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Fe(TSPc)-Catalysed Benzylic Oxidation and Subsequent Dealkylation of a Non-Phenolic Lignin Model

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**Fe(TSPc)-CATALYSED BENZYLIC OXIDATION AND SUBSEQUENT
DEALKYLATION OF A NON-PHENOLIC LIGNIN MODEL**

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ABSTRACT

The mechanism by which the phthalocyanine complex trisodium tetra-4-sulfonatophthalocyanineiron(III) (Fe(TSPc)) promotes oxidation and dealkylation of non-phenolic benzyl alcohol units in lignin under alkaline conditions was investigated using simple lignin model compounds. The iron complex effectively oxidised benzylic hydroxyl groups in 2-hydroxyethyl apocynol (**5**), with the extent of oxidation increasing with the amount of Fe(TSPc) added. To a limited extent, Fe(TSPc) also catalysed the oxidation of **5** by small amounts of oxygen in the reaction mixture. However, the extent of oxidation did not increase on adding excess air or oxygen, as greater amounts of oxygen also increased complex degradation. Phenolic products were formed in these reactions in the presence of Fe(TSPc), but at a rate slower than that of the benzylic oxidation. Further experiments indicated that the phenolic products were formed by base-promoted loss of the ether group at C4 and that such dealkylation occurred more readily in oxidised products.

INTRODUCTION

The rate of delignification during the bulk phase of kraft or soda pulping is determined by the rate of hydrolysis of non-phenolic β -O-4 bonds in the lignin.¹ This reaction is suggested to involve ionisation of the benzylic hydroxyl, followed by intramolecular epoxide formation as the phenoxyl ether bond is replaced by the alkoxide in the rate determining step. One method shown to increase the rate of hydrolysis of these bonds is to make the phenoxyl group a better leaving group by oxidising its attached benzylic hydroxyl to a carbonyl group. Gierer and Norén² showed that by pretreating wood with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), a reagent known to oxidise benzylic hydroxyls in lignin to the corresponding ketones,³ the rate of delignification during kraft pulping was increased. However, better methods for oxidation of the lignin are required, as the DDQ pretreatment also increased carbohydrate degradation.

More recently, it has been shown that the complexes trisodium tetra-4-sulfonatophthalocyanineiron(III) (Fe(TSPc)) and trisodium *meso*-tetra-4-sulfonatophenylporphinerhodium(III) (Rh(TSPP)) promote the degradation of both phenolic and non-phenolic β -ethers and milled wood lignin under alkaline pulping conditions.⁴⁻⁶

For the non-phenolic β -ether model veratrylglycol- β -guaiacyl ether (1), the major products detected on alkaline degradation in the presence of both catalysts were the oxidised compounds acetoveratrone (3) and acetovanillone (4), as well as guaiacol (2) (Figure 1).^{5,6} These oxidised products were produced under the alkaline conditions in spite of the fact that the reactions were performed in the absence of oxygen or other added oxidants. The authors proposed that these oxidation reactions occur via one electron oxidations of the lignin model compound by the catalyst, with the oxidised form of the catalyst being regenerated

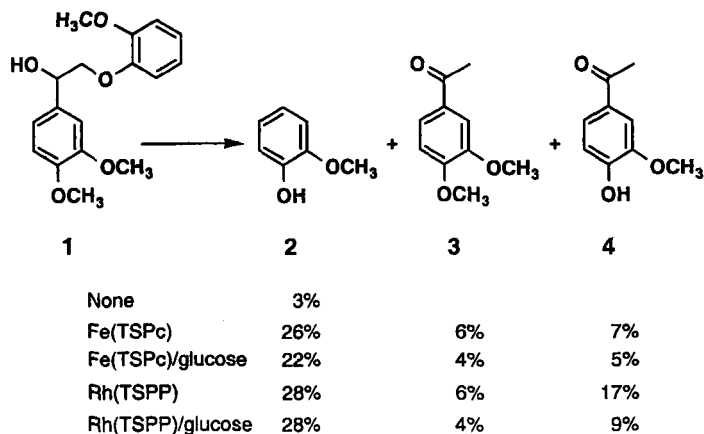
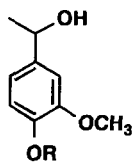
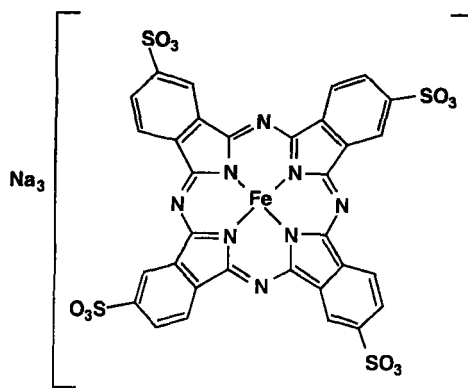


