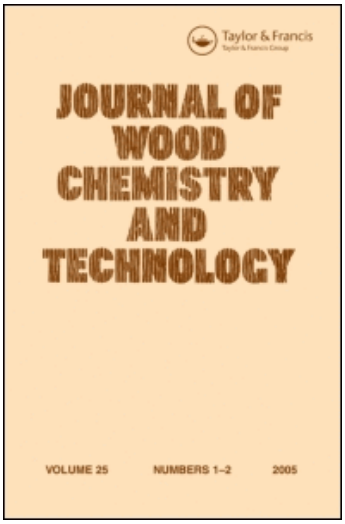

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ANTIOXIDANT PROPERTIES OF PHENOLIC LIGNIN MODEL COMPOUNDS

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ABSTRACT

Antioxidant activities of phenolic lignin model compounds were determined by measurements of inhibition rate constants (k_{inh}) during inhibited peroxidation of styrene in chlorobenzene initiated by azobisisobutyrylnitrile with known rates of initiation (R_i). The number of peroxyl radicals trapped by each antioxidant, the stoichiometric factors (n), were determined by comparison with pentamethylhydroxychroman, PMHC, n = 2. Monomeric lignin models, 4-propylguaiacol (**1**), eugenol (**2**), isoeugenol (**3**), coniferyl alcohol (**4**), coniferyl aldehyde (**5**), and 4-allyl-2,6-dimethoxyphenol (**6**) were all more active antioxidants than the commercial inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT). Two dimer models, bis(2-hydroxy-3-methoxyl-5-allylphenyl)methane (**7**) and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethoxymethylbiphenyl (**8**) and a synthetic tetramer, bis[2-hydroxy-5-(2'-hydroxy-3'-methoxy-5'-methylbenzyl)-3-methoxyphenyl]methane (**9**) were more active antioxidants. The overall relative activity was tetramer > dimers > monomers > BHT. The stoichiometric factors of **1** to **6** ranged from 1.6 to 1.7 compared to PMHC. The n factors for **7**, **8**, and **9**, showed an additive effect per phenolic hydroxyl. Phenolic groups in lignin may protect lignin-containing pulps and paper against damaging free radical peroxidation.

INTRODUCTION

Undesirable photoyellowing of wood pulp and derived paper from thermal-mechanical processes is attributed to free radical initiated autoxidation of the

residual lignin components in the pulp. Research by various groups on the photochemistry of lignin model compounds indicates that the facile formation of carbon-centered radicals such as ketyl radicals and derived peroxyl and phenoxyl radicals during photooxidation are involved in the photoyellowing process.[1-12] These pathways of photoyellowing are applicable to lignin as found earlier[13] and to lignin-containing wood pulps.[14-16] These studies have been summarized in recent reviews.[17,18] While these studies have identified the main pathways for photo-yellowing of mechanical pulps (e.g. see ref. 15), the effect of lignin oxygen-centered radicals on the cellulose of the pulp is still a relatively unknown factor. For example, recent evidence showed that lignin can have a beneficial effect on the pulp by inhibiting free radical peroxidation. In particular, controlled free radical peroxidation of lignin-containing thermal mechanical pulp compared to that of lignin-free pulp showed that the latter exhibited depolymerization and loss of tensile strength of the cellulose whereas the lignin-containing paper exhibited no such change. Paper that contained lignin showed discolouration and it was concluded that "the discolouration of lignin is a manifestation of its antioxidant properties".[19] If this is indeed the case, the phenolic chromophores, known to be present in lignin, may be responsible for the apparent antioxidant property of lignin.

The structural features in effective phenolic antioxidants have been established by the research of Ingold et al.[20] For effective antioxidant action, in other words to optimize the rate of trapping peroxyl radicals (R-O-O•) by a phenolic antioxidant (ArOH) under known conditions, the antioxidant should possess:

(1) Ortho-groups so that the hindered phenoxyl radical, ArO•, initially formed cannot itself initiate new reaction chains, and (2) an ether oxygen positioned on the aromatic ring and in a ring system which stabilizes the phenoxyl radical Ar-O• by stereoelectronic effects.

