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Review

Metabolisms and multiple functions of laminaran in marine algae under global change: A critical review

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ABSTRACT

Laminaran is a major storage of carbohydrate in marine algae. Its high content and potential functions draw increasing attention. However, our understanding of its metabolisms and functions is still fragmented. After reviewing, marine algae exhibit a spectacular capacity of laminaran accumulation especially in the diatom *Odontella aurita* (65 % DW). Marine particulate organic carbon (POC) also has high contents of laminaran (42 ± 21 % DW). Laminaran shows a diel variation trend in marine algae, the content of which increases in the day but decreases at night. Laminaran also significantly accumulates in the stationary phase of algal growth. Furthermore, the metabolic pathway of laminaran and the remolding carbon mechanism in response to marine nitrogen limitation are proposed and comprehensively discussed. Laminaran production in marine phytoplankton is predicted to increase in future warmer and CO_2-enriched oceans. Laminaran has diverse biological functions, including antioxidant, antimicrobial, anti-cancer, immunomodulatory, wound healing, and prebiotics. In addition, laminaran is also a major carbon storage compound in marine algae, suggesting its significant ecological function in marine carbon cycle. This study provides new insight into algal laminaran functions and its response mechanisms to environmental and climate changes.

1. Introduction

Carbon dioxide and solar energy are converted into carbohydrates via photosynthesis and intracellular carbon metabolism in autotrophic algae (Chauton et al., 2013). One of the major carbohydrates in marine algae is laminaran, a vacuolar β-1, 3 glucan, mainly composed of glucose (Huang et al., 2021). It is also known as laminarin, chrysolaminarin, and mycolaminarin in different species (Kamoun, 2003; Vogler et al., 2018). Laminaran, a water-soluble polysaccharide, consists of an ordinary β-1, 3 glucan backbone chain and a diversiform of β-1, 6 side chain (Beattie et al., 1961; Paulsen & Myklestad, 1978). The reducing end of the laminaran chain makes it of two different types; one is the M chain and the other is the G chain. The M type laminaran chain is the end of mannitol residue, while the G type is the end of glucose residue (Rioux et al., 2007). The production of laminaran occurs in various algal groups, including Bacillariophyta (Beattie et al., 1961), Phaeophyceae (Percival & Ross, 1951), Oomycetes (Wang & Bartnicki-Garcia, 1974), Eustigmatophyceae (Vogler et al., 2021), and Chrysophyte (Ma et al., 2021), making it a widespread carbon storage. According to phylogenetic analysis, the laminaran synthases (β-1, 3 glucan synthetase) of the GT48 family is conserved in most eukaryotic phyla (Phaeophyceae and Stramenopiles) but it is absent in Archaea and bacteria. Its presence in the last eukaryotic common ancestor of β-1, 3 glucans implies that laminaran is the common ancestral metabolite in the Stramenopiles. Moreover, cell wall β-1, 3 glucans were found in fungal groups (Oomycetes, Laminariales etc.) and plants, which are believed to be evolved from intracellular β-1, 3 glucans (Michel et al., 2010). The widespread occurrence of laminaran in various algae and the role of ancestral carbohydrate suggest its potential biological and ecological functions in aquatic plants.

Laminaran is abundantly synthesized by marine algae and serves as source of intracellular energy and carbon stock. However, the multiple bioactivities of laminaran indicate its potential for broad applications. The bioactivities of laminaran, e.g., inducing apoptosis, antioxidant, immunomodulatory, and antitumor activity, etc., have been stated in an array of studies. The laminaran extract from *Phaeodactylum tricornutum*

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shows a high level of antioxidant activity (Carballo et al., 2018). Similar antioxidant activity was also reported for laminaran extracted from two seaweeds *Ascophyllum nodosum* and *Laminarina hyperborean* (Shekhar et al., 2015). Laminaran also shows high immunomodulatory activity to Senegalese sole (Carballo et al., 2018). Laminaran can inhibit cell proliferation and apoptosis (Park et al., 2012). Moreover, laminaran could kill cancer cells, while exhibiting no toxicity to the normal cells (Kusaikin et al., 2010). In addition, laminaran can serve as prebiotic for improving the dietary structure (Nguyen et al., 2016). The diverse laminaran bioactivities, e.g., antioxidant, anti-cancer, immunomodulatory, prebiotics, and regulating gut microbial homeostasis, can be applied in many fields.

In the ocean, laminaran is an underestimated carbon pool. According to estimates, diatom can generate 5–15 Gt/y of laminaran making it a big carbon pool in the ocean (Alderkamp et al., 2007). During the algal bloom, β glucans especially laminaran is generated in abundance (Unfried et al., 2018). The particulate organic carbon contains 26 ± 17 % of laminaran, and the content can reach up to 42 ± 21 % in Arctic field samples. The wide distribution of laminaran in intertidal and upper sublittoral zones of rocky shores, together with sustainable seaweed farming, exhibits a huge potential as a global carbon sink (Duarte et al., 2005).

In spite of increasing concerns on laminaran due to its multiple biological and ecological functions, our understanding of its distribution, metabolism characteristic and response to environmental changes is still fragmented. Previous review articles focus on extraction and biofunctional activities of laminaran (Dobrinčić et al., 2020; Kadam et al., 2015; Karuppusamy et al., 2022). In this study, we review the distribution features of laminaran, diel variation trends, potential productivity and multiple functions in various marine algal species, and explore the response of laminaran to nitrogen limitation and climate change.

2. Structure of laminaran in marine algae

The structure of laminaran varies among marine algae, including Bacillariophyta, Phaeophyta, Chrysophyte and Eustigmatophyceae (Table 1). In diatom, the molecular weight of laminaran ranges from 4 to 13 kDa. While, the seaweed *Eisenia bicyclis* shows a high molecular weight of laminaran from 19 to 26 kDa (Belik et al., 2022). The degree of polymerization of laminaran ranges from 5 to 30 for diatom and *Nannochloropsis*. However, the seaweed *Laminaria digitata* showed a higher degree of polymerization (Kim et al., 2000). The usual structure of laminaran is composed of a β-1, 3 glucan backbone chain and a β-1, 6 glucose side chain (Fig. 1). It has been reported that the main and the side chains contain high content of β-1, 6 glucose residues (ratio of bonds β-1, 3: β-1, 6 = 1.5:1) in *E. bicyclis* (Menshova et al., 2014). The molecule weight of laminaran in *Poterioochromonas malhamensis* is 16.7 kDa while on or β-1, 6 glucose side chain was found purified sample (Ma et al., 2021).

The branch of laminaran is β-1, 6 glucose sidechains in seaweeds and *Nannochloropsis*, while the branch of laminaran in diatom varies with species. *Skeletonema costatum*, *Stauroneis amphioxys*, and *Achnanthes longipes* contain two β glucose sidechains, β-1, 6 glucose sidechains, and β-1, 2 glucose sidechains. *Chaetoceros muelleri* contains another β-1, 3 glucose sidechain, β-1, 3 glucose sidechains (Størseth et al., 2005).

3. Laminaran production in marine algae

3.1. Laminaran content in various marine algae

Marine algae contribute nearly 50 % of the global primary productivity, by assimilating CO_2 into organic carbon (Becker et al., 2017). One of the forms of organic carbon is carbohydrate that contributes ~80 % of the algae biomass (Myklestad, 1974). Laminaran, a major carbohydrate in marine algae, occupies 4.5 % to 64.86 % of the biomass in dry weight among various marine algal species (Table 2). The highest content was found in *Odontella aurita*, cultured in low nitrogen and high light condition. Laminaran content varies not only in the diel cycle but also among the species as well as under varying culture conditions. Interestingly, the laminaran content of *P. tricornutum* stayed low during the exponential stage, ranging from 9.95 % to 16 % (DW), under 75–300 μmol photons m^{-2} s^{-1} of light intensity and 2.9–14.5 mM of nitrogen concentration (Gao et al., 2017; Jiang et al., 2022; Yang et al., 2019). Meanwhile, the laminaran content of *O. aurita* was reported to rise in the exponential stage, ranging from 39 % to 60 % (DW), under two-factor coupled culture conditions (100–300 μmol photons m^{-2} s^{-1} of light intensity and 6–18 mM of nitrogen concentration) (Xia et al., 2014). The discrepancies in the laminaran content might be due to the differences of

Table 1
The structural features of laminaran in marine algae.

