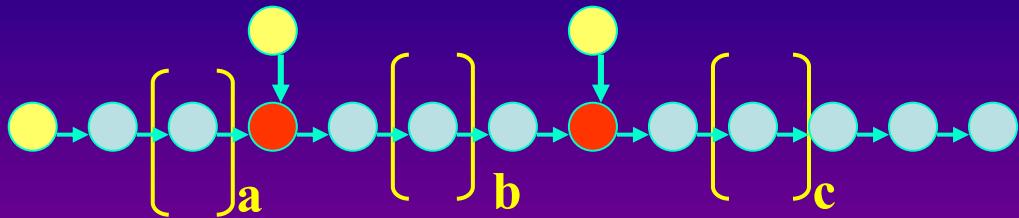


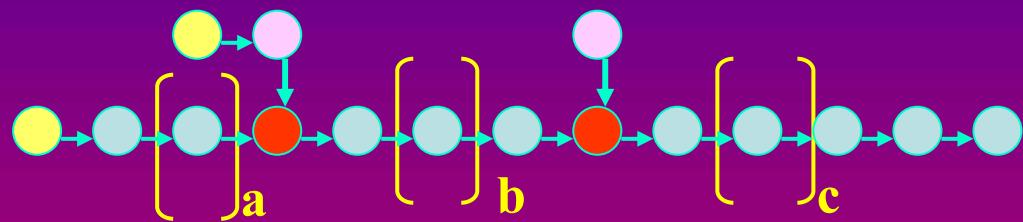
PIBOC Polysaccharide Collection

Laboratory of Enzyme Chemistry

1,3;1,6- β -D-Glucans



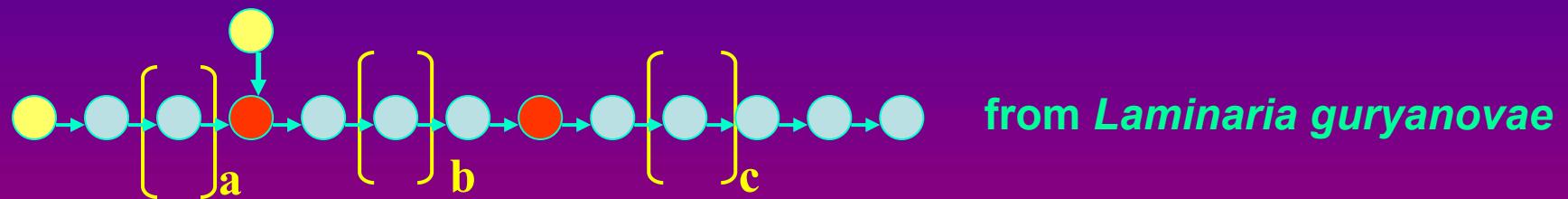
from *Laminaria cichorioides*
5 kDa



from *Fucus evanescens*
5 kDa

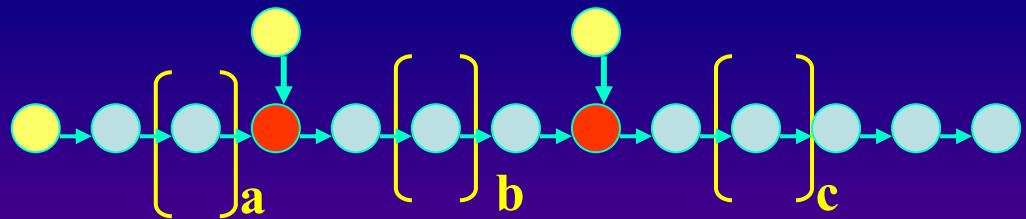
- - nonsubstituted Glc residue
- - 3-O-substituted Glc residue
- - 3,6-O-di-substituted Glc residue
- - 6-O-substituted Glc residue

