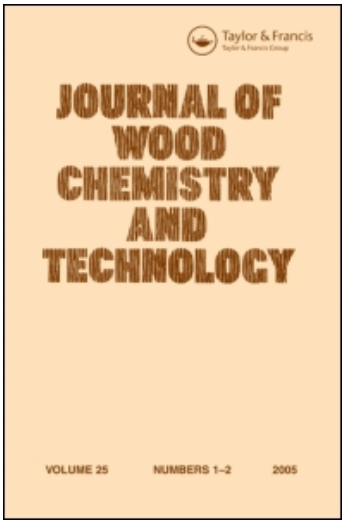

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R. G. Hise[ab]; C.-L. Chen[a]; J. S. Gratzl[a]
[a] Department of Wood and Paper Science, North Carolina State University, Raleigh, North Carolina, USA [b] Westvaco Corporation, Charleston Research Center, North Charleston

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SYNTHESIS OF BETA-ARYL LIGNIN MODEL COMPOUNDS

R. G. Hise*, C.-L. Chen and J. S. Gratzl
Department of Wood and Paper Science
North Carolina State University
Raleigh, North Carolina, USA 27695-8005

ABSTRACT

A Claisen-Schmidt type aldol addition reaction was used to synthesize erythro- and threo-ethyl-3-hydroxy-3-(4-benzyloxy-3-methoxyphenyl)-2-phenylpropanoate (1a, 1b) and erythro-2,3-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (9). The key aldol addition step was facilitated by adding a molar equivalent of Zn (II) cations to stabilize the addition product, thus inhibiting the reverse aldol reaction. This allowed the reaction to be carried out at moderate temperatures (-20 to 0°C) and rather short reaction times (10 to 20 minutes). The H-alpha—H-beta coupling constants in the PMR spectra were used for assignment of the stereoisomers.

INTRODUCTION

With about 16-20% of the monomeric lignin units linked by carbon-carbon bonds from the β-carbon of the propyl side chain to either C-1 (β-1 type) or C-5 (β-5 type) of the aromatic ring of another unit, these substructures represent a major portion of structural elements of softwood lignins.[1,2]

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* Present address: Westvaco Corporation, Charleston Research Center, Box 5207, North Charleston, SC 29406.

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Previous work on phenylcoumaran models for β-5 substructures has shown that the carbon-carbon interunit linkages are virtually stable under conventional soda and kraft pulping conditions, while carbon-carbon bonds along the propyl side chain suffered minor fragmentations.[3,4] As a consequence of their stability and abundance, one may assume that carbon-carbon linked substructures place certain restrictions on rate and extent of lignin removal and may be in part responsible for the rather incomplete delignification in conventional alkaline pulping processes.

Model studies performed in our laboratory on soda-anthraquinone (AQ) pulping demonstrated clearly that hydroxyl groups in α and γ positions in side chains are oxidized to the corresponding carbonyls and thus facilitate base-catalyzed hydrolytic carbon-carbon bond cleavage.[5] This observation led us to the speculation that such oxidative-hydrolytic splitting may contribute to the substantially enhanced fragmentation and removal of lignin in alkaline pulping in presence of AQ. In order to gain a more detailed understanding of the principal mechanisms involved, we have selected C-1 type models for further investigations. The compounds offer the advantage of avoiding complications one would expect to encounter from models with arylether linkages due to their instability towards base catalyzed splitting reactions.

The objective of the present study was to develop a procedure whereby significant quantities of β-1 model compounds could be synthesized. When this work began, three syntheses for β-1 diols had been published.[6,7,8] Since then, three others have been reported.[9,10,11] The procedure described in the following represents an attempt to shorten and simplify the method by Nakatsubo and Higuchi[7] by incorporating a modification published by House.[12]

DISCUSSION

An aldol type addition constitutes the key step in almost all of the syntheses known for β-1 diol model compounds. The basic differences among the procedures arise from the techniques used

