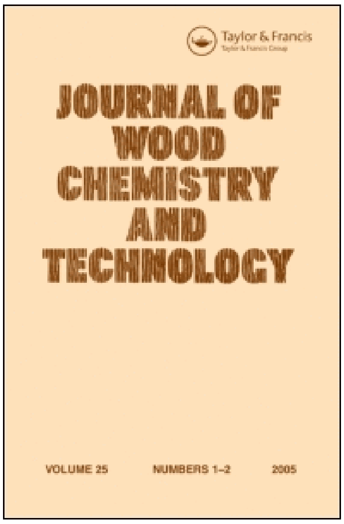

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Reactions of Metal Ion Complexes with Lignin Model Compounds Part I. Co(TSPP) as a Single Electron Transfer Catalyst and Implications for the Mechanism of AQ Pulping

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REACTIONS OF METAL ION COMPLEXES WITH LIGNIN MODEL COMPOUNDS, PART I. Co(TSPP) AS A SINGLE ELECTRON TRANSFER CATALYST AND IMPLICATIONS FOR THE MECHANISM OF AQ PULPING.

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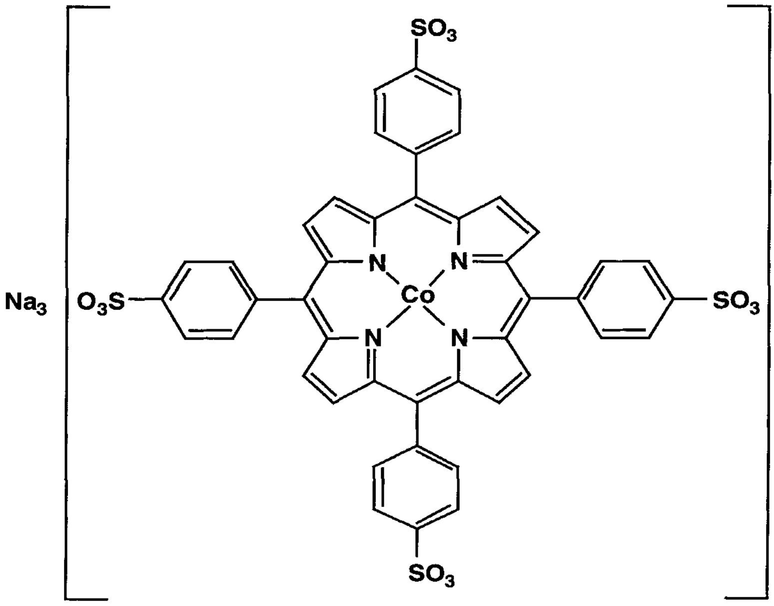
ABSTRACT

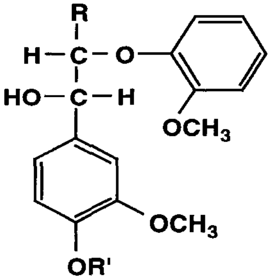
Cleavage of the β-aryl ether bonds of the lignin model compounds guaiacylglycol β-guaiacyl ether (**1**) and guaiacylglycerol β-guaiacyl ether (**11**) to form guaiacol was found to be catalyzed by the water soluble porphyrin complex trisodium meso-tetra-4-sulfonatophenylporphinecobalt(III), (Co(TSPP)). The resulting product distributions were remarkably similar to those obtained for the anthraquinone (AQ) catalyzed reactions under the same conditions. Studies of the reactions of Co(TSPP) with proposed intermediate compounds indicate that the major route to guaiacol formation involves reaction of the reduced catalyst, Co^{II}(TSPP), with the quinone methides **9** and **13** which are derived from the phenolic model compounds **1** and **11** respectively. It is proposed that the mechanisms of these reactions involve single electron transfer to the quinone methide as the first step. The implications of this proposal for the AQ catalyzed reactions of **1** are discussed.

INTRODUCTION

The discovery that anthraquinone (AQ) catalyzes pulping reactions has stimulated research in the area of pulping catalysts.[1] We have noted previously



Trisodium <u>meso</u> -tetra-4-sulfonatophenylporphinecobalt(III) (Co(TSPP))



R=H, R'=H;	**guaiacylglycol β-guaiacyl ether (1)**
R=H, $R'=CH_3$;	**veratrylglycol β-guaiacyl ether (10)**
$R=CH_2OH$, R'=H;	**guaiacylglycerol β-guaiacyl ether (11)**

FIGURE 1. The catalyst Co(TSPP) and the lignin model compounds **1**, **10** and **11**

that water soluble metalloporphyrins and metallophthalocyanines display many of the features of AQ that are thought to be essential for its catalytic activity, i.e. stability and solubility in sodium hydroxide solution at high temperatures, and the ability to be reduced by carbohydrates.[2,3,4] Our initial investigations have identified that the complexes trisodium meso-tetra-4 sulfonatophenylporphinecobalt(III) (Co(TSPP)) and iron trisodium tetra-4-sulfonatophenylphthalocyanineiron (Fe(TSPc)) are very active catalysts for the cleavage of the β-aryl ether bond in lignin model compounds, under both soda and kraft conditions and in the absence of oxygen.