1,3;1,6- β -D-Glucans



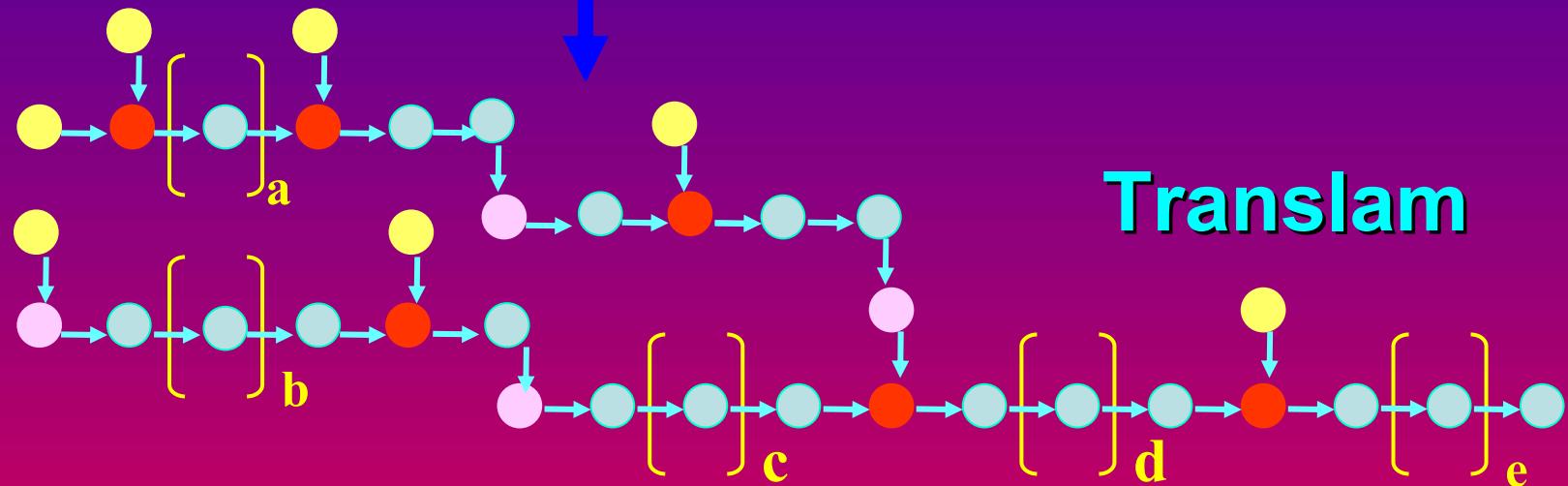
from *Laminaria guryanovaе*

Molecular weight : 5-16 kDa



Laminaran from *Laminaria cichorioides*

1,3- β -D-glucanase from *Chlamys albidus*



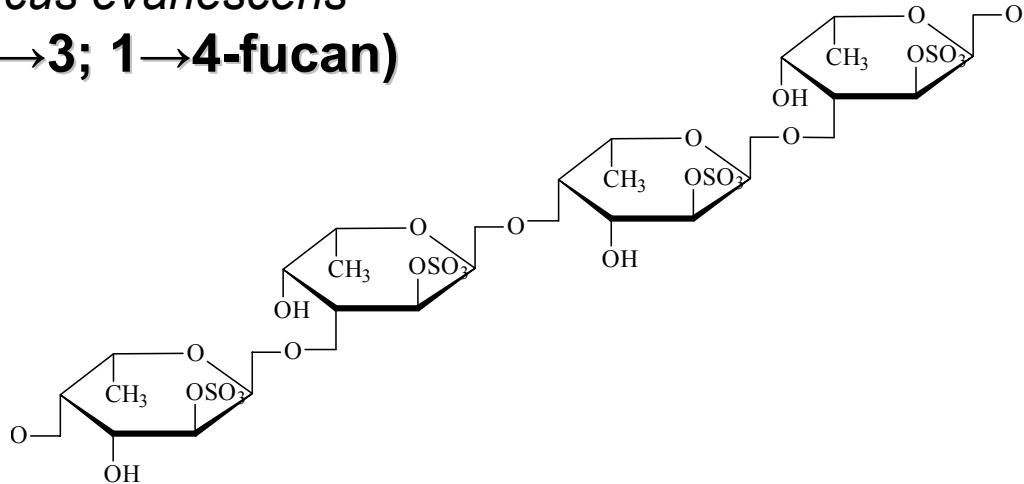
Translам

- - 3,6-O-di-substituted Glc residue
- - 3-O-substituted Glc residue
- - 6-O-substituted Glc residue
- - nonsubstituted Glc residue