FIGURE 1. Products detected by GC on treatment of veratrylglycol- β -guaiacyl ether in the presence of 0.1 equivalents of Fe(TSPc) or Rh(TSPP) and 2.15 equivalents of glucose.^{5,6} Conditions: 1 M NaOH, 135 °C, 2 h.

by reaction with the added lignin model or its degradation products. Consistent with this suggestion, lower levels of oxidised products were produced when glucose, a sugar capable of reducing the oxidised catalyst, was added.

Interestingly, alkaline degradation of **1** in the presence of Fe(TSPc) and Rh(TSPP) afforded substantial amounts of the phenolic product acetovanillone (**4**).^{5,6} This suggested that addition of Fe(TSPc) or Rh(TSPP) during alkaline pulping should facilitate lignin breakdown. It was proposed that demethylation might involve a single electron transfer step between the catalyst and the substrate.

In this study, the mechanisms of Fe(TSPc)-promoted benzylic oxidation and dealkylation of non-phenolic lignin units were investigated in more detail using the simpler model 2-hydroxyethyl apocynol (**5**) (Figure 2). Although more effective, the Rh complex was not investigated because of its higher cost. The 2-







5 R = CH₂CH₂OH

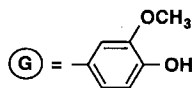
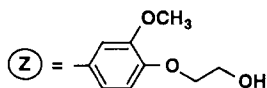
6 R = CH₃

FIGURE 2. Fe(TSPc) and lignin models.

hydroxyethyl ether model **5** was used in preference to the simpler methyl ether **6**, as it more closely resembles the type of non-phenolic interunit linkages found in lignin. It is also more soluble in alkali, avoiding the need for an organic co-solvent in the reactions. With the simple model **5**, the oxidised form of the catalyst cannot be regenerated by reaction of the reduced catalyst with lignin model compound degradation products. This is in contrast to the case during our earlier model compound investigation - and during pulping - where the reduced catalyst can react with lignin degradation products, such as quinone methides, to reform the oxidised catalyst.

TABLE 1.
Reactions of **5** in the Presence of Additives.^a

Additive (mole equivalents)				
	5	8	7	4
None	103	0	1	1
Fe(TSPc) (1.0)	0	0	41	25
Fe(TSPc) (0.1)	57	0	12	18
Fe(TSPc) (0.065)	71	0	4	13
Co(TSPP) (1.0)	64	1	17	9
Co(TSPP) (0.1)	72	1	13	7
AQ (1.0)	78	3	12	7
AQ (1.0) + glucose (2.15)	68	3	9	5
glucose (2.15)	97	2	1	1



^a Reaction conditions: 1M NaOH, 135 °C, 2 h, N₂ atmosphere.

RESULTS AND DISCUSSION

Reactions of Hydroxyethyl Apocynol (**5**)

The reactions were performed by dissolving the model compound and metal complex in 1 M sodium hydroxide in a teflon-lined stainless steel vessel. Nitrogen was bubbled through the solution to minimise the amount of oxygen present prior to sealing and heating in an oil bath for the required time. The reaction products were analysed by reverse phase high performance liquid chromatography (HPLC).

