STABILITY OF HYDROGENATED SAURY (*COLOLABIS SAIRA*) AND WHALE OILS DETERMINED BY THE RATE OF INCREASE OF THEIR PEROXIDE VALUES

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The stability of hydrogenated oil has been studied by many authors, but previous studies are concerned mostly with hydrogenated vegetable oils such as hydrogenated soybean and cottonseed oils, whereas the stability of hydrogenated fish and whale oils appears not to have been studied in detail. The production of saury oil in this country has remarkably increased due to an abundant catch of saury in recent years, and this oil in place of sardine and herring oils in former times has become most important among Japanese fish oils. Hydrogenated saury oil appears to be used not only for industrial purpose but also for edible purpose. Hydrogenated whale oil is used as an important ingredient in the manufacture of shortening and margarine in Europe and Japan.

In this study, stabilities of several series of saury and whale oil samples hydrogenated to varying degrees have been determined, and the relationship between the stability, the degree of hydrogenation and the fatty acid composition of hydrogenated oil samples has been discussed.

1. Samples of Hydrogenated Saury and Whale Oils

The following samples of hydrogenated oils were used in this study. The melting points and iodine values of these samples are given in Table 1.

Samples SA.—Supplied by the courtesy of the plant A. SA-0 and SA-0′ are saury oil samples before hydrogenation. SA-1 to SA-6 are hydrogenated oil samples obtained from a batch of SA-0 in the course of its hydrogenation. SA-1′ to SA-6′ are hydrogenated oil samples obtained from a batch of SA-0′ in the course of its hydrogenation.

Samples SB.—Supplied by the courtesy of the plant B. SB-0 is a saury oil sample before hydrogenation. SB-1 to SB-11 are hydrogenated oil samples obtained from a batch of SB-0 in the course of its hydrogenation.

Samples WB.—Supplied by the courtesy of the plant B. WB-0 is a whale oil sample before hydrogenation. WB-1 to WB-3 are hydrogenated oil samples obtained from a batch of WB-0 in the course of its hydrogenation. WB-R Nos. 1–4 are samples of edible hydrogenated whale oil regularly produced at the same plant.

Samples WC.—Supplied by the courtesy of the plant C. WC-0 is a whale oil sample before hydrogenation. WC-1 to WC-5 are hydrogenated oil samples obtained from a batch of WC-0 in the course of its hydrogenation. WC-R is a sample of edible hydrogenated whale oil regularly produced at the same plant.

WC-R′ is a sample obtained from the same batch as WC-R just before deodorization.

Samples WD.—Supplied by the courtesy of the plant D. WD-1 to WD-3 are hydrogenated whale oil samples obtained ftom a batch of whale oil in the course of its hydrogenation. WD-R Nos. 1–3 are deodorized samples of hydrogenated whale oil obtained from the same lot of whale oil as used for the preparation of WD-1 to WD-3.

Samples WE.—Supplied by the courtesy of the plant E. WE-0 is a whale oil sample before hydrogenation. WE-1 to WE-4 are hydrogenated oil samples obtained from a batch of WE-0 in the course of its hydrogenation. WE-R is a sample of edible hydrogenated whale oil regularly produced at this plant. WE-R′ is a sample obtained from the same batch as WE-R just before deodorization.

2. Stability Test

Twenty g. of each sample listed in Table 1 was placed in a 50 cc. wide-mouth bottle and kept at 50°C in a constant-temperature air bath. One g. of each sample was periodically taken out from the bottle for the determination of peroxide value. Two samples of hydrogenated soybean oil, for reference, were submitted to the same test. The peroxide value (milliequivalent/kg.) was determined by the method of Wheeler except that 1 g. of sample was weighed. The results are shown in Tables 2 A-2 D.

