NOTE

Extraction of Carotenes from Palm Oil. I. Molecular Distillation Method

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Crude palm oil was treated with phosphoric, poly-phosphoric, tartaric or oxalic acid at 80°C for 1 h followed by molecular distillation. Carotene fractions were collected at 215°C and 225°C under a pressure of $6\sim 8 \times 10^{-3}$ mmHg after removal of the lower boiling fractions. Carotene content was determined as β -carotene by spectrophotometry. The color number of residual oils was measured by a Lovibond Tintometer, type E.

Carotene recovery and enrichment ratio of the fractions at 215°C were 11.9~18.2% and 2.6~3.4, respectively, and the highest values of both were obtained for oil treated with poly-phosphoric acid. As for the fractions at 225°C, the highest enrichment ratio and carotene recovery were obtained in the case of oil treated with phosphoric acid, the respective values were 3.8 and 28.1%.

The loss of carotene during distillation was observed in all cases. The degree of bleaching of residual oil was inadequate in all cases.

The distillation of hybrid palm oil containing carotenes more than ordinary crude palm oil was also carried out.

1 Introduction

Carotenoids are present in palm oil in concentration which varies from 250 to 1,000 ppm*¹ according to the variety, the locality, and the degree of the maturity of oil palm trees. The carotenoids are α -, β -, and γ -carotene, xanthophylls, and lycopene, and α - and β -carotene constitute ca. 91% of them¹⁾. Based on the annual production quantity of 3.5 million tons of crude palm oil in 1984 in Malaysia²⁾ and on the assumption that the carotene content of the oil is 600 ppm, carotenes have been produced in the quantity of 2,100 tons in Malaysia in the year. However, most of all of the carotenes would have been destroyed as coloring impurities during refining.

It is well known that β -carotene possesses activity toward living bodies as provitamin A. Recently, β -carotene is being proved to have

anti-tumor activity toward the tumor induced by light³⁾, anti-cancer activity⁴⁾, and a certain activity strongly related with reproduction⁵⁾. Therefore, it is advisable that the carotenes in palm oil are extracted before the oil is undergone refining process.

Meanwhile, among all the components of palm oil, triglycerides is the most important substance, and the objective of palm oil refining is exactly to refine this substance. Hence, the extraction of carotenes from palm oil should not be the process which affects the quality of the oil. In the present study, the feasibility of molecular distillation method for both the extraction of carotenes and the refining of palm oil was studied.

Molecular distillation has already been applied to palm oil by Ueno *et al.*⁶⁾ to extract the carotenes in the oil. They submitted crude palm oil directly to molecular distillation. In the present study, crude palm oil pretreated under various conditions was submitted to molecular distillation and the results were

*1 Recently, a certain variety was found to produce palm oil containing carotenes in the concentration of 3,500 ppm.

discussed in connection with the pretreating conditions. In addition, molecular distillation of hybrid palm oil containing carotenes more than ordinary palm oil was also carried out to extract carotenes from the oil.

2 Experimental

2.1 Materials

Crude palm oil and hybrid palm oil were obtained from Lam Soon Oil & Soap Mfg. Sdn. Bhd. and United Plantations, Malaysia, respectively. Some characteristics of both oils are shown in Table-1.

Table-1 Some characteristic of crude and hybrid palm oils.

	Crude	Hybrid
% of free fatty acid (as palmitic acid)	4.5	2.5
Carotene content (ppm) (as β -carotene)	602	103 $\times$ 10
Fatty acid composition		
Lauric	0.2	Tr.
Myristic	1.1	0.2
Palmitic	43.9	25.3
Stearic	4.2	2.2
Oleic	39.8	60.1
Linoleic	9.8	12.2

All the reagents used were of GR grade.

Poly-phosphoric acid was prepared by heating the mixture of phosphoric acid (100 g) and phosphorous pentoxide (20 g) at 150°C for 5 h in an oven with occasional stirring.

2.2 Pretreatment of crude palm oil

Phosphoric, polyphosphoric, tartaric, and oxalic acids were used as pretreating agents. The amounts of the pretreating agents used are shown in Table-2.