Species		MW/DP	Branches	Reference
Bacillariophyta	*Phaeodactylum tricornutum*	−/17	β-1, 6	(Caballero et al., 2016)
	Phaeodactylum tricornutum	–	β-1, 6	(Ford & Percival, 1965)
	Skeletonema costatum	6– 13 kDa/−	β-1, 6 β-1, 2	(Paulsen & Myklestad, 1978)
	Stauroneis amphioxys	4 kDa/ 24	β-1, 6 β-1, 2	(McConville et al., 1986)
	Achnanthes longipes	–	β-1, 6 β-1, 2	(Wustman et al., 1998)
	Craspedostauros australis	>10 kDa/−	β-1, 6	(Chiovitti et al., 2003)
	Chaetoceros muelleri	−/22–24	β-1, 6 β-1, 3	(Størseth et al., 2005)
	Chaetoceros debilis	4.9 kDa/30	β-1, 6	(Størseth et al., 2006)
	Thalassiosira weissflogi	−/5– 8	–	(Størseth et al., 2005)
	Odontella aurita	7.75 kDa/−	β-1, 6	(Xia et al., 2014)
Phaeophyta	*Laminaria digitata*	−/28	β-1, 6	(Caballero et al., 2016)
	Laminaria digitata	−/13	β-1, 6	(Vogler et al., 2018)
	Laminaria digitata	−/30.3	β-1, 6	(Read et al., 1996)
	Laminaria digitata	3.9 kDa/−	β-1, 6	(Alderkamp et al., 2007)
	Laminaria digitata	−/33	β-1, 6	(Kim et al., 2000)
	Eisenia bicyclis	−/21.5	β-1, 6	(Becker et al., 2017; Maeda & Nisizawa, 1968)
	Eisenia bicyclis	–	β-1, 6	(Shin et al., 2009)
	Eisenia bicyclis	19– 26 kDa/−	β-1, 6	(Belik et al., 2022)
	Laminaria hyperborea	−/20–25	β-1, 6	(Nelson & Lewis, 1974)
	Saccharina longicruris	2.9–3.3 kDa/−	β-1, 6	(Rioux et al., 2010)
	Saccharina cichorioides	4– 6 kDa/ <24.7	β-1, 6	(Belik et al., 2022)
Chrysophyte	*Poterioochromonas malhamensis*	16.7 kDa/	β-1, 6	(Ma et al., 2021)
Eustigmatophyceae	*Nannochloropsis gaditana*	−/8	β-1, 6	(Vogler et al., 2018)
	Nannochloropsis gaditana	−/8.1–9.2	β-1, 6	(Vogler et al., 2018)

Note: MW, molecule weight; DP, degree of polymerization; Branches, side chain; −, no report.

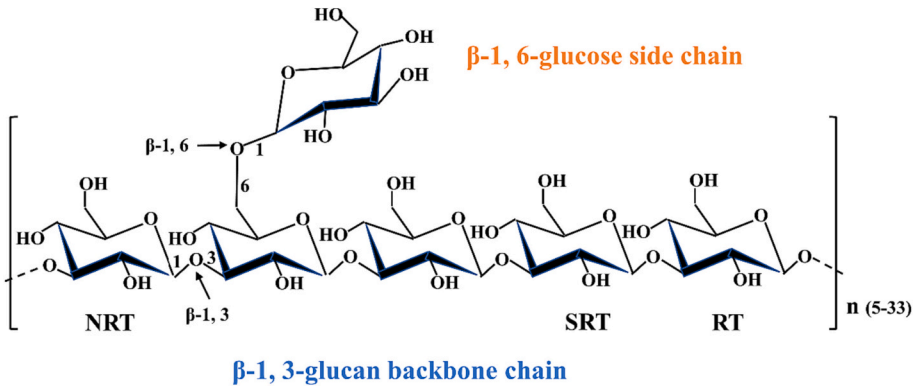

Fig. 1. Structure of laminaran in marine algae. Note: NRT, nonreducing terminal group; RT, reducing α-anomer; SRT, second to the reducing terminal group.

Table 2
Laminaran content in marine algae under various conditions.

Species		Culture condition	Content (DW)		References
			Exponential	Stationary	
Bacillariophyta	*Phaeodactylum tricornutum*	300 μmol photons m^{-2} s^{-1}; 25 ± 1 °C; ① LN: 2.9 mM, ② HN: 14.5 mM	① 14.66 % ② around 16 %	① Around 12.5 % ② 17 %	(Gao et al., 2017)
	Phaeodactylum tricornutum	200 μmol photons m^{-2} s^{-1}; 21 ± 0.5 °C;	10 %	–	(Yang et al., 2019)
	Phaeodactylum tricornutum	75 μmol photons m^{-2} s^{-1}; 20 ± 1 °C	9.95 %	–	(Jiang et al., 2022)
	Phaeodactylum tricornutum	18 °C; 50 μmol photons m^{-2} s^{-1}; LC: 400 ppm; HC: 20,000 ppm; ① LC, ② HC	① About 14 pg·$cell^{-1}$ ② About 17.5 pg·$cell^{-1}$	① About 14 pg·$cell^{-1}$ ② About 20 pg·$cell^{-1}$	(Jensen et al., 2020)
	Skeletonema costatum	f/10 medium	–	32 %	(Paulsen & Myklestad, 1978)
	Skeletonema costatum	① LN: 0.5 mM, ② HN: 1.5 mM	①-② 4.5 pg C·$cell^{-1}$	① 21 pg C·$cell^{-1}$ ② 17 pg C·$cell^{-1}$	(Granum et al., 2002)
	Odontella aurita	25 ± 2 °C; LL: 100 μmol photons m^{-2} s^{-1}; HL: 300 μmol photons m^{-2} s^{-1}; LN: 6 mM; HN: 18 mM ① LL-LN, ② LL-HN, ③ HL-LN, ④ HL-HN	① Around 54 % ② Around 39 % ③ Around 60 % ④ Around 39 %	① 61.34 % ② 39.67 % ③ 64.86 % ④ Around 52.5 %	(Xia et al., 2014)
	Chaetoceros affinis	f/10 medium	35 pg·$cell^{-1}$	200 pg·$cell^{-1}$	(Myklestad, 2013)
	Chaetoceros debilis	200 μmol photons m^{-2} s^{-1}; continuous light; 18 °C;	10 %; 15.8 pg·$cell^{-1}$	–	(Størseth et al., 2006)
	Thalassiosira pseudonana	18 °C; 50 μmol photons m^{-2} s^{-1}; LC: 400 ppm; HC: 20,000 ppm; ① LC, ② HC	① About 5 pg·$cell^{-1}$ ② <5 pg·$cell^{-1}$	① About 8 pg·$cell^{-1}$ ② About 5 pg·$cell^{-1}$	(Jensen et al., 2020)
	Navicula pelliculosa	18 °C; 50 μmol photons m^{-2} s^{-1}; LC: 400 ppm; HC: 20,000 ppm; ① LC, ② HC	① <2 pg·$cell^{-1}$ ② <2 pg·$cell^{-1}$	① About 7 pg·$cell^{-1}$ ② About 8 pg·$cell^{-1}$	(Jensen et al., 2020)
Chrysophyte	*Poterioochromonas malhamensis*	inorganic-nitrogen culture condition 1.0 g·L^{-1} NH4Cl	55 %		(Ma et al., 2021)
	Isochrysis zhangjiangensiss	LL: 80 μE·m^{-2}·s^{-1} HL: 150 μE·m^{-2}·s^{-1} 25 °C; NR: nutrient replete; -N: nitrogen deprivations; -P: phosphorus deprivations; -S: sulfur ① LL-N; ② LL-P; ③ LL-S; ④ HL-N; ⑤ HL-P; ⑥ HL-S	LL-NR: 3.48 ± 0.69 pg·$cell^{-1}$ HL-NR: 8.71 ± 0.09 pg·$cell^{-1}$; ① 40.97 ± 1.90 pg·$cell^{-1}$; ② 8.95 ± 0.84 pg·$cell^{-1}$; ③ 45.31 ± 1.30 pg·$cell^{-1}$; ④ 40.58 ± 1.21 pg·$cell^{-1}$; ⑤ 23.10 ± 1.56 pg·$cell^{-1}$; ⑥ 50.72 ± 1.50 pg·$cell^{-1}$;		(Ran et al., 2022)
Phaeophyta	*Saccharina latissima*	Field sampling	<55 %		(Adams et al., 2009)
	Ascophyllum nodosum	Field sampling	4.5 %		(Holdt & Kraan, 2011)
	Ascophyllum nodosum	Field sampling	5.82 %		(Shekhar et al., 2015)
	Laminaria digitata	Field sampling	14.4 %		(Holdt & Kraan, 2011)
	Laminaria hyperborea	Field sampling	36.8 %		(Rajauria et al., 2021)
	Laminaria hyperborea	Field sampling	6.24 %		(Shekhar et al., 2015)
POC pool		Field sampling	42 ± 21 %		(Becker et al., 2020)

Note: LL, low light intensity; HL, high light intensity; LN, low nitrogen concentration; HN, high nitrogen concentration; POC pool, particulate organic carbon;

the species and the sampling time. Interestingly, both phases showed higher content of laminaran in *O. aurita* compared to *P. tricornutum*. It was also observed that the high CO_2 concentration could induce the accumulation of laminaran in *P. tricornutum* in exponential (increased about 4 pg cell^{-1}) and stationary phases (increased over 5 pg cell^{-1}), while showed no significant influence to *Navicula pelliculosa* and inhibit the accumulation of laminaran on *Thalassiosira pseudonana* in exponential (decreased about 1 pg cell^{-1}) and stationary phases (decreased about 4 pg cell^{-1}) (Jensen et al., 2020). The Chrysophyte alga *P. malhamensis* recently found in high Arctic marine ecosystem contained ~55 % of the laminaran content which indicated that laminaran might be abundant at high latitude marine areas (Ma et al., 2021; Zhang et al., 2021). Chrysophyte algae *Isochrysis zhangjiangensiss* were found to accumulate laminaran in both low and high light intensity under the deficiency of nitrogen, phosphorus and sulfur (Ran et al., 2022). Nitrogen deprivation led to over 11-fold and 4.6-fold accumulation of laminaran in low light and high light, respectively (Ran et al., 2022). Moreover, sulfur deprivation stimulated *I. zhangjiangensiss* to accumulate over 13-fold of laminaran content, which was more significant than the other two stresses (Ran et al., 2022). In addition, the laminaran content of macroalgae from field sampling showed a very large range (4.5 % to 55 % DW) (Adams et al., 2009; Holdt & Kraan, 2011; Rajauria et al., 2021; Shekhar et al., 2015). While the particulate organic carbon pool (POC, 0.7 to 3 μm of glass fiber filters) contained about 26 ± 17 % of the laminaran content to shows a great potential for laminaran storage. It is worth noting that POC contains about 42 ± 21 % of the laminaran content in the Arctic (Becker et al., 2020). Obviously, laminaran having a great potential in reaching over 40 % of the biomass in marine algae, makes it a large carbon pool in the oceans.

