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Assessing the volatile composition of seaweed (*Laminaria digitata)* suspensions as function of thermal and mechanical treatments

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ABSTRACT

Macroalgae are a rich source of dietary fibre, protein, lipids and bioactives. However, more research is needed to understand how processing methods impact macroalgae techno-functional properties. In this work, aqueous suspensions of the fibre-rich brown algae *Laminaria digitata* were prepared by conventional food processing methods. The impact of sequence of processing steps (thermal and mechanical treatments), and heating time (15, 30 and 45 min), on volatile aroma composition were investigated. Changes in volatile composition were monitored with headspace GC-FID/MS analysis. Our results showed that both parameters impacted the volatiles profile of the suspensions. From an overall volatile perspective, short heating times (90 °C for 15 min) led to similar profiles, independently of the sequence of thermal and mechanical treatments. However, longer heating times induced a larger release of several aldehydes, specific for each processing method. Our results bring new insights on the volatile composition of suspensions of *Laminaria digitata*, which are related to flavour properties, and aid design of food products containing seaweed.

1. Introduction

One of the greatest challenges of our society is to ensure access to food for the entire world population, without having a negative impact on the environment. Algae are considered one of the most promising sources for sustainable production of foods. Their potential is reflected in their increasing value on the world market with a current prognosis that, in 2024, seaweed market value worldwide will be 9.98 billion U.S. dollars, twice the value in 2017 (Leandro, Pereira, & Gonçalves, 2020). The inclusion of algae or algae-derived products is increasing in Western countries (Lucas, Gouin, & Lesueur, 2019; Mouritsen, Williams, Bjerregaard, & Duelund, 2012; Palmieri & Forleo, 2020), in the context of innovative cooking and healthy food (Mouritsen et al., 2018, 2019; Rioux, Beaulieu, & Turgeon, 2017). However, despite the fact that macroalgae are present across coastal Europe and can be consumed either fresh or in processed foods, their consumption in Western countries is not yet as common as in Asian countries (Leandro et al., 2020).

Macroalgae, *i.e.* seaweeds, can be divided into three groups: Chlorophyta (green algae), Rhodophyta (red algae), and Ochrophyta – Phaeophyceae (brown algae) (Barsanti & Gualtieri, 2014; Leandro et al., 2020). This classification is mainly based on the colour of their thallus; however, the different types of macroalgae have also large differences in their chemical composition. For example, edible brown algae such as *Laminaria digitata* are a rich source of polysaccharides such as alginates and fucoidans (Lahaye, 1991; Malafronte et al., 2021).

Several studies have investigated the potential use of algae as a source of phenolic compounds (Agregán et al., 2017), polysaccharides (Garcia-Vaquero, Rajauria, O'Doherty, & Sweeney, 2017) and minerals for applications in cosmetics (Lourenço-Lopes, Fraga-Corral, & Jimenez-Lopez, 2020), pharmaceutical industry and as animal feed (Leandro et al., 2020), as well as for their therapeutic properties (Patel, 2012; Roohinejad et al., 2017). Furthermore, the use of macroalgae compounds in the food industry is not new, as they have been used as a source of thickeners and texturisers for decades (Saha & Bhattacharya, 2010), however the interest to use them for other applications is also increasing, for example as stabilisers against oxidation of canola oil (Agregán et al., 2017; Agregán et al., 2017), and to replace bentonite for wine clarification (Cabello-Pasini, Victoria-Cota, Macias-Carranza,

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Hernandez-Garibay, & Muñiz-Salazar, 2005; Marangon et al., 2013).

In order to develop new food products with seaweed, more studies are needed to understand the impact of processing conditions on their techno-functional properties relevant for the perception of texture, flavour (aroma), and taste. Whilst several studies investigate the effect of processing on the rheological properties of microalgae (Magpusao, Giteru, Oey, & Kebede, 2021; Martínez-Sanz et al., 2020; Zhang et al., 2013), less is known about macroalgae suspensions (Malafronte et al., 2021), and most studies focus on biofuels applications and extractability of seaweed components (Hentati, Delattre, et al., 2020; Hentati, Pierre, et al., 2020; Hentati, Tounsi, et al., 2020; Qin, 2018). Furthermore, the safety of algae consumption, for example regarding concentrations of iodine and heavy metals (Ho & Redan, 2020) as well as their impact on sensory properties (Peinado, Girón, Koutsidis, & Ames, 2014) and consumers' willingness to eat algae products (Wendin & Undeland, 2020) should also be considered for product development strategies.

The investigation of the volatile fingerprint of different algae species is attracting great interest (Berneira et al., 2020; Garicano Vilar, O'Sullivan, Kerry, & Kilcawley, 2020a; Jerković et al., 2018; López-Pérez, Picon, & Nuñez, 2017; Peinado et al., 2014; Yamamoto et al., 2014; Zuo, 2019), due to the implications for the sensory properties and acceptability of food products. The relationship between volatile profile of edible algae and processing conditions (Pina, Costa, Lage-Yusty, & López-Hernández, 2014; Stévant et al., 2018; Wang et al., 2019), harvesting season (spring or autumn) and mild pre-treatments (salting and dehydration versus raw material) (Mirzayeva, Castro, Barroso C., & Durán-Guerrero, 2021) has been also investigated in recent years.

Previous studies on suspensions of fruits and vegetables showed that the volatile profile was affected by the sequency of processing steps as well as the heating time (Bi et al., 2021; Lopez-Sanchez, De Vos et al., 2015). Lopez-Sanchez et al. (2015) showed that lipid oxidation related volatile compounds, such as hexanal or decadienal were found to be higher when blending was followed by heating, compared to heating and blending, in all three vegetables. However, the processing order seemed to affect differently the release of other volatiles (*e.g.*, pentanal, heptanal and 1-penten-3-one), highlighting the relevance of the food matrix. The release of lipid oxidation compounds could also be enhanced by the cooking time. A better understanding of how different food processes influence the volatiles profile of seaweed is essential, as it would be a powerful tool to tailor sensory properties and improve the final consumer acceptance of algae in food products (Stévant et al., 2018, 2020).