8-10 kDa

Fucoidans

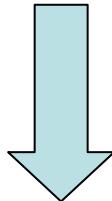
FUCOIDAN from
Fucus evanescens
(α -1→3; 1→4-fucan)



Molecular weight: 20-40 kDa
Fucose – 81 %
Fucose: SO₄²⁻ = 1:0.8

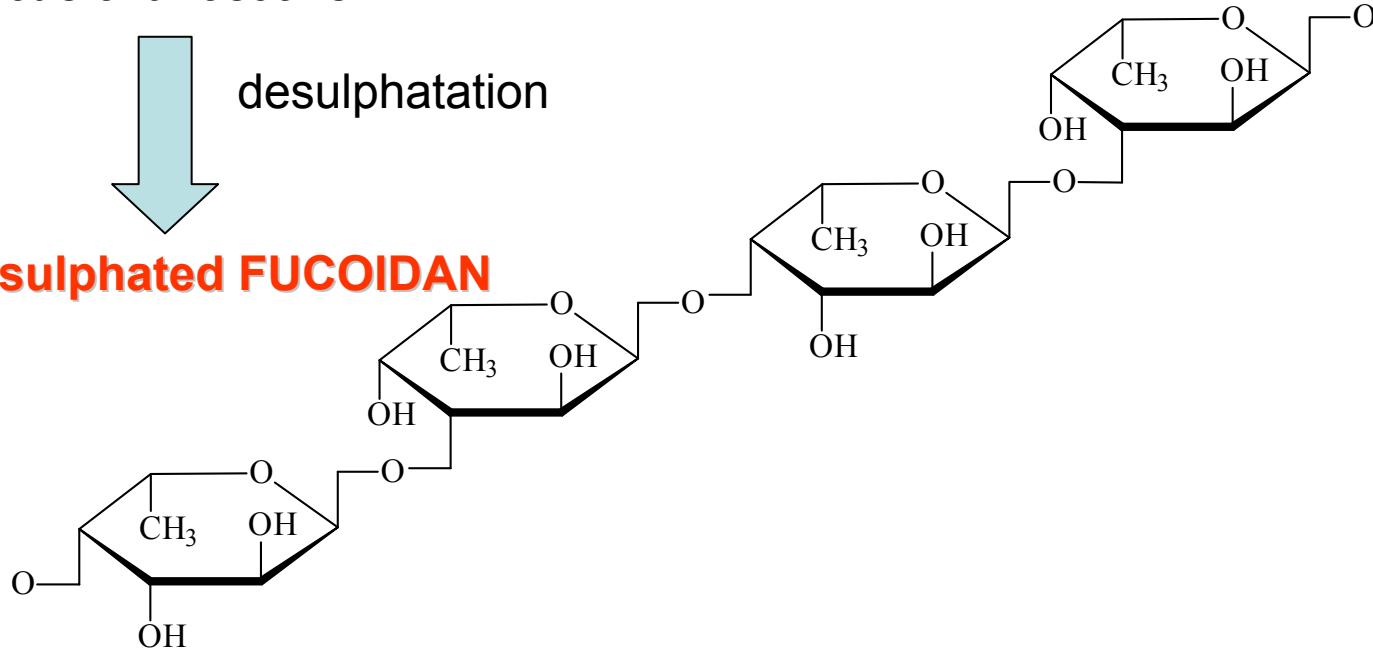
Fucoidans

FUCOIDAN from
Fucus evanescens



desulphatation

