

SOME NOTES ON OILS EXTRACTED FROM DRIED SAURY

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The fatty oil contained in dried fish has various influences upon the quality of dried fish. Particularly the discoloration of dried fish, the deterioration of its nutritional value and the development of toxicity caused by the oxidation of oil are a matter of vital importance. According to Nonaka *et al.*,¹⁾ some carbonyl compounds formed by the oxidation of oil are responsible as the primary cause for the discoloration of dried fish. Saruya *et al.*^{2) 3) 4)} and Matsushashi *et al.*^{5) 6)} found butylated hydroxyanisole and butylated hydroxytoluene to be effective to inhibit the discoloration of dried fish. The nutritional value of oxidized oils has been studied by many authors. A recent work of Kaneda *et al.*⁷⁾ confirmed that among the oxidation products of various types from the highly unsaturated fish oil fatty acids, the peroxides show the most strong toxicity in the biological test on rat.

This study has been undertaken with the object of contributing to the improvement of the quality of dried fish. At the outset of this study, the oils extracted from the saury which had been dried to varying extents were analyzed.

1. Properties of the oils extracted from half-dried saury with a particular reference to the influence of extraction procedure on the peroxide value of oil

The half-dried saury used for this experiment was purchased at a retail shop in the city of Nagoya in middle January, 1957. This material, so far as we are informed, was produced a few days before our purchase at a fishing coast in Shizuoka-ken or Mie-ken in the following way. The fresh saury was splitted along the back. After removal of the viscera, the open-backed fish was dipped in a 3-5% solution of sodium chloride for 1-2 hr. and then exposed to the sun for 2-3 hr.

The material, fifty in number and 3,650 g. in total weight, still contained roughly 60% of water. It was cut into small pieces and divided into three portions. Oils were extracted from each portion by the following procedures.

Oil A. A 1,200 g.-portion of the material was boiled with 5 l. of water for 15 min. and the liquor was separated from the residue by decantation. The residue was again boiled with water as before. The liquors obtained by two boilings were united and allowed to settle until a creamy layer separated at the upper part. The oil in the creamy layer was collected using ether. The ether solution was dehydrated over anhydrous sodium sulfate and filtered. It required about one hour for these procedures. The ether was removed from the ether solution by heating on a water bath in the usual way, last traces of ether being removed under vacuum. The yield of oil was 21 g. or 1.8%.

Oils B_1 and B_2 . A 1,600 g.-portion of the material was dipped in 1 l. of methanol for 1 hr. at room temperature, and the methanol was removed by decantation. The residue was then soaked in 1.5 l. of ether for 24 hr. After decantation of the ether

solution, the residue was washed twice with ether using 500 cc. each time. The ether solution and washings were united, washed several times with water to remove methanol, dehydrated over anhydrous sodium sulfate, and filtered. The filtered solution was divided into two portions. From one portion, the ether was distilled off in the usual way to give the oil B_1 . From the other portion, the ether was distilled off at a temperature below about 30°C by applying vacuum from the beginning of distillation, giving the oil B_2 . The total yield of the oils B_1 and B_2 was 119 g. or 6.8%.

Oil C. A 850 g.-portion of the material was spread on a wire-netting and roasted to such an extent as to suit our accustomed meal. The roasted material weighed 645 g. or 76% of the material before roasting. The oil was extracted from the roasted material by soaking in ether, without previous dipping in methanol, followed by distilling off ether from the ether solution in the usual way. The yield of oil was 72 g. or 8.5% of the material before roasting.

Properties of these oils are given in Table 1.

TABLE 1. Properties of the Oils from Half-dried Saury

Oil	A	B_1	B_2	C
Color	Yellowish orange	Reddish orange	Reddish orange	Dark reddish orange
d_4^{20}	0.9165	0.9131	0.9123	0.9172
n_D^{20}	1.4736	1.4740	1.4738	1.4741
Acid value	5.6	10.0	8.8	10.4
Saponif. value	189.0	186.9	186.7	189.1
Iodine value (Wijs)	134.9	137.7	137.1	134.7
Unsaponifiable matter (%)	—	0.53	0.57	0.58
Hydroxyl value	—	11.7	10.4	12.3
Peroxide value (meq./kg.)	48.3	40.7	62.4	10.9
Conjugated diene (%)	1.59	1.53	1.32	1.10
Fatty acids				
Neutralization value	189.7	190.3	190.7	191.8
Iodine value	138.2	143.0	142.6	139.5
Ether-insoluble bromide (%)	36.5	37.4	36.6	—
Hexane-insoluble bromide (%)	23.4	23.1	23.1	23.0

Notes: The peroxide value was determined by the Wheeler method immediately after the preparation of oil. Although the spectrophotometric method can not be strictly applied to find the content of conjugated diene in an oil containing oxidized acids, the figures for conjugated diene in Table 1 were calculated from the absorption value, k_{233} , of the oil in *n*-heptane by applying the usual equation; conjugated diene (%) = $0.84 (k_{233} - 0.07)$.

