ALKALINE PULPING OF WOOD AND LIGNIN MODEL COMPOUNDS IN AQUEOUS DMSO

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DONALD R. DIMMEL, DONALINE SHEPARD, AND LOIS F. PERRY

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and

A Mechanistic Study of DMSO Pulping Reactions of Lignin Model Compounds

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One of the goals of Project 3475, Fundamentals of Selectivity in Pulping and Bleaching, has been to establish a firm understanding of the chemistry of anthraquinone pulping. Toward this end, we examined the fragmentation reactions of some β-aryl ether lignin model compounds with anthrahydroquinone (AHQ) derivatives in mixed organic-water solvent systems at 150°C. We observed that the models extensively fragmented in alkaline aqueous DMSO; in fact, the fragmentation efficiency paralleled that of a soda/AHQ system.

Subsequent research under Exploratory Project 3534-1, Pulping with DMSO, focused on the practical and mechanistic aspects of DMSO as a pulping aid. The research established that DMSO promotes the pulping of wood, when used at moderate levels, and acts by sets of complex oxidation and reduction reactions. The details are provided in the two attached papers.
ALKALINE PULPING OF WOOD AND LIGNIN MODEL COMPOUNDS IN AQUEOUS DMSO

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ABSTRACT

Lignin model fragmentation studies done in alkaline aqueous DMSO exhibited a high degree of β-aryl ether cleavage, a degree equal to that of a comparable soda/AQ system. Pulping studies with loblolly pine in aqueous DMSO demonstrated that DMSO accelerates delignification, but the quantities required appear impractical.

INTRODUCTION

In view of the difficulties of working with actual lignin, researchers have often examined the reactions of model compounds and assumed that the observed chemistry approximates the chemistry of lignin. However, because models and lignin differ greatly in complexity and solubility, some are skeptical of the value of model compound studies in understanding the actual chemistry of wood. Among other things, this report will show how model studies can provide useful information on pulping.

In order to understand the chemistry of anthraquinone (AQ) pulping, we began looking at the reactions of anthrahydroquinone dianion (AHQ−2), and methylated analogs, with lignin model compounds in aqueous alkali. Our initial experimental design dictated that a nonalkaline solution of the model compound be preheated and then mixed with a preheated alkaline solution of an AHQ−2 species. The model compounds and some of the methylated AHQ−2 species required dimethyl sulfoxide (DMSO) as a cosolvent with water for
complete dissolution. Thus, our initial studies involved a reaction solvent system containing 75% DMSO and 25% water. Later studies, using small pressure vessels, allowed us to decrease or eliminate the use of an organic solvent.

The model studies established that DMSO promoted the fragmentation of β-aryl ether bonds; bonds of this type are prominent in lignin. The effects of DMSO on the pulping of wood were then examined. This report concerns these two subjects; the succeeding article concerns reaction studies aimed at unraveling the mechanism of action of DMSO with model compounds.

RESULTS

Preliminary Model Studies

Lignin model compound 1 was heated with alkali at 153°C for 1 hour in small reactors, both with and without AHQ⁻² present, in order to ascertain what effects AHQ⁻² had on the extent of cleavage of the β-aryl ether bond of the model. Fragmentation of this bond produces guaiacol (2). The amount of guaiacol liberated was determined by a sensitive gas chromatography-mass spectroscopy (GC-MS) technique. A known quantity of 3,5-dideuteroguaiacol was added as an internal standard prior to each reaction, and following work-up of the reaction, the ratio of guaiacol to guaiacol-d₂ was determined by selected ion monitoring (SIM) of masses 124 and 126 by GC-MS. This method of analysis allows the use of very small sample sizes (i.e., 2 mg of 1 per experiment) and should alleviate the problems associated with efficient recovery of the partially water soluble guaiacol.¹

![Chemical structures](image)
The yield of guaiacol from the fragmentation of 1 with OH\textsuperscript{-} and OH\textsuperscript{-}/AHQ\textsuperscript{-} \textsuperscript{2} varied considerably with changes in the composition of the solvent system. Figure 1 shows the variability of guaiacol yields as the solvent composition is changed from 75% dioxane to pure water to 75% DMSO. The data of Fig. 1 point out several interesting features of these degradation reactions.

