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Review Article

Volatile Components in Seaweeds



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Abstract

Marine environment comprehends a large geographic area, occupying about 71% of the surface of this planet. This environment has a great diversity of plants and animals which constitute an enormous amount in the food chain, comprising of organisms living in complex habitats where they are exposed to extreme conditions, which help them to produce a wide range of potent and active substances. These are commonly not found in other environments, that results in a source of nutrients, pharmaceuticals and characteristic flavor compounds. One of these plants which are very important to the food industry is the seaweed.

Introduction

Seaweeds are a group of photosynthetic plant-like organisms that generally thrive attached to rock or other hard substrata in coastal areas [1-5]. They have high amounts of macronutrients (proteins, carbohydrates and lipids) and thus characterize for important nutritional value [6,7]. Seaweeds are also sources of bioactive and antioxidant compounds, besides their extracts can have antihypertensive and anti-inflammatory properties [8-11]. Another important characteristic of seaweeds is their volatile compounds profile, which plays an important role in marine ecosystems, including in the chemical communication. Volatile compounds in seaweeds act as sexual pheromones, chemical defenses against herbivores and inhibitors of bacteria and fungi [12-14]. Some volatile compounds present in seaweeds such as ammonia, methylamine, and trimethylamine are generated by microorganisms or by chemical reactions. Processes like roasting are responsible for the formation of volatile compounds, especially dimethyl sulfide which stimulates the aroma of edible green and red seaweeds, which are very much appreciated by Japanese. Other volatile compounds could act like a protection for the seaweeds, for example, the diterpene holohedral, which defends seaweeds against herbivorous fishes and invertebrates [15].

The volatile compounds of some edible seaweeds have been analyzed by GC-MS systems and it showed that volatile compounds depend on the species, its geographical origin, processing method and environmental conditions [16,17]. In relation to the species, some studies revealed that green seaweed produces mainly cymopole, a product of condensation of reaction between bromophenols and monoterpenes. Brown seaweeds produce sulfur compounds, \mathbf{C}_{11} -hydrocarbons and diterpenes while red seaweeds are known to produce halogenated compounds containing bromine

and iodine, which contribute to a sweet note in the aroma of this specie of seaweeds. Organic compounds present in seaweeds also function as therapeutic drugs, flavoring agents, odorants in perfume industry and indicator of water pollutants. For these reasons, many studies were performed with the aim of determining the volatiles from seaweeds using different analytical methods as shown in the Table 1 which cites the volatile compounds identified in brown, green and red seaweeds [18,19]. Some compounds have great impact on the aroma of seaweeds and are considered "character-impact compounds", and these include iodoethane, iodopentane and isoprene (2-methyl-1-3-butadiene) present especially in red seaweeds [20]. Volatile halogenated compounds such as dibromoethane, bromoform, dibromochloromethane, bromodichloromethane and chloroiodomethane contribute to the characteristic aroma of the seaweeds with notes like marine, crustacean and green. Moreover, these compounds play an important role in chemical defense against predators [21,22].

The profile of volatile compounds can be very diverse between the various types of seaweeds [23]. This diversity is occasioned due to different species that can be capable of producing a variety of volatile compounds. The detailed identification of such compounds is very important to elucidate their aroma properties of the final product [24,25]. In the green seaweeds, a higher number of compounds have been identified in comparison to brown and red seaweeds (Table 1). The diversity of volatiles compounds presents in seaweeds produce different odors which involve main notes defined like "marine" and "seafood". Showed that other odor notes like "fatty", "fish", "licorice", "spices", "green", "honey" were detected in species of green, red and brown seaweeds. In these species, carboxylic acids were related to odor notes such as of licorice, honey

