



How the Ecology of Calcified Red Macroalgae is Investigated under a Chemical Approach? A Systematic Review and Bibliometric Study

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Abstract

Characteristics such as calcareous morphology and life cycle are used to understand the ecology of calcified rhodophytes. However, there is limited information regarding their chemical profiles and biological activities. Therefore, a systematic review (PRISMA) was conducted to assess the influence of the chemistry of calcareous rhodophytes on ecological interactions in the marine environment. The keywords used were: ["Chemical AND [Ecology OR Interaction OR Response OR Defense OR Effect OR Cue OR Mediated OR Induce]"] AND ["Red Seaweed" OR "Red Macroalgae" OR Rhodophy?] AND [Calcified OR Calcareous] in Science Direct, Scielo, PUBMED, Springer, Web of Science, and Scopus. Only English articles within the proposed theme were considered. Due to the low number of articles, another search was conducted with three classes and 16 genera. Finally, 67 articles were considered valid. Their titles, abstracts, and keywords were analyzed using IRaMuTeQ through factorial, hierarchical and similarity classification. Most of the studies used macroalgae thallus to evaluate chemical mediation while few tested crude extracts. Some substances were noted as sesquiterpene (6-hydroxy-isololiolide), fatty acid (heptadeca5,8,11-triene) and dibromomethane. The articles were divided into four classes: Herbivory, Competition, Settlement/Metamorphosis, and Epiphytism. Crustose calcareous algae were associated with studies of Settlement/Metamorphosis, while calcified algae were linked to herbivory. Thus, the importance of chemistry in the ecology of these algae is evident, and additional studies are needed to identify the substances responsible for ecological interactions. This study collected essential information on calcified red algae, whose diversity appears to be highly vulnerable to the harmful impacts of ongoing climate change.

Keywords Calcareous macroalgae · Chemical ecology · Allelopathy · Rhodophytes · Herbivorous · Corals

Introduction

Carbonate skeletons and shells are produced by various marine organisms, including the three marine macroalgal lineages (Phaeophyceae, Ulvophyceae, and Eurhodophytina) (Hofmann & Bischof 2014). Calcification refers to different forms of calcium carbonate (CaCO₃) mineralization (calcite, aragonite, dolomite) in distinct areas of the thallus such as cell or thallus surface, cell wall, or inside cells itself (Nelson 2009; Nash et al. 2019). Initially, this strategy imposes metabolic and physical disadvantages on photosynthetic organism, including interference in light absorption,

reduced flexibility, and an energy cost for biomineral production (Smith et al. 2012). Moreover, CaCO₃ crystals may take on rhomboidal or orthorhombic shapes, rendering them less soluble in seawater (Hofmann and Bischof 2014). This reduced solubility, combine with the Mg:CaCO₃ ratio, may render the macroalgal thallus more susceptible to dissolution in an ocean acidification scenario (Hurd et al. 2014). Nevertheless, the benefits of enhancing thallus strength, increasing resistance to wave action, providing greater protection against predators, serving as a calcium storage, enabling metal co-precipitation, and improving nutrient absorption appear to outweigh the disadvantages. This is evident as approximately 5-6% of marine macroalgae are calcified (Littler 1976; Foster et al. 1977; Smith et al. 2012).

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Calcified rhodophytes are unique organisms characterized by their calcareous thallus morphology, typically exhibiting a pinkish or reddish color, featuring either articulated/geniculate fronds or crustose/non-geniculate fronds (Johansen 1981). The calcification strategy has proven to be an evolutionary success for these organisms, having evolved independently within at least three subclasses: Corallinophycidae (Corallinales, Corallinapetrales, Hapalidales, Rhodogorgonales, and Sporolithales), Nemaliophycidae (Nemaliales), and Rhodymeniophycidae (Nemastomatales, Peyssonneliales). These three subclasses exhibit the greatest diversity among calcareous algae (Guiry and Guiry 2023). Fossil evidence traces calcareous red algae back to the Permian period, around 300 million years ago (Riding and Guo 1991). Abundant and well-documented calcareous red algae, primarily belonging to Corallinales, have been found from the Upper Cretaceous period, approximately 100 million years ago, up to the present-day (Barattolo 1991). It's worth noting that different orders of red macroalgae use distinct ways for depositing calcium carbonate. For example, Nemaliales and Nemastomatales deposit aragonite, while Corallinales species exhibit a high ratio of magnesium calcite on their cell surfaces and within the cell walls. This suggests a higher vulnerability to herbivory and potentially reduced ability to biomineralize in Nemaliales and Nemastomatales (Littler 1976; Johnson et al. 2014). When discussing calcareous algae, Corallinales is the most referenced order, boasting nearly 1,000 species, all of which display calcification (Littler 1976; Guiry and Guiry 2023).

Red calcified macroalgae are essential components in intertidal and reef ecosystems, serving as primary producers and providing substrates for settlement and shelter for organisms on rocky shores, structuring and protecting reefs from erosion (McCook et al. 2001; Nelson 2009), being an important source of carbon sink in the ocean (Van der Heijden & Kamenos 2015; Cornwall et al. 2023), as well as performing a wide range of biotic interactions (Morcom and Woelkerling 2000). These algae have a global distribution, with the highest abundance in tropical and subtropical environments, and occur throughout the euphotic zone (Nelson 2009). Littler (1976) correlated the abundance of calcareous macroalgae in these regions with the concentration of dissolved calcium carbonate in seawater, temperature, and partial pressure of carbon dioxide. However, this correlation remains unclear due to exceptions, such as massive banks of crustose coralline algae in subpolar waters (Hofmann and Bischof 2014).

Although morphology, life cycle, and habitat have long been used to understand the ecology of marine macroalgae, several studies have focused on exploring chemically mediated interactions involving macroalgae (Whittaker and Feeny 1971; McClintock and Baker 2001). Furthermore, secondary metabolites may have contributed

to macroalgae occurrence in environments with a high diversity of herbivores, such as tropical regions (Hay et al. 1994; Amsler 2008). So far, chemical studies on Rhodophyta uncovered their ability to synthesize a diverse array of chemical structural classes, including terpenes, steroids, polyketides, polyphenols, and acetogenins, except for phlorotannins (Maschek and Baker 2001). However, what sets these organisms apart from other macroalgal lineages is their significant production of halogenated compounds, accounting for approximately 90% of the known metabolites, including bromine and chloride (Maschek and Baker 2001).

Some of the compounds found in red macroalgae exhibit ecological properties (*e.g.*, antifouling action, inhibition of biofilm formation, repellence of bivalve mollusks, and ichthyotoxic) and biotechnological properties (*e.g.*, antiviral, antitumor, antifungal, anti-inflammatory). (Blunt et al. 2010; Manilal et al. 2010; Teixeira 2013). Despite the abundance of information regarding the chemistry of red algae, there is scant literature available about the identification of secondary metabolites and their biological activities in red calcified macroalgae, especially when compared to green calcified algae (Ohsawa et al. 2001; Martins et al. 2012; Boopathy and Kathiresan 2013).