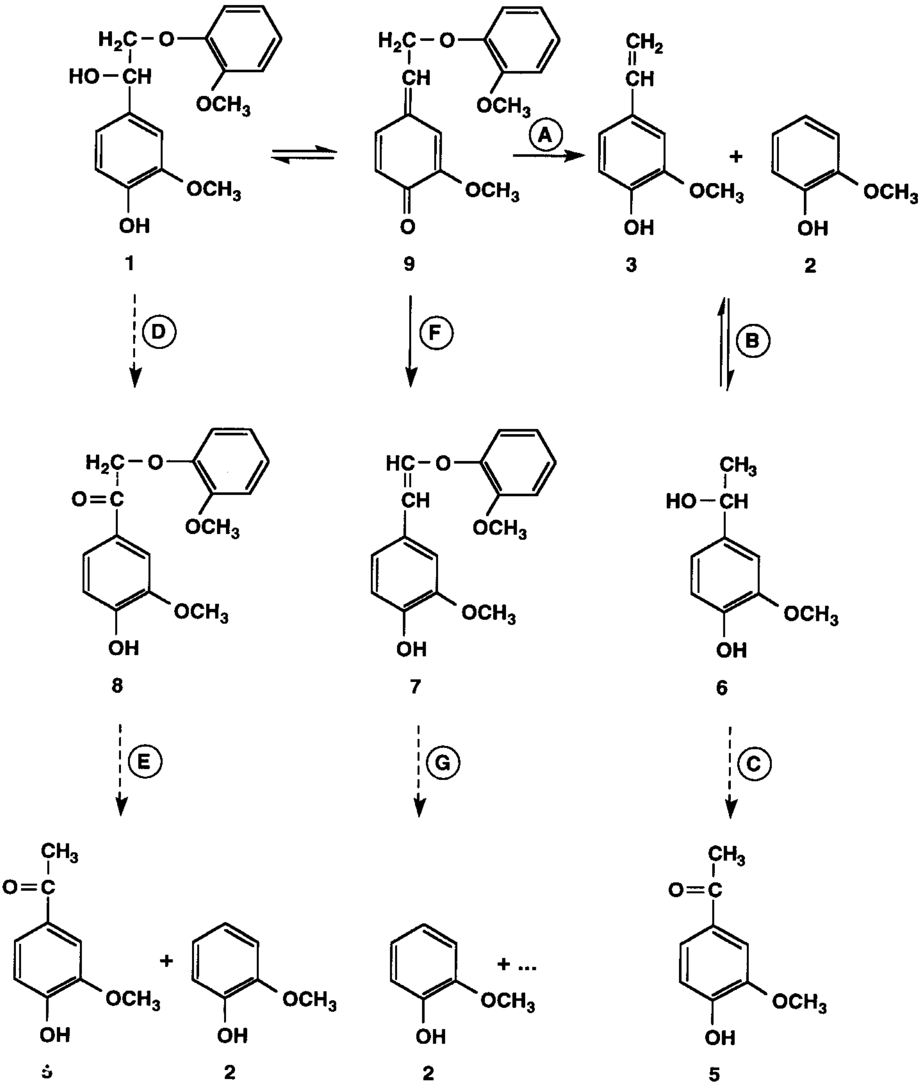
In this and the two following papers we report details of our studies which provide information concerning the mechanisms of these catalytic reactions, and also describe our studies with trisodium meso-tetra-4-sulfonatophenylporphinerhodium (Rh(TSPP)), which we have recently discovered is also a very active catalyst for β-aryl ether cleavage in lignin model compounds. Although the product distributions formed on reaction of guaiacylglycol β-guaiacyl ether (**1**) with each of these catalysts are very different, the results can be rationalized in terms of a common reaction scheme (Scheme 1). This paper deals with our preliminary studies of the mechanism of the Co(TSPP) catalyzed reactions.

RESULTS AND DISCUSSION

Reactions Of The β–Ether Lignin Model Compound **1**.

