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Short communication

Rapid identification of volatile compounds in fresh seaweed

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ABSTRACT

Volatile component profiles of fresh seaweed *Laminaria* spp and *Undaria pinnatífida* were analyzed using dynamic headspace for volatile profile evaluation, which allows the direct analysis of small quantities of sample without previous treatment and have been identified by GC–MS.

Alcohols were the most important class of volatile compounds identified in Wakame and Kombu (25 and 29% respectively); nine alcohols were identified. The hydrocarbons group constitute the second most important family of volatiles, in both samples entire similar % area total 13–14%, being the butane the most abundant hydrocarbon. Aldehydes and halogenated compounds are higher in *Laminaria* spp (10–9% total area), whereas *Undaria pinnatifida* presents 4–0.23% respectively.

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1. Introduction

Seaweds have been used in human consumption at a very early date, especially in the Far East countries. Their apparition in the western food came several centuries later. Nevertheless, thanks to a strong development of their harvesting and their cultivation during the last century, they have taken more important place in the European consumption. Many studies have verified that the seaweeds are healthy food with interesting nutritional properties [1–3] and compounds with biological activity [4,5]. In addition, seaweeds also have interesting organoleptic properties, such as aroma, with marine, crustacean and green notes, that could enable them to be included in processed foods, as condiments, or vegetables, and could lead to the development of new marine foodstuffs.

Marine biota produce a great variety of volatile organic compounds and these compounds are of diverse biosynthetic origins. The volatile organic compounds which comprise the essential oil are molecules with low molecular weight, low to moderate hydrophilicity and high vapor pressure. A wide range of volatile secondary metabolites such as halogenated and sulfur compounds, hydrocarbons, alcohols, phenols, aldehydes, ketones, acids, esters, terpenes and other compounds, are distributed among the seaweeds [6].

Volatile components are considered as the most important parameters of food flavor and the quality. Consumers' acceptance of foodstuffs is closely related to its flavor. Moreover, the volatile components have been studied to estimate the freshness of seafood [7]. Seaweed can be eaten raw, cooked or processed and depending on the method of their preparation the volatiles content may vary greatly. Authors studied the influence of storage conditions [3] and drying methods [8] on the volatile compounds of different seaweeds.

Studies of the volatiles in algae were conducted by extraction and pre-concentration by conventional methods: liquid–liquid extraction [9], distillation [6,10–14] and pre-evaporation [15]. These methods present several disadvantages as use of expensive and hazardous organic solvents, lose analytes during extraction and high time consuming. Headspace-solid phase microextraction (HS-SPME) [16–18] are simple and solvent free methods, although presenting the risk of possible artefact generation and occasionally, poor reproducibility.

Dynamic headspace volatile concentration a purge-and-trap, the volatile organic compounds are removed and collected in an analytical trap, without the use of solvent extraction. The trap is heated and the volatile organic compounds (VOCs) are released and delivered to a gas chromatograph for separation and detection. This technique is frequently used for the analysis of crude material such as honey and oyster. It has also been used for the extraction of volatile compounds of dried Kombu but it has never been used for the extraction of fresh seaweed volatiles [8].

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This paper uses a simple and rapid analytical method using dynamic headspace for volatile profile evaluation on two fresh brown seaweeds and analysis by GC–MS.

2. Materials and methods

2.1. Samples

Fresh seaweed Kombu (Laminaria spp) and Wakame (*Undaria pinnatífida*) were collected in February 2011 in the Atlantic coastal region in Galicia (NW Spain) and were obtained from the factory Algamar (Redondela, Pontevedra, Spain). Algae are immediately analyzed in our laboratory.

2.2. Dynamic headspace sampling

In this work we have used Stratum PTC Purge and Trap Concentrator equipped with probe for solid and system of heating, which allows the direct analysis of small quantities of sample without treatment previous to these. We have tested with 1 and 2 g of fresh seaweed, presenting in both cases a similar profile. The sample is warmed to 35 °C during 20 min, avoiding the direct contact with the probe.

Sampling conditions: sample temperature 35 °C; purge time 15 min; purge flow 40 ml/min; dry purge flow 100 ml/min; dry purge time: 2 min; dry purge temperature: 20 °C; desorb preheat temperature 245 °C; desorb temperature 250 °C; bake temperature 260 °C.

2.3. Gas-chromatography.

The trapped components were coupled via a heated interface to a GC–MS system (THERMO Finnigan Trace GC ultra chromatograph with a TraceDSQ mass detector) and directed into an in-line GC capillary column (30 m, 0.25 mm i.d. 1 mm film of 5% diphenyl-polysiloxane and 95% dimethyl-polysiloxane) (DB-5, J&W Scientific). Helium was used as the carrier gas at 1 ml/min. Injector temperature was 170 °C. Split flow: 10 ml/min.

The oven temperature was programmed as follows: initial temperature 40 °C 4 min to 200 °C at a rate of 10 °C/min, with equilibration time 0.1 min.

All analysis were conducted under the same MS conditions. The MS detector was operated in the full scan mode with 70 eV electron ionization, by scanning a mass range of m/z 35–400. The system was computed-controlled using the XCalibur Home Page version 1.4 SRI, Windows XP software.

3. Results and discussion

The system Stratum PTC Purge and Trap Concentrator is a non-invasive, solvent-free method, presenting major advantages: simplicity, quickness, high sensitivity and small sample requirement. This method is appropriate for the volatile profile study of seaweed and frequently used in different samples. It allowed the identification of 24 and 26 compounds, in fresh Wakame and Kombu respectively. Table 1 lists the compounds identified in both samples.

