Chapter 11

Biomimetic Initiation of Lignol Dehydropolymerization with Metal Salts

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Dehydropolymerization of *p*-hydroxycinnamyl alcohols with metal salt oxidants can lead to dehydropolymerisates (DHPs) that more closely resemble native lignin than those prepared by conventional techniques. Intermediate dimers, trimers, and tetramers obtained by this technique have provided the building blocks that are necessary for precise characterization of the DHPs by ^{13}C NMR spectroscopy. Individual dilignols have been used for specific preparation of higher oligolignols with readily definable (*i.e.* interpretable) features. Guaiacyl DHPs prepared with metal salts exhibit, in certain cases, distributions of interunit linkages more representative of native lignin than those prepared by conventional enzymatic techniques.

The use of reliable models for complex lignin macromolecules are essential in many areas of lignin, wood, and plant research. Dehydropolymerisates of *p*-hydroxy cinnamyl alcohols, commonly referred to as 'DHPs', are currently the best models available. DHPs are prepared by either oxidative coupling of coniferyl, sinapyl, or *p*-coumaryl alcohols and their mixtures through enzymatic catalysis involving peroxidase and hydrogen peroxide (*1,2*).

There are many reasons for using DHPs rather than natural isolated lignins, such as a milled wood lignin (MWL). One is that the DHP structure is free of extraneous wood components such as extractives, tannins, proteins, etc. Also, it is very difficult to remove all of the carbohydrate material from isolated lignins, especially because a certain fraction of it is thought to be chemically bound to the lignin. Another significant advantage of DHPs is that they are relatively simple to label isotopically in specific positions by using appropriately labeled *p*-hydroxycinnamyl alcohols (*3-5*). The use of isotopically labeled DHPs is very important in the study of enzymatic delignification (pulping) and bleaching, and in microbial degradation studies (*6*). It is also possible to incorporate into DHPs minor structures (labeled or unlabeled) that are known to be present in natural lignins but are not formed from *p*-hydroxycinnamyl alcohols during dehydropolymerization. Experiments that utilize labeled DHPs supplement more difficult and time-consuming experiments involving the labeling of natural lignins by feeding labeled precursors to the plant (*7-11*).

DHP Types

DHPs can be formed from *p*-hydroxycinnamyl alcohols as illustrated in Figure 1. The most commonly produced DHP is that formed from coniferyl alcohol. The resulting guaiacyl- or G-DHP is generally used as a model for gymnosperm lignin. DHPs formed from a mixture of coniferyl and sinapyl alcohols or from all three alcohols are designated as guaiacyl-syringyl (GS) and guaiacyl-syringyl-*p*-hydroxyphenyl (GSH) DHPs, and are used as models for angiosperm and grass lignins, respectively. If pure *p*-coumaryl or sinapyl alcohols are used, DHPs which do not have any analog in Nature are obtained, but they are very useful in certain instances. One such example involves the sorting out of chemical shift assignments in NMR spectra associated with specific dimeric entities, which in natural lignin would be. difficult to find and characterize because of their relatively low abundance.

Comparison of Conventional DHPs with MWLs.

The key step in both natural lignification processes and conventional laboratory dehydropolymerizations is the enzyme-initiated generation of a phenoxy radical that engenders a complex variety of non-enzymatic processes which include radical coupling reactions, nucleophilic additions to quinone methide structures, rearrangements, side-chain oxidations and eliminations to generate the complicated lignin macromolecule (12). Some of the more common dimeric entities that are formed by radical coupling reactions are illustrated in Figure 2. According to Adler (*13*) these six linkage types account for about 80% of the total in a gymnosperm lignin. The predominant linkage is the β-*O*-4′, which accounts for about half of the total. There are about 10% each of β−5′ and 5-5′, and smaller amounts of β−1′, β−β′ and 4-*O*-5′.

Although there are claims in the early literature (*1*, *2*) that DHPs essentially duplicate natural lignins, they turn out to be rather poor models for actual lignin structure. This is especially true for guaiacyl DHPs. In typical G-DHPs the abundance of the β−5′ linkage is generally greater than or comparable to that of the β−*O*-4′ linkage, and the β−β′ linkages are much more abundant than in natural lignins. In addition, the presence of an appreciable quantity of α-*O*-4′ linkages in G-DHPs has been revealed by NMR spectroscopy.

The α-*O*-4′ linkage is not formed by radical coupling, but by the nucleophilic addition of a phenolic group to a quinone methide, as illustrated in Figure 3 (*1*). The characterization of this structural entity in DHPs depended heavily on the availability of NMR spectroscopic data from trilignols of this type (*14*).

Comparisons of the ^{13}C NMR spectra of MWLs with those of DHPs indicate that the latter are much simpler in structure and consist primarily of four linkage types: β−5′, β−β′, β−*O*-4′, and α−*O*-4′. The existence of other linkage types such as β−1′, 5-5′, and 4-*O*-5′ structures has been more difficult to substantiate with NMR spectroscopic techniques. This is primarily due to the lack of appropriate model compounds embodying these linkages and/or to their low abundance in both natural lignins and DHPs. Thioacidolysis studies have indicated their presence in small amounts in lignins and in even much smaller amounts in DHPs (*15*).

