Note

Cooked Odor of *Euphausia pacifica* Hansen*Kikue KUBOTA, Akio KOBAYASHI
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In the series of our research on the cooked odor of Antarctic krills (*Euphausia superba* Dana),^{1,2)} the odor of *Euphausia pacifica* Hansen (Tsunonashi-okiami in Japanese), the same family as Antarctic krills, was investigated.

Tsunonashi-okiami is one of the harvest of coastal fishery in north-east of Japan, and utilized for various processed products, not only for man's food but also food for fish feeding.

This paper reports the isolation and identification of *N,N*-dimethyl-2-phenylethylamine, which is a main constituent of cooked *E. pacifica* odor and has not been found in other *Euphausia* family.

The sample of *E. pacifica* was caught off the coast of Kinkazan, Miyagi prefecture, May 1979, and directly frozen and stored in the refrigerator below -25°C until just before the use.

The cooked odor concentrate was prepared by simultaneous distillation and extraction in a modified Likens and Nickersons apparatus.³⁾ One kg of frozen samples and 1 liter of water was refluxed for 2 hours, using 50 ml of purified diethyl ether for extracting solvent. The sample (4.8 kg) yielded 136 mg of the cooked odor concentrate (2.8 mg% in wet weight), which has a fishy odor. The concentrate was subjected to glass capillary gas chromatography, (GC)²⁾.

The result and conditions are shown in Fig. 1. Main components in the odor concentrate were peaks 1 and 2, which accounted for about 90% in the concentrate by peak area of the gas chromatogram (GLC). These two peaks were trapped by preparative GLC respectively, and subjected to spectrometric investigation.

Peak 1 was separated to two peaks on apolar column (4 mm $\times$ 3 m glass column packed with 10% SP-2100 on chromosorb AW-DMCS 60/80), used for combined gas chromatography-mass spectrometry (GC-MS). The ionizing electron voltage was 70 eV. Consequently, peak 1 was composed of ethanol (92.9%) and isovaleraldehyde (7.1%).

FIG. 1. Gas Chromatogram of the Cooked Odor Concentrate from *Euphausia pacifica* (1979).

Conditions: instrument, Shimadzu model GC-6A gas chromatograph; column, FFAP glass SCOT column (0.28 mm $\times$ 30 m); column temperature, 60°C (12 min hold) $\rightarrow 190^{\circ}\text{C}$ ($2^{\circ}\text{C}/\text{min}$); injection and detector temperature, 190°C ; carrier gas, nitrogen 2 ml/min; detector, FID.

Peak identities: (1), isovaleraldehyde and ethanol; (2), *N,N*-dimethyl-2-phenylethylamine.

The trapped peak 2 was a colorless oil and had a heavy amine-like odor, and confirmed to be consisted of single pure compound on both (GC)²⁾ and apolar column above mentioned. Mass spectra obtained by GC-MS analysis, showed the base peak at m/e 58 and the ratio of abundance of any other peaks were below 10%, even at the condition of lower ionizing voltage (20 eV). High MS showed, however, the M^{+} is 149.11831 and its molecular formula was determined as $\text{C}_{10}\text{H}_{15}\text{N}$. Because of the absence of ν_{NH} in IR spectrum, the fragment of the base peak should be $[\text{CH}_2\text{N}(\text{CH}_3)_2]^{+}$. The IR spectrum (KBr disk) also suggested the presence of aromatic nucleus (3060, 3020, 1605, 1495 cm^{-1}) and resembles to that of *N,N*-dimethylbenzylamine. Phenylethylamine skeleton was determined by CMR (100 MHz, $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 34.350, t, $\text{C}_6\text{H}_5\text{-CH}_2$; 61.549, t, $\text{CH}_2\text{-N-}$) and other peaks were reasonably assigned to *N,N*-dimethyl-2-phenylethylamine (45.403, q, $\text{CH}_3\text{-N-CH}_3$; 126.025, d, $\text{C}_6\text{H}_5\text{-R}$; 128.409, 128.625, d, $\text{C}_6\text{H}_5\text{-R}$; 140.489, s, $\text{C}_6\text{H}_5\text{-R}$). The PMR (100 MHz) data also supported the structure as follows: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 2.31 (s, 6H, $\text{CH}_3\text{-N-CH}_3$), 2.53 (m, 2H, $\text{CH}_2\text{-N-}$), 2.81 (m, 2H, $\text{C}_6\text{H}_5\text{-CH}_2$), 7.23 (m, 5H, C_6H_5). The authentic compound showed the same MS, IR and PMR spectra and had the same t_R on (GC)²⁾ under the same condition described in Fig. 1.

N,N-Dimethyl-2-phenylethylamine was first found in *Eria jarensis* as natural product in 1969⁴⁾ and has been known as a precursor of alkaloids in plants,⁵⁾ but it was never found in the literature as the odor constituent of any food stuffs.

To certify the presence of the amine in *E. pacifica* we repeated the same experiment to the newly caught

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samples of *E. pacifica* in May 1980, and found *N,N*-dimethyl-2-phenylethylamine as a predominant component in odor concentrate (81.9% calculated from peak area of GLC).

The evidence that *N,N*-dimethyl-2-phenylethylamine was also detected in the methanol extract of the fresh samples, explains that this amine in the cooked odor concentrate was not produced by heat reaction but naturally occurring compound in *E. pacifica*. The source of the amine in the fresh samples may be plant planktons, some baits for *E. pacifica*. On the other hand, since a crustacean contains a larger quantity of betain (one of quarternary amines) than other fishes. Quarternary amines may take part in the formation of this *tert*-amine. Thus *N,N*-dimethyl-2-phenylethylamine seems to be a very interesting compound with consideration of its origin, as well as the fact that the amine is a predominant and contributory component in the odor concentrate from Tsunonashi-okiami.

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