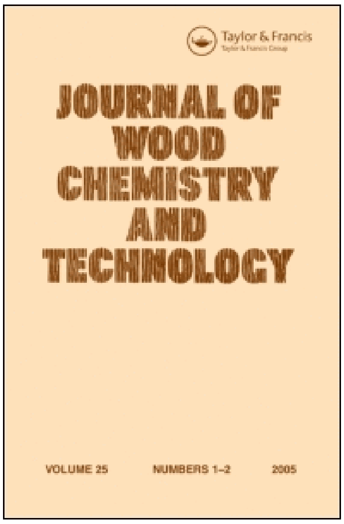

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REACTION OF *p*-HYDROXYCINNAMYL ALCOHOLS WITH TRANSITION METAL SALTS. 1. OLIGOLIGNOLS AND POLYLIGNOLS (DHPs) FROM CONIFERYL ALCOHOL

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ABSTRACT

Treatment of coniferyl alcohol with iron, cobalt, or manganese salts gave a variety of oligolignols and polylignols (DHPs). Conditions could be adjusted to favor high or low molecular weight products and to give different inter-unit linkage distributions. Oxidation with iron and manganese salts generally gave structures containing β-O-4, β-5, and β-β linkages. Oxidation with iron and manganese salts under highly alkaline conditions also generated α-O-4 structures. The cobalt salt $K_3Co(CN)_6$ was unique in that a novel β–γ linkage was generated in high yield. Reactions in the absence of solvent also resulted in the formation of oligolignols and DHPs.

INTRODUCTION

The enzyme catalyzed dehydropolymerization of coniferyl alcohol (CA) to give oligolignols and polylignols (DHPs) was first reported by Freudenberg.[1,2] Since then, DHPs have become popular lignin models in the lignin, wood, and plant science fields. Although it was claimed

TABLE 1
Comparison of Linkage Distribution

	Linkage (%)						
	β-O-4	β-5	β–β	α-O-4	5-5′	β-1	5-O-4
Guaiacyl DHP	27	45	17	11	---	---	---
Softwood lignin	48	9-12	2	---	10	7	4

that natural lignins were truly duplicated by the enzymic dehydropolymerization in the laboratory,[1] subsequent comparisons of milled wood lignins (MWLs) and DHPs revealed significant differences.[3-6] In particular, recent comparisons of ^{13}C NMR spectra of DHPs and MWLs revealed major qualitative and quantitative differences.[7,8] For example, the ^{13}C NMR spectrum of a high molecular weight (MW) fraction from a typical DHP prepared from CA (peroxidase/H_2O_2) indicated the presence of only four linkage types. The linkage distribution is compared to that of a typical softwood lignin[9] in Table 1. In addition to the linkages shown in the table, many others were reported to be present in softwood lignin in smaller amounts.[9] Early comparisons of DHPs and lignins by ^{13}C NMR spectroscopy focused on the similarities; differences were not as apparent with the lower field (25 MHz ^{13}C) instrumentation due to poorer signal resolution.[10–12] A quantitative estimation of hydroxyl groups in a spruce MWL and a guaiacyl DHP, utilizing quantitative ^{13}C NMR spectroscopy (62.9 MHz), indicated that the benzylic alcohol groups in the DHP are only half as abundant as in the MWL.[13] This is consistent with the high α-O-4 content shown in Table 1. Significant differences between lignins and DHPs have also been revealed by thioacidolysis studies,[14] but with much less detail than is possible with NMR techniques. Consequently, although DHPs remain the best models of natural lignins available and are invaluable in studies involving specific isotopic labeling, experimental results obtained by using DHPs may be distorted relative to the results that would have been obtained had corresponding lignins been used. Most importantly, the major crosslink in natural lignin is presumably the very stable 5-5′ linkage because of its reported abundance.[9] In contrast, in DHP, the predominant crosslink is the labile α-O-4 linkage, which is formed by heterolytic quinone methide reactions rather than by radical coupling.[1,8,15]

