Algal Chemical Ecology

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Editor

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Dedicated to Rick Searles, Fritz Kapraun, and to the memory of Mike Neushul, three wonderful mentors and friends who taught me so much about the biology of algae

Preface

Studies of biotic interactions of algae that involve chemical defenses or signals are currently vibrant, active components of both marine ecological and phycological research. This field is rapidly growing, not only by delving deeper into relatively well-known aspects such as secondary metabolite defenses of tropical and temperate macroalgae to herbivores but also by broadening such work into new habitats and by expanding the field to include many other aspects of the chemical interactions of algae with other organisms or with their environments.

This book has attempted to span the breadth of algal chemical ecology from the perspective of basic ecology. To keep it of manageable length, its scope is restricted primarily to ecological aspects of the field and in doing so, it is unfortunate that a great deal of excellent work in applied areas of algal chemical ecology could not be included. Likewise, algal natural products chemistry is not emphasized in most chapters but the book begins with an introduction to the chemistry of algal defenses that is intended as a primer on natural products chemistry for algal ecologists. In addition, although intended to be broad, it could not be so comprehensively and consequently each author was asked to highlight new areas of research and simply refer a reader to previously published reviews where appropriate. Nevertheless, regardless of previous reviews, the authors were asked to go into depth in one or more areas that they felt would be particularly valuable to illustrate important concepts that could be incorporated into undergraduate- or graduate-level ecology or phycology courses.

As noted, Chap. 1 was intended to help algal ecologists understand the chemistry underlying chemical ecological studies. Chapters 2–5 focus on defenses of macroalgae, primarily though not exclusively on their defenses against herbivores. These chapters are divided by geography and habitat with the relatively well-studied tropical and temperate marine communities the focus of the first two and the relatively understudied freshwater and polar marine communities the focus of the latter two. Chapters 6 and 7 unify these by collectively examining new ways of looking at macroalgal chemical defenses as well as the utility of macroalgae across latitudes and habitats as models for testing and expanding broad ecological theories. Chapter 8 follows with a focused examination of a relatively new area of macroalgal chemical ecology, the multiple potential roles of dimethylsulfoniopropionate in algal ecology and physiology.

The chemical ecology of phytoplankton has been a major new focus of research over the past decade. Chapter 9 was originally intended as a detailed review of this field but unfortunately, for reasons both understandable and unforeseeable, the author was unable to complete it. Fortunately, most individual aspects of the field have been reviewed in a number of recent publications and I am very grateful to Professor Pohnert, himself the author of several of those reviews, for preparing this relatively short chapter that reviews these reviews and that can serve the reader as a unifying introduction into this literature.

Chapters 10–12 all deal with exciting and relatively new areas of study in both macroalgal and microalgal chemical ecology. Chapter 10 examines how herbivores "fight back" in adaptive response to the chemical defenses elaborated by their algal prey. Chapter 11 reviews the relatively few (and comparatively recent) studies of algal secondary metabolite defenses against biofoulers and pathogens that have been conducted with ecologically relevant methodology while Chap. 12 examines the relatively new field studying oxidative burst responses of algae as a defense against these same threats.

Finally, Chaps. 13 and 14 both review other areas of macroalgal and microalgal chemical ecology that have been studied to some extent for a number of years but which are both active areas of current research. Chapter 13 focuses on the multiple ways in which algae utilize defensive compounds to limit damage from ultraviolet radiation. Chapter 14 reviews studies of the behavioral sensory ecology of algae, which is very much understudied in comparison to such work on terrestrial and aquatic animals.

With the exception of Chap. 9, all of the chapters were peer-reviewed and the thoughtful assistance of all the peer-reviewers is deeply appreciated. In almost every case there were at least two anonymous reviews of each chapter and I am grateful to Drs. Katrin Iken and Maureen Callow for coordinating the anonymous reviews of Chaps. 4 and 14, respectively. I am also grateful to Dr. James McClintock, Craig Aumack, and in particular to Margaret Amsler for help in editing several of the chapters. In addition, I thank Dr. Christina Eckey for inviting me to take on this project and Dr. Andrea Schlitzberger for a myriad of assistance in seeing it through to completion. In closing, I am sincerely grateful for the continuing financial support of my own work in algal chemical ecology from the Office of Polar Programs at the United States National Science Foundation and also past support from the Mississippi–Alabama Sea Grant Consortium.

August 2007 Charles D. Amsler

Contents

1 The Chemistry of Algal Secondary Metabolism 1
J.A. Maschek and B.J. Baker
1.1 Introduction 1
1.2 Conceptual Framework 1
1.2.1 Natural Products 1
1.2.2 Natural Product Names 3
1.2.3 Bioactivity of Natural Products 5
1.3 Compound Classes 7
1.3.1 General Overview 7
1.3.2 Terpenes 8
1.3.3 Polyketides 9
1.3.4 Amino-Acid-Derived Natural Products 10
1.3.5 Shikimates 11
1.3.6 Miscellaneous Classes of Algal Natural Products 11
1.4 Algal Chemistry 11
1.4.1 Natural Products Chemistry of Rhodophyta 12
1.4.2 Natural Products Chemistry of Phaeophyta 14
1.4.3 Natural Products Chemistry of Chlorophyta 16
1.4.4 Natural Products Chemistry of Cyanobacteria and Microalgae 17
1.5 Summary 19
References 20

2 Macroalgal Chemical Defenses and Their Roles in Structuring Tropical Marine Communities 25
R.C. Pereira and B.A. P. da Gama
2.1 Introduction 25
2.2 The Tropical Marine Environment 26
2.3 Tropical Macroalgal Natural Products 27
2.4 Tropical Chemically Defended Macroalgae 28
2.5 Tropical Macroalgal Chemical Defenses and Community Structure 29
2.5.1 Are Tropical Macroalgae Better Defended Than Their Counterparts? 39

2.5.2 The Causes and Effects of Ecological Dominance 39
2.5.3 Associational Defenses 40
2.5.4 Chemically Defended Isomorphic Macroalgal Life Stages 41
2.5.5 Intrapopulational Variation 42
2.5.6 Surface Ecology 43
2.5.7 Is Inducible Resistance to Herbivores Common Among Tropical Macroalgae? 45
2.5.8 The Invasive Potential of Chemically Defended Tropical Macroalgae 46
2.6 Conclusions 48
References 49

3 Macroalgal Chemical Defenses and Their Roles in Structuring Temperate Marine Communities 57
V. Jormalainen and T. Honkanen
3.1 Interactions in Diverse Macroalgal Communities 57
3.2 Defense Strategies 58
3.2.1 Induced Defenses against Herbivory 60
3.2.2 Within-Plant Variation in Defenses: Watch Your Valuables! 66
3.3 Consequences of Algal Defenses to Grazers 68
3.3.1 From Defenses to Herbivore Population Dynamics 68
3.3.2 Defenses as Selective Agents 69
3.4 Allelopathy in Space Competition and in Resisting Epibiotism 71
3.4.1 Epibiotism as a Natural Enemy 72
3.4.2 Community Context Matters: Interactions among Hosts, Epibiota, and Grazers 74
3.5 Case Study of *F. vesiculosus* in the Eutrophic Northern Baltic Sea: Genotypically Variable, Plastic Phlorotannins as Chemical Defenses 76
3.6 Conclusions 80
References 81

