Chemical Ecology of Plants: Allelopathy in Aquatic and Terrestrial Ecosystems

Edited by Inderjit and Azim U. Mallik

Editors:

Prof. Azim U. Mallik   Dr. Inderjit
Biology Department   Department of Botany
Lakehead University   University of Delhi
Thunder Bay   Delhi 110007
Ontario P7B 5E1   India
Canada

Contents

List of contributors

Prasanta C. Bhowmik, Department of Plant and Soil Sciences, Stockbridge Hall, University of Massachusetts, Amherst, MS 01003-7245, USA; e-mail: pbhowmik@pssci.umass.edu

José L.G. Galindo, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain; e-mail: joseluis.garciagalindo@alum.uca.es

Maria T. Gallardo-Williams, Laboratory of Molecular Toxicology, National Institute of Environmental Health Sciences, P.O. Box 1233, Mail drop E1-06, Research Triangle Park, NC 27709, USA; e-mail: Gallardo@niehs.nih.gov

Institute for Environmental Studies, Department of Chemistry–SCA 400, University of South Florida, 4202 East Fowler Avenue, Tampa, FL 33620-5202, Florida, USA; e-mail: @

Stephen R. Gliessman, Center for Agroecology, Department of Environmental Studies, University of California Santa Cruz, Santa Cruz, California 95064, USA; e-mail: gliess@zzyx.ucsc.edu

Inderjit, Department of Botany, University of Delhi, Delhi 110007, India; e-mail: allelopathy@satyam.net.in

Shibu Jose, School of Forest Resources and Conservation, University of Florida, 5988 Hwy 90, Building 4900, Milton, FL 32583, USA; e-mail: sjose@ufl.edu

Harleen Kaur, Department of Botany, Panjab University, Chandigarh 160 014, Sector 14, India; e-mail: harleen786@rediffmail.com

K.I. Keating, Department of Environmental Sciences, Rutgers University of New Jersey, Cook Campus, New Brunswick, New Jersey 08903, USA; e-mail: KKeating@rci.rutgers.edu

Julia Koricheva, Section of Ecology, Department of Biology, University of Turku, FIN-20014 Turku, Finland; e-mail: julkoric@utu.fi

Francisco A. Macías, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain; e-mail: famacias@uca.es

Azim U. Mallik, Department of Biology, Lakehead University, Thunder Bay, Ontario P7B 5E1, Canada; e-mail: azim.mallik@lakeheadu.ca

Dean F. Martin, Institute for Environmental Studies, Department of Chemistry –SCA 400, University of South Florida, 4202 East Fowler Avenue, Tampa, FL 33620-5202, Florida, USA; e-mail: dmartin@chuma1.cas.usf.edu

José M.G. Molinillo, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain; e-mail: chema.gonzalez@uca.es

Stephen D. Murphy, Department of Environment and Resource Studies, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada; e-mail: sd2murph@fes.uwaterloo.ca

Dale G. Nagle, Department of Pharmacognosy and National Center for Natural Products Research, Research Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, University, MS 38677-1848, USA; e-mail: dnagle@olemiss.edu

Harsh Nayyar, Department of Botany, Panjab University, Chandigarh 160 014, India; e-mail: harshnayyar@hotmail.com

Erik Tallak Nilsen, Biology Department, Virginia Polytechnic Institute and State University, 2119 Derring Hall, Blacksburg, VA 24061, USA; e-mail: enilsen@vt.edu

François Pellissier, Dynamics of Altitude Ecosystems Laboratory, University of Savoie, 73376 Le Bourget-du-Lac, France; e-mail: pellissier@univ-savoie.fr

Anna Shevtsova, Department of Forest Vegetation Ecology, Swedish University of Agricultural Sciences, S-90183 Umeå, Sweden; e-mail: Anna.Shevtsova@svek.slu.se

X. Carlos Souto, Departamento de Ingeniería de los Recursos Naturales y Medio Ambiente, E.U.E.T. Forestal, Universidade de Vigo, 36005 Pontevedra, Spain; e-mail: csouto@uvigo.es

Ascensión Torres, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain; e-mail: chon.torres@uca.es

Rosa M. Varela, Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, 11510 Puerto Real, Cádiz, Spain; e-mail: rosa.varela@uca.es

David E. Wedge, United States Department of Agriculture, Agricultural Research Service, Natural Products Utilization Research Service, Thad Cochran National Center for Natural Products Research, University, MS 38677-8048, USA; e-mail: dwedge@olemiss.edu