The present study aims to bring new insights regarding the processability of seaweed as a whole ingredient. The impact of sequence of conventional food processing techniques (thermal and mechanical treatments), and heating time (15, 30 and 45 min) on volatile aroma compounds of *Laminaria digitata* suspensions were investigated. Tailoring processing conditions may help optimise flavour and reduce the possible appearance of undesired aromas, helping the design of sustainable food products containing algae.

2. Materials and methods

2.1. Raw materials and sample preparation

Frozen *Laminaria digitata* was purchased from a Swedish grower (KosterAlg Sweden). The composition (expressed in dry weight as provided by the supplier) was total fat 0.68 % wt., total carbohydrate 55.8 % wt., total protein 9.12 % wt., and total ash 25.4 % wt. Frozen algae were stored at −20 °C prior to the study. The *Laminaria digitata* suspensions were prepared as follows: firstly, algae were thawed at room temperature overnight and washed with water. The seaweed was then mixed with water (ratio of 1:1 seaweed/water) and cooked in glass beakers at 90 °C (selected as a conventional cooking temperature, and monitored with a thermometer inmersed in the suspension (TESTO 735–2, Testo AG; Germany)) for 15, 30 and 45 min using two different processing methods, namely blending followed by heating (BH) or heating followed by blending (HB). For the blending step, a kitchen blender (6700 OBH Nordica, Sweden) was used at maximum speed for 3 min. The total solids content of the aqueous suspensions was adjusted to 3% wt. with deionised water. Algae suspensions were kept in the fridge at 4 °C. All measurements were performed within 48 h of sample preparation.

2.2. Dry matter content

The dry matter was measured by drying 5 g of each suspension in an oven (Memmert ULE 400, Memmert GmbH + Co. KG, Germany) at 105 °C for 24 h. Samples were measured in triplicate.

2.3. Assesment of the volatile composition by DHS-TD-GC-FID/MS

2.3.1. Headspace sampling

The volatile profile was assessed on frozen/thawed (unprocessed) and on processed *Laminaria digitata* suspensions cooked at 90 °C for 15, 30 and 45min. Extraction of the aroma compounds was performed by Dynamic Headspace Sampling (DHS) on 20 g of sample, which were placed on a 500 mL bottle, followed by an equilibration time of 30 min at 35 °C. Volatile compounds released on the bottle headspace were trapped with 1 L of Helium (flow rate 40 mL/min) on thermal desorption tubes (Perkin Elmer - Norwalk, CT, USA) filled with Tenax-TA adsorbent.

2.3.2. Volatile analysis by TD-GC-FID/MS

Thermal desorption was carried out with an automated thermal desorption unit (ThermoMatrix 650, Perkin Elmer - Norwalk, CT, USA). TD Tenax tubes were desorbed at 250 °C for 5 min onto the cold trap held at −30 °C (following a ramp of 40 °C/min), followed by a heating to 280 °C. The temperature of the transfer line was held at 220 °C.

Separation was carried on a Trace GC ULTRA (Thermo Fisher Scientific- Austin, TX, USA) equipped with a flame ionisation detector (FID). The mass spectrometer (MS) detector used was a DSQ II (Thermo Fisher Scientific Austin, TX, USA) operating in electron ionisation mode (EI) at 70eV, with a mass range of 24–300. Separation was performed using DB-WAXetr column (30 m length x 0.32 mm i.d. x 1 μm film thickness, Agilent Tachnologies). The chromatographic conditions used were as described by Peinado et al. (Peinado et al., 2014). Initial oven temperature was set at 40 °C and held for 5 min. A ramp of 8 °C/min until 200 °C followed by a second ramp of 8 °C/min 250 °C and hold for 5 min was applied. Volatile compounds in the sample were tentatively identified by comparing the relative retention time (RT), with respect to the external standard nonane, and by matching the mass spectra with the spectral library NIST14 (National Institute of Standards and Technology, Gaithersburg, MD, USA). The RT was also compared with the original method form Peinado et al. (2014). Compounds that did not exceed the mass spectral match threshold (≥70%) were not considered for the data analysis. Individual peak quantification was done using of Xcalibur™ 4.0 software (Thermo Fisher Scientific, San Jose, California, USA). Calibration was done using one solution containing heptane and nonane (200 ng/L) as external standards. Samples were prepared in triplicate. Values are expressed as nonane equivalent in ng/g of *Laminaria digitata* suspension.

2.4. Statistical analysis

The analysis of variance of the different volatile compounds was performed with a two-way ANOVA (processing method and heating time) and significant differences between treatments were defined using post-hoc Tukey's honest significant difference (HSD) test ($p < 0.05$). Individual volatile compounds were submitted to Principal Component Analysis (PCA) and subsequent Hierarchical Cluster Analysis (HCA),

with Euclidean distances and Ward's agglomeration. XLSTAT 2021.3.1 software (Addinsoft, New York, NY) was used.

3. Results and discussion

3.1. Multivariate analysis to assess the volatile composition as function of processing method and heating time

The chemical composition of *Laminaria digitata* has been previously determined in several studies (Bravo-Linares, Mudge, & Loyola-Sepulveda, 2010; Nitschke, Walsh, McDaid, & Stengel, 2018; Peinado et al., 2014). This species of brown macroalgae was found to be rich in iodinated compounds (Bravo-Linares et al., 2010) and aldehydes, especially hexanal (Peinado et al., 2014). Here, we report on the volatile profile as result of processing conditions, namely thermal and mechanical treatments and heating time. To assess differences on the volatile composition, an analysis of variance was performed (Table 1). The *p-values* displayed in Table 1 represent the significant (*p-value* <0.05) interaction between processing technique and heating time for each individual volatile. The volatile composition of frozen/thawed (unprocessed) *Laminaria digitata* is also reported in Table 1, as an indicator of the initial profile of the samples.