This report, the first in a series, deals mainly with the scope and flexibility of reactions of CA with salts of iron, manganese and cobalt to produce a variety of oligolignols and DHPs. The initial generation of phenoxy radicals by the metal oxidants is analogous to the action of the conventional peroxidase/H_2O_2 system.[16,17] However, the metal salt approach is more flexible than the corresponding enzymic methods in that the reaction conditions are not constrained within the pH and temperature limits imposed by the enzymes. Subsequent reports will address the tailoring of oxidation reactions to generate low MW products, such as di-, tri-, or tetralignols, or high MW products such as DHPs. One goal of the overall study is to obtain a number of trilignols or higher oligolignols of guaiacyl, syringyl, and coumaryl C_9 units linked by at least one β-O-4 bond in combination with minor linkages such as β-5 (coumaran), β-β (resinol), 5-5′ (biphenyl), β-1, and 5-O-4 bonds. These compounds, which can be precisely characterized by ^{13}C NMR spectroscopy, serve as more accurate models of lignin substructures than those that have been used previously.[10,18] Ultimately, this technique will be used to prepare DHPs that more closely approximate the structure of native lignins.

RESULTS AND DISCUSSION

Reaction Products

All of the compounds isolated and/or detected in the reaction mixtures in this study are illustrated in Figure 1 and are identified by

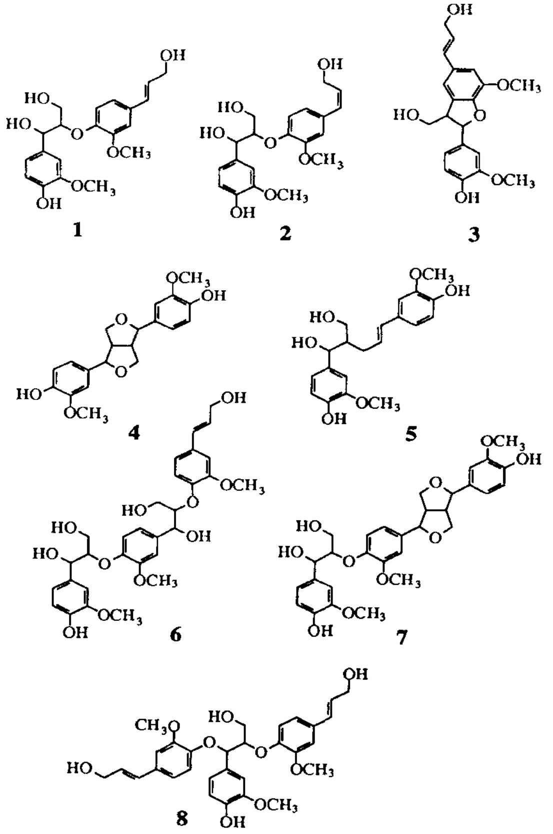


FIGURE 1. Oligolignols from Coniferyl Alcohol/Metal Salt Reactions.

number in the text. The underivatized products are shown although, in most cases, the fully acetylated products were isolated. The compounds were identified by ^{1}H and ^{13}C NMR spectroscopy and by comparison with the spectra of authentic compounds in the FPL/DFRC (Forest Products Lab/Dairy Forage Research Center) NMR database.[19] Linkages represented in the figure are β-O-4 in dilignols **1** and **2** and trilignols **6** - **8**; β-5 (coumaran) in **3**; β–β (resinol) in **4** and **7**; a novel β–γ linkage in **5**; and α-O-4 in **8**. In addition to these compounds, unidentified higher oligolignols and DHPs were also obtained.

Analysis of Linkage Distributions

To estimate the abundances of linkages in oligolignol mixtures and/or DHPs, the areas of ^{13}C NMR signals attributed to side chain carbons were determined. These carbons can generally be associated with four linkage types: α-O-4, β-O-4, β-5, and β–β. With the exception of α-O-4, these linkage types can be represented by dilignols. A trilignol is the smallest entity in which the α-O-4 linkage occurs. The "α-O-4" actually refers to an α-O-4/β-O-4 trilignol entity such as **8**, On the other hand, "β-O-4" will be used only to designate dilignol entities with un-etherified α-carbons.