It is seen from Table 1 that the four oils are not alike in their properties. Especially the peroxide values show a remarkable variance for four oils. The reason for this will be discussed later in this paper. Some properties other than peroxide value also show a noticeable variance for four oils. Thus, the oil A has a considerably lower acid value than other oils, while the oils B_1 and B_2 , as compared with other two oils, have a little lower saponification values and a little higher iodine values. These variances may possibly be caused by the different extraction procedures for four oils. For the preparation of the oil A, the half-dried saury was boiled with a relatively large amount of water so that a part of the free fatty acids remained, dissolved or dispersed, in the aqueous layer, giving an oil of relatively

low acid value. The oils B_1 and B_2 were prepared by dipping in methanol followed by soaking in ether. Accordingly, these two oils contain some lipid components which are soluble in methanol but not extractable with ether alone, resulting in a little lowering of the saponification value and a little elevation of the iodine value of these oils.

2. Effects of the period of sun-drying on properties of the oil extracted from sun-dried saury

Another lot (fifty in number and 3,340 g. in weight) of open-backed half-dried saury purchased at a retail shop in the city of Nagoya in late January, 1957 was cut into small pieces and divided into four portions. Oil was extracted from a portion on the day of purchase. Other three portions were sun-dried for different periods and then oils were extracted (Table 2). For the extraction of the oils D and E in Table 2, the material was first dipped in methanol and then soaked in ether, as was the case with the oil B_1 in Table 1. The oils F and G in Table 2 were prepared using ether alone.

TABLE 2. Properties of Oils Extracted from the Saury sun-dried for Different Periods

Sample	D	E	F	G
Period of sun-drying (day)	0	8	15	22
Wt. {before drying (g.)	835	835	835	835
{after drying (g.)	835	423	380	360
Yield of oil {(g.)	76	91	96	97
{(%)	9.1	10.8	11.5	11.6
d_4^{20}	0.9202	0.9412	0.9513	0.9564
n_D^{20}	1.4739	1.4759	1.4761	—
Specific viscosity (30°C)	42.2	102.7	—	—
Acid value	9.3	17.1	18.7	25.8
Saponification value	187.6	199.6	202.9	208.6
Iodine value (Wijs)	134.9	113.7	103.9	96.4
Unsaponifiable matter (%)	0.62	1.51	1.54	1.55
Hydroxyl value	9.9	31.3	51.6	54.0
Peroxide value (meq./kg.)	16.6	64.6	106.5	173.1
Conjugated diene (%)	1.91	2.33	—	—
Fatty acids				
Iodine value	143.0	118.0	105.9	101.1
Ether-insoluble bromide (%)	39.9	21.5	16.4	15.3
Hexane-insoluble bromide (%)	21.7	20.9	17.3	13.9

Notes: The material was exposed to the sun during the day time and placed indoors during the night time. The average period of sun-drying per day during 22 days was 7hr.

The oils in Table 2 have a reddish orange color which is darker for the oil extracted after longer period of sun-drying. Comparing the characteristics of oils given in Table 2, it is seen that the oxidation of oil proceeds to a larger extent as the period of sun-drying increases. The ether-insoluble bromide from fatty acids increases with the period of sun-drying, indicating that highly unsaturated acids in the oil tend to decrease by the autoxidation during sun-drying. However, the ultra-violet absorption curves (Fig. 1) for the fatty acids of the oils D and G after alkali-

isomerization under the condition of 21% KOH-ethylene glycol, 180°C and 15 min. show the characteristic maxima, $k_{374}=2.1$ and $k_{374}=1.1$, respectively, suggesting that unchanged hexaenoic acid remains, though in a small amount, even in the oil *G* extracted from the material which had been sun-dried for the longest period. Although it can not be exactly known to what extent the oil *D*, as compared with the oil from fresh saury, has already undergone autoxidation, an inspection of the characteristics of the oil *D* appears to indicate that it has already been autoxidized to a considerable extent. The oil *E* extracted from the material after sun-drying for a further eight days (actually, sun-drying for 50-60 hr.) shows a specific viscosity (30°C) which is higher by more than double, a saponification value which is higher by 12 units and an iodine value which is lower by 21 units than the corresponding values for the oil *D*. Accordingly, the oxidation of oil appears to proceed further to a marked extent during the sun-drying for eight days. Although the sun-drying of open-backed whole saury may cause the deterioration of oil to a lesser extent than the sun-drying of small pieces of fish body, like the case with our experiments, it seems advisable to restrain the sun-drying to the least allowable extent to lessen the deterioration of oil.

