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Semi-dry storage as a maturation process for improving the sensory characteristics of the edible red seaweed dulse (*Palmaria palmata*)



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ABSTRACT

The potential of seaweeds as food is gaining increasing interest among Western consumers. This trend is supported by the nutritional benefits of several species such as *Palmaria palmata*. Product flavor is a major factor governing consumer acceptance. Developing more attractive flavors in edible seaweeds is a key to sustain the current health food movement based on this resource in Europe. Semi-dry (SD) storage of *P. palmata* was investigated as a mean to increase its sensory quality. SD-samples containing 20% moisture and dried (D) samples (6% moisture) stored up to 126 days were studied. SD-samples stored for a long period (61 and 126 days) developed a distinct sweet, rich, complex flavor and odor as well as a softer texture compared to SD-samples stored for a shorter period (12 days) and D-samples stored for 126 days. Variations in nutritional compounds and physico-chemical properties among samples along with increasing levels and diversity of volatile compounds in SD-samples during storage compared to D-126 suggest that a variety of flavor compounds arise from biochemical reactions involving lipids, proteins and carbohydrates. These reactions are either endogenous or the result of the activity of microorganisms naturally present in the seaweed. They are promoted by a higher moisture content than in dried material (20% vs 6%) and long storage times. These results provide a basis which can be applied to control the storage conditions of seaweeds to produce flavor-rich ingredients attractive to Western consumers.

1. Introduction

Seaweeds have to a small degree been regarded as food in Western countries during the past centuries [1]. They are now increasingly recognized as a source of nutrients and bioactive substances as well as natural and sustainable food ingredients with a great potential in culinary applications. In particular, some species common to the coast of Europe such as dulse (*Palmaria palmata*) have flavor and physico-chemical characteristics that can be used to enhance the palatability of foods to which they are added [2,3]. Yet, food neophobia [4] and negative associations from the consumer (e.g. with rotting biomass on the foreshore) have been identified as major obstacles to a broader use of seaweeds in the Western diet [1,5,6]. Flavor is a major factor determining consumer acceptance of foods [7]. To sustain the current movement promoting this resource as natural and healthy food ingredient, there is a need to develop products from seaweeds that are attractive to Western consumers.

In Asia, seaweeds are part of the culinary culture and prized for their flavors and textures. Umami is the most characteristic flavor described from seaweeds. Umami is the fifth basic taste (along with sweet, salty, sour and bitter) and was first described by Kikunae Ikeda in 1909 as brothy, meaty and savory (*umai*) [8]. Ikeda described this specific taste from the traditional broth (*dashi*) prepared from the Japanese kelp *kombu* (*Saccharina japonica*) and used as soup base. He attributed the umami taste sensation to the notably high amount of monosodium glutamate (MSG) present in its free chemical form in *kombu* and released to the broth during its preparation.

After harvest, *S. japonica* is sun dried to prevent rapid spoilage by microorganisms then aged in cellars, usually two years and up to ten years, to fade the strong marine taste in favor of mild, rich and savory flavors [9]. A white precipitate consisting of salts, mannitol and free glutamate is observed on the surface of the dried and matured *kombu* blades, providing a combination of salty, sweet and umami flavors [2]. Similar observations were reported from historical records from Iceland

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Table 1
Sensory attributes and their definitions, associated to the *P. palmata* samples.

Sensory attribute	Label	Scale anchors	Definition
<i>Odor</i>			
Seaweed	O-Seaweed	None much	Odor of seaweed or sea shore
Sweet	O-Sweet	None much	Sweet odor that reminds of sweet soy sauce
Hay	O-Hay	None much	Odor of dry hay
Fish skin	O-Fish skin	None much	Odor of dried fish skin or dried fish heads
<i>Flavor</i>			
Salty	F-Salty	None much	Salty taste
Seaweed	F-Seaweed	None much	Flavor of seaweed or sea shore
Flavor richness	F-Richness	None much	Flavor richness, stock, umami
Processing	F-Processing	None much	Processed seaweed, heavy and complicated flavor, green tea, honey
Dried fish	F-Dried fish	None much	Skin of dried fish
Bitter	F-Bitter	None much	Bitter aftertaste
<i>Texture</i>			
Crunchy	T-Crunchy	None much	Crunchiness at the beginning of chewing
Tough	T-Tough	Tender tough	When chewing. Tough: takes long time to disintegrate

depicting the collection of *dulse* from the shore by gatherers since the 8th century [10]. The seaweed was handpicked during the summer, rinsed and spread over the fields for sun drying. A white precipitate (*hneita*) tasting both salty and sweet, forming on the surface of the fronds during drying, was indicative of the quality of the seaweed. Storing the dried fronds in closed barrels for several months was reported to increase the precipitate formation and the flavor value of the product [10]. Though, no scientific-based descriptions are today explaining the chemical changes occurring during storage of edible seaweeds.

Due to variable weather conditions during the process, sun dried seaweeds typically contain higher moisture than material dried under controlled conditions in air-ovens [11]. While the product must remain safe for the consumer, a higher moisture content (MC) usually increases the rate of enzymatic and non-enzymatic reactions and can result in the formation of flavor compounds e.g. free amino acids (FAAs), mono- and oligosaccharides and volatile compounds, from the hydrolysis of proteins and carbohydrates, lipid oxidation and from subsequent secondary reactions [12]. Changes of this kind are typically observed during the maturation (also referred to as “curing” or “ripening”) of many food products such as ham, cheese and soy sauce [12]. The food products obtained from these processes are highly valued by consumers worldwide for their rich and complex taste and aroma. Despite some efforts to study the sensory profile of edible seaweed species and identify changes in the composition of flavor-active compounds from fresh storage [13], drying [14,15] and cooking treatments [16], potential methods to increase the sensory value of seaweeds do not appear to be addressed in the scientific literature.

The objective of this study was to analyze the changes in quality of *P. palmata* during storage in a dried (D) and so-called semi-dried (SD) state with emphasis on the sensory properties of the product. The variations in flavor, odor and texture between samples of different MC and storage duration were investigated by sensory evaluation. Flavor-active compounds i.e. FAAs and volatile compounds were analyzed to determine their influence on the flavor and odor characteristics of the samples. The macronutrient content (soluble proteins and carbohydrates, lipid and mineral fractions), physico-chemical properties (water activity, water and oil binding capacities, swelling capacity) and microbial load were also determined to describe the overall changes in key parameters reflecting the quality of this edible seaweed species of commercial importance. The general aim of this study was to optimize the processing conditions of *P. palmata* in order to achieve high-quality products attractive to the consumer and to provide a basis to better understand the reactions occurring in the product during storage.

2. Material and methods

2.1. Seaweeds and processing

Wild biomass of *P. palmata*, free from epiphytes, was harvested at Roscoff in France in November 2017 (Biocean, France) and air-dried at 32 °C in a shelf-dryer for 24 h. At reception to the laboratory, the MC of the material was measured, and the biomass divided into 2 batches: a semi-dry (SD) and a dry (D) control group, each comprising 3 sample replicates of 900 g and 650 g respectively. The SD-samples were partially rehydrated by spraying the required amount of water (unfiltered tap water) on the seaweeds to achieve a MC of 20%, as preliminary tests showed microbial stability of *P. palmata* at this level of moisture (unpublished data). The D-samples did not receive any treatment at reception to the laboratory. All samples were sealed in polyethylene bags (not vacuumed) then stored in the dark at a constant temperature of 12 °C. Samples of the SD-group were taken after 12, 61 and 126 days of storage (labelled SD-12, SD-61 and SD-126 respectively) and were freeze-dried, vacuum-packed and stored at −80 °C until analysis. D-samples were taken at reception to the laboratory (D-0) and after 126 days of storage (D-126) under the conditions described above. The chemical and physico-chemical analyses were conducted on freeze-dried samples, to exclude the potential bias of comparing samples of different MC. Only the MC, water activity (a_w) and microbial analyses were performed on the samples in their original form.

