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Biochemical study of attached macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands: multivariate analysis to determine bioresource potential

Abstract: Fifteen attached macroalgae from the Madeira Archipelago, comprising three green, three red and nine brown algal species, as well as two beach-cast macroalgal samples, collected along the north shore of Gran Canaria, were assessed for their biochemical properties. The analysis included the determination of total minerals, total carbohydrates, protein, lipids, chlorophyll *a*, total carotenoids, total phenolic content, fucoxanthin and phycobilins (allophycocyanin, phycocyanin and phycoerythrin). The results showed a high variability of biochemical composition, allowing for the targetting of specific bioresources for particular purposes, including functional foods. This work provides the foundation for a biorefinery strategy implementation plan, for which specific macroalgae may be targeted for valuable and beneficial compounds.

Keywords: carotenoids; fucoxanthin; lipids; phycobilins; protein.

Introduction

Marine macroalgae have a high potential as an alternative source of biochemical compounds since they possess

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several specific metabolic pathways. They contain nutrients, such as proteins, minerals, fiber, carotenoids, vitamins and fatty acids, all of which provide beneficial bioactivity (Kılınç et al. 2013). For instance, macroalgal protein is considered an excellent source of essential amino acids necessary for human metabolism (Galland-Irmouli et al. 2000). Similarly, fiber is recognized in preventing the occurrence of colon cancer, obstipation, obesity and cardiovascular diseases (Dreher 1987). Additionally, liposoluble and hydrosoluble vitamins such as tocopherols, β-carotene, thiamine, and riboflavin have been shown to reduce the risk of thrombosis, atherosclerosis and heart disease (Mishra et al. 1993). Furthermore, phenolics and carotenoids, found in these resources, have the ability to neutralize free radicals, delaying oxidative degradation (Miyashita 2014). These compounds could neutralize reactive oxygen species (ROS) produced in human metabolism, related to degenerative processes associated with ageing, cancer and other human diseases (Aruoma 1999).

In-depth studies on the potential of bioresources may yield several, as yet undiscovered, valuable compounds, making a biorefinery industry potentially feasible. Screening the biochemical composition would be the first step in predicting an alga's potential for further investigation. Presently, the macroalgal industry is focused mainly on single-product (e.g. xanthophylls, polysaccharides, hydrocolloids, proteins) extractions and more recently, the production of biofuels, with little to no use for the remaining biomass (Van Hal et al. 2014). A cascade extraction envisions a primary extraction of a valuable compound followed by a set of subsequent extractions of other compounds found in the target bioresource, in order to maximize extraction efficiency and monetize the process and resource. This method coupled with an efficient fragmentation of the resource increases the potential for a cost-effective biocompound industry (Gilbert-López et al. 2015). For example, a coupled effect of an efficient biorefinery and an eco-friendly process could co-produce both bioethanol and biogas, using the green macroalga *Chaetomorpha linum* (O.F. Müller) Kützing, (Ben Yahmed et al. 2016). Similarly, a cascade extraction study was conducted using *Gelidiella acerosa* (Forsskål) Feldmann & Hamel, *Gelidium pusillum* (Stackhouse) Le Jolis

and *Gracilaria dura* (C. Agardh) J. Agardh, to determine the feasibility of these red macroalgae as a multi-product bioresource to produce purified bioethanol, lipids, agar, R-phycoerythrin (R-PE), R-phycocyanin (R-PC) and liquid fertilizer (Baghel et al. 2015). More recently Nunes et al. (2018) showed the potential of *Asparagopsis taxiformis* (Delile) Trevisan for integration into a cascade extraction for the production of a bioactive extract, lipids, carrageenan and cellulose, with minimum waste.

Madeira Archipelago has 810 km^2 of land surface, but an exclusive economic zone of 10,823 km^2 of sea area (Portuguese Navy 2015). There is thus great potential for new sea-related economic industries. Macroalgae are usually collected in the intertidal and subtidal areas, although several nutrient-enriched areas exist that develop large masses of free-floating, beach-cast macroalgae. These beach-casts have a huge economic impact as they tend to cover large expanses of the coastline, which inevitably harms traditional fishery, negatively impacts on tourism and disturbs aquaculture production (Oyesiku and Egunyomi 2014). It is thus imperative to develop mitigation strategies to effectively reduce the negative impact of such beach-casts (Smetacek and Zingone 2013). One strategy could be to use these beach-casts as raw materials (e.g. biocompound extraction) for industrial purposes (Nunes et al. 2019a,b). Still other applications could be the direct use of the beach-cast macroalgae as soil fertilizers for crop production (Franzén et al. 2019).

In view of ongoing mitigation strategies, this study aimed to: 1) assess and compare the biochemical composition of three green (Chlorophyta), three red (Rhodophyta) and nine brown (Ochrophyta, Phaeophyceae) macroalgae from the intertidal and subtidal zone of the Madeira Archipelago and two samples of beach-cast macroalgae from the Island of Gran Canaria; and 2) identify potential new sources of valuable biocompounds that can be extracted and purified from these resources.

Materials and methods

Bioresources from Madeira Archipelago and Canary Islands

Macroalgal samples were collected in the spring of 2017 to a maximum depth of 10 m by means of free-diving round the Madeiran Archipelago; collection sites included the Madeira and Porto Santo Islands. Macroalgal samples comprised three green, three red and nine brown species. The following macroalgae were collected: green, *Dasycladus vermicularis* (Scopoli) Krasser, *Ulva intestinalis*

Linnaeus and *Ulva* Linnaeus Sp.; red, *Asparagopsis taxiformis* (Delile) Trevisan, *Corallina officinalis* Linnaeus and *Halopithys incurva* (Hudson) Batters; brown, *Cystoseira compressa* (Esper) Gerloff & Nizamuddin, *Cystoseira humilis* Schousboe ex Kützing, *Cystoseira usneoides* (Linnaeus) M. Roberts, *Dictyota dichotoma* (Hudson) J.V. Lamouroux, *Halopteris filicina* (Grateloup) Kützing, *Halopteris scoparia* (Linnaeus) Sauvageau, *Lobophora variegata* (J.V. Lamouroux) Womersley ex E.C. Oliveira, *Padina pavonica* (Linnaeus) Thivy and *Sargassum vulgare* C. Agardh.
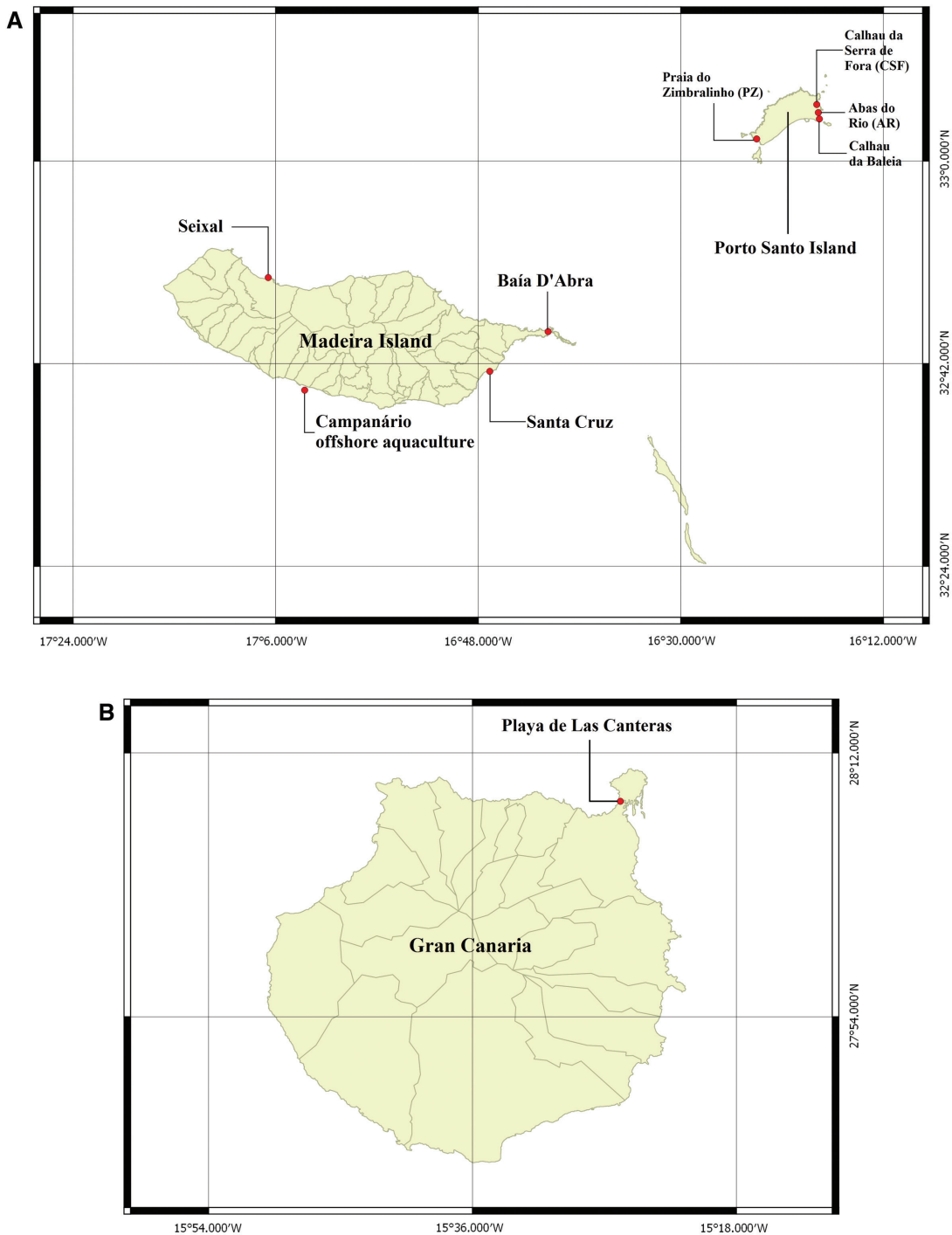
Study sites

