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Review

Phytohormones and Pheromones in the Phycology Literature: Benchmarking of Data-Set and Developing Critical Tools of Biotechnological Implications for Commercial Aquaculture Industry

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Abstract: Plant hormones and pheromones are natural compounds involved in the growth, development, and reproductive processes. There is a plethora of studies on hormones and pheromones in terrestrial plants, but such investigations are few in the phycological literature. There are striking similarities between the chemical diversity, biosynthetic processes, roles, and actions of hormones and pheromones in both higher angiospermic plants and algae. However, there are substantial knowledge gaps in understanding the genes responsible for hormone biosynthesis and regulation in algae. Efforts have focused on identifying the genes and proteins involved in these processes, shedding light on lateral gene transfer and evolutionary outcomes. This comprehensive review contributes to benchmarking data and essential biotechnological tools, particularly for the aquaculture industry where seaweed is economically crucial. Advanced techniques in plant hormones and pheromones can revolutionize commercial aquaculture by using synthetic analogs to enhance growth, yield, and reproductive control, thereby addressing seasonal limitations and enabling sustainable seedling production. To the best of our knowledge, this is the first comprehensive review that focuses on biosynthetic pathways and modes of action (of five plant hormones and five pheromones), roles (of 11 hormones and 29 pheromones), and extraction protocols (of four hormones and six pheromones) reported in the phycological domain.

Keywords: aquaculture; biosynthetic pathways; hormones; pheromones; phycology; seedling production

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1. Introduction

Algae are a diverse group of photosynthetic organisms that are unrelated ecologically as well morphologically to other groups [1]. They range from microscopic unicellular forms to large multicellular seaweeds, representing a crucial component of aquatic ecosystems, contributing significantly to oxygen production and serving as fundamental sources of nutrition [2,3]. Classified into various taxonomic groups, including green, brown, and red algae, they showcase a remarkable adaptability to diverse environments, highlighting their significance in both freshwater and marine ecosystems [4]. The forms around which considerable trade and economics are developed are marine macroalgae. They represent heterogeneous artificial groups, forms of marine polyphyletic origin, and different evolutionary lineages [5].

The perennial, multilayered seaweed stands of large 'kelps' represent the most productive ecosystems, which can sequester significant blue carbon and consequently increase oxygen in the oceanic environment [6]. Seaweeds have a long-standing history of exploitation by humankind for food, fodder, and agriculture, especially in Asia, Polynesia, and

South America [7]. Propelled by emerging applications in day-to-day commodity products and biotechnological and medical use, seaweeds have been industrially farmed. In 2018, the commercial production of seaweeds globally reached more than 30 million tons, 97% of which was harvested through aquaculture [8]. Currently, 47 species and two varieties of 27 genera are commercially cultivated—largely in Asian countries [9]. The industry is expected to improve its performance by 12% annual growth and is anticipated to reach USD 30.2 billion by 2025 [10]. The burgeoning global population necessitated substantial improvement in food production even at the cost of limited availability of agricultural land, fast-deteriorating soil quality, shortages of water for irrigation, and protuberances by climate change. It should be noted that, considering current consumption trends, there is an urgent need to produce 50–70% additional food by 2050 [11]. The seaweeds or their extracts have been used since ancient times as soil conditioners or fertilizers in agriculture [12]. Their large-scale application has considerable potential to improve food production [13]. This is because they are needed only in small dosages—often diluted in volume by a factor of 20–500 [14]—as growth stimulants to enhance yield [15], impart disease resistance [16], elevate drought tolerance [17], reduce pest infestation [18], and improve shelf-life of produce [19]. These applications need in-depth scientific understating to unravel their mode of action, which is largely unknown. The empirical evidence showed that the growth responses elicited by seaweed extracts cannot be attributed to the presence of macro- and micro-elements alone, but plant growth regulatory compounds might also play a catalytic role [20]. The discovery of different classes of hormones in seaweeds or their extracts was evident from the work that was carried out during the late 1960s to early 1970s [21].

This comprehensive review deals with the critical aspects of phytohormones and pheromones reported in algae (encompassing both macro- and microscopic forms). It is well evident that plant hormones play a pivotal role in regulating growth and development while pheromones are needed for induction of reproduction and sexual maturity in algae. Further, we tried to elucidate on how their biosynthetic pathways are similar to those in higher angiospermic plants, e.g., response to climate change and stress from the herbivores. We have tried to figure out the detailed ways these substances work in macroalgae as well as microalgae, especially in their defense mechanisms. If we understand this process better, it could help us to have effective control over algal growth and dealing with infestations. The study also highlights the importance of understanding the reproduction of commercially valuable macroalgae and microalgae, suggesting that hormones and pheromones may play a crucial role in advancing spore-based cultivation technologies. We believe that the data synthesis provided here would be useful in developing critical tools of biotechnological implications for the commercial aquaculture industry.

2. Hormones and Pheromones Reported in the Phycology Literature

Phytohormones are produced within the plant cells at extremely low concentrations. They act as signaling molecules and control almost all aspects of development and growth. The hormones acquire a greater significance as messenger or signaling molecules, where contact between adjacent cells plays a key role in regulating metabolism at the tissue level [22]. Eleven different plant hormones have been discovered in algae (Table 1), i.e., auxin, cytokinin, gibberellin, abscisic acid, ethylene, rhodomorphin, jasmonic acid, brassinosteroids, salicylic acid, strigolactones, and polyamines. More recently, strigolactones have been identified from freshwater alga *Chara coralina* as a new branching inhibiting hormone [23]. Polyamines, e.g., thermospermine, are considered to be one of the plant hormones and are present in various seaweeds like *Ascophyllum nodosum*, *Fucus vesiculosus*, and *Sargassum horneri* (Table 1).

Table 1. Role of hormones in algae.

Category	Hormone Name	Name of Alga	Role	Reference
Auxin	Phenylacetic acid (PAA)	*Ulva compressa* (as *Enteromorpha compressa*)	Induces the thallus growth	[24]
	Indole acetic acid (IAA)	*Neoporphyra perforata* (as *Porphyra perforata*)	Stimulates the growth and cell division	[25]
	Indole acetic acid (IAA)	*Ulva lactuca*	Induces the filamentous sporelings and promotes their growth	[26]
	Indole acetic acid (IAA)	*Chara zeylanica*	Antagonistic effect, inhibits gibberellic acid and its stimulatory effect on the growth	[27]
	Indole-3-acetic acid (IAA)	*Caulerpa paspaloides*	Enhanced initiation of leaf-like structures	[28]
	Indole acetic acid (IAA)	*Fucus spiralis*	Tissue differentiation	[29]
	Indole acetic acid (IAA)	*Tretraselmis* sps.		
Cytokinin	Isoprenoid and aromatic cytokinins	*Cladophora capensis*	Growth and morphogenesis	[30]
		Ulva sp.		
		Caulerpa tongaensis (as *Caulerpa filiformis*)		
		Halimeda cuneata		
		Brassicophycus sisymbrioides (as *Bifurcaria brassicaeformis*)		
		Ecklonia maxima		
		Laminaria pallida		
		Macrocystis pyrifera (as *Macrocystis angustifolia*)		
		Splachnidium rugosum		
		Dictyota sp.		
		Sargassum incisifolium (as *Sargassum heterophyllum*)		
		Pachymenia orbitosa (as *Aeodes orbitosa*)		
		Gigartina bracteata (as *Gigartina clathrata*)		
		Gigartina polycarpa		
		Sarcothalia scutellata		
		Hymenena venosa		
		Hypnea spicifera		
		Mazzaella capensis		
		Nothogenia erinacea		
		Plocamium corallorhiza		
		Carradoeriella virgata		
		Porphyra capensis		
		Sarcothalia stiriata		
		Gelidium vittatum (as *Suhria vittata*)		
		Amphiroa bowerbankii		
		Amphiroa ephedraea		
		Arthrocardia sp.		
		Cheilosporum sp.		
		Corallina sp.		
		Jania sp.		
	Kinetin	*Sphacelaria rigidula* (as *Sphacelaria furcigera*)	Increases the length of lateral branches	[31]

Table 1. *Cont.*

Category	Hormone Name	Name of Alga	Role	Reference
Cytokinin	Kinetin	*Kappaphycus alvarezii*	Promotes cell division	[32]
	Zeatin	*Kappaphycus alvarezii*		
		Sargassum tenerrimum		
		Hydropuntia edulis (as *Gracilaria edulis*)		
	Isopentenyladenine	*Sargassum muticum*	Early growth of the receptacles	[33]
	cis-zeatin riboside			
	Isopentenyladenine	*Neoporphyra perforata* (as *Porphyra perforata*)	Helps in maturation of spermatangia and carpogonia	
	cis-zeatin riboside			
	Cytokinin	*Fucus vesiculosus*	Regeneration and morphogenesis	[34]
Gibberellic acid	Gibberellin (GA1/GA3)	*Fucus spiralis*	Tissue differentiation	[29]
	Gibberellin (GA4/GA7)	*Tretraselmis* sps.		
	Gibberellin (GA3)	*Chara vulgaris*	Promotes the number of antheridial filaments and spermatids	[35]
	Gibberellin (GA3)	*Fucus vesiculosus*	Increases adventitious branches	[34]
Abscisic acid	Abscisic acid (ABA)	*Ulva lactuca*/*Ulva linza* (as *Ulva fasciata*)	Releases in extreme conditions and inhibits growth	[36]
		Dictyota humifusa		
	Abscisic acid (ABA)	*Phycocalidia acanthophora* (as *Porphyra acanthophora* (red))	Releases in stress conditions and inhibits growth	[37]
		Phycocalidia acanthophora (as *Porphyra acanthophora*)		
		Gelidium floridanum		
		Crassiphycus birdiae (as *Gracilaria birdiae*)		
		Gracilaria cervicornis		
		Gracilariopsis tenuifrons		
		Chondracanthus teedei		
		Hypnea nigrescens		
		Hypnea musciformis (brown)		
		Hypnea musciformis (green)		
		Dunaliella parva	Releases during salinity stress, causes reduction in growth, and in some cases promotes senescence	[38]
		Draparnaldia mutabilis		
		Dunaliella acidophila	Reduction in growth and photosynthesis with increase in pH	
Rhodomorphin	Rhodomorphin	*Griffithsia pacifica*	Repairs shoot cell and normal regeneration	[39]
		Anotrichium tenue		
		Antithamnion kylinii		
	Rhodomorphin (as glycoprotein)	*Volvox carteri*	Sexual hormone	[40]
Ethylene	1-aminocyclopropane-l-carboxylicacid (ACC) (Ethylene precursor)	*Neoporphyra perforata* (as *Porphyra perforata*)	Stimulates cell division and apical cap development	[25]
	Ethylene	*Acetabularia acetabulum* (as *Acetabularia mediterranea*)	Influences the developmental pattern of cap	[41]
Brassinosteroids	Brassinolide (BR)	*Ecklonia maxima*	Improves stress response to various biotic and abiotic stresses	[42]
	Castasterone (CS)			
Jasmonic acid	Jasmonate	*Scenedesmus incrassulatus*	Provides tolerance to the temperatures and infections stress	[43]
	Methyl jasmonate			
	Jasmonic acid and its derivatives	*Chondrus crispus*	Induces defense reaction	[44]

Table 1. *Cont.*

Category	Hormone Name	Name of Alga	Role	Reference
Polyamines	Polyamines	*Chlorella vulgaris*	Enhances cell division, DNA replication, and autospore release	[45]
	Polyamines	*Chlamydomonas reinhardtii*	Enhances cell division	[46]
	Putrescine	*Ulva lactuca* (as *Ulva fasciata*)	Releases during hyposaline stress causes and decreases the chlorophyll and growth rate	[47]
	Spermidine			
	Putrescine	*Grateloupia doryphora*	Releases during hyposaline shock and helps in physiological performance during acclimation by increasing photosynthetic rate	[48]
	Spermidine			
	Spermine			
	Polyamines	*Grateloupia doryphora*	Enhances cell division, elongation, and morphogenesis	[49,50]
	Putrescine	*Grateloupia* sp.	Induction of cystocarp, development, and release	[51]
	Spermidine			
	Spermine			
	Putrescine	*Gracilaria cornea* (as *Crassiphycus corneus*)	Promotes cystocarp maturation and liberation and develops cell masses	[52,53]
Salicylic acid	Salicylic acid	*Saccharina japonica* (as *Laminaria japonica*)	Imparts thermotolerance	[54]
Strigolactone	Strigolactone	*Chara coralina*	Stimulates rhizoid elongation	[23]

The concept and different terminologies related to hormone research in the phycology literature have been adopted largely from higher plants. The studies on hormones in algae are uncoordinated and not as advanced as in higher plants. This review primarily utilizes the literature on seaweeds and other algal forms like microalgae (of marine as well as freshwater origin) wherever necessary to substantiate the phycological origin of data. The presence of gibberellin activity was first reported in *Enteromorpha prolifera* (now *Ulva prolifera*) and *Ecklonia radiata* [55]; auxin activity in *Ulva pertusa* (now *Ulva australis*), *Undaria pinnatifida*, and *Hizikia fusiformis* (now *Sargassum fusiforme*) [56]; and cytokinin activity in species of *Laminaria* and *Fucus* [57]. Even the concentration of hormones like IAA has been studied in zygotes and mature tissues of *Fucus distichus*, which was 2–9 ng g^{-1} fr wt and is in a slightly lower proportion than in higher plants [58].

