

The results of the biospecific chromatography of the giant hornet venom are shown in Figure 1. It can be seen that the bulk of the protein substances, possessing no lysophospholipase activity, passed through the column without being bound to the adsorbent. When the column was washed with a solution of ammonia having pH 11, about 16% of the total activity of the initial venom was eluted. At this stage, the specific activity of the enzyme increased 5-fold. The noneluted part of the lysophospholipase (i.e., the immobilized form of the enzyme) also cleaved lysolecithin with a specific activity of 35-50 units per 1 g of sorbent. Analysis of the protein composition of the fraction eluted from the adsorbent showed two bands on an electrophoretogram with molecular weights of 32 and 44 kD. The gel filtration of this fraction on a column of Sephadex C-75 permitted the lysophospholipase to be separated from the accompanying component.

Thus, the lysophospholipase from giant hornet venom has been obtained in a highly purified form. An analysis of the terminal amino acids showed that phenylalanine was present at the N-end of the enzyme and lysine at the C-end which agrees with results obtained previously [9].

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INHIBITION OF THE OXIDATION OF LIGNIN BY SYNERGISTIC COMPOSITIONS

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UDC 547.992.3

As is known, the most effective inhibiting properties are possessed by systems in which there is a constant regeneration of the active forms of the inhibitors and which can act by several mechanisms: the inhibition of the formation of peroxides or their decomposition, the recombination of the inhibitor radicals with radicals of the substrate, or the disproportionation of the radicals formed. A substantial increase in the rate and selectivity of the alkaline delignification of wood is achieved with the use of anthraquinone [1], which forms reduced varieties: anthrasemiquinone and anthrahydroquinone [2].

We have established that the addition to anthraquinone of N,N-dimethyl-p-phenylenediamine under the conditions of an alkaline wood cook leads to the formation of a synergistic system, as is shown by an acceleration of delignification and a rise in the yield of cellulose by 2% as compared with an anthraquinone cook [3]. The possibility of increasing the antioxidant activity of the system by the addition of inhibitors of radical processes indicates a substantial contribution of redox transformations of the lignin in the wood-cooking process.

Siberian Scientific-Research Institute of Cellulose and Board, Bratsk. Translated from *Khimiya Prirodnikh Soedinenii*, No. 2, pp. 314-315, March-April, 1987. Original article submitted October 13, 1986.

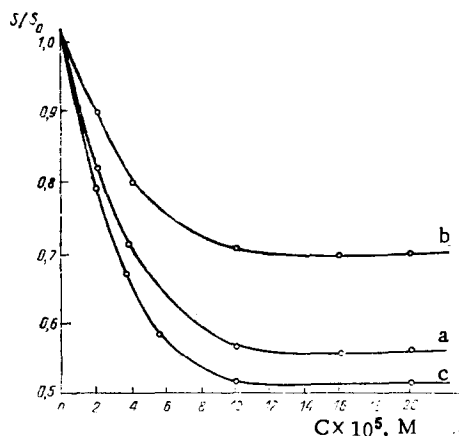


Fig. 1. Influence of additions of N,N-dimethyl-p-phenylenediamine and of N,N-dimethylaniline on the light sum of the chemiluminescence of the anthraquinone-2-sulfonic acid-lignin system. The concentration of anthraquinone-2-sulfonic acid was $3 \cdot 10^{-5}$ M.

We give the results of an investigation of the mechanism of the action on the process of oxidation of lignin in an alkaline medium of the following synergistic compositions: anthraquinone-2-sulfonic acid-N,N-dimethyl-p-phenylenediamine, and anthraquinone-2-sulfonic acid-N,N-dimethylaniline.

It was established by the chemiluminescence method that the addition of anthraquinone-2-sulfonic acid (ANS) to lignin leads to an inhibition of the oxidative transformations in lignin in an alkaline medium (Fig. 1c). The results obtained show that under the conditions of anthraquinone cook it is not only the products of the one- and two-electron reduction of anthraquinone but also the oxidized form of the delignification catalyst that exert an inhibiting action on the oxidation of lignin.

The addition of N,N-dimethyl-p-phenylenediamine (DPA) and of N,N-dimethylaniline (DMA) in the range of concentrations studied ($2 \cdot 10^{-5}$ – $2 \cdot 10^{-4}$ M) did not affect the intensity of luminescence in the oxidation of lignin in an alkaline medium, while their combined addition with ANS led to a fall in the fluorescence light sum (Fig. 1, curves a and b). The efficacy of the inhibition of the oxidative transformations of lignin reflected in the dependence of the chemiluminescence light sum on the concentration of additive is characterized by saturation. Consequently, the addition of ANS and of compositions based on it enables only partial suppression of the oxidation process to be achieved. The limiting achievable level of addition depends on the type of synergist: on the addition of PDA the fall in the light sum of fluorescence was 46%, while the DMA it was 30%.

To confirm the hypothesis that the synergistic effect of the inhibition of the oxidative transformations of lignin observed on the addition of the compositions under investigation is explained by an additional generation of anthrasemiquinone in the solution, we used the method of spectrophotometry. It was shown that the addition of PDA to an alkaline solution of anthraquinone-2-sulfonic acid led to an increase in the concentration of anthrasemiquinone, as was shown by a rise in the optical density in the 840 nm band, which is assigned to the radical anion of anthrasemiquinone [2].

It may be assumed that the synergistic effect of the quenching of chemiluminescence in the oxidation of lignin in alkaline solutions arises through an increase in the concentration of anthrasemiquinone in the solution.

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