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Artículo original de investigación

Chemical composition *of Padina fernandeziana* (Phaeophyceae, Dictyotales) from Juan Fernandez Archipelago, Chile

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Abstract

The chemical composition of the endemic brown macroalga *Padina fernandeziana* (Skottsberg & Levring) from Juan Fernández Archipelago, Chile was analyzed. Dry matter, crude protein, ether extract (lipids), carbohydrates, ash and total dietary fiber content of three samples were determined by standard methods. *P. fernandeziana* showed a high content of ashes (35-53%), carbohydrates (30-44%) and total dietary fiber (32-44% on dry basis). The content of proteins (6-8%) and lipids (1.8-2%) were low. The species showed temporal variations in the percentages of proteins, lipids, minerals, dietary fiber contents, and non-nitrogenous extracts. *Padina fernandeziana* presented comparable values to those of algae used actually as food in the region.

Keywords: *Brown algae, dietary fiber, lipids, proteins, Robinson Crusoe Island*

Composición química de Padina fernandeziana (Phaeophyceae, Dictyotales) del Archipiélago de Juan Fernández, Chile

Resumen

Se determinó la composición química de la macroalga parda *Padina fernandeziana* (Skottsberg & Levring), endémica del archipiélago de Juan Fernández, Chile. Mediante métodos estándar y en triplicado se determinó en base a peso seco el porcentage de proteínas crudas, extracto etéreo (lípidos), carbohidratos, cenizas y el contenido de fibra dietética total. *P. fernandeziana* presentó un alto contenido de cenizas (35-53%), carbohidratos (30-44%) y de fibra dietética total (32-44% en base a peso seco). El contenido proteico (6-8%) y lípidico (1,8-2%) fue bajo. La especie demostró variaciones temporales en el porcentage de proteínas, lípidos, minerales, fibra dietética y extracto no-nitrogenado. *Padina fernandeziana* presentó valores comparables a los de algas que se utilizan actualmente como alimento en la región.

Palabras clave: *Algas pardas, fibra dietética, lípidos, proteínas, Isla Robinson Crusoe*

1. Introduction

The use of macroalgae in Asia as food source is well known and established. During the last decades they are attracting increasing attention as a valued food source in western societies (MacArtain *et al.*, 2007). 221 macroalgal species have been listed worldwide as commercially utilized (Zemke-White & Ohno, 1999). This commercial utilization includes: Human food, fodder, fertilizer, drugs, paper production, and the "roe on kelp" industry. The industrial utilization of macroalgae is at present largely confined to extraction for phycocolloids and, to a much lesser extent, certain fine biochemicals. Recently in Chile, macroalgae have been used for the production of industrial aquaculture (feed for *Oncorhynchus mykiss*) increasing the added value of this natural resource (Mansilla & Ávila, 2011). Health, food and drug industries are interested in new sources for novel products.

Although the chemical content and nutritional value of some macroalgae from Chile were examined earlier (*i.e.* Quilhot, 1970; Chapman & Chapman, 1980; Pak & Araya, 1996; Ortiz *et al.*, 2006; Goecke *et al.*, 2010), there are about 550 species of macroalgae in this country, but only 1% of them are widely known (Santelices, 1991; Ortiz *et al.*, 2009). Thus, the coast of Chile harbors a huge food and biomedical potential that has not been investigated yet. In this sense, the latest addition of highly valuable macroalgal species, such as the edible *Callophyllis variegata* (Bory de Saint-Vincent) Kützing and *Chondracanthus chamissoi* (C.Agardh) Kützing to the Chilean exports (Buschmann *et al.*, 2005), are clear examples of the importance of developing novel macroalgal products.

The algal genus *Padina* Adanson is well defined, widely distributed throughout the tropics and very easy to recognize (Geraldino *et al.*, 2005). Its geographical distribution reaches South America and Southeast Asia, from the tropics to cool temperate waters, where they occur in intertidal and subtidal habitats. Ramírez & Osorio (2000) have reported it as endemic from Juan Fernández Archipielago. With 43 currently recognized species, *Padina* is the second most speciose dictyotalean genus after *Dictyota*, and can be especially abundant in certain regions as well (Silberfeld *et al*., 2012,)

A few species of *Padina* spp. have been traditionally used as food source in some coastal cultures, e.g. as a gelatin-like sweetmeat (Robledo & Freile-Pelegrín, 1997), seasoning in dry flake forms or as salt replacement for high blood pressure patients (Novaczek & Athy, 2001) and for treatment of goiter and scrofula (Anggadiredja, 1992). The Chilean macroalga *Padina fernandeziana* is not listed in the 145 edible seaweeds of the world (Zemke-White & Ohno, 1999), and its chemical constituents have never been studied before. The aim of this work is to investigate the chemical composition of the common and endemic macroalga *P. fernandeziana* from the Juan Fernández Archipelago, Chile.