3. Fatty Acid Composition of Saury and Whale Oils and Their Hydrogenated Oils

TABLE 1. Properties of Saury and Whale Oils and Their Hydrogenated Oils

Sample	m.p. (°C)	Iodine value
SA-0	Liquid	152.2
SA-1	〃	143.8
SA-2	Liquid with some solid	133.7
SA-3	〃	124.8
SA-4	〃	110.8
SA-5	〃	102.3
SA-6	35.8	75.7
SA-0′	Liquid	152.9
SA-1′	Liquid with some solid	134.4
SA-2′	〃	124.3
SA-3′	Soft solid	102.2
SA-4′	〃	89.0
SA-5′	33.8	80.5
SA-6′	39.7	68.7
SB- 0	Liquid	152.2
SB- 1	Liquid with some solid	131.4
SB- 2	〃	119.1
SB- 3	Soft solid	109.8
SB- 4	〃	98.9
SB- 5	〃	94.6
SB- 6	〃	89.5
SB- 7	〃	83.6
SB- 8	37.2	70.5
SB- 9	40.7	68.5
SB-10	42.3	64.3
SB-11	44.5	53.2
WB-0	Liquid with some solid	114.3
WB-1	34.5	67.0
WB-2	35.3	64.9
WB-3	36.8	61.0
WB-R, No. 1	33.8	71.0
〃 No. 2	33.5	70.9
〃 No. 3	36.8	68.7
〃 No. 4	36.8	68.7
WC-0	Liquid with some solid	112.6
WC-1	〃	82.9
WC-2	34.0	69.1
WC-3	37.6	62.8
WC-4	39.2	59.8
WC-5	40.9	53.6
WC-R	39.1	57.0
WC-R′	39.1	57.0
WD-1	Liquid with some solid	96.0
WD-2	34.0	73.2
WD-3	40.1	55.6
WD-R, No. 1	34.9	69.6
〃 No. 2	36.5	63.7
〃 No. 3	41.0	54.3
WE-0	Liquid with some solid	111.2
WE-1	35.0	68.4
WE-2	37.0	62.9
WE-3	41.5	52.1
WE-4	44.9	41.6
WE-R	37.9	58.9
WE-R′	37.9	58.9

The fatty acids freed from the unsaponifiable matter were separated in the

usual way from several of the samples listed in Table 1. These were isomerized under the condition of 21% KOH-ethylene glycol, 180°C and 15 min. with a current of nitrogen. Ultraviolet absorption spectra of the isomerized fatty acids were measured, and the compositions of polyethenoid acids were tentatively calculated from the absorption data by applying the formula of Hammond and Lundberg.[1)]

TABLE 2 A. Increase of Peroxide Values of Hydrogenated Saury Oil Samples Kept at 50°C in an Air Bath

Sample	Peroxide value immediately before the experiment	Increase of peroxide value			
		After 8 hrs.	After 11 hrs.	After 15 hrs.	After 18.5 hrs.
SA-0	25.4	13.2	15.4	19.0	24.8
SA-1	13.2	15.4	20.7	45.5	61.6
SA-2	17.9	21.9	27.9	45.7	67.0
SA-3	12.2	10.5	12.6	22.7	33.2
SA-4	12.1	—	—	20.4	24.4
SA-5	7.5	—	—	19.1	23.0
SA-6	4.6	—	—	18.3	21.1
Hydrogenated soybean oil, No. 1	3.6	—	—	3.6	4.4
〃 No. 2	4.1	—	—	—	<1

Notes: Hydrogenated soybean oil samples, No. 1 and No. 2, had iodine values 68.6 and 62.8, respectively.

TABLE 2 B. Increase of Peroxide Values of Hydrogenated Saury Oil Samples Kept at 50°C in an Air Bath

Sample	Peroxide value immediately before the experiment	Increase of peroxide value			
		After 9.5 hrs.	After 13 hrs.	After 17 hrs.	After 22 hrs.
SA-0′	8.8	4.4	13.7	15.4	26.1
SA-1′	20.9	42.1	81.2	115.9	196.0
SA-2′	6.4	5.1	22.8	39.6	112.0
SA-3′	7.4	—	6.1	9.1	23.7
SA-4′	5.8	—	—	—	2.4
SA-5′	4.4	—	—	—	<1
SA-6′	3.3	—	—	—	<1

TABLE 2 C. Increase of Peroxide Values of Hydrogenated Saury Oil Samples Kept at 50°C in an Air Bath

Sample	Peroxide value immediately before the experiment	Increase of peroxide value			
		After 9.5 hrs.	After 13.5 hrs.	After 18.5 hrs.	After 34.5 hrs.
SB- 0	7.6	8.5	10.5	22.3	64.5
SB- 1	4.8	31.5	36.7	54.8	115.9
SB- 2	4.6	26.6	32.5	49.0	89.1
SB- 3	5.0	12.4	14.4	24.5	54.1
SB- 4	3.6	7.9	11.9	17.2	35.8
SB- 5	1.2	7.8	9.2	15.5	32.2
SB- 6	2.9	3.6	3.5	6.5	16.7
SB- 7	3.5	—	2.5	4.1	13.5
SB- 8	3.8	—	2.5	3.1	10.3
SB- 9	2.7	—	—	1.0	5.5
SB-10	2.4	—	—	—	2.8
SB-11	1.9	—	—	—	<1