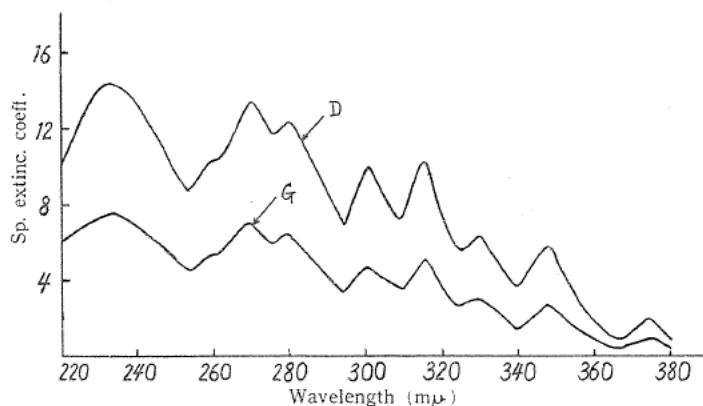


FIG. 1. Ultraviolet absorption curves for the alkali-isomerized fatty acids of the oils *D* and *G*.

3. Some notes on the peroxide value of saury oil

As shown in Table 1, four oils from the same lot of half-dried saury have widely different peroxide values. Comparing the oils *B*₁ and *B*₂, the former has a lower peroxide value of 40.7 while the latter a higher peroxide value of 62.4. The procedures for their preparation differ only in that for the preparation of the oil *B*₁, the ether was distilled off from the solution by heating on a water bath in the usual way, whereas for the preparation of the oil *B*₂, the ether was driven off at a temperature below 30°C under vacuum. Accordingly, the peroxides initially contained in the oil *B*₁ must have decomposed to a considerable extent by the heating during the distillation of ether. For the preparation of the oil *A*, the ether was distilled by heating on a water bath as in the case of the oil *B*₁. In this case, however, the oil must have undergone autoxidation during the previous boiling of half-dried

saury with water and the settling of the creamy layer containing the oil, resulting in an increase of the peroxide value of oil. Thus, the oil *A* has a little higher peroxide value than the oil *B*₁. In the case of the oil *C*, the previous roasting of half-dried saury must have caused to decompose the peroxides in oil to a marked extent, so that the oil *C* has a remarkably lower peroxide value than other oils. Kaneda *et al.*⁷⁾ also reported that the roasting of dried saury caused the peroxide value of oil to decrease by 55-70%. That the peroxides in saury oil are prone to decompose is indicated also by the following experiments. The oil *B*₂ having a peroxide value of 62.4 was kept in a tightly stoppered bottle filled with nitrogen at room temperature. After one month, the peroxide value of oil was decreased to 36.7. Two samples of autoxidized oil prepared by exposing a saury oil to the sun, having peroxide values of 186.2 and 394.1, respectively, were kept at room temperature avoiding the contact with air. After a few months, the peroxide values of these oils were found to be 150.1 and 328.1, respectively. Thus, the peroxides in saury oil have a marked tendency to decompose not only at an elevated temperature but even at ordinary temperature. Accordingly, the peroxide value for saury oil can not be taken in most cases as an index indicating the extent to which the oil has undergone autoxidation. Such may be the case not only with saury oil but also with other fish oils. In the authors' opinion, some components of the highly unsaturated acids in saury and other fish oils are highly reactive with peroxides and act as acceptors for the active oxygen in peroxides. According to this postulation, the peroxides in a vegetable oil which does not contain such reactive highly unsaturated acids are expected to be less liable to decompose. This proved to be true in the case of a sample of autoxidized corn oil having a peroxide value of 90. A portion of this oil was heated at 70°-80°C for 30 min. under an atmosphere of nitrogen. Another portion of the same oil was dissolved in ether, and the oil was recovered from the ether solution by distilling off ether. The peroxide value of oil did not show any noticeable decrease by these treatments.

Summary

1. Oils extracted from half-dried saury by different procedures showed some variance in their properties. Especially the peroxide values of oils showed a remarkable variance.

2. On examining the oils extracted from the samples prepared by a further sun-drying of half-dried saury, it was found that the oil contained in saury undergoes autoxidation to a larger extent as the period of sun-drying increases.

3. The peroxides in autoxidized saury oil are relatively unstable and tend to decompose not only at an elevated temperature but even at ordinary temperature. It has been postulated by the authors that some components of the highly unsaturated acids of saury oil are highly reactive with peroxides and act as acceptors for the active oxygen in peroxides.

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