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Volatile compounds and odour characteristics of seven species of dehydrated edible seaweeds

O. López-Pérez, A. Picon, M. Nuñez *

Departamento de Tecnología de Alimentos, INIA, Carretera de la Coruña, km 7, Madrid 28040, Spain

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ABSTRACT

The volatile fraction of dehydrated edible seaweeds belonging to seven species (*Himanthalia elongata*, *Laminaria ochroleuca*, *Palmaria palmata*, *Porphyra umbilicalis*, *Saccharina latissima*, *Ulva lactuca* and *Undaria pinnatifida*) was analyzed by gas chromatography–mass spectrometry, after solid-phase microextraction of samples. Thirty-six hydrocarbons, 34 ketones, 28 aldehydes, 23 alcohols, 8 carboxylic acids, 6 halogenated compounds, 4 furans, 3 esters, 2 sulphur compounds, 2 pyrazines, 1 pyridine and 1 amine were detected among the 151 volatile compounds found in seaweeds. There were significant differences between seaweed species for all the volatile compounds. Hydrocarbons reached their highest levels in *U. pinnatifida*, ketones in *P. umbilicalis*, aldehydes in *P. palmata* and *P. umbilicalis*, alcohols in *P. umbilicalis*, carboxylic acids in *S. latissima*, and halogenated compounds in L. *ochroleuca* and *S. latissima*. Sensory analysis revealed that *P. palmata*, *U. lactuca* and *H. elongata* were the seaweeds showing the most potent seafood odour and seaweed odour characteristics.

1. Introduction

Seaweeds constitute an estimable source of functional ingredients and bioactive compounds (Gómez-Ordóñez, Jiménez-Escrig, & Rupérez, 2010; Gupta & Abu-Ghannam, 2011; Samarakoon & Jeon, 2012). However, and in spite of their nutritional benefits, seaweeds still remain of minor importance in the diet of Western countries (MacArtain, Gill, Brooks, Campbell, & Rowland, 2007).

Chemical composition and bioactive compounds present in fresh seaweeds and in seaweed products have deserved worldwide attention from researchers (Kumar, Ganesan, Suresh, & Bhaskar, 2008; Marsham, Scott, & Tobin, 2007; O'Sullivan et al., 2011). Also, the antioxidant activities of purified compounds and extracts from seaweeds and their anti-hypertensive and anti-inflammatory properties have been investigated (Balboa, Conde, Moure, Falqué, & Domínguez, 2012; Rafiquzzaman et al., 2015; Tierney, Croft, & Hayes, 2010).

Seaweeds release volatile compounds to the surrounding marine ecosystems which play important roles in chemical communications. These volatile compounds act as sexual pheromones involved in the mating process, deterrents or chemical defenses against herbivores, feeding attractants and incitants also directed towards herbivores, inhibitors of bacteria and fungi, and suppressors of competitive neighbours (Akakabe & Kajiwara, 2008; Amsler & Fairhead, 2006). The emission of volatile compounds by seaweeds is influenced by environmental conditions (García-Jiménez, Brito-Romano, & Robaina, 2013) and some of them are bothersome pollutants that play an important role in climate functioning (Gschwend, MacFarlane, & Newman, 1985; Paul & Pohnert, 2011).

The volatile fraction of some edible seaweed species has been investigated, generally by means of gas chromatography–mass spectrometry (GC–MS). Volatile compounds found in seaweeds depend on the species, its geographical origin, processing such as drying, and the method used for volatile extraction. Dynamic headspace extraction (Ferraces-Casais, Lage-Yusty, Rodríguez-Bernaldo de Quirós, & López-Hernández, 2013; Le Pape, Grua-Priol, Prost, & Demaimay, 2004), distillation-solvent extraction (Kamenarska et al., 2002, 2006), and, more recently, solid-phase microextraction (Balbas et al., 2015; Peinado, Girón, Koutsidis, & Ames, 2014; Yamamoto et al., 2014) have been used for the extraction of volatile compounds from seaweeds.

