Use of NMR to Evaluate the Oxidative Deterioration of Niboshi, Boiled and Dried Fish

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Drying has been used for many years to preserved fish; particularly in Japan, there were many kind of products which were boiled and dried. For example, boiled and dried products of small fish such as young sardines (Sardina pelamis) and Japanese anchovies (Engraulis japonica) are called niboshi, and are widely used for preparing soup stock termed dashi in Japanese.

Since these fishes as raw material contain a large amount of fat, and niboshi is generally stored for a long time because it is a seasonal product, it is always exposed to deterioration due to lipid oxidation during processing and preservation. An appropriate method for estimation of the degree of oxidative deterioration in niboshi has long been required by the processor and trader. For measuring the degree of oxidative degradation of lipids in niboshi, the peroxide value (PV) and acid value (AV) are conventionally used. The PV and AV used generally as indices of deterioration of edible oil are not always useful for evaluation of the deterioration of oil in dried and boiled marine products, because the PV increases rapidly during the active oxygen absorption period, and passes a maximum value and subsequently decreases during the propagation period of radical chain reaction. The AV hardly changes in the boiled products because the increase of AV is chiefly caused by enzymatic hydrolysis of oil, but the enzyme is destroyed during the boiling process and no longer participates in hydrolysis.7,11

On the other hand, the ratios of olefinic protons to that of aliphatic protons (abbreviated as Ro) and divinylmethylene protons to that of aliphatic protons (abbreviated as Rm) in fish oils, which can be measured by nuclear magnetic resonance (NMR) decreased steadily with elapse of storage time.4 Therefore, the use of an NMR method for estimating the oxidative deterioration of oils in niboshi was attempted.

Different samples of niboshi were prepared in the ordinary way by boiling juvenile sardines and anchovies for 30 min and drying under forced ventilation at 50°C for 18 hr. The samples were pulverized with a meat chopper into fine uniform granules and left at 20°C in contact with air throughout the experimental period (about 30 days), and the oil was periodically extracted from each pulverized sample with a mixture of chloroform and methanol (2:1) by the procedure of Folch et al.25 With a view to estimating of oil deterioration, the PV, Ro, and Rm of the extracted oil were measured.

As shown in Figs. 1 and 2, PVs of both oils extracted from sardine and anchovy niboshi increased very rapidly at the beginning of storage and reached the maximum value, and then decreased. For example, the PV in the oil of sardine niboshi increased to as much as 600 meq/kg on 3 days storage, and decreased gradually to below 250 meq/kg after 20 days, which was much the same as the value of the starting materials. This finding suggests that a simple PV measurement may be misleading in the quality judgement of oil in boiled dried products during long storage.

On the contrary, the Ro and Rm values in the measurement of NMR decreased continuously and monotonously as shown in Figs. 1 and 2. For example, the Ro decreased rapidly from 17.0% to 11.0% after in the first 3 days, while PV showed a rapid increase, then decreased gradually to 6.1% during the next 27 days, while PV decreased moderately as shown in Fig. 1.

These combined findings indicate that the PV does not always reflect the proceeding of oil deterioration in the case of niboshi, which is a typical marine dried product. The values of Ro and Rm are closely parallel to the deterioration because the oxidative deterioration generally proceeds steadily with the elapse of storage time.

Because the NMR method only estimates progress of the oxidative deterioration of oil, this method will be suitable for comparing the storage condition of boiled and dried fish, and for estimating the effects of

Fig. 1. Changes in PV, Ro, and Rm for the Oil of Sardine Niboshi.

Fig. 2. Changes in PV, Ro, and Rm for the Oil of Anchovy Niboshi.

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antioxidants added in them.
The applicability and limitations of this NMR method to the evaluation of oil in many different kinds of dried marine products should be examined in further detail. It might be an adequate method at least for measurement of the oil deterioration, *i.e.*, the quality of *niboshi*.

**References**