In spring, the Madeira Archipelago sea surface temperature varies from 18.5 to 22.5°C, salinity from 32 to 39, conductivity from 54.8 to 55.4 mS · cm^{-1}, pH from 8.1 to 8.2 and the dissolved oxygen from 8.7 to 9.2 mg · l^{-1} which were determined using a seawater multiparameter device (Multi 3430 Set G, WTW, Weilheim, Germany). The seawater here is within an oligotrophic range, with phosphate (0–0.8 μM), silicic acid (0.2–9.2 μM), nitrite (0–0.6 μM) and nitrate (0–34 μM) present in low concentrations throughout the year (Kaufmann and Maranhão 2017). The photosynthetically active radiation (PAR) at a depth of 11 m ranges from 0 to 26% of the surface PAR (Kaufmann and Maranhão 2017). Collection sites are shown in Figure 1A.

Beach-cast macroalgae were collected in Playa de Las Canteras, along the northern shore of the Island of Gran Canaria, Canary Islands. Beach-cast macroalgae 1 was composed of 95% *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira and 5% others, while beach-cast macroalgae 2 was composed of 57% *Halopithys incurva* (Hudson) Batters, 32% *Dictyota* J.V. Lamouroux, 10.7% *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira and 0.3% others. At this site, the sea surface temperature averages 23°C and salinity 36 (Pelegrí et al. 2005). The seawater here is also oligotrophic, with 0.4 μM of nitrate, 0.3 μM of silicon dioxide and 0.01 μM of phosphate, with an average pH of 8.0 (Pérez et al. 2001). The collection site is shown in Figure 1B.

Treatment samples

After harvesting the attached macroalgae, samples were transported to the laboratory in seawater, where they were gently rinsed with filtered freshwater. Thereafter the macroalgae were frozen at −35°C and freeze-dried under reduced pressure (4 × 10^{-4} mbar) with a cooling trap (Scanvac Coolsafe Model 55-4, Labogene, Lynge, Denmark) set at −56°C for 5 days. Finally, lyophilized samples were milled to 200 mesh particle size in an electric mill (IKA

A

Calhau da
Serra de
Fora (CSF)

Praia do
Zimbralinho (PZ)

Abas do
Rio (AR)

Calhau
da Baleia

Porto Santo Island

Seixal

Baía D'Abra

Madeira Island

**Campanário
offshore aquaculture**

Santa Cruz

B

Playa de Las Canteras

Gran Canaria

Figure 1: Maps of both locations showing sampling sites from which macroalgae or beach-cast macroalgae were collected. (A) Madeira Archipelago, including Madeira and Porto Santo Islands; (B) Gran Canaria Island.

Werke Model M20, Staufen, Germany), vacuum-packed with a vacuum sealer (AudionVac Model VMS 153, Derby, UK) and stored at –35°C until further use. Beach-cast macroalgae were cleaned of sand and epiphytes and rinsed with fresh water. The different species were identified, and subsequently air dried at ambient temperature.

Major constituent analysis

Moisture content was determined according to AOAC 925.10 (2000). Samples were oven (Memmert Model UF 260, Schwabach, Germany) dried at 105°C until a constant weight was achieved. Total minerals were determined

according to AOAC 923.03 (2005). Samples were calcinated in a furnace (Vulcan Model 3-550, NEY, USA) at 550°C for 5 h and the mineral content determined gravimetrically. Protein content was determined as described by AOAC 978.04 (2005). The process began with the digestion of the samples at 420°C in a Velp Scientifica digester (DK 8S Digester Heater, Velp Scientifica, Usmate, Italy) using potassium and selenium sulfate. The ammonium sulfate that formed in the reaction was titrated in a distillation and titration unit (Model UDK 152, Velp Scientifica, Usmate, Italy) using sodium hydroxide. Ammonia condensation, using boric acid with bromocresol green and methyl red indicators, allowed for the quantification of total nitrogen. The conversion factors used to convert nitrogen to protein were 5.13 for green, 5.38 for brown and 4.59 for red macroalgae (Lourenço et al. 2002). The protein content (nitrogen-to-protein conversion factor) calculated for the beach-cast macroalgae was determined by considering the % variability of the different macroalgal compositions in each of these beach-cast masses. Lipids were quantified as described by Folch et al. (1957). Initially, freeze-dried milled macroalgae were mixed with $CHCl_3$:MeOH (2:1, v/v), sonicated for 10 min and then centrifuged at room temperature. The extract was filtered, added to a 0.9% NaCl solution, vortexed and centrifuged again for phase separation. The upper phase was removed and the remaining lipophilic phase evaporated in a rotary evaporator (Heidolph, Model Hei-Vap HL, Schwabach, Germany) at 35°C and then weighed on a scale (Precisa, Model ES 225SM-DR, Dietikon, Switzerland). Total carbohydrates were calculated as the difference between 100% of dry matter and the sum of the other biocomponents.

Minor constituent analysis

Chlorophyll a (Chl-a) and total carotenoids (TCC) were extracted with methanol and absorbance read on a spectrophotometer (Shimadzu, Model UV-2401 PC, Kyoto, Japan) at 470, 652.4 and 665.2 nm as per Kumar et al. (2010) and their contents calculated using equations 1 and 2, respectively. Total phenolic content (TPC) was measured as per Chew et al. (2008) and expressed in gallic acid equivalents (GAE). Phenol extraction was performed using 50% methanol and quantified by mixing with Folin Ciocalteu reagent and sodium carbonate at 7.5% (w/v), followed by the absorbance reading at 765 nm.

$$\text{Chlorophyll } a\left(\frac{\mu g}{ml}\right) = 16.72(A665.2) - 9.16(A652.4) \quad (1)$$

$$Cx+c\left(\frac{\mu g}{ml}\right) = (1000(A470)) - (1.63(\text{Chl } a)) - (104.96(\text{Chl } b)) \quad (2)$$

Phycobilins from red macroalgae were extracted with 1 M acetic acid-sodium acetate buffer (pH 5.5) and 0.01% of sodium azide as per Francavilla et al. (2014), and absorbance read at 498.5, 614 and 651 nm, to quantify the allophycocyanin (equation 3), phycocyanin (equation 4) and phycoerythrin (equation 5) content, using the equations developed by Kursar et al. (1983).

$$APC\left(\frac{\mu g}{ml}\right) = 181.3(A651) - 22.3(A614) \quad (3)$$

$$PC\left(\frac{\mu g}{ml}\right) = 151.1(A614) - 991(A651) \quad (4)$$

$$PE\left(\frac{\mu g}{ml}\right) = 155.8(A498.5) - 40(A614) - 10.5(A651) \quad (5)$$