Most of the research carried out to discuss the physical and chemical defense of calcified macroalgae has primarily focused on calcified chlorophytes, specifically species of the genus *Halimeda*, with herbivory as the ecological interaction in tropical environments (Hay 1984; Schupp and Paul 1993; Hay et al. 1994; Hay 1996). Paul and Hay (1986) conducted a study involving several species of red and brown macroalgae, some of which were calcified, and evaluated their anti-herbivory activity. This work gave rise to hypotheses suggesting that morphological defenses might not suffice for these macroalgae in regions with high levels of herbivory (*i.e.*, tropical environment). It emphasized the necessity to supplement secondary metabolites for effective defense. Consequently, the diversity and adaptation of herbivory may lead to the selection of calcified algae species with chemical defense mechanisms over time. Simultaneously, herbivores with weak mouthparts and a tolerance for chemical defense may contribute to the selection of calcification (Paul and Hay 1986; Martone et al. 2021).

In acknowledgment of the ecological significance of calcified red macroalgae, this review endeavors to comprehend what is the influence of the chemistry of different calcified red macroalgae on the ecology of benthic organisms in relation to their interactions in the marine environment. To achieve this, information was gathered on the existing knowledge related to the chemical ecology of calcified red macroalgae, including insights into the most studied taxa, their biological activities, and potential substances or crude extracts responsible for these activities.

Materials and Methods

Study Design

This systematic review followed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines (Page et al. 2021). The research question was formulated using the PICOS (problem, intervention, comparison, outcome, and scenario) framework as recommended by the PRISMA method: "Regarding ecological interactions (P) in the marine environment (S), what is the influence (O) of the chemistry (I) of different calcified red macroalgae on the ecology of benthic organisms? (C)." Given the specific focus of this systematic review, which centers on the examination of ecological interactions involving calcified red macroalgae and other benthic organisms, it was not registered in an electronic systematic reviews database.

Search Strategy

The systematic review was independently conducted, involving searches in six electronic databases: PubMed, Scielo, Science Direct, Scopus, Springer, and Web of Science. Each reviewer cross-checked the references in their respective database lists for potential discrepancies. When inconsistencies were identified, they were adjusted by aligning with majority of the authors. These searches encompassed studies up to July 2023. The initial search utilized the following keywords: ["chemical ecology" OR "chemical interaction" OR "chemical response" OR "chemical defense" OR "chemical effect" OR "chemical cue" OR "chemical mediated" OR "chemical induce"] AND ["red seaweed" OR "red macroalgae" OR "red algae" OR rhodophy?] AND [calcified OR calcareous].

After the initial search, limited number of valid articles were encountered suitable for information extraction and discussion. One plausible hypothesis was that many articles did not employ the terms "calcareous" or "calcified" when referring to this specific group of algae. Conducting a new search without these terms would encompass the entire clade of red algae and jeopardize the study's specificity. Therefore, building upon the results of the initial search, all discarded review articles underwent thorough critical evaluation to identify classes and families of calcified red algae with records of ecological interaction studies in the literature up to that point. Thus, a new search was executed by combining the initial keywords with the names of the identified classes and families. As a result, the combinations for the new search were as follows: ["chemical ecology" OR "chemical interaction" OR

"chemical response" OR "chemical defense" OR "chemical effect" OR "chemical cue" OR "chemical mediated" OR "chemical induce"] AND [corallin? OR nemaniales OR peyssonneliales OR *Jania* OR *Amphiroa* OR *Lithophyllum* OR *Titanoderma* OR *Dichotomaria* OR *Galaxaura* OR *Tricleocarpa* OR *Sporolithon* OR *Phymatolithon* OR *Lithotrix* OR *Hydrolithon* OR *Ellisolandia* OR *Porolithon* OR *Lithothamnium* OR *Neogoniolithon*].

Eligibility Criteria

The searches were performed using titles, abstracts, and keywords of each article. Complete scientific articles written in English were eligible for inclusion, with no geographical restrictions. All other document types, such as reviews, books, case studies/reports, theses, dissertations, and others, were excluded. In this study, two rounds of article validation occurred during the search phase. In the first selection, two independent reviewers assessed all titles, abstracts, and keywords. Any discrepancies in this inclusion/exclusion phase were resolved through consensus, and when necessary, a third reviewer provided the final decision. In the second selection phase, which involved data extraction, the complete texts of the articles were reviewed by two evaluators. During this phase of inclusion/exclusion, any differences were resolved through consensus, or in cases where consensus could not be reached, a third reviewer made the final decision.

Inclusion and Exclusion Criteria

Articles that contained information pertaining to the influence of the chemistry of calcified red macroalgae on ecological interactions of marine organisms were considered. Articles exclusively focused on non-calcified algae, algae from other phyla, only fingerprints and chemical data without ecological interaction discussions, or those intended solely for biotechnological purposes (lacking ecological information) were disregarded.

Processing and Data Extraction

To compile the material, all identified articles were systematically organized into a table, including details such as the database source, title, publication year, and DOI. Duplicate entries were removed from the collected documents, and a new file was generated to consolidated all the information (Fig. 1). Two reviewers compiled data using a standardized spreadsheet, gathering specific details such as "article, algae family, cited species name, updated species name (following AlgaeBase), sampling site, chemical material, ecological interaction, and target species (updated following WoRMS)." The compiled data underwent cross-verification to ensure