and spices, while esters and Sulphur compounds were related to green odor. Notes like fish odor, marine odor, fatty odor, seafood odor are related to presence of amines and pyridines. Important volatiles responsible for the odor of green marine algae [26]. In a recent study it is reported that compounds when present in higher concentrations contribute to fruity notes in aroma characteristics of some seaweeds [27]. Another class of compounds commonly found in the aroma composition of seaweeds are the ketones. Ketones, such as β -ionone and δ -methyl- δ -hepten- δ -one are formed by the

oxidative cleavage of carotenoids such as lycopene and phytoene [28]. These compounds are formed from the pigments contained in the seaweeds and are metabolized while capturing light and scavenging radicals [29]. β -ionone is a potent odorant in seafood and has been found in all three types of seaweeds. Other ketone frequently found in aroma of seaweeds which have an odor impact is 6-methyl-5-hepten-2-one. This ketone is also found in other foods, such as tomato as a metabolite of lycopene which results in compounds having more pleasant odors [30-32].

Table 1

Volatile compounds	Odor description*	Туј	Types of microalgae		
		Green	Brown	Red	
	Aldehydes	'			
(E)-2-Heptenala	Green, pungent	Х	X	X	
(E)-2-Hexenalf,i	Green, banana	X	X	X	
(E)-2-Octenale, f	Fresh, cucumber, green	X	X	X	
(E)-2-nonenale	Fatty, green	Х			
(E)-2-Butenala	flowery	Х	X	X	
(E)-2-Pentenala	Green, fruity	Х	X	X	
(E,E)-2,4-decadienala,e	Fatty, cucumber	Х			
(E,E)-2,4-Heptadienala	Green, fatty	X	X	X	
(E,E)-2,6-Nonadienala, e	Green, fatty	X	X	X	
(Z)-4-Heptenala	Green, fatty	X	X	X	
(Z)-8-Heptadecenal	-	Х			
(Z,E)-2,4-Heptadienala, j	Fried	X	X	X	
(Z,Z)-8,11-Heptadecadienale	-	Х			
(Z,Z)-9,12-Octadecadienale	-	Х			
(Z,Z,Z)-8,11,14-Heptadecatrienale	Seaweed	Х			
(Z,E)-2.6-Nonadienala	Green	Х			
2,4-Decadienale	Fatty, orange	X			
2-Methyl-2-propenala	Fresh	Х	X	X	
2-Heptenald	Green, fatty	Х			
3-Methylbut-2-enalb	Fruity	Х	X		
3-Methylbutanala,b, i	Peach-like	X	X	X	
2-Methylbutanala	Chocolate	X	X	X	
2,4-Heptadienald	Green, fruity	X			
4-Heptenalc	Green			Х	
Benzaldehydea,b, d, f	Fruity	X	X	Х	
Ethanala	Ethereal	X	X	X	
Butanala	Chocolate, cocoa	X	X	Х	
Decanala,b	Sweet, aldehydic			X	
Heptanala, f, j	Green, fresh	X	X	X	
Hexanala,b, d, e, f, j	Fresh, green	X	X	X	
Pentadecanal	Fresh, waxy	X			
Nonanala,b, f, i	Aldehydic	X	X	X	
Furfurald	Sweet, woody	X			

