Technical

Tocopherol Contents of Nine Vegetable Frying Oils, and Their Changes under Simulated Deep-Fat Frying Conditions

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ABSTRACT

The tocopherol contents and active oxygen method values of nine vegetable oils were determined and compared before and after the oils were treated under simulated deep-fat frying conditions. The saturated oils, coconut and palm, had much higher initial active oxygen method values than the unsaturated oils, soybean, safflower, etc., but the treatments caused a much sharper decrease of the active oxygen method value in saturated oils than in unsaturated ones. The ratio of tocopherol loss after treatment is also much greater in the saturated oils than the unsaturated ones. A similar tendency was observed when the saturated oils enriched with commercial tocopherol mixture were treated under the same conditions.

INTRODUCTION

Each vegetable frying oil has a particular stability against autoxidation, depending upon the composition of fatty acids and the content and composition of tocopherol (Tocol) in it. When used in deep-fat frying, the oils does not only deteriorate as reactions, such as thermal oxidation and hydrolysis, proceed but also loses Tocol and causes a decrease of its stability. This is an important problem connected with the shelf-life of fried foods.

Although much information is available on the deterioration of frying oils (1-17), few works have been done on the changes of Tocol content during deep-fat frying (18-20). Recently, Pokorny et al. (21) have reported the changes of Tocol content in soybean and sunflower oils treated under deep-fat frying conditions and showed that Tocol destruction proceeded according to the kinetics of a first-order reaction, and the rate of Tocol destruction was increased by the addition of acids, such as citric, ascorbic, palmitic, and phosphoric.

Tocol contents in edible oils were determined by several investigators (22-25). In this paper, Tocol contents of nine vegetable oils normally used as frying oil in Japan were determined. The relation between Tocol content and autoxidative stability of the oils before and after frying was examined.

EXPERIMENTAL PROCEDURES

Frying oils: Nine vegetable oils–soybean, rapeseed, rice bran, corn, cottonseed, safflower, oleic safflower, palm, and coconut–were commercially refined, bleached, and deodorized, and they contained no antioxidants, except 20 ppm of citric acid. As shown in Table I, their general properties are compatible with those of oils commonly used. The purity of commercial tocopherol mixture (M-Tocol) was ca. 80%, and its composition was α-Tocol 8.5%, γ-Tocol 57.8%, and δ-Tocol 33.7%. The purity of dl-α-Tocol was ca. 100%.

Analytical procedures of Tocol: Tocol was determined by Slover's method (25) slightly modified by us. Several grams of an oil sample (depending on the Tocol content of each oil) was saponified with a mixture of potassium hydroxide and pyrogallol, and unsaponifiable matter was extracted with ether. An aliquot of this solution (corresponding to ca. 1 mg of Tocol) was subjected to thin layer chromatography (TLC). The conditions of TLC were as follows: plate, 0.5 mm thickness of Kieselgel HF_{254}; developing solvent, benzene. The bands of Tocols from α- to δ-Tocol, detected by an ultraviolet lamp, were scraped off in the lump from each plate and extracted with ethanol after the addition of squalane (0.1 mg) as an internal standard for gas liquid chromatography (GLC). After concentration, the ethanol solution was injected for analysis by GLC. Only in the case of rice bran oil, α-Tocol and other Tocol bands were scraped off separately, and subsequent treatment was done in the same way as described above. This was because the bands corresponding to γ- and δ-Tocols contained substances interfering the α-Tocol analysis by GLC. The conditions of GLC were as follows: apparatus, Shimadzu GC-5A gas chromatograph equipped with flame ionization detector (FID); column, 0.3% Silicon GE-SE 30, 200 cm glass column; column temperature, 235 C; flow rate of nitrogen, 50 ml/min. Correction factors for correcting areas in response variations and analytical losses were as follows: α-Tocol 1.42, γ-Tocol 1.33, and δ-Tocol 1.34.

In addition to the Tocol content which was determined by TLC-GLC method described above, the amount of total reducing substances in unsaponifiable matter was also determined by Emmerie-Engel's colorimetric method by using dl-α-Tocol as a standard and defined as "total Tocol by EE method." In the case of autoxidized oil having a high peroxide value, the determination was done after heating at 210 C under reduced pressure to remove interfering substances (27). The reason why total Tocol content by EE method was determined in addition to that by TLC-GLC, was based on the prediction of the presence of reducing Tocol dimers in the treated oils.