4 Macroalgal Chemical Defenses in Polar Marine Communities 91
C.D. Amsler, J.B. McClintock, and B.J. Baker
4.1 Introduction 91
4.2 Western Antarctic Peninsula 92
4.3 McMurdo Sound, Antarctica 98
4.4 The Arctic 99
References 100

5 Macroalgal and Cyanobacterial Chemical Defenses in Freshwater Communities 105
F.A. Camacho
5.1 Introduction 105
5.2 Cyanobacteria and Macroalgae: Evolutionary and Ecological Perspectives 106
5.3 Cyanotoxin Structure and Synthesis 107
5.3.1 Hepatotoxins 107
5.3.2 Neurotoxins 108
5.4 Macroalgal Secondary Metabolites 110
5.5 Inducible Synthesis of Secondary Metabolites 111
5.6 Effects on Consumers 111
5.7 Allelopathic Effects 112
5.7.1 Allelopathy in Cyanobacteria 112
5.7.2 Allelopathic Effects of *A. flos-aquae* on a Motile Alga 113
5.7.3 Allelopathy in Algae 113
5.8 Secondary Metabolites and Trophic Interactions 114
5.9 Bioaccumulation of Metabolites at Higher Trophic Levels 115
5.10 Summary 115
References 116

6 New Perspectives for Addressing Patterns of Secondary Metabolites in Marine Macroalgae 121
K.N. Pelletreau and N.M. Targett
6.1 Interpreting Patterns of Chemical Defense in the Marine Environment 121
6.2 A Brief Review of Macroscale Patterns of Algal Chemical Defenses 122
6.3 Patterns of Secondary Metabolites at the Microscale 125
6.3.1 Metabolite Distribution Within the Thallus 125
6.3.2 Temporal Responses Within Algae: Seconds to Weeks 128
6.4 Advances in the Characterization of Patterns of Chemical Defenses 130
6.4.1 Phylogeny Meets Ecology 130
6.4.2 Metabolic Similarities Between Algal Groups 132
6.4.3 The Use of Molecular Tools to Characterize Patterns of Gene Response Involved in Macroalgal Defenses 136
6.5 Conclusion 138
References 139

7 Macroalgal Models in Testing and Extending Defense Theories 147
H. Pavia and G.B. Toth
7.1 Introduction 147
7.2 Defense Theories 148
7.2.1 Optimal Defense Model 148
7.2.2 Carbon-Nutrient Balance Model 149
7.2.3 Growth-Differentiation Balance Model 149
7.3 The Status of Defense Models in Terrestrial Plant Ecology 150
7.4 Empirical Tests of Defense Theories in Marine Studies 151
7.4.1 Optimal Defense Model 151
7.4.2 Carbon-Nutrient Balance Model 161
7.4.3 Growth-Differentiation Balance Model 163
7.4.4 Tests of Hypotheses from More Than One Model 164
7.5 Summary and Conclusions 166
References 167

8 Ecological and Physiological Roles of Dimethylsulfoniopropionate and its Products in Marine Macroalgae 173
K.L. Van Alstyne
8.1 Introduction 173
8.2 Dimethylsulfoniopropionate 174
8.2.1 DMSP Synthesis 174
8.2.2 The Distribution of DMSP in Marine Macroalgae 176
8.2.3 Physiological and Ecological Functions of DMSP 177
8.3 The DMSP Cleavage Reaction and Its Products 178
8.3.1 The DMSP Cleavage Reaction 178
8.3.2 The Functional Significance of the DMSP Cleavage Reaction 179
8.4 Summary 188
References 188

9 Influence of Algal Secondary Metabolites on Plankton Community Structure 195
G. Pohnert
9.1 Introduction 195
9.2 Early Studies 196
9.3 General Considerations 197
9.4 Specific Aspects 198
9.5 Single Metabolites 199
9.6 Conclusions 199
References 200

10 Herbivore Offense in the Sea: The Detoxification and Transport of Secondary Metabolites 203
E.E. Sotka and K.E. Whalen
10.1 Introduction 203
10.2 Proximate Mechanisms of Herbivore Tolerance 204
10.2.1 Defining "Tolerance" 204
10.2.2 Mechanisms of Detoxification and Transport 205
10.3 Detoxification and Macroalgal-Herbivore Interactions 214
10.3.1 Do Detoxification Rates Limit Feeding Rates of Large Grazers? 214
10.3.2 Are Tropical Herbivores More Tolerant of Lipophilic Metabolites Than Are Temperate Herbivores? 215
10.3.3 Is Host Breadth Mediated by Tolerance of Lipophilic Metabolites? 216
10.3.4 Are There Phylogenetic Constraints on Tolerance of Lipophilic Metabolites? 218
10.3.5 Do Herbivores "Eavesdrop" on Their Macroalgal Hosts? 219
10.4 Using Population-Level Variation in Herbivore Traits as an Analytical Tool 219
10.5 Conclusion 221
References 221

11 Secondary Metabolite Defenses Against Pathogens and Biofoulers 229
A.L. Lane and J. Kubanek
11.1 Introduction 229
11.2 Defenses Against Settlement and Attachment 230
11.2.1 Larval Attachment Defenses of *Ulva reticulata* 231
11.2.2 Disruption of Microbial Communication Pathways: An Effective Inhibitor of Settlement and Attachment 233
11.3 Lethal and Growth-Inhibitory Antimicrobials 234
11.3.1 Lobophorolide: A Potent Antifungal Chemical Defense 234
11.3.2 Antifungal Chemical Defenses of Penicillus spp. 236
11.4 Future Perspective and Conclusions 238
References 239

12 Oxidative Burst and Related Responses in Biotic Interactions of Algae 245
P. Potin
12.1 Introduction 245
12.2 Reactive Oxygen Species and Detection Methods 246

12.3 Inducers and Sources of ROS Emission in Biotic Interactions of Marine Algae 248
12.3.1 Elicitors and Sources of ROS in Terrestrial Plant-Pathogen Interactions 248
12.3.2 A Growing Repertoire of ROS Inducers 249
12.3.3 New Insights into ROS Sources in Algae 249
12.4 Oxidative-Burst-Associated Responses 254
12.4.1 Emission of Volatile Halogenated Organic Compounds 254
12.4.2 Lipid Peroxidation and Generation of Oxylipins 255
12.4.3 Phenolics, Cell-Wall Cross-Linking, and Responses to Wounding 256
12.4.4 Gene-Regulated Responses 258
12.5 Functions of the Oxidative Burst in an Ecological Context, the Hallmark of Parasite or Disease Resistance 259
12.5.1 Ecological Functions of the Oxidative Burst 259
12.5.2 Toward New Approaches to Test the Ecological Relevance of Oxidative-Burst-Associated Responses 262
12.6 Conclusions 263
References 264

13 Defense Strategies of Algae and Cyanobacteria Against Solar Ultraviolet Radiation 273
U. Karsten
13.1 Introduction 273
13.1.1 Solar Spectrum and UVR 274
13.1.2 UVR in Aquatic Ecosystems 275
13.2 Effects of UVR on Algae 276
13.2.1 Molecular Targets 276
13.2.2 Induction of Reactive Oxygen Species 277
13.2.3 Ultrastructure of Cells 277
13.2.4 Physiological Processes 278
13.2.5 Ecological Consequences 278
13.3 Protective Mechanisms to Counteract Harmful UV Effects 279
13.3.1 Avoidance 279
13.3.2 Physiological Acclimation 281
13.3.3 Physical Properties 281
13.3.4 DNA Repair 281
13.3.5 De Novo Protein Biosynthesis 282
13.3.6 Antioxidative Potential 282
13.3.7 Photoprotective Substances 283