Comparison of the linkage distribution of a typical G-DHP with that of a pine MWL is shown in Table I. Clearly, the predominant linkage in the DHP is the β−5′ or phenyl coumaran linkage. Even in the best of the conventional preparations the abundance of the β−5′ linkage is comparable to that of the β−*O*-4′. The β−β′ linkage is also abnormally frequent in the DHP. However, perhaps the most serious discrepancy in the DHPs is a relatively large abundance of α−*O*-4′ linkages. This linkage appears to be the main branchpoint in G-DHPs in contrast with natural lignins where presumably the branchpoints occur primarily at 5-5′ linkages and also to a lesser extent at 4-*O*-5′ and β−1′ linkages.
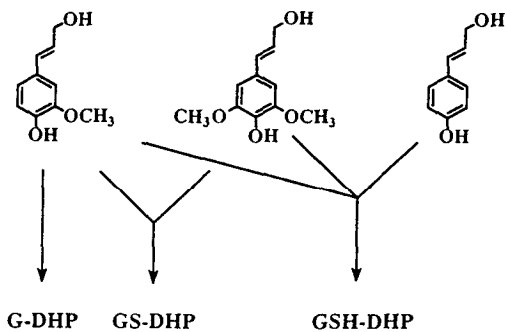
Figure 1. DHP types from coniferyl, sinapyl and coumaryl alcohols; G: guaiacyl; GS: guaiacyl-syringyl; GSH: guaiacyl-syringyl-*p*-hydroxyphenyl.
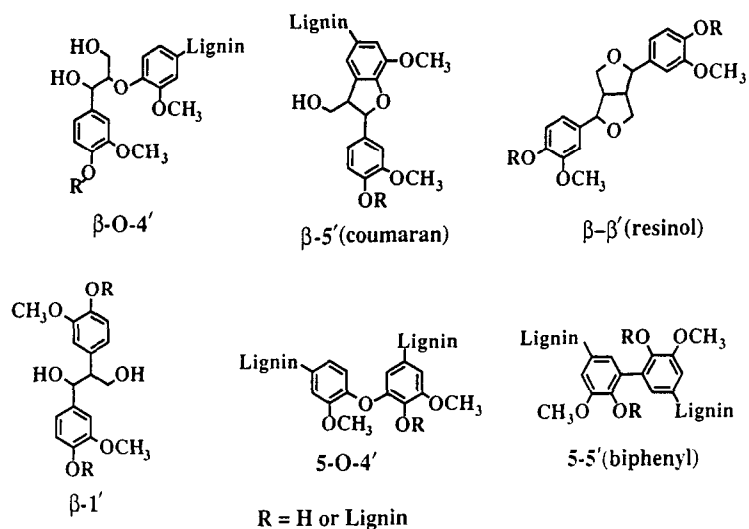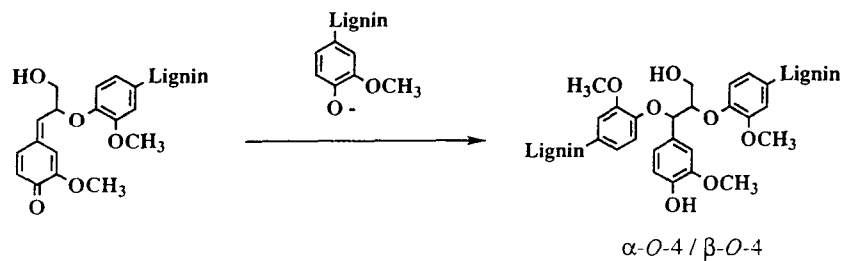

Figure 2. Common linkage types in lignin.

Figure 3. Formation of α–*O*-4′ linkages *via* quinone methides.

Table I. Comparison of Linkage Distributions in G-DHP and G-MWL

	Linkage (%)						
	β–O–4′	β–5′	β–β′	α–O–4′	5–5′	β–1′	4–O–5′
G-DHP	27	45	17	11	---	---	---
G-MWL	48	10	2	---	10	7	4

Another disadvantage of G-DHPs is that the content of coniferyl alcohol sidechains is enormous in comparison with a MWL where the unsaturated sidechain content is barely noticeable. This is illustrated in Figure 4 with both proton decoupled ^{13}C NMR spectra (all carbons) and DEPT spectra (CH's only) for a G-DHP and a pine MWL. The presence of the unsaturated sidechain in the G-DHP is indicated by the strong signal at about 135 ppm. In the corresponding spectrum of the MWL this signal is not apparent, not even in the DEPT spectrum which removes interfering quaternary carbon signals in this region.

Biomimetic Initiation of Dehydropolymerization.

The significant discrepancies between DHPs and natural lignins prompted an investigation of alternative methods of dehydropolymerization aimed toward improved fidelity in polymeric models for lignin. One promising method involves the use of metal salt oxidants (*16,17*). It was found that an approach using transition metal salts as one-electron oxidants provided a convenient biomimetic route to phenoxy radicals analogous to the enzymatic generation of phenoxy radicals in conventional techniques. Subsequent radical coupling and other reactions, eluded to above, then ultimately lead to oligolignols and DHPs. These DHPs will be termed 'biomimetic' to distinguish them from DHPs prepared by conventional enzymatic techniques. The biomimetic approach is far more flexible than the corresponding enzymatic technique in that the reaction conditions are not constrained within the limits required by the enzyme. With the non-enzymatic system it is easy to vary the reaction conditions over a very large range. For example, temperatures from ambient to 100°C have been used; solutions from totally aqueous to totally nonaqueous; and in aqueous systems, the entire pH range was covered. In fact, with some metal salts the technique even works in the solid state. The advantage of this flexibility is that the reaction can be induced to generate a wide variety of product mixtures that differ in both molecular weight and linkage distributions.