3.2. Diel fluctuation of laminaran content

The laminaran content in algae varies in the diel cycle (Fig. 2A). It has been reported that laminaran is a diurnal energy reserve (Huang et al., 2016). The cellular content of laminaran increased to the maximum in the end of light period (~50 % of total carbon) in *S. costatum* while decreased to the minimum (ranged from 4 %–25 %) during the dark periods (Vårum et al., 1986). A longer dark period leads to low laminaran content implying that light is the driving force in the accumulation of laminaran (Vårum et al., 1986). Laminaran content in *P. tricornutum* show a similar variation pattern to that of *S. costatum* in diel cycle, especially the nearly complete consumption in the dark period (Caballero et al., 2016). In *P. tricornutum* a sharp increase in the total water-soluble carbohydrate content (5 to 11.5 pg cell^{-1}) in the light period, followed by decline to the original content of ~5 pg cell^{-1} during the dark period was reported in an earlier study (Chauton et al., 2013). Analogously, the glucose content, a laminaran component also showed a similar variation pattern in *Nannochloropsis oceanica* (Poliner et al., 2015). The LamC: POC ratio (Laminaran carbon: particulate organic carbon) of field phytoplankton samples also increased by 80 % during the day and declined by 60 % during the night. The diurnal variation of LamC: POC suggests that laminaran is a major carbon reserve and a fast turnover compound in the whole ocean (Becker et al., 2020).

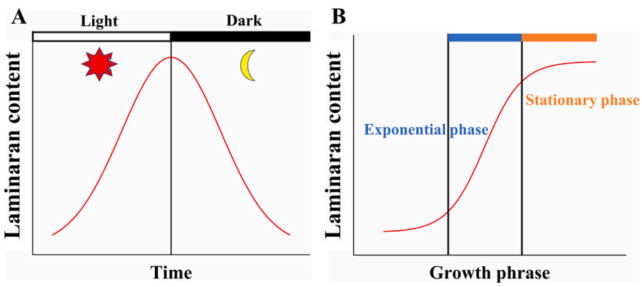

Fig. 2. Conceptual illustration of laminaran accumulation patterns in marine algae under different stages. Note: A, the accumulation of laminaran under the diel cycle; B, the accumulation of laminaran in two growth phases.

3.3. Fluctuation of laminaran content in different growth phases

The laminaran content usually increases with the expansion of exponential phase and approach the highest values in stationary phase of algal growth (Fig. 2B). An increasing of laminaran content from the exponential phase to the stationary phase of (4.5 pg C cell^{-1} to 17 pg C cell^{-1}) was reported in *S. costatum* (Granum et al., 2002). Similarly, a 6.7 fold increase in the laminaran content from about 30 pg cell^{-1} in the exponential phase to about 200 pg cell^{-1} in the stationary phase was reported in *Chaetoceros affinis* (Myklestad, 2013). Similar results were also reported for *S. costatum*, *O. aurita*, and *C. affinis* (Granum et al., 2002; Myklestad, 2013; Xia et al., 2014). The laminaran content can be influenced by culture conditions, e.g., nitrogen concentration, light intensity and CO_2 concentration whereas laminaran always has higher content in stationary phase compared to exponential phase, which has been reported in *S. costatum* (Granum et al., 2002), *O. aurita* (Xia et al., 2014), *P. tricornutum* (Gao et al., 2017), *T. pseudonana* (Jensen et al., 2020), *N. pelliculosa* (Jensen et al., 2020) and *I. zhangjiangensiss* (Ran et al., 2022) (Table 2). Similar results were also reported under changing light intensities (Xia et al., 2014).

4. Metabolism pathways of laminaran in marine algae

The metabolic mechanisms of laminaran are not clearly stated for marine algae. To date, the metabolic pathway has been proposed in *P. tricornutum* (Huang et al., 2018; Kroth et al., 2008; Yang et al., 2019), *Thalassiosira psudonana* (Hildebrand et al., 2017), *N. oceanica* (Poliner et al., 2015), and the seaweed *Ectocarpus siliculosus* (Michel et al., 2010). In this study, we have proposed the core metabolic pathway of laminaran in the marine algae (Fig. 3). In the beginning of core biosynthesis of laminaran, Glc-6-P is converted to UDP-Glc via phosphoglucomutase (PGM) and UDP-glucose pyrophosphorylase (UGP) or via the fusion enzyme UGP/PGM through the intermediate product Glc-1-P (Poliner et al., 2015). Five PGM enzymes had been identified in *P. tricornutum*

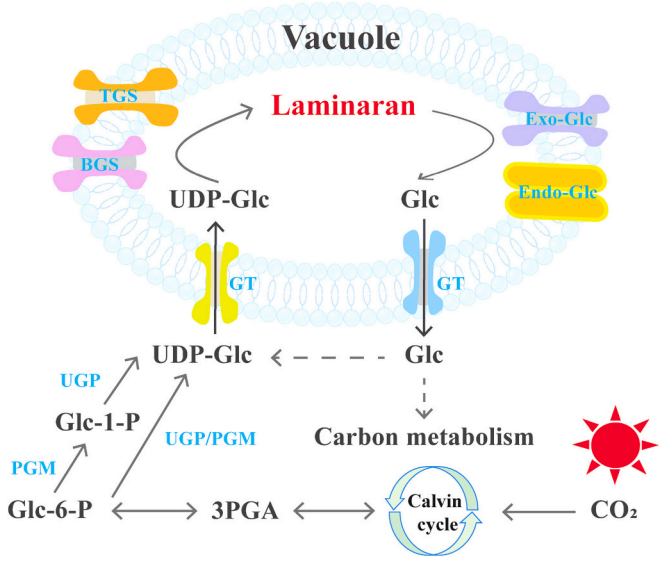

Fig. 3. Metabolism pathway of laminaran in marine algae. Note: 3PGA, 3-phosphoglycerate; Glc, glucose; Glc-1-P, glucose-1-phosphate; Glc-6-P, glucose-6-phosphate; UDP-Glc, UDP-glucose; BGS, β-1, 3 glucan synthetase; TGS, β-1, 6 transglycosylase; Exo-Glc, Exo-β-1,3 glucosidase; Endo-Glc, Endo-β-1,3 glucosidase; GT, glucose transporter; UGP, UDP-glucose pyrophosphorylase; PGM, phosphoglucomutase; UGP/PGM, a fusion enzyme of UGP and PGM.

(Chauton et al., 2013). It is demonstrated that the overexpression of PGM (50444) would lead to a 2.54-fold elevation of laminaran content in *P. tricornutum* (Yang et al., 2019). The functioning in the carbon allocation and laminaran synthesis indicate that UGP is a rate-limiting enzyme. The silencing of UGP would lead to a significant cut down in the laminaran content in *P. tricornutum* (Zhu et al., 2016). Two cytosolic isoforms of UGP (Esi0144_0004 and Esi0430_0005) have been identified in *E. siliculosus*. After the formation of UDP-Glc from Glc-6-P, it is transported to the vacuole via glucose transporter (GT) for the synthesis of laminaran. GT (12520) is predicted to be located in the vacuole (WoLF PSORT) that may play a role in shuttling of glucose between cytosol and vacuole (Chauton et al., 2013). Laminaran biosynthesis is catalyzed via β-1, 3 glucan synthetase (BGS) and β-1, 6 transglycosylase (TGS) for the backbone chain and side chain, respectively (Huang et al., 2016). Only one gene (56808) encoding BGS was confirmed to be in the tonoplast of *P. tricornutum*. The silencing of BGS was attributed for thylakoid impairment and significant reduction of laminaran content (maximum reduce about 30 %) through energy shuttling to soluble sugars and lipids (Huang et al., 2018). Similarly, knocking down of the transcript levels of β-1,3 glucan synthase (12695) would cause lowering of laminaran content and increase in TAG content in *T. psudonana* (Hildebrand et al., 2017). Two TGS viz. 50238 and 56509 were identified in the vacuole and were credited for catalyzing the synthesis of β-1, 6 side chain in *P. tricornutum* (Huang et al., 2016).