2. Materials and Methods

2.1 Seaweed material

Padina fernandeziana (Fig. 1) was collected by SCUBA diving in April 2002 and January 2003. Samples were taken from a distinct site of the Cumberland bay of the Robinson Crusoe Island, Juan Fernández Archipelago (33º37'S, 78º49'W), Chile. They were transported to the laboratory at 4°C. All the samples were washed with distilled water to remove associated debris and salt water. Epibionts were removed and the macroalgae were dried 48 hours at 35°C, grounded and stored in a dry place. Part of the macroalgae was fixed in 4% formaldehyde for its taxonomic identification. Algae were identified by examination of their thallus architecture and special morphological characters: Fronds, cell layers and reproductive structures (as in Gaillard, 1973; Geraldino *et al*., 2005). A voucher specimen was deposited in the Herbarium of Museo de Historia Natural, Santiago, Chile (code SGO).

2.2Chemical Composition

Dry matter, ether extract, total dietary fiber contents and ash of three samples were determined by standard AOAC methods (AOAC, 1997). Crude protein (N x 5.38) was determined according to Lourenco *et al.* (2002). Carbohydrate contents were calculated with the formula: Carbohydrates = [100% - (%protein + %lipid + %ashes + %water)] according to Ortiz *et al*. (2009). All inorganic salts, reagents, and buffers were analytical reagent grade.

Total dietary fiber content was determined with the Dietary Fiber Kit was from Sigma Chemical Co. (St. Louis, CA, USA). The results were expressed as a percentage of the dry weight.

3. Results and Discussion

The chemical composition of the endemic macroalga *Padina fernandeziana*, from Juan Fernandez Archipelago from two sampling campaigns, is shown in Table 1. The water content of the samples was less than 11.5%.

Table 1. Chemical composition (mineral ashes, proteins, lipids, carbohydrates and total dietary fiber) in the brown algae *Padina fernandeziana* expressed as a percentage of the dry weight, all values are means ±sd (n=3).

Padina fernandeziana	**April 2002**	**January 2003**
Water content	9.23 ±2.04	7.33 ±0.49
Mineral ashes	35.75 ±2.10	53.79 ±0.19
Total lipids	2.01 ±0.03	1.86 ±0.15
Proteins	8.31 ±1.60	6.54 ±1.43
Total dietetic fiber	44.61 ±0.66	32.29 ±0.52
Carbohydrates	44.07 ±1.28	30.48 ±1.03

3.1 Mineral Ashes

The marine habitats in which macroalgae grow allow them to absorb a wide diversity and high amounts of minerals (Rupérez, 2002). In fact, trace elements and minerals are more abundant in macroalgae compared to terrestrial food sources (MacArtain *et al*., 2007) (Table II). In the present study, the mineral ashes content in the macroalgae collected in April 2002 and January 2003 was high (35.75% and 53.79% respectively, Table 1). Variations in the ash content according to species and origin of the samples have been noticed in prior studies (see Table II). Behairy & El-Sayed (1983) explained the high content of ash in brown macroalgae by the presence of polysaccharides and divalent cations. For example, *Padina gymnospora* (Kützing) Sonder have showed a higher content of copper, chromium, iron, lead, sulphur, potassium and calcium, than five other macroalgae (Manivannan *et al*., 2009). Species of *Padina* contained relatively high concentrations of SO_4^{-2} (60%) comparable to those of highly acidic macroalgal species like *Desmarestia* spp. (Sasaki *et al*., 1999). Sulphate seems to be a typical component of marine macroalgal polysaccharides, related to high salt concentration in the environment and to specific aspects of ionic regulation (Manivannan *et al*., 2009).

Padina species are an important source of calcium carbonate and organic matter in the shallow waters of tropical and subtropical areas (Wefer, 1980). This genus produces extracellular calcium in their erect and conspicuous fan-like fronds (Okazaki *et al*., 1986). This mineral is precipitated in the form of aragonite within the apical portions of the frond and deposited as needles on the proximal dorsal surfaces (Geraldino *et al*., 2005) (Fig. 1). This is an important aspect not only from a taxonomical, but also from a nutritional and biogeochemical point of view. It has been calculated that *Padina sanctae-crucis* Børgesen produces 240 g m^2 calcium carbonate per year (Wefer, 1980). The specific content of calcium on *Padina* spp. has been reviewed by Basson & Abbas (1992), Santoso *et al*. (2004), Manivannan *et al*. (2009) and Carrillo *et al*. (2003).