The Building Blocks. In order to characterize the biomimetic DHPs, an intensive effort was made to isolate the intermediate building blocks of the polymer. Dilignol, trilignol, and tetralignol entities were of interest, as these relatively simple structures could be precisely characterized by NMR and mass spectroscopy, and signals in the ^{13}C spectra could be unambiguously assigned by an assortment of modern NMR experiments. The chemical shift data from these components is necessary for subsequent characterization of the DHPs. Oligolignols that have been isolated to date from a variety of reactions with coniferyl and sinapyl alcohols are shown in Figure 5. The abbreviated nomenclature associated with each of the structures in Figure 5 was developed in order to simplify discussion, and is presented in Table II.
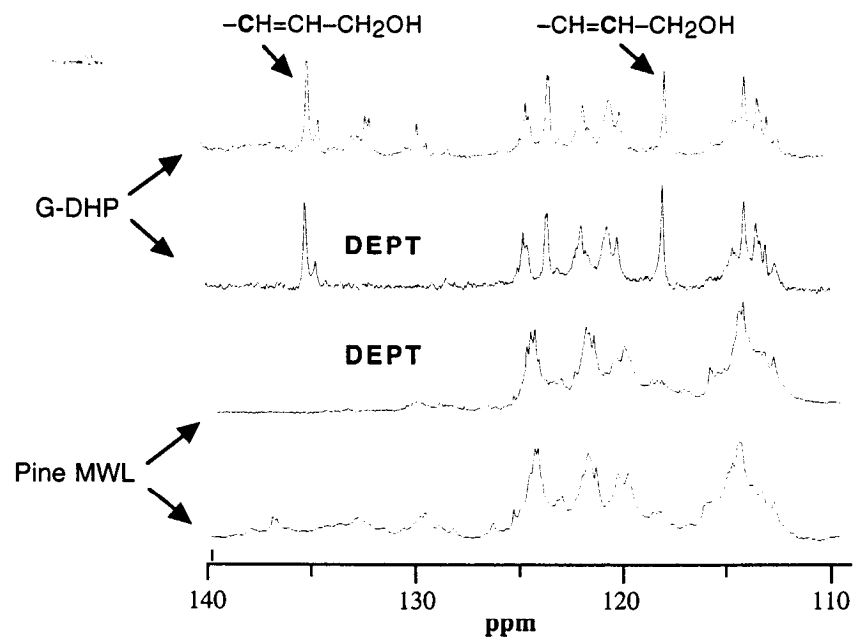
Figure 4. Proton decoupled and DEPT ^{13}C NMR spectra of a G-DHP and a pine MWL. [DEPT: distortionless enhancement polarization transfer].
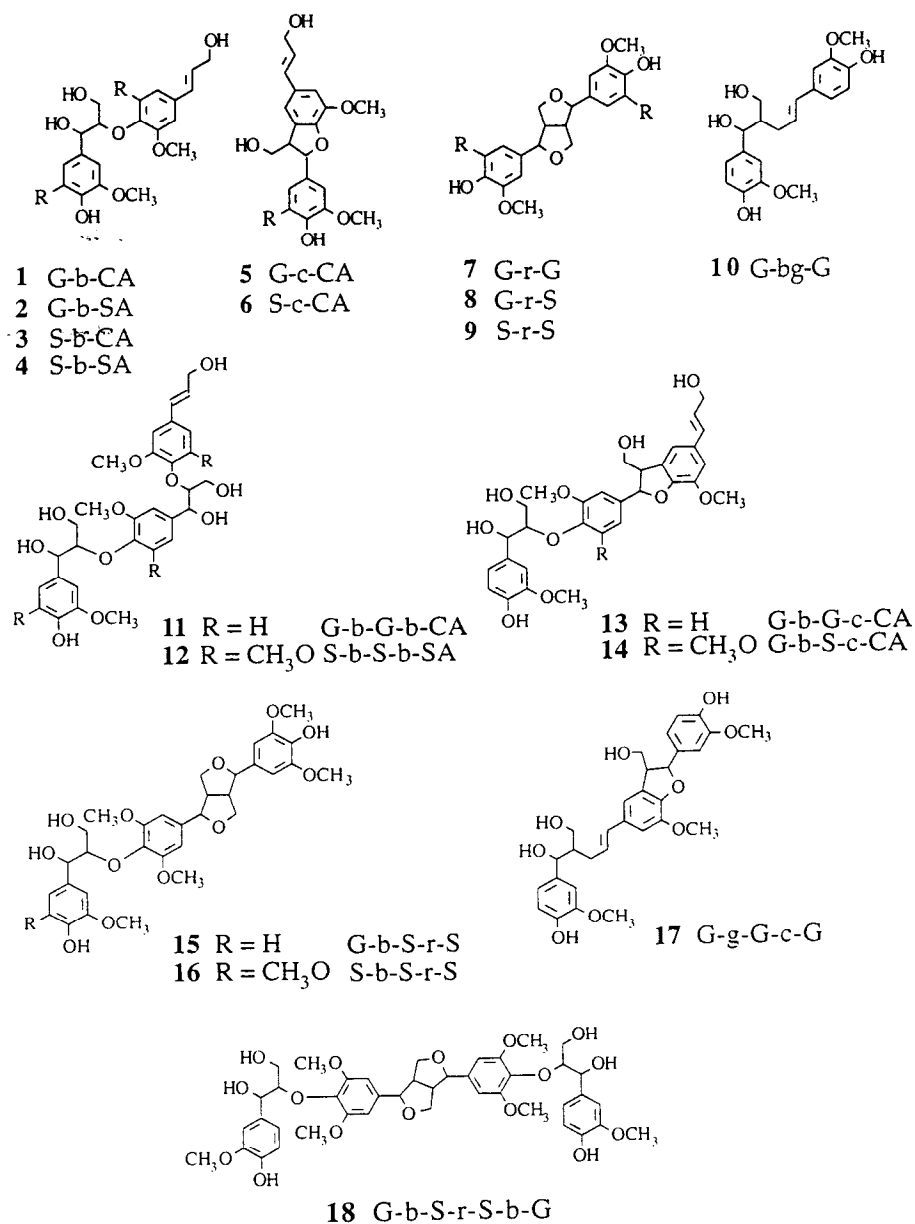
1 G-b-CA
2 G-b-SA
3 S-b-CA
4 S-b-SA