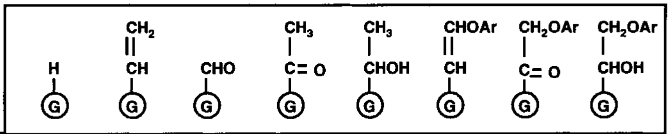
Typical model pulping reactions were carried out as follows. The lignin model compound, the catalyst, and glucose (when added) in mole ratios of 1.0 : 0.1 : 2.15, were placed in 1M sodium hydroxide solution, sealed in a glass tube under nitrogen and heated in an oil bath in the dark at 135°C for two hours. The products were analyzed quantitatively by gas liquid chromatography (see experimental section for details).

The product distributions obtained for the Co(TSPP) catalyzed reactions of the lignin model compound **1** are summarized in Table 1. Values obtained for

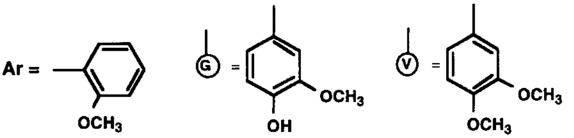


SCHEME 1. Rationalization of product distribution obtained from reaction of **1** with Co(TSPP)

TABLE 1. Total Reaction Component Analysis for **1**[a]



Catalyst	%**2**	%**3**	%**4**	%**5**	%**6**	%**7**	%**8**	%**1**
Control	23		3			37		40
Control/Gl	33	4			1	29		32
AQ	30	9	4	1	2	16		10
AQ/Gl	65	18	1	2	5	2		17
Co(TSPP)	44	10	5	5	2	21	2	28
Co(TSPP)/Gl	80	22	3	8	18	8		10



Gl = glucose, **AQ** = anthraquinone

[a] Conditions: 135°C, N_2, 1 M NaOH, 2hr; control = 1 M NaOH solution alone; mole ratios, model compound : catalyst : glucose = 1 : 0.1 : 2.15

the AQ catalyzed reactions are also given for comparison. Striking features of Table 1 are the large amount of guaiacol (**2**) formed when Co(TSPP)/glucose is the catalyst and the similarity in the overall product distribution for the Co(TSPP) and AQ catalyzed reactions. The products obtained from these reactions can be rationalized in terms of the overall reaction pathways depicted in Scheme 1.

Our previous studies have shown that significant amounts of guaiacol (**2**) are only produced at temperatures greater than ca. 100°C in the Co(TSPP) catalyzed reactions of **1**.[5] In addition, only small amounts of guaiacol (**2**) are formed in the reactions of the methylated lignin model compound **10** (see Table

3). This strongly suggests that the major reaction pathway leading to guaiacol (**2**) formation proceeds via the quinone methide **9**.

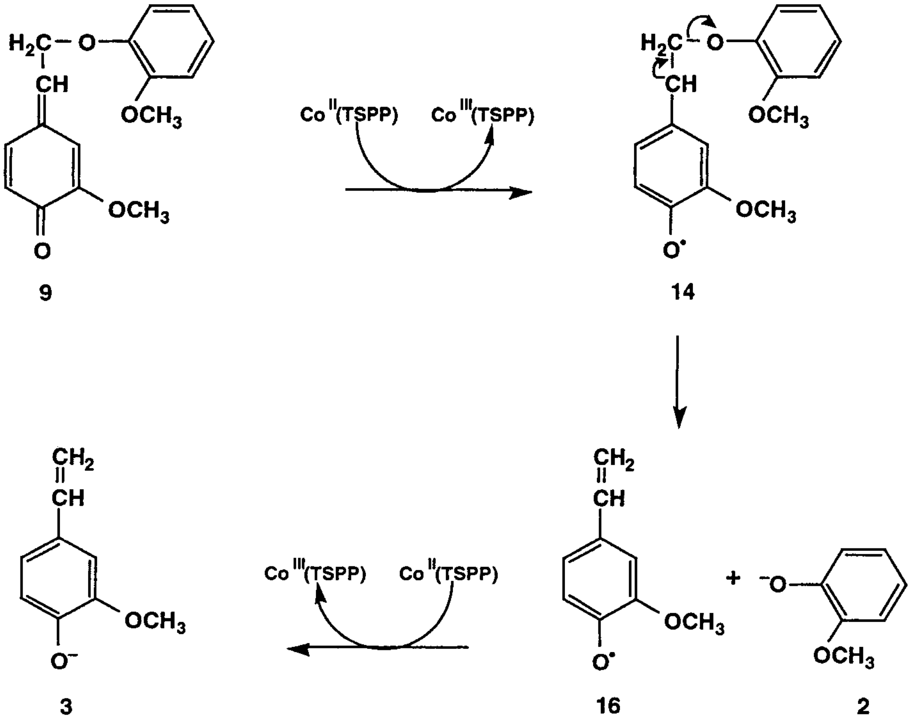
The large increase in guaiacol (**2**) formation observed for the Co(TSPP)/ glucose catalyzed reaction of **1** compared to the reaction catalyzed by Co(TSPP) alone suggests that a reduced form of the catalyst is active in the β-aryl ether cleavage reaction. It was found that Co^{III}(TSPP) is rapidly and quantitatively reduced to Co^{II}(TSPP) by glucose at 135°C in 1 M sodium hydroxide solution. The reduction can be conveniently monitored by UV-vis spectroscopy.[6] No evidence was obtained for further reduction to Co^{I}(TSPP) under these conditions. It has been reported that Co^{I}(TSPP) can be formed as a short lived species in water by reduction of Co^{II}(TSPP) using pulse radiolysis.[7] However, Co^{I}(TSPP) was found to be a very strong reductant which decomposes by rapidly reducing water. It is therefore very unlikely that this oxidation state plays an important role in the catalytic reactions described here.