![Figure 1](image)

Figure 1. The percent guaiacol liberated from \(\alpha\)-hydroxy model 1 at 153\(\degree\) after 60 minutes in an alkaline solution, with and without AHQ. Solid area on the top of each bar indicates the range of duplicate runs.

Increasing the relative amounts of organic solvent (dioxane or DMSO) in the system retards the fragmentation reaction. In fact, pure water is the best medium for efficient fragmentation by AHQ\textsuperscript{-} \textsuperscript{2}. Obst has also observed that dioxane suppresses the rate of alkaline cleavage of models similar to 1.\textsuperscript{2} Some of this suppression was attributed to a phase separation at 170\(\degree\)C with 50\% or more dioxane-water mixtures; the model may preferentially remain in the dioxane phase and receive low exposure to the water-soluble, active chemicals.

Degradations in DMSO produced higher yields of guaiacol than those in dioxane. An even more significant finding is the fact that DMSO/OH\textsuperscript{-} control degradations were nearly as effective as the corresponding AHQ\textsuperscript{-} \textsuperscript{2} degradations. As the level of DMSO decreased, the fragmentation efficiency of the model both increased and
approached more closely that of the AHQ\textsuperscript{-2} case. The efficiency of 5% DMSO in aqueous alkali was indistinguishable from AHQ\textsuperscript{-2} in water or water-5% DMSO mixtures. [At a 5% solvent level, the DMSO was still in large excess relative to the model. The AHQ\textsuperscript{-2} experiments employed three equivalents of AHQ\textsuperscript{-2} per equivalent of model.]

The model degradations indicated that DMSO promoted fragmentation. The efficiency of model fragmentation has been related to wood delignification efficiencies.\textsuperscript{3,4} Thus, the results of the model reactions of 1 suggested that an alkaline DMSO-water mixture may be as good as soda-AQ for the delignification of wood.

Pulping Studies

The rate of soda pulping of loblolly pine chips was significantly accelerated by the addition of DMSO (Table 1). In fact, pulping with soda/25% DMSO gave the same yield, kappa number, and rejects as an analogous cook with 0.1% AQ. At 75% DMSO, there was no free liquid phase after pulping; the chips were very swollen. Although the model studies' prediction was confirmed, pulping with 25% DMSO is not very practical.

<table>
<thead>
<tr>
<th>DMSO, %</th>
<th>DMSO, %</th>
<th>AQ, %</th>
<th>Total Yield, %</th>
<th>Screened Rejects, %</th>
<th>Screened Pulp Kappa No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquor vol. o.d. wood</td>
<td>o.d. wood</td>
<td>o.d. wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>54.0</td>
<td>8.6</td>
<td>100.0</td>
</tr>
<tr>
<td>25</td>
<td>110</td>
<td>0</td>
<td>42.6</td>
<td>1.1</td>
<td>25.6</td>
</tr>
<tr>
<td>25</td>
<td>110</td>
<td>0.1</td>
<td>42.2</td>
<td>0.4</td>
<td>25.1</td>
</tr>
<tr>
<td>75</td>
<td>330</td>
<td>0</td>
<td>44.0</td>
<td>21.0</td>
<td>25.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Constant conditions: 18% Na\textsubscript{2}O on o.d. wood, liquor-to-wood ratio 4.0, 90 minutes rise to 173°C, 120 minutes at 173°C, loblolly pine chips (air-dry).

The results of pulping with low levels of DMSO are given in Table 2 and Fig. 2. A DMSO level of roughly 3% based on oven-dry
wood was needed to observe a significant delignification rate increase. The ineffectiveness of the first 1% DMSO may be due to its consumption by some minor wood component. Pulping with mixed systems of DMSO and AQ or sulfide indicated some complementary effects with AQ, but not with sulfide. A 3% DMSO/0.05% AQ/soda system behaved similarly to a 0.1% AQ/soda system.

