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Polarographically Active Structural Fragments of Lignin. I. Monomeric Model Compounds

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POLAROGRAPHICALLY ACTIVE STRUCTURAL FRAGMENTS
OF LIGNIN. I. MONOMERIC MODEL COMPOUNDS

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ABSTRACT

Electrochemical properties of compounds modeling typical structural units of lignin were determined by differential pulse polarography in dimethylsulfoxide with tetrabutylammonium perchlorate as a supporting electrolyte. *p*-Quinonemethides; derivatives of cinnamyl aldehyde and cinnamic acid; aromatic aldehydes, ketones, diketones, and carboxylic acids; isoeugenol; and coniferyl alcohol were studied. Structural effects on the reduction potentials of lignin units were estimated. The potentials, which correspond to the first polarographic peak, varied from -0.8 (*p*-quinonemethide) to -2.8 V (coniferyl alcohol). The compounds containing nonconjugated carbonyl or carboxyl groups were not polarographically active. The autoprotonation reaction had a profound effect on the electrochemical reduction of compounds containing hydroxyl groups.

INTRODUCTION

The advantages and limitations of polarography for analyzing lignin have not been established. Systematic studies of the electrochemical reactions of lignin are needed. To this end the polarographically active functional groups and bonds in lignin should be determined. This is especially important because of the

recent encouraging development of electrochemical technologies in wood processing.¹

Reports²⁻⁶ have dealt with the reactivity and mechanisms of electrochemical reduction of carbonyl-containing lignin model compounds in aqueous and aqueous-organic media. As a result of the low solubility of lignin in water *per se*, polarographic studies of lignin have been mostly conducted in alkaline solutions. Lignin catalytic waves have been determined in ammonia buffer solutions,⁷⁻⁹ but under the chosen conditions these may correspond only to the reduction of structural fragments which form a complex with cobalt ion. Up to three lignin polarographic waves were detected in aqueous solutions containing KOH or NaOH.¹⁰⁻¹² Ascribing these waves to certain types of functional groups in the polymer would be difficult due to the known fact that lignin sorption on the dropping mercury electrode (DME) results in "false" polarographic waves.^{13,14} Using a mixed solvent such as dioxane:water (9:1) decreases the sorption and thus allows the establishment of a relationship between the lignin reduction potential and pH.¹⁵

Non-aqueous solvents, such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF), can be used as media in lignin functional group analysis. In these media, the use of tetraalkylammonium salts as supporting electrolytes permits the measurement of a wide range of reduction potentials, reduces adsorption on the DME and, prevents protonation. Thus, their use simplifies the electrochemical analysis.¹⁶⁻¹⁸ Up to four¹⁹ or five¹⁵ polarographic waves were registered for lignin using this approach.

Lignin contains several types of electrochemically active functional groups and bonds. Therefore, it is of primary importance to choose a polarographic method which provides good resolution. A comparative study on several types of lignins has shown that classical polarographic waves usually

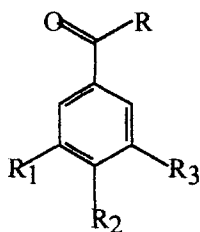
overlap. Therefore, their half-wave potentials and amplitudes are difficult to determine. In the alternating-current polarograms of lignin, there are five distinctive peaks of reduction and a tensymmetrical peak. These peaks result from reduction of carbonyl groups at -1.0 through -2.0 V.²⁰

RESULTS AND DISCUSSION

Carbonyl-Containing Compounds

Lignin contains carbonyl groups in the α -, β - and γ -positions of its phenylpropane units (PPU). In spruce MWL, their combined content is 20 per 100 PPU,²² including 7 α - and 10 β -carbonyl groups. γ -Carbonyl groups (3 per 100 PPU) are normally a part of coniferyl aldehyde-like structures, and will be discussed later. α,β -Dicarbonyl compounds were reported to be found during ethanolysis and acidolysis of spruce MWL.²² Quinone methides are usually considered as carbonyl-containing intermediates in lignification and delignification reactions. The presence of quinone methide structures in lignin macromolecule itself was suggested by Freudenberg and Harkin.²³ Being highly reactive intermediates, quinone methide structures could potentially exist in lignin because of steric hindrance and other stabilization provided by the macromolecule.

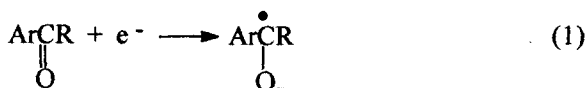
Aromatic aldehydes and ketones - Derivatives of benzaldehyde (1-8), acetophenone (9-15), and propiophenone (16-22) were examined as lignin model compounds containing an α -carbonyl group:



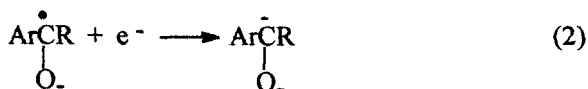
1-8 R=H, 9-15 R=Me, 16-22 R=Et

R₁,R₂,R₃=H,OH,OMe (see Tables 1-3)

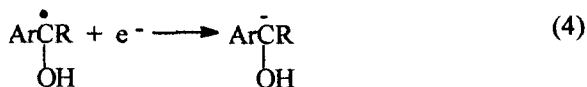
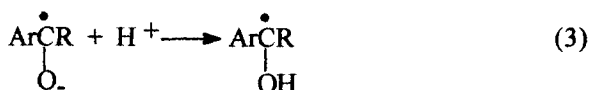
The electrochemical reduction mechanism for benzaldehyde, acetophenone, and propiophenone in nonaqueous aprotic media has already been described.^{16,17} In the first stage, a one-electron transfer (Reaction 1) yields a radical-anion:



The radical-anion can diffuse into solution and then dimerize or be reduced (Reaction 2) to the dianion:



Usually, the first stage (Reaction 1) is reversible and the second stage (Reaction 2) is irreversible. In the presence of a proton donor (e.g., phenol), the radical-anion formed in the first stage (Reaction 1) accepts a proton (Reaction 3) and the second electron transfer (Reaction 4) follows:



The protonated structures can be reduced more easily than the radical-anion. Therefore, if a proton donor is present in sufficient concentration, reactions 1, 3, and 4 occur at the same potential (a two-electron polarographic wave).