Components were identified by matching their mass spectra with the Wiley *Xcalibur and Mainlib* spectral library. Compounds were identified with a resemblance percentage above 75%. The values are arithmetic means of two samples. These correspond to the following chemical families: alcohols, hydrocarbons, aldehydes, halogenated compounds, esters, and others. These compounds accounted for 77.5% and 81.3% of the total integrated peak areas in Kombu and Wakame respectively.

Table 1
Identified volatile compounds and their average area in fresh seaweed.

Name	No CAS	RT (min)	%Area Wakame	%Area Kombu
Ethanol	64-17-5	3,04	0,37	1,37
Butane	106-97-8	3,33	13,10	11.45
Dicloromethane	75-09-2	3,84	1,59	2,99
1-Propanol	71-23-8	4,16	0,69	0,42
Butanal	123-72-8	4,77		0,26
Hexane	110-54-3	4,87	1,24	1,53
Acetic acid ethyl ester	141-78-6	5,17	0,40	
Methane, trichloro	67-66-3	5,43		0,61
1-Penten-3-ol	616-25-1	6,71	6,84	16,36
1-Penten-3-one	1629-58-9	6,75	3,21	
2-Ethyl-furan	3208-16-0	7,09	0,27	
Propane, 2 yodo	75-30-9	7,62		0,34
(2E)-2-Pentenal	1576-87-0	8,37	1,52	0,49
2-(Chloromethyl)-1-Butene	23010-02-8	8,44		0,39
cis-2-Penten-1-ol	1576-95-0	8,65	2,46	6,27
5-Hexenal	764-59-0	9,09	0,51	0,31
(3Z)-3-hexenal	6789-80-6	9,31	3,33	
n-Hexanal	66-25-1	9,36	8,87	12,03
3-Hexen-1-ol	544-12-7	10,4	11,25	4,15
5-Hexen-1-ol	821-41-0	10,61	0,43	
(2E)-2-Hexen-1-ol	928-95-0	10,69	2,81	
n-Hexanol	111-27-3	10,75	17,16	2,51
Heptanal	111-71-7	11,47		0,63
1-Iodopentane	628-17-1	12,07	0,23	2,22
Ciclopentane,iodo	1556-18-9	1 2,12		5,44
1-Octen-3-ol	3391-86-4	12,93	0,49	0,51
2,4-Heptadienal, (E,E)	#4313-03-5	13,31	0,23	
Octanal	124-13-0	13,40		1,45
Nonanal	124-19-6	15,16	0,22	3,30
n-Decanal	112-31-2	16,79	0,16	3,51
Undecanal	112-44-7	18,31		0,34
Pentanedioic acid, dibutylester	6624-57-3	18,4	0,14	1,88
Dodecanal	112-54-9	19,73		0,57

Alcohols were the most important class of volatile compounds identified in Wakame and Kombu (25 and 29% respectively). Nine alcohols were identified. Two alcohols are superior to 10% of total peak area in Wakame: 3-hexen-1-ol and n-hexanol. The pentenol is the predominant alcohol in Kombu 16%. 3-hexen-1-ol and 1-octen-3-ol were also found in *Fucus serratus* [15].

The hydrocarbons group constitute the second most important family of volatiles from a quantitative point of view in seaweed analyzed. In both samples entire similar % area total: 13–14%, being the butane the most abundant hydrocarbon.

In analyzed Laminaria spp. seaweed has more aldehydes and halogenated compounds (10–9% total area), whereas *Undaria pinnatifida* presents 4–0.23% respectively. A great number of halogenated compounds have been identified in several species of red algae [19,20], may be produced by a range of marine organisms including marine bacteria, algae and several classes of marine invertebrates, in response to oxidative stress, antimicrobial action and other reasons [18]. Hexanal is the most abundant aldehyde in two analyzed seaweed. Akakabe and Kajiwara [14] have reported that in marine seaweed short and middle-chain aldehydes are produced from fatty acids. Aldehydes such as hexanal, heptanal, nonanal and decanal were also found in some species of brown algae from the Black sea [12]. Sugisama et al. [21] have reported aldheydes in the seaweed aroma.

Esters are in small proportion in both seaweeds. 2-ethyl-furan and 1-penten-3 one were only found in Laminaria spp.

These results are that the major volatile compounds found in seaweeds are hydrocarbons, terpenes, phenols, alcohols, aldehydes, ketones, esters, fatty acids and halogen or sulfur-containing compounds [4,22] and that marine macroalgae can produce a broad variety of volatile organic compounds [16]. They are also consistent with those found in other algae, among the volatile components observed in *Palmaria palmata*, the halogenated compounds were the most characteristic, followed by the aldehydes [8].

4. Conclusions

Dynamic headspace with system Stratum PTC Purge and Trap Concentrator and GC–MS is a convenient method for volatile profile evaluation on fresh seaweeds, presenting major advantages as simplicity, quickness, solvent free, high sensitivity and small sample requirement. It allowed the identification of 24 and 26 compounds, in fresh Wakame and Kombu respectively and accounted for 81.3% and 77.5% of the total integrated peak areas, corresponding to the following chemical families: alcohols, hydrocarbons, aldehydes, halogenated compounds, esters, and others.

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