NEW STRUCTURES OF OXIDIZED DEXTRANES

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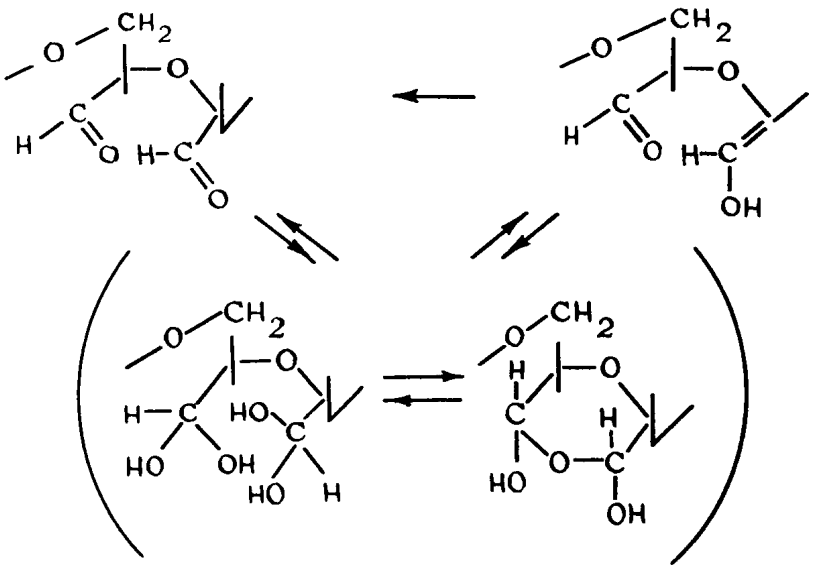
Oxidation of polysaccharides with sodium periodate was proposed in 1958 and has been widely used for the study of natural polysaccharides and for the synthesis of biologically active polysaccharide derivatives till now. It was found by chemical methods (in the case of dextranes) that such oxidation leads to the formation of two aldehyde groups in every oxidized cycle. However, these aldehyde groups have not been detected yet by physical methods. This was explained by the fact that the aldehyde groups exist in hydrate forms, such as semiacetals and hemdiols, which are not detectable by the spectral methods.

The new method of separation and purification of the oxidized dextranes elaborated in the Laboratory of Organic Synthesis of the LNPI has given an opportunity to get preparations which absorb light in the UV-region, characteristic for the aldehyde groups. The study of dextrane oxidation and methods of its purification showed that the structure of oxidized dextranes depended on the pH of the media. It was first shown (with the help of UV-, IR-, and NMR-spectroscopy and chemical reactions) that there was aldoenol tautomerism in oxidized dextranes: at pH below 4 the dialdehyde structure is stable, at pH above 5,2 the aldoenol structure appears. The transformation of these structures appears to take place through the hydrate or hemdiols forms which do not absorb light in UV and visible regions.

The separation of the dialdehyde and the aldoenol forms of oxidized dextrane and the investigation of their chemical properties, for example, the reaction with primary amines, gave an opportunity not only to believe in the existence of the aldoenol structure, but to identify the chemical structures of the reaction products. In the case of the aldehyde structure, it is the Schiff bases, in the case of the aldoenol structure — the nitrogen containing cycles with an unsaturated bond.