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Amino acids, fatty acids, and dietary fibre in edible seaweed products

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Abstract

The nutritional compositions of 34 edible seaweed products of the *Laminaria* sp., *Undaria pinnatifida*, *Hizikia fusiforme* and *Porphyra* sp. varieties were analyzed.

This study determined amino acid and fatty acid (FA) distributions and contents of protein, fat, and total fibre of these seaweed varieties. In general, the marine macroalgae varieties tested demonstrated low lipid contents with 2.3 ± 1.6 g/100 g semi-dry sample weight (s.w.) and proved to be a rich source of dietary fibre (46.2 ± 8.0 g/100 g s.w). The pure protein content of seaweed products varied widely (26.6 ± 6.3 g/100 g s.w. in red algae varieties and 12.9 ± 6.2 g/100 g s.w. in brown algae varieties). All essential amino acids were detected in the seaweed species tested and red algae species featured uniquely high concentrations of taurine when compared to brown algae varieties. Interestingly, the FA distribution of seaweed products showed high levels of n-3 FA and demonstrated a nutritionally ideal n-6/n-3 FA ratio. The predominante FA in various seaweed products was eicosapentaenoic acid (C20:5, n-3) which was at concentrations as high as 50% of total FA content.
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Keywords: Edible seaweed; Fat; Protein; Fatty acids; Amino acids; Dietary fibre

1. Introduction

Commercially available varieties of marine macroalgae are commonly referred to as "seaweeds". Macroalgae can be classified as red algae (Rhodophyta), brown algae (Phaeophyta) or green algae (Chlorophyta), depending on their nutrient and chemical composition. Red and brown algae are mainly used as human food sources.

The protein content of seaweed varieties varies greatly and demonstrates a dependence on such factors as season and environmental growth conditions. For example, the protein content of brown algae species, e.g., *Laminaria japonica*, *Hizikia fusiforme* or *Undaria pinnatifida*, is relatively low with 7–16 g/100 g dry weight (d.w.) (Jurković, Kolb, & Colić, 1995; Kolb, Vallorani, & Stocchi, 1999; Rupérez & Saura-Calixto, 2001). In contrast, red algae, e.g., *Palmaria palmata* (Dulse) and *Porphyra tenera* contain 21–47 g protein/100 g d.w. (Fleurence, 1999; Rupérez & Saura-Calixto, 2001).

Abbreviations: AA, amino acids; AAS, amino acid score; Ala, alanine; ALA, α-linolenic acid; Arame, Eisenia bicyclis; Arg, arginine; Asp, aspartic acid; Cys, cysteine; d.w., dry weight; Dulse, *Palmaria palmata*; EAA, essential amino acids; EAAI, essential amino acid index; essential AA/non-essential AA, EAA/NEAA; EPA, eicosapentaenoic acid; FA, fatty acids; FAO, Food and Agriculture Organization of the United Nations; FAME, fatty acid methyl esters; Glu, glutamic acid; Gly, glycine; Hijiki, *Hizikia fusiforme*; Ile, isoleucine; *Konbu*, *Laminaria* sp.; LA, linoleic acid; LCFA, long-chain fatty acids; LC-PUFA, long-chain polyunsaturated fatty acids; Leu, leucine; Lys, lysine; MCFA, middle-chain fatty acids; Met, methionine; MUFA, monounsaturated fatty acids; N, nitrogen; Nori, *Porphyra* sp.; NPN, non-protein nitrogen; Phe, phenylalanine; P- Ser, phosphoserine; PUFA, polyunsaturated fatty acids; SCFA, short-chain fatty acids; SD, standard deviation; SDA, stearidonic acid; SFA, saturated fatty acids; semi-dry sample weight, s.w.; Tau, taurine; Thr, threonine; Trp, tryptophan; Val, valine; Wakame, *Undaria pinnatifida*; WHO, World Health Organization.

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The protein in algae contains all essential amino acids (EAA) and all EAA are available throughout the year although seasonal variations in their concentrations are known to occur (Galland-Irmouli et al., 1999). For example, the proportion of EAA is 45–49% in *Hizikia* sp. and *Eisenia bicyclis* (Arame). In both these brown algae varieties, Trp is the first limiting EAA, followed by Lys (Kolb et al., 1999). The EAA contents of some species (e.g., *Porphyra* sp.) can be compared with those of soy and egg protein (Fleurence, 1999; Galland-Irmouli et al., 1999). In addition, high concentrations of Arg, Asp and Glu are found in many seaweed species (Fleurence, 1999).

The fat content of marine macroalgae accounts for 1–6 g/100 g d.w. (Fleurence, Gutbier, Mabeau, & Leray, 1994; Jurković et al., 1995; Herbreteau, Coiffard, Derrien, & De Roeck-Holtzhauer, 1997). In some brown algae varieties, such as *Hizikia* sp. and Arame, only 0.7–0.9 g/100 g d.w. of fat content were found (Kolb et al., 1999).

Red algae (e.g., *Porphyra* sp.) have high concentrations of eicosapentaenoic acid (C20:5, n-3, EPA), with 48.0–51.0% of total FAME, and marginal concentrations of arachidonic acid (C20:4, n-6), with 2.1–10.9% of total FAME and, linoleic acid (C18:2, n-6, LA), with 1.3–2.5% of total FAME (Fleurence et al., 1994; Takagi, Asahi, & Itabashi, 1985). In contrast, brown algae (e.g., *Laminaria* sp., *Undaria* sp., *Hizikia* sp.) have high concentrations of oleic acid (C18:1, n-9) with 4.1–20.9% of total FAME, LA with 4.0–7.3% of total FAME as well as α-linolenic acid (C18:3, n-3, ALA) with 3.6–13.8% of total FAME but low concentrations of EPA with 5.9–13.6% of total FAME (Fleurence et al., 1994; Takagi et al., 1985). Interestingly, in *Porphyra* sp., *Laminaria* sp., and *Undaria* sp., the concentrations of docosahexaenoic acid (C22:6, n-3, DHA) and docosapentaenoic acid (C22:5, n-3) were below the detection limit (less than 0.1% of total FAME) (Fleurence et al., 1994; Takagi et al., 1985).