13.4 Conclusions 291
References 291

14 Algal Sensory Chemical Ecology 297
C.D. Amsler
14.1 Introduction to Sensory Chemical Ecology 297
14.2 Sexual Communication 298
14.2.1 Gamete Attraction 298
14.2.2 Inducers of Gamete Production or Release 299
14.3 Chemoattraction to Nutrients 300
14.4 Sensory Ecology of *Ulva* Spores 301
14.5 Chemical and Physicochemical Modulation of Spore Settlement in Brown Algae 303
References 305

Index 311

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1
The Chemistry of Algal Secondary Metabolism

J.A. Maschek and B.J. Baker(✉)

1.1 Introduction

Natural product chemistry is a branch of organic chemistry that touches upon many other fields of science, especially applied sciences such as medicine, agriculture, and engineering. It is fundamentally a basic science, involved in the discovery, characterization and cataloging of new chemical substances found in nature. Among other basic scientists, biologists and ecologists recognized some time ago that natural products might help explain species composition, distribution, and diversity in some settings, establishing the field of chemical ecology (Harborne 1989). The field has developed largely around collaborations of chemists and biologists, each bringing their own knowledge base to chemical ecological questions. This chapter is intended as an overview of natural product chemistry with an emphasis on the chemical aspects of algal defensive metabolites. It is our hope that algal ecologists will gain insight into the chemistry in the same manner that chemists will acquire a deeper understanding of the ecology from the remaining chapters of this book.

1.2 Conceptual Framework

1.2.1 Natural Products

Similar to those of other sessile organisms, successful life history strategies employed by algae must include adaptations to their biological communities. Such survival strategies may include behavioral, physical, or chemical means (Hay and Fenical 1988; Lobban and Harrison 1994; Dawes 1998; Stachowicz 2001). Chemical strategies, whereby an organism may produce a toxic defensive compound or an

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antifouling metabolite, utilize what chemists refer to as "natural products," literally alluding to products made by living organisms. Defining what a natural product is can be a slippery slope; generally, we know one when we see it, but describing the identifying characteristics inevitably invites divisiveness. It is not the intent of our discussion here to devolve into the philosophy behind the concept, but rather to present typical characteristics observed among natural products.

The term natural product is used synonymously with "secondary metabolite ," the latter of which may have more obvious characteristics. In particular, "secondary" is used here in the context of functional significance, so that something that is secondary is less important than something that is primary. Indeed, primary metabolites are the nuts and bolts of a living system: amino acids, cofactors, and lipids, for example. Cellular function is not possible without primary metabolites. Similarly, organismal function is dependant on primary metabolism, extending "primacy" to large molecules, such as proteins, but perhaps enveloping other small molecules such as visual pigments and neurotransmitters. Primary metabolites tend to be ubiquitous; proteins and enzymes from all organisms are composed from a selection of 20-odd amino acids, and genes are built from combinations of four purine and/or pyrimidine bases. Thus primary metabolites are largely limited to several dozen small molecules, and polymers thereof, and drive all living systems, providing energy, structure, and reproductive capacity.

One of the ways to identify a secondary metabolite, then, is to establish that it is not a primary metabolite. For example, only a small group of red algae make C_{15} halogenated acetogenins (Sect. 1.3.1). These fatty-acid-derived compounds are not nuts and bolts, nor are they ubiquitous, and so they are clearly secondary. Consider, however, steroid derivatives produced by algae and plants known as phytosterols (Parish and Nes 1997). These sterols (cholesterol-like compounds) bear alkylation at C-24, differentiating them from animal sterols. They have roles in membrane structure, a primary characteristic, but they are often species-specific and usually fall under the guise of secondary metabolites. Most often, secondary metabolites are found to be associated with an organism's interaction with its environment. Phlorotannins (Sect. 1.4.2), for example, can impart distastefulness to potential predators, which is a secondary characteristic even though phlorotannins can have primary roles in brown algal cell wall biosynthesis (Ragan and Glombitzka 1986; Amsler and Fairhead 2006). Thus, in the modern use of the term, when we speak of a secondary metabolite or a natural product, we are referring to compounds that are not involved in the development or maintenance of an organism, limited in their biological distribution, often species-specific, and most often produced by an organism for intervention in ecological interactions (Williams et al. 1989). Note that the lack of a demonstrated ecological role for a natural product does not mean one does not exist, and even the failure to identify a particular role is not sufficient to argue against ecological relevance. Careful and thorough investigations of the ecological roles for many natural products remain to be accomplished.

Chemical structure can often be used by itself to recognize a secondary metabolite because of their common biosynthetic origin. Terpenes and polyketides, for

example, account for most of the secondary metabolites (Buckingham 2002) and can be recognized as oligomers of the primary metabolites isoprene and acetate, respectively. An expert can discern arrangements of these oligomers and their associated source(s). Specific details of these chemical classes will be discussed in Sect. 1.3.

1.2.2 Natural Product Names

Like in other fields of science involved in characterizing and cataloging, natural product chemists name their discoveries. The International Union of Pure and Applied Chemistry (IUPAC) has rules of nomenclature, much to the chagrin of many a student of organic chemistry. However, systematic names of natural products, as IUPAC dictates, are inappropriate for common usage, bearing multiple nests of convoluted descriptions of functionalization (IUPAC 1976; Giles 1999; Favre et al. 2004). Common usage allows for nicknames, which are bestowed at the time a new compound is described in the literature, and are generally more succinct and easy to pronounce, and especially, more easily associated mentally with a chemical structure. As an example, most of us are aware of our personal cholesterol level, but few of us would fully comprehend the significance of our (3*S*,10*R*,13*R*,17*R*)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-1H-cyclopenta[a]phenanthren-3-ol level. Thus, a common naming system is critical for natural product chemists. Nonetheless, many scientists outside the field of natural products can be baffled by the odd amalgamation of terms that comprise the common names assigned, and perhaps worse, may still find difficulty in pronouncing them. A brief explanation is presented here to assist the nonspecialist.

A newly described natural product will normally be assigned a common name based either on its species of origin or, alternately, on a geographic characteristic associated with its acquisition. **Laurin**terol (Fig. 1.5a), for example, is a common name assigned to a compound first isolated from a red alga of the genus ***Lauren****cia* (Irie et al. 1966), while **kahala**lide (Fig. 1.7e) describes a series of compounds isolated from a green alga (and its sacoglossan predator) from the **Kahala** district of O'ahu, Hawaii (Hamann and Scheuer 1993). Purists will argue the capriciousness of the latter, and certainly a natural product isolated from a Caribbean brown alga may one day turn up in another collected from Okinawan waters. However, as biological taxa undergo constant revision, genus and species names may become obsolete or their members reassigned, so that neither of these guidelines bestows durability or accuracy. Biologically based names can also suffer the discovery of a symbiotic or dietary source, such as the case for aplysiatoxin, which was first described from Hawaiian sea hares (Aplysiidae) (Watson and Rayner 1973; Kato and Scheuer 1974) but later proved to be of cyanobacterial origin. The ultimate aim in assigning a common name is to achieve uniqueness with some semblance of historical origin, be it biological or geographical.

