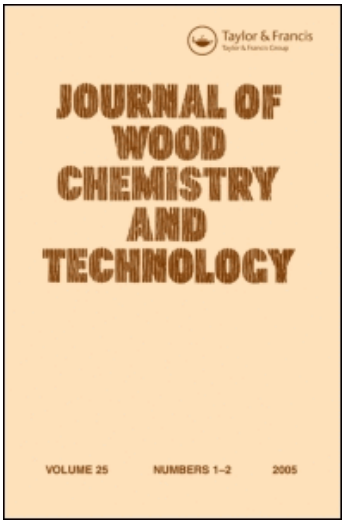


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Electron Transfer Reactions in Pulping Systems VIII. Reactions of Syringyl Alcohol in Aqueous Alkali

Dean A. Smith[a]; Donald R. Dimmel[a]
[a] Institute of Paper Science and Technology, Atlanta, Georgia

To cite this Article Smith, Dean A. and Dimmel, Donald R.(1994) 'Electron Transfer Reactions in Pulping Systems VIII. Reactions of Syringyl Alcohol in Aqueous Alkali', Journal of Wood Chemistry and Technology, 14: 2, 279 — 295
To link to this Article: DOI: 10.1080/02773819408003098
URL: http://dx.doi.org/10.1080/02773819408003098

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 14(2), 279-295 (1994)

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (VIII): REACTIONS OF SYRINGYL ALCOHOL IN AQUEOUS ALKALI

Dean A. Smith and Donald R. Dimmel
Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, Georgia 30318

ABSTRACT

Syringyl alcohol, a simple lignin model compound, has been heated in lM NaOH at 135°C. Five products - three monomers and two dimers - were identified from the reaction mixture; two of the products were presumably formed by radical processes. One of the radical products, 4-methylsyringol, was shown by deuterium labeling to incorporate a benzylic hydrogen from syringyl alcohol. Alkaline reactions of syringyl alcohol in the presence of radical initiators and inhibitors were not able to establish if the condensation reactions proceeded by a radical mechanism.

INTRODUCTION

Lignin condensation reactions during the alkaline pulping of wood consist of combining small, water-soluble lignin fragments into larger, insoluble macromolecules.[1,2] The condensation may involve carbohydrates or lignin materials. The condensed material is believed to contain many strong carbon-carbon linkages between monomers and to be at least partially responsible for that lignin (residual lignin) which is resistant to removal under typical pulping conditions.[2]

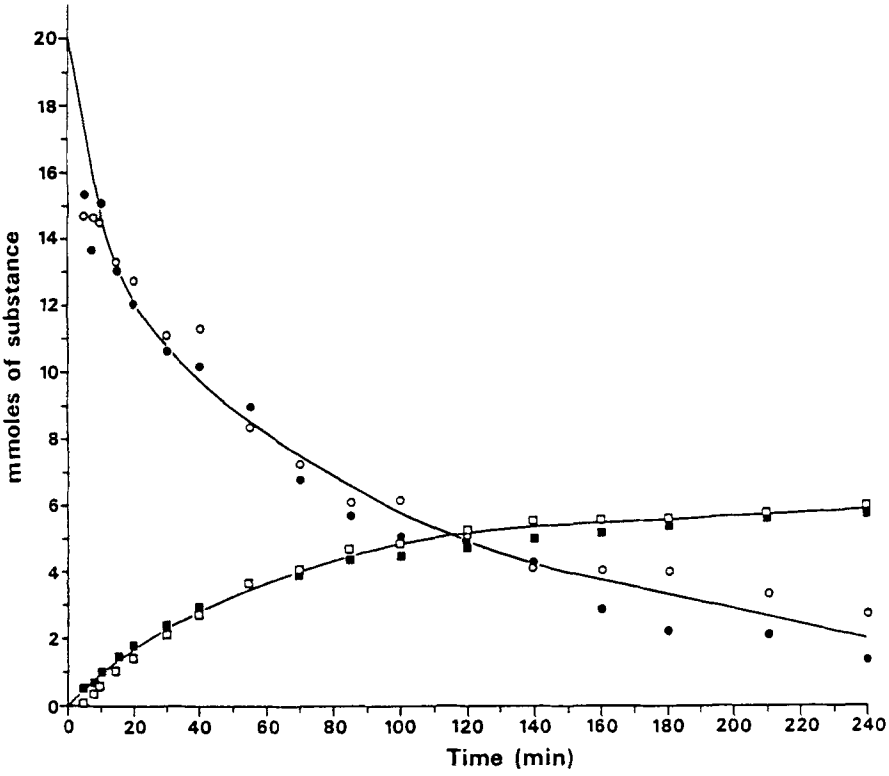


Figure 1. The concentrations of syringyl alcohol (○,●) and of disyringylmethane (□,■) for duplicate experiments involving heating 20 mmol/L of syringyl alcohol in 1M NaOH at 135°C for various time periods.

