

Molecular Distillation of Sperm Whale Blubber Oil

Seiichi Ishikawa, Yoshimori Omote, Hideo Kanno

1. Introduction.

Tsujimoto and Koyanagi¹⁾ report that when sperm whale blubber oil was distilled in vacuum, only 60.25% of distilled oil was obtained at a reduced pressure of 2 mm. and distilled up to 295°C, and a greater part of the glycerides remained as residue. The authors undertook this research with the presumption that it will be possible to distill a greater part of the sperm whale blubber oil by molecular distillation, and the relation between temperature and quantity of distillate was examined, together with the general characteristic of each fraction. Also, quantitative analysis of each fraction was carried on. It was of great interest to find out to what extent cholesterol, which is present in minute quantities in this whale blubber oil, is contained in each fraction, which is related with analytical distillation of vitamin D.

2. Molecular Distillation with Pot Still.

At first, molecular distillation was carried out with pot still with the object of observing the general conditions such as the extent glycerides will distill over by molecular distillation. The result of this shows that 74.7% distilled over at 130—269°C. The characteristic and cholesterol content of each fraction is as shown in Table 1.

Experiment 1. Molecular Distillation with Pot Still.

The characteristic of the sperm whale blubber oil sample was as follows: specific gravity d_4^{17} 0.8599, refractive index n_D^{20} 1.4673, acid value 1.46, saponification value 158, iodine value 60.5, unsaponifiable matter 23.5%, cholesterol content 0.15% (0.12% in free state and 0.03% as ester).

40 g of sample was used each time and distilled in a vacuum of 10^{-3}

Table 1. Molecular Distillation with Pot Still

Fraction	Temperature Range (°C)	Quantity of Distillate (g)	Quantity of Distillate (%)	Refractive Index n_D^{20}	Acid Value	Saponification Value	Iodine Value	Cholesterol %
1	130—215	6.5	16.5	1.4645	2.74	95.5	52.4	19.0
2	215—225	12.9	32.4	1.4654	0.91	100.3	54.7	20.5
3	225—245	8.5	21.2	1.4674	0.87	132.4	63.8	12.4
4	245—269	1.7	4.2	1.4697	15.34	145.3	77.0	4.1
Residue	269	10.1	25.3	1.4735	1.57	224.2	64.4	44.0

mm. The average of each trial is shown in Table 1. The temperature was measured in the still. Micro-colorimetric method using Liebermann-Burchard color reaction was used for quantitative analysis of cholesterol in each fraction.

3. Molecular Distillation with Cyclic Still.

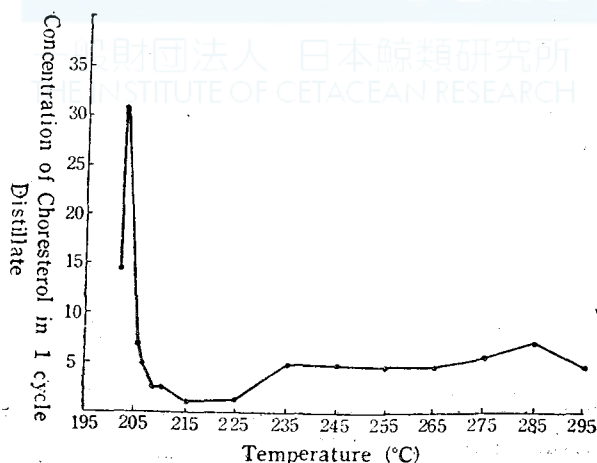
Next distillation was carried on with falling-film type cyclic still and 17 fractions were obtained between 195–295°C. Quantity of distillate was 90% of the sample, and a greater part of the distillate was obtained at 205°C, about 60% of the sample and about 75% of the distillate. The characteristic and cholesterol content of each fraction are summarized in Table 2.

On examining the result indicated in Table 2, with reference to Toyama and Tsuchiya's²⁾ report on the composition of sperm whale blubber oil, it is concluded that higher alcohol ester was the principal component of the distillate at a temperature below fraction 12, reached the maximum at 205°C and glycerides distilled over at higher temperatures (See Fig. 1).

Furthermore, observations were made of fraction No. 5 as a representative of the 205°C fraction and it was shown that the fraction was a mixture of oleyl oleate and cetyl oleate, its mol-ratio being 3 : 2.

Also, the distillation of cholesterol was at the maximum from the first distillate to the 205°C fraction, its concentration increasing again near the end of the distillation. (See Fig. 2). It is assumed that the former is cholesterol in the free state and the latter, cholesterol in ester form. The presence of cholesterol in the free state and as an ester was also verified by quantitative separation analysis using digitonin.