### TABLE 2

Effects of Small Amounts of DMSO in Soda Pulping

<table>
<thead>
<tr>
<th>DMSO, %</th>
<th>Total Rejects, % Screened o.d. wood Yield, %</th>
<th>Screened o.d. wood Kappa No.</th>
<th>Carbohydrate Yield, %</th>
<th>Lignin Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.6</td>
<td>6.2</td>
<td>87.1</td>
<td>44.0</td>
</tr>
<tr>
<td>0.2</td>
<td>50.8</td>
<td>3.4</td>
<td>87.2</td>
<td>44.2</td>
</tr>
<tr>
<td>0.4</td>
<td>50.1</td>
<td>2.8</td>
<td>89.5</td>
<td>43.4</td>
</tr>
<tr>
<td>0.8</td>
<td>50.5</td>
<td>5.9</td>
<td>89.8</td>
<td>43.7</td>
</tr>
<tr>
<td>1.6</td>
<td>50.7</td>
<td>2.7</td>
<td>86.4</td>
<td>44.4</td>
</tr>
<tr>
<td>3.2</td>
<td>49.4</td>
<td>1.3</td>
<td>83.1</td>
<td>43.3</td>
</tr>
<tr>
<td>6.4</td>
<td>48.5</td>
<td>1.2</td>
<td>72.5</td>
<td>43.2</td>
</tr>
</tbody>
</table>

*Constant conditions as in Table 1, except chips soaked in water before cooking liquor addition; final pH = 13.4 in each case. Total yield = lignin yield. Lignin yield = 0.0015 x kappa x total yield.*

**Figure 1.** The effects of small amounts of DMSO on lignin yield.
Technology is available for paper mills to produce inexpensive dilute aqueous solutions of DMSO; however, DMSO would have to cost 4¢/lb to partially replace AQ at $2.40/lb. Chemical recovery of DMSO from pulping liquors would probably be costly. Thus pulping with DMSO appears impractical.

The use of dilute DMSO water solutions for alkaline pulping appears to be a novel finding. The literature has numerous references to the use of DMSO in pulping systems in which the DMSO is the only solvent and/or acid catalysts are present. Also, DMSO has been used in amine pulping and in pulping pretreatments.

The effectiveness of DMSO in alkaline pulping systems is probably related to a chemical reaction between the DMSO and lignin. This fact is borne out by the previously described model studies and the effective concentration range of DMSO (5-25%) in the pulping studies. Physical effects, such as the swelling of cell walls and solvation of the lignin, may also play a role.

**EXPERIMENTAL**

A JEOL FX 100 spectrometer and a Hewlett-Packard Model 5985 spectrometer were used to obtain NMR and GC-MS data, respectively. The pulping experiments were done with loblolly pine chips in 500 mL bombs rotated in an oil bath, using the conditions given in Tables 1 and 2.

**Guaiacol-3,5-d$_2$.** A solution of 10 g of guaiacol in 50 g of 100% D$_3$PO$_4$ was stirred for several days in a nitrogen atmosphere. [All glassware was oven-dried before use.] The solution was extracted three times with comparable volumes of 50/50 ether-benzene. Emulsions and solubility problems cause the loss of roughly half of the organic solvent mixture. Much of the deuterated guaiacol should be in the organic phase; however, the following additional steps were taken to remove the rest of the guaiacol. The D$_3$PO$_4$ phase was dripped slowly into an excess of stirred aqueous NaHCO$_3$ and the resulting solution was extracted with
50/50 ether-benzene. The latter was washed with aqueous NaHCO₃ and then water, dried (Na₂SO₄), combined with the first ether-benzene extracts, and gently distilled to give 6.8 g of partially deuterated guaiacol. Without further purification the guaiacol was treated again with 50 g of D₃PO₄ for several days and worked up as described above to give roughly 5 g of extensively deuterated guaiacol. Both NMR and GC-MS indicated that the ring protons were nearly completely replaced with deuteriums.

The crude deuterated guaiacol was placed in a titanium bomb with 15 mL of 4N NaOH, flushed with nitrogen gas, sealed, and heated at 153°C for 2 hours. The bomb was cooled, opened, and the contents were neutralized with aqueous HCl. The resulting solution was extracted several times with 50/50 benzene-ether. The combined organic extracts were dried (Na₂SO₄) and distilled to give 3 g of guaiacol-3,5-d₂, b.p. 200-210°C; ¹H-NMR (CDCl₃) δ 3.85 (s, OCH₃), 5.66 (s, OH) and 6.84, 6.92 (singlets, C₄ and C₆ protons) [nondeuterated guaiacol shows a multiplet in the 6.8-7.0 region]; ¹³C-NMR (CDCl₃) PPM 55.8 (s, OCH₃), 114.4 (d, C₆), 119.9 (d, C₄), 145.6 and 146.5 (singlets, C₁ and C₂), signals for C₃ and C₅ were absent; MS m/e 126 (guaiacol-d₂, 100%) and 124 (guaiacol, 1.4%).

