Short Paper

Occurrence of the Green Aroma Compound,
1,5-Octadien-3-hydroperoxide, in Stored
Sardine OilShun Wada^{*1,2} and Robert C. Lindsay^{*1}

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Health benefits of long-chain n-3 polyunsaturated fatty acids found in seafoods have been recently recognized to aid in the prevention of diseases such as cardiovascular and neural disorders.¹⁾ Sardine oil, which is the most abundant domestic fish oil currently produced in Japan, is prepared with conventional refining techniques, and is mainly exported to Europe. Many food industries in the world are now attempting to use fish oils as food ingredients because of potential health benefits, but many problems with fishy flavors and/or off-flavors that develop during storage still remain. These off-flavors are initiated enzymatically by lipooxygenases as well as by other chemically initiated free radical degradations of polyunsaturated fatty acids.²⁾

Among the off-flavors noted in freshly deodorized fish oils, a green aroma develops early and contributes to distinctly fishy odors. A number of green aroma compounds, nonadienal, *trans*-2-hexenal, and 1,5-octadien-3-one, were recently identified in cod liver oil by Karahadian and Lindsay.³⁾ In this paper, we report the characterization of a new aroma compound in oxidized sardine oil.

Sardine oil was obtained commercially (Asama Chem. Co., Tokyo), and was stored in cold storage (4°C) for one year after normal production in Japan. The peroxide value⁴⁾ of this sample was 35.1×10^{-3} mol/l. Aroma volatiles were collected from sardine oil samples by nitrogen purging onto Tenax GC adsorbent traps using a method described in detail elsewhere.⁵⁾ After collection, volatiles in Tenax GC traps were eluted with redistilled diethyl ether to obtain solutions of aroma compounds. Concentrated aroma compounds were then subjected to gas chromatography-mass spectrometry (GC-MS) using a Finnegan 4500 mass spectrometer fitted with SE-54 capillary column (30 m $\times$ 0.25 μ m; J & W Scientific Co., Rancho Cordova, CA). Identification of peaks in chromatograms was achieved by matching electron impact (EI; 70 eV) mass spectral data to those published in "EPA/NIH" Mass Spectral Data Base⁶⁾ and the retention indices (I_R).⁷⁾

Figure 1(A) indicates the portion of the total ion chromatogram of the oxidized sardine oil that was of interest. The peak associated with the scan number 878 ($I_R=7.30$) in Fig. 1(A) was identified as 1,5-octadien-3-hydroperoxide, a new aroma compound in fish oils. It contributes to the green-like odor and flavor of sardine oil, and was recently reported as a component contributing to the green-like flavor of soybean oil that forms oxidatively during storage.⁸⁾ The fragmentation pattern shown in Fig. 1(B) has characterizing fragments of m/z 41 ($-\text{CH}_2-\text{CH}=\text{CH}_2$), 55 ($-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$), 69 ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2$), 73 ($-\text{CH}(\text{OOH})-\text{CH}=\text{CH}_2$), 57, 39, and 67 which corresponds to the recently published spectrum for this compounds. The concentration of 1,5-octadien-3-hydroperoxide in the sardine oil sample was approximately 20 ppb. 1,5-Octadien-3-hydroperoxide has been reported to have a threshold of 0.03–0.12 ng/l

Fig. 1. Portion of total ion chromatogram (A) and fragmentation pattern (B) for green aroma in oxidized sardine oil.

* Obtained by MS Scan 878, $I_R=7.3$ (SE-54).

** C_7 and C_8 are internal standards of ethyl heptanoate and ethyl octanoate.

*** Shows scan number of MS.

(air), and to have a green geranium-like and metallic aroma.⁹⁾

Josephson²⁾ has summarized the mechanisms of oxidative degradation of eicosapentaenoic acid and other n-3 polyunsaturated fatty acids by free radical processes. It has not been established as yet whether 1,5-octadien-3-hydroperoxide would result from direct degradation of n-3 fatty acids or from some oxidative reaction involving 1-*cis*-5-octadien-3-ol. However, the hydroperoxide is easily decomposed with formation of the corresponding alcohol or ketone. Other green aroma compounds found in fish oil³⁾ were also identified, and therefore the green aroma of sardine oil reflects a combination of all of these compounds, including nonadienal, *trans*-2-hexenal, 1, *cis*-5-octadien-3-one, and 1,5-octadien-3-hydroperoxide.

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*1 Department of Food Science, University of Wisconsin-Madison, Madison, WI 53706, U.S.A. (和田 俊, ロバート C. リンゼイ: ウィスコンシン大学食品科学科).

*2 Department of Food Science and Technology, Tokyo University of Fisheries, Konan, Minato, Tokyo 108, Japan (東京水産大学食品生産学科).