Table 1 shows the products obtained on heating 2-hydroxyethyl apocynol (**5**) in the presence of Fe(TSPc), Co(TSPP), anthraquinone (AQ) or glucose under

identical conditions to those used in previous studies^{5,7} (135 °C, 2 hours). Consistent with these earlier studies, addition of Fe(TSPc) led to the most extensive benzylic oxidation, with the extent of oxidation decreasing in the order Fe(TSPc) >> Co(TSPP) > AQ >> glucose ≈ control. Formation of phenolic products, principally acetovanillone (**4**), was also greatest in the presence of Fe(TSPc). All further studies were carried out using Fe(TSPc).

The results in Table 1 indicate that the extent of both oxidation and dealkylation increase as the amount of Fe(TSPc) added was increased. This suggested that oxidation of the model compound was a stoichiometric rather than a catalytic reaction. However, the extent of oxidation in the presence of 0.065 and 0.1 mole equivalents of Fe(TSPc) was significantly greater than expected on the basis of the number of moles of the complex added, implying that the complex was acting as a catalyst for the benzylic oxidation, and that there was some regenerant present in the reaction mixture. Evidence discussed in more detail below suggested that, although the reactions were purged with nitrogen, some oxygen still remained in the reaction medium and it was this which was regenerating the active form of the catalyst.

Oxidation of the model by Fe(III)(TSPc) probably occurs via a single electron transfer (SET) mechanism. Such SET reactions have been commonly proposed for redox reactions involving metallophthalocyanines⁸⁻¹⁰ and also proposed for benzylic oxidation of lignin models by species including nitrobenzene, AQ, metalloporphyrins and metallophthalocyanines.^{5-7,11-14} The metal centre in Fe(TSPc) can exist in three oxidation states, Fe(III), (II), or (I), and the corresponding complexes are coloured blue, green and red respectively. Reactions of Fe(TSPc) with the alcohol **5** change in colour from the blue that is characteristic of Fe(III)(TSPc) to red by the end of the reaction, indicating that Fe(I)(TSPc) is ultimately the dominant species in the final medium. The red Fe(I) complex rapidly forms the green Fe(II)(TSPc) complex when air is admitted to the

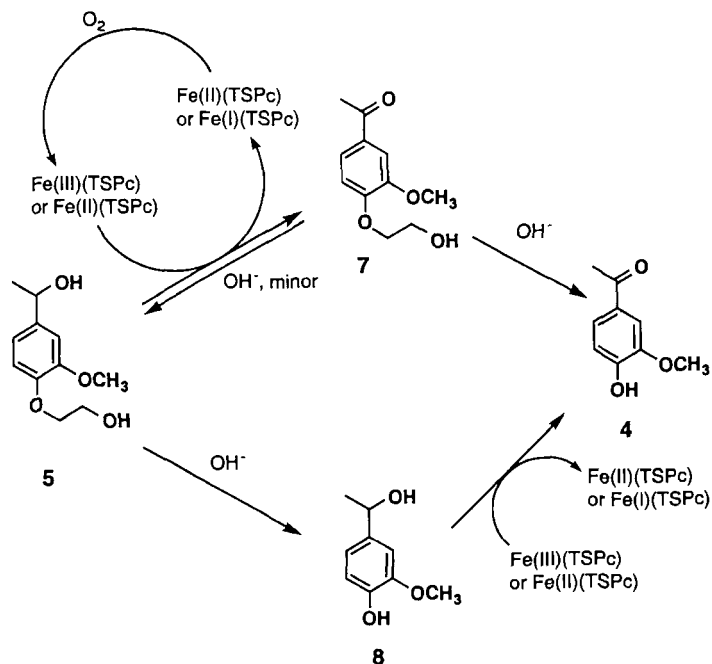






FIGURE 3. Possible reactions of hydroxyethyl acetovanillone in the presence of Fe(TSPc).

reaction vessel and the Fe(II) complex is then slowly oxidised to the blue Fe(III)(TSPc). However, it is not clear which of these three possible oxidation states of the iron centre are important in the catalytic cycle involving the Fe(TSPc) catalysed oxidation of 5 in the presence of small amounts of oxygen.

