

Prof. Giorgio Sartor

# I glucidi

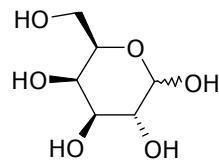
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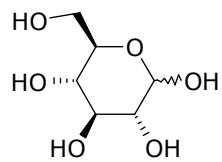
## Glicosidasi

- Così come per le proteine anche i polimeri glucidici vengono scissi in monomeri attraverso l'idrolisi di un legame glicosidico.
- Diversi sono i monomeri coinvolti nella formazione dei polisaccaridi di origine algale marina:
  - fucoso,
  - glucoso,
  - galattoso,
  - mannoso,
  - xyloso,
  - ramnoso

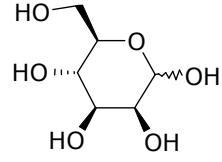
# Monomeri



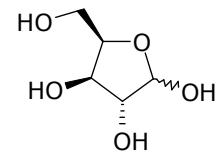
Galattoso



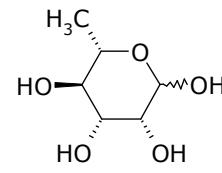
Glucoso



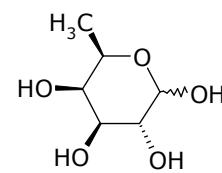
Mannoso



Xiloso



Ramnoso



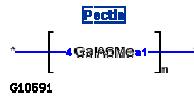
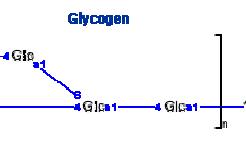
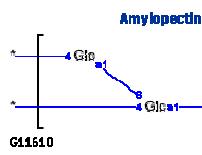
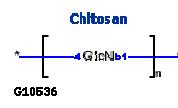
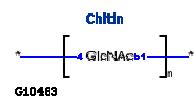
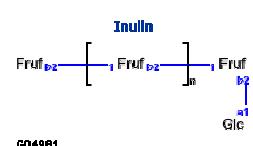
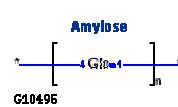
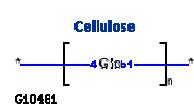
Fucoso

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# Omopolisaccaridi

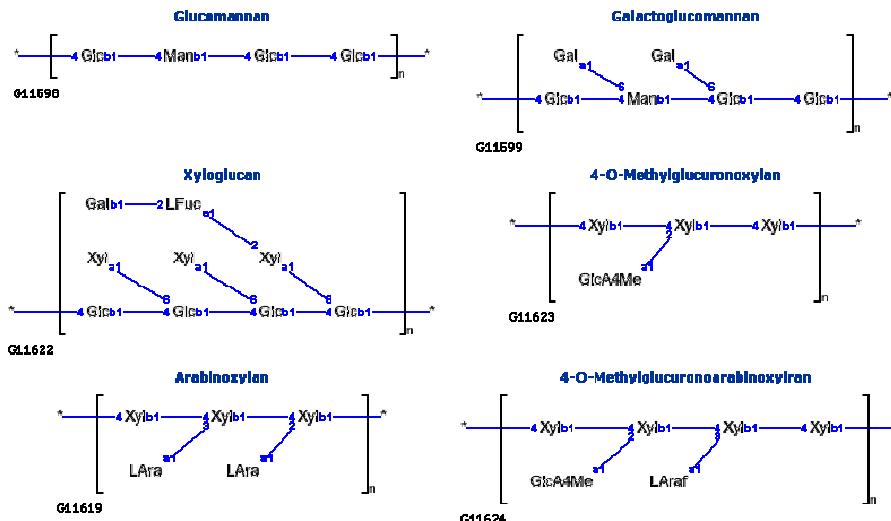


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# Eteropolisaccaridi

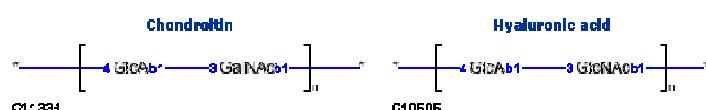


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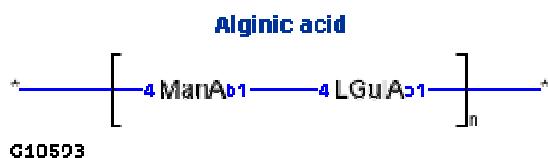
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- Glucosaminoglicani



