Chemical Reactions Involved in Deep Fat Frying of Foods: VI. Characterization of Nonvolatile Decomposition Products of Trilinolein[1,2]

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ABSTRACT

A laboratory apparatus that could be used to treat pure triglycerides under simulated deep fat frying conditions was designed and built. By the use of this apparatus, the volatile decomposition products produced during frying could be quantitatively collected at the same time. Pure trilinolein was treated in this apparatus at 185 C for 74 hr. The volatile decomposition products were collected quantitatively. Their fractionation and identification will be reported in a subsequent paper. The nonvolatile decomposition products were isolated from the treated trilinolein as the non-urea-adduct-forming methyl esters. They constituted 26.3% of the treated trilinolein and were separated into seven fractions by repeated liquid column chromatography. Chemical and physical analyses of these fractions indicated that the chemical reactions taking place under simulated deep fat frying conditions were not entirely the same as those during simple heating under air. One of the seven fractions was further purified by thin layer chromatography and then identified as a cyclic carbon to carbon linked dimer which amounted to 4.9% of the treated trilinolein. Another fraction was further purified by thin layer chromatography, followed by gas chromatography, and then identified as noncyclic hydroxy dimers formed through carbon to carbon linkages. The noncyclic dimers constituted 2.8% of the treated trilinolein. The other four fractions were depolymerized by hydroiodic acid. The depolymerization products were fractionated by thin layer chromatography and then analyzed. It was estimated that the treated trilinolein contained 8.4% of trimers formed through carbon to carbon linkages, and 4.9% of dimers and trimers joined through carbon to carbon or carbon to oxygen linkages in the same molecule and also trimers, in which all the three monomeric units were joined through carbon to oxygen linkages.

INTRODUCTION

Deep fat frying is one of the most commonly used procedures for the manufacture and preparation of foods in the world. Approximately 500 million pounds of fats and oils are used each year for the manufacture of potato chips alone in the U.S. Another 200 million pounds of fats and oils are used each year for the manufacture of doughnuts. During deep fat frying, the oil is continuously or repeatedly used at elevated temperatures in the presence of air. Under such conditions, both thermal and oxidative decomposition of the oil may take place. Such unavoidable chemical reactions cause formation of both volatile and nonvolatile decomposition products which might have a significant effect upon the flavor, flavor stability, color and texture of the fried food, as well as the length of time a batch of oil can be used for frying. In addition, these decomposition

