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Structure of a fucoidan from the brown seaweed *Fucus serratus* L.☆

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Abstract—A fucoidan consisting of L-fucose, sulfate and acetate in a molar proportion of 1:1:0.1 and small amounts of xylose and galactose were isolated from the brown seaweed *Fucus serratus* L. The fucoidan structure was investigated by 1D and 2D ^{1}H and ^{13}C NMR spectroscopy of its desulfated and de-O-acetylated derivatives as well as by methylation analysis of the native and desulfated polysaccharides. A branched structure was suggested for the fucoidan with a backbone of alternating 3- and 4-linked α-L-fucopyranose residues, →3)-α-L-Fuc*p*-(1→4)-α-L-Fuc*p*-(1→, about half of the 3-linked residues being substituted at C-4 by trifucoside units α-L-Fuc*p*-(1→4)-α-L-Fuc*p*-(1→3)-α-L-Fuc*p*-(1→. Minor chains built up of 4-linked α-fucopyranose and β-xylose residues were also detected, but their location, as well as the position of galactose residues, remained unknown. Sulfate groups were shown to occupy mainly C-2 and sometimes C-4, although 3,4-diglycosylated and some terminal fucose residues may be nonsulfated. Acetate was found to occupy C-4 of 3-linked Fuc and C-3 of 4-linked Fuc in a ratio of about 7:3.
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1. Introduction

Sulfated fucans present in brown algae and some marine invertebrates have a wide variety of biological activities.[2] Invertebrate polysaccharides have usually simple ordered structures differing in the specific sulfation patterns and/or position of glycosidic linkages within their oligosaccharide repeating units.[3,4] As a result, the structures of these repeating units can be determined unambiguously, especially by using high-field NMR spectroscopy,[5] and hence, important correlations between structures and biological activities of polysaccharides may be outlined.[6,7] In contrast, algal sulfated fucans, usually named fucoidans, have much more complex and heterogeneous structures devoid of regularity.[8] There is only one example of an algal polysaccharide, a highly sulfated fraction of fucoidan from *Fucus distichus*, which has a ^{13}C NMR spectrum corresponding to a structure with repeating disaccharide units: →3)-α-L-Fuc*p*(2,4-di-SO_3^-)-(1→4)-α-L-Fuc*p*(2SO_3^-)-(1→, but even in this case some minor deviations from the regular structure were observed using chemical methods of structural analysis.[9] Several fucoidans isolated from closely related species of brown algae belonging to the same order Fucales seem to have similar backbones of alternating 3- and 4-linked α-L-fucopyranose residues, although the regularity of their molecules is masked by random sulfation and acetylation.[10,11] Representatives of Chordariales[12] and Laminariales[13,14] may have another backbone built up of 3-linked α-L-fucopyranose residues. Branched structures were postulated for several fucoidans,[12,14,15] but the presence of sulfate groups often prevents the unambiguous identification of branching points and determination of

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their position. Several minor monosaccharide constituents (galactose, xylose, etc.) were found in many fucoidan preparations, but their structural significance, as a rule, also remains unknown.[16]

In order to elucidate structural features of fucoidans responsible for their biological activities, we continue the investigation of sulfated polysaccharides from different species of brown algae. The present work is devoted to the structural analysis of a fucoidan isolated from *Fucus serratus* L.

2. Results and discussion

Water-soluble polysaccharides were extracted from the defatted[17] biomass of *F. serratus* and fractionated by anion-exchange chromatography (see Section 4). The yields and composition of the four fractions obtained are given in Table 1. Fraction F_4, which was essentially a homofucan sulfate containing fucose and sulfate in a molar ratio of about 1:1 and only traces of other monosaccharide constituents, was subjected to structural analysis.

The IR-spectrum of F_4 contained an intense absorption band at 1240 cm^{-1} (S=O) common to all the sulfate esters. An additional sulfate absorption band at 824 cm^{-1} (C–O–S, secondary equatorial sulfate) and a shoulder at 844 cm^{-1} (C–O–S, secondary axial sulfate) indicated that the majority of sulfate groups occupy positions 2 and/or 3, and only a minor part of sulfate is located at position 4 of fucopyranose residues.