One hundred grams of crude palm oil was heated in the presence of a pretreating agent at 80°C for 1 h with stirring. Then, the pretreating agent was removed by centrifugation or by the use of a separatory funnel. The pretreated oil was washed with hot distilled water for several times, dried at 80°C for 3 h under reduced pressure, and undergone molecular distillation.

Table-2 Amounts of pretreating agents used.

Sample No.	Pretreating agent	Amount (wt%)	Phase
P-5	Phosphoric acid	5	Conc.
P*-2	" "	2	Conc.
PP-2	Poly phosphoric acid	2	Neat
T-2	Tartaric acid	2	5 wt% aq. soln.
O-2	Oxalic acid	2	" "

* Deacidified with alkali after the pretreatment.

One hundred grams of oil was submitted to pretreatment.

2.3 Molecular distillation

A Breger's falling film semi-micro molecular still was used to obtain a distillation curve of crude palm oil. The conditions are shown in Fig.-1. A Shibata molecular still MS-300 was used for the distillation of the pretreated oils and hybrid oil. The conditions are shown in Table-3 and -4.

2.4 Analyses

2.4.1 Determination of carotene content

Carotene content was calculated as β -carotene using the following equation:

$$\text{Carotene content (ppm)} = \frac{E_{\text{obs}}}{d} \times \frac{10^6}{2610} \quad (1)$$

where E_{obs} are $E_{1\text{cm}}^{1\%}$ values at 446 nm obtained by the experiments, d is the width of the spectrophotometer cell, and 2610 is the $E_{1\text{cm}}^{1\%}$ value of pure β -carotene at the same wavelength⁷⁾.

The measurement of absorption spectra in visible region were done by using a HP 7550 UV-VIS Spectrophotometer with 1 cm quartz cells. Purified isooctane was used as a solvent.

2.4.2 Determination of tocopherol content

Total tocopherol content was determined under the same analytical conditions as those reported by Tanabe *et al.*⁸⁾. The calibration coefficients of individual tocopherols obtained by Tanabe *et al.*⁹⁾ were used.

2.4.3 Determination of color number

The residual oil after distillation was heated at 65°C to melt uniformly, and a portion was transferred into a cell (width: 2.54 cm). The color number of the oil was immediately determined by the use of a Lovibond Tintometer type E.

3 Results and Discussion

3.1 Distillation curve

Prior to the distillation of the pretreated oils, crude palm oil was distilled in the temperature range from 100°C to 240°C at intervals of every 10°C to obtain a distillation curve (Fig.-1). In Fig.-1, recovery curves of free fatty acids, of total tocopherols, and of total carotenes calculated as β -carotene are also shown. The recovery curve of free fatty acids was obtained on the basis of the acid values of individual fractions.

As can be seen, the distillation curve has two peaks. The first peak appears at 110°C. This peak is attributable to the distilling of free fatty acids, since the position of the peak and slopes are consistent with those of the recovery curve of free fatty acids. The second peak which locates at 200°C is probably due to the distilling of partial glycerides. Tocopherols come out in the temperature range between 140°C and 200°C. The weight of distillate increases steeply at temperature higher than 200°C. The increase in the weight of distillate may be due to the distilling of triglycerides.

Fig.-1 seems to indicate that the intention of raising carotene recovery leads to lowering the enrichment ratio of carotenes, or *vice versa*. Since one aim of the present study is to obtain

Starting oil: AV 9.8, tocopherols 650ppm
(100g) Carotenes 418ppm as β -carotene
Pressure: $7-9 \times 10^{-3}$ mmHg
Apparatus: Breger's falling film molecular still

Fig.-1 Distillation curve of crude palm oil.

carotene fractions with higher values of recovery and enrichment ratio, it is difficult to choose the temperature for the removal of lower boiling fractions and the collection of carotene fractions. In the case of the pretreated oils, the temperatures of 215°C and 225°C were selected for the collection of carotene fractions, and the lower boiling fractions were removed at 160°C and 180°C.