Laminaran is catalyzed via Endo-β-1,3 glucosidase (Endo-glc) and Exo-β-1,3 glucosidase (Exo-Glc) enzymes. Three Endo-Glcs, 54681 and 54973 pertained to glycosyl hydrolase family 16 (GH16), one (46976) pertained to GH81, cleaving the backbone chain into glucose and oligosaccharides, have been identified in *P. tricornutum* (Chauton et al., 2013; Kroth et al., 2008). In addition, *P. tricornutum* contains four putative Exo-glcs (56510, 49610, 49294 and 56506), while cleaving of the nonreducing ends to free glucoses was pertained to GH16 (Kroth et al., 2008). Finally, glucose would be transported outside the vacuole to participate in the other carbon metabolism processes.

5. Laminaran-related response to changing ocean environments

5.1. Response to nitrogen limitation

Being an integral constituent of cellular products like protein and nucleic acids, nitrogen is an essential element for organisms (Yang et al., 2014). Global warming mainly caused by the rising atmospheric carbon dioxide can drive ocean stratification. Intensified ocean stratification would hinder the nutrient transport from deeper to surface waters, which may lead to the nitrogen limitation for marine algae in upper oceans (Gao et al., 2021; Steinacher et al., 2010). Nitrogen limitation would lead to the reprogramming of nitrogen-carbon metabolism as described in Fig. 4. To date, a great deal of studies have elucidated that

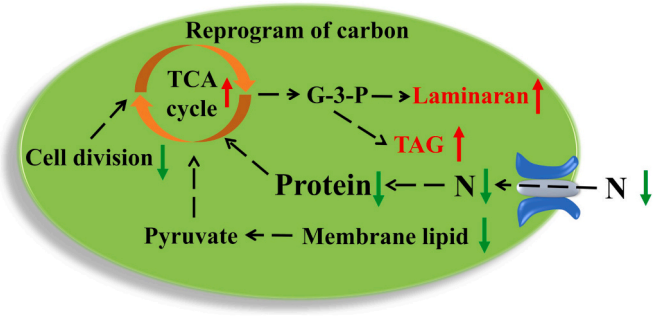

Fig. 4. Laminaran-related response to nitrogen limitation. Note: G-3-P, glyceraldehyde-3-phosphate; TCA cycle, tricarboxylic acid cycle; TAG, triacylglyceride. Red and green arrows represent increasing and decreasing trends, respectively.

nitrogen stress would induce the production of TAG in *P. tricornutum* and *N. oceanica* through physiological, transcriptomic, proteomic, and metabolomic processes (Abida et al., 2015; Alipanah et al., 2015; Jia et al., 2015; Levitan et al., 2015; Remmers et al., 2018). Uniformly, the content of major carbohydrate laminaran increased under nitrogen stress in *P. tricornutum* (Frick et al., 2023). Three strains of *P. tricornutum* showed an increase in the laminaran content under nitrogen-stress suggesting that diatom tend to accumulate laminaran under nitrogen-limitation. Especially, the laminaran content of *O. aurita* under low nitrogen culture was 15 % higher than that under nitrogen rich culture condition at both low and high light intensities (Xia et al., 2014). Nitrogen limitation may lead to unbalanced growth, causing cell cycle arrest in which a portion of energy is redirected and stored as carbohydrate (Kim et al., 2017). Additionally, the lipid and carbohydrate content of *Chlamydomonas reinhardtii* and *Scenedesmus subspicatus* were induced under nitrogen stress (Dean et al., 2010). Nitrogen limitation can induce the accumulation of carbohydrate and TAG due to the remobilization of additional energy from plastid protein, polar lipids, and membrane lipids in marine algae (Jia et al., 2015; Levitan et al., 2015). It was reported that the higher carbohydrate content was accompanied with enhanced sinking rate in diatom *Coscinodiscus concinnus* (Granata, 1991), *Rhizosolenia spp* (Villareal et al., 1993), and *T. weissflogii* (Richardson & Cullen, 1995). Therefore, the increased accumulation of storage compounds, mainly laminaran and TAG, may lead to carbon export from the surface to the deep water.

5.2. Response to ocean warming and acidification

The increased CO_2 emission by human activities is causing global warming and ocean acidification. The oceans are becoming warmer and CO_2 enriched (IPCC, 2023). Ocean warming can promote the growth rate of phytoplankton and macroalgae due to the increased activity of photosynthesis (Hou et al., 2023; Zou & Gao, 2013). The polar region is the most sensitive area to ocean warming, in which the arctic kelp *Saccharina latissimi* was reported to accumulate more laminaran content (about 70 mg g^{-1} DW) when experiencing a 4 °C warming (Scheschonk et al., 2019). The laminaran content shows seasonal fluctuation in kelp and temperature is the dominant factor causing this fluctuation. The laminaran content of *L. digitata* and *L. hyperborean* show the highest level in summer and autumn while reduced by 90 % to 96 % in winter (Schiener et al., 2015). Adams et al. (Adams et al., 2011) has also reported a similar result that the laminaran content of *L. digitata* is pretty low until June, reaches the peak of 24.6 % DW in July and then gradually reduces in the remaining time of the year. These results indicate that warming may stimulate both growth and laminaran content in algae and thus algal laminaran productivity. Ocean is CO_2 limited for phytoplankton photosynthesis and thus enriched CO_2 could generally stimulate the growth of phytoplankton (Gao et al., 2020; Hein & Sand-Jensen, 1997). High concentration of CO_2 was reported to accelerate the growth rate of diatom, e.g., *P. tricornutum* (since 5th day), *N. pelliculosa* seawater specie (since 3th day), and *A. formosa* (since 2th day) (Jensen et al., 2020). Moreover, the biomass productivity of diatoms, e.g., *P. tricornutum*, *N. pelliculosa*, and *A. Formosa*, can be boosted by high CO_2 in both exponential and stationary phases (Jensen et al., 2020). The laminaran content of *P. tricornutum* can also be induced by high CO_2 from about 14 pg·$cell^{-1}$ to 17.5 pg·$cell^{-1}$ and 20 pg·$cell^{-1}$ in exponential and stationary phase respectively (Jensen et al., 2020). Therefore, it seems that ocean acidification would also enhance laminaran productivity of algae and laminaran production is predicted to incease in future warmer and CO_2-enriched oceans.

5.3. Laminaran production in future oceans

Different from the stimulative effects of ocean warming and acidification on laminaran, the effects of nitrogen limitation may be complicated. Although nitrogen limitation can enhance laminaran

accumulation as described above, it can also inhibit algal photosynthesis and growth (Abida et al., 2015; Frick et al., 2023). Therefore, laminaran productivity under nitrogen limitation conditions depends on the balance between growth and laminaran content. Contrary to open oceans, nutrient levels in many coastal waters show an increasing trend due to riverine and mariculture inputs (Feng et al., 2023). In coastal waters, the excess nutrient input caused to eutrophication is mainly due to fertilizer usage, sewage discharge, and population density etc. and lead to harmful algal blooms (Wang et al., 2021). In addition, the submarine groundwater discharge is an underestimated nutrient fluxes, sometimes exceed river input, which can mitigate the nitrogen limitation in coastal water (Santos et al., 2021). Increased nutrient availability can stimulate algal growth while it may reduce laminaran content in algae. Therefore, algal laminaran productivity in open oceans and coastal waters may demonstrate different patterns in future oceans (Fig. 5). To date, the studies on laminaran production under the context of climate change are very scarce. Considering that ocean warming, acidification and nutrient change simultaneously occur, more studies are needed to understand the combined effects of them on laminaran production by marine algae.

6. Biological activities of laminaran

As mentioned above, laminaran content in algae accumulates during the day but decreases at night. That is due to the intracellular role of energy stock in the day while energy resource for cell division at night (Liu et al., 2023). Interestingly, laminaran seems to play an important role in the photosynthesis apparatus. Reducing laminaran content via silencing BGS would interfere with photosynthesis, especially thylakoid by increasing thickness and reducing the quantity (about 2 thylakoids) in every plastid (Huang et al., 2018). The increase of laminaran content via over expression of PGM and TGS is beneficial for carbohydrate accumulation but results in lowering of lipid content and cell division (Yang et al., 2019, 2022). The accumulation of laminaran content may detain the energy that can be used for cell division and lipid synthesis.