Degradations of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxyphenoxy)-1-propanol (1). - Stock solutions containing 10.0 mg of model 1²⁰ and 4.1 mg (1 equiv.) of guaiacol-3,5-d₂ per mL of either DMSO or dioxane were prepared. Another stock solution of NaOH in water (0.0484 g/mL) was also prepared. Reactions involving AHQ employed 29 mg (3 equiv. based on 1) of anthrahydroquinone diacetate and an extra 12 equivalents of NaOH. The diacetate is hydrolyzed rapidly by the base in the early stages of the reactions: AHQ-diacetate + 4NaOH → Na₂AHQ + 2NaOAc.

The reactions were performed in small stainless steel bombs of 5.5 mL capacity. Except for the pure water experiments, the bombs were charged with AHQ-diacetate (where necessary), 1 mL of model/internal standard stock solution, 0.63 or 0.95 mL of NaOH.
solution (depending on whether AHQ diacetate was present) to give 23 equivalents of NaOH (after AHQ diacetate hydrolysis), and varying levels of water and pure organic solvent to obtain 4 mL of the desired solvent mixture. The bombs were flushed with N₂, sealed and immersed in a 153°C thermostatically regulated oil bath for 1 hour. After cooling, the bombs were opened and the contents were acidified and stirred in air until the AHQ⁻² (red colored) had oxidized to colorless AQ. The solids were filtered and washed with a small amount of organic solvent (DMSO or dioxane). The water diluted filtrate was extracted with 2 mL of CHCl₃.

A sample, 1 μL, of the CHCl₃ solution was injected into a GC-MS equipped with a 2 foot column packed with 3% OV-1 on Chrom WHP (100-120 mesh) and held at 110°C. Both guaiacol and guaiacol-d₂ eluted at 2.0 minutes. Only masses 124 and 126 were monitored and the ratio of the two ions determined. The observed ratio was compared to ratios obtained with standard guaiacol/guaiacol-d₂ mixtures to determine the yield of guaiacol produced in the reaction. Only one 2-mL CHCl₃ extract was analyzed since additional extracts gave the same guaiacol/guaiacol-d₂ ratios.

For pure water degradation runs, both the model 1 and AHQ-diacetate were weighed into the bomb; guaiacol-d₂ was dissolved in dilute NaOH and pipetted into the bomb. Again, the quantities of reagents were adjusted so that the 4 mL bomb solutions contained 1 equiv. of model and guaiacol-d₂, 3 or zero equiv. of AHQ-diacetate, and either 23 or 35 equivalents of NaOH.

Each degradation was done in an identical way, and in duplicate, to give the results shown in Fig. 1.

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A MECHANISTIC STUDY OF DMSO PULPING: REACTIONS OF LIGNIN MODEL COMPOUNDS

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ABSTRACT
Several lignin model compounds have been heated at 150°C with alkali in aqueous DMSO to give complex product mixtures containing oxidation, reduction, and methyl sulfide addition products. Low temperature reactions of DMSO and dimsyl anion with in situ generated quinonemethides afforded unique products. Reactions attributed to DMSO were not observed when an oxidized analog, dimethylsulfone, was substituted for the DMSO.

INTRODUCTION
In the preceding paper we established that dimethylsulfoxide (DMSO) facilitates cleavage of β-aryl ether bonds in lignin model compounds and accelerates the pulping of wood.1 The level of DMSO needed as an additive to alkaline pulping systems appears too high for a commercially successful operation. Even so, we undertook the brief investigation described here in hopes that the mechanism of action of DMSO as a pulping aid could be understood and that the knowledge gained might reveal new practical pulping techniques. The only previous lignin model mechanistic studies with DMSO involved the acid-catalyzed elimination of benzyl alcohol groups from dibenzyl ether structures in DMSO-water mixtures.2

RESULTS
A detailed GC-MS analysis of the product mixture obtained in the aqueous DMSO/alkali treatment of lignin model 1 showed three main components: starting model and fragmentation products
guaiacol 2 and isoeugenol 3. Two minor components were also detected; based on mass spectral fragmentation patterns and GC elution times, they were tentatively identified as ketone 4 and vinyl ether 5 [Eq. (1), where Ar = o-methoxyphenyl]. The mass spectra of 5 and 1 are very similar, since 1 readily dehydrates to 5 upon electron impact. We are certain if the vinyl ether 5 is a primary reaction product or formed during reaction workup and/or GC analysis.