The word pheromone is derived from a Greek word that means 'to carry', which signifies its role as it carries information regarding the availability and favorability of conditions for the organism to sexually reproduce [59]. There have been a number of studies related to the bioactive metabolites and hormones produced by seaweeds that can effectuate interspecific signaling, but very little is known about the chemical cues that affect the members of the same species, i.e., interspecific interaction of the seaweeds. These cues are the pheromones, which can help in deciphering the factors that induce sexual reproduction in those seaweeds. A number of pheromones have been identified in various seaweeds (Table 2).

Table 2. Role of pheromones in algae.

Class	Name of Pheromone	Name of Alga	Role	Reference
Chlorophyceae	*Sporulation inhibitor-1a* (Glycoprotein)	*Ulva compressa* (as *Ulva mutabilis*)	Suppresses gametogenesis	[60]
	Swarming inhibitor	*Ulva compressa* (as *Ulva mutabilis*)	Inhibits gamete swarming	
	Sporulation inhibitor-2 (Non-protein)	*Ulva compressa* (as *Ulva mutabilis*)	Suppresses gametogenesis	

Table 2. *Cont.*

Class	Name of Pheromone	Name of Alga	Role	Reference
Phaeophyceae	Ectocarpene (S(+)l-*cis*-buten-l-yl-cyclohepta-2,5-diene)	*Ectocarpus siliculosus*	Releases female gamete and helps in attracting male gametes	[61]
		Sphacelaria rigidula	Acts as a chemoattractant	[62]
		Adenocystis longissima (as *Adenocystis utricularis*)		[63]
	Dictyotene (C11 metabolite)	*Dictyopteris polypodioides* (as *Dictyopteris membranacea*)	Helps in gamete attraction and acts as a deterrent to mesograzers	[64]
		Dictyota dichotoma		
		Dictyota diemensis		
		Sargassum filipendula		
	C11 sulphur metabolite	*Dictyopteris polypodioides* (as *Dictyopteris membranacea*)		
	Dictyotene (C11 metabolite)	*Dictyota dimensis*	Acts as a sperm attractant	[65]
	Diterpene alcohols	*Dictyota dichotoma*	Acts as a deterrent to herbivores	[66]
	C11 hydrocarbons	*Dictyopteris delicatula*		[67]
	Thiopyranone (Thiopyran-4-one)	*Dictyopteris polypodioides* (as *Dictyopteris membranacea*)	Acts as a deterrent to herbivores	[68]
	Dithiepanone (Dithiepan-5-one)			
	Multifidene	*Halosiphon tomentosus* (as *Chorda tomentosa*)	Acts as a chemoattractant	[69]
	Ectocarpene			
	Dictyopterene			
	Viridiene			
	Fucoserratene (1,3-trans-5-*cis*-octatriene)	*Fucus serratus*	Acts as a chemoattractant	[70]
		Fucus vesiculosus		[71]
		Fucus spiralis		
	Finavarrene	*Ascophyllum nodosum*	Acts as a chemoattractant	[71]
	Cystophorene	*Cystophora siliquosa*	Acts as a chemoattractant	[71]
	Hormosirene	*Hormosira banksii*	Acts as a chemoattractant	[71]
		Xiphophora chondrophylla		
		Xiphophora gladiate		
		Durvillaea potatorum		
		Durvillaea antarctica		
		Durvillaea willana		
		Colpomenia peregrina		[72]
		Planosiphon complanatus (as *Scytosiphon lomentaria*)		
		Analipus japonicus		[73]
	Ectocarpene	*Ectocarpus flagelliformis* (as *Ectocarpus fasciculatus*)	Acts as a chemoattractant	[71]
		Adenocystis longissima (as *Adenocystis utricularis*)		
		Sphacelaria rigidula		
		Analipus japonicus		[73]
	Dictyopterene C′	*Dictyota dichotoma*	Acts as a chemoattractant	[71]
	Dictyotene	*Dictyota diemensis*	Acts as an erotactin	[74]

Table 2. *Cont.*

Class	Name of Pheromone	Name of Alga	Role	Reference
Phaeophyceae	Desmarcstene	*Desmarestia aculeata*/*Desmarestia menziesii* (as *Desmarestia aculeata*)	Acts as a chemoattractant	[71]
		Desmarestia confervoides (as *Desmarestia viridis*)		
		Cladostephus hirsutus/*Cladostephus kuetzingii* (as *Cladostephus spongiosus*)		
	Lamoxirene	*Laminariaceae*	Acts as a chemoattractant	[71]
		Alariaceae		
		Lessoniaceae		
		Pleurophycus gardneri	Acts as an erotactin	[74]
		Agarum clathratum (as *Agarum cribrosum*)		
		Sachharina gyrata (as *Kjellmaniella gyrata*)		
		Hedophyllum sessile		
		Cymathaere triplicate		
		Undaria pinnatifida		
		Pterygophora californica		
		Eisenia bicyclis (as *Eisenia arborea*)		
		Ecklonia biruncinata (as *Ecklonia radiata*)		
		Macrocystis pyrifera		
		Macrocystis pyrifera (as *Macrocystis integrifolia*)		
		Nereocystis luetkeana		
		Pelagophycus porra		
		Dictyoneurum reticulatum (as *Dictyoneuropsis reticulata*)		
		Lessoniopsis littoralis		
	Multifidene *cis*-4-vinyl-5-*cis*-buten-l-yl-cyclopentene)	*Cutleria multifida*	Responsible for chemotaxis of the male microgametes	[75]
		Zonaria angustata	Acts as a chemoattractant	[73]
	Viridiene	*Microzonia phinneyi* (as *Syringoderma phinneyi*)		[71]
	Caudoxirene	*Perithalia caudata*		
	Giffordene	*Feldmannia mirchelliae*/*Hincksia mitchelliae* (as *Giffordia mitchelliae*)		[72]
Rhodophyceae	Ochtodene (Monoterpene)	*Ochtodes secundiramea*	Acts as a deterrent to herbivores	[76]
	Octodiol			

3. Biosynthetic Pathways

3.1. Hormones

3.1.1. Auxin

Auxin (IAA) biosynthesis occurs mainly by two pathways, i.e., tryptophan-dependent (Figure 1) and tryptophan-independent (Supplementary Figure S1). The tryptophan-dependent pathway follows four different routes: indole-3-pyruvic acid (IPA) pathway, indole-3-acetaldoxime pathway, tryptamine pathway, and IAM pathway, of which indole-3-pyruvic acid (IPA) pathway and tryptamine pathway (TAM) are the main routes for

IAA biosynthesis in the plant [77]. In algae, the tryptamine pathway (TAM) could be the most probable pathway for auxin biosynthesis. The tryptophan decarboxylase enzyme has been reported from microalgae *Chlamydomonas reinhardtii* [78]. Algal counterparts of many auxin biosynthetic enzymes from higher plants like C-S lyase, and nitrilases have also been reported in *Ectocarpus siliculosus*, *Ostreococcus lucimarinus*, *Micromonas pusilla*, *Chlorella variabilis*, *Volvox carteri*, etc. [78]. Amino acid sequence comparison of the Flavin-containing mono-oxidases, YUCCA and FLOOZY, involved in auxin biosynthesis has been carried out between algae like *Ectocarpus siliculosus*, *Ostreococcus lucimarinus*, *Ostreococcus tauri*, and *Chlorella variabilis* and higher plant Arabidopsis. Their comparison has revealed homology with a high confidence value, suggesting parallels in the biosynthetic pathways of both groups [78]. Similar analysis performed for the enzyme tryptophan aminotransferase did not result in any sequence similarity, suggesting the absence of the indole-3-pyruvate pathway of auxin biosynthesis in algae [78].

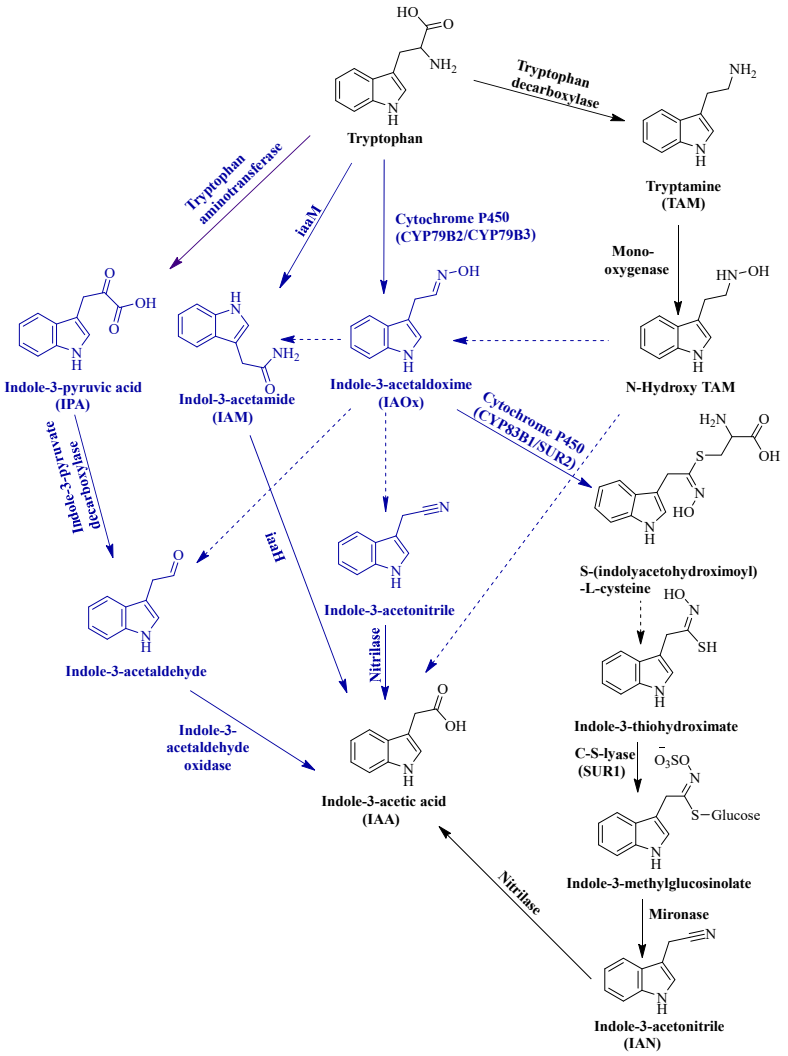

Figure 1. Tryptophan-dependent biosynthesis of IAA (modified from [78,79]). Solid arrows: enzymes/genes responsible for the steps identified. Dashed arrows: proposed steps, but enzymes/genes have not been conclusively determined. Black color: pathway reported in algae. Blue color: pathway reported in higher plants.

