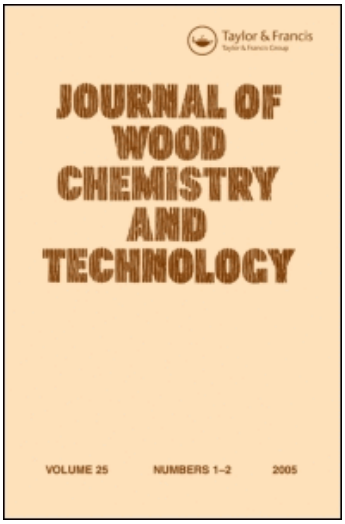

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PULPING CATALYSTS FROM LIGNIN (7). NITROGEN DIOXIDE OXIDATION OF A LIGNIN MODEL DIMER

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ABSTRACT

Oxidation of a lignin model disyringyl dimer with nitrogen dioxide (NO_2) in the presence of air and N-hydroxysuccinimide led to C_1-C_α cleavage with the formation of approximately equal amounts of 2,6-dimethoxy-*p*-benzoquinone (DMBQ) and glyceraldehyde-2-syringyl ether type structures. The result indicates that only the phenolic end syringyl units of a lignin polymer will be converted to DMBQ upon treatment with the current NO_2 reaction conditions. Internal (non-phenolic) lignin units, bonded by β-O-4 linkages, will resist oxidation.

INTRODUCTION

We have been investigating the feasibility of preparing low-cost anthraquinone (AQ) catalysts from lignin. The synthesis involves oxidation of lignin, or a lignin-related compound, to methoxy-substituted benzoquinones and then treatment of the latter with a diene (Diels-Alder reaction) to generate AQ-type structures (Figure 1).[1]

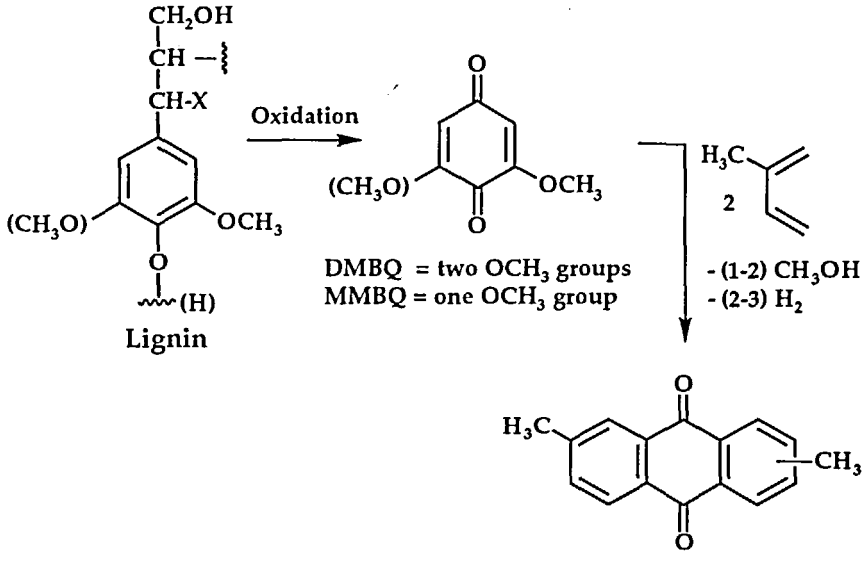


Figure 1. Chemical steps in the conversion of lignin to an AQ.[1]

Many phenolic syringyl lignin models (those having two CH_3O- groups per aromatic ring) have been oxidized to 2,6-dimethoxy-*p*-benzoquinone (DMBQ) in high (~90%) yields with nitrogen dioxide (NO_2) in the presence of air and N-hydroxysuccinimide (NHS).[2] The yields of DMBQ from lignin oxidations are much lower, typically 4-15% for a low-molecular-weight hardwood lignin and <4% for a high-molecular-weight lignin.[3] This result suggests that few of the internal (non-phenolic) lignin units are being oxidized. The present study addresses the issue of internal lignin unit reactivity in NO_2 oxidations.

