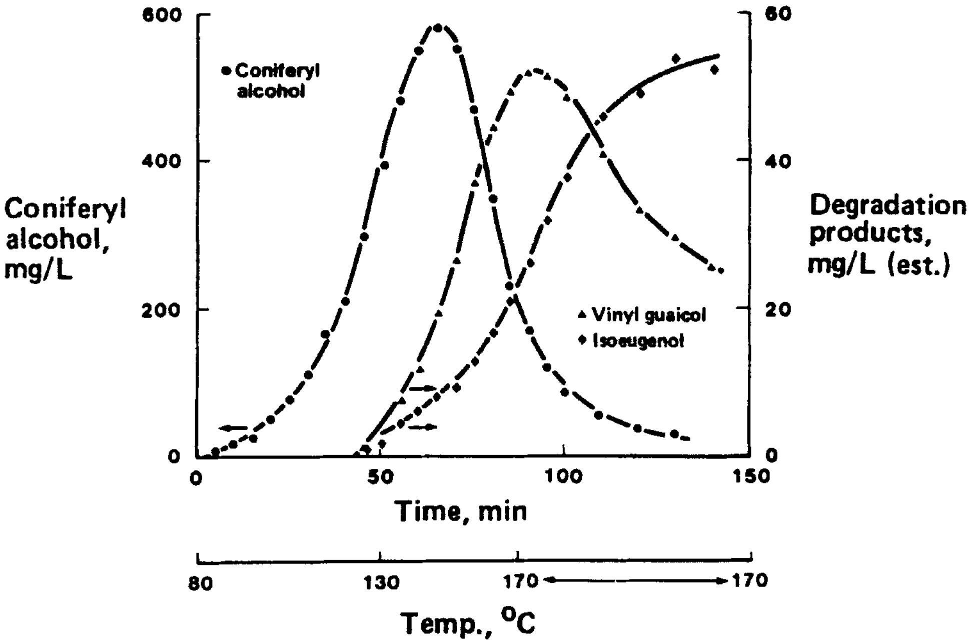


Figure IX. Concentration profiles of coniferyl alcohol and two of its degradation products during soda-AQ pulping of black spruce chips. Acetonitrile extracts of the pulping liquor were analysed by HPLC for vinyl guaiacol and isoeugenol, whereas coniferyl alcohol was measured in the liquor directly.

lignin sulphonate. By the time the reaction vessel has reached temperature (25-125°C in 47 min.), the maximum concentration of coniferyl alcohol has been reached (a further 60 min at 125°C was required for wood [Fig. 7]. In a series of cooks with anthraquinone monosulphonate (8%), a maximum yield of CA of 0.93% was attained within 30 min of adding the reaction vessel to the oil bath at 125°. Whether the faster rate is due to the homogeneous conditions or to a modification of the CA precursor under sulphite pulping conditions is not yet known.

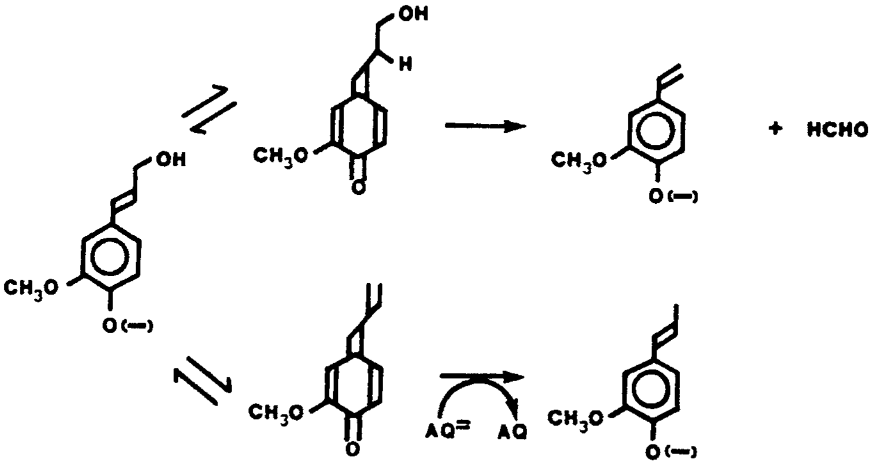
c) The possibility of developing coniferyl alcohol as a chemical product like vanillin was explored, but no simple, low-cost isolation method has been found. Coniferyl alcohol was not steam volatile from the cooking liquor, even after neutralization; and unlike vanillin, it could not be extracted from the alkaline liquor with n-butanol (23). Furthermore, no success was achieved in attempts to adsorb CA from alkaline liquor with either XAD-2 resin or sawdust (24). The laboratory procedure for isolating coniferyl alcohol requires extraction of neutralized liquor and is probably impractical. Neither hexane nor toluene extracted CA to any extent, although toluene has potential for counter-current methods. It was necessary to use solvents such as ethyl acetate, ether, methyl ethyl ketone or methylene chloride. When cooking liquors from wood are neutralized, the precipitated lignins tend to emulsify the extracting solvents. The resulting emulsions were slow to separate unless centrifuged. In the case of lignin sulphonate cooks, however, there is no precipitate on neutralization and the problem of emulsions is minimized.