Different aldehydes were tentatively identified on the frozen/thawed samples, with hexanal as the major component, followed by propanal and 2-hexenal. The presence of aldehydes in seaweeds has been previously reported in the literature (Garicano Vilar, O'Sullivan, Kerry, & Kilcawley, 2020b; Takahashi, Sumitani, Inada, & Mori, 2002), being particularly higher in *Laminaria digitata* than in other macroalgae (Ferraces-Casais, Lage-Yusty, Rodríguez-Bernaldo De Quirós, & López-Hernández, 2013; Peinado et al., 2014). The presence of propanal and 2-hexenal has also been shown in other *Laminaria* species (*Laminaria ochroleuca*) (López-Pérez et al., 2017). Six alcohols were identified in the unprocessed samples, with ethanol and 1-penten-3-ol being the most abundant, which remained present in all the processed algae suspensions. The main alcohol reported in the literature in *Laminaria* spp is 1-penten-3-ol (Ferraces-Casais et al., 2013). Additionally, three iodinated compounds were tentatively identified: iodoethane, iodo-1-propane, and iodo-2-propane. The presence of some iodinated compounds has been reported in different algae (Lukić, Carlin, Horvat, & Vrhovsek, 2019), and specially in *Laminaria digitata* (Bravo-Linares et al., 2010; Nitschke, Dixneuf, Ruth, Schmid, & Stengel, 2013). The level of benzaldehyde was higher in frozen/thawed samples (unprocessed) compared to any of the processed samples (Table 1). The presence of benzaldehyde has been previously reported in *Laminaria ochroleuca* (Garicano Vilar et al., 2020a).

3.1.1. Impact on individual aldehydes

Regarding processed samples, a majority of volatile compounds were found at higher concentrations in samples thermally treated for longer heating times, especially in HB samples, suggesting that mechanical disruption of thermally treated algae enhanced release of volatile compounds (Table 1). Nevertheless, some aroma compounds such as ethanol and benzaldehyde did not show variation, irrespective of time or type of processing (Table 1). Our results showed a trend towards a larger release of hexanal and heptanal at heating times longer than 15 min however, the differences were only significant for HB suspensions. For BH, the level of hexanal tended to increase, but remained statistically similar independently of the heating time (Table 1). However, for HB samples, a

Table 1
Average content (in ng/g of algae expressed as nonane equivalents) of the individual volatiles in *Laminaria digitata* suspensions. The corresponding p-value for each compound was obtained from a two-way ANOVA (processing technique and heating time). Significant differences (p-value < 0.05) between samples for each individual volatile compound are indicated with different letters (Tukey's HSD test).

					BH			HB			
	RT	RRT	m/z	Frozen/thawed	15 min	30 min	45 min	15 min	30 min	45 min	***p*-value**
Propanal	9.62	0.75	58	6.69 ± 0.4	8.44 ± 1.0 ab	12.15 ± 2.3 ab	10.10 ± 0.7 ab	5.33 ± 1.0 b	14.65 ± 0.4 a	11.74 ± 1.9 ab	0.221
Acetone	10.46	0.82	43	1.44 ± 0.1	1.52 ± 0.0 bc	2.20 ± 0.1 ab	3.06 ± 0.1 a	1.30 ± 0.1 b	2.32 ± 0.2 ac	2.41 ± 0.3 ac	0.203
2-Propenal	11.55	0.91	56	0.53 ± 0.1	0.52 ± 0.1 b	0.95 ± 0.2 ab	0.64 ± 0.3 b	0.38 ± 0.1 b	1.79 ± 0.4 a	1.77 ± 0.5 a	0.026
Ethane, iodo	12.57	0.99	156	2.31 ± 0.0	3.25 ± 0.7 a	5.13 ± 1.8 a	3.92 ± 0.7 a	2.17 ± 0.4 a	4.86 ± 0.5 a	4.79 ± 0.2 a	0.322
Propane, 2-iodo	13.61	1.07	170	1.95 ± 0.2	1.15 ± 0.1 b	1.92 ± 0.5 b	0.46 ± 0.7b	1.61 ± 0.3 b	4.16 ± 0.7 a	4.32 ± 0.2 a	0.003
3-methylbutanal	14.19	1.11	44	0.37 ± 0.0	0.50 ± 0.1 b	0.93 ± 0.2 ab	0.83 ± 0.2 ab	0.21 ± 0.1 b	1.55 ± 0.5 a	1.50 ± 0.4 a	0.027
Ethanol	14.85	1.16	31	11.7 ± 0.6	7.82 ± 1.2 a	9.61 ± 5.6 a	11.06 ± 6.5 a	4.90 ± 0.1 a	5.80 ± 0.1 a	10.13 ± 1.1 a	0.828
Propane, 1-iodo	16.25	1.27	170	0.74 ± 0.0	1.35 ± 0.4 ab	2.19 ± 0.7 a	1.64 ± 0.4 ab	0.87 ± 0.2 b	0.57 ± 0.1 b	0.88 ± 0.3 ab	0.119
Pentanal	17.05	1.34	44	1.64 ± 0.1	3.12 ± 0.8 a	4.27 ± 1.1 a	4.95 ± 0.2 a	3.79 ± 0.3 a	5.41 ± 0.6 a	5.56 ± 1.2 a	0.955
1-Penten-3-one	18.80	1.47	55	3.71 ± 0.4	6.45 ± 1.6 bc	9.74 ± 0.0 ac	6.41 ± 2.1 bc	3.51 ± 0.5 c	16.31 ± 2.2 a	14.40 ± 4.5 ab	0.015
2-Butenal	19.87	1.56	39	1.05 ± 0.1	1.72 ± 0.1 c	2.61 ± 0.3 bc	2.27 ± 0.4 bc	1.41 ± 0.1 c	5.24 ± 0.7 a	4.37 ± 1.2 ab	0.022
2,3-pentanedione	20.28	1.59	57	0.49 ± 0.0	0.53 ± 0.1 c	0.90 ± 0.3 ac	0.76 ± 0.2 bc	0.48 ± 0.0 c	1.74 ± 0.0 a	1.65 ± 0.6 ab	0.028
Hexanal	21.25	1.67	44	18.61 ± 2.2	29.49 ± 8.3 ab	42.83 ± 0.3 a	35.78 ± 7.7 ab	14.42 ± 2.5 b	54.87 ± 4.4 a	57.05 ± 15.2 a	0.021
1-penten-3-ol	24.10	1.89	57	7.03 ± 0.2	6.05 ± 0.9 c	7.61 ± 0.3 bc	5.92 ± 1.0 c	5.35 ± 0.1 c	12.68 ± 1.2 a	11.01 ± 1.7 ab	0.002
Heptanal	25.60	2.01	44	0.71 ± 0.1	0.96 ± 0.1 bc	1.43 ± 0.0 ab	1.34 ± 0.4 ab	0.56 ± 0.1 c	1.84 ± 0.1 a	1.76 ± 0.4 a	0.033
2-Hexenal	27.21	2.13	41	7.3 ± 0.5	7.94 ± 1.3 ab	10.33 ± 1.3 a	8.83 ± 1.9 ab	4.42 ± 0.5 b	11.13 ± 0.3 a	9.31 ± 1.5 ab	0.154
2-penten-1-ol	30.49	2.39	57	1.54 ± 0.1	1.04 ± 0.1 a	1.18 ± 0.1 ab	0.97 ± 0.2 a	1.03 ± 0.0 a	1.78 ± 0.4 b	1.65 ± 0.2 b	0.022
1-octen-3-ol	35.10	2.75	57	3.4 ± 0.2	4.02 ± 0.5 cd	6.29 ± 0.8 abc	5.03 ± 0.7 bd	3.16 ± 0.3 d	7.48 ± 0.8 ab	8.04 ± 1.6 a	0.017
2,4-heptadienal	36.78	2.88	81	0.98 ± 0.1	1.55 ± 0.4 c	2.31 ± 0.5 bc	1.48 ± 0.6 c	1.23 ± 0.1 c	4.50 ± 0.8 ab	4.63 ± 1.2 a	0.006
Benzaldehyde	39.61	3.10	77	7.54 ± 0.1	3.82 ± 0.2 a	3.64 ± 0.1 a	3.60 ± 0.3 a	3.21 ± 0.3 a	3.43 ± 0.1 a	4.38 ± 0.2 a	0.551
2,6-nonadienal	41.40	3.24	81	0.76 ± 0.1	0.80 ± 0.1 bd	1.23 ± 0.1 ab	0.97 ± 0.2 bdc	0.72 ± 0.1 d	1.36 ± 0.1 ac	1.50 ± 0.2 a	0.021
2,4-decadienal	49.60	3.89	81	0.84 ± 0.0	1.36 ± 0.2 bd	1.95 ± 0.0 ab	1.51 ± 0.2 bdc	1.10 ± 0.1 d	2.48 ± 0.2 ac	2.48 ± 0.3 a	0.001