A typical example of the signals of interest in an acetylated guaiacyl DHP is shown in Figure 2 and sample calculations are illustrated in Table 2. The signal cluster in the 74 - 76 ppm region is due exclusively to the α-carbon of the *erythro* and *threo* forms of the β–O–4 linkage and the area under this cluster is arbitrarily set to 1 unit.

The signal cluster in the 79-82 ppm region arises from both the α- and β-carbons of α-O-4 entities as well as the β-carbon of β-O-4 units. Therefore, the contribution of the α-O-4 entity is determined as illustrated in Table 2. Signals from α-carbons of β-5 units (88-90 ppm) can be measured directly and the α- and γ-carbons of the β–β entities each account for two carbons because of the symmetry of the linkage. The above technique can not be used for natural lignins because of the numerous overlapping signals in this region due to other lignin bonds, carbohydrate impurities and extraneous wood components.

Metal Systems

The metal systems and associated reaction conditions used in this study are shown in Table 3. Under some conditions the actual oxidant may be different from the formula in the table because of hydrolysis and/or disproportionation reactions.[20]

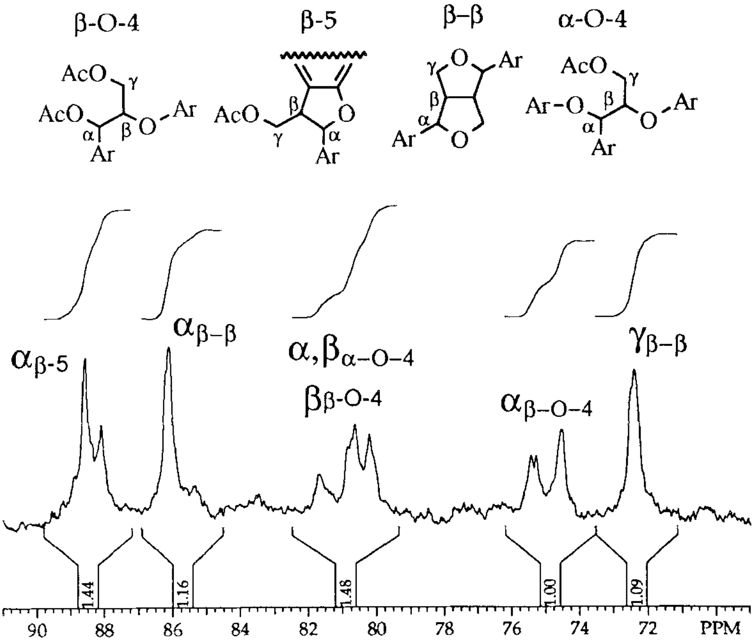


FIGURE 2. Partial ^{13}C NMR Spectrum of an Acetylated Guaiacyl DHP.

TABLE 2
Sample Calculations of Linkage Distributions

Linkage	Calculate	Area	Percent of Total
β-O-4		1.00	31
α-O-4	(1.48 - 1.00)/2	0.24	7
β-5		1.44	44
β-β	(1.16 + 1.09)/4	0.57	18
	Total	3.25	100

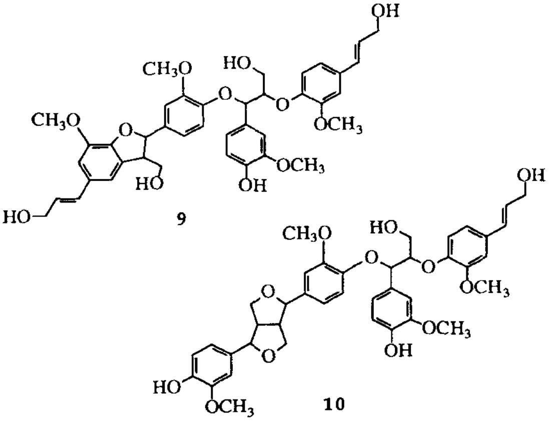
TABLE 3
Metal Systems and Reaction Conditions