Apparatus and method of simulation of deep-fat frying: The experimental apparatus, including the continuous water spraying and heating system (16,17), is shown in Figure 1. The experimental conditions were as follows: 400 g of oil was placed in stainless steel beaker (A) and heated by pipe and base heaters (B,G) and maintained at 180 ± 2 C by pipe heater and thermister temperature controller (F,I). The lower layer of the oil was gently agitated by magnetic stirrer (C,H) to prevent the over heating at heat transfer surface. One hundred grams of water/hour was discharged continuously from glass sprayer (D) as a jet stream at a point on the surface of the oil. The jet stream was produced by the pressure from the nitrogen bomb (M), and, at the same time, the nitrogen gas exerts a pressure to volumetric cylinder (K) and glass bottle (L) to maintain the water in the bottle at a given level. The sprayed water flows down into the oil layer, dispersing homogeneously, but very rapidly vaporizes out from the oil layer by receiving the

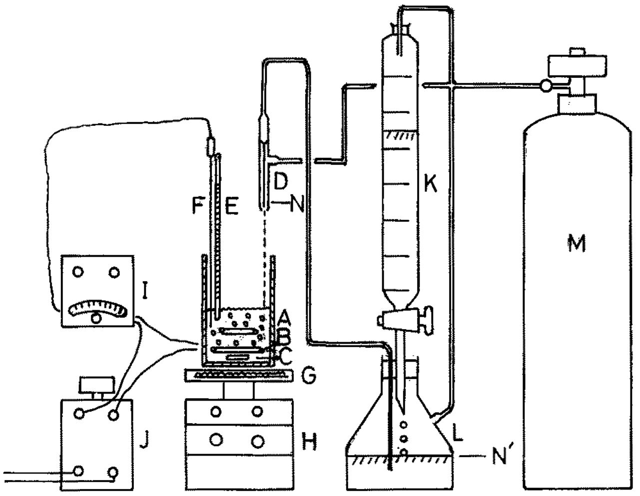

FIG. 1. Apparatus for the continuous water spraying and heating system. A = stainless steel beaker, B = pipe heater, C = stirring bar, D = glass sprayer, E = thermometer, F = thermister element, G = base heater, H = magnetic stirrer, I = thermister temperature controller, J = volt slider, K = volumetric cylinder, L = glass bottle, M = nitrogen gas bomb, and N and N′ are maintained at the same level.

supply of heat from surrounding high temperature oil. These conditions simulate deep-fat frying. The other main factors affecting the rate of fat deterioration were as follows: specific surface area of oil exposed to air, 0.159 cm^2/g; rate of water vaporization, 25 g/100g.oil/hr. Oil samples were subjected to the examination after 2, 5, and 10 hr treatments.

RESULTS AND DISCUSSION

Tocol contents in nine oils, which were determined by TLC-GLC and EE methods, are shown in Table I. Large differences were not observed in Tocol contents measured by the two different methods, except in the case of rice bran and palm oils. This suggests that other reducing substances in addition to Tocol are present in the two oils. Tocol contents in soybean, corn, and cottonseed oils were the highest, while those in palm and coconut oils were the lowest. Tocol contents in rapeseed, rice bran, safflower, and oleic safflower oils fall between the two groups described above. The composition of Tocol isomers differed from one another, that is, rice bran, cottonseed, safflower, oleic safflower, and palm oils had α-Tocol as their main ingredient, whereas soybean, rapeseed, and corn oils had γ-Tocol.

In spite of the lower content of Tocol, coconut and palm oils had higher initial active oxygen method (AOM) value than soybean, rapeseed, rice bran, cottonseed, and safflower oils. This is because the former oils had higher saturated ones in their fatty acids.

General properties, Tocol content, and AOM value of each oil treated under the simulated deep-fat frying conditions for 10 hr are shown in Table II. The most remarkable difference observed between saturated and unsaturated oils is the decrease of their AOM value after the treatment. The AOM value of palm and coconut oils dropped drastically after the treatment, but the degree of AOM value drop in the unsaturated oils was relatively small. Thermal oxidative deterioration, as indicated by the changes in iodine value and viscosity increase, however, was larger in unsaturated oils than in saturated oils. Therefore, the decrease in AOM value of the treated oils was mainly dependent upon the decrease of their Tocol contents. As shown in Table II, a large amount of Tocol remained in the unsaturated oils, but only a small or trace amount of Tocol remained in palm and coconut oils. The residual ratio of Tocol in the treated oils increased in proportion to the degree of unsaturation of oil, being largest in safflower oil, the most unsaturated oil, followed by soybean oil. This was further confirmed from the fact that, although safflower and oleic safflower oils have almost the same content and composition of Tocols as shown in Table II, the former was superior to the latter in the amount of Tocol remaining after the treatment. These results indicate that Tocols in unsaturated oils are more stable than those in saturated oils under the simulated deep-fat frying conditions.