The types and abundance of carbohydrates vary strongly between algae species. Typical carbohydrates in red algae varieties consist of floridean starch (α-1.4-binding glucan), cellulose, xylan, and mannan. The water-soluble fibre fraction is formed by sulfur-containing galactans, e.g., agar and carrageen (Jiménez-Escrig & Sánchez-Muniz, 2000; Van den Hoek, Jahns, & Mann, 1993). The typical carbohydrates in brown algae varieties consist of fucoidan, laminaran (β-1.3-glucan), cellulose, alginates, and mannitol. Brown algae fibres are mainly cellulose and insoluble alginates. Alginates are Ca, Mg, or Na salts of alginic acid (1.4-linked polymer of β-D-mannuronic acid and α-L-guluronic acid). The amorphous, slimy fraction of brown algae fibres consists mainly of water-soluble alginates and/or fucoidan. Main reserve polysaccharides of Phaeophyta are laminaran (β-1.3-glucan) and mannitol (Kolb et al., 1999; Van den Hoek et al., 1993). The typical algae carbohydrates are not digestible by the human gastrointestinal tract and, therefore, they are dietary fibres. The content of total dietary fibre ranges from 33–50 g/100 g d.w. (Jiménez-Escrig & Cambrodon, 1999; Lahaye, 1991; Rupérez & Saura-Calixto, 2001). Accordingly, the fibre content of seaweed varieties is higher than those found in most fruits and vegetables. The human consumption of algal fibre has been proven to be health-promoting and it benefits are well documented in the scientific literature. The consumption of this dietary fibre has been related to the following health promoting effects: (1) its consumption promotes the growth and protection of the beneficial intestinal flora (Fujii, Kuda, Saheki, & Okuzumi, 1992; Goni, Guidel-Urbano, Bravo, & Saura-Calixto, 2001; Kuda, Yokoyama, & Fujii, 1997; Kuda, Goto, Yokoyama, & Fujii, 1998a, Kuda, Goto, Yokoyama, & Fujii, 1998b), (2) its consumption, in combination with high glycemic load foods, reduces the overall glycemic response, seaweed fibre acts as a hypoglycaemic (Goni, Valdivieso, & Garcia-Alonso, 2000), (3) its consumption greatly increases stool volume (Jiménez-Escrig & Sánchez-Muniz, 2000) and (4) its consumption reduces the risk of colon cancer (Guidel-Urbano & Goni, 2002).

In addition, seaweed varieties are rich sources of vitamin C, vitamin B-complex, e.g., folic acid and B12, and vitamin A precursors, such as β-carotene (McDermid & Stuercke, 2003; Takenaka et al., 2001; Watanabe et al., 1999, Watanabe, Takenaka, Kittaka-Katsura, Ebara, & Miyamoto, 2002; Yamada, Yamada, Fukuda, & Yamada, 1999; Yon & Hyun, 2003).

Because seaweed species are rich in beneficial nutrients, in countries such as China, Japan, and Korea, they have been commonly utilised in human alimentation (since ancient times) (Lahaye, 1991). For example, Japanese people consume more than 1.6 kg algae (d.w.) per year *per capita* (Fleurence, 1999). In addition to their importance as traditional Asian foods, seaweed species are utilised industrially as a source of hydrocolloids, such as agar, carrageen, and alginate (Jiménez-Escrig & Sánchez-Muniz, 2000).

Over the past few decades, the consumption of seaweed products has increased in European countries. Currently, approximately 15–20 edible algae strains are being commonly marketed for consumption in Europe. These seaweed varieties differ greatly in their quality, colour, consistency, and nutrient content. Therefore, this investigation evaluates and compares the nutrient and chemical contents of 34 commercially available seaweed products which were locally purchased in German food stores and speciality shops.

2. Materials and methods

2.1. Samples

Thirty four dried macroalgae were analysed, which are classified as 17 brown algae (Phaeophyta) and 17 red algae (Rhodophyta). The brown algae samples were dried and consisted of eight *Laminaria* sp. (Konbu), seven *Undaria pinnatifida* (Wakame), and two *Hizikia fusiforme* (Hijiki) products. The brown algae varieties originate from China,

Japan, and Korea. The dried red algae varieties are commercially named Nori and are *Porphyra* sp. Twelve of this variety originated from Japan and Korea. Eight products of this group were dried and additionally roasted. The remaining five dried red algae varieties of different consistency were from China. On the package there was no more information about the processing of the analysed seaweed products.

2.2. Methods

Crude dried seaweed materials were collected, then blended to obtain homogeneous samples, and pulverised before representative samples were taken for chemical analysis.

For determination of the oven-dry weight, samples were dried at 105 °C for 24 h.

Seaweed sample organic nitrogen content was quantified by the Kjeldahl method and an estimate of the crude protein content was calculated by multiplication of the organic nitrogen content by a factor of 6.25 (Lourenço, Barbarino, & De-Paula, 2002). The content of non-protein nitrogen (NPN) species was obtained after precipitation of proteins with trichloracetic acid (10%). Pure protein content resulted from the difference between crude protein and NPN contents. The content of total fibre was enzymatically determined (α-amylase, protease, amyloglucosidase; BIOQUANT® Total Dietary Fibre, Merck).

2.3. AA analysis

Acid hydrolysis and analysis of free amino acids were conducted according to the guidelines of the European Community (98/64/EG). AA samples were separated, and identified using the AA analyser LC-3000 (Eppendorf-Biotronik; Germany) by post-column derivatisation with ninhydrin. AA concentrations were calculated by ChromStar32, version 6.0.

While acid hydrolysis has been the accepted method for pre-treatment of proteins to prepare them for AA analysis, all of the Try is destroyed. Therefore, Try analysis requires dissolution of the protein by treatment of the sample with a solution of lithium hydroxide (4 M) and autoclaving in the absence of air at 110 °C for 20 h before Try analysis (Degussa, 1998; Lucas & Sotelo, 1980).