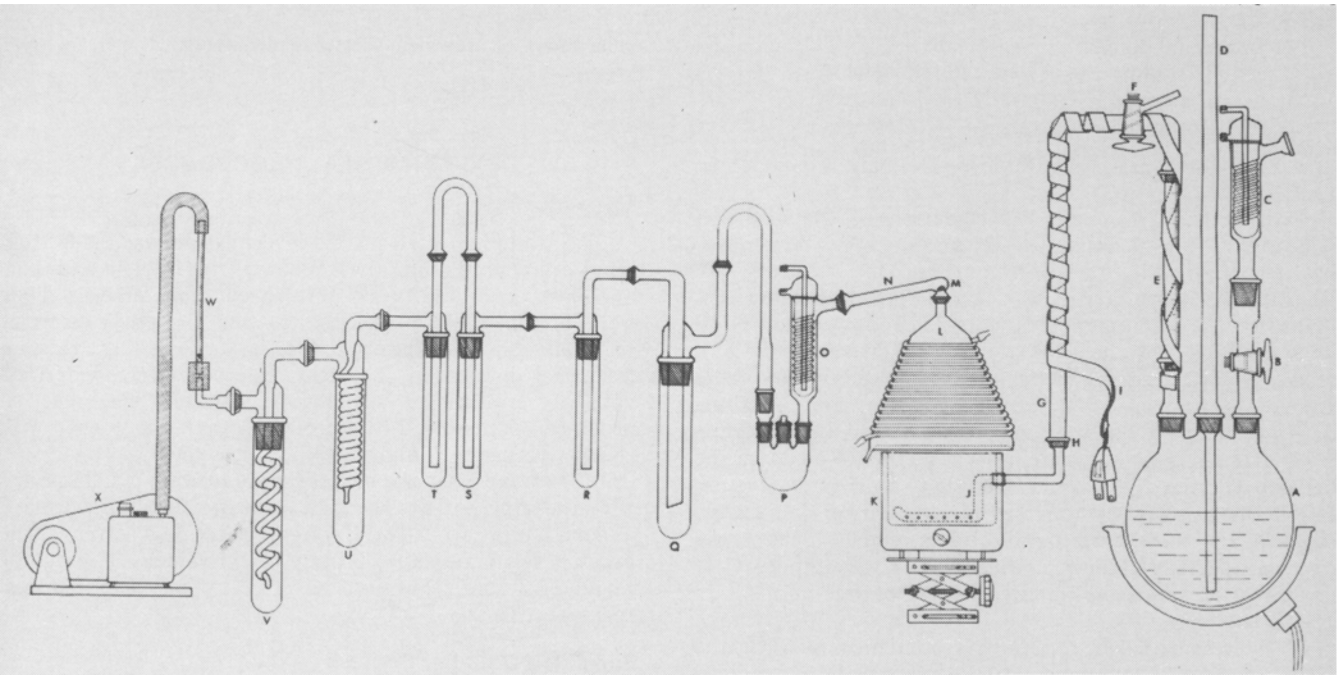

FIG. 1. Apparatus used for treating triglycerides under simulated deep fat frying conditions.

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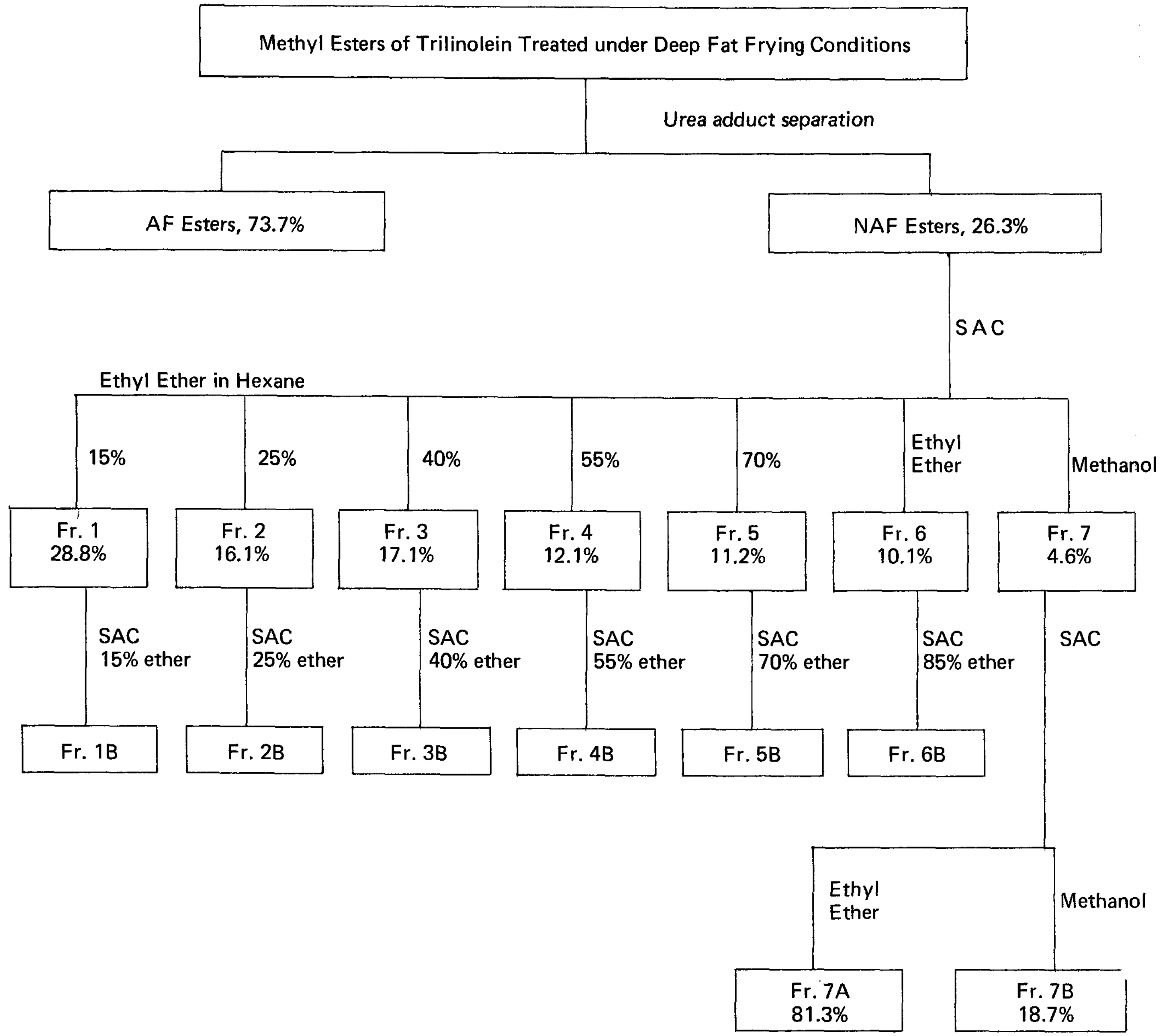

FIG. 2. Liquid column chromatography of the non-urea-adduct-forming esters of trilinolein treated under simulated deep fat frying conditions. SAC = silicic acid column chromatography.

products, both volatile and nonvolatile, may affect human health.

