

INTERESTERIFICATION OF CUTTLE-FISH OIL AND SOYBEAN OIL

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In the preceding paper,¹⁾ the authors studied on the interesterification of sardine oil, and examined the drying property of the oils obtained by winterization after the reaction. This paper deals with the interesterification of cuttle-fish oil and soybean oil.

1. Cuttle-Fish Oil

The sample oil used in these experiments was a refined oil which had been thoroughly dehydrated by heating at 100–110°C under a vacuum of 2 mm Hg and then filtered. It had acid value 0.86 and iodine value (Wijs method) 179.5. On gradually cooling this oil to 1°C and removing solid by suction filter, a winterized oil having acid value 0.76 and iodine value 180.6 was obtained in a yield of 97%.

One kg of the sample oil or the winterized sample oil with 0.6% of catalyst (as sodium methylate) was placed in a 2 l three necked flask equipped with a stirrer, and dry nitrogen was passed through the flask. The temperature was lowered stepwise from 25°C to 7°C in the total reaction period of 24 hours. When the temperature was lowered to 16°C after 9 hours since the beginning of the experiment, the reaction mixture became solid, so that the reaction hereafter was performed without stirring. Catalyst used throughout these experiments was a suspension of sodium methylate in xylene containing 0.11–0.07 g of sodium methylate per 1 cc. The results of experiments are shown in Table 1, in which tri-saturated glyceride is crystalline glyceride which separated on cooling a solution of 10 g of each oil in 100 cc of petroleum ether at 0°C. Although a minor amount of tri-saturated glyceride occurs in the sample oil and the winterized sample oil before interesterification, it did not separate from the petroleum ether solution. Table 1 indicates that 3.4–4.7% of tri-saturated glyceride is formed by interesterification.

TABLE 1. Properties of Interesterified Cuttle-Fish Oil (1)

	Acid value	Cloud point (°C)	Cold point (°C)	Tri-saturated glyceride (%)
{Sample oil	0.86	–4	–8	0
{Interesterified oil I	3.0	28	24	4.7
{Winterized sample oil	0.77	–8.5	–10	0
{Interesterified oil II	3.7	26	23	3.6

The interesterified oils I and II were brought to melting, and the melted oils were gradually cooled to about 5°C in the course of 20 hours. After removal of solid by suction filter, the winterized oils I_a and II_a were separated (Table 2). Satu-

rated acids in the mixed fatty acids of I_a and II_a were calculated from the amount and iodine value of solid acids obtained by means of the lead salt alcohol method on the assumption that the acid responsible to the iodine value of solid acids is oleic acid. Since the amounts of saturated acids in the mixed fatty acids of the sample oil and the winterized sample oil are 16.9%* and 15.4% respectively, the amounts of saturated acids which were removed by winterization after the reaction are found to be 8.8-7.3%. These figures are a little larger than the amounts of tri-saturated glyceride formed by interesterification, 3.6-4.7%, indicating that not only tri-saturated glyceride but also some di-saturated glyceride is removed by winterization after the reaction.

TABLE 2. Winterized Oil from Interesterified Cuttle-Fish Oil (1)

	Yield (%)	Iodine value	Saturated acids (%) based on mixed fatty acids
I_a	49	195.8	8.1
II_a	57	194.4	8.1

Interesterification for 18 hours at 25-4°C by using 0.6% of catalyst gave the results shown in Table 3. The interesterified oils I' and II' were obtained from the sample oil and the winterized sample oil, respectively. Winterization of I' and II' at 17-18°C gave the winterized oils I'_a and II'_a , respectively, as shown in Table 4. The yields of I'_a and II'_a are higher than those of I_a and II_a in Table 2, but the iodine values of I'_a and II'_a are a little lower than those of I_a and II_a . Since the mixed fatty acids of these oils obtained by winterization after the reaction still contain over 8% of saturated acids, as is the case with sardine oil reported previously, it is indicated that the interesterification under the conditions of the present experiments does not proceed so extensively that all of the saturated acids in the glyceride of the sample oils are rearranged to tri-saturated glyceride.

TABLE 3. Properties of Interesterified Cuttle-Fish Oil (2)

	Acid value	Cloud point (°C)	Cold point (°C)
I'	3.1	22.5	16
II'	2.3	22	12

TABLE 4. Winterized Oil from Interesterified Cuttle-Fish Oil (2)

	Yield (%)	Iodine value	Saturated acids (%) based on mixed fatty acids
I'_a	63	185.1	8.9
II'_a	68	188.7	8.4

The fatty acids of the sample oil before interesterification and those of the oils I'_a and II'_a were examined by spectrophotometric method, and the amounts of con-

* The content of saturated acids in this sample oil seems to be considerably lower than the average content of saturated acids in cuttle-fish oil.

jugation were estimated with the results shown in Table 5 which indicate that practically no conjugation occurs in the course of interesterification.