2.2. Sensory analysis

A generic descriptive analysis (GDA) [17] was used to characterize and compare the sensory profiles of SD- (SD-12, SD-61, SD-126) and D-126 samples of *P. palmata*. The sensory panel consisted of 9 judges selected and trained according to the guidelines in ISO:8586 [18]. All assessors had some experience with sensory evaluation of seaweeds. The panelists were all members of the Matis ohf staff and gave their consent to participate in the sensory evaluation according to the guidelines in Lawless and Heymann [17]. All samples, i.e. including the dry control group, were rehydrated to 20% MC prior to the evaluation to avoid the potential bias of evaluating samples of different MC [19]. During a first training phase, the assessors developed a vocabulary describing the samples' odor, flavor and texture characteristics and agreed upon a total of 12 attributes listed in Table 1. The panel members were then trained in the evaluation of samples of *P. palmata*, using a 15-cm unstructured scale for each attribute, ranging from lowest to highest intensity. The GDA results were transformed to numbers from 0 to 100 (lowest to highest intensity) for the data analysis. Both the training and sensory evaluation phases were conducted in a sensory test facility equipped with individual booths. Red lights were used during

the evaluation to mask any possible differences in the appearance of the samples. Four samples, coded with three-digit numbers, were evaluated in each of the three replicate sessions. The sensory evaluation program FIZZ (2.50B, Biosystèmes, Couternon, France) was used to collect sensory data. The program Panelcheck (V1.4.0, Nofima, Tromsø, Norway) was used to evaluate performance of the sensory panel and individual panelists. The sensory data was processed according to the General Data Protection Regulation (GDPR).

2.3. Moisture, a_w and chemical characterization

2.3.1. Moisture and a_w

The MC of both D- and SD-samples was determined gravimetrically by drying ca. 5 g of sample at 105 °C until constant weight (typically 24 h). Three replicate measurements were made on each sample. The subsequent results from chemical analyses were expressed as part of the dry weight (DW) of the samples. The a_w was measured with a LabMaster-aw (Novasina AG, Lachen, Switzerland).

2.3.2. Ash

Ash content was determined in triplicate after combustion of the dried samples at 590 °C for 12 h in a laboratory muffle furnace (Type 62700, Barnstead Thermolyne, Ramsey, MN, USA). The ashes were quantified as the residue from combustion.

2.3.3. Lipids

The lipid content of the samples was determined according to the method of Bligh and Dyer [20] with modifications. Ground samples were rehydrated at a 1/4 ratio (w/v) with ultrapure water. Lipids were extracted in triplicate with a mixture of dichloromethane and methanol (2/1, v/v). The extract was filtered on fritted glass then KCl (0.88%) was added to the filtrate to improve phase separation. The lipid content was determined gravimetrically.

2.3.4. Water-soluble carbohydrates and proteins

Crude extracts were obtained from ground samples in liquid nitrogen homogenized with sodium phosphate buffer (20 mM, pH = 7.1) at a 1/20 ratio (w/v) under stirring for 20 min at 4 °C. After centrifugation at 25000 g and 4 °C for 20 min, the resulting supernatant contained the water-soluble compounds. Three replicate extracts were obtained from each sample. The content of water-soluble carbohydrates were analyzed using the modified colorimetric phenol-sulfuric acid method [21]. Phenol at 5% (200 µL) was added to 200 µL of extract or glucose solution followed by 1 mL of sulfuric acid (96%). The solutions were allowed to stand for 10 min at room temperature before vortexing (10 s at 2000 g), then 15 min at room temperature and 30 min at 35 °C (in a water bath) before the absorbance was measured at 490 nm. Glucose was used as a standard. The protein content of the extracts was quantified using the bicinchoninic acid (BCA) protein reagent assay (Thermo Fisher Scientific, Waltham, MA, USA) according to the manufacturer instructions. The R-phycoerythrin (R-PE) content was determined spectrophotometrically using the Beer and Eshel [22] Eq. (1) and the measured absorbance (A) from the extracts at 455, 565 and 592 nm:

$$[R - PE] = [(A_{565} - A_{592}) - (A_{455} - A_{592}) \times 0.20] \times 0.12 \quad (1)$$

2.3.5. Total nitrogen

The nitrogen content was quantified by the Kjeldahl method [23] and an estimate of the total protein content was calculated by multiplying the nitrogen content by a factor of 5 as previously reported suitable to predict the protein content of seaweeds [24].

2.3.6. Free amino acids

The FAAAs of the samples were extracted in triplicate using the method of Osnes and Mohr [25] and determined by high-performance

liquid chromatography (HPLC) as described by Stévant et al. [15]. The results were expressed in mg g⁻¹ DW of the seaweed samples.

2.4. Physico-chemical properties

Water- and oil binding capacity (WBC, OBC), swelling capacity (SC) were measured using the modified methods of Rupérez and Saura-Calixto [26] as described in Stévant et al. [15]. Three replicate measurements were made.

2.5. Microbial load

The microbial load of both D- and SD-samples at the end of the storage period (D-126 and SD-126) were analyzed. Approximately 5 g of each sample were diluted in a ratio 1:10 using peptone water (pH 7.0 ± 0.2) and homogenized in a stomacher (Seward Ltd., Worthing, UK). Five serial dilutions were then plated (1 mL) onto different types of count plates, namely aerobic, coliform, and yeast and mold count plates (3M Petrifilm, Maplewood, MN, USA). The incubation time was 72 h at 30 °C for aerobes, 24 h at 37 °C for coliforms and 48 h at 25 °C for yeasts and molds as validated by standard methods [27]. The total viable count (TVC) was enumerated following the manufacturer guidelines for each type of plate. The microbial load of the samples was expressed in colony forming unit (CFU) per g sample. Microbial analyses of the samples were conducted in triplicate.

2.6. Analysis of volatile compounds by headspace solid phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS)

The extraction of volatile compounds of D-126 and SD-samples of *P. palmata* was carried out using a SPME fiber (65 µm polydimethylsiloxane–divinylbenzene, 23 Ga needles, StableFlex™) supplied by Supelco (Bellefonte, PA, USA). Prior to extraction, the fiber was conditioned (270 °C for 1 h) and placed into the SPME adapter for a CTC autosampler (CTC Analytics, Zwingen, Switzerland) fitted with a vial heater. Two of three sample replicates were analyzed and accurately weighed (1 g) into eight 20 mL headspace vials and pre-incubated in vial heater for 15 min at 50 °C. The samples were extracted for 30 min before injecting the fiber and desorbing in the GC injection port for 5 min at 230 °C under splitless conditions as described by López-Pérez et al. [28]. The volatile compounds were separated on a ZB-5MS column, 30 m long, 0.25 mm internal diameter, 0.25 µm film thickness (Phenomenex, Torrance, CA, USA). Measurements were performed on a Shimadzu Q2010 GC–MS. Helium was used as a carrier gas and the temperature program was as follows; 35 °C for 3 min, 35 °C to 70 °C at 3 °C min⁻¹, 70 °C to 200 °C at 10 °C min⁻¹, 200 °C to 260 °C at 20 °C min⁻¹ and held for 3 min. Injection temperature was 230 °C and ion source was kept at 250 °C. Interface temperature was 265 °C. The mass detector was set to scan from 35 to 400 m/z. Tentative and qualitative identification of volatile compounds was performed by comparing mass spectra of peaks to the NIST's library (Gaithersburg, MD, USA) based on the calculated degree of similarity. All samples were evaluated using the same integration parameters, i.e. using peak height as set minimum. Only volatile compounds detected in both sample replicates were selected. Relative standard error (RSD) between two replicate measurements was calculated for each detected compound and 42% (i.e. $\sqrt{2} \times 30\%$, RSD being 30% at limit of detection) was defined as the threshold value above which the detected compounds were discarded for further data analysis. It should be noted that the HS-SPME GC–MS method used is not validated by analysis of known standards to fully confirm the identity and quantity of the detected volatiles.

2.7. Data analysis

Raw data were pre-processed for descriptive statistics and the

results expressed as mean \pm standard error ($n = 3$, unless stated otherwise) using R (version 3.4.4, R Development Core Team [29]). A mixed model ANOVA (R function lmer [30]) with individual panelists and replicate sessions as random factors was used to detect differences in sensory profile (mean scores for each attribute) among sample groups. The estimation of significance was achieved by sequential elimination of non-significant random effects, following a procedure proposed by Kuznetsova et al. [31]. Tukey's honest significant differences (HSD) were computed for the pairwise comparison of sample groups. A principal component analysis (PCA, R function prcomp) based on covariance matrix (no scaling) was applied to visualize differences in sensory profiles among samples. A one-way analysis of variance (ANOVA, R function aov) was used to detect significant differences ($p < 0.05$) among sample groups regarding their MC, a_w , nutrient content, and physico-chemical properties. A Tukey's HSD test was used for post-hoc comparisons of significant ANOVA results. The Benjamini-Hochberg procedure was applied to control the false discovery rate under multiple testing. The FAA content and profiles of the samples were analyzed using the ANOVA and PCA (no scaling) respectively. A PCA based on correlation matrix (i.e. scaling applied) was used to visualize differences in volatile compounds. The relationship between chemical characteristics (volatile compounds and FAAs) and sensory attributes (flavors and odors) was analyzed by partial least-squares regression (PLSR) using the Unscrambler 10.5 software package (CAMO software AS, Oslo, Norway). The PLSR was performed on averaged data over sample replicates ($n = 3$ for sensory and FAA data, $n = 2$ for volatile compounds). The chemical data i.e. volatiles and FAAs, was standardized to equal variance (1/StD) and full cross-validation (leaves-one-out at a time) was used as a validation method.