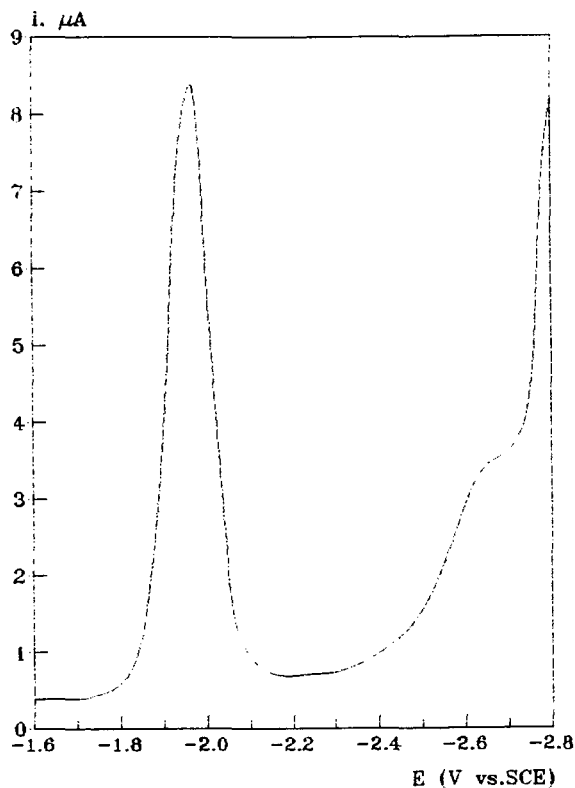


FIGURE 1. DP polarogram of propiophenone (16).

Under the current conditions (DMSO with TBAP), benzaldehyde, acetophenone and propiophenone were reduced in two stages. Figure 1 shows a polarogram of propiophenone (16) as an example. The CV method demonstrated that the first stage corresponded to a reversible one-electron transfer followed by a chemical reaction (an EC-mechanism²¹) and that the second stage was irreversible. Thus, reduction of the compounds can be described by the conventional scheme (Reactions 1 and 2).

The related lignin model compounds (Tables 1-3) were also reduced in two stages (Fig. 2). On DP polarograms of all the carbonyl-containing

TABLE 1
Polarographic Characteristics of Benzaldehyde Derivatives

Cmpd.	R ₁	R ₂	R ₃	-E _p ¹ , V	i _p ¹ , μA	r*
1	H	H	H	1.77	7.5	+
2	H	OH	H	1.88	2.0	-
3	H	OMe	H	1.92	6.8	+
4	H	OH	OMe	1.86	2.1	-
5	H	OMe	OMe	1.91	4.5	+
6	OMe	OH	OMe	1.83	2.1	-
7	OMe	OMe	OMe	1.79	4.5	+
8	OH	OH	OMe	1.87	1.8	-

*r - reversibility of electrochemical reaction by CV measurements; "+" - reversible, "-" - irreversible

TABLE 2
Polarographic Characteristics of Acetophenone Derivatives

Cmpd.	R ₁	R ₂	R ₃	-E _p ¹ , V	i _p ¹ , μA	r*
9	H	H	H	1.95	7.7	+
10	H	OH	H	2.04	2.6	-
11	H	OMe	H	2.11	5.9	+
12	H	OH	OMe	2.02	2.4	-
13	H	OMe	OMe	2.07	5.3	+
14	OMe	OH	OMe	1.99	2.3	-
15	OMe	OMe	OMe	1.97	4.7	+

*See footnote to Table 1

compounds, the second peak was observed in close proximity to the supporting electrolyte reduction potential (Figs. 1 and 2). Therefore, it was not possible to define the exact value of E_p² and Tables 1-3 include only the first peak potentials (E_p¹). A linear correlation between the amplitude of the first peak and the concentration suggests a diffusional type electrochemical process (Fig. 3).

TABLE 3
Polarographic Characteristics of Propiophenone Derivatives

Compd.	R ₁	R ₂	R ₃	-E _p ¹ , V	i _p ¹ , μA	R*
16	H	H	H	1.97	8.0	+
17	H	OH	H	2.07	2.9	-
18	H	OMe	H	2.12	6.7	+
19	H	OH	OMe	2.03	2.7	-
20	H	OMe	OMe	2.09	5.5	+
21	OMe	OH	OMe	2.01	2.3	-
22	OMe	OMe	OMe	1.99	4.6	+
23	H	OH	OMe	1.86	2.0	-
24	H	OMe	OMe	1.91	3.4	-
25	H	OMe	OMe	1.94	4.9	-

*See footnote to Table 1

The data from CV and DPP experiments suggested that mechanism for reduction of model compounds containing blocked phenolic hydroxyl groups was similar to that for their non-substituted analogues, such as benzaldehyde, acetophenone, and propiophenone. Thus, for example, the first stage of reduction of propioveratrone (20) would be a reversible electron transfer, followed by a chemical reaction. This reaction is likely to be dimerization. The CV measurements (Fig. 4) provides evidence that the differential between the potentials of the cathode and anode peaks is close to the theoretical value (*ca.* 70 mV), but the amplitude of the anode peak is less than that of the cathode peak. The anode peak amplitude became closer to that of the cathode peak as the polarization rate of the potential increased. The second stage was irreversible, also typical of the non-substituted analogues (for the criteria of reversibility, see reference 21).

Polarographic characteristics of model compounds containing a free phenolic hydroxyl group showed that these compounds were being reduced via an

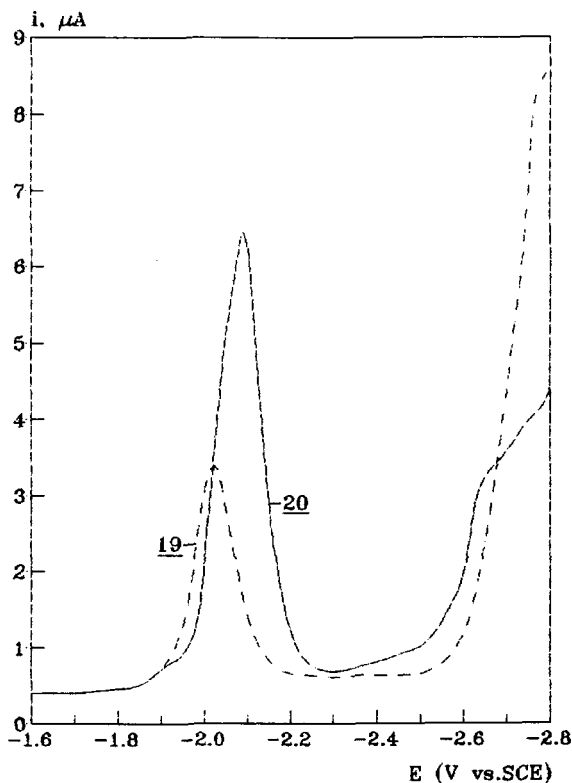


FIGURE 2. DP polarograms of propioguaiacone (19) and propioveratrone (20).

alternative mechanism. The effect of a phenolic hydroxyl on the electrochemical reaction is illustrated by the correlation between E_p^1 and i_p^1 in the pairs of hydroxyl-containing compounds and their methylated analogs (2 and 3, 10 and 11, and 17 and 18, see Tables 1-3). It is interesting to compare the changes in the reduction potential that the p-hydroxy and p-methoxy substituents cause. The Hammett constants of the substituents are -0.37 and -0.27, respectively.²⁴ Thus, the carbonyl groups of p-hydroxy-derivatives were expected to be more difficult to reduce than p-methoxy-derivatives. However, the data presented in Tables 1-3 show the opposite, except for the syringyl compounds.

