# POLYSACCHARIDES OF BROWN SEAWEEDS

## X. THE STRUCTURE OF THE SIDE CHAINS OF THE PELVECYAN MOLECULE

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The results of a study of pelvecyan – a glucuronoglycan from Pelvetia wrightii [1] – have shown that the molecule is based on a linear carbohydrate chain of alternating mannose and glucuronic acid residues [2]. The present paper gives the results of an investigation of the structure of the side chains of pelvecyan.

The partial hydrolysis of this polysaccharide with dilute oxalic acid [2], and also the acetolysis of desulfurated pelvecyan, formed, in addition to a glucuronomannan, a complex mixture of mono and oligosaccharides which we separated partially by the column chromatography of the corresponding acetates on Woelm kieselguhr followed by preparative paper charomatography (PC) of the deacetylated fractions enriched in the oligosaccharides. Eight chromatographically individual oligosaccharides (A-H, Table 1) were isolated. The acid hydrolysis of the compounds obtained and of their tetrahydroborate-reduced analogs enabled their monosaccharide compositions and the reducing terminal residues of all the oligosaccharides to be determined (see Table 1). The quantitative monosaccharide compositions [3] and the chromatographic mobilities of the acetylated oligosaccharides in a thin layer of silica gel showed that oligosaccharides A-C and E-G are disaccharides and D and H are trisaccharides.

Further information on the structures of these oligosaccharides was obtained by analyzing the products of the methanolysis of the fully methylated oligosaccharides by gas–liquid chromatography. Table 1 gives the methyl ethers of methyl glycosides found in the products of the methanolysis of the permethylated oligosaccharides.

TABLE 1. Composition and Structure of the Oligosaccharides Isolated by the Partial Hydrolysis and Acetolysis of Pelvecyan

| Method of cleaving the pelvecyan | Oligosaccharides | Monosaccharide composition | Reducing end | Methylated sugars | Structure |
|---|---|---|---|---|---|
| Acetolysis | A | Xyl : Fuc (1 : 1) | Fuc | 2, 3, 4-Xyl<br>2, 4-Fuc | Xylp 1→3 Fuc |
| | B | Fuc : Gal (1 : 1) | Gal | ? | ? |
| | C | Xyl : Gal (1 : 1) | Gal | 2, 3, 4-Xyl<br>2, 3, 6-Gal | Xylp 1→4 Gal |
| | D | Xyl : Gal : Man (1 : 1 : 1) | Man | 2, 3, 4-Xyl<br>2, 3, 4-Gal<br>2, 3, 4-Man | Xylp 1→6 Gal 1→<br>→6 Man |
| Hydrolysis with 0.5 M oxalic acid | E | Fuc | Fuc | 2, 3, 4-Fuc<br>di-O-Me-Fuc | ?<br>Fucp 1→2 Fuc |
| | F | Fuc : Xyl (1 : 1) | Xyl | 2, 3, 4-Fuc<br>3, 4-Xyl | Fucp 1→2 Xyl |
| | G | Xyl : Gal (1 : 1) | Gal | 2, 3, 4-Xyl<br>2, 3, 6-Gal | Xylp 1→4 Gal |
| | H | Fuc : Xyl : Gal (1 : 1 : 1) | Gal | 2, 3, 4-Fuc<br>3, 4-Xyl<br>tri-O-Me-Gal | Fucp 1→2 Xyl 1→<br>→? Gal |

Notes: Xyl) D-xylose; Fuc) D-fucose; Gal) D-galactose; Man) D-mannose; p) pyranose; 2,3,4-Xyl) 2,3,4-tri-O-methyl-D-xylose, etc.

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Thus, the following fragments are present in the side chains of pelvecyan: Xyl1 → 3 Fuc; Xyl1 → 4 Gal; Xyl1 → 6 Gal 1 → 6 Man; Fuc 1 → 2 Xyl1 → Gal; Fuc 1 → 2 Xyl and Fuc 1$\frac{?}{-}$ → 2 Fuc.