A similar degradation of model 6 gave, upon GC-MS analysis, the following product mixture: starting material, guaiacol, acetoguaiacone 7, two sulfides 8 and 9, vinyl ether 10, and a component tentatively identified as 11 (Eq. 2). The fragmentation product analogous to 3, except no α-CH₃ (i.e., 29) was not detected; it (4-vinylguaiacol) is prone to be lost by polymerization side reactions. The identification of minor component 11 was based on its GC retention time and MS signals at m/e 274 (molecular ion) and 137 (benzyl ion from C₈−C₆ cleavage). Attempts to independently synthesize 11 failed.
The two sulfides were unexpected products. Confirmation of their structures was provided by independent syntheses and comparison of GC retention time and MS characteristics. The syntheses were accomplished by the set of reactions outlined in Eq. (3).

\[
\begin{align*}
R & \text{CHOH} \quad & R & \text{CHCl} \quad & R & \text{CHSMe} \\
12, R = H & \xrightarrow{\text{AcCl}} & 14, R = H & \xrightarrow{\text{MeS}^-} & 16, R = H & \xrightarrow{\text{1} \text{OH}^-} \xrightarrow{\text{2} \text{H}^+} 8 \text{ or } 9 \\
13, R = \text{CH}_3 & & 15, R = \text{CH}_3 & & & \\
\end{align*}
\]

The reasons why one model gave sulfide products and the other did not are not clear. Additional studies appeared appropriate. Therefore, \( p \)-hydroxybenzyl alcohol 18 and syringyl alcohol 21 were subjected to aqueous DMSO/alkali cooks. The results are given in Eq. (4) and (5). The sulfide product 24 was identified by comparison with an authentic sample synthesized using a procedure analogous to that given by Eq. (3). Authentic samples of the non-sulfur compounds were available for direct comparison. Condensation products 20 and 25 were expected.
The reactions outlined above were done with commercial DMSO with no prior purification. However, repetition of two of the cooks with freshly purified DMSO gave identical results. Thus, the methyl sulfide products do not arise from a contaminant (CH$_3$SH) in the DMSO. Apparently methyl sulfide ion is generated by a reduction of DMSO during the reaction and thus adds to the quinone-methide intermediates present in the mixture to give the observed sulfide products [Eq. (6)].

$$\text{CH}_3\text{S}^-\text{CH}_3 \xrightarrow{\text{reduction}} \text{CH}_3\text{S}^-$$

Several of the model reactions showed oxidation products, reduction products, or both (i.e., 1 \(\rightarrow\) 4; 6 \(\rightarrow\) 7 + 11; 21 \(\rightarrow\) 22 + 23). The mechanisms for these multiple oxidation/reduction reactions are not obvious. Base and DMSO in organic systems can function as an oxidizing agent, converting alcohols to carbonyl groups. Possibly, similar reactions occur in water at elevated temperatures.

Acid/base reactions of DMSO and hydroxide ion, which give rise to dimsyl anions 26, may be prominent at 150°C [Eq. (7)]. The basicity of hydroxide increases dramatically with temperature. Dimsyl anion might react with the models and lignin in some manner to produce fragmentation and delignification.

$$\text{CH}_3\text{S}^-\text{CH}_3 + \text{HO}^- \xrightarrow{\text{high temp.}} \text{CH}_3\text{S}^-\text{CH}_2^- + \text{H}_2\text{O}$$
The key reactive intermediates in model and lignin reactions are probably quinonemethides. At 150°C the lifetimes of quinonemethides will be extremely short. Quinonemethides can be generated under mild conditions by the hydrolysis of p-acetoxybenzylchlorides, such as 14 and 15. A few reactions of DMSO and dimysyl anions with quinonemethides generated from chloroacetates were investigated.