Fig. 1. Relation Between Temperature and Quantity of Distillate



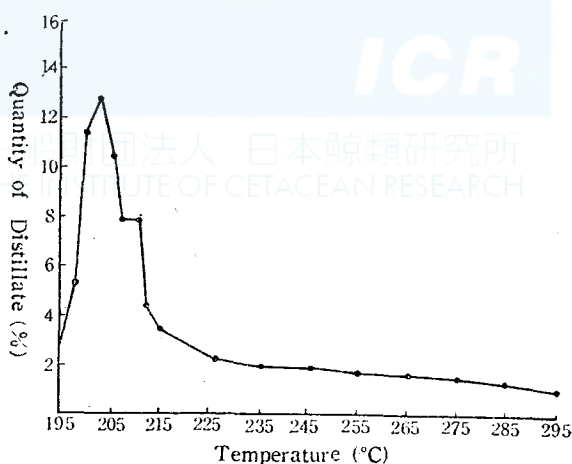
Experiment 2. Molecular Distillation with Cyclic Still.

285 g of sample was used, vacuum of 10^{-3} mm., temperature determination made at the central part of the heating oil bath within the evaporating column, and about 30 minutes were required for one cycle. Experimental result is summarized in Table 2.

Table 2. Molecular Distillation with Cyclic Still

Fraction No.	Temp ^t (°C)	Number of Cycle	Quantity of Distillation		Refractive Index n_D^{17}	Acid Value	Saponification Value	Iodine Value	Cholesterol %
			(g)	(%)					
1	195	2	6.9	2.4	1.4700	2.36	94.5	49.4	—
2	205	1	15.2	5.3	1.4678	1.06	121.8	53.6	14.6
3	205	1	31.8	11.8	1.4661	1.32	123.5	41.5	30.5
4	205	2	35.3	12.8	1.4668	0.78	136.1	64.9	6.6
5	205	2	29.1	10.4	1.4662	1.05	129.0	54.9	4.6
6	205	2	22.4	7.9	1.4666	1.10	128.2	64.6	3.5
7	205	2	22.7	7.9	1.4070	0.98	134.0	66.8	2.1
8	205	2	12.5	4.4	1.4670	1.10	125.1	67.5	2.1
9	215	2	10.1	3.5	1.4680	0.74	131.6	69.7	0.8
10	225	1	6.8	2.4	1.4680	1.69	126.5	78.1	1.1
11	235	1	6.2	2.0	1.4680	4.09	160.0	78.3	3.6
12	245	1	5.3	1.9	1.4680	4.82	151.8	76.9	4.6
13	255	1	4.8	1.7	1.4707	2.56	211.4	72.5	4.6
14	265	1	4.8	1.7	1.4710	2.44	216.4	69.1	4.6
15	275	1	4.5	1.6	1.4713	3.60	215.0	67.9	5.3
16	285	1	4.1	1.4	1.4724	2.44	221.6	67.2	6.5
17	295	1	3.1	1.1	1.4726	1.72	223.8	66.6	4.1

Fig. 2. Relation between Temperature and Quantity of Cholesterol Distillation



Experiment 3. Confirmation of Composition of Fraction No. 5.

5.4 g of Fraction No. 5 of Table 2 was used, unsaponifiable matter

extracted with ether after saponification, and from this a light yellow, semi-solid was obtained. This substance had an iodine value of 56.4, and referring to the report of Koyanagi and Tsujimoto¹⁾, its ratio, assuming that it is a mixture of cetyl alcohol and oleyl alcohol, was 2 : 3. Also an yellow oil was obtained from the saponifiable matter by ether extraction after acidifying with hydrochloric acid. The acid value of this oil was 187.8, iodine value 92.0 (theoretical value of oleic acid, acid value 190, iodine value 90) so it was confirmed that this oil was oleic acid.

4. Conclusion.

(1) By using pot still, about 80% of distillate was obtained between 195—295°C by molecular distillation of sperm whale blubber oil. Its principal component, about 75% of the entire distillate distilled over at 205°C and its components were confirmed as being oleyl oleate and cetyl oleate.

(2) Quantitative analysis of cholesterol in each fraction was carried out and it was possible to observe the presence of two maximum concentrations, which corresponds to the free state and ester state.

References

- 1) Mitsumaru Tsujimoto and Hanji Koyanagi, *J. Soc. Chem. Ind. (Japan)* **40**, 694 (1937).
- 2) Shushi Toyama and Chitaro Tsuchiya, *J. Soc. Chem. Ind. (Japan)* **30**, 519 (1927).

ICR

一般財団法人 日本鯨類研究所
THE INSTITUTE OF CETACEAN RESEARCH