TABLE 2 D. Increase of Peroxide Values of Hydrogenated Whale Oil Samples Kept at 50°C in an Air Bath

Sample	Peroxide value immediately before the experiment	Increase of peroxide value				
		After 43 hrs.	After 88 hrs.	After 160 hrs.	After 232 hrs.	After 328 hrs.
WB-0	2.1	22.9	35.6	100.7	155.2	178.9
WB-1	1.0	—	2.0	2.4	2.5	3.3
WB-2	2.7	—	—	—	—	<1
WB-3	1.9	—	—	—	—	<1
WB-R, No. 1	3.4	—	—	—	—	<1
〃 No. 2	33.9	—	9.0	49.7	120.3	205.6
〃 No. 3	3.7	—	—	—	—	<1
〃 No. 4	3.2	—	—	—	—	<1
WC-0	13.7	10.3	17.5	51.9	85.4	127.5
WC-1	17.8	—	32.7	62.0	92.5	127.8
WC-2	5.1	—	36.3	70.5	105.6	147.9
WC-3	3.9	—	2.5	32.7	61.8	122.0
WC-4	3.9	—	—	24.4	31.0	97.8
WC-5	2.8	—	—	—	—	<1
WC-R	4.7	—	—	—	—	<1
WC-R′	6.0	—	—	3.0	9.6	32.3
WD-1	3.2	19.2	36.3	68.2	95.1	122.6
WD-2	1.5	5.2	19.3	43.9	69.4	104.2
WD-3	2.8	—	—	26.6	30.9	38.7
WD-R, No. 1	1.9	—	1.2	—	—	1.7
〃 No. 2	1.9	—	—	—	—	1.4
〃 No. 3	1.8	—	—	—	—	1.2
WE-0	54.5	16.5	43.3	205.7	321.3	—
WE-1	3.7	—	—	—	—	<1
WE-2	3.7	—	—	—	—	<1
WE-3	2.7	—	—	—	—	<1
WE-4	3.1	—	—	—	—	<1
WE-R	3.0	—	—	—	—	<1
WE-R′	3.2	—	—	—	—	<1
Hydrogenated soybean oil, No. 1	10.4	10.3	25.4	49.6	77.7	104.8
〃 No. 2	6.1	—	—	—	—	<1

TABLE 3. Fatty Acid Compositions of Saury and Hydrogenated Saury Oils

Sample	Saturated acids (%)	Mono-ethenoid acids (%)	Polyethenoid acids (%)					Iodine value of the total fatty acids	
			Di-	Tri-	Tetra-	Penta-	Hexa-	Observed	Calcd.
SA-0	26.2	39.5	4.7	7.0	9.3	7.3	6.0	156.4	152.7
SA-2	28.8	44.3	6.8	6.0	6.0	3.7	4.4	137.9	124.0
SA-5	30.4	60.5	5.5	2.0	1.0	0.6	0	106.4	75.6
SA-6	33.3	66.7	0	0	0	0	0	79.5	60.0
SA-0′	23.5	39.9	5.0	6.7	9.4	7.0	8.5	156.9	162.0
SA-1′	25.8	45.8	5.4	5.5	6.6	4.8	6.1	138.9	135.5
SA-3′	28.8	61.4	5.7	2.6	0.8	0.7	0	106.4	78.5
SA-6′	33.4	66.6	0	0	0	0	0	72.7	59.9
SB-0	24.3	39.1	4.5	9.1	9.7	6.1	7.2	156.9	158.0
SB-1	26.4	44.3	4.7	6.7	7.0	5.1	5.8	136.0	137.8
SB-4	28.9	54.6	10.8	3.2	1.5	1.0	0	102.8	86.4
SB-8	34.2	65.3	0.5	0	0	0	0	74.6	59.6

In the case of saury oils and their hydrogenated oils, the saturated acids were estimated by submitting the methyl esters of total fatty acids to the permanganate acetone oxidation method, and the monoethenoid acids were calculated by subtracting the saturated and polyethenoid acids from the total fatty acids. The results are shown in Tables 3 and 4, in which the percentage for polyethenoid acids is the average of the percentages obtained, respectively, by taking pentaethenoid acids as C_{22} and as C_{20}. The calculated iodine value of the total fatty acids in Table 3 was obtained by assuming monoethenoid acids to be C_{18}.