Preface

There has been significant progress in plant allelochemical research with the recent advancement of conceptual understanding of ecological processes and breakthroughs in biotechnological and molecular techniques. Allelochemicals play a major role in influencing community structure, nutrient dynamics, substratum and mycorrhizal ecology, and resource competition. There is a wide gap between ecologists and natural product chemists in understanding the significance of an allelochemical in the natural environment. While natural product chemistry is an integral part of allelochemical research, ecological understanding of allelochemicals is required to generate ecologically relevant data. We feel that merely isolating allelochemicals from a plant or its habitat is not enough to argue the occurrence of allelochemical interactions in field conditions. We must unfold the chain of events initiated with the release of allelochemicals in the environment to the manifestation of their impact in community organization.

This book is devoted to highlighting the recent findings in allelochemical research from an ecological standpoint. The aim of the book is to provide an up-to-date insight into examples of allelochemical research from aquatic, forest, and agricultural ecosystems. Chapter 1 summarizes the problems and prospects in the study of allelopathy and serves as brief introduction for the book. Chapters 2 and 3 specifically discuss algal allelochemicals having ecological roles in plant defense and community structure. Chapter 4 discusses the role of allelochemicals in the aquatic weed *Typha domingesis*. Chapter 5 discusses in-depth chemical and applied aspects of sunflower allelochemicals. The significance of abiotic and biotic soil factor in determining allelochemical response is discussed in Chapters 6 and 7. The role of allelochemicals in forest and agroecosystems is reviewed in Chapters 8 through 12. Plants generally have to cope with abiotic stresses. Chapter 13 raises several questions on shifts in allelochemical functioning that are due to selected abiotic stresses. Chapter 14 argues that if the focus of a study is on the mechanisms rather than the consequences of variation in plant allelochemical composition, other methods of chemical data analysis and interpretation should be used. Chapter 15 highlights the update information of pollen allelochemicals. All in all, the book illustrates the different aspects of allelochemical research in aquatic and terrestrial ecosystems.

We are grateful to the authors for submitting their valuable work for this book within the given time lines. We are indebted to the following referees for their critical and timely reviews: Hans Lambers, Jeffrey Weidenhamer, John

Azim U. Mallik and Inderjit
January 2002

Problems and prospects in the study of plant allelochemicals: a brief introduction

Azim U. Mallik[1] and Inderjit[2]

[1] Department of Biology, Lakehead University, Thunder Bay, Ontario P7B 5E1, Canada
[2] Department of Botany, University of Delhi, Delhi 110007, India

A series of simplistic experiments followed by a broad and bold generalization by Hans Molisch in the late 1930s regarding the influence of one plant on another through release of chemicals into the environment initiated the foundation of allelopathy [1]. However, the phenomenon of a plant's growth suppression by chemicals released from plants in its vicinity has been known since ancient times [2]. Molisch articulated the phenomenon by defining and coining the term allelopathy. As a plant physiologist, Molisch drew his conclusions from controlled experiments, mostly by exposing his test plant(s) or plant parts to ethylene emitting from apples. Around the same time, F. Boas conducted controlled experiments with aquatic extracts of leaves of buttercup (*Ranunculus* spp.), camomile, and several conifers such as fir, pine, and juniper and found inhibitory as well as stimulatory effects on test plant(s) depending on the type of extract. From these limited tests, he developed far-reaching conclusions of plant community structuring [3, 4]. Our intention is not to dismiss or undermine the contributions of these pioneers of allelopathy research but to emphasize the fact that a complex phenomenon like allelopathy cannot be demonstrated by such a simplified experimental approach [5]. Many researchers in the past, and to some extent present, have taken this bad lesson of using inappropriate and simplified approaches draw unjustifiable conclusions and extrapolation in the study of allelopathy [6–9]. The discipline has suffered a great deal because of it [10].