All our efforts to produce high yields of coniferyl alcohol were also thwarted. The maximum yield of coniferyl alcohol that we have produced was 3.5% based on lignin. This level was attained with black spruce woodmeal after 60 min at 125°C in 1N NaOH (L:W = 10) containing 0.8% AQ and 20% glucose based on o.d. wood.

Degradation of Coniferyl Alcohol in Alkaline Liquors

The salts of vinyl guaiacol (I) and isoeugenol (II) are reported to be among the numerous products formed when coniferyl alcohol is treated with white liquor (7, 35, 36) or soda-AQ (37) at 170°C, and certainly these two products are revealed in the

HPLC chromatograms of the liquor extracts. The efficiencies of extraction of these substances into acetonitrile are presently unknown; therefore, the concentrations plotted in Figure 9 are only estimated values. The concentration increases of these two compounds, nevertheless, correspond to the disappearance of coniferyl alcohol from the liquor, supporting the concept (7) that the compounds are degradation products of CA (equations 1 and 2).



(1)

(2)

GENERAL DISCUSSION

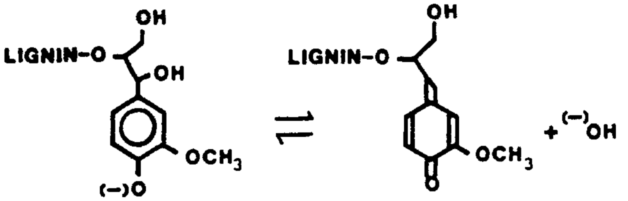
It is evident from Figure 2 that the maximum concentration of coniferyl alcohol results from a balance between a reaction forming CA and a reaction destroying CA. In this respect, the overall process can be represented by a series first-order reaction as in equation 3 (25). In this series, A would be the CA

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (3)$$

precursor, B would be coniferyl alcohol and C, the degradation product(s) of coniferyl alcohol. Equation 3 can produce more than one concentration profile for B depending on whether k_1 and k_2 have similar temperature coefficients; i.e., similar activation energies, and whether [A] is constant or not. The component A, of course, cannot be constant if it is being consumed except in the case where B is generated by cleavage of a terminal unit from a chain of like units in such a way that another terminal precursor unit is regenerated after each cleavage until the whole chain is consumed. Whereas such a series of events may be occuring to some extent in the formation of coniferyl alcohol, our present knowledge of delignification indicates that the process is far more complex. In subsequent discussion, the statement that [A] is constant simply means that the precursor unit is not depleted during the early phase of the reaction.

If we assume that [A] is constant and that k_1 and k_2 have similar temperature coefficients, we would expect the concentration of coniferyl alcohol to rise with temperature and approach a plateau level at or near cooking temperature. This does not occur (Figure 2); therefore, either [A] is not constant or the temperature coefficients are substantially different.

