Preparation of Powdered Seasoning with Shrimp-like Flavor from the Aqueous Residue of Isada Krill by Subcritical Water Treatment and Spray-drying

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The aqueous residue formed after the recovery of oil–soluble functional components in Isada krill caught on the Sanriku coast in 2018 was treated under subcritical water conditions at 140°C. Maltodextrins (MDs) with different dextrose equivalents (DEs) were added to the residue, and the mixtures were spray-dried to produce the powdered seasonings. Sensory evaluation of the odor of the powdered seasonings was conducted by a panel of volunteers. The DE of MD was found to affect palatability, and MDs with larger DEs exhibited higher preference scores. GC-MS analysis revealed that all the powdered seasonings contained pyrazines related to shrimp-like flavor, although no pyridines were detected.

Keywords: Isada krill, powdered seasoning, spray–drying, subcritical water

1. Introduction

Isada krill (Euphausia pacifica) are small euphausiids caught abundantly on the Sanriku coast seasonally between February and April [1, 2]. Most Isada krill are used as fishing bait and as feed for cultured fish, but their use in food is limited due to the rapid deterioration in quality by endogenous enzymes [1, 3]. However, Isada krill contain many functional lipids, such as eicosapentaenoic and docosahexaenoic acids [4], as well as 8-hydroxyeicosapentaenoic acid, which can reduce plasm and hepatic triacylglycerols [5], and are recommended as supplements. A large amount of aqueous residue is formed while recovering useful oily ingredients from Isada krill which, at present, is discarded.

We have previously reported that the treatment of Isada krill [6–10], or that of its residual waste solution [11], under subcritical water conditions at 140–200°C reduced the fishy odor and enhanced shrimp–like flavor. Treatment of the aqueous residue formed after the recovery of oil–soluble functional components in Isada krill under subcritical water conditions also reduced the fishy odor of the residue and exhibited a shrimp–like flavor [12]. The residue treated at 140°C had the highest palatability [12].

The aqueous residue with shrimp–like flavor should be refrigerated or stored frozen until use. However, the storage of the liquid residue is costly due to its large amount. If the liquid residue is converted to powder, its amount is largely reduced and the powder can be stored at room temperature.

To this end, we prepared powdered seasoning by spray–drying the aqueous residue treated at 140°C, to which maltodextrin (MD) with different dextrose equivalents (DEs) was added as an excipient. The effects of DE and drying conditions on the smell of the powdered seasonings were then evaluated by a panel of volunteers.

2. Materials and Methods

2.1 Materials

The aqueous residue obtained after the recovery of useful oil–soluble ingredients from Isada krill caught in 2018 was supplied by Kokuyo (Ofunato, Japan). The residue was stored in a freezer at ~80°C prior to use. The frozen residue was thawed at room temperature and centrifuged (H–3Ga, Kokusan, Saitama, Japan) at 1500×g for 10 min to remove the insoluble matter. The supernatant was treated under subcritical water conditions. MDs with DEs of 19, 25, and 29 were supplied by Matsutani Chemical Industry (Itami, Japan).
2.2 Treatment of the residue under subcritical water conditions

The aqueous residue was treated under subcritical water conditions using a pressure-resistant batch-type SUS-316 vessel with a maximum volume of 117 mL (Taiatsu Techno, Osaka, Japan). The aqueous residue (ca. 80 mL) was poured into the vessel and the vessel was tightly sealed and heated at 140°C using a heating mantle with power of 200 W. The temperature inside the vessel was measured using a K-type thermocouple. After reaching 140°C, the vessel was maintained for an additional 5 min at that temperature to perform the treatment. The vessel was then cooled using running tap water to terminate the treatment. The treated residue was centrifuged at 1500×g for 10 min to remove insoluble matter and the supernatant was used for preparation of powdered seasonings. These operations were repeated 33 times to obtain ~2.6 L of the treated residue. The treated residues were pooled in a vessel to make the content uniform. The Brix concentration of the residue was 15%.