In addition to its intracellular role, laminaran has a promising application prospect due to its series of bioactivities in the animal cells. Various bioactivities such as antioxidant, antimicrobial, anti-cancer, immunomodulatory, wound healing, prebiotics, regulating gut microbial homeostasis and enteric drugs give laminaran a promising position in the future applications in human health. The laminaran extracted from macroalgae *L. hyperborea* and *A. nodosum* showed 87.57 % and 93.23 % of inhibition on 2,2-diphenyl-1-picrylhydrazyl (an indicator for antioxidant activity), respectively (Shekhar et al., 2015). Laminaran also shows antimicrobial activity to four bacteria *Staphylcoccus aureus*, *Listeria monocytogenes*, *E. coli* and *S. typhimurium*, with the minimum inhibition concentrations being 5.3, 2.6, 13.1, and 13.1 mg mL^{-1} respectively (Shekhar et al., 2015). Besides, the laminaran extracted from microalgae *O. aurita* shows significant antioxidant activity (42.46 ± 4.67 % of scavenging activity with laminaran concentration of 100 mg mL^{-1}) and hydroxyl radical scavenging activity (83.54 ± 6.71 % of scavenging activity with laminaran concentration of 10 mg mL^{-1}) (Xia et al., 2014). Similarly, noticeable antioxidant activity (7.5 % to 15 % with laminaran concentration of 3.75 mg mL^{-1}) in *I. zhangjiangensis* signify laminaran an additive and antimicrobial agent (Ran et al., 2022). Laminaran could induce the death of cancer cells while exhibiting no cytotoxicity to intestinal epithelial cells with doses of 2.5 mg mL^{-1} and 5.0 mg mL^{-1} (Park et al., 2012). The bioactivity of inducing cancer cell apoptosis makes laminaran a potential therapeutic cancer drug. Laminaran extracted from *P. tricornutum* could induce 29.4 % of cumulated mortality of flatfish Senegalese sole after six days of injection with 1 mg per fish while no death occurred after reinjected which exhibits excellent immunostimulating capacity for aquaculture (Carballo et al., 2018). Laminaran supplemented diet can result in the modulation of immune cells of liver via enhancing about 40 % of ED2-positive cells, i.e. Kupffer cells, and inhibiting about 25 % of peroxidase-positive cells (Neyrinck et al., 2007). Laminaran serving as prebiotic can reduce the negative effects of high-fat diet (Nguyen et al., 2016).

Additionally, hard digestion and absorption in the human small intestine make laminaran a potential dietary fiber (Devillé et al., 2004). However, the human gut commensal *Bacteroides uniformis* JCM 13288^T could digest laminaran by four glycoside hydrolases enzymes (*Bu*GH3, *Bu*GH16, *Bu*GH30 and *Bu*GH158) and share glycans with other gut bacteria, helping to maintain the gut microbial homeostasis (Singh et al., 2020). Furthermore, Cui et al. (2021) found that SHNP (laminaran-type homogeneous polysaccharide) could be digested by gut microbiota, which accelerated the growth of *g_Unspecified_Enterobacteriaceae* and *E. coli* while inhibited the growth of *Haemophilus parainfluenzae* and *Gemmiger formicilis*, suggesting laminaran's role in regulating the composition of intestinal microbiota. In addition, laminaran can restrain the abundance of Firmicutes and induced Bacteroidetes as well (Takei et al., 2020). *Bacteroides intestinalis ALB-11* (laminaran-susceptible indigenous bacteria) isolated from the mice fermented laminaran and contributed to the production of lactate, suggesting the laminaran consumption and gut microbiota regulation in intestinal tract (Takei et al., 2020). Moreover, Gotteland et al. (2020) summarized that laminaran could be fermented, which promoted the population of *Bacteroides*, *Lactobacillus*, and *Coprobacillus* and enhanced the production of short chain fatty acids while decreased the putrefactive metabolites of H_2S, phenol and indole in the cecum of the animals, implying laminaran's role in the energy supply and prebiotics in intestinal tract. More noteworthy aspect is the role of laminaran synthetic substances in intestinal therapy. The laminaran zwitterion carboxylate and laminaran zwitterion sulfonate can cure the injury of colonic tissue and can increase the number of goblet cells to improve the balance of intestinal flora without posing any harm to the normal cells (Li et al., 2022). Moreover, the laminaran purified from seaweed *Cystoseira barbata* shows faster healing rate of 87.81–98.57 % compared to 68.30 ± 1.59 % in control group in 13 days suggesting its use in modern medicine (Sellimi et al., 2018). Therefore, the multiple bioactivities of laminaran make it a great potential curative agent in the field of health care.

7. Ecological functions of laminaran

Laminaran plays a critical role in marine carbon cycle, especially due to its widely distribution (from nearshore to ocean) and high concentrations. For instance, perennial *Ecklonia* can assimilate ~10 t/ha of carbon dioxide per year (Chung et al., 2013), where the laminaran content reaches up to 35 % of the dry weight, suggesting a big carbon sink in the form of laminaran (Kadam et al., 2015). Similar to macroalgae, laminaran is also a major carbon storage compound in the cosmopolitan genus *Phaeocystis*, driving global geochemical cycles (Schoemann et al., 2005). According to Stefan Becker et al. (Becker et al., 2020). Laminaran, obtained from POC samples in the northern equatorial upwelling region shows a higher concentration than that in the other regions (Northern and Southern gyres). It might be related to the higher biomass in the upwelling region, suggesting a positive correlation of biomass to laminaran proportion. As for the size fraction, larger POC samples (over 10 μm) contained more laminaran than the small samples (3–10 μm). It can be related to the community structure because larger cells contain more diatoms. In addition, larger microalgae (over 10 μm) drive the laminaran production during the 2017 algal bloom in the North Sea. Intriguingly, 10 times higher laminaran concentration than starch suggests its prior role in the marine carbohydrate production. As a ubiquitous marine carbon source, laminaran plays an important role in the marine food resource, particularly for heterotrophic bacteria (Unfried et al., 2018). Bacterial laminaranase activities are abundant among surface water, deep water, and sediments, which implies the high abundance and large scare of vertical transport of laminaran (Keith & Arnosti, 2001). During a phytoplankton bloom, the laminaranse of the GH16 family showed high abundance in *Flavobacteria* and *Gammaproteo* bacteria and a maximal expression level during the preliminary phase of algal death (Teeling et al., 2012). It is suggested

that bacteria are vital in the conversion of laminaran. Likewise, laminaran could be ingested and utilized by zooplankton as food (Saborowski & Buchholz, 1999). When adding laminaran-containing algae, the laminaranase activity of *Euphausia pacifica* could be induced regardless of day or night, which implies a critical food supply of laminaran (Cox, 1981). Overall, laminaran is not only an underestimated carbon sink but also a critical food resource for bacteria and zooplankton.

8. Perspectives

In this study, we reviewed the structure, variation tendency, distribution, metabolisms and functions of laminaran in marine algae. Laminaran content shows significant differences among species, culture conditions, and the sampling time. Laminaran content shows an interesting tendency of accumulating during the day and declining at night. Laminaran production also varies with the growth phases. Furthermore, the metabolism and response mechanisms of laminaran to changing ocean environments have also been analyzed here. In particular, laminaran shows both biological and ecological functions that are crucial for human health and marine carbon cycle. To further understand and utilize laminaran, there are some recommendations for future studies:

(1) Build an algal platform for stable and efficient production of laminaran via genetic tools. This can be achieved by using biotechnology techniques, e.g., over expression and gene editing, to identify the function of key genes involved in the mechanism of laminaran biosynthesis and further clarify the whole mechanism of laminaran. Subsequently, introduce efficient industrial algae cultivation, purification, and extraction methods for a large-scale production of laminaran.
(2) Develop laminaran modification techniques to produce specific laminaran products. Firstly, take efficient and specific modification methods, e.g., adding zwitterion carboxylate and zwitterion sulfonate to develop more laminaran-derivatives. Secondly, employ more tests of these products to explore its applicative properties and broaden the application area, e.g., foods, medicine, additive, and even clothing material.
(3) Clarify the transition mechanisms of laminaran to refractory dissolved organic carbon (RDOC). RDOC is an important form of DOC and contributes to carbon sink of oceans. The understanding of the transformation from laminaran to RDOC, particularly in future scenarios, will help us understand the contribution of laminaran production to carbon sequestration and climate change mitigation.
(4) Assess laminaran productivity in coastal waters and open oceans. The different nutrient levels and algal community can result in different productivities of laminaran. The understanding of laminaran productivity in different waters helps to evaluate its contribution to marine carbon cycle.
(5) Predict the changing trends of laminaran production in marine algae under climate change. Climate change is drawing increased attention, while the impacts of ocean warming and acidification on laminaran production in marine algae remain unclear (Fig. 5). Laminaran is a big and underestimated carbon pool. In the context of global climate change, the response of laminaran production will bring up a new insight to changing marine carbon cycle.

CRediT authorship contribution statement

Jichen Chen and Guang Gao put forward the conceptualization; Jichen Chen validated the data, and prepared the original draft; Guang Gao, Xiaojuan Liu, Azhar Rashid, and Shuqi Wang reviewed and edited the manuscript; all authors read and approved the final manuscript.