Seaweeds are commonly marketed as dried products, which once rehydrated are directly consumed or used as ingredients of different dishes. Information on the volatile compounds of commercial dehydrated seaweeds, which contribute to their sensory profile, is scant. To our knowledge, only the volatile compounds found in dried *Palmaria palmata* and *Ulva* sp. (Michel, Priol, Galaup, & Demaimay, 1997), dried *Monostroma nitidum*, *Ulva linza* and *U. prolifera* (Yamamoto et al., 2014), and dried *Undaria pinnatifida* (Balbas et al., 2015) have been reported.

* Corresponding author.
E-mail address: nunez@inia.es (M. Nuñez).

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The objective of the present study was to investigate the volatile compounds present in seven species of dehydrated edible seaweeds: *Himanthalia elongata* (sea spaghetti), *Laminaria ochroleuca* (kelp, kombu), *P. palmata* (dulse), *Porphyra umbilicalis* (laver, nori), *Saccharina latissima* (sugar kelp, sugar kombu), *Ulva lactuca* (sea lettuce), and *U. pinnatifida* (wakame), which were analyzed by GC–MS after solid-phase microextraction (SPME) of samples. Five of the seven dehydrated seaweed species had not been previously investigated for volatile compounds and in the case of the other two seaweed species the analytical methods used had not permitted the detection of most of the volatile compounds found in the present study. In addition, the odour characteristics of dehydrated seaweeds were evaluated by trained panellists by means of descriptive sensory analysis, and the relationships between volatile compounds and odour characteristics of dehydrated seaweeds were elucidated by principal component analysis.

2. Materials and methods

2.1. Seaweed material

Dehydrated edible seaweeds used in experiments were four brown seaweeds (*H. elongata*, *L. ochroleuca*, *S. latissima* and *U. pinnatifida*), two red seaweeds (*P. palmata* and *P. umbilicalis*) and one green seaweed (*U. lactuca*). They were harvested along the North Western coast of Spain and dehydrated at a temperature of 46–48 °C at the facilities of an industrial plant (Porto Muiños, Cerceda, Spain).

Before chemical and sensory analysis, dehydrated seaweeds were minced to pieces of a maximum size of 2 mm by means of a mechanical grinder. Minced samples were stored in screw-capped glass flasks with practically no head space left on top, at room temperature in the dark, for no > 15 days until analysis. Volatile compounds and odour characteristics were determined on two different batches from each of the seven seaweed species.

2.2. Extraction and analysis of volatile compounds

The extraction of volatile compounds was carried out using a 2-cm 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane SPME fibre (Supelco, Bellefonte, PA, U.S.). The fibre was conditioned before use according to manufacturer instructions in the GC injection port with Merlin Microseal™ at 270 °C for 1 h and afterwards placed into the SPME adapter for a CombiPAL autosampler (CTC Analytics, Zwingen, Switzerland) fitted with a vial heater. Seaweed samples (1 g) were weighed in 20 mL glass vials with magnetic steel caps and PTFE/Sil (100 pk) vial septa (Agilent Technologies, Wilmington, DE, U.S.). After equilibration at 50 °C for 15 min, the SPME fibre was exposed to the seaweed headspace for 30 min and then desorbed in the GC injection port at 250 °C for 5 min under splitless conditions and 2.5 split vent.

Prior to the analysis of volatile compounds, the best extraction conditions were determined by comparing equilibration time before extraction (5 and 15 min), time of extraction (5, 15, 30 and 45 min), temperature of extraction (40 and 50 °C) and sample size to headspace volume ratio (1 g/85% vial and 2 g/40% vial). In addition, the extraction of volatile compounds from the headspace of different aqueous extracts of seaweeds was tested, with less satisfactory results. Different chromatographic temperature programmes were assayed in order to optimize the separation of compound peaks and permit the quantification of the highest number of volatile compounds.

