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Fatty acids, total lipid, protein and ash contents of processed edible seaweeds

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Abstract

The total lipid, protein, ash and individual fatty acid contents of edible seaweeds that had been canned (Saccorhiza polyschides and Himanthalia elongata) or dried (H. elongata, Laminaria ochroleuca, Undaria pinnatifida, Palmaria sp. and Porphyra sp.) were determined (fatty acids by gas chromatography). Total lipid content ranged from 0.70 ± 0.09 to 1.80 ± 0.14 g/(100 g dry weight). The four most abundant fatty acids were C16:0, C18:1o9, C20:4o6 and C20:5o3. Unsaturated fatty acids predominated in all the brown seaweeds studied, and saturated fatty acids in the red seaweeds, but both groups are balanced sources of ω 3 and ω 6 acids. Ash content ranged from 19.07 ± 0.61 to 34.00 ± 0.11 g/(100 g dry weight), and protein content from 5.46 ± 0.16 to 24.11 ± 1.03 g/(100 g dry weight). These protein, ash and ω 3 and ω 6 fatty acid contents show that processing (canning or drying) leaves these seaweeds with substantial nutritional value.

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Keywords: Seaweeds; Fatty acids; Protein; Ash

1. Introduction

Seaweeds have been used since ancient times as food, fodder and fertilizer and as sources of medicinal drugs. Today seaweeds are the raw material for industrial production of agar, carrageenan and alginates (Bárbara [& Cremades, 1993\)](#page-4-0), but they continue to be widely consumed as food in Asian countries ([Mishra, Temelli,](#page-5-0) [Ooraikul, Shacklock, & Craigie, 1993](#page-5-0)). They are nutritionally valuable as fresh or dried vegetables, or as ingredients in a wide variety of prepared foods (Robledo & Pelegrín, 1997). In particular, certain edible seaweeds contain significant quantities of lipids, protein, vitamins and minerals (Norziah $& Ching, 2000; Sán$ chez-Machado, López-Hernández & Paseiro-Losada, [2002; Wong & Cheung, 2000](#page-5-0)), although nutrient contents vary with species, geographical location, season and temperature ([Dawes, Kovach, & Friedlander, 1993;](#page-4-0) [Kaehler & Kennish, 1996\)](#page-4-0).

Studies of fatty acids in seaweeds have investigated their seasonal variation [\(Floreto, Hirata, Ando, &](#page-5-0) [Yamasaki, 1993; Nelson, Phleger, & Nichols, 2002\)](#page-5-0), differences among different plant tissues [\(Khotim](#page-5-0)[chenko & Kulikova, 2000](#page-5-0)), the effect of growth conditions ([Dawes et al., 1993](#page-4-0)), the compositional characterization of a genus [\(Khotimchenko, 1995\)](#page-5-0) and applications to aquaculture ([De Roeck-Holtzhauer,](#page-4-0) [Claire, Bresdin, Amicel, & Derrien, 1993\)](#page-4-0). The fatty acids of seaweeds generally have linear chains, an even number of carbon atoms, and one or more double bonds ([Shameel, 1990](#page-5-0)). In particular, seaweeds can be a source of essential fatty acids such as eicosapentaenoic acid, C20:5o3 ([Khotimchenko, Vaskovsky, & Titlya](#page-5-0)[nova, 2002](#page-5-0)); o3 fatty acids such as C20:5o3 are thought to reduce the risk of heart disease, thrombosis and atherosclerosis [\(Mishra et al., 1993\)](#page-5-0). It has also been reported that the fatty acids of certain seaweeds have antiviral activity [\(Kamat et al., 1992\)](#page-5-0).

For quantitative determination of fatty acids in foods by gas chromatography it is usual either for crude extracts of samples to be derivatized to form fatty acid methyl esters, or for one-step transesterification with methanolic HCl to be followed by extraction with an

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apolar solvent [\(Adrian, Potus, Poiffait, & Dauvillier,](#page-4-0) [2000\)](#page-4-0). The latter procedure is efficient and easier than the former (De la Cruz García, López-Hernández, & [Simal-Lozano, 2000; Ulberth & Henninger 1995](#page-4-0)).