Investigations concerning elucidation of the chemical structure of these decomposition products and their possible toxicity were reviewed by Artman in 1969 (1). Recently, he and Smith also systematically isolated and identified the monomeric, less volatile decomposition products produced by heating cottonseed oil under air (2). However understanding of the chemical structure of volatile and nonvolatile products produced during deep fat frying of foods is still far from complete. Without such information, it is impossible to obtain deep fat fried foods with the utmost in flavor, flavor stability, color and texture. Furthermore, such information is essential for a thorough study of possible physiological effects of these decomposition products on human health and development of analytical methods for quality control of fats and oils in fried foods in our diet.

The present paper reports a systematic study of the chemical nature of nonvolatile decomposition products produced by trilinolein under simulated deep fat frying conditions.

EXPERIMENTAL PROCEDURES

Materials

The trilinolein used in this investigation was made from ethyl esters containing 0.4% olein, 99.1% linolein and 0.5% linolenin, according to gas chromatographic analysis. They were obtained by repeatedly treating the ethyl esters of safflower oil with powdered urea, followed by vacuum fractional distillation. The ethyl esters were transesterified with glycerol, using an alkaline catalyst. The reaction product was dissolved in petroleum ether and washed with aqueous ethanol. Trilinolein thus produced was recrystallized from acetone, and excess ethyl linoleate was discarded with the supernatant. The trilinolein was finally deodorized under vacuum up to 180 C to remove residual solvents. The product has acid value, 0.0; hydroxyl value, <1; peroxide value, 25.8; and ethyl linoleate <1% by thin layer chromatography (TLC).

Simulated Deep Fat Frying

The apparatus used for treating the synthetic trilinolein under simulated deep fat frying conditions, with quantitative collection of volatile decomposition products at the same time, is shown in Figure 1. This is a modified version of the apparatus used by Krishnamurthy et al. (3), who fried moist cotton balls to simulate the frying of foods. Since cotton balls would absorb a significant amount of the expensive trilinolein, they could not be used in this experiment. The apparatus was therefore modified so that steam could be periodically injected into the heated trilinolein.

The steam generator was constructed from a three-necked round-bottomed flask (A). In one neck, a reflux condenser (C) was connected through a large bore stopcock (B). The center neck was fitted with a long glass tubing (D) extending to the bottom of the flask. The third neck was connected to an aluminum tubing (H) through a flowmeter (E) and a three-way stopcock (F). The aluminum tubing was extended into the deep fat fryer by soldering through the wall of the fryer. The section of aluminum tubing insdie the fryer was perforated with pin holes at equidistance with the end closed and was bent to form a loop (J) lying on the bottom of the fryer. A heating tape (I) was wrapped around the connecting tube (G) to prevent condensation of steam.

With stopcock (B) open, the water in the round-bottomed flask was heated to a vigorous boil. To simulate frying, the stopcock (B) was closed. When the desired degree of steam pressure was built up in the flask, the three-way stopcock (F) was opened to allow the steam to bubble through the 2 kg of trilinolein maintained at 185 C in the Sunbeam deep fat fryer (K). To stop the steam flow, stopcock B was opened. The three-way stopcock (F) was added to avoid back suction. It was open to air at all times, except when steam was bubbled through the triglycerides.

The fryer was fitted snugly into a stainless steel, alembic type cone (L). It was cooled with running water through aluminum coils wrapped around the outside of the cone. Condensate collected in the cone was prevented from dripping back into the triglycerides by the alembic structure. The cone was connected to a condenser (O) cooled with running water and a series of traps (P-V) cooled with dry ice.

By turning on the vacuum pump (X), a current of air was drawn through the top of the fryer and the series of cold traps at a rate of 7.2 liters/min, as indicated by the flowmeter (W). The air flew over the surface of the triglycerides without bubbling through them. This simulated the conditions of a commercial deep fat fryer placed underneath an efficient hood. Steam, equivalent to 15 ml water, was bubbled through the trilinolein in 2 min. The operation was repeated at intervals of 30 min. Fifteen operations were performed each day in 7 hr. After the last operation, the trilinolein was cooled to room temperature and allowed to stand overnight. Total time of simulated frying was 74 hr. The study of the volatile decomposition products carried by the current of air into a series of traps as condensates will be reported in a subsequent paper.