3.1.2. Cytokinins

In higher plants, isoprenoid cytokinin biosynthesis takes place via two different pathways. The direct route includes the formation of N6-isopentenyladenosine monophosphate (iPMP) from AMP and pyrophosphate, catalyzed by isopentenyltransferase (IPT)

(Figure 2) [80]. In the second pathway, the synthesis of isoprenoid cytokinin takes place by making changes in the structure of tRNA containing cis-zeatin [30]. This pathway can be found in all organisms except Archea [81]. In marine macroalgae (chlorophyta, pheophyta, and rhodophya), both isoprenoid and aromatic cytokinins and their conjugates have been detected, indicating the presence of complex inter-conversion systems and regulation of their activities, but this second indirect pathway, which includes tRNA degradation, seems to be a characteristic feature of marine macroalgae [30]. Cytokinin biosynthesis has been reported from different macro- as well as microalgae. The macroalgae include *Cladophora capensis*, *Ulva fasciata*, *Caulerpa filiformis*, *Sargassum heterophyllum*, *Porphyra capensis*, *Amphiroa bowerbankii*, *Dictyota humifusa*, etc. [30,36], and the microalgae include *Protococcus viridis*, *Chlorella minutissima*, *Chlorella* sp., and *Scenedesmus* sp. [82]. Interestingly, isopentenyladenine (iP) and cis-zeatin (cZ) forms have been detected in higher concentrations than dihydrozeatin (DHZ) conjugates; whereas, no N-glucosides have been reported from various marine macroalgae like *Ulva*, *Caulerpa*, *Sargassum*, *Macrocystis*, *Porphyra*, *Hypnea*, *Amphiroa*, etc. This suggests that they may have the tRNA-dependent pathway as the preferred route for cytokinin biosynthesis [83]. On BlastP search of amino acid sequence of biosynthetic enzymes like isopentenyltransferase from higher plants, a strong homology with proteins from various algal species like *Ectocarpus siliculosus*, *Volvox carteri* f. *nagariensis*, *Micromonas pusilla*, and *Chlorella variabilis* was observed. It could be concluded that the cytokinin biosynthesis in microalgae (*Micromonas*, *Chlorella*, *Ostreococcus*, *Volvox*, *Thalassiosira*, and *Phaeodactylum*) and macroalgae (*Ectocarpus siliculosus*) possibly occurs via pathways similar to higher plants [78].

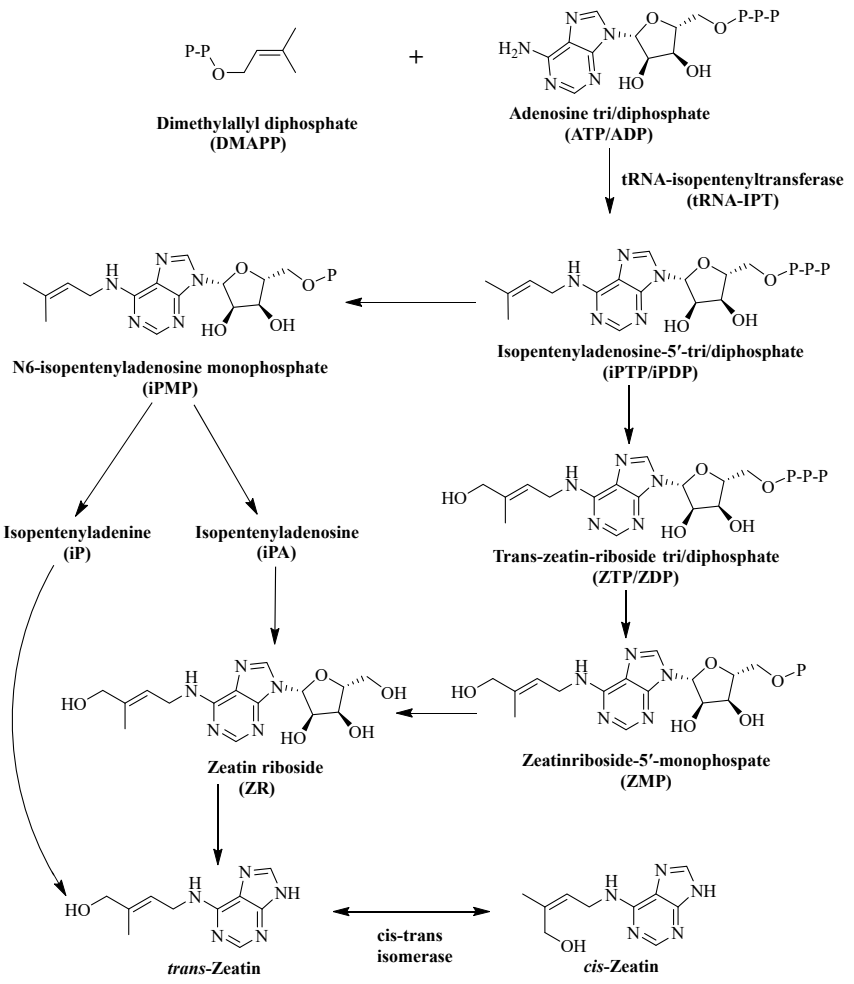

Figure 2. Biosynthesis of cytokinin (modified from [78,84]).

3.1.3. Gibberellins

GAs are chemically diterpenes, and their synthesis, at the early stages, takes place via one of two pathways of isoprenoid biosynthesis, i.e., through the mevalonic acid pathway or methylerythritol phosphate pathway [85]. In higher plants, GA is mostly synthesized through the methylerythritol phosphate pathway, which occurs in plastids [86]. The main reaction of GA biosynthesis is the cyclization of geranylgeranyl pyrophosphate (GGPP) into copalyl pyrophosphate and the final conversion into ent-kaurene (Figure 3). The reactions are catalyzed via the copalyl pyrophosphate synthase (CPS) and ent-kaurene synthase, respectively. Protein sequences similar to the Arabidopsis enzymes, copalyl pyrophosphate synthase, ent-kaurene synthase, and ent-kaurenoic acid oxidase have not been reported from algae [78]. The reason may not be the absence of corresponding enzymes, but the shortage of the available proteomic data. GA-20 oxidase enzyme has been characterized in a green alga *Chlamydomonas reinhardtii*. The BlastP search of this enzyme showed a considerable homology to *A. thaliana* sequence of late-stage enzymes of GA synthesis. This suggests that the GA biosynthesis pathway in algae may not differ too much from the higher plants. At the same time, it is also clear that more research-based evidence is required to understand the exact pathway in algae [78].

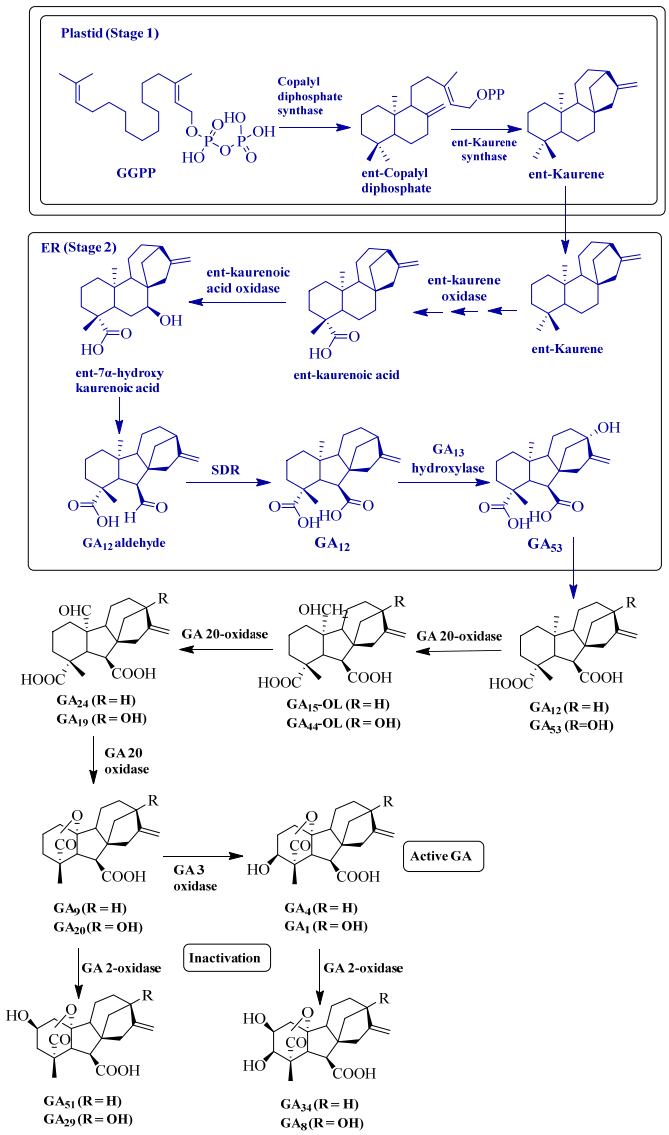

Figure 3. Biosynthesis of gibberellin (modified from [78,84]). Black color: pathway reported in algae. Blue color: pathway reported in higher plants.

3.1.4. Abscisic Acid (ABA)

ABA biosynthesis occurs through the precursor isopentenyl pyrophosphate or directly via the degradation of carotenoids (Figure 4). Carotenoid synthesis is the first stage of ABA biosynthesis where all the isoprenoids and carotenoids are produced from isopentenyl pyrophosphate (IPP) [87]. For the carotenoid synthesis, geranylgeranyl pyrophosphate (GGPP) is formed from the isopentenyl diphosphate (IPP), and GGPP is converted into phytoene, which is catalyzed by phytoene synthase (PSY). Phytoene desaturase (PDS) catalyzes the conversion of phytoene into ζ-carotene and sequentially converts it into lycopene, β-carotene until the zeaxanthin [78], or via the direct pathway in which zeaxanthin forms from the isopentenyl pyrophosphate (IPP) via farnesyl-diphosphate [84,88]. The first key reaction of ABA biosynthesis is a conversion of zeaxanthin into trans-violaxanthin via two-step de-epoxidation catalyzed by zeaxanthin epoxidase (ZEP). The trans-violaxanthin is then converted into 9-cis-neoxanthin by the enzyme neoxanthin synthase. After that, xanthoxin is synthesized by the oxidative splitting of 9-cis-violaxanthin and/or 9-cis-neoxanthin, and the reaction is catalyzed by the 9-cis-epoxycarotenoid dioxygenase (NCED) [78,84]. Finally, there are three possible ways for the last step of ABA biosynthesis from xanthoxin, i.e., three different intermediate compounds can be formed before finally yielding ABA. These intermediates are ABA aldehyde (as shown), xanthoxinic acid, or abscisic alcohol [89].

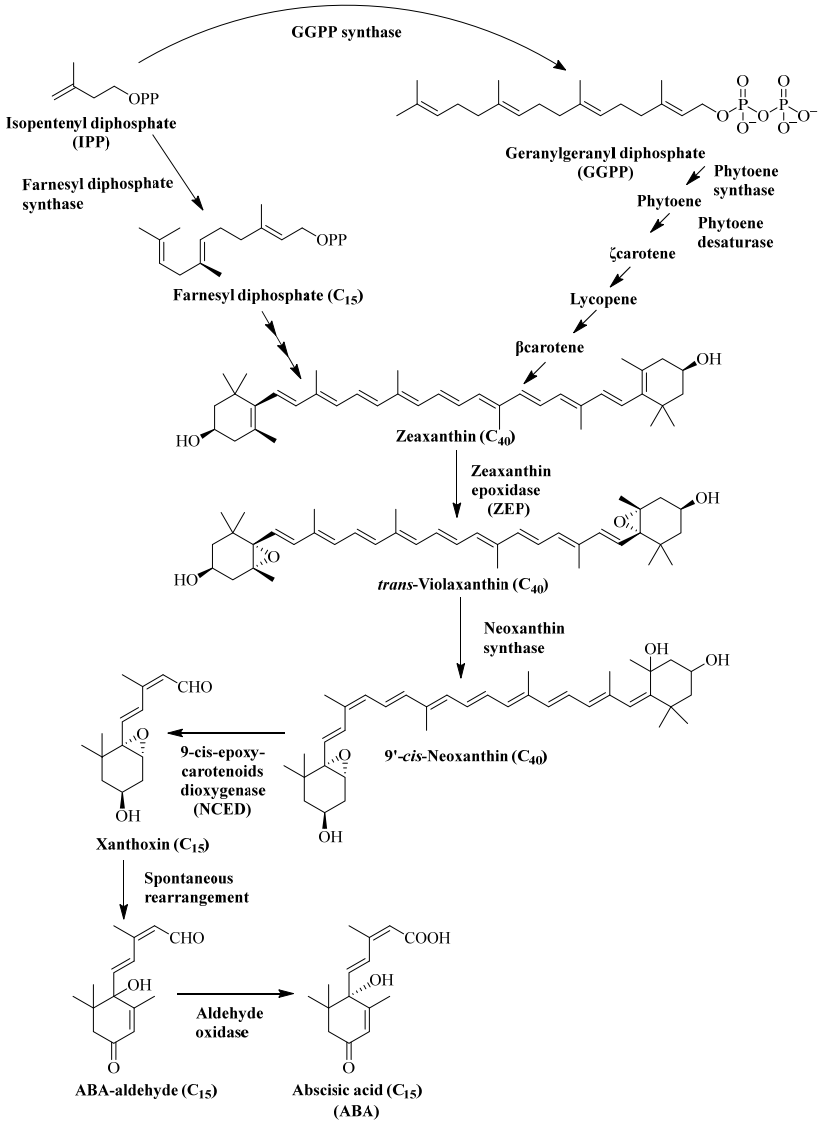

Figure 4. Biosynthesis of abscisic acid (modified from [78,84]).