TABLE 5. Amounts of Conjugation

	Diene (%)	Triene (%)	Tetraene (%)	Total conjugation (%)
Sample oil before interesterification	1.47	0.15	0.08	1.70
I _a '	1.60	0.17	0.09	1.86
II _a '	1.71	0.13	0.07	1.91

A series of drying test was carried out with the winterized oils obtained from interesterified oils in Table 2, I_a and II_a, the winterized sample oil before interesterification, a sample of linseed oil for contrast, the boiled oils prepared therefrom by adding cobalt resinate, and the white paints prepared from the boiled oils and zinc oxide. The results are shown in Table 6. The oils I_a and II_a, either of raw oil, boiled oil and white paint, are superior to the winterized oil before the reaction and are comparable to linseed oil in their drying property. Also the oils I_a' and II_a' in Table 4 were found to be superior to the winterized oil before the reaction in their drying property, though they were a little inferior to the linseed oil.

TABLE 6. Drying Test

	Time for drying					
	Raw oil		Boiled oil		White paint	
	Room temp. 5-18°C	40°C	Room temp. 5-18°C	40°C	Room temp. 5-18°C	40°C
Winterized sample oil before interesterification	200	163	187	95	50	25
I _a	76	40	50	30	25	17
II _a	76	40	50	30	25	17
Linseed oil	80	45	52	32	25	18

2. Soybean Oil

The sample oil was prepared from crude extraction soybean oil of acid value 11.7 by alkali-refining followed by thorough removal of moisture. It had acid value 0.29, saponification value 194.9 and iodine value 130.5. Fifty g of sample oil added with catalyst was placed in a 150 cc gas washer, and the interesterification was performed in a similar way as described in the previous report on sardine oil. Table 7 shows the results of the experiments in which the reaction temperature was lowered from 20°C to 5°C in the total reaction period of 10 hours in the following way: 1 hr each at 20°, 16°, 14° and 12°C; 1.5 hrs at 10°C; 2 hrs at 8°C; 2.5 hrs at 5°C. Table 8 shows the results of the experiments in which the reaction temperature was lowered stepwise from 30°C to 2°C in the total reaction period of 24 hours. As is seen from both tables, the interesterification with less than about 0.5% of catalyst proceeds only to a very insufficient extent. By using more than 0.5% of catalyst, the progress of interesterification is nearly the same for both the reaction periods of 10 hours and 24 hours.

Since the cloud and cold points of the sample oil used in the above experiments are notably lower than those of an ordinary soybean oil, another sample of refined

TABLE 7. Interesterification of Soybean Oil (1)

Expt. No.	Before interesterification	Interesterified oil				
		1	2	3	4	5
Catalyst (%)	—	0.14	0.29	0.49	0.70	0.98
Acid value	0.29	1.4	2.1	2.7	3.2	4.0
Cloud point (°C)	0	3	9	17	18	18.5
Cold point (°C)	-5.5	-5	-4.5	-4	-3.5	-3.5

TABLE 8. Interesterification of Soybean Oil (2)

Expt. No.	Before interesterification	Interesterified oil				
		1	2	3	4	5
Catalyst (%)	—	0.14	0.34	0.55	0.74	1.02
Acid value	0.29	1.0	2.2	2.8	5.5	7.1
Cloud point (°C)	0	3	10	18	18.5	19
Cold point (°C)	-5.5	-5	-4.5	-4	-3.5	-3

extraction soybean oil was used in the experiments described below. This sample oil had acid value 0.41, saponification value 191.3, iodine value 133.7, cloud point -8°C and cold point -13°C . It was subjected to interesterification for 11 hours at $30-2^{\circ}\text{C}$ by stepwise lowering of the reaction temperature. The properties of interesterified oil are given in Table 9. Expt. No. 4 in Table 9 was performed in a separate vessel equipped with a stirrer. Since the interesterified oil of No. 4 has a little higher cloud and cold points than that of No. 3, the progress of interesterification seems to be accelerated a little by stirring.