RESULTS AND DISCUSSION

Model Selection and Synthesis

In order to establish the reactivity of internal lignin units, we decided to examine the yields of DMBQ that result from oxidation of

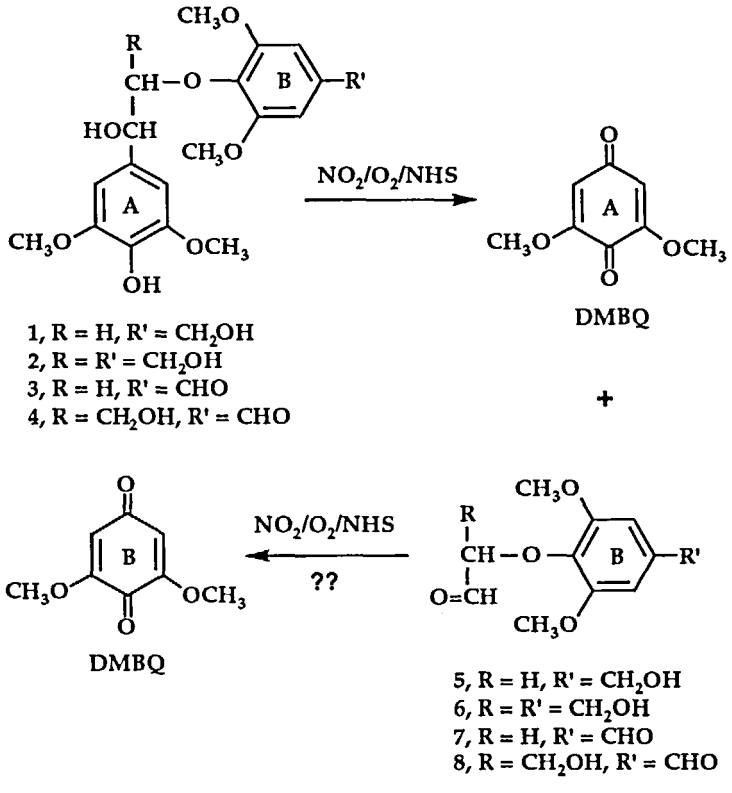


Figure 2. Potential NO_2 oxidation reactions of syringyl-syringyl dimers.

syringyl-syringyl dimers, such as **1-4**, Figure 2. The dimer was expected to give one equivalent of DMBQ from oxidation of the phenolic A-ring unit. We anticipated that the other oxidation product would be a non-phenolic structure (such as **5-8**) composed of the B-ring joined to the A-ring side chain. The question was whether this structure would also be oxidized under the reaction conditions to give another equivalent of DMBQ. If the dimer provided two equivalents of DMBQ upon treatment with NO_2/NHS, we rationalized that internal (non-phenolic) lignin units would also be susceptible to oxidation by NO_2. A syringyl-type dimer was selected for study because DMBQ yields are high from

the NO_2 oxidations of syringyl compounds, while monomethoxybenzoquinone (MMBQ) yields are generally low for the corresponding oxidation of guaiacyl units.[2,4]

We first attempted a synthesis of the β-O-4 dimer **1**, using the synthetic route shown in Figure 3. β-Bromoacetosyringone (**9**) was coupled with sodium 4-formyl-2,6-dimethoxyphenoate (**10**) to get β-(4'-formyl-2',6'-dimethoxyphenoxy)acetosyringone (**11**) in 66% yield, and $NaBH_4$ reduction of **11** gave **1** in 72% yield. Various attempts to obtain a pure product were not successful. Analysis of the synthesized dimer by NMR indicated a purity of about 90%.

Syringyl-syringyl dimer **2** was prepared in 52% overall yield by the reactions shown in Figure 4. Compound **2** has been prepared by Miksche in 1973;[5] however, we selected a route analogous to that employed by Katayama et al. to prepare guaiacyl dimers.[6] The key step in the synthesis involved condensing 4-O-benzyl syringaldehyde (**12**) with ester acetal **13**. The acetal group in **13** prevents self condensation in the presence of base; the benzyl group in **12** prevents ionization of the phenolic-OH in base and thereby facilitates a nucleophilic addition to the aldehyde group.

The ester acetal **13** and the resulting condensed acetal product were unstable; Katayama et al. observed similar instabilities in the guaiacyl analogs.[6] Each acetal was carried into the next step soon after preparation. Consequently, the dimer product from condensing **12** with acetal **13** was not characterized, but immediately hydrolyzed with acid to give a 7:1 mixture of stable erythro/threo aldehydes (**14e/14t**). Column chromatography resulted in partial separation of the two aldehydes. The minor threo isomer was easily crystallized; the major erythro isomer was about 95% pure; further purification attempts were not successful.