If we continue to assume that [A] is constant, but now consider that the reaction destroying coniferyl alcohol may have a substantially higher activation energy than the one forming CA, we could produce a concentration profile for CA similar to the ones in Figure 2. Present evidence is not sufficient to dismiss this possibility entirely, but there are indications that it is unlikely. The rate determining steps for formation (eq. 4) and for degradation (eq. 5) of coniferyl alcohol are thought to involve elimination of a hydroxyl group to form a quinone methide and a vinylogous quinone methide, respectively (9). The nature of these two steps is too similar to expect substantially different activation energies. Because of the increased conjugation



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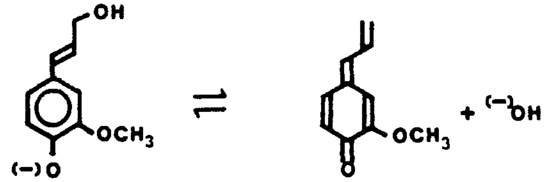


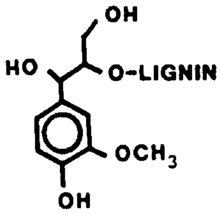
(5)

in the structures of equation 5 compared to equation 4, the activation energy for k_2 might even be lower than that for k_1.

If k_1 and k_2 do have similar activation energies, then the first assumption must be incorrect; i.e., the concentration of precursor A cannot be constant but must decrease as the temperature rises in the cooking cycle. Figure 7 shows a concentration profile for coniferyl alcohol formed at 140°C. A plot of log[CA] versus time for the last four points gives a straight line whose slope, the rate constant for coniferyl alcohol degradation, is -1.45×10^{-4} mmol.L^{-1}.sec^{-1}. Gierer *et al* (7) measured the decay of coniferyl alcohol at 140°C in 1.06 *N* NaOH (no AQ). A similar plot of their data produced a line with a slope of -1.50×10^{-4} mmol.L^{-1}.sec^{-1}. The equivalence of these two values suggests that little or no further coniferyl alcohol is formed once the maximum concentration is reached. This conclusion is supported by the result of the following experiment. Wood chips were cooked with NaOH to 140°C, then washed and re-cooked with NaOH-AQ to the same temperature. The amount of coniferyl alcohol measured in the second part of the two-stage NaOH- AQ cook was only 25% of that measured in a normal NaOH-AQ cook. The initial alkali treatment clearly destroyed a high proportion of the coniferyl alcohol precursor; therefore, [A] cannot be constant.

The most satisfactory explanation for the coniferyl alcohol concentration profile is that CA is formed by the reductive process illustrated in Figure 1 from a lignin structural unit which is present in the lignin macromolecule in only limited amount. By the end of the initial delignification phase, this unit has been entirely consumed, no further CA is produced at that temperature, and the already formed CA is rapidly destroyed by alkaline degradation reactions. As hydroxide ion cleaves β-aryl ether groups from the etherified lignin macromolecule at the higher temperature of the bulk delignification phase, the concentration of the precursor unit can be renewed. At this temperature (170°C), however, the CA formed is quickly degraded and is not easily observed.

What is the nature of the coniferyl alcohol precursor? All the evidence suggests that it is the terminal group III.



III

It is unlikely that the α-position of III is occupied by either phenoxy ether or by carboxylic ester groups. Both of these units are excellent leaving groups under basic conditions and would be expected to form quinone methides even at room temperature (9). Coniferyl alcohol begins to form (from wood) only at 110°C. The leaving group is likely, therefore, to be a hydroxyl or alkoxy group. The faster rate of CA production from lignin sulphonate may be due to sulphonation at the α-position.

The need for a free phenolic hydroxyl group in the precursor was demonstrated by the large reduction in CA concentration when the woodmeal was methylated with excess CH_2N_2.

The precursor is not simply an esterified coniferyl unit. If that were so, CA concentration would not be a function of the AQ charge. Coniferyl alcohol is a product of a reduction sequence; most likely, that proposed by Landucci (11) and Gierer (12). This necessitates a leaving group at the β-position, probably an aryl ether group.