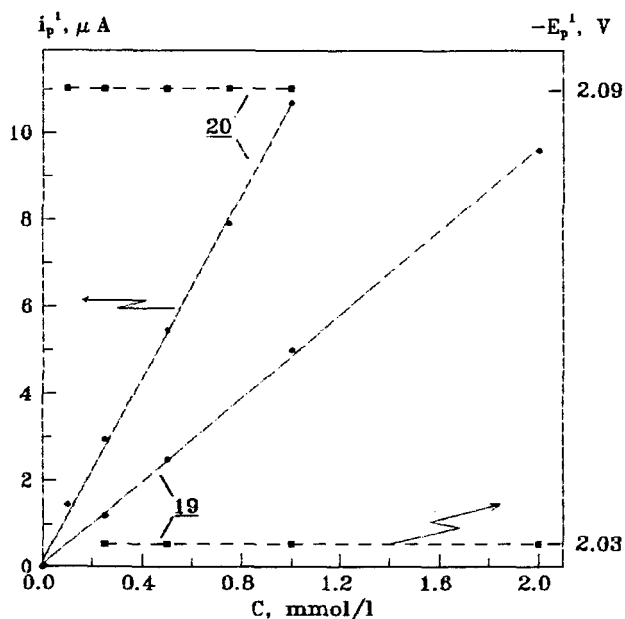


FIGURE 3. Concentration relationships of peaks i (solid lines) and E (dashed lines) on DP polarograms of propioguiaiacone (19) and propioveratrone (20).

The *p*-hydroxy- and *p*-methoxy derivatives of the aromatic aldehydes and ketones also differed in the magnitudes of the first peaks in the DP (Fig. 2, Tables 1-3). Similar results were previously obtained using classical polarography.²⁰ Another characteristic of hydroxy-containing compounds was the irreversibility of their electrochemical reduction, which was shown by CV (see Fig. 4) and ACP measurements.²⁰

Considering that carbonyl compounds of the *p*-hydroxyphenyl, guaiacyl and syringyl type are both depolarizers and proton donors, we suggest the following scheme for their electrochemical reduction:

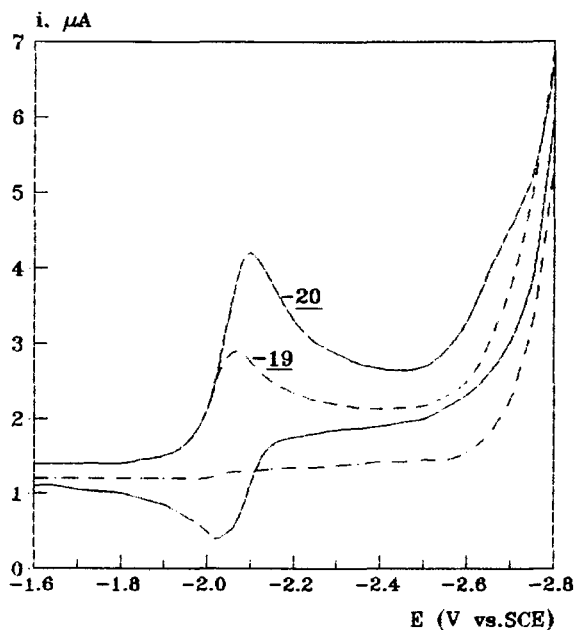
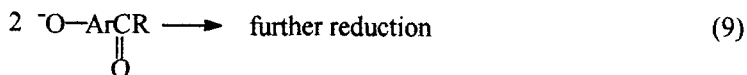
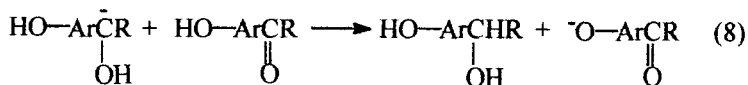
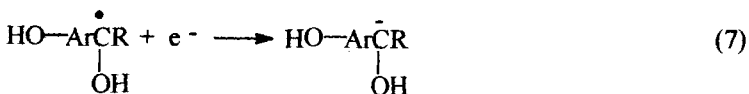
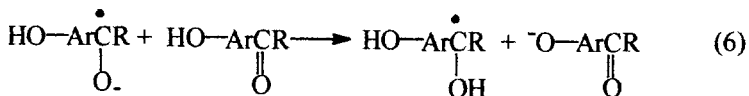
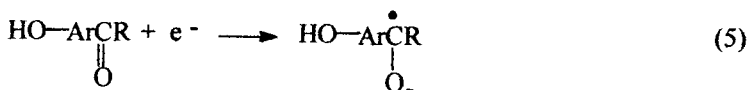


FIGURE 4. Cyclic voltammograms of propioguaiacone (19) and propioveratrone (20). The polarization rate was 200 mV/s.



HO-Ar = p-hydroxyphenyl, guaiacyl, syringyl.

This scheme is similar to the reduction scheme for aromatic aldehydes and ketones in the presence of a proton donor (Eqs. 1, 3 and 4). On DP polarograms of the compounds studied, the reactions described by Eqs. 5-8 occurred at the potential of the first peak. The autoprotection reaction was the main one (Eq. 6). Near the electrode, molecules of hydroxyl-containing compounds protonate radical-anions formed in the first stage, yielding the carbonyl derivative with a phenoxy anion. It is much more difficult to reduce the carbonyl groups of the compounds with phenoxy anions than neutral molecules. Therefore, the second peak on a polarogram is likely to account for reduction of the anion (Eq. 9). The second peak was easily distinguishable only on polarograms of a few aldehydes, such as syringaldehyde (6) and 5-hydroxyvanillin (8) (Fig. 5).