ABA biosynthesis in the unicellular green alga *C. reinhardtii* occurs via a neoxanthin-mediated pathway [90]. It has been reported that 9′-cis-neoxanthin, a suitable substrate for ABA production, was present in the green algae containing chlorophyll a and b, whereas 9′-cis-neoxanthin was not found in other algal divisions, such as Heterokontophyta and Rhodophyta. However, all of these organisms do synthesize ABA, which could very well be via the direct pathway involving farnesyl-diphosphate [88]. Furthermore, the inhibition of known carotenoid precursors did not affect the ABA accumulation in cyanobacteria, Dinophyta, and Rhodophyta, suggesting either a new or unknown carotenoid precursor or a direct route of ABA biosynthesis from IPP precursors, which needs to be studied in detail [87]. Since the preliminary steps of ABA biosynthesis occur with those of carotenoid biosynthesis, it may be anticipated that homogeneous enzymes catalyzing these reactions are present in a wide set of algae. In the BlastP results of amino acid sequences of enzymes PSY, PDS, and ZEP from *A. thaliana*, a considerable number of similarities were found with diverse algae. Similarly, the homologs of enzymes NCED and xanthoxin dehydrogenase like SDR (dehydrogenase/reductase, which is involved in spontaneous rearrangement from xanthoxin to ABA aldehyde) specific for ABA biosynthesis were also identified in different algae, i.e., *Ectocarpus siliculosus*, *Chlamydomonas reinhardtii*, and *Chlorella variabilis*. It can therefore be concluded that the algal representatives contain homologous enzymes participating in ABA biosynthesis since its biosynthetic pathway in algal representatives is similar to that in higher plants [78].

3.1.5. Ethylene

Ethylene formation in marine algae was first reported by Watanabe and Kondo [91]. Methionine acts as an efficient precursor for the dimethylsulphoniopropionate (DMSP) (dimethyl-β-propiothetin) biosynthesis. DMSP is converted into acrylate and dimethyl sulfide by the unknown enzyme protein (now, DMSP lyase). Acrylate is finally converted into the ethylene by the action of acrylate decarboxylase (as yeast decarboxylase) (Figure 5) [91]. The different steps in this pathway were reported in numerous algae *Ulva lactuca*, *Polysiphonia fastigiata*, *Pyropia tenera* (as *Porphyra tenera*), *Ulva pertusa*, *Codium fragile*, *Laminaria* sp., *Fucus vesiculosus*, and *Digenea simplex* [91]. A similar pathway of ethylene biosynthesis was also reported in *Ulva intestinalis*, which is initiated with the methionine and converted into dimethylsulphoniopropionate (DMSP) by the enzyme methionine transaminase, and further, DMSP lyase converts DMSP to acrylate and acrylate is then finally converted into ethylene via action of enzyme acrylate decarboxylase [92]. In contrast, a different pathway of ethylene biosynthesis was reported in unicellular green algae (*Haematococcus pluvialis*), which is similar to higher plants. In *H. pluvialis*, ethylene biosynthesis initiates with L-methionine as precursors, and further, methionine is converted to S-adenosylmethionine (SAM/AdoMet), 1-aminocyclopropane-1-carboxylic acid (ACC), and finally to ethylene via the action of ACC oxidase. The enzymatic complex of the last step of ethylene biosynthesis to ACC oxidase differs from the higher plants. In *Haematococcus pluvialis*, this enzyme is stimulated by Co^{2+}, Mn^{2+}, and Ag^{2+}, inhibited by Cu^{2+}, salicylhydroxamic acid, and by dark, while not affected by Zn^{2+}, Fe^{2+}, or Mg^{2+}. In plants, this enzyme is stimulated by Fe^{2+}, Mn^{2+}, or Cu^{2+} and inhibited by Co^{2+} [93]. Intermediate compound ACC treatment increases the ethylene production in the chlorophytes *Haematococcus pluvialis* and *Ulva intestinalis*, and the red algae *Pterocladiella capillacea*, like in the higher plant [90]. Therefore, seed plants, red and green algae convert ACC to ethylene, and this pathway is consistent and conserved throughout the plant kingdom [94].

3.2. Pheromones

Pheromones are sex hormones involved in the highly synchronized and regulated process of induction of reproduction in algae [71]. The paucity in the knowledge of exact life cycle stages and reliable methods to induce sexual reproduction are major impediments in identifying the pheromones. These things considered, direct structural elucidation is cumbersome because of the minuscule quantities at which these compounds are secreted

in cultured uni-algal samples [95]. The pheromones produced by algal cells act as chemoattractants, facilitating recognition of motile gametes of the opposite sex, thereby enhancing fertilization efficiently [74]. The diversity of pheromone and signaling systems showed considerable diversity and complexity, both within and between algal groups [96]. This section deals with types, biosynthetic pathways, roles, and modes of action of pheromones reported from seaweeds. The pheromones reported from brown, green, and red algae are described below.

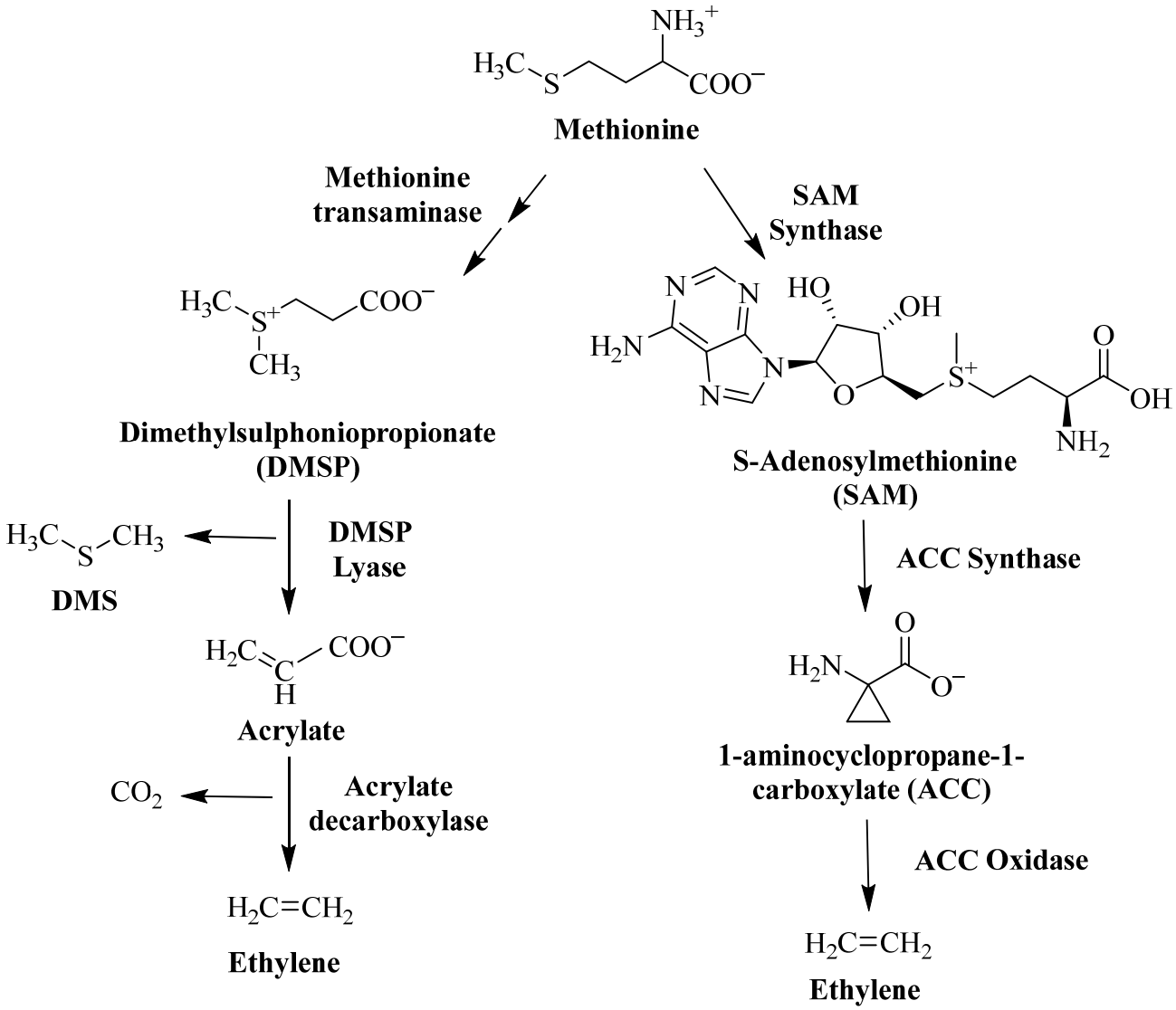

Figure 5. Biosynthesis of ethylene (modified from [92,94]).

3.2.1. Giffordene

Giffordene (2Z,4Z,6E,8Z)-undeca-2,4,6,8-tetraene) has been isolated from *Feldmannia mitchelliae* (as *Giffordia michellae*) gyno-gametophytes. Eicosapentaenoic acid is the precursor of giffordene biosynthesis via hydroperoxide HPEPE as an intermediate. The enzymatic carboxylation of 3Z,6Z,9Z-dodecatrienoic acid forms 1,3Z,5Z,8Z-undecatetraene, which ultimately shifts 1,7-sigmatropic hydrogen to obtain giffordene (Figure 6) [97].

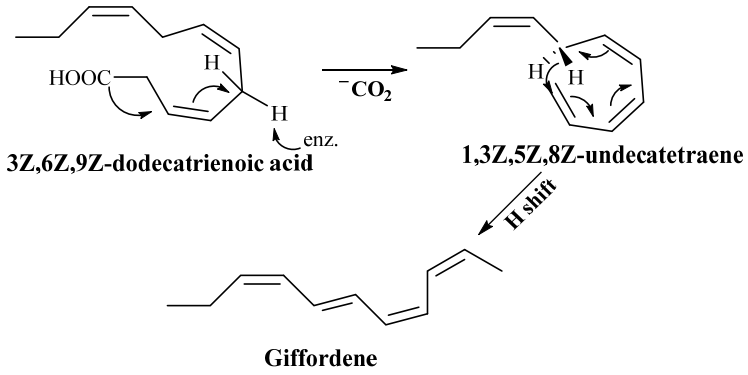

Figure 6. Biosynthesis of giffordene [98].

3.2.2. Dictyotene

Ectocarpus siliculosus, secretes dictyotene along with ectocarpene, hormosirene, and finavarrene, which act as chemoattractants for male gametes [99]. When *E. siliculosus* female gametes were externally supplemented with arachidonic acid, there was de novo synthesis of dictyotene (6-butylcyclohepta-l,4-diene), and undeca-(1,3E,5Z)-triene was observed (Figure 7) [100].

3.2.3. Cystophorene

Cystophorene fits in the class of organic compounds as alkatrienes. These are acyclic hydrocarbons that contain exactly three C:C double bonds [101]. Cystophorene (<1%) was also found to be released in trace amounts from suspensions of female gametes of *Ectocarpus siliculosus* along with ectocarpene (>95%) and dictyotene (ca. 3–4%). First, the fatty acid is activated to the (9S)-hydroperoxide-(9S) HPETE via lipoxygenase. It is followed by an oxidative breakdown into the polar fragment 9-oxonona-5(Z), (E-)dienoic acid, and a respective hydrocarbon (Figure 7) [102].

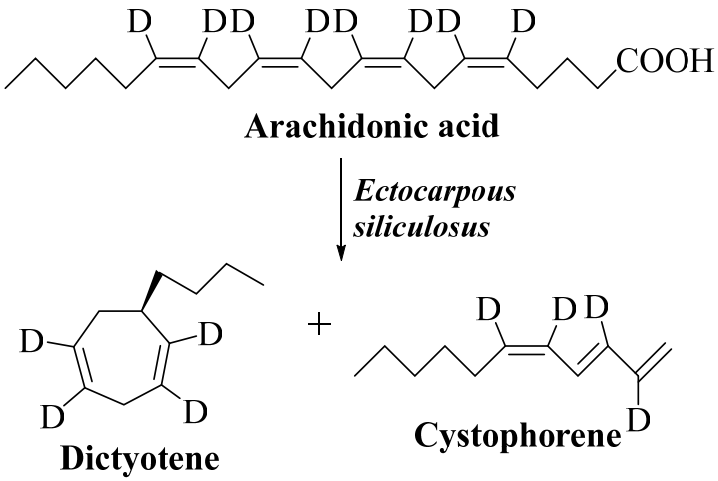

Figure 7. Biosynthesis of dictyotene and cystophorene (C11 hydrocarbons) in brown algae *Ectocarpous siliculosus* [103].