The major route to guaiacol (**2**) formation for this catalyst therefore appears to involve the reaction of Co^{II}(TSPP) with the quinone methide **9**. To test this, an aqueous solution of Co^{II}(TSPP) was generated by reducing Co^{III}(TSPP) with zinc amalgam. This was then added to a dichloromethane solution containing a stoichiometric quantity of the quinone methide **9**, and the two phase mixture stirred at room temperature in the dark for one hour. Subsequent analysis of the organic phase revealed that the major products were guaiacol (**2**) (21%) and vinyl guaiacol (**3**) (5%). Control experiments in which **9** was reacted with excess zinc amalgam alone gave only guaiacol (**2**) (2%) and β-(2'-methoxyphenoxy)-4-hydroxy-3-methoxystyrene (**7**) (1%). Reaction with a stoichiometric amount of Co^{III}(TSPP) alone gave guaiacol (**2**) (2%) and **7** (4%). The facile formation of guaiacol (**2**) and vinyl guaiacol (**3**) from Co^{II}(TSPP) and the quinone methide **9** under these mild conditions strongly supports the proposal that pathway A in Scheme 1 is indeed a major route for guaiacol (**2**) and vinyl guaiacol (**3**) formation in the reactions of **1** at 135°C.

The mechanism for the reaction between Co^{II}(TSPP) and the quinone methide **9** can be discussed in terms of the two main mechanisms that have been proposed for the reaction of anthrahydroquinone (AHQ) with this quinone methide. These mechanisms involve either (i) adduct formation with the quinone methide **9** followed by heterolytic bond cleavage and overall transfer of two electrons from the catalyst,[8,9] or (ii) single electron transfer from the catalyst to the quinone methide **9** followed by homolytic cleavage of the β-aryl ether bond and then further single electron transfer from the reduced catalyst.[10] If Co^{II}(TSPP) reacted via mechanism (i), transfer of the two electrons on breakdown of the corresponding adduct would yield the oxidized form of the catalyst, Co^{IV}(TSPP) (or equivalent). It has been reported that Co^{III}(TSPP) can be oxidized electrochemically in aqueous solution at +1.06 V (vs NHE). The electron is removed from the porphyrin ring rather than the metal and the product formed is the porphyrin radical cation complex, $Co^{III}(TSPP^{+\cdot})$.[11] Although the intermediacy of this species in the catalytic cycle cannot be completely ruled out, it is very unlikely that it is formed in view of the weak oxidizing power of the quinone methide **9.**[12]

This strongly suggests that Co^{II}(TSPP) and Co^{III}(TSPP) are the only oxidation states involved and that the mechanism of the reaction with the quinone methide must therefore involve separate, single electron transfer steps. A plausible mechanism involving single electron transfer is depicted in Scheme 2. Following transfer of the first electron, the resulting organic radical **14** breaks down to yield guaiacol (**2**) and the vinyl guaiacol radical (**16**). Reduction of the latter by a further Co^{II}(TSPP) molecule then produces vinyl guaiacol (**3**).

An alternative breakdown mode of **14** to give vinyl guaiacol (**3**) and the guaiacol radical is also possible, and would lead to the same products after further reduction by Co^{II}(TSPP). If vinyl guaiacol radicals were formed in this reaction some dimerization might have been expected. However, high molecular weight compounds of this type were beyond the detection limits of the glc method of analysis used. Thus, no clear information concerning the formation of species such as this was obtained. It is noteworthy, however, that the overall mass of the products detected for many of the reactions was less than that of the starting lignin model compound. This is consistent with the possibility that higher molecular weight fragments were formed, but remained undetected.