It has generally been assumed that the mechanism of condensation involves the conjugate addition of carbanions to quinone methides (QMs), or in other words, involves ionic pathways.[3] However, the fact that anthrahydroquinone (AHQ) reduces the level of dimers and trimers formed during the heating of vanillyl alcohol in alkali does not support an ionic mechanism of condensation.[4] Both sodium sulfide and AHQ reduce the amount of condensation exhibited by coniferyl alcohol reacting with an isolated lignin.[5]

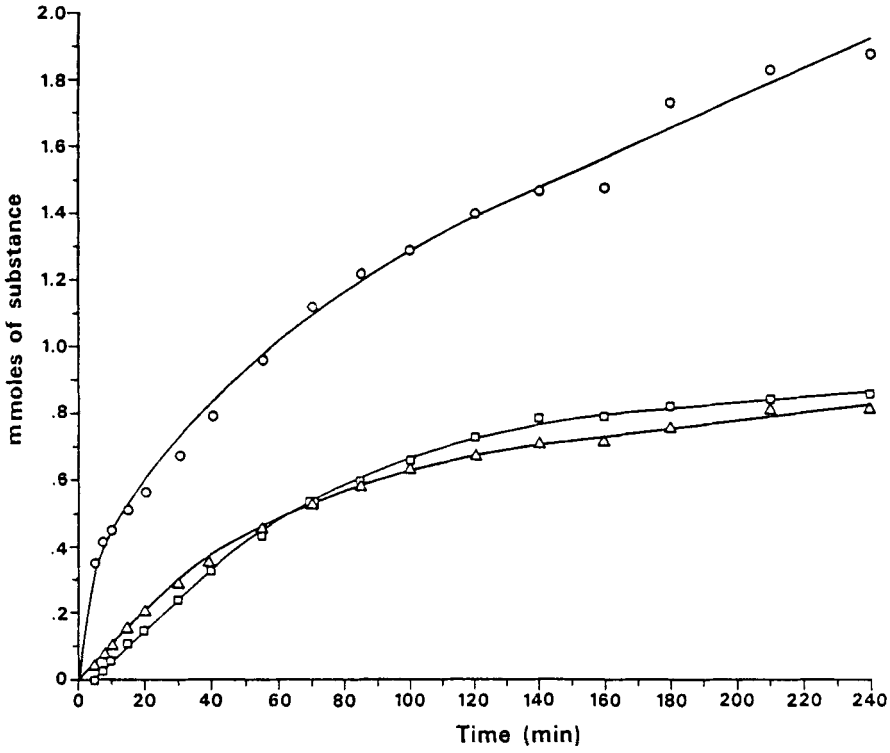


Figure 2. The concentrations of syringol (Δ), 4-methylsyringol (□), and syringaldehyde (○) observed after heating 20 mmol/L of syringyl alcohol in 1M NaOH at 135°C for various time periods.

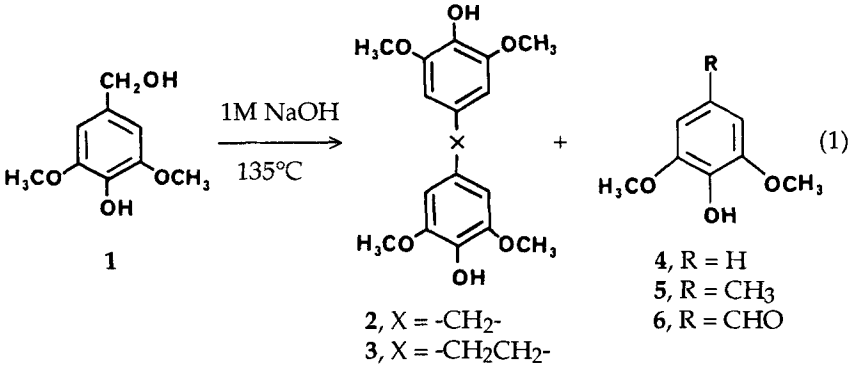
In order to learn more about the mechanism of lignin-lignin condensation reactions, we have examined the reaction of syringyl alcohol (**1**) in hot aqueous alkali. Syringyl alcohol should not form products larger than dimers, thus simplifying the product analysis. The study reported here examines NaOH-induced reactions and the affects of suspected radical initiators and inhibitors on syringyl alcohol condensation reactions; the paper which follows[6] considers syringyl alcohol reactions with typical pulping reagents.

RESULTS AND DISCUSSION

Sodium Hydroxide Reaction

Heating syringyl alcohol in 1M NaOH at 135°C produced five products. Disyringylmethane (**2**), the expected condensation dimer, was the major product. Another dimer, bisyringyl (**3**), was formed in a trace amount. Three monomers, syringol (**4**), 4-methylsyringol (**5**), and syringaldehyde (**6**) were produced in moderate yields (Eq. 1). [Note: common names will be used throughout this report to help the readability; however, the common names are a bit confusing.[7]]

The concentrations of syringyl alcohol and its products (except bisyringyl), as a function of reaction time, are shown in Figures 1 and 2. The syringyl alcohol-NaOH reaction was done three times. The concentration profiles of the major components were very similar from one run to the next (as can be seen in Fig. 1); however, the profiles of the minor monomer products varied considerably from one run to the next. The general trend of concentrations of **6** > **5** ≈ **4** was maintained, but, in the additional runs, compounds **4-6** had final concentrations of 40-60% of those shown in Fig. 2.