3.2.4. Ectocarpene

Ectocarpene is biosynthesized in numerous species of brown algae and was the first isolated pheromone in *Ectocarpus siliculosus* [61]. PUFAs, such as 9-hydroperoxyeicosatetraenoic acid (9-HPEPE) in the brown algae, are converted to biosynthesized ectocarpene via the consecutive catalytic action of lipoxygenase and hydroxyperoxide lyase (Figure 8) [102].

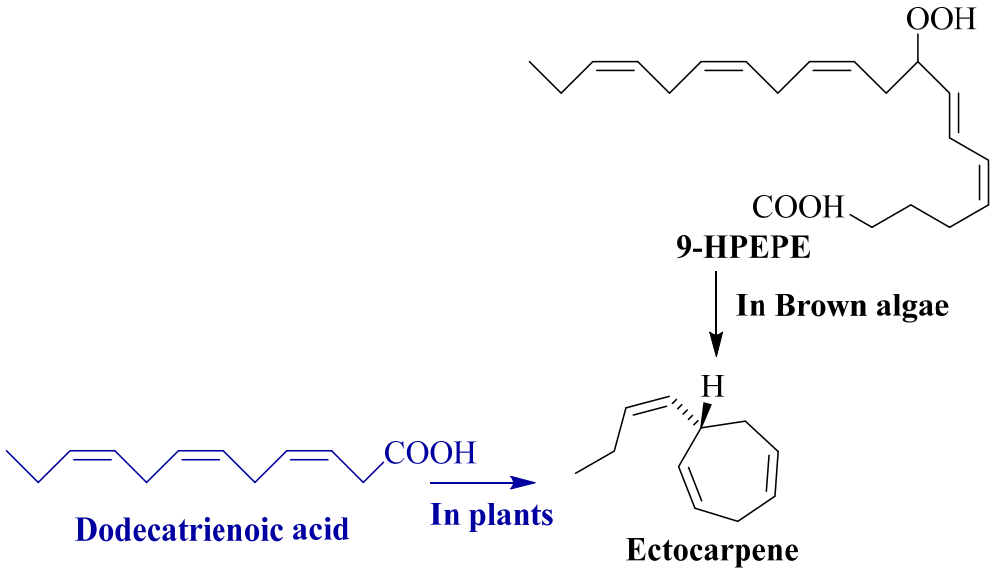

Figure 8. Biosynthesis of ectocarpene in brown algae from (9-hydroperoxyicosa-(5Z,7E,11Z,14Z,17Z)-pentaenoic acid (9-HPEPE) (modified from [104,105]). Black color: pathway found in algae. Blue color: pathway reported in higher plants.

3.2.5. Dictyopterene

Dictyopterenes are characteristic volatile substances, which are the main constituents of oceanic odor. Additionally, some gamete-attracting substances and flavors, which is a characteristic feature in brown algae, also consist of dictyopterenes, which are mainly C11 hydrocarbon compounds [106]. Neodictyoprolenol [(3S,5Z,8Z)-1,5,8-undecatrien-3-ol; (3S)-1] was assumed to be a possible reaction intermediate of the biosynthesis of the pheromones in the brown seaweed [61,107]. The stereospecific shifting of the hydroxyl group from (9,S)-hydroperoxides (Carbon-9 to Carbon-12) via a six-membered ring ultimately leads to the formation of dictyopterenes (Figure 9).

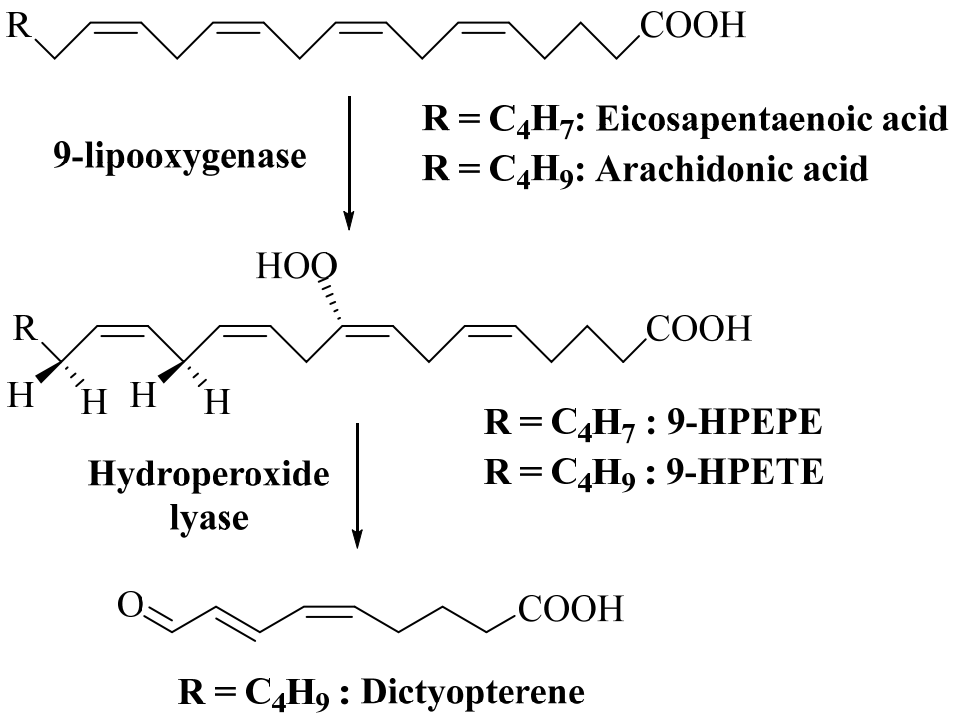

Figure 9. Biosynthesis of dictyopterene [102].

4. Role of Hormones in Algae

4.1. Auxin

Auxin, found in higher plants, algae, microorganisms, fungi, and animals [108,109], plays a key role in plant growth and development. Generally, the hormone concentration found in algae is much lower as compared to the higher plants [110]. Its function in the growth and development of algae is similar to that in higher plants [111]. Auxin plays a key role in cell division and elongation, suppresses branching at the apical and intercalary regions in red algae *Grateloupia dichotoma* [112], and has a significant role in the determination of zygote polarization in fucoid algae, i.e., *Fucus distichus* and *Fucus vesiculosus* [58,113]. Supplementing the axenic culture of *Ulva lactuca* germlings in enriched seawater with kinetin and IAA resulted in the formation of a normal flat blade, which further increased the length of the filament with the addition of gibberellin [26]. Similar results were also found with different algae, like *Fucus spiralis*, *Porphyra tenera*, and *Enteromorpha compressa*, when exogenously supplied auxins, p-hydroxy-phenylacetic acid (OH-PAA), and PAA, inducing branching and broadening of fronds [24,114,115]. Inhibition of apical dominance was also found in macroalgae when the apical meristem was removed or damaged, thereby inducing the growth of axillary buds and the formation of lateral branches [116]. IAA concentration in *Caulerpa* was in the same range as in angiosperms [117]. The activity of IAA in cultured *Caulerpa* triggered the initiation of leaf-like structures and slower elongation of rhizome-like structures [28]. The synergistic effect of IAA, kinetin, and gibberellic acid (GA) studied in *Ulva lactuca* induced significant growth higher than each of these hormones individually [26]. The role of IAA in tissue differentiation in multicellular algae has been evident in the literature, in addition to the role in cell elongation and cell division, as observed in higher plants [29]. IAA application also induces cell division by upregulating the genes that encode CDKs, Cycs, CDCs, and tubulins, resulting in increased branch number and promotion of rhizoid branching in *Gracilariopsis lemaneiformis* [118].

4.2. Cytokinins

Cytokinins regulate key processes like cell division and growth activation in algae just like in higher plants [82]. Kinetin (cytokinin) shows a positive effect on the growth of thallus when added simultaneously with GA, resulting in the formation of adventitious branches from the apical portion of *Fucus vesiculosus* [34]. Independently as well, kinetin or GA can partly replace the apical cells in *Sphacelaria furcigera* and increase the length of newly formed lateral branches (apical dominance) from the injured parts of the alga [31]. Cytokinins show less diversity in algae than higher plants but they perform a vital role in the growth and morphogenesis of algae [85]. Cytokinin-like activity occurred in *Sargassum heterophyllum* during gamete release and at the beginning of receptacle development [119]. Intercalary meristem of young blades of the *Macrocystis pyrifera* exhibit cytokinin activity in the form of free bases or ribosides and are responsible for cell division, whereas older blades contained cytokinins in the form of O-glucoside as a storage form [120]. Cytokinin, present in seaweed, in the form of free bases and ribosides are the physiologically active forms and can be detected in low concentrations, as they are actively utilized in several developmental processes [36]. Cytokinins, play an important role in the early growth of the receptacles in *Sargassum muticum* and are also responsible for thalli to possess mature spermatangia and carpogonia in *Porphyra perforata* [33].

4.3. Gibberellins (GAs)

The regulatory action of GA is well studied in higher plants; however, very few studies have been undertaken to understand their role in algae. In *Fucus spiralis* and *Tetraselmis* sp., just like the higher plants, the gibberellins significantly contribute to inducing tissue differentiation via cell elongation and cell division [29]. Such GA-like activities were also reported in *Fucus vesiculosus*, *F. spiralis* (Phaeophyceae) [121], and *Caulerpa paspaloides* (Chlorophyta) [122]. GA treatments of red and brown algal cultures can induce branching and control the growth of axial structures similar to the higher plants. GA3 increases

the number of antheridial filaments and spermatids in *Chara vulgaris*, while the anti-gibberellin, in this case, AMO-1618, inhibits its effect [35]. Exogenous application of GA3 distinctly increases the number of adventitious branches formed on fragments from the apical parts. GA3 also shows a positive effect, in combination with kinetin, on the growth and regeneration of *Fucus vesiculosus* [34]. In contrast, GA3 inhibits the morphogenesis in the tissue culture of the red alga *Grateloupia doryphora* [49].

4.4. Abscisic Acid (ABA)

In higher plants, abscission of buds and leaves and dormancy in seeds is caused by ABA and can also inhibit its growth. ABA can be detected in higher concentrations during stress conditions in vascular plants [123]. Similarly, ABA can also be found in many algal groups during stress conditions [124]. However, the concentrations in algal cells are lower as compared to the higher plants [88]. Exogenous ABA accelerates sorus development in addition to its role as a suppressor of vegetative growth in the brown alga *Laminaria* [125]. In *Laminaria*, ABA regulates the transition of sporophyte from growth to the stage of propagation [78]. ABA levels in *Dunaliella parva*, *Draparnaldia mutabilis*, and *Dunaliella acidophila* increase with the increase in salinity and pH of the culture media [38,124]. Therefore, changes in endogenous ABA levels due to different environmental conditions may provide pieces of evidence for their possible roles in algae. Higher ABA in *Ulva fasciata* was observed when collected from a rock pool of the upper intertidal zone since it was more exposed to adverse conditions as compared to *Dictyota humifusa*, which was collected from a mid-intertidal zone. Therefore, ABA acts as a stress hormone in seaweeds and performs a role in growth inhibition [36].

4.5. Ethylene

In higher angiospermic plants, ethylene biosynthesis occurs during the ripening process, in which biosynthesis may be activated via IAA or by any other physiological stress [84]. Ethylene promotes cap production in *Acetabularia acetabulum* (as *Acetabularia mediterranea*) [41], and its precursor 1-aminocyclopropane-l-carboxylicacid (ACC) promotes cell division and cap development in *Neoporphyra perforata* (as *Porphyra perforata*) [25]. During sexual reproduction, ethylene regulates gamete formation and protects against stress-induced damage in *Neopyropia yezoensis*, whereas its precursor, 1-aminocylopropane-1-carboxylic acid, regulates sexual reproduction by inducing the gametophytes to form spermatangia in *Neopyropia yezoensis* [126,127]. Ethylene also plays a key role in cell wall metabolism, photosynthesis, and abiotic stress responses in *Spirogyra pratensis* [128].