3. Results and discussion

3.1. Sensory analysis

The effects of two different levels of moisture during 126 days of storage on the quality of *P. palmata* as food was investigated in this study with emphasis on the sensory characteristics of the product. Both dry (D-126) and semi-dry (SD-12, SD-61, SD-126) samples of *P. palmata* were evaluated by nine trained panel members in a GDA based on 12 sensory attributes (Table 1).

Significant differences were detected between samples regarding most of the sensory attributes, except for bitterness, associated with low scores, and saltiness, perceived as intense in all samples (Table 2). The PCA of the mean scores (averaged over panelists) for each attribute explains 81.6% of the variance in the dataset (72.0 and 9.6% by PC-1 and -2 respectively, Fig. 1). Strong marine flavor and odor ("seaweed" and fishy) were identified from the evaluation of the control stored

during the entire period (D-126) and SD-samples stored for 12 days (SD-12) as well as a tough and crunchy texture, supporting previous reports from the sensory evaluation of dried *P. palmata* samples [14,28]. In stark contrast, SD-samples stored for a longer period i.e. 61 and 126 days (SD-61 and SD-126), were characterized by "hay" and sweet odors, a complex flavor ("processing" flavor attribute) and a softer texture than SD-12 and D-126 (Fig. 1, Table 2). The marine flavors and odors characteristic of the control (D-126) and SD-12 samples faded in the SD-61 and SD-126 samples, as observed during the maturation of *kombu* [9] and semi-dry storage of *Saccharina latissima* [19]. However, no salt precipitate was formed on the surface of these samples as reported for the *kombu* [9] and traditional storage of *P. palmata* in Iceland [10]. The attribute "flavor richness" which includes the perception of umami (Table 1) was somehow more pronounced in SD-samples although this trend was not significant (Table 2). Sweet, umami and bitter tastes are particularly related to food acceptance, or rejection in the case of bitterness [32,33]. Some of the most common unpleasant feelings from tasting seaweeds are related to prominent fishy and marine flavors as well as a tough texture [1,6]. The relative increase in sweetness, green notes, complex flavor and tender texture, along with the decrease in marine flavors and odors as well as low bitterness of the SD-samples of *P. palmata* stored over an extended period, suggest a higher potential of these samples compared to the dried control, to be used as flavor-enhancing ingredients in culinary applications.

3.2. Moisture, a_w and chemical characterization

The MC of the control samples during storage (D-0 and D-126) was ca. 6% while the moisture level of SD-samples was close to the targeted value of 20% (Table 3). The a_w of the SD-samples was in a range between 0.60 and 0.65 (Table 3). Although these levels are considerably higher than those of D-samples (close to 0.30), they are below the typical threshold critical for the growth of most microorganisms (i.e. 0.80) [34]. Higher a_w in SD- compared to D-samples may allow for enzymatic and non-enzymatic (e.g. hydrolysis, Maillard) reactions to occur at higher rates.

The ash, and thereby the mineral content, of *P. palmata* was high (> 40% DW), as previously reported in the literature [35,36] (Table 3), which correlates with the intense salty taste of the samples. This species, like most seaweeds, is known to be a rich source of macro-minerals (i.e. Na, K, Ca and Mg) and is characterized by a particularly low Na/K ratio (between 0.1 and 0.4) [19,37,38] compared to other species. This feature is interesting from a nutritional perspective given that diets rich in Na (i.e. with a high Na/K ratio) are associated with health risks such as high blood pressure and cardiovascular diseases. Therefore, *P. palmata* has the potential to be used as a salt replacing ingredient to improve the mineral profile of food products.

Table 2

Mean sensory scores (on a scale from 1 to 100) from panelists ($n = 9$) from the generic descriptive analysis (GDA) of *P. palmata* samples stored in dry (D) and semi-dry (SD) state over a period of 126 days, based on 12 sensory attributes including odor (O), flavor (F) and texture (T) characteristics.

Sensory attribute	D-126	SD-12	SD-61	SD-126	<i>p</i> -value
O-Seaweed	40.6 \pm 3.9 ^b	38.1 \pm 4.0 ^{ab}	31.9 \pm 1.3 ^{ab}	31.1 \pm 1.6 ^a	0.029
O-Sweet	30.2 \pm 2.3 ^a	29.7 \pm 1.4 ^a	38.9 \pm 2.6 ^b	40.2 \pm 0.6 ^b	0.002
O-Hay	31.0 \pm 0.8 ^a	35.9 \pm 3.8 ^a	47.1 \pm 3.3 ^b	47.8 \pm 3.2 ^b	0.001
O-Fish skin	29.1 \pm 5.4 ^b	22.8 \pm 3.6 ^b	11.4 \pm 0.5 ^a	10.5 \pm 1.1 ^a	< 0.001
F-Salty	60.7 \pm 4.2 ^a	59.7 \pm 1.9 ^a	58.3 \pm 1.4 ^a	63.1 \pm 3.5 ^a	0.460
F-Seaweed	42.4 \pm 3.1 ^b	39.0 \pm 1.6 ^{ab}	33.9 \pm 1.2 ^a	34.9 \pm 2.4 ^a	0.024
F-Flavor richness	39.5 \pm 2.4 ^a	43.8 \pm 0.5 ^a	47.0 \pm 2.7 ^a	43.8 \pm 2.0 ^a	0.180
F-Processing	32.4 \pm 2.3 ^a	35.7 \pm 1.0 ^{ab}	43.0 \pm 1.1 ^b	41.4 \pm 2.8 ^{ab}	0.022
F-Dried fish	22.4 \pm 0.8 ^b	18.4 \pm 1.2 ^{ab}	12.3 \pm 0.7 ^a	14.6 \pm 1.1 ^a	0.002
F-Bitter	8.5 \pm 0.8 ^a	9.0 \pm 1.9 ^a	7.6 \pm 1.4 ^a	10.9 \pm 1.1 ^a	0.262
T-Crunchy	57.3 \pm 1.1 ^b	51.6 \pm 3.2 ^{ab}	44.5 \pm 1.1 ^a	44.4 \pm 1.8 ^a	0.001
T-Tough	60.9 \pm 3.5 ^c	59.0 \pm 4.4 ^c	47.8 \pm 2.6 ^b	39.2 \pm 1.2 ^a	< 0.001

Values are given as mean \pm standard error ($n = 3$). Significant ANOVA results ($p < 0.05$) following correction with the Benjamini-Hochberg procedure are in bold. Different superscript letters in the same row indicate significant differences among samples (Tukey HSD, $p < 0.05$).

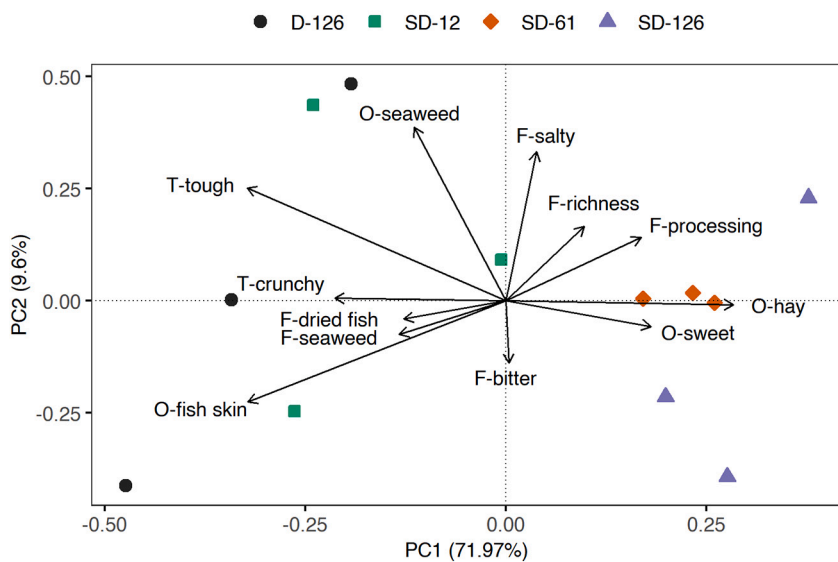


Fig. 1. Biplot (1st and 2nd principal component axes) obtained from the principal component analysis (PCA) of the sensory scores of *P. palmata* samples after dry (D) and semi-dry (SD) storage over a period of 126 days. Average scores over panelists ($n = 9$) were used for the PCA. Vectors indicate loadings representing the variation in intensity for individual sensory attributes including odor (O), flavor (F) and texture (T) characteristics, among all samples.