Mechanism of Dealkylation

As shown in Figure 3, acetovanillone (4) could potentially be formed either via initial oxidation to the ketone 7 followed by dealkylation, or by dealkylation to apocynol (8) followed by oxidation. The following results suggested that acetovanillone (4) is formed largely via the intermediacy of the etherified ketone 7, but that some formation via apocynol (8) cannot be ruled out:

TABLE 2.
Products from Possible Intermediate Compounds^a.

					
	Mole equivalents Fe(TSPc)	5	8	7	4
5	1.0	0	0	41	25
7	1.0	2	0	47	33
7	-	2	0	42	40
8	1.0	-	0	0	84

^a Reaction conditions and definition of symbols given in Table 1.

- Treating hydroxyethyl acetovanillone (**7**), either in the presence or absence of one mole equivalent of Fe(TSPc), gave a similar product distribution to reactions of hydroxyethyl apocynol (**5**) in the presence of one mole equivalent of Fe(TSPc) (Table 2).
- Apocynol (**8**) was effectively converted to acetovanillone in the presence of Fe(TSPc) (Table 2).
- Treating **5** with larger amounts of Fe(TSPc) leads to significantly higher levels of the ketone **7** (Table 1).
- On treatment of hydroxyethyl apocynol (**5**) with alkali in the absence of Fe(TSPc), neither **7** nor **8** were formed to an appreciable extent (Table 1).

The presence of Fe(TSPc) did not have a great effect on the extent of dealkylation of hydroxyethyl acetovanillone (**7**) (Table 2). This suggests that dealkylation of this compound occurs largely through an alkali-promoted reaction, rather than through interaction with Fe(TSPc). Gierer and Ljunggren¹⁵ suggested that alkali-promoted dealkylation of both hydroxyethyl apocynol (**5**) and hydroxyethyl acetovanillone (**7**) occurred via a neighbouring group mechanism analogous to that suggested for non-phenolic β -ether cleavage (Figure 4). The significantly greater base-induced dealkylation of the ketone **7** compared to that of

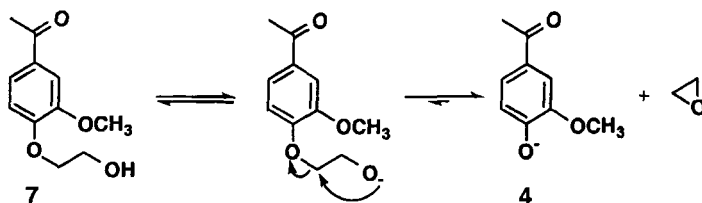


FIGURE 4. Mechanism for dealkylation of 7.¹⁵

the corresponding alcohol 5 is consistent with earlier studies reported by both Gierer and Ljunggren¹⁵ and more recent work at Mississippi State.^{16,17}

The ratio of acetovanillone (4) to the etherified ketone 7 found during alkaline degradation of hydroxyethyl apocynol (5) in the presence of both Co(TSP) and AQ is very similar to that seen in the presence of 1 equivalent of Fe(TSP) (Table 1). This suggests that acetovanillone is also formed from 5 mainly via the intermediacy of the etherified ketone 7 in the presence of these additives. Interestingly, while the extent of oxidation is reduced in the presence of lower doses of Fe(TSP), proportionately more acetovanillone is formed. While this observation was not investigated further, it does suggest that other mechanisms of acetovanillone formation may be operative in the presence of catalytic amounts of Fe(TSP).

Effect of Temperature

Figure 5a shows the results from separate reactions of hydroxyethyl apocynol (5) with alkali in the presence of 0.1 equivalents of Fe(TSP) at temperatures ranging from ambient up to 165 °C. The extent of oxidation of 5 reached a maximum around 100 °C. The slightly higher recovery of the starting material (5) at temperatures above 100 °C may be associated with some oxidative breakdown of the Fe(TSP) at these higher temperatures.¹⁰ In agreement with this, a brown solid which was presumably iron(III) hydroxide, was found in