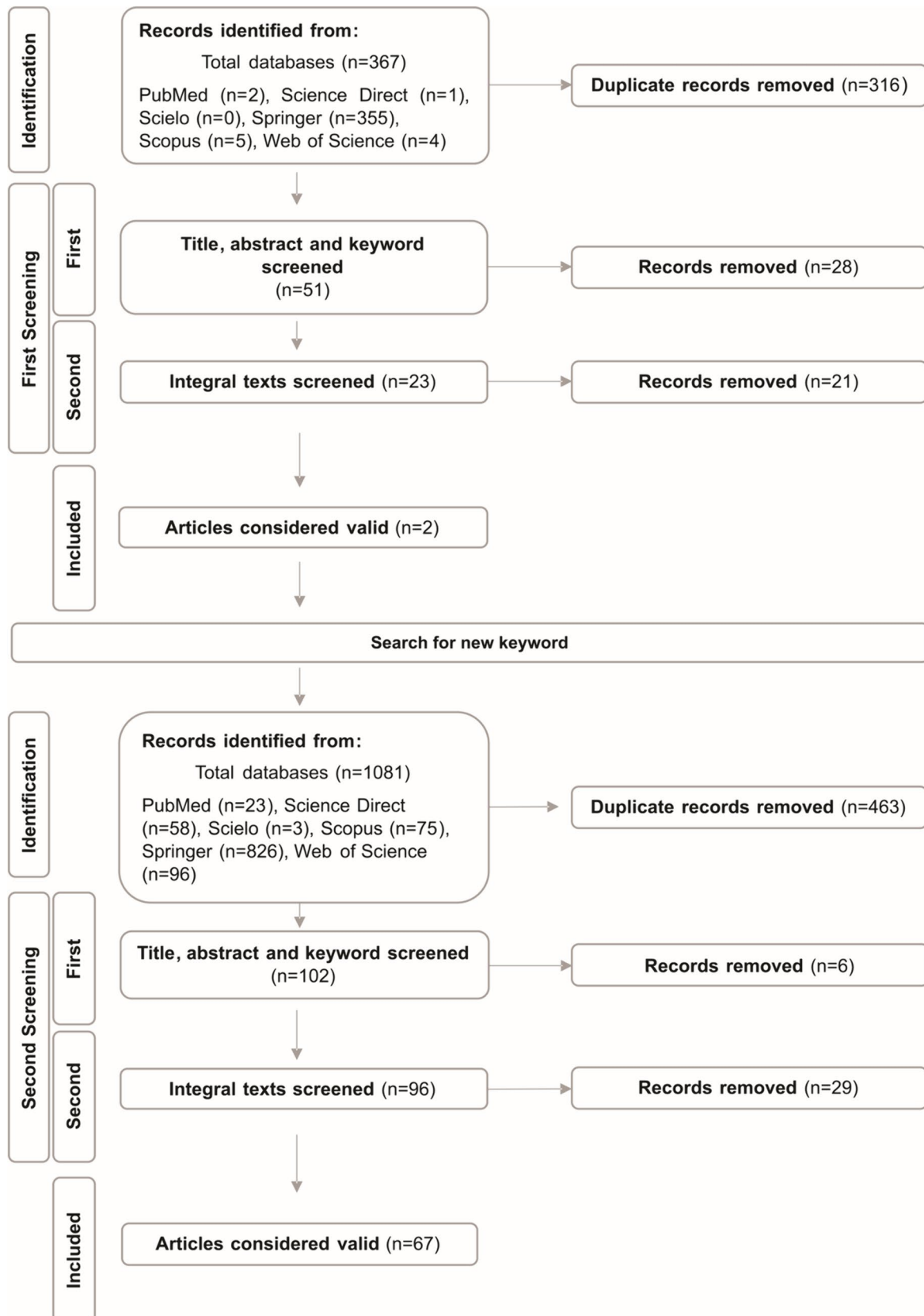


Fig. 1 Preferred Reporting Items for Systematic Reviews and Meta-Analysis (PRISMA) workflow chart of the screening process

completeness and accuracy, with any discrepancies being addressed through discussion and resolved by consensus or, when necessary, by a third reviewer. Maps were generated to verify the spatial distribution of publications on the theme and the origins of the researched species, using their geographic coordinates and plotted in QGIS software (version 3.36 Maidenhead).

Bibliometric Analysis

For text content analysis, the IRaMuTeQ software v. 0.7 alpha 2 (Interface de R pour les Analyses Multidimensionnelles de Textes et de Questionnaires) was used. The articles were consolidated into a single text file (.txt) known as a textual corpus. Each article, including title, abstract, and keywords, underwent evaluation (Online Resource 1). The language and dictionary selected in the software for recognition of words was English, the character extension used was *utf_8_sig*, and the separation of the *corpus* into text segments was determined by *ucesize* 450. This approach

facilitated the execution of multivariate analyses that enable both qualitative and quantitative assessment of the articles. Several evaluations were conducted, including similarity tree analysis, descending hierarchical classification (Reinert method), and factorial classifications.

The Current Frame on the Chemical Ecology of Calcified Red Macroalgae

After the search within the databases, 67 articles were found that discuss or mention any information about the ecology involving chemically mediated interactions of calcified red macroalgae. Among the orders featuring calcified red species, only Corallinales, Hapalidiales, Nemaliales, Peyssonneliales, and Sporolithales had species with reported biological activity (Online Resource 2). *Corallina* and *Amphiroa* were the most extensively studied genera in the collected literature (5 species each), followed by *Galaxaura* and *Lithophyllum* (3 species each), *Dichotomaria*,

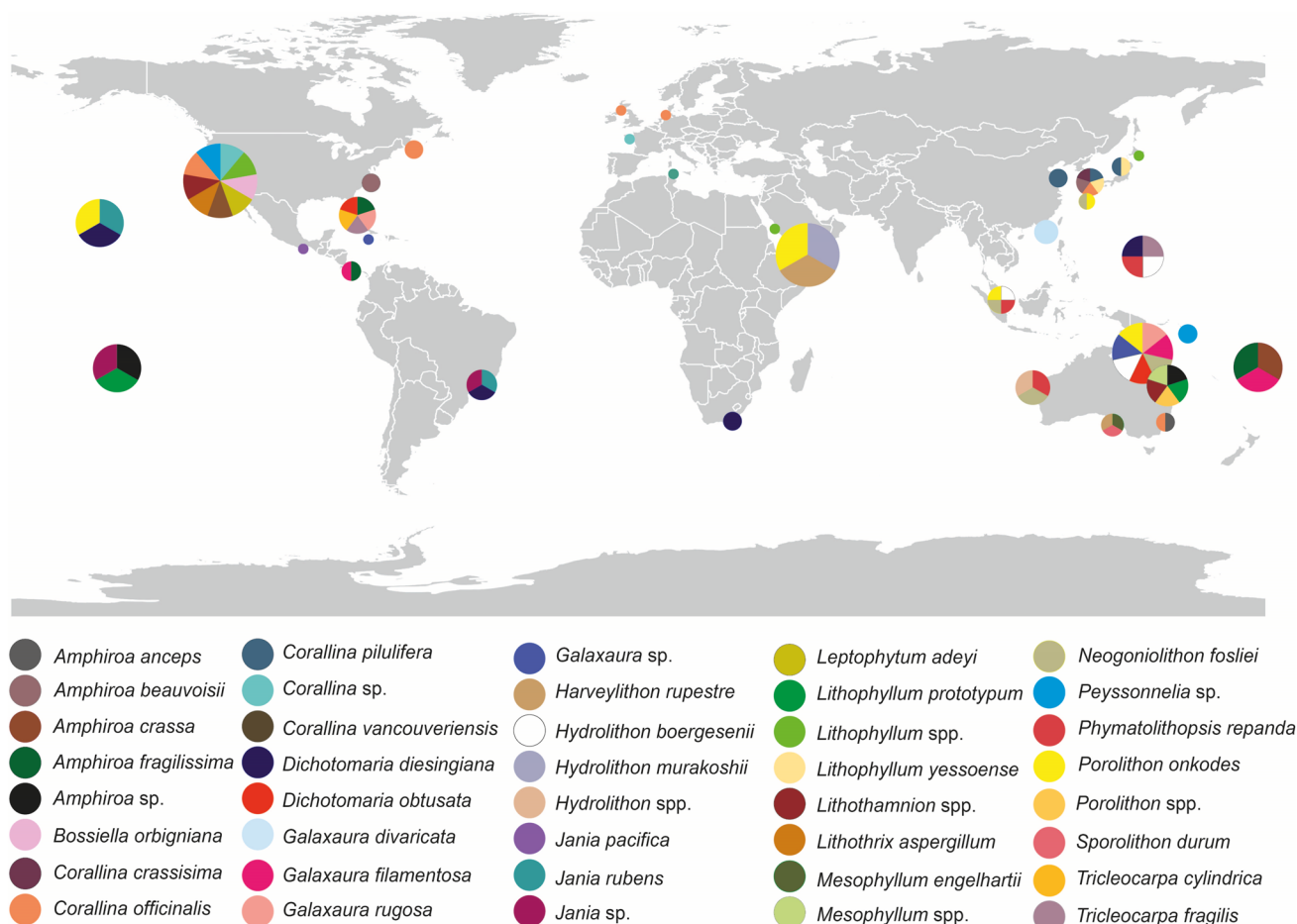


Fig. 2 Areas where calcified algae species were collected in the gathered papers (n= 67). The size of the circle represents the sampling effort in the area, and the division of the circles corresponds to the number of species found in the given area

Jania, *Tricleocarpa*, *Hydrolithon*, *Mesophyllum* (2 species each) in different areas of the globe (Fig. 2). It is worth noting that there is a study which analyzed the chemistry of calcified algae species from an ecological perspective, but it does not provide information on their sampling locations.