There have been legitimate concerns regarding the definition of allelopathy and allelochemicals. The all-encompassing definition of allelopathy by E.L. Rice [11] "*as any direct or indirect harmful or beneficial effect by one plant (including microorganisms) on another through production of chemical compounds that escape into the environment*" has been criticized for being "boundless and therefore meaningless" as a definition [12]. The working definition of the International Allelopathy Society [13], "*any process involving secondary metabolites produced by plants, algae, bacteria and viruses that influence the growth and development of agricultural and biological systems; a study of the functions of secondary metabolites, their significance in biological organiza-*

tion, their evolutionary origin and elucidation of the mechanisms involving plant–plant, plant–microorganisms, plant–virus, plant–insect, plant–soil–plant interactions," also suffers from the similar problem of all-inclusiveness and boundlessness. However, the fact remains that the phenomenon of plant–plant interaction through the release of secondary compounds in nature is undeniable. Even one of the most influential ecologists and a vocal critics of allelopathy of our time, J.L. Harper, said, "*Demonstrating allelopathy has proved extraordinarily difficult—it is logically impossible that it does not happen and perhaps nearly impossible to prove that it does*" [10]. Therefore, the concern is the burden of proving the existence of allelopathy in natural ecosystem amongst all other interacting phenomena rather than the existence of allelopathy. Terminology and trends in allelopathy research were convincingly reviewed by Willis [14]. He suggested that allelopathy should be considered under plant ecology and should be kept as sub-discipline of allelochemicals [14].

The other challenge is in the definition of allelochemicals. There are several questions which need to be addressed. For example, do allelochemicals include only secondary metabolites or also primary metabolites? Are allelochemicals necessarily a specialized group of compounds that are exudates or volatilized or degraded products of non-allelopathic compounds at certain concentration and/or in certain mixtures influencing the growth of the neighboring plants? We all know that many usual secondary metabolites of plants such as phenolics are considered allelochemicals under certain concentrations or in certain mixtures. Are there non-allelopathic compounds that become allelopathic under certain circumstances? When does a compound become allelopathic? These are the sorts of questions we have yet to resolve in order to develop a solid conceptual basis of allelochemical research.

Having highlighted some of the academic questions that we have yet to answer in order to better articulate the premise of allelopathy, there is no denying that we have experienced significant progress in allelopathy research in the last four decades. Development of new and sophisticated methods of isolation and identification of allelochemicals and development of innovative experimental designs for the study of allelopathy have contributed significantly to this success. Better methods are able to detect the effects of dominant chemical and environmental factors that play important roles in the manifestation of allelopathy. Although some researchers were able to demonstrate the separation of allelopathic effects from competition under controlled conditions [15–17], others [18] advocated against the separation of allelopathy from resource competition. Inderjit and Del Moral [18] opined that nature is too complex to be explained by one factor. Several factors—allelopathy, resource competition, nutrient immobilization, mycorrhizae, substratum—operate sequentially and/or simultaneously and influence community structure. We can separate allelopathy from other interference factors under controlled condition, but the question is: Does this actually happen in nature? By using sophisticated, modern equipment and techniques, the mode of action and fate

of allelochemicals in soil and their effects on microorganisms and nutrient availability have been investigated [19, 20]. A methodological impasse in allelopathy research has been further elevated by the recent advances in molecular biology and digital technology. As a result, the discipline has been diversified from molecular genetics, to pollen allelopathy, to weed management in agriculture and forestry. Scientists with many different specializations are working independently and in collaboration to gain a better understanding of the workings of allelochemicals and allelopathic phenomenon. Breakthroughs in allelopathic research in molecular biology will play a leading role in developing practical methods for sustainable agriculture and forestry. Digital imaging techniques and information technology will play an increasingly important role in in-depth study of allelochemical origin and function and will elucidate the phenomenon of allelopathy [21].

Recently, ecosystem-level understanding of allelopathy has been explored in agriculture and forestry by several researchers [16, 22]. The concept of keystone species and their role as ecosystem engineers has been linked to substrate ecology and allelopathy, which can preempt competition in structuring plant communities (Mallik, this volume).

Research areas need in-depth investigations

While many unanswered questions remain in the study of allelopathy, new discoveries on the behavior of secondary compounds as allelochemicals, new tools for sophisticated chemical analyses, and renewed understanding of ecosystem function together provide an exciting opportunity to resolve the challenging fundamental questions [23]. On the application side, there is a bright prospect of applying allelopathic principles in sustainable agriculture and forestry by refining agronomic and silvicultural techniques, allelopathic gene transfer, and biological weed control. The future lies in understanding the ecosystem perspective of allelopathic phenomena and allelochemical effects on soil chemistry. Demonstration of the subtlety of the phenomenon and its interconnectedness with other ecological processes that influence ecosystem functioning will make a significant contribution to science and natural resources management. We feel that the following areas can be used as examples for understanding the diversity and complexity of allelochemical functioning in ecosystems.
1. Significance of algal metabolites and their importance in pharmaceutical and community structure (Nagle and Wedge, this volume; Nagle and Inderjit, this volume).
2. Compared to terrestrial ecosystems, little attention has been paid to allelochemical interactions in aquatic ecosystems. Gallardo-Williams and Martin (this volume) discuss allelochemicals from *Typha domningesis* and their ecological significance.