2.3 Preparation of powdered seasoning by spray-drying

MD with DE of 19, 25, or 29 (141.2 g) was added to 658.8 g of the treated residue to prepare the solution of the solid content of 30% (w/w). The residue was fed to an L-8 spray-dryer (Ohkawara Kakouki, Yokohama, Japan) at a flow rate of 20 mL/min and sprayed from the atomizer at a rotation speed of 3.0×10^4 or 1.5×10^4 rpm. The temperatures of the inlet and outlet air, the flow rate of which was 110 kg/h, were 160°C or 180°C and 99-119°C, respectively. Four kinds of powdered seasonings were prepared under different conditions (Table 1).

2.4 Particle size of powdered seasoning

Spray-dried powder (0.4 g) was dispersed in 2-methyl-1-propanol (12 mL), and the particle size distribution was measured using a SALD-7100 particle size analyzer (Shimadzu, Kyoto, Japan). The light intensity distribution was converted to the particle size distribution, and the volume–surface mean diameter was calculated. The measurement was repeated three times.

2.5 Observation of powered seasonings by scanning electron microscopy

A scanning electron microscope (SEM) JSM-6060 (JEOL, Tokyo, Japan) was used to observe the external structure of the powdered seasonings. The powdered seasoning sample was placed on the SEM stage using a two-sided carbon tape (Nisshin EM, Tokyo, Japan). The SEM stub was subsequently coated with Pt–Pd using a magnetron sputter coater (Model MSP-1S, Vacuum Device, Tokyo, Japan). The electron accelerating voltage was 20 kV with magnification ranging from 50× to 1500×.

2.6 Gas chromatography–mass spectrometry (GC–MS) analysis of the odor

Gas chromatography mass spectrometry analysis of the odor was performed in the same manner as in our previous studies [11, 12], using a GC–MS QP–2010 (Shimadzu, Kyoto) with electron ionization (EI) and a DB–WAX Ultra Inert column (0.25 mm×30 m, Agilent, Santa Clara, CA, USA). The column temperature was programmed as follows: 40°C for 5 min, 40°C to 140°C at 5°C/min, and 140°C for 10 min. The powdered seasoning (0.5 g) was dissolved in water (2.0 mL) and placed in a 20-mL screw-capped vial. A fiber for solid-phase microextraction (SPME (Carboxen™/PDMS), Sigma–Aldrich, St. Louis, MO, USA) was inserted into the head space of the vial and stored at 40°C for 5 min to adsorb the volatile compounds. The odors of shrimp cracker (Calbee, Tokyo, Japan) and dried shrimp (Akiyomo Suisan, Numazu, Japan) were also measured after crushing under the same conditions as references.

| Sample | A | B | C | D |
|--------|---|---|---|---|
| DE of MD | 19 | 25 | 29 | 29 |
| Temperature of inlet air [°C] | 160 | 160 | 160 | 180 |
| Rotational speed of atomizer [rpm] | 3.0×10^4 | 3.0×10^4 | 3.0×10^4 | 1.5×10^4 |
| Mean particle size [µm] | 15.43±0.31 | 15.60±0.32 | 18.24±0.26 | 44.38±0.16 |
| Preference score | -0.07±0.81 | 0.67±0.94 | 1.13±0.62 | 0.40±1.02 |

MD: maltodextrin, DE: dextrose equivalent
Mean±standard deviation
2.7 Sensory evaluation of the odor of the powdered seasonings

The powdered seasoning is likely to be often used by dissolving it in water such as soup. However, since the smell of the powdered seasoning seems to affect consumers’ behavior to use, sensory evaluation was performed on the powder.

About 1 g of powdered seasoning was placed in an amber glass vial with a cap, and the vial was served to 15 well-informed panelists at room temperature. Preference was evaluated on a five-point hedonic scale (-2: Dislike extremely, -1: Dislike, 0: Neither like nor dislike, +1: Like and +2: Like extremely), and smell properties (shrimp-like, fragrant, burnt, rotten, and fishy odor) were also evaluated by grading the odor on a five-point intensity scale (0: Odorless to 4: Strong).