Metal Salt	Condition	Medium	Time/Temp[a]	Comments[b]
$K_3Fe(CN)_6$	A	borate buffer, pH 9	1 hr/100 °C	met-->CA
	B	borate buffer, pH 9	15 hr/RT[a]	CA-->met
	C	borate buffer, pH 9	15 hr/RT	met--->CA
	D	0.1 M NaOH	20 min/RT	fast/simul
	E	K_2CO_3, solid state[c]	20 min/RT	fast/simul
	F	K_2CO_3, solid state[c]	15 hr/RT	fast/simul
$K_3Co(CN)_6$	G	acetate, pH 4.5	2 hr/RT	no reaction
	H	borate buffer, pH 9	4-15 hr/RT	fast/simul
	I	0.1 M NaOH	2 hr/RT	no reaction
$K_3Mn(CN)_6$	J	acetate, pH 4.5	15 hr/RT	no reaction
	K	0.1 M NaOH	1 hr/RT	fast/simul
	L	borate buffer, pH 9	15 hr/RT	CA-->met
	M	borate buffer, pH 9	15 hr/RT	met-->CA
$Mn(OAc)_3$	N	acetic acid	30 min/RT	fast/simul
	O	solid state[c]	15 min/RT	fast/simul
			15 hr/RT	fast/simul

[a] RT = room temperature.
[b] met-->CA indicates slow addition of metal salt soln. to CA soln.; CA-->met indicates slow addition of CA soln. to metal salt soln.; fast/simul indicates fast or simultaneous addition of reactants.
[c] See Experimental.

Potassium Ferricyanide Reactions

Reaction of CA with ferricyanide (condition A, Table 3) gave a mixture of the three dilignols, **1**, **3**, and **4**, representing the β-O-4, β-5, and β-β linkages. A typical reaction gave 28% of **1**; 12% of **3**; 6% of **4**; and a 14% recovery of CA. When a mixture of *cis* and *trans* CA was used, dilignol **2** was also isolated. The stereochemistry of the β-O-4 linkage formed by radical coupling with ferricyanide/borax systems was always about 90:10 *erythro:threo* (*e:t*). In most cases a few percent of a



9

10

FIGURE 3. α-O-4 Tetralignols.

*mixture of higher oligolignols was also obtained, but was not character*ized further because of the complexity of the mixtures and the small scale of the reactions. When the oligolignol fractions from several similar reactions were combined and subjected to chromatographic separation, the *erythro* α-O-4 trilignol **8** was identified. This compound has been previously obtained by treatment of CA with silver oxide[15]. The silver oxide treatment also gave the two *erythro* α-O-4 linked tetralignols **9** and **10**, (Fig. 3). Although the components were not isolated, the ^{1}H and ^{13}C NMR spectra of a tetralignol fraction from a ferricyanide oxidation of CA in NaOH solution (condition D) are consistent with a mixture of **9** and **10**. No β-O-4 dilignols were detected because under these conditions all of the β-O-4 dilignols that are generated rapidly undergo quinone methide additions to form α–O–4 oligolignols. Similar product mixtures, high in α-O-4 linkages, were obtained by simply grinding dry CA, potassium ferricyanide, and anhydrous potassium carbonate together in a mortar. If the reaction mixture was worked up in a few minutes (condition E), low MW products were obtained; left overnight (condition F), a DHP was

TABLE 4

Linkage Distributions of Products High in α-O-4 Linkages

			Linkage (%)			
Condition	Medium	Time	α-O-4	β-O-4[a]	β-5	β–β
D	NaOH solution	20 min	53	nd[b]	25	22
E	K_2CO_3, solid state	20 min	50	nd	25	25
F	K_2CO_3, solid state	15 hr	45	22	15	18

[a]With an un-etherified benzylic carbon; [b]nd, not detected.

obtained. The large difference between the MW of the products present in the two preparations is apparent from the ^1H NMR spectra in Figure 4. Linkage distribution in the α-O-4 rich products, calculated from ^{13}C NMR spectra, are compared in Table 4.