2.4. Lipid extraction and preparation of fatty acid methylesters (FAME)

Total lipids in algae were extracted using a solvent mixture of methanol/chloroform/water 1:2:1 (v/v/v) according to the method of Folch, Lees, and Sloane-Stanley (1957). For the preparation of FAME, $NaOCH_3$ and 1.1.3.3-tetramethylguanidine were used. The analyses of sample FAME extracts were conducted via gas chromatography (GC, GC-17 V3, Shimadzu, Japan) equipped with an auto-sampler (AOC-5000) and flame ionization detector. One GC procedure was required to analyze the FAME distribution of these samples. This method determined the identity and general FA distribution of 4–22 carbon length FAs (including straight and branched structures) using a fused-silica capillary column DB-225ms (30 m × 0.25 mm, i.d. with 0.2 μm film thickness; Jand W, Scientific, USA) and H_2 as carrier gas. The results are expressed as percentage of total FAME.

2.5. Statistics

The results were expressed as means with standard deviation (SD). All statistical analysis was performed using the SPSS software package, version 11.5 (SPSS Inc., Chicago). The unpaired *t*-test was employed to compare the values between red and brown algae varieties. The ANOVA multivariate test was utilized to evaluate the variance between the nutrient characteristics of red and brown algae subclasses. Differences were considered significant at $P < 0.05$.

3. Results and discussion

3.1. Dry weight, contents of protein, lipids, and dietary fibre

Samples of commercially available seaweed products were oven-dried and their d.w. determined (93 g/100 g s.w. in red algae varieties and 90 g/100 g s.w. in brown algae varieties) (Table 1). The results demonstrate that

Table 1
Chemical composition given in means ± SD (g/100 g s.w.; $n = 34$)

Nutrimental components	Red algae			Brown algae			
	Porphyra sp.[A]	*Porphyra* sp.[B]	Overall average	*Undaria pinnatifida*	*Laminaria* sp.	*Hizikia fusiforme*	Overall average
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Dry weight	93.5 ± 1.5^{a}	$92.3 \pm 0.7^{a,c}$	93.1 ± 1.3^{a}	89.3 ± 1.4^{b}	$91.0 \pm 2.2^{c,d}$	$89.4 \pm 0.5^{b,d}$	90.0 ± 1.9^{a}
Crude protein	31.4 ± 8.4^{a}	30.9 ± 3.9^{a}	31.3 ± 7.3^{a}	19.8 ± 1.4^{b}	7.5 ± 1.9^{c}	$11.6 \pm 0.8^{b,c}$	13.8 ± 6.2^{b}
Pure protein	27.0 ± 7.3^{a}	25.6 ± 3.6^{a}	26.6 ± 6.3^{a}	$18.9 \pm 9.8^{a,b}$	6.3 ± 3.8^{c}	$10.9 \pm 1.0^{b,c}$	12.9 ± 6.2^{b}
NPN	4.4 ± 1.4^{a}	5.3 ± 0.6^{a}	4.6 ± 1.2^{a}	0.4 ± 0.3^{b}	1.6 ± 0.9^{b}	0.7 ± 0.2^{b}	0.9 ± 0.6^{b}
Fats	2.8 ± 1.0^{b}	1.0 ± 0.2^{c}	2.1 ± 1.2^{a}	4.5 ± 0.7^{a}	1.0 ± 0.3^{c}	1.4 ± 0.1^{c}	2.4 ± 1.8^{a}
Dietary fibre	49.8 ± 6.6^{b}	45.7 ± 1.9^{b}	48.6 ± 5.9^{a}	45.9 ± 1.5^{b}	36.0 ± 5.7^{c}	62.3 ± 0.7^{a}	43.8 ± 9.2^{a}

[a,b,c,d] Values in a row without a common superscript are significantly different ($P < 0.05$).
[A] *Porphyra* sp. from Japan and Korea.
[B] *Porphyra* sp. from China.

commercially available seaweed products are semi-dried before packaging. The following results refer to the semi-dry weight (s.w.) and not to the analysed oven-dry weight.

In general, red and brown algae species demonstrated large differences in their protein contents. The crude protein content of red seaweed varieties was 31 g/100 g s.w. whereas the crude protein content of brown algae was only 14 g/100 g s.w. (Table 1). Similar protein contents for these macroalgae classes were described in other studies (Fleurence, 1999; Jurković et al., 1995; Kolb et al., 1999; Rupérez & Saura-Calixto, 2001).

In red algae species, the amount of the NPN fraction was much higher than in brown algae (Table 1). The NPN-fraction of algae consists mainly of chlorophyll and phycoerythrine, nitrite, nitrate, nucleic acids, and ammonium compounds (Lourenço, Barbarino, Marquez, & Aidar, 1998), as well as free AA.

The lipid content of edible seaweed varieties studied was about 2 g/100 g s.w.. The low lipid contents of *Porphyra* sp. from China, *Laminaria* sp. and *Hizikia fusiforme* differed significantly ($P < 0.05$) from the lipid content of *Undaria pinnatifida* and *Porphyra* sp. from Japan and Korea (Table 1) and no significant differences in the lipid content were determined between the red and brown algae classes.

The contents of dietary fibres in red algae and *Undaria pinnatifida* were comparable. The highest fibre content was found in *Hizikia fusiforme* with 62 g/100 g s.w., whereas *Laminaria* sp. had the lowest content of fibre (Table 1). No significant differences in dietary fibre content were determined between the red and brown algae classes. Altogether, seaweed species were low in fat and high in dietary fibre. The analysed fat and dietary fibre contents agree with previous studies (Fleurence et al., 1994; Herbreteau et al., 1997; Jiménez-Escrig & Cambrodon, 1999; Jurković et al., 1995; Lahaye, 1991; Rupérez & Saura-Calixto, 2001).

3.2. Amino acid analysis

Asp and Glu were the most abundantly occurring amino acids (AA) in the 34 seaweed species tested. Red algae contained 8 g Asp/16 g nitrogen (N) and 10 g Glu/16 g N. In brown algae, the quantities of these AA were significantly higher ($P < 0.05$; Table 2). *Laminaria* sp. had the highest concentrations of these AA, with 13 g Asp/16 g N and 24 g Glu/16 g N. The Asp concentration of the *Laminaria* sp. was significantly higher than those of *Undaria pinnatifida* and *Hizikia fusiforme* ($P < 0.05$).