A DMSO solution of dimysyl anions, produced from DMSO and NaH, was mixed with chloroacetate 14 at room temperature. The major product detected by GC/MS was 4-vinylguaiacol (29). The presumed course of reactions giving rise to this product is shown in Eq. (8).

\[
\begin{align*}
\text{14} + \text{26} & \rightarrow \text{27} \\
& \rightarrow \text{28} \\
& \rightarrow \text{29}
\end{align*}
\]

The degradation of chloroacetate 30 with anthrahydroquinone in alkaline 75% DMSO-water at 25°C produced an interesting by-product, ketone 33. The level of ketone produced varied inversely with the level of NaOH used. None was observed when dioxane was substituted for DMSO. A plausible mechanism for the DMSO-related occurrence of 33 is outlined in Eq. (9). A key intermediate is probably the quinonemethide 31, which is the initial product of 30 reacting with dimysyl anion. The quinonemethide can also be formed in situ from an AHQ-adduct, and is rapidly destroyed by base. However, 31 may also be captured by dimysyl anion to give intermediate 32, which subsequently gives rise to ketone 33. Intermediates similar to 32 have been proposed in the oxidation of alcohols with DMSO/(CF3CO)2O/Et3N.
Dimethylsulfone (CH$_3$SO$_2$CH$_3$) is a close relative of DMSO and may be expected to exhibit some of the characteristics of DMSO. Yet, wood pulping and model cooks with dimethylsulfone showed no enhanced delignification rates or $\beta$-aryl ether cleavage. No sulfide products were observed in model cooks. Any mechanistic projections will have to reconcile these vast behavior differences with just a small change in the oxidation state of the sulfur.

CONCLUSIONS

Dimethyl sulfoxide accelerates the cleavage of $\beta$-aryl ether bonds in lignin model compounds and the dissolution of lignin from wood during pulping. Its exact mechanism of action is unclear from the experiments performed here with selected model compounds. However, the DMSO/alkali system produces several oxidation and reduction products of the models and of DMSO. The observed methyl sulfide addition products indicate that some DMSO is converted to CH$_3$S$^-$ during the high temperature reaction.

Part of DMSO's "delignification effect" might be attributable to the generated CH$_3$S$^-$, which is a known pulping aid. The conditions of pulping are strenuous enough that some dimsyl anions are probably generated; these anions can add to intermediate quinonemethides and possibly facilitate cleavage of neighboring interlinkage lignin bonds. Electron transfer reactions may be
important to efficient delignification.\textsuperscript{10} Dimethylsulfoxide, a frequently used solvent for electron transfer reactions,\textsuperscript{11} may facilitate delignification by promoting such reactions.

**EXPERIMENTAL**

The mass spectra were obtained with a Hewlett-Packard Model 5985 GC-MS spectrometer equipped with a 2' column packed with 3% OV-1 on Chrom WHP (100-120 mesh). The GC employed a helium flow of 30 mL/min and a temperature program as follows (unless stated otherwise): hold at 120°C for 3 min, raise at 25°C/min to a final temperature of 285°C.

**Standard Procedure.** - Low temperature reactions were done in small round-bottomed flasks under a nitrogen atmosphere and agitation with a magnetic stirring bar. High temperature reactions were done in 5.5 mL capacity stainless steel bombs; the reactants were placed in the bomb, flushed with nitrogen, sealed, and immersed in a thermostatically controlled oil bath set at 153°C for 1 hr. Reactions were worked-up by cooling, neutralizing with 3M HCl, and extracting (2-3 times) with small amounts of CHCl\textsubscript{3}; the combined chloroform solutions were washed several times with water, dried (Na\textsubscript{2}SO\textsubscript{4}), filtered, and analyzed by GC-MS.

**Degradation of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2'-methoxyphenoxy)-1-propanol (1).** - The standard procedure described above was employed for a 1 hr, 153°C degradation of 10 mg of model 1\textsuperscript{12} with 100 mg of NaOH in 3 mL of 50/50 DMSO-water. The GC-MS analysis showed starting material (1), guaiacol (2), and isoeugenol (3) as major components of the product mixture. Their presence was confirmed by comparing GC retention times and mass spectra with authentic samples. Several minor components were also present. One, with a retention time a little longer than isoeugenol, was assigned structure 4, 1-(4'-hydroxy-3'-methoxyphenyl)-2-propanone, based on a molecular ion at m/e 180 (20%) and a base peak at m/e 137, which could be the benzyl ion from C\textsubscript{1}-C\textsubscript{2} bond cleavage; however, the m/e signal, expected for CH\textsubscript{3}CO\textsuperscript{+}, was rather weak (7%). A small component preceding model 1 in the GC displayed a
m/e 286 ion which would correspond to the molecular weight of vinyl ether 5.