- Alginati



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## Fucoidan hydrolase and glycosidase activities in marine invertebrates

<b>COELENTERATA</b>		<b>MOLLUSCA</b>	
Anthozoa		Monoplacophora	
<i>Actinia</i> sp.	DT	<i>Onchidiopsis</i> sp.	HP
<i>Cnidoplatus japonicus</i>	all	<i>Tritia tratercula</i>	HP
<i>Anthopleura orientalis</i>	all	<i>Plicifucus plicatus</i>	HP
<i>Tialia fellina</i>	all	<i>Neptunaea bulbacea</i>	HP
		<i>Neptunaea lyrata</i>	HP
		<i>Astarte borealis</i>	HP
		<i>Lussiovolutopsis</i> sp.	HP
<b>ANNELIDA</b>		Bivalvia	
Polychaeta	all		
Palynoidae	all	<i>Cyclocardia rjabininae</i>	HP
Sabellidae	all	<i>Modiolus difficilis</i>	CS
Sabellidae	all		HP
<i>Tubulamus punctatus</i>	all		
<i>Chaetopterus cautus</i>	all		
<i>Eudistylia polymorpha (Bispira)</i>	all		
<i>Sipunculida phascolosoma</i>	all		
<b>NEMERTINI</b>		<b>ECHINODERMATA</b>	
Nemertini		Ophiuroidea	
<i>Collarenemertes bimaculata</i>	proboscis	<i>Ophiuira sarsi</i>	DT
		Echinoidea	
		<i>Strongylocentrotus pallidus</i>	DT
<b>ARTHROPODA</b>		Asterioidea	
Crustacea		<i>Leptoasterias arctica</i>	DT
<i>Pandalus hypsiotus</i>	HP	<i>Distolasterias aligans</i>	DT
<i>Chiohocetes opilio elongatus</i>	HP	<i>Hemicrilia</i> sp.	DT
<i>Pagurus beringanus</i>	all	Crinidea	DT

\*\* Specific activity was expressed in nmol of *p*-nitrophenol/h per mg protein. Designations: DT, digestive tract; HP, hepatopancreas; CS, crystalline style;

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## Fucoidan hydrolase and glycosidase activity in marine invertebrates

<b>CNIDARIA</b>					
Anthozoa					---
<i>Metridium</i> sp.	All	<b>Bivalvia</b>			
SIPUNCULA		<i>Crassostrea gigas</i>	Hp	<b>ECHINODERMATA</b>	
Phascolosomatidae		<i>Crenomytilus grayanus</i>	Hp	Holothuroidea	
<i>Phascolosoma agassizii</i>	All	<i>Glycymeris yessoensis</i>	Hp	<i>Eupentacta fraudatrix</i>	All
ARTHROPODA		<i>Spisula sachalinensis</i>	Hp	<i>Apostichopus japonicus</i>	All
Crustacea				Echinoidea	
<i>Balanus rostratus</i>	All	<i>Mactra chinensis</i>	Crs	<i>Strongylocentrotus nudus</i>	Dt
<i>Pagurus</i> sp.	All		Hp	<i>S. intermedius</i>	Dt
<i>Cancer amphioctetus</i>	Hp	<i>Mercenaria stimpsoni</i>	Crs	<i>Scaphechinus mirabilis</i>	Dt
<i>Hemigrapsus sanguineus</i>	Hp		Hp	<i>S. griseus</i>	Dt
MOLLUSCA		<i>Peronidia venulosa</i>	Crs	<i>Echinocardium cordatum</i>	Dt
Polyplophorpha				Asterioidea	
<i>Lepidozona albrechtii</i>	Hp	<i>Mizuhopecten yessoensis</i>	Hp	<i>Asterias amurensis</i>	Dt
Gastropoda			Crs	<i>Lysastrosoma anthosticta</i>	Dt
<i>Lottia</i> spp.	All			<i>Patiria pectinifera</i>	Dt
<i>Littorina brevicula</i>	Hp			<i>Distolasterias nikon</i>	Dt
<i>L. squalida</i>	Hp			CHORDATA	
<i>L. sitkana</i>	Hp			Asciidiacea	
<i>Acmaea pallida</i>	All			<i>Botryllus tuberatus</i>	All
<i>Musella heyseana</i>	Hp				

