## ACTION OF OXIDIZING ENZYMES ON THE LIGNIN-CARBOHYDRATE COMPLEX OF SPRUCE WOOD

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The action of the wood-destroying fungi of storage rot is connected with the presence of oxidizing enzymes in them. An anatomical study of wood destroyed by the enzyme complex has shown that there is no appreciable difference between such wood and wood destroyed by the fungi themselves [1]. It has been shown [2] that such active lignin-destroying fungi as <u>Coriolus hirsutum</u> 073 and <u>Stereum hirsutum</u> 204 have a high productivity of the oxidizing enzyme peroxidase and laccase. As a result of the preliminary treatment of birch wood with culture filtrates of these strains before neutral sulfite delignification, an increased selectivity of the elimination of lignin and an increased yield of semicellulose are observed [3].

In the present paper we present the results of an investigation of the influence of enzymatic treatment on the change in the physicochemical properties of samples of spruce wood.

To characterize the change in the lignin-carbohydrate complex (LCC) of the wood we used the relative optical densities (RODs) at 3400 and 1600 cm<sup>-1</sup> in the IR spectra of the samples. As internal standard we selected the band at 895 cm<sup>-1</sup>, which does not change with various forms of treatment of the wood.

As a result of the action of the enzymes laccase and peroxidase there was a fall in the ROD at 1600 cm<sup>-1</sup>, which indicated the occurrence of a partial delignification of the samples of spruce wood investigated (Fig. 1, a) when thin sections were treated for 30 hours, the ROD fell from 1.65 to 1.15 under the action of peroxidase- $H_2O_2$  and to 0.77 on the oxidation of the wood by oxygen in the presence of laccase. The fall in the relative amount of lignin in the enzyme-treated spruce wood was apparently due to an increase in solubility and its passage into solution. This hypothesis was confirmed by the increase with time of the absorption of the solution in the UV region at  $\lambda$  280 nm. The change in the

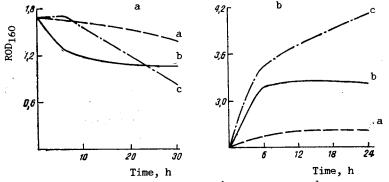


Fig. 1. Dependence of the ROD ( $v = 1600 \text{ cm}^{-1}$ , internal standard 895 cm<sup>-1</sup>) (a) and of the concentration of free radicals (b) on the time of treatment of samples of spruce by enzymes: a) control; b) laccase; c) peroxidase-H<sub>2</sub>O<sub>2</sub>.

Siberian Scientific Research Institute of Cellulose and Board, Bratsk. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 663-664, September-October, 1986. Original article submitted August 13, 1985; revision submitted April 25, 1986. solubility of the lignin was connected with the presence on its macromolecules of carboxylic and phenolic hydroxy groups. During the enzymatic treatment of the samples of spruce wood, a fall in absorption in the  $1720 \text{ cm}^{-1}$  region was observed, which may be connected, in the view of the specific action of the enzymes, with a decrease in the amount of carboxy groups in the lignin molecule.

As a result of the action of the oxidative enzymes, the number of hydroxy groups in the treated wood rose considerably. This phenomenon was responsible for a rise in the ROD at  $3400 \text{ cm}^{-1}$ , which reaches its maximum value on treatment for 24 h, almost doubling in comparison with the initial wood.

The action of enzymes on samples of spruce wood led to a rise in the number of free radicals as compared with the untreated samples. The greatest influence on the process of forming stable radicals was exerted by the enzyme laccase. Thus, as the result of the treatment of sections for 24 hours the concentration of paramagentic centers almost doubled in comparison with the control (Fig. 1, b). The formation of stable radicals in spruce wood indicates an oxidative process taking place under the catalytic action of enzymes.

Thus, enzymatic oxidation of the lignin-carbohydrate complex of spruce wood is accompanied by partial delignification and by an increase in the number of hydroxy groups and of free radicals.

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