POLYSACCHARIDES OF BROWN SEAWEEDS

VIII. THE STRUCTURE OF THE SIDE CHAINS OF THE SARGASSAN MOLECULE

V. A. Khomenko and Yu. S. Ovodov

UDC 547.917+639.64

The results of a study of sargassan, a glucuronoglycan from Sargassum pallidum (brown seaweed) [1], have shown that its molecule is based on a linear carbohydrate chain of alternating glucuronic acid and mannose residues [2]. We have attempted to determine individual features of the structure of the side chains of the sargassan molecule by analyzing the oligosaccharide fragments formed on partial hydrolysis with 1% sulfuric acid or 0.5 M oxalic acid by a previously described method [2]. The mixture of oligo- and monosaccharides was fractionated on Bio-Gel P-6 (elution with water), then by column chromatography on cellulose (with water-saturated butanol), and, finally, by preparative paper chromatography in the butanol–ethanol–water (40 : 11 : 19) and butan-1-ol–acetic acid–water (4 : 5 : 1, upper layer) systems. Six chromatographically individual oligosaccharides, A-F, were isolated (Table 1). The results of acid hydrolysis of the compounds obtained and of their tetrahydroborate-reduced analogs showed the monosaccharide compositions and reducing terminal residues of all the oligosaccharides (see Table 1). The quantitative monosaccharide compositions (by gas-liquid chromatography of the acetates of the aldononitriles [3]) and chromatographic mobility showed that the oligosaccharides A-D are disaccharides, while oligosaccharide E is apparently a trisaccharide.

Preliminary results obtained by means of color reactions with TTC [4] and with the diphenylamine–aniline reagent [5] indicate a 1,2-bond at the reducing end of oligosaccharides B, C, E, and F, a 1,3 bond in disaccharide A, and a 1,4 bond in disaccharide D. In addition, on alkaline hydrolysis [6], disaccharide A decomposed into its constituent monosaccharides, while the other oligosaccharides remained unchanged. As is well known, this shows that disaccharide A has a 1,3 bond.

The higher proportion of disaccharides A and D in the hydrolyzate from sargassan permitted them to be isolated in amounts sufficient for study by the methylation method. In the methanolyzate of the fully methylated disaccharide A, gas-liquid chromatography showed the presence of the methyl glycosides of 2,3,4-tri-O-methyl-D-xylose and 2,4-di-O-methyl-L-fucose. Thus, disaccharide A is 3-O-D-xylopyranosyl-L-fucose.

TABLE 1

Oligosaccharide	R_{Gal}	Monosaccharide composition*	Reducing terminal residue	Reaction with TTC†	Reaction with diphenylamine
A	1,23	Xyl, Fuc	Fuc	+	—
B	1,13	Fuc, Xyl	Xyl	—	—
C	0,90	Fuc, Gal	Gal	—	—
D	0,77	Xyl, Gal	Gal	+	+
E	0,47	Xyl, Fuc, Gal	Gal	—	—
F	0,19	Gal	Gal	—	—

*Xyl = D-xylose; Fuc = L-fucose; Gal = D-galactose.

† TTC = triphenyltetrazolium chloride.

Institute of Biologically Active Substances, Far-Eastern Scientific Center. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 107-108, January-February, 1973. Original article submitted July 12, 1972.

The methanolyzate of disaccharide D was found to contain the methyl glycosides of 2,3,4-tri-O-methyl-D-xylose and 2,3,6-tri-O-methyl-D-galactose. Consequently, disaccharide D is 4-O-D-xylopyranosyl-D-galactose.

Thus, the side chains of sargassans contain the following oligosaccharide fragments: Xyl 1→3 Fuc; Fuc 1→2 Xyl; Fuc 1→2 Gal; Xyl 1→4 Gal; Xyl–Fuc 1→2 Gal; $(Gal)_n$1→2 Gal.

LITERATURE CITED

1. Yu. S. Ovodov, V. A. Khomenko, and T. F. Guseva, Khim. Prirodn. Soedin., 285 (1970).
2. V. A. Khomenko, A. F. Pavlenko, T. F. Solov'eva, and Yu. S. Ovodov, Khim. Prirodn. Soedin., 393 (1971).
3. V. M. Easterwood and B. J. L. Huff, Svensk Papperstidn., 72, 768 (1969).
4. G. Avigad, R. Zelinson, and S. Hestrin, Biochem. J., 80, 57 (1961).
5. S. Schwimmer and A. Bevenue, Science, 123, 543 (1956).
6. T. J. Painter, Chem. Ind. (London), 34 (1963).