The yield of (II) was 0.9 g, syrup; $[\alpha]_D^{20}$ −57.8° (c 1.1; methanol). R_f 0.48. R_T 1.18 [5].

The yield of (I) was 1.0 g, mp 39-41°C, $[\alpha]_D^{20}$ −18.8° (c 1.8; methanol). R_f 0.30. R_T 3.76 [3].

The methyl ethers of (I) were identified by ^{13}C NMR spectroscopy in D_2O with allowance for the effects described previously [6]. The assignment of the ^{13}C signals in I was made in [7].

Compound	C-1	C-2	C-3	C-4	C-5	Quaternary C's	Acetonide CH₃	CH₃		
I	105.1	85.4	74.6	81.8	60.0	113.2	25.8; 26.3			
II	105.2	84.2	81.9	81.4	59.7	113.2	25.9; 26.3			58.2
III	105.1	85.3	74.8	80.4	70.7	113.2	25.8; 26.3			59.2
IV	105.2	84.4	81.8	79.6	70.4	113.2	25.9; 26.3	58.2;	59.3	

LITERATURE CITED

1. E. V. Evtushenko and Yu. S. Ovodov, Khim. Prir. Soedin., 178 (1985).
2. E. V. Evtushenko and Yu. S. Ovodov, Khim. Prir Soedin., 682 (1975).
3. O. Svanberg and K. Sjoberg, Chem. Ber., 56, 863 (1923).
4. R. A. Laidlaw, J. Chem. Soc., 2941 (1952).
5. P. A. Levene and A. L. Raymond, J. Biol. Chem., 102, 331 (1933).
6. A. S. Shashkov and O. S. Chizhov, Bioorg. Chem. 2, 437 (1976).
7. A. S. Shashkov, A. I. Shienok, M. Islomov, A. F. Sviridov, and O. S. Chizhov, Bioorg. Khim., 3 102 (1977).

STABILIZATION OF CARBOHYDRATES IN THE ALKALINE DIGESTION OF WOOD

WITH ANTHRAQUINONE AND POLYSULFIDES

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The experimentally established facts of the stabilization of carbohydrates and an increase in the yield of cellulose in alkaline cooks of wood with additions of anthraquinone and polysulfide and an increase in the amount of carboxy groups in the cellulosic materials in these cooks are explained by the selective oxidation of the terminal carbonyl groups to carboxy groups, the formation of which "stabilizes" the breakdown of the polysaccharide [1, 2]. The influence of reducing agents (NH_2−NH_2, $NaBH_4$, Na_2S) causes the stabilization of the carbohydrate fraction and an increase in its yield [3], and, therefore, in alkaline cooks a considerable contribution to the degradation of the polysaccharides is also provided by their oxidative breakdown.

If the opinion is held that the "peeling" mechanism, as a depolymerization process, is determinative in the breakdown of carbohydrates, then in alkaline treatments no appreciable fall in the degree of polymerization (DP) of celluloses should be observed. However, a number of authors, including in particular, Yu. V. Brestkin, have convincingly shown that in a sulfate cook a statistical degradation of cellulose takes place [4].

We have performed investigation by the chemiluminescence method with the aim of elucidating the mechanism of the stabilizing action of anthraquinone-2-sulfonic acid (AMS) and polysulfide on the degradation of carbohydrates. It has been established that when glucose is oxidized the addition of anthraquinone-2-sulfonic acid at concentrations of 10^{-5}-10^{-4} M intensively quenches luminescence (Fig. 1). Thus, the oxidized form of AMS is itself an inhibitor of the oxidation of carbohydrates, which does not fall within the framework of the explanation of the mechanism of the stabilization of carbohydrates through the selective oxidation of ter-
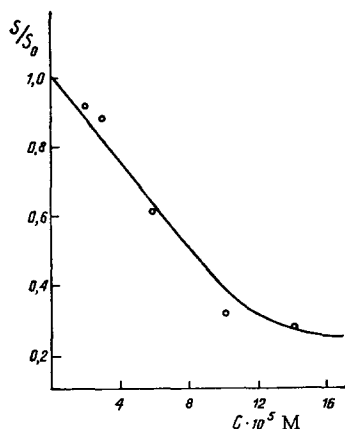
Fig. 1   Fig. 2