1

2, X = -CH_2-
3, X = -CH_2CH_2-

4, R = H
5, R = CH_3
6, R = CHO

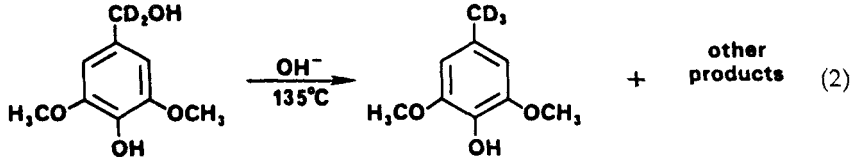
Except for dimer **3**, quantification of reaction components was done by spiking reaction samples with known amounts of deuterated analogs of the components and analyzing the extracted samples by gas chromatography-mass spectroscopy (GC-MS) using selected ion moni-

toring (SIM) and standard response curves. The method described has the advantage of using internal standards (deuterated analogs) which will have solubility characteristics very close to that of the compounds and, therefore, provide accurate determinations. Also, the SIM technique is extremely sensitive, allowing analysis of small sample sizes.

The overall material balance for the NaOH run, considering that two molecules of **1** give one molecule of dimer was 75% at <10 min, 83% at 10-60 min, and 93% at 2-4 hr. The lower balance and concentration peculiarities at earlier times may be reflecting (1) poor initial mixing and heating in the reactor, (2) an induction period, and/or (3) a higher level of a reactive intermediate, which upon quenching gives a non-volatile product; an example would be oxidation of a radical intermediate upon exposure to air to a polar product.

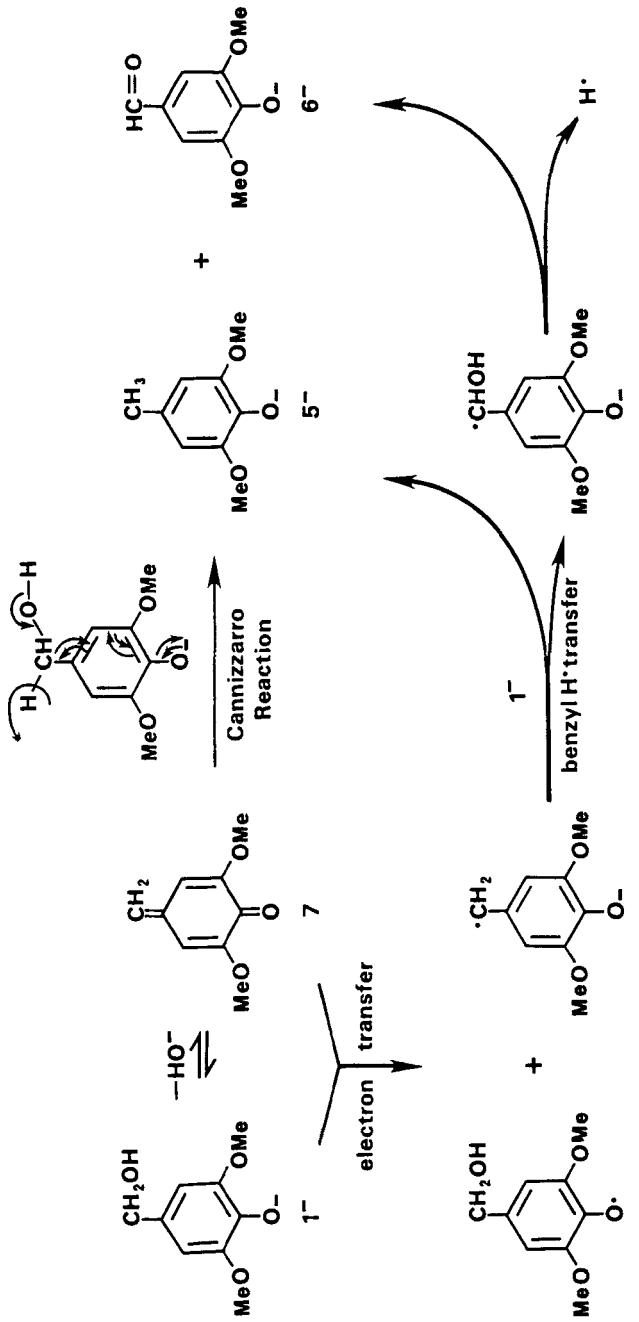
The yield of syringol (**4**) was only about 5% after 4 hours; its yield was often < 5% in NaOH/additive runs.[6] Its mechanism of formation is assumed to be an ionic reverse aldol reaction (loss of CH_2O from the keto form of syringyl alcohol).[3] The formation of syringol, although determined in each case, will not be presented or discussed further.

