Complete Recovery of Vitamin A from Molecular Distillation Residue of Whale-liver Oil

By
Yoshimori Omote

When the whale-liver oil is treated with molecular distillation, more than 100% of vitamin A (to be abbreviated A hereafter) can be recovered in a distilled concentrate, as the thermal decomposition of kitol produces A during distillation. The residual oil has an absorption maximum at 290 mμ and gives a bluish violet color with antimony tricholride. The absorption maximum which is identical with that of kitol indicates the presence of kitol, while the color reaction is considered due to the blue color by A and red by kitol. Now it is probable that the thoroughgoing molecular distillation can recover not only the remaining A in the residue, but also the newly produced A from kitol. The presumption is discussed with several fundamental experiments and the pratical thoroughgoing distillation, with the result of which this paper is concerned.

Analysis of Absorption Spectrum of Residue Oil.—Table I shows an example of absorption spectrum of molecular distillation residue of whale-liver oil. For the sake of convenience, Oser's correction[1] was directly applied to Table I, though the method strictly must be used upon the unsaponifiable fraction. The corrected coefficient, E (1%, 1 cm, 325 mμ) was much lower than that of the original. The authors' so-called AK method, which is grounded on the assumption that the absorption spectrum of sample is mainly due to A and kitol, was also applied (see Table II). Both corrected values showed

Table I. Absorption Spectrum of the Residue Oil

wave length, (mμ)	Absorption coefficient, E (1%, 1 cm.)
280	49.65
290	52.05
310	48.1
325	37.75
328	35.1
330	33.55
334	29.95

Table II. Comparison of Corrections about the Absorption Spectrum of Residue

Method	E (1%, 1 cm)	
Non-corrected	E (325) 37.75	E (328) 35.1
Oser's	E (325) 6.8	—
AK	—	E (328) 22.5

a considerable difference, the true A value probably being between them, and their mean value of ca. 15 for E (328 mμ) was taken as that of A. Kitol content was calculated with AK method to be nearly five times as much weight as A.

Distillation Time and Recovery of A.—The residual oil was distilled in a semi-micro molecular pot still at a constant temperature of 200°, the relation between distillation temperature and A recovery being studied (Table III). As Table III shows that one hour heating was able to distil A, but not enough to decompose kitol, heating time was extended (Table IV).

Table III. Distillation Time and Recovery of A (in case of short time)

Time (min.)	A Unit *	Time, total (min.)	Unit, total
0—2	17.9	2	17.9
2—5	17.9	5	35.8
5—10	11.2	10	47.0
10—15	8.97	15	56.0
15—20	3.58	20	59.6
20—25	3.58	25	63.2
25—55	7.16	55	70.4

* Cod Liver Oil Unit, cf. Experiment 2.

Table IV. Distillation Time and Recovery of A (in case of long time)

Time (hr.)	A Unit	Time, total (hr.)	A Unit, total
0.0—0.5	71.7	0.5	71.7
0.5—1.0	8.96	1.0	80.7
1.0—1.5	7.17	1.5	87.9
1.5—2.0	2.39	2.0	90.3

By making distillation curves based on data from Table III and IV one can recognize the discontinuous point near 10 minutes' heating, where A is almost recovered and kitol begins to decompose to form new A. The recovery of A, however, was about 100% after 30 mins., and 130% after 2 hrs., so the decomposition rate of kitol seemed very small at a temperature 200°.

Distillation Temperature and Recovery of A.—Using the same apparatus as above the recovery of A at discontinuously elevated temperature was measured (Table V).

As shown in Table V, the recovery of A was about 60 units at 200°, about 220 units at 270°, so the difference of 160 units may be considered to represent newly produced A from kitol pyrolysis. This

Table V. Relation between Distillation Temperature and Recovery of A

Temperature °C*	Time (min.)	Recovered A**	Time, total (hrs.)	Recovered A total
200	30	57.8	0.5	57.8
220	30	76.1	1.0	133.9
250	40	71.6	1.67	205.5
270	40	10.8	2.33	216.3

* Cf. experiment 4 ** Cod Liver Oil Unit for the source oil.

corresponds to about 2.7 times as much as first contained A. If it is assumed that kitol content in the sample was about five times as much as A and one mole of kitol can produce two moles of A[2], five times as much A as first A must be newly obtained theoretically. On the other hand, 2.5 times of A must be produced under the assumption of one mole A being obtainable from one mole kitol[3]. Considering the destructions of A during distillation the result of above experiments seems accorded with theoretical value of 5 times, nevertheless it is close to 2.5 times in case of neglecting the destruction of A.