The synthesis of **2e** and **2t** was completed by reduction of the carbonyl groups in **14e** and **14t** with lithium aluminum hydride and removal of the benzyl protecting groups by hydrogenation. The threo isomer again crystallized; it had a sharp melting point (equal to a literature value). The erythro isomer, a solid with a broad melting point range, again resisted various recrystallization attempts. This isomer is

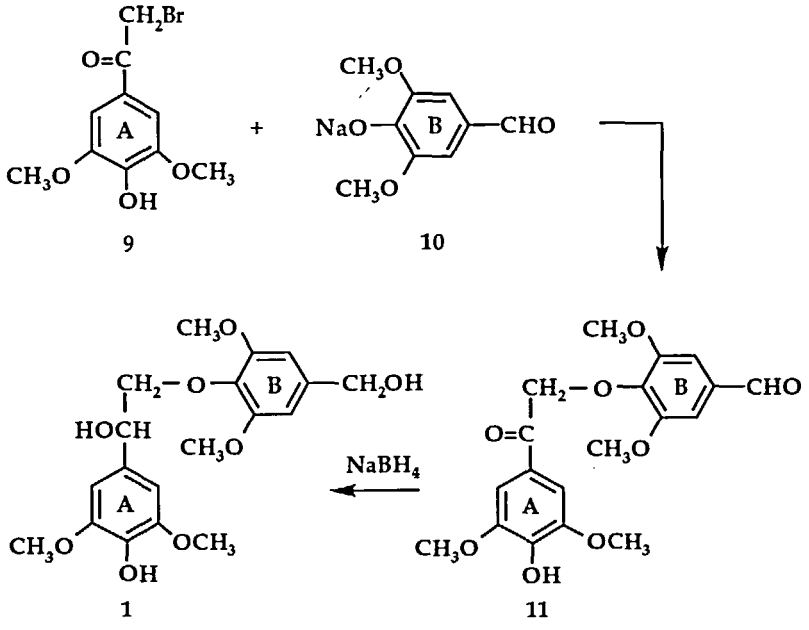


Figure 3. Synthesis of the β-O-4 dimer **1**.

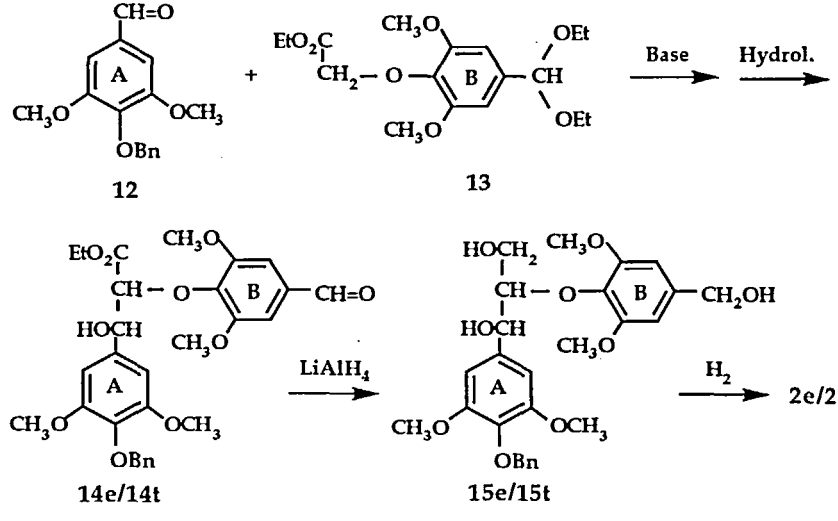


Figure 4. Synthesis of lignin model dimer **2**.

Table 1. Yields of DMBQ from the NO_2 Oxidations of Dimers **1** and **2**, and Selected Monomeric Models.[a]

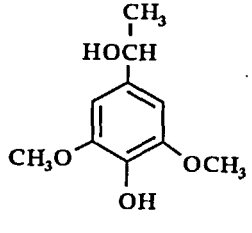
Compound	DMBQ Yield (%)
Dimer **1**	~37[b]
Dimer **2e**	37, 38[c,d]
Dimer **2t**	44, 46[c,d]
α-Methylsyringyl Alcohol **16**	88
3,4,5-Trimethoxybenzyl Alcohol **17**	0

[a]In air with an excess of NO_2 and NHS in methanol at 22°C for 2 hours. [b]The reported yield was obtained by dividing the observed 33% yield by the purity (estimated by NMR to be ~90%). [c]Duplicate determinations. [d]If both syringyl units had been completely converted to DMBQ, the yield would be 100%; if one had been completely converted, then 50%.

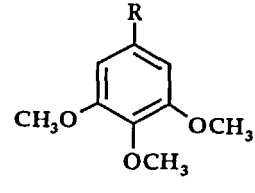
reported to be difficult to purify.[7] NMR analysis, indicated that the compounds were ≥95% pure.