significant increase was observed from 15 min to 30 min and 45 min. Similar results were found for heptanal. High levels of hexanal in *Laminaria digitata,* compared to other algae species, had been previously reported by Peinado et al. (Peinado et al., 2014). The formation of short-chain and medium-chain aldehydes in seaweeds, such as hexanal or heptanal, has been associated with the degradation of fatty acids (Akakabe & Kajiwara, 2008; Le Pape, Grua-Priol, Prost, & Demaimay, 2004). Longer heating times may induce the formation of hexanal and heptanal from fatty acids, which are associated with "fresh" and "green" but also with "fishy", "rancid" and "fatty" smells (Peinado et al., 2014; Stévant et al., 2020). The formation of 2-hexenal (with "green" and "fatty" smell (Stévant et al., 2020)) did not seem to be influenced by the processing method. However, other unsaturated aldehydes such as 2, 4-Heptadienal and 2,4-Decadienal, both associated with "fatty" smells (Stévant et al., 2020) were significantly higher in HB, especially after 45 min. Apart from lipid oxidation, the concentration of aldehydes in processed foods might increase after thermal processing due to chemical reactions occurring at high temperatures, such as degradation of amino acids or carbohydrates (Diez-Simon, Mumm, & Hall, 2019). Thus, the larger concentration of hexanal and heptanal in HB samples may be a consequence of the initial heating prior to blending, blending softer material could lead to higher disruption and release of cell components. The presence of these aldehydes throughout the heating process has been reported in other food products (Chai et al., 2019). Other aldehydes such as propanal and pentanal were not significantly influenced by the processing method or time. A recent study has found a decrease in aldehydes (statistically significant in the case of hexanal) in the green algae *Ulva rigida* after cooking for 15 min (Sánchez-García et al., 2020), highlighting the differences between macroalgae species. Blending in combination with longer heating times may lead to an increase in the lipid content and exposure time to oxygen, resulting in the formation of these aldehydes. The levels of 3-methylbutanal, which is the main key odorant in miso soup (Stévant et al., 2020) were significantly higher at longer heating times, but no significant differences were found between processing methods (HB and BH).

3.1.2. Impact on individual alcohols and ketones

The content of alcohols was influenced by the processing method and heating time, being significant for 1-penten-3-ol, 2-penten-1-ol and 1-octen-3-ol. The concentration of these compounds tended to be higher in HB samples. Interestingly, the highest concentration of these compounds in HB samples was found after 30 min of heating, showing a decrease in 45 min samples. This decreasing trend was observed for all the alcohols with the exception of 1-penten-3-ol, that reached its maximum level after 45 min (Table 1). A study in edible red seaweed showed that out of the different alcohols identified only ethanol and 1-penten-3-ol were found after cooking (Pina et al., 2014). The level of ketones, 1-penten-3-one and 2,3-pentanedione, were also significantly higher in HB samples compared to BH samples.

3.1.3. Impact on individual halogenated compounds

Regarding the presence of halogenated compounds, the release of iodinated compounds is usually associated with oxidative stress, but some of these compounds seemed to be also influenced by the processing method (Table 1). Different trends were observed, the level of iodoethane remained stable regardless of processing method and time, whilst 2-iodopropane increased after 15 min for HB samples (but remained constant for BH). Llittle is known regarding the impact of these iodinated compounds on the sensory properties of the algae. The study of Takahashi and co-workers (Takahashi et al., 2002) showed that only 1-iodooctane had an active odour and was found to be the major contributor to Kombu aroma. However, further research needs to be done to investigate whether these iodinated compounds have a direct or indirect contribution to the organoleptic properties of *Laminaria digitata*.