Lignin is a complex polymer of substituted phenylpropanoid groups bearing a significant number of free phenolic groups reported to vary from 6-12 in black

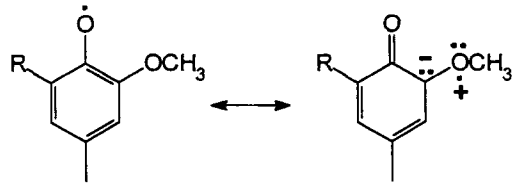


Figure 1. Stabilization of a phenoxyl radical by resonance with an ortho methoxy group.

spruce wood[21] to 15-30 per 100 C_9 units in isolated lignin.[22] Such structures are expected to exhibit antioxidant properties since some of them contain ortho - disubstituted phenolic groups. In addition, the ortho-methoxy might provide stabilization to the incipient phenoxyl radical formed, by resonance of the type indicated in Figure 1, not unlike the stereoelectronic effect exhibited by para methoxy.[20]

Quantitative determination of kinetics for autoxidation and antioxidant action are commonly performed by controlling the rate of initiation (R_i) by the use of azo initiators. The general mechanism for autoxidation is outlined in Equations (1) - (7)

Initiation: $R—N{=}N—R \xrightarrow{2k_i} 2R\cdot + N_2$ (1)

Propagation: $R\cdot + O_2 \xrightarrow{fast} R—O—O\cdot$ (peroxyl) (2)

$R—O—O\cdot + RH\ (substrate) \xrightarrow{k_p} ROOH + \dot{R}$ (3)

Termination: $2\,R—O—O\cdot \xrightarrow{2k_t}$ non-radical products $+ O_2$ (4)

Uninhibited oxygen uptake is given by Equation (5):

$$-\frac{d[O_2]}{dt} = k_p[R\dot{O}_2][R\text{-}H] \quad (5)$$

Equation (6) is obtained from the steady state approximation where the rate of initiation = the rate of termination.

$$R_i = 2k_i \times e\,[RN_2R] = 2k_t\,[ROO\cdot]^2 \qquad (6)$$

(e = initiator efficiency)

The [ROO•] from Equation (6) is substituted into Equation (5) to obtain the general Equation (7) for uninhibited autoxidation.

$$-\frac{d[O_2]}{dt} = \frac{k_p}{2k_t^{1/2}} \times [R\text{-}H] \times R_i^{1/2} \qquad (7)$$

During inhibition by phenolic antioxidants (ArOH), the chain-carrying peroxyl radicals are terminated by reactions given by Equations (8) and (9).

$$ROO\cdot + ArOH \xrightarrow{k_{inh}} ROOH + ArO\cdot \qquad (8)$$

$$ROO\cdot + ArO\cdot \xrightarrow{fast} \text{nonradical products} \qquad (9)$$

Under these conditions, a steady state approximation gives Equations (10) and (11)

$$R_i = k_{inh} \times 2\,[ArOH] \times [ROO\cdot] \qquad (10)$$

$$[ROO\cdot] = \frac{R_i}{k_{inh}} \times 2\,[ArOH] \qquad (11)$$

Substitution for [ROO•] into equation (5) gives the expression for oxygen uptake during inhibition.

$$-\frac{d[O_2]}{dt} = \frac{k_p}{k_{inh}} \times \frac{[R\text{-}H] \times Ri}{2[ArOH]} \qquad (12)$$

In quantitative determinations, the rate of free radical initiation (R_i) must be measured and this is done by adding an efficient phenolic inhibitor known to trap two peroxyl radicals (e.g. the stoichiometic factor, n, is 2) and by measuring the inhibition period (τ) during which oxidation is suppressed. Under these conditions, Equation (13) applies.

$$R_i = \frac{n \times [ArOH]}{\tau} \quad (13)$$

RESULTS AND DISCUSSION

Three classes of model lignin phenolic compounds shown in Figure 2 were selected for examination of antioxidant properties: Monomeric Models, which are compounds commonly derived from degradation of lignin; Dimeric Models and a Tetrameric Model. The latter classes are synthetic model compounds which might be expected to mimic the antioxidant properties of typical cross linked structures in lignin.