Heating α,α-dideuteriosyringyl alcohol in lM NaOH at 135°C gave α,α,α-trideuterio-4-methylsyringol (Eq. 2). This result suggests the possibility of a hydride transfer (Cannizzarro-type reaction) or a set of electron and hydrogen atom transfer reactions (Scheme 1). The transfer of an electron from a phenolate ion to a quinone methide has been observed by us in a closely related system.[8]

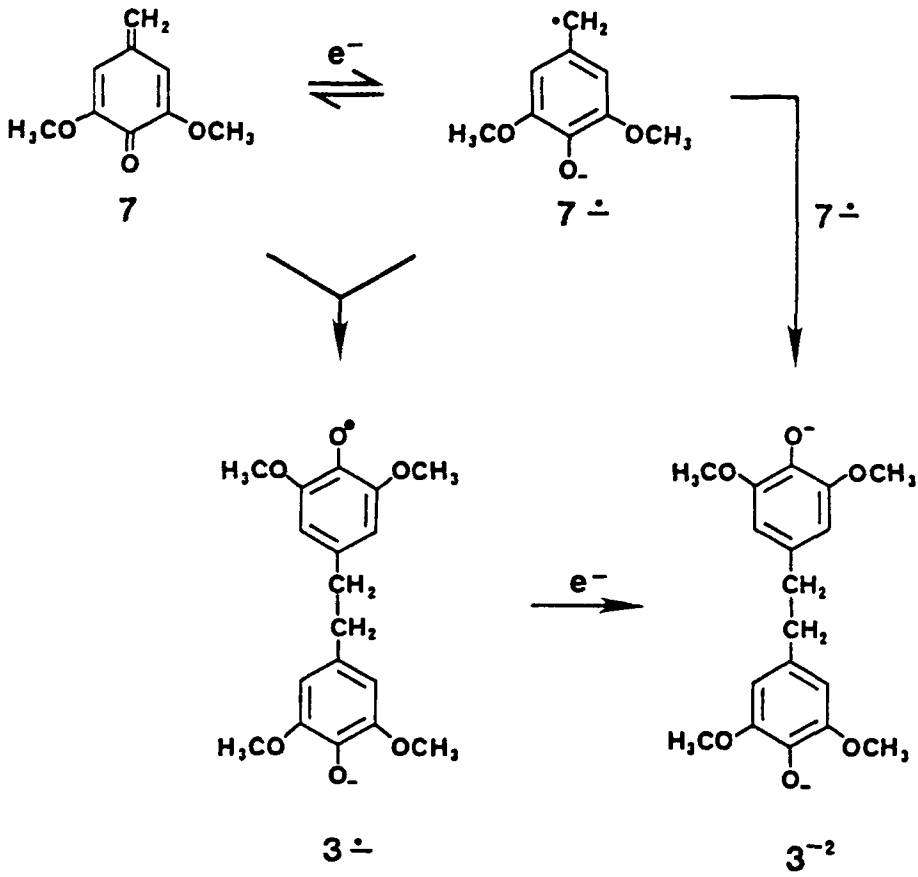


(2)

The trace levels of bisyringyl (**3**) must arise by a dimerization of two $7^{\cdot}$ intermediates or the addition of $7^{\cdot}$ to QM **7**, followed by electron transfer (Scheme 2). The fact that only trace levels of bisyringyl were observed suggests that the concentrations of quinone methide **7** and its radical anion $7^{\cdot}$ are low in the NaOH reaction of syringyl alcohol.