Overall reaction:

$$(9) + 2\ \mathrm{Co^{II}\ (TSPP)} \xrightarrow{+2H^+} 2\ \mathrm{Co^{III}\ (TSPP)} + (2) + (3)$$

SCHEME 2. Proposed mechanism for reaction of Co^{II}(TSPP) with quinone methide **9**.

In a series of recent papers,[10,12,13] Dimmel *et al.* have reported evidence that suggests the reaction of AHQ with the lignin model compound **1** also proceeds via single electron transfer to the quinone methide **9**, rather than by direct adduct formation followed by heterolytic bond cleavage with overall transfer of two electrons to **9**.[8,9] The mechanism in Scheme 2 is essentially the same as that already proposed by Dimmel for the reaction involving AHQ.[10] The close similarity in the product distributions for both the Co(TSPP) and AQ catalyzed reactions of **1** is supportive of a common mechanism for these two catalysts, viz. one involving single electron transfer steps.

Reactions Of Proposed Intermediate Compounds

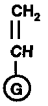
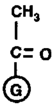
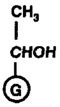
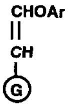
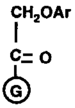
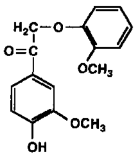
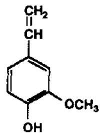
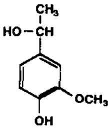
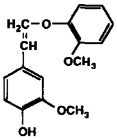
An attempt was made to determine the relative importance of each of the pathways A-G shown in Scheme 1 for the cobalt catalyzed reactions. To this end compounds **3**, **6**, **7**, and **8** were each reacted with Co(TSPP) (10%) and the products analyzed. The results are presented in Table 2.

The α-carbonyl compound **8** reacted to give guaiacol (**2**) and acetovanillone (**5**) as the only detected products. This reaction was particularly efficient in the presence of glucose (Table 2). However, inspection of the product distribution in Table 1 shows very little acetovanillone (**5**) was formed in the Co(TSPP)/glucose catalyzed reactions of **1**. Therefore pathways D and E in Scheme 1 were of minor importance here. A small amount of the α-carbonyl compound **8** (2%) was formed in the absence of the reducing glucose, indicating Co^{III}(TSPP) oxidized **1**, but only to a very minor extent. (The oxidation reactions of **1** are discussed in Part II of this series).

Significant quantities of the vinyl ether **7** were recovered from the reaction of **7** with Co(TSPP), either with or without glucose present (Table 2). Thus pathway G (Scheme 1) is also relatively unimportant here. The small amount of the vinyl ether **7** (8%) formed on reaction of **1** with Co(TSPP)/glucose indicates that in this case pathway A successfully competes with pathway F. This latter reaction is well documented for the quinone methide **9** in alkaline solution.[14] In the absence of glucose, the catalyst was largely in the Co^{III}(TSPP) form and thus could not react with the quinone methide **9** via pathway A. Therefore the vinyl ether **7** accumulated (21%) via pathway F and correspondingly smaller amounts of guaiacol (**2**) (44%) and vinyl guaiacol (**3**) (10%) were formed via pathway A. (Table 1).

Apocynol (**6**) is known to equilibrate with vinyl guaiacol (**3**) in hot alkaline solution,[8] and significant quantities of **3** were formed in both the control and

TABLE 2. Products from Proposed Intermediate Compounds[a]

								
	Catalyst	%**2**	%**3**	%**4**	%**5**	%**6**	%**7**	%**8**
 8	Control	9						89
	Control/Gl	11			5			87
	Co(TSPP)	24			9			70
	Co(TSPP)/Gl	67			61			21
 3	Control		22			12		
	Control/Gl		23		10			
	Co(TSPP)		25		3	12		
	Co(TSPP)/Gl		22		10			
 6	Control		29			10		
	Control/Gl		24			12		
	Co(TSPP)		28		17	15		
	Co(TSPP)/Gl		25		2	13		
 7	Control	9					65	
	Control/Gl	7					31	
	Co(TSPP)	13	1				42	
	Co(TSPP)/Gl	16	5			1	41	

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

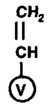
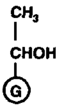
Co(TSPP) catalyzed reactions of apocynol (**6**) (Table 2). The only other product detected was acetovanillone (**5**). Larger amounts (17%) were obtained in the Co(TSPP) catalyzed reaction in which glucose was absent. In this case the catalyst was predominantly in the oxidized form Co^{III}(TSPP) and hence capable of oxidizing **6** to **5**. However, the product distribution for the Co(TSPP) catalyzed reactions of **1** (Table 1) shows that overall very little acetovanillone (**5**) was formed, regardless of whether glucose was present or not. Pathway C (Scheme 1) is therefore unimportant for this catalyst.