Dt—digestive tract; hp—hepatopancreas; Crs—crystalline style;

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# Glicosidasi

## O-GLYCOSYLHYDROLASES OF MARINE INVERTEBRATES

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Table 2. O-Glycosylhydrolases from hepatopancreas of *L. kurila*

Enzyme	Substrate	Activity, nmol/h per mg protein
Fucoidan hydrolase	fucoidan from <i>F. evanescens</i>	71
1,3- $\beta$ -D-Glucanase	laminaran from <i>L. cichorioides</i>	35 714
Amylase	amylopectin	11 309
Cellulase	CM-cellulose	15 550
Agarase	agar (galactoglycan)	1237
Pustulanase	1,6- $\beta$ -D-glucan	1524
$\beta$ -D-Galactosidase	<i>p</i> -Nph- $\beta$ -D-galactopyranoside	11 103
$\beta$ -D-Glucosidase	<i>p</i> -Nph- $\beta$ -D-glucopyranoside	11 401
$\alpha$ -D-Mannosidase	<i>p</i> -Nph- $\alpha$ -D-mannopyranoside	3447
Arylsulfatase	<i>p</i> -Nph-sulfate	12 000
$\alpha$ -L-Fucosidase	<i>p</i> -Nph- $\alpha$ -L-fucopyranoside	4370

## Glicosidasi (EC 3.2.1.-)

- **1. Ossidorettiasi**
- **2. Transferasi**
- **3. Idrolasi**
  - 3.1 Agisce su legami esterei
  - 3.2 Glicosilasi
    - **3.2.1 Glicosidasi, idrolizzano composti O- e S-glicosilici**
      - 3.2.2 Idrolizzano composti N-glicosilici
      - 3.2.3 sottoclasse cancellata (Idrolizzano composti S-glicosilici)
  - 3.3 Agisce su legami etere
  - 3.4 Agisce su legami peptidici (peptidasi)
  - 3.5 Agisce su legami C-N diversi da legame peptidico
  - 3.6 Agisce su legami anidride
  - 3.7 Agisce su legami C-C
  - 3.8 Agisce su legami alide
  - 3.9 Agisce su legami P-N
  - 3.10 Agisce su legami S-N
  - 3.11 Agisce su legami C-P
  - 3.12 Agisce su legami S-S
  - 3.13 Agisce su legami C-S
- **4. Liasi**
- **5. Isomerasi**
- **6. Ligasi**