Nearly half of the studies (31) were conducted within the biogeographic realm of Central Indo-Pacific, followed by the Temperate Northern Pacific (15), following Spalding et al. (2007). Albeit the Islands of Guam and French Polynesia were territories of the United States of America and France, respectively, this paper considers their geographic location within the provinces and realms (Fig. 3). The higher concentration of studies in these regions can be attributed to the presence of prolific research laboratories focused on marine biology, as well as the presence of the Coral Triangle and Great Barrier Reef. These locations represent the largest coral reef ecosystems globally, with remarkable biodiversity and intricate ecological interactions (Fig. 1 - Online Resource 3) (Fine et al. 2019; Mellin et al. 2019).

Over the course of nearly four decades, it is noteworthy how frequently these macroalgae have undergone species or genus changes. The species analyzed in the papers had their names verified in AlgaBase, and it was found that 15 of them had experienced name changes. This can be attributed to the challenges in macroalgae identification based on thallus morphology, the complexity of investigating their reproductive structures, and the limited number of experts in the field of calcareous algae. These challenges become even more pronounced when dealing with crustose calcareous algae, given their high morphological variability and difficulty in collection, making field identification exceptionally challenging (Woelkerling et al. 1993). Consequently, other techniques are currently employed for species identification of these algae, such as the utilization of DNA sequence data, phylogenetic analyses, and descriptive metabolomics

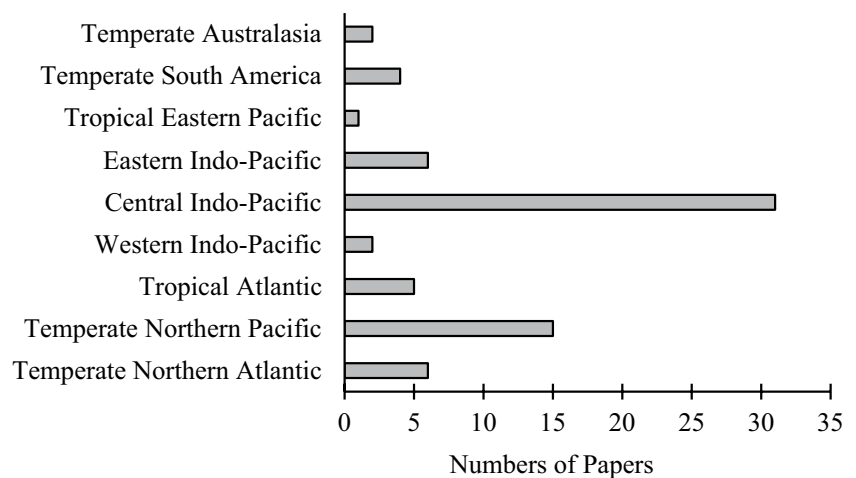
to determining chemotypes (Santos et al. 2020; Chhetri et al. 2023).

The descriptive results of bibliometric analysis showed that the number of sets comprising of title, abstract and keywords corresponds to the number of texts segments, with 15,583 occurrences, 2,819 number of forms, and 1,345 hapax (words used once). For the analyses in this work, only three textual forms were utilized: nouns, verbs, and unrecognized forms.

Initially, the title, abstract and keywords (*i.e.* corpus) were used for constructing a similarity tree. In this tree, terms with higher frequency were represented by larger nodes, and the strengths of the relationships between the terms was indicated by their thickness (Fig. 4). Thus, studies that explore the chemical interactions involving calcified red macroalgae and other marine organisms frequently incorporate terms such as 'red_macroalgae', 'coral_reef', 'reef', 'herbivorous', 'chemical_defense', 'larva', 'settlement', 'metamorphosis', 'cca' (calcareous crustose algae) and 'surface'.

The primary interactions explored in these articles included herbivory, settlement, metamorphosis, and allelochemical process. Each interaction was associated with specific terms that exhibited higher frequency of use. For instance, the term 'herbivorous' was frequently linked with words such as 'reef', 'chemical defense', 'preference', 'consumption', indicating the ecosystem where this interaction involving red calcified macroalgae was predominantly investigated and how it was assessed. Some of the macroalgae species examined in this study appeared together with terms representing particular interactions. For example, *Jania rubens* was associated with 'secondary metabolites' and 'herbivorous', while *Galaxaura divaricata* (Linnaeus) Huisman & R.A. Townsend, *Corallina pilulifera* Postels & Ruprecht 1840, and *Lithophyllum yessoense* Foslie were linked to 'allelochemical' interactions. Additionally, *Jania* sp. was connected with 'epiphytic' interactions and *Gambierdiscus toxicus* R.Adachi & Y.Fukuyo, 1979, and *Sporolithon durum*