4.6. Brassinosteroids (BRs)

Brassinosteroids are polyhydroxylated steroid hormones with ubiquitous distribution that regulate the growth and development of higher angiospermic plants. The first report of Brassinosteroids viz, brassinolide (BR), and castasterone (CS) from algae was from the extract of *Ecklonia maxima* [42]. BRs stimulate the cell division and growth in *Chlorella vulgaris*, mostly influencing the number of algal cells, phosphorus, chlorophyll, and monosaccharide content in this alga [129]. In *Chlorella vulgaris*, BRs can regulate protein and lipid content, thereby enhancing the energy storage capacity of the alga during stress conditions like high temperatures [130,131]. It can also boost the stress-responsive ABA content with temperature rise [132]. BRs also play an important role during stress and defense, either individually or along with the primary defense hormones [133].

4.7. Jasmonic Acid (JA)

Jasmonic acid is one of the primary plant defense hormones in addition to SA and ethylene [134]. JA and its derivatives play a vital role as hormones and can induce defense responses by producing oxylipins (defense mediators) and prostaglandins (defense chemicals against grazers) in the red macroalga *Chondrus crispus* [44]. However, contradictory observations have been made, which suggested that JA- and methyl jasmonate (MeJA)-like

compounds may be active just in higher plants and do not play any role in the algal defense system. JA and MeJA may not be ubiquitous in all red algae, as none were detected in the *Gracilaria chilensis* even after exposure to pathogen attack [135]. Therefore, the role of JA in algae needs to be re-evaluated extensively using the latest analytical techniques on various algal taxa.

4.8. Polyamines (PAs)

The polyamine biosynthetic pathway is conserved in bacteria, animals, and higher angiospermic plants [136]. Polyamines play an important role in physiological metabolism, which eliminates the active oxygen-free radicals, giving the plant tolerance to oxidative stresses [137]. Consequently, polyamines like putrescine and spermidine can help in the acclimation due to the oxidative stress caused by hyposaline conditions in green macroalga *Ulva fasciata* [47]. Similarly, in the red alga *Grateloupia doryphora*, during hyposaline shock, the level of putrescine, spermidine, and spermine rises, which has been attributed mainly to the decrease in transglutaminase activity [48]. Exogenous application of PAs can lead to effects similar to 2,4-D in *Grateloupia* and plays an important role in the development of cystocarp and in the release and development of spores in cultivated species of red macroalga *Grateloupia* sp. [49,51]. Putrescine and spermidine also play important roles in the transformation of the carposporelings into cell masses that produce shoots. Furthermore, the combination of putrescine, spermidine, and spermine leads to the formation of bigger sizes of cell masses and ultimately to a higher amount of shoot per cell mass [49]. These three are ubiquitous aliphatic amines that are also involved in reproduction in higher angiospermic plants and algae. A higher level of PA (putrescine) in immature cystocarps as compared to mature cystocarps of *Crassiphycus corneus* (as *Gracilaria cornea*) was observed, which declined in the transition event of reproduction from the infertile to the fertile state [52,53]. These reports suggest the involvement of polyamines in the reproductive events and other cellular processes in the algae as well.

4.9. Salicylic Acid (SA)

Salicylic acid (SA) is best known for mediating host responses against pathogen infection as it plays an important role in eliciting the defense responses [138]. Some evidence shows that SA plays an important role in the oxidative defense for protection against environmental stresses in seaweeds in a similar way as found in higher plants. SA treated *Saccharina japonica* (as *Laminaria japonica*) sporophytes before heat stress improved their thermotolerance by altering antioxidant enzymatic activity with increased superoxidase dismutase (SOD), peroxidase (POD), and catalase (CAT) activity [79].

4.10. Strigolactone (SL)

Strigolactones (SLs) are the newly categorized phytohormones that regulate plant growth, development, and metabolism. Strigolactones have been linked to a variety of physiological processes such as seed germination, nodulation, inhibition of bud outgrowth and shoot branching, photomorphogenesis, and physiological responses to abiotic stimuli [139]. SLs are present in basal Embryophytes, where they are involved in signaling role promoting the arbuscular mycorrhizal (AM) symbiosis [140]. This hypothesis, however, can be challenged by the fact that Charales, which do not participate in AM symbiosis, also synthesize and exude SLs into the medium. Such evidence, supported by sequence and metabolite profile, concluded that the widespread existence of SLs in the green lineage was probably more hormonal than symbiotic [23]. The closest freshwater green algal relatives of land plants, Charales, produce and exude strigolactones, which help them to survive fungal colonization. It was also proven experimentally that the exogenous SLs stimulate rhizoid elongation in *Chara coralina* [23]. Based on the literature survey, it has been suggested that strigolactones are not found in marine macroalgae. But, the lack of complete genome sequences for lower-order plants, including marine macroalgae, may make such assumptions difficult [141]. However, the strigolactones have been found in the

liquid seaweed extract (Seasol™, Seasol International Pty Ltd, Bayswater, Australia), which is made from the biomass of *Durvillaea potatorum* and *Ascophyllum nodosum*, which have extensive applications in agriculture [142].

4.11. Rhodomorphin

Rhodomorphin is produced by rhizoidal cells in *Griffithsia pacifica*, a red alga [139], and is a species-specific growth regulator [21]. A study on *Griffithsia* sp. revealed its role in the repair of rhizoids, decapitated filament, and its elongation, but no such role has been observed in shoot cell repair [39,143].

5. Role of Pheromones in Algae

5.1. Sporulation Inhibitors

Axenic culture of *Ulva mutabilis* produces two such inhibitors. Sporulation inhibitor-1a (SI-1a), which is a glycoprotein, is produced by their cell wall, and Sporulation inhibitor (SI-2), which is a non-protein, is produced in the space between the two blade cell layers. Both SI-1 and SI-2 play important roles in keeping the thalli in a vegetative state by suppressing gametogenesis. The absence or removal of these sporulation inhibitors causes induction in gametogenesis from the mature blades in *Ulva mutabilis* [60].

5.2. Swarming Inhibitors

Swarming inhibitors act as regulatory factors during gametogenesis and are excreted during the determination phase of the gametes and can inhibit the gamete formation event in *Ulva compressa* (as *Ulva mutabilis*) [60,144].

5.3. Ectocarpene

Ectocarpene is a chemoattractant hydrocarbon released by female gametes to attract its male counterparts [61]. In most of the brown algae, the fertilization is boosted by such chemical messengers. Ectocarpene is also released by female gametes of *Chorda tomentosa* to attract male gametes [69]. Ectocarpene is the first reported pheromone in brown algae *Ectocarpus siliculosus* and is known to induce chemokinesis. It has also been reported in *Sphacelaria rigidula*, *Adenocystis utricularis* [63], and in *Ectocarpus fasciculatus* [62].

5.4. Dictyotene and C11 Sulfur Compounds

Dictyotene and other C11 compounds generally found in brown algae can perform functions like saving the spores, zygotes, and germlings against mesograzers like amphipods [68]. These compounds and their free products also play an essential role in the chemoattraction of gametes in addition to keeping the mesograzers away from the developing zygotes. These are the volatile compounds, reported mainly in *Dictyota diemensis*, *Dictyota dichotoma*, *Dictyopteris membranacea*, *D. delicatula*, and *Sargassum filipendula* [64–67]. *Volvox* is reported to produce protein erogens; similarly, Allomyces and brown algae have been reported to secrete terpenoids and hydrophobic hydrocarbons, respectively. In *Dictyota diemensis*, dictyotene has also been reported to act as erotactins, the compounds attracting sperms [74].

5.5. Ochtodene

It is a monoterpene pheromone reported from the *Ochtodes secundiramea*, which protects this alga against predation by many rapacious herbivores. It also has antibacterial activity against Staphylococcus aureus. Therefore, its antimicrobial role is also important [76].

5.6. Other Chemoattractants

Most of the pheromones perform similar kinds of roles during sexual reproduction. Some of the pheromones in seaweeds and their discovery as chemoattractants are given in Table 2.

6. Mode of Action of Hormones in Algae

Certain plant/algal hormones, unlike animal hormones, have multiple physiological functions [145]. They are produced in cells and then bind to specific receptor proteins to carry out downstream signaling. Their liaison results in a change in cell function and the activation of a signal transduction pathway. The concentration of individual hormones is not important, but the response of hormones is usually governed by the sum effect of other hormones either in tandem or vice versa [146].

In higher angiospermic plants, auxin signal may be perceived at the extracellular matrix, at ER, or inside the nucleus with the help of a receptor ABP1 (Auxin-Binding Protein1) [147,148]. ABP1 homologs have also been found in genomes of *Chlorella variabilis* NC64A, *Chlorella pyrenoidosa*, and *Chlamydomonas reinhardtii*. These proteins form the auxin-binding pocket, which in the presence of auxin, induces transcription of auxin responsive genes [149]. These findings suggest the early emergence of a primitive form of auxin receptors in microalgae [150]. Additionally, more genome sequences of a variety of algae are required to elucidate the origin of auxin signaling in them.

Cytokinin signaling involves the phosphorylation of cytokinin, which binds to the extracellular portion of cytokinin response1 (CRE1), known as the CHASE domain, localized at the plasma membrane [84]. The cytokinin signaling components have evolved in microalgae, and further analogous evolution occurred among different algal lineages [150]. In Arabidopsis, cytokinin is perceived by AHK receptors located in the endoplasmic reticulum, triggering their histidine kinase activity [151]. These receptors are also common in the algal genome [152]. This histidine kinase activity leads to a cascade of phosphorylation from the cytoplasm to the nucleus, ultimately activating the transcription of type-A Arabidopsis Response Regulators (ARRs) and CRFs. Homologous components of these proteins (type-B Arabidopsis Response Regulators and Histidine-Containing Phosphotransmitter 1) have also been found in green microalgae (*Nannochloropsis oceanica*), suggesting the similarities in their mode of action in microalgae (*Nannochloropsis*) and plant (*Arabidopsis*) [152]. The phosphorylated type-A ARRs then interact with various effectors to bring about cytokinin responses [84,151].

Gibberellic acid (GA) molecules bind to the GID1 (GIBBERELLIN INSENSITIVE DWARF1) receptor in higher angiospermic plants, which then interacts with DELLA proteins [153]. DELLA proteins interact with DNA-binding proteins, which are regulated by PIFs (Phytochrome-Interacting Factors) [154]. GID1 receptor orthologs have been identified in microalgae via the functional motif analysis and revealed that the GID homologs have the catalytic triad (S, D, and H) of the hormone-sensitive lipase (HSL) family in microalgae [150]. Therefore, this supports the inheritance of GA signaling from microalgae, which might be the crucial source for the foundations of the higher plant hormone systems. However, some proteins (DELLA and the F-box protein SLEEPY1) involved in mediating GA signaling have been found only in land plants and not in microalgae [155]. This warrants a thorough exploration of downstream signaling molecules involved in GA [150].

Three abscisic acid (ABA) receptors have been identified in higher angiospermic plants, i.e., chloroplast envelope-localized ABA receptor (ChlH/ABAR), plasma membrane-localized GTG1/GTG2 (GPCR-type G protein 1 and 2), and nucleo-cytoplasmic PYR/PYL/RCARs (pyrabactin resistance/pyrabactin resistance-like/regulatory component of ABA receptors) [156,157]. Among these, the nucleo-cytoplasmic PYR/PYL/RCAR receptors are considered the most established ABA perception receptors. These receptors have not been identified in microalgae to date, even though the downstream phosphatases (SNF1-Related Protein Kinase 2) of the ABA signaling pathway are conserved from microalgae to higher plants [158]. Nevertheless, ABA-related genes in algae have not been explored, and it is necessary to compare them to gain more definite proof of the evolutionary origin of ABA-related genes [159].

Ethylene perception in higher angiospermic plants occurs through membrane-bound receptors embedded in the endoplasmic reticulum (ER). *Arabidopsis* has five known ethylene receptors, which are ETR1 (Ethylene Response1), ETR2, ERS1 (Ethylene Response Sensor1),

ERS2, and EIN4 (Ethylene Insensitive 4) [160]. Ethylene receptor complexes, comprising ETR1, ERS, and EIN4, have been widely reported in microalgae (*Micromonas* sp.) [150]. In addition to that, ethylene binding sites have also been confirmed in a cyanobacterial protein [161].

In silico genome-wide homology search analysis revealed the biosynthetic pathways of iP and ABA in red seaweeds similar to those in terrestrial plants. However, the mode of action in these seaweeds (*Neopyropia yezoensis* and *Bangia fuscopurpurea*) are dissimilar to those in terrestrial plants for IAA, iP, and ABA [162] and are yet to be investigated. Hormones like brassinosteroids (BRs), jasmonic acid, salicylic acid, and rhodomorphin have been reported from algae, but their possible signaling mechanism is yet to be investigated [54,141,163]. To date, their mode of action has not been elucidated. However, it has been proposed that their mode of action in algae could be similar to those of higher plants, which has been provided in Supplementary Materials.