Fig. 1. Dependence of the change in the relative light sum of the luminescence of glucose on the concentration of anthraquinone-2-sulfonic acid (T = 100°C, C_{gl} = 2• 10^{-4} M, 0.1 M NaOH).
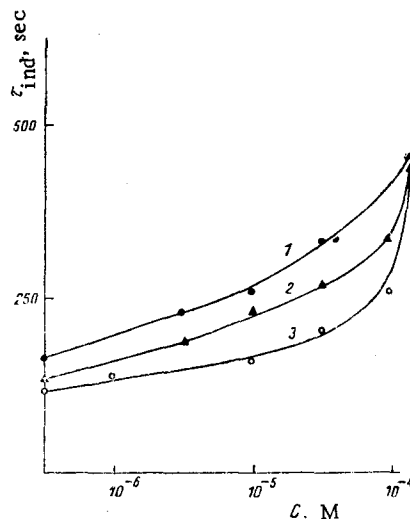
Fig. 2. Change in the induction period of the oxidation of glucose as a function of the concentration of polysulfide (0.1 M NaOH, C_{gl} = 2•10^{-4} M): 1) 80; 2) 90; 3) 100°C.

minal groups to carboxy groups, since additions of antnraquinone-2-sulfonic acid prevent the oxidative decomposition of monomeric carbohydrates.

When polysulfide was added, a similar quenching of the chemiluminescence in the oxidation of carbohydrates took place, and with an increase in the concentration of polysulfide the induction period lengthened greatly (Fig. 2), while the rate of oxidation in time did not reach the same values as in inhibited oxidation. At the same time, it was established by a micromanometric method that, at the same temperatures and comparable concentrations, the rate of oxidation of the polysulfide (from the consumption of oxygen) exceeds the rate of oxidation approximately 100-fold. Consequently, it is impossible to speak of "oxidative stabilization." The stabilization of carbohydrates in cooks with anthraquinone and polysulfides must be considered as a case of inhibited oxidation.

Carbonyl groups, having reducing properties, are oxidized, to carboxy groups, in preference to the C—C— and alcohol groups in a glycoside residue and to the glycosidic bond, the breakdown of which is what is primarily responsible for the degradation of the polysaccharide. These facts do not contradict one another but explain (although from different aspects) Samuelson's results [2] showing an increase in the yield of saccharic acids on the addition of anthraquinone to an alkaline cook.

We have observed a similar situation on the introduction of inhibitors with different oxidation potentials in the inhibited oxidation of lignin, since the majority of additives act ing positively on wood cooks inhibit oxidation partially, apparently in accordance with the oxidation potentials of individual fragments of the lignin [5].

Thus, polysulfide and anthraquinone stop the oxidative process at the stage of the formation of carboxy groups and prevent the decomposition of the bonds and functional groups (alcohol groups) more resistant to oxidative transformations, thereby preventing the far-reaching breakdown of polysaccharides.

LITERATURE CITED

1. A. Teder, Svensk Papperstidning, No. 9, 294 (1969).
2. L. Lowendahl and O. Samuelson, Polym. Bull., 1, No. 3, 205 (1978).
3. G. A. Pazukhina, Author's abstract of dissertation for Candidate of Technical Sciences, Leningrad (1966).
4. Yu. V. Brestkin, Zh. Prikl. Khim., 40,, No. 11 2562 (1967).
5. E. I. Chipka, A. D. Sergeev, and V. N. Gvozdov, Khim. Drev., No. 5, 43 (1983).