The origin of the natural product occupies the part of the compound name that IUPAC refers to as the "parent" structure. Appended to the name of the parent is a suffix that indicates the primary chemical function (functional group) of the molecule. For instance, in the earlier-mentioned example, laurinterol has an alcohol functional group, which is denoted by IUPAC systematic nomenclature with the "-ol" ending. The "-ide" ending of kahalalide similarly identifies a lactone functionality. Caulerpenyne (Fig. 1.7a), isolated from the green algae ***Caulerp****a flexilix* (Amico et al. 1978), contains a carbon-carbon double bond, which is referred to as an alk**en**e, as well as a carbon-carbon triple bond, known as an alk**yne**. Alternately, the suffix may convey biological activity information, or may categorize the structural class (Sect. 1.2) to which the natural product belongs. Aplysiatoxin (Fig. 1.8g), for example, is broadly cytotoxic and has been implicated in "swimmers itch" in shallow water environs of the South Pacific (Fujiki et al. 1985). Table 1.1 illustrates several other ways the suffix of a compound may provide further information.

There are exceptions to these guidelines. Ilimaquinone, for example, is a compound isolated from a Hawaiian sponge (Luibrand et al. 1979). The suffix, as guidelines suggest, imparts information about the chemical function present in the natural product, the quinone function. Ilima, rather than deriving from the species binomial or a geographical region, is the Hawaiian word for yellow, the characteristic color of the natural product. Putricine and menthol have obvious odoriferous characteristics associated with their constitution. Honorific names are rare among natural products (Herb et al. 1990; Cooray et al.1988).

Nomenclature based on a parent term with an appended suffix accounts for most natural product names. However, as related compounds are identified, or even when a suffix has to denote multiple functional groups, a variety of modifying terms can be employed. For example, the common prefix "nor-" denotes the removal of a skeletal atom from the parent structure; the loss of two or more skeletal atoms is indicated by combining an appropriate numerical prefix with "nor-", e.g., "dinor-", "trinor-" (Giles 1999). Table 1.2 lists additional examples of commonly encountered modifying terms.

Table 1.1 Examples of natural product nomenclature suffix usage

Functional group	Structural class	Bioactivity	Biological origin
-al (aldehyde)	-sterol (steroid)	-toxin (toxin)	-mycin (Actinomycete)
-ol (alcohol)	-oside (sugar)	-statin (inhibitor)	-gorgin (gorgonian)
-one (ketone)	-ceramide (ceramide)	-lysin (lytic)	-spongin (sponge)

Table 1.2 Nomenclature modifying terms

Atom replacement	Bond rearrangements	Skeletal modifications
Aza (C → N)	Abeo (general rearrangement)	Apo (side chain loss)
Oxa (C → O)	Cyclo (cyclic rearrangement)	De (functional group loss)
	Iso (isomeric form)	Homo (add skeletal atom)
	Seco (bond removal)	Nor (skeletal atom loss)

The pronunciation of natural product names stresses the individual contributions. Thus, biological or geographical names incorporated into parent names of natural products are generally pronounced the way they are as biological or geographical names. Caulerpenyne, with its alkene and alkyne functionality described earlier, is pronounced to emphasize each of those three units: Caulerp en yne (kôl erp ĕn īn). Isocyanopupukeanane (Burreson et al. 1975) looks like a mouthful, but when dissected into its functional group, the isocyano (ī sō sī an ōh) group, its geographical origin, Pupukea, Hawaii (pu pu kay a), and finally its structural class, an alk**ane** (-ān), it is much more manageable: īsō sīanōh pu pu kay ən ān. Structural classes can often combine some of the same terms, so that a diterpene (dī tûr pēn) that has been metabolized to remove two carbon atoms from its skeleton becomes a "dinor" (dī nôr) diterpene or a dinorditerpene (dī nôr dī tûr pēn). Select common names and terms used in this chapter will include phonetic pronunciation.

1.2.3 Bioactivity of Natural Products

Natural products are inherently bioactive. Bioactivity is a physiological response to a molecule or ion binding to a ligand, with downstream cascading consequences. Natural products are themselves products of enzymatic processes, demonstrating their ability to interact with receptors. Whether they bind other, nonsynthetic receptors likely depends on whether they have evolved in response to environmental pressures or whether they accumulate as a result of diverted primary metabolic pathways (Williams et al. 1989; Clardy 1995).

Receptor binding requires exquisite molecular organization, as generalized in Fig. 1.1. Proteins and enzymes present a plethora of functional groups on their surface, providing opportunity for molecular interactions. It is only when a potential binding molecule has its own array of functionality that complements those presented on the surface, or more likely in a pocket of an enzyme, that binding can take place. Binding, as measured by the ratio of bound to unbound natural product, is dependent on the strength of the molecular interactions depicted in Fig. 1.1 in order of decreasing strength: ionic bonds (**A**, structure II), hydrogen bonds (**B**, structure II), π-stacking interactions (**C**, structure II), which involve noncovalent aromatic interaction in which p-orbitals of flat aromatic molecules overlap and align parallel to each other, much like stacked coins, and, finally, van der Waals forces (**D**, structure II), also referred to as London dispersion forces.

The receptors of ecological interactions are still not well understood. In fact, many ecological studies have failed to demonstrate well-defined roles for natural products (Pawlik 1993). Most experimental evidence for natural product receptors derives from biomedical applications. Kahalalide F, for example, is a potent cytotoxic depsipeptide (see Sect. 1.3.2.3) initially found in the sacoglossan mollusc *Elysia rufescens* and later in the green alga it feeds upon (Hamann and Scheuer