Scheme 1

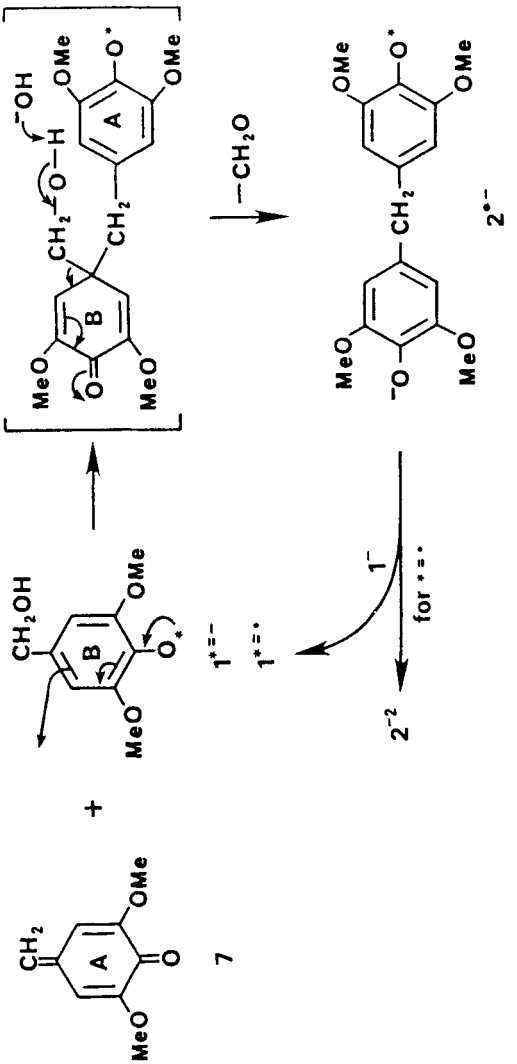


Scheme 2

Finally, a proposed mechanism of formation of the major dimeric product **2** is presented in Scheme 3. An ionic mechanism (* = :) has generally been assumed, but a radical chain mechanism (* = ·) is also a possibility, especially considering the presence of other radical-derived products and our additional studies with syringyl alcohol.[6]

Radical Initiators and Inhibitors

The extent of radical reactions in a system should be influenced by radical initiators and inhibitors. We therefore undertook a brief in-



Scheme 3

vestigation of what affects certain suspected radical initiators and inhibitors had on the condensation reactions of syringyl alcohol. We were limited in the scope of this study by the lack of water soluble reagents which would be stable in lM NaOH at 135°C.

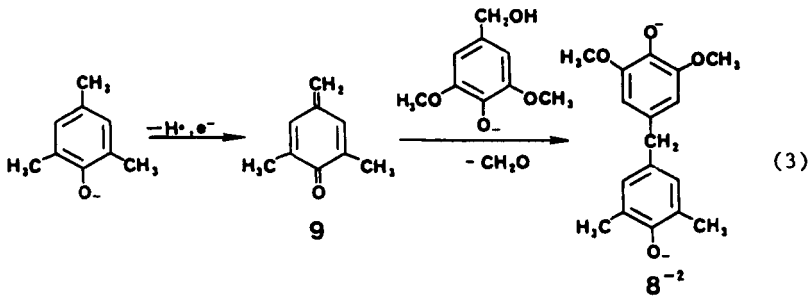
Two radical initiators, sodium persulfate and potassium ferricyanide, were added to syringyl alcohol condensation reactions with the expectation that the conversion of phenolate ions to phenoxy radicals would be facilitated. Unfortunately, the principal reaction turned to a rapid conversion of syringyl alcohol to syringaldehyde. Disyringylmethane production was inhibited, but probably only because syringyl alcohol was being consumed in the competing oxidation reaction.

A known radical inhibitor, butylated hydroxytoluene (BHT),[9] was added to a 135°C alkaline reaction of syringyl alcohol. While BHT is known to be insoluble in alkali at room temperature,[10] it was hoped that (being a phenol) BHT would dissolve at 135°C in alkali. However, this apparently was not the case. Samples of the reaction mixture liquors, removed at various times, were void of BHT and exhibited product compositions similar to the control NaOH reaction. [The sampling techniques only removed soluble components; the metal pressure vessel did not allow visual inspection of the reaction mixture.]

A compound of good alkali solubility, 2,4,6-trimethylphenol, was added in two molar equivalents to a syringyl alcohol reaction. Trimethylphenol was used in the hope that, by donating electrons, it would quench reactive radicals. Although it lacks the steric hindrance of BHT, we reasoned that an excess of trimethylphenol could possibly quench reactive radicals, at least temporarily, and thus reduce condensation. However, addition of trimethylphenol had no significant effect on NaOH-induced product composition.

A minor compound with a molecular weight of 288 was observed in the trimethylphenol product mixture. This mass number corresponds to a diphenylmethane dimer between trimethylphenol and syringyl alcohol. A logical structure is dimer **8**. Such a compound would be difficult to form by a traditional ionic mechanism; the radical mechanism presented in Eq. (3) appears more likely.

Previously, 3,5-dinitrobenzoic acid (DNBA) was observed to decrease the amount of dimers and trimers formed during the alkaline reaction of vanillyl alcohol.[4] By accepting electrons, dinitrobenzenes can quench radical-anions in electron transfer reactions.[11] Addition of DNBA to a syringyl alcohol reaction, however, proved only to increase



(3)

the production of syringaldehyde; the rate of disyringylmethane production was reduced, probably because less syringyl alcohol was available for dimerization. Apparently, syringyl alcohol donates electrons to DNBA and becomes oxidized to syringaldehyde. The previous[4] lower levels of condensation products observed with vanillyl alcohol/DNBA were probably due to similar oxidation reactions; oxidized dimers, along with a greater formation of vanillin, were observed.

The rate of production of 4-methylsyringol (**5**) was impeded by the presence of DNBA; there was a 15 minute delay in its appearance and the level after 4 hours was ~10% of that observed in the control run. The production of 4-methylsyringol was similarly delayed 15 minutes with potassium ferricyanide; however, the production then steadily increased to give a final yield which was about 10% greater than the control. It is interesting that 4-methylsyringol, a reduction product, should increase in the presence of a powerful oxidant for phenol compounds. Possibly syringaldehyde, which is produced in large amounts in the presence of potassium ferricyanide, might be involved, i.e., $7^{\cdot-} + 6^{-} \rightarrow 5^{-}$ + syringic acid$^{\cdot-}$ (Scheme 1 analogy).