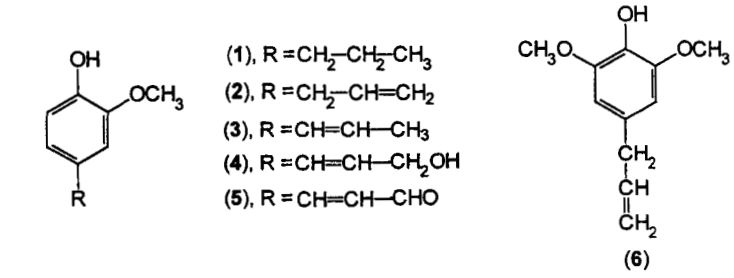
1. The Profiles of Inhibited Peroxidation

(a) Phenolic Lignin Monomeric Models Compared to 2,6-Di-*tert*-butyl-4-methylphenol (BHT)

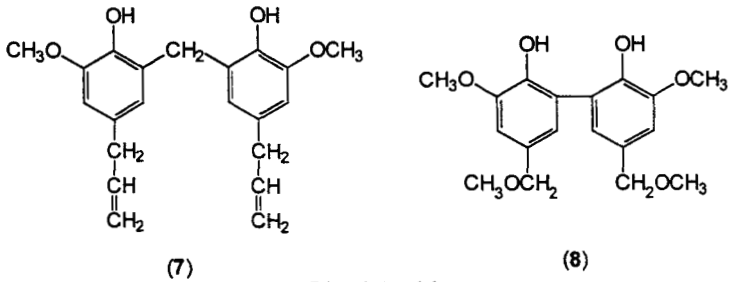
The inhibited peroxidation of styrene in chlorobenzene was used to determine the antioxidant properties of model lignins. This method has proven to be a reliable one to measure antioxidant action of a wide variety of phenolic compounds.[20] The experimental profiles of peroxidation of styrene, initiated by azo-bis-isobutyrylnitrile (AIBN), and inhibited by the various model lignin monomers are shown in Figure 3 for the initial stages of the inhibition periods. These results indicate that the model phenolic monomers are all superior in suppressing peroxidation than is the commercial antioxidant, BHT, as studied under those comparable conditions.

(b) Phenolic Lignin Dimeric Models and a Tetramer Compared to BHT

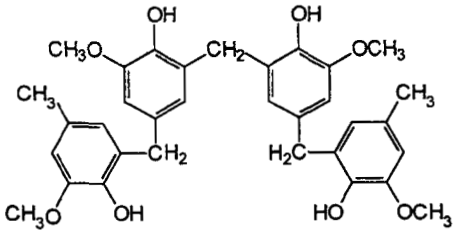
The profiles of AIBN-initiated peroxidation of styrene inhibited by the model dimers, **7** and **8** , and tetramer **9** are shown in Figure 4. Again it is clear that these phenolic lignin model compounds are more active than BHT at suppressing oxygen uptake.



Monomeric Models



Dimeric Models



A Tetrameric Model

Figure 2. Structures for the model lignin phenolic compounds used in this study.