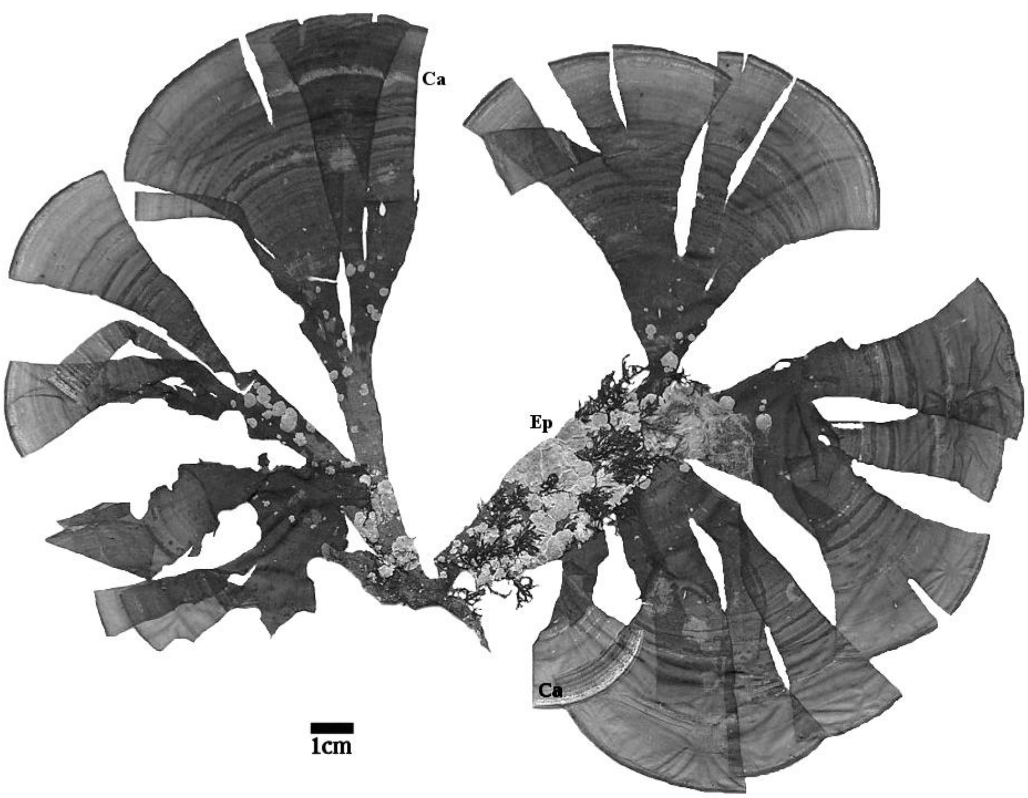

Fig. 1. Pressed thalli of the brown macroalga *Padina fernandeziana*, endemic from the Juan Fernandez Archipelago, Chile. Calcification deposits (Ca) over the frond and the presence of epiphytes (Ep) are showed in the figure. Scale bar = 1 cm.

3.2 Proteins

From a nutritional point of view macroalgae are a good source of proteins (Lahaye, 1991; Jiménez-Escrig & Goñi, 1999). But brown macroalgae, with the exception of *Ecklonia* spp., consist of only 5% to 15% protein (Mabeau & Fleurence, 1993; Norziah & Ching, 2000). Consequently, *P. fernandeziana* collected in April 2002 and January 2003 showed low content of protein (8,31% and 6,54% respectively, Table I). As in our results, prior chemical studies of different *Padina* species showed a low and variable protein content too (see Table II). It has been observed that the protein content of macroalgae is dependent on season and environmental growth conditions (Dawczynski *et al.*, 2007). Besides the low protein content, it has been shown that those macroalgae are rich in essential amino acids.

The specific content of amino acids in *Padina* spp. has been reviewed by Lewis (1962), Khafaji *et al*. (1992) and Wahbeh (1997).