Yang and Goring's determination of 0.1 free phenolic groups per C_9-unit (26) suggests that a yield of coniferyl alcohol of 10% or more based on lignin would be possible. Our failure to achieve more than a third of this level suggests that some of the free phenolic groups may lack a satisfactory leaving group at the β-position or have links at C-5. This may be due to phenylcoumaran- or pinoresinol-types of structures adjacent to the C_9-unit with the free phenolic group.

It is probably no coincidence that the transition from initial delignification phase to bulk delignification phase (140-150°C) occurs at the same temperature as that at which the production of coniferyl alcohol ceases. The formation of coniferyl alcohol shares a number of characteristics of the initial phase: it is independent of the alkali concentration, it is independent of the rate of rise-to-temperature and it ends between 140 and 150°C. The precise relationship of CA formation and initial phase delignification remains to be determined. Bihani and Samuelson (27) have observed a catalytic effect of AQ on delignification at 120°C. Their results support a $\sqrt{\text{AQ charge}}$ relationship for initial phase delignification. Similarly, an increase in sulphide causes proportionately more delignification in the initial stage (28).

Our conclusion is that the coniferyl alcohol observed during the rise-to-temperature is most likely a product of initial phase delignification and that it is formed in the manner depicted in Figure 1 when sulphide or AQ is present. Considering the evidence that initial phase delignification occurs predominantly, if not completely, in the secondary wall (29), it is also possible that the precursor of coniferyl alcohol is a characteristic unit of the secondary wall lignin but not of the middle lamella lignin. This relates to the free, phenolic hydroxyl content of each region.

EXPERIMENTAL

General

Coniferyl alcohol (Fluka, puriss.) and isoeugenol (Aldrich) were used as received. Anthraquinone (Anachemia) was recrystallized from dimethylformamide then ground to a fine powder. Anthraquinone sodium 2-sulfonate (Anachemia) was recrystallized from water. Ligninsulphonates (Norlig A, Maracarb N_1 and N_2, Marasperse N22) were obtained as dry powders from American Can. Co., Streator, Illinois.

Kraft lignin was obtained by filtration of an acidified (H_2SO_4) fresh black liquor from a black spruce cook (18% AA, 30% S, 1400 H). The recovered solid was air dried then extracted with CH_2Cl_2 for 24 hrs (Soxhlet).

Vinyl guaiacol was prepared by decarboxylating ferulic acid (Aldrich) in quinoline (200°C, 15 min) followed by steam distillation of the reaction mixture. The condensate was acidified and extracted with CH_2Cl_2. The extract was evaporated and the residue was distilled bulb to bulb (10mm Hg). The colourless distillate (10% yield) had a molecular ion of 150 a.m.u. and a single peak on HPLC (RP-18, gradient 15-90% CH_3CN in H_2O, pH 3).

Routine mass spectra were run on a Hewlett-Packard 5985 in the E.I. mode (70 ev, ion source = 200°C). HPLC analyses were done on a Hewlett-Packard 1084B liquid chromatograph. Melting points were done on a Fisher-Johns apparatus and are uncorrected.

Initial and residual alkali concentrations were determined by potentiometric titration to pH 10.5 with dilute HCl.

Cooking Procedures

The laboratory cooks were done in autoclaves of 250 mL, 1000 mL and 20 L capacity. The 250 mL bombs were maintained stationary in an oil bath and, in order to ensure complete wood contact with the liquor, the L:W ratios were 5 and 10 for chips and woodmeal respectively. The 1000 mL bombs were attached at an angle to a rotating shaft immersed in ethylene glycol. Only chips were cooked in these bombs and the L:W ratio was always 4. The 20 L digester had a recirculation line with a sampling valve. A coil of stainless steel capillary tubing (1m long) attached to the valve was immersed in cold water during sampling. The chips for cooks in the 20 L digester and in the 1L autoclaves were presteamed and L:W ratio was 4 excluding wood moisture. Samples taken during mill trials were obtained through a sampling valve on the recirculation line fitted with a cooling coil. The coil dead volume was well flushed before a sample was taken for analysis.