Vinyl guaiacol is relatively unstable in alkaline solution at high temperatures and this is reflected in the small quantities of low molecular weight products obtained from the reactions of this compound (Table 2). Apocynol (**6**) (12%) was isolated from both the control and the Co(TSPP) (glucose free) reactions. In addition, some acetovanillone (**5**) (3%) was detected in the Co(TSPP) reaction and this was probably formed by partial oxidation of (**6**) by Co^{III}(TSPP) (see above). Acetovanillone (**5**) (10%) was formed as the only product in both the control/glucose and the Co(TSPP)/glucose reactions. The formation of **5** probably involved direct reaction of vinylguaiacol (**3**) with glucose in both cases. This same reaction could well be responsible for much of the acetovanillone (**5**) (8%) formed on reaction of **1** with Co(TSPP)/glucose (Table 1).

Reaction Of Co(TSPP) With The Non-phenolic β-Ether Lignin Model Compound **10**.

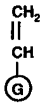
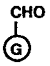
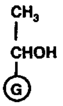
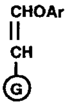
The products formed on reaction of the non-phenolic lignin model compound veratrylglycol β-guaiacyl ether (**10**) with the Co(TSPP) catalyst are presented in Table 3. The products formed when AQ was the catalyst are also included for comparison. The smaller amount of guaiacol (**2**) produced compared with the phenolic analogue **1** is consistent with the quinone methide **9** being an important intermediate in the reactions of **1**. Other features of Table 3 worthy of note are the close similarity in the product ratios for both the AQ/glucose and Co(TSPP)/glucose catalyzed reactions and the virtual absence of demethylated products. In this manner the AQ and Co(TSPP) catalysts behave very differently

TABLE 3. Products from the Non-phenolic Model Compound **10**[a]

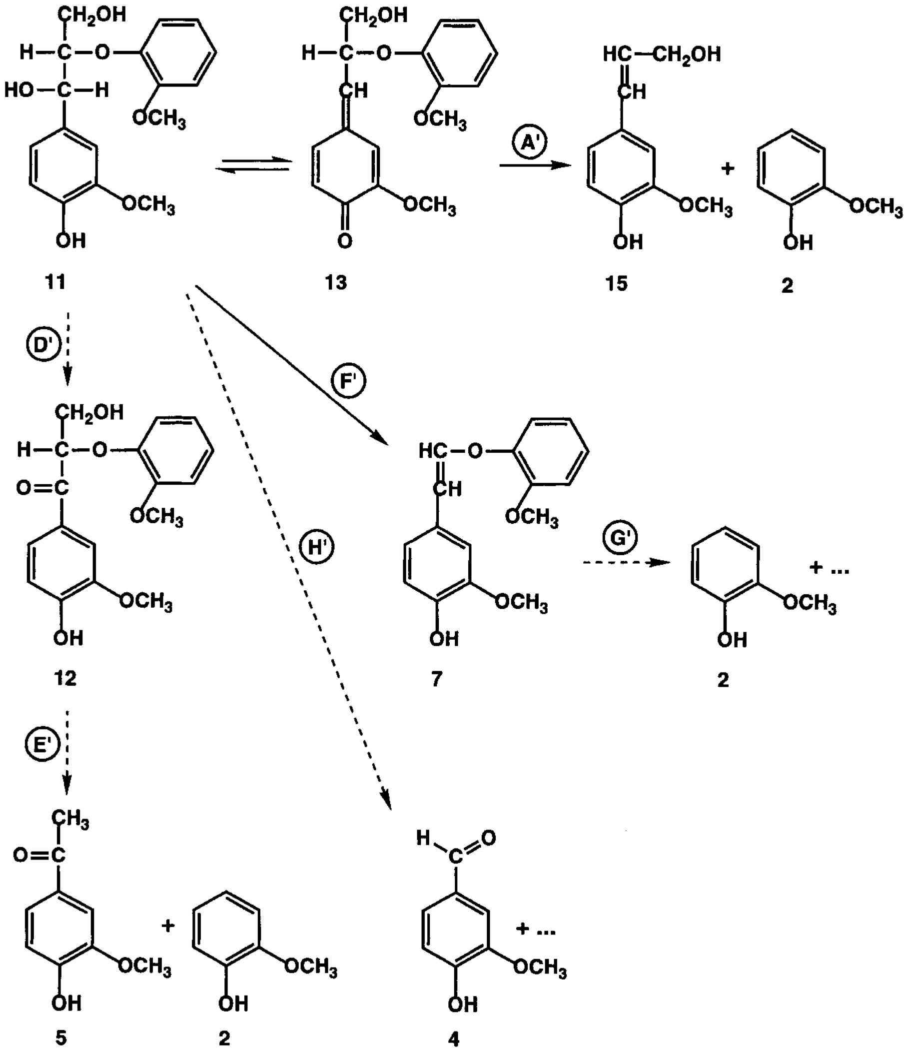
	 $\mathrm{H{-}}\textcircled{G}$	 $\mathrm{CH_2{=}CH{-}}\textcircled{V}$	 $\mathrm{CH_3{-}CHOH{-}}\textcircled{G}$
Catalyst	%**2**	%**27**	%**6**
Control	3		
Control/Gl	10		
AQ/Gl	17	3	
Co(TSPP)	14		
Co(TSPP)/Gl	18	5	1