Degradation of 1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2'-methoxyphenoxo)ethanol (6). - The standard procedure was employed for a 2 hr, 153°C degradation of 0.10 g of model 612 with 0.32 g of NaOH in 3 mL of water and 0.15 mL of DMSO. The three major product components, identified by comparison to authentic samples, were guaiacol (2.0 min), vinyl ether 10 (8.4 min), and 6 (8.6 min). Minor components consisted of: acetoguaiacone (7) (4.1 min), m/e 166 (45%, M+), 151 (100%, ArCH2+) and 123 (25%, Ar+); methyl 4-hydroxy-3-methoxybenzyl sulfide (8) (5.0 min), m/e 184 (45% M+) and 137 (100%, ArCH2+); methyl 4-hydroxy-3-methoxy-α-methylbenzyl sulfide (9) (5.1 min), m/e 198 (13%, M+) and 151 (100%, ArCHCH3).

A corresponding degradation using 0.168 g of dimethylsulfone, 0.100 g of model 6 and 0.321 g of NaOH in 3 mL of water gave a product mixture containing model 6, vinyl ether 10, and guaiacol. Even with selected ion monitoring (SIM), products analogous to sulfides 8 and 9 were not detected. The same set of products in roughly the same ratios were observed when model 6 was degraded in the absence of either dimethylsulfone or DMSO.

Methyl 4-Hydroxy-3-methoxybenzyl Sulfide (8). - In a RB flask fitted with a condenser, magnetic stirring bar, nitrogen inlet/outlet, dropping funnel and two traps (one aq. KMnO4 and the other sat. aq. Pb(OAc)2 to capture CH3SH), was added 25 mL of water, and 1.3 g (1 equiv.) of 2-methyl-2-thiopseudourea sulfate. A solution of 0.56 g of NaOH in 20 mL of water was slowly dripped into the stirred, 60°C solution to generate CH3SNa. After stirring an additional 15 min at 60°, the solution was cooled to room temperature and 1 g of 4-acetoxy-3-methoxybenzyl chloride (14)7 in 20 mL of dioxane was added dropwise. After stirring for 90 min, the solution was acidified and extracted with CHCl3. Analysis of the CHCl3 extract showed only two signals; one corresponded to 14 and the other to methyl 4-acetoxy-3-methoxybenzyl sulfide (16): MS m/e 214 (3% M+), 184 (4%, M-ketene) and 137 (100%, ArCH2+–ketene).
A portion of the CHCl₃ solution of the odorous 14 was evaporated and taken up in CH₃OH. The methanol solution was stirred at 60°C with 15 mL of 1N NaOH for 90 min, cooled, acidified and extracted with CHCl₃. Analysis of the CHCl₃ extract by GC-MS showed two principal components in nearly equal amounts; one corresponded exactly in GC retention time and MS to sulfide 8 observed in the previous reaction. The other appeared to be methyl 4-hydroxy-3-methoxybenzyl ether: m/e 168 (38%, M⁺), 167 (12%, M⁻1), 137 (100%, ArCH₂⁺) and 122 (21%).

**Methyl 4-Hydroxy-3-methoxy-α-methylbenzyl Sulfide (9).** - A procedure similar to that described above was employed to treat 0.314 g of 4-acetoxy-3-methyl-α-methylbenzyl chloride (15) with 6 equiv. of in situ generated CH₃SNa. The workup of the reaction afforded the desired product directly, i.e., no hydrolysis was needed. The major component of the odorous product mixture corresponded exactly in GC retention time and MS to the sulfide (9) observed in the degradation of model 6. Two minor low retention compounds were also observed: 29, MS m/e 150 (100%, M⁺), 135 (96%, M⁻15), 107 (41%) and 77 (54%) and α-methyl-4-hydroxy-3-methoxybenzyl alcohol, MS m/e 168 (50%, M⁺), 153 (78%, M⁻15) and 93 (100%).