DMBQ Yields from NO_2 Oxidations

The syringyl dimers **1** and **2**, along with selected monomeric compounds (**16** and **17**), were oxidized with NO_2/NHS. The yields of DMBQ, as shown in Table 1, were similar for dimers **1** and **2** , namely



16



17, R = CH_2OH
18, R = CHO
19, R = CH_2OCH_3

~40 mole % (~0.8 equiv. of DMBQ/dimer model). The yield difference between the two isomers of **2** was probably due more to a stereochemical difference than to a possible purity difference.

The DMBQ yields from oxidation of the dimers fit predictions based on the oxidation results of monomers **16** and **17**. The phenolic model, α-methylsyringyl alcohol (**16**), gave an 0.88 equiv. of DMBQ, while the non-phenolic model, 3,4,5-trimethoxybenzyl alcohol (**17**), provided no DMBQ. The former mimics the A-ring and side chain, while the latter mimics the non-phenolic B-ring of the dimer models. If we consider that the dimers are composed of a "combination" of **16** and **17**, the ceiling yield of DMBQ from the dimer should be ~45%.

Gas chromatography/mass spectroscopy (GC/MS) analysis of the NO_2 reaction solution from the non-phenolic model **17** showed starting material (60%) and a signal (40%) which contained two components: an oxidation product 3,4,5-trimethoxybenzaldehyde (**18**) and an (acid-catalyzed) solvent reaction product 3,4,5-trimethoxybenzyl methyl ether (**19**). The results indicate that a free phenolic hydroxyl group in the substrate is needed for DMBQ production and that the NO_2 conditions result in some benzyl alcohol oxidation to an aldehyde.

Other Dimer Oxidation Products

Apart from DMBQ, the product mixture from oxidation of dimer **2** contained two other principal components: non-phenolic compounds **6** and **8**, that are from the B-ring portion of the molecule. The structures of these components were established by GC/MS and by conversion of the components to a product (**21**) that was synthesized by a separate route, as shown in Figure 5. The product mixture containing **6** and **8** was treated with sodium borohydride to reduce the aldehyde groups in each component to alcohols, giving rise to the same product (**21**). The three component product mixture (DMBQ, **6** and **8**) became a two component mixture (reduced DMBQ and **21**). Compound **21** was identical to that prepared by coupling α-chloro diethyl malonate with syringaldehyde, followed by $LiAlH_4$ reduction.

The production of aldehydes **6** and **8** indicates that cleavage has occurred between C_1-C_α, without other alterations of the side chain. A

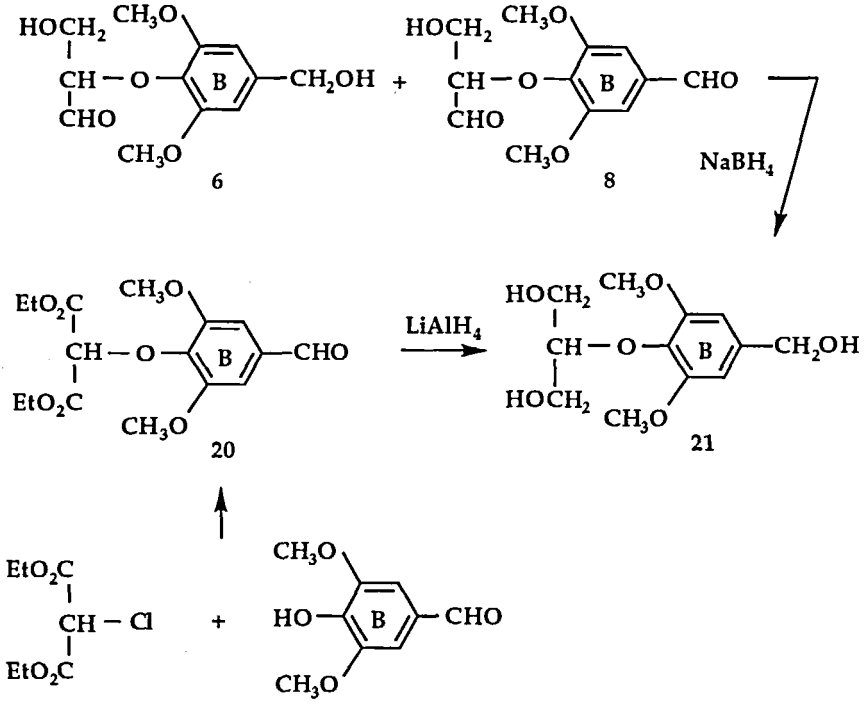
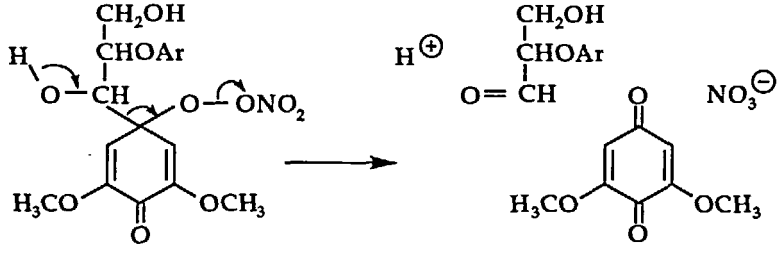