TABLE 4. Compositions of Polyethenoid Acids of Whale and Hydrogenated Whale Oils

Sample	Polyethenoid acids (%)				
	Di-	Tri-	Tetra-	Penta-	Hexa-
WB-0	3.9	2.3	4.0	7.0	4.1
WB-3	0	0	0	0	0
WB-R, No. 1	0.3	0	0	0	0
〃 No. 2	0.4	0	0	0	0
〃 No. 3	1.2	0	0	0	0
〃 No. 4	1.2	0	0	0	0
WC-0	4.1	1.8	3.7	7.4	5.8
WC-1	5.8	0.9	0.5	0.3	0
WC-4	0.3	0.2	0	0	0
WC-5	0.1	0	0	0	0
WC-R	0	0	0	0	0
WD-1	5.9	2.8	2.1	1.8	0.6
WD-2	0.9	0	0	0	0
WD-3	0	0	0	0	0
WD-R, No. 2	0.7	0	0	0	0
WE-0	3.8	2.4	3.7	6.2	4.1
WE-2	0	0	0	0	0
WE-R	0	0	0	0	0
Hydrogenated soybean oil, No. 1	2.0	0	0	0	0
〃 No. 2	0.5	0	0	0	0

4. Discussion of Results

As shown in Tables 2 A–2 D, every oil sample used in this study has some peroxide values just before the experiment. Among the samples in Tables 2 A and 2 B, the samples SA-0 and SA-1′, respectively, have highest peroxide values. Among the samples in Table 2 D, the samples WB-R, No. 2 and WE-0 have especially high peroxide values. Thus every sample has already been at a certain stage of oxidation prior to the experiment, and the extent of the oxidation which each sample has undergone before the experiment is considered to be different for each sample. Although it may not be always reasonable to estimate the stability of such samples by the increase of their peroxide values in a definite time, an inspection of Tables 2 A–2 D shows an interesting relationship between the extent of hydrogenation and the increase of peroxide value. Thus in the case of hydrogenated saury oil samples (Tables 2 A–2 C) the increase of peroxide value becomes greater with the progress of hydrogenation at the relatively early stage of hydrogenation until it reaches

the maximum (samples SA-2, SA-1′ and SB-1), but it becomes smaller with the further progress of hydrogenation. Accordingly, the hydrogenation to a slight extent is considered to have an adverse effect on the stability of saury oil. On the other hand, the hydrogenation brings about a decrease in the content of polyethenoid acids of saury oil, excepting a slight increase for diethenoid acids, as is seen by a comparison of the samples, SA-2, SA-1′ and SB-1, and the samples, SA-0, SA-0′ and SB-0, respectively, in Table 3. This is worthy of a particular note, for it is known that the stability of vegetable oils is generally improved by hydrogenation.[2] According to a patent literature,[3] the stability of soybean oil is significantly improved even when the oil is hydrogenated under a suitable condition to such a slight extent that the iodine value is reduced only by 2–4 units. As for whale oil, the samples at a very early stage of hydrogenation are not examined in this study, but an inspection of Table 2 D shows that the hydrogenated sample WC-2 of iodine value 69.1 is found to have a greater increase of peroxide value than the sample before hydrogenation, WC-0. Hence the hydrogenation of whale oil to a slight extent is considered to lower its stability likewise the case with saury oil. The reason for this wants yet to be confirmed, but it is conceivable that some natural antioxidants occurring in saury and whale oils may undergo destruction even at the initial stage of hydrogenation and also that oil samples may become to be contaminated with some pro-oxidants, such as copper, iron and nickel, in the course of hydrogenation process.

Table 3 indicates that in the hydrogenation of saury oil the highly unsaturated acids such as hexaethenoid, pentaethenoid and tetraethenoid acids decrease with the progress of hydrogenation while the diethenoid acids show a small increase at the relatively early stage of hydrogenation. Also in the case of the hydrogenation of whale oil shown in Table 4, the diethenoid acids show a small accumulation in the course of hydrogenation, yielding the hydrogenated sample WC-1 which has a little larger content of diethenoid acids than the sample before hydrogenation, WC-0. This agrees with the fact reported in our previous study on the hydrogenation of sardine oil.[4] Among the hydrogenated saury oil samples having an iodine value below 80, the samples SA-6 (I.V. 75.7) and SA-6′ (I.V. 68.7) contain no ethenoid acids while the sample SB-8 (I.V. 70.5) contains only 0.5% of diethenoid acids. While the figures for polyethenoid acids in Table 3 are obtained on an assumption that all polyethenoid acids in the samples are alkali-isomerizable and the formula of Hammond and Lundberg is applicable to these samples, the three samples mentioned above should contain, calculating from the observed iodine values of their total fatty acids, some polyethenoid acids besides saturated and monoethenoid acids. If these polyethenoid acids are assumed entirely to be C_{18}-diethenoid acids, the percentages of C_{18}-diethenoid acids in the total fatty acids are found by a calculation from the iodine values of total fatty acids as follows: 21.6% for the sample SA-6, 14.3% for the sample SA-6′ and 17.5% (0.5% being alkali-isomerizable) for the sample SB-8. As is expected from the consideration that such diethenoid acids of the difficultly alkali-isomerizable nature affect the stability of hydrogenated oil samples, the increase of peroxide value is greater for the sample SA-6 containing a larger amount of such diethenoid acids than for the samples SA-6′ and SB-8. On the other hand, however, comparing the sample SA-6 and the sample SA-5′, the increase of peroxide value is greater for the sample SA-6 having a lower iodine value (75.7) than for the sample SA-5′ having a higher