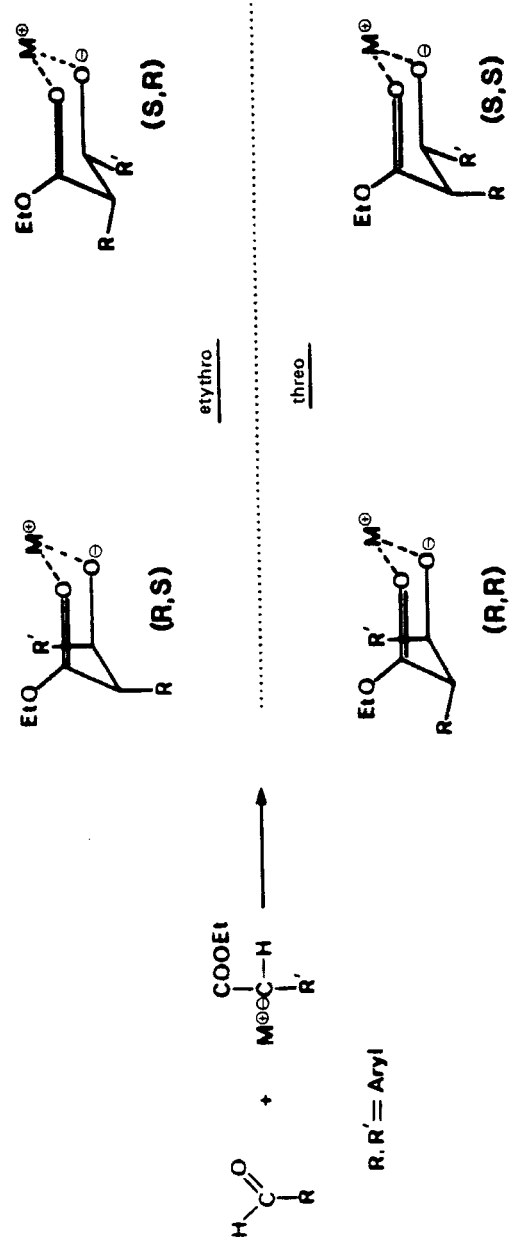
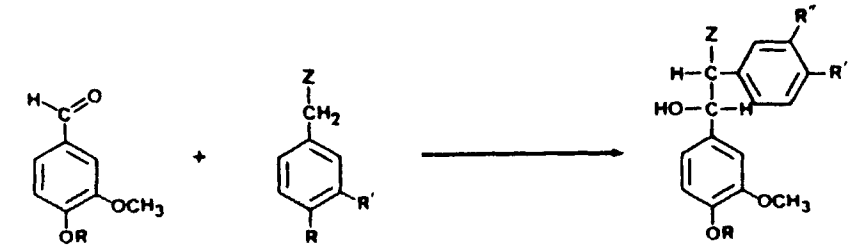


Figure 1. Possible Diastereoisomerism for Intermediates of Aldol Addition Reaction.

for stabilizing the initially formed addition product, which is generally less stable than either reactant. Various means for displacing the unfavorable equilibrium that exists between the forward and reverse reactions have been employed. At sufficiently low temperatures and in non-polar solvent systems it has been shown that a metal cation can form a rather stable chelate with the addition product, thus inhibiting the reverse reaction.[12] Nakatsubo and Higuchi[7] employed this concept by pre-forming the enolate with a lithium amide base and then adding the electrophilic carbonyl component very slowly at -70°C. The addition product reportedly formed a six-member cyclic metal chelate with the lithium cation (Figure 1) leading to high yields. Following this procedure on a larger scale and with 4-benzyloxy-3-methoxybenzaldehyde (3) rather than 4-benzyloxy-3,5-dimethoxybenzaldehyde (3a) as the carbonyl component (Figure 2), we obtained only very poor yields. Since the chelate forming property of metal ions improves with increased charge to mass ratio, cations with small ionic radii (around 0.7°A) such as Mg^{++} and Zn^{++} are, according to House,[12] even more effective than Li^{+} at trapping the adduct. By employing $ZnCl_2$ we were able to carry out the synthesis at somewhat more moderate temperatures (-20-0°C) and drastically shorter reaction times (10 minutes versus 5 hours). The yields obtained were still rather moderate.