Fucoxanthin from brown macroalgae was extracted using 80% ethanol at 40°C for 1 h, the absorbance read at 445 nm, and the content calculated using equation 6 as per Wu et al. (2014).

$$\text{Fucoxanthin}\left(\frac{mg}{g}\right) = \frac{A445 \times n \times V \times 1000}{A \times m \times 100} \quad (6)$$

Statistical analysis

Data are expressed as an average of three replicates ± standard deviation, using the SPSS 24 software. Tests included the post hoc Tukey's b test, with a significance level of $p < 0.05$ applied to assess the statistical variance of individual compounds between macroalgae. A Pearson correlation was also performed to determine the relationship between the biochemical parameters. STATISTICA 10 software was used to perform a principal component analysis (PCA), frequently used for establishing predictive models and exploratory data analysis. PCA improved the perception of the results, since a score plot (Figure 2) was performed, enabling a visual analysis of the influence of each biochemical parameter in the 2D distribution of the samples. A loading plot (Figure 3) was used to explain a probable sample grouping. A dendrogram (Figure 4) was constructed, based on Euclidean distances, to determine the linkage distance between the different samples.
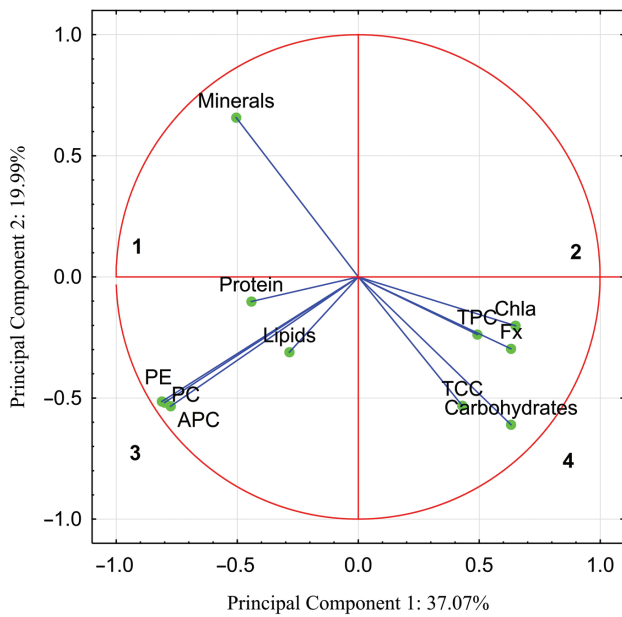
Figure 2: Principal component analysis of the biochemical analysis carried out for the 19 samples of macroalgae from the Madeira Archipelago and beach-cast macroalgae from Gran Canaria, with a projection of the variables on the factor-plane.
Quadrant 1: minerals; Quadrant 3: protein, lipids and phycobilins, including allophycocyanin (APC), phycocyanin (PC) and phycoerythrin (PE); Quadrant 4: chlorophyll *a* (Chl*a*), total phenolic content (TPC), fucoxanthin (Fx), carbohydrates and total carotenoid content (TCC).

Results

Total minerals

Among the macroalgae analyzed, the highest mineral content was observed in *Dasycladus vermicularis* (Scopoli) Krasser and in *Corallina officinalis* Linnaeus, and the lowest mineral content in *Cystoseira humilis* Schousboe *ex* Kützing (Table 1). The red macroalgae *Asparagopsis taxiformis* (Delile) Trevisan from Abas do Rio (AR) (32.37 g · 100 g^{-1} dry weight (dw)) and Praia do Zimbralinho (PZ) (50.12 g · 100 g^{-1} dw), collected in Porto Santo Island (Table 1), showed significant differences in mineral content. Beach-cast macroalgae 1 and 2 had statistically different mineral contents, 38 and 46 g · 100 g^{-1} dw (Table 1).

Protein

The highest protein content was found in the green alga *Ulva intestinalis* Linnaeus (16.85 g of protein per 100 g dw) from Madeira Island, sampled in the offshore fish cages located at Campanário (Table 1). The lowest protein content was found in the red alga *Corallina officinalis* Linnaeus (2.69 g · 100 g^{-1} dw; Table 1). Protein content in the red alga

Asparagopsis taxiformis (Delile) Trevisan varied between 12 and 16 g · 100 g^{-1} dw in the samples collected in Abas do Rio and Praia do Zimbralinho, in Porto Santo Island (Table 1). Beach-cast macroalgae showed protein contents that ranged from 6 to 8 g · 100 g^{-1} dw (Table 1).

Lipid content

The highest lipid content was found in the brown alga *Dictyota dichotoma* (Hudson) J.V. Lamouroux (10.00 g · 100 g^{-1} dw) and the lowest was found in the green alga *Dasycladus vermicularis* (Scopoli) Krasser (2.11 g · 100 g^{-1} dw), both collected from Porto Santo Island (Table 1). A high lipid content was observed in the red alga *Asparagopsis taxiformis* (Delile) Trevisan, collected in Abas do Rio and Praia do Zimbralinho, ranging between 7 and 8 g · 100 g^{-1} dw (Table 1). Beach-cast macroalgae from Playa de Las Canteras, Gran Canaria, had a moderate lipid content, containing from 4 to 5 g · 100 g^{-1} dw (Table 1).

Carbohydrates

The highest carbohydrate contents were found in the brown macroalgae *Cystoseira humilis* Schousboe *ex* Kützing and *Sargassum vulgare* C. Agardh, nom. illeg. (Table 1). Low carbohydrate contents were found in *Dasycladus vermicularis* (Scopoli) Krasser and in *Corallina officinalis* Linnaeus (Table 1). Beach-cast macroalgae showed a medium carbohydrate content, between 34 and 48 g · 100 g^{-1} dw (Table 1).

Chlorophyll *a*

The analysis of macroalgal samples shows that higher concentrations of chlorophyll *a* were present in the Chlorophyta *Ulva intestinalis* Linnaeus (15.23 mg · g^{-1} dw) and Phaeophyceae *Cystoseira usneoides* (Linnaeus) M. Roberts (11.84 mg · g^{-1} dw; Table 2). Lowest chlorophyll *a* contents were detected in *Asparagopsis taxiformis* (Delile) Trevisan from both locations, Abas do Rio and Praia do Zimbralinho (Table 2). Chlorophyll *a* content in Canary Islands beach-cast macroalgae varied between 7 and 8 mg of chlorophyll *a* per g dw (Table 2).

