

# Anodic Cleavage of Lignin Model Dimers in Methanol

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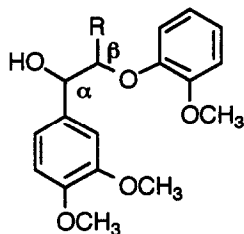
**Abstract:** The anodic oxidation in methanol of some lignin model compounds, the C<sub>17</sub>-C<sub>18</sub> compounds (1) - (5), has been studied to ascertain factors influencing cleavage of C<sub>α</sub>-C<sub>β</sub> bonds *cf.* substitution. Cyclic voltammetric oxidation peak potentials were influenced by structure but not by pH. Preparative-scale electrolyses gave 3,4-dimethoxybenzaldehyde as the major product from compounds (1) - (3), corresponding to cleavage of the C<sub>α</sub>-C<sub>β</sub> bonds. In contrast compounds (4) and (5) were not cleaved with significant efficiency. The results are convincingly rationalised in terms of rapid cleavage of the C<sub>α</sub>-C<sub>β</sub> bonds in the first-formed radical cations.

Lignins are three dimensional natural polymers composed of oxygenated phenylpropane units<sup>1</sup>. Their oxidative degradation to useful low molecular weight aromatic compounds such as vanillin and syringaldehyde has been much studied and is commercially important. It can be achieved, among other methods, by oxidation with nitroaromatics<sup>2</sup> or air in alkaline solution at high temperatures<sup>3</sup>, electrochemical oxidation<sup>4</sup> and a combined nitroaromatic/electrochemical oxidation<sup>5</sup>. Recently Umezawa<sup>6</sup> and others<sup>7</sup> showed that relevant enzymes, e.g. ligninase, are able to oxidize relatively simple lignin models. The key reaction for all these processes is the cleavage of C<sub>α</sub>-C<sub>β</sub> bonds and this reaction may involve electron transfer in at least some of the above described processes. For lignin model compounds the role of electron transfer, using a radical-cation mediator, has been elucidated in detail<sup>8</sup>; Ce(IV) is also known<sup>9</sup> to induce cleavage *via* electron-transfer. Competition between the modes of side-chain cleavage for aromatic radical-cations (C-C, C-H and C-O) has been recently reviewed<sup>10</sup>, and much seems to depend on the solvent. For anodic oxidation of simple lignin model compounds in methanol previous results<sup>11-13</sup> led us to investigate the electrochemical behaviour, under similar conditions, of some arylglycol β-aryl ethers; the β-O-aryl ether bond is the most abundant linkage in lignins (48 to 60%)<sup>1</sup>. We here report the results of the electrochemical oxidation of ethers (1) - (5) in sodium methoxide/methanol solution.

## RESULTS AND DISCUSSION.

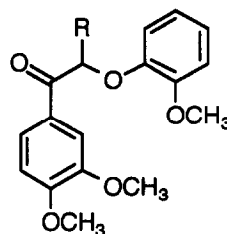
Table 1 shows the oxidation peak potentials (E<sub>pa</sub>) for the model compounds (1) - (5), determined by cyclic voltammetry, together with comparative values for compounds (11) - (15) [see below]. The oxidation waves are irreversible and a considerable decrease of current was observed during the second cycle which is

consistent with electrode fouling due to polymerization. The  $E_{pa}$  values were measured in neutral and alkaline media but they varied little with pH. In contrast, structural effects are important.



R: H CH<sub>3</sub> CH<sub>2</sub>OH

(1) (2) (3)



R: H CH<sub>3</sub>

(4) (5)

Electrochemical oxidation of the aromatic ethers will involve electron transfer from the  $\pi$ -system as normally observed for oxidation of aromatic compounds to cation-radicals<sup>14</sup>. Carbonyl substituents on the aromatic ring will lower the energy of the HOMO causing an anodic shift of the corresponding oxidation peak potentials<sup>15</sup>. This can be seen by comparison of the potentials for (11) and (12) with that of (15) -Table 1. The anodic shifts are 0.32 and 0.25V respectively. When a similar comparison is made between (13), (14) and (15) only a slight influence of the side chains is observed, which is consistent with relatively small substituent effects of H and OH.