7. Mode of Action of Pheromones in Algae

Green algae undergo sexual reproduction during their life cycle to survive unfavorable environmental conditions. Induction of gametogenesis in *Chlamydomonas reinhardtii* is activated via a reduced nitrogen supply in the environment [164]. After gametogenesis, the agglutinins, sex-specific glycoproteins located on the flagella, are synthesized, which promotes the interactions between different mating types and may lead to their fusion [165]. The gamete fusion takes place only when two compatible gametes come in contact with each other [164]. This contact induces the production of certain enzymes, which facilitate their fusion and form a cell having four flagella, ultimately giving rise to a non-motile zygote [96]. The attraction between the gametes and the level of compatibility between cells in *C. reinhardtii* decides the mating success. Similarly, in other species of *Chlamydomonas*, chemotactic behavior of gametes can be observed [74]. At low concentrations of pheromone lurlene, motile MT− gametes of *Chlamydomonas allensworthii* attract the motile MT+ gametes [166].

In *Volvox carteri* f. *nagariensis*, the male clones produce inducer molecules, extracellular matrix (ECM) glycoproteins called pherophorins, which can control sexualization. This protein is originally of somatic origin but can induce the production of respective gametes in both male and female algae [167,168]. After the gamete production, the sperm cells attain the ability to produce this inducer, which is now called pheromone [169]. The release of this pheromone can also lead to the production of hydroxyproline. Remarkably, the wounding of *Volvox* also produces a similar protein. Such expression of the same genes, which are activated by the wounding as well as pheromone induction, hints toward an existing relationship between environmental stress, sexual reproduction, and wound healing at the molecular level [170].

The blade cells of green macroalga *Ulva mutabilis* secrete some regulatory factors, which control the gametogenesis and are important to keep its thallus in a vegetative state. One of these factors, a sporulation inhibitor, prevents the differentiation of blade cells into gametangia [60]. During the maturation of the thallus, the production of this factor gradually decreases and stops until the concentration drops to the inhibitory concentration of 10^{-14} M. At this point, another sporulation inhibitor is released into the environment, which can supposedly control the distribution of gametangia spatially while they are developing. After induction, a swarming inhibitor is produced, which inhibits the release of gametes from *U. mutabilis* and *U. lactuca* [96].

Ectocarpene was identified as the first male-attracting chemical released by female plants. It was the first identified from *Ectocarpus siliculosus*. The compound is apolar and derived from a fatty acid, 9-hydroperoxyicosa (5Z,7E,11Z,14Z,17Z)-pentaenoic acid [61]. This compound is formed after the precursor is subjected to thermal rearrangement [104]. The inactivation process is wholly controlled by temperature and does not require any enzymatic activity [96]. Ectocarpene functions as a chemoattractant not only in many *Ectocarpus* species [62] but also in other brown algal genera like *Adenocystis* and *Sphace-*

laria [63]. However, it has not yet been determined if the ectocarpene is as native in these species as in *E. siliculosus*. The gamete recognition and union in this alga is mediated by the lectin–glycoprotein complexes present in the membranes [171]. In another example, a structurally related epoxidized hydrocarbon from *Laminaria digitata* synchronizes the release of male gametes [172].

In marine brown algae *Hormosira banksiii*, *Durvillea* sp., *Xiphophora* sp., *Scytosiphon lomentaria*, and *Colpomenia peregrina*, chemical signal hormosirene was found to be released by female gametes (1–1000 pmol) to attract their conspecific male gametes [104]. Various life cycle stages of *Giffordia mitchellae* produce odoriferous compounds comprising mainly of giffordene and its stereoisomers because its male gametes are strongly attracted to settled female gametes [98]. In the orders Laminariales, Sporochnales, and Desmarestiales, sexual pheromones induce spermatozoid release from antheridia. In *Laminaria*, Maier et al. summarized the regulation of sexual reproduction by pheromones and other environmental factors [173]. The chemotactic movement of spermatozoids of *Hormosira banksii* and *Laminaria digitata* has also been reported in the literature [174,175]. Wirth and Boland recognized spermatozoid-attracting and spermatozoid-releasing factors in *Perithalia caudata* [176].

The interactions between various receptor–pheromone complexes have been studied in many species utilizing a number of pheromone analogs synthesized chemically [173]. But still, there seems to be no clarity on the molecular nature and cellular localization of various pheromone receptors. The first stage in the binding of brown algal pheromones is probably the partitioning into the cellular membrane due to the hydrophobic nature of this compound. Binding to the receptor protein strongly depends on the steric characteristics of the pheromone molecules and is intermediated by non-covalent dispersion forces, like how the double bonds are arranged in the molecule [74]. In chemotaxis assays, the binding process involves a strict enantiomer differentiation, which occurs as per the enantiomer specificity; the higher the specificity, the better the binding. Boland et al. hypothesized computer scheming for the identification of minimum energy conformations and a receptor-bound metal cation acting as the coordination center in pheromone binding [177].

8. Methods for Extraction, Identification, and Quantification of Hormones from Algae

A number of traditional extraction (with solvent) and novel extraction methods have been used to extract the phytohormones from plant samples. Of late, novel methods including microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), pressurized liquid extraction (PLE), enzyme-assisted extraction (EAE), and supercritical fluid extraction (SFE) have been standardized for hormone extraction from algae [178,179]. From the analytical point of view, some of the most common and advantageous methods to extract phytohormones are liquid–liquid extraction (LLE), different types of liquid microextraction (LME), solid-phase extraction (SPE), or molecularly imprinted extraction (MIPE) [180]. Different protocols for the identification and quantification of phytohormones from algae are summarized in the flow chart (Supplementary Figure S2).

Seaweed sap, obtained mechanically by expelling water from fresh *Kappaphycus alvarezii*, is filtered with a nylon cloth (20–50 µm mesh size). Auxins, gibberellins, and cytokinins can then be extracted from sap using DEE, ethyl acetate, and n-butanol, respectively. Samples are kept overnight for solvent evaporation, and the pellets are then dissolved in 1–2 mL of HPLC-grade methanol. Phytohormones are then identified using MS/MS followed by quantification with ESI-MS, and quantification is validated against HPLC [32]. Among other techniques, auxin, cytokinin, and abscisic acid have been extracted from red algae (*Porphyra*, *Gelidium*, *Gracilaria*, and *Hypnea*), endogenous auxin can be extracted with cold phosphate buffer containing 0.02% sodium diethyldithiocarbamate, cytokinin can be extracted with ice-cold ethanol (70%), and abscisic acid can be extracted with ice-cold methanol: water: acetic acid (10:89:1, v/v) containing sodium diethyldithiocarbamate (400 µg g^{-1} dwt). Subsequently, solid-phase extraction followed by immune affinity chromatography can be used for purification and analyzed with liquid chromatography–tandem mass spectrometry [37]. The simultaneous determination of

broad classes of phytohormones in *Monostroma* and different species of *Ulva* (*U. fasciata*, *U. lactuca*, *U. taeniata*, and *U. linza*), using the extraction buffer methanol: water: formic acid (15:4:1) and subsequent purification with help of dispersive liquid–liquid microextraction (DLLME) [181], followed by the HPLC coupled to ultraviolet detector has also been reported [182].

A mixture of acetonitrile 80% (*v*/*v*) and acetic acid 1% (*v*/*v*) can also be used as an extraction solvent for the comprehensive quantification of phytohormones (auxin (IAA), N6-(Δ2-isopentenyl) adenine (iP), abscisic acid (ABA), and salicylic acid) in red seaweeds (*Bangia fuscopurpurea* and *Pyropia yezoensis*). After extraction, the acetonitrile extract is purified with solid-phase extraction and analyzed with an LC-ESI-MS/MS system [183]. Simultaneous analysis methodology of nine phytohormones from *Cladophora glomerata* and *Spirulina* sp. was developed and optimized by Górka and Wieczorek. In this, the samples were extracted with the SFE-CO_2 extraction method with controlled condition of 500 bar pressure at 40 °C and analyzed using reversed-phase high-performance liquid chromatography (RP-HPLC) with a photodiode array detector (PDA) [180]. In another method, the aqueous extracts of dried *Padina durvillaei* and *Ulva lactuca* (1:10 *w*/*v*) are lyophilized. The lyophilized extract is then suspended in 80% methanol (MeOH) (1% acetic acid). This is followed by centrifugation, drying of supernatant, and dissolution in 1% (*v*/*v*) acetic acid. It is then passed consecutively through the reverse-phase column. Finally, the acidic hormones are eluted with MeOH and basic hormones with 60% MeOH with 5% aqueous ammonia. Dried final residues are dissolved in 5% (*v*/*v*) acetonitrile, 1% (*v*/*v*) MeOH, and 1% acetic acid. The hormones can then be quantified using ultra-high-performance liquid chromatography–mass spectrometry (UHPLC-MS) [184].

Reliable analytical techniques such as GC/MS and UPLC-MS/MS can also be used to identify phytohormones in microalgae (*Chlorella minutissima*) [185]. Gibberellins and brassinosteroids can be extracted from the different microalgae using 80% acetonitrile containing 5% formic acid as a solvent and analyzed with ultra performance chromatography–tandem mass spectrometry (UPLC-MS/MS) [186]. Endogenous hormones in *Chlorella minutissima* are extracted in cold 50 mM phosphate buffer (pH 7.0) with sodium diethyldithiocarbamate and analyzed using ultra-high-performance liquid chromatography (UPLC) equipped with an electrospray interface (ESI) [185,187].

9. Methods for Extraction, Identification, and Quantification of Pheromones from Algae

Volatile compounds like pheromones can be isolated using different methods, namely: CO_2 extraction method, cold trap condensation, head-space, and closed-loop-stripping method. Among all the methods, the closed-loop extraction method by Grob and Zurcher has proven to be the most efficient [188,189]. Different protocols for the identification and quantification of pheromones from algae are summarized in the flow chart (Supplementary Figure S3).

The closed-loop extraction method was used by Maier et al. [190] for the Lamoxirene extraction from the egg secretions in Laminariales and by Maier and Clayton [191] for the Hormosirene extraction from *Hormosira banksii*. Volatile compounds (chemoattractants) from the seaweed *Ulva pertusa* (now *Ulva australis*) can be extracted by distillation method with CH_2Cl_2 or Pentane used as solvent [192]. To extract the volatiles from microalgae, the cold trap condensation method is widely used, e.g., ectocarpene was obtained using this method [193]. In this method, a purified air stream is passed briefly through female gametes' culture media or suspensions of *Skeletonema costatum* and *Lithodesmium undulatum*, which is then directed into a cold trap (−50 °C), containing 4–5 mL of n-pentane [194]. Trapped volatile compounds from *Ectocarpus*, *Fucus*, and *Cutleria* can then be adsorbed on an activated carbon bed of 1.5 mg and then desorbed with dichloromethane [71]. Finally, the eluates are purified using glass-capillary gas chromatography and analyzed with GC-MS [71,194]. Another method of extraction is where the cultures of the bloom-forming dinoflagellate *Alexandrium tamarense* have been subjected to suction filtration onto 45 mm GF/F filters for cell lysis, which causes the release of pheromone compounds from cells.

The cell-free filtrate is then pumped through a 100 mg ENV + SPE column to trap the exudates. The eluate is concentrated in a centrifugal concentrator and resolved in methanol: water (80:20) having 20 mM ammonium acetate. Further eluted compounds are analyzed using Fourier transform ion cyclotron resonance (FT-ICR) MS. The stable isotope pattern (SIP), a novel algorithm, and an automated workflow can be used for comparison with theoretical isotope intensity profiles to produce the empirical formulae of the detected metabolites [195].

10. Perspectives

The primary objective of this review is to provide a comprehensive account of hormones and pheromones from an algal point of view. This article can form the basis for benchmarking future investigations. A lot of parallels could be drawn between the higher plants and the algae, e.g., exposure to rapid climate changes, seasonal growth cycles, and biotic stress from herbivores. This and similar factors underline the fact that algal growth and development, like in higher plants, are influenced and controlled by hormones and pheromones. Similarly, hormones have a major role to play in defense mechanisms in higher angiospermic plants, and this could be said about algae as well but its molecular mechanism in algae has not been established thus far. Deciphering this mechanism could be a game changer in technological interventions in the cultivation of various algae, which are frequently infested by epi/endophytes. A lot of focus is being put on understanding the reproduction of various commercially important species, which could revolutionize the spore-based commercial cultivation technologies, and the study of hormones and pheromones might hold the key for future development. Recent studies have unequivocally provided evidence for the use of algal-based bio-stimulants in micro-algal and seaweed cultivation to enhance circular blue economy [196,197].