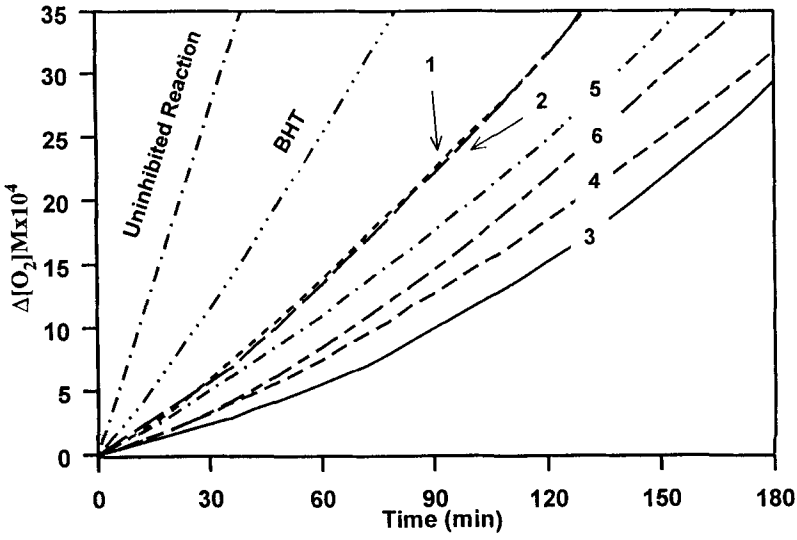


Figure 3. Autoxidation of styrene (1.02M) in chlorobenzene (2.0mL.) initiated by AIBN (4.0×10^{-5}mol.). Inhibition profiles are shown during the initial parts of the inhibition period for BHT and monomeric lignin models **1** to **6**. The typical lengths of the inhibition periods and amounts of antioxidants used are given Table 1.

2. Quantitative Determination of Antioxidant Activities, k_{inh}, and Stoichiometric Factor, n

Quantitative determinations of antioxidant activities of the model compounds were made by measuring oxygen uptake during the inhibited peroxidation and using the known methods[20,23,24] to calculate the k_{inh} from the integrated equation for the kinetics during inhibition, Equation (14),

$$\Delta [O_2]_t = \frac{-k_p}{k_{inh}} \times \ln\left(1-\frac{t}{\tau}\right) \times [RH] \qquad (14)$$

where τ is the inhibition period and the suppressed oxygen uptake, $[O_2]_t$ is measured at known times, t, during the inhibition reaction. Plots of oxygen

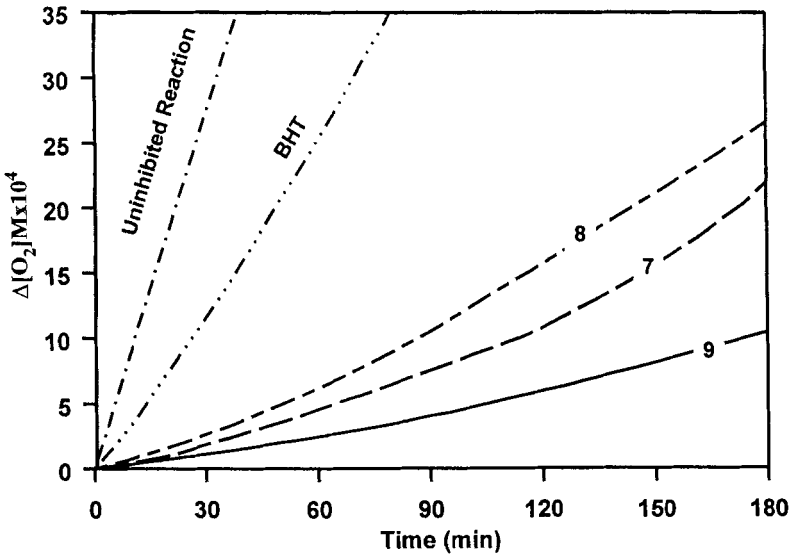


Figure 4. Autoxidation of styrene (1.02M) in chlorobenzene (2.0mL) initiated by AIBN (4.0 $x10^{-5}$mol.) and (8.10)x 10^{-5}mol.). Inhibition profiles are shown during the initial parts of the inhibition period for BHT and dimeric models **7** and **8** (using 8.10 x 10^{-5}mol. AIBN) and tetramer **9**. The amounts of antioxidants and inhibition periods are given in Table 1.

consumed during inhibition periods versus $-\ln(1-t/\tau)$ should be linear and the k_{inh} is calculated from the slope, $k_p/k_{inh}[RH]$, by using the known value[20] for the chain propagation rate constant of peroxidation of styrene, 41 $M^{-1}s^{-1}$. Typical linear plots obtained for inhibited peroxidation of styrene by BHT, used as a standard, and the various model phenolic compounds are illustrated in Figures 5 and 6.