The amount of soluble carbohydrates tended to be higher in SD-compared to D-samples, with the highest amounts obtained from the SD group after 61 days of storage (Table 3). However, this trend is weakly supported by the statistical analysis of the results. Water-soluble extracts of *P. palmata* typically contain low molecular weight storage carbohydrates, mainly floridoside (α -D-galactopyranosyl-(1-2)-glycerol) and floridean starch (amylopectin-like glucan), which are minimal during the winter season [37] explaining the low levels measured in these samples (from 2.1 to 3.5% DW, Table 3) harvested in November. The total carbohydrate content of wild *P. palmata* is reported to be between 42 and 64% DW, mainly consisting of xylans (composed of β -(1 \rightarrow 4)- and β -(1 \rightarrow 3)-linked D-xylose units) as the main cell-wall constituent [35,37]. The hydrolysis of this compound as a result of a higher rate of enzymatic or non-enzymatic reactions in SD-samples can explain the relatively higher levels of soluble sugars in these samples compared to the D-samples. It also correlates with increased sweet odor and a more tender texture (due to a loss of cellular rigidity). The degradation products of such reactions can however be involved as reducing agents in Maillard reactions which may occur in food systems even at ambient temperatures during long storage periods [12].

Given a N-to-protein conversion factor of 5, the total protein content of these samples was estimated between 15.3 and 16.3% DW (Table 3), which is comparable to the values reported in the literature for this species [36,37,39]. Only a small fraction of the total protein was found

in the water-soluble extracts (13% in the initial dried samples, D-0) mainly consisting of the red protein-pigment R-PE. While the soluble fraction of the proteins, including R-PE, did not differ significantly during storage of the D-samples, it decreased in the SD-samples. The reactions occurring within the product at higher MC during storage may induce changes in the protein conformation of the pigment resulting in denaturation, as suggested by Munier et al. [40] who measured a reduced absorption over time of R-PE extracts even stored at low temperature (4 °C) in darkness. Other factors such as aggregation of proteins and their degradation through enzymatic reactions are known to affect their solubility. Besides their bioactivity as antioxidant compound, R-PE has applications in the food and cosmetic industries as natural colorant [41].

As major flavor-active compounds in foods [12,42], the FAA composition of the *P. palmata* samples was analyzed. The total FAA content decreased by approximately 50% in both D- and SD-samples compared to the initial D-0 samples (Table 4). This trend is in contradiction with the results obtained from a similar experiment conducted on *S. latissima* in which increasing FAA contents were observed during storage of the samples regardless of their MC [19]. The accumulation of FAAs and small peptides is typically observed during the ripening process of fruit, ageing of cheese and curing of meat as a result of proteolysis by endogenous enzymes and/or the activity of microorganisms [12,42]. Secondary reactions usually involve the conversion of FAAs into flavor-active derivatives from different reactions such as Strecker and Maillard

Table 3

Moisture content (MC, % of dry weight (DW)), water activity (a_w , dimensionless), chemical content (in g (100 g)⁻¹ DW) and physico-chemical properties i.e. water binding capacity (WBC in g water g⁻¹ (dry sample)), oil binding capacity (OBC in g oil g⁻¹ (dry sample)), swelling capacity (SC in mL g⁻¹ (dry sample)) of dry (D) and semi-dry (SD) samples of *P. palmata* during storage over a period of 126 days.

	D-0	D-126	SD-12	SD-61	SD-126	p-value
MC	5.5 ± 0.2 ^a	6.2 ± 0.3 ^a	18.5 ± 0.3 ^b	21.5 ± 0.9 ^c	18.9 ± 0.9 ^{bc}	< 0.001
a_w	0.28 ± 0.01 ^a	0.29 ± 0.01 ^a	0.62 ± 0.00 ^b	0.65 ± 0.01 ^b	0.60 ± 0.02 ^b	< 0.001
Ashes	43.0 ± 0.9 ^{ab}	40.2 ± 1.0 ^a	45.0 ± 0.6 ^b	42.4 ± 1.1 ^{ab}	43.0 ± 1.4 ^{ab}	0.110
Lipids	2.0 ± 0.1 ^a	2.1 ± 0.2 ^a	1.8 ± 0.4 ^a	1.8 ± 0.3 ^a	1.8 ± 0.1 ^a	0.853
Soluble carbohydrates	2.7 ± 0.4 ^{ab}	2.1 ± 0.3 ^a	3.1 ± 0.1 ^{ab}	3.5 ± 0.1 ^b	2.8 ± 0.3 ^{ab}	0.052
Soluble proteins	2.0 ± 0.2 ^b	1.9 ± 0.1 ^b	1.8 ± 0.0 ^b	1.2 ± 0.1 ^a	1.1 ± 0.0 ^a	< 0.001
R-Phycocerythrin (R-PE)	1.7 ± 0.2 ^b	1.4 ± 0.0 ^b	1.6 ± 0.0 ^b	0.7 ± 0.1 ^a	0.6 ± 0.0 ^a	< 0.001
Total proteins (N * 5)	15.3 ± 0.7 ^a	15.1 ± 0.0 ^a	15.4 ± 0.3 ^a	15.8 ± 0.8 ^a	16.3 ± 0.8 ^a	0.853
WBC	4.7 ± 0.2 ^b	4.3 ± 0.2 ^{ab}	3.7 ± 0.1 ^a	3.9 ± 0.0 ^a	3.8 ± 0.2 ^a	0.009
OBC	3.4 ± 0.3 ^b	2.4 ± 0.0 ^a	2.9 ± 0.2 ^{ab}	2.8 ± 0.1 ^{ab}	2.3 ± 0.1 ^a	0.016
SC	3.3 ± 0.1 ^{ab}	3.7 ± 0.1 ^b	2.9 ± 0.3 ^{ab}	2.5 ± 0.2 ^a	3.5 ± 0.3 ^{ab}	0.027

Values are given as mean ± standard error ($n = 3$). Significant ANOVA results ($p < 0.05$) following correction with the Benjamini-Hochberg procedure are in bold. Different superscript letters in the same row indicate significant differences among samples (Tukey HSD, $p < 0.05$).

Table 4
Free amino acid (FAA) content (in mg g⁻¹ DW) of dry (D) and semi-dry (SD) samples of *P. palmata* during storage over a period of 126 days.