5 G-c-CA
6 S-c-CA

7 G-r-G
8 G-r-S
9 S-r-S

1 0 G-bg-G

11 R = H   G-b-G-b-CA
12 R = CH₃O S-b-S-b-SA

13 R = H   G-b-G-c-CA
14 R = CH₃O G-b-S-c-CA

15 R = H   G-b-S-r-S
16 R = CH₃O S-b-S-r-S

17 G-g-G-c-G

18 G-b-S-r-S-b-G

Figure 5. Oligolignols isolated from dehydropolymerization mixtures.
(In **1-9,** R = H for G and CA groups, and R = OCH₃ for S and SA groups.)

Table II. Terminology of Abbreviated Structural Representations

Entity	Abbreviation
guaiacyl ring	G
syringyl ring	S
α–O–4′ linkage	a
β–O–4′ linkage	b
β–5′ (phenylcoumaran)	c
β–γ′ linkage	bg
β–β′ (resinol)	r
coniferyl alcohol end unit	CA
sinapyl alcohol end unit	SA
erythro	*e*
threo	*t*

All of the possible dilignols containing guaiacyl and/or syringyl rings and with either a β–O-4′ β–5′, or b-b′ linkage have been isolated from biomimetic dehydropolymerization mixtures (**1-9** in Figure 5). Although these dilignols are valuable for chemical shift assignments in higher oligolignols, they are not particularly good models for lignin or DHPs because it is unlikely that the combination of the unsaturated side chain and the free phenolic moiety would exist on the same C9 unit in either polymer. The smallest oligolignol that can be reliably used as a model for lignin or DHP is a trilignol. However, of the 24 possible trilignols (G, S, or GS) that contain at least one b-O-4′ linkage plus a β–5′ or β–β′ or another β–O-4′ linkage, only six **(11**-**16** in Figure 5) have been isolated in pure form from dehydropolymerization mixtures. The trilignols are generally much more difficult to isolate and purify because of the number of possible structures, their isomeric complexity, and because the trilignol content in the reaction mixtures usually ranges between 5 and 15%, with the exception of those from some of the reactions in which SA is present. With SA or CA/SA mixtures, the β–β′ linkage is sometimes predominant and di- and trilignols containing this linkage are isolated in high yield. The facile formation of some structures of this type is in keeping with previous reports of their presence in plant extracts (*18-20*).

Metal and Media Effects. The flexibility of using metal salts as oxidants in dehydropolymerization is illustrated by noting some of the results obtained under a variety of reaction conditions with various metal salts. In an effort to determine some of the controlling factors in these interesting reactions, several different metal/medium combinations were investigated (16, 17). One interesting series is illustrated in Figure 6 with the hexacyano complexes of Mn(III), Fe(III), and Co(III) in borate and NaOH solutions. With the iron compound in borate media, the three dilignols were obtained in comparable amounts. It should be noted that the β–O-4′ dilignol was primarily obtained in the *erythro* form (90%). In NaOH solution, quinone methide reactions dominated after initial radical coupling so the major products were α–O-4′ linked structures, the smallest being a trilignol. With the cobalt complex, a quantitative yield of a single compound was obtained. It was identified as a novel β–γ′ linked dilignol, **10** (Figure 5). Signals from this entity were not observed in any MWL or DHP that was examined, so the reaction was not further investigated. However, there was a recent report in the literature by Yoshida and coworkers where the S-S analog of this compound was isolated from a mixture produced when sinapyl alcohol was dehydrogenatively oxidized in the presence of pectin (21). In NaOH solution, the cobalt complex was unreactive and only starting material was recovered.

With the manganese complex in borate, the β–O-4′ dilignol was identified along with an unknown dilignol that is presently being identified. In NaOH solution, both the β–O-4′ and β–5′ dilignols were obtained. An interesting finding is that, contrary to the predominately *erythro* form in the iron reaction, a 50/50 mixture of *e* and *t* diastereomers were obtained.