3.3 Carbohydrates

Macroalgae are rich in carbohydrates (Mabeau & Fleurence, 1993; Rupérez, 2002). The typical carbohydrates in brown macroalgae are fucoidan, laminaran, cellulose and alginates (Dawczynski *et al.*, 2007). The levels of carbohydrates detected in the present study were within the ranges previously reported for other *Padina* species (Table II). *P. fernandeziana* presented high contents of non-structural carbohydrates ranging from 30% to 44% dry weight (Table I). According to earlier works, mannitol constitutes the major carbohydrate of low molecular weight in *Padina* spp. (Mian & Percival, 1973). Silva *et al.* (2005) showed that brown macroalgae produce a great variety of acidic polysaccharides, such as alginic acids and different heterofucans that were found in *P. gymnospora*. Different species of *Padina* contained at least five different types of polysaccharides (Mian & Percival, 1973; Prasada Rao *et al*., 1984; Karmakar *et al*., 2010). These heterofucans comprised variable proportions of glucuronic acid, galactose, glucose, mannose, xylose, fucose or fucosyl residues in addition to a protein moiety and sulfate (Salgado *et al*., 2005).

3.4 Lipids

Our results further confirm that the lipid fraction in macroalgae represents only 1 - 5 % of algal dry matter (Tables I & II, Jiménez-Escrig & Goñi, 1999; Carrillo *et al.*, 2002; McDermid & Stuercke, 2003). Although macroalgae have been reported to have low lipid contents (Mabeau & Fleurence, 1993), their polyunsaturated fatty acid (PUFA) composition is superior to those of terrestrial vegetables in regard to the human diet (Goecke *et al*., 2010; Kumari *et al*., 2010). Some of those essential fatty acids like omega-3 and omega-6 PUFAs must be consumed by humans and animals in their normal diet (MacArtain *et al*., 2007). The fatty acid content of different *Padina* species, from different biogeographycal regions, have been reviewed by Arao & Yamada (1989), Heiba *et al*. (1997), Wahbeh (1997), Kamenarska *et al*. (2002), Orhan *et al*. (2003), and Kumari *et al*. (2010), confirming this assumption.

3.5 Dietary fiber

Macroalgae are also potentially good sources of dietary fiber (Dawczynski *et al.*, 2007). They are known to contain a variety of soluble and insoluble fibers including agar, carrageenans, xylans, alginates, fucans, laminarans, sulfated rhamnoxyloglucurons, celluloses and mannans (McDermid *et al.*, 2005). In *P. fernandeziana* the content of total dietary fibers was high (32.29 – 44.61%, Table I). Our results presented are in the same range as described for other Dictyotales (see McDermid *et al.*, 2005). In previously studies, macroalgal fibers accounted for up to 50% of total dry mass (Mabeau & Fleurence, 1993), although for the genus *Padina* much lower values of crude fiber have been observed (Table 2).

Table 2. Chemical composition of different *Padina* species from around the world.
Two common edible macroalgae (*Durvillaea antarctica* and *Ulva lactuca*) from Chile and two commonly consumed terrestrial vegetables (lettuce and soybeans) are used as reference. Values expressed as a percentage of the dry weight except: (fw) values in fresh weight, (cf) crude fiber, (-) = not determined. CBH = carbohydrates. Chile-2002 and 2003 correspond to the present work.

Species	Ashes	Protein	CBH	Lipids	Fibers	Origin
P. australis	5.50±0.4	1.50±0.1	-	0.80±0.1	9.60±0.6	Indonesia[14 fw]
P. distromatica	-	5.30	-	-	-	India[7]
P. durvillei	34.43	5.24±0.1	44.18	0.69	7.57	Mexico[5 cf]
P. fernandeziana	35.75	8.31	44.07	2.01	44.61	Chile-2002
P. fernandeziana	53.79	6.54	30.48	5.52	32.29	Chile-2003
P. gymnospora	-	5.33	-	-	-	India[7]
P. gymnospora	-	17.08±0.3	21.88±1.2	1.40±0.3	-	India[8 fw]
P. gymnospora	6.5	2.2±0.6	-	-	-	India[1]
P. gymnospora	36.61±2.1	9.86	1.86	0.11±0.5	9.07±0.5	Mexico[13 cf]
P. gymnospora	44.41	6.76	40.84	0.71	7.29	Puerto Rico[4]
P. gymnospora	-	14.30	-	-	-	US[12]
P. pavonica	33.08±0.8	11.83±1.4	-	1.79±0.5	11.6±0.5	Iran[15 cf]
P. pavonica	23.1±4.3	17.40±4	-	4.40±2	-	Jordan[16]
P. pavonica	7.50±0.1	6.70±1	32.00±6	5.10±2	-	Pakistan[2]
P. pavonica	28-32.9	5.46-7	33.2-41	4.4-4.6	9-10.11	Pakistan[11]
P. tetrastromatica	-	6.55	-	-	-	India[7]
P. tetrastromatica	-	-	-	2.07±0.3	-	India[6]
P. vickersiae	21.74	18.62	-	1.43	9.78	Saudi Arabia[3]
Ulva lactuca	11.0±0.1	27.2±1.1	61.5±2.3	0.3±0.0	60.5±0.6	Chile[10]
D. antarctica	17-25,7	10-11.6	58-70.9	0.8-4,3	56-71.4	Chile[10]
Lettuce	0.7	1.2	-	0.1	0.5	Malaysia[9 fw]
Soybeans	4.8	33.8	-	18.9	5.5	Malaysia[9 fw]