The mode and rate of addition of reactants also had a major effect on the MW of the products. Condition A (slow addition of metal salt to CA) produced primarily low MW products wereas slow addition of CA to ferricyanide solution at ambient temperature (condition B) produced a DHP with a distribution of linkages similar to that obtained under condition A. As would be expected, reversing the addition (slowly adding metal salt to CA; condition C) significantly altered the linkage distribution as a relatively large concentration of CA was always present. Table 5 compares the distributions in DHPs obtained by normal (CA-->met) as opposed to reverse (met-->CA) addition and with a guaiacyl DHP prepared by the conventional "Zutropfverfahren" mode with the hydrogen peroxide/peroxidase system.[2,8]

The typical predominance of the β-5 linkage in conventionally prepared G-DHPs illustrated here (45%), is considerably greater than that in the DHPs produced by dehydropolymerization with ferricyanide (32-33%). Another observation obtained from Table 5 is the potential of β-O-4 production which can be considered as the sum of the β-O-4 and α-O-4 linkages. Prevention of quinone methide reactions on β-O-4

TABLE 5
Linkage Distribution in Ferricyanide-Produced DHPs and Conventional G-DHP

	Linkage (%)		
Linkage	CA-->Met	Met-->CA	G-DHP
β-O-4	37	22	30
α-O-4	8	19	8
β-5	33	32	45
β–β	22	26	17

sidechains would raise the β-O-4 content of the DHPs by a value equal or greater than the original α-O-4 content.

Potassium Cyanocobaltate(III) Oxidations

Cyanocobaltate did not react with CA under either acidic (condition G, Table 3) or highly alkaline conditions (condition I). In borate buffer (condition H), however, a single product, dilignol **5**, was obtained in high yield (97%). An analogous syringyl compound has recently been isolated in low yield from an enzymic dehydrogenation mixture containing pectin.[21] Presumably, formation of the extended quinone methide of CA[22,23] is the intermediate responsible for the formation of **5**. When the reaction was repeated with slow addition of CA over a 15 hour period, the same product was obtained (20% yield) along with an unidentified β–γ dilignol (16% yield). The unidentified dilignol appeared to be a dehydration product of dilignol **5** as both the benzylic and methylol acetate entities were absent from the ^{13}C NMR spectrum of the fully acetylated product. Examination of the remaining material by ^{13}C NMR spectroscopy indicated that it was polyphenolic in nature and had no aliphatic sidechain carbons. The acetylated β–γ dilignols have chemical shifts at 32.4 ppm (32.2 for the dehydrated product) corresponding to the γ–carbon in **5**, and 44.0 ppm (41.8 for the dehydrated product) corresponding to the saturated β-carbon in **5**. Because these signals are absent in MWLs and conventionally prepared DHPs, the β–γ lignols were not investigated further.

Potassium Cyanomanganate(III) Oxidations

CA did not react with cyanomanganate in acetate buffer (condition J, Table 3). In highly alkaline medium (condition K), a high yield (90%) of crude product was obtained. Upon thick-layer chromatography on silica gel, a mixture of dilignols **1** (19% yield), **3** (28%), and **4** (20%) was obtained along with recovered CA (3%). Examination of the crude product by ^{13}C NMR spectroscopy prior to chromatography also indicated the presence of α-O-4 entities. These were likely present as trilignols, such as **8** but, under the conditions of the plate development, were not resolved from other oligolignols. The ^{13}C NMR spectrum of the crude mixture indicated 26% β-O-4, 9% α-O-4, 34% β-5, and 28% β–β. This result is in contrast to the analogous reaction with ferricyanide (condition D) in which no un-etherified β–O–4 entities were detected.

Reaction of CA with cyanomanganate in borate buffer (condition K, L) gave DHPs in 85% yield with both normal and reverse addition. Unlike the corresponding experiments with ferricyanide, (Table 5) both addition modes gave similar linkage distributions and considerably fewer α-O-4 entities, as shown in Table 6. This is consistent with less quinone methide participation and/or a lack of stability of α-O-4 structures in the cyanomanganate system. Evidence for the latter is that β-O-4 dilignols isolated from cyanomanganate/NaOH reactions had an approximately 50:50 *e:t* ratio in contrast with cyanomanganate/borax or ferricyanide/borax reactions in which the *erythro* isomer predominated (>90%). Approximately equal *erythro* and *threo*

TABLE 6
Linkage Distribution in Cyanomanganate produced DHPs

	Linkage (%)	
Linkage	CA-->met	met-->CA
β-O-4	42	45
α-O-4	3	5
β-5	29	29
β-β	25	21

forms of the β-O-4 linkage is consistent with alkaline hydrolysis of α-O-4 structures such as 8.