Consequently, the side chains of pelvecyan are constructed of xylose, fucose, and galactose residues, which are present in them in various sequences and are bound to one another by various types of glycosidic bonds. Oligosaccharide D may indicate the attachment of one of the side chains to a mannose residue of the main chain by a 1,6-glycosidic bond.

## EXPERIMENTAL

Chromatography was performed on FN-3, FN-4, and Whatman No. 1 papers in the following solvent systems: 1) butan-1-ol–ethanol–water (40 : 11 : 19); 2) butan-1-ol–pyridine–water (6 : 4 : 3); 3) butan-1-ol–acetic acid–water (4 : 1 : 5, upper layer).

The benzene–ethyl acetate (7 : 3) system was used for chromatography in a thin layer of silica gel (more than 200 mesh). The oligosaccharides were methylated by Purdie's method and the methylation products were analyzed as described previously [4].

Partial Hydrolysis. A mixture of 2.5 g of pelvecyan and 150 ml of 0.5 M oxalic acid was heated and was then worked up as described previously [2]. The resulting mixture of mono- and oligosaccharides (yield 2.0 g) was acetylated with acetic anhydride in pyridine.

Acetolysis of Desulfurated Pelvecyan. Desulfurated pelvecyan [4] (2 g) was stirred by means of a magnetic stirrer with 50 ml of acetolysis mixture (1.5 ml of conc. $H_2SO_4$ and 48.5 ml of $Ac_2O$) at room temperature for six days. The resulting mixture was poured onto ice and extracted with chloroform, and the combined chloroform extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated in vacuum. The yield of acetolysis products was 2.1 g.

Separation of the Oligosaccharides. A mixture of mono- and oligosaccharides in the form of the full acetates (0.9 g) was deposited on a column (32 × 2.0 cm) of Woelm silica gel in benzene and was eluted with benzene containing increasing concentrations of ethyl acetate. The fractions corresponding to the acetates of the oligosugars were dried and deacetylated. The separation of the fractions was monitored by the TLC method. Further purification was performed by chromatography on paper in systems 1, 2, and 3. From the complex mixture of acetolysis products the following were isolated in the individual state (see Table 1): oligosaccharide A (11.5 mg), $[\alpha]_D^{22}$ −40° (in water); oligosaccharide B (8.3 mg), $[\alpha]_D^{22}$ +50.4° (in water); oligosaccharide C (13.4 mg); and oligosaccharide D (5.1 mg).

From the mixture of products of partial hydrolysis we obtained the following compounds in the individual state: oligosaccharide E (9.2 mg) $[\alpha]_D^{22}$ −158° (in water); oligosaccharide F (6.2 mg), $[\alpha]_D^{22}$ −60° (in water); oligosaccharide G (5.2 mg); and oligosaccharide H (10.7 mg).

Reduction of the Oligosaccharides. A solution of 1-2 mg of an oligosaccharide in 0.5 ml of water was treated with 5 mg of sodium tetrahydroborate and the mixture was left at room temperature for 18 h. Then it was treated with Amberlite IR-120 ($H^+$) and was evaporated several times with methanol to eliminate boric acid. The reduced products were hydrolyzed with 2 N sulfuric acid. The hydrolyzates were investigated by PC in system 3 (see Table 1).

## SUMMARY

The compositions and structures of some oligosaccharides isolated by the partial acid hydrolysis and acetolysis of pelvecyan have been established. It has been shown that the side chains of the pelvecyan molecule consist of residues of fucose, xylose, and galactose connected with one another in various sequences and by various types of glycosidic bonds.

## LITERATURE CITED

1. Yu. S. Ovodov and A. F. Pavlenko, Khim. Prirodn. Soedin., 400 (1970).
2. V. A. Khomenko, A. F. Pavlenko, T. F. Solov'eva, and Yu. S. Ovodov, Khim. Prirodn. Soedin., 393 (1971).
3. I. N. Krasikova, T. F. Solov'eva, V. A. Khomenko, and Yu. S. Ovodov, Khim. Prirodn. Soedin., 253 (1972).
4. A. F. Pavlenko, A. V. Kurika, V. A. Khomenko, and Yu. S. Ovodov, Khim. Prirodn. Soedin., 142 (1973).