When an equal molar mixture of coniferyl and sinapyl alcohols was subjected to the dehydropolymerization conditions optimized for lower oligolignols, very different results were obtained for different metal/medium combinations (*17*). For example, Table III summarizes the varying distribution of dilignols obtained in three systems.

Table III. Product Distribution in CA/SA Dilignol Fractions[a].

Dilignol	Mn(OAc)$_3$[b]	K$_3$Mn(CN)$_6$[c]	Cu(OAc)$_2$[d]
1 (G-b-CA)	6	6	8
2 (G-b-SA)	11	nd[e]	2
3 (S-b-CA)	11	nd[e]	1
4 (S-b-SA)	19	nd[e]	2
5 (G-c-CA)	5	7	5
6 (S-c-CA)	2	2	4
7 (G-r-G)	nd[e]	nd[e]	nd[e]
8 (G-r-S)	2	4	7
9 (S-r-S)	1	11	2

[a]Values are wt% of total acetylated products from ethyl acetate soluble material; [b] in pyridine; [c] in 0.1 M NaOH; [d] in 0.05 M borate buffer (pH = 9.2); [e] nd, not detected.

With the Cu(OAc)$_2$ system, the predominant dilignol was *erythro* G-b-CA, with only small amounts of the other possible combinations. With hexacyanomanganate in NaOH solution, the dilignol content consisted almost exclusively of 50/50 *e/t* G-b-CA. With manganese acetate in pyridine, all four β–O-4′ dilignols were obtained in comparable amounts. In this experiment the G-b-CA was almost exclusively *erythro*.

In addition to having some control over linkage types and distribution, the molecular weight distribution may be controlled somewhat by choosing appropriate reaction conditions. This is illustrated in Table IV with the polymerization of CA with manganese and copper systems. For example, with the manganese

Table IV. Effect of Metal/Medium on Molecular Weight Distribution.

Metal salt/Media	Degree of Polymerization					Major linkages
	1	2	3	4	≥5	
Mn(OAc)$_3$/CH$_2$Cl$_2$/HOAc (fast addition)	2	78	6	6	5	β–O–4′ >> β–5′ >> β–β′
Mn(OAc)$_3$/CH$_2$Cl$_2$/HOAc (slow addition)	5	19	2	4	70	β–O–4′ >> β–5′ >> β–β′
Cu(OAc)$_2$/borate	5	55	12	1	10	β–O–4′ ≈ β–5′ ≈ β–β′

acetate/methylene chloride/acetic acid combination, when the reactants were quickly mixed together, 78% of the total product was dilignols. On the other hand, if the CA was slowly added to the oxidant over a period of 8 h, 70% of the total product was high molecular weight, and only 20% of the total were dilignols. In between these two extremes was the copper borate system in which 55% of the total were dilignols. However, with the copper borate system, the β−O-4′, β−5′, and β−β′ linkages were roughly comparable, whereas with the manganese system the β-O-4′ linkages predominated over β−5′ and β−β′ which were present in only trace amounts.

It should be noted that an approximate indication of molecular weight can be obtained from an ^{1}H NMR spectrum of the sample. If relatively sharp signals like those seen in the upper spectrum of Figure 7 are present, it can be concluded that the material-is perhaps composed mainly of di-, tri-, and tetralignols. This contrasts with the lower spectrum which is of a mixture containing predominantly polymeric material. Typically, with many of the metal systems, the crude product mixtures consist of material with molecular weights ranging from monomers to 20-mers, and they must be fractionated by preparative gel permeation chromatography.

Missing Building Blocks. In order to adequately elucidate the structures of the DHPs prepared by using metal salts, several additional tri- and tetralignols are needed. Some of these are undoubtedly present in the product mixtures already obtained, but their yields are too low or they could not be separated from numerous similar compounds. For example, trilignols that would be expected to be highly elusive in such complicated mixtures are those containing only β−O-4′ linkages. Considering all possible combinations of G and S rings, there are a total of 8 expected trilignols: G-b-G-b-CA, G-b-G-b-SA, G-b-S-b-CA, S-b-G-b-CA, G-b-S-b-SA, S-b-G-b-SA, S-b-S-b-CA, and S-b-S-b-SA. Of these components, only the pure guaiacyl **(11)** and the pure syringyl **(12)** trilignols (Figure 5) have been isolated.

Other missing building blocks are structures containing 5-5′, β−1′ and 4-O-5′ linkages. Some of these may not be overly important in elucidating the structures of many of the existing DHPs, since the latter are also thought to be lacking these linkages. However, as more improved DHPs are prepared that more closely resemble native lignin, these missing building blocks will become more important.

Tailored Syntheses of Oligolignols. Because of the difficulty of obtaining a sufficiently wide range of pure oligolignols from dehydropolymerization mixtures, it was necessary to consider modified approaches to obtain these vital components. As mentioned above, two of the main stumbling blocks are the difficulty of isolating β−O-4′ trilignols, because of the wide variety of possible trilignol structures, and the absence of certain linkages, such as 5-5′, β–1′, and 4-O-5′, in the mixtures. Both of these problems can conceivably be overcome by the dehydropolymerization of CA or SA in the presence of well characterized pure dilignols.