Furthermore, the protein of 34 seaweed varieties tested was consistently rich in the AA Thr, Val, Leu, Lys, Gly and Ala (Table 2).

The EAA concentrations amounted to 35 g/16 g N in red algae varieties and 32 g/16 g N in brown algae varieties. In *Porphyra* sp. and *Undaria pinnatifida*, the ratio of essential AA/non-essential AA (EAA/NEAA) was higher than in *Laminaria* sp. and *Hizikia fusiforme* (Table 2).

The concentration of EAA was comparable among red algae varieties but differed substantially in brown algae varieties. The concentrations of Thr, Val, Ile, Leu, Phe,

Table 2
Amino acid composition given in means ± SD (g/16 g N; $n = 34$)

Amino acids	*Porphyra* sp.[A]	*Porphyra* sp.[B]	*Undaria pinnatifia*	*Laminaria* sp.	*Hizikia fusiforme*
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
P-Ser	0.7 ± 0.8^{b}	0.3 ± 0.7^{b}	1.5 ± 1.3^{b}	1.8 ± 2.8^{b}	5.6 ± 0.2^{a}
Tau	4.3 ± 2.1^{a}	2.4 ± 1.1^{b}	0.1 ± 0.1^{d}	$0.3 \pm 0.2^{c,d}$	$0.6 \pm 0.2^{b,d}$
P-Eta	0.2 ± 0.5^{a}	0.1 ± 0.1^{a}	0.0 ± 0.0^{a}	0.3 ± 0.4^{a}	0.1 ± 0.2^{a}
Asp	8.5 ± 1.0^{b}	8.2 ± 1.3^{b}	8.7 ± 1.1^{b}	12.5 ± 2.8^{a}	9.1 ± 1.0^{b}
Thr	5.3 ± 0.8^{a}	$5.2 \pm 0.6^{a,b}$	4.4 ± 0.6^{c}	3.5 ± 0.6^{d}	$4.1 \pm 0.5^{b,c,d}$
Ser	4.0 ± 0.5^{b}	4.9 ± 0.4^{a}	4.0 ± 0.4^{b}	3.3 ± 0.6^{c}	$3.7 \pm 0.3^{b,c}$
Glu	$10.2 \pm 2.6^{c,d}$	9.3 ± 1.1^{c}	14.5 ± 3.2^{b}	23.8 ± 7.5^{a}	$18.7 \pm 2.4^{a,b}$
Gly	$5.1 \pm 1.3^{a,c}$	$4.1 \pm 0.4^{b,c}$	5.1 ± 0.7^{c}	4.0 ± 1.1^{b}	$4.8 \pm 0.5^{b,c}$
Ala	6.2 ± 2.2^{a}	4.2 ± 0.4^{a}	4.7 ± 0.6^{a}	5.7 ± 2.8^{a}	4.3 ± 0.4^{a}
Val	5.2 ± 1.0^{a}	$4.5 \pm 0.4^{a,b}$	5.2 ± 0.5^{a}	3.8 ± 1.0^{b}	$4.9 \pm 0.5^{a,b}$
Ile	3.1 ± 0.5^{c}	$3.3 \pm 0.2^{b,c}$	4.1 ± 0.3^{a}	2.7 ± 0.9^{c}	$4.0 \pm 0.4^{a,b}$
Leu	$5.5 \pm 0.9^{c,d}$	$5.9 \pm 0.4^{c,d}$	7.4 ± 0.6^{a}	$4.9 \pm 1.7^{b,c}$	$6.7 \pm 0.6^{a,d}$
Tyr	3.4 ± 2.1^{a}	$3.2 \pm 0.5^{a,b}$	$2.9 \pm 0.5^{a,b}$	$1.\ 7 \pm 0.5^{b}$	$2.8 \pm 0.4^{a,b}$
Phe	3.3 ± 0.4^{b}	3.5 ± 0.4^{b}	4.7 ± 0.3^{a}	3.2 ± 1.0^{b}	4.6 ± 0.4^{a}
His	2.6 ± 0.4^{a}	2.4 ± 0.5^{a}	2.5 ± 0.3^{a}	2.2 ± 0.4^{a}	2.6 ± 0.4^{a}
Lys	4.9 ± 0.9^{a}	5.2 ± 0.6^{a}	5.6 ± 0.4^{a}	3.9 ± 1.4^{b}	3.1 ± 0.3^{b}
Arg	5.9 ± 0.4^{a}	5.9 ± 0.7^{a}	5.2 ± 0.2^{b}	3.3 ± 1.1^{c}	4.5 ± 0.3^{b}
Pro	3.5 ± 1.0^{a}	3.6 ± 0.4^{a}	3.6 ± 1.6^{a}	3.1 ± 1.1^{a}	3.8 ± 0.4^{a}
Cys	1.2 ± 0.2^{a}	1.3 ± 0.2^{a}	0.9 ± 0.2^{b}	1.2 ± 0.3^{a}	0.9 ± 0.1^{b}
Met	1.8 ± 0.7^{a}	1.7 ± 0.3^{a}	1.7 ± 0.5^{a}	0.9 ± 0.2^{b}	$1.6 \pm 0.1^{a,b}$
Trp	0.7 ± 0.1^{a}	0.7 ± 0.1^{a}	0.7 ± 0.1^{a}	0.5 ± 0.5^{a}	0.4 ± 0.0^{a}
Total	85.5 ± 9.1^{a}	81.9 ± 8.7^{a}	87.3 ± 7.9^{a}	$86.5 \pm\ 14.1^{a}$	90.9 ± 7.9^{a}
EAA/NEAA	$0.7{:}1 \pm 0.1^{a,b}$	$0.8{:}1 \pm\ 0.1^{a}$	$0.7{:}1 \pm 0.1^{a}$	$0.5{:}1 \pm 0.2^{c}$	$0.6{:}1 \pm 0.0^{b,c}$

[a,b,c,d] Values in a row without a common superscript are significantly different ($P < 0.05$).
[A] *Porphyra* sp. from Japan and Korea.
[B] *Porphyra* sp. from China.