3.1.4. Impact of processing on the overall volatile profile

Multivariate analyses were performed to determine the impact of processing method and heating time on the overall volatile profile of *Laminaria digitata* suspensions. The PCA biplot plot illustrates the sample distribution according to the overall volatile composition of the samples (Fig. 1), including unprocessed samples. The first two components accounted for 84.86% of the total explained variance. Statistical analysis on the compounds quantified from the DHS-TD-GC-FID/MS analyses showed that both the heating time and the sequence of blending and thermal treatments played a role on the release of volatile compounds. The impact of sequence of thermal and mechanical treatments on the volatile profile was previously observed in different vegetable purées (Koutidou, Grauwet, Van Loey, & Acharya, 2017; Lopez-Sanchez, de Vos et al., 2015). The results showed that most of the individual volatile compounds, especially aldehydes, had a positive contribution to the positive side of PC1 (70.99%). On the overall, a greater volatile release in HB 30 and 45 suspensions was already described in Table 1. More specifically, hexanal, heptanal, and 1-pentan-3-one were found to be the major contributors to the separation along PC11, whereas compounds such as 1-iodopropane, 2-penten-1-ol and benzaldehyde showed a larger contribution to PC2 (13.87%). Benzaldehyde is one of the volatile compounds driving the separation between unprocessed and processed samples. Similarities between samples as a result of heating time and sequential treatment were also evaluated with the corresponding HCA (Fig. 2), which showed the formation of two clusters. The first cluster was formed by HB samples after 30 and 45 min, characterised by a larger concentration of most volatiles (Table 1). The second cluster, two subclusters were formed. The first subcluster was formed by unprocessed samples, and HB 15 min and one of the replicates from BH15. The second subgroup included BH after 15, 30 and 45 min. Therefore, the present findings indicate that when cooked for only 15 min, the sequence of mechanical and thermal treatment does not seem to have large impact on the volatile release however, when cooked for longer times differences could be observed between processing methods. Additionally, HB cooked for 15min present a similar volatile profile to unprocessed samples.

The formation of volatile compounds in macroalgae, has been related to fatty acid degradation (López-Pérez et al., 2017) and they might be

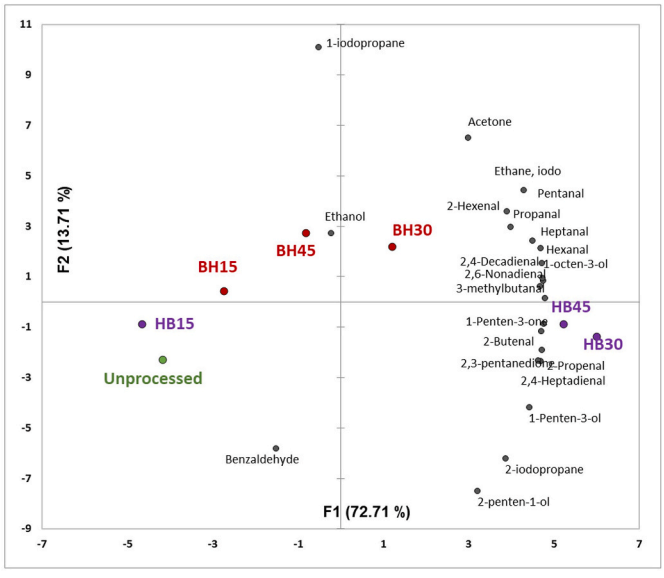

Fig. 1. Biplot illustrating the sample distribution (HB and BH) according to the overall volatile profile of the samples. Samples are coloured according to the processing technique (green - unprocessed; purple - HB; burgundy - BH). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

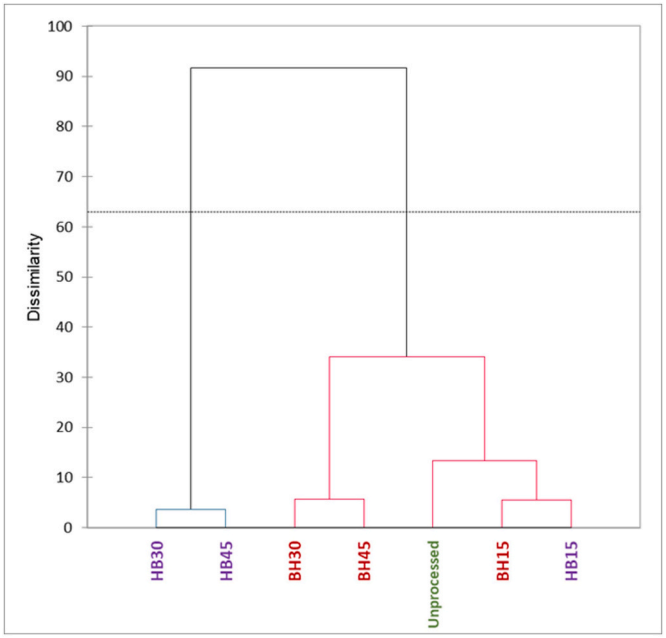

Fig. 2. Hierarchical cluster analysis of the principal components. Samples are coloured according to the processing technique (green - unprocessed; purple - HB; burgundy - BH). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

associated with rancidity (Peinado et al., 2014). Lopez-Sanchez and colleagues (Lopez-Sanchez, De Vos et al., 2015) showed that initial blending followed by heating may favour the release of lipid soluble compounds in some vegetables. Based on these findings, we could expect having greater aldehyde levels on BH. However, the present results showed a higher level on HB samples. It is necessary to take into account that the impact of blending of *Laminaria digitata* might also be favouring the release of other bioactive compounds, such as alginate, laminarin and fucoidan (Malafronte et al., 2021). The greater level of these compounds in the suspensions may be affecting the formation, but also the subsequent release of compounds such as aldehydes. A study on pork patties, showed that when adding laminarin and fucoidan (extracted from *Laminaria digitata*) reduced lipid oxidation in cooked patties (Moroney, O'Grady, O'Doherty, & Kerry, 2013). Moroney and co-workers highlighted that heating may enhance the antioxidant activity of these two active polysaccharides from *Laminaria digitata*. The volatile release of individual compounds such as 2-hexenal has already been shown to be affected by the presence of polysaccharides, such as propylene glycol alginate (Terta, Blekas, & Paraskevopoulou, 2006). This could be an explanation for the lower levels of some aldehydes in BH.