Most studies on the nutrient contents of seaweeds have concerned fresh plants. Little is known of the effects of processing by drying, canning or other pre- or post-marketing procedures. In this paper we report results on the total lipid, protein, ash and individual fatty acid contents of edible seaweeds that had been collected on the northwest Iberian coast and had been either canned (Saccorhiza polyschides and Himanthalia elongata) or dried (H. elongata, Laminaria ochroleuca, Undaria pinnatifida, Palmaria sp. and Porphyra sp.). Fatty acids were determined by gas-chromatography. For fresh H. elongata and U. pinnatifida collected on the Atlantic coast of France, complete fatty acids profiles have been published [\(Herbreteau, Coiffard, Derrien, &](#page-5-0) [De Roeck-Holtzhauer, 1997\)](#page-5-0), but hitherto there has been little available information on the fatty acids contents of the other seaweeds studied in this work.

2. Materials and methods

2.1. Chemicals

Fatty acid methyl ester mix (PUFA No. 3) used as GC standard was obtained from Supelco (Bellefonte, PA, USA). Methanol, chloroform, hydrochloric acid, sodium sulfate and sodium hydroxide were of analytical grade from Merck (Darmstadt, Germany). Toluene and potassium carbonate anhydrous were of analytical grade from Sigma (ST Louis, MO, USA). All other reagents were of analytical grade.

2.2. Samples

2.2.1. Dried seaweeds

The following seaweeds were collected at the following times at the following sites on the northwest Iberian coast: H. elongata at Finisterre in July 2001; L. ochroleuca at Bayona in July 2001; U. pinnatifida at Limens in April 2002; Palmaria sp. at Rinlo in September 2001; and Porphyra sp. at Viana do Castelo in August 2001. Plants were harvested manually by cutting the fronds, and were transported, in plastic mesh bags and at ambient temperature, to the seaweed processing plant of Algamar (Redondela, Pontevedra, Spain), where they were successively dried at 45° C for 24 h, stored at room temperature for 3 days, and sealed in 100 g lots in polypropylene bags.

2.2.2. Canned seaweeds

In August 2001, H. elongata and Saccorhiza polyschides were harvested at sites in, or on the Atlantic coast adjoining, the Ría de Arousa (A Coruña, Spain) and were transported to the processing plant of Conservas y Ahumados Lou (Ribeira, A Coruña, Spain), where they were prepared for canning and sterilized at 112 °C for 40 min. Prior to analysis, these seaweeds were drained and dried in an oven at 40 \degree C for 48 h.

2.2.3. All samples

For analysis, all samples were ground and passed through a 0.5 mm mesh sieve.

2.3. Fatty acid contents

Fatty acids were determined by gas chromatographic quantification of their methyl esters (FAMEs), which were prepared by a slightly modified version of the method of De la Cruz García et al., (2000). Specifically, 0.75 g of ground dry sample was weighed into a 160×16 mm screw-topped tube and treated with 2 ml of toluene and 3 ml of freshly prepared 5% methanolic HCl. This mixture was carefully mixed with a vortex mixer, and the tube was closed under nitrogen and then heated for 2 h in a water bath at 70 \degree C. After cooling to room temperature, 4 ml of 6% aqueous K_2CO_3 and 2 ml of toluene were added and the mixture was mixed in a vortex mixer and then centrifuged for 5 min at 373 g in an Ettich EBA 12 centrifuge, after which the organic phase was drawn off and dried with anhydrous $Na₂SO₄$.

The compositions of FAME samples prepared as above were determined using a Fison 8000 gas chromatograph with a 30 $m \times 0.32$ mm Supelco-Wax capillary column (stationary phase thickness, $0.25 \mu m$) and a Fison EL-980 flame ionization detector. The injection volume was 1 μ l, the injection temperature 240 °C, the split ratio 1:40, the carrier gas helium and the detector temperature 260 °C. The column temperature regime was 160 °C for 1 min, followed by a 3.5 °C/min ramp up to 230 °C, followed by 14 min at 230 °C. FAME peaks were identified by comparison of their retention times with those of a standard mixture (PUFA No.3), and peak areas were quantified using Chrom-Card for Windows (v.1.18).

2.4. Total lipid contents

To evaluate total lipid content, lipids were extracted from the samples with 2:1 chloroform/methanol ([Erick](#page-4-0)[son, 1993](#page-4-0)). Specifically, 2 g of ground dry sample was weighed into a tube, 14 ml of the solvent mixture was added, the tube was closed in an atmosphere of nitrogen, and after 2 min in a vortex mixer the contents of the tube were filtered through Whatman No. 41 paper. The residue was re-extracted by 30 s treatment with 5 ml of solvent mixture in the vortex mixer, the resulting extract was filtered through Whatman No. 41 paper, the two filtrates were pooled and concentrated to dryness

under nitrogen, and the weight of the resulting residue was taken as the total lipid content of the sample.