3.2 Distillation of the pretreated oils

Each of phosphoric, polyphosphoric, tartaric, and oxalic acids was used as pretreating agent in the present study. The main purpose of the

Table-3 Recovery of carotenes from pretreated crude palm oils by molecular distillation.

Apparatus: Shibata MS-300 molecular still.
Pressure: $6-8 \times 10^{-3}$ mmHg.

Sample No.	Starting oil	Fraction at 215°C			Fraction at 225°C			Residue		
	Wt. (g) TC conc.*	Wt. (g) TC conc.*	Rec.** %	E.R.***	Wt. (g) TC conc.*	Rec. %	E.R.	Wt. (g) TC conc.*	TC remained %	Color**** No.
P-5	50.0 49.7*	2.3 129*	11.9	2.6	3.7 189*	28.1	3.8	37.5 23.2*	35.0	Y20 R 7
P-2 ^{a)}	51.0 58.6*	2.0 193*	12.9	3.3	3.5 199*	23.3	3.4	41.2 22.4*	30.8	Y32 R 4
PP-2	49.0 44.7*	2.7 150*	18.4	3.4	3.5 145*	22.8	3.2	34.9 20.7*	32.9	Y40 R 4
T-2	49.6 51.4*	2.7 126*	13.3	2.5	3.6 155*	21.9	3.0	37.0 21.3*	30.9	Y35 R 5
O-2	50.4 53.3*	2.5 156*	14.5	2.9	3.5 141*	18.4	2.6	35.4 18.7*	24.6	Y23 R 4

* Total carotene concentration calculated as β -carotene $\times 10^{-1}$ ppm.

** Carotene recovery. *** Enrichment ratio of carotenes.

**** Color numbers were obtained by use of Lovibond Tintometer type E with 2.54 cm cell.

a) Deacidified with alkali after pretreatment.

use of the pretreating agents is to remove metal ions, particularly, iron ions from crude palm oil, since the deterioration of carotenes is accelerated by the presence of iron ions at higher temperature¹⁾. Phosphoric¹⁰⁾, tartaric¹⁰⁾, and polyphosphoric¹¹⁾ acid were used for this purpose. Oxalic acid was used as a decoloring agent for chlorophyll pigments¹²⁾.

The results of the distillation of the pretreated oils are summarized in **Table-3**.

The carotene concentration of starting oil, or pretreated oil, depends on the pretreating condition, but this will be discussed in another paper¹³⁾.

In the case of sample P-5, the carotene concentration of the fraction at 215°C is 1,290 ppm, accordingly, the enrichment ratio becomes $2.6 (=1,290/497)$. The carotene recovery of the same fraction is 11.9% $\{=(1,290 \times 2.3 \times 100)/$

$(497 \times 50)\}$. The amount of carotenes remaining in the residue corresponds to 34.5% of that of the starting oil.

As shown in **Table-3**, among the fractions at 215°C, the highest value of enrichment ratio was obtained in the case of PP-2, and the value was 3.4, which was followed by that of P-2. The recovery of carotenes was the highest in the case of PP-2, and the value was 18.2%. Meanwhile, among the fractions at 225°C, the highest enrichment ratio was obtained in the case of P-5, and the value was 3.8, being followed by that of P-2. As for carotene recovery, the highest value was 28.1%, and the value was obtained in the case of P-5.

Regarding the total of the carotene recoveries at 215°C and 225°C, the values of P-5 and PP-2 are almost the same and the highest, both values were *ca.* 40%. The next highest

Table-4 Recovery of carotenes from hybrid palm oil by molecular distillation.

Apparatus : Shibata MS-300 molecular still.