CONCLUSIONS

Two of the products observed when syringyl alcohol is heated in NaOH appear to be derived via radical (electron transfer) processes; further confirmation of the radical nature of the reactions which produce 4-methylsyringol and bisyringyl will follow.[6] However, various attempts to determine if radical processes were involved in the formation of disyringylmethane, the principal product, were inconclusive. Radical inhibitors proved to be either insoluble or not suitable; radical initiators only oxidized syringyl alcohol to syringaldehyde. It may be difficult to find an initiator which can generate a phenoxy radical without forming syringaldehyde and is stable under the reaction conditions.

EXPERIMENTAL

Proton- and ^{13}C-NMR spectra were recorded on a Jeol FX 100 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Gas chromatography (GC) analyses of samples were done with a Hewlett Packard 5840 GC chromatogram using either a 2-foot 3% OV-17 on gas-chrom Q or a 6-foot 3% silicone OV-17 on 100/120 Chromosorb W-HP; detection was by a Hewlett Packard 5985 mass spectrometer. The all glass system employed helium (30 mL/min) as the carrier gas, a jet separator at 250°C, a source temperature of 200°C, and an ionization voltage of 70 eV for the electron impact mode.

Oxygen-free water was prepared by boiling distilled water for about 30 min, dispersing nitrogen into the water as it cooled, and sealing until needed. Ultrapure sodium hydroxide was obtained as a 30% solution from Alfa Products, Danvers, Massachusetts. Silica gel 60 (70-230 mesh ASTM) was used in all chromatographic separations.

Syringaldehyde, syringol, lithium aluminum deuteride, and syringic acid were purchased from the Aldrich Chem. Co., Milwaukee, WI. Bisyringyl (**3**) was prepared from syringol (graciously supplied by Dr. I. A. Pearl) by the method of Pearl.[12] Samples of 4-methylsyringol (**5**) and its deuterium-enriched ring analog were available.[13]

Syringyl Alcohol Condensation Reaction - The reaction vessel, described in detail elsewhere,[14] consisted of a 250 mL capacity, Teflon-lined brass reactor which contained an inlet port for the introduction of starting materials and an outlet port for the sampling of the reaction solution. Stirring was by an external air driven magnet.

Reaction solutions were prepared in a nitrogen atmosphere. To the reaction vessel was added 128.3 g of oxygen-free water and 19.8 g of 30% ultrapure NaOH. Syringyl alcohol[15] (0.553 g, 3 mmoles) was dissolved in a mixture of 4.5 g of oxygen-free water and 0.6 g of 30% ultrapure NaOH. This solution was then drawn into a 1/16" ID Teflon tube. Into another Teflon tube was drawn 2.9 g of oxygen-free water. The syringyl alcohol solution, followed by the oxygen-free water, was connected to the reaction vessel by a slider injection valve. The reaction vessel was placed in a 135°C oil bath and heated to temperature. Introduction of the syringyl alcohol solution was done with nitrogen at 100 psi. The final reaction solution had a volume of 150 mL (assuming a density of 1 g/mL) and a syringyl alcohol concentration of 20 mM.

A second slider injection valve with Teflon tubing was used for periodic sampling. Samples (~ 1.5 mL) were expelled from a valve into preweighed 4-mL glass vials and the weight recorded. The density of the reaction solution was found to be 1.044 g/mL, allowing the volumes of the samples to be determined. Approximately 0.15 g of an accurately weighed standard solution was added to each of the recovered samples. The standard solution contained 3.8 g of oxygen-free water, 0.55 g of 30% ultrapure NaOH, and the following amounts of deuterium-enriched compounds: 0.0740 g syringyl alcohol, 0.0213 g disyringylmethane, 0.0100 g syringaldehyde, 0.0067 g 4-methylsyringol, and 0.0025 g syringol. The samples were acidified with 2M H_2SO_4 until a precipitate was observed and then extracted with 1.0 g of chloroform.

Reaction samples were analyzed by mass spectrometry selective ion monitoring system (SIMS). The compounds were separated by GC and the ions representing the molecular weights of the deuterated and nondeuterated compounds were recorded. Just prior to each product analysis, eight standard solutions of known molar ratios of deuterated to nondeuterated syringol, 4-methylsyringol, syringaldehyde, syringyl

alcohol, and disyringylmethane were analyzed by the SIMS technique; a standard response factor curve for each compound was obtained. The areas of the molecular weight ions were measured, allowing the concentration at the time of sampling to be calculated for each compound from the observed peak ratios for the nondeuterated and deuterated compounds (i.e., 184 signal for syringyl alcohol/186 signal for deuterium-enriched syringyl alcohol) and the response factor curves.