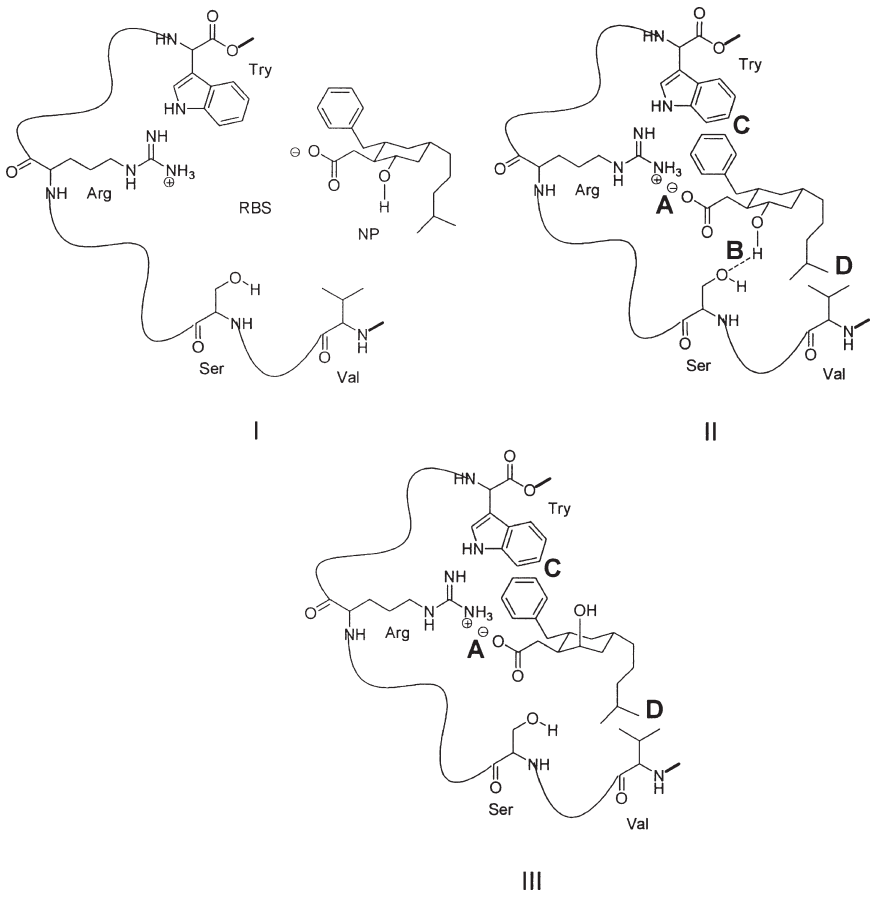

Fig. 1.1 Illustration of a hypothetical natural product (NP) interacting with a receptor binding site (RBS). I. Receptor is indicated by four amino acids (*Val* valine, *Ser* serine, *Arg* arginine, *Try* tryptophan) arrayed along a peptide chain (*wavy lines*); NP approaches RBS from open face. II. NP binds with four amino acids: A, carboxylate of NP forms ionic bond with *Arg* guanidinium group of RBS; B, alcohol group of NP forms hydrogen bond with alcohol group of *Ser*; C, phenyl ring of NP interacts with RBS via π-stacking with *Try* indole ring; D, lipophilic chains of NP and *Val* associate using van der Waals forces. III. The stereochemical configuration of NP functional groups is critical to strong binding; notice that the change in stereochemical configuration of NP alcohol results in the absence of a hydrogen bond in structure III, which would make III less stable than II

1993). Currently in phase II clinical trials as a treatment for melanoma, hepatocellular carcinoma, and non-small-cell lung cancer (Hamann 2004), the compound has a mode of action that is not well understood, though it has been deemed necrosis-like and characterized by cytoplasmic swelling and DNA clumping (Janmaat et al. 2005).

1.3 Compound Classes

1.3.1 General Overview

Secondary metabolites are classified according to the biosynthetic pathway from which they are derived. Biosynthetic and genetic studies have revealed that a limited number of core biosynthetic pathways, generalized in Fig. 1.2, are responsible for the production of most of the natural products (boxed in Fig. 1.2). The Bioinformatics Center of Kyoto University and the Human Genome Center of the University of Tokyo have created a remarkable bioinformatics resource called the Kyoto Encyclopedia of Genes and Genomes (Kanehisa et al. 2004). This user-friendly database provides a graphical representation of biological pathways, replete with diagrams of molecular interactions, reactions, and relations, as well as structures of primary and secondary metabolites. Moore (2005, 2006) has authored two recent reviews on the biosynthesis of marine natural products from both micro- and macroorganisms.

While common biosynthetic pathways may provide the framework for the various classes of secondary metabolites, their functionality is imparted by specialized tailoring enzymes that are often unique to natural products (Walsh 2004; Hertweck et al. 2007). Whether it is the addition of alcohol groups, halogenation (Gribble 1998), oxidation, reduction, stereochemical manipulation, or cyclization, it is often these functionalities that make secondary metabolites unique and bioactive.

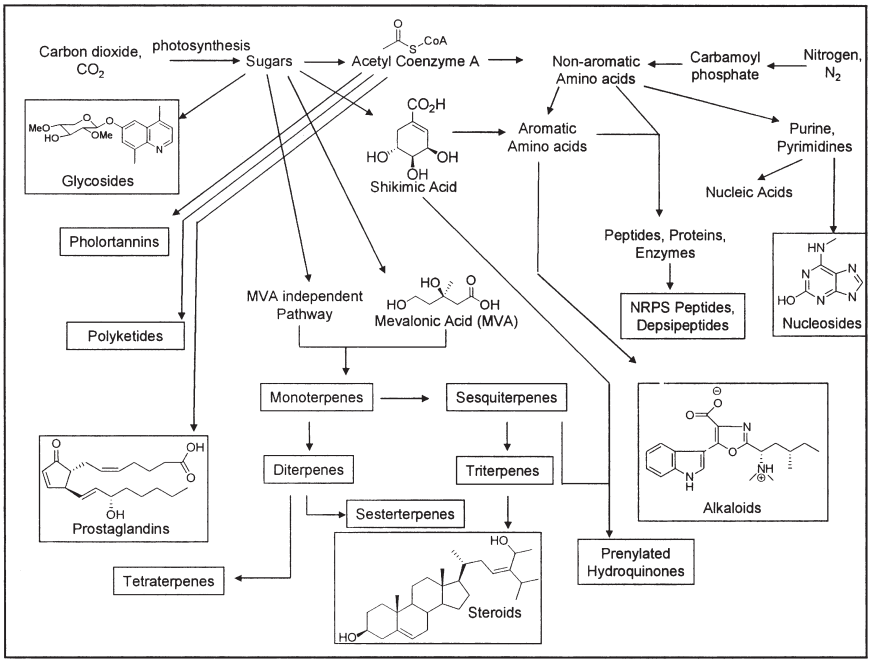

Fig. 1.2 Biosynthetic origin of the major classes of natural products

1.3.2 Terpenes

Terpenes are a large and diverse class of compounds produced by a wide variety of organisms, though plants are an especially prolific source. The terms terpenoid and isoprenoid can be used interchangeably with terpene, though, strictly, terpenes are hydrocarbons (composed only of carbon and hydrogen) while terpenoids and isoprenoids have been further functionalized.

More than half of the reported secondary metabolites from macroalgae are isoprenoids. Terpenes, steroids, carotenoids, prenylated quinines, and hydroquinones make up the isoprenoid class, which is understood to derive from either the classical mevalonate pathway, or the mevalonate-independent pathway (Stratmann et al. 1992). Melavonic acid (MVA) (Fig. 1.2) is the first committed metabolite of the terpene pathway. Dimethylallyl (dī měth əl ăləl) pyrophosphate (DMAPP) (Fig. 1.3) and its isomer isopentenyl pyrophosphate (IPP, Fig. 1.3) are intermediates of the MVA pathway and exist in nearly all life forms (Humphrey and Beale 2006). Geranyl (jə rən əl) (C_{10}) and farnesyl (C_{15}) units are generated by head-to-tail (Fig. 1.3) condensation of two (for C_{10}) or three (for C_{15}) 5-carbon DMA-like isoprene units, identifiable in final products by the characteristic fish-tail repeating units, as traced over the structure of a sesquiterpene in Fig. 1.3 (Humphrey and Beale 2006). Additional IPP condensation with farnesyl pyrophosphate (FPP)