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

TABLE 4. Total Reaction Component Analysis for **11**[a]

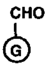
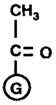
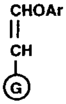
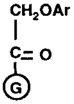
	 $\mathrm{H{-}}\textcircled{G}$	 $\mathrm{CH_2{=}CH{-}}\textcircled{G}$	 $\mathrm{CHO{-}}\textcircled{G}$	 $\mathrm{CH_3{-}CHOH{-}}\textcircled{G}$	 $\mathrm{CHOAr{=}CH{-}}\textcircled{G}$
Catalyst	%**2**	%**3**	%**4**	%**6**	%**7**
Control	16		5		56
Control/Gl	15		2		50
AQ/Gl	43	2	6	1	22
Co(TSPP)	23	1	8		29
Co(TSPP)/Gl	49	3	4	1	9

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote



SCHEME 3. Rationalization of the product distribution obtained from the reaction of **11** with Co(TSPP)

TABLE 5. Products from **12**[a]

					
Catalyst	%**2**	%**4**	%**5**	%**7**	%**8**
Control	16	3	1	5	10
Control/Gl	21	2	3	2	24
AQ/Gl	22	2	4		30
Co(TSPP)	20	5	5	2	11
Co(TSPP)/Gl	53	2	34		14

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

from the Fe(TSPc) and Rh(TSPP) catalysts described in Parts II and III of this series.

Reactions Of Co(TSPP) With The Phenylpropane Lignin Model Compounds **11** And **12**.

Reactions with the phenylpropane model compound guaiacylglycerol β-guaiacyl ether (**11**) were also investigated and the products obtained are listed in Table 4. Again very similar distributions were obtained for both the AQ and Co(TSPP) catalyzed reactions. Reasonable quantities of guaiacol (**2**) were formed in the presence of glucose and the catalyst, but only minor amounts of other compounds were apparent.

The products can be rationalized in terms of the overall reaction pathways in Scheme 3. Pathways D' and E' are unimportant for this catalyst since no 3-methoxy-4-hydroxy-α-(2'-methoxyphenoxy)-β-hydroxypropiophenone (**12**) was detected in the reaction products of **11** by ^{13}C NMR spectroscopy. In addition, in separate reactions with **12**, considerable quantities of acetovanillone (**5**) were produced (Table 5). However this compound was also completely absent from the products of **11** (Table 4). Only a small amount of the vinyl ether **7** was formed in the reaction containing glucose and catalyst, although more was formed when glucose was absent. As **7** was only slowly degraded by the catalyst (Table 2), this means pathway F' in Scheme 3 is only important when glucose is absent. The small amount of vanillin (**4**) formed indicates that pathway H' is also relatively unimportant for this catalyst. By analogy with **1**, it seems likely that reaction of the reduced catalyst with the quinone methide **13** (pathway A') provides the major route for guaiacol formation. Coniferyl alcohol (**15**) was not detected among the products, probably because it is very reactive under the conditions used. In the absence of glucose, the catalyst is largely in the Co^{III}(TSPP) form and pathway A' is therefore suppressed. Pathway F' then increases in importance. A slightly larger amount of guaiacol (**2**) and a smaller amount of the vinyl ether **7** was obtained for the Co(TSPP)/glucose catalyzed reaction of **11** compared with that catalyzed by AQ/glucose. This suggests Co^{II}(TSPP) may be more reactive towards the quinone methide **13** than AHQ. The mechanism of the reaction of **13** with Co^{II}(TSPP) is probably the same as that depicted for **9** in Scheme 2 with single electron transfer from Co^{II}(TSPP) to the quinone methide **13** occurring in the first step.