3. Sunflower has long been a source of interest to chemist and agroecologists. Macías et al. (this volume) provide an update on the chemistry, bioactivity, and application of sunflower allelochemicals.

4. An in-depth insight on ecological relevance of allelochemicals in forest and agroecosystems can contribute significantly to developing sustainable land management, and these are discussed by several authors in this book (e.g., Nilsen, Mallik, Jose, Inderjit and Bhowmik, and Gliessman).

5. The functioning of allelochemicals is greatly influenced by abiotic stress factors in field situations. Inderjit and Nayyar (this volume) raise several questions about allelochemical functioning and abiotic stress.

6. Koricheva and Shevtsova (this volume) argue that if the focus of a study is on the mechanisms rather than on the consequences of variation in plant allelochemical composition, presentation of data in terms of concentrations, contents, and plant biomass should be encouraged.

7. Pollen allelopathy is of great interest to eco-physiologists and weed ecologists. Recent information on the biochemical and physiological aspects of pollen allelopathy is reviewed by Murphy (this volume).

Topics covered in this volume provide information not only on the recent developments in allelochemical research in relation to sustainable agriculture and forestry but also on our latest understanding about the complexity of interaction between allelochemicals and various biotic and abiotic factors.

References

1 Molisch H (1937) *Der Einfluß einer Pflanze auf die andere, Allelopathie*. Verlag von Gustav Fischer, Jena, Germany. English translation (2001) LJ LaFleur, MAB Mallik (translators): *Influence of one plant on another*, Scientific Publisher, Jodhpur

2 Theophrastus (ca. 300 B.C.) *Enquiry into plants and minor works on odorous and weither signs*. 2 Vols. Transl. to English by A Hort, Loeb Classical Libr., W. Heinemann, London (1916)

3 Boas F (1934) Beiträge zur Wirkungsphysiologie einheimischer Pflanzen, I [Contributions to the metabolic physiology of indigenous plants, I]. *Berichte Deutsch Bot Gesell* 52: 126–131

4 Boas F (1935) Vergleichende Untersuchungen über Wachstumsanreger in einheimischen Pflanzen, Beiträge zur Wirkungsphysiologie einheimischer Pflanzen, II [Comparative investigations of growth stimulants in indigenous plants: contributions to the metabolic physiology of indigenous plants, II]. *Berichte Deutsch Bot Gesell* 53: 495–511

5 Inderjit, Weiner J (2001) Plant allelochemical interference or soil chemical ecology? *Perspect Plant Ecol Evol Syst* 4: 3–12

6 Willis RJ (1985) The historical basis of the concept of allelopathy. *J Hist Biol* 18: 71–102

7 Inderjit, Dakshini KMM (1995) On laboratory bioassays in allelopathy. *Bot Rev* 61: 28–44

8 Inderjit, Weston LA (2000) Are laboratory bioassays for allelopathy suitable for prediction of field responses? *J Chem Ecol* 26: 2111–2118

9 Romeo J (2000) Raising the beam: moving beyond phytotoxicity. *J Chem Ecol* 26: 2011–2014

10 Harper JL (1975) Allelopathy. *Q Rev Biol* 50: 493–495

11 Rice EL (1974) *Allelopathy*. Academic Press, New York

12 Watkinson AR (1998) Reply from A.R. Watkinson. *Trends Ecol Evol* 13: 407

13 International Allelopathy Society (1998) Allelopathy: is this the definition we want? *In*: R Willis (ed): *IAS Newsletter 2: 5*, University of Melbourne, Australia

14 Willis RJ (1994) Terminology and trends in allelopathy. *Allelo J* 1: 6–28

15 Weidenhamer JD, Hartnett DC, Romeo JT (1989) Density-dependent phytotoxicity: distinguish-

ing resource competition and allelopathic interference in plants. *J Appl Ecol* 26: 613–624

16 Zackrisson O, Nilsson M-C (1992) Allelopathic effects by *Empetrum hermaphroditum* on seed germination of two boreal tree species. *Can J For Res* 22: 1310–1319

