OXIDATION POTENTIAL OF COMPOUNDS MODELING LIGNIN AS A MEASURE OF THEIR OXIDATIVE CAPACITY

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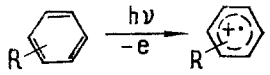
Oxidative processes play a large role both in the formation of the complex polymeric molecule of lignin and in its enzymatic degradation under natural conditions. The capacity of lignin precursors for undergoing oxidation determines the probability of the participation of each of them in oxidative coupling, and the accessibility of the individual fragments of the lignin molecule to the action of oxidizing agents shows the reaction center in the lignin-degrading reaction. Consequently, information characterizing the capacity of certain compounds modeling lignin for undergoing oxidation is of interest.

The results of the electrochemical oxidation of these compounds in an alkaline medium [1, 2] characterize the capacity of oxidation of the ionized forms of the molecules (phenolate ions) and do not always reflect the oxidative properties of the substrate itself. To evaluate the capacity of lignin-modeling compounds for undergoing one-electron oxidation it is possible to use the ionization potential (IP) of the molecule, which reflects the energetics of the following process:



Since, in the method under consideration, ionization takes place in the gas phase, a knowledge of IPs is of particular interest, since they are not complicated by various types of intermolecular interactions. The ionization potentials of lignin-modeling compounds determined by the photoionization method are as follows (eV): isoeugenol, 7.5 ± 0.1; veratrole, 7.7 ± 0.05; apocynol, 7.75 ± 0.05; acetoguaiacone, 8.0 ± 0.1; guaiacol, 8.0 ± 0.05; creosol, 8.2 ± 0.1; vanillin, 8.3 ± 0.05.

The sequence of increasing values of the IP obtained corresponds, on the whole, to the electronochemical characteristics of the substituents bound to the aromatic ring. The low value of the IP for isoeugenol, which contains a conjugated double bond in the side chain, agrees well with the high reactivity of coniferyl alcohol in oxidative coupling reactions in the biosynthesis of lignin. The alkylation of a phenolic hydroxyl substantially lowers the IP, the difference in the IPs of guiacol and veratrole amounting to 0.3 eV, which is close to the difference between the IPs found for alkylphenols and their methyl ethers [3]. Consequently, in a neutral medium veratrole derivatives should be oxidized more readily than the corresponding guaiacol. The similar IP values for acetoguaiacone and guaiacol show that the introduction of an acetyl group does not change the IP; the difference in the IPs for acetophenone and benzene amounts to 0.05 eV [4].

Creosol, acetoguaiacone, and apocynol were synthesized by known methods. All the substances were purified by fractional distillation or by crystallization, and their physical constants agreed with those given in the literature.

A MKh-1311 mass spectrograph with photoionization was used [5]. The initial sections of the curves of the efficiency of ionization of the compounds under investigation, i.e., the dependences of the yields of molecular ions on the energy of the ionizing photons, were measured. The adiabatic potentials of the ionizing photons were determined from the appearance threshold of the molecular ions.

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THE LIGNINS OF RIPE RICE-PLANT STEMS AND OF RICE HUSKS

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Studying the structure of lignin, we have performed the nitrobenzene oxidation and cleavage with sodium and liquid ammonia of the natural and the dioxane lignins of rice husks and ripe stems of rice plants. The isolation, characterization, and oxidation of the DLA (dioxane lignin) of rice husks has been described previously [1]. When the DLA of ripe rice-plant stems was oxidized, 44% of products were obtained, of which the following compounds were identified (in % on the total): p-hydroxybenzaldehyde, 17.08; p-hydroxyacetophenone, 2.1; guaiacol, 2.71; vanillin, 33.9; acetoguaiacone, 1.45; syringaldehyde 14.08. The ratio of p-coumaryl, guaiacyl, and syringyl structures was 0.51:1:0.38.

To determine the nature of the propane chains of the phenylpropane structural units of the lignin, we performed the reductive degradation with metallic sodium and liquid ammonia of the natural and DLA lignins of rice husks and of ripe rice-plant stems as described previously [2]. The total yield of products amounted to 26% for the DLA of the ripe stems, 24.8% for the DLA of the rice husks, 12.5% for the ripe stems, and 11.5% of the rice husks of the DLA and the Komarov lignins, respectively. Of the total materials at pH 8 the following products of cleavage by sodium and liquid ammonia were identified by the GLC method on a Chrom-4 instrument (4% on the total).

Substance	Rice husks	Rice husk DLA	Ripe rice stems	DLA of ripe rice stems
p-Hydroxyphenylethane	1.66	0.41	11.07	5.0
p-Hydroxyphenylpropane	13.64	23.28	1.29	10.47
1-(p-Hydroxyphenylpropan)-1-ol	—	1.3	0.93	—
Guaiacol	—	6.33	0.37	—
Vanillin	7.40	6.27	2.00	13.12
Guaiacylethane	—	2.17	0.74	—
Guaiacylpropane	2.85	14.0	4.64	5.72
1-Guaicylpropan-1-ol	5.54	—	—	2.90
3-Guaicylpropan-3-ol	—	5.32	2.80	—
Syringylpropane	9.74	27.5	17.33	24.26

Thus, by the nitrobenzene oxidation and reductive degradation with sodium and liquid ammonia of natural and dioxane lignins from rice husks and the ripe stems of rice plants we have shown the presence of three structural units of lignin — p-coumaryl, guaiacyl, and syringyl — in ratios of 0.73:1:0.79 for the rice husks DLA and 0.71:1:1.12 for the ripe rice stem DLA. The presence of a number of phenols in the products of cleavage with sodium and liquid ammonia shows that the initial lignins contain phenylpropane structural units

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