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Phenolic compounds from three brown seaweed species using LC-DAD–ESI-MS/MS

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ABSTRACT

The phenolic compounds of extracts from *Ascophyllum nodosum* (ANE), *Bifurcaria bifurcata* (BBE) and *Fucus vesiculosus* (FVE) from Galicia (NW Spain) were analyzed by liquid chromatography-diode array detection coupled to negative electrospray ionization-tandem mass spectrometry (LC-DAD–ESI-MS/MS) with the interest to evaluate their potential application as functional ingredients. Phlorotannins were tentatively identified as the main phenolic compounds in the three extracts, followed by phenolic acids, and flavonoids. Fuhalols were present in ANE and BBE, while hydroxyfuhalols were identified in BBE and FVE. Eckol derivatives were present in the three extracts. Quinic acid derivatives were tentatively identified in the three seaweed species; in addition, ANE showed specifically hydroxybenzoic and rosmarinic acid derivatives, BBE showed rosmarinic acid, and FVE contained *p*-coumaric and ferulic acid derivatives. Regarding flavonoids, acacetin derivatives were tentatively identified in the three extracts, hispidulin and a gallocatechin derivative were specifically detected in ANE, and cypellocarpin C was present in BBE. In conclusion, all brown seaweed extracts studied could be exploited as sources of antioxidant phenolic compounds with potential applications in the food and health sectors.

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1. Introduction

Seaweeds are consumed as part of traditional food in Asian countries and more recently they have been included in the diet of Western countries due to their contents of bioactive compounds such as polysaccharides (including dietary fiber), minerals, vitamins (B12, C and E), polyphenols and carotenoids (Burtin, 2003; Garcia-Vaquero & Hayes, 2016; Gómez-Ordóñez, Jiménez-Escrig, & Rupérez, 2010). Brown seaweeds (phaeophyta, *e.g. Ascophyllum nodosum*, *Himanthalia elongata*, *Bifurcaria bifurcata*, *Fucus vesiculosus* and *Laminaria saccharina*) are particular interesting sources of bioactive compounds such as soluble fiber, iodine and proteins (Garcia-Vaquero, Lopez-Alonso & Hayes, 2017). This group is also an interesting source of carotenoids since fucoxanthin is the compound associated with their characteristic yellowish or brownish color. Brown algae bioactive compounds are also associated with health benefits as anti-viral, anti-tumoral and anti-cancer activity (Gupta & Abu-Ghannam, 2011; Michalak & Chojnacka, 2015; Garcia-Vaquero, Rajauria, O'Doherty & Sweeney, 2017).

The chemical composition of brown seaweeds is still under constant investigation and recent few studies have elucidated, at least in part, the phenolic composition of this seaweed family. The phenolic composition of brown seaweeds can be largely composed by phlorotannins that are oligomers of phloroglucinol (1,3,5-trihydroxybenzene). The oligomer phlorotannins can be classified according to the intermolecular linkage of phloroglucinol units in 3 major groups that are known as fucols (phenyl/aryl linkages), phlorethols (arylether bonds) and fucophlorethols (both types of linkages) (Burtin, 2003; Martínez & Castañeda, 2013).

Phlorotannins are synthetized *via* the acetate-malonate pathway and stored in physodes (vesicles). They are the most researched group of polyphenols in seaweeds. Their highest content is reported in brown seaweeds, wherein it ranges from 5 to 15% of the dried weight (Burtin, 2003). These tannins are highly hydrophilic with wide range of molecular sizes from 100 to more than 100,000 Da depending on the species as reported in previous studies (Arnold & Targett, 2000; Ferreres et al., 2012). In contrast to the terrestrial phenolic compounds (*e.g.* flavanols, flavones and phenolic acids), little knowledge exists about the potential health benefits and technological applications of marine polyphenols (phloroglucinol and phlorotannins) (Steevensz et al., 2012).