Like many other native algal fucoidans, fraction F_4 had a very complex ^{13}C NMR spectrum, which was difficult to interpret completely (Fig. 1). It contained several intense signals in the anomeric (97–102 ppm) and high-field (16.5–16.7 ppm) regions, which are typical of α-fucopyranosides. The signals at 21–22 ppm confirmed the presence of *O*-acetyl groups. Unfortunately, the ^1H NMR spectrum of F_4 was poorly resolved, so we could not apply 2D procedures to assign other resonances in the ^{13}C NMR spectrum of the native polysaccharide.

Several chemical modifications were carried out to simplify the structure of F_4. Three modified polysaccharide preparations were obtained as the result of desulfation (deS), deacetylation (deAc) and both desulfation and deacetylation (deSdeAc). Molar proportions of constituents of F_4 and modified preparations are given in Table 2. Deacetylation was carried out by treatment of polysaccharides with aqueous ammonia.[14] A solvolytic desulfation procedure[18] was used to remove sulfate groups. The yield of desulfated polysaccharide (deS) was 34.8% of theoretical value. The preparation still contained about 4% of residual sulfate. High negative values of optical rotation of deAc and deSdeAc were consistent with α-configuration of L-fucopyranose residues in these polysaccharides.

Both ^1H (Fig. 2) and ^{13}C (Fig. 3) NMR spectra of desulfated and de-O-acetylated polysaccharide (deSdeAc) were resolved enough to apply 2D spectroscopy for the assignment of resonances in the 1D spectra. Analysis of COSY, TOCSY and HSQC (Fig. 4) spectra revealed the presence of α-fucose, β-xylose and β-galactose residues

Table 1. Yields and composition of fucoidan fractions obtained by ion-exchange chromatography of crude polysaccharide preparation (F)

Fraction	Yield, % of F	Neutral monosaccharides (%)					Sulfate (SO_3Na) (%)	Acetate (CH_3CO) (%)
		Fuc	Xyl	Gal	Man	Glc		
F_1	23.2	—	—	—	2.8	92.8	—	—
F_2	2.6	35.3	10.2	2.1	4.0	3.3	14.8	0.7
F_3	18.1	54.8	4.0	2.6	1.4	0.6	21.9	0.7
F_4	43.9	46.6	1.5	1.6	—	—	31.8	1.1

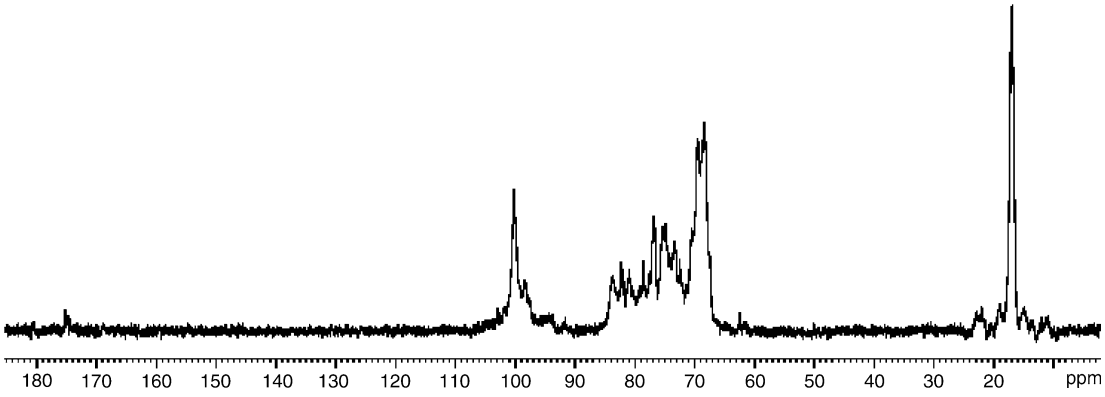

Figure 1. The ^{13}C NMR spectrum of native fucoidan F_4 (recorded at 333 K).

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