β−O-4 Trilignols. An initial attempt using this approach involved the reaction of CA with a 65/35 *e/t* mixture of G-b-CA in a $Mn(OAc)_3$ system (*22*). The trilignol fraction, which amounted to about 13% of the total, was composed mainly of G-b-G-b-CA. The complex pattern in the expanded β-carbon region of the ^{13}C spectrum in Figure 8 illustrates the stereochemical complexity of the trilignol. With a trilignol of this type there are 4 chiral centers giving rise to 16 optical isomers that include 8 distinct chemical isomers. Chemical shift assignments for the individual isomers in a case like this is generally not feasible because of the small differences involved. However, for the purposes of correlation with analogous lignin or DHP entities, these stereochemical considerations were somewhat redundant in that the small chemical shift differences between the various stereochemical configurations in an individual trilignol were generally not detected in the corresponding polymeric components because of much increased line widths in the spectra of the latter. It is only a problem when it comes to assigning precise chemical shifts for lower molecular weight components when the signals are still relatively narrow.
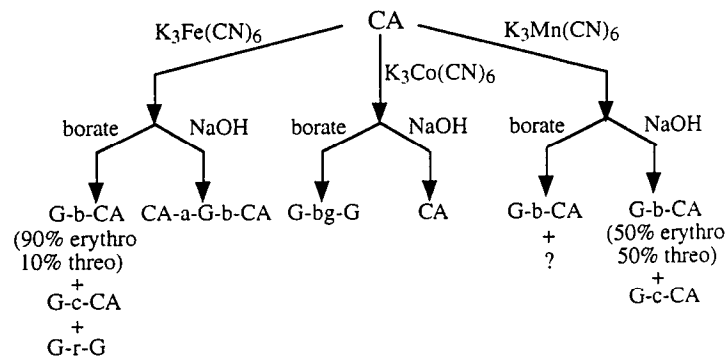
Figure 6. Dehydropolymerization of coniferyl alcohol with hexacyanometalates.
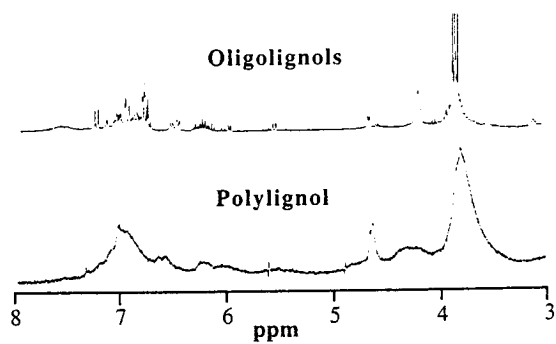

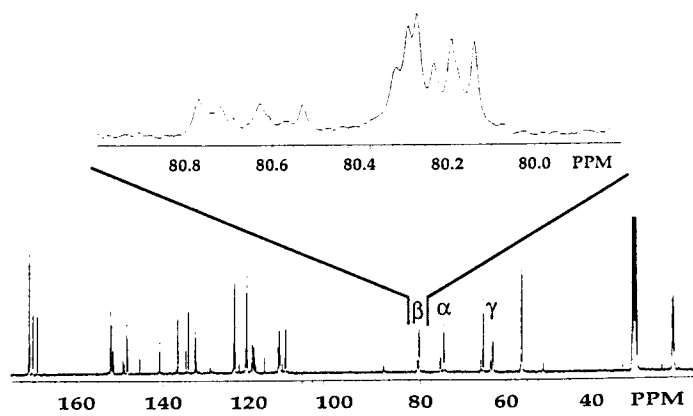Figure 7. ^{1}H NMR spectra of oligolignols and polylignol (DHP).

Figure 8. Isomers of trilignol G-b-G-b-CA.

If a stereochemically pure dilignol is used in the above experiment, the number of distinguishable isomers among the products is cut in half. Also, by imposing such a restriction on one of the linkages and two of the rings, a much simpler reaction mixture is obtained when we limit the self-coupling reactions of the monolignol. The use of dilignols also allows a greater flexibility in choice of structures for the terminal side chain of the resulting trilignol. A study of chemical shift substituent effects indicates that the terminal side chain typically has little effect on the chemical shifts of the internal C9 unit (*23*).

β–1/β–*O*-4 Trilignols. The coupling of a monolignol to a dilignol as a means of introducing a β–1′ linkage into a trilignol is illustrated in the contemplated scheme in Figure 9. In this example, the CA could conceivably add to either end of the dilignol to give two possible structures. A reaction such as this one would be expected to be quite complicated in that eight isomers could result from each coupling mode. However, the reaction could be simplified by using an isomerically pure dilignol. Also, the coupling reaction may possibly be induced to conform to only one of the pathways if the depicted precursor to G-bl-G (deoxyvanilloin) is used. Following the formation of the trilignol, formaldehyde addition and reduction (preferably by a stereoselective method) would afford the desired trilignol. This strategy is presently under investigation.