Unlike the corresponding iron and cobalt cyano complexes, the manganese complex is not stable in neutral or alkaline aqueous solution. Disproportionation of the Mn(III) to Mn(II) and Mn(IV) presumably occurs under these conditions so the active oxidant may simply be MnO_2.[20]

Manganese(III) Acetate Oxidations

Reaction of CA with $Mn(OAc)_3$ in acetic acid (condition N) gave both low (dilignols) and high MW fractions. This was apparent as ^1H NMR spectra similar to those of Figure 4 were obtained. Analysis of the corresponding ^{13}C NMR spectra gave the linkage distribution results shown in Table 7. In addition to the greater β-O-4 content than was observed with previous metal systems, it is also noteworthy that the β-O-4 entites have an *e:t* ratio of about 65:35, whereas, with the ferricyanide/borax and cyanomanganate/borax systems, the *erythro* form predominated (>90%).

$Mn(OAc)_3$ readily reacted with CA in the solid state (condition O). If the metal salt was ground with CA in a mortar and then quenched (by adding the solid to water) after a few minutes, di- and trilignols

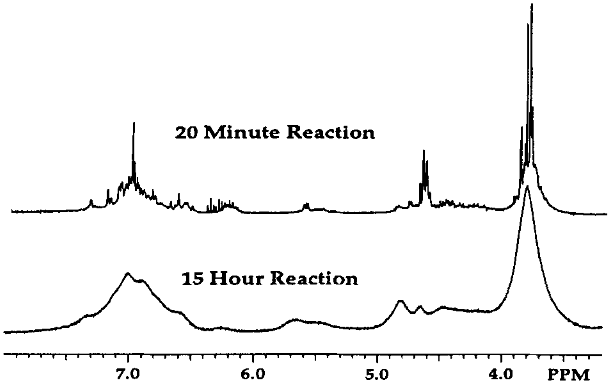


FIGURE 4. ^1H NMR spectra of products from solid-state reactions.

TABLE 7

Linkage Distribution in Manganese(III) Acetate Produced Lignols

	Molecular weight (%)	
Linkage	Low	High
β-O-4	59	55
α-O-4	nd[a]	8
β-5	35	26
β–β	6	11

[a] Not detected

were obtained. If the solid mixture was allowed to remain overnight at room temperature and then quenched, a DHP was obtained. Further investigations of solid state reactions are in progress.

EXPERIMENTAL

Starting Materials.

Coniferyl alcohol (CA) was prepared according to a literature procedure.[24] The CA was free of α,β-dihydro-CA, a common impurity in other preparations.[25] The potassium ferricyanide, $K_3Fe(CN)_6$, was A.C.S. reagent grade from Baker & Adamson, the potassium hexacyanomanganate, $K_3Mn(CN)_6$, was from Alfa Inorganics, the manganese acetate, $Mn(OAc)_3$-$2H_2O$, 97%, was from Aldrich Chemical Company and the potassium cyanocobaltate, $K_3Co(CN)_6$, was prepared by the author while a student at the University of Minnesota. The 0.05 M borax buffer (pH 9) was prepared from Mallinckrodt AR grade sodium borate ($Na_2B_4O_7$-$10H_2O$).

Potassium Ferricyanide Reactions.

Condition A, Table 3:

Typically, the CA (180 mg, 1.00 mmol) was dissolved in 0.05 M borax (50 ml, 2.50 mmol) at 100 °C under a nitrogen atmosphere while stirring magnetically. A solution of the metal salt (395 mg, 1.20 mmol) in water (3 ml) was then added to the CA solution over a period of 40–50 m. The resulting suspension was heated for an additional 10 m, cooled to room temperature, neutralized with acetic acid, and extracted with ethyl acetate (5 x 20 ml). The extract was dried over $MgSO_4$, and evaporated under vacuum to give an oil/boric acid mixture. Methanol (5 ml) was added and evaporation was repeated. This methanol evaporation sequence was repeated 5 times to drive off all of the boric acid as methyl borate. Reaction mixtures were examined by ^1H and ^{13}C NMR spectroscopy and/or acetylated with 1/1 acetic anhydride/pyridine (2-4 h) prior to NMR examination.