House et al[12] found that the maximum number of substituents on the intermediate six-member cyclic metal chelate tend to occupy equatorial positions. This suggests the erythro-form[13] should predominate for these model compounds on thermodynamic considerations alone.

House also demonstrated that the initially formed ester addition product (such as 1 and 7), through intramolecular hydrogen bonding may also form a six-member ring (in non-polar, aprotic solvent systems). The stereochemistry of the two possible configurational isomers can often be assigned based on the magnitude of the vicinal H-alpha—H-beta coupling constants in the PMR



3. R = $CH_2C_6H_5$, R′ = H

3a. R = $CH_2C_6H_5$, R′ = OCH_3

2. R, R′ = H, Z = $COOC_2H_5$

4. R = OH, R′ = OCH_3, Z = $COOCH_3$

5. R = OH, R′ = OCH_3, Z = COOH

6. R = $OCH_2C_6H_5$, R′ = OCH_3, Z = $COOCH_3$

1. R = $CH_2C_6H_5$, R′, R″ = H, Z = $COOC_2H_5$

7a,b. R = $CH_2C_6H_5$, R′ = $OCH_2C_6H_5$, R″ = OCH_3, Z = $COOCH_3$

8. R = $CH_2C_6H_5$, R′ = $OCH_2C_6H_5$, R″ = OCH_3, Z = CH_2OH

9. R = H, R′ = OH, R″ = OCH_3, Z = CH_2OH

Figure 2. General Scheme for Synthesis of β-1 Lignin Model Compounds.

spectra. The erythro-isomer (Figure 3) has the vicinal protons oriented trans diaxially, giving rise to a coupling constant on the order of 6-9 Hz. In contrast, the threo-isomer exhibits a much smaller coupling constant (2-4 Hz), as would be expected from the cis axial-equatorial interaction. This concept was employed in assigning the configuration of 1a and 1b; overlapping signals in critical regions prevented using this technique for assignment of compound 7, as noted in the Syntheses Section.

SYNTHESES

Ethyl-3-Hydroxy-3-(4-Benzyloxy-3-Methoxyphenyl)-2-Phenylpropanoate (1)

This compound was prepared according to Nakatsubo and Higuchi[7], using ethyl-2-phenylethanoate 2 and 4-benzyloxy-3-

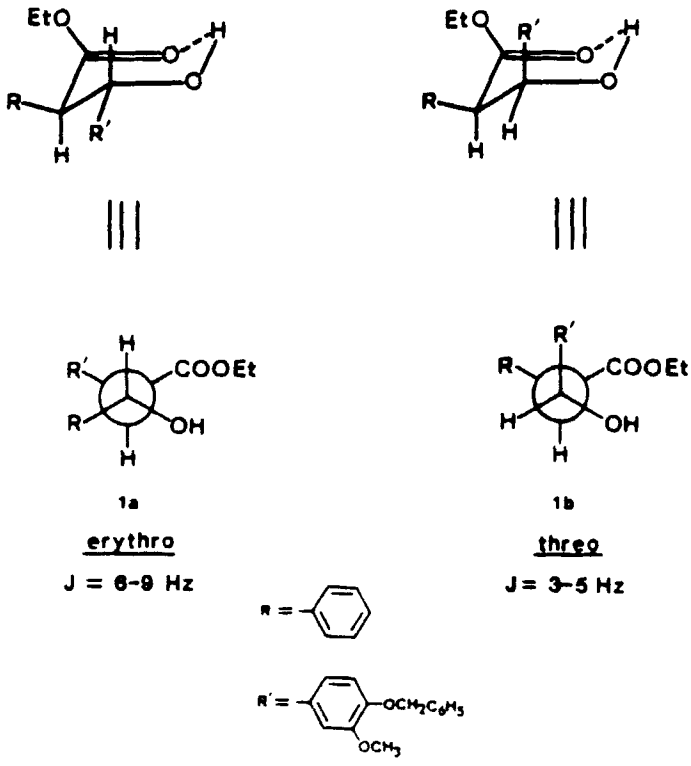


Figure 3. Relationship between Arrangement of Hydrogen Atoms on Vicinal Carbon Atoms and Observed Coupling Constants in PMR Spectra.

methoxybenzaldehyde 3 as starting materials. Crystals of the erythro-isomer 1a were obtained in about 15% yield of theoretical from the crude product after five weeks in the freezer. Separation of the mother liquor on a thick layer silica gel plate afforded a small amount of the threo-isomer 1b as a syrup.