**EC 3.2.1.1 – EC 3.2.1.165**

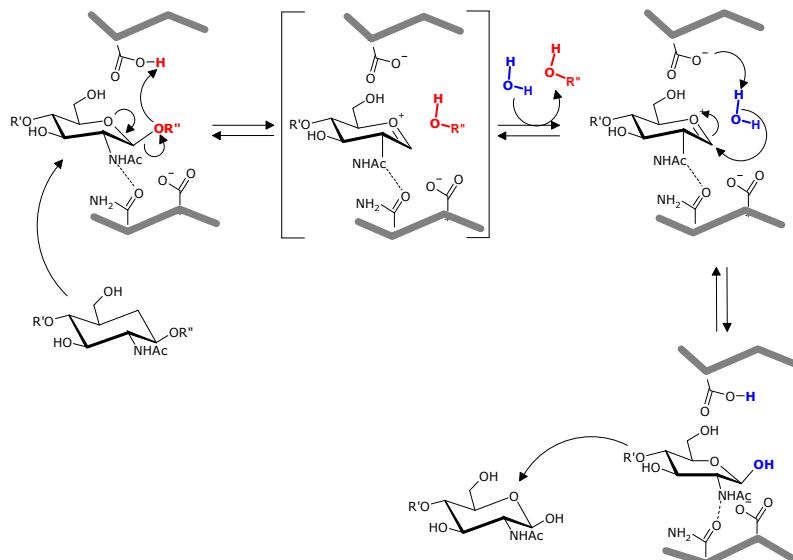
# Meccanismi catalitici

- Le glicosidasi agiscono con idrolisi del legame glicosidico con due prodotti principali:
  - Monomeri con medesima configurazione del carbonio anomero
    - Intermedio ione ossonio (lisozima)
    - Intermedio covalente ( $\beta$ -1,4-glicosidasi)
  - Monomeri con inversione della configurazione del carbonio anomero
    - Stato di transizione ione ossicarbene

# Meccanismi catalitici

- Le glicosidasi agiscono con idrolisi del legame glicosidico con due prodotti principali:
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    - Intermedio covalente ( $\beta$ -1,4-glicosidasi)
  - Monomeri con inversione della configurazione del carbonio anomero
    - Stato di transizione ione ossicarbene

## Intermedio ione ossonio

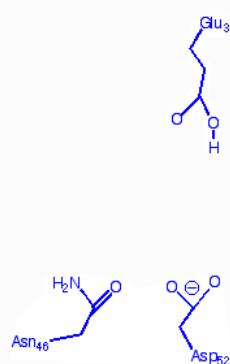


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## Lisozima

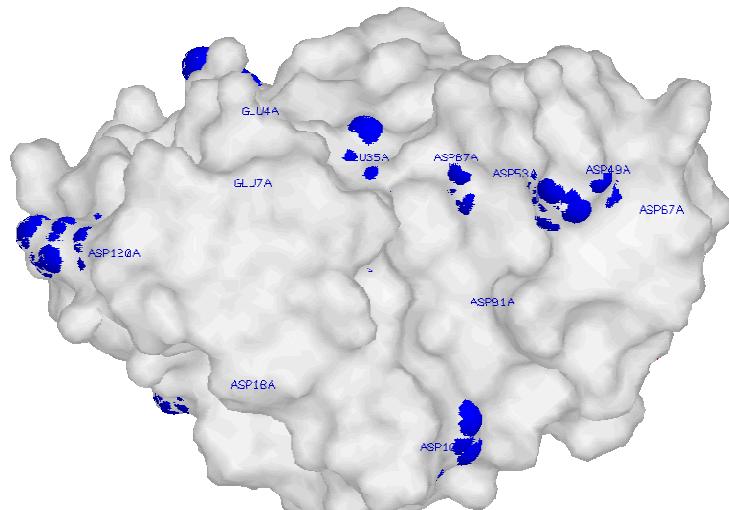


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## Lisozima (EC 3.2.1.17)

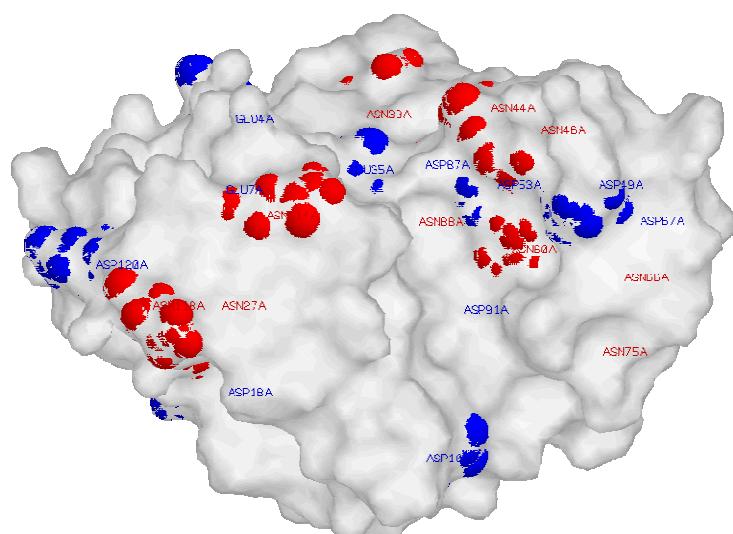


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## Lisozima (EC 3.2.1.17)