Conditions B & C:

In the normal addition experiment (condition B), a N_2-sparged solution of CA (90 mg, 0.5 mmol) in 0.05M borax (50 ml) was added over a period of 15 h (using a peristaltic pump) to a solution of $K_3Fe(CN)_6$ (332 mg, 1.0 mmol) in 0.05 M borax (10 ml), under N_2 while stirring magnetically. The pH of the resulting suspension was then adjusted from 9 to about 5 with acetic acid, and the mixture was filtered. The residue was washed with water and freeze-dried, yielding a cream colored solid (57 mg, 63% wt yield). The polymeric product was acetylated and examined by NMR (see Table 4). Workup of the filtrate according to the technique described for condition A gave a small amount (8% wt yield) of a low MW fraction which was not further investigated.

In the reverse addition experiment (condition C), the same weights were used but the CA was dissolved in 15 ml of the borax solution and the iron salt was dissolved in 45 ml of borax solution. Workup as above gave a 80% and 7% wt yield of polymeric and low MW products, respectively. The polymeric product was acetylated and examined by NMR. Table 5 shows the linkage distribution.

Condition D:

A solution of $K_3Fe(CN)_6$ (200 mg, 0.61 mmol) in water (3 ml) was added over a 1 m period to a solution of CA (100 mg, 0.56 mmol) in 0.1M NaOH under a N_2 atmosphere with stirring. Stirring was continued for 20 m, and then acetic acid (3 drops) was added. The resulting white suspension (pH ~ 4) was then filtered and the residue was washed with water and freeze-dried, giving a cream-colored solid (74 mg, 74% wt yield). Acetylation of the product with 1/1 acetic anhydride in pyridine gave 82 mg of a pale yellow oil. Table 4 shows the linkage distribution.

Conditions E & F:

For the short reaction (condition E), CA (100 mg, 0.56 mmol), $K_3Fe(CN)_6$ (200 mg, 0.61 mmol) and anhydrous K_2CO_3 (124 mg, 0.90 mmol) were ground together in a mortar for 20 m. The solid was then transferred to a small beaker with water (10 ml) and the mixture was neutralized with two drops of acetic acid. The resulting suspension was filtered and the residue was washed with water and freeze-dried, giving a white solid (69 mg, 69 wt%). A ^1H NMR spectrum of the acetylated product indicated that it was predominately low MW material. For the long reaction (condition F), CA (50 mg, 0.28 mmol), $K_3Fe(CN)_6$ (100 mg, 0.30 mmol) and anhydrous K_2CO_3 (85 mg, 0.62 mmol) were ground together for 10 m, then allowed to remain at room temperature overnight. Workup as above gave a pink solid (46 mg, 92 wt%). The ^1H NMR spectrum of the acetylated product confirmed its polymeric nature. Table 4 shows linkage distributions in the low and high MW products.

Potassium Cyanocobaltate Reactions

Condition G:

A solution of CA (25 mg, 0.14 mmol) and $K_3Co(CN)_6$ (94 mg, 0.28 mmol) in 0.1 M sodium acetate buffer (10 ml, pH 4.6) was stirred at room temperature for 1.5 h. The colorless solution was then extracted with ethyl acetate (4 x 15 ml). Evaporation of the solvent and azeotroping off residual acetic acid with toluene gave a quantitative recovery of CA.

Condition H:

A solution of CA (90 mg, 0.50 mmol) and $K_3Co(CN)_6$ (335 mg, 1.00 mmol) in 0.05 M borax (25 ml) was stirred at room temperature, under N_2 for 4 h. Acidification of the yellow solution with acetic acid gave a colorless solution that was extracted with ethyl acetate (6 x 10 ml). Evaporation of the solvent under vacuum and driving off residual boric acid as methyl borate, as described under condition A, gave a yellow oil (87 mg, 97%). The ^1H and ^{13}C NMR spectra of the oil were consistent with dilignol **5**.