1a. Erythro: m.p. 88-90°C. Elemental analysis: calc. for $C_{25}H_{26}O_5$; C%, 73.84, H%, 6.45. Found; C%, 73.77, H%, 6.48. MS: m/e(rel.int. with respect to m/e 243) 406(M^+,4), 243(100), 165(12), 164(63), 151(11), 136(21), 107(21), 105(18), 91(100),

77(30), 65(100). PMR ($CDCl_3$): δ 1.04(3H,t, J=8.0 Hz, $OCH_2\underline{CH_3}$), 3.76(1H,d, J=8.0 Hz, C-beta-H), 3.78(3H,s,$ArOCH_3$), 4.01(2H,q, J=8.0 Hz, OCH_2CH_3), 5.09(2H,s,Ar''CH_2OAr), 5.18(1H,d, J=8.0 Hz, C-alpha-H), 6.82(3H,broad s,ArH-2,5,6), 7.19-7.43(10H,m,Ar'H-2—H-6, Ar''H-2—H-6).

1b. Threo: PMR ($CDCl_3$): δ 1.20(3H,t, J=8.0 Hz, OCH_2CH_3), 3.70(3H,s,$ArOCH_3$), 3.72(1H,d, J=3.5 Hz, C-beta-H), 4.20(2H,q, J=8.0 Hz, OCH_2CH_3), 5.40(2H,s,Ar''CH_2OAr), 5.13(1H,d, J=3.5 Hz, C-alpha-H), 6.45-6.71(3H,m,ArH-2—H-6), 7.03-7.37(10H,m,Ar'H-2—H-6, Ar''H-2—H-6).

Methyl-2-(4-Hydroxy-3-Methoxyphenyl)Ethanoate (4)

Commercially available 2-(4-hydroxy-3-methoxyphenyl)ethanoic acid (5) (2.2g, 12.0 mM) was esterified using 14% (w/v) BF_3-MeOH solution (13.2 ml, 27.0 mM), following a procedure by Hallas[14]. The solution was refluxed for two hours, cooled and washed with 50 ml saturated $NaHCO_3$, and extracted with 3 x 20 ml of diethylether. After drying the combined organic phase overnight with $MgSO_4$ and filtering, the solvent was removed under vacuum, leaving a light brown syrup which crystallized slowly unless seeded. The crude crystals of methyl-2-(4-hydroxy-3-methoxyphenyl)ethanoate (4), obtained in 98% yield, were sufficiently pure to be used in the subsequent step. MS: m/e(rel.int.) 196(M^+,68), 137(100), 123(23), 94(18), 43(16). 108.6(M*,137-122), 95.8(M*,196-137). PMR (CD_3COCD_3): δ 3.48(2H,s,$ArCH_2COOCH_3$), 3.58(3H,s,$COOCH_3$), 3.68(3H,s,$ArOCH_3$), 5.53(1H,s,ArOH), 6.66-6.90(3H,m,ArH).

Methyl-2-(4-Benzyloxy-3-Methoxyphenyl)Ethanoate (6)

The ester was further derivatized by a standard benzylation procedure: to a stirred solution of 5.0 g (25.0 mM) of the methyl ester 4 described above in 30 ml acetone was added (in small portions) 3.75 g (27.0 mM) anhydrous K_2CO_3. Benzylchloride (3.75 g, 30.0 mM) was added dropwise over a period of one hour and the