Lys and Met were significantly higher ($P < 0.05$) in *Undaria pinnatifida* than in *Laminaria* sp. *Undaria pinnatifida* had significantly higher concentrations of Lys than had *Hizikia fusiforme* ($P < 0.05$) and *Laminaria* sp. had significantly higher concentrations of Cys than had *Undaria pinnatifida* ($P < 0.05$, Table 2).

Interestingly, taurine (Tau) is not a typical component of traditional European food and the Tau content represents a nutrient feature which is characteristic of red algae varieties. The abundance of Tau in red algae varieties and in *Porphyra* sp. from Japan and Korea amounted to 4 g Tau/16 g N. This concentration was significantly higher ($P < 0.05$, Table 2) than those observed in red algae from China. Tau was detected at low concentrations in brown algae varieties (Table 2). However brown algae contained phosphoserine (P-Ser) and the content of this AA was significantly higher than those in red algae varieties that were studied ($P < 0.05$, Table 2). *Hizikia fusiforme* had the highest concentrations of P-Ser and, finally, phosphoethanolamine was observed in small concentrations within the seaweed varieties analyzed (Table 2).

3.3. Evaluation of protein quality

The amino acid score (AAS) evaluates the actual abundance of individual EAA in a food material and relates it to dietary requirements or a reference protein (FAO/WHO/UNU, 1985; FAO, 1991). The AAS of red algae species varied greatly and ranged from 40% to 90% and were significantly higher than those of brown algae species whose AAS varied from 20% to 70% ($P < 0.05$; Table 3). Among brown algae varieties, the AAS of *Undaria pinnatifida* were significantly higher than those of *Laminaria* sp. and *Hizikia fusiforme* ($P < 0.05$).

The essential amino acid index (EAAI) compares the protein quality by means of the geometrical mean value of EAA compared to a reference protein (FAO/WHO/UNU, 1985; FAO, 1991). The EAAI is more closely associated with the biological quality of a protein than is the AAS. *Porphyra* sp. (from China) and *Undaria pinnatifida* had the highest EAAI (Table 3) and *Laminaria* sp. had the lowest EAAI. The differences in EAAI between both *Porphyra* sp. and *Undaria pinnatifida* to *Laminaria* sp. were significant ($P < 0.05$).

Trp was the first limiting AA in algae protein for all seaweed species evaluated. The Trp concentrations were 0.5 g/16 g N in brown algae varieties and 0.7 g/16 g N in red algae varieties analysed. Other limiting AAs in the protein of red algae varieties that were present at low concentrations included Leu and Ile, whereas, the AAs in the protein of the brown algae varieties that were present at low concentrations included Met, Cys, and Lys (Table 2).

The availabilities of the AA Lys, Met/Cys, Trp, and Thr are generally at low levels in the protein consumed in a typical human diet and, therefore, the Lys–Met–Cys–Trp–Thr-score can be a useful tool for the evaluation of the protein quality (Kolb et al., 1999). The Lys–Met–Cys–Trp–Thr-score of red algae varieties and *Undaria pinnatifida* was higher than those in *Laminaria* sp. and *Hizikia fusiforme* (Table 3). All parameters used for protein assessment indicated that the protein qualities of *Laminaria* sp. and *Hizikia fusiforme* were lower than those of *Porphyra* sp. and *Undaria pinnatifida* (Table 3).

The AA profile is important for evaluating the nutritional value of algae proteins, but the digestibility of those proteins is the primary factor of the availability of their AA. In this investigation, the digestibility of algae protein was not analysed. Other studies showed that the digestibility seems to be limited by the algal non-protein fraction (Galland-Irmouli et al., 1999).

Table 3
Evaluation of protein quality in analysed algae given in means ± SD (%; $n = 34$)

Algae species	AAS[A]	EAAI[A]	Lys–Met–Cys–Trp–Thr-score[A]
	Mean ± SD	Mean ± SD	Mean ± SD
Porphyra sp.[B]	61.7 ± 14.0[a]	89.6 ± 9.8[a]	1.0 ± 0.0[a]
Porphyra sp.[C]	64.0 ± 5.5[a]	91.2 ± 7.2[a]	1.0 ± 0.1[a]
Undaria pinnatifida	61.3 ± 13.6[a]	95.9 ± 6.7[a]	0.9 ± 0.1[a]
Laminaria sp.	31.4 ± 14.6[b]	65.9 ± 14.8[b]	0.7 ± 0.1[b]
Hizikia fusiforme	40.0 ± 0.0[b]	80.9 ± 5.0[a,b]	0.7 ± 0.1[b]

[a,b] Values in a row without a common superscript are significantly different ($P < 0.05$).
[A] FAO/WHO/UNU, (1985); FAO (1991).
[B] *Porphyra* sp. from Japan and Korea.
[C] *Porphyra* sp. from China.

3.4. FA composition

3.4.1. Saturated fatty acids (SFA)

In the analysed seaweed varieties, palmitic acid (C16:0) was the most abundant SFA (Table 4). The content of C16:0 was highest in *Porphyra* sp. from China with 37% of total FAME and lowest levels were in *Undaria pinnatifida* with 14% of total FAME (Table 4). Furthermore, the algae varieties tested had minor levels of myristic acid (C14:0) and trace levels of pentadecanoic acid (C15:0) and heptadecanoic acid (C17:0). Similar results were found in other analyses, but *Laminaria* sp., and *Hizikia* sp. had higher levels of myristic acid (Fleurence et al., 1994; Takagi et al., 1985).

The sum of SFA ranged from 18% of total FAME in *Undaria pinnatifida* to 45% of total FAME in *Porphyra* sp. from China (Table 5). The total levels of SFA were considerably higher in red algae varieties and *Laminaria* sp. than *Undaria pinnatifida* ($P < 0.05$).