Fig. 3 Biogeographical realms where the studies were conducted



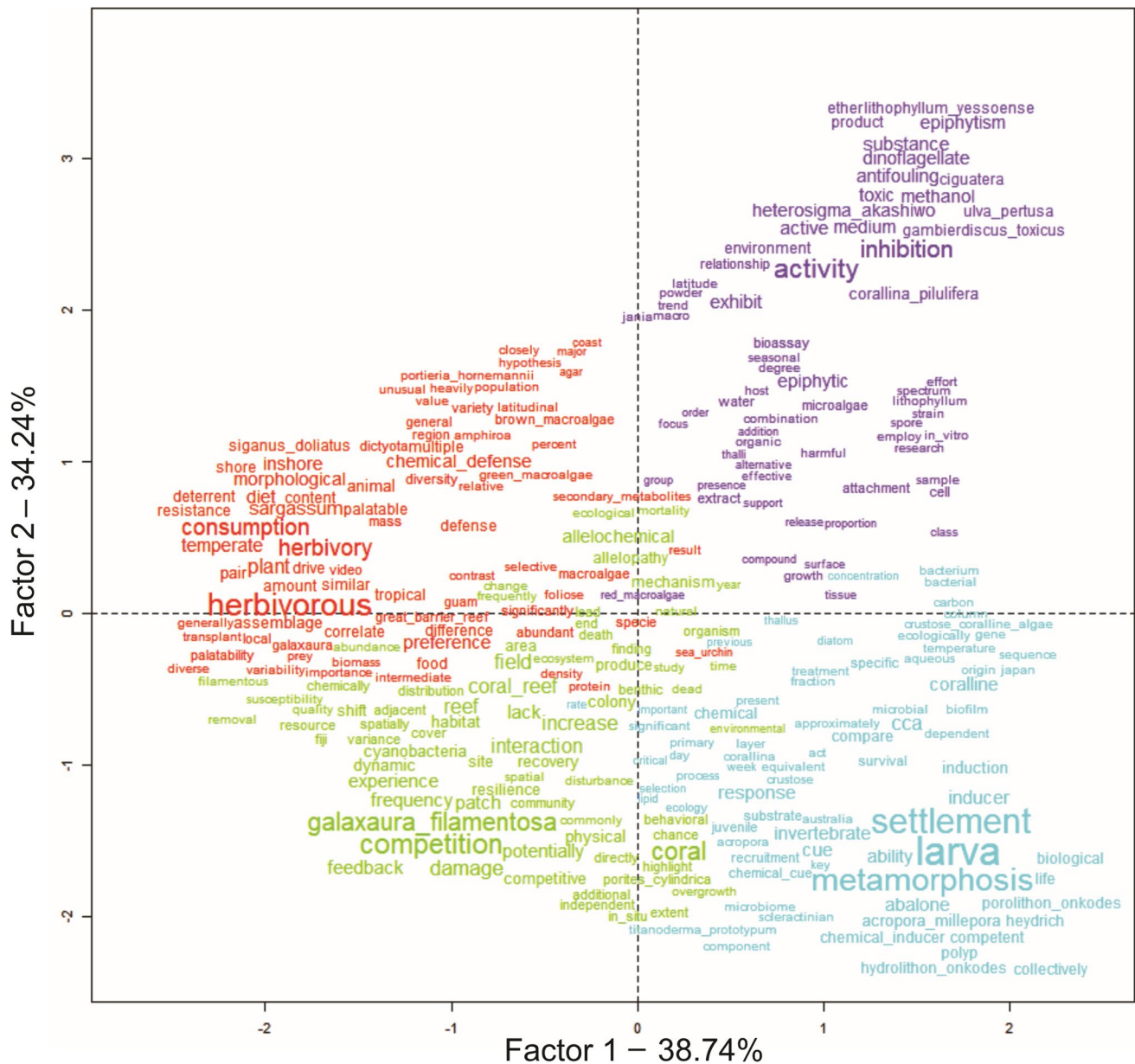


Fig. 5 Correspondence factorial analysis representation provided by IRAMUTEQ software

The combination of CaCO_3 and secondary metabolites has already shown both additive and synergistic effects on the defense of these calcified macroalgae (Hay et al. 1994; Meyer and Paul 1995). These defense mechanisms appear to function simultaneously in tropical marine macroalgae, and the common co-occurrence of the multiple defenses (morphological and chemical defense) has been proposed to be adaptive due to the high diversity of herbivorous found in this area (Littler and Littler 1980; Littler et al. 1983; Duffy and Hay 1990).

Besides the discussion about multiple defenses of calcified macroalgae, there is also a general hypothesis of

tropical macroalgae having stronger chemical defense compared to temperate ones in herbivory interactions (Bolser and Hay 1996). The genus *Halimeda*, tropical green calcified macroalgae, is one of the most studied taxa regarding the concurrent action of physical and chemical defense (Hay et al. 1988; McClintock and Baker 2001). Anti-herbivory activity was also seen in tropical red macroalgae with calcified thallus. Eleven species of Nemaniales had records of deterrence or low preference against the isopod *Paridotea rubra* Barnard, 1914, the amphipod *Cymadusa filosa* Savigny, 1816, the sea hare *Dolabella auricularia* (Lightfoot, 1786), and several reef fishes,

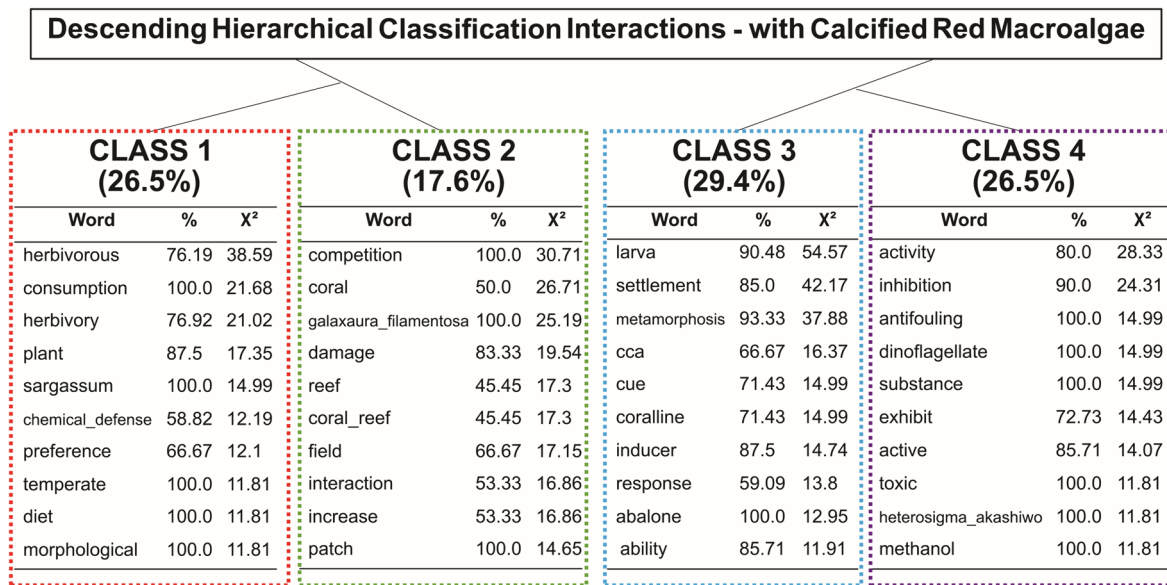


Fig. 6 Dendrogram of the Descending Hierarchical Classification (DHC) with the percentage of each class and word and chi-square values

including *Chlorurus sordidus* (Forsskål, 1775), *Naso lituratus* (Forster, 1801) and *Zebрасoma flavescens* (Bennett, 1828) (Table 1 – Online Resource 2). On a smaller scale, Corallinales had seven species with deterrence by herbivorous associated, such as *Corallina officinalis* Linnaeus against the periwinkle *Littorina littorea* (Linnaeus, 1758), *Bossiaella orbigniana* (Decaisne) P.C.Silva against the sea urchin *Strongylocentrotus purpuratus* (Stimpson, 1857), *Lithothrix aspergillum* J.E. Gray against the fishes *Girella nigricans* (Ayres, 1860) and *Kyphosus azureus* (Jenkins & Evermann, 1889) (Watson and Norton 1985; Barry and Ehret 1993; Thornber et al. 2008). Other studies investigated the herbivorous preference utilizing green and brown calcified and non-calcified macroalgae (such as *Ulva* sp. and *Sargassum* sp.) against red calcified macroalgae and highlighted the lower consumption of it by sea urchin and reef fishes (Bolser and Hay 1996; Solandt and Campbell 2001; Loffler et al. 2015a,b).