FAA	D-0	D-126	SD-12	SD-61	SD-126	p-value
Glu	3.638 ± 0.072 ^c	1.400 ± 0.137 ^a	2.131 ± 0.057 ^b	2.132 ± 0.169 ^b	1.973 ± 0.224 ^{ab}	< 0.001
Asp	3.116 ± 0.159 ^b	0.609 ± 0.004 ^a	0.807 ± 0.091 ^a	0.914 ± 0.106 ^a	0.760 ± 0.097 ^a	< 0.001
Ala	1.586 ± 0.037 ^a	1.816 ± 0.010 ^a	1.901 ± 0.089 ^a	1.930 ± 0.321 ^a	2.039 ± 0.193 ^a	0.470
Val	0.354 ± 0.024 ^b	0.136 ± 0.006 ^a	0.155 ± 0.005 ^a	0.134 ± 0.020 ^a	0.141 ± 0.014 ^a	< 0.001
Leu	0.352 ± 0.025 ^b	0.148 ± 0.007 ^a	0.168 ± 0.010 ^a	0.144 ± 0.012 ^a	0.138 ± 0.021 ^a	< 0.001
Gly + Arg	0.310 ± 0.020 ^a	0.235 ± 0.012 ^a	0.246 ± 0.004 ^a	0.273 ± 0.018 ^a	0.239 ± 0.029 ^a	0.096
Asn	0.237 ± 0.022 ^b	0.136 ± 0.008 ^a	0.132 ± 0.09 ^a	0.124 ± 0.015 ^a	0.123 ± 0.023 ^a	0.004
Phe	0.227 ± 0.018 ^b	0.106 ± 0.004 ^a	0.113 ± 0.007 ^a	0.080 ± 0.014 ^a	0.077 ± 0.008 ^a	< 0.001
Ile	0.212 ± 0.013 ^b	0.082 ± 0.002 ^a	0.094 ± 0.002 ^a	0.081 ± 0.009 ^a	0.079 ± 0.011 ^a	< 0.001
Gln	0.201 ± 0.022 ^b	0.095 ± 0.008 ^a	0.143 ± 0.005 ^{ab}	0.123 ± 0.013 ^a	0.093 ± 0.024 ^a	0.007
Lys	0.158 ± 0.011 ^b	0.089 ± 0.001 ^a	0.105 ± 0.005 ^a	0.079 ± 0.012 ^a	0.073 ± 0.011 ^a	0.001
Met	0.124 ± 0.016 ^b	0.028 ± 0.002 ^a	0.024 ± 0.001 ^a	0.001 ± 0.000 ^a	0.001 ± 0.001 ^a	< 0.001
Tyr	0.106 ± 0.007 ^b	0.064 ± 0.004 ^a	0.066 ± 0.002 ^a	0.057 ± 0.007 ^a	0.064 ± 0.005 ^a	0.001
Thr	0.092 ± 0.004 ^a	0.111 ± 0.007 ^a	0.130 ± 0.001 ^a	0.124 ± 0.016 ^a	0.130 ± 0.012 ^a	0.100
Ser	0.046 ± 0.003 ^a	0.032 ± 0.005 ^a	0.046 ± 0.018 ^a	0.034 ± 0.009 ^a	0.019 ± 0.005 ^a	0.340
His	0.012 ± 0.004 ^b	0.010 ± 0.001 ^{ab}	0.008 ± 0.002 ^{ab}	0.002 ± 0.001 ^{ab}	0.002 ± 0.000 ^a	< 0.030
Σ FAAs	10.772 ± 0.000 ^b	5.097 ± 0.097 ^a	6.267 ± 0.223 ^a	6.234 ± 0.683 ^a	5.951 ± 0.600 ^a	< 0.001

Values are given as mean ± standard error (n = 3). Significant ANOVA results (p < 0.05) following correction with the Benjamini-Hochberg procedure are in bold. Different superscript letters in the same row indicate significant differences among samples (Tukey HSD, p < 0.05).

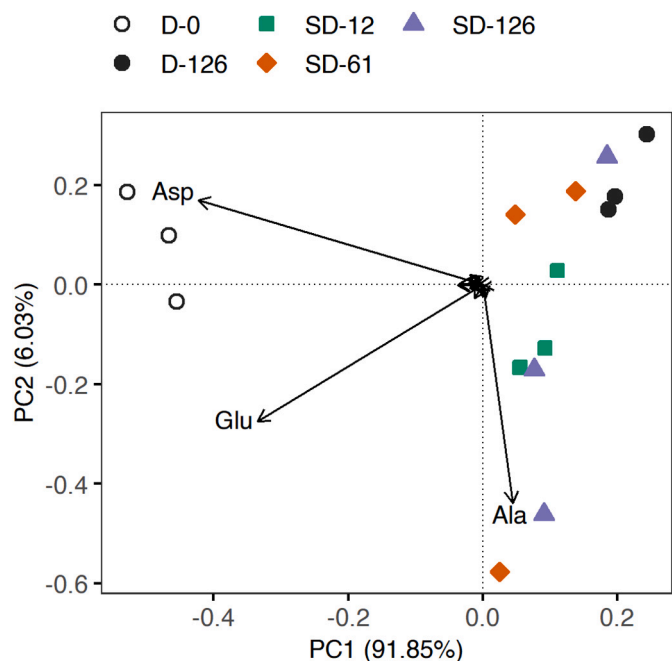


Fig. 2. Biplot (1st and 2nd principal component axes) obtained from the principal component analysis (PCA) of the free amino acid (FAA) profile of dry (D) and semi-dry (SD) samples of *P. palmata* during storage over a period of 126 days. For each sample, average values from repeated extractions (n = 3) and high-performance liquid chromatography (HPLC) runs (n = 2) were used. Vectors indicate loadings representing the variation in the content of individual FAAs among the samples.

reactions [12] which, in the present study, may occur at higher rates than proteolysis. Glutamate, aspartate and alanine were the main FAAs representing 77% of the total FAA content of the D-0 samples (Table 4). The variation in FAA composition among samples was analyzed by PCA. Most of the variance (almost 92%) in FAAs among samples is explained by the first component (PC1) (Fig. 2). A considerable reduction in free glutamate and aspartate was observed after storage of D- and SD-samples compared to the initial D-0 samples. In contrast the levels of free alanine remained relatively stable. Both free glutamate and to a lesser extent aspartate in their salt form are elicitors of umami flavor, enhancing the palatability of foods [42]. The lowest glutamate levels were measured in D-126. An average difference of 0.7 mg Glu

g⁻¹ DW was measured between SD-samples on the one hand and D-126 samples on the other, which may affect the product flavor given the low flavor threshold of this compound [12]. In previous studies, *P. palmata* was distinguished and considered a promising ingredient providing umami flavor to a wide range of dishes such as ice cream, bread and pasta [2,3]. The levels measured in D-0 samples in this study i.e. 3.6 mg g⁻¹ DW are in the range of those reported by Mouritsen et al. [2] from dried *P. palmata* of different origin (1–4 mg Glu g⁻¹ DW) but lower than those measured in kombu (up to 16 mg g⁻¹ DW) [42]. The perception of umami not only depends on the glutamate content but also on other molecules e.g. guanylate and inosinate [42], pyroglutamate peptides, succinyl amino-acids [12] as well as other flavors influencing the overall taste experience [43]. The present results suggest that such compounds are involved in the differences in flavor and odor perceived in SD- compared to D-samples.

3.3. Physico-chemical parameters

WBC was lower in the SD- compared to the D-samples, but this parameter was not significantly affected by the storage time (Table 3). A significant decrease in OBC was observed in both D- and SD-samples after 126 days of storage compared to D-0. Although some variations in SC were observed across samples, no significant differences were detected between stored samples (D-126 and SD-samples) and D-0. WBC and SC depend largely on the content and structure of insoluble fibers present in the raw material [44] while OBC is mostly related to the hydrophilic nature of the polysaccharides as well as the levels of non-polar residues in the protein fraction [26,45]. Xylans represent the main source of fibers in *P. palmata* and are present in both soluble and insoluble forms [44]. The changes in WBC and OBC in both D- and SD-samples of *P. palmata* reflects structural modifications involving this major cell-wall constituent during storage. It should be noted that the particles sizes can have affected the subsequent results. Even all samples were ground using the same method, relatively smaller particles were obtained from grinding the samples SD-61 and SD-126 prior to analysis, compared to SD-12, D-0 and D-126. However, this heterogeneity may also be a direct consequence of the structural alterations during storage, correlating with changes in texture observed during the sensory evaluation of the samples.

3.4. Microbial load

The microbial load of both D- and SD-samples at the end of the storage period (126 days) was compared. The levels of aerobes were

low and comparable in both samples (10.4×10^3 and 5.9×10^3 CFU g⁻¹ in D-126 and SD-126 respectively). Some molds were detected in D-126 (5.4×10^2 CFU g⁻¹) and not in SD-126 samples. Neither yeasts nor coliforms were detected in any of the samples. These results are in the range of those of a previous study of the microbial load of dried seaweeds using similar methods [46]. Some fungal species (mainly of the genera *Aspergillus*, *Cladosporium* and *Penicillium*) originating from marine environments have been isolated from salted food and may persist even when the water activity is low thus inhibits the growth of most microorganisms [47], as the conditions at the surface of the D-samples. It should be noted that these preliminary results based on standard protocols to evaluate food safety (including seafood) only provide a comparison between the D-126 and SD-126 samples and may not reflect their real microbial load. Adapted growing medium (e.g. marine agar) or other methods (e.g. based on molecular DNA) would be necessary to provide detailed information on the microbiology of seaweeds.