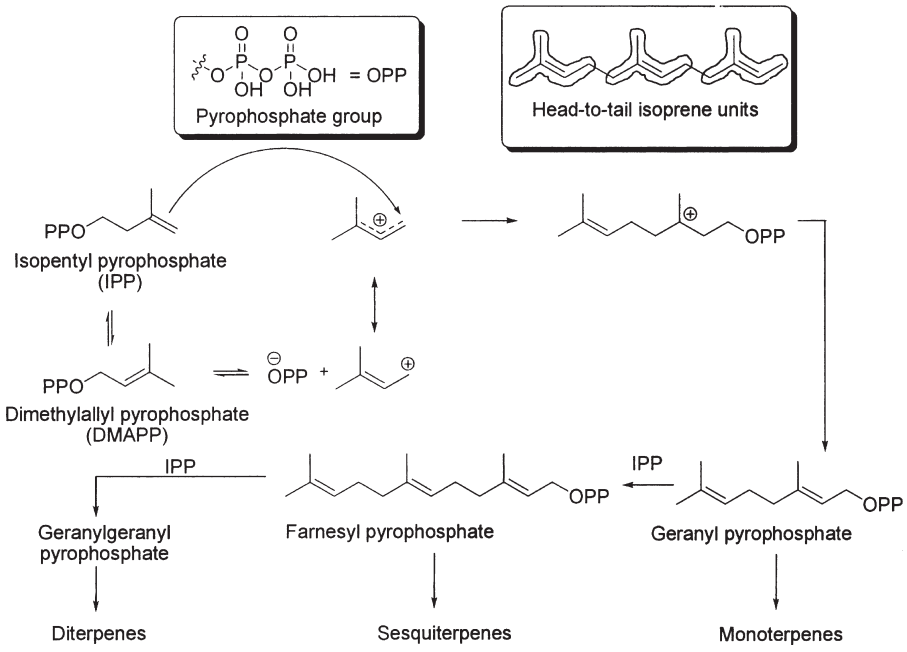

Fig. 1.3 Summary of terpene biosynthetic pathway

yields geranylgeranyl pyrophosphate, which is the precursor of all diterpenes (C_{20}), while the condensation of two FPP, in a head-to-head fashion, leads to squalene, the precursor of all triterpenes (C_{30}) and sterols (Brown 1998).

1.3.3 Polyketides

The second largest class of compounds reported from macroalgae is the polyketides, which comprise approximately a quarter of known algal compounds (Blunt et al. 2007). Polyketides are polymers of acetate (C_2) and occasionally propionate (C_3) and are very similar to fatty acids in their biosynthetic origin. Polyketides can be found in plants, animals, bacteria, and fungi. With a range of activities as broad as their structures, the polyketides are a diverse family of natural products classified based upon the polyketide synthases (PKSs) responsible for their biosynthesis, primarily type I and type II.

All polyketides use the same general mechanism for chain elongation. Acetyl coenzyme A provides acetate (C_2) units, which are condensed by a ketosynthase (KS). This in turn catalyzes condensation of the growing chain onto an acyl carrier protein (ACP), as generalized in Fig. 1.4. Enzymes such as ketoreductase (KR), enoyl reductase (ER), and dehydratase (DH) establish the oxidation state of carbon during translation, imparting structural diversity. Successive translation of each module leads to a chain of the required length that is eventually passed to thioesterase (TE), which releases the chain as a free acid or lactone.

Type I polyketides include linear and macrolide -type structures, including algal toxins such as the brevetoxins (Fig. 1.8a) as well as microbially derived antibiotics such as erythromycin (Staunton and Weissman 2001). Type II polyketide synthases yield condensed aromatic ring systems (Hertweck et al. 2007), such as those found in plant flavonoids, algal phlorotannins (Fig. 1.7), and, perhaps most well-known, microbe-derived antibiotics such as tetracyclin. General enzyme terminology is the same for type I and type II; however, the enzymes are fundamentally different. Type I PKSs are large, multifunctional enzyme complexes where intermediates translate along modules, whereas type II PKSs involve iterative multienzyme complexes of single proteins. Polyketides synthesized by type II PKS will typically have chain lengths of 16 (octaketides), 20 (decaketides), or 24 (dodecaketides) (Hertweck et al. 2007). Other PKSs have been described, and it is becoming apparent that the diversity of these systems is greater than previously recognized (Shen 2003).

Structurally related to polyketides are another class of linear, acetate-derived compounds, the acetogenins ("genesis in acetate"). These compounds are often indistinguishable from polyketides based purely on inspection of their chemical structure. However, with their origin in the fatty acid pathway, they are not biosynthesized by polyketide synthases but rather by fatty acid synthases (FASs). Algal acetogenins are often odd numbered (C_{11} and C_{15} are the major algal acetogenins) due to decarboxylative degradation of the parent fatty acid (Sect. 1.4.1).

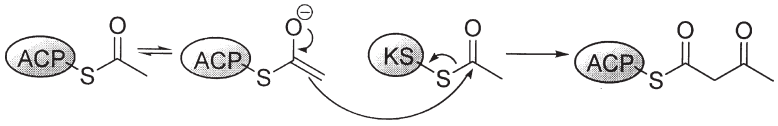

Fig. 1.4 Chain extension during polyketide biosynthesis

1.3.4 Amino-Acid-Derived Natural Products

Natural products derived from amino acids form a broad and divergent group, including simple amino acid derivatives, alkaloids, and small, often cyclic, polypeptides. Simple amino acid derivatives, which are not uncommon in algae, are often oxidation or rearrangement products of one of the 20 common amino acids. Alkaloids and polypeptides are more complex in their structural modifications.

Alkaloids

The term alkaloid has a long history and has been applied to compounds of many different pathways and structures. Originally, the term was used to describe any compound with a basic nitrogen (amine), often bitter tasting, and usually aromatic in structure. Alkaloids are more often recognized now as highly condensed amino acids, which may or may not have a *basic* nitrogen, bitter taste, or aromatic structure, but can also include lipophilic nitrogen containing compounds whose origin from amino acids is less clear. There is no unifying biosynthetic pathway for alkaloids, but rather many different classes of alkaloids have related pathways. The KEGG database describes two fundamentally different schemes of interrelationships, but even that only addresses a fraction of known alkaloids.

Nonribosomal Peptides

Peptide bonds are formed from the condensation of the carboxylic acid carbon of an amino acid with the α-nitrogen of a second amino acid. Large molecular weight polymers of amino acids constitute the proteins and enzymes of primary metabolism. A number of smaller polymers ("oligomers") are found in nature in a species-specific manner. Too small for structural roles or enzymatic activity, these peptides have demonstrated a number of bioactivities, including biomedical as well as ecological (Tan 2007). Recent research has shown that these small peptides are not produced by the translational biochemistry of the ribosome, where structural peptides and enzymes originate, but rather are biosynthesized by a group of enzymes referred to as nonribosomal peptide synthases (NRPS). NRPS products and polyketides share a similar model of biosynthesis. Both are created on modular enzymatic assembly lines, with their structural diversity governed by optional

enzymes within the enzyme complexes (Walsh 2004). In fact, it is not uncommon to find secondary metabolites of mixed PKS-NRPS biosynthetic origin (see curacin in Sect. 1.4.4). Products from NRPSs are secondary metabolites and often include ester linkages among the peptide bonds, producing natural products known as depsipeptides, such as the kahalalides, discussed previously. Most of the NRPS products found in algae are isolated from cyanobacteria and microalgae (Sect. 1.4.4).

1.3.5 Shikimates

Shikimates, which include phenylalanine, tyrosine, tryptophan, and their derivatives, are represented by many aromatic natural products, including hydroquinones found in brown algae such as *Sargassum* (Segawa and Shirahama 1987). Flavonoids are a structural class of shikimates found in plants, including isoflavonoids or neoflavonoids, as is the γ-pyrone (coumarin) core structure (Knaggs 2003).

1.3.6 Miscellaneous Classes of Algal Natural Products

Other natural product classes are found less frequently in algae. Nucleosides are constructed from nucleobases often linked to sugars derived from nucleic acids (Rosemeyer 2004). Terpenes, polyketides, and amino acid derivatives can be sugar-bound, or glycosylated, (Pfander and Stoll 1991). Glycosylated compounds are known as glycosides, the sugar is referred to as the glycone, and the remaining portion of the molecule is the aglycone. Arsenic-containing sugars are produced by brown algae (Usov et al. 2001). Prenylated quinones and hydroquinones are examples of mixed biogenesis, as their aromatic rings are derived from the shikimic acid pathway while isoprene units constitute their side chain. The term prenyl denotes an isoprene group.