3.4.2. Monounsaturated fatty acids (MUFA)

Of the 34 seaweed species investigated, the red algae varieties and *Laminaria* sp. had the highest proportion of MUFA in their FAME distribution (Table 5) and oleic acid was the predominant FA within this class (Table 4).

Table 4
Fatty acid composition given in means ± SD (% of total FAME; $n = 34$)

Fatty acids	*Porphyra* sp.[A]	*Porphyra* sp.[B]	*Undaria pinnatifia*	*Laminaria* sp.	*Hizikia fusiforme*
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
C12:0	0.02 ± 0.02^{b}	0.09 ± 0.06^{a}	n.d.	$0.06 \pm 0.03^{a,b}$	n.d.
C14:0	2.68 ± 2.17^{a}	4.07 ± 4.84^{a}	2.25 ± 0.07^{a}	2.88 ± 3.92^{a}	0.30 ± 0.09^{a}
C15:0	0.34 ± 0.13^{a}	0.45 ± 0.23^{a}	0.21 ± 0.03^{a}	0.40 ± 0.21^{a}	0.17 ± 0.03^{a}
C16:0	30.8 ± 4.60^{a}	37.1 ± 17.74^{a}	13.5 ± 0.67^{b}	36.0 ± 10.04^{a}	$26.8 \pm 3.84^{a,b}$
C17:0	0.19 ± 0.14^{a}	0.18 ± 0.07^{a}	0.20 ± 0.06^{a}	0.16 ± 0.06^{a}	0.04 ± 0.02^{a}
C18:0	0.66 ± 0.02^{b}	1.89 ± 0.52^{a}	0.86 ± 0.06^{b}	1.49 ± 0.35^{a}	0.76 ± 0.31^{b}
C20:0	0.21 ± 0.19^{a}	0.45 ± 0.63^{a}	0.39 ± 0.05^{a}	0.28 ± 0.49^{a}	0.04 ± 0.06^{a}
C22:0	0.41 ± 0.36	n.d.	n.d.	n.d.	0.01 ± 0.02^{b}
C24:0	0.17 ± 0.15	n.d.	n.d.	n.d.	n.d.
$C14:1_{n5}$	0.02 ± 0.02^{a}	0.03 ± 0.05^{a}	n.d.	n.d.	n.d.
$C16:1_{n7}$	2.24 ± 1.89^{a}	1.82 ± 2.14^{a}	0.44 ± 0.02^{a}	1.71 ± 1.08^{a}	0.15 ± 0.07^{a}
$C17:1_{n7}$	0.19 ± 0.03^{a}	0.20 ± 0.11^{a}	0.12 ± 0.02^{a}	0.13 ± 0.10^{a}	n.s.
ΣC18:1	7.16 ± 3.58^{a}	15.3 ± 11.43^{a}	5.95 ± 0.15^{a}	12.8 ± 8.27^{a}	7.68 ± 4.22^{a}
$C20:1_{n9}$	1.42 ± 2.29^{a}	1.52 ± 2.11^{a}	n.d.	1.55 ± 1.31^{a}	4.09 ± 2.13^{a}
$C22:1_{n11}$	2.96 ± 2.58^{a}	n.d.	n.d.	0.02 ± 0.04^{b}	n.d.
$C22:1_{n13}$	0.20 ± 0.25^{a}	0.96 ± 1.35^{a}	n.d.	0.96 ± 0.84^{a}	0.64 ± 0.32^{a}
$C18:2_{n6}$	3.86 ± 1.47^{a}	7.06 ± 4.65^{a}	7.41 ± 0.47^{a}	5.48 ± 3.44^{a}	3.56 ± 1.45^{a}
$C20:2_{n6}$	$0.51 \pm 0.43^{a,b}$	0.90 ± 0.71^{a}	0.12 ± 0.03^{b}	0.87 ± 0.31^{a}	0.97 ± 0.27^{a}
$C18:3_{8t,10t,12c}$	0.81 ± 0.37^{a}	0.24 ± 0.17^{a}	0.34 ± 0.34^{a}	n.d.	0.56 ± 0.21^{a}
$C18:3_{n6}$	0.31 ± 0.01^{a}	2.04 ± 2.32^{a}	1.71 ± 0.13^{a}	1.60 ± 2.25^{a}	0.42 ± 0.06^{a}
$C18:3_{n3}$	5.66 ± 4.74^{b}	$0.94 \pm 1.15^{b,c,d}$	11.2 ± 0.53^{a}	$0.76 \pm 0.93^{c,d}$	0.41 ± 0.23^{d}
$C20:3_{n6}$	1.20 ± 1.28^{b}	0.97 ± 0.84^{b}	0.57 ± 0.04^{b}	1.17 ± 0.73^{b}	3.21 ± 0.56^{a}
$C20:3_{n3}$	0.15 ± 0.02^{a}	$0.04 \pm 0.05^{b,c}$	0.14 ± 0.02^{a}	0.01 ± 0.02^{c}	0.09 ± 0.00^{b}
$C18:4_{n3}$	3.37 ± 2.72^{b}	1.51 ± 2.14^{b}	25.8 ± 1.55^{a}	1.24 ± 2.15^{b}	n.d.
$C20:4_{n6}$	$8.00 \pm 4.69^{a,b}$	$9.84 \pm 1.60^{a,b}$	13.3 ± 0.41^{a}	12.4 ± 1.61^{a}	5.30 ± 1.98^{b}
$C20:5_{n3}$	20.9 ± 26.54^{a}	10.4 ± 7.46^{a}	13.2 ± 0.66^{a}	16.2 ± 8.90^{a}	42.4 ± 11.88^{a}
$C22:5_{n3}$	0.05 ± 0.09^{a}	n.d.	n.d.	n.d.	0.09 ± 0.04^{a}
$C22:6_{n3}$	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detectable (values < 0.001% of FAME).
[a,b,c,d] Values in a row without a common superscript are significantly different ($P < 0.05$).
[A] *Porphyra* sp. from Japan and Korea.
[B] *Porphyra* sp. from China.