The above reaction was repeated under similar conditions except that a CA solution (0.50 mmole in 50 ml 0.05 M borax) was added to $K_3Co(CN)_6$ (1.00 mmol in 10 ml borax) over a 15 h period. Workup as above and acetylation of the crude product gave a white solid (77 mg 86%). Thick-layer chromatography on silica gel indicated at least 9 products. The two major ones were dilignol **5** (10 mg) and an unidentified dehydration product of **5**. The remaining products were much slower moving on the silica gel and appeared to be polymeric.

Condition I:

A solution of CA (90 mg, 0.50 mmol) and $K_3Co(CN)_6$ (335 mg, 1.00 mmol) in 0.1 M NaOH was stirred at room temperature for 2 h. Neutralization of the yellow solution with acetic acid and extraction of the resulting white suspension with $CHCl_3$ gave only starting material (83 mg, 92% recovery).

Potassium Cyanomanganate Reactions

Condition J:

A reaction analogous to that described above with the cobalt salt (condition G) gave a quantitative recovery of CA.

Condition K:

CA (180 mg, 1.00 mmol) was dissolved in 0.1 M NaOH in a large vial with agitation provided by bubbling N_2. When dissolved, $K_3Mn(CN)_6$ (360 mg, 1.10 mmol) was rapidly added and N_2 bubbling was continued for 1 h. The resulting dark suspension was filtered and the yellow-orange filtrate was acidified with 1 M HCl to give a white suspension, that was extracted with ethyl acetate (4 x 20 ml). The extract was washed with water, saturated NaCl solution, and dried over $MgSO_4$. Evaporation of the solvent left a pale yellow foam (162 mg, 90% wt yield). Thick-layer chromatography on silica gel, with 5%

CH_3OH/CH_2Cl_2 as developer, gave the three dilignols, **1** (19%), **3** (28%) and **4** (16%), along with unidentified material.

Conditions L & M:

CA was reacted with $K_3Mn(CN)_6$ under conditions analogous to those of conditions B & C with ferricyanide. In both cases DHPs were obtained in 85% yield. Table 6 shows the linkage distributions.

Manganese Acetate Oxidations

Condition N:

A mixture of $Mn(OAc)_3$-$2H_2O$ (154 mg, 0.57 mmol) and acetic acid (15 ml) was added over a 15 m period to a solution of CA (93 mg, 0.52 mmol) in acetic acid (1 ml) under N_2. After 15 m of stirring, the pale tan solution was added to water (100 ml). No precipitation occurred until the colorless solution was neutralized with NaOH solution, at which time a pale pink flocculent precipitate formed. The solid was filtered off, washed with water and freeze-dried, yielding a pink solid (38 mg, 41% wt yield). The colorless filtrate was concentrated under vacuum (to 30 ml) and the resulting pale yellow turbid solution was extracted with ethyl acetate (3 x 10 ml). The extract was dried over $MgSO_4$ and evaporated under vacuum, leaving a pale yellow oil (43 mg, 46% wt yield). Acetylation of the two fractions and examination by ^1H NMR indicated that the oil was a mixture of dilignols and the solid was composed of higher oligolignols and a DHP. The linkage distributions, as determined by ^{13}C NMR, are shown in Table 7.

Condition O:

Equimolar amounts of CA and $Mn(OAc)_3 \cdot 2H_2O$ were ground together in a mortar for 10 m, quenched with water, and worked up as above. The main products were di- and trilignols, as indicated by the ^1H NMR spectrum. When the solid mixture was allowed to remain in the mortar overnight and then worked up, a DHP was obtained. The small scale of these reactions prevented detailed ^{13}C NMR analysis.

NMR spectroscopy

NMR spectra were obtained with a Bruker WM250 spectrometer controlled by an Aspect 2000A minicomputer and fitted with a 5 mm broad-band probe. Samples were dissolved in acetone-d_6, and TMS was used as internal reference. Typically, the ^{13}C (62.9 MHz) spectra were obtained with the standard Bruker Powgate microprogram. Quantitation of the side chain carbons in oligolignol and DHP preparations were performed as described in the text. Because of small sample quantities in most cases, it was not feasible to acquire quantitative spectra (inverse-gated). However, over the small chemical shift range that was quantified, it was found that there was no significant difference between results obtained with qualitative and quantitative spectra.

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