4. Conclusions

The presented results demonstrated that the sequence of mechanical and thermal processing, as well as the severity of thermal treatment, affected the volatile profile of *Laminaria digitata* aqueous suspensions. In general, thermal processing prior to mechanical treatment softens the algae tissues and this may enhance the release of cell compounds, including cell wall polysaccharides, phenolics and lipids. Multivariate analysis showed that for short heating times (90 °C 15 min) the sequence of mechanical and thermal treatments did not have a significant impact on the volatile composition compared to unprocessed *Laminaria digitata*. However, longer heating times can lead to the formation of aldehydes such as hexanal and heptanal related to the degradation of fatty acids, especially when the algae is thermally treated prior to blending (HB). Thus, processing conditions could be tailored to optimise the use of this macroalgae in food products. Our study contributes to the knowledge regarding processing of seaweed to enhance their organoleptic properties, which in combination with nutritional quality, would aid design of food products making use of these aquatic resources.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Gonzalo Garrido-Bañuelos: Conceptualization, Experimental design, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Ana Miljkovic:** Processing experiments, Data curation, Formal analysis, Investigation, Writing – original draft. **Clément Morange:** Volatile experiments, Investigation, Writing – original draft. **Mihaela Mihnea:** Conceptualization, Methodology, Writing – review & editing. **Patricia Lopez-Sanchez:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Validation, Writing – original draft, Writing – review & editing.

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References

Agregán, R., Lorenzo, J. M., Munekata, P. E. S., Dominguez, R., Carballo, J., & Franco, D. (2017). Assessment of the antioxidant activity of Bifurcaria bifurcata aqueous extract on canola oil. Effect of extract concentration on the oxidation stability and volatile compound generation during oil storage. *Food Research International, 99*, 1095–1102. https://doi.org/10.1016/j.foodres.2016.10.029

Agregán, R., Munekata, P. E., Domínguez, R., Carballo, J., Franco, D., & Lorenzo, J. M. (2017). Proximate composition, phenolic content and in vitro antioxidant activity of aqueous extracts of the seaweeds Ascophyllum nodosum, Bifurcaria bifurcata and Fucus vesiculosus. Effect of addition of the extracts on the oxidative stability of canola oil unde. *Food Research International, 99*, 986–994. https://doi.org/10.1016/j.foodres.2016.11.009

Agregán, R., Munekata, P. E. S., Franco, D., Dominguez, R., Carballo, J., & Lorenzo, J. M. (2017). Phenolic compounds from three brown seaweed species using LC-DAD–ESI-MS/MS. *Food Research International, 99*, 979–985. https://doi.org/10.1016/j.foodres.2017.03.043

Akakabe, Y., & Kajiwara, T. (2008). Bioactive volatile compounds from marine algae: Feeding attractants. *Journal of Applied Phycology, 20*(5), 661–664. https://doi.org/10.1007/s10811-007-9309-x

Barsanti, L., & Gualtieri, P. (2014). *Algae: Anatomy, biochemistry and biotechnology, second edition. Boca Raton*. https://doi.org/10.1007/s007690000247

Berneira, L., da Silva, C., Poletti, T., Ritter, M., dos Santos, M., Colepicolo, P., et al. (2020). Evaluation of the volatile composition and fatty acid profile of seven Antarctic macroalgae. *Journal of Applied Phycology, 3*. https://doi.org/10.1007/s10811-020-02170-9

Bi, J., Lin, Z., Li, Y., Chen, F., Liu, S., & Li, C. (2021). Effects of different cooking methods on volatile flavor compounds of chicken breast. *Journal of Food Biochemistry, 45*(8). https://doi.org/10.1111/jfbc.13770

Bravo-Linares, C. M., Mudge, S. M., & Loyola-Sepulveda, R. H. (2010). Production of volatile organic compounds (VOCs) by temperate macroalgae. The use of Solid Phase Microextraction (SPME) coupled to GC-MS as method of analysis. *Journal of the Chilean Chemical Society, 55*(2), 227–232. https://doi.org/10.4067/S0717-97072010000200018

Cabello-Pasini, A., Victoria-Cota, N., Macias-Carranza, V., Hernandez-Garibay, E., & Muñiz-Salazar, R. (2005). Clarification of wines using polysaccharides extracted from seaweeds. *American Journal of Enology and Viticulture, 56*(1), 52–59.

Chai, D., Li, C., Zhang, X., Yang, J., Liu, L., Xu, X., et al. (2019). Analysis of volatile compounds from wheat flour in the heating process. *International Journal of Food Engineering, 15*(10). https://doi.org/10.1515/ijfe-2019-0252

Diez-Simon, C., Mumm, R., & Hall, R. D. (2019). Mass spectrometry-based metabolomics of volatiles as a new tool for understanding aroma and flavour chemistry in processed food products. *Metabolomics, 15*(3), 1–20. https://doi.org/10.1007/s11306-019-1493-6

Ferraces-Casais, P., Lage-Yusty, M. A., Rodríguez-Bernaldo De Quirós, A., & López-Hernández, J. (2013). Rapid identification of volatile compounds in fresh seaweed. *Talanta, 115*, 798–800. https://doi.org/10.1016/j.talanta.2013.06.049

Garcia-Vaquero, M., Rajauria, G., O'Doherty, J. V., & Sweeney, T. (2017). Polysaccharides from macroalgae: Recent advances, innovative technologies and challenges in extraction and purification. *Food Research International, 99*, 1011–1020. https://doi.org/10.1016/j.foodres.2016.11.016

Garicano Vilar, E., O'Sullivan, M. G., Kerry, J. P., & Kilcawley, K. N. (2020a). Volatile compounds of six species of edible seaweed: A review. *Algal Research, 45*, Article 101740. https://doi.org/10.1016/j.algal.2019.101740. December 2019.

Garicano Vilar, E., O'Sullivan, M. G., Kerry, J. P., & Kilcawley, K. N. (2020b). Volatile compounds of six species of edible seaweed: A review. *Algal Research, 45*, Article 101740. https://doi.org/10.1016/j.algal.2019.101740. December 2019.