The residual ratio of Tocol was also changeable due to difference of Tocol isomers. Comparing corn and cottonseed oils having almost the same unsaturation, the former which has γ-Tocol as the main ingredient was much smaller in the residual ratio than the latter, which has α-Tocol. Pokorny et al. (21), however, obtained experimental results contrary to ours in the oxidation of soybean and safflower oils.

As shown in Table III, Tocol content and AOM value of palm and coconut oils enriched with M-Tocol decreased very rapidly when they were treated under the same conditions. This was similar to the result of unriched oils.

TABLE I

General Properties of Oils Used in the Test

	Soybean	Rapeseed	Rice bran	Corn	Cottonseed	Safflower	Oleic safflower	Palm	Coconut
Acid value	0.06	0.07	0.09	0.06	0.06	0.06	0.05	0.05	0.03
Iodine value	133.2	107.8	109.3	108.4	110.0	150.2	85.2	52.1	9.2
Peroxide value[a]	0.7	0.6	1.3	1.5	1.2	0.3	1.1	0.8	0.5
Total carbonyl value[b]	8.8	3.7	9.3	4.8	15.2	10.9	4.9	6.4	2.8
Lovibond color Y/R[c]	6/0.8	13/1.1	20/2.7	10/1	11/1	5/0.5	3/0.3	14/1.2	3/0.3
Fe (ppm)	0.80	0.92	0.70	0.85	0.60	0.50	0.88	0.58	0.40
Cu (ppm)	0.04	0.04	0.06	0.04	0.02	0.03	0.08	0.04	0.02
Total Tocol (TLC-GLC)[d]	66.8	37.8	38.8	85.7	62.6	33.0	34.2	18.9	1.7
α-Tocol	4.8	13.0	32.3	20.4	38.2	28.1	31.6	12.4	0.5
γ-Tocol	47.1	25.2	6.1	65.2	25.1	3.4	2.5	6.5	0.5
δ-Tocol	12.7	Trace	Trace	Trace	Trace	1.2	Trace	Trace	0.5
Total Tocol (EE)[e]	72.3	44.1	83.0	93.8	68.2	35.1	37.3	38.5	5.4
Active oxygen method value (hr)	11.5	19.2	17.5	19.0	15.5	8.0	27.3	45.0	220.0

[a] meq/kg.

[b] meq/kg, Henick's method (26).

[c] 133.5 mm cell.

[d] mg/100 g.

[e] EE = Emmerie-Engel's colorimetric method.

TABLE II

General Properties of Oils Treated under Simulated Deep-Fat Frying Conditions for 10 Hr

	Soybean	Rapeseed	Rice bran	Corn	Cottonseed	Safflower	Oleic safflower	Palm	Coconut
Acid value	0.31	0.55	1.02	0.29	0.16	0.27	0.28	0.39	0.73
Iodine value	127.6	104.0	107.1	104.9	107.2	142.7	82.5	49.5	8.3
Total carbonyl value	40.0	32.2	32.1	41.2	60.3	49.9	34.3	44.0	30.8
Lovibond color Y/R	16/1.9	20/2.9	30/7.5	15/2.3	18/2.8	13/1.0	12/1.2	13/1.5	10/0.9
Viscosity increase (%)[a]	20.7	18.6	9.7	15.4	11.4	17.8	11.5	10.7	3.4
Fe (ppm)	0.80	0.90	0.80	0.95	0.60	0.70	0.80	0.95	0.40
Cu (ppm)	0.04	0.04	0.08	0.04	0.03	0.04	0.08	0.04	0.03
Total Tocol (TLC-GLC)[b]	53.6	25.2	27.5	41.0	47.2	30.0	17.3	6.2	0
	(80.2)[c]	(63.7)	(72.0)	(53.5)	(74.7)	(91.2)	(50.0)	(32.6)	(0)
α-Tocol	4.4	12.0	25.0	13.1	30.8	24.6	15.6	4.0	0
γ-Tocol	37.8	13.2	2.5	27.9	16.2	3.0	1.7	2.1	0
δ-Tocol	11.5	0	0	0	0	2.4	0	0	0
Total Tocol (EE)[d]	53.1	26.5	61.1	52.5	48.7	27.1	16.0	9.2	Trace
	(73.5)	(60.0)	(73.3)	(55.9)	(71.4)	(77.5)	(43.2)	(24.0)	(0)
Active oxygen method value (hr)	6.0	8.0	11.5	8.3	9.0	4.0	7.5	4.5	8.2