Octanala, i	Aldehydic	X	X	X
Octadecanalb,c	Oily	A	A	X
β-Cyclocitrala,b, d	Tropical	X	X	X
4-Propylbenzaldehydea	-	X	X	X
Pentanala		X	X	X
	Fermented, bready		Λ	X
Tridecanale	Aldehydic	X		
Perillaldehydee	Herbal	X		
4-Ethylbenzaldehydea	Fruity, almond	X	X	X
Hydrocarbons				
1-Hexadecenea	-	X		
1-Nonadecenef	-			X
1-Pentadecenea	-	X	X	
1-Tetradecenea	-	X		
3-Heptadecenec	-			X
4,6-Dimethyldodecanea	-	X	X	X
4,8-Dimethylundecanea	-	X	X	X
Heptadecadiene	-	X		
Heptadecanea, c, d	-	X	X	X
Heptadecened, f	-	X		X
4-Methyldecanea	-	X	Х	X
7-Heptadecenee	Alkane	X		
4-Ethyldecanea	-	X	X	X
2,4-Dimethylhexanea	-	X	X	X
2,4-Dimethylundecane	-	X	Х	X
2,4-Dimethylheptanea	-	X	X	X
2-Methylheptanea	-	X	X	X
2-Methylnonanea	-	X	X	X
2,7-Dimethyloctanea	-		X	X
5-Methyldecanea	-	X	X	X
Nonadecanea	-	X		
Hexadecanee	-	X		
Octanea	Gasoline	X	X	X
Octadecenee	-	X	Λ	A
		Λ	V	V
Nonanea	Gasoline	77	X	X
Hexadecenee	-	X		
Tetradecanee	Mild, waxy	X		
Tetradecenee	-	X		
Tridecanee	-	X		1
Pentadecanea	Waxy	X	X	1
Pentadecenee	-	X		
Ketones				
2-Octanonea	Earthy	X		
3-Octen-2-onea	Earthy, spicy	X	X	X
α-Iononea, f	Floral	X		X
γ-Butyrolactonea	Cream, caramellic	X	X	X

γ-Hexalactonea	Herbal, coconut	X	X	X
γ-Valerolactonea	Herbal, sweet		X	X
ß-iononea,b,d,e	Floral	X	X	X
(E,E)-3,5-Octadien-2-onea	Fruity, green	X	X	X
(E,Z)-3,5-Octadien-2-onea	Herbal	X	X	X
1-Octen-3-onea	Herbal, mushroom	X	X	X
1-Phenylethanonea	Floral, sweet	X	X	X
2,3-Butanedionea	Buttery, sweet	X	X	X
2,3-Octanedionef	Dill, aspargus			X
2,5-Octadionea	-	X	X	X
2-Butanonea	Etheral, acetone	X	X	X
2,2,6-Trimethylcyclohexanonea	Thujonic	X	X	X
2-Heptanonea, f	Fruity, spicy	X	X	X
2,6,6-Trimethyl-2-hydroxycyclohexanonea	Sweet, herbal	X		
2-Pentadecanonec	Floral, fresh, jasmin			X
2-Pentanonea	Sweet, fruity	Х	X	X
3-Hydroxy-2-butanonea	Sweet, buttery	Х	X	X
3-Penten-2-onea	Fruity, acetone	X	X	X
6-Methyl-3,5-heptadien-2-onea	Spicy, cinnamom		X	X
6-Methyl-5-hepten-2-onea, d	Citrus, green	X	X	X
5-Ethyl-2(5H)-furanonea	Caramel	X	X	Х
trans-β-Iononea	Floral, sweet	X	X	X
Alcohols				
(E)-2-Ethyl-1-hexanola	Citrus, fresh	X	X	X
(E)-2-Penten-1-ola, e	Mushroom	X	X	X
(Z)-1,5-Octadien-3-ol	Green, marine	X	X	X
(Z)-2-Ethyl-1-hexanola	Citrus		X	
(Z)-2-Penten-1-ola	Green	X	X	X
1,7-Octadien-3-ola	-		X	
1-Hexadecanolc	Waxy, green			X
1-Hexanola,b	Herbal	X	X	X
1-Octanola,f	Waxy, green	X	X	X
1-Octen-3-ol	Earthy, mushroom	X	X	X
1-Pentanola	Fermented, oily, sweet	X	X	X
1-Penten-3-ola, i	Green	X	X	X
2-(2-Methoxypropoxy)-1-propanola	-	X	X	X
2,3-Butanediola	Fruity, creamy			X
2-Methyl-3-pentanola	-	X	X	X
2-Octen-1-ola	Green, vegetable	X	X	X
2-Penten-l-ola	Green	X		
3-Pentanole	Herbal	X	X	X
Isophytolc	Floral, herbal			X
Benzyl alcohold	Floral, rose	X		X
Delizi i dicultud		1 -*		
Perillyl alcohole	-	X		

