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Seaweeds from the Portuguese coast as a source of proteinaceous material: Total and free amino acid composition profile

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ABSTRACT

The total protein content and the (total and free) amino acid composition of nine edible species of red, brown and green seaweeds collected in the Portuguese North-Central coast were quantified to assess their potential contribution to the recommended dietary intake. Whenever possible, the protein and amino acid composition was compared with that of commercial European seaweeds. The protein content was the highest ($P < 0.05$) in red species (19.1–28.2 g/100 g dw), followed by the green seaweed *Ulva* spp. (20.5–23.3 g/100 g dw), with the lowest content found in brown seaweeds (6.90–19.5 g/100 g dw). Brown seaweeds presented the lowest mean contents of essential amino acids (EAAs) (41.0% protein) but significantly ($P < 0.05$) higher concentrations of non-essential amino acids (36.1% protein) and free amino acids (6.47–24.0% protein). Tryptophan, methionine and leucine were the limiting EAAs in all species. In contrast, lysine was found in high concentrations, especially in red (2.71–3.85% protein) and green (2.84–4.24% protein) seaweeds.

1. Introduction

Seaweeds have been traditionally used as a food source in many Asian countries, with a contribution ranging from 10% to 25% of food intake (Mišurcová et al., 2014). In Europe, although seaweeds have received great attention for human food in the last decades, they have been mostly exploited for a variety of biotechnological purposes, including cosmeceuticals, animal feed, fatty acids and alginates production, wastewater treatment, and as biofuel (Makkar et al., 2016; Bleakley & Hayes, 2017). Norway, France and Ireland are the dominant seaweed suppliers, whereas Spain, Portugal and the United Kingdom are small producers and suppliers (Peinado, Girón, Koutsidis, & Ames, 2014).

Seaweeds are macroscopic marine algae, taxonomically classified as red (*Rhodophyta*), brown (*Phaeophyta*) or green (*Chlorophyta*), depending on the nature of their pigments (Peinado et al., 2014; Mišurcová et al., 2014; Bleakley & Hayes, 2017). In general, seaweeds are recognized for their richness in minerals and certain vitamins, as well as the presence of bioactive substances such as polysaccharides, proteins, lipids and polyphenols claimed to have a medicine-like effect in treating or preventing certain diseases (Déléris, Nazih, & Bard, 2016; Rioux, Beaulieu, & Turgeon, 2017). The nutritional composition of seaweeds depends on the developmental stage and mostly on environmental factors, namely, geographical location, habitat, season and nutrient content of the growth medium (Holdt & Kraan, 2011; Peinado et al., 2014).

The protein content presents high variability, ranging from 10 to 30% of dry weight (dw) in red seaweeds, 5 to 15% dw in brown seaweeds and 3 to 47% dw in green seaweeds (Kadam, Álvarez, Tiwari, & O'Donnell, 2017; Rodrigues et al., 2015). According to literature, the highest protein contents in seaweeds are found during the period of winter-early spring and the lowest during summer-early autumn (Pangestuti & Kim, 2015). The essential amino acids (EAAs) composition represents almost half of total amino acids (Černá, 2011) and meets the Food and Agriculture Organization of the United Nations requirements for EAAs (FAO, 1991) with levels comparable to those found in traditional high-protein sources such as meat, egg, soybean and milk (Bleakley & Hayes, 2017). This gives seaweeds great potential to be exploited as a source of proteins and as supplement in functional food or for the extraction of valuable compounds (Holdt & Kraan, 2011).

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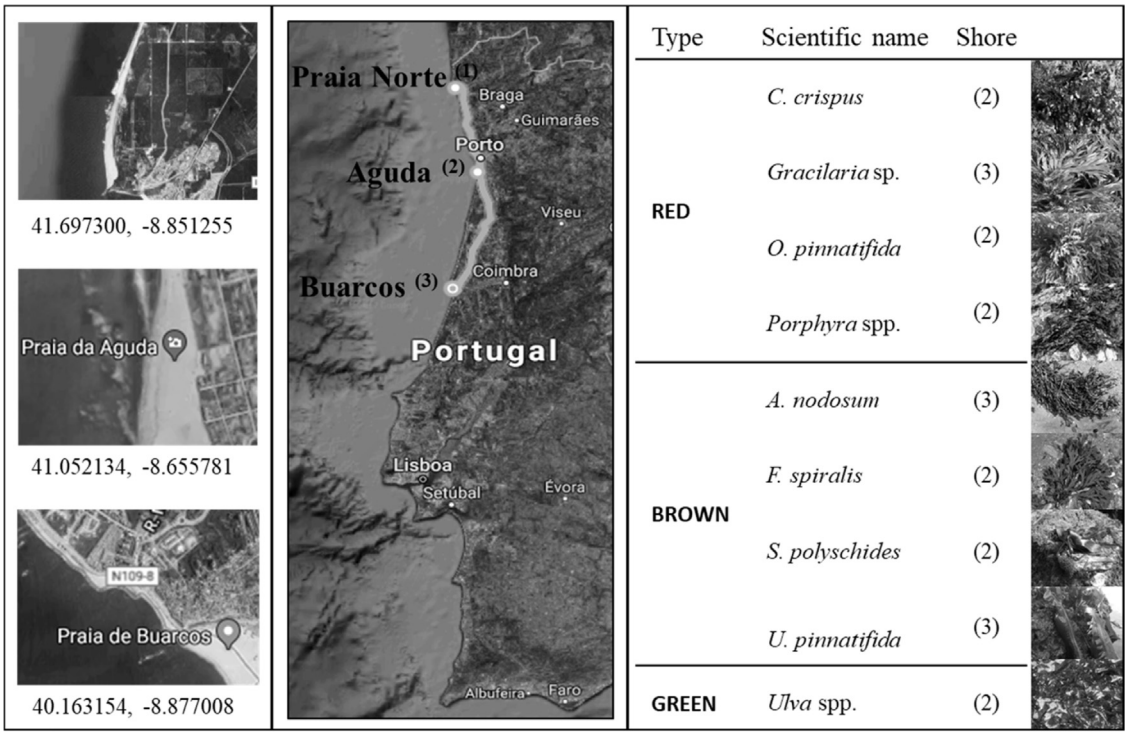