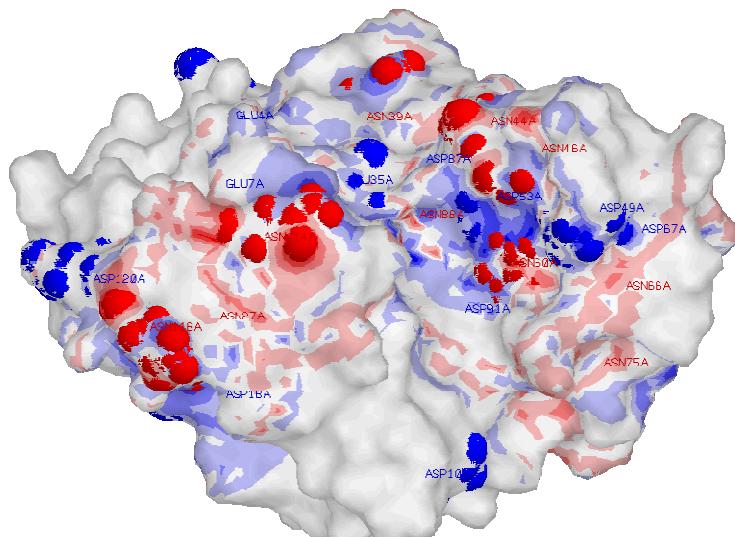


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## Lisozima (EC 3.2.1.17)