Syringyl Alcohol Additive Reactions - The additive reactions were conducted in the same manner as the control reaction. Some of the additives were placed in the reaction vessel; these included butylated hydroxytoluene (1.32 g, 2 equiv.), 2,4,6-trimethylphenol (0.82 g, 2 equiv.), and 3,5-dinitrobenzoic acid (0.19 g, 0.3 equiv.). The other additives were added as solutions to the reaction vessel simultaneously with syringyl alcohol. The amount of oxygen-free water necessary to dissolve these additives was subtracted from that added to the reaction vessel. The additives added as solutions included sodium persulfate (0.21 g, 0.3 equiv. in 4.2 g water), and potassium ferricyanide (1.98 g, 2 equiv. in 5.5 g water). Sampling and analysis for the additive reactions was done in the same manner as the control.

Disyringylmethane - Syringyl alcohol was added to a 1M NaOH solution in the previously described reaction vessel and heated at 135°C for six hours. The reaction solution was then neutralized with 5M H_2SO_4 and extracted with chloroform. The chloroform was separated, dried (anhyd. Na_2SO_4), and reduced to a minimum volume. Separation of the products was accomplished by placing the chloroform solution on a silica gel column and eluting with chloroform. Disyringylmethane co-eluted with syringaldehyde; the aldehyde was removed by extraction of a chloroform solution containing the two compounds with an aqueous $NaHSO_3$ solution. The chloroform (now containing only disyringylmethane) was dried (anhyd. Na_2SO_4) and evaporated. The resulting solid (63% yield) was recrystallized from toluene/35-60°C petroleum ether: mp 110.5-111.5°C; ^{1}H-NMR ($CDCl_3$) δ 3.83 (s, 16, -C$\underline{H}_2$- and -OC$\underline{H}_3$), 5.42 (s, 2, -O$\underline{H}$), 6.39 (s, 4, aryl); ^{13}C-NMR ($CDCl_3$) ppm 41.7 (t, -$\underline{C}H_2$-), 56.1 (q, -O$\underline{C}H_3$), 105.34 (d, C-2, C-6), 131.8 (s, C-1), 132.8 (s, C-4), 146.6 (s, C-3, C-5).

Deuterium-Enriched Syringaldehyde - The two aromatic hydrogens of syringaldehyde were exchanged for deuteriums by heating syringaldehyde in 100% D_3PO_4.[16,17] The 100% D_3PO_4 was prepared in a nitrogen atmosphere by adding 35.5 g of P_2O_5 to 100 g of stirred 85% D_3PO_4. To an oven-dried 250-mL three-necked round-bottom flask was added the 100% D_3PO_4 and 9.5 g of syringaldehyde. Nitrogen was flowed through the flask as the contents were stirred in a 50°C water bath for four days. Quenching of the reaction was accomplished by adding water to the cooled flask, pouring the reaction solution into a larger volume of water, and carefully adding solid NaOH until the pH was near neutral. The solid product was removed by filtration of the aqueous mixture, washed with water, and dried. The filtered solution was extracted with chloroform, which in turn was dried (anhyd. Na_2SO_4) and evaporated to yield additional product. Analysis of the combined product (9.0 g) by ^{1}H-NMR showed, with respect to the methoxyl protons, an exchange of the aromatic protons corresponding to 95.7% d_2.

Deuterium-Enriched Syringyl Alcohol - This compound was obtained by reducing deuterium-enriched syringaldehyde with $NaBH_4$.[15]

Deuterium-Enriched Syringol - Two consecutive exchanges, done in the same manner as for deuterated syringaldehyde, converted 2.00 g of syringol to 1.38 g of solid, which by GC/MS showed 156 (d_2) as the major signal, with no 154 (d_0) signal.

α,α-Dideuteriosyringyl Alcohol - The ethyl ester of syringic acid was prepared by stirring for 30 min a solution of 70 mL of ethanol containing 5.00 g (25 mmoles) of syringic acid and saturated HCl gas . The volume of ethanol solution was then halved by distillation and the resulting solution poured into 300 mL of a 2% $NaHCO_3$ solution. Filtration provided 4.25 g of a colorless solid. The filtrate was extracted with $CHCl_3$, which was dried (anhyd. Na_2SO_4) and evaporated to yield an additional 1.17 g of product. The total yield of ester was 5.42 g (95.0%): ^{1}H-NMR ($CDCl_3$) δ 1.39 (t, 3, J = 7 Hz, -C<u>H</u>$_3$), 3.93 (s, 6, -OC<u>H</u>$_3$), 4.36 (q, 2, J = 7 Hz, -C<u>H</u>$_2$-), 5.99 (s, 1, -O<u>H</u>), 7.32 (s, 2, aryl).