The applications in terms of biotechnological implications for the commercial aquaculture industry include induction of reproduction, germplasm enhancement, micropropagation, and seedling production. The commercial farming of seaweeds—where clonal propagation is not practiced—overwhelmingly depends on the availability of reproductive cells, e.g., zoospores, gametes for seeding [*Ulva*, *Porphyra* (*Pyropia*), *Undaria*, etc.]. The use of hormones and pheromones can ascertain and ensure the timely availability of carpospores, tetraspores, zoospores, and gametes for seeding. Research has shown that treating the thalli of *Grateloupia imbricata* with methyl jasmonate reported a ~7.5-fold increase in cystocarp numbers. Further, the maturation occurred within 48 h of treatment, thereby shortening the typical >3-week maturation period [198]. Similarly, the use of ethylene as a physiological regulator in the tetrasporogenesis of *Pterocladiella capillacea* has been established [199]. The thalli exposed to ethylene for 15 and 30 min produced a high number of tretrasporangia. Polyamines like spermidine and spermine were reported to enhance cystocarp maturation followed by spore release in *Gracilaria cornea* [52]. The exogenous application of ABA to *Saccharina japonica* enhanced the formation of sporophytic sori [125]. These studies unequivocally confirmed the role and thus potential role of plant hormones in spore-mediated aquaculture of economically important seaweeds.

Another application is their use in germplasm enhancement. Studies have shown that the use of ethylene precursor, which is 1-aminocylopropane-1-carboxylic acid (ACC), provides *Neopyropia yezoensis* gametophytes tolerance to heat stress [126,127,200]. It was shown that *Pyropia orbicularis* had 4–7 times higher free ABA levels during water deficit conditions [201]. Further, ABA is known to regulate the activation of the antioxidant enzymes during desiccation. The long distance transportation of planting material in red seaweed *Kappaphycus alvarezii* reported low survival and vigor. Thus, exogenous application of ABA to these seedlings could provide desiccation stress tolerance for germplasm improvement.

The role of plant hormones in micro-propagation and seedling production is well known. The use of indole-3-acetic acid, 2,4-dichlorophenoxyacetic acid (2,4-D), and kinetin on callus formation, growth, and regeneration of *Gracilaria tenuistipitata* and *G. perplexa* was reported [202]. Similarly, auxins and cytokinins are known to help the tissue culture of

Grateloupia dichotoma [112]. The plant growth hormones like 2,4-D, IAA, and α-naphthalene acetic acid were found to be effective in successful micro-propagation for the production of clonal planting materials in *Gracilaria changii* and *Kappaphycus alvarezii* through tissue culture [203]. The plant hormones individually as well as in combination have reported improved survival and regeneration in *Gracilaria dura* [204].

Therefore, the understating of endogenous level and exogenous application have several pivotal implications in seaweed aquaculture. Unlike higher plants, the application domain for plant hormones and pheromones has yet to expand for seaweeds. Decreasing genetic variability of seaweeds due to repeated conventional vegetative propagation methods in seaweed cultivation causes decreased growth rates and productivity and makes them more susceptible to diseases [205]. Micro-propagation through tissue culture has been an alternative to this conventional method. Plant growth regulators and their role in the tissue culture of marine macroalgae (seaweeds) have been extensively reviewed [21,111,206], suggesting that the phytohormones play an important role in the growth and development of algae. Further, significant efforts are needed to better understand the physiological effects and varied functions of hormones, which depend on the development of different groups of algal taxonomy. Male-sterile *Gelidium vagum* macroalgae exhibited notably faster growth rates compared to plants from the different lines, indicating that male-sterile gametophytes might be more suitable for aquaculture than the typical wild-type plants of this species [207].

Exogenous application of α-naphthaleneacetic acid (NAA), gibberellin (GA3), and 6-benzyl adenine (BAP) has been used to induce regeneration of *Sargassum fusiforme* to obtain more regenerative seedlings within a short time, thereby improving economic efficiency [208]. Plant growth hormone (zeatin + phenylacetic acid) has been used for micropropagation in three color morphotypes of *Kappaphycus alvarezii* var. "adik-adik" [209]. The successful regeneration of young plants from various *Kappaphycus* varieties was achieved using a culture medium composed of zeatin and phenylacetic acid (PAA) along with Ascophyllum/Acadian marine plant extract powder (AMPEP) obtained from the brown seaweed *Ascophyllum nodosum* [210]. AMPEP concentrations with 0.1, 1.0 mg L^{-1} stimulate the growth in macroalgae *Gracilaria caudata* and *Gracilaria corticata* var. *cylindrica*, and at higher concentrations of 5.0 mg L^{-1}, it stimulates the growth in *Laurencia catarinensis* [211,212]. Seaweed extracts containing hormones (auxins, gibberellins, cytokinins, gibberellins, abscisic acid, ethylene, betaine, and polyamines) have more potential as biostimulants in agriculture [213]. Phytohormones' abscisic acid (ABA), 24-epibrassinolide (EBL), brassinolide (BL), and indole-3-acetic acid (IAA) showed the stimulatory effects on microalga *Scenedesmus quadricauda* cell growth, biomass production, intracellular concentrations of chlorophyll-a, carotenoid, and lipids biosynthesis [214]. Phytohormones in combination are widely used to enhance algal cultivation. In *Chlorella sorokiniana*, combined treatments of NAA_{5ppm} + $GA3_{10ppm}$ + $zeatin_{1ppm}$ increased the biomass production by 170% as compared to control, followed by treatments of NAA_{5ppm} + $GA3_{10ppm}$ and $NAA_{2.5ppm}$ + $zeatin_{1ppm}$ stimulating the biomass production by 138% and 136%, respectively [215]. Similarly, in freshwater microalgae, the combination of phytohormones has been reported to stimulate biomass and lipid production [216]. Pheromones can be used to facilitate the selective release of male and female gametes in marine macroalgae by controlling the release and response to specific pheromones [217,218]. Breeders can choose the desired individuals for mating, leading to the development of seaweed strains with desirable traits. Sexual signaling in marine benthic diatom *Seminavis robusta* is controlled by a complex and unknown pheromone system called sex-inducing pheromone (SIP+), which activates the shift from mitosis to meiosis in the opposing mating type. Additionally, it stimulates the activation of genes related to proline biosynthesis and the release of an attraction pheromone derived from proline [219].

In seaweed, gene regulation can occur in response to changes in environmental conditions, including hormone signaling. For example, the levels of certain genes related to growth or stress response can be upregulated or down-regulated in response to hormonal

signals [141,220]. Stress hormone ABA increases in concentration in response to abiotic stress, initiating a range of physiological processes aimed at enhancing their survival chances [221]. In filamentous green alga *Stigeocloflium* cf. *tenue*, exogenous application of ABA (10^{-7} to 10^{-5} M) in a culture medium for the 3 weeks reported a slight reduction in growth and senescence. So the physiological concentrations of ABA below 10^{-7} to 10^{-5} M show tolerance and healthy growth, whereas concentrations above this for a longer period (3 weeks) may start growth reduction and senescence in *Stigeocloflium* cf. *tenue* [38]. Also, the endogenous ABA was reported to increase (10×) in microalga *Draparnaldia mutabilis* and JA increased (15×) in *Draparnaldia salina* when grown in osmotic stress (50 and 85 mM NaCl), suggesting that the endogenous ABA and JA play important roles in salt tolerance in microalgae [38]. In seaweeds, CRISPR technology can be used to target and modify genes involved in hormone production or response pathways in seaweed and shed light on the regulatory mechanisms [222].

It is worth mentioning that the field of seaweed hormone and pheromone research is relatively young compared to terrestrial plants, and there is ongoing research to better understand the role of hormones and pheromones in seaweed growth, health, and defense mechanisms. While these studies provide some insights, further research is needed to fully explore the potential of hormone and pheromone calibration for identifying elite, healthy, and disease-free seaweed germplasm.

11. Way Forward

It is well evident that plant hormones play a pivotal role in regulating growth and development while pheromones are needed for induction of reproduction and sexual maturity in seaweeds. Although plant hormones possess specific functions, they tend to mediate with other hormones either antagonistically or cooperatively via complex crosstalk for achieving optimal outcomes, and their mode of action in isolation is most unlikely in nature.

The present review for the first time provides types and diversity of biosynthetic pathways of five phytohormones and five pheromones reported in algal representatives (along with six hormones and two pheromones in higher angiospermic plants but possibly also operational in algal representatives); modes of action of five hormones and five pheromones reported in algal representatives (along with the modes of action of five hormones in higher angiospermic plants but possibly also operational in algal representatives); roles of 11 hormones and 29 pheromones reported in algal representatives; and extraction protocols of four hormones and six pheromones reported in algal representatives. The application of endogenous plant hormones as environmentally friendly or organic biostimulants for higher crops and seaweeds is well documented [196]. It has been shown that in higher plants, hormones, besides their usual known functions, are also involved in the interactions between them and beneficial microbes [223]. Further, these microbial-derived hormones assist in imparting tolerance to biotic and abiotic stress in higher angiospermic plants. However, such studies are seldom attempted in seaweeds and are necessary so that such knowledge can be applied to sustainable seaweed aquaculture. Similarly, the use of plant hormones for alleviating stress tolerance and disease resistance would be critical to retard the aggravated impacts of climate change in terms of mass mortality and failure of commercial seaweed crops. The diversity in sexual strategies in seaweeds provides ample opportunity in the presence of chemical diversity of pheromones, but the research in elucidating functional roles is slow. The successful application of pheromones in triggering sexual reproduction and life cycle transition in *Ulva* has been evident [60,144]. The microbial-derived chemicals are also known to enhance reproduction in green and red seaweeds [224]. Unlike plant hormones, analogs for pheromones are not widely studied. This is essentially due to the minuscule amount released into the environment, the absence of standard extraction procedures, and a vast range of active chemical moieties, e.g., non-polar small hydrocarbons to polar glycoproteins of high molecular weight with respect to pheromones. Further studies in this direction would help elicit physiological

responses reminiscent of pheromones to aid control over reproduction; successful breeding; and continuous and sustainable seedling production by removing seasonality barriers to enhance aquaculture prospects.

The exact identification and quantification of plant hormones and pheromones from seaweeds have been usually performed using ultra-high-performance liquid chromatography–mass spectrometry methodology. The current technical advancements in methodologies have focused on developing protocols that are less labor-intensive and comprehensive rather than improving sensitivity and accuracy [162]. However, fine quantification is difficult to conduct due to the interfering effects of cellular constituents. Novel methods in extraction and further identification and quantifications are needed for quick and reliable outcomes. Consequently, sophisticated imaging tool kits applied with a fluorescence-compatible clearing approach with synthetic transcriptional reporters for specific plant hormones or pheromones in seaweeds may be used for determining the precise spatial and temporal regulation. The implementation of such cutting-edge techniques would open new possibilities of enhancing our ability to understand the mode of action and characterize hormone and pheromone dynamics at the cellular level. In the high-throughput-mediated multi-omics era, the understating of the mechanism of hormones and pheromones at the metabolomics, proteomics, transcriptomics, and genomics levels would shed more light not only on their biosynthesis, mode of action, and signal transduction but also in a micro-evolutionary context. There seems enormous potential for involving multidisciplinary teams including bioinformatics promoting a paradigm shift in our understating.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/phycology4010001/s1, The Biosynthetic pathways and mode of actions in higher angiospermic plants are given in the Supplementary Information, Supplementary Figure S1, and Supplementary Figures S4–S10. References [225–257] are cited in the Supplementary Materials. Figure S1: Tryptophan-independent pathway of auxin biosynthesis in higher plants; Figure S2: Flow chart summarizing the protocols for identification and quantification of phytohormones from algae; Figure S3. Flow chart summarizing the protocols for identification and quantification of pheromones from algae; Figure S4. Biosynthesis of brassinosteroids in higher plants; Figure S5: Biosynthesis of jasmonic acid (JA) in higher plants; Figure S6: Biosynthesis of polyamines in higher plants; Figure S7: Biosynthesis of salicylic acid (SA) in higher plants; Figure S8: Biosynthesis of strigolactones (SL) in higher plants; Figure S9: Biosynthesis of finavarrene from dodeca-3,6,9-trienoic acid in higher plants; Figure S10: Biosynthesis of Hormosirene in higher plants.

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