The number of peroxyl radicals trapped per molecule of antioxidant, the stoichiometric factor 'n', was determined by comparison with an efficient phenolic antioxidant, e.g., pentamethylhydroxychroman (PMHC), known to trap two peroxyl radicals[23] The inhibition period, τ, is measured for a known amount of the antioxidant for which n is to be determined. The R_i is measured by PMHC under

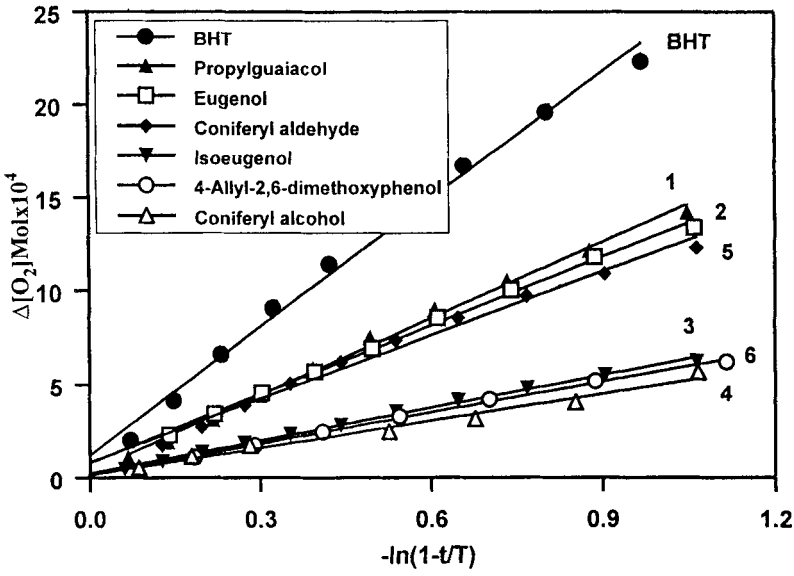


Figure 5. Plots of oxygen consumed versus $-\ln(1-t/\tau)$ for peroxidation of styrene in chlorobenzene initiated by AIBN and inhibited by BHT and monomeric lignin models **1** to **6**. Amounts are those given in Table 1. The antioxidant activities, k_{inh}, are obtained from the slopes which equal k_p/k_{inh} x [R-H]. (see text).

the same conditions and Equation (15) is used to calculate the stoichoimetric factor relative to PMHC.

$$n = R_i \times \frac{\tau}{[\text{inhibitor}]} \qquad (15)$$

The Antioxidant Activities, k_{inh}

Values for the absolute rate constant of inhibition (k_{inh}) are given in Table 1 of the various model compounds and of BHT and 2,6-di-*tert*-butyl-4-methoxyphenol (DBHA). So that comparison of antioxidant properties of the different compounds and with BHT and DBHA could be made, each experiment

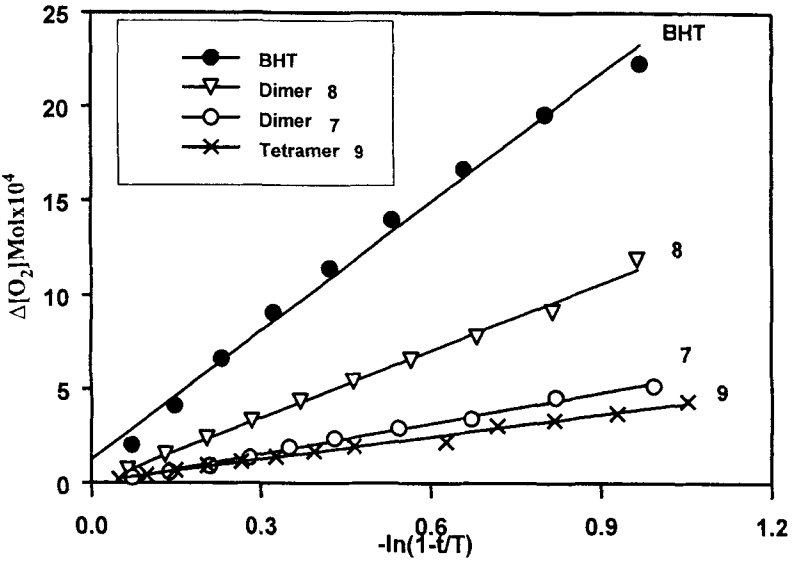


Figure 6. Plots of oxygen consumed versus -ln(1-t/τ) for inhibited peroxidation of styrene in chlorobenzene initiated by AIBN and inhibited by BHT and dimeric models dimers **7** and **8** and tetramer **9**. Amounts are given in Table 1. Antioxidant activities, k_{inh}, are obtained from the slopes which equal k_p/k_{inh} x [R-H] (see text).

employed similar conditions in the amount of substrate and initiator. Comparable rates of free radical chain initiation, R_i, as measured separately by PMHC, were observed.