5–5/β–*O*-4 Trilignols. Another example of incorporating a linkage into a trilignol that has been difficult to obtain otherwise is illustrated in Figure 10 by the reaction of CA with the 5-5' linked dilignol **21.** Interestingly, the expected trilignol 22 was not obtained; instead, the cyclic structure **23** was obtained which is analogous to one recently reported by Brunow and coworkers (*24*). The 5-5′ linkage has been particularly troublesome to characterize partly because of its rarity in conventionally prepared DHPs. Some results of work not yet published indicate an upper of 1 or 2% for the frequency of 5-5′ linkages in a G-DHP prepared by the so-called 'Zutropf' method. This is consistent with the thioacidolysis results obtained by Lapierre and coworkers who reported only a trace of 5-5′ linkages in this type of DHP. Other problems in the characterization of the 5-5′ entity is that there is extensive overlap of most of the pertinent signals with others, and that suitable etherified or partly etherified models such as **21** have not been available. It should be noted here that 3,4-dimethoxy (veratryl) derivatives are very poor models for P-ether linkages with respect to the observed ^{13}C NMR chemical shifts (*23*).

Polylignols (Biomimetic DHPs). Initial attempts to prepare DHPs with metal salts resulted in a variety of novel products (16). Similar to conventionally prepared G-DHPs, most of them were composed mainly of the four linkage types, β−*O*-4′, β−5′, β−β′, and α−*O*-4′. Relative contributions of these linkages in selected biomimetic G-DHPs are compared with a conventional G-DHP and a pine MWL in Table V. The wide range of results obtained with the biomimetic approach again attests to its inherent flexibility. With all four biomimetic DHPs, the predominant linkage is β−*O*-4′, in contrast to the predominance of β−5′ in the conventional DHP. G-DHP-1, obtained from a solid state reaction, contained a very high content of α-O-4′ linkages. In the biomimetic systems, in aqueous solution, the α−*O*-4′ content correlates somewhat with the pH. For example, G-DHP-2 is obtained with ferricyanide at pH 9 and the α−*O*-4′ content is 8%. In contrast, ferricyanide in NaOH solution (not shown in table) yields products with much higher α−*O*-4′ contents, and some do not contain any un-etherified benzylic carbons (*16*). It is thought that the formation of DHPs in the hexacyanomanganate/NaOH system also proceeds through α−*O*-4′ linked intermediates. However, as seen from the low a-*O*-4′ content in G-DHP-3, these linkages are cleaved during workup. This contention is supported by the 50/50 *e/t* character (expected ratio upon alkaline hydrolysis of α−*O*-4′ entities) of the β−*O*-4′ linkages in G-DHP-3, in contrast to a more typical 90/10 ratio in DHPs obtained at pH 9 or less.
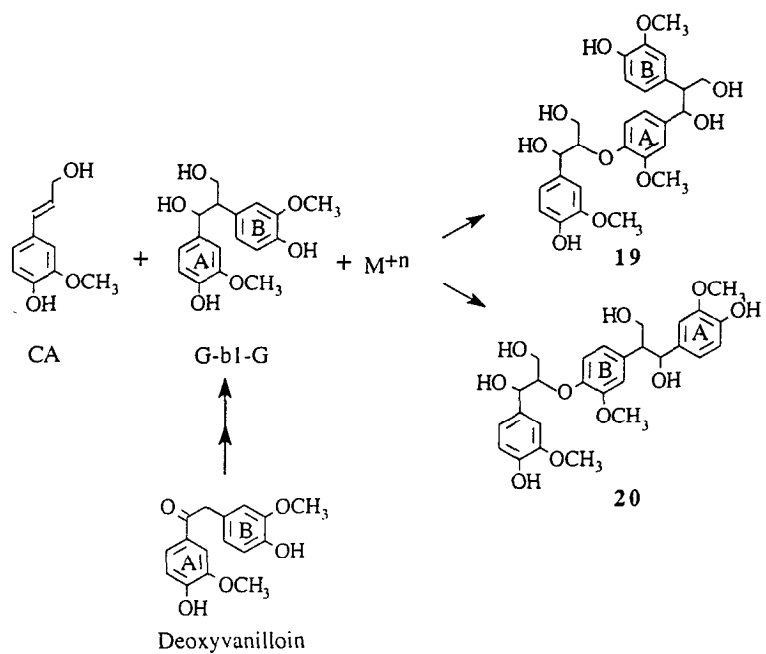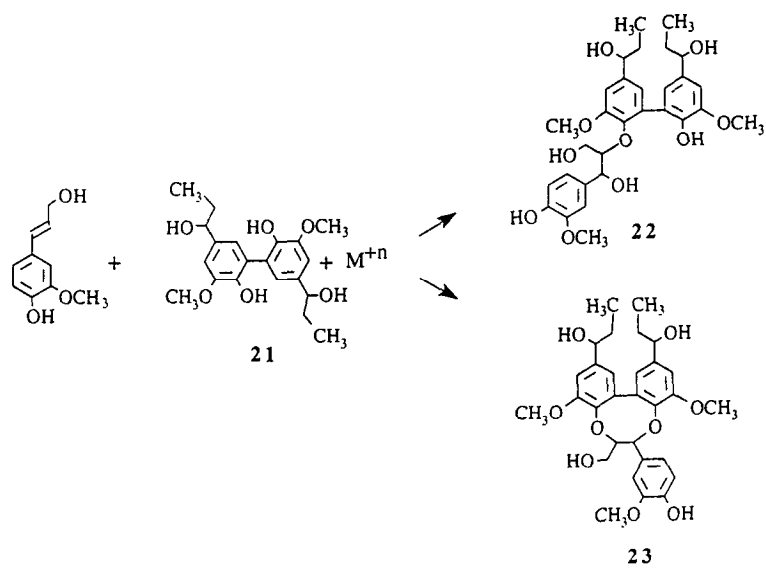
Figure 9. Formation of a β–1/β–O-4 trilignol.