solution was then refluxed for 8-10 hours. After removing the solvent in vacuo the residue was poured into 40 ml of 1N KOH in a separatory funnel. The mixture was agitated thoroughly, extracted several times with $CHCl_3$ and the combined organic phase was dried over Na_2SO_4. After filtering, the solvent was removed under vacuum and the resulting oil was crystallized from methanol. Yield of methyl-2-(4-benzyloxy-3-methoxyphenyl)ethanoate (6) was 61%; m.p. 60-62°C. MS: m/e(rel.int.) 286(M^+,20), 195(7), 151(3), 107(5), 91(100), 65(10), 59(5), 46.4(M*,91-65). PMR ($CDCl_3$): δ 3.51(2H,s,ArCH_2COOCH_3), 3.64(3H,s,COOCH_3), 3.84(3H,s,ArOCH_3), 5.10(2H,s,Ar'CH_2OAr), 6.64-6.87(3H,m,ArH), 7.21-7.46(5H,m,Ar'H). CMR (DMSO-d_6): δ 51.5(q,COOCH_3), 55.5(q,ArOCH_3), 69.9(t,C-alpha), 113.5(d,ArC-2,5), 121.2(d,ArC-6), 127.1-127.7(m,Ar'C-2 - C-6) 137.1(s,Ar'C-1), 137.2(s,ArC-1), 146.6(s,ArC-4), 148.9(s,ArC-3), 171.7(s,$COOCH_3$).

Methyl-3-Hydroxy-2,3-Bis(4-Benzyloxy-3-Methoxyphenyl) Propanoate (7)

The aldol addition step was based on a method published by House[12], which allows the reaction to be performed at more convenient temperatures and requires less time than other methods. All reagents were carefully purified and dried, glassware was dried in a 100°C oven for two days prior to use, and the reaction was conducted under nitrogen. Material transfers were either via a double needle technique or done in a dry box. Commercially available n-butyllithium (in n-hexane) was titrated by the method of Jones and Gilman[15] and used immediately.

Freshly distilled diisopropylamine (1.5 ml, 10.7 mmol) and 10 ml dry Et_2O were added to a 300 ml reaction flask. This solution was cooled to -15°C and 8.5 ml (10.5 mmol) of 1.24 M n-butyllithium solution was added quickly with stirring. After stirring for 10 minutes, a pre-cooled solution of 3.0 g (10.5 mmol) methyl-2-(4-benzyloxy-3-methoxyphenyl)ethanoate (6) in 75 ml dry Et_2O was added over one minute to the -15°C lithium

diisopropylamide solution. The temperature was allowed to rise to 0°C and stirring maintained for 10 minutes. Saturated (0.69 M) $ZnCl_2/Et_2O$ solution (7.6 ml. 10.5 mmol) was added slowly, and the temperature was lowered to -15°C. Dropwise addition of 2.54 g (10.5 mmol) 4-benzyloxy-3-methoxybenzaldehyde (3) (Aldrich Chemical Co.) in Et_2O turned the yellow transparent solution creamy white and opaque as the addition proceeded. Temperature was allowed to rise to 0°C while adding the aldehyde and maintained there for five minutes, with stirring. The reaction mixture, a white suspension, was poured into 100 ml NH_4Cl solution (pH 8) at 0°C. After shaking, the yellow organic phase was separated and the aqueous phase washed twice with 75 ml Et_2O. The combined organic phase was washed with saturated NaCl solution and dried overnight with $MgSO_4$. As the solvent was removed in vacuo, erythro-methyl-3-hydroxy-2,3-bis(4-benzyloxy-3-methoxyphenyl)-propanoate (7a) precipitated and was later separated; yield was 20% of theoretical. Crystalline threo isomer 7b was obtained in a 10% yield from the yellow oil that remained by dissolving in benzene and adding hexane.