The concentrations of oleic acid were at high levels in *Porphyra* sp. from China and *Laminaria* sp. and accounted for more than 20% of total FAME but such a high content was only found in single samples. The oleic acid content of *Porphyra* sp. from Japan and Korea, *Undaria pinnatifida* and *Hizikia fusiforme* was at 2.6–9.3% of total FAME. Other studies showed similar concentrations of oleic acid in *Laminaria* sp., *Undaria pinnatifida* and *Hizikia fusiforme*, but lower concentrations in *Porphyra* sp. (Fleurence et al., 1994; Takagi et al., 1985). Furthermore, seaweed varieties

Table 5
Fatty acid groups given in means ± SD (% of total FAME; $n = 34$)

Fatty acid groups	*Porphyra* sp.[A]	*Porphyra* sp.[B]	*Undaria pinnatifia*	*Laminaria* sp.	*Hizikia fusiforme*
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Σ_{SFA}	$35.7 \pm 7.9^{a,b}$	44.5 ± 12.5^{a}	17.5 ± 0.8^{c}	$41.5 \pm 6.0^{a,b}$	$28.1 \pm 4.3^{b,c}$
Σ_{MUFA}	18.6 ± 6.9^{a}	20.7 ± 9.0^{a}	7.8 ± 0.4^{a}	17.4 ± 7.3^{a}	13.4 ± 6.4^{a}
Σ_{PUFA}	$44.8 \pm 15.3^{b,c,d}$	33.9 ± 3.1^{c}	73.7 ± 1.1^{a}	$39.9 \pm 3.3^{b,c,d}$	$57.0 \pm 11.6^{a,d}$
Σ_{MCFA}[C]	2.7 ± 2.2^{a}	4.2 ± 4.8^{a}	2.3 ± 0.1^{a}	2.9 ± 3.9^{a}	0.3 ± 0.1^{a}
Σ_{LCFA}[D]	96.3 ± 2.7^{a}	94.9 ± 5.3^{a}	96.8 ± 0.4^{a}	95.9 ± 3.6^{a}	98.2 ± 1.0^{a}
$\Sigma_{trans\ FA}$	0.8 ± 0.4^{a}	$0.3 \pm 0.1^{a,b}$	0.3 ± 0.3^{b}	0.1 ± 0.1^{b}	$0.6 \pm 0.2^{a,b}$
$\Sigma_{n6\text{-}FA}$	13.9 ± 4.5^{b}	$20.8 \pm 7.0^{a,b}$	23.1 ± 0.9^{a}	$21.6 \pm 4.2^{a,c}$	$13.5 \pm 0.4^{b,c}$
$\Sigma_{n3\text{-}FA}$	$30.1 \pm 19.2^{a,c,d}$	$12.9 \pm 4.1^{c,d}$	$50.3 \pm 1.8^{a,b}$	18.3 ± 5.9^{d}	42.9 ± 11.7^{a}
n6/n3	$0.6{:}1 \pm 0.4^{a,b}$	$1.8{:}1 \pm 1.1^{a}$	$0.5{:}1 \pm 0.0^{b}$	$1.3{:}1 \pm 0.8^{a,b}$	$0.3{:}1 \pm 0.1^{b}$
$\Sigma_{n9\text{-}FA}$	$8.3 \pm 0.9^{a,b}$	17.1 ± 8.3^{a}	5.9 ± 0.2^{b}	$14.1 \pm 6.8^{a,b}$	$11.6 \pm 6.3^{a,b}$

[a,b,c,d] Values in a row without a common superscript are significantly different ($P < 0.05$) .
[A] *Porphyra* sp. from Japan and Korea.
[B] *Porphyra* sp. from China.
[C] MCFA: C11–C14.
[D] LCFA: C15–C24.

tested had low levels of palmitoleic acid (16:1, n-7) and the concentrations of this FA ranged from 0.1% to 3.6% of total FAME. *Porphyra* sp. and *Laminaria* sp. had higher concentrations of palmitoleic acid and, in *Undaria pinnatifida* and *Hizikia fusiforme*, the lowest concentrations of this FA were found.

In *Hizikia fusiforme*, *Laminaria* sp. and *Porphyra* sp., higher amounts of eicosenoic acid (C20:1; n-9) were detected. Red algae from Japan and Korea contained particularly higher quantities of docosenoic acid (C22:1, n-11; Table 4).

3.4.3. Polyunsaturated fatty acids (PUFA)

The lipids of most algae varieties tested consisted mainly of PUFA (Table 5). The amounts of this FA class varied between 34% of total FAME in *Porphyra* sp. to 74% in *Undaria pinnatifida* (Table 5). LA, ALA, stearidonic acid (C18:4, n-3, SDA), arachidonic acid, and EPA represented the predominant proportions of this FA class. The amount of LA averaged from 2.2% of total FAME in *Porphyra* sp. (from Japan and Korea) to 10.3% of total FAME in *Porphyra* sp. from China (Table 4). The highest LA content was observed in the *Porphyra* sp. from China and in *Undaria pinnatifida*, with 7% of total FAME (Table 4).

The concentration of γ-linolenic acid (C18:3, n-6) was relatively low and varied from 0.3% to 4.2% of total FAME (Table 4). However, the concentrations of ALA varied from 0.1% to 11.7 % of total FAME in the investigated seaweed products. *Undaria pinnatifida* and some *Porphyra* sp. from Japan and Korea had the highest concentrations of ALA (Table 4). *Undaria pinnatifida* was particularly rich in SDA; the concentrations of this FA varied from 24.8% to 27.5% of total FAME. In the other algal species, the concentrations of this n-3 PUFA were very low with 0.0–5.2% of total FAME (Table 4). These findings agree with other investigations (Fleurence et al., 1994; Takagi et al., 1985). SDA is an interesting FA for human nutrition because there is a high relative effectiveness for SDA in increasing EPA concentrations in tissues such as erythrocytes and plasma lipids (James, Ursin, & Cleland, 2003).

Arachidonic acid, another important PUFA, was detected in *Undaria pinnatifida* and *Laminaria* sp. at concentration that varied from 11.3% to 14.3% of total FAME and similar levels of this PUFA were observed in red algae (Table 4). In contrast, *Hizikia fusiforme* had low concentrations of arachidonic acid, with 5 % of total FAME.