1.4 Algal Chemistry

Macroalgae have accounted for almost 3,000 natural products representing ~20% of the chemistry reported from the marine realm. During the 1960s, the period when dedicated marine natural product laboratories were being established worldwide, more than 50% of newly reported natural products came from macroalgae, though that number has steadily decreased and now hovers around 10% annually (Munro and Blunt 2005; Blunt et al. 2007). Research into the chemistry of marine microalgae and cyanobacteria is thriving, representing almost 50% of the literature accumulated since 2000 (Blunt et al. 2007). Despite the recent shift away from macroalgal chemistry, interest in several macroalgal compounds is high for

pharmaceutical application (e.g., sulphated polysaccharides, kahalalides) (Smit 2004) and as antifouling agents (e.g. fimbrolides) (Bhadury and Wright 2004).

1.4.1 Natural Products Chemistry of Rhodophyta

With more than 1,500 compounds reported, the secondary metabolite chemistry of Rhodophyta is richer than those of other macroalgae, both in terms of abundance and diversity. With the exception of phlorotannins, all major classes of natural products are represented among Rhodophyta (Munro and Blunt 2005). Red algae elaborate predominantly isoprenoid and acetogenin derivatives, along with some amino acid, shikimate and nucleic acid derivatives. What truly distinguishes red algae is that they are impressive producers of halogenated compounds, with over 90% of those reported containing bromine or chlorine, compared with only 7% of green algal compounds and less than 1% of those from brown algae (Harper et al. 2001). These halogenated terpenoids have shown only a paucity of nonecological bioactivity, which may explain the decline in interest in red algal chemistry (Blunt et al. 2007).

More than half of the reports (57%) on Rhodophyta chemistry come from Family Rhodomelaceae and the vast majority (85%) of that represents chemistry of the genus *Laurencia*, which produces a wealth of halogenated sesquiterpenes and C_{15} acetogenins, along with a few higher terpenes (C_{20} and greater), as seen in Fig. 1.5. *Laurencia* sesquiterpenes, like those from several other rhodomelacean genera, are typically cyclized, often polycyclic, as seen in laurinterol (lō rĕn tûr ôl) (Fig. 1.5a) (Irie et al. 1966) and pacifenol (Fig. 1.5b) (Sims et al. 1971). Chemically unusual spiro-ring fusions, rings connected through just one atom, observed in elatol (Fig. 1.5c) (Sims et al. 1974), are not uncommon among *Laurencia* sesquiterpenes. Higher terpenes in Rhodophyta are largely limited to *Laurencia*, with some exceptions (see Kubanek et al. 2005). Diterpenes are primarily monobrominated polycycles, such as the irieol (Fig. 1.5d) (Fenical et al. 1975), while triterpenes are most often polyether in nature, such callicladol (Fig. 1.5e) (Suzuki et al. 1995). In fact, among all the families of Rhodophyta, polyhalogenated higher terpenes are rare, represented by a couple of dozen dibromominated polycycles and a few monobromo, monochloro *Laurencia* polycycles. Sesterterpenes are not represented in Rhodophyta.

Laurencia is nearly alone in elaborating a rather unique series of C_{15} acetogenins, such as laurepinnacin (Fig. 1.5f) (Fukuzawa and Masamune 1981), and laurallene (Fig. 1.5g) (Fukuzawa et al. 1979). The C_{15} carbon backbone (Fig. 1.5h) (Kigoshi et al. 1986) is hypothesized to originate from a C_{16} carboxylic acid precursor via apparent decarboxylation to the enyn e functionality commonly found terminating this family of largely halogenated compounds. Besides the enyne, or its isomeric form, the allene, the C_{15} acetogenins are generally adorned with bromine and chlorine (or both) with oxygenation on the adjacent carbon. This pattern of halogen with vicinal (adjacent) oxygenation reflects their assembly on the carbon skeleton via carbocation chemistry (Staunton and Weissman 2001).

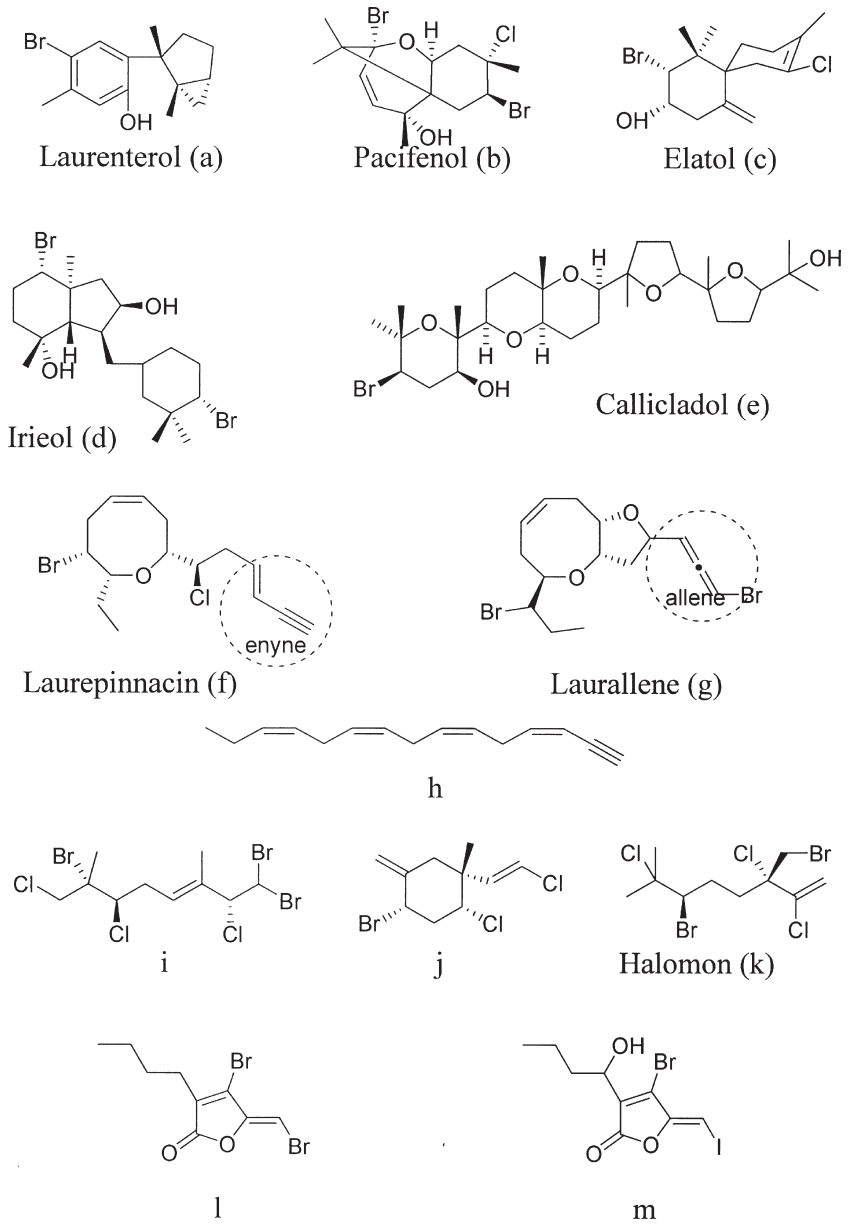

Fig. 1.5 Representative Rhodophyta chemistry

Three other Rhodophyta families, Rhizophyllidaceae, Plocamiaceae, and Delesseriaceae, distinguish themselves from the Rhodomelaceae by producing largely halogenated monoterpenes. The Rhizophyllidaceae genera *Chondrococcus*, *Desmia*, and *Ochtodes*, the plocamiacen *Plocamium*, and the delesseriacean *Pantoneura*, are,

with few exceptions, the only sources of monoterpenes among the red algae. These red algal monoterpenes are often highly halogenated linear (Fig. 1.5i) (Bates et al. 1979) or monocyclic (Fig. 1.5j) (Crews et al. 1978). One notable exception is the rhizophyllidacean *Portiera*, which elaborates one of the most intensely studied red algal anticancer metabolites, halomon (Fig. 1.5k) (Fuller et al. 1992).