As pointed out before,[20, 24] for the method of oxygen uptake to be useful there must be appreciable kinetic chain lengths during the inhibition periods. This requirement is met for all the experiments (Table 1, Column 5) and large variations in the range of chain lengths between antioxidants are a reflection of their different activities. It is evident from the k_{inh} values that all of the model compounds listed are appreciably more active as antioxidants than the commercial antioxidant, BHT. This is especially clear from the relative values, k_{rel}, shown in Column 7, and it is probably due to the effect of the ortho methoxy group, absent in BHT, to stabilize

Table 1. Antioxidant Activities, k_{inh}, and Stoichiometric Factors, n, of Model Lignin Phenolic Compounds, and BHT and DBHA, in Styrene[a] / Chlorobenzene During Peroxidation Thermally Initiated by AIBN[a] at 30 °C.

Antioxidant	molx10^8	Inhibition[b] period, τx10^{-3}s	R_i[c] $Ms^{-1}x10^9$	Chain length[d] Range	k_{inh}[e] $M^{-1}s^{-1}x10^{-4}$	k relative	n
BHT	1.29	5.18-5.22	2.22±0.04	264-560	1.82±0.02(1.4[20])	1.00	1.84±0.01
1	1.51	5.54-5.80	2.08±0.06	111-310	3.07±0.07	1.69	1.68±0.02
2	1.80	6.48-6.55	2.12±0.04	141-247	3.33±0.07	1.83	1.62±0.03
3	1.40	5.89-6.05	2.07±0.05	51-126	7.19±0.05	3.95	1.64±0.01
4	1.11	4.23-4.39	2.06±0.05	63-125	7.74±0.41	4.25	1.69±0.03
5	1.40	6.05-6.17	2.03±0.08	118-280	3.58±0.05	2.00	1.68±0.02
6	1.04	4.28-4.33	1.98±0.02	63-205	7.45±0.08	4.09	1.73±0.02
7	0.91	5.15-5.84	2.44±0.09	26-151	9.76±0.13	5.36	3.19±0.08
8	1.47	7.65	3.98	69-174	8.45	4.48	3.25±0.05
	1.27	4.43-5.02	4.17-4.19	197-300	8.02 (8.16±0.23)		
9	5.36	6.59-7.74	2.28±0.18	82-219	14.1±0.14	7.75	6.38±0.11
DBHA	0.83	3.27-3.37	2.29-2.62	40-113	17.7-19.2	9.95	1.97
	1.65	6.88	2.21	27-83	18.1±0.79		2.07±0.14

[a] Styrene (1.02M) and AIBN (40 μm) in a 2.0 mL volume. **8** used 81 μm AIBN.
[b] The range of inhibition periods for duplicated experiments.
[c] The rate of chain inhibition measured with PMHC where $Ri = 2x[PMHC]/\tau$ (see text).
[d] The kinetic chain length range for the series of at least three runs during inhibition periods.
[e] Inhibition rate constants determined from linear plots of $\Delta[O_2]_t$ versus $-\ln(1-t/\tau)$ where the slope $= k_{inh}/k_p$ x [R-H] and $k_p = 41\ M^{-1}s^{-1}$ (see text).

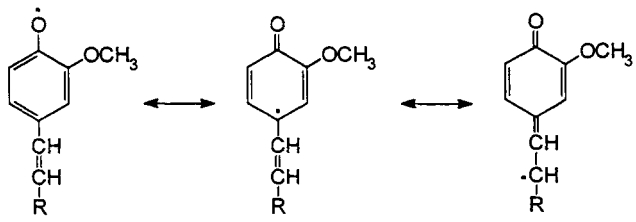
the phenoxyl radical (e.g. Figure 1) formed in the rate-determining step of the antioxidant action, Equation (8).

