POLYSACCHARIDES OF BROWN SEAWEEDS

VII. A COMPARATIVE STUDY OF THE PRODUCTS OF THE SMITH DEGRADATION OF PELVECYAN AND ITS DESULFURATED DERIVATIVE

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In a preceding communication [1] preliminary results on the structure of pelvecyan were given. The present paper describes the results of an investigation of the fragments isolated from the Smith degradation of pelvecyan and its desulfurated derivative. The polysaccharides obtained were studied analytically (Table 1).

As the curves of gel filtration of Bio-Gel P-100 show, during desulfuration the degradation of the initial pelvecyan and of the desulfurated pelvecyan takes place (Fig. 1, curves 1 and 2). However, the desulfurated pelvecyan has the same quantitative monosaccharide composition as the initial material (see Table 1). The different behaviors of the initial and the desulfurated pelvecyans on Smith degradation can be explained by the presence and absence, respectively, of sulfo groups. The desulfuration of the pelvecyan during the Smith treatment leads to a considerable splitting off of fucose residues and to the accumulation of the other monosaccharides.

In the degraded polysaccharide from pelvecyan (PSII), fucose predominates among the sugars, and in the degraded polysaccharide from desulfurated pelvecyans (PSIII) the amount of fucose falls (see Table 1). The desulfurated pelvecyan is oxidized more intensively than the initial material. The consumption of periodate increases, probably because of the desulfurated fucose residues, in which there are α-glycol groupings. The low-molecular-weight products of the Smith degradation of PSIII contain propylene glycol. Consequently, some of the fucose residues have the sulfo group at C-4 and are attached to the carbohydrate chain by a 1,2 bond or (and) are at the nonreducing end of the polysaccharide chain and are sulfurated in position 3. The periodate oxidation of desulfurated pelvecyan leads mainly to the destruction of the fucose residues, no appreciable depolymerization of the polysaccharide being observed (Fig. 1, curve 3). It may be assumed that the fucose residues are located on the periphery of the pelvecyan molecule.

The polysaccharide (III) obtained as the result of the primary Smith degradation undergoes additional cleavage with periodate. This shows the presence of branchings in the polysaccharide chain: The side chains are oxidized by periodate and are therefore split off on hydrolysis, liberating monosaccharide links capable of being oxidized. When PSIII is desulfurated, the amount of sulfurated monosaccharide residues falls fourfold. However, the oxidations of PSIII and PSIV consume the same amounts of periodate and form PSV and PSVI with similar monosaccharide compositions (see Table 1). The gel filtration curves for these polysaccharides are also similar (see Fig. 1, curves 4 and 5). The weak oxidation of PSIV and PSIII by periodate is obviously due not to the presence of sulfo groups but to the position of the glycosidic linkages (1,3 bonds, branchings). The appreciable accumulation of residues of mannose in the degraded polysaccharides (see Table 1) permits the assumption that in the partially desulfurated pelvecyan they do not undergo oxidation, or only to a small extent. The amount of sulfate groups in the degraded polysaccharides (see Table 1) shows that a part of the mannose residues is not sulfated. The mannose residues are not oxidized, and therefore they can be taken as the points of branching of the polysaccharide chain or else the

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TABLE 1

Polysaccharides	Amount, %							
	S	N	COOH	monosaccharides				
				Fuc	Xyl	Man	Gal	Y*
Pelvecyan (pyridinium salt)	5,79	4,2	5,63	19,6	10,7	5,7	2,9	0,0
	5,76	4,4	5,93	—	—	—	—	
Desulfurated pelvecyan (PSI)	1,19	2,93	7,24	18,2	9,7	5,6	3,0	0,0
	1,16	2,95	—	—	—	—	—	
Degraded pelvecyan (PSII)	9,14	0,18	3,71	25,4	8,2	10,6	3,6	0,0
	9,06	0,22	3,11	—	—	—	—	
Degraded polysaccharide I (PSIII)	2,53	0,24	6,81	7,6	18,6	26,0	2,0	7,7
	2,43	0,25	6,65	—	—	—	—	—
Desulfurated polysaccharide III (PSIV)	0,65	—	—	6,0	15,5	22,3		6,0
Degraded polysaccharide III (PSVI)	—	—	—	3,0	12,4	22,5	1,7	7,2
Degraded polysaccharide IV (PSV)	—	—	—	4,7	13,5	22,8	2,7	6,8

*Y represents an unidentified compound.