iodine value (80.5). This is difficultly explicable on the basis of their fatty acid compositions, and is possibly due to the effect of some other factors, such as the contamination of oil samples with pro-oxidants. In the case of hydrogenated whale oils, a comparison of the increase of peroxide value for four samples, WB-3 (I.V. 61.0), WC-4 (I.V. 59.8), WD-3 (I.V. 55.6) and WE-2 (I.V. 62.9), whose iodine values do not differ greatly from each other, shows that the increase of peroxide value is largest for the sample WC-4 and larger for the sample WD-3 than for the samples WB-3 and WE-2. Among these four samples, only the sample WC-4, as shown in Table 4, contains diethenoid and triethenoid acids, though in small amounts. Hence, that the increase of peroxide value is largest for the sample WC-4 is reasonably explained on the basis of the fatty acid composition. However, that the sample WD-3 shows a larger increase of peroxide value than the samples WB-3 and WE-2 should be attributed to the effect of some other factors, such as the possible contamination of oil samples with pro-oxidant.

As for the effect of deodorization process on the stability of hydrogenated whale oil, Table 2 D shows that the increase of peroxide value is smaller for the deodorized sample WC-R than for the sample before deodorization WC-R′ so that the deodorization process appears to affect favorably the stability of hydrogenated whale oil, whereas the effect of deodorization process is not evident for the samples WE since both samples WE-R and WE-R′ show a small increase of peroxide value of nearly same level. Meanwhile the deodorized samples WD-R, No. 1 (I.V. 69.6) and No. 2 (I.V. 63.7) show a smaller increase of peroxide value than the sample WD-3 having a lower iodine value (55.6), and so it appears that the deodorization process improves in most cases the stability of hydrogenated whale oil. This is possibly caused by the removal or inactivation of pro-oxidants in the course of deodorization process. If pro-oxidants are not all removed or inactivated, the stability of oil would not be improved by the deodorization process alone. This may be the case with the samples WB-R, No. 1–4. These four samples were produced at the same plant under the same processing condition and have nearly same iodine values, and their contents of diethenoid acids are all small (Table 4), but the No. 2 sample shows a remarkably larger increase of peroxide value than other three samples. This is possibly due to some unnoticed variance in the processing condition resulting in an exceptionally high contamination of the No. 2 sample with pro-oxidants.

5. Summary

1. Several series of samples prepared by hydrogenating saury and whale oils to different degrees were kept at 50°C in a constant-temperature air bath, and the increase of their peroxide values was periodically determined. Fatty acid composition of these oil samples was also estimated, and the relationship between the stability, the degree of hydrogenation and the fatty acid composition was discussed.

2. The stability of saury oil is lowered at the early stage of hydrogenation until it reaches a minimum, and then it becomes higher with the further progress of hydrogenation. A similar tendency is also observed in the course of hydrogenation of whale oil. The reason for the lowering of stability at the early stage of hyrogenation is not exactly known, but it is possibly due to the effect of some factors, including the contamination of the oil sample with pro-oxidants such as

copper, iron and nickel, and the destruction of natural antioxidants in the oil sample in the course of hydrogenation process.

3. The stability of hydrogenated oil appears to be affected not only by its iodine value and fatty acid composition but also by some other factors, especially by the contamination of the oil sample with pro-oxidants in the course of hydrogenation process.

4. The stability of hydrogenated oil is generally improved by the deodorization process, possibly for the reason that the removal or inactivation of pro-oxidants in the oil sample is effected in the course of deodorization process.

References

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