Herbivorous may show distinct responses to interaction with the chemical defense of diverse macroalgae since it tends to be a species-specific interplay resulting from a biochemical reaction between the precise secondary metabolite and their digestive processes (Hurd et al. 2014). The primary goal of most of the papers analyzed was related to deterrence, but some studies showed a higher preference or consumption of *Galaxaura* sp. and *Corallina vancouveriensis* Yendo by the sea urchin *Diadema antillarum* (Philippi, 1845) and *S. purpuratus* respectively (Solandt and Campbell 2001; Thornber et al. 2008). Calcium carbonate may have an essential role in the diet of sea urchins since they have a neutral gut pH, they frequently consume this material while feeding, incorporate organic compounds despite

a large amount of inorganic material, and utilize it for their structural defense (Pennings and Svedberg 1993, Asnaghi et al. 2013; Rich et al. 2018).

Class 2 (Allelopathic Competition)

One of the most registered interactions in the literature for red calcified species is allelopathy. Allelopathic substances of these algae have an essential role in the structure, ecology, and conservation of benthic communities and coral reefs, allowing competition for space (Morcom and Woelkerling 2000). These photosynthetic organisms may negatively affect corals through several mechanisms, such as overgrowth, shading, abrasion, and/or chemical effects, as shown in studies performed in the field (Lirman 2001; Rasher and Hay 2010). Corallinales species, such as *Amphiroa crassa* J.V. Lamouroux and *Amphiroa fragilissima* (Linnaeus) J.V.Lamouroux, have shown to present bleaching activity and suppression of the photosynthetic efficiency of the corals *Acropora millepora* (Ehrenberg, 1834), *Pocillopora damicornis* (Linnaeus, 1758), and *Porites porites* (Pallas, 1766) (Rasher and Hay 2010; Rasher et al. 2011). In Brazil, nearly 700 macroalgae species occur in coral reefs along the coast; among them, Corallinales is the least studied group despite their role in reef formation (Figueiredo et al. 2008).

Galaxaura filamentosa R.C.Y.Chou (order Nemaniales) has shown to cause damage in the settlement of the adult phase of several corals such as *Acropora aspera* (Dana, 1846), *Montipora digitata* (Dana, 1846), *Porites cylindrica* Dana, 1846, *Porites lobata* Dana, 1846, among others (Rasher and Hay 2010; Rasher et al. 2011; Bonaldo and Hay 2014). Species of *Galaxaura* are ubiquitous

macroalgae on coral reef ecosystems, thriving in waters from warm temperate to tropical regions of the Atlantic, Pacific, and Indian Ocean, and are known as coral-killing due to their allelochemicals (Liu et al. 2013; McCormick et al. 2017; Nieder et al. 2022). Nieder et al. (2019) registered the interaction between the herbivorous fish and epiphytic organisms of *Galaxaura divaricata* (Linnaeus) Huisman & R.A. Townsend and how they avoid eating the host itself, probably due to their allelochemicals and nutrient-poor thallus. Once established locally, this species could represent a serious ecological issue for coral recovery in degraded patch reefs (Rasher et al. 2011; Nieder et al. 2022). Species of the genus former known as *Galaxaura obtusata*, *Dichotomaria obtusata* (J. Ellis & Solander) Lamarck, was also shown to have allelochemicals mediating interactions with the coral *Porites astreoides* Lamarck 1816 and injuring its microbial community (Thurber et al. 2012).

Macroalgae as the dominant phase on coral reefs is a well-known process, which usually originates from the competition between these organisms with coral under reef degradation (Jompa and McCook 2003). However, there is variability about the effects of algae on corals since corals are considered superior competitors, and only on specific situations (e.g., reef degradation) and mediation by herbivory to obtain a higher cover of algae (McCook et al. 2001). For instance, *Peyssonnelia* sp. may overgrow and kill corals, but *Lithophyllum* spp. may induce larvae settlement and metamorphosis of different coral species (James et al. 1988; Gómez-Lemos et al. 2018). Likewise, decadal research on the Abrolhos bank in Southwestern Atlantic highlighted that high cover of macroalgae should neither necessarily represent a phase-shift symptom of coral reefs nor an overfishing scenario, and they may benefit Brazilian endemic corals by avoiding coral-allelopathic cyanobacteria interaction (Teixeira et al. 2021).

Allelopathic substances may influence the community surrounding the macroalgae by altering the behavior of neighboring organisms. In the case of red calcified algae, such as *D. obtusata* and *Galaxaura rugosa* (J. Ellis & Solander) J.V. Lamouroux, allelopathic interactions have been observed with specific herbivores. McCormick et al. (2017) registered the influence of allelochemicals produced by *D. obtusata* on nullifying alarm odors for the reef damselfish *Pomacentrus amboinensis* Bleeker 1868, weakening their antipredator responses. The role of coral reefs as nurseries for the early stages of fish is crucial, as these stages are likely vulnerable to changes in the chemistry of the surrounding habitat, intensified by the high abundance of chemically defended macroalgae (McCormick et al. 2017). Rasher and Hay (2014) recorded a peculiar coral-macroalgae-herbivorous interaction, in which the competition between coral and macroalgae increase the palatability of *Galaxaura filamentosa* to herbivorous and make this calcified macroalgae

more susceptible to herbivory. On the other hand, *G. rugosa* may serve as a refuge for the highly palatable algae *Acanthophora spicifera* (M. Vahl) Børgesen due to its secondary metabolites that dissuade herbivores from feeding on it and algae or coral in her vicinity (Rasher and Hay 2014; Löffler et al. 2015a,b; Brooker et al. 2017). This highlights the intricate chemical interactions between red calcified algae and herbivores, ultimately shaping the dynamics of marine reef ecosystems.

Class 3 (Settlement and Metamorphosis). Although the disharmonic interaction between epibionts and macroalgae is frequently documented in the literature, several authors already registered the ability of coralline algae to chemically stimulate the recruitment of invertebrates larva, indicating the relevance of these organisms for the ecology of coastal ecosystems (Fusetani 2003; Li et al. 2004; Tebben et al. 2015; Barner et al. 2016). However, the study of this larval-coraline ecological interaction must be made critically and carefully since recent studies showed a significant role of the bacterial biofilm together with the thallus of the coral-line algae in the settlement of larva (Huggett et al. 2006; Swanson et al. 2006).

Corallina species are largely associated with larval settlement and/or metamorphosis of the sea urchins *Heliocidaris crassispina* (A. Agassiz, 1864), *Mesocentrotus nudus* (A. Agassiz, 1864), *Pseudocentrotus depressus* (A. Agassiz, 1864), *Strongylocentrotus droebachiensis* (O.F. Müller, 1776), *S. purpuratus* (Stimpson, 1857) and *Paracentrotus lividus* (Lamarck, 1816). Alongside them, calcareous crustose algae (cca) such as *Lithophyllum* spp., *Mesophyllum printzianum* Woelkerling & A.S. Harvey, *Phymatolithopsis repanda* (Foslie) S.Y. Jeong, Maneveldt, P.W. Gabrielson, W.A. Nelson & T.O. Cho, and *Pneophyllum coronatum* (Rosanoff) Penrose was investigated as an inducer of abalone and coral larva (Harrington et al. 2004; Gómez-Lemos et al. 2018). For instance, metamorphosis of *Haliotis iris* Gmelin, 1791 occurred in response to the chemical cues of *P. repanda*, suggesting the importance of this calcareous macroalgae for the survival and growth of this abalone (Roberts and Lapworth 2001). This ecological activity was investigated largely on the Southwest Pacific coast, possibly due to the mass production of these economically important marine species to their culinary (Kitamura et al. 1993; Li et al. 2004).