Total phenolic content

TPC was assessed in macroalgae from Madeira Archipelago and was not detected in *Ulva* Linnaeus species, *Asparagopsis taxiformis* (Delile) Trevisan, *Corallina officinalis* Linnaeus, and *Padina pavonica* (Linnaeus) Thivy. The highest
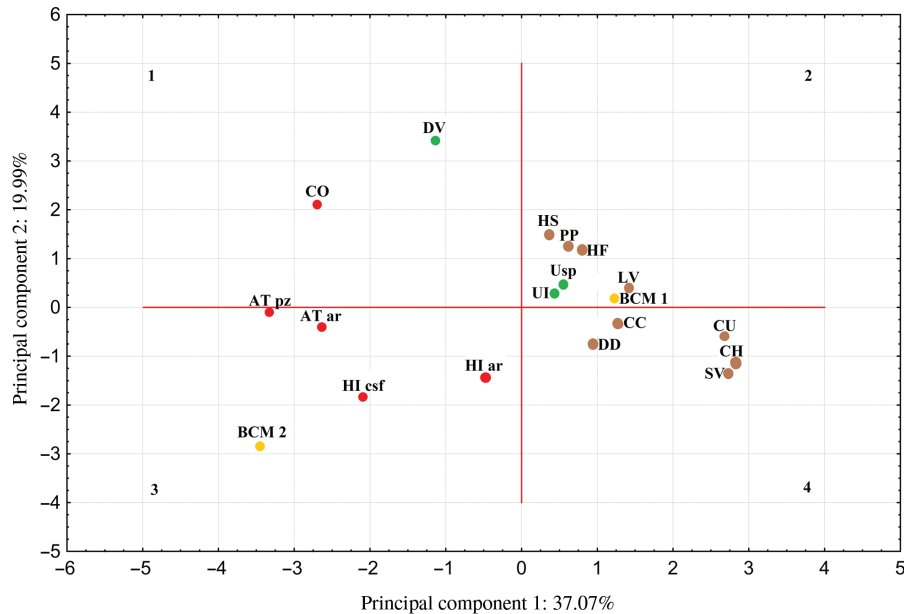
Figure 3: Principal component analysis of the biochemical analysis carried out for the 19 samples of macroalgae from the Madeira Archipelago and beach-cast macroalgae from Gran Canaria, with a projection of the samples on the factor-plane.
Quadrant 1: *Corallina officinalis* Linnaeus (CO) and *Dascladus vermicularis* (Scopoli) Krasser (DV); Quadrant 2: *Halopteris scoparia* (Linnaeus) Sauvageau (HS), *Padina pavonica* (Linnaeus) Thivy (PP), *Halopteris filicina* (Grateloup) Kützing (HF), *Ulva* Linnaeus sp. (Usp), *Ulva intestinalis* Linnaeus (UI), *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira (LV), Beach-cast macroalgae 1 (BCM 1); Quadrant 3: *Asparagopsis taxiformis* (Delile) Trevisan from Praia do Zimbralinho (AT pz) and Abas do Rio (AT ar), *Halopithys incurva* (Hudson) Batters from Calhau da Serra de Fora (HI csf) and Abas do Rio (HI ar), Beach-cast macroalgae 2 (BCM 2); Quadrant 4: *Cystoseira compressa* (Esper) Gerloff & Nizamuddin (CC), *Dictyota dichotoma* (Hudson) J.V. Lamouroux (DD), *Cystoseira usneoides* (Linnaeus) M. Roberts (CU), *Cystoseira humilis* Schousboe *ex* Kützing (CH), *Sargassum vulgare* C. Agardh (SV). The color of each dot represents the color of each macroalga, except for beach-cast macroalgae that are shown in yellow, since these could contain all three groups of macroalgae.
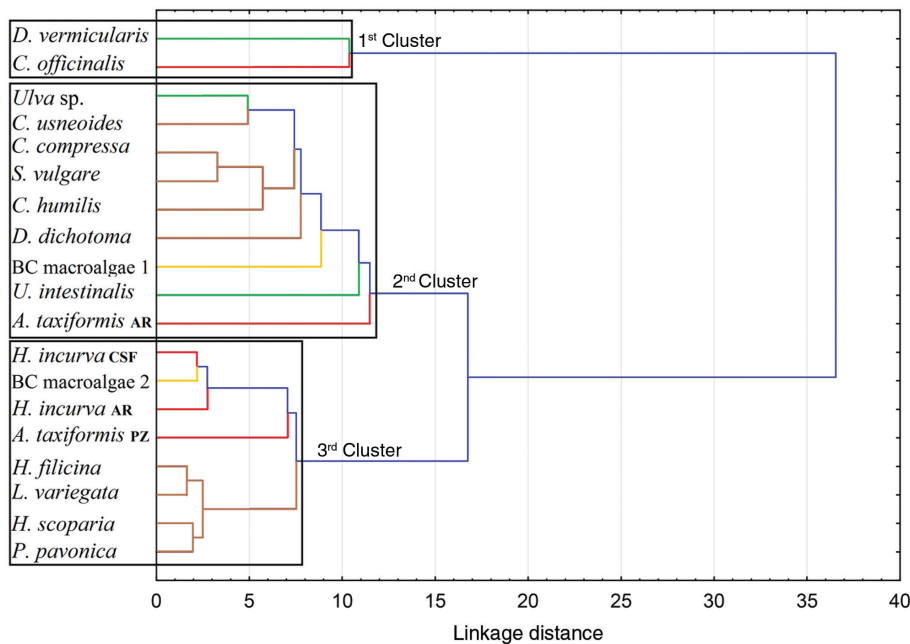
Figure 4: Hierarchical cluster analysis in a dendrogram format, for a single linkage, using Euclidean distance.
The biochemical analysis carried out for the 19 samples of macroalgae from the Madeira Archipelago and beach-cast macroalgae (BC macroalgae) from Gran Canaria were included. The color of each line represents the color of each macroalga, except for beach-cast macroalgae which are shown in yellow. Blue lines indicate mixed algal groups. Algal species names as in Figure 3; BC, beach-cast; AR, Abas do Rio; CSF, Calhau da Serra de Fora; PZ, Praia do Zimbralinho.

Table 1: Biochemical constituents of attached macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands.

Bioresource	Moisture (g · 100 g^{-1} dw)	Total minerals (g · 100 g^{-1} dw)	Protein (g · 100 g^{-1} dw)	Lipids (g · 100 g^{-1} dw)	Total carbohydrates (g · 100 g^{-1} dw)
Green macroalgae					
1 *Dasycladus vermicularis*[1]	3.64 ± 1.03^a	86.96 ± 1.27^n	10.14 ± 0.36^{abc}	2.11 ± 0.63^a	0.00^a
2 *Ulva* sp.[2]	8.15 ± 0.23^{def}	30.25 ± 0.12^e	2.76 ± 0.02^a	5.85 ± 0.83^{ef}	53.73 ± 1.97^{gh}
3 *Ulva intestinalis*[3]	8.83 ± 0.79^{cdef}	26.10 ± 0.39^d	16.85 ± 0.59^c	5.29 ± 0.5^{cdef}	41.81 ± 10.68^{fgh}
Red macroalgae					
4 *Asparagopsis taxiformis* AR[4]	7.77 ± 0.50^{bcdef}	32.37 ± 1.08^e	15.83 ± 0.16^{bc}	7.88 ± 0.64^g	39.73 ± 10.49^{efg}
5 *Asparagopsis taxiformis* PZ[5]	6.35 ± 0.47^{abcdef}	50.12 ± 0.40^i	11.76 ± 0.12^{abc}	6.97 ± 0.79^{fg}	28.68 ± 6.72^{cde}
6 *Corallina officinalis*[5]	3.64 ± 1.60^a	85.19 ± 0.17^n	2.69 ± 0.06^a	5.24 ± 0.91^{cdef}	6.02 ± 1.89^{ab}
7 *Halopithys incurva* AR[4]	5.89 ± 0.89^{abcd}	48.88 ± 1.45^{hi}	9.41 ± 0.19^{abc}	3.83 ± 0.35^{abcd}	34.70 ± 4.62^{ef}
8 *Halopithys incurva* CSF[1]	6.78 ± 0.63^{bcdef}	47.88 ± 0.67^{gh}	7.69 ± 0.04^{abc}	5.05 ± 0.86^{cde}	33.35 ± 4.92^{cdef}
Brown macroalgae					
9 *Cystoseira compressa*[2]	9.08 ± 0.41^f	23.58 ± 0.92^c	4.05 ± 0.17^a	5.61 ± 1.12^{def}	56.55 ± 1.34^{gh}
10 *Cystoseira humilis*[6]	7.60 ± 0.74^{bcdef}	20.44 ± 0.18^b	4.68 ± 0.03^{ab}	2.95 ± 0.10^{ab}	63.51 ± 4.01^h
11 *Cystoseira usneoides*[6]	8.20 ± 1.83^{def}	30.70 ± 0.14^e	3.78 ± 0.14^a	3.50 ± 0.54^{abc}	51.50 ± 4.28^{gh}
12 *Dictyota dichotoma*[5]	5.04 ± 1.47^{ab}	27.51 ± 0.71^d	7.22 ± 0.01^{abc}	10.00 ± 0.67^h	49.76 ± 1.39^{fgh}
13 *Halopteris filicina*[4]	6.06 ± 1.96^{abcde}	55.34 ± 0.50^{jk}	5.47 ± 0.05^{ab}	3.10 ± 0.65^{ab}	31.43 ± 1.16^{cde}
14 *Halopteris scoparia*[7]	5.20 ± 0.70^{abc}	57.20 ± 1.69^{km}	5.54 ± 0.01^{ab}	3.64 ± 0.44^{abc}	29.86 ± 4.06^{cde}
15 *Lobophora variegata*[8]	5.05 ± 0.90^{ab}	54.67 ± 0.47^j	5.92 ± 0.04^{ab}	4.20 ± 0.99^{bcde}	30.88 ± 3.76^{cde}
16 *Padina pavonica*[6]	5.66 ± 0.65^{abcd}	57.85 ± 1.68^m	3.74 ± 0.15^a	3.50 ± 0.60^{abc}	30.17 ± 2.83^{cde}
17 *Sargassum vulgare*[9]	5.79 ± 0.49^{abcd}	22.74 ± 0.16^c	5.49 ± 0.01^{ab}	5.06 ± 0.07^{cde}	59.17 ± 0.74^h
Miscellaneous					
18 Beach-cast macroalgae 1[10]	6.80 ± 0.64^{bcdef}	37.88 ± 0.82^f	6.32 ± 0.09^{abc}	3.67 ± 0.37^{abc}	48.27 ± 6.06^{fgh}
19 Beach-cast macroalgae 2[10]	6.26 ± 0.65^{abcdef}	46.43 ± 1.29^g	8.23 ± 0^{abc}	4.80 ± 0.26^{bcde}	34.04 ± 1.72^{def}