The sensory evaluation was conducted with the approval of the ethical review board of Kyoto Gakuen University, which is the former name of Kyoto University of Advanced Science.

3. Results and Discussion

3.1 Powder size

Figure 1 shows the particle size distributions of the powdered seasonings, based on which the volume–surface mean diameters were calculated. The mean and standard deviation values for triplicated measurements are listed in Table 1. The powdered seasonings A, B, and C, which were prepared at the same inlet–air temperature (160°C) and atomizer speed (3.0×10⁴ rpm), had almost the same particle size of 15–19 mm, although the DE of excipient MD was different. On the other hand, the powdered seasoning D had a large particle size (44 mm) because the atomizer speed was slow (1.5×10⁴ rpm).

Figure 2 shows the SEM images of the powdered seasonings observed under 500× magnification. The powdered seasoning prepared by adding MD with the smallest DE, i.e. the largest molecular size, had relatively few aggregates. The SEM images clearly show that the powdered seasoning D has a mean diameter larger than those of other seasonings.

3.2 Sensory evaluation

The preference scores for the seasonings A–D are listed in Table 1. The score depended on the DE of the MD used as excipient, and the seasoning prepared using MD with larger DE showed higher preference score. The powdered seasoning C, which was prepared using MD with DE=29 at the inlet–air temperature of 160°C and the atomizer–rotation speed of 3.0×10⁴ rpm, exhibited the highest palatability. This is probably because MD with larger DE forms a denser dry layer in the early stages of drying, which efficiently retained the odor components in the powdered seasoning.

Figure 3 shows the individual odor characteristics (shrimp-like, fragrant, burnt, rotten, and fishy) of the powdered seasonings A–D. The powdered seasoning C, which had the highest palatability, had the highest scores for shrimp-like flavor and fragrance, and the lowest scores for rotten and fishy odor. Among the four seasonings, the powdered seasoning A, which had a negative mean value in preference score (Table 1), had a low score for shrimp-like flavor. These observations suggest that the strength of shrimp-like flavor affected the palatability of the seasonings.
3.3 GC–MS analysis

Figure 4 shows the GC–MS chromatograms for the powdered seasonings A–D, as well as those for shrimp crackers and dried shrimp as references. The odor com-

![Diagrams showing GC–MS chromatograms](image)

Fig. 3 Odor characteristics of powdered seasonings A–D evaluated by 15 well-informed panelists. Circles and bars indicate the mean and standard deviation values, respectively.

![Diagrams showing GC–MS chromatograms](image)

Fig. 4 GC–MS chromatograms in the headspace analysis of powdered seasonings (A–D) and of crushed shrimp crackers (R1) and dried and crushed shrimp (R2). The label in the vertical axis (TIC) represents the total ion chromatogram.
powdered seasonings could scarcely be detected by GC–MS. However, the odor components could be detected when the seasonings were dissolved in water. This indicates that these components were trapped in the powders upon spray drying. It has been reported that the shrimp–like flavor is ascribed to pyridines and pyrazines formed during shrimp roasting and krill boiling [13, 14]; the aqueous residue treated under subcritical water conditions contained both pyridines and pyrazines [12]. All the powdered seasonings also contained some pyrazines, although no pyridines were detected in any of the seasonings. The reason to this remains unclear. The range in which pyrazines are detected is indicated by a dashed rectangle. The peaks at the retention times of 17.55, 22.2, 23.1, 24.05, and 24.7 seemed to be 3-ethyl-2,5-dimethylpyrazine, 2-isomethyl-6-methylpyrazine, 3-isomethyl-2,5-dimethylpyrazine, or 5-isomethyl-2,3-dimethylpyrazine, and 2-isomethyl-3,5,6-trimethylpyrazine, although the attributions have not fully identified.