Class 4 (Antifouling). Compared with other phyla, Rhodophytes exhibit the highest number of isolated substances known with antifouling activity and constitute the most significant proportion of species along the Brazilian coast (Da Gama et al. 2008; Leal et al. 2013). Secondary metabolites with antifouling activity hold significant ecological functions for the development of macroalgae and their adaptive value, as epibionts can have direct effects (e.g., tissue damage through anchoring) and indirect effects (e.g., increasing susceptibility

to herbivory) (Gonzalez and Goff 1989; Pereira et al. 2003). A significant portion of these antifouling substances comprises terpenes and halogens, with the genus *Laurencia* being the primary source of this type of substance (e.g., elatol) (Da Gama et al. 2014). Regarding red calcareous macroalgae, antifouling activity was seen through surface sloughing of the thallus, which is considered a physical defense mechanism (Fujita and Masaki 1985; Keats et al. 1997). However, studies have shown that allelopathic compounds produced by the articulated algae *Jania rubens* (Linnaeus) J.V.Lamouroux exhibit antifouling activity against the brown mussel *Perna perna* (Linnaeus 1758) (Medeiros et al. 2007; Da Gama et al. 2008).

Other important organisms that live on the surface of macroalgae and may have an indirect influence on the fouling process by attracting organisms are microalgae and bacteria (Hellio et al. 2001). Growth inhibition of epiphytes and other epibiont competitors by allelochemicals of red calcified macroalgae have been reported (Bedoux and Bourgougnon 2015). The crustose calcareous algae *Lithophyllum yes-soense* Foslie has active substances that suppress or inhibit the growth of epiphytic microalgae, as well as *Corallina pilulifera* Postels & Ruprecht, and that lyse macroalgae spores (Ohsawa et al. 2001; Kim et al. 2004; Luyen et al. 2009). On the contrary, *J. rubens* exhibited antimicrobial activity against the marine bacteria *Shewanella* sp. localized in the surrounding water and not against the bacteria residing on its surface, suggesting an intimate association between *J. rubens* and its associated bacteria (Ali et al. 2012).

The biofilm found on the surface of calcareous algae is diverse and different interactions can be observed between the substrate (macroalgae) and the microbiome. Although there is evidence that *Gambierdiscus* species live as free-swimming forms, the epiphytic *Gambierdiscus toxicus* R.Adachi & Y.Fukuyo, 1979 has been recorded attached to species of *Jania*, *Amphiroa*, and *Galaxaura* (Nakahara et al. 1996; Lobel et al. 1988). Thus, it has been hypothesized that these macroalgae may have chemical signals that influence the epiphytic behavior of this dinoflagellate, as allelochemical substances from *J. rubens* and *D. obtusata* have led to the proliferation of *G. toxicus* (Parsons et al. 2011). However, individuals of *C. pilulifera* collected on the coasts of China and South Korea and its methanol extracts inhibited the growth and was toxic, causing mortality in at least seven species of microalgae, such as *Heterosigma akashiwo* (Y.Hada) Y. Hada ex Y. Hara & M.Chihara, 1987, and *Procentrum triestinum* J.Schiller, 1918 (Jeong et al. 2000; Wang et al. 2007; Wang and Tang 2016). Hence, the secondary metabolites produced by red calcified macroalgae may have a variety of biological activities associated with it and play a crucial role in the dynamics of marine ecosystems.

Chemically Mediated Ecological Interaction

Secondary metabolites found in calcified red algae encompass a range of chemical classes, including sterols, terpenes, phenols, hydrocarbons, fatty acids, etc. (Sheu et al. 1997; Rosa et al. 2003; El-Din and El-Ahwany 2016). Some substances were found in extracts of red coralline algae, such as the fatty acids palmitic acid and 5Z,8Z,11Z,14Z,17Z-eicosapentaenoic acid EPA, the pigments chlorophyll *a* and phycoerythrin R-phycoerythrin (Fleury et al. 2011; Mogstad and Johnsen 2017). The advancement of DNA analysis techniques, spectrometry, spectrophotometry, and chromatography should enable the exploration of chemotypes in calcified red algae to facilitate the identification and promote integrative taxonomy studies. However, only the red crustose calcified macroalgae *Peyssonnelia* spp. were investigated through non-target metabolomics and biomolecular analysis, which pointed out to four triterpene glycosides peyssonbaricanosides with antifungal activity against the marine fungus *Paradendryphiella salina* (G.K. Sutherl.) Woudenb. & Crous, 2013 (Chhetri et al. 2023).

The secondary metabolites of red calcified macroalgae receive significant attention and are frequently annotated for their pharmaceutical, nutritional, or cosmetic properties, unlike the studies that primarily focus on their ecological effects (Khairy and El-Sheikh 2015; Dixit and Reddy 2017; Lefranc et al. 2019; Nekooei et al. 2021). When considering this type of activity, the information about the chemical profile of red calcified macroalgae is investigated mainly using hydrophilic or polar extracts and volatile compounds (Awad 2004; Ryu et al. 2009). Nonetheless, regarding the chemical ecology of benthic organisms, authors raised the hypotheses: 1) tropical algae may be particularly rich in lipophilic secondary metabolite, supporting the idea of an evolutionary response to higher diversity of herbivory, and 2) allelopathic compounds could be hydrophobic rather than hydrophilic in benthic marine systems due to interactions with direct contact registered in papers (Rasher et al. 2011; Hurd et al. 2014). These indicate that further analyses should be done with hydrophobic extracts to annotate compounds responsible for relevant ecological interactions.

Most of the assays done in the literature by the authors utilized the macroalgae thallus itself live or frozen (32 papers) without investigating extracts or annotating compounds responsible for the activity. Assays evaluating the chemical mediation of *Corallina* spp. on larval settlement of sea urchins used its conditioned water since it is known that coralline red algae provides higher metamorphosis rate for sea urchins by inductive effect (Pearce and Scheibling 1990; Li et al. 2004; Castilla-Gavilán et al. 2018). Moreover, the establishment of dense populations of young sea

urchins in areas colonized by crustose coralline algae has been observed in the field (Rowley 1989).

When crude extracts were made to evaluate ecological interaction mediated by secondary metabolites, the solvents used were methanol, dichloromethane, and ethanol (Table 1- Online Resource 2). In this case, extracts with higher to intermediate polarity or their aqueous fraction were used to produce artificial food or substrate to assess several interactions as anti-herbivory, antifouling, antimicrobial, algaecide, induction of coral larvae settlement (Meyer et al. 1994; Jeong et al. 2000; Harrington et al. 2004; Da Gama et al. 2008).

Few studies were able to annotate the compounds accountable for the activity. Rasher et al. (2011) identified the biological activity of two sesquiterpenes 6-hydroxy-isololiolide (Fig. 7A) and isololio (Fig. 7B), from extracts of *G. filamentosa* against the corals *A. millepora*, *M. digitata*, and *P. damicornis*. Also, the fatty acids arachidonic (Fig. 7C), eicosapentaenoic (Fig. 7D) (*C. pilulifera* and *Tricleocarpa cylindrica* (J.Ellis & Solander) Huisman & Borowitzka) and heptadeca5,8,11-trien (HpDTE: C17:3) (Fig. 7E) (*L. yessoense*) induced to larval settlement and metamorphosis, was unpalatable for scaridae and acanthuridae fishes, and lysed algae spores, respectively (Paul and Hay 1986; Kitamura et al. 1993; Luyen et al. 2009).