Isolation of Coniferyl Alcohol [3-(4'-hydroxy-3'-methoxyphenyl)-2-propen-1-ol]

A 1000 ml autoclave was charged with black spruce chips (250 g o.d., 66.1% solids), AQ (1.0 g) and NaOH solution (1.0 L, 45 g/L as Na_2O) and sealed. The bomb was heated from 25°C to 141°C in 73 minutes then chilled. The bright red cooking liquor was poured into a plastic bottle and stored in the refrigerator (3 days). The coniferyl alcohol concentration was 560 mg/L (HPLC analysis).

A portion (0.5 L) of the cooking liquor (pH ~12) was oxidized by bubbling air for 0.5 h then extracted with CH_2Cl_2 (100 mL x 4). The extract was discarded. The cooking liquor was then adjusted to pH 7 and re-extracted with CH_2Cl_2 (100 mL x 3). The extract was washed with saturated NaCl, dried over anhydrous, Na_2SO_4 and then filtered. The CH_2Cl_2 was removed on a rotary evaporator to yield a light brown oil (0.54 g).

The extracted mixture was eluted through a column of silica gel (50 g, 0.08 mm grains; Mackerey, Nagel and Co.) with CH_2Cl_2-EtOAc (1:1). Flow was 1 mL/min. The collected fractions were examined by TLC (SiO_2, CH_2Cl_2-EtOAc, 1:1) and like fractions were combined. Coniferyl alcohol was isolated as a pale yellow oil which crystallized on standing (222 mg, 80% yield based on the HPLC analysis, mp. 70-71°C, M^+ = 180 a.m.u.). The mass spectrum, the UV spectrum and the retention times on TLC (SiO_2) and HPLC (RP-18) of the isolated material were identical with those of commercial coniferyl alcohol (Fluka).

Analysis of Coniferyl Alcohol in Pulping Liquor

A 1.0 mL aliquot of cooking liquor was diluted with 9.0 mL de-ionized water and, then, filtered through a glass fibre disc

(Gelman, Type A/E, 25 mm). A 10 µL sample of the filtrate was injected onto a Spherisorb-ODS column (25 cm x 4.6 mm, 5 µm particles, Laboratory Data Control) coupled to a UV detector monitoring at 254 nm (0.1 AUFS). The mobile phase was 12% CH_3CN-H_2O (pH 2.5-3.0) for 12 min then the acetonitrile content was increased linearly to 90% CH_3CN-H_2O (pH 2.5-3.0) during 8 min to remove lignin, AQ and resinous materials. The oven temperature was 45°C and the flow rate was 1.5 mL/min. The retention time of coniferyl alcohol was 9.80 ± 0.05 min.

Methylation of Woodmeal

Black spruce woodmeal (40-60 mesh) was extracted with THF (Fisher) under N_2 for 24 hr in a Soxhlet apparatus. Diazomethane was generated as an alcohol-free ether solution from N-methyl-N-nitroso-p-toluenesulfonamide (25 g, Aldrich) and used immediately. Portions of the ice-cold, CH_2N_2 solution (25-50 mL) were added to a thick slurry of woodmeal (25 g o.d.) in THF at 25°C. Evolution of N_2 was vigorous and the yellow colour was soon discharged. Excess solvent was poured off from the woodmeal slurry as the reaction progressed. The reaction slowed noticeably only towards the end of the additions in spite of the large excess of CH_2N_2 [25-30 times the phenolic content of wood, (26)]. After all colour was discharged from the final addition, the woodmeal was filtered, washed with fresh ether and air dried.

Klason lignin determinations for the original unextracted woodmeal and for the methylated woodmeal were 28.0 and 28.8%, respectively.

A sample of methylated woodmeal (5g o.d.) was cooked in a stainless steel autoclave charged with 1<u>N</u> NaOH (50 mL), AQ (50 mg) and glucose (2g). The temperature of the autoclave was raised from 25°C to 125°C in 71 min and then held at 125°C for 60 min. A control cook of extracted woodmeal was done in the same way.