17 Nilsson MC (1994) Separation of allelopathy and resource competition by the boreal dwarf shrub *Empetrum hermaphroditum* Hagerup. *Oecologia* 98: 1–7

18 Inderjit, Del Moral R (1997) Is separating resource competition from allelopathy realistic? *Bot Rev* 63: 221–230

19 Einhellig FA (2001) An integrated view of phytochemicals amid multiple stresses. *In*: Inderjit, KMM Dakshini, CL Foy (eds): *Principles and practices in plant ecology: allelochemical interactions*. CRC Press, Boca Raton, 479–494

20 Blum U, Shafer SR, Lehman ME (1999) Evidence of inhibitory allelopathic interactions involving phenolic acids in field soils: concepts *vs.* an experimental model. *Crit Rev Plant Sci* 18: 673–693

21 Weston LA, Czarnota MA (2001) Activity and persistence of sorgoleone, a long-chain hydroquinone produced by *Sorghum bicolor*. *J Crop Prod* 4: 363–377

22 Wardle DA, Nilsson MC, Gallet C (1998) An ecosystem-level perspective of allelopathy. *Biol Rev* 73: 305–319

23 Mallik AU (2000) Challenges and opportunities in allelopathy research: a brief overview. *J Chem Ecol* 26: 2007–2009

Antifungal properties of cyanobacteria and algae: ecological and agricultural implications

Dale G. Nagle[1] and David E. Wedge[2]

[1] Department of Pharmacognosy and National Center for Natural Products Research, Research
Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, University,
MS 38677-1848, USA
[2] United States Department of Agriculture, Agricultural Research Service, Natural Products
Utilization Research Service, Thad Cochran National Center for Natural Products Research,
University, MS 38677-8048, USA

Introduction

Scientific reports of fungi associated with marine algae date back to the late
nineteenth century [1, 2]. Since then, many species of fungi have been identi-
fied from marine macroalgae [3]. As many as one-third of the described spe-
cies of marine higher fungi and many species of lower fungi are associated
with marine algae [4, 5]. Similarly, aquatic fungi are often found in association
with freshwater algae and microscopic cyanobacteria [6]. While most reports
are primarily taxonomic, the ecological nature of the interactions between
these associations is diverse. Saprophytic fungi are common, and parasitic fun-
gal species can seriously affect vast populations of macroalgae raised in com-
mercial sea-farming enterprises [7].

It is often difficult to establish the nature of the algal-fungal relationship
without careful observation of the ecological process of fungal attack on the
alga. The overall health of the alga before fungal infestation must be consid-
ered. The intertidal brown marine algae *Pelvetia canaliculata* (L.) Dcne et
Thur. and *Ascophyllum nodosum* (L.) Le Jol. are reported to be permanently
and systemically infected by the ascomycete fungus *Mycosphaerella asco-
phylli* Cotton [8, 9]. While much of the work has focused on *A. nodosum*, a
mutualistic interrelationship has been suggested to exist between these organ-
isms [10, 11]. More recent studies have failed to find any significant benefit
that the algae derive from the fungus and have questioned the implied mutual-
istic nature of this relationship [12].

In terrestrial systems, algae and fungi appear to exist in pathogenic, com-
petitive, and symbiotic relationships, as observed in lichens. In much the same
way, evidence suggests that freshwater and marine algae are intimately asso-
ciated with fungi. It is our intention neither to exhaustively examine the inter-
actions between algae and fungi nor to describe all aspects of algal defense

strategies. However, this review does briefly examine the pathogenic nature of the relationship between these two distinctly different groups of organisms that somehow seem inexorably bound. Significant research efforts have probed the chemical arsenal produced by cyanobacteria and algae as new sources of biologically active natural products for use in both agriculture and medicine. Numerous reports exist concerning the production of antifungal compounds by cyanobacteria and algae [13–17]. However, most reports of antifungal activity by compounds from algae and cyanobacteria concern their evaluation for pharmaceutical activity. There are substantially fewer reports on the evaluation of these organisms for antifungal activity against economically important plant pathogenic fungi. Very little is known with regard to the chemical ecology of algae and fungi associations in marine and aquatic systems. In order to spur new research efforts and suggest possible avenues for future chemical ecology research, we have elected to specifically discuss the substances produced by cyanobacteria and algae with clearly documented antimicrobial activities against only those species of fungi that are recognized as pathogenic to either plants or algae. In addition, a discussion of antifungal algae natural products in agricultural pest control and the approaches that we are currently using to discover antifungal compounds from algae and cyanobacteria is presented.