Table 1. Oxidation Peak Potentials of Lignin Model Dimers by Cyclic Voltammetry<sup>a</sup>

Compound	neutral medium		alkaline medium	
	$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)	$E_{pa}(1)$ (V)	$E_{pa}(2)$ (V)
(1)	1.87	2.20	1.87	2.20
(2)	1.84	2.15	1.80	2.15
(3)	1.77	2.15	1.77	2.15
(4)	2.00	2.19	2.00	2.19
(5)	1.91	2.10	1.91	2.10
(11)	2.20	-	-	-
(12)	2.13	-	-	-
(13)	1.90	-	-	-
(14)	1.85	-	-	-
(15)	1.88	-	-	-

a ; V vs Ag/AgI; Pt bead anode, 60 mVs<sup>-1</sup>; MeCN-NaClO<sub>4</sub> (0.1M); substrate 3 to 8 mM

When the side chain contains the  $\beta$ -O-aryl linkage, as in lignins, the anodic shifts for the  $\alpha$ -carbonyl derivatives (4) and (5) relative to (15) decrease to 0.12 and 0.03V respectively. This rather large influence

of the oxygen substituent may be a result of a conformational preference, e.g. *cisoid* as observed for  $\omega$ -methoxy-acetophenone<sup>13</sup>. In such cases stereoelectronic effects<sup>10</sup> can significantly alter the electronic interaction between the carbonyl group and the aromatic  $\pi$ -system, e.g. in (11) and (12).

A significantly smaller influence of side-chain substitution is observed for (1), (2) and (3), the corresponding hydroxy-derivatives. Their  $E_{pa}(1)$  values are less anodic than for (15) by 0.01, 0.05 and 0.11V respectively. These structural differences occur at the  $\beta$ -carbon and involve replacement of H by  $CH_3$  and  $CH_2OH$ ; the latter change is the most significant. The changes in oxidation peak potentials observed for H and  $CH_3$  substitution are much smaller than for the  $CH_2OH$  group. A field effect is unlikely because substitution at the  $\beta$ -carbon by  $CO_2Et$  causes only a small shift [ $E_{pa}(1)$ , 1.84V for that and for (2)]. The hydroxymethyl group participates intramolecularly in rapid follow-up reactions which are known to result in redox potential shifts in the direction observed.

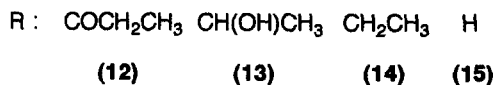
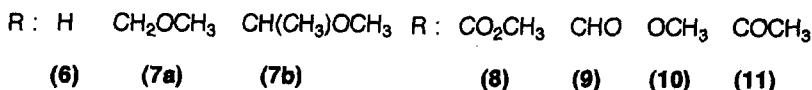
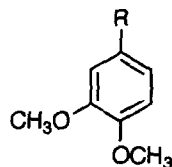
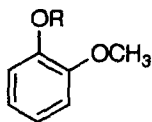
Table 2. Electrochemical Oxidation of Some Lignin Model Dimers<sup>a</sup>

<u>Starting</u> <u>Material</u>	<u>Products (%)</u>								<u>S.M.</u> <sup>b</sup>	<u>M.F.</u> <sup>c</sup>	<u>Total</u>
	(6)	(7)	(8)	(9)	(10)	(11)	(12)				
(1)	1.7	14.1	---	30.0	4.4	---	---	43.3	2.0	95.5	
(2)	19.0	---	---	37.0	4.0	---	---	21.0	8.0	89.0	
(3)	11.0	---	1.0	35.0	6.2	---	---	16.1	12.0	90.9 <sup>d</sup>	
(4)	8.2	---	7.9	---	1.5	22.0	---	16.3	16.0	71.9	
(5)	5.6	---	2.3	---	6.0	---	31.0	29.5	19.0	93.4	

- a; 0.1M NaOMe/0.2M NaClO<sub>4</sub>/MeOH-CH<sub>2</sub>Cl<sub>2</sub> (7:3 v/v); undivided cell; Pt foil anode (2.5 x 3.5 cm); W wire cathode; constant current (50mA); substrate 20-39mM and charge = 3F mol<sup>-1</sup>
- b; S.M. - recovered starting material
- c; M.F. - methanolic fraction obtained from chromatographic column (polymeric material)
- d; unidentified product (9.6%), probably a nuclear methoxylated derivative of 3,4-dimethoxybenzaldehyde (m/z= 196)

The lignin model compounds (1) - (5) were electrolysed amperostatically in a 0.2M NaClO<sub>4</sub> methanol/dichloromethane (7:3 v/v) solution containing sodium methoxide (0.1M). After passage of the appropriate amount of electricity the cell contents were worked-up and the products analyzed by GC-MS. The results of these electrolyses are displayed in Table 2.