7a. Erythro: m.p. 165-167°C. Elem. Analysis: calc. for $C_{32}H_{32}O_7$; C%, 72.71, H%, 6.10. Found; C%, 72.59, H%, 6.34. MS: m/e(rel.int.) 510(M^+) ($-H_2O$,0.2), 419(0.2), 362(0.4), 314(1.3), 287(35), 286(100), 243(15), 242(79), 227(18), 195(69), 163(3), 137(4), 135(10), 107(28), 106(11), 105(12), 91(>100). PMR ($CDCl_3$): δ 3.50(3H,s,$COOCH_3$), 3.78(3H,s,$ArOCH_3$), 3.82(3H,s,$Ar'OCH_3$), 5.11(4H,s,2xAr''CH_2OAr), 6.78-6.87(6H,m,ArH-2,5,6,Ar'H-2,5,6), 7.20-7.45(10H,m,2xAr''H-2--H-6). (Using double irradiation techniques and from peak integration, it was found that the C-alpha proton signal lies underneath the methylene peak at 5.11 delta, and the C-beta proton signal is obscured by the methoxy peaks. Exact assignment was not possible.) CMR ($CDCl_3$): δ 51.9(q,$COOCH_3$), 55.9(q,$ArOCH_3$,$Ar'OCH_3$), 59.1(d,C-beta), 79.9(t,2xArCH_2OAr), 74.8(d,C-alpha), 110.2(d,ArC-2), 112.5(d,Ar'C-2), 113.6(d,ArC-5,Ar'C-5), 118.8(d,ArC-6),

121.3(d,Ar'C-6), 127.1-128.4(m,2xAr''C-2—C-6), 133.9(s,ArC-1,Ar'C-1), 137.0(s,2xAr''C-1), 147.6 and 147.9(s,ArC-4,Ar'C-4), 149.3 and 149.5(s,ArC-3,Ar'C-3), 172.8(s,$COOCH_3$).

7b. Threo: m.p. 110-112°C (not recrystallized). Elem. Analysis: calc. for $C_{32}H_{32}O_7$; C%, 72.71, H%, 6.10. Found; C% 72.79, H% 6.25. MS: m/e(rel.int.) 528(M^+,0.1), 510(0.5), 362(0.5), 314(1), 286(100), 254(17), 243(13), 242(46), 227(9), 195(63), 163(51), 151(12), 137(7), 135(11), 107(108), 91(>100). PMR ($CDCl_3$): δ 3.71(9H,s,$COOCH_3$,$ArOCH_3$,$Ar'OCH_3$), 5.03(4H,s,2xAr''CH_2OAr), 6.41-6.80(6H,m,ArH-2,5,6,Ar'H-2,5,6), 7.20-7.45(10H,m,2xAr''H-2—H-6). (As noted for the erythro isomer, the proton signals on C-alpha and C-beta were present but distorted.) CMR ($CDCl_3$): δ 52.1(q,$COOCH_3$), 55.8(q,$ArOCH_3$,$Ar'OCH_3$), 59.5(d,C-beta), 70.8(t,2xAr''CH_2OAr), 76.3(d,C-alpha), 110.1(d,ArC-2), 112.3(d,ArC'-2), 113.5 and 113.7(d,ArC-5,Ar'C-5), 118.8(d,ArC-6), 120.6(d,Ar'C-6), 127.1-128.4(m,2xAr''C-2—C-6), 133.9(s,ArC-1,Ar'C-1), 136.9(s,2xAr''C-1), 147.5(s,ArC-4,A'C-4), 149.2 and 149.3(s,ArC-3,Ar'C-3), 173.8(s,$COOCH_3$).

Erythro-2,3-Bis(4-Benzyloxy-3-Methoxyphenyl)-1,3-Propanediol (8)

The erythro-isomer of the ester 7a (2.00 g, 3.8 mmol) was dissolved in 60 ml dry THF and added dropwise to a stirred solution of 11.0 ml(12.0 mmol) of 1.1 M $LiAlH_4$ (in THF) over one hour. The resulting solution was refluxed three hours, cooled, and excess $LiAlH_4$ was decomposed by adding small portions of THF containing 10% H_2O. When bubbling ceased, 100 ml saturated sodium potassium tartrate solution was added[16] and the two phase system was extracted several times with Et_2O. The combined organic phase was dried over $MgSO_4$ and evaporated in vacuo at room temperature the following day to yield quantitatively crude crystals of erythro-2,3-bis(4-benzyloxy-3-methoxyphenyl)-1,3-propanediol (8). 8. Erythro: m.p. 104-106°C (lit. 106-108°C[7]) obtained in 44% yield by recrystallizing from $CHCl_3$:heptane (7:1). Elem.