Hentati, F., Delattre, C., Gardarin, C., Desbrières, J., Le Cerf, D., Rihouey, C., et al. (2020). *Structural features and rheological properties of a sulfated Xylogalactan-rich fraction isolated from Tunisian red seaweed Jania adhaerens*. Switzerland: Applied Sciences. https://doi.org/10.3390/app10051655

Hentati, F., Pierre, G., Ursu, A. V., Vial, C., Delattre, C., Abdelkafi, S., et al. (2020). Rheological investigations of water-soluble polysaccharides from the Tunisian brown seaweed Cystoseira compressa. *Food Hydrocolloids*. https://doi.org/10.1016/j.foodhyd.2019.105631

Hentati, F., Tounsi, L., Djomdi, D., Pierre, G., Delattre, C., Ursu, A. V., et al. (2020). Bioactive polysaccharides from seaweeds. *Molecules, 25*(14), 1–29. https://doi.org/10.3390/molecules25143152

Ho, K. K. H. Y., & Redan, B. W. (2020). Impact of thermal processing on the nutrients, phytochemicals, and metal contaminants in edible algae. *Critical Reviews in Food Science and Nutrition*, 1–19. https://doi.org/10.1080/10408398.2020.1821598, 0 (0).

Jerković, I., Marijanović, Z., Roje, M., Kus, P. M., Jokić, S., & Čož-Rakovac, R. (2018). Phytochemical study of the headspace volatile organic compounds of fresh algae and seagrass from the Adriatic Sea (single point collection). *PLoS One, 13*(5), 1–13. https://doi.org/10.1371/journal.pone.0196462

Koutidou, M., Grauwet, T., Van Loey, A., & Acharya, P. (2017). Potential of different mechanical and thermal treatments to control off-flavour generation in broccoli puree. *Food Chemistry*. https://doi.org/10.1016/j.foodchem.2016.09.003

Lahaye, M. (1991). Marine algae as sources of fibres: Determination of soluble and insoluble dietary fibre contents in some 'sea vegetables. *Journal of the Science of Food and Agriculture*. https://doi.org/10.1002/jsfa.2740540410

Le Pape, M. A., Grua-Priol, J., Prost, C., & Demaimay, M. (2004). Optimization of dynamic headspace extraction of the edible red algae palmaria palmata and identification of the volatile components. *Journal of Agricultural and Food Chemistry*. https://doi.org/10.1021/jf030478x

Leandro, A., Pereira, L., & Gonçalves, A. M. M. (2020). Diverse applications of marine macroalgae. *Marine Drugs, 18*(1). https://doi.org/10.3390/md18010017

López-Pérez, O., Picon, A., & Nuñez, M. (2017). Volatile compounds and odour characteristics of seven species of dehydrated edible seaweeds. *Food Research International, 99*, 1002–1010. https://doi.org/10.1016/j.foodres.2016.12.013

Lopez-Sanchez, P., De Vos, R. C. H., Jonker, H. H., Mumm, R., Hall, R. D., Bialek, L., et al. (2015). Comprehensive metabolomics to evaluate the impact of industrial processing on the phytochemical composition of vegetable purees. *Food Chemistry, 168*, 348–355. https://doi.org/10.1016/j.foodchem.2014.07.076

Lourenço-Lopes, C., Fraga-Corral, M., & Jimenez-Lopez, C. (2020). Metabolites from macroalgae and its applications in the cosmetic industry : A circular economy approach. *Resources*. https://doi.org/10.3390/resources9090101. August.

Lucas, S., Gouin, S., & Lesueur, M. (2019). Seaweed consumption and label preferences in France. *Marine Resource Economics, 34*(2), 143–162. https://doi.org/10.1086/704078

Lukić, I., Carlin, S., Horvat, I., & Vrhovsek, U. (2019). Combined targeted and untargeted profiling of volatile aroma compounds with comprehensive two-dimensional gas chromatography for differentiation of virgin olive oils according to variety and geographical origin. *Food Chemistry, 270*, 403–414. https://doi.org/10.1016/j.foodchem.2018.07.133. March 2018.

Magpusao, J., Giteru, S., Oey, I., & Kebede, B. (2021). Effect of high pressure homogenization on microstructural and rheological properties of A. platensis, Isochrysis, Nannochloropsis and Tetraselmis species. *Algal Research, 56*, Article 102327. https://doi.org/10.1016/J.ALGAL.2021.102327

Malafronte, L., Yilmaz-Turan, S., Krona, A., Martinez-Sanz, M., Vilaplana, F., & Lopez-Sanchez, P. (2021). Macroalgae suspensions prepared by physical treatments: Effect of polysaccharide composition and microstructure on the rheological properties. *Food Hydrocolloids, 120*, Article 106989. https://doi.org/10.1016/j.foodhyd.2021.106989. December 2020.

Marangon, M., Stockdale, V. J., Munro, P., Trethewey, T., Schulkin, A., Holt, H. E., et al. (2013). Addition of carrageenan at different stages of winemaking for white wine protein stabilization. *Journal of Agricultural and Food Chemistry, 61*(26), 6516–6524. https://doi.org/10.1021/jf401712d

Martínez-Sanz, M., Garrido-Fernández, A., Mijlkovic, A., Krona, A., Martínez-Abad, A., Coll-Marqués, J. M., et al. (2020). Composition and rheological properties of microalgae suspensions: Impact of ultrasound processing. *Algal Research*. https://doi.org/10.1016/j.algal.2020.101960

Mirzayeva, A., Castro, R., Barroso, C. G., & Durán-Guerrero, E. (2021). Characterization and differentiation of seaweeds on the basis of their volatile composition. *Food Chemistry, 336*, Article 127725. https://doi.org/10.1016/j.foodchem.2020.127725. April 2020.