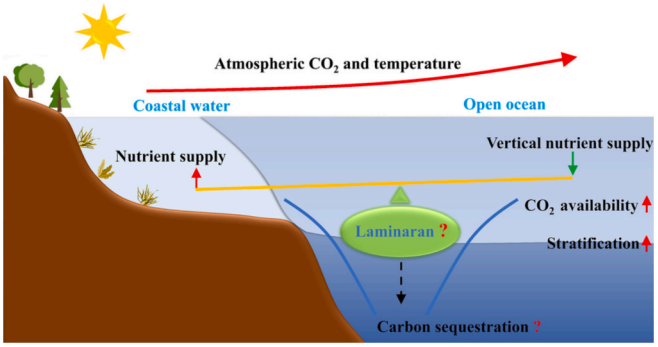

Fig. 5. Conceptual illustration of laminaran production in marine algae under climate change. TAG means triacylglyceride. Red and green arrows represent increasing trend and decreasing trend respectively.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

Abida, H., Dolch, L. J., Meï, C., Villanova, V., Conte, M., Block, M. A., … Maréchal, E. (2015). Membrane glycerolipid remodeling triggered by nitrogen and phosphorus starvation in *Phaeodactylum tricornutum*. *Plant Physiology, 167*(1), 118–136.
Adams, J. M., Gallagher, J. A., & Donnison, I. S. (2009). Fermentation study on *Saccharina latissima* for bioethanol production considering variable pre-treatments. *Journal of Applied Phycology, 21*(5), 569–574.
Adams, J. M. M., Ross, A. B., Anastasakis, K., Hodgson, E. M., Gallagher, J. A., Jones, J. M., & Donnison, I. S. (2011). Seasonal variation in the chemical composition of the bioenergy feedstock *Laminaria digitata* for thermochemical conversion. *Bioresource Technology, 102*(1), 226–234.
Alderkamp, A. C., Van Rijssel, M., & Bolhuis, H. (2007). Characterization of marine bacteria and the activity of their enzyme systems involved in degradation of the algal storage glucan laminarin. *FEMS Microbiology Ecology, 59*(1), 108–117.
Alipanah, L., Rohloff, J., Winge, P., Bones, A. M., & Brembu, T. (2015). Whole-cell response to nitrogen deprivation in the diatom *Phaeodactylum tricornutum*. *Journal of Experimental Botany, 66*(20), 6281–6296.
Beattie, A., Hirst, E. L., & Pervical, E. (1961). Studies on the metabolism of the Chrysophyceae. Comparative structural investigations on leucosin (chrysolaminarin) separated from diatoms and laminarin from the brown algae. *Archives of Ophthalmology, 79*(6), 531–537.
Becker, S., Scheffel, A., Polz, M. F., & Hehemann, J. H. (2017). Accurate quantification of laminarin in marine organic matter with enzymes from marine microbes. *Applied and Environmental Microbiology, 83*(9), 1–15.
Becker, S., Tebben, J., Coffinet, S., Wiltshire, K., Iversen, M. H., Harder, T., … Hehemann, J. H. (2020). Laminarin is a major molecule in the marine carbon cycle. *Proceedings of the National Academy of Sciences of the United States of America, 117*(12), 6599–6607.
Belik, A. A., Rasin, A. B., Kusaykin, M. I., & Ermakova, S. P. (2022). Two GH16 Endo-1,3-β-D-Glucanases from *Formosa agariphila* and *F. algae* bacteria have complete different modes of laminarin digestion. *Molecular Biotechnology, 64*(4), 434–446.
Caballero, M. A., Jallet, D., Shi, L., Rithner, C., Zhang, Y., & Peers, G. (2016). Quantification of chrysolaminarin from the model diatom *Phaeodactylum tricornutum*. *Algal Research, 20*, 180–188.

Carballo, C., Chronopoulou, E. G., Letsiou, S., Maya, C., Labrou, N. E., Infante, C., … Manchado, M. (2018). Antioxidant capacity and immunomodulatory effects of a chrysolaminarin-enriched extract in Senegalese sole. *Fish & Shellfish Immunology, 82*, 1–8.

Chauton, M. S., Winge, P., Brembu, T., Vadstein, O., & Bones, A. M. (2013). Gene regulation of carbon fixation, storage, and utilization in the diatom *Phaeodactylum tricornutum* acclimated to light/dark cycles. *Plant Physiology, 161*(2), 1034–1048.

Chiovitti, A., Bacic, A., Burke, J., & Wetherbee, R. (2003). Heterogeneous xylose-rich glycans are associated with extracellular glycoproteins from the biofouling diatom *Craspedostauros australis* (Bacillariophyceae). *European Journal of Phycology, 38*(4), 351–360.

Chung, I. K., Oak, J. H., Lee, J. A., Shin, J. A., Kim, J. G., & Park, K. (2013). Installing kelp forests/seaweed beds for mitigation and adaptation against global warming: Korean project overview. *ICES Journal of Marine Science, 70*(5), 1038–1044.

Cox, J. L. (1981). Laminarinase induction in marine zooplankton and its variability in zooplankton samples. *Journal of Plankton Research, 3*(3), 345–356.

Cui, Y., Zhu, L., Li, Y., Jiang, S., Sun, Q., Xie, E., Chen, H., Zhao, Z., Qiao, W., Xu, J., & Dong, C. (2021). Structure of a laminarin-type β-(1→3)-glucan from brown algae *Sargassum henslowianum* and its potential on regulating gut microbiota. *Carbohydrate Polymers, 255*(117389), 1–12.

Dean, A. P., Sigee, D. C., Estrada, B., & Pittman, J. K. (2010). Using FTIR spectroscopy for rapid determination of lipid accumulation in response to nitrogen limitation in freshwater microalgae. *Bioresource Technology, 101*(12), 4499–4507.

Devillé, C., Damas, J., Forget, P., Dandrifosse, G., & Peulen, O. (2004). Laminarin in the dietary fibre concept. *Journal of the Science of Food and Agriculture, 84*(9), 1030–1038.

Dobrinčić, A., Balbino, S., Zorić, Z., Pedisić, S., Kovačević, D. B., Garofulić, I. E., & Dragović-Uzelac, V. (2020). Advanced technologies for the extraction of marine brown algal polysaccharides. *Marine Drugs, 18*(3), 1–29.

Duarte, C. M., Middelburg, J. J., & Caraco, N. (2005). Major role of marine vegetation on the oceanic carbon cycle. *Biogeosciences, 2*(1), 1–8.

Feng, Y., Xiong, Y., Hall-Spencer, J. M., Liu, K., Beardall, J., Gao, K., … Gao, G. (2023). Shift in algal blooms from micro- to macroalgae around China with increasing eutrophication and climate change. *Global Change Biology, 8*, Article e17018.

Ford, C. W., & Percival, E. (1965). The carbohydrates of *Phaeodactylum tricornutum*. Part I. Preliminary examination of the organism, and characterisation of low molecular weight material and of a glucan. *Journal of the Chemical Society (Resumed)*, 7035–7041.

Frick, K., Yeh, Y. C., Schmid-Staiger, U., & Tovar, G. E. M. (2023). Comparing three different *Phaeodactylum tricornutum* strains for the production of chrysolaminarin in flat panel airlift photobioreactors. *Journal of Applied Phycology, 35*(1), 11–24.

Gao, B., Chen, A., Zhang, W., Li, A., & Zhang, C. (2017). Co-production of lipids, eicosapentaenoic acid, fucoxanthin, and chrysolaminarin by *Phaeodactylum tricornutum* cultured in a flat-plate photobioreactor under varying nitrogen conditions. *Journal of Ocean University of China, 16*(5), 916–924.

Gao, G., Zhao, X., Jiang, M., & Gao, L. (2021). Impacts of marine heatwaves on algal structure and carbon sequestration in conjunction with ocean warming and acidification. *Frontiers in Marine Science, 8*, 1–12.

Gao, K., Gao, G., Wang, Y., & Dupont, S. (2020). Impacts of ocean acidification under multiple stressors on typical organisms and ecological processes. *Marine Life Science and Technology, 2*(3), 279–291.

Gotteland, M., Riveros, K., Gasaly, N., Carcamo, C., Magne, F., Liabeuf, G., Beattie, A., & Rosenfeld, S. (2020). The pros and cons of using algal polysaccharides as prebiotics. *Frontiers in Nutrition, 7*(163), 1–15.

Granata, T. C. (1991). Diel periodicity in growth and sinking rates of the centric diatom *Coscinodiscus concinnus*. *Limnology and Oceanography, 36*(1), 132–139.

Granum, E., Kirkvold, S., & Myklestad, S. M. (2002). Cellular and extracellular production of carbohydrates and amino acids by the marine diatom *Skeletonema costatum*: Diel variations and effects of N depletion. *Marine Ecology Progress Series, 242*, 83–94.

Hein, M., & Sand-Jensen, K. (1997). CO_2 increases oceanic primary production. *Nature, 388*(6642), 526–527.

Hildebrand, M., Manandhar-Shrestha, K., & Abbriano, R. (2017). Effects of chrysolaminarin synthase knockdown in the diatom *Thalassiosira pseudonana*: Implications of reduced carbohydrate storage relative to green algae. *Algal Research, 23*, 66–77.

Holdt, S. L., & Kraan, S. (2011). Bioactive compounds in seaweed: Functional food applications and legislation. *Journal of Applied Phycology, 23*(3), 543–597.

Hou, X., Mu, L., Hu, X., & Guo, S. (2023). Warming and microplastic pollution shape the carbon and nitrogen cycles of algae. *Journal of Hazardous Materials, 447*(130775), 1–10.

Huang, G., Vidal-Melgosa, S., Sichert, A., Becker, S., Fang, Y., Niggemann, J., … Hehemann, J. (2021). Secretion of sulfated fucans by diatoms may contribute to marine aggregate formation. *Limnology and Oceanography, 66*(10), 3768–3782.