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Seaweeds contain complex mixtures of phenolic components, and liquid chromatography-mass spectrometry (LC-MS/MS) has been demonstrated to be a powerful analytical tool for rapid analysis of these polar, nonvolatile, and thermally labile constituents (Hossain, Rai, Brunton, Martin-Diana, & Barry-Ryan, 2010).

Thus, the aim of this study was to characterize the phenolic compounds of *Ascophyllum nodosum*, *Bifurcaria bifurcata* and *Fucus vesiculosus* extracts using liquid chromatography-diode array detection coupled to negative electrospray ionization-tandem mass spectrometry (LC-DAD–ESI-MS/MS). This will give information on their potentiality as sources of natural antioxidants to be later used as functional ingredients in the food industry.

2. Material and methods

2.1. Seaweed material and extraction procedure

The brown seaweeds used in the present study were kindly supplied by Porto-muiños company (A Coruña, Spain). Three different samples from each seaweed species were collected in the months of August and September in the Atlantic Ocean, at three different places in the area of Camariñas (A Coruña, Spain). To obtain the *Ascophyllum nodosum* (ANE), *Bifurcaria bifurcata* (BBE) and *Fucus vesiculosus* (FVE) extracts, seaweeds were dried in a conventional oven at 40 °C and then they were grounded to obtain a particle size less than 500 μm. Extraction was performed in a magnetic stirrer, using water as a solvent in a liquid/solid ratio of 30 g/g for 5 min to obtain a correct hydration. Then an aliquot of 800 mL from algae/water suspension was sonicated for 10 min in an ultrasonic Hielscher UIP1000HD homogenizer (Hielscher Ultrasonics GmbH, Teltow, Germany) equipped with a flow cell with a residence time of 30 s and 90 percentage of amplitude and with continuous recirculation. The process was stopped if the temperature reached a value higher than 40 °C. Finally the extract was centrifuged at 2000 × *g* and filtered through a cellulose filter of 20–25 μm pore size (Filter-lab, Filtros Anoia, S.A., Barcelona, Spain).

2.2. Phenolic profile by LC-DAD–ESI-MS/MS

Phenolic compounds of seaweed extracts were separated and analyzed by UV/VIS DAD chromatography. Next, these compounds were evaluated according to their *m/z* ratio in the ESI mass spectrometer. Tentative identification of phenolic compounds was performed by matching UV/VIS and mass spectral data with already published data in literature or by tentative based on mass spectra and/or UV data.

The analysis of phenolic compounds was carried out in an Agilent 1100 HPLC system equipped with G1312B binary gradient pump, G1379A degasser, G1316A column thermostat, G1329A auto-sampler and G1315C diode array detector (DAD) (Agilent Technologies, Waldbronn, Germany). Chromatography separation was performed using a Zorbax SB C18 (Agilent Technologies, Inc., Santa Clara, CA, USA) (150 × 3.0 mm I.D., 3.5 μm particle size) column, operated at 25 °C. The mobile phase was composed by acetic acid (2.5%, v/v) in water (solvent A), and methanol containing 2.5% acetic acid (solvent B). The extracts were diluted to obtain 2 mg/mL with mobile phase A. A flow rate of 1.0 mL/min was used with the following gradient program: 0 min 95:5 (A:B, v/v), 15 min 85:15 (A:B, v/v), 35 min 70:30 (A:B, v/v), 40 min 60:40 (A:B, v/v), 50 min 40:60 (A:B, v/v), 55 min 10:90 (A:B, v/v), 55.01 min 0:100 (A:B, v/v), 75 min 0:100 (A:B, v/v). The wavelengths of 240 and 370 nm were used to collect spectral data. When the absorbance at 240 nm and 370 nm exceeded a predetermined value (1% with respect to the baseline), a full spectral data was collected between 190 and 600 nm.