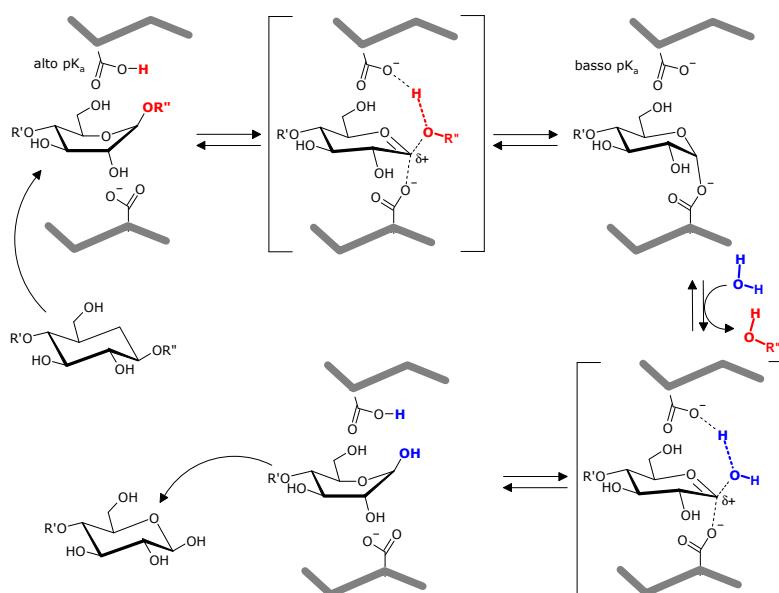


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## Intermedio covalente

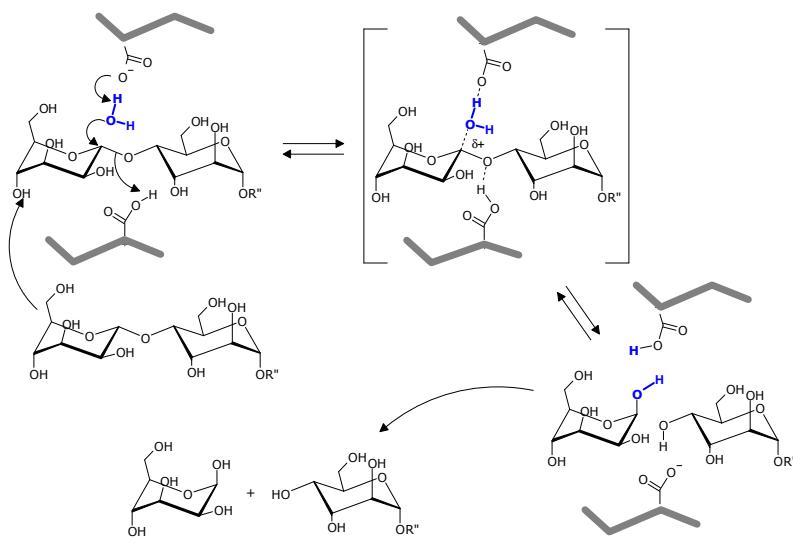


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## Stato di transizione ione ossicarbene

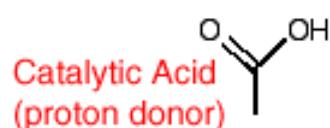
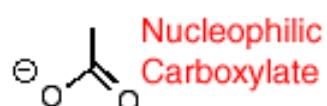


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## Ritenzione della configurazione

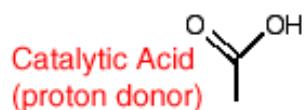
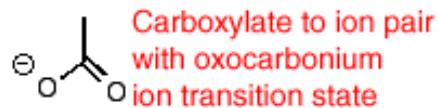


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## Ritenzione della configurazione



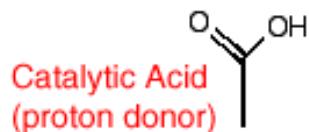
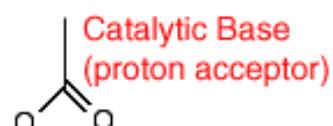
- Senza formazione di un intermedio covalente

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## Inversione della configurazione

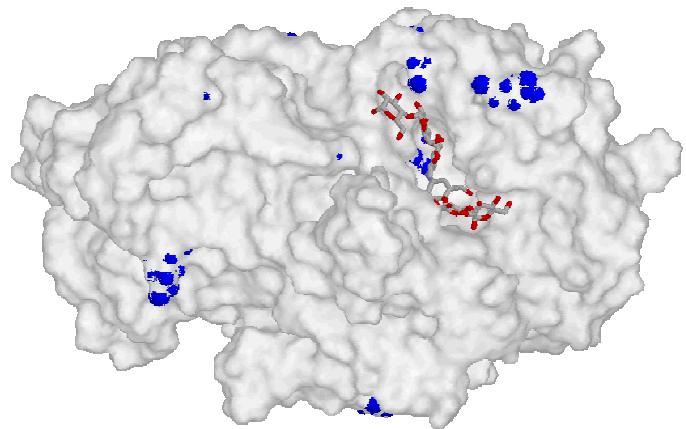


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## GLicogenasi (EC 3.2.1.1)

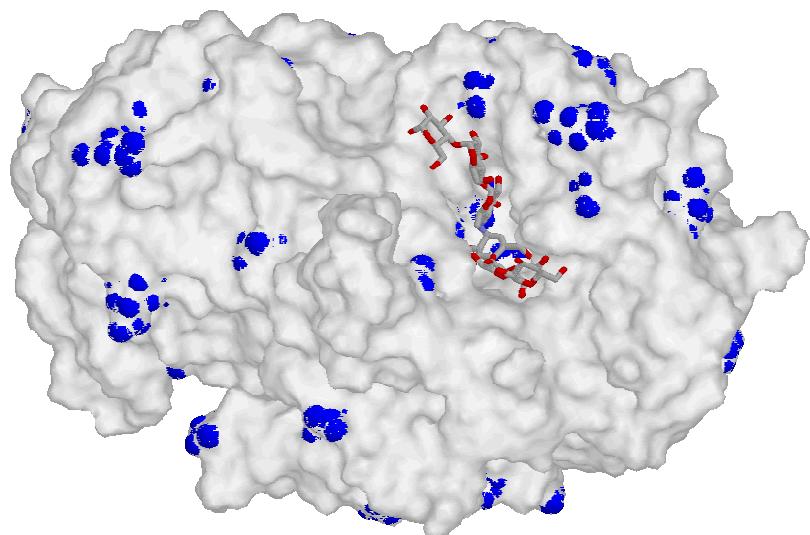


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## GLicogenasi (EC 3.2.1.1)