2.5. Ash contents

Ground dried samples were ashed by heating for 5 h in an electric oven at 525 °C (AOAC, 1995).

2.6. Protein contents

Total protein content was calculated by multiplying Kjeldahl nitrogen (AOAC, 1995) by 6.25.

2.7. Expression of data and statistical analysis

All data presented are means \pm standard deviations. The statistical significance of differences between means $(P<0.05)$ was estimated by Student's *t*-tests using SPSS 11.0.

3. Results and discussion

Although the most numerous macroalga phylum on the northwest Iberian coast is Rhodophyta (red seaweeds), the brown seaweeds (Phaeophyta) are more conspicuous, and are currently more exploited commercially, because of their large size (Bárbara et al., [1993\)](#page-4-0). Of the species studied in this work, two are red algae (Palmaria sp. and Porphyra sp.) and four brown (S. polyschides, H. elongata, L. ochroleuca and U. pinnatifida).

3.1. Fatty acid contents

Although seaweeds are not a conventional source of energy (their total lipids content is low; see below), their polyunsaturated fatty acids contents can be as high as those of terrestrial vegetables ([Darcy-Vrillon, 1993\)](#page-4-0). In this work, fifteen fatty acids were identified (Table 1). The fatty acid composition of the seaweeds studied are shown in [Table 2](#page-3-0), and [Fig. 1](#page-3-0) shows a typical chromatogram of the FAMEs of Palmaria sp.

In all the seaweeds studied except U . pinnatifida the single most abundant fatty acid was C16:0 (which in Porphyra sp. accounted for 63.19% of all fatty acid), and in U. *pinnatifida* the C16:0 content (16.51%) was only exceeded by that of C18:4o3 (22.6%). However, all the seaweeds also contained the essential fatty acids C18:2o6 (linoleic acid) and C18:3o3 (linolenic acid) and the eicosanoid precursors C20:4o6 (arachidonic acid) and C20:5o3 (eicosapentaenoic acid), which have also been reported in macroalgae from southern Yemen [\(Banaimoon, 1992\)](#page-4-0). Furthermore, the o6/o3 ratio, which the WHO currently recommends should be no higher than 10 in the diet as a whole, was at most 1.32

(falling to only 0.13 in *Palmaria* sp., which had a very low o6 content), so that the seaweeds studied in this work may be of use for reduction of $\omega/(\omega^3)$ ratio [\(Mahan & Escott-Stump, 2000\)](#page-5-0).

Variations in fatty acid contents are attributable both to environmental and genetic differences [\(Nelson et al.,](#page-5-0) [2002\)](#page-5-0). In this work, relative saturated fatty acid contents (saturated fatty acid contents as percentages of total fatty acid contents) were higher in the red seaweeds than in the brown seaweeds, and vice versa for relative total unsaturated fatty acid contents. Whereas in the red seaweeds, in keeping with reports on other red seaweeds [\(Khotimchenko et al., 2002; Mishra et al.,](#page-5-0) [1993\)](#page-5-0), C20 polyunsaturated fatty acids (PUFAs) were as a class 8–12 times more abundant than C18 PUFAs, in brown seaweeds these two classes of fatty acid were more or less equally abundant. Relative essential fatty acid contents were higher in brown seaweeds than in red, as were (in most cases) relative arachidonic acid contents, but the highest relative eicosapentaenoic acid content was that of Palmaria sp., 24.05%.

In keeping with reports on other brown seaweeds [\(Herbreteau et al., 1997; Khotimchenko, et al., 2002\)](#page-5-0), the most abundant fatty acids in those studied in this work, apart from C16:0, were generally C18:1o9 and C20:4o6 (Table 1). The highest relative total PUFA levels were found in L. ochroleuca and U. pinnatifida.

The fatty acid profiles of dried and canned H. elongata were very similar, at least as regards their major components (C16:0, C18:1o9 and C20:4o6, in that order), and there were no statistically significant differences between them as regards relative C18:1o9, C₂₀:4₀₀6 or total monounsaturated fatty acid contents, although there were statistically significant differences $(P<0.05)$ as regards relative C16:0, saturated fatty acid and PUFA contents. These differences may be due to their having been harvested at different sites and/or to the effects of drying [\(Chan, Cheung, & Ang, 1997](#page-4-0)).

