Changes of Volatile Sulfur Compounds of 'Nori' Products, *Porphyra* spp. during Storage

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The changes in the flavor of dried and toasted laver *Porphyra* spp. stored over three months were examined by focusing on the changes in three volatile sulfur compounds, hydrogen sulfide (H₂S), methyl mercaptan (MM) and dimethyl sulfide (DMS) monitored by gas chromatography.

In dried laver with 8% moisture content, the decline of H₂S and DMS and the increase of MM were negligible only when stored at -30°C with air or at 5°C with nitrogen gas or an oxygen absorber. When the moisture content declined to 4.5%, changes in the H₂S and MM levels were minimized by the nitrogen gas and by the oxygen absorber at both 5° and 25°C. DMS, however, increased with nitrogen gas at both 5° and 25°C.

In toasted laver, the levels of the three compounds were well preserved when stored at 5°C with nitrogen gas or an oxygen absorber. At 25°C with nitrogen gas or an oxygen absorber, however, H₂S and MM declined moderately. Meanwhile DMS was well preserved, resulting in the maintenance of good flavor.

Therefore, the storage of all nori products at 5°C with nitrogen gas or an oxygen absorber is recommended.

Besides the apparent properties such as color, luster, taste, compactness and smoothness, flavor are important factors of the quality of commercial dried and toasted laver 'Nori', *Porphyra* spp. As the flavor substances of dried laver, terpenes, organic acid, carbonyl and sulfur compounds have been detected.¹⁻⁵⁾ It is reported that dimethyl sulfide (DMS) and its precursor dimethyl-β-propiothetin affect the flavor of dried laver.⁶⁾ In the case of toasted laver, bases and aldehydes are also detected together with carbonyl, pyrazines and γ-butyrolactone.⁷⁻⁹⁾

Dried laver just after being manufactured has 7-15% moisture content, and can not be preserved in excellent quality for a long time. Commercially the dried laver is, therefore, heated at 50-60°C after mechanically drying until the moisture content is reduced to less than 5%, and stored at room temperature. Even by this method, the flavor of dried laver becomes unfavorable with prolonged storage. By the monitoring of changes in the volatile sulfur concentrations in dried laver during storage, it is reported that moisture increased slightly the DMS concentration at a water activity

lower than 0.2.¹⁰⁾ But the high moisture content decreased the DMS level and increased the methylmercaptan (MM) level with the increase of hydrogen sulfide (H₂S) at a high storage temperature.¹¹⁾ However, not only the changes of concentrations of volatile sulfur compounds in *Porphyra* from harvesting through manufacturing to toasted laver, but also the best storage conditions for preserving the flavor of dried and toasted laver requires more detail investigation.

This paper describes the changes of volatile sulfur concentrations in dried and toasted laver stored under various conditions, and the best storage conditions for the nori products.

Materials and Methods

Materials

Fresh and dried laver 'Nori', *Porphyra* spp. were obtained from culture grounds in Hyogo Prefecture. The quality of dried laver was guaranteed as excellent by the inspection of Hyogo Prefectural Fisheries Association. Dried laver with 8% and 4.5% moisture content were

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prepared by using a drying machine. Toasted laver was produced by a commercial toasting machine from the dried laver with the 4.5% moisture content mentioned above. Dried and toasted laver were stored under varying conditions for three months.

Storage Conditions

Each kind of dried laver and toasted laver was packed in gas barrier bags made of alumin laminate film (polyvinyliden chloride coated polypropylene/polyethylene/aluminium/polyethylene). Each bag was filled with either air, an oxygen absorber or nitrogen gas. Both the dried and toasted laver were stored at 5° and 25°C for half a month, one, two and three months, respectively. Also, dried laver with 8% moisture content was stored at -30°C with air. The oxygen content in the bags sealed with nitrogen gas or an oxygen absorber was less than 0.1%.