3.5. Analysis of volatile compounds

A semi-quantitative analysis of the volatile compounds of the *P. palmata* samples that were used in the sensory evaluation was performed using a HS-SPME coupled to GC-MS method. A total of 42 compounds were identified across the four samples, including 16 aldehydes, 11 alcohols, 8 hydrocarbons, 5 ketones and 2 carboxylic acids (Table 5). Some of the compounds detected in the present samples, especially most of the aldehydes, have been reported previously from both fresh [14,48] and dried samples of *P. palmata* [14,28] as well as in brown [43,49] and green seaweed species [13]. Differences were observed in the diversity and abundance (reflected by the relative peak area) of volatile compounds between samples. A slightly larger diversity was detected in SD-61 and SD-126 (39 and 38 compounds respectively) compared to SD-12 and D-126 (35 and 34 compounds respectively). Higher levels of volatile compounds were measured in SD-samples compared to D-126, along with a trend showing an increasing abundance of these compounds in SD-samples with increasing storage time. This is mainly attributed to an increase in the total levels of aldehydes, alcohols and ketones in the SD-samples during storage. The relative proportion of hydrocarbons, representing more than 50% of the total abundance in D-126, decreased from 44% in SD-12 to 36% in SD-126 (Table 5). The biplot from the PCA of the results illustrates the differences in volatile profiles between samples (Fig. 3). The first principal component (PC1) explains 68% of the variation across samples and clearly discriminates D-126 and to a lesser degree SD-12 on the right-hand side against SD-61 and SD-126 on the left-hand side of the plot. PC2 explains 18% of the variance and discriminates SD-12 on top and D-126 at the bottom of the plot. The proximity of SD-61 and SD-126 indicates the similarity of the volatile compounds profile of these samples. Most of the compounds are positively correlated with SD-61 and SD-126 reflecting higher levels in these samples compared to the two others and in some cases, their absence in one or both of SD-12 and D-126 (Table 5).

Typical aldehydes from seaweeds found in the present *P. palmata* samples such as hexanal, (*E*)-2-hexenal, octanal, nonanal and (*E,E*)-2,4-heptadienal may arise from the degradation of polyunsaturated fatty acids (PUFA) either from autooxidation or the action of enzymes [48]. The levels of PUFA in *P. palmata* are highly variable depending on the location of harvest and age of the plant and can represent up to 60% of the total lipids [39]. Although higher levels of these volatile compounds were measured in SD-samples compared to D-126 (Table 5) no significant differences were detected across these samples regarding their total lipid content (Table 3). 3-Methylbutanal which is identified as a key compound of *miso* soup flavor, is a characteristic product of leucine catabolism [50] from the action of microorganisms or under Strecker degradation. These reactions in *P. palmata* are very likely promoted by higher MC and longer storage times. In food systems, the level of a

compound does not necessarily reflect its flavor contribution due to variable flavor thresholds. Volatile aldehydes can both contribute to desirable aromas as well as an unpleasant rancid odor during spoilage of lipid-rich foods, due to their low threshold values (high odor strength). (*Z*)-4-Heptenal which arises from the oxidation of *n*-3 unsaturated fatty acids, has a very low odor threshold in water and has been associated with rancid odors in fish products [51]. Since fishy off-flavors were not characteristic of the samples in this study, this compound at the levels measured in SD-61 and SD-126 may contribute with fatty and grassy odors.

Branched alcohols were detected in higher relative amounts in SD-samples compared to D-126 (Fig. 3, Table 5) and can be derived from the peroxidation of lipids, glycosylation of carbohydrates or from amino acid catabolism [49]. Among these, 1-octen-3-ol particularly abundant in SD-61 and SD-126, is associated with pleasant mushroom aroma and results from the oxidative cleavage of linoleic acid. Some aromatic alcohols were also measured at relatively high levels in these two samples, such as 2,6-dimethylcyclohexanol which has been identified previously from green tea and apricots. The increasing levels of volatile alcohols in SD-samples and considerably lower signals (i.e. lower peak area) in D-126 samples suggest that both storage time and MC of the product are important factors governing the synthesis and accumulation of these compounds.

Among the ketones identified in the samples, 3,5-octadien-2-one was found in higher relative amount in SD-samples compared to D-126. This compound is most likely a product of autooxidation of unsaturated fatty acids and has also been reported in fish products [51]. α -Ionone, another volatile compound commonly found in seaweeds [16,28] is derived from the oxidative cleavage of carotenoid pigments [28]. It is associated with sweet, floral and fruity notes and is presumed to be an important flavor contributor in seaweeds [13].

Heptadecane was the most abundant volatile compound detected in all samples as previously observed in dried *P. palmata* [28]. Other saturated hydrocarbons, i.e. tetradecane and pentadecane were also detected at higher relative levels in D-126 compared to SD-samples (Fig. 3, Table 5). These compounds may be involved as precursors in biochemical reactions during storage of the SD-samples. In general, storage conditions [13], preservation (e.g. drying) [14] and cooking treatments [16] have a great impact on the profile and content of volatile compounds with consequences on the sensory profile of the seaweed product.

3.6. Correlation between flavor compounds and sensory analysis

The correlation between the sensory scores for flavor and odor attributes (Y-variables) and measured flavor-active compounds in the samples i.e. volatiles and FAAs (X-variable), was investigated by PLSR. The first two PLSR components explained 83% of the X-variables and 99% of the Y-variables (Fig. 4). The first principal component discriminates rich and processing flavors, sweet and hay odor characteristic of both SD-61 and SD-126 samples together with most of the volatile compounds detected in higher relative amounts in these samples, against fishy and seaweed flavors and odors associated with D-126 and to a lesser extent to SD-12 samples. As expected, flavor richness correlated with higher levels of free glutamate and aspartate measured in SD-samples compared to D-126 as well as with 1-penten-3-ol, and (*E*)-2-hexenal which also have been reported in matured *kombu* [52]. Volatile compounds associated with fatty and green odors such as (*E,E*)-2,4-heptadienal, 3,5-octadien-2-one, hexanal, (*Z*)-4-heptenal also correlated with flavor richness as well as processing flavors (described by “heavy”, “complicated”, “green tea”, “honey”, Table 1) and hay odor. A variety of compounds characterized by sweet and woody (2,6,6-trimethyl-2-cyclohexene-1,4-dione), sweet and floral (α -ionone; benzaldehyde) as well as sweet and/or fruity odors (3-methylbutanal; benzaldehyde; octanal; 2,6-dimethylcyclohexanol; (*E,Z*)-2,6-nonadienal, decanal, nonanal) are correlated with sweet and green (hay)

Table 5
Volatile compounds of *P. palmata* samples after dry (D) and semi-dry (SD) storage over a period of 126 days.

