Alkaloid	f	$\overline{X}$	S^2	S	P	$t_{p,f}$	ΔX	E,%	E_m,%
Vincarine	9	0,625	0,000149	±0.012210	95	2,26	±0,027596	4,41	±2,55
Herbadine	9	1,128	0,000479	±0,021899	95	2,26	±0,049493	4,39	±2,53
Herbamine	9	1,881	0,001405	±0,037491	95	2,26	±0,084730	4,50	±2,60

The investigation was performed under the direction of the Head of the Division of Analytical Chemistry, V. S. Bostoganashvili.

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FORMATION OF THE RADICAL ANIONS $O_2^{\dot{-}}$ IN THE OXIDATION OF LIGNIN

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It is known that the oxygen radical anion ($O_2^{\dot{-}}$) is formed in the autooxidation of phenols in alkaline media [1]. In the opinion of Renard et al. [2], $O_2^{\dot{-}}$ plays an active part in the oxidation of lignin by a radical chain mechanism. However, there are no experimental proofs of the formation of the oxygen radical anion in the oxidation of lignin and its model compounds in the literature.

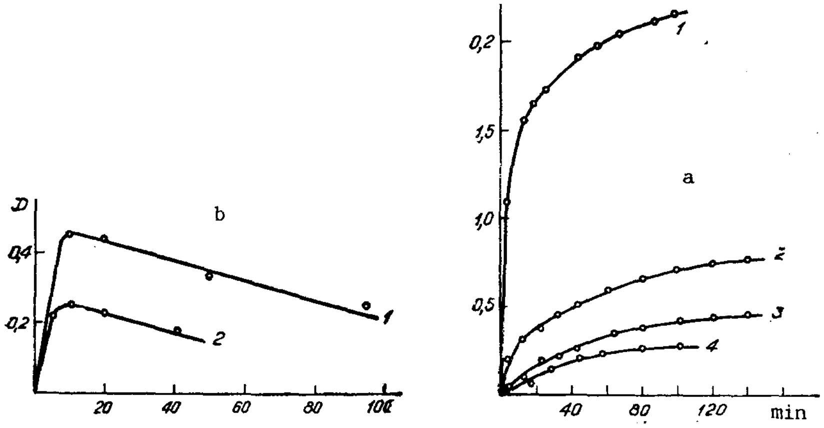

Fig. 1. Change in the optical density in the zone of the maximum absorption of diformazan on the oxidation of lignin (1.67 × 10^{-2} M), in the presence of Tetrazolium Blue ($5 \cdot 10^{-4}$ M): a) air, 30°C: 1) 1 N NaOH; 2-4) aqueous buffer, pH 9.3—DMF (1:2); 2) C_{SOD} = 0; 3) $S_{SOD} = 9 \cdot 10^{-6}$ M; 4) $C_{SOD} = 3.6 \cdot 10^{-5}$ M. b) pO_2 = 1 atm, 60°C, aqueous buffer, pH 3—DMF (1:2): 1) C_{SOD} = 0; 2) $C_{SOD} = 10^{-5}$ M.

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To check the hypothesis of the formation of $O_2^{\cdot-}$ we have studied the autooxidation of lignin in an aqueous organic medium [universal buffer, pH 9.3—dimethylformamide (1:2)] and in 1 N NaOH in the presence of the dye Tetrazolium Blue (TB). Nitrotetrazolium Blue, which belongs to the same series of dyes, is widely used in the determination of $O_2^{\cdot-}$ [3]. The results show that on the oxidation of lignin in the presence of TB (30°C) absorption appeared in the spectrum in the 515-525 nm in the aqueous organic medium and at 555-560 nm in 1 N NaOH, due to the formation of a diformazan — the product of the reduction of TB (Fig. 1a). At 60°C and a partial pressure of O_2 of 1 atm, the absorption at 515-525 nm rapidly passed through a maximum in the course of the reaction (Fig. 1b), which may be connected with an instability of the diformazan under the given conditions.

To determine whether the formation of the diformazan took place on the interaction of TB with the oxygen radical anion we performed control experiments on the autooxidation of lignin in an aqueous organic medium using superoxide dismutase (SOD), which causes the specific inhibition of reactions with the participation of $O_2^{\cdot-}$ [3, 4]. The results of these experiments showed that the addition of SOD inhibited the increase in absorption at 515-525 nm (see Fig. 1), which confirmed the formation of the oxygen radical anion during the oxidation of lignin. In experiments on model lignin compounds it was shown that $O_2^{\cdot-}$ is formed rapidly in the oxidation of isoeugenol and slowly in the oxidation of vanillin.

Thus, the formation of the oxygen radical anion in the oxidation of lignin has been shown experimentally.

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ROLE OF SINGLET OXYGEN IN THE OXIDATION OF LIGNIN IN ALKALINE SOLUTIONS

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When lignin is oxidized in alkaline solutions, luminescence can be detected the spectra of which has a maxima at 470, 560, and 640 nm [1]. According to the literature [2, 3], the maximum at 560 nm is due to the radiative deactivation of carbonyl groups from the excited (triplet) state and the maximum at 640 nm reflects the passage of singlet oxygen, $^1O_2$, into the ground (triplet) state. Lymarev et al. [4] have assigned the radiation in the 500 and 630 nm regions to carbonyl-containing compounds and to singlet oxygen, respectively. However, no direct proofs have been given (apart from the spectral characteristics) of the formation of $^1O_2$ in the oxidation of lignin. The role of $^1O_2$ in the subsequent transformation of the lignin also remained unexplained.

It is known that furfuryl alcohol is a selective quenching agent for $^1O_2$ [5]. To prove the realization of processes connected with the formation of $^1O_2$ in the oxidation of lignin, we investigated the influence of furfuryl alcohol on the change in the intensity of chemiluminescence (I_{chl}) when Pepper lignin [6] was heated in 1 N NaOH solution in the temperature range from 40 to 100°C.

The results, which are presented in Fig. 1, show that I_{chl} and the total emission of light $\left(S = \int_{\tau=0}^{n} I_{chl}\, d\tau_i\right)$ decreased with an increase in the concentration of added furfuryl alcohol. The dependence in the change in I_{chl} on the concentration of furfuryl alcohol is described by an equation analogous to the Stern—Volmer equation (Fig. 2). The activation energy

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