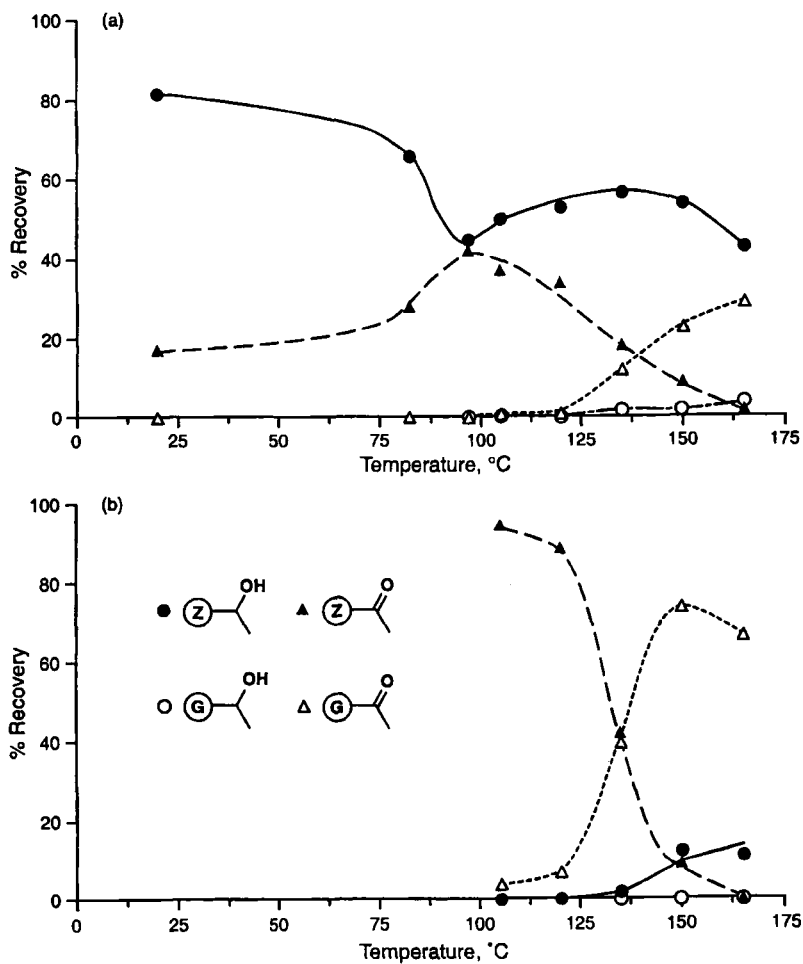


FIGURE 5. Effect of temperature on the reaction of (a) hydroxyethyl apocynol (5) with alkali in the presence of 0.1 mole equivalents Fe(TSPc) and (b) hydroxyethyl acetovanillone with alkali. Time 2 h.

reactions at these higher temperatures. Additional alkali-promoted degradation reactions may account for the decreased total product recovery seen at 165 °C. Consistent with this, cooks of hydroxyethyl apocynol (**5**) at 165 °C in alkali alone showed that only about 80% of the starting material was recovered, and that additional products, observed as late-eluting peaks in the HPLC trace, were formed. In the higher temperature reactions the amounts of acetovanillone (**4**) grew as the alkylated ketone **7** decreased, suggesting that the dealkylation of **7** to **4** occurred more readily under these more forcing conditions. Support for this came from reactions of hydroxyethyl acetovanillone (**7**) in alkali alone (Figure 5b), which showed that dealkylation increased as the temperature was raised. Interestingly, up to 11% of hydroxyethyl apocynol (**5**) was formed in cooks of the corresponding ketone **7** in alkali alone. The mechanism by which this occurs is not clear.

Effect of Oxygen

As the extent of oxidation of the model **5** was greater than expected on the basis of the number of moles of Fe(TSPc) added (Table 1), it is reasonable to expect that traces of oxygen remaining in the reaction medium could be regenerating the active oxidised form of the metal complex.^{10,18,19} Support for this was obtained when the reactions of **5** were carried out in the normal way, except that glass vessels were used and the solutions were subjected to several freeze-thaw-degas cycles before heating to 100 °C. In reactions that contained 0.1 mole equivalents of Fe(TSPc) only 12% of **5** was converted to oxidised products, which is very close to the 10% that would be expected if no regeneration of the reduced metal complex occurred.