Compound	Retention time (min)	Peak area (10^{-6})				Ref	Odor descriptor ^d	Odor strength ^d
		D-126	SD-12	SD-61	SD-126			
Aldehydes								
3-Methylbutanal	3.40	2.0 ± 0.2	1.7 ± 0.1	2.1 ± 0.3	2.1 ± 0.0	a, b	Fruity, chocolate	High
Hexanal	7.32	3.8 ± 0.3	6.0 ± 0.8	9.0 ± 0.6	8.3 ± 0.3	a, b	Fresh, green, fatty	High
(E)-2-Hexenal	9.56	3.3 ± 0.9	6.6 ± 1.1	8.9 ± 0.0	8.0 ± 0.4	a, b, c	Fresh, leafy, green	High
(Z)-4-Heptenal	11.78	2.3 ± 0.1	4.6 ± 1.2	7.2 ± 0.1	7.5 ± 0.1	b	Fatty, green	Very high
Heptanal	11.90	4.3 ± 0.4	3.3 ± 0.2	3.7 ± 0.1	4.0 ± 0.3	a, b	Fresh, green, fatty	High
Benzaldehyde	14.83	9.8 ± 1.8	9.4 ± 0.2	10.0 ± 1.6	10.1 ± 0.8	b, c	Sweet, bitter, almond	High
Octanal	16.62	5.5 ± 0.5	5.1 ± 0.3	6.6 ± 0.6	8.4 ± 0.8	a, b	Citrus	High
(E,E)-2,4-Heptadienal	16.87	4.6 ± 0.3	10.7 ± 2.6	15.5 ± 2.2	11.5 ± 0.3	b, c	Fatty, green	High
(E)-4-Oxohex-2-enal	17.51	n.d.	3.4 ± 0.0	4.1 ± 0.4	6.8 ± 0.3			
Benzeneacetaldehyde	17.85	2.5 ± 0.1	2.2 ± 0.2	2.6 ± 0.1	3.1 ± 0.1		Honey, floral	High
Nonanal	19.44	16.1 ± 2.4	17.7 ± 1.1	20.9 ± 0.9	21.7 ± 1.1	a, b	Citrus	High
(E,Z)-2,6-Nonadienal	20.46	4.7 ± 0.3	8.1 ± 1.6	11.8 ± 1.5	10.6 ± 0.1		Cucumber, melon	High
Decanal	21.47	6.7 ± 0.2	8.4 ± 0.8	10.6 ± 0.6	13.4 ± 1.6	b, c	Sweet, citrus	High
2,6,6-Trimethyl-cyclohexene-1-carboxaldehyde	21.75	3.4 ± 0.2	4.6 ± 0.9	5.7 ± 0.7	5.6 ± 0.3	c		
Undecanal	23.14	4.5 ± 0.4	3.9 ± 0.5	3.3 ± 0.4	4.4 ± 0.2		Soapy	High
(E,E)-2,4-Decadienal	23.33	n.d.	2.0 ± 0.5	3.5 ± 0.7	3.4 ± 0.3		Fatty, chicken	High
Σ aldehydes		73.6 ± 0.6	97.8 ± 11.8	125.5 ± 5.2	128.8 ± 6.5			
Alcohols								
1-Penten-3-ol	3.87	4.4 ± 0.1	4.8 ± 0.1	5.6 ± 0.7	4.9 ± 0.0	a	Pungent, green	High
1-Octen-3-ol	15.77	5.8 ± 0.4	8.3 ± 1.5	10.9 ± 1.2	11.5 ± 0.1	a	Mushroom, earthy	High
1-(2-Methoxy-1-methylethoxy)-propan-2-ol	16.56	4.8 ± 0.0	7.6 ± 0.3	3.3 ± 0.4	3.9 ± 0.2			
1-(2-Methoxypropoxy)-2-propanol	16.93	7.6 ± 0.1	12.8 ± 1.8	n.d.	5.4 ± 0.9	b		
Benzyl alcohol	17.58	3.8 ± 0.2	2.8 ± 0.1	n.d.	4.0 ± 0.5		Floral, rose	Medium
2,4,4-Trimethylcyclohex-2-en-1-ol	18.12	2.7 ± 0.3	5.3 ± 1.6	7.5 ± 0.2	10.4 ± 1.6			
2,6-Dimethylcyclohexanol	19.57	7.2 ± 0.4	19.9 ± 7.4	28.0 ± 3.6	38.8 ± 1.7			
3-Cyclohexene-1-ethanol	21.29	2.9 ± 0.1	4.9 ± 1.2	8.1 ± 1.0	7.0 ± 0.5			
2-Amino-4-methoxyphenol	21.92	n.d.	n.d.	5.1 ± 0.6	8.2 ± 0.4			
2,3,6-Trimethyl-7-Octen-3-ol	22.62	2.5 ± 0.1	n.d.	4.1 ± 0.1	n.d.			
1-(1-Adamantyl)-1-phenylethanol	23.92	n.d.	n.d.	3.0 ± 0.4	3.2 ± 0.2			
Σ alcohols		41.8 ± 1.0	66.4 ± 13.4	75.5 ± 3.8	97.4 ± 4.6			
Hydrocarbons								
3,5,5-Trimethyl-2-hexene	15.51	27.5 ± 1.4	34.1 ± 3.0	35.8 ± 8.7	37.9 ± 0.9			
7-Methyl-3-octyne	17.45	n.d.	n.d.	2.3 ± 0.2	2.6 ± 0.1			
3-Dodecylcyclohexane	22.52	7.2 ± 0.7	15.4 ± 4.6	21.8 ± 0.7	22.8 ± 1.0			
1-Butenylidene-cyclohexane	22.76	2.6 ± 0.2	3.0 ± 0.2	3.6 ± 0.3	3.4 ± 0.3			
3-[(E)-3-Methylbut-1-enyl] cyclohexene	24.31	1.7 ± 0.1	n.d.	2.8 ± 0.0	n.d.			
Tetradecane	24.47	3.7 ± 0.3	3.1 ± 0.5	2.2 ± 0.1	n.d.		Mild, waxy	Low
Pentadecane	25.81	19.9 ± 2.0	7.9 ± 0.2	6.8 ± 0.2	7.9 ± 0.6	b, c	Waxy	Low
Heptadecane	28.22	89.4 ± 0.9	103.5 ± 4.6	88.9 ± 11.3	96.7 ± 4.2	b, c	Waxy	Low
Σ hydrocarbons		152.0 ± 1.5	166.9 ± 11.8	164.3 ± 19.2	171.4 ± 3.0			
Ketones								
3,5,5-Trimethylcyclohex-3-en-1-one	18.79	3.2 ± 0.2	n.d.	n.d.	n.d.			
3,5-Octadien-2-one	19.17	6.4 ± 0.2	14.0 ± 5.0	22.3 ± 1.7	21.2 ± 0.4	c	Fruity, mushroom	High
3,4,4-Trimethyl-2-cyclopenten-1-one	19.40	n.d.	n.d.	3.4 ± 0.1	5.6 ± 0.2			
2,6,6-Trimethyl-2-cyclohexene-1,4-dione	20.31	n.d.	2.9 ± 0.8	4.6 ± 0.0	7.4 ± 0.4		Sweet, woody, tea	Medium
α -Ionone	24.87	8.1 ± 1.0	15.9 ± 4.5	22.1 ± 0.2	31.7 ± 4.3	a, b, c	Sweet, woody, floral	Medium
Σ ketones		17.7 ± 1.3	32.8 ± 10.3	52.4 ± 1.6	65.9 ± 5.3			
Carboxylic acids								
Diethylacetic acid	21.69	n.d.	4.2 ± 0.1	3.7 ± 0.1	2.2 ± 0.2		Acidic, fruity	Medium
Bis[2-(Trimethylsilyl)ethyl] malonic acid	22.95	11.4 ± 0.2	11.0 ± 0.0	11.6 ± 0.2	11.9 ± 0.1			
Σ carboxylic acids		11.4 ± 0.2	15.2 ± 0.0	15.4 ± 0.4	14.1 ± 0.3			
Σ volatiles compounds		296.5 ± 3.1	379.2 ± 47.2	433.2 ± 19.0	477.7 ± 13.7			

Values are given as mean ± standard error ($n = 2$). n.d. (no data) indicates that the compound was either not detected in one or both duplicates or that RSD exceeds the threshold value of 42%.

^a Le Pape et al. [48].

^b López-Pérez et al. [28].

^c Michel et al. [14].

^d Odor descriptors and strengths from <http://www.thegoodscentscompany.com>.

notes and processing flavor. Free alanine, which is a sweet tasting amino acid [42] is also highly correlated with sweet odors.

On the other side of the plot, the FAAs asparagine, histidine, methionine and phenylalanine as well as the hydrocarbons pentadecane

and tetradecane are correlated with fishy and marine odors and flavors. Histidine is an active compound contributing to the savory taste of dried skipjack (*katsuobushi*) stock [53] and in combination with methionine, to the overall taste of Vietnamese fish-sauce (*Nuoc mam*) [54].