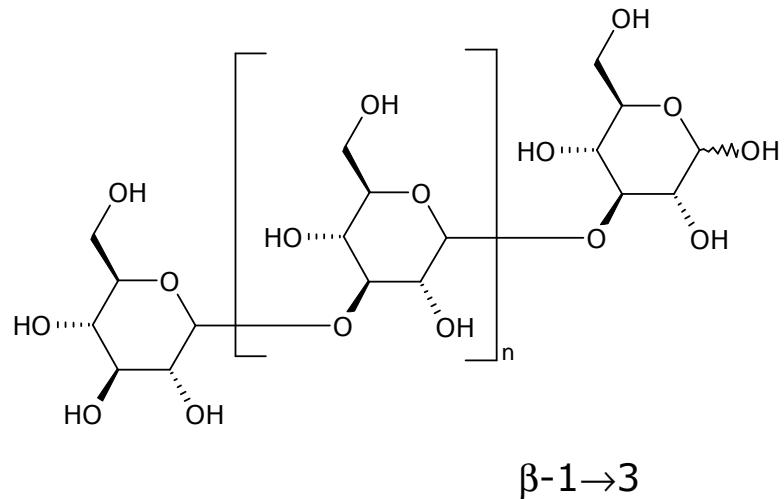


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## Laminarina



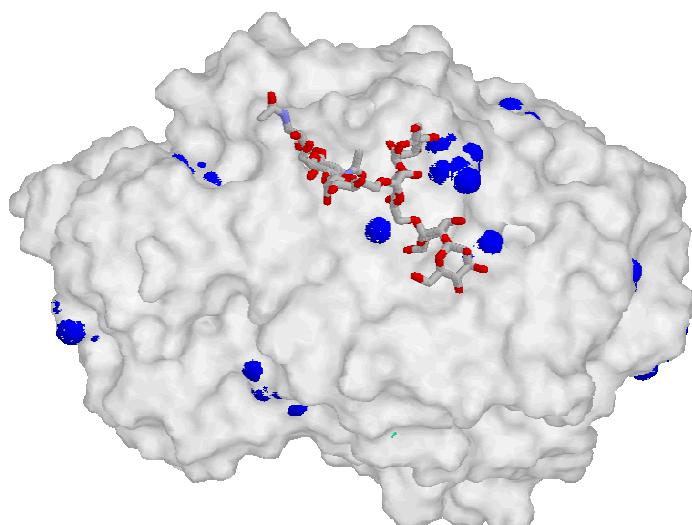
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## Laminaranasi - EC 3.2.1.6



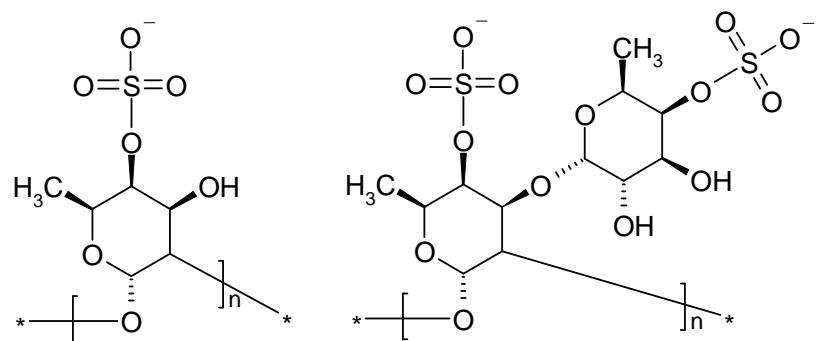
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## Fucoidan

