POLYSACCHARIDES OF BROWN ALGAE

V. SMITH DEGRADATION OF SARGASSAN AND PELVECYAN

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In the preceding communication [1] we have described the fragmentation of sargassan and pelvecyan by partial hydrolysis. In the present paper we give the results of a study of these polysaccharides by means of Smith degradation [2].

In the periodate oxidation of sargassan and pelvecyan the consumption of periodate amounted to 0.3-0.4 mole per anhydro unit. We reduced the resulting polyaldehydes to polyalcohols and subjected these to further investigation.

The complete acid hydrolysis of both polysaccharides formed as the main components mannose, glucuronic acid, galactose, fucose, glycerol, glycolaldehyde, and glyceraldehyde, and also small amounts of xylose, erythritol, and threitol. Consequently, the xylose was oxidized to a considerable extent, contained practically no sulfate groups, and was present in the carbohydrate chain in which it was bound by a 1,2- or a 1,4- linkage. The presence in the polyalcohols of considerable amounts of glyceraldehyde shows that the 1,2- linkage with the xylose residues is predominant. The small amounts of erythritol and threitol show the small number of galactose and mannose residues substituted in positions 4 accessible to oxidation (linear carbohydrate chain consisting of 1,4-bound residues or points of branching with substitution in positions 4 and 6).

The periodate oxidation of desulfurated sargassan and pelvecyan with subsequent tetrahydroborate reduction gave reaction products of approximately the same composition as the compounds obtained from sargassan and pelvecyan.

On partial hydrolysis of the polyalcohols, degraded sargassan and pelvecyan were formed, low-molecular-weight fragments – mainly glycerol, glyceraldehyde, and glycolaldehyde and only a small amount of propylene glycol – being split off. The latter shows the low degree of oxidation of the fucose residues.

The degraded polysaccharides were subjected to mild oxidation and on hydrolysis gave all the monosaccharides of the initial glucuronoglycans, the xylose being found in only very small amounts. The great complexity of the fragments studied does not permit their characterization in more detail. However, there is no doubt that in these fragments the monosaccharide residues have a high degree of substitution (sulfate groups, branching), which, in its turn, shows the high degree of substitutuion of the monosaccharide residues in the initial polysaccharides.

EXPERIMENTAL

The general experimental conditions have been given in preceding papers [1, 3].

Periodate Oxidation of Sargassan and Pelvecyan. A cooled solution of polysaccharide (1 g) was mixed with a cold solution of sodium periodate (4 g), and water was added to make 1 liter. Oxidation was performed in the dark at +5° C for 4 days. The consumption of periodate was 0.40 mole per anhydro unit for sargassan and 0.28 mole for pelvecyan. Ethylene glycol was added to the reaction mixture, and it was dialyzed against distilled water. The dialyzed solution was treated with 0.7 g of sodium tetrahydroborate

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and left overnight with stirring. The excess of tetrahydroborate was decomposed with acetic acid, and the resulting mixture was dialyzed and evaporated to dryness. The residue was mixed with methanol and evaporated three times in order to remove the boric acid completely. The yield of polyalcohols from sargassan (I) was 0.88 g and from pelvecyan (II) 0.91 g.

Complete Hydrolysis of the Polyalcohols. A mixture of 30 mg of a polyalcohol (I or II) and 1 ml of 2 N sulfuric acid was heated in a sealed tube in the boiling water bath for 12 h. The hydrolysate was neutralized with barium carbonate and evaporated. The resulting mixture of monosaccharides was investigated by gas-liquid chromatography in the form of the corresponding acetates and the acetates of the aldononitriles.

The following compounds were found in the hydrolysates of both polyalcohols: glycolaldehyde and glyceraldehyde, glycerol, fucose, mannose, galactose, and a small amount of xylose, threitol, erythritol, and propylene glycol.

Chromatography of the hydrolysates in thin layers of impregnated silica gel [4] in the butan-1-ol–acetone–water (4 : 5 : 1) system showed the presence of glucuronic acid in them, in addition to the compounds mentioned above.

Partial Hydrolysis of the Polyalcohols. A solution of 0.3 g of the polyalcohol (I) in 6 ml of 1 N sulfuric acid was stirred with a magnetic stirrer for 24 h and was centrifuged. A small brown precipitate was separated off, and the liquid phase was poured into an excess of ethanol. A white precipitate of degraded sargassan precipitated, and this was washed with alcohol and dried in the air. Yield 0.18 g. The ethanol was distilled off from the supernatant liquid, and the acid solution was neutralized with barium carbonate and filtered. Evaporation of the filtrate gave a mixture of low-molecular-weight decomposition products in the form of a sirup. Yield 0.03 g.

The polyalcohol (II) (0.1 g) was partially hydrolyzed in a similar manner. Degraded pelvecyan was isolated with a yield of 60 mg and a mixture of low-molecular-weight decomposition products with a yield of 22 mg.

The hydrolysates of the degraded polysaccharides were found by thin-layer and gas-liquid chromatography to contain fucose, galactose, mannose, glucuronic acid, and a small amount of xylose. The mixture of of low-molecular-weight decomposition products contained glycerol, glycolaldehyde and glyceraldehyde, and a small amount of propylene glycol, threitol and erythritol (gas-liquid chromatography) and polyol glycosides (paper chromatography).

SUMMARY

It has been shown that in pelvecyan and sargassan the monosaccharide residues have a high degree of substitution (sulfate groups, branching). The xylose residues present in these polysaccharides are oxidized by periodate to a considerable degree.

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