TABLE 9. Interesterification of Soybean Oil (3)

Expt. No.	Before interesterification	Interesterified oil				
		1	2	3	4	5
Catalyst (%)	—	0.21	0.49	0.69	0.69	0.97
Acid value	0.41	2.2	4.4	5.8	6.0	5.5
Cloud point (°C)	-8	-7	11	13	15	13.5
Cold point (°C)	-13	-10	-6	-6	-4.5	-5.5

In order to prepare a large quantity of interesterified oil, 500 g of the sample oil added with 0.7% of catalyst was interesterified for 26 hours in a 2 l three necked flask equipped with a stirrer in an atmosphere of nitrogen, the temperature being lowered stepwise from 30°C to 2°C . As is seen from Table 10, cloud and cold points of interesterified oil are considerably higher than those of the sample oil before interesterification, while the amount of tri-saturated glyceride formed by interesterification is very small.

On removal of solid from the interesterified oil at about 5°C by suction filter, there was obtained a winterized oil of iodine value 137.7 in a yield of 85%. Since the amounts of saturated acids in the mixed fatty acids of the oil obtained by winterization after interesterification and the sample oil were determined as 8.5% and 11.2% respectively, the amount of saturated acids removed by winterization after

TABLE 10. Interesterification of Soybean Oil (4)

	Acid value	Cloud point (°C)	Cold point (°C)	Tri-saturated glyceride (%)
Sample oil	0.41	-8	-13	0
Interesterified oil	5.3	13.5	-5.5	0.35

the reaction is 2.7%, which is found to be larger than the amount of tri-saturated glyceride formed by interesterification. Accordingly, some di-saturated glyceride besides tri-saturated glyceride is removed by winterization after the reaction. As is the case with cuttle-fish oil, the oil obtained by winterization after the reaction in this case, likewise, still contains over 8% of saturated acids in the mixed fatty acids. Thus it is quite difficult to effect the interesterification so extensively as to rearrange all the saturated acids of glyceride into tri-saturated glyceride, and consequently the winterization after the reaction is not much effective to obtain a winterized oil of high unsaturation from the oils which, like soybean oil, contain originally a relatively small amount of saturated acids, because only a small proportion of saturated acids is removed by winterization after the reaction. The iodine value of the oil winterized after the reaction in Table 10 is higher than that of the sample oil before the reaction by only 4 units, and the content of saturated acids in the former oil is less than that in the latter oil by only 2.7%. Accordingly, it is expected that the both oils do not differ much in their drying property. This was verified by the results of drying test with the both oils, the boiled oils prepared therefrom and the white paints prepared from the boiled oils and zinc white. For instance, the time for drying at a room temperature of 4-10°C was 221 hours for the sample oil before the reaction, 216 hours for the oil winterized after the reaction and 77 hours for the linseed oil used for contrast.

Spectrophotometric examination on the mixed fatty acids of the oil winterized after the reaction and the sample oil before the reaction indicated 0.65% and 0.25% of diene conjugation, and 0.08% and 0.01% of triene conjugation, respectively, so that no noticeable amount of conjugation occurs in the course of interesterification.

3. Summary

1. Cuttle-fish oil and winterized oil prepared therefrom were subjected to interesterification for 24 hours by using a suspension of sodium methylate in xylene as catalyst in an amount of 0.6% as sodium methylate, the reaction temperature being lowered stepwise from 25°C to 7°C. Interesterified oils were then winterized at about 5°C, by which there were obtained winterized oils in which the contents of saturated acids in the mixed fatty acids were less than those in the oils before the reaction by 8.8-7.3%, but winterized oils had still over 8% of saturated acids. Since the amounts of tri-saturated glyceride formed by interesterification were found to be 3.6-4.7%, some di-saturated glyceride besides tri-saturated glyceride must have been removed by winterization after the reaction.

2. The amount of tri-saturated glyceride formed by the interesterification of soybean oil with 0.7% of catalyst for 20 hours at 30-2°C by stepwise lowering of the reaction temperature was found to be only 0.35%. On removal of tri-saturated glyceride together with some di-saturated glyceride by winterization of interesterified

oil, there was obtained a winterized oil having iodine value 137.7 and 8.5% of saturated acids in the mixed fatty acids. Comparing the oil obtained by winterization after the reaction and the oil before the reaction, it is found that the iodine value and the amount of saturated acids are decreased by only 4 units and 2.7%, respectively, by the winterization after the reaction. The oil obtained by winterization after the reaction was little superior to the oil before the reaction in its drying property. Thus, winterization even after the reaction is not notably effective to obtain an oil of higher unsaturation from the oils which, like soybean oil, contain originally a relatively small amount of saturated acids.

3. Conjugation of polyethylenic acids does not occur in the course of interesterification.

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Reference

- 1) Y. Toyama, S. Igarashi and T. Yamamoto: *Memoirs Faculty Engineering Nagoya Univ.* 4, 239 (1952).