Data are means ± standard deviation in grams per 100 grams of sample (g · 100 g^{-1}) on a dry weight (dw) basis. All determinations were carried out in triplicate (n = 3). Different letters within the same column indicate significant differences (p < 0.05) determined using Tukey b test. Collection locations are identified by superscript values after each scientific or sample name as follows: (1) Calhau da Serra de Fora, Porto Santo; (2) Praia do Zimbralinho, Porto Santo; (3) Campanário, Madeira; (4) Abas do Rio, Porto Santo; (5) Praia do Zimbralinho, Porto Santo; (6) Piscinas naturais Seixal, Madeira, (7) Baía D'Abra, Madeira; (8) Calhau da Baleia, Porto Santo; (9) Santa Cruz, Madeira; (10) Playa de Las Canteras, Gran Canaria.

content of TPC was determined in *Cystoseira usneoides* (Linnaeus) M. Roberts, 35.20 mg · g^{-1} dw (Table 2). The two beach-cast macroalgae analyzed showed distinct amounts of TPC, varying between 1 and 3 mg per g of dw (Table 2).

Total carotenoid content

Among the macroalgae analyzed, the highest TCC was determined in *Halopithys incurva* (Hudson) Batters from Abas do Rio and Calhau da Serra de Fora (Porto Santo Island) with values ranging from 5 to 7 mg · g^{-1} dw (Table 2). The brown algae *Sargassum vulgare* C. Agardh and *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C.Oliveira also had high TCC, with values around 4 mg · g^{-1} dw (Table 2). For beach-cast macroalgae, TCC was between 3 and 4 mg · g^{-1} dw (Table 2).

Phycobilins

In the red macroalgae analyzed, the allophycocyanin (APC) content varied between 0.12 mg · g^{-1} dw in *Corallina officinalis* Linnaeus and 0.33 mg · g^{-1} dw in *Halopithys incurva*

(Hudson) Batters from Calhau da Serra de Fora (Table 3). On the other hand, phycocyanin (PC) oscillated between 0.08 mg · g^{-1} dw in *Asparagopsis taxiformis* (Delile) Trevisan from Abas do Rio and 0.14 mg · g^{-1} dw in *H. incurva* (Hudson) Batters from Calhau da Serra de Fora (Table 3). Finally, phycoerythrin (PE) presented the lowest value in *C. officinalis* Linnaeus, 0.46 mg · g^{-1} dw and the highest in *H. incurva* (Hudson) Batters from Calhau da Serra de Fora, 0.85 mg · g^{-1} dw (Table 3). Among the two samples of beach-cast macroalgae, only beach-cast macroalgae 2 showed phycobilins due to the presence of Rhodophyta macroalgae (57% *H. incurva* (Hudson) Batters). APC, PC and PE values for this resource, were the highest detected in this work (Table 3).

Fucoxanthin

Fucoxanthin content was assessed in the nine brown macroalgae and the two beach-cast macroalgae. Fucoxanthin yield varied from 0.34 mg · g^{-1} dw in *Halopteris scoparia* (Linnaeus) Sauvageau to 1.19 mg · g^{-1} dw in *Sargassum vulgare* C. Agardh (Table 4). Both beach-cast macroalgae, due to the presence of brown seaweeds in their composition, were

Table 2: Chlorophyll, carotenoids and phenolic compounds of attached macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands.

Bioresource	Chlorophyll a (mg·g^{-1} dw)	TCC (mg·g^{-1} dw)	TPC (mg GAE·g^{-1} dw)
Green macroalgae			
1 *Dasycladus vermicularis*	4.97 ± 0.06^{cdef}	0.26 ± 0.01^a	17.31 ± 0.36^f
2 *Ulva* sp.	5.61 ± 0.66^{defg}	1.69 ± 0.11^b	0.00^a
3 *Ulva intestinalis*	15.23 ± 0.33^n	0.00^a	0.00^a
Red macroalgae			
4 *Asparagopsis taxiformis* AR	0.58 ± 0.04^a	0.26 ± 0^a	0.00^a
5 *Asparagopsis taxiformis* PZ	0.88 ± 0.04^a	0.31 ± 0.02^a	0.00^a
6 *Corallina officinalis*	3.43 ± 0.06^{bcd}	0.30 ± 0.01^a	0.00^a
7 *Halopithys incurva* AR	11.38 ± 0.43^m	6.59 ± 0.42^g	16.52 ± 0.76^f
8 *Halopithys incurva* CSF	7.07 ± 0.43^{fghi}	4.58 ± 0.25^f	14.99 ± 0.19^e
Brown macroalgae			
9 *Cystoseira compressa*	4.53 ± 0.38^{bcde}	2.88 ± 0.10^{bcde}	9.11 ± 0.33^d
10 *Cystoseira humilis*	9.65 ± 0.09^{jkm}	4.05 ± 0.09^{def}	33.14 ± 1.41^g
11 *Cystoseira usneoides*	11.84 ± 0.86^m	2.90 ± 0.18^{bcde}	35.20 ± 2.22^g
12 *Dictyota dichotoma*	7.82 ± 1.41^{ghij}	2.74 ± 0.17^{bcd}	2.38 ± 0.20^{bc}
13 *Halopteris filicina*	8.85 ± 1.09^{hijk}	2.77 ± 0.09^{bcd}	1.98 ± 0.02^{bc}
14 *Halopteris scoparia*	8.15 ± 0.16^{hij}	2.15 ± 0.08^{bc}	1.90 ± 0.17^{bc}
15 *Lobophora variegata*	9.04 ± 1.49^{ijk}	4.27 ± 0.18^{ef}	8.99 ± 0.70^d
16 *Padina pavonica*	7.83 ± 0.26^{ghij}	3.60 ± 0.13^{cdef}	0.00^a
17 *Sargassum vulgare*	11.07 ± 2.72^{km}	4.37 ± 0.26^f	14.60 ± 1.03^e
Miscellaneous			
18 Beach-cast macroalgae 1	7.78 ± 0.25^{ghij}	3.58 ± 0.10^{cdef}	3.22 ± 0.20^c
19 Beach-cast macroalgae 2	6.49 ± 1.17^{efgh}	2.88 ± 0.25^{bcde}	1.42 ± 0.10^{ab}

Data are mean ± standard deviation in milligrams per gram (mg·g^{-1}) of sample on a dry weight (dw) basis. All determinations were carried out in triplicate (n = 3). Different letters within the same column indicate significant differences (p < 0.05) determined using Tukey b test. TCC, Total carotenoids; TPC, total phenolic compounds; GAE, gallic acid equivalents. Collection sites: AR, "Abas do Rio"; CSF, "Calhau da Serra de Fora"; PZ, "Praia do Zimbralinho".

Table 3: Phycobilins of attached macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands.