Some interesting differences are exhibited in the antioxidant activities between the model lignin compounds. For example, isoeugenol (**3**) and coniferyl alcohol (**4**) exhibit about twice the antioxidant activity of 4-propylguaiacol (**1**) and

of eugenol (**2**). This is attributed to the presence of the conjugated double bond in **3** and **4** compared to the saturated propyl group of **1** and the remote double bond in **2**. A conjugated double bond is expected to provide additional stabilization of the phenoxyl radical though extended conjugation in structures such as those shown in Figure 7.

It is surprising that additional conjugation provided by the carbonyl group in coniferyl aldehyde (**5**) does not increase the antioxidant activity. In fact, the k_{inh} drops back to be only marginally greater than **1** and **2**. Spectroscopic studies of related 2-alkanonyl radicals indicated that resonance stabilization "contributes in a small but chemically significant way to the structure."[25] We conclude that the electron attracting inductive effect of the electropositive carbon in the CHO group destabilizes **5** resulting in the decrease of k_{inh} for coniferyl aldehyde compared to that of **3** and **4**. The relative high antioxidant activity of the dimethoxy compound, **6**, compared to that of eugenol, **2**, with one methoxy, is probably due to additional resonance stabilization of the type shown in Figure 1 provided by the two ortho methoxy groups of **6**.

The antioxidant activities of model phenolic dimers **7** and **8**, and the tetramer **9** are of particular interest because they "model" the more complex polyphenolic structure in lignin. The dimer **7**, two eugenol units joined by an ortho methylene bridge, exhibits three times the activity of eugenol, **2**. This result illustrates the importance of the inductive effect of an ortho alkyl (-CH_2-) to further stabilize the phenoxyl radical formed in the inhibition step (Equation 8). On the other hand, the dimer **8** is only 2.5 times more active than eugenol. We speculate that steric hindrance between the phenolic hydroxyls may interfere with a planar conformation for **8** which would be required for optimal stabilization of the phenolic radical by resonance. Finally the most active antioxidant of the series is the model tetramer, (**9**), which reflects again the role of the ortho connecting -CH_2- bridge to stabilize the phenoxyl radical(s) thereby facilitating the rate determining step of the inhibition (Equation 8).



R = CH_3 (**3**); R = CH_2OH (**4**); R = CHO (**5**)

Figure 7. Stabilization of the phenoxyl radicals derived from isoeugenol (**3**), coniferyl alcohol (**4**) and coniferyl aldehyde (**5**).

The Stoichiometric Factors, n.

The overall property of an antioxidant takes into account the number of peroxyl radicals trapped per molecule of antioxidant. Efficient antioxidants, such as hydroxychromans of the α-tocopherol (vitamin E) class, are known to trap two peroxyl radicals, n = 2, according to Equations (8) and (9). The stoichiometric factor for the model lignin compounds, compared to n = 2 for the efficient antioxidant, pentamethylhydroxychroman,[24] are given in Table 1. The n factors for the monomeric lignin models **1**, **2**, **3**, **4**, **5** and **6** are all consistently in the range of approximately 1.6 to 1.7, compared to 1.84 for BHT. Stoichiometric factors less than the normal 2.0 have been observed before. This is probably due to ArO• "wasting" reactions competing with reaction (9) such as a self termination of ArO• and a chain transfer reaction especially with styrene.[27] It is interesting to note that the stoichiometric factors for the two model dimers and the tetramer exhibit almost exactly the additive effect expected for the phenolic antioxidant moiety present. The dimeric phenols, **7** and **8**, exhibit twice the stoichiometric factor of eugenol (**2**) or isoeugenol (**3**), and the tetramer, (**9**), four times the number of peroxyl radicals trapped compared to **2** or **3** within experimental error.

CONCLUSIONS

1. Phenolic model compounds, recognized as indigenous to the lignin structure, possess significant antioxidant properties as measured by their rate constants of peroxyl trapping and stoichiometric factors measured in solution.

2. Structures with conjugated double bonds in the propyl side chain have higher (e.g. twice) the antioxidant activities compared to structures with a saturated side chain, or an isolated double bond as in eugenol.