Isolation and Preliminary Fractionation of Nonvolatile Decomposition Products

The trilinolein, after treatment under simulated frying conditions for 74 hr, was freed from volatile decomposition products by vacuum steam distillation at 150 C under 0.01 mm Hg for 1 hr. Free fatty acids left in the products were removed by treatment with Amberlite IRA-400 ion exchange resin, according to the method of Hornstein et al. (4). The treated trilinolein was then converted into methyl esters by transesterification, using sodium methoxide as a catalyst (5). The methyl esters were then separated into urea-adduct-forming (AF) esters and non-urea-adduct-forming (NAF) esters by the method of Firestone et al. (6).

The NAF esters were fractionated by liquid chromatography with the use of silicic acid, according to the method of Sahasrabudhe and Chapman (7). By eluting with hexane containing stepwise increasing amounts of ethyl ether, as shown in Figure 2, the NAF esters were separated into seven fractions, 1-7. Each of the first six fractions was rechromatographed on a silicic acid column, and the major peak material was collected as fraction 1B-6B. Fraction 7 was rechromatographed on a silicic acid column to obtain fractions 7A and 7B, with the use of ethyl ether and methanol as eluents, respectively.

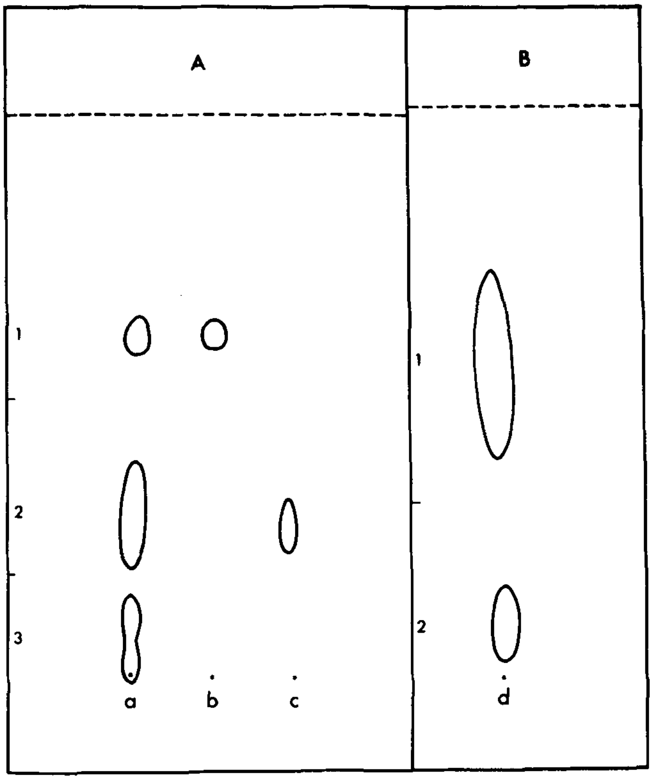

FIG. 3. Thin layer chromatogram of fractions 1B (a), 1B1 (b), 1B2 (c) and 2B (d).

Isolation of Cyclic Dimer

Fraction 1B from silic acid column chromatography was further separated by preparative TLC using a 1 mm thick 20 x 20 cm Silica Gel G plate. Approximately 75 mg of fraction 1B was applied to each plate and elution was done with benzene, according to the method of Paschke et al (8). A portion of the plate was sprayed with 2,7-dichlorofluoresceine and viewed under UV light. Three well separated spots–1B1 (R_f, 0.61), 1B2 (R_f, 0.29) and 1B3 (R_f, 0.08)–were obtained as shown in Figure 3. Each of the three spots was scraped from the unsprayed portion of the plate. The sample was then recovered by extracting with ethyl ether. Preparative TLC was repeated a number of times until a sufficient amount of each fraction was accumulated. In order to improve its purity, fraction 1B2 was rechromatographed twice with a thin layer Silica Gel G plate.

Isolation of Noncyclic Dimer

Fraction 2B, from silicic acid column chromatography, was further separated into two fractions–2B1 (R_f, 0.55) and 2B2 (R_f, 0.09)–by preparative TLC, using Silica Gel G as the adsorbent and benzene-ethyl ether 9:1 as the eluent (Figure 3). Fraction 2B1 was further separated into a major peak and several small peaks by gas chromatography on a 3 ft x 1/4 in. stainless steel column packed with 1% methyl silicone OV-1 on 60/80 mesh Chromosorb G (Analabs, North Haven, Conn.), with temperature programed from 150 to 300 C. Gas chromatography was repeated until a sufficient amount of the major peak was collected as fraction 2B1B.