Thoroughgoing Molecular Distillation in Falling-film Still.—Being clarified fundamental conditions about the complete distillation in a molecular pot still, two hundred grams of the sample was distilled in a falling-film still. The' sample was somewhat different from that used by the foregoing fundamental experiments, so that assays were conducted again in detail. The result of the distillation was that about two times as much as original A was obtained (Table VI).

Table VI. Recovery of A from Residual Oil with Complete Molecular Distillation in Falling-film Still

	Temperature, °C	Weight, g	Vitamin A Unit (U.S.P.)* Oshima's	Whole-oil	Oser's	AK
Original	—	(200)	30,400	31,200	15,800	26,000
Fr. 1	190—205	90	185,000	124,000	93,700	121,800
Fr. 2	205—215	40	46,800	50,000	41,200	49,200
Residual	—	70	—	8,500	133	5,500

	Recovery of Vitamin A			
	Oshima's	Whole-oil	Oser's	AK
Original	(100)	(100)	(100)	(100)
Fr. 1	266	180	268	211
Fr. 2	30.8	32.0	52	37.8
Residual	—	9.5	0.3	7.4

* Conversion factor, Oshima's Cod Liver Oil Unit was multiplied by 380, others by 1900.

Further discussions may be described below. Contents of A and kitol in the original residue was calculated with AK method, A being ca. 0.76% from (328 mμ)=13.7, kitol ca. 1.5% from K (290 mμ)=10.6. Assuming that kitol changes into A completely, and one mole kitol forms two moles A, the content of A must be about three times as much as that of original A, the result of the experiment corresponding with the calculation. Furthermore, the calculation on this experiment led to the conclusion that one mole kitol produced 1.69 moles A considering the distillate only, and 1.53 moles A considering both the distillate and residue.

Experimental Part

1. Analysis of Absorption Spectrum Curve.—Oser's correction[1] was made through the following revised equation, employing data from Table I.

$$f=7-2.625E(310/325)-4.375E(334/325)$$

Also AK method was adopted as stated in the previous paper,[2] A(328)=22.5 and K(290)=43.4 being obtained.

2. Distillation Time and Recovery of A (Short Time).—The semi-micro molecular still was of great value,in which 279 mg. of the sample was taken. The distillation was effected under the vacuum of 10^{-3} to 10^{-4} mm. and a constant oil bath temperature of 200°. As the distillate was cooled, little or no A was destroyed. At first, after two minutes' heating, the distillation was stopped and the condenser was taken out to be washed in an aliquot of benzene, which, after suitable dilution with chloroform was treated with Oshima's colorimetry to determine the blue value. Cod liver oil unit was tentatively calculated using 279 mg as the weight of oil. Similarly the process was carried on as follows (see Table II). Cod liver oil unit of the original sample was found to range 80 to 90, though the violet color prevented exact colorimetry.

3. Distillation Time and Recovery of A (Long Time).—The same conditions as Experiment 2 were adopted except for the range of heating time extended (Table III). The final residual of this experiment gave a reddish color with antimony trichloride, while the original residual oil showed bluish violet.

4. Distillation Temperature and Recovery of A.—Also the same apparatus was appreciated, but the temperature was raised step by

step (cf. Table V). In spite of its strong fluorescence, the yellow distillate at 270° had a low potency of A. And the gray black final residue gave a reddish brown color with antimony trichloride.

5. Complete Distillation with Falling-film Still.—The sample was the residual oil obtained from the Antarctic whale-liver oil, distilled in the molecular still to concentrate A in a distillate, about 30% of the total oil being distilled (The sample used in Experiment 1 to 4 was about the same as this). The still was falling-film cyclic type, the temperature was of falling liquid (Table VI). The process of distillation was not so smooth because of occasional sudden bubbling on the distilling surface.

6. Calculation of A Formation Ratio from Kitol.—Mole of A formed from one mole of kitol is expressed as follows:[2]

$$\text{A mole} = [\text{A}(328\,\text{m}\mu)\ \text{increased/K}\ (290\,\text{m}\mu)\ \text{decreased}] \times 0.786.$$

A (328) and K (290) were calculated by AK from the absorption spectrum data of each fraction, the result of which already appeared in the preceding explanation.

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Summary

Molecular distillation residue of whale-liver oil, containing vitamin A and kitol of about 1% and 5% respectively, was distilled in a semi-micro molecular pot still. At a constant temperature of 200°, about 100% of A was recovered through thirty minutes' heating, yet only 130% of A by two hours' heating; while, by raising the temperature up to 270°, approximately 400% of A could be recovered.

Furthermore, the practical thoroughgoing distillation showed that kitol in the residue was completely converted into A, the absorption curve analysis proving that one mole kitol produced two moles A.

References

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