Huang, W., Haferkamp, I., Lepetit, B., Molchanova, M., Hou, S., Jeblick, W., … Kroth, P. G. (2018). Reduced vacuolar β-1,3-glucan synthesis affects carbohydrate metabolism as well as plastid homeostasis and structure in *Phaeodactylum tricornutum*. *Proceedings of the National Academy of Sciences of the United States of America, 115*(18), 4791–4796.

Huang, W., Río Bártulos, C., & Kroth, P. G. (2016). Diatom vacuolar 1,6-β-Transglycosylases can functionally complement the respective yeast mutants. *The Journal of Eukaryotic Microbiology, 63*(4), 536–546.

IPCC. (2023). IPCC, 2023: Summary for policymakers. In *Climate Change 2023: Synthesis report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*.

Jensen, E. L., Yangüez, K., Carrière, F., & Gontero, B. (2020). Storage compound accumulation in diatoms as response to elevated CO_2 concentration. *Biology, 9*(1), 1–17.

Jia, J., Han, D., Gerken, H. G., Li, Y., Sommerfeld, M., Hu, Q., & Xu, J. (2015). Molecular mechanisms for photosynthetic carbon partitioning into storage neutral lipids in *Nannochloropsis oceanica* under nitrogen-depletion conditions. *Algal Research, 7*, 66–77.

Jiang, X., Zhu, B., Tu, C., Li, Y., Zhao, Y., Yang, G., & Pan, K. (2022). Silencing 1,3-β-glucan synthase gene promotes total lipid production and changes fatty acids composition by affecting carbon flow distribution in *Phaeodactylum tricornutum*. *Algal Research, 67*(5), 1–9.

Kadam, S. U., Tiwari, B. K., & O'Donnell, C. P. (2015). Extraction, structure and biofunctional activities of laminarin from brown algae. *International Journal of Food Science and Technology, 50*(1), 24–31.

Kamoun, S. (2003). Molecular genetics of pathogenic oomycetes. *Eukaryotic Cell, 2*(2), 191–199.

Karuppusamy, S., Rajauria, G., Fitzpatrick, S., Lyons, H., McMahon, H., Curtin, J., … O'Donnell, C. (2022). Biological properties and health-promoting functions of laminarin: A comprehensive review of preclinical and clinical studies. *Marine Drugs, 20*(12), 1–26.

Keith, S. C., & Arnosti, C. (2001). Extracellular enzyme activity in a river-bay-shelf transect: Variations in polysaccharide hydrolysis rates with substrate and size class. *Aquatic Microbial Ecology, 24*(3), 243–253.

Kim, J., Brown, C. M., Kim, M. K., Burrows, E. H., Bach, S., Lun, D. S., & Falkowski, P. G. (2017). Effect of cell cycle arrest on intermediate metabolism in the marine diatom *Phaeodactylum tricornutum*. *Proceedings of the National Academy of Sciences of the United States of America, 114*(38), 1–10.

Kim, Y. T., Kim, E. H., Cheong, C., Williams, D. L., Kim, C. W., & Lim, S. T. (2000). Structural characterization of β-D-(1→3, 1→6)-linked glucans using NMR spectroscopy. *Carbohydrate Research, 328*(3), 331–341.

Kroth, P. G., Chiovitti, A., Gruber, A., Martin-Jezequе, V., Mock, T., Parker, M. S., … Bowler, C. (2008). A model for carbohydrate metabolism in the diatom *Phaeodactylum tricornutum* deduced from comparative whole genome analysis. *PLoS One, 3*(1), Article e1426.

Kusaikin, M. I., Ermakova, S. P., Shevchenko, N. M., Isakov, V. V., Gorshkov, A. G., Vereshchagin, A. L., … Zvyagintseva, T. N. (2010). Structural characteristics and antitumor activity of a new chrysolaminaran from the diatom alga *Synedra acus*. *Chemistry of Natural Compounds, 46*(1), 1–4.

Levitan, O., Dinamarca, J., Zelzion, E., Lun, D. S., Guerra, L. T., Kim, M. K., … Falkowski, P. G. (2015). Remodeling of intermediate metabolism in the diatom *Phaeodactylum tricornutum* under nitrogen stress. *Proceedings of the National Academy of Sciences of the United States of America, 112*(2), 412–417.

Li, Y., Udayakumar, V., Sathuvan, M., Liu, Y., Liu, X., Zhang, Y., Ma, W., Zhang, W., Tang, S., & Cheong, K. (2022). Effects of laminarin zwitterionic carboxylate and sulfonate on the intestinal barrier function and gut microbiota. *Carbohydrate Polymers, 278*(118898), 1–10.

Liu, X., Chen, J., Du, H., Liu, Z., Du, H., Rashid, A., Wang, Y., Ma, W., & Wang, S. (2023). Resolving the dynamics of chrysolaminarin regulation in a marine diatom: A physiological and transcriptomic study. *International Journal of Biological Macromolecules, 252*(126361), 1–10.

Ma, M., Li, Y., Chen, J., Wang, F., Yuan, L., Li, Y., Zhang, B., Ye, D., Han, D., Jin, H., & Hu, Q. (2021). High-cell-density cultivation of the flagellate alga *Poterioochromonas malhamensis* for biomanufacturing the water-soluble β-1,3-glucan with multiple biological activities. *Bioresource Technology, 337*(125447), 1–8.

Maeda, M., & Nisizawa, K. (1968). Fine structure of laminaran of *Eisenia bicyclis*. *Journal of Biochemistry, 63*(2), 199–206.

McConville, M. J., Bacic, A., & Clarke, A. E. (1986). Structural studies of chrysolaminaran from the ice diatom *Stauroneis amphioxys* (Gregory). *Carbohydrate Research, 153*(2), 330–333.

Menshova, R. V., Ermakova, S. P., Anastyuk, S. D., Isakov, V. V., Dubrovskaya, Y. V., Kusaykin, M. I., … Zvyagintseva, T. N. (2014). Structure, enzymatic transformation and anticancer activity of branched high molecular weight laminaran from brown alga Eisenia bicyclis. *Carbohydrate Polymers, 99*, 101–109.

Michel, G., Tonon, T., Scornet, D., Cock, J. M., & Kloareg, B. (2010). Central and storage carbon metabolism of the brown alga *Ectocarpus siliculosus*: Insights into the origin and evolution of storage carbohydrates in eukaryotes. *New Phytologist, 188*(1), 67–81.

Myklestad, S. (1974). Production of carbohydrates by marine planktonic diatoms. i. Comparison of nine different species in culture. *Journal of Experimental Marine Biology and Ecology, 15*(3), 261–274.

Myklestad, S. M. (2013). Production, chemical structure, metabolism, and biological function of the (1→3)-linked, β3-D-glucans in diatoms. *Biological Oceanography, 6*(3), 313–326.

Nelson, T. E., & Lewis, B. A. (1974). Separation and characterization of the soluble and insoluble components of insoluble laminaran. *Carbohydrate Research, 33*(1), 63–74.

Neyrinck, A. M., Mouson, A., & Delzenne, N. M. (2007). Dietary supplementation with laminarin, a fermentable marine β (1-3) glucan, protects against hepatotoxicity induced by LPS in rat by modulating immune response in the hepatic tissue. *International Immunopharmacology, 7*(12), 1497–1506.

Nguyen, S. G., Kim, J., Guevarra, R. B., Lee, J. H., Kim, E., Kim, S. I., & Unno, T. (2016). Laminarin favorably modulates gut microbiota in mice fed a high-fat diet. *Food & Function, 7*(10), 4193–4201.

Park, H. K., Kim, I. H., Kim, J., & Nam, T. J. (2012). Induction of apoptosis by laminarin, regulating the insulin-like growth factor-IR signaling pathways in HT-29 human colon cells. *International Journal of Molecular Medicine, 30*(4), 734–738.