Bioresource	APC (mg·g^{-1} dw)	PC (mg·g^{-1} dw)	PE (mg·g^{-1} dw)
Red macroalgae			
1 *Asparagopsis taxiformis* AR	0.13 ± 0.02^a	0.08 ± 0.01^a	0.51 ± 0.03^a
2 *Asparagopsis taxiformis* PZ	0.21 ± 0.02^b	0.12 ± 0.01^{ab}	0.67 ± 0.03^b
3 *Corallina officinalis*	0.12 ± 0.03^a	0.09 ± 0.01^a	0.46 ± 0.03^a
4 *Halopithys incurva* AR	0.12 ± 0.06^a	0.010 ± 0.01^a	0.82 ± 0.05^c
5 *Halopithys incurva* CSF	0.33 ± 0.03^c	0.14 ± 0.02^b	0.85 ± 0.07^c
Miscellaneous			
6 Beach-cast macroalgae 2	0.48 ± 0.06^d	0.27 ± 0.03^c	1.14 ± 0.06^d

Data are mean ± standard deviation in milligrams per gram (mg·g^{-1}) of sample on a dry weight (dw) basis. All determinations were carried out in triplicate (n = 3). Different letters within the same column indicate significant differences (p < 0.05) determined using Tukey b test. APC, Allophycocyanin; PC, phycocyanin; PE, phycoerythrin. Collection sites: AR, "Abas do Rio"; CSF, "Calhau da Serra de Fora"; PZ, "Praia do Zimbralinho".

also assessed. Fucoxanthin values for beach-cast macroalgae were between 0.52 and 0.65 mg·g^{-1} dw (Table 4).

Statistics

The Pearson correlation coefficients (Table 5) discriminated the macroalgal samples by negative or positive correlations between the compositional parameters. A significant negative correlation was found between total minerals and total carbohydrates ($R^2 = -0.948$). Furthermore, significant positive correlations were found between chlorophyll a and TCC ($R^2 = 0.463$), and between fucoxanthin and TCC ($R^2 = 0.462$).

The PCA (Figures 2 and 3) determined a total of 57.06% of the cumulative variance with two principal components

Table 4: Fucoxanthin content of attached brown macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands.

Bioresource	Fucoxanthin (mg·g^{-1} dw)
Brown macroalgae	
1 *Cystoseira compressa*	0.49 ± 0.01[a]
2 *Cystoseira humilis*	0.59 ± 0.01[ab]
3 *Cystoseira usneoides*	0.75 ± 0.0[abc]
4 *Dictyota dichotoma*	0.77 ± 0.03[abc]
5 *Halopteris filicina*	0.59 ± 0.04[ab]
6 *Halopteris scoparia*	0.34 ± 0.02[a]
7 *Lobophora variegata*	1.07 ± 0.07[bc]
8 *Padina pavonica*	0.39 ± 0.01[a]
9 *Sargassum vulgare*	1.19 ± 0.07[c]
Miscellaneous	
10 Beach-cast macroalgae 1	0.52 ± 0.01[a]
11 Beach-cast macroalgae 2	0.65 ± 0.03[ab]

Data are mean $\pm$ standard deviation in milligrams per gram (mg·g^{-1}) of sample on a dry weight (dw) basis. All determinations were carried out in triplicate (n = 3). Different letters within the same column indicate significant differences (p < 0.05) determined using Tukey b test.

(PC), in which PC 1 had 37.07% and PC 2 19.99%. This projection (Figure 2) showed that protein, lipids and phycobilins were positioned in the 3rd quadrant. The TPC, chlorophyll *a*, fucoxanthin, TCC and carbohydrates were grouped in the 4th quadrant and mineral content was isolated in the 2nd quadrant. Three parameters, namely chlorophyll *a*, TPC and fucoxanthin were located close together, as were TCC and carbohydrates. The phycobilins overlapped in the projection, due to the intrinsic correlation of these compounds. Furthermore, the projection of the cases for individual species (Figure 3) shows that the macroalgae were scattered in the projection plane according to their biochemical composition. *Dasycladus vermicularis* (Scopoli) Krasser and *Corallina officinalis* Linnaeus, are located in the 1st quadrant, influenced by their high mineral content.

Furthermore, the green macroalgae, *Ulva* Linnaeus sp. and *Ulva intestinalis* Linnaeus were located close together in the 2nd quadrant, due to their biochemical resemblance. Two more distinct groups were located in this quadrant: the brown algae *Halopteris scoparia* (Linnaeus) Sauvageau, *Padina pavonica* (Linnaeus) Thivy and *Halopteris filicina* (Grateloup) Kützing, and the brown alga *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira with the beach-cast macroalgae 1. This is due to their intermediate biochemical content, with no distinct parameters. Phycobilins accounted for the isolation of beach-cast macroalgae 2 in the 3rd quadrant, due to its high content of *Halopithys incurva* (Hudson) Batters (57%). In the 3rd quadrant, protein content also imprinted a strong influence, separating *Asparagopsis taxiformis* (Delile) Trevisan from its two locations. Similarly, lipids imprinted a strong influence, separating *H. incurva* (Hudson) Batters from its two locations. In the 4th quadrant, two groups of brown algae were formed, namely *Cystoseira compressa* (Esper) Gerloff & Nizamuddin and *Dictyota dichotoma* (Hudson) J.V. Lamouroux, and also *Cystoseira usneoides* (Linnaeus) M. Roberts, *Cystoseira humilis* Schousboe *ex* Kützing and *Sargassum vulgare* C. Agardh. These two groups were separated due to the influence of five biochemical parameters, namely chlorophyll *a*, TPC, fucoxanthin, TCC and carbohydrates.

With regard to the distance between samples, three well-defined clusters were obtained (Figure 4). The 1st cluster (Euclidean linkage distance of 36) included *Dasycladus vermicularis* (Scopoli) Krasser and *Corallina officinalis* Linnaeus that were well separated from the remaining samples due to their high mineral content. The 2nd and 3rd clusters have a Euclidian linkage distance of 16. The 2nd cluster comprised nine samples, namely two green (*Ulva* Linnaeus sp. and *Ulva intestinalis* Linnaeus), five brown (*Cystoseira usneoides* (Linnaeus) M. Roberts, *Cystoseira compressa* (Esper) Gerloff & Nizamuddin, *Sargassum*

Table 5: Pearson correlation coefficients showing relationships among different chemical components of attached macroalgae from the Madeira Archipelago and beach-cast macroalgae from the Canary Islands.

	Total minerals	Protein	Lipids	Carbohydrates	Chlorophyll *a*	TCC	TPC	Fucoxanthin
Total minerals	1							
Protein	−0.085	1						
Lipids	−0.356[a]	0.294[b]	1					
Carbohydrates	−0.948[a]	−0.105	0.208	1				
Chlorophyll *a*	−0.319[b]	−0.046	−0.350[a]	0.372[a]	1			
TCC	−0.247	−0.398[a]	−0.267[b]	0.340[a]	0.463[a]	1		
TPC	−0.216	−0.235	−0.427[a]	0.268[b]	0.377[a]	0.429[a]	1	
Fucoxanthin	−0.349[a]	−0.419[a]	−0.061	0.416[a]	0.371[a]	0.462[a]	0.276[b]	1

Statistical significance at 0.01 level (a) or at 0.05 level (b) bilateral using Pearson correlation test; Signaling (−) reveal the negative relation between parameters, or, in its absence, their positive correlation. Values presented are for R^2. TCC, Total carotenoid content; TPC, total phenolic content. Data for allophycocyanins (APC), phycocyanins (PC) and phycoerythrins (PE) were not in compliance with Pearson coefficient assumptions and therefore are not shown in this table.

vulgare C. Agardh, *Cystoseira humilis* Schousboe *ex* Kützing and *Dictyota dichotoma* (Hudson) J.V. Lamouroux), one red (*Asparagopsis taxiformis* (Delile) Trevisan AR) macroalgae, and the beach-cast macroalgae 1. The 3rd cluster comprised eight samples, namely three red (*Halopithys incurva* (Hudson) Batters CSF, *H. incurva* (Hudson) Batters AR and *A. taxiformis* (Delile) Trevisan PZ), four brown (*Halopteris filicina* (Grateloup) Kützing, *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira, *Halopteris scoparia* (Linnaeus) Sauvageau and *Padina pavonica* (Linnaeus) Thivy) macroalgae and the beach-cast macroalgae 2.

Discussion

Mineral composition

The mineral content of macroalgae is an essential trait to determine their nutritional, industrial, pharmaceutical, or agricultural uses. Macroalgae are recognized as a rich source of minerals, mainly iodine and iron, and have a high potential to become a source for daily nutrition or to be used as a nutraceutical product (Mišurcová et al. 2011a).

