腐敗した海産物の不快臭の除去

誌名	日本水産學會誌
ISSN	00215392
著者	川合, 哲夫 石田, 祐三郎 東田, 敏久
巻/号	56巻6号
掲載ページ	p. 1013-1013
発行年月	1990年6月

Short paper

Elimination of Unpleasant Odors of Putrefied Seafoods

Tetsuo Kawai,*1 Yuzaburo Ishida,*2 and Toshihisa Higashida*1

(Received December 1, 1989)

Suppression of fish odors arising from seafoods has frequently aimed at elimination of trimethylamine (TMA) due to its fish odor.[1] Many reactions of TMA with spices, acids, and phenol compounds have been studied,[1] however, their reactants are not well understood.

On the other hand, Vitamin U chloride (VU, an anti-ulcer factor, DL-[3-amino-3-carboxypropyl]dimethylsulfonium chloride) has been registered as a GRAS (Generally Recognized As Safe) Substance.[2] VU, with the large usage level (maximum 1000 ppm), has been allowed to be used for fish as a flavoring ingredient, in spite of its weak odor for nonvolatility. The ground for using VU, and the reaction of VU with TMA were obscure in literature.

We report here this reaction, and its application to the elimination of unpleasant odors of spoiled seafoods.

We dissolved VU (32 g, 0.16 mol) in aqueous TMA containing 70% of water (48 g, 0.24 mol) in a vessel at room temperature. In a few hours, the transparent liquid produced white masses, giving off an odor of dimethyl sulfide (DMS). After standing at room temperature for a few days, the masses were isolated and then recrystallized from water. The imbricate crystals (15 g, 62% yield) were identified as DL-methionine (Met), based on the following proof; $C_5H_{11}NO_2S$ (Found: N, 8.91; S, 21.60; Cl^-, 0.5. Calculated: N, 9.39; S, 21.49), $[\alpha]_D^{18.5}$–6.5 (C=0.8, H_2O), $[\alpha]_D^{19.2}$–1.4 (C=3.0, *N*-HCl), mp 254°C (decomp., ref. 281°C[3]), IR (KBr; 1587, 1415, 1345 cm^{-1} on a Jasco IRA-1), and NMR (δ=1.9–2.5, *m*, 2*H*; δ=2.15, *s*, 3*H*; δ=2.70, *t*, 2*H*, *J*=7 Hz; δ=3.90, *t*, 1*H*, *J*=6 Hz on a Hitachi R-24B/60 Mz). Furthermore, the crude masses showed a larger peak at δ=3.22 (*s*) than the crystals, with other peaks of Met on the NMR spectrum. The peak agreed completely with that of tetramethylammonium chloride (TAC) when an authentic was loaded on the NMR. Therefore, the reaction of VU with TMA probably occurred mainly as follows:

$$(CH_3)_2S^+(Cl^-)CH_2CH_2CH(NH_2)COOH+(CH_3)_3N \rightarrow CH_3SCH_2CH_2CH(NH_2)COOH+(CH_3)_4NCl$$

The reaction proceeded almost spontaneously even at room temperature, yielding both odorless resultants of Met and TAC.

We applied the reaction to the elimination of fishy odors from spoiled marine products. Raw shucked shrimps having no heads (ca. 4 cm length), along with raw sardines (ca. 10 cm length), were purchased from a local supermarket. After being tied individually with each thread, they were respectively incubated for 3 and 4 days at 35°C in order to be putrefied. After that, they were emitting nauseous fish and rotting odors. Each group of those ten shrimps and five sardines was suspended and immersed in a 1% VU solution (1 *l*) for 1 day. Every sample, after being picked up from the solution, gave no terrible odor, having merely a moderate odor associated with the ocean in stead. The odor was most likely caused by DMS formed from VU as a by-product. Thus, the fish and rotting odors disappeared. Immersion for 1 hr already began to suppress those odors. However, the 0.1% solution afforded little effect, and the 10% solution behaved the same as the 1% solution, so that some excess amounts of VU seemed to be required. As described above, the disappearance of fishy odors together with the generation of DMS was probably due to the reaction of VU with TMA, while, that of the rotten odors was indistinct.

We wish to thank S. Nakamura for the elementary analyses, and also M. Ishihara for the NMR procedures.

References

1) K. Mori: in "Odor of Marine Products" (ed. by C. Koizumi), Koseishakoseikaku, Tokyo, 1989, pp. 110–121.
2) B. L. Oser and R. A. Ford: *Food Tech.*, **29**, 70–72 (1975).
3) I. Chihata: in "Methionine, Cysteine, and Cystine" (ed. by The Editorial Committee for Amino Acids Series), Sekaihokentsushinsha, Osaka, 1962, pp. 10–67.

*1 Laboratory of Flavor Substances, Shiono Koryo Kaisha, Ltd., Niitakakita Yodogawaku, Osaka 532, Japan (川合哲夫, 東田敏久: 塩野香料).
*2 Laboratory of Microbiology, Department of Fisheries, Faculty of Agriculture, Kyoto University, Kyoto 606, Japan (石田祐三郎: 京都大学農学部水産学科水産微生物学教室).