High concentrations of EPA were observed in the 34 macroalgae varieties investigated (Table 4). Some members of *Porphyra* sp. (from Japan and Korea) and *Hizikia fusiforme* showed more than 50% of total FAME for this PUFA. The EPA concentrations varied highly between algae samples tested (Table 4), but there was no correlation between EPA content and origin or drying process.

Interestingly, DHA was not found in the analysed seaweed species (Table 4). These results were also found in other studies (Fleurence et al., 1994; Takagi et al., 1985).

The main proportion of PUFA consisted of n-3 FA. The amounts of n-3 FA varied between 10% of total FAME in a sample of *Porphyra* sp. from China and 51% of total FAME in a sample of *Hizikia fusiforme*. The concentrations of n-3 PUFA in *Porphyra* sp. (from China) and *Laminaria* sp. were significantly lower than those in *Undaria pinnatifida* and *Hizikia fusiforme* ($P < 0.05$).

The proportion of n-9 FA varied between 7.3% of total FAME in red algae (from Japan and Korea) and 22.9% of total FAME in *Porphyra* sp. from China (Table 5). Furthermore, all seaweed varieties contained small amounts of n-7 and n-11 FA, as well as *trans* FA (Table 4).

The results showed that palmitic acid, EPA, arachidonic acid, oleic acid, LA, and ALA were the primary FAs in red algae and brown algal varieties, such as *Laminaria* sp. and *Hizikia fusiforme* (Table 4).

The FA content varied strongly within algal strains and, therefore, a unique FA distribution for any given algal strain can not easily be produced because lipid composition changes, depending on various factors, such temperature, characteristics, intensity of light, levels of minerals, nitrogen compounds, and the period in the life cycle of the algae (Takagi et al., 1985).

The one exception to this statement is *Undaria pinnatifida*, in which the variation of the FA distribution was comparably small. This algal variety had the highest concentrations of SDA and this concentration was significantly different from that observed in the other strains of brown algae ($P < 0.05$). Additionally, *Undaria pinnatifida* contained less palmitic acid ($P < 0.05$) than did *Porphyra* sp. or *Laminaria* sp. (Table 4). The results agreed with the specific features of the PUFA concentrations in red and brown algae varieties reported in previous papers (Fleurence et al., 1994; Takagi et al., 1985).

The analysis of the data revealed that red and brown algae varieties tested contained approximately 90% of total FAME as long-chain fatty acids (LCFA; C15–C24). In contrast, the short-chain fatty acids (SCFA; C4–C10) were not detected in algal species investigated. The proportions of middle-chain fatty acids (MCFA; C11–C14) were generally low in the analysed seaweed species and varied between 0.3% of total FAME in *Hizikia fusiforme* and 4.2% of total FAME in *Porphyra* sp. from China (Table 5).

Seaweed products represent an important source of LC-PUFA (n-3; n-6), that are fundamental for the formation of important structural lipids and elements of cell membranes. In addition, these LC-PUFA are precursors of eicosanoids, which influence inflammation processes and immune reactions (Calder & Grimble, 2002; De Pablo & Àlvarez de Cienfuegos, 2000). The two classes of PUFA have opposing physiological functions and their balance is important for normal growth and development. These FAs are beneficial for the prevention of cardiovascular diseases and other chronic diseases, such as diabetes, hypertension, and autoimmune diseases. The European Nutritional Societies have recommended that human diet with an-6/n-3 ratio of 5:1 is health-promoting (D-A-C-H,

2000). At present, the most traditional European food products possess a n-6/n-3 ratio of approximately 15–17:1. This would suggest that Western diets are deficient in n-3 FA and high in n-6 FA (Simopoulos, 2002). The results of this study show that the percentage of n-6 FA is comparably low in seaweed varieties (Table 5). Therefore, the n-6/n-3 ratio of seaweed varieties (1.1:1 in red algae and 0.8:1 in brown algae) is beneficial (Table 5).

This n-6/n-3 ratio is comparable with those of cold water fishes. Thus, consumption of seaweed products can contribute to the improvement of the dietary supply of n-3 FA. The intake of food rich in n-3 LC-PUFA can have a positive influence on the composition of blood lipids and can therefore be used for the prevention of arteriosclerosis (Erkkilä, Lehto, Pyörälä, & Uusitupa, 2003; Murata, Sano, Ishihara, & Uchida, 2002; Nestel et al., 2002).

4. Conclusions

It can be concluded that, particularly, red algae varieties represent an important source of protein which contains all EAAs. The AAS and the EAAI was higher in red algae and *Undaria pinnatifida*, while *Laminaria* sp. and *Hizikia fusiforme* have a low nutritive value protein. With respect to their high protein level and their AA composition, *Porphyra* sp. and *Undaria* sp. tested appear to be an interesting potential source of food proteins.

The content of Tau in red algae varieties studied was especially noteworthy since this sulphonic acid is not often found in conventional European food proteins. Generally, the most abundant AAs in seaweed varieties investigated were Asp and Glu.

The contents of dietary fibres were comparable between red and brown algae classes (29.1–62.8 g /100 g s.w.) with the lowest concentrations of dietary fibre in *Laminaria* sp. and the highest concentrations of dietary fibre in *Hizikia fusiforme*.

The lipid concentrations of the 34 seaweed varieties analysed were low (2 g/100 g s.w.). The n-3 FA content of some algae species was also noteworthy; EPA concentrations were high (greater than 50.0% of total FAME) in *Hizikia fusiforme* and some red algae varieties. In addition, the macroalgae varieties tested contained high concentrations of PUFA (31.8–74.7% of total FAME). In *Porphyra* sp. from Japan and Korea, *Undaria pinnatifida*, and *Hizikia fusiforme* n-3 LC-PUFAs are the main representatives of this group. Therefore, these seaweed varieties are a very rich source of n-3 PUFA (17.9–52.3% of total FAME).

This investigation of edible macroalgae verified the presence of several health-promoting and beneficial nutrients, such as EAAs, important FAs, and dietary fibres.

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