The mineral content in macroalgae can fluctuate due to endogenous factors intrinsic to a specific species, or due to several exogenous environmental factors such as the concentration of minerals, the temperature and the pH of seawater (Circuncisão et al. 2018). This may explain why *Asparagopsis taxiformis* (Delile) Trevisan, collected along the southern shore of Porto Santo Island, displayed a mineral content that fluctuated between 1.36 and 2.11, values higher than those previously reported for the species collected on Madeira Island (Nunes et al. 2017). The variation in mineral content between these samples of *A. taxiformis* (Delile) Trevisan (Nunes et al. 2017, this study) was potentially a result of the differences in the ecological conditions of the intertidal and subtidal zones between Madeira and Porto Santo Islands. Additionally, *A. taxiformis* (Delile) Trevisan was rich in bioaccumulated iodine, which could be used to produce nutraceutical iodine-rich supplements (Nunes et al. 2018). *Corallina officinalis* Linnaeus and *Dasycladus vermicularis* (Scopoli) Krasser collected in Porto Santo Island contained the highest mineral contents, similar to *Galaxaura rugosa* (J. Ellis & Solander) J.V. Lamouroux (Rhodophyta) collected from Reis Magos beach in Madeira Island (Nunes et al. 2017). Similarly, Marsham et al. (2007) found a high mineral content (78 g · 100 g⁻¹ dw) in *C. officinalis* Linnaeus collected from North Yorkshire, UK. Moreover, *Dictyota dichotoma* (Hudson) J.V. Lamouroux had more than twice the mineral content of the same species collected in India, although *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira had a similar content compared with Verma et al. (2017). The two beach-casts of macroalgae differed in their mineral yields notably due to the variation in macroalgal composition collected at different periods.

Potential as a protein source

Ulva intestinalis Linnaeus collected in offshore cages at the *Sparus aurata* Linnaeus fish farm was rich in protein. Protein contents for the species reported in this study were similar to those reported for the species from Southern Thailand by Benjama and Masniyom (2011). The high protein content in our study is likely the result of unconsumed feed from the fish farm that dissolves into the surrounding waters, providing available nutrients. This is known as eutrophication, which can be substantially reduced with the incorporation of macroalgae that then increase in growth rate and protein content as a consequence (Shpigel et al. 2018). This strategy reduces the environmental impact of fish aquaculture and enables the development of a macroalgal resource that has a market potential (Ellis and Tiller 2019).

Asparagopsis taxiformis (Delile) Trevisan collected from Porto Santo Island (this study) has also proven to be a prominent protein source, but with slightly lower values than those collected on the south coast of Madeira Island (Nunes et al. 2017). The differences in the protein contents of the two *A. taxiformis* (Delile) Trevisan populations can likely be attributed to the higher human impact (increased eutrophication through increased population density and industrialization) on Madeira Island. Furthermore, the protein content of *Corallina officinalis* Linnaeus in this study was significantly lower than that reported by Marsham et al. (2007) for the species. Verma et al. (2017) assessed a total of 30 macroalgae collected in India and measured a higher protein content (12 g · 100 g⁻¹ dw) in *Dictyota dichotoma* (Hudson) J.V. Lamouroux. The beach-cast macroalgae in this study were considered a moderate protein source, being similar to the pelagic macroalgal mixtures of *Sargassum natans* (Linnaeus) Gaillon and *S. fluitans* (Børgesen) Børgesen (Oyesiku and Egunyomi 2014). These pelagic masses stay afloat, and previous research by Oyesiku and Egunyomi (2014) demonstrated that these masses contain a moderate protein yield. These could be extensively collected, when located near to the coastline, highlighting its potential use as a protein source for multiple applications.

Macroalgae are regularly consumed whole or in supplement form due to their protein content, which is comparable to other plant sources (Phong et al. 2016). Some selected species of macroalgae are a staple food in some Asian countries. Increased protein content increases the

potential of a macroalga to be introduced as a nutraceutical ingredient, providing essential amino acids. The fortification of several food products is a viable strategy to improve the products' nutritional value and thus achieve the recommended daily intake (RDI).

Low-fat bioresource

The macroalgae investigated in this study had a low lipid content, not exceeding 10%. Such low lipid contents were previously reported by Lorenzo et al. (2017) who evaluated the edible brown macroalgae *Ascophyllum nodosum* (Linnaeus) Le Jolis and *Fucus vesiculosus* f. subglobosus Kjellman. Nonetheless, the lipid composition of macroalgae is an important determinant because bioactive lipids, in particular, activate several biochemical mechanisms in the consumers of macroalgae (Mišurcová et al. 2011b). The lipid content of *Asparagopsis taxiformis* (Delile) Trevisan from Madeira Island was previously determined by Nunes et al. (2018). This macroalga is known to be a traditional staple food in Hawaii, identified as "limu kohu" (Burreson et al. 1976). Nunes et al. (2019c) recently published the nutraceutical and bioactive potential of lipid extracts obtained from three macroalgae collected from Madeira Island, identifying their fatty acid composition, anti-cholinesterase activity, and *in vitro* cytotoxicity to the A549 tumor cell line. Moreover, in this study, *Corallina officinalis* Linnaeus had a higher lipid content than the same species examined by Marsham et al. (2007), demonstrating the biochemical dissimilarity of these resources when propagated under different conditions. Similarly, in this study the lipid content of *Dictyota dichotoma* (Hudson) J.V. Lamouroux and *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira were approximately triple those found in these macroalgae by Verma et al. (2017). The beach-cast macroalgae in this study were not a noticeable lipid source. In contrast, Oyesiku and Egunyomi (2014) described a higher lipid content in pelagic macroalgal masses, highlighting the influence of the macroalgal composition on the lipid yield. These comparisons show the importance of assessing different resources due to the biochemical differences that can occur. Total lipid content and composition can vary between species/assemblages and can fluctuate due to differing environmental conditions and geographical positions (Miyashita et al. 2013).

Carbohydrate content inference

Vizetto-Duarte et al. (2016) assessed the biochemical composition of five *Cystoseira* C. Agardh species, collected on the mainland of Portugal. They found that *Cystoseira* *humilis* Schousboe *ex* Kützing had 64.09 g of carbohydrates per 100 g dw, similar to our results. The beach-cast macroalgae in this study showed a high polysaccharide content, which was lower than the macroalgal pelagic masses collected offshore of the coast of Nigeria (Oyesiku and Egunyomi 2014). The variation in carbohydrate content is likely related to the different species composition of these algal masses, ranging from almost monospecific to mixed species compositions. Additionally, specific biochemical pathways and habitat features force these organisms to biosynthesize different contents and types of polysaccharides (Sudha et al. 2014).

Chlorophyll *a* as a potential nutraceutical

Chlorophyll *a* is an important feature for macroalgae due to the capability of this molecule to chelate several chemical carcinogens and mutagens, thus potentially decreasing the risk of cancer in consumers (Chen and Roca 2018). Chlorophyll *a* content was highly variable in the different species sampled in this study, with *Ulva intestinalis* Linnaeus being the most prominent source. Furthermore, *Dictyota dichotoma* (Hudson) J.V. Lamouroux and *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira contained significantly higher chlorophyll *a* values than those reported for these species from India (Verma et al. 2017). This could indicate, at least for these species, that the production of chlorophyll *a* is higher in Madeira Archipelago, promoting this location for producing or collecting macroalgae when targeting higher chlorophyll *a* biomass.

Total phenolic content (TPC) in brown macroalgae

Phenolic compounds are used by algae as protection against marine grazers, epiphytes, pathogens, and in photoprotection mechanisms (Audibert et al. 2010).

In this work, TPC analysis demonstrated a high content of these compounds in *Cystoseira humilis* Schousboe *ex* Kützing and *Cystoseira usneoides* (Linnaeus) M. Roberts. This finding corroborates the statement by Deniaud-Bouët et al. (2014) who stated that brown macroalgae will tend to have higher TPC contents due to the possible enzymatic cross-linking of alginates by phenols in regulating the strengthening of the cell wall. Habitat conditions greatly influence the composition and concentration of phenolic compounds in macroalgae. The biosynthesis and accumulation are determined by the action of long desiccation periods in the intertidal zone, high levels of UV radiation (O'Sullivan et al. 2011), or grazing activity (Alstyne 1988).

Macroalgae as a source of carotenoids with antioxidant potential

TCC is an important parameter that can determine the selection of macroalgae as a source of antioxidants and provide functional activity.