Thus, not all of the molecules in this class undergo an electrochemical reaction at the first peak potential if they bear proton-donor groups. Protonation of an initial depolarizer and the corresponding radical-anion is also possible. In the first scenario, the peak potential is expected to drift to less negative values as the concentration of the compound increases, due to a positive charge on the protonated forms. In the second scenario, there is no dependence between the potential and concentration, because the reductions in the two stages occur at the same potential (see above). As shown in Fig. 3, the peak potential was not affected by the concentration in the reduction of propioguaiacone (19), where the radical-anions are protonated. Autoprotection of dianions does not affect the peak potential occurring after the electron transfer stage. Published data on the effect of phenol on the electrochemical reduction of aromatic aldehydes and ketones in DMSO²⁰ are in line with the proposed scheme. Depending on the concentration of phenol, two polarographic waves merged into one two-electron wave. The same phenomenon was observed in p-hydroxy-derivatives of propiophenone, but in that case the concentration was 50 times higher than with the corresponding p-methoxy-derivatives. It happened because a large excess of an "external" proton-donor (phenol) was required to suppress the autoprotection reaction (Eq. 6) and to enhance protonation (Eq. 3). For example, in

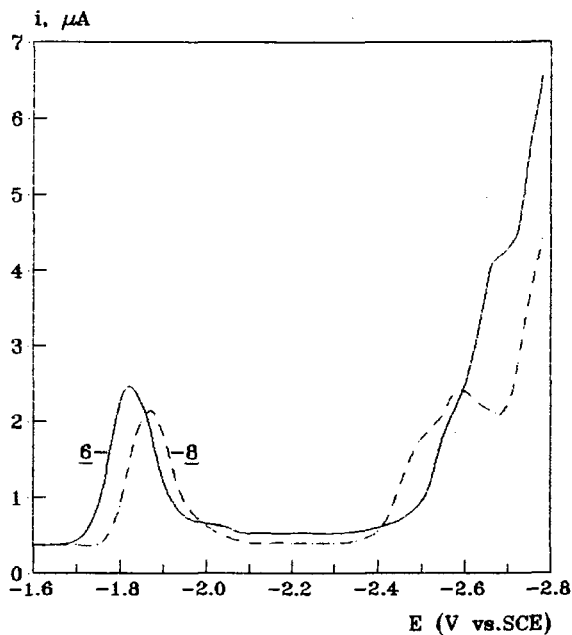
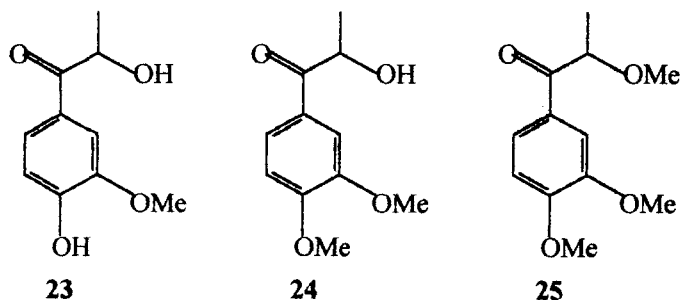


FIGURE 5. DP polarograms of syringaldehyde (6) and 5-hydroxyvanillin (8).

propioguaiacone (19), two polarographic waves merged at a molar concentration ratio of phenol:depolarizer of 460:1.

Aromatic ketones with side-chain substituents - Derivatives of propiophenone (23, 24, 25) substituted in the β -position of the side chain were studied.



They were reduced more easily than other derivatives and had lower potentials than E_p^1 of propiophenone (Table 3). We could suggest that this is an effect of autoprotonation in compounds **23** and **24**. However, compound **25** does not contain any hydroxyl groups and another explanation of the phenomenon is required.

It is known¹⁸ that the electron withdrawing effect of a carbonyl group makes reductive cleavage of an adjacent C-X bond easier (Reaction 10).



X = OH, OAlk, OPh etc.

Usually, reduction of the carbonyl group follows the reductive cleavage. However, sometimes (e.g. when X = OH) the C-X bond splits and the C=O group is reduced at the same potential.¹⁷ Merging of the two processes is likely to occur during reduction of propiophenone derivatives **23** and **24**. On the polarogram of ketone **25**, there is a peak at E = -2.08 V, besides the peak at E = -1.94 V (Fig. 6). This peak can be assigned to the reduction of propioveratrone (**20**) formed via the reductive cleavage of compound **25** (Eq. 10).

The effect of autoprotonation on the electrochemical process is responsible for the appearance of two peaks in the polarogram of compound **23** (Fig. 6, $E_p = -1.86, -2.62$ V). The second peak is two times higher than the first one. In line with the proposed scheme of electrochemical reduction of p-hydroxy-derivatives of aromatic aldehydes and ketones (Eqs. 5-9), the first peak can be assigned to reduction of compound **23** in the neutral form and the second one to its reduction in the anionic form.

β -Carbonyl compounds - Compounds of this type (**26** and **27**) did not demonstrate any polarographic activity under the current conditions (DMSO and

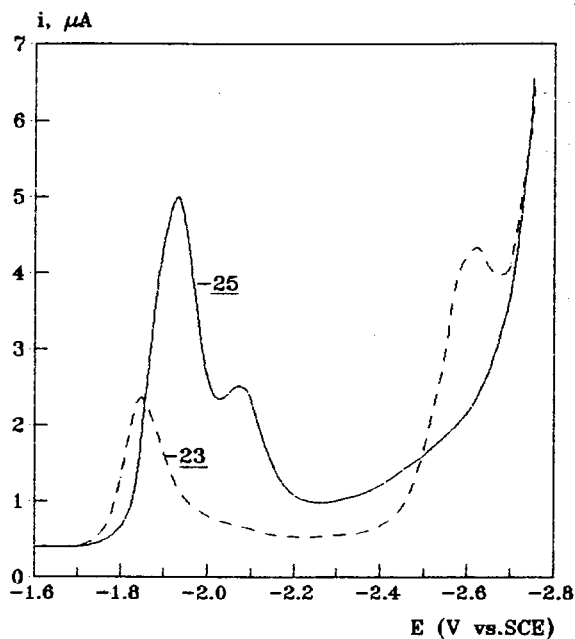
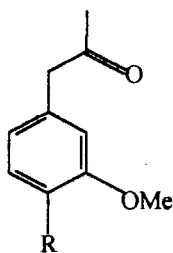


FIGURE 6. DP polarograms of α -hydroxypropioquiaceone (23) and α -methoxypropioveratrone (25).

TBAP). The carbonyl groups in these ketones are not conjugated and are less reactive than compounds with conjugated carbonyl groups.¹⁶⁻¹⁸



26 R=OH

27 R=OMe

α,β -Dicarbonyl compounds - PD polarograms of diketones 28 and 29 are presented in Fig. 7.