Analysis: calc. for $C_{31}H_{32}O_6$; C%, 74.38, H%, 6.44. Found; C% 74.44, H% 6.44. MS: m/e(rel.int.) 452(M^+-H_2O,-CH_2O,23), 361(49), 271(11), 240(100), 181(17), 167(27), 165(17), 149(37), 135(12), 107(34), 91(100), 77(36). PMR ($CDCl_3$): δ 2.90-3.12(1H,m,C-beta-H), 3.71(2H,d,J=6Hz,CH_2OH), 3.77(3H,s,ArOCH_3), 3.80(3H,s,ArOCH_3), 4.87(1H,d,J=7.5Hz,C-alpha-H), 5.10(4H,s,2xAr''CH_2OAr), 6.62-6.98(6H,m,ArH-2,5,6,Ar'H-2,5,6), 7.27-7.47(10H,m,2xAr''H-2--H-6). CMR (DMSO-d_6): δ 55.1(s,C-beta), 55.5(q,ArOCH_3,Ar'OCH_3), 62.8(t,C-gamma), 70.1(t,2xAr''CH_2OAr), 72.3(d,C-alpha), 110.8(d,ArC-2), 113.1(d,ArC-5,Ar'C-5), 114.1(d,Ar'C-2), 118.4(d,ArC-6), 121.7(d,Ar'C-6), 127.7-128.4(m,2xAr''C-2--C-6), 133.7(s,ArC-1,Ar'C-1), 137.5(s,Ar''C-1), 138.1(s,Ar''C-1), 146.3(s,ArC-4,Ar'C-4), 148.4(s,ArC-3,Ar'C-3).

Erythro-2,3-Bis(4-Hydroxy-3-Methoxyphenyl)-1,3-Propanediol (9)

The final product was obtained by removing the benzyl protecting groups by catalytic hydrogenolysis. The diol 8 (0.47 g, 0.95 mmol) was dissolved with mild heating in 130 ml absolute ethanol, and shaken for one hour at 60 psig H_2 with 0.047 g 10% Pd-C. After removing the catalyst by filtration the solvent was evaporated, leaving a clear viscous oil. The oil was taken up in ethyl acetate from which crystallized erythro-2,3-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (9) in a 76% yield. M.p. 140-141°C (lit. 146.5-149)[7]. Elem. Analysis: calc. for $C_{17}H_{20}O_6$; C%, 63.74, H%, 6.29. Found; C% 63.66, H% 6.25. MS: m/e(rel.int.) 302(M^+- H_2O,4), 272(46), 167(20), 151(27), 150(100), 137(37), 107(31), 93(35), 77(34), 65(44). PMR (CD_3COCD_3): δ 2.82-3.08(1H,m,C-beta-H), 3.67(3H,s,ArOCH_3), 3.71(3H,s,Ar'OCH_3), 3.72-3.90(2H,m,C-gamma H_2), 5.02(1H,d,J=6Hz,C-alpha-H), 6.58-6.72(6H,m,ArH-2,5,6,Ar'H-2,5,6). CMR (DMSO-d_6): δ 55.1(d,C-beta), 55.6(q,ArOCH_3,Ar'OCH_3), 62.8(t,C-gamma), 72.6(d,C-alpha), 111.1(d,ArC-2), 114.2(d,Ar'C-2), 114.6(d,ArC-5,Ar'C-5), 118.8(d,ArC-6), 122.0(d,Ar'C-6), 131.6(s,ArC-1), 136.0(s,Ar'C-1), 144.7 and 144.9(s,s,ArC-4 and Ar'C-4), 146.7(s,ArC-3,Ar'C-3).

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13. "Erythro" and "threo" have been assigned (as in Ref. 16) in analogy with the parent molecules, using the convention that the gamma carbon of the lignin model compound side chain is located at the top of the Fischer projection and the aromatic ring connected to the alpha carbon of the chain is at the bottom. For clarity, the Cahn-Ingold-Prelog nomenclature is included in the Figures.

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