Paulsen, B. S., & Myklestad, S. (1978). Structural studies of the reserve glucan produced by the marine diatom *Skeletonema costatum* (grev.) Cleve. *Carbohydrate Research, 62*(2), 386–388.
Percival, E. G. V., & Ross, A. G. (1951). 156. The constitution of laminarin. Part II. The soluble laminarin of *Laminaria digitata*. *Journal of the Chemical Society (Resumed), 720*, 1–7.
Poliner, E., Panchy, N., Newton, L., Wu, G., Lapinsky, A., Bullard, B., … Farré, E. M. (2015). Transcriptional coordination of physiological responses in *Nannochloropsis oceanica CCMP1779* under light/dark cycles. *Plant Journal, 83*(6), 1097–1113.
Rajauria, G., Ravindran, R., Garcia-Vaquero, M., Rai, D. K., Sweeney, T., & O'Doherty, J. (2021). Molecular characteristics and antioxidant activity of laminarin extracted from the seaweed species *Laminaria hyperborea*, using hydrothermal-assisted extraction and a multi-step purification procedure. *Food Hydrocolloids, 112*(106332), 1–10.
Ran, X., Shen, Y., Jiang, D., Wang, C., Li, X., Zhang, H., Pan, Y., Xie, C., Xie, T., Zhang, Y., & Yao, C. (2022). Nutrient deprivation coupled with high light exposure for bioactive chrysolaminarin production in the marine microalga *Isochrysis zhangjiangensis*. *Marine Drugs, 20*(6), 1–19.
Read, S. M., Currie, G., & Bacic, A. (1996). Analysis of the structural heterogeneity of laminarin by electrospray-ionisation-mass spectrometry. *Carbohydrate Research, 281*(2), 187–201.
Remmers, I. M., D'Adamo, S., Martens, D. E., de Vos, R. C. H., Mumm, R., America, A. H. P., … Lamers, P. P. (2018). Orchestration of transcriptome, proteome and metabolome in the diatom *Phaeodactylum tricornutum* during nitrogen limitation. *Algal Research, 35*, 33–49.
Richardson, T. L., & Cullen, J. J. (1995). Changes in buoyancy and chemical composition during growth of a coastal marine diatom: Ecological and biogeochemical consequences. *Marine Ecology Progress Series, 128*(1–3), 77–90.
Rioux, L. E., Turgeon, S. L., & Beaulieu, M. (2007). Characterization of polysaccharides extracted from brown seaweeds. *Carbohydrate Polymers, 69*(3), 530–537.
Rioux, L. E., Turgeon, S. L., & Beaulieu, M. (2010). Structural characterization of laminaran and galactofucan extracted from the brown seaweed *Saccharina longicruris*. *Phytochemistry, 71*(13), 1586–1595.
Saborowski, R., & Buchholz, F. (1999). A laboratory study on digestive processes in the Antarctic krill, *Euphausia superba*, with special regard to chitinolytic enzymes. *Polar Biology, 21*(5), 295–304.
Santos, I. R., Chen, X., Lecher, A. L., Sawyer, A. H., Moosdorf, N., Rodellas, V., … Li, L. (2021). Submarine groundwater discharge impacts on coastal nutrient biogeochemistry. *Nature Reviews Earth and Environment, 2*(5), 307–323.
Scheschonk, L., Becker, S., Hehemann, J. H., Diehl, N., Karsten, U., & Bischof, K. (2019). Arctic kelp eco-physiology during the polar night in the face of global warming: A crucial role for laminarin. *Marine Ecology Progress Series, 611*, 59–74.
Schiener, P., Black, K. D., Stanley, M. S., & Green, D. H. (2015). The seasonal variation in the chemical composition of the kelp species *Laminaria digitata*, *Laminaria hyperborea*, *Saccharina latissima* and *Alaria esculenta*. *Journal of Applied Phycology, 27*(1), 363–373.
Schoemann, V., Becquevort, S., Stefels, J., Rousseau, V., & Lancelot, C. (2005). Phaeocystis blooms in the global ocean and their controlling mechanisms: A review. *Journal of Sea Research, 53*(1–2), 43–66.
Sellimi, S., Maalej, H., Rekik, D. M., Benslima, A., Ksouda, G., Hamdi, M., … Hajji, M. (2018). Antioxidant, antibacterial and in vivo wound healing properties of laminaran purified from *Cystoseira barbata* seaweed. *International Journal of Biological Macromolecules, 119*, 633–644.
Shekhar, K., Colm, O., Dilip, R., Mohammad, H., Catherine, B., Des, W., & Brijesh, T. (2015). Laminarin from Irish brown seaweeds *Ascophyllum nodosum* and *Laminaria hyperborea*: Ultrasound assisted extraction, characterization and bioactivity. *Marine Drugs, 13*(7), 4270–4280.
Shin, H. J., Oh, S. J., Kim, S. I., Won Kim, H., & Son, J. H. (2009). Conformational characteristics of β-glucan in laminarin probed by terahertz spectroscopy. *Applied Physics Letters, 94*(11), 2012–2015.
Singh, R. P., Rajarammohan, S., Thakur, R., & Hassan, M. (2020). Linear and branched β-glucans degrading enzymes from versatile *Bacteroides uniformis JCM 13288^T* and their roles in cooperation with gut bacteria. *Gut Microbes, 12*(1), 1–18.
Steinacher, M., Joos, F., Frölicher, T. L., Bopp, L., Cadule, P., Cocco, V., … Segschneider, J. (2010). Projected 21st century decrease in marine productivity: A multi-model analysis. *Biogeosciences, 7*(3), 979–1005.
Størseth, T. R., Hansen, K., Reitan, K. I., & Skjermo, J. (2005). Structural characterization of β-D-(1→3)-glucans from different growth phases of the marine diatoms *Chaetoceros mülleri* and *Thalassiosira weissflogii*. *Carbohydrate Research, 340*(6), 1159–1164.
Størseth, T. R., Kirkvold, S., Skjermo, J., & Reitan, K. I. (2006). A branched β-d-(1→3,1→6)-glucan from the marine diatom *Chaetoceros debilis* (Bacillariophyceae) characterized by NMR. *Carbohydrate Research, 341*(12), 2108–2114.
Takei, M. N., Kuda, T., Taniguchi, M., Nakamura, S., Hajime, T., & Kimura, B. (2020). Detection and isolation of low molecular weight alginate- and laminaran-susceptible gut indigenous bacteria from ICR mice. *Carbohydrate Polymers, 238*(116205), 1–7.
Teeling, H., Fuchs, B. M., Becher, D., Klockow, C., Gardebrecht, A., Bennke, C. M., … Amann, R. (2012). Substrate-controlled succession of marine bacterioplankton populations induced by a phytoplankton bloom. *Science, 336*(6081), 608–611.
Unfried, F., Becker, S., Robb, C. S., Hehemann, J. H., Markert, S., Heiden, S. E., … Schweder, T. (2018). Adaptive mechanisms that provide competitive advantages to marine bacteroidetes during microalgal blooms. *ISME Journal, 12*(12), 2894–2906.
Vårum, K. M., Østgaard, K., & Grimsrud, K. (1986). Diurnal rhythms in carbohydrate metabolism of the marine diatom *Skeletonema costatum* (Grev.) Cleve. *Journal of Experimental Marine Biology and Ecology, 102*(2–3), 249–256.
Villareal, T. A., Altabet, M. A., & Culver-Rymsza, K. (1993). Nitrogen transport by vertically migrating diatom mats in the North Pacific Ocean. *Nature, 363*(6431), 709–712.
Vogler, B. W., Ashford, A., & Posewitz, M. C. (2021). CRISPR/Cas9 disruption of glucan synthase in *Nannochloropsis gaditana* attenuates accumulation of β-1,3-glucose oligomers. *Algal Research, 58*(102385), 1–7.
Vogler, B. W., Brannum, J., Chung, J. W., Seger, M., & Posewitz, M. C. (2018). Characterization of the *Nannochloropsis gaditana* storage carbohydrate: A 1,3-beta glucan with limited 1,6-branching. *Algal Research, 36*(2018), 152–158.
Wang, M., & Bartnicki-Garcia, S. (1974). Mycolaminarans: Storage (1→3)-β-D-glucans from the cytoplasm of the fungus *Phytophthora palmivora*. *Carbohydrate Research, 37*(2), 331–338.
Wang, Y., Liu, D., Xiao, W., Zhou, P., Tian, C., Zhang, C., Du, J., Guo, H., & Wang, B. (2021). Coastal eutrophication in China: Trend, sources, and ecological effects. *Harmful Algae, 107*(102058), 1–13.
Wustman, B. A., Lind, J., Wetherbee, R., & Gretz, M. R. (1998). A model of adhesives based on chemical characterization and localization of polysaccharides from the marine diatom *Achnanthes longipes* and other diatoms. *Plant Physiology, 116*(4), 1059–1069.
Xia, S., Gao, B., Li, A., Xiong, J., Ao, Z., & Zhang, C. (2014). Preliminary characterization, antioxidant properties and production of chrysolaminarin from marine diatom *Odontella aurita*. *Marine Drugs, 12*(9), 4883–4897.
Yang, Y., Li, D., Balamurugan, S., Wang, X., Yang, W., & Li, H. (2022). Chrysolaminarin biosynthesis in the diatom is enhanced by overexpression of 1,6-β-transglycosylase. *Algal Research, 66*(102817), 1–8.
Yang, Y., Li, D., Chen, T., Hao, T., Balamurugan, S., Yang, W. D., … Li, H. Y. (2019). Overproduction of bioactive algal chrysolaminarin by the critical carbon flux regulator phosphoglucomutase. *Biotechnology Journal, 14*(3), 1–8.
Yang, Z., Ma, Y., Zheng, J., Yang, W., Liu, J., & Li, H. (2014). Proteomics to reveal metabolic network shifts towards lipid accumulation following nitrogen deprivation in the diatom *Phaeodactylum tricornutum*. *Journal of Applied Phycology, 26*(1), 73–82.
Zhang, F., Tian, Y., & He, J. (2021). Occurrence of the freshwater Chrysophyte *Poterioochromonas malhamensis* in a high arctic marine ecosystem. *Water, 13*(15), 1–8.
Zhu, B., Shi, H., Yang, G., Lv, N., Yang, M., & Pan, K. (2016). Silencing UDP-glucose pyrophosphorylase gene in *Phaeodactylum tricornutum* affects carbon allocation. *New Biotechnology, 33*(1), 237–244.
Zou, D., & Gao, K. (2013). Thermal acclimation of respiration and photosynthesis in the marine macroalga *Gracilaria lemaneiformis* (Gracilariales, Rhodophyta). *Journal of Phycology, 49*(1), 61–68.