3. The dimeric and tetrameric phenolic model compounds examined have significantly higher antioxidant properties. The phenolic groups exhibit an additive effect on the stoichiometric factor, n. A tetrameric model compound exhibits similar peroxyl radical trapping activities to di-*tert*-butylhydroxyanisole, a known active commercial antioxidant. Such phenolic structures in high lignin pulp and papers probably play an important role in protecting cellulose fibers from damaging attack from active oxygen centred radicals.

EXPERIMENTAL

Materials. Commercially available antioxidants, BHT, DBHA, eugenol (**2**), isoeugenol (**3**), coniferyl alcohol (**4**), coniferyl aldehyde (**5**), and 4-allyl-2,6-dimethoxyphenol (**6**) were obtained from Aldrich Chemicals. 4-Propylguaiacol (**1**), a known liquid compound,[26] was prepared by catalytic hydrogenation of eugenol over palladium-activated carbon in ethanol in a Parr hydrogenation apparatus. The compound (**1**) showed one component in GCMS analysis and it gave M^+ ion = 166 as calculated for **1**. The ^{1}HNMR gave signals at δ 0.94 (t, 3H, CH_3), 1.59 (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 3.85 (s, 3H, CH_3O), 5.52 (s, 1H, OH), 6.65-6.74 (m 2H, Ar-H) and 6.83 (d, 1H, Ar-H), and ^{13}C-NMR ($CDCl_3$) signals at δ 13.8 (CH_3), 24.8 (CH_2), 37.8 (CH_2), 55.8 (CH_3O), and 111, 121, 135, 144, 146, 146 (aryl carbons) ppm as expected. The model dimer (**8**), and tetramer (**9**), were synthesized by approaches described in earlier work.[28] Bis(5-allyl-2-

hydroxy-3-methoxyphenyl)methane (7), was synthesized by the condensation reaction of formaldehyde (37%, 0.2 moles) with eugenol (0.12 moles) in 2N NaOH solution (0.24 moles) at 100 °C for 1 h. Recrystallization from 50% ethanol gave white crystals (46%), m.p. 81-83 °C (lit.[28], 85 °C). The ^{1}H-NMR ($CDCl_3$) showed signals at δ 3.26 (d, 4H, CH_2), 3.84 (s, 6H, CH_3O), 3.93 (s, 2H, CH_2), 2.00-2.08 (m, 4H, CH_2=), 5.84-5.99 (m, 2H, CH=), 6.01 (s, 2H, OH), 6.52 (d,2H, ArH), and 6.62 (d, 2H, ArH), and ^{13}C ($CDCl_3$) signals at δ 29.32 (CH_2), 39. 96 (CH_2), 55.97 (CH_3O), 109.21 (CH_2=), 115.37 (CH=), 122.56, 126.27, 131.28, 137.93, 141.93, 141.38, 146 (aryl carbons). The AIBN was obtained from Polysiciences, Inc. and recrytallized from ethanol before use, m.p. 103-104 °C. Solutions of known AIBN concentrations in chlorobenzene were prepared just before use or stored at -30 °C in the dark. Styrene was obtained from Aldrich Chemicals and the commercial inhibitor removed by passage of styrene through an inhibitor removal column supplied to remove *tert*-butylcatechol just before use in an autoxidation experiment.

The Autoxidation / Inhibition Procedure. The autoxidations and inhibition studies of oxygen uptake were carried out at 30 °C / 760 Torr under oxygen in a sensitive dual-channel calibrated pressure transducer system that is described elsewhere.[23, 30] The apparatus was designed for sensitive measurements of oxygen uptake; for each experiment, it was conditioned for the solution used, styrene in chlorobenzene. For this purpose, the sample cell and reference cell were charged with the solution and allowed to equilibrate under oxygen for several hours, or overnight. After a steady baseline on a recorder was established, oxygen uptake was started by injecting a known amount of AIBN in chlorobenzene. The uninhibited autoxidation was measured, followed by injection of a known amount of PMHC and the R_i determined by measuring the time until the rate returned to the uninhibited rate of oxygen uptake. Then the lignin model compound dissolved in chlorobenzene was added and the inhibition period measured as before. At least three experiments were used to determine the antioxidant activity and stoichiometric factor for each model compound.

ACKNOWLEDGEMENTS

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