The Agilent 6410B triple quadrupole equipped with an electrospray ionization (ESI) source (Agilent Technologies, Inc., Palo Alto, CA, USA) was used for mass spectrometric analysis. ESI conditions were as follows: temperature 350 °C, nebulizer pressure 35 psi, N_2 drying gas flow rate 10 L/min, fragmentor voltage 135 V, and capillary voltage 4500 V. Full mass scan spectra were recorded in negative ionization mode over the range of *m/z* 100–1600 Da (5 scan/s). The Agilent MassHunter Qualitative Analysis B.04.00 software (Agilent Technologies, Inc., Santa Clara, CA, USA) was used for data acquisition and qualitative analysis.

3. Results and discussion

3.1. Extraction of the phenolic compounds

The stability of phenolic compounds in brown algae extracts and extraction conditions may influence the extraction of phenolic compounds from seaweeds. Phenolic compounds in algae seem to be particularly sensible to heating and UV radiation exposure as Le Lann, Jégou, and Stiger-Pouvreau (2008) pointed out. These authors reported significant reduction of phenolic content and antioxidant activity due to oven-drying (4 h at 50–60 °C) or greenhouse-drying (72 h at 15–30 °C) in *Sargassum muticum* and *Bifurcaria bifurcata* extracts.

Regarding extraction conditions, an aqueous mixture of solvents may provide better yields of extraction than using only water as solvent. This outcome was reported by Koivikko, Loponen, Honkanen, and Jormalainen (2005) who evaluated several pure solvents and mixtures and they observed the highest extraction yield for acetone:water (70:30, v/v) compared to other aqueous mixtures and organic solvents in *Fucus vesiculosus*. Such considerations may explain, at least in part, the reduced number of compounds tentatively identified in the extracts obtained in the present study. Nevertheless, and despite of this, currently water is preferred instead organic solvents to obtain extracts to be used in formulation of foods, due to economic, toxicological, and environmental reasons.

3.2. Tentative identification of phenolic compounds from seaweed extracts

The evaluation of ANE composition by HPLC-DAD-ESI-MS (Fig. 1) revealed the presence of 22 peaks (named from A1 to A22). The evaluation of BBE composition (Fig. 2) revealed the presence of 18 peaks (B1 to B18), and evaluation of the FVE (Fig. 3) showed the presence of 19 peaks (C1 to C19). Some of these compounds were tentatively identified and their characteristics are shown in Table 1. Fourteen phenolic compounds were tentatively identified from ANE. Phlorotannins (5 compounds, peaks **A2**, **A4**, **A6**, **A8** and **A9**) and flavonoids (5 compounds, peaks **A7**, **A10**, **A11**, **A15** and **A22**) were the main groups in ANE, followed by phenolic acids (4 compounds, peaks **A1**, **A16**, **A17** and **A18**). In the BBE extracts, fourteen phenolic compounds were tentatively identified. Most of these compounds belong to the phlorotannins group (peaks **B2**, **B3**, **B5**, **B9**, **B13**, **B16**, **B17** and **B18**). Phenolic acids (peaks **B1**, **B12** and **B14**) and flavonoids (peaks **B7**, **B8** and **B11**) were also observed. Finally, thirteen phenolic compounds

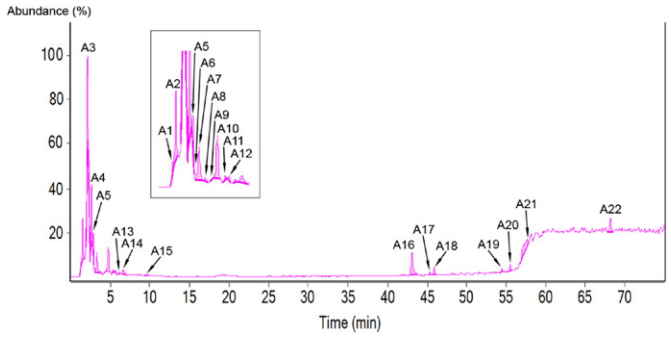

Fig. 1. Representative chromatogram of phenolic compounds from *Ascophyllum nodosum* extract (*ANE*) obtained by liquid chromatography-diode array detection (LC-DAD).

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