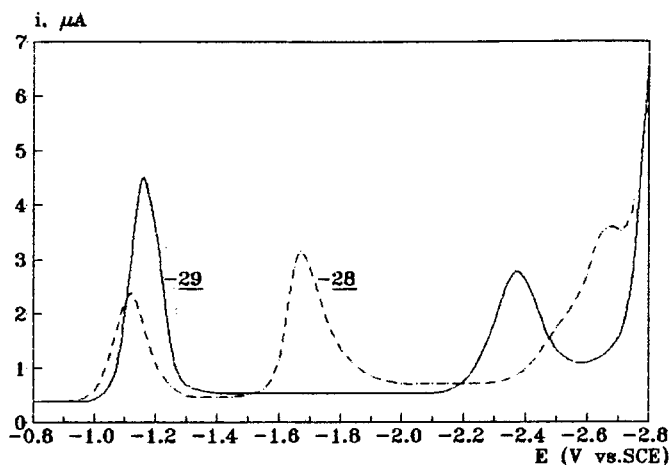
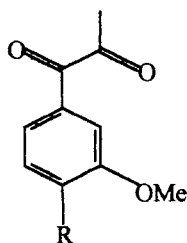


FIGURE 7. DP polarograms of vanilloyl methyl ketone (28) and veratroyl methyl ketone (29).



28 R=OH

29 R=OMe

Electrochemical reduction of similar compounds in an aprotic medium occurs in two stages; the first one being reversible (Reactions 11 and 12).¹⁶

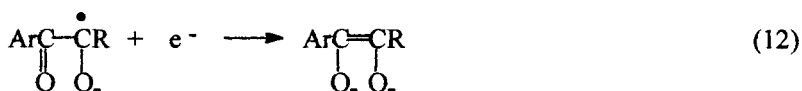
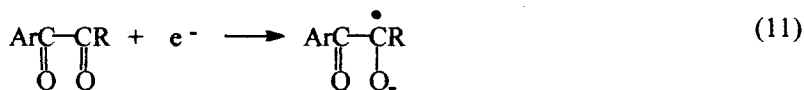


TABLE 4
Polarographic Characteristics of α,β -Dicarbonyl Compounds

Compd.	$-E_p$, V	i_p , μA	r
28	1.12	2.1	-
	1.68	2.7	-
	2.67	*	-
29	1.16	4.3	+
	2.37	2.3	-

* Peak is overlapped by the current of a supporting electrolyte discharge

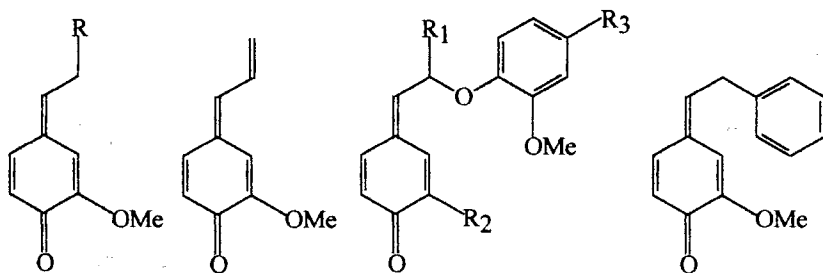
This scheme may be useful in interpreting the data for diketone **29**. From CV data the first stage of its reduction appears to be a one-electron reversible process, while the second one is irreversible. Comparison of the polarographic characteristics of compounds **28** and **29** shows the same autoprotonation effect on the electrochemical reaction mechanism as that observed for aromatic aldehydes and ketones (Table 4). The scheme proposed for the compounds with aromatic OH groups (Eqs. 5-9) could be also used for diketone **28**. In the polarogram of compound **28** (Fig. 7), the first peak corresponds to the reduction of an initial depolarizer; the second to the reduction of anions, and the third comes from the electron transfer to a compound with a conjugated double bond formed according to Eqs. 11 and 12. The fact that $i_p^2 > i_p^1$ is consistent with the scheme because two moles of an anion are generated by complete reduction of one mole of a hydroxyl-containing depolarizer. It should be noted that the magnitude ratio of the first and second peaks was affected by the stoichiometry, and also by the ratio of the electron transfer rate and the rate of protonation.

p-Quinone methides - Recently we studied the physico-chemical properties and chemical reactivity of some lignin model quinone methides (**30-36**).^{25,26} Their reduction potentials are presented in Table 5. Because of the low

TABLE 5
Reduction Potentials of Model p-Quinone Methides

Compd.	30	31	32	33	34	35	36
$-E_p, V$	1.10	1.10	0.90	0.83	0.95	0.95	1.08

stability of these compounds, they could not be isolated under normal conditions. They were prepared in a dichloromethane solution, and this solution was added to DMSO containing TBAP (10% v/v or less). Under these conditions the model quinone methides were stable for not less than 1 h. It was demonstrated in experiments with stable quinone methides that the presence of dichloromethane in the solution did not affect the value of E_p of a compound.



30 R=H

32

33 $R_1=R_2=R_3=H$

36

31 R=Me

34 $R_1=Me$ $R_2=OMe$ $R_3=H$

35 $R_1=Me$ $R_2=OMe$

$R_3=CH=CHMe$

The DP polarograms exhibited one peak, which, as could be seen from the CV measurements, corresponded to irreversible reduction. Quinone methide 34 and two other related quinone methides were studied using CV under similar conditions (DMSO and TBAP, 1-5% $CHCl_3$) and exhibited the same results.²⁷

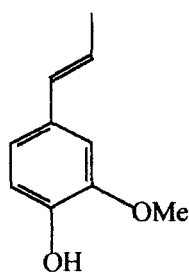
Stable sterically-hindered quinone methides are reduced in a nonaqueous medium in two stages (Reactions 13 and 14). The first stage is reversible; the second one is followed by dimerization and dismutation of radical-anions.^{28,29} The irreversibility of the reduction of the quinone methides does not permit the number of transferring electrons to be determined by CV. However, other evidence favors the electrochemical reaction being described by Eq. 13, followed by a fast chemical reaction of the radical-anion to yield a polarographically inactive product.²⁷ The chemical reactivities of quinone methides **30-36** and related compounds were discussed earlier.³⁰



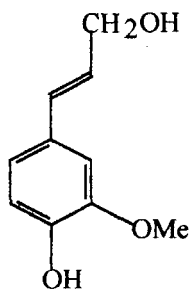
Compounds with Conjugated Double Bonds

The content of conjugated double bonds in spruce MWL is 7 per 100 PPU. They are almost evenly divided between coniferyl aldehyde- and coniferyl alcohol-type structures. Their content in kraft pine lignin is 7-8 per 100 PPU (they are included in stilbene structures).² The compounds used to model α,β -unsaturated structures in lignin were isoeugenol, coniferyl alcohol, cinnamyl aldehyde derivatives, and coniferyl aldehyde. Derivatives of cinnamic acid were also included in an attempt to determine the effect of a γ -substituent on the reactivity of the double bond. Some of these structures are precursors of lignin or are chemically bound to lignin, e.g., ferulic acid in grassy plants.²²

Isoeugenol and coniferyl alcohol - Isoeugenol **37** and coniferyl alcohol **38** were reduced at potentials close to the discharge potential of the supporting electrolyte (about -2.80 V), thus making it difficult to measure the values of E_p and i_p . Thus, the conjugated α,β -double bonds are not among the easily reducible structures in lignin.