Gas-Liquid Chromatography

The volatile sulfur compounds in the head space vapor were analyzed by gas chromatography as follows:

Twenty grams of fresh laver and two grams of the powder of dried or toasted laver were kept in a vial bottle (50 ml) with distilled water (30 ml), respectively. After being kept for 20 min at 40°C in a water bath, the head space vapor (5 ml) was applied to a Shimadzu GC-9A gas chromatograph equipped with a flame photometric detector and a glass column (3 mm×3 m) packed with 25% 1, 2, 3-tris [2-cyanoethoxy] propane on Shimalite (60-80 mesh). The flow rate of nitrogen as carrier gas was 50 ml/min and the column temperature was 40°C. The identification and estimation of sulfur compounds were made on the basis of retention time and a standard curve established by standard gas.

Results

Contents of Volatile Sulfur Compounds in the Manufacturing Process of Dried and Toasted Laver

The gas chromatograms of the head space vapor obtained from fresh laver, dried laver with 8% and 4.5% moisture content and toasted laver

Fig. 1. Gas chromatogram of volatile sulfur compounds in the head space vapor.

A, fresh laver; B, dried laver with 8% moisture content; C, dried laver with 4.5% moisture content; D, toasted laver; E, authentic specimen. Peak No. 1, 2 and 3 represent hydrogen sulfide, methyl mercaptan and dimethyl sulfide, respectively.

are illustrated in Fig. 1. From the comparison with standard gas, peak No. 1, 2 and 3 were identified as H_2S , MM and DMS, respectively.

As shown in Table 1, the contents of each compound increased during processing.

Hydrogen Sulfide H_2S was contained at a higher concentration than MM and DMS except in the case of fresh laver and increased remarkably in toasted laver. In toasted laver, the flavor of H_2S was discerned organoleptically. When authentic

Table 1. Contents of volatile sulfur compounds in fresh, dried and toasted laver

		(ppm)		
		Dried laver		
	Fresh laver	Moisture content		Toasted laver
		8%	4.5%	
Hydrogen sulfide	0.1	11.8	13.8	131.4
Methyl mercaptan	Trace	Trace	Trace	3.9
Methyl mercaptan	Trace	Trace	Trace	3.9
Dimethyl sulfide	0.4	0.3	3.1	7.5

Fig. 2. Changes of the levels of volatile sulfur compounds in dried laver with 8% moisture content. Dried lavers were stored with nitrogen gas, an oxygen absorber and air at -30° , 5° and 25°C , respectively.

■—■—, -30°C with air; ○—○—, 5°C with N_2 ; △—△—, 5°C with an oxygen absorber; ●—●—, 5°C with air; ○—○—, 25°C with N_2 ; △—△—, 25°C with an oxygen absorber; ●—●—, 25°C with air.

H₂S was added to the head space vapor, the peculiar flavor of toasted laver was apparently strengthened.

Methyl Mercaptan Trace amounts of MM were found in both fresh and dried laver. In toasted laver, however, MM increased by 2.7% of the total sulfur compound. Even though authentic MM was added to the head space vapor, the flavor of toasted laver was not strengthened. Apparently only small amounts of this compound seemed to contribute to the toasted aroma.

Dimethyl Sulfide Levels of DMS, one of the main components in fresh laver, is almost the same as that in dried laver with 8% moisture content. The DMS level, however, increased markedly in dried laver with 4.5% moisture content and toasted laver, resulting in the increase

of the levels as much as 8–19 times in fresh laver. The increasing rate of DMS was low compared with that of H₂S.

Changes of the Levels of Volatile Sulfur Compounds during Storage of Dried and Toasted Laver

(1) Dried Laver with 8% Moisture Content

Hydrogen Sulfide The H₂S level of dried laver with 8% moisture content increased as much as 1.3 times the initial level when stored at –30°C with air for half a month (Fig. 2A). But during the first month storage at 25°C with nitrogen gas, an oxygen absorber or air, the level of H₂S declined sharply to 66%, 51% and 40% of the initial level, respectively. Thereafter, H₂S levels remained nearly unchanged. On the other

Fig. 3. Changes of the levels of volatile sulfur compounds in dried laver with 4.5% moisture content. Dried laver was stored with nitrogen gas, an oxygen absorber and air at 5° and 25°C, respectively.