Figure 5. Structural confirmation of oxidation products 6 and 8.

possible mechanism could involve cleavage of a nitrate ester[2] (Eq. 1). The dialdehyde component 8 probably is a secondary oxidation product of 6 or an oxidation of the A-ring -CH_2OH group before oxidative cleavage of dimer 2. Its formation is analogous to the NO_2 oxidation of the -CH_2OH group in the non-phenolic model 17 which gives rise to aldehyde 18.



Eq. 1

CONCLUSIONS

The results obtained from this investigation indicate that the NO_2 oxidation of an α-syringyl-β-syringyl ether glycerol lignin model dimer (**2**) leads to formation of DMBQ and glyceraldehyde-β-syringyl ether structures via a C_1-C_α cleavage. Under present reaction conditions, NO_2 does not oxidatively cleave non-phenolic model compounds; also, the β-O-4 linkages in model dimers are not broken. These conclusions suggest that only phenolic (terminal) syringyl units in a lignin macromolecule will be converted to DMBQ upon NO_2 oxidation. In order to significantly improve DMBQ yields from lignin by NO_2 oxidation, we apparently will have to degrade lignin into smaller pieces, either before or during the NO_2 oxidation. Such an approach is being taken.[3]

EXPERIMENTAL

The description of chromatography and NMR equipment and conditions were presented earlier.[2]

Synthesis of Lignin Model Compounds

Syringaldehyde, acetosyringone, 3,4,5-trimethoxybenzyl alcohol (**17**) and 3,4,5-trimethoxybenzaldehyde (**18**) are commercial products. α-Methylsyringyl alcohol (**16**)[8] was prepared by $NaBH_4$ reduction of acetosyringone in 80% yield; recrystallized from hexane/ethyl acetate gave mp 93-94°C (Lit.[9] mp 95-95.5°C). 4-O-Benzyl syringaldehyde (**12**) was prepared in 68% yield from syringaldehyde and benzyl bromide in the presence of potassium carbonate in ethanol and recrystallized from hexane/ethanol: mp 60-61°C (Lit.[9] mp 62.5°C); ^{1}H-NMR ($CDCl_3$) δ 3.90 (s, 6, 2 -OC<u>H</u>$_3$), 5.13 (s, 2, PhC<u>H</u>$_2$-), 7.12 (s, 2, Ar<u>H</u>), 7.27 - 7.50 (m, 5, <u>Ph</u>CH$_2$), and 9.87 (s, 1, -C<u>H</u>O).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-formyl-2',6'-dimethoxyphenoxy)ethanone (11). Syringaldehyde sodium salt (**10**) was prepared by freeze-drying an aqueous solution of syringaldehyde (12 g, 66 mmol) and NaOH (2.7 g, 67 mmol). β-Bromoacetosyringone (**9**) was prepared

in a manner analogous to the preparation of β-bromoacetoguaiacone;[10] 2.9 g (10 mmol) of 9 in 45 mL of DMF was added dropwise to a stirred solution of **10** (66 mmol) in 600 mL of DMF. The reaction conditions and work up were identical to that described for guaiacyl dimers prepared in a similar manner.[10] Column chromatography on silica gel provided 2.5 g (66% yield) of **11**: mp 152-5°C; ^{1}H-NMR ($CDCl_3$) δ 3.89 (s, 6, two -OC$\underline{H}_3$), 3.95 (s, 6, two -OC$\underline{H}_3$), 5.32 (s, 2, β-C$\underline{H}_2$), 7.15 (s, 2, Ar$\underline{H}$), 7.35 (s, 2, Ar$\underline{H}$), and 9.88 (s, 1, -C$\underline{H}$O).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-hydroxymethyl-2',6'-dimethoxyphenoxy)-1-ethanol (1). To a stirred solution of **11** (100 mg, 0.27 mmol) in 5 mL of ethanol was added an excess of $NaBH_4$ (130 mg, 3.4 mmol) in 5 mL of water. After 8 hr., another 100 mg (2.6 mmol) of $NaBH_4$ was added and stirring was continued overnight. The solution was neutralized by adding 6 N HCl to a pH of 2 and then extracted with chloroform. The extracts were combined and dried over Na_2SO_4, and evaporated to give 72 mg (72% yield) of an oily residue (**11**), that resisted crystallization from several solvent combinations: ^{1}H-NMR (acetone-d_6/D_2O) δ 3.68 (d of d, J = 9.3 and 10.6 Hz, 1, β-C$\underline{H}_A$H$_B$), 3.81 (s, 6, two -OC$\underline{H}_3$), 3.87 (s, 6, two -OC$\underline{H}_3$), 4.23 (d of d, J = 3.2 and 10.6 Hz, 1, β-CH$_A$$\underline{H}_B$), 4.59 (s, 2, ArC$\underline{H}_2$OH), 4.80 (d of d, J = 9.3 and 3.2 Hz, 1, α-C$\underline{H}$OH), 6.71 (s, 2, Ar$\underline{H}$), and 6.75 (s, 2, Ar$\underline{H}$).