After the passage of 3F mol<sup>-1</sup> compound (1) afforded 3,4-dimethoxybenzaldehyde (9), acetal (7a) and 1,2,4-trimethoxybenzene (10) besides recovered starting material. Aldehyde (9) was also the major product of similar electrolysis of compound (2). Guaiacol (6) was probably formed during the acidic work-up procedure by hydrolysis of acetal (7b); (7a) is stable under similar conditions.



Electrolysis of compound (3) (3Fmol<sup>-1</sup>) produced 3,4-dimethoxybenzaldehyde (9), guaiacol (6), 1,2,4-trimethoxybenzene (10) and a small amount of methyl 3,4-dimethoxybenzoate (8). When 6F mol<sup>-1</sup> was passed in the electrolysis of compound (3), similar amounts of (6) and (10) were formed, but a slight increase in the yield of aldehyde (9) (39.6%) and ester (8) (3.6%) was observed. No starting material was recovered. The presence of ester (8) is noteworthy but a plausible explanation for its formation is not obvious. Oxidation of aldehyde (9) can be excluded in the light of the results obtained with (1) and (2). A possible pathway is the oxidation of (3) to the corresponding keto compound which would undergo electro-oxidative cleavage as observed for compound (4). The presence of the CH<sub>2</sub>OH group in (3), the major structural difference in relation to (1) and (2), seems to be responsible for this behaviour. Labat and Meunier<sup>7</sup> observed that 3,4-dimethoxybenzaldehyde (9) and 2-methoxy-1,4-benzoquinone were cleavage products of (3) when potassium monopersulfate and iron or manganese porphyrin derivatives were used as oxidant. The total yield of these two products was below 40%. Their formation results from the oxidative C<sub>α</sub>-C<sub>β</sub> bond cleavage of (3), a process which involves guaiacol as an intermediate<sup>7</sup>. This can be oxidized by peroxidases to 2-methoxy-1,4-benzoquinone<sup>17</sup>.

Although (4) and (5) gave (8), no efficient oxidative cleavage was observed. In both cases the reductive cleavage occurred to a larger extent with formation of (11) and (12) from (4) and (5) respectively. This behaviour is in contrast to the electrochemical oxidation at nickel in alkaline aqueous solution which gave good yields of 3,4-dimethoxybenzoic acid<sup>8</sup>.

In all cases compound (10) was an electrolysis product. Weinberg and Belleau<sup>18</sup> electrolyzed 1,2-dimethoxybenzene in methanolic KOH solution and isolated 1,2,4-trimethoxybenzene (15%). This suggests that its formation during the electrolysis of model compounds (1) - (5) originates from the guaiacyl unit via 1,4-dimethoxylation. Compound (7a) was electrolyzed under the same conditions as dimers (1) - (5) and the product distribution supports this hypothesis. Recovered starting material (7a, 35%), 1,2,4-trimethoxybenzene (10, 27%), guaiacol (6, 7%) and a nuclear methoxylated product were present in the electrolysis product.

The results in Table 2 can be rationalized in terms of the usual mechanism<sup>14,19</sup> involving cation radical (**16**) as the first-formed intermediate after the electron transfer (Scheme). This species can undergo a variety of reactions, e.g., with nucleophiles and fragmentations with cleavage of carbon-carbon bonds<sup>10,14</sup>. In methanol containing sufficient methoxide, as in this work, the formation of 1,2- and 1,4- nuclear addition products is a well-established pathway<sup>13</sup>. Due to the substitution pattern of the side chains of compounds (**1**) - (**5**) it seems reasonable that cleavage of the C $_{\alpha}$ -C $_{\beta}$  bonds can compete efficiently with addition because stabilized radicals and carbocations result, e.g. (**17**) and (**18**) or (**19**) and (**20**), whose formation eventually can be assisted by such nucleophiles as methoxide or methanol. The results to hand do not allow a distinction between the competing pathways to (**17**)/(**18**) *vis à vis* (**19**)/(**20**). It may be that both routes are involved. Cleavage of C-O bonds in such cases has been deemed<sup>10</sup> to be uncommon although in the case of dibenzyl ether radical-cation there is strong evidence for it from isotope-labelling experiments<sup>20</sup>.