To see if increasing amounts of oxygen in the reaction medium would lead to greater oxidation of the lignin model compound, a number of experiments were carried out with 0.1 mole equivalents of Fe(TSPc) at 100 and 135 °C in air and oxygen atmospheres. While the results were not very reproducible, it was clear

that increasing the amount of oxygen did not increase lignin model oxidation, apparently because increasing the amount of oxygen in the reaction led to greater and more rapid oxidative degradation of the metal complex.¹⁰

CONCLUSIONS

The complex Fe(TSPc) was shown to be a highly effective oxidant of benzylic hydroxyl units in the non-phenolic lignin model **5**, with the extent of oxidation increasing as the amount of Fe(TSPc) added was raised. The Fe(TSPc) was able to act as a catalyst for this oxidation, with small amounts of oxygen in the reaction mixture regenerating the active form of the metal complex. However, performing the reactions under an air or oxygen atmosphere did not increase the extent of oxidation, as oxidative degradation of the metal complex increased in the presence of more oxygen. During alkaline pulping, other processes, such as reaction of the reduced metal complex with quinone methides leading to β -ether cleavage, may provide alternative pathways for regeneration of the oxidised form of the catalyst.

Loss of the hydroxyethyl ether at C4 occurs readily for the oxidised intermediate **7**, but not to any great extent for the starting model compound **5**. Oxidation of the benzylic alcohol function in **5** by Fe(TSPc) proceeds much faster than the subsequent base-induced dealkylation reaction. This latter reaction appears to proceed via a neighbouring group mechanism.

EXPERIMENTAL

Materials and Methods

¹H NMR and ¹³C NMR spectra were recorded at 25 °C in CDCl₃ on a Bruker AC-200 NMR spectrometer with a 5 mm probe operating at 200.13 and

50.33 MHz respectively and were referenced against tetramethylsilane or internal chloroform. Ultraviolet-visible spectra were recorded on a Phillips PU 8740 spectrometer and mass spectra on a VG 70-SE mass spectrometer. Microanalyses were determined by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Trisodium tetrasulfophthalocyanineiron(III) trihydrate (Fe(TSPc)) was prepared using the procedure of Weber and Busch,²⁰ and apocynol (7) by catalytic hydrogenation of acetovanillone (4). Other materials and reagents used were obtained commercially and used as received except for acetovanillone and veratraldehyde, which were recrystallised from hot water and diethyl ether/hexanes respectively prior to use.

4-(-2'-bromoethoxy)-3-methoxyacetophenone

A mixture of acetovanillone (4) (1.00 g, 6.0 mmol), 1,2-dibromoethane (5.6 mL, 60 mmol), dry K₂CO₃ (8.29 g, 60 mmol) and KI (0.05 g, 0.3 mmol) were heated under reflux in acetone (300 mL) for eight hours. The mixture was filtered and the filtrate concentrated to give a yellow solid. This was heated in hexane and the hexane, containing any excess dibromoethane, filtered off to afford 1.23 g (74%) of 4-(-2'-bromoethoxy)-3-methoxyacetophenone. ¹H NMR δ_H: 2.57 (s, 3H, COCH₃); 3.68 (t, 2H, CH₂); 3.93 (s, 3H, OCH₃); 4.40 (t, 2H, CH₂); 6.9 - 7.6 (m, 3H, Ar-H).

4-(-2'-hydroxyethoxy)-3-methoxyacetophenone (7)

A mixture of 4-(-2'-bromoethoxy)-3-methoxyacetophenone (5.00 g, 20 mmol) and potassium carbonate (15.0 g, 0.1 mol) was heated under reflux in water (200 mL) for 2.5 days. The mixture was cooled to ambient temperature and extracted with dichloromethane. The combined organic extracts were dried and concentrated under reduced pressure. Recrystallization from dichloromethane - hexanes gave 2.67 g (69%) of 4-(-2'-hydroxyethoxy)-3-methoxyacetophenone (7),

m.p. 101.5 - 102 °C (uncorrected). $^1\text{H NMR } \delta_{\text{H}}$: 2.56 (s, 3H, COCH₃); 3.91 (s, 3H, OCH₃); 4.01 (t, 2H, CH₂); 4.18 (t, 2H, CH₂); 6.9 - 7.6 (m, 3H, Ar-H). $^{13}\text{C NMR } \delta_{\text{C}}$: 26.1; 55.8; 60.9; 70.5; 110.3; 111.6; 123.2; 130.7; 149.1; 152.4; 180.8. EIMS (probe) $m/z = 210 \text{ M}^+$. Analysis: C, 63.15; H, 6.83. C₁₁H₁₄O₄ requires: C, 62.85; H, 6.71.