Fig. 1. Location and GPS coordinates of the shores considered for seaweeds harvesting in the North-Central coast of Portugal: Praia Norte in Viana do Castelo, Aguda in Vila Nova de Gaia and Buarcos in Figueira da Foz.

Nevertheless, seaweed protein digestibility appears to be limited by the presence of various anti-nutritional compounds, such as polysaccharides (xylans, agar, carrageenan, or alginates), lectins, protease inhibitors, goitrogens, allergens, anti-vitamins, saponins, tannins and phytate (Silva et al., 2015; Fleurence, Morançais, & Dumay, 2018; Mišurcová, Kráčmar, Klejdus, & Vacek, 2010). The presence of toxic compounds, such as heavy metals or fucotoxins – if present in its natural environment – can also be a limiting factor for their use in food industry (Mišurcová et al., 2010).

Portugal presents one of the largest exploration marine areas in Europe, with a very rich and diverse seaweed flora (Mare, 2014). To date, whilst scientific research has been carried out on the nutritional composition of potentially edible seaweeds of this region, such as *Osmundea pinnatifida*, *Saccorhiza polyschides*, *Fucus spiralis*, and *Porphyra* sp. (Paiva, Lima, Patarra, Neto, & Baptista, 2014; Patarra, Leite, Pereira, Baptista, & Neto, 2013; Rodrigues et al., 2015), scarce information exists concerning the amino acid content, particularly, the free fraction recognized for its role in the taste sensation referred to as 'umami' (Yamaguchi, & Ninomiya, 2000). Moreover, most of the previous studies of the amino acid content of seaweeds have considered species obtained from aquaculture and do not take in account the seasonal variations of the protein material.

This study aimed to characterize nine different edible seaweeds (four species of red seaweeds, four species of brown seaweeds and one species of green seaweed) collected on the North-Central coast of Portugal in terms of *(i)* protein content, *(ii)* total and free amino acid profile, *(iii)* amino acid score and their contributions to recommended daily intakes (RDIs) of EAAs, and *(iv)* seasonal variations of the protein material. In addition, the amino acid profiles of wild seaweeds collected in the North-Central coast of Portugal were compared with those of ten commercial European seaweeds available in the Portuguese market (wild and from aquaculture).

2. Material and methods

2.1. Chemicals and reagents

HPLC-grade acetonitrile and methanol, tetrahydrofuran (THF), orthoboric acid, methanesulfonic acid (MSA); *o*-phthalaldehyde (OPA); 9-fluorenylmethyl chloroformate (FMOC) and tryptamine [3-(2-aminoethyl)indole] were purchased from Sigma-Aldrich (Steinheim, Germany). Ultrapure water used for the preparation of all reagents, eluents, and buffers was obtained from a Milli-Q-simplicity 185 system (Millipore, Bedford, MA, USA). All solutions and reagents were filtered through 0.2 μm MS® Nylon membrane filters. The amino acid standards alanine (Ala), aspartic acid (Asp), arginine (Arg), asparagine (Asn), glutamic acid (Glu), glycine (Gly), hydroxyproline (Hyp); histidine (His), isoleucine (Ile), leucine (Leu), lysine (Lys), methionine (Met), norvaline (Nva), phenylalanine (Phe), proline (Pro), serine (Ser), taurine (Tau), tyrosine (Tyr), threonine (Thr) and valine (Val) were from Sigma-Aldrich (Steinheim, Germany); the amino acid standards glutamine (Gln) and tryptophan (Trp) were purchased from Merck (Darmstadt, Germany).

2.2. Seaweeds sampling

Fifty four samples of seaweeds were collected between April and July 2016 (batch A) and between October and November 2016 (batch B), including four species of red seaweeds: *Chondrus crispus* (*C. crispus*), *Gracilaria* sp., *Osmundea pinnatifida (O. pinnatifida)* and *Porphyra* spp.; four different species of brown seaweeds: *Ascophyllum nodosum (A. nodosum), Fucus spiralis (F. spiralis), Saccorhiza polyschides (S. polyschides)* and *Undaria pinnatifida (U. pinnatifida)*; and one species of green seaweed (*Ulva* spp.; no other green species was available). The sampling sites in the North-Central coast of Portugal included Praia Norte in Viana do Castelo, Aguda in Vila Nova de Gaia and Buarcos in Figueira da Foz (Fig. 1). Seaweed material was collected manually cutting the fronds, washed with seawater and stored in opaque plastic bags with excess water during transportation to the laboratory.