Mass spectrometry shows that considerable bond-weakening may be associated with the removal of an electron from an organic molecule<sup>14</sup>. Fragmentation of radical-cations is common in the gas phase; in solution similar reaction would be expected although greatly modified by the presence and nature of the solvent. However, despite the numerous cases where product analysis shows that cleavage of a carbon-carbon bond has taken place during an oxidation reaction, in only a few cases has it been shown that cleavage of the cation radical is involved. In most cases the initially formed cation radical reacts so rapidly that a direct characterization of the intermediate, as well as kinetic and mechanistic analysis of its decay, is precluded.

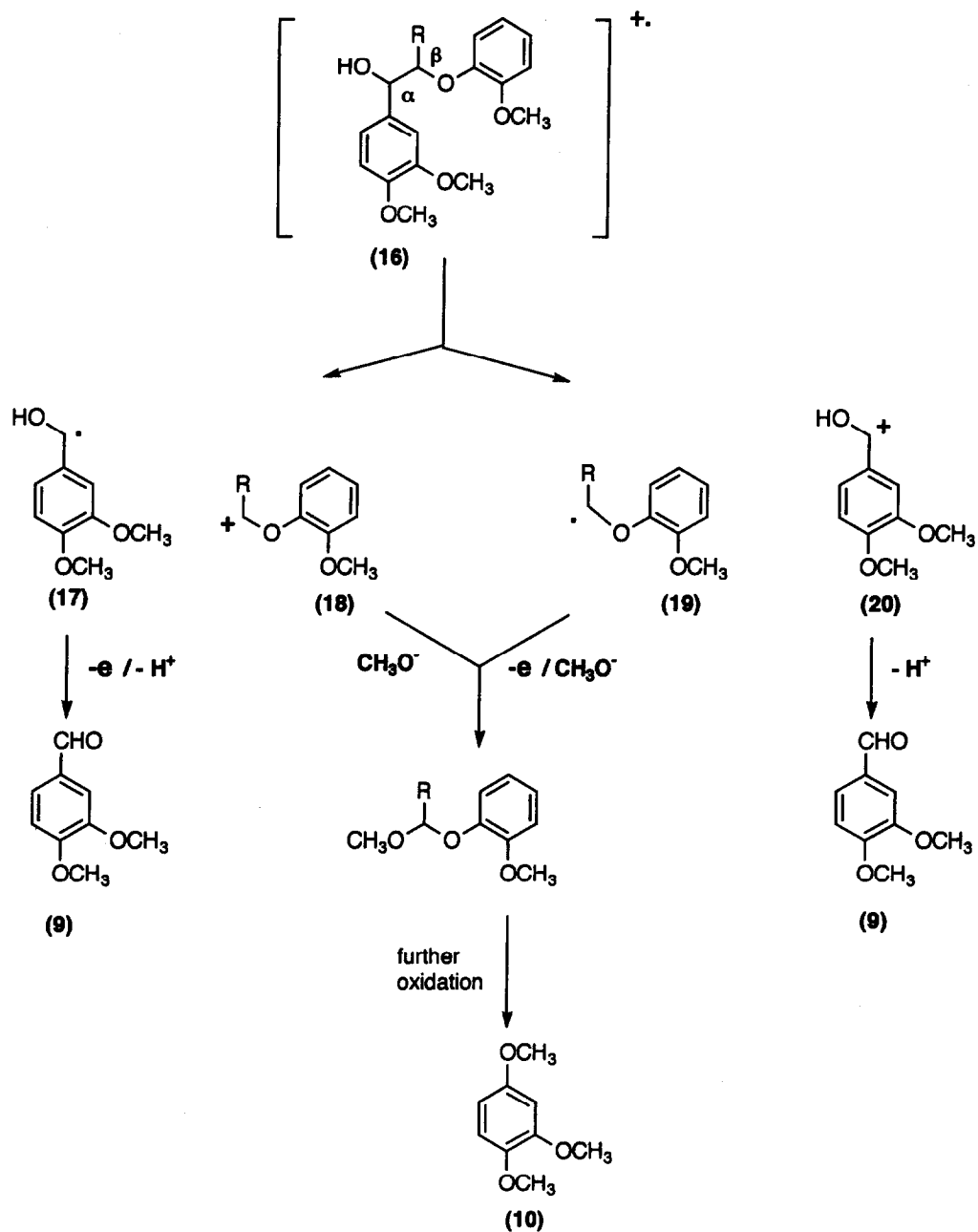
Electrochemical oxidation using triaryl amines as mediators is in many cases by single electron transfer (SET). This homogeneous process is followed by proton abstraction<sup>8</sup>. Lignin model dimers containing *p*-aryl ether structures were so cleaved and afforded vanillin and syringaldehyde derivatives. Tris-(4-bromophenyl)-amine in acetonitrile was the electron transfer agent with the necessary presence of 2,6-lutidine. The products, benzaldehyde derivatives, result from C $_{\alpha}$ -C $_{\beta}$  bond cleavage. In the mass spectra of the dimers (**1**) - (**5**) a dominating feature is their fragmentation *via* rupture of the C $_{\alpha}$ -C $_{\beta}$  bond<sup>21</sup>. In methanolic solutions, with or without sodium methoxide, the C $_{\alpha}$ -C $_{\beta}$  cleavage of the electrochemically generated cation radical may have competition, e.g. from nuclear methoxylation. Even so there is a correlation between the electrolysis products and the fragments in mass spectra which shows that cleavage of C $_{\alpha}$ -C $_{\beta}$  bond is the main reaction and lends credence to the routes outlined in the Scheme.