Cedrolc	Woody			X
යි-terpineole	Woody	X		
Esters				
2-Propenoic acida	-	X		
3-Methylbutanoic acida	Cheesy	X	X	X
Butanoic acida	Cheesy	X	X	X
Ethanoic acida	Acidic	X	X	X
Ethyl acetatec	Fruity, sweet	X		X
Hexanoic acida,e	Fatty, cheesy	X	X	X
Heptanoic acida	Cheesy, rancid	X	X	X
Methyl hexanoatec	Waxy fatty	X		X
2-Methylpropanoic acida	Acidic	X	X	X
2-propenoic acid,2-methyl dodecylesterc	-			X
Methyl linolenate	-	X		
Methyl tetradecanoatec	Waxy, fatty	X		
Nonanoic acidd	Waxy, dirty	X		
Ethyl hexanoatea	Fruity, pineapple			X
Octanoic acida	Fatty, waxy	X	X	X
Octyl acetatee	Floral, green	X		
Isobutyl acetate	Fruity, sweet	X		
Sulfur compounds				
Dimethyl sulfidea,d,e,c	Sulfurous, onion, sweet	X	X	Х
Dimethyl sulfoxidea,d	Fatty, oily	X	X	Х
Dimethyl trisulfidec	Sulfurous, onion			Х
Other compounds				
2-Iodo-propanea	-		X	
Iodo-ethanea	-		X	
Iodo-methanea	-		X	
1-Iodo-pentanea,b	-	Х	X	Х
1-Iodo-octanea	-		X	
2-Ethylfurana	Sweet, burnt	Х	X	Х
Germacrene Db	-		X	
2-Pentylfurana,f	Fruity, green	Х	X	Х
m-Cymenee	-	X		
2-Methylfurana	Chocolate	Х	X	X
Trans-2-(2-pentenyl)furanf	-			Х
Tribromomethaneh,i	-	X	X	

A large quantity of compounds present in the aroma of seaweeds is due to the significant contribution of lipid-derived volatiles, such as aldehydes and alcohols, which relate to the non-appreciable aroma characteristics of microalgae. It is for this reason that prevention and control of lipid oxidation is recommended to ensure good flavor quality of the product [33]. In some species of seaweed it is possible to find compounds which belong to furans. This class consists of a family of important chemicals in the formation of crab flavor and are sourced from the oxidative degradation of linolenic acid [34]. The aroma diversity of seaweeds is a result of the variety

and concentration range of the aroma compounds. Since microalgae could possess important odor characteristics, it can be used in food and feed formulations. Some of these aroma characteristics may be desirable in some applications but unwanted in others. For example, while sulfur-containing compounds are highly appreciated in certain foods such as oysters, roasted coffee, fried meat, toasted bread or cheddar cheese, these can lead to very irritating off-flavors, for example, in milk [35,36]. This review reveals that the odor characteristics of seaweeds can be very distinct, and it varies between the three types: red, brown and green. Ulva sp., a specie

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of green seaweed, received notes like seaweed odor, marine odor and seafood odor. However, *Laminaria digitate*, brown seaweed, showed stronger seaweed aroma and milder honey aroma [37] and the red seaweeds received the highest scores for the seaweed odor attribute.

Conclusion

The volatile profiles of brown, green and red microalgae have been presented in this review on seaweeds. Volatile compounds in seaweeds also act as sexual pheromones and inhibitors of bacteria and fungi. Moreover, the specific aroma notes of these seaweeds as reported in publications are also detailed. Among the three types of seaweeds, the green has been studied much more and relatively a large number of volatile compounds have been identified in this seaweed as compared to brown and red types. The characteristic marine odor is much more appreciated in food preparations and is very prominent in green seaweed.

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