Fungal growth and parasitism on algae

Ecological interactions between parasitic fungi and freshwater algae are well documented [6]. Marine algae are raised commercially throughout the world as both food and commercial sources of polysaccharides such as carrageenin, alginic acid, and agar. Several Oomycete species of fungi have been directly implicated in pathological infestations of maricultured red algae. *Petersenia pollagaster* (Petersen) Sparrow has been found to infect a cultured strain of *Chondrus crispus* Stackh. [18]. This polysaccharide-rich strain of *C. crispus*, termed "T4", is cultured in Nova Scotia as a major commercial source of κ-carrageenin.

Nori (*Porphyra yezoensis* Ueda, *Porphyra tenera* Kjellum) mariculture is a multi-billion-dollar food industry in Japan and throughout coastal Asia [19]. The Oomycete *Pythium porphyrae* Takahashi et Sasaki commonly infects *Porphyra* sp. growing in cultivation farms. This process is known as red rot disease or "aka-gusare" [20]. Red rot disease is reported to have nearly destroyed entire crops of *Porphyra* sp. in Japan and Korea within only a few weeks [7, 21, 22]. *Pythium porphyrae* has since been found to infect other species including *Porphyra miniata* (Lyngbye) C. Agardh [23]. Oomycete species have been observed to infect other red algae, brown algae, and green algae [24]. The Oomycete *Ectrogella perforans* Petersen acts as an endobiotic parasite of marine diatoms and is reported to cause epidemic infections of *Licmorphora* and other diatom species [25].

The large marine kelp *Laminaria saccharina* (L.) Lam. is subject to parasitic infection by the ascomycete *Phycomelaina laminariae* (Rostrup) Kohlm [26]. *Phycomelaina laminariae* infects the meristematic tissue of the algal stipe, forming black patches, and appears to increase algal susceptibility to invasion by otherwise non-pathogenic species of fungi. Deuteromycete fungi are known to infect several species of large marine algae. *Sargassum* sp. and *Cystoseira* sp. are parasitized by *Spaceloma cecidii* Kohlm. [27]. In addition, numerous species of fungi have recently been isolated and cultured from the surfaces of marine algae as part of modern microbial drug-discovery programs [28–33].

Disease cycle

Although considerable research has focused on the process of fungal invasion of terrestrial plant tissues [34], far less is known about the process of fungal infection in algae. An overview of the fungus disease cycle in plants is provided. However, considerable research is needed before the true nature of the algae infection process and the role(s) of antifungal chemical defenses in the control of fungal invasion of algae are clear. A plant or alga becomes diseased in most cases when it is attacked by a pathogen. In order for successful infection to occur, each of the three following components must be present: (1) the pathogen must be virulent, (2) environmental conditions must be present that favor infection, and (3) the host must be susceptible. In every infectious disease, whether in plants or animals, a series of distinct events occurs in succession that leads to disease development: (1) attachment of the pathogen to the host; (2) recognition between the host and pathogen; (3) penetration/invasion by the pathogen; (4) growth and reproduction of the pathogen within the host; and (5) subsequent survival of the pathogen in the absence of the host [34].

All plant pathogens, in their vegetative state, can initiate infection. Eight thousand fungal species are known to cause plant diseases, compared with only 100 fungal species that cause human mycosis. Fungal spores are most often the initial infectious propagule. Spore germination is often stimulated by nutrient diffusion from the plant surface, and the subsequent development of germ tube, appressorium, and penetration peg is influenced by the presence or absence of numerous plant chemicals.

Almost all plant pathogens are mobile and are transported to an immobile host. This situation is in contrast to human diseases, in which the host is mobile and most pathogens are immobile. Before a pathogen can colonize its host, it must first become attached to the host surface. Pathogen propagules have evolved sophisticated processes to locate, attach to, and recognize suitable hosts. Most pathogens have on their cellular surface mucilaginous substances, glycoproteins, and/or fibrillar materials that aid in adherence to the host surface [35]. Successful invasion, infection, and disease development occur when the pathogen successfully overcomes the physical and biochemi-