[a] Increasing ratio of viscosity in treated oils to that of original oils.

[b] mg/100 g.

[c] Figures in parentheses show the ratio of Tocol content remained in treated oils to that of original oils.

[d] EE = Emmerie-Engel's colorimetric method.

TABLE III

Changes of Tocol Content and Active Oxygen Method Value in Palm and Coconut Oils Enriched with 0.04% M-Tocol and Treated under Simulated Deep-Fat Frying Conditions

	Tocol content (mg/100 g, EE[a])				Active oxygen method value (hr)			
	Treating time (hr)				Treating time (hr)			
	0	2	5	10	0	2	5	10
Palm oil	61.5	23.5	16.2	9.0	60.0	30.5	15.2	8.0
		(38.2)[b]	(26.3)	(14.6)				
Coconut oil	37.8	15.3	3.0	1.0	535.0	380.0	25.0	14.5
		(40.5)	(7.9)	(2.6)				

[a] EE = Emmerie-Engel's colorimetric method.

[b] Figures in parentheses show the ratio of Tocol content remained in treated oils to that of original oils.

TABLE IV

Changes of Tocol Content and Peroxide Value in Soybean and Enriched Coconut Oils Treated under Active Oxygen Method Conditions

		Treating time (hr)						
		0	5	10	15	20	30	50
Tocol content (mg/100 g, EE[a])	Soybean oil	72.3	71.2	58.2	33.8	8.5	-	-
			(98.5)[b]	(80.5)	(46.7)	(11.8)		
	Enriched coconut oil	37.8	33.1	30.8	30.4	30.0	29.2	28.5
			(87.5)	(81.6)	(80.5)	(79.5)	(77.2)	(75.4)
Peroxide value (meq/kg)	Soybean oil	0.27	1.5	56.7	155.6	374.5	-	-
	Enriched coconut oil	0.15	0.25	0.30	0.35	0.40	0.57	0.75

[a] EE = Emmerie-Engel's colorimetric method.

[b] Figures in parentheses show the ratio of Tocol content remained in treated oils.

On the other hand, Tocol in enriched coconut oil was more stable than those naturally present in soybean oil after a long period under the conditions of the AOM test without severe heating, although the Tocol in soybean oil was more stable initially (Table IV).

Evans et al. (28) obtained similar results on the oxidation of soybean and partial hydrogenated soybean oils and showed that the initial rate of Tocol loss in the hydrogenated oil was greater than in the unhydrogenated oil until the peroxide value accumulated to a peroxide level of ca. 50. Frankel et al. (29) also reported that Tocol loss during autoxidation was much smaller in the highly unsaturated vegetable oils than in cottonseed oil and lard, suggesting that the hydroperoxide formed in highly unsaturated oils decomposed rapidly before they reacted with Tocol.

The mechanism of Tocol destruction under the simulated deep-fat frying conditions was thought to be similar to one described by Evans et al. (28) and Frankel et al. (29).

The reasons for a rapid Tocol destruction in saturated oils under the simulated deep-fat frying conditions are as follows: on autoxidation at a lower temperature, saturated oils are very stable, for example, the rate of oxygen absorption in methyl linoleate at 100 C is about one hundred times of that in methyl stearate (30). On the other hand, on thermal oxidation at a higher temperature, saturated oils are not always stable, that is, the formation of functional groups in methyl stearate at 180 C is about one half of that in methyl linoleate or methyl linolenate (31). Such large differences in the oxidation rate of saturated oils at lower and elevated temperatures may cause the rapid Tocol loss in saturated oils under the simulated deep-fat frying conditions, although the loss is very small under AOM conditions.

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