Short Communication

Estimation of the Oxidative Deterioration of Fish Oils by Measurements of Nuclear Magnetic Resonance

Hiroaki SAITO

*Tokai Regional Fisheries Research Laboratory,
Fisheries Agency,**Kachidoki 5-5-1, Chuo-ku, Tokyo 104, Japan*

Received June 26, 1987

The deterioration of food caused by lipid oxidation during processing and preservation often poses serious problems. For example, some food poisonings are attributed to the toxicity of autoxidised fats and hydroperoxides. Therefore, a regulative standard based on the measurement of peroxide value (POV) is applied to vegetable and animal oils. However, this is inapplicable to fish oils because of the high content of unstable polyunsaturated fatty acids (PUFA).¹⁾ In fact, the POV of oils of dried fish often exceeds hundreds meq/kg.²⁾

This study was undertaken to devise a simple and adequate method for estimating the oxidative deterioration of fish oils during storage, and an attempt was made to use nuclear magnetic resonance (NMR) for this purpose. The autoxidation of PUFA is a free radical chain reaction, in which hydroperoxides are generally recognized as the primary major products. Hydroperoxides of PUFA are easily decomposed into a very complex mixture of secondary products with the decrease of olefinic protons.^{3~5)}

NMR absorption peaks of the olefinic protons of fish oils were found to appear at $\delta 4.9 \sim 5.8$ ppm as the relative position to that of tetramethylsilane (0.00 ppm) as an internal standard. The amount of the protons could be

calculated by integrating the peaks. The measurement of NMR is considered to be convenient for estimating oxidative deterioration and any increase of secondary products during storage, because it is known that the percentage of olefinic protons in fish oils containing a large amount of PUFA is relatively high,⁶⁾ and that the ratio (Ro) of olefinic protons ($\delta 4.9 \sim 5.8$ ppm) to aliphatic protons ($\delta 0.5 \sim 3.0$ ppm) decreases markedly as the oxidative deterioration proceeds. Therefore, the relationship between the POV and ratio (Ro) of olefinic protons was examined.

Pollack liver oil, sardine oil and their methyl esters were allowed to stand at 40°C, and POV and Ro were periodically measured.

As shown in Fig. 1, good correlation was obtained between POV and Ro. The correlation coefficients were -0.972 for pollack liver, -0.995 for sardine oil, -0.955 for the methyl ester of pollack liver oil, and -0.988 for the methyl ester of sardine oil. In addition, the NMR method was simply compared with the measurement of POV, because the operation of NMR is very easy and the quantity of the specimen necessary for analysis is quite small (less than 100 mg).

Although the regression curves for different samples were parallel, the points obtained by extrapolating the POV plots to zero differed according to oils from different species of fish. The numerical values thus obtained were 13.4 for pollack liver oil and 18.4 for sardine oil. The difference between the two values depended on the difference in percentage of the olefinic protons of PUFA that was contained in the samples. Figure 2 gives the relationship between POV and the value (Ro/p[PUFA]) obtained from dividing Ro by each original percentage of PUFA in the fish oils. This was attempted to generalize a relationship that would be applicable to fish oils of different species. For convenience, p[PUFA] can be substituted by the percentage of EPA plus DHA being most contributive to the ratio of

FIG. 1. Relationships between POV and Ro for Pollack Liver Oil, Sardine Oil, the Methyl Ester of Pollack Liver Oil, and the Methyl Ester of Sardine Oil.

FIG. 2. Relationship between POV and Ro/p[PUFA] for Pollack Liver Oil and Sardine Oil.

PUFA.

Consequently, the relationship produced a straight line, for which correlation coefficient appeared to be -0.982 . The results of this study suggest the possibility that POV could be easily determined by the fraction Ro/p [PUFA], although the validity was proved for only two kinds of fish oil in the present study, where Ro was obtained from the NMR measurements and p[PUFA] was determined by gas chromatographic analysis.⁷⁾ Since the decrease of Ro was quite small compared with the increase of POV, a very accurate measurement of NMR was required. (Most of the errors of Ro were 0.1 percent at the most.)

The applicability and limitations of this method to various kinds of fish oil are now under investigation.

REFERENCES

- 1) Kōseishōkokuji, 17 (1977).
- 2) K. Nakamura and S. Ishikawa, *Bull. Tokai Reg. Fish. Res. Lab.*, **102**, 67 (1980).

- 3) N. A. Porter, L. S. Lehman, B. A. Weber and K. J. Smith, *J. Am. Chem. Soc.*, **103**, 6447 (1981).
 - 4) W. A. Pryor and J. P. Stanley, *J. Org. Chem.*, **40**, 3615 (1975).
 - 5) S.-Y. Cho, K. Miyashita, Y. Miyazawa, K. Fujimoto and T. Kaneda, *J. Am. Oil Chem. Soc.*, **64**, 876 (1987).
 - 6) M. Ohtsuru, M. Fujii, M. Ishinaga and M. Kito, *Nippon Nōgeikagaku Kaishi*, **58**, 35 (1984).
 - 7) M. Saito, Y. Kobatake, K. Tagaya, T. Yoshida, H. Yamazaki and E. Nishide, *Jap. J. Nutr.*, **43**, 301 (1985).
-