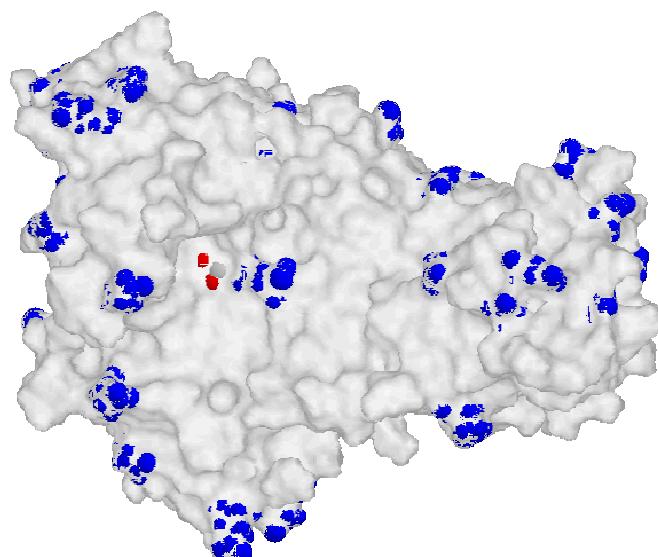


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## $\alpha$ -L-fucosidasi - EC 3.2.1.44



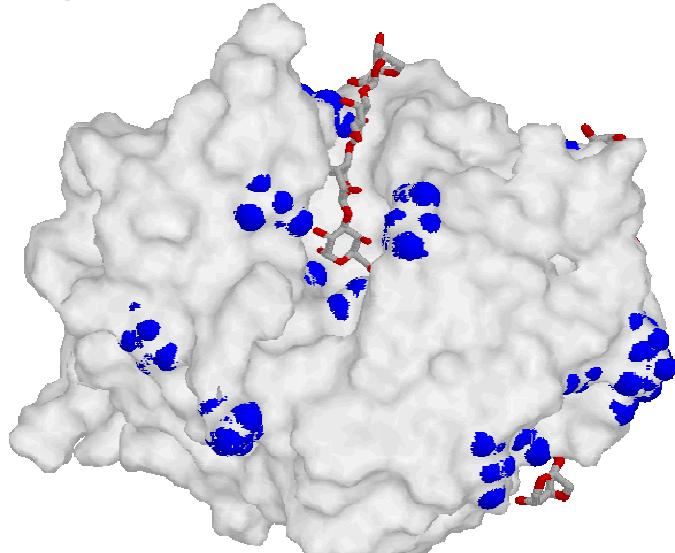
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2CL2

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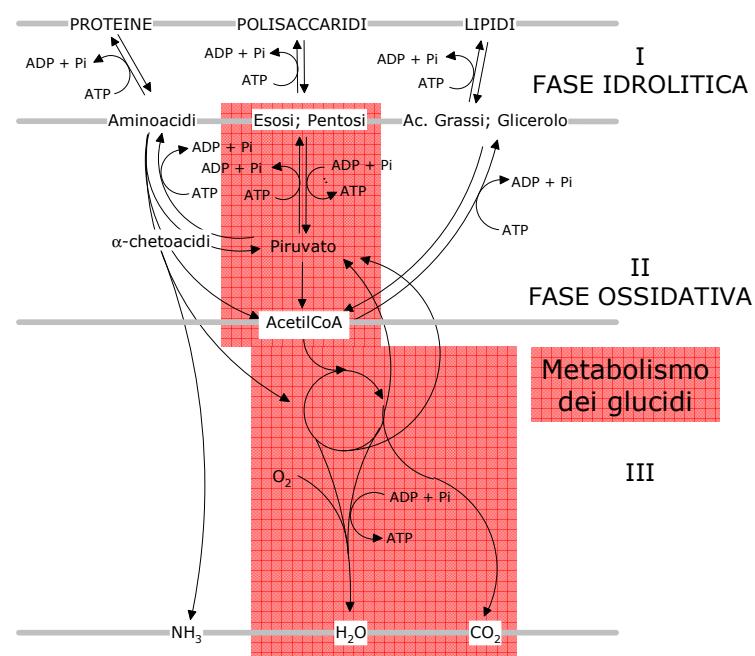
# Agarasi (EC 3.2.1.81)



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Università di Bologna a Ravenna

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