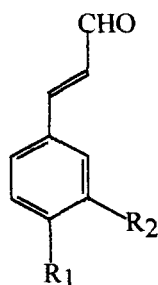


37



38

Derivatives of cinnamyl aldehyde - Data for polarographic reduction of cinnamyl aldehyde and its derivatives (compounds 39-41) are presented in Table 6 and Fig. 8. In nonaqueous media (DMSO or DMF) electrochemical reduction of unsaturated carbonyl-containing compounds, such as cinnamyl aldehyde (39) proceeds as a consecutive addition of two electrons and protons to form the analogous saturated compounds.

39 $R_1=R_2=H$ 40 $R_1=OH$ $R_2=OMe$ 41 $R_1=R_2=OMe$

This complex reaction begins with a transfer of one electron to the carbonyl group followed by electron transfer stages and rearrangement of the depolarizer, and ends with regeneration of the carbonyl group.^{16,17,31} Radical-anions generated in the first stage of reduction are unstable and quickly dimerize.³¹ This may explain why $i_a \ll i_c$ in a cyclic voltammogram of cinnamyl

TABLE 6
Polarographic Characteristics of Cinnamyl Aldehyde Derivatives

Compd.	$-E_p$, V	i_p , μA	r
39	1.45	6.7	-
	2.08	2.1	-
40	1.48	1.8	-
	2.02	2.7	-
41	1.55	4.6	-
	2.25	1.3	-

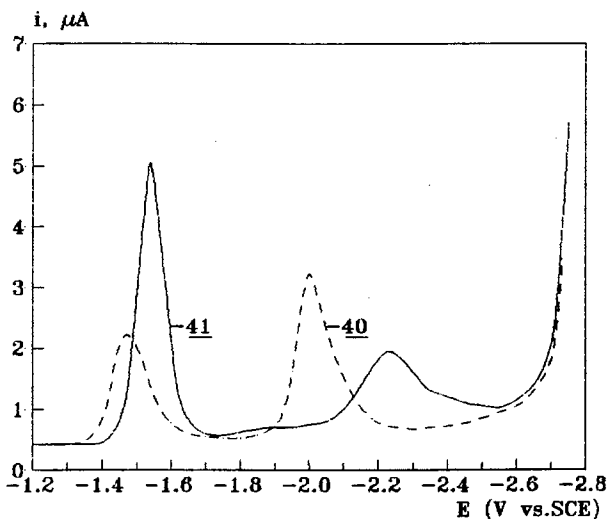


FIGURE 8. DP polarograms of conferyl aldehyde (40) and methylconferyl aldehyde (41).

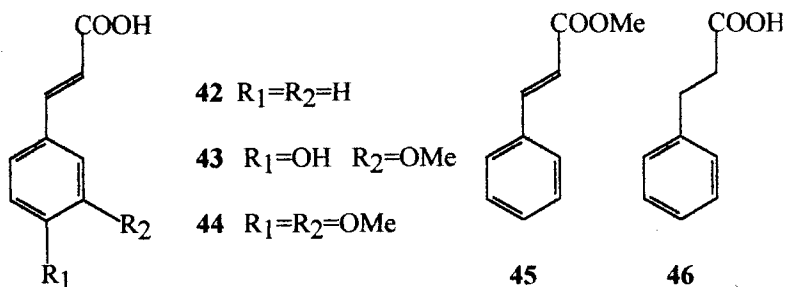
aldehyde. A comparison of the CV and DPP data showed that this scheme is also applicable to the reduction of methylconferyl aldehyde (41). However, with conferyl aldehyde (40), a comparison of the polarograms in Fig. 8 demonstrates that the autoprotonation reaction has a profound effect on the process. Analysis

TABLE 7
Polarographic Characteristics of Cinnamic Acid Derivatives

Compd.	$-E_p$, V	i_p , μA	r
42	1.70	2.6	-
	2.44	4.5	-
43	1.83	2.2	-
	2.60	1.0	-
44	1.80	2.4	-
	2.58	3.4	-
45	1.73	4.9	-
	2.28	2.7	-

of the E_p and i_p values for cinnamyl aldehyde derivatives leads to the conclusion made earlier about the effect of a phenolic hydroxyl group on the electrochemical reduction of aromatic aldehydes and ketones (see above).

Derivatives of cinnamic acid - The results for cinnamic acid and its derivatives (42-46) are presented in Table 7 and Fig. 9.



In non-aqueous aprotic media (DMF, acetonitrile), the electrochemical reduction of esters of cinnamic acid, e.g. ethyl cinnamate, proceeds through two

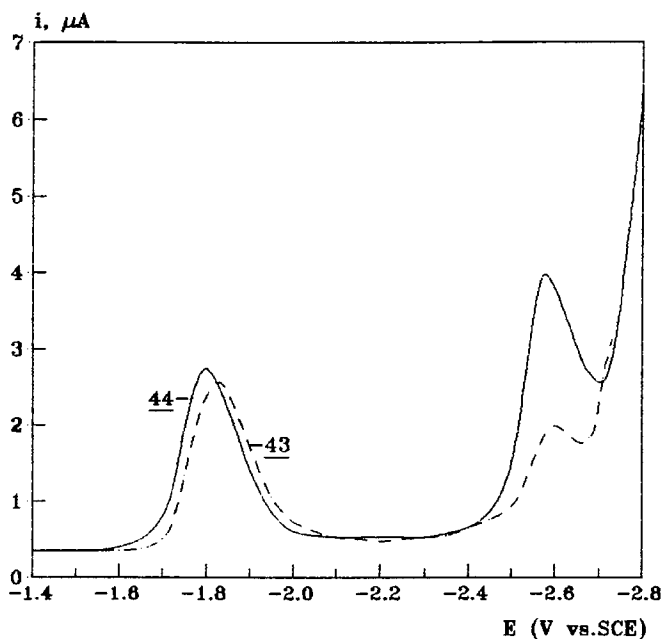


FIGURE 9. DP polarograms of ferulic acid (43) and methylferulic acid (44).

one-electron stages resulting in saturation of the double bond. The reaction is complicated by dimerization of the products that are generated at the potential of the first wave.^{32,33} Under similar conditions (DMSO and TBAP), methyl cinnamate 45 was also reduced in two stages, the amplitude of the first peak being higher than that of the second peak (Table 7). In the case of cinnamic acid (42), the ratio of the peak amplitudes was reversed (see Table 7). The same effect can be achieved in a number of aromatic aldehydes and ketones by introduction of a phenolic hydroxyl group. In cinnamic acid, the carboxylic acid group serves not as a substrate for reduction but as a proton donor. This was confirmed by an experiment on dihydrocinnamic acid (46). No reduction peaks were observed in the polarograms of the compound. Only a small increase of current at potentials close to the potential of the supporting electrolyte discharge (approximately -2.8

V) was observed. Similar to cinnamic acid, model compound **44**, with a substituted phenolic hydroxyl group, was reduced with $i_p^1 < i_p^2$ (Fig. 9). With ferulic acid (**43**), which contains both a phenolic hydroxyl and a COOH group, the mechanism of reduction is likely to be more complicated and requires additional research that is beyond the scope of our present work.