Ethyl 4-diethylacetal-2,6-dimethoxyphenoxyacetate (13). A mixture of syringaldehyde (6.94g, 37 mmol), ethyl chloroacetate (5.86, 47 mmol), K_2CO_3 (6.49 g, 47 mmol), and KI (0.78 g, 4.7 mmol) in 100 mL of acetone was stirred at room temperature for 2 hr. The inorganics were filtered off and washed with ethyl acetate. The filtrates and washings were combined and concentrated. The residue was dissolved in ethyl acetate, washed with water, dried over Na_2SO_4, concentrated, and dissolved in 20 mL of anh. ethanol.

To this solution was added triethyl orthoformate (56 g, 370 mmol) and *p*-toluenesulfonic acid (110 mg). After stirring for 30 min, the mixture was neutralized by the addition of $NaHCO_3$. The excess $NaHCO_3$ was removed by filtration and washed with ethyl acetate. The filtrates and washings were combined and concentrated. The residue was dis-

solved in ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated with first a simple vacuum evaporation and then with high vacuum. Analysis by TLC showed one principal component, presumedly the acetal **13**, and only minor impurities. The acetal **13** was unstable, even towards crystallization from ethanol and, therefore, was used quickly after preparation without purification.

Ethyl 1 - (4'-formyl-2',6'-dimethoxyphenoxy) - 2 - (4-benzoxy-3,5-dimethoxyphenyl) - 2 - hydroxypropanoate (14). To a stirred solution of 1.34 g (13 mmole) of diisopropylamine (freshly distilled from sodium metal) in 20 mL of anh. THF (freshly distilled from $LiAlH_4$) was added dropwise 5.4 mL (13 mmole) of a solution of 2.5 M n-butyllithium in hexane at 0°C under nitrogen. After another 30 min at 0°C, the resulting lithium diisopropylamine solution was cooled to -78°C and stirred while 3.56 g (10 mmole) of **13** in 20 mL of anh. THF was added dropwise at -78°C. Thirty minutes later, a solution of benzyl syringaldehyde **12** (2.45 g, 9 mmole) in 20 mL of anh. THF was added dropwise to the stirred -78°C solution. After stirring for additional 90 min at -78°C, the reaction solution was neutralized by the addition of powdered dry ice and partitioned between ethyl acetate and water. The aqueous layer was extracted twice with ethyl acetate. The combined ethyl acetate extracts was stirred for 2 hr with 1 N HCl solution in order to hydrolyze the acetal dimers contained in the ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to yield 6.6 g of crude product.

Analysis of the product mixture by TLC showed one major component, without any significant amount of remaining starting materials. The major component was most likely an erythro/threo mixture of the desired product. Silica gel column chromatography, with solvent elution by methylene chloride/ethyl acetate (4:1), was used to give 2.3 g (70% yield) of **14e** and 0.3 g (10% yield) of **14t**. The latter was recrystallized from ethyl acetate/hexane: mp 126-8°C; ^{1}H-NMR ($CDCl_3$) δ 1.04 (t, 3, -$CH_2\underline{CH_3}$), 3.79 (s, 6, two -$OC\underline{H_3}$), 3.93 (s, 6, two -OCH_3), 3.98-4.06 (two q, 2, -$\underline{CH_2}CH_3$), 4.19 (d, 1, β-C$\underline{H}$), 4.97 (s + d, 3, α-C$\underline{H}$ and $PhC\underline{H_2}$-), 6.56 (s, 2, Ar$\underline{H}$), 7.16 (s, 2, Ar$\underline{H}$), 7.3-7.5 (m, 5, $\underline{Ph}CH_2$), and 9.90 (s, 1, -C$\underline{H}$O). The

