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![structural formula (I)]()

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Figure 1: structural formula (I)

Abstract

Full Text

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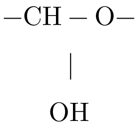
ON OPEN RINGS IN THE CELLULOSE MOLECULE

Numerous studies have established that the cellulose molecule contains carboxyl and aldehyde groups in positions 2, 3, and 6 of the anhydroglucose unit ([6]-[11]). Consequently, the structural formula of the cellulose molecule previously accepted in the literature ([5]) does not fully describe its chemical properties. The structure of the real cellulose molecule may be represented by formula (I)* ([12]):

(I)

Carboxyl and aldehyde groups in positions 2, 3, and 6 weaken the stability of the 1—4-β-glycosidic bond ([1],[2],[14]).

An open pyranose ring, if such is present in the cellulose molecule, creates hemiacetal bonds in position 1—4, which are characterized by low stability in an acid medium ([15]). In higher sugars, the existence of bonds ([13]) of the type



$$-\underset{\displaystyle OH}{\underset{|}{CH}}-O-$$

is admitted, but there is no experimental confirmation of this.

The study of the interaction of chlorine water with carbohydrates ([16]) gave grounds to suppose that at acidic pH rupture of the 1—5 bond occurs with the formation of a hemiacetal hydroxyl.

In our work, the task was set of experimentally confirming the supposition that, in the cellulose macromolecule, part of the anhydroglucose residues are present in a state opened at the 1—5 bond.

The experiments were carried out on samples of hydrate cellulose with DP-3290. The hydrate-cellulose samples were preliminarily treated with 97% acetic reaction scheme

Figure 2: reaction scheme

acid, which hydrolyzes the weakened glycosidic-glucose bonds of the cellulose macromolecule (17).

The samples were then treated with a hydrochloric-acid solution of pH 1.8 in order to open part of the pyranose rings at the 1–5 bond. The samples obtained were methylated with dimethyl sulfate in an alkaline medium. The methylated cellulose samples were hydrolyzed with a 1% aqueous solution of HCl for 1 hour at a temperature of 40−50°. This process is represented by the scheme:

$$\text{cellulose unit} \longrightarrow \text{opened unit} \xrightarrow[\text{NaOH}]{(\mathrm{CH_3})_2\mathrm{SO_4}}$$

* Dots denote anhydroglucose units of the molecule omitted in the scheme.

$$\text{—O—[methylated anhydroglucose residue]—O—} \xrightarrow[\text{hydrolysis}]{1\%\,\mathrm{HCl}} \text{—O—[residue with hemiacetal OH]—O—} + \mathrm{CH_3OH}$$

Probable methylation of the hydroxyls at C_2, C_3, C_6 leads to the formation of simple methyl ethers that are stable under the given conditions. Methyl groups attached through a hemiacetal hydroxyl are, under these conditions, extremely unstable and readily pass into the hydrolysate.

The methyl alcohol formed as a result of hydrolysis was determined in the form of 3,5-dinitrobenzoates by the method of ascending-descending chromatography with solvent overflow on preliminarily acetylated paper (18–20).

Methanol appeared unambiguously. The methanol detected cannot be attributed to its cleavage from the hydroxyl at the terminal C_1 of the cellulose macromolecule, since the amount of methanol that could be formed in this way is one order of magnitude lower than the sensitivity of the chromatographic method used (3 γ).

It follows from these data that, in the cellulose macromolecule, part of the anhydroglucose units under certain conditions may be present in an open state through the 1-5 bond.

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Note: Figure translations are in progress. See original paper for figures.