In light of the ability of rhodophytes to synthesize halogenated compounds containing bromine and chloride, bromoform (Fig. 7F) and dibromomethane (Fig. 7G) were

isolated and tested. The former compound was isolated from *C. pilulifera* and *L. yessoense*, resulting in the inhibition of epiphytic microalgae growth (Ohsawa et al. 2001). Conversely, the latter compound was obtained from *Alatocladia yessoensis* (Yendo) P.W.Gabrielson, K.A.Miller & Martone, *Amphiroa ephedraea* (Lamarck) Decaisne, *Corallina maxima* (Yendo) K.R.Hind & G.W.Saunders, *C. pilulifera*, and *L. yessoense*, and it influenced the metamorphosis of the sea urchin *M. nudus* (Taniguchi et al. 1994). Furthermore, Tebben et al. (2015) isolated the followed compounds (2*S*)-1-O-(7*Z*,10*Z*,13*Z*-hexadecatrienoyl)-3-O- β -D-galactopyranosyl-sn-glycerol (Fig. 7H) and (2*R*)-1-O-(palmitoyl)-3-O- α -D-(6'-(2*R*)-1-O-(palmitoyl)-3-O- α -D-(6'-sulfoquinovosyl)-sn-glycerol (Fig. 7I) which were associated with larva settlement, attachment and metamorphosis of the corals Acroporidae, Siderastreidae, Favidae.

Methodological Limitations of the Studies

The studies found in this systematic review discussed major orders of calcified red macroalgae, mentioning highly representative species from this group. Other species could have been included to enrich this review with a greater diversity of chemical and biological information about this group. However, it was observed that a significant portion of the literature does not specify the calcareous morphology of these organisms, meaning that they do not include terms such as "calcareous" and "calcified" in

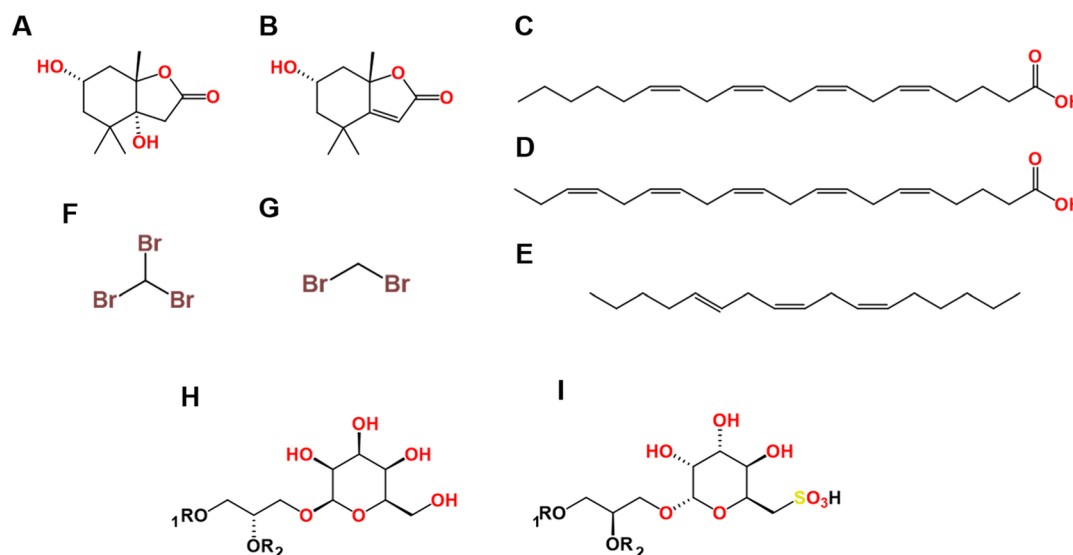


Fig. 7 Compounds produced by red calcified macroalgae with associated ecological interaction. Monogalactosyldiacylglycerol [MGDG] ($R_1 = R_2 =$ acyl side chain) and Monogalactosylmonoacylglycerol [MGMG] ($R_1 =$ acyl side chain, $R_2 =$ H) are represented by OR_1 and

OR_2 of figure H; Sulphoquinovosyldiacylglycerol [SQDG] ($R_1 = R_2 =$ acyl C16:0 side chain) and Sulphoquinovosylmonoacylglycerol [SQMG] ($R_1 =$ acyl C16:0 side chain, $R_2 =$ H) are represented by OR_1 and OR_2 of figure I

their titles, abstracts, and keywords. So, there is a limitation in accessing this information and fully understanding the importance of the chemical ecology of these calcareous species for marine ecosystems and the coastal biodiversity as a whole, exceptionally in the scenario facing climate changes and degradation of these environments.

Future Perspectives of the Chemical Ecology of Red Calcified Macroalgae

The investigations encompassed in this review revealed numerous interactions facilitated by the secondary metabolites of calcified red algae, which can significantly influence the dynamics of benthic communities. Nevertheless, most experiments were conducted solely in laboratory settings using isolated macroalgal thalli and do not specify its life stage (sporophyte or vegetative), posing challenges in comprehending the complete chemical profile and identifying the specific substances responsible for their ecological activity. In this particular scenario, employing bio-guided assays and advanced chemical analysis techniques such as NMR, LC-MS, and GC-MS could serve as valuable options for gaining a deeper understanding of the interactions between these macroalgae and other organisms. It is worth noting that there are limitations to adopting these new techniques, as they will require funding for methods and supplies or the establishment of collaborations for broader studies.

Different authors pointed out the need to investigate the ecology and chemical profile of red calcified macroalgae due to its importance on the trophic chain and the current condition of climate changes (McCormick et al. 2017; McCoy and Kamenos 2018; Nieder et al. 2019). The alteration of habitats (by overexploitation, reduced water quality, global warming, and ocean acidification) in wilderness areas is a significant factor contributing to the worldwide decline in biodiversity (Doney et al. 2012). Coralline macroalgae, as calcifying algae, are vulnerable to community processes and ocean acidification. Their resistance to grazers primarily relies on thallus thickness and morphology, in which species with higher content of calcium carbonate may undergo structural changes as becoming thinner and slimmer species exhibiting reduced internal density under ongoing acidification (McCoy and Kamenos 2015). These changes in skeletal material quantity and quality may impact the ecosystem function of coralline algae related to competition and trophic interactions, leading to substantial changes in the dynamics of marine habitats (McCoy and Kamenos 2018).

Conclusion

In summary, the studies addressed in this review showed the crucial role of the chemistry produced by red calcified algae in marine ecosystems due to its variety of interactions registered and its abundance in tropical and subtropical areas. However, it is necessary to carry out in-depth studies on the chemical profile of these macroalgae and biological activities associated with this chemical profile since there is a scenario of constant climate change with deleterious effects on the biodiversity of marine environments (Doney et al. 2012).

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Declarations

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