Figure 10. Formation of a 5–5/β–O-4 trilignol.

Table V. Comparison of Linkage Distributions in Selected DHPs and a MWL.

Substrate	Metal salt	Medium	Linkage			
			$\beta-O\text{-}4$[a]	$\alpha-O\text{-}4'$	$\beta-5'$	$\beta-\beta'$
Pine MWL	—	—	48	nd[b]	10	2
conventional G-DHP	—	H_2O/Peroxidase/H_2O_2	27	11	45	17
biomimetic G-DHP-1	$K_3Fe(CN)_6$	K_2CO_3, solid state	45	22	15	18
biomimetic G-DHP-2	$K_3Fe(CN)_6$	Borate buffer, pH 9	37	8	33	22
biomimetic G-DHP-3	$K_3Mn(CN)_6$	NaOH solution	42	3	29	25
biomimetic G-DHP-4	$Mn(OAc)_3$	Acetic acid	75	nd[b]	23	2

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

Of the biomimetic DHPs, G-DHP-4 is the only one of the four in Table V that has realistic levels of $\beta-5'$ and $\beta-\beta'$ linkages (as compared to the MWL). The very high content of $\beta-O\text{-}4'$ in G-DHP-4 reflects the relative simplicity of DHPs in contrast to the MWL in which the four linkages in question only represent 60% of the total. By introducing other linkages such as 5-5', $\beta-1'$, and 4-O-5' into biomimetic DHPs of this type, it is expected that a closer resemblance to native lignins will be obtained.

Partial ^{13}C NMR spectra of the pine MWL, the conventional G-DHP, and the biomimetic DHP with the highest $\beta-O\text{-}4'$ content (G-DHP-4) are compared in Figure 11. Pertinent differences between the three materials not apparent from Table V are found in the content of unsaturated side chains and the benzylic hydroxyl frequency as reflected by the corresponding acetoxy carbonyl in the acetylated material. The α–carbon of CA sidechains is present as a very strong signal at about 134 ppm in the DHPs. The benzylic acetoxy carbonyl is the middle signal in the inset expansion at about 170 ppm. Clearly, the conventional DHP has a greater content of unsaturated side chains and a lower content of benzylic alcohol groups than does the biomimetic DHP. This difference can be largely attributed to the very high contents of $\beta-5'$ and $\beta-\beta'$ linkages in the conventional DHP, as reflected in the α–carbon signals of the corresponding C9 units between 86 and 88 ppm. More complete characterization and ^{13}C NMR signal assignments of selected biomimetic DHPs is presently in progress.

Conclusions

Dehydropolymerization of *p*-hydroxycinnamyl alcohols with metal salt oxidants results in the formation of a variety of oligolignols, which are valuable model compounds for the ^{13}C NMR characterization of DHPs and lignins. Novel guaiacyl DHPs can be obtained by this biomimetic approach that mimic natural lignin much better than those prepared by conventional techniques. A combination of the biomimetic with conventional syntheses allows introduction of rare linkages into oligolignols and will ultimately result in the capability of tailoring DHPs to certain specifications.
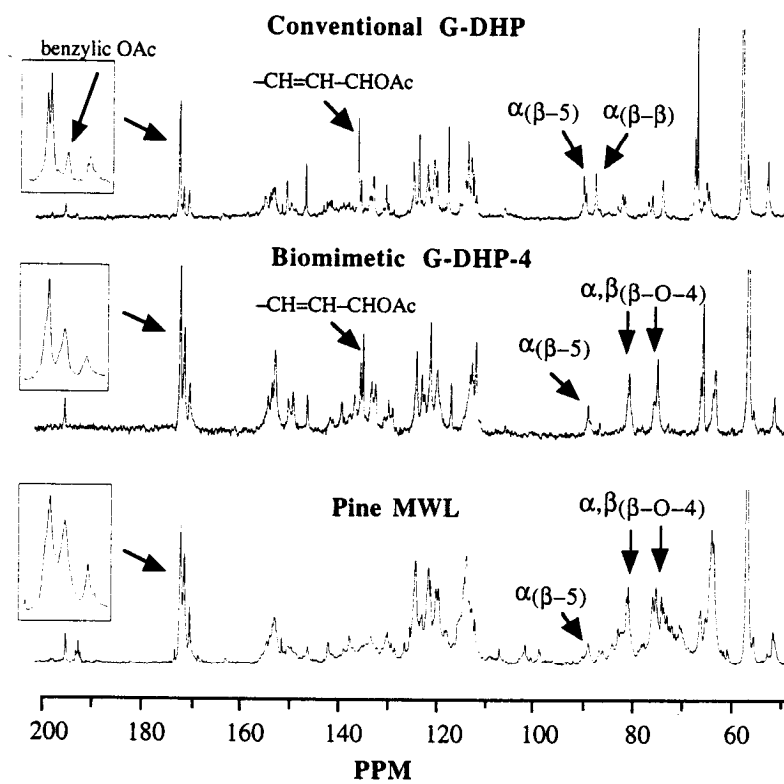
Acknowledgments

Figure 11. Partial ^{13}C NMR spectra of conventional G-DHP, biomimetic G-DHP, and pine MWL.

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