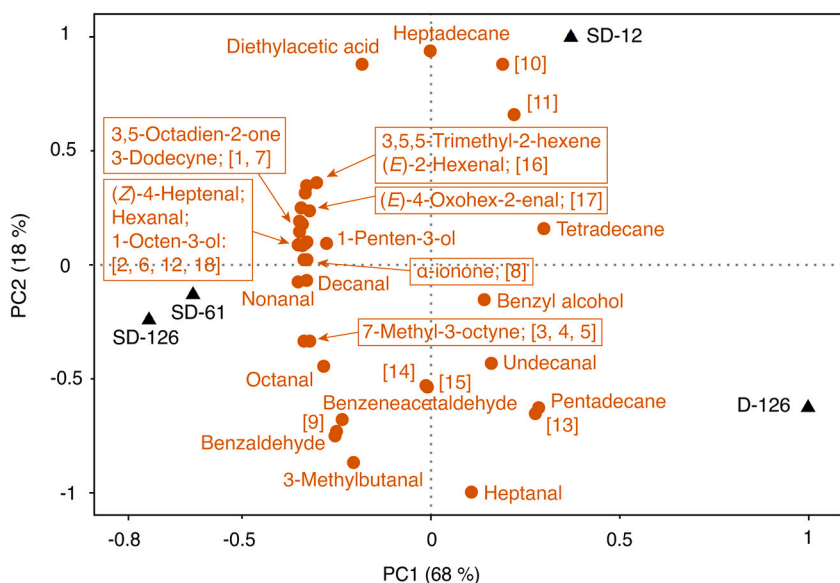


Fig. 3. Biplot (1st and 2nd principal component axes) obtained from the principal component analysis (PCA) of the volatile compounds of dry (D) and semi-dry (SD) samples of *P. palmata* during storage over a period of 126 days. For each group of samples, average values for the gas chromatography–mass spectrometry (GC–MS) analysis ($n = 2$) were used. For clarity of the figure, the name of some compounds were abbreviated: [1]: 2,6,6-Trimethyl-cyclohexene-1-carboxaldehyde; [2]: 1-Butenylidene-cyclohexane; [3]: 1-(1-Adamantyl)-1-phenylethanol; [4]: 2-Amino-4-methoxyphenol; [5]: 3,4,4-Trimethyl-2-cyclopenten-1-one; [6]: 2,6-Dimethylcyclohexanol; [7]: (*E,Z*)-2,6-Nonadienal; [8]: 2,4,4-Trimethylcyclohex-2-en-1-ol; [9]: Bis[2-(Trimethylsilyl)ethyl] malonic acid; [10]: 1-(2-Methoxy-1-methylethoxy)propan-2-ol; [11]: 1-(2-Methoxypropoxy)-2-propanol; [12]: 2,6,6-Trimethyl-2-cyclohexene-1,4-dione; [13]: 3,5,5-Trimethylcyclohex-3-en-1-one; [14]: 3-[(*E*)-3-Methylbut-1-enyl] cyclohexene; [15]: 2,3,6-Trimethyl-7-Octen-3-ol.; [16]: (*E,E*)-2,4-Heptadienal; [17]: (*E,E*)-2,4-Decadienal; [18]: 3-Cyclohexene-1-ethanol.

Methionine has also been reported to be an essential component responsible for the flavor of sea-urchin roe [53]. The levels of both histidine and methionine reported in the cited literature largely exceed those measured in the present *P. palmata* samples. However, the levels

of these FAAs are lower in SD-61 and SD-126 compared to D-126 and SD-12 (Table 4) which may contribute to the observed flavor differences between these samples.

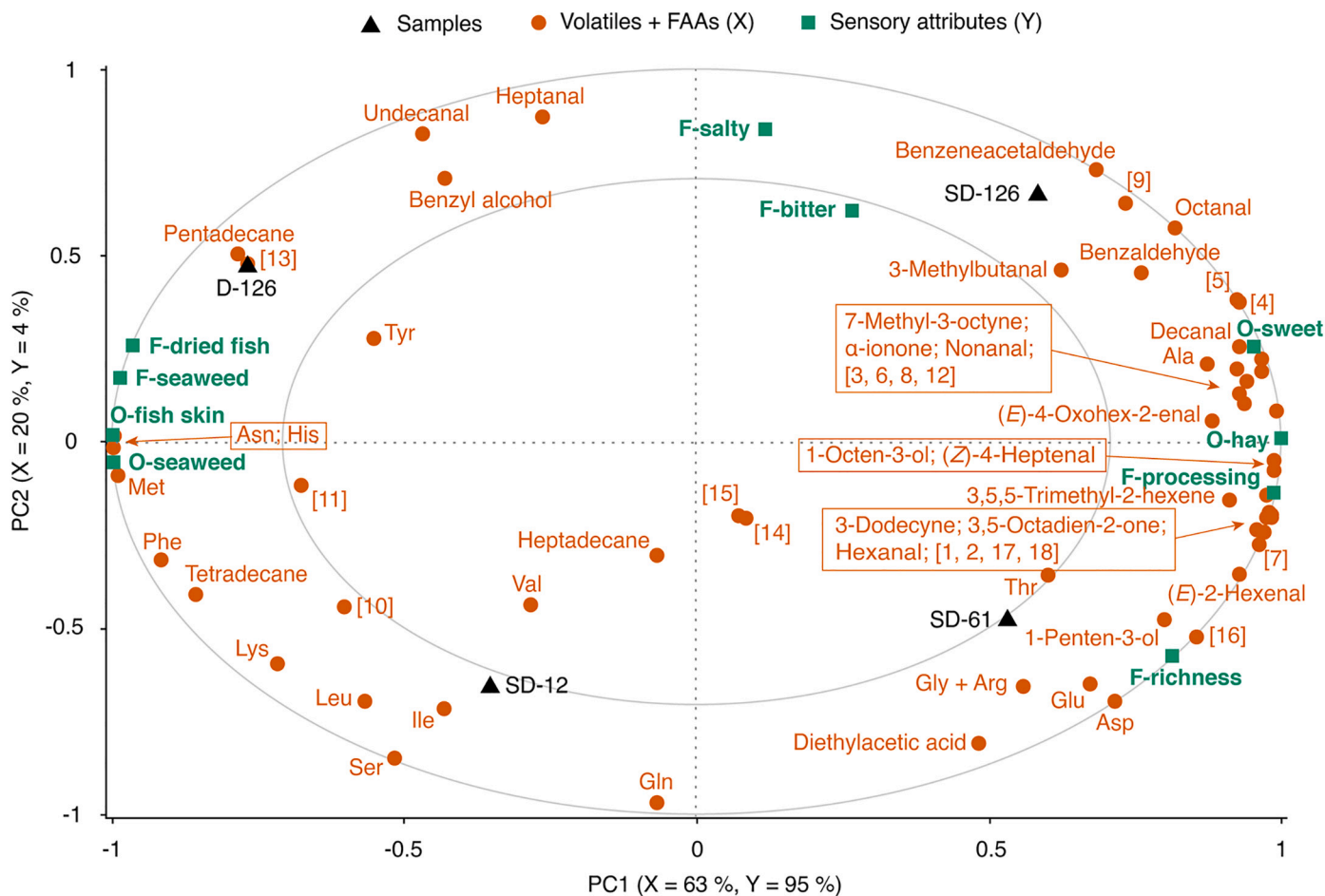


Fig. 4. Correlation loading plot for a partial least-squares regression (PLSR) model based on volatile compounds and free amino acids (FAAs) as predictors (X-variables, scaled) and sensory odor (O) and flavor (F) attributes as response variables (Y-variables, not scaled) in *P. palmata* samples after dry (D) and semi-dry (SD) storage over a period of 126 days. Results for the predictors are the mean of two (volatiles) and three (FAAs) sample replicates. The outer and inner ellipses indicate 100% and 50% explained variance respectively. For the full names of abbreviated volatile compounds, see the caption of Fig. 3.

4. Conclusions

The SD-storage of *P. palmata* in this study can be compared to a maturation process commonly employed in a wide range of foodstuffs. In general, the food products obtained from these processes are highly valued by consumers worldwide for their rich and complex flavors. This study demonstrates that increasing the MC of dried *P. palmata* samples to ca. 20% significantly altered the sensory profile of the products compared to dried material containing ca. 6% moisture. During storage under controlled conditions, the characteristic marine and fishy flavors and odors of the dried seaweed faded, as described for the maturation of *kombu* in Japan, while sweet, rich and complex notes arose during storage of SD material. Based on the analysis of the chemical content, physico-chemical properties and flavor-active compounds, the variations observed among samples suggest that lipids, proteins and FAAs as well as carbohydrates are involved in enzymatic and/or non-enzymatic reactions during storage. These reactions can be the result of endogenous processes and/or the action of microorganisms naturally present and cause the formation of a variety of volatile flavor contributors and a softer texture. Higher MC and longer storage times clearly promoted these biochemical reactions. The hedonic effect of matured *P. palmata* from SD-storage should be tested in future studies.

Further understanding of the biochemical and chemical patterns involved in flavor development will enable the optimization of processing and storage conditions of edible seaweeds to achieve tastier food products attractive to Western consumers and support the current movement promoting seaweeds as natural and healthy food ingredients. This study provides a scientific basis for future work on the quality of seaweeds in food applications and more specifically on processes to increase the sensory value of seaweed products.

CRedit authorship contribution statement

Pierrick Stévant: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Aðalheiður Ólafsdóttir**: Methodology, Investigation, Writing - review & editing. **Paul Déleris**: Investigation, Writing - review & editing. **Justine Dumay**: Investigation, Writing - review & editing. **Joël Fleurence**: Methodology, Resources, Supervision, Writing - review & editing. **Berggrós Ingadóttir**: Investigation. **Rósa Jónsdóttir**: Resources, Writing - review & editing. **Émilie Ragueneau**: Investigation. **Céline Rebours**: Methodology, Resources, Supervision, Writing - review & editing, Project administration, Funding acquisition. **Turid Rustad**: Methodology, Resources, Supervision, Writing - review & editing.

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.

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Statement of informed consent, human/animal rights

No conflicts or animal rights applicable. The sensory research procedures in this study followed the guidelines that constrain the use of

human subjects from the Nuremberg code of ethics in medical research and the declaration of Helsinki (as revised in 2013).

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