—○—○—, 5°C with N₂; —△—△—, 5°C with an oxygen absorber; —●—●—, 5°C with air; —○—○—, 25°C with N₂; —△—△—, 25°C with an oxygen absorber; —●—●—, 25°C with air.

hand, the initial levels of H_2S were well maintained when stored at $5^\circ C$ with nitrogen gas or an oxygen absorber.

Methyl Mercaptan The MM level of dried laver stored at $25^\circ C$ for three months with air, an oxygen absorber or nitrogen gas was 3.8–5 times the initial level (Fig. 2B). Use of nitrogen gas or an oxygen absorber slowed down the rate of MM's increase to 53–56% of the rate of the increase which occurred at $25^\circ C$ with air. Therefore, to prevent the increase of MM, freezing or storing at $5^\circ C$ with air, an oxygen absorber and nitrogen gas are necessary.

Dimethyl Sulfide Fig. 2C shows that levels of DMS changed slightly when dried laver was stored at $-30^\circ C$ with air and at $5^\circ C$ with nitrogen gas or with an oxygen absorber, but declined by 30% during half a month storage at $5^\circ C$ with air. While dried laver was stored at $25^\circ C$ with an oxygen absorber for three months, the DMS level in dried laver declined to 80% of the initial concentration. However, the DMS level in dried laver stored at $25^\circ C$ with nitrogen gas for three months declined sharply to 55% of the initial level. The magnitude of the decline of DMS was the largest when dried laver was stored at $25^\circ C$ with air.

From the results obtained above, the levels of H_2S , MM and DMS in dried laver fluctuated during storage for three months. The fluctuation of these compounds were considerable during one month storage. Since the increase of H_2S level in dried laver stored at $-30^\circ C$ with air strengthened the good flavor of dried laver, freezing or storage at $5^\circ C$ with nitrogen gas or an oxygen absorber are recommended to preserve the flavor of dried laver. However, an oxygen absorber or nitrogen gas are not effective to preserve the flavor of dried laver when stored at $25^\circ C$.

(2) Dried Laver with 4.5% Moisture Content

Hydrogen Sulfide H_2S levels in dried laver with 4.5% moisture content stored at 5° or $25^\circ C$ with air declined to 79% and 65% of the initial level after three months storage, respectively (Fig. 3A). With an oxygen absorber, however, the H_2S levels were stabilized from 97% to 90% of the initial level. The H_2S level in dried laver stored with nitrogen gas approximated the initial level, even after three months (109% in storage at $5^\circ C$ and 103% in storage at $25^\circ C$). Oxygen is a more important factor in reducing the H_2S level than the storage temperature.

Methyl Mercaptan As shown in Fig. 3B, only the dried laver stored at $25^\circ C$ with air showed a marked increase in the MM level. This increase peaked at three months storage. Five other test groups revealed H_2S levels after three months that approximated the initial concentration. Therefore, dried laver with 4.5% moisture content produced smaller amounts of MM when nitrogen gas or an oxygen absorber were used.

Dimethyl Sulfide The dried laver stored at $5^\circ C$ with air or with an oxygen absorber and at $25^\circ C$ with an oxygen absorber showed similar DMS levels during the storage period (Fig. 3C). When stored at $25^\circ C$ with air, however, the DMS levels declined to 54% of the initial level during half a month, and to 12% during three months. On the other hand, use of nitrogen gas at $5^\circ C$ and at $25^\circ C$ increased the DMS levels to 1.7 and 2.2 times the initial level during three months, respectively. Therefore, to preserve the flavor of dried laver with 4.5% moisture content, storage at 5° or $25^\circ C$ with nitrogen gas are recommended.