1-(4'-(-2"-hydroxyethoxy)-3'-methoxyphenyl)-1-hydroxyethane (5)

Sodium borohydride (0.37 g, 9.74 mmol) was added to a cold, 0 °C, stirred solution of 4-(-2'-hydroxyethoxy)-3-methoxyacetophenone (7) (0.35 g, 1.67 mmol) in ethanol (50 mL) and the solution warmed to room temperature. After five hours, solid NH₄Cl was added until gas evolution ceased. The mixture was stirred for ten minutes, filtered and the inorganic solid was washed with dichloromethane. The filtrate was placed in a separating funnel, diluted with water and extracted three times with dichloromethane. The combined organic extracts were dried and concentrated under reduced pressure to give 1-(4'-(-2"-hydroxyethoxy)-3'-methoxyphenyl)-1-hydroxyethane (5) (0.30 g, 85%) as a colourless viscous oil. $^1\text{H NMR } \delta_{\text{H}}$: 1.44 (d, 3H, $J=6.4 \text{ Hz}$, H β); 3.73 (s, 3H, OCH₃); 3.90 (t, 2H, OCH₂CH₂OH); 4.04 (t, 2H, OCH₂CH₂OH); 4.80 (q, 1H, $J=6.4 \text{ Hz}$, H α); 6.75-6.95, (m, 3H, ArH). $^{13}\text{C NMR } \delta_{\text{C}}$: 24.9; 55.5; 60.8; 69.8; 70.8; 108.9; 113.1; 117.7; 139.3; 147.0; 148.9.

Model Pulping Reactions

In a typical reaction, the model compound 5 (20 mg, 77.2 μmol), Fe(TSPc) 6.8 mg, 7.7 μmol) and 1M sodium hydroxide (5 mL) were placed in a teflon-lined stainless steel vessel. Nitrogen was bubbled through the resulting solution to minimise the oxygen content and the vessel sealed. The vessel was heated at 135 °C for two hours in an oil bath, removed and cooled by immersion in water. The contents of the vessel were adjusted to pH 6 with dilute aqueous H₃PO₄, transferred to a separating funnel and extracted three times with dichloromethane (15 mL). The combined organic extracts were dried, concentrated under reduced

TABLE 3.
Recoveries and Relative Response Factors for Model Compounds.

	Recovery ^a , %	Relative response factor ^b
Hydroxyethyl apocynol (5)	67	7.6
Apocynol (8)	89	4.7
Hydroxyethyl acetovanillone (7)	75	1.35
Acetovanillone (4)	97	1.18

^a Average of duplicate determinations.

^b Mass response relative to 3,4-dimethoxybenzaldehyde.

pressure and the residue redissolved in methanol (40 mL) before transferring to a 100 mL volumetric flask. A solution of veratraldehyde (10 mL of a 1.00 mg/mL in methanol) was added as internal standard and the flask then made up to volume with 50% aqueous methanol.

HPLC Analysis

Aliquots (20 μ L), which had been filtered through a 0.45 μ m syringe filter, were analysed by reverse phase HPLC on a C18 column (5 μ m, 150 mm x 4.6 mm i.d., Alltech Econosphere), eluting at 1 mL/min with 30% methanol in water containing 0.1% phosphoric acid. The column eluate was monitored at 280 nm and the column flushed with methanol between each run to remove possible contaminants. Corrections were made to account for incomplete recovery of the reaction products during the extractive workup. Table 3 gives the measured recoveries of each of the reaction products, together with their detector responses relative to the internal standard.

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