## EXPERIMENTAL SECTION

Glc analyses were performed on a HP5890 instrument, (fused silica capillary column SE-30, 12m x 0.2mm) and mass spectra were recorded on a Hewlett Packard HP5988A GLC/MS instrument at 70eV (EI). NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were recorded on a Bruker AC-200 from solutions in CDCl<sub>3</sub>. Chemical shifts are reported as  $\delta$  values relative to tetramethylsilane as internal reference. The cleavage products have been identified by comparison to authentic samples.

## ELECTROCHEMICAL EXPERIMENTS

Cyclic voltammetry experiments were run in a three compartment cell. The reference electrode was Ag/AgI (a silver wire immersed in a acetonitrile solution 0.1M in NaClO<sub>4</sub> and 0.01M in tetrabutylammonium



SCHEME

iodide), platinum bead as working electrode and platinum foil as counter electrode. Solvent/supporting electrolyte was 0.1M NaClO<sub>4</sub> in acetonitrile, the substrate concentration was 3 to 8mM, and the sweep rate was 60mV s<sup>-1</sup>.

**General Procedure for Electrolysis.** The compounds (1) - (5) (0.9-1.8 mmol) were electrolyzed at constant current (50mA) in 60ml of 0.2M NaClO<sub>4</sub> in methanol/dichloromethane (7:3 v/v) solution containing sodium methoxide (0.1M). An undivided cell made of glass was equipped with a platinum foil (2.5 x 3.5cm) as working electrode, and a tungsten wire as counter electrode. After the passage of the appropriate amount of electricity the cell contents were worked-up. The solution was quenched with diluted perchloric acid solution until pH 3.0. The solvent was evaporated and water (100ml) was added to the residue. The mixture was extracted with 3 x 50ml dichloromethane, washed with water (3 x 10ml) and dried over magnesium sulfate. The solvent was stripped in vacuo and the mixture of phenolic compounds was passed through to a chromatographic column (SiO<sub>2</sub>- Merck 60G) using n-hexane/ethyl acetate (3:2, v/v) as eluent. The fractions were quantified and analyzed by GC-MS and NMR.

**Synthesis.** The preparation of compounds (1)-(5) has been described previously<sup>8</sup>.

1-Methoxy-2-(methoxymethoxy)-benzene (**7a**) was prepared by the method of Rosenberg and Rapaport<sup>22</sup> and its mass spectrum compared with that of the electrolysis product. (**7a**): <sup>1</sup>HNMR-200 MHz- $\delta$ (CDCl<sub>3</sub>-TMS): 3,47(s, 3H), 3,79(s, 3H), 5,18(s, 2H), 6,79-6,99(m, 3H), 7,13(m, 1H); <sup>13</sup>CNMR-50MHz- $\delta$ (CDCl<sub>3</sub>-TMS): 55.0(q), 55.3(q), 94.8(t), 111.3(d), 116.1(d), 120.2(d), 121.9(d), 145.9(s), 149.3(s); MS (relative intensity): 168(86), 138(100), 123(28), 122(25), 95(25), 77(37), 52(25), 45(64).

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