Nonsulphated FUCOIDAN

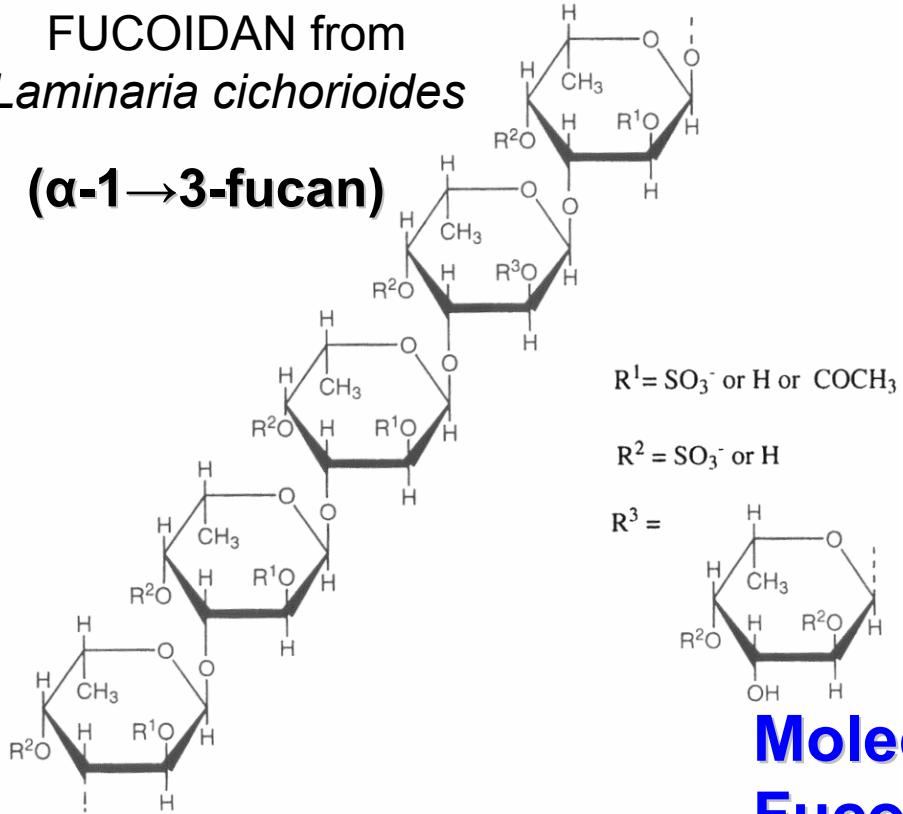


Fractions	Monosaccharide composition, % Fuc:Glc:Gal:Man:Xyl:Ram:GlcA	Level of sulphation, %
1	73:0:6:6.7:0:0	1.5

Fucoidans

FUCOIDAN from
Laminaria cichorioides

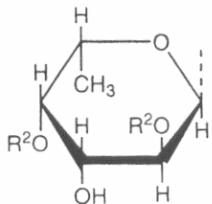
(α -1→3-fucan)