No.	Conditions		Weight (g)	Total carotenes* ($\times 10^{-1}$ ppm)	E.R.**	Recovery (%)
	Temp. (°C)	Pressure ($\times 10^{-3}$ mmHg)				
HP-1-0	—	—	100.0	110	—	—
HP-1-1	180	15	2.1	—	—	—
HP-1-2	220	10	3.4	366	3.3	11.2
HP-1-3	230	10	3.2	437	4.0	12.7
HP-1-4	240	10	3.6	264	2.4	3.7
HP-1-R	—	—	82.6	18.9	—	14.2
						Total 41.8
HP-2-0	—	—	100.0	103	—	—
HP-2-1	180	10	2.9	—	—	—
HP-2-2	235	10	4.2	324	3.1	13.2
HP-2-3	235	15	1.7	255	2.5	4.2
HP-2-4	235	10	1.2	400	3.9	4.7
HP-2-R	—	—	82.2	30.2	—	24.1
						Total 46.2
HP-3-0	—	—	100.0	103	—	—
HP-3-1	140	15	1.5	—	—	—
HP-3-2	240	13	4.0	268	2.6	10.4
HP-3-3	240	10	2.0	352	3.4	6.8
HP-3-4	240	10	2.0	312	3.0	6.1
HP-3-R	—	—	86.2	31.0	—	25.9
						Total 49.2

* Calculated as β -carotene.

** Enrichment ratio of carotenes.

value was *ca.* 36% which was obtained in the case of P-2. O-2 gave the least value of *ca.* 33%.

The total of the percentage of recovered and remaining carotenes does not reach 100% in every case. This indicates that a certain amount of carotene in starting oil is lost during distillation. The degree of the loss of carotene during distillation can not be accurately estimated because the weight of individual residues are different as shown in **Table-3**, but the loss of carotene increases in the following order: P-5 $\cong$ PP-2 < P-2 = T-2 < O-2. The order is possibly due to the difference in the degree of the removal of iron ions in crude palm oil.

The color numbers of the residues were those shown in the right column of **Table-3**. In every case, the color of the residue was certainly improved comparing with that of corresponding starting oil, but the degree of bleaching was still inadequate from practical point of view.

3.3 Distillation of hybrid palm oil

It is of interest to extract carotenes from hybrid palm oil, because the oil contains carotenes in about one and a half or two-fold concentration of ordinary crude palm oil. In the present study, hybrid palm oil without pretreatment was subjected to molecular distillation under various conditions. The results are shown in **Table-4**.

As can be seen, the pressure is slightly higher than that in the case of the distillation of pretreated crude palm oils, but the following results were obtained.

a) The carotene concentration of distilled fractions are higher than those of pretreated crude palm oils, reflecting the higher carotene concentration of hybrid palm oil.

b) The value of enrichment ratio of carotenes are almost the same as those obtained through the distillation of pretreated crude palm oils.

c) The loss of carotene during distillation is larger than that in the case of the distillation of pretreated crude palm oils.

The larger loss of carotene is considered to be partly due to the lack of the removal of iron ions by pretreatment and the higher distillation temperature.

In summary, the pretreatment of crude palm oil with phosphoric or polyphosphoric acid was effective to protect carotenes against deterioration during distillation. The values of enrichment ratio were lower than the aimed value of 10 fold concentration of starting oil. The degree of bleaching of residual oils was also inadequate.

Because of the difference in analytical method, no effort is done in comparing the present data with those obtained by Ueno *et al.*⁶⁾.

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カロテンのパーム油からの抽出 (第1報)

分子蒸留法

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パーム原油をリン酸、ポリリン酸、酒石酸、及びシュウ酸のおのおのをい 80°C, 1 h 処理し、蒸留に供した。カロテン留分は、140°C 及び 180°C で低沸点留分を除いたのち、 $6\sim 8\times 10^{-3}$ mmHg の圧力下 215°C 及び

225°C で捕集した。カロテン含量は分光光度法によって β -カロテンとして求めた。残油の色数はロビボンデ E 型色度計により測定した。

215°C 画分のカロテン回収率及び濃縮倍率はそれぞれ 11.9~18.2% 及び 2.6~3.4 で、両者の最高値はポリリン酸処理油のとき得られた。225°C 留分についてはリン酸処理油が 28.1% 及び 3.8 と回収率及び濃縮倍率それぞれの最高値を示した。どの処理油の場合でも蒸留中にカロテンが一部消失することを認めた。残油の脱色の程度はいずれも不十分であった。通常のパーム原油よりカロテンを多く含有しているハイブリッドパーム油の蒸留も行った。

話しながら学ぶ化学英語

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