EXPERIMENTAL

^{1}H and ^{13}C nmr spectra were determined on a Bruker AC200 FT spectrometer. UV-visible spectra were obtained in aqueous solution on a Phillips PU8700 UV-visible spectrometer. Low resolution mass spectra were determined on a Hewlett Packard HP 5985 spectrometer operating under EI using an ionisation potential of 70eV.

Gas liquid chromatography (glc) was performed on a Hewlett Packard 5890 gas chromatograph fitted with an autoinjector (3 μl per injection) and a 5 m x 0.32 mm x 0.3 μm Carbowax 20M capillary column using helium as the carrier gas at a flow rate of 4-5 ml per minute, a column head pressure of 4 psi and purged splitless injection. The temperature program was:

60°C (0 min), 20°C/min to 100°C, 6°C/min to 170°C, 20°C/min to 220°C and hold at 220°C for 20 min.

Response factors and approximate retention times for all compounds were as follows:

Compound	Response Factor	Retention Time (min)
guaiacol (**2**)	1.04	4.3
p-cresol	internal standard	6.5
vinyl guaiacol (**3**)	1.12	8.0
3,4-dimethoxystyrene (**18**)	1.20	8.2
vanillin (**4**)	1.33	12.8
acetovanillone (**5**)	1.00	13.0
apocynol (**6**)	1.03	14.3
β-(2'-methoxyphenoxy)-4-hydroxy-3-methoxy styrene (**7**)	1.46	22.7 cis 25.3 trans
1-(3",4"-dimethoxyphenyl)-1-hydroxy-2-(2'-methoxyphenoxy) ethane (**10**)	2.70	30.3
4'-hydroxy-3'-methoxy-1-(2"-methoxy-phenoxy) acetophenone (**8**)	2.31	32.6
guaiacylglycol β-guaiacyl ether (**1**)	2.10	35.2

The phenolic lignin model compounds guaiacylglycol β-guaiacyl ether (**1**), 4'-hydroxy-3'-methoxy-1-(2"-methoxyphenoxy)acetophenone (**8**),[16] β-(2'-methoxyphenoxy)-4-hydroxy-3-methoxystyrene (**7**),[17] vinyl guaiacol (**3**),[18] guaiacylglycerol β-guaiacyl ether (**11**)[19] and 3-methoxy-4-hydroxy-α-(2'-methoxyphenoxy)-β-hydroxypropiophenone (**12**)[19] were prepared by literature methods. The non-phenolic lignin model compounds 3,4-dimethoxy styrene (**18**) and 1-(3",4"-dimethoxyphenyl)-1-hydroxy-2-(2'-methoxyphenoxy) ethane (**10**) were prepared by diazomethane methylation of the corresponding phenolic compounds in methanol. The metal ion complex $Na_3[Co(TSPP)]$ was also prepared by literature methods.[20,21,22]

Model Compound Reactions: General Procedure

The lignin model compound **1** (30.0 mg), D-glucose (40.0 mg, 2.15 eq) and Na_3 [Co(TSPP)] (10.5 mg, 0.1 eq) were placed in a glass tube and 1M sodium hydroxide solution (4 ml) added. The solution was purged with a stream of nitrogen for 1-2 min then sealed. The tube was suspended in an efficiently stirred oil bath at 135°C for 2 h in the dark, removed, cooled to room temperature, opened and the contents quantitatively poured onto 90 ml of 0.75M hydrochloric acid. The solution was extracted with 3 x 15 ml of dichloromethane. The dichloromethane extract was dried over anhydrous magnesium sulfate and made up to 50 ml. The solution was analysed by glc on a Carbowax 20M capillary column using *p*-cresol as the internal standard. The by-products were identified by gc mass spectrometry and by comparison with authentic samples.

CONCLUSIONS

Our results indicate that Co(TSPP) catalyzes β-aryl ether bond cleavage in the lingin model compounds **1** and **11**, most likely by single electron transfer from the reduced metalloporphyrin, Co^{II}(TSPP), to a quinone methide intermediate. A significant portion of the vinyl guaiacol cleavage product then undergoes further reaction under the conditions employed.

Recent studies by Dimmel *et al.*[10,12,13] have shown that the mechanism by which AHQ reacts with **1** probably involves single electron transfer from AHQ to the quinone methide **9** as the key step. The fact that the product distributions obtained for both the AQ/glucose and Co(TSPP)/glucose catalyzed reactions of **1** are so similar (Table 1) suggests a common mechanism and adds further support to the proposed single electron transfer mechanisms for the AQ/glucose catalyzed reactions.

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