14e spectra: ^{1}H-NMR ($CDCl_3$) δ 1.07 (t, 3, -$CH_2C\underline{H}_3$), 3.83 (s, 6, two -$OC\underline{H}_3$), 3.93 (s, 6, two -$OC\underline{H}_3$), 4.05-4.10 (two q, 2, -$C\underline{H}_2CH_3$), 4.82 (d, 1, β-C$\underline{H}$), 4.99 (s + d, 3, α-C$\underline{H}$ and Ph$C\underline{H}_2$-), 6.68 (s, 2, Ar$\underline{H}$), 7.17 (s, 2, Ar$\underline{H}$), 7.3-7.5 (m, 5, $\underline{Ph}CH_2$), and 9.90 (s, 1, -C$\underline{H}$O).

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-(4'-hydroxymethyl-2',6'-dimethoxyphenoxy)-1,3-propandiol (2). Compound **14**, erythro (1.2 g, 3.2 mmol) or threo (150 mg, 0.4 mmol), was dissolved in anh. THF and added to a stirred solution of $LiAlH_4$ (6 equiv.) in anh. THF at 50°C under nitrogen. After 1 hr, ethyl acetate was added to destroyed the excess $LiAlH_4$. The reaction mixture was neutralized with 1 N HCl and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated to give an oil (**15e** or **15t**) which was dissolved in methanol and stirred with 10% palladium/charcoal and hydrogen (1 atm) at room temperature until hydrogen consumption ceased. After 30 min, the catalyst was filtered off and washed with methanol. The filtrate and the washings were combined, concentrated, and chromatographed on a silica gel column with chloroform containing 5% methanol.

In the erythro isomer case, we obtained 630 mg (69% yield) of **2e**, a white solid that could not be successfully recrystallized: ^{1}H-NMR (acetone-d_6/D_2O) δ 3.40 (d of d, 1, γ-C$\underline{H}_A$$H_B$OH), 3.79 (s, 6, two -$OC\underline{H}_3$), 3.84 (s, 6, two -$OC\underline{H}_3$), 3.86 (shoulder on the large 3.84 signal, assumed to be d of d, 1, γ-$CH_A\underline{H}_B$OH), 4.12-4.16 (m, 1, β-C$\underline{H}$), 4.56 (s, 2, Ar$C\underline{H}_2$OH), 4.96 (d, 1, α-C$\underline{H}$OH), 6.70 (s, 2, Ar$\underline{H}$), and 6.73 (s, 2, Ar$\underline{H}$). In the threo isomer case, we obtained 71 mg (62% yield) of **2t**: mp 153-4°C, from ethyl acetate/ hexane, (Lit.[5] mp 154-5°C); ^{1}H-NMR (acetone-d_6/D_2O) δ 3.27 (d of d, 1, γ-C$\underline{H}_A$$H_B$OH) and 3.65 (d of d, 1, γ-C$\underline{H}_A$$H_B$OH), 3.77 (s, 6, two -$OC\underline{H}_3$), 3.85 (s, 6, two -$OC\underline{H}_3$), 3.88-3.92 (m, 1, β-C$\underline{H}$), 4.54 (s, 2, Ar$C\underline{H}_2$OH), 4.95 (d, 1, α-C$\underline{H}$OH), 6.72 (s, 2, Ar$\underline{H}$), and 6.74 (s, 2, Ar$\underline{H}$). Previous NMR spectra for **2e** and **2t** report only the tetraacetate derivatives.[4,11]

3,4,5-Trimethoxybenzyl methyl ether (19). A solution containing syringyl alcohol (**7**) (420 mg, 2 mmol), 4 mL of dioxane, 4 mL of 4 N NaOH, and 4 mL (40 mmol) of dimethyl sulfate was stirred at room temperature overnight. The pH of the mixture was maintained near

11 by adding 4 N NaOH. After acidification with HCl, the mixture was extracted with chloroform. The organic layers were dried over Na_2SO_4 and concentrated to yield a pale yellow oil material. Silica gel column chromatography with toluene/ethyl acetate gave 370 mg (87% yield) of a pale yellow oil, compound **19**: ^{1}H-NMR ($CDCl_3$) δ 3.42 (s, 3, ROC<u>H</u>$_3$), 3.84 (s, 3, ArOC<u>H</u>$_3$), 3.87 (s, 6, two ArOC<u>H</u>$_3$), 4.39 (s, 2, -C<u>H</u>$_2$OCH$_3$), and 6.57 (s, 2, Ar<u>H</u>); MS *m/z* (%) 212 (M^+, 88), 197 (10), 181 (100), 169 (17), 151 (14), 138 (20), 123 (7), 111 (7), 95 (9), 77 (9), 66 (7), and 53 (9).