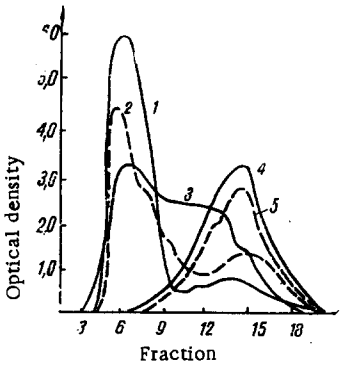

Fig. 1. Elution curves of gel filtration on Bio-Gel P-100: 1) pelvecyan; 2) desulfurated pelvecyan; 3) polysaccharide (III); 4) polysaccharide (V); 5) polysaccharide (VI).

existence of a 1,3 bond between them may be assumed. Thus, the pelvecyan molecule contains a nucleus resistant to periodate oxidation consisting mainly of residues of mannose, glucuronic acid, and, probably, xylose,

It is interesting to note the appearance in the degraded polysaccharide of a hitherto unknown compound which has the same R_f value on paper chromatograms as glucose and has the same retention time as the glucose derivative in the gas chromatography of the aldononitrile acetates. Its identification is being performed.

EXPERIMENTAL

The substances were analyzed on a Tswett-2 chromatograph on columns containing Chromosorb W (AW, DMCS 45-60 mesh) bearing 8% (w/w) of poly(butane-1,4-diol succinate). The rate of flow of the carrier gas (nitrogen) was 60 ml/min, that of hydrogen 60 ml/min, and that of air 300 ml/min. The temperature of the thermostat was 190-225°C, the temperature being raised at the rate of 2°C/min. The derivatives used for GLC analysis were the full acetates and the acetates of the aldononitriles [2]. The quantitative monosaccharide compositions of the polysaccharides were determined by methods described previously [2, 3], the amounts of sulfate groups by Gustaffson's method [4], and the amounts of uronic acids by decarboxylation [5]. The results of these determinations are given in Table 1.

Gel Filtration of the Polysaccharides. A solution of 1.0-1.5 mg of a polysaccharide in 0.2 M sodium chloride was transferred to a standard column (1.1 × 17.5 cm) containing Bio-Gel P-100 and elution was performed with the same solution. The fractions collected (0.5 ml each) were analyzed by the phenol–sulfuric acid method [6].

Desulfuration of Pelvecyan [7]. A mixture of 1.5 g of the dried pyridinium salt of pelvecyan and 150 ml of dimethyl sulfoxide containing 2.2 ml of pyridine was heated at 85-92°C for 9 h. The reaction mixture was dialyzed and freeze-dried. A desulfurated polysaccharide (PSI) was obtained with a yield of 66.6% (see Table 1).

Periodate Oxidation of Pelvecyan and of Desulfurated Pelvecyan. A solution of 2.6 g of periodic acid dehydrate in 750 ml of water was brought to pH 5.4 with a solution of sodium carbonate and was cooled to + 5°C. Then 1.5 g of polysaccharide was added. The resulting solution was kept in the refrigerator for 6 h. The course of oxidation was monitored by the consumption of periodate [8]. Oxidation was complete after 4 h (the consumption of periodate ceased); the amount of periodate consumed was 0.35 mole/162. The reaction was stopped by adding ethylene glycol. The reaction mixture was dialyzed and then 1.5 g of potassium tetrahydroborate was added and the resulting mixture was kept overnight in the refrigerator. The excess of potassium tetrahydroborate was decomposed by the addition of a solution of acetic acid. The resulting mixture was dialyzed and evaporated to dryness. Methanol was added to the residue and it was evap-

orated, this operation being repeated three times. The yield of polyalcohol (I) was 1.03 g (66.6%). The desulfurated pelvecyan was oxidized as described above. The consumption of periodate was 0.44 mole/162 and the yield of the polyalcohol (II) was 69.4%.

Partial Hydrolysis of the Polyalcohol. A mixture of 0.9 g of the polyalcohol (I) and 18 ml of 2 N sulfuric acid was stirred with a magnetic stirrer for 24 h. The brown precipitate that deposited was centrifuged off, and the solution was poured into ethanol. The precipitate of degraded polysaccharide was separated off by centrifuging, washed with ethanol, and dried in the air. The weight of PSII was 0.32 g (35.5%). The centrifugate was evaporated until the ethanol had been eliminated and was neutralized with barium carbonate. The precipitate of barium sulfate was separated off and the filtrate was evaporated to dryness. The weight of low-molecular-weight products was 0.18 g (20.0%). When 0.81 g of the polyalcohol (II) was hydrolyzed in the same way, the yield of PSIII was 0.28 g (34.5%) and that of low-molecular-weight compounds was 0.31 g (38.4%). Among the low-moleular-weight products, compounds with the retention times of propylene glycol, ethylene glycol, glyceraldehyde, and glycerol were detected by the GLC method.

The desulfuration of the degraded polysaccharide and the Smith degradation of the degraded polysaccharides were performed by the methods given above. They gave rise to the polysaccharides (IV) (yield 75%), (V) (yield 22.1%), and (VI) (yield 20.5%). The oxidation of the polysaccharides (V) and (VI) consumed 0.23 mole/162 of periodate in each case.

SUMMARY

The fucose residues in pelvecyan are mainly sulfurated and are present on the periphery of a molecule, the nucleus of which consists of a glucuronomannan, The mannose residues are feebly oxidized by periodate and, at least for some of them, this is due not to the presence of sulfate groups but to the nature of the glycosidic linkages in the polysaccharide.

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