Table 1 Identification of fatty acid in edible seaweeds

Peak	Retention time (min)	Fatty acid
1	5.43	C14:0
2	8.42	C16:0
3	8.78	$C16:1\omega$
4	9.71	$C16:2 \omega$
5	11.23	$C16:3$ ω 4
6	12.12	C18:0
7	12.41	$C18:1\omega9$
8	12.55	$C18:1\omega$
9	13.24	$C18:2\omega$
10	14.46	$C18:3\omega3$
11	15.02	$C18:4 \omega$
12	16.49	C ₂₀ :1 ω 9
13	18.22	$C20:4\omega$
14	19.08	$C20:4\omega$ 3
15	19.51	$C20:5 \omega3$

^a Means \pm standard deviation (*n* = 10).

 $^b FA=fatty acid; PUFA=polyunsaturated fatty acids.$ </sup>

Fig. 1. A chromatogram of the fatty acid methyl esters (FAMEs) of a dried sample of the red seaweed Palmaria sp.

3.2. Protein, ash and total lipid contents

Protein contents ranged from 5.46 $g/(100 g)$ dry weight) in H . elongata to 24.11 g/(100 g dry weight) in Porphyra sp., a span within the range reported by Fleurence (1999), Table 3. The protein content of Porphyra sp. is comparable with that of high-protein plant foods such as soybean [\(Norziah & Ching, 2000](#page-5-0)). It should be borne in mind that not all our samples were collected at the same time of year, and that the protein content of seaweeds varies not only between species (Fleurence, 1999) but also between seasons [\(Mishra et](#page-5-0) [al., 1993\)](#page-5-0).

Ash contents, which ranged from 19.07 ± 0.61 to 34.00 ± 0.11 g/(100 g dry weight) (Table 3), were considerably higher than the 21.3–22.8% reported by [Wong](#page-5-0) [et al. \(2000\)](#page-5-0) but lower than the 20.6–39.3% reported by Rupérez (2000). The ash contents of seaweeds, which are generally much higher than those of terrestrial vegetables other than spinach (Rupérez, 2002), vary between species, between geographical locations and between seasons ([Kaehler & Kemish, 1996\)](#page-5-0).

In keeping with reports that the total lipid contents of seaweeds are always less than 4% ([Herbreteau et al.,](#page-5-0) [1997\)](#page-5-0), those of the seaweeds studied in this work ranged from 0.7 ± 0.09 g/(100 g dry weight) in S. polyschides to 1.8 ± 0.14 g/(100 g dry weight) in *Palmaria* sp. (Table 3). [Mishra et al. \(1993\)](#page-5-0) also found a relatively high total lipid content in Palmaria. By contrast, the levels measured in this work in H . elongata and U . pinnatifida $(0.97 \pm 0.07$ and 1.05 ± 0.01 g/(100 g dry weight), respectively) are lower than those reported by [Her](#page-5-0)[breteau et al. \(1997\)](#page-5-0) for these species.

In Europe, the development of novel foods such as functional foods could be a new possibility for the use of this seaweeds, especially for the protein-rich species, in human nutrition. In addition, high ash content was a common feature in algae studied, and based on our results this seaweeds my serve as a food supplement to

Table 3

Protein, ash and total lipid contents of some processed edible seaweeds, in g/(100 g dry weight)

Seaweed	Protein ^a	Ash ^a	Lípid ^a
Canned seaweeds			
Himanthalia elongata	10.95 ± 0.27	22.98 ± 0.60	0.93 ± 0.05
Saccorhiza polyschides	13.10 ± 0.12	$26.58 + 0.65$	0.70 ± 0.09
Dried seaweeds			
Himanthalia elongata	$5.46 + 0.16$	$26.78 + 0.24$	$0.97 + 0.07$
Laminaria ochroleuca	7.49 ± 0.12	29.47 ± 1.05	0.92 ± 0.01
Undaria pinnatifida	18.00 ± 1.46	$31.24 + 0.22$	1.05 ± 0.01
Porphyra sp.	24.11 ± 1.03	19.07 ± 0.61	1.03 ± 0.04
Palmaria sp.	13.87 ± 0.28	34.00 ± 0.11	1.80 ± 0.14

 a Means values of triplicate determinations \pm standard deviations.

help meet the recommended daily adult intakes of some minerals. In general, the lipid contents of all edible seaweeds were low, and high levels of polyunsaturated fatty acids of the omega-3 and omega-6 families.

4. Conclusions

The dried and canned seaweeds examined in this work have high ash contents, appreciable protein contents, low total lipid contents, and relatively high levels of polyunsaturated fatty acids, making them a healthy low-fat food.

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