A solution of 10.92 g (48 mmole) of the ethyl ester in 150 mL was added over a 2-hour period to a stirred suspension of 3.00 g of $LiAlD_4$

(1.14 equiv.) in 50 mL of anhyd. ether. After refluxing for three hours, the cooled, stirred reaction was quenched by slowly adding saturated aq. Na_2SO_4. The reaction mixture was filtered and the collected aluminum salts washed with ether. The salts were then dissolved in dilute HCl and extracted with ether. The combined ether solutions were dried (anhydrous Na_2SO_4) and evaporated to afford a solid which, when recrystallized from $CHCl_3$/hexane, yielded 3.0 g (33%) of α,α-dideuteriosyringyl alcohol. Analysis of the product by ^{1}H-NMR showed no Ar$C\underline{H}_2$OH signal at δ 4.61.

α,α-Dideuteriodisyringylmethane - In a nitrogen atmosphere, the previously described 250 mL reactor vessel was loaded with 2.26 g (12 mmole) of α,α-dideuteriosyringyl alcohol, 110 g of oxygen-free water, and 16.2 g of 30% ultrapure NaOH. The reaction vessel was sealed and placed in a 135°C oil bath. After six hours, the reaction solution was cooled, acidified, and extracted with $CHCl_3$. The $CHCl_3$ solution was dried (anhyd. Na_2SO_4), reduced in volume, placed on a silica gel column, and eluted with $CHCl_3$. The first compounds eluted were syringol and 4-methylsyringol, which by GC/MS analysis had molecular weights of 154 and 171, respectively. Thus, the alkaline reaction of α,α-dideuteriosyringyl alcohol yielded nondeuteriosyringol and trideuterio-4-methylsyringol.

Disyringylmethane and syringaldehyde quickly eluted next from the column. The $CHCl_3$ solution which contained these compounds was reduced in volume, extracted with a $NaHSO_3$ solution to remove the aldehyde, dried (anhyd. Na_2SO_4), and evaporated. The resulting solid was recrystallized from toluene/35-60°C petroleum ether to yield 1.33 g (68%) of α,α-dideuteriodisyringylmethane. Analysis by ^{1}H-NMR showed no Ar$C\underline{H}_2$Ar signal.

ACKNOWLEDGMENTS

Portions of this work were used by Smith as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper

Chemistry (now the Institute of Paper Science and Technology). We would like to thank Dr. Leland Schroeder for his helpful suggestions.

REFERENCES

1. Martin, J., in Lignins, Chapter 16, K. V. Sarkanen and C. H. Ludwig (eds.), John Wiley and Sons, Inc., New York, 1971.

2. Bryce, J. R. G., in Pulp and Paper, Chemistry and Chemical Technology, J. P. Casey (ed.), Vol. I, 3rd Edition, John Wiley and Sons, Inc., New York, 1980, p. 425-429. Also, W. G. Glasser, ibid, p. 69-76.

3. Gierer, J., Wood Science Technol., 19, 289 (1985).

4. Dimmel, D. R., Shepard, D., and Brown, T. A., J. Wood Chem. Technol., 1, 123 (1981).

5. Kondo, R. and McCarthy, J. L., J. Wood Chem. Technol., 5, 37 (1985).

6. Smith, D. A. and Dimmel, D. R., J. Wood Chem. Technol., following article.

7. The names appear to be derived from syringaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde (ArCHO). Syringyl alcohol is the reduction product of syringaldehyde; therefore, syringyl = $ArCH_2$-. The corresponding compound which has no side chain, ArH, is known as syringol. On this basis, $ArCH_2CH_2Ar$ is bisyringyl, $ArCH_3$ is methylsyringol, and $ArCH_2Ar$ should be syringylsyringol; however, the latter is known as disyringylmethane - a name that will be used in this report.

8. Smith, D. A. and Dimmel, D. R., J. Org. Chem., 53, 5428 (1988).

9. Howard, J. A., in Free Radicals, J. K. Kochi (ed.), Vol. II, John Wiley and Sons, Inc., New York, 1973, p. 3.

10. Stillson, G. H., Sawyer, D. W., and Hunt, C. K., J. Amer. Chem. Soc., 67, 303 (1945).

11. Kornblum, N., Angew. Chem. Intern., Engl. Ed., 14, 734 (1975).

12. Pearl, I. A., J. Org. Chem., 22, 1229 (1957).

13. Apfeld, P. B., Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wisconsin, June, 1986; D. R. Dimmel and L. F. Schuller, J. Wood Chem. Technol., 6, 345 (1986).

14. Millard, E. C., Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, WI, June, 1976.

15. Sarkanen, K. V., Kakehi, K., Murphy, R. A., and White, H., Tappi, 45 (1), 24 (1962).

16. Dimmel, D. R., Shepard, D., Perry, L. F., Joachimides, T., McDonough, T. J., and Malcolm, E. W., J. Wood Chem. Technol., 5, 229 (1985).

17. Ericsson, B., Nist, B. J., and Sarkanen, K. V., Khim. Biokhim. Lignina, Tsellyul. Gemitsellyul, 21 (1969); ABIPC, 74, 127845.