A few other genera in Rhodomelaceae (for example, *Odonthalia*, *Polysiphonia*, *Rytiphloea*, *Vadalia*, *Symphyocladia*) elaborate brominated phenol s. The genus *Acanthophora* stands out as a producer of nonhalogenated steroids. Several genera in Bonnemaisoniaceae (*Delesea*, *Asparagopsis*, *Bonnemaisonia*, *Ptilonia*) are notable as producers of small, linear halongenated ketones and branched lactones. The fimbrolides, for example (Fig. 1.5l, m), are a series of halogenated furanones from *Delisea pulchra* (Kazlauskas et al. 1977) that have been shown to interfere with signaling in bacteria and provide an antifouling defense (Kjelleberg and Steinberg 2001) by functioning as an intracellular signal antagonist (Rasmussen et al. 2000).

1.4.2 Natural Products Chemistry of Phaeophyta

More than 1,140 secondary metabolites have been reported from Phaeophyceae. The characteristic compounds of these brown algae include diterpenes, phlorotannins, and small C_{11} acetogenins, all with very little halogenation (Blunt et al. 2007). Phlorotannins are the true niche compound from brown algae, often accounting for an astonishing 10–20% of dry weight (Ragan and Glombitzka 1986; Amsler and Fairhead 2006).

Almost a third of the reported brown algal chemistry comes from a single genus, *Dictyota*, which has elaborated a wealth of terpenes (>250) (Munro and Blunt 2005). Diterpenes dominate *Dictyota* chemistry and are typically di- and tricyclized, as seen in dictyol E (Fig. 1.6a) (Danise et al. 1977), amijiol (Fig. 1.6b) (Ochi et al. 1980), Fig. 1.6c (Tringali et al. 1984), and dictyoxetane (Fig. 1.6d) (Pullaiah et al. 1985).

Another dictyotalean genus, *Dictyopteris*, has been reported to produce an array of C_{11} cyclic or acyclic acetogenins derived from higher fatty acids (Stratmann et al. 1992). Examples include the hydrocarbons dictyopterene A (Fig. 1.6e) (Moore et al. 1968) and dictyopterene D'[B1] (Fig. 1.6f) (Moore and Pettus 1971), which act as pheromones in sexual reproduction (Stratmann et al. 1992). The compounds are short lived and undergo facile degradative oxidation to yield compounds such as dictyoprolene (Fig. 1.6g) (Yamada et al. 1979) and dihydrotropone (Fig. 1.6h) (Moore and Yost 1973). In a true exhibition of efficiency, these degradative products have also been shown to act as a chemical defense (Hay et al. 1998).

Phlorotannins, or polyphenols, are structural classes of polyketides found exclusively in brown algae and classified into six groups based upon variations in their assemblage from the polymerization of phloroglucinol (Fig. 1.6i) (1,3,5-trihydroxybenzene) units (Ragan and Glombitzka 1986; Targett and Arnold 2001). Fucols (Fig. 1.6j) (Geiselman and McConnell 1981), phlorethols, fucophlorethols, fuhalols, isofuhalols (Fig. 1.6k) (Grosse-Damhues and Glombitzka 1984), and eckols differ in

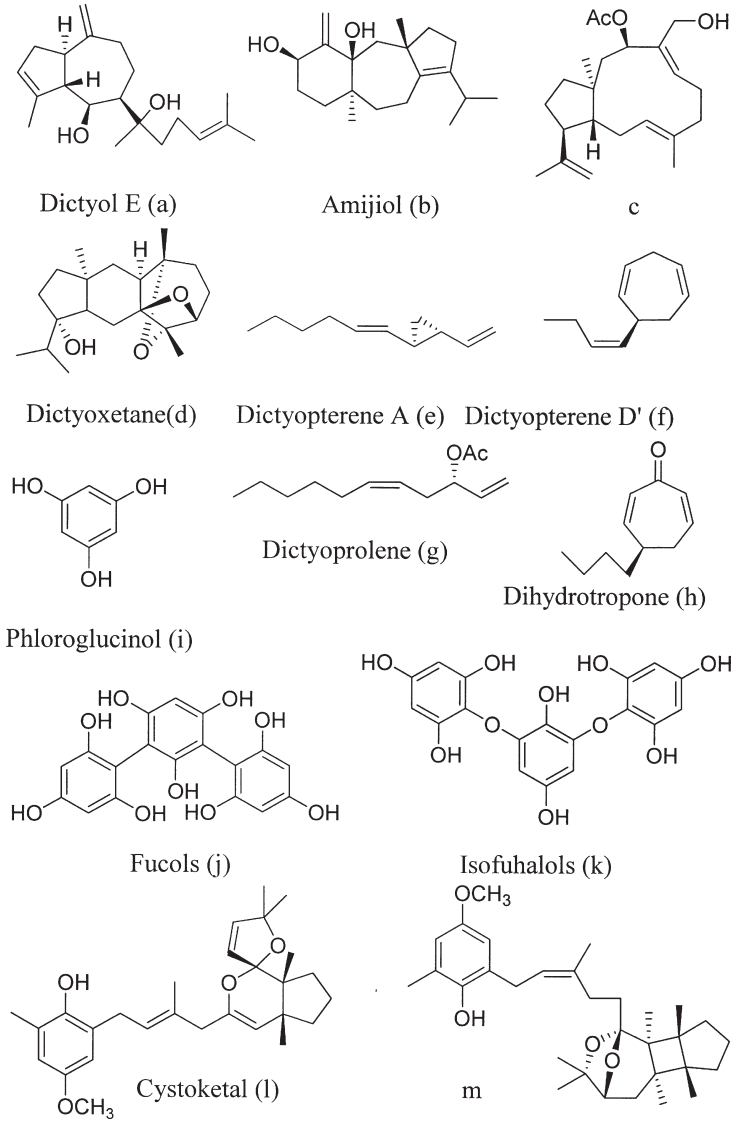

Fig. 1.6 Representative Phaeophyta chemistry

the number of hydroxyl groups present and in their bond linkages. All but the fucols are attached by ether bonds. The phloroglucinol units are often esterified or acylated, and can dimerize or polymerize into larger units. These compounds also exhibit a broad range in size, thought to polymerize as they age and thereby grow larger. They are typically 10–100 kDa, although their range spans from as small as 126 Da to as large as 650 kDa (Targett and Arnold 2001; Boettcher and Targett 1993). Stored within cells in vessels called physodes, phlorotannins have been reported from