Aromatic Carboxylic Acids

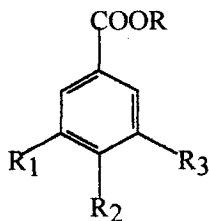
The carboxyl acid group is not a typical functional group of native lignin and it was not included into the structural scheme of softwood MWL by Freudenberg.³⁴ However, about 5 COOH groups per 100 PPU were reported in MWL.^{35,36} The content of these groups is much higher in technical lignins. Thus, 16 COOH per 100 PPU were found in pine kraft lignin.³⁶ A higher content of carboxyl groups was found in oxidized lignins and lignins from alkaline oxygen bleaching of kraft pulp.³⁷

The nature of lignin carboxyl groups is still a controversial subject. Thus, in kraft lignin all COOH-groups were first believed to be aromatic,³⁸ but later data indicated aliphatic COOH-groups.³⁶ Aromatic and aliphatic carboxyl groups were suggested to be present in kraft lignin in equal amounts.^{39,40} The considerable amount of oxidized lignin being produced by oxidative methods of cooking and bleaching justify including aromatic acids into the scope of this research. It was shown above that an aliphatic carboxyl group is not polarographically active. Therefore, only derivatives of benzoic acid (**47-57**) were studied. The results are presented in Table 8.

The autoprotonation reaction had a dominant effect on the electrochemical reduction of benzoic acid in a non-aqueous, aprotic medium. For example, only about 20% of benzoic acid was reduced (to benzaldehyde and benzyl alcohol); the remaining 80% played the role of a proton donor.¹⁷

TABLE 8
Polarographic Characteristics of Derivatives of Benzoic Acid

Compd.	R ₁	R ₂	R ₃	-E _p , V	i _p , μA	r
47	H	H	H	2.11	2.7	-
48	H	OH	H	2.38	2.2	-
49	H	OMe	H	2.29	2.0	-
50	H	OH	OMe	2.35	2.0	-
51	H	OMe	OMe	2.25	2.0	-
52	OMe	OH	OMe	2.31	1.2	-
53	OMe	OMe	OMe	2.19	2.2	-
54	H	H	H	2.16	6.0	+
55	H	OH	H	2.36	3.1	-
56	H	OMe	H	2.33	5.5	+
57	OMe	OMe	OMe	2.23	5.0	+



47 - 53 R=H 54 - 57 R=Me

R₁, R₂, R₃=H, OH, OMe (see Table 8)

In the DMSO-TBAP medium, the reduction of benzoic acid and its derivatives is likely to occur through similar routes, thereby allowing direct comparison of the DP polarogram peak amplitudes of the compounds (Table 8). Considering the peak amplitude of methyl benzoate (54) as a reference, and assuming that the electrochemical reduction process is reversible and not affected by autoprotonation (as suggested by CV data), in the DMSO medium, 45% of the benzoic acid (47) was reduced. For its derivatives (48-53) the percentage of reduction was lower.

The effect of a substituent on the aromatic ring on the reduction potentials

is shown by the E_p values of the pairs of compounds **48** and **49**, **50** and **51**, and **52** and **53** (Table 8). *p*-Hydroxy-derivatives were harder to reduce than the analogous *p*-methoxy-derivatives. This suggests that the phenolic hydroxyl group is not involved in autoprotonation. A methoxyl group in a *m*-position caused E_p to shift to less negative values (see **48**, **50**, and **52**, and **49**, **51**, and **53** in Table 8). Of the derivatives of methyl benzoate, only compound **55**, which contains a phenolic hydroxyl group, was reduced irreversibly. It had approximately half the DP polarogram amplitude of methyl benzoate **54**. In this case, the electrochemical reduction evidently includes autoprotonation of radical-anions.

CONCLUSIONS

Comparison of E_p^1 values for a number of aromatic aldehydes, ketones and acids (Tables 1-3, 8) showed that the chemical reactivity of these compounds decreases in the series: syringyl, guaiacyl, *p*-hydroxyphenyl. The presence of acidic groups (phenolic or carboxylic) in a molecule complicated the mechanism of electrochemical reduction due to autoprotonation. Therefore, from an analytical point of view, lignin model compounds that contain such groups can be studied more easily in the ether or ester forms.

Model compounds representing lignin structural fragments can be arranged in the order shown in Table 9, based on their reduction potentials.

The compounds with a non-conjugated carbonyl (**26**, **27**) or carboxyl (**46**) group were not polarographically active. The data in Table 9 show that polarographically active functional groups and bonds of lignin differ considerably in their reactivities, and that there is little overlap between the reduction potentials ranges typical of different groups. This, along with chemical analytical data could facilitate peak identification in DP polarograms of lignin. The results of a polarographic study of dimeric lignin model compounds containing basic types of lignin interunit bonds will be presented in the next report.

TABLE 9
Potentials of the First Polarographic Peak of Lignin Model Compounds

Compounds	$-E_p^1$, V vs. SCE
p-Quinone methides	0.83 - 1.10
Aromatic diketones	1.12 - 1.16
Derivatives of cinnamyl aldehyde	1.45 - 1.55
Derivatives of cinnamic acid	1.70 - 1.83
Aromatic aldehydes	1.77 - 1.92
Aromatic ketones	1.95 - 2.12
Aromatic acids	2.11 - 2.38
Isoeugenol	about 2.80
Coniferyl alcohol	about 2.80

EXPERIMENTAL

Differential pulse polarograms were recorded on a PA-2 polarograph at 0 to -2.8 V. The measurements were performed in a three-electrode vessel with a saturated calomel electrode (SCE) as the reference, using a scanning rate 5 mV/s with a 50 mV pulse. A dropping mercury electrode had a controlled drop life of 1 s. All the experiments were carried out at 25°C in DMSO containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. A platinum electrode was used as an auxiliary electrode. Oxygen was removed by bubbling argon through the solution for 10 min. Cyclic voltammograms were recorded on a PA-2 polarograph at 50-500 mV/s on a hanging mercury drop. The concentration of model compounds was 0.5 mmol/L.