(3) Toasted Laver

Hydrogen Sulfide As shown in Fig. 4A the H_2S level in toasted laver stored at $5^\circ C$ with nitrogen gas or an oxygen absorber declined slightly. The H_2S level after storage for three months was 83% of the initial level in the former and 87% in the latter. The H_2S levels of toasted laver stored at $5^\circ C$ with air or at $25^\circ C$ with nitrogen gas declined moderately. When stored at $25^\circ C$ with air or with an oxygen absorber the H_2S levels in toasted laver declined vigorously to 7% and 33% of the initial level, respectively. Preservation of the H_2S level at the initial level was difficult at $25^\circ C$ with air.

Therefore, the use of nitrogen gas or an oxygen absorber at $5^\circ C$ was very effective, maintaining 90% of the initial level of H_2S .

Methyl Mercaptan The MM levels in toasted laver declined slightly when stored at $5^\circ C$ with nitrogen gas or an oxygen absorber (Fig. 4B). The levels, however, declined sharply during the first half month when stored at $5^\circ C$ with air. Marginal decline of the MM level in toasted laver stored at $25^\circ C$ occurred regardless of the use of air, nitrogen gas or an oxygen absorber. Therefore, the recovery was mainly dependent on the storage temperature.

Dimethyl Sulfide As shown in Fig. 4C, the DMS levels during three months storage changed slightly regardless of nitrogen gas or an oxygen absorber when stored at 5° and $25^\circ C$. However,

Fig. 4. Changes of the levels of volatile sulfure compounds in toasted laver. Dried laver was stored with nitrogen gas, an oxygen absorber and air at 5° and 25°C, respectively.

—○—○—, 5°C with N₂; —△—△—, 5°C with an oxygen absorber; —●—●—, 5°C with air; —○—○—, 25°C with N₂; —△—△—, 25°C with an oxygen absorber; —●—●—, 25°C with air.

the levels declined dramatically when stored with air at 25°C.

From the results obtained above, the flavor of the toasted laver can be well preserved with either nitrogen gas or an oxygen absorber at 5°C and moderately well at 25°C.

Discussion

The threshold of odor of H₂S, MM and DMS are 0.0047, 0.0021 and 0.001 ppm, respectively.¹²⁾ In the present experiment, contents of these three sulfur compounds during nori manufacturing processes were sufficient for organoleptic detection except for MM in fresh and dried laver. These three compounds increased during the processing of dried laver. The increase was greatest in H₂S in the toasted laver. The higher

the heating temperature and the longer the heating time, the more the H₂S levels increased. Therefore, drying and heating procedures may accelerate the formation of H₂S.

In contrast, the rate of increase of DMS during processing was less than that of H₂S. Also, the DMS level in toasted laver approximated that of dried laver. This observation seems to indicate that the evolution of DMS may be accelerated in the heating process.

The results obtained above provide us information not only on the initial level of flavor, but also on the changes in the flavor of nori products. In newly prepared nori products H₂S and DMS are abundant. MM levels increased in all nori products when stimulant flavor was detected organoleptically. If MM levels surpassed 10% of the total content of H₂S, MM and DMS, an

odor associated with deterioration occurred.* Therefore, to preserve the flavor of nori products, it is important to track quantitatively the changes in these three compounds.

Iida *et al.*,¹¹⁾ reported that dried laver with 9.5–12% moisture content showed increases of MM and decreases of DMS during three months storage at 30°C with air and caused the deterioration of flavor. They also reported that in dried laver stored at 5°C with air, the deterioration of flavor was slight.¹¹⁾ On the contrary, in the present study, the rate of decrease of DMS slowed down only when we used nitrogen gas or an oxygen absorber at 5°C.

As for toasted laver, MM content at 25°C was lower than that at 5°C. Also, the laver was virtually unaffected by environmental gas. MM seemed volatilize during the storage period. The subsequent rate of MM exceeded the levels of H₂S, resulting in the increase of the relative concentration in the total amounts of sulfur compounds. Therefore, MM seems to reduce the flavor of toasted laver to a level equal to that in dried laver.

These past several years, consumers have preferred toasted laver and seasoned laver over dried laver. Currently, storage facilities preserve all nori products at room temperature. If the 'Nori' industry wishes to continue this practice,

sealing of toasted laver with nitrogen gas or an oxygen absorber is essential.

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