$R^1 = SO_3^-$ or H or $COCH_3$

$R^2 = SO_3^-$ or H

$R^3 =$



Molecular weight: 60-80 kDa

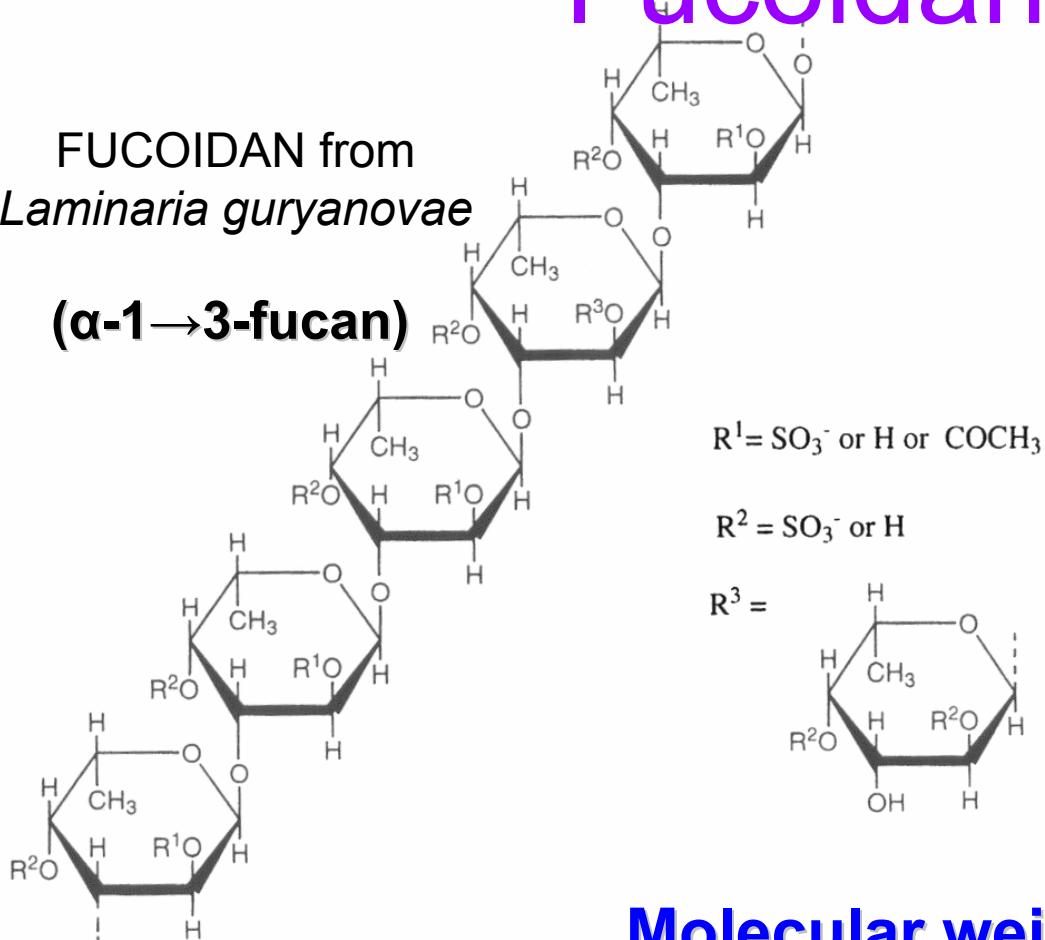
Fucose: 98%

Fucose: SO_4^{2-} = 1:1.7

Fucoidans

FUCOIDAN from
*Laminaria guryanova*e

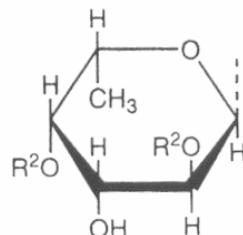
(α -1→3-fucan)