4. Conclusion

Powdered seasonings with shrimp–like flavor were prepared by treating the aqueous residue from the recovery of oily components of Isada krill under subcritical water conditions at 140°C, then combining with MDs of different DEs and spray-drying the aqueous residue. Sensory evaluation of the odor of the powdered seasonings by a panel of volunteers indicated that the powdered seasoning prepared using MD with DE = 19 at an inlet-air temperature of 160°C and atomizer speed of 3.0 × 10^4 rpm had the highest preference score. GC–MS analysis revealed that all the seasonings contained pyrazines related to shrimp–like flavor.

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イサダからの水溶性残渣液の亜臨界処理と噴霧乾燥によるエビ風味調味粉末の調製

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早春に三陸沿岸で漁獲されるイサダ（学名ツノナシオキアミ、別名アミエビ）は、資源量が豊富な小型のアミ類であるが、内在性の酵素活性が強く、漁獲後短時間で品質が低下するので、食品としての利用は限定的であり、大半は釣りの撒き餌や養殖魚の餌として利用されている[1-3]。しかし、イサダはエイコサペンタエン酸やドコサヘキサエン酸、脂肪燃焼効果をもつ8-ヒドロキシエイコサペンタエン酸[5]を多く含有するため、脂溶性成分はサプリメントなどへの利用が期待されている。一方、これらの有効成分を回収する工程で大量に排出される水溶性残渣液は、現状では用途がない。

著者らは、イサダ[6-10]やその煮汁[11]を亜臨界水（常圧での沸点である100℃から臨界温度の374℃の範囲で加圧することにより液体状態を保った水）の条件下で処理すると、生臭さが大幅に低減し、香ばしいエビ風味を発現することを見出した。脂溶性成分を回収したあとの水溶性残渣液についても同様に、亜臨界処理すると、エビ風味調味液が得られることを見出し、嗜好性の高い処理液を調製する条件を明らかにした[12]。

しかし、水溶性残渣液から調製したエビ風味調味液は、冷蔵または冷凍して保存する必要がある。そこで、エビ風味調味液を噴霧乾燥することにより、調味粉末を調製する条件について検討した。粉末にすることにより、常温での保存と大幅な減容化が可能になる。

2018年に漁獲されたイサダから脂溶性の有用成分を回収したあとの水溶性残渣液を140℃で亜臨界処理し、エビ風味調味液を調製した。エビ風味調味液の固形分濃度はBrix値で15%であり、そのまま噴霧乾燥するには濃度が低い。そこで、賦形剤として、デキストロース当量（dextrose equivalent, DE）の異なるマルトデキストリン（MD）を15%（w/w）の濃度で調製したのも、喷霧乾燥し、使用したMDのDEは19, 25および29であり、熱風の入口温度は160℃または180℃、噴霧乾燥機のアトマイザ回転数は3.0×10^4または1.5×10^4 rpmとした（Table 1）。

DE 29のMDを用い、アトマイザ回転数1.5×10^4 rpm、熱風入口温度180℃で調製した調味粉末の体面積平均粒子径は44 μmであり、他の条件で調製した粉末のそれは15〜19 μmであった（Fig. 1, Fig. 2およびTable 1）。

調製した粉末の嗜好性を官能評価したところ、DEが大きい（すなわち、分子が小さい）MDで調製した粉末の嗜好性が高い傾向があった（Table 1およびFig. 3）。これは、DEの大きいMDは乾燥初期に液滴表面に形成する皮膜が緻密で、匂い成分が保持されやすいことに起因すると推測される。また、GC-MSを用い、調味粉末を溶解した液のヘッドスペース分析を行ったところ、嗜好性がもっとも高い調味粉末がもっとも強いピーク強度を示した（Fig. 4）。また、すべての調味粉末で、エビ風味を示す成分と考えられているピラジン類の生成が認められた。しかし、水溶性残渣液を亜臨界処理して得られたエビ風味調味液で検出され

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