The analysis of volatile compounds was carried out by means of an Agilent 6890 gas chromatograph equipped with a 5973 quadrupole mass analyzer detector (Agilent Technologies). A fused-silica capillary column, 60 m long, 0.25 mm internal diameter, 0.5 μm film thickness (Zebron ZB-WAX plus; Phenomenex, Torrance, CA, U.S.) was used to achieve chromatographic separation. The oven temperature was maintained at 50 °C for 2.5 min and increased to 90 °C at 3 °C/min, to 140 °C at 6 °C/min, to 180 °C at 2 °C/min, to 230 °C at 20 °C/min, and finally held at that temperature for 15 min to ensure cleanliness of the column before the following analysis. Helium was used as the carrier gas with a constant flow rate of 1 mL/min. The injector, detector transfer line and ion source temperatures were 250, 280 and 230 °C, respectively. The MS detector was operated in the full scan mode at 70 eV electron ionization, collecting data at 1.74 scans/s over the *m/z* range of 35 to 300 u.m.a. The linear retention indexes of volatile compounds were calculated by analysing the C5-C20 n-alkanes included in a retention index mixture for GC (Sigma-Aldrich, Tres Cantos, Spain) under the same conditions. All samples were analyzed in triplicate, using the same fibre throughout the whole experiment.

Identification of volatile compounds was performed by injection of commercial standards (Sigma-Aldrich), by spectra comparison using the Wiley7Nist05 Library (Wiley & Sons Inc., Weinheim, Germany), and/or by calculation of linear retention indexes (LRI) relative to the C5-C20 series of alkanes. Integration of chromatograms was carried out using the method of ion selective integration by selecting the most abundant ions, generally at least four ions. The sums of peak areas were multiplied by 10^{-5} for easier comprehension and used for the semi-quantitative determination of compounds.

2.3. Sensory analysis

Minced seaweed 20 g samples were dispensed into 100 mL screw-capped glass flasks and held at 21–23 °C for 1 h before analysis. A panel of 19 members (11 female, 8 male), with a minimum 2-year experience in food sensory analysis, evaluated 12 odour characteristics which had been previously selected by four assessors from the descriptors used in the sensory analysis of seaweeds and their products (Peinado et al., 2014; Yamamoto et al., 2014). Four odour characteristics were sea-related attributes (fish, marine, seafood, seaweed), five were vegetal-related attributes (green grass, hay, honey, licorice, spices) and three were animal-related attributes (fatty, faecal, leather). Seaweed samples, coded with 3 digits, were randomly presented to panellists, who were asked to gently shake the flasks before opening and approaching them to the nose. Odour characteristics were evaluated using 10-cm long horizontal scales, marked with 0 at the left end (lowest intensity) and 10 at the right end (highest intensity).

2.4. Statistical analysis

One-way analysis of variance (ANOVA) with seaweed species as the main effect was carried out on the levels of volatile compounds and the scores of odour characteristics using the SPSS 19.0 statistical package (SPSS Inc., Chicago, IL, U.S). Comparison of the means of volatile compounds levels and odour characteristics scores between seaweed species was performed by Tukey's test using the same package, with the statistical significance assigned at $P < 0.05$. Principal component analysis (PCA) with Varimax rotation was carried out on the total levels of the chemical groups of volatile compounds, on the levels of individual volatile compounds, on the scores of odour characteristics, on the total levels of the chemical groups of volatile compounds and the scores of odour characteristics, and on the levels of individual volatile compounds and the scores of odour characteristics using the same package.

3. Results and discussion

3.1. Volatile compounds

One hundred and fifty-one volatile compounds were detected in the seven seaweed species as a whole. The number of volatile compounds in individual seaweed species was similar, with 129 compounds in *H. elongata*, 128 in L. *ochroleuca*, 136 in *P. palmata*, 131 in *P. umbilicalis*, 137 in *S. latissima*, 127 in *U. lactuca,* and 140 in *U. pinnatifida*. These numbers were higher than the 38 volatile compounds in dried samples of *Dictyopteris membranaceae* (El Hattab, Culioli, Piovetti, Chitour, &