$\text{R}^1 = \text{SO}_3^-$ or H or COCH_3

$\text{R}^2 = \text{SO}_3^-$ or H

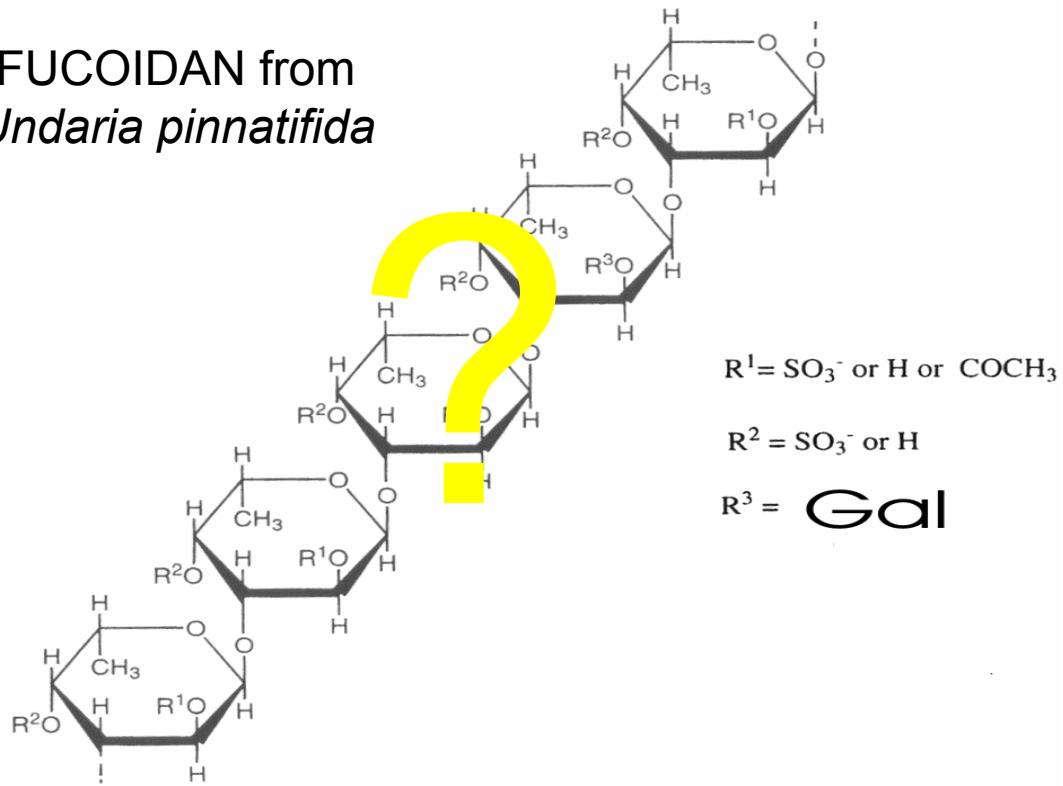
$\text{R}^3 =$



Molecular weight: 20-50 kDa
Fucose – 96%
Fucose: SO_4^{2-} = 1:0.4

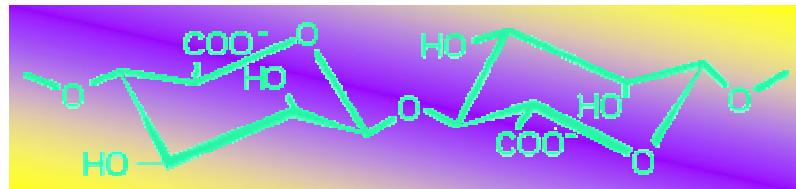
Fucoidans

FUCOIDAN from
Undaria pinnatifida



Fractions	Monosaccharide composition, %	Fucose: SO_4^{2-}
	Fuc:Glc:Gal:Man:Xyl:Ram:GlcA	
1	55:0:45:0:0:0:0	1:0.7

Polymannuronic acids



M-block

Sources:

Alaria fistulosa

Fucus evanescens

Laminaria cichorioides

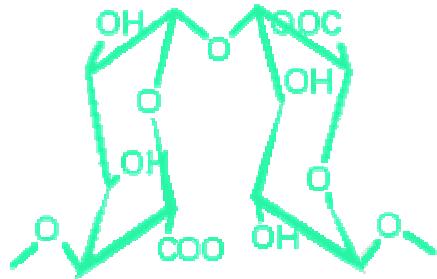
Molecular weight:

20kDa - 300 kDa

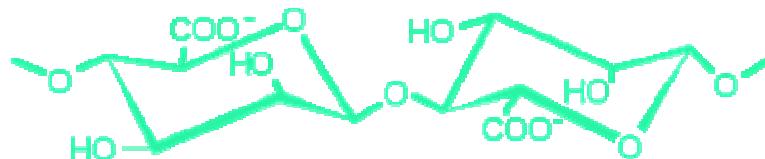
20 kDa-40 kDa

100-300 kDa

Alginic acids



G-block



M-block

Sources:

Alaria fistulosa

Fucus evanescens

Laminaria cichorioides 900 kDa

Undaria pinnatifida 900 kDa

Molecular weight:

Ratio M and G-block

2.8:1

1.0:1

2.5:1

3.0:1

Enzyme transformation of the FUCOIDAN

Fucoidans, highly sulfated polysaccharides of brown algae, possess diverse biological activities. The most interesting are antitumor, anticoagulant, and antiviral activities, e.g., against HIV, hepatitis virus, and herpes virus. For the last decade, the structure of these polysaccharides has been extensively studied. A close correlation between structural characteristics of fucoidans and the taxonomy of the corresponding brown algae was hypothesized: it is known that α -(1,3)-L-fucans are found in *Laminaria*, whereas species of *Fucus* genus mainly contain α -(1,3, 1,4)-L-fucans.

Structure/ activity correlations for these polysaccharides are poorly studied. **Usually fucoidans have a high d. p., so depolymerisation is needed for medicinal applications.**

The enzymes degrading polysaccharides are widely used in structural studies, in studies of biological activities, and in preparation of drugs.

Enzyme transformation of the FUCOIDAN from *Fucus evanescens*

The products of enzymatic cleavage of fucoidans by fucoidanases

Enzyme (pH-optimum)	Substrate, m. wt, kDa	Characteristics			
		HMP, yields*, %	n**	LMP, yields***, %	n
Acidic fucoidanase from <i>Littorina kurila</i> (5.4)	fucoidan from <i>F. evanescens</i> , 20-40	85	$n > 7$	15	$7 > n > 15$
	fucoidan from <i>L. cichorioides</i> , 60-80	95	$n > 7$	5	$7 > n > 15$
Basic fucoidanase from <i>L. kurila</i> (8.5)	fucoidan from <i>F. evanescens</i> , 20-40	55	$n > 7$	45	$7 > n > 15$
Fucoidanase from <i>P. citrea</i> KMM 3296 (7.2)	fucoidan from <i>F. evanescens</i> , 60-80	30	$n > 7$	70	$5 > n > 15$

HMP: highly molecular products obtained by precipitation with 80 % aqueous ethanol

*n (% of total amount of products) **n: degree of polymerization ***LMP: low molecular products

Enzyme transformation of the FUCOIDAN from *Fucus evanescens*

The characteristics of low-molecular products of enzymatic cleavage of fucoidan from *F. evanescens* by action of fucoidanase from hepatopancreas of *L. kurila* and *P. citrea* KMM 3296

A source of enzyme	Products	Yield, % from the starting substrate	M. wt., kDa or n^*	Carbohydrate composition, %						Molar ratio Fuc :SO ₄ ²⁻
				Fuc	Gal	Xyl	Rha	Glc	Man	
<i>Pseudoalteromonas citrea</i> KMM 3296	P-1-Ps	26	$5 \geq n \geq 2$	96	4	0	0	0	0	1:0.31
	P-2-Ps	8	2-3	97.2	0.4	2.1	0.3	0	0	1:0.53
<i>Hepatopancreas Littorina kurila</i> ,	P-1-L	30	3-10	92	1	1.8	0	2.5	3.7	1:0.59
	P-2-L	8	$7 \geq n \geq 2$	50	0	0	0	50	0	0
	P-1-1-L	17	3-10	92	1	1.8	0	2.5	3.7	1:0.59

*n: degree of polymerization of products

Enzyme transformation of the FUCOIDAN from *Fucus evanescens*

The fucoidanases from the marine mollusk *L. kurila* and the marine bacterium *P. citrea* KMM 3296 have a similar specificity: they catalyze the predominant cleavage of α -(1→3)-glycosidic bonds between fucose residues in the polysaccharide. In contrast to fucoidanase from *L. kurila*, the bacterial fucoidanase cleaves fucoidan forming mainly di-, tri-, tetra-, and pentafucooligosaccharides, whereas the action of the basic form of fucoidanase from *L. kurila* yields higher molecular weight products of 3-10 kDa.

Probably, these differences are related to structural peculiarities of active centers of enzymes and the mechanism of action of the enzymes on the polymer substrate.