**Methyl 4-Hydroxy-3,5-dimethoxybenzyl Sulfide (24).** - A procedure identical to that described above was employed using 30 mg of 4-acetoxy-3,5-dimethoxybenzyl chloride. The latter was prepared by treating syringyl alcohol with acetylchloride: ¹H-NMR δ (CDCl₃) 2.32 (s, 3, Ac), 3.82 (s, 6, OCH₃), 4.54 (s, 2, -CH₂Cl) and 6.63 (s, 2, aryl); IR (mull) 1760 cm⁻¹ (ester C=O). Analysis of the sulfide addition product mixture showed starting chloroacetate, MS m/e 202/204 (35%, M⁺) and 167 (100%, ArCH₂⁺) and sulfide 24, MS m/e 214 (19%, M⁺), 167 (100%, ArCH₂⁺) and 123 (14%).

**Degradation of p-Hydroxybenzyl Alcohol (18).** - The standard procedure was employed for a 1 hr, 153°C degradation of 0.1 g of 18 with 0.1 g of NaOH in 3 mL of 50/50 DMSO-water. Analysis of GC-MS showed only two main components: the low retention time
component was methyl-p-hydroxybenzyl sulfide (19), MS m/e 154 (21%, M+), 107 (100%, ArCH2+) and 77 (18%); the high retention time peak was bis-(p-hydroxyphenyl)methane (20), MS m/e 200 (74%, M+), 199 (31%, M-1) and 107 (100% ArCH2+).

Degradation of Syringyl Alcohol (21). - The standard procedure was employed for a 1 hr, 153°C degradation of 0.1 g of syringyl alcohol (21) with 0.1 g of NaOH in 3 mL of 50/50 DMSO-water. Analysis by GC-MS showed an abundant component at 9.8 min which corresponded to the dimer 25, MS m/e 320 (100%, M+), 289 (50%, M-CH3) and 167 (75%, ArCH2+), a moderate component (6.5 min) corresponding to sulfide 24, which had an identical retention time and MS to the material prepared above, and minor components at 3.7 min and 5.5 min corresponding to 2,6-dimethoxy-4-methyl phenol (22), MS m/e 168 (100%, M+) and 153 (61%, M-CH3), and syringaldehyde (23), MS m/e 182 (100%, M+) and 181 (65%, M-H).

A degradation of syringyl alcohol without DMSO or with dimethylsulfone gives the same product mixture except no sulfide 24 was observed.

Dimsyl Anion Reaction with Chloroacetate (14). - A mixture of 2.0 g (83 mmoles) of sodium hydride in 50 mL of freshly distilled DMSO (in dry glassware, under a nitrogen atmosphere) was stirred for 2 1/2 hr at 75°C, cooled to room temperature, and then 2.0 g (9 mmoles) of 4-acetoxy-3-methoxybenzyl chloride (14)7 dissolved in 10 mL of DMSO was added dropwise. After stirring overnight, the solution was poured into an excess of water, acidified with 3N HCl, and extracted with CHCl3. The combined CHCl3 extracts were washed with water, dried (Na2SO4), and evaporated. Analysis of the resulting residue showed only a single component, 4-vinylguaiacol (29), identical to an authentic sample; MS m/e 150 (100%, M+), 135 (75%, M-CH3), 107 (20%), and 77 (22%).

A similar reaction done with dimethylsulfone gave starting material (14) at 5.0 min in large amounts, 1,2-di(4-hydroxy-3-methoxyphenyl)ethane, MS m/e 274 (12%, M+) and 137 (100% ArCH2+), at 8.5 min in small-moderate amounts, and several minor components in the 8-11 min region.
Degradation of 1-Chloro-1-(4'-hydroxy-3'-methoxyphenyl)-2-(2"methoxyphenoxy)ethane (30). - A mixture of 302 mg (3 equiv.) of AHQ-diacetate in 40 mL of 75% DMSO-water, containing 301 mg (22 equiv.) of NaOH and 48.5 mg (1 equiv.) of cresol (internal standard), was stirred for 15 min at 25°C and then 120 mg (1 equiv.) of solid chloroacetate 3012 was added. Samples were withdrawn at various time intervals, worked-up in the standard manner and analyzed by GC-MS. Each sample contained 3-(o-methoxyphenoxy)-4-hydroxy-3-methoxyacetophenone (33). The level of 33 increased (relative to the cresol) with time.

Similar runs were done with higher and lower NaOH concentrations. The observed level of ketone 33 decreased with increasing base concentration. No ketone 33 was observed when dioxane was substituted for DMSO.

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