DMSO was purified by repeated freezing, kept over barium oxide, and distilled in vacuum. Benzaldehyde (1), acetophenone (9), propiophenone (16), cinnamyl aldehyde (39), cinnamic acid (42), methyl cinnamate (45), dihydrocinnamic acid (46), derivatives of benzoic acid and methyl benzoate (47-57) were commercial samples purified by distillation in vacuum or

recrystallization from suitable solvents. Model compounds (2-8, 10-15, 17-29, 37, 38, 40, 41, 43, and 44) were prepared by known methods.⁴¹ Their physical constants agreed with published values. The synthesis of p-quinone methides in solution (30-36) was described earlier.^{25,26}

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REFERENCES

1. H.L. Chum and M.M. Baizer, The Electrochemistry of Biomass and Derived Materials, Amer. Chem. Soc., Washington, D.C., 1985.
2. J.J. Lindberg, K. Penttinen and C. Majani, *Acta Chem. Scand.*, **19**, 1991 (1965).
3. J.J. Lindberg, K. Penttinen, and F. Sundholm, *Paperi ja Puu*, **51**, 823 (1969).
4. F. Peter, J. Polcin, and W.H. Rapson, *Pulp Paper Mag. Can.*, **74**, 89 (1973).
5. J. Polcin, F. Peter, and W.H. Rapson, *Trans. Tech. Sect. Can. Pulp Paper Assoc.*, **2**, 7 (1976).
6. E.I. Chupka, L.V. Bronov, and V.M. Nikitin, In Khimiya Drevesiny, Zinatne, Riga, **15**, 57 (1974).
7. T. Kanda and H. Kawakami, *J. Japan Wood Res. Soc.*, **2**, 124 (1956).
8. T. Kanda, N. Terashima, and H. Kawakami, *J. Japan Wood Res. Soc.*, **7**, 258 (1961).
9. N. Terashima, M. Tamao, and T. Kanda, *J. Japan Wood Res. Soc.*, **14**, 220 (1968).
10. O.F. Gorbunova and B.D. Bogomolov, *Izv. VUZov, Lesn. Zh.*, **N3**, 114 (1973).
11. E.I. Chupka, T.A. Khrapkova, I.L. Maleva, and V.M. Nikitin, *Izv. VUZov, Lesn. Zh.*, **N4**, 103 (1976).

12. E.I. Chupka, G.I. Stromskaya, G.P. Martynova, and V.V. Verthal, *Khimiya Drevesiny*, **N6**, 90 (1979).
13. E.I. Evstigneyev, L.V. Bronov, and V.M. Nikitin, *Izv. VUZov, Lesn. Zh.*, **N5**, 114 (1978).
14. E.I. Evstigneyev, *J. Appl. Chem. (USSR)*, **54**, 265 (1981).
15. E.I. Evstigneyev, L.V. Bronov, and V.M. Nikitin, *Izv. VUZov, Lesn. Zh.*, **N6**, 95 (1978).
16. C.K. Mann and K.K. Barnes, Electrochemical Reactions in Nonaqueous Systems (in Russ.), *Khimiya*, Moscow, 1974.
17. S.G. Mairanovsky, J.P. Stradins, and V.D. Bezugly, Polarography in Organic Chemistry (in Russ.), *Khimiya*, Leningrad, 1975.
18. Organic Electrochemistry, M.M. Baizer and H. Lund (eds.), M. Dekker, Inc., New York and Basel, 1983.
19. E.I. Chupka and G.I. Stromskaya, *Khimiya Drevesiny*, **N2**, 65 (1978).
20. E.I. Evstigneyev, L.V. Bronov, and V.M. Nikitin, *Khimiya Drevesiny*, **N6**, 71 (1979).
21. A.M. Bond, Modern Polarographic Methods in Analytical Chemistry, M. Dekker, Inc., New York and Basel, 1980.
22. Lignins: Occurrence, Formation, Structure, and Reactions, (in Russ.), K.V. Sarkanen and C.H. Ludwig, (eds.), *Lesnaya promyshlennost*, Moscow, 1975.
23. K. Freudenberg and J.M. Harkin, *Holzforschung*, **18**, 166 (1964).
24. N.S. Isaacs, Experiments in Physical Organic Chemistry, Macmillan Ltd., London, 1969.
25. S.M. Shevchenko, S.G. Semenov, E.I. Evstigneyev, A.V. Pranovich, and V.A. Gindin, *Zhurn. Org. Khim.*, **23**, 1891 (1987).
26. S.M. Shevchenko, S.G. Semenov, A.G. Apushkinsky, A.V. Pranovich, and E.I. Evstigneyev, *Zhurn. Org. Khim.*, **26**, 1839 (1990).
27. D.R. Dimmel, L.F. Perry, P.D. Palasz, and H.L. Chum, *J. Wood Chem. Technol.*, **5**, 15 (1985).

28. J. Krupicka, B. Koutek, L. Musil, L. Pavlickova, and M. Soucek, *Coll. Czechosl. Chem. Commun.*, **46**, 861 (1981).
29. B. Koutek, M. Pisova, J. Krupicka, A. Lycka, D. Šnobl, and M. Soucek, *Coll. Czechosl. Chem. Commun.*, **47**, 1645 (1982).
30. E.I. Evstigneyev, S.M. Shevchenko, A.G. Apushkinsky, and S.G. Semenov, In Lignocellulosics: Science, Technology, Development, and Use, J.F. Kennedy, G.O. Phillips, and P.A. Williams (eds.), p. 658-670, Ellis Harwood, New York, 1992.
31. V.N. Nikulin, N.M. Kargina, and Yu.M. Kargin, *Zhurn. Obchsh. Khim.*, **44**, 2520 (1974).
32. J.P. Petrovich, M.M. Baizer, and M.R. Ort, *J. Electrochem. Soc.*, **116**, 743, 749 (1969).
33. L.H. Klemm, D.R. Olson, and D.V. White, *J. Org. Chem.*, **36**, 3740 (1971).
34. K. Freudenberg and A.C. Neish, Constitution and Biosynthesis of Lignin, Berlin, Heidelberg, and New York, 1968.
35. K. Ekman and J. Lindberg, *Paperi ja Puu*, **42**, 21 (1960).
36. J. Marton and E. Adler, *Tappi*, **46**, 92 (1963).
37. G. Gellerstedt and E.-L. Lindfors, *Tappi J.*, **70**, 119 (1987).
38. H. Mikawa, K. Sato, C. Takasaki, and K. Ebisawa, *Bull. Chem. Soc. Japan*, **29**, 265 (1956).
39. T. Enkvist, *Paperi ja Puu*, **43**, 657 (1961).
40. A.A. Sokolova, In Khimiya Drevesiny, Zinatne, Riga, **1**, 63 (1968).
41. G.F. Zakis, Synthesis of Lignin Model Compounds (in Russ.), Zinatne, Riga, 1980.