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REFERENCES

1. K. Freudenberg, Nature, 183 1152 (1959).
2. J. Gierer, Svensk Papperstidn., 73 (18) 571 (1970).
3. A. Sakakibara and N. Nakayama, Nippon Mokuzai Gakkaishi, 8 153 (1962).
4. S. Raisanen, Suomen Kemistilehti, B40 35 (1967).
5. T. Ashorn, Societas Scientiarum Fennica, Commentationes Physico-Mathematicae XXV-8, Helsinki, 1961.
6. L. Lowendahl, G. Petersson and O. Samuelson, Svensk Papperstidn., 81 (12) 392 (1978).
7. J. Gierer and O. Lindeberg, Acta. Chem. Scand., B32 (8) 577 (1978) and references therein.
8. J. Gierer, I. Petterson, L-A. Smedman and I. Wennberg, Acta Chem. Scand., 27 (6) 2083 (1973).
9. G. Brunow and G. Miksche, Applied Polymer Symp., No. 28, 1155 (1976).
10. H. Holton, Pulp and Paper Mag. Can., 78 (10) T218 (1977).
11. L. Landucci, Tappi, 63 (7) 95 (1980).
12. J. Gierer, O. Lindeberg and I. Noren, Holzforschung, 33 213 (1979).

13. R.D. Mortimer and B.I. Fleming, Tappi 64 (11) 114 (1981).

14. D.P. Werthemann and O. Pekkala, Trans. Tech. Sect. CPPA 6 (3):TR77 (1980).

15. D.P. Werthemann, Tappi 64 (3) 140 (1981).

16. K.V. Sarkanen and H,L. Hergert, in "Lignins: Occurrence, Formation, Structure and Reactions," K.V. Sarkanen and C.H. Ludwig (eds.), Wiley-Interscience, New York; 1971, Chapter 3.

17. J. Gierer, Wood Sci. Technol., 14 241 (1980).

18. L. Olm and G. Tistad, Svensk Papperstidn., 82 (15) 458 (1979).

19. S. Lemon and A. Teder, ibid., 76 (11) 407 (1973).

20. S. Rekunen, E. Jutila, E. Lahteenmaki, B. Lonnberg and N-E. Virkola, Paperi ja Puu 61 (2) 80 (1980).

21. S. Ljunggren, Svensk Papperstidn., 83 (13) 363 (1980).

22. G.J. Kubes, B.I. Fleming, J.M. MacLeod and H.I. Bolker, Tappi 61 (8) 46 (1978).

23. D.W. Goheen, in "Lignins: Occurrence, Formation, Structure and Reactions," K.V. Sarkanen and C.H. Ludwig (eds.), Wiley-Interscience, New York; 1971, Chapter 19.

24. J.R. Wood, P.A. Ahlgren, E. Slatinska and D.A.I. Goring, Tappi 54 (12) 2056 (1971).

25. A.A. Frost and R.G. Pearson, "Kinetics and Mechanism", p. 166-167, John Wiley and Sons, 2nd Edition, 1962.

26. J.M. Yang and D.A.I. Goring, Can. J. Chem., 58 2411 (1980).

27. B. Bihani and O. Samuelson, Svensk Papperstidn., 83 (6) 161 (1980).

28. N. Hartler, B. Skogberg and G. Tistad, ibid., 75 (13) 528 (1972).

29. D.A.I. Goring, SPCI International Symposium Wood and Pulping Chemistry (Stockholm) Preprints vol. 1:3-10 (June 9-12, 1981).

30. J. Gierer and O. Lindberg, Acta Chem. Scand., 34 161 (1980).

31. J. Gierer, B. Lenz and N-H, Wallin, ibid., 18 1469 (1964).

32. J. Gierer amd L-A. Smedman, ibid., 19 1103 (1965).

33. G. Brunow and G. Miksche, ibid., 23 1444 (1969).

34. G. Brunow, T. Ilus and G. Miksche, ibid., 26 1117 (1972).

35. G. Brunow and G. Miksche, ibid., 26 1123 (1972).

36. H. Aminoff, G. Brunow, K. Falck and G. Miksche, Acta Chem. Scand., 28 373 (1974).

37. O. Lindeberg, Chemical Communications, University of Stockholm, No. 6, 31 (1979).