(1) Abbas *et al*., 1992; (2) Akhtar & Sultana, 2002; (3) Behairy & El-Sayed, 1983; (4) Burkholder *et al*., 1971; (5) Carrillo *et al*., 2002; (6) Kumari *et al*., 2010; (7) Lewis, 1962; (8) Manivannan *et al*., 2008; (9) Norziah & Ching, 2000; (10) Ortíz *et al*., 2006; (11) Rashida & Rashida, 1993; (12) Renaud *et al*., 1990; (13) Robledo & Freile-Pelegrín, 1997; (14) Santoso *et al*., 2004; (15) Tabarsa *et al*., 2012; (16) Wahbeh, 1997.

As mentioned before, most of the macroalgal polysaccharides are not digested; therefore they can be regarded as dietary fibers (Wahbeh, 1997; Fleurence, 1999). Major non-digestible components in plant foods include not only dietary fiber but also resistant starch and proteins, minerals and other compounds such as oligosaccharides, polyphenols, lipids, that resist digestion (Rupérez & Toledano, 2003). The nature of soluble macroalgal fibers is such that their passage throughout the gastrointestinal tract occurs largely without digestion, and therefore it can increase feelings of satiety and aid digestive transit trough their bulking capacity (MacArtain *et al*., 2007). The human consumption of macroalgal fiber has been proven to be health-promoting and its benefits include promotion of growth and protection of the beneficial intestinal flora, hypoglycaemic and reduction of risk of colon cancer (Dawczynski *et al*., 2007).

4. Conclusions

Many macroalgal species have been used traditionally as ingredients in both medicinal and food preparations in different regions across the world (Anggadiredja, 1992; Novaczek & Athy, 2001; Kumari *et al*., 2010), but in general, the nutritional properties of macroalgae are not known completely yet (Mabeau & Fleurence, 1993). Over the past 50 years, the utilization of algae has increased considerably, with the consequent increase in applied research in various related fields (Jiménez-Escrig & Sánchez-Muniz, 2000). Macroalgae are considered as low caloric foods with high contents of minerals, vitamins and carbohydrates (Kumari *et al*., 2010). Accordingly, *Padina fernandeziana* showed a high content of ashes, carbohydrates and total dietary fiber. The content of proteins and lipids were low, as normal for these brown macroalgae. The studied macroalga presented comparable values to those of algae used actually as food in Chile (see Table 2). The chemical composition of macroalgae varied considerably, depending on factors such as the species, geographical distribution and habitat, season, developmental stage and nutrient concentrations in the environment, among others (Fleurence, 1999; Goecke *et al.*, 2010; Mancilla & Ávila, 2011). In this sense, we observed seasonal variations in the chemical composition of the sampled macroalgae.

The mineral content in macroalgae is higher compared to that of land plants and animal products (Table 2, Mabeau & Fleurence, 1993; Rupérez, 2002; MacArtain *et al*., 2007). As aquaculture, poultry culture and heliciculture need further calcium and other mineral complement diets, algal biomass could serve as dietary supplement. Seaweed meal has important benefits for animal health and nutrition that could be applied or tested in marine organisms of commercial importance (Mansilla & Ávila, 2011).

In addition, different extracts and compounds of a variety of *Padina* species have shown promising biological activities (e.g. anticoagulant, antiviral, antioxidant and gastroprotective action), and could serve as a functional food (see Prasada Rao *et al*., 1984; Rocha de Souza *et al*., 2007; Chew *et al*., 2008; Amornlerdpison *et al*., 2009; Karmakar *et al*., 2010).

Macroalgae are a renewable natural resource existing in large quantities all along the Pacific Coast, nevertheless, there has been little exploration for diversification of the uses of macroalga (Ortiz *et al.*, 2006). In Chile, the exploitation of macroalgae has been carried out for more than 60 years (Mansilla & Ávila, 2011), but is still concentrated in very few species. The chemical characterization of macroalgae is necessary to attract interest in developing novel seaweed products in order to increase the profitability of algal markets (Buschmann *et al*., 2005). Chile with its long coast, rich in macroalgal resources, is an interesting source of novel products.

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