In this work, elevated amounts of TCC were detected in the red macroalga *Halopithys incurva* (Hudson) Batters and the browns *Sargassum vulgare* C. Agardh and *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira. They could be selected for further analysis to determine the specific carotenoids that comprise the physiological composition of these macroalgae. In our study, *Dictyota dichotoma* (Hudson) J.V. Lamouroux and *L. variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira had considerably higher TCC values than isolates of the same species investigated by Verma et al. (2017). Beach-cast macroalgae were not a prominent source of TCC, and the variation was strongly imprinted by the algal composition. Macroalgae are known to biosynthesize β-carotene and other carotenoids that are specific to the algal class. These terpenoids and their oxygenated derivatives, xanthophylls are antioxidants, scavenging reactive oxygen species (ROS) throughout the metabolic processes (von Elbe and Schwartz 1996).

Beach-cast macroalgae and *Halopithys incurva* (Hudson) Batters as prominent sources of phycobilins

Phycobilins are water-soluble macromolecules present in red algae, which have different bioactivities (Apt et al. 1995). Biological tests performed *in vitro* and *in vivo* have shown their performance for anti-tumor, anti-viral and anti-inflammatory activity, as well as their hepatoprotective or neuroprotective potential (Sekar and Chandramohan 2008). *Halopithys incurva* (Hudson) Batters from Calhau da Serra de Fora possessed the highest content of all the three classes of phycobilins among the red algae analyzed in this study. Interestingly, beach-cast macroalgae 2, which comprised 57% of *H. incurva* (Hudson) Batters, had a higher phycobilin content than *H. incurva* (Hudson) Batters from Calhau da Serra de Fora, possibly due to the different ecosystem dynamics (e.g. available nutrients, exposure to sunlight, hydrodynamics, grazing, epiphytes, etc) that these macroalgae were exposed to. Similar values for allophycocyanin were found in this study to those reported by Verma et al. (2017), who assessed 14 red macroalgae collected from India, but with higher values for phycocyanin and phycoerythrin than those presented in this study.

Environmental effects on fucoxanthin yield

Fucoxanthins are exclusively present in the photosynthetic complex of brown algae (Haugan and Liaaen-Jensen 1992), contributing to about 10% of the total carotenoids found in nature (Kim et al. 2012). Different environmental conditions can trigger different adaptation mechanisms, enabling strategic metabolic pathways and leading to an increase or decrease in carotenoid production. Any environmental factor that influences carotenoid production will thus influence fucoxanthin production.

The brown macroalga *Sargassum vulgare* C. Agardh had the highest fucoxanthin content in this study. Although beach-cast macroalgae 1 had significantly more brown macroalgae (95% *Lobophora variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira) than beach-cast macroalgae 2 (32% *Dictyota* J.V. Lamouroux sp. and 10.7% *L. variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira), no significant difference in fucoxanthin content was observed between them. These results are in line with the brown macroalgae analyzed in this study. Moreover, *Dictyota dichotoma* (Hudson) J.V. Lamouroux and *L. variegata* (J.V. Lamouroux) Womersley *ex* E.C. Oliveira from this study had approximately four times more fucoxanthin than the same species collected from India (Verma et al. 2017). Due to their biological and therapeutic activities (e.g. anticancer, antidiabetic, antitumor, etc.; Rajauria et al. 2016), macroalgae are screened to find new and abundant sources of these compounds.

Statistical analysis of the biochemical parameters

Correlation analysis among all eight biochemical parameters (Table 5) showed 15 correlations significant at 1% and five correlations significant at 5%. Of these, the three correlations with the highest Pearson coefficient values involved just five parameters (carbohydrates, chlorophyll *a*, fucoxanthin, TCC and total minerals). The highest coefficient was found for the negative relationship between carbohydrates and mineral content. Marinho-Soriano et al. (2006) also found this correlation in their assessment of two tropical macroalgae collected in the northwest of Brazil. Moreover, in a previous study, Nunes et al. (2017), examining seven macroalgae from the Madeira Archipelago, also found a negative correlation between carbohydrates and minerals, as well as a positive correlation between chlorophyll *a* and TCC which was confirmed in the present study. The third highest coefficient was for the positive correlation between fucoxanthin and TCC, but this could be explained by the fact that fucoxanthin

contributes to the total amount of carotenoids in macroalgal resources.

Principal component analysis closely related the phycobilins with protein content. Verma et al. (2017) reported similar results. Phycobilins are linked to proteins, forming phycobiliproteins, which are light-harvesting pigment-protein complexes present in red algae (Sudhakar et al. 2015). In the projection of algal samples (Figure 3), several small groups were formed, due to their biochemical similarity. A total of eight groups and one single sample were displayed in the four quadrants. *Dasycladus vermicularis* (Scopoli) Krasser and *Corallina officinalis* Linnaeus formed one group, as did the *Asparagopsis taxiformis* (Delile) Trevisan and *Halopithys incurva* (Hudson) Batters collected in different locations. Also, the two species of *Ulva* Linnaeus were located close together, but beach-cast macroalgae 2 (BCM 2) did not form a group with any of the remaining macroalgae. The dendrogram (Figure 4) elucidates the biochemical relations between this heterogeneous group of macroalgae and beach-cast macroalgae. These samples formed three distinct clusters, based on their biochemical analysis, and environmental conditions were found to influence their linkage distance. *Halopithys incurva* (Hudson) Batters from the two locations, Calhau da Serra de Fora and Abas do Rio, were closely related, but *A. taxiformis* (Delile) Trevisan from Abas do Rio and Praia do Zimbralinho were separated between clusters 2 and 3, in contrast to their close positions in Figure 3. This discrepancy can be attributed to the two different statistical analyses. Furthermore, the two samples of beach-cast macroalgae were statistically different from each other in terms of their phycobilin, total mineral and TPC content, and this demonstrates that if this resource is considered for biocompound extraction or any economic utilization, a deeper study is needed to understand the compositional variability of these resources throughout the year, to improve its industrial integration.

Conclusion

The green macroalga *Ulva intestinalis* Linnaeus is a good potential source of protein, lipids, carbohydrates and chlorophyll *a*. *Ulva* Linnaeus as a genus is permitted for food consumption in the European Union, and it can be harvested in offshore seabream aquaculture on Madeira Island. This macroalga has the potential to be upscaled into an integrated *Ulva*-fish aquaculture system, increasing profitability by providing an additional commercial resource and reducing nitrate emissions to the environment, by capturing this nutrient. The brown macroalga

Dictyota dichotoma (Hudson) J.V. Lamouroux has potential as a source of lipids and could be used to produce lipid-related supplements. Similarly, the red macroalga *Halopithys incurva* (Hudson) Batters can be used for phycobilin extraction. This species could be used for extracting these compounds with a lower purity index for the food industry, functioning as a natural dye or as a source of bioactive compounds. The brown macroalga *Sargassum vulgare* C. Agardh has potential as a source of fucoxanthin and can be used to produce rich fucoxanthin extracts using "Green Chemistry" techniques, supplements or additives for food products. Beach-cast macroalgae were found to be a source of several biocompounds, but their value is strongly dependent on their algal composition, which is unpredictable; further study is needed here.

Several significant correlations were found including the negative correlation between carbohydrates and minerals, and positive correlations between TCC, chlorophyll *a* and fucoxanthin. Principal component analysis and dendrogram analysis helped to determine the biochemical parameters that strongly characterize these macroalgae and their biochemical groups. It is of the utmost importance to determine the biochemical composition of these new bioresources, thus determining the potential applications and strategies appropriate to each resource. Moreover, multi-compound extraction could be optimized for these resources, implementing biorefinery strategies to maximize extraction and improve income and sustainability. It is important to link this biochemical knowledge with an efficient and eco-friendly extraction design in order to build a profitable and sustained, long-lasting industry.

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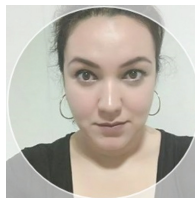
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Graphical abstract

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Maria Carmo Barreto and Miguel A.A.
Pinheiro de Carvalho

**Biochemical study of attached macroal-
gae from the Madeira Archipelago and
beach-cast macroalgae from the Canary
Islands: multivariate analysis to deter-
mine bioresource potential**

Research article: Macroalgae
from the Madeira Archipelago
and beach-cast macroalgae
from Gran Canaria are
valuable sources of important
biochemical compounds,
necessary for human nutrition
and industrial applications.

Keywords: carotenoids;
fucoxanthin; lipids;
phycobilins; protein.