cal defenses of the host. In the process of invasion, numerous enzyme types (e.g., cutinases, pectinases, cellulases, hemicellulases, amylases, and lipases) can degrade the host cell into chemical fragments, which in turn may elicit the biochemical defenses of the host organism [36, 37]. Research suggests that a disease cycle, similar to that observed in fungal infection of plants, is responsible for the fungal infection process observed in marine algae [38]. The pathogenic nature of the marine fungus *Pythium porphyrae* that infects red algae (*Porphyra* spp.) has been the subject of considerable research [38]. *Pythium porphyrae* infects only a relatively small number of algae species. Studies have demonstrated that *Pythium porphyrae* will attach to and encyst on many species of red algae [38]. However, *P. porphyrae* was shown to infect *Porphyra* spp. and *Bangia atropurpurea* (Roth) only in laboratory culture. Research has implicated porphyran, a sulfated galactan polysaccharide, as a surface determinant on the thallus surface of the marine red alga *Porphyra* spp. that is recognized by zoospores of the pathogenic marine fungus *Pythium porphyrae* [38]. Under laboratory conditions, *P. porphyrae* zoospores attach, encyst, germinate, and form appressoria on thin films of porphyran in suspension. Films composed of agar or agarose media also induced *P. porphyrae* zoospore attachment and cyst formation. However, no appressoria were formed. Films composed of agarose media and either water-soluble extracts of *Porphyra yezoensis* or purified porphyran polysaccharide induced *Pythium porphyrae* appressoria formation [38].

Plants and algae defend themselves against pathogens by a combination of structural characteristics that act as physical barriers to inhibit the invasion and colonization of a host by the pathogen. Biochemical reactions take place in the host tissues to produce substances that either are directly toxic to the pathogen or indirectly create conditions that inhibit infection and further growth and development of the pathogen. It is becoming increasingly clear that plant resistance to pathogen attack depends more on the production of biochemical metabolites in cells before or shortly after infection than on preexisting physical or structural barriers [35].

Antibiotics, antineoplastics, herbicides, and insecticides often originate from plant and microbial chemical defense mechanisms [39]. Secondary metabolites, once considered unimportant products, are now thought to mediate chemical defense mechanisms by providing chemical barriers against animal and microbial predators [35, 39]. This chemical warfare between algae and their pathogens shows promise to provide new natural product leads for biomedical research and agricultural pest control.

Direct acting defense chemicals

Since the discovery of the vinca alkaloids in 1963, many of the major known antitubulin agents used in today's cancer chemotherapy arsenal are products of secondary metabolism. These "natural products" are probably defense chemi-

cals that target and inhibit cell division in invading pathogens [39]. Other phytochemicals such as resveratrol [40], ellagic acid, beta-carotene, and vitamin E may possess anti-mutagenic and cancer-preventive activity [41, 42]. Therefore, it is reasonable to hypothesize that plants and algae produce chemicals that act in defense directly, by inhibiting pathogen proliferation, or indirectly, by disrupting chemical signal processes related to growth and development of pathogens or herbivores.

Indirect acting defense chemicals

Plant resistance to pathogens is considered to be systemically induced by some endogenous signal molecule produced at the infection site that is then translocated to other parts of the plant [43]. Search and identification of the putative signal is of great interest to many plant scientists because such molecules have possible uses as "natural product" disease-control agents. However, research indicates that there is not a single compound but rather a complex signal-transduction pathway in plants that can be mediated by a number of compounds and that appears to influence octadecanoid metabolism. In response to wounding or pathogen attack, fatty acids of the jasmonate cascade are formed from membrane-bound α-linolenic acid by lipoxygenase-mediated peroxidation [44]. Analogous to the prostaglandin cascade in mammals, α-linolenic acid is thought to participate in a lipid-based signaling system where jasmonates induce the synthesis of a family of wound-inducible defensive proteinase inhibitors [45] and low- and high-molecular-weight phytoalexins such as flavonoids, alkaloids, and terpenoids [46, 47].

Fatty acids are known to play an important role in signal-transduction pathways *via* the inositol phosphate mechanism in both plants and animals. In animals, several polyunsaturated fatty acids, such as linolenic acid, are precursors for hormones. Interruption of fatty acid metabolism produces a complex cascade of effects that are difficult to separate independently. In response to hormones, stress, infection, inflammation, and other stimuli, a specific phospholipase present in most mammalian cells acts upon membrane phospholipids, releasing arachidonate. Arachidonic acid is parent to a family of very potent biological signaling molecules that act as short-range messengers, affecting tissues near the cells that produce them. The role of various phytochemicals and their ability to disrupt arachidonic acid metabolism in mammalian systems by inhibiting cyclooxygenase-mediated pathways are of major pharmacological importance.