Moroney, N. C., O'Grady, M. N., O'Doherty, J. V., & Kerry, J. P. (2013). Effect of a brown seaweed (Laminaria digitata) extract containing laminarin and fucoidan on the quality and shelf-life of fresh and cooked minced pork patties. *Meat Science, 94*(3), 304–311. https://doi.org/10.1016/j.meatsci.2013.02.010

Mouritsen, O. G., Rhatigan, P., & Pérez-Lloréns, J. L. (2018). World cuisine of seaweeds: Science meets gastronomy. *International Journal of Gastronomy and Food Science, 14* (August), 55–65. https://doi.org/10.1016/j.ijgfs.2018.09.002

Mouritsen, O. G., Rhatigan, P., & Pérez-Lloréns, J. L. (2019). The rise of seaweed gastronomy: Phycogastronomy. *Botanica Marina, 62*(3), 195–209. https://doi.org/10.1515/bot-2018-0041

Mouritsen, O. G., Williams, L., Bjerregaard, R., & Duelund, L. (2012). Seaweeds for umami flavour in the new nordic cuisine. *Flavour, 1*(1), 1–12. https://doi.org/10.1186/2044-7248-1-4

Nitschke, U., Dixneuf, S., Ruth, A. A., Schmid, M., & Stengel, D. B. (2013). Molecular iodine (I2) emission from two Laminaria species (Phaeophyceae) and impact of irradiance and temperature on I2 emission into air and iodide release into seawater from Laminaria digitata. *Marine Environmental Research, 92*, 102–109. https://doi.org/10.1016/j.marenvres.2013.09.006

Nitschke, U., Walsh, P., McDaid, J., & Stengel, D. B. (2018). Variability in iodine in temperate seaweeds and iodine accumulation kinetics of Fucus vesiculosus and Laminaria digitata (Phaeophyceae, Ochrophyta). *Journal of Phycology, 54*(1), 114–125. https://doi.org/10.1111/jpy.12606

Palmieri, N., & Forleo, M. B. (2020). The potential of edible seaweed within the western diet. A segmentation of Italian consumers. *International Journal of Gastronomy and Food Science, 20*(January), Article 100202. https://doi.org/10.1016/j.ijgfs.2020.100202

Patel, S. (2012). Therapeutic importance of sulfated polysaccharides from seaweeds: Updating the recent findings. *3 Biotech, 2*(3), 171–185. https://doi.org/10.1007/s13205-012-0061-9

Peinado, I., Girón, J., Koutsidis, G., & Ames, J. M. (2014). Chemical composition, antioxidant activity and sensory evaluation of five different species of brown edible seaweeds. *Food Research International, 66*, 36–44. https://doi.org/10.1016/j.foodres.2014.08.035

Pina, A. L., Costa, A. R., Lage-Yusty, M. A., & López-Hernández, J. (2014). An evaluation of edible red seaweed (Chondrus crispus) components and their modification during the cooking process. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology, 56*(1), 175–180. https://doi.org/10.1016/j.lwt.2013.08.006

Qin, Y. (2018). Seaweed hydrocolloids as thickening, gelling, and emulsifying agents in functional food products. In *Bioactive seaweeds for food applications: Natural ingredients for healthy diets*. https://doi.org/10.1016/B978-0-12-813312-5.00007-8

Rioux, L. E., Beaulieu, L., & Turgeon, S. L. (2017). Seaweeds: A traditional ingredients for new gastronomic sensation. *Food Hydrocolloids, 68*, 255–265. https://doi.org/10.1016/j.foodhyd.2017.02.005

Roohinejad, S., Koubaa, M., Barba, F. J., Saljoughian, S., Amid, M., & Greiner, R. (2017). Application of seaweeds to develop new food products with enhanced shelf-life, quality and health-related beneficial properties. *Food Research International, 99*, 1066–1083. https://doi.org/10.1016/j.foodres.2016.08.016

Saha, D., & Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: A critical review. *Journal of Food Science & Technology, 47*(6), 587–597. https://doi.org/10.1007/S13197-010-0162-6, 47(6) 2010.

Sánchez-García, F., Mirzayeva, A., Roldán, A., Castro, R., Palacios, V., Barroso, C. G., et al. (2020). Effect of different cooking methods on sea lettuce (Ulva rigida) volatile compounds and sensory properties. *Journal of the Science of Food and Agriculture*. https://doi.org/10.1002/jsfa.10705

Stévant, P., Indergård, E., Ólafsdóttir, A., Marfaing, H., Larssen, W. E., Fleurence, J., et al. (2018). Effects of drying on the nutrient content and physico-chemical and sensory characteristics of the edible kelp Saccharina latissima. *Journal of Applied Phycology, 30*(4), 2587–2599. https://doi.org/10.1007/s10811-018-1451-0

Stévant, P., Ólafsdóttir, A., Déléris, P., Dumay, J., Fleurence, J., Ingadóttir, B., et al. (2020). Semi-dry storage as a maturation process for improving the sensory characteristics of the edible red seaweed dulse (Palmaria palmata). *Algal Research, 51*, Article 102048. https://doi.org/10.1016/j.algal.2020.102048. November 2019.

Takahashi, H., Sumitani, H., Inada, Y., & Mori, D. (2002). Identification of volatile compounds of kombu (Laminaria spp.) and their odor description. *Nippon Shokuhin Kagaku Kogaku Kaishi, 49*(4), 228–237. https://doi.org/10.3136/nskkk.49.228

Terta, M., Blekas, G., & Paraskevopoulou, A. (2006). Retention of selected aroma compounds by polysaccharide solutions: A thermodynamic and kinetic approach. *Food Hydrocolloids, 20*(6), 863–871. https://doi.org/10.1016/j.foodhyd.2005.08.011

Wendin, K., & Undeland, I. (2020). Seaweed as food – attitudes and preferences among Swedish consumers. *International Journal of Gastronomy and Food Science, 22*, Article 100265. https://doi.org/10.1016/j.ijgfs.2020.100265. June.

Yamamoto, M., Baldermann, S., Yoshikawa, K., Fujita, A., Mase, N., & Watanabe, N. (2014). Determination of volatile compounds in four commercial samples of Japanese green algae using solid phase microextraction gas chromatography mass spectrometry. *The Scientific World Journal*. https://doi.org/10.1155/2014/289780. January) 2014.

Zhang, X., Jiang, Z., Chen, L., Chou, A., Yan, H., Zuo, Y. Y., et al. (2013). Influence of cell properties on rheological characterization of microalgae suspensions. *Bioresource Technology*. https://doi.org/10.1016/j.biortech.2013.03.195

Zuo, Z. (2019). Why algae release volatile organic compounds - the emission and roles. *Frontiers in Microbiology, 10*, 1–7. https://doi.org/10.3389/fmicb.2019.00491. MAR.