Diethyl 2-(4-formyl-2,6-dimethoxyphenoxy)malonate (20). The sodium salt of syringaldehyde was prepared by freeze-drying an aqueous solution containing 3.14 g (16 mmole) of syringaldehyde and 0.69 g (17 mmole) of NaOH. To a stirred solution of 4.05 g (21 mmole) of diethyl chloromalonate in 20 mL of DMF at 60°C was added dropwise 15 mL DMF containing the syringaldehyde sodium salt. The mixture was allowed to stir for another 1 hr at 60°C, then poured into 100 mL ice water, neutralized with 4 N HCl solution, and finally extracted with chloroform. The chloroform extract was washed with 1 N NaOH solution, dried over Na_2SO_4, and evaporated. The residue was chromatographed on a silica gel column using ethyl acetate/hexane as solvent to obtain 4.2 g (77% yield) of a pale yellow oil, which resisted crystallization. The ^{1}H-NMR showed a single product: ($CDCl_3$) δ 1.30 (t, 6, -CH$_2$C<u>H</u>$_3$), 3.89 (s, 6, two -OC<u>H</u>$_3$), 4.31 (two q or a finely split q, 4, -C<u>H</u>$_2$CH$_3$), 5.28 (s, 1, -C<u>H</u>-), 7.13 (s, 2, Ar<u>H</u>), and 9.88 (s, 1, -C<u>H</u>O).

2-(4-Hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propandiol (21). Compound **20** from above was reduced by $LiAlH_4$, following the same procedure used for compound **14**. The reduced product was purified by silica gel column chromatography with chloroform containing 10% methanol. ^{1}H-NMR (acetone-d_6/D_2O) δ 3.72-3.75 (m, 4, -C<u>H</u>$_2$OH), 3.86 (s, 6, two -OC<u>H</u>$_3$), 3.97 (p, 1, -C<u>H</u>-), 4.58 (s, 2, ArC<u>H</u>$_2$OH), and 6.75 (s, 2, Ar<u>H</u>); MS *m/z* (%) 258 (M^+, 15), 184 (100), 167 (14), 155 (9), 123 (14), 109 (11), 95 (6), 81 (5), 65 (2), and 53 (3).

Nitrogen Dioxide Oxidations

NO_2 Oxidation of 3,4,5-trimethoxybenzyl alcohol (17). The standard NO_2/NHS oxidation conditions[2] with **17** provided a product mix-

ture showing one principal GC signal (40%), besides that of the starting material (60%). The new GC signal was not symmetrical, suggesting that there were two components. Analysis by GC-MS indicated that the signal was a mixture of 3,4,5-trimethoxybenzaldehyde (**18**) and 3,4,5-trimethoxybenzyl methyl ether (**19**). A direct comparison of GC retention time and mass spectra with authentic samples of **18** and **19** confirmed the structural assignments. Compound **18** was available as a commercial product; compound **19** was synthesized, as described above.

NO_2 Oxidation of Dimer 2e and 2t. The standard NO_2/NHS oxidation conditions[2] with either dimer **2e** or **2t** provided a product mixture showing three principal GC signals: DMBQ at retention time 6.3 min, compound **8** at 9.5 min, and compound **6** at 11.3 min. The preliminary structural assignments for **6** and **8** were based on mass spectral data: **3-hydroxy-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)propanal (6)** *m/z* (%) 256 (M^+, 33), 226 (12), 197 (3), 183 (100), 168 (33), 155 (18), 127 (40), 109 (10), and 95 (18), and **3-hydroxy-2-(4-formyl-2,6-dimethoxyphenoxy)propanal (8)** *m/z* (%) 254 (M^+, 27), 224 (7), 195 (3), 181 (100), 166 (29), 153 (9), 125 (14), 107 (9), and 93 (9).

The crude product was dissolved in ethanol and stirred with an excess of $NaBH_4$ (100 mg) for 2 hr. The solution was neutralized by adding 1 N HCl and then extracted first with chloroform and then with ethyl acetate. The extracts were combined and dried over Na_2SO_4. An examination of the solution by GC showed that components **6** and **8** had been converted to a single component of retention time 12.4 min. A GC-MS indicated that this compound was 2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propandiol (**21**). This compound was identical in GC retention time and MS to a synthesized sample of **21**.

NO_2 Oxidation of Dimer 1 and Compound 16. The standard NO_2/NHS oxidation conditions[2] were employed with each substrate; only the yields of DMBQ were examined.

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