Eicosanoids, which include prostaglandins, prostacyclin, thromboxane A2, and leukotrienes, are a family of very potent autocoid signaling molecules that act as chemical messengers with a wide variety of biological activities in various tissues of vertebrate animals. It was not until the general structure of prostaglandins was determined, a 20-carbon unsaturated carboxylic acid with a cyclopentane ring, that the role of fatty acids was realized. Eicosanoids are

formed *via* a cascade pathway in which the 20-carbon polyunsaturated fatty acid arachidonic acid is rapidly metabolized to oxygenated products by several enzyme systems including cyclooxygenases [48], lipoxygenases [49, 50], or cytochrome P450s [51] (Fig. 1). The eicosanoids maintain this 20-carbon scaffold, often with cyclopentane-ring, (prostaglandins), double cyclopentane-ring (prostacyclin), or oxirane-ring (thromboxanes) modifications. The first enzyme in the prostaglandin synthetic pathway is prostaglandin endoperoxide synthase, or fatty acid cyclooxygenase. This enzyme converts arachidonic acid to unstable prostaglandin endoperoxide intermediates. Aspirin, derived from salicylic acid in plants, irreversibly inactivates prostaglandin endoperoxide synthase by acetylating an essential serine residue on the enzyme, thus producing anti-inflammatory and anti-clotting actions [52].

Jasmonic acid (Fig. 2), a 12-carbon pentacyclic polyunsaturated fatty acid derived from α-linolenic acid, plays a role in plants similar to that of arachidonic acid metabolites [53] and has a structure similar to the prostaglandins. It is synthesized in plants from α-linolenic acid by an oxidative pathway analo-
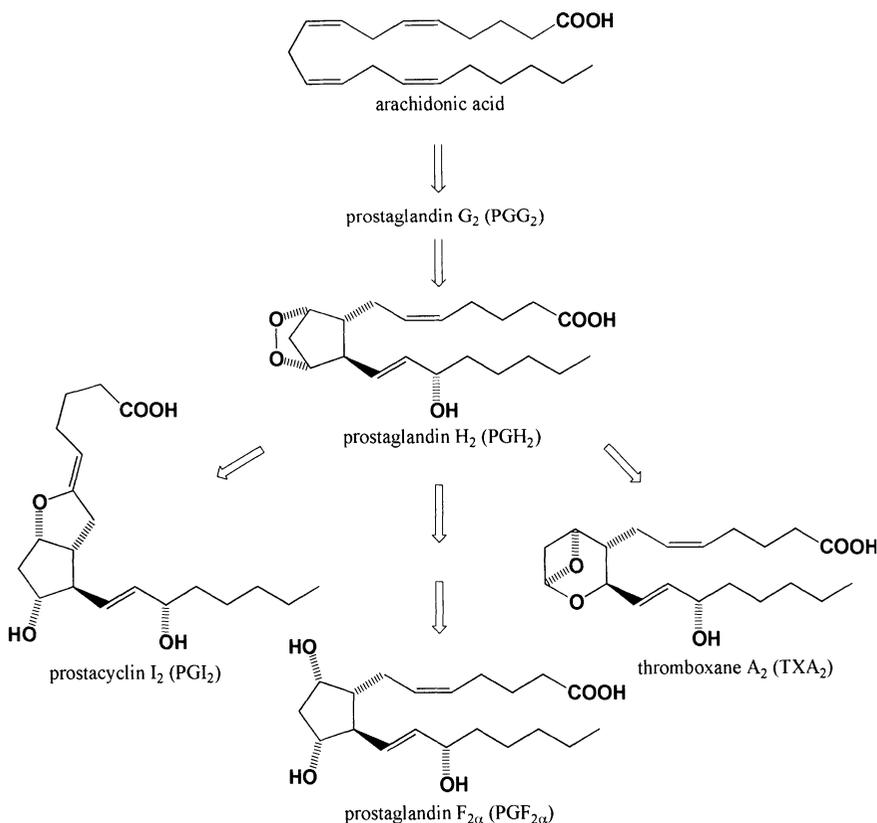

Figure 1. Cyclooxygenase-catalyzed metabolism of arachidonic acid to eicosanoids.