TABLE I

Physical and Chemical Changes of Trilinolein during Simulated Deep Fat Frying

Characteristic	Trilinolein	
	Before treatment	After frying
Color (photometric)	3.55	76.00
Free fatty acid content, %	0.04	2.6
Iodine value, Wijs	176.0	155.4
Peroxide value, meq/kg	25.8	4.7
Viscosity, centistokes, 30 C	36.2	200.6
Refractive index 40 C	1.4728	1.4793
NAF esters, %	—	26.3

Depolymerization Studies

Two different depolymerization procedures were used. The method of Chang and Kummerow (9), using 2.5 N dry hydrochloric acid in anhydrous methanol, was used to break polymers joined through peroxide linkages. The method of Williamson (10), using anhydrous hydroiodic acid, was used to break polymers joined through ether linkages.

Fractions 3B-6B were each depolymerized by the two procedures. The depolymerized product obtained from each of the four fractions by treating with hydroiodic acid was dehalogenated with zinc dust in acetic acid (10) and then esterified with anhydrous methanol using sulfuric acid as a catalyst. The methyl esters of the depolymerized product of each fraction were then separated into four fraction by TLC, using Silica Gel G plates with benzene as the developer (Fig. 4).

Analytical Methods

Iodine value, free fatty acids, peroxide value, oxirane oxygen and photomeric color were determined according to AOCS official methods (11). Saponification value, hydroxyl value and conjugated diene were determined according to the method described by Mehlenbacher (12). Carbonyl value was analyzed by the method of Bhalerao et al. (13).

Viscosity was measured with a Cannon Fenske Viscometer (No. 200, Cannon Instrument Co.). Molecular weight was determined with a Mechrolab Vapor Pressure Osmometer, Model 301A. Elemental analysis was carried out by Schwarzkopf Micro Analytical Lab., Woodside, N.Y.

Dehydrogenation analysis was carried out by heating the samples, fractions 1B-7B, at 280 C for 5 hr under a nitrogen atmosphere with 10% Pd on charcoal as a catalyst. Absorption of the dehydrogenated product in the UV region was measured with a Beckman DB-G spectrophotometer.

IR studies were carried out with a Beckman IR-8 IR spectrophotometer. NMR studies were conducted with a Varian Associates A-60 instrument.

RESULTS AND DISCUSSION

Deterioration of Trilinolein during Simulated Deep Fat Frying

After the trilinolein was used for simulated deep fat frying for 74 hr, there were relatively large increases in free fatty acids, color, viscosity and refractive index, as well as a decrease in iodine value (Table I). The low peroxide value was expected, as peroxides tend to decompose at frying temperature. It was interesting to note that there was no sign of foaming when steam was injected into the trilinolein after it had been used for 74 hr, even though there had been a large increase in viscosity.

The methyl esters of the used trilinolein contained

TABLE II

Analysis of AF Esters and Fractions of NAF Esters Obtained from Trilinolein after Being Used for Simulated Deep Fat Frying

Characteristic	AF esters	Fractions of NAF esters							
		1B	2B	3B	4B	5B	6B	7A	7B
Molecular weight	297	485	605	656	752	832	818	613	833
Carbon, %	—	76.35	74.54	72.44	72.68	71.35	69.84	70.33	65.04
Hydrogen, %	—	11.23	10.82	9.81	10.35	10.06	10.00	10.22	9.31
Oxygen, % (by difference)	—	12.42	14.64	17.75	16.97	18.59	20.16	19.45	25.65
Iodine value	159.0	116.0	107.5	99.2	72.0	77.5	70.8	63.3	69.7
Double bond/mole	1.87	2.22	2.57	2.56	2.14	2.54	2.28	1.53	2.29
Hydroxyl value	17.5	25.7	56.8	42.1	67.6	64.4	161.3	86.7	183.7
Hydroxyl/mole	0.09	0.22	0.61	0.49	0.91	0.96	2.35	0.97	2.80
Saponification value	193	181	193	194	183	206	215	257	207
Ester/mole	1.02	1.56	2.05	2.27	2.45	3.11	3.13	2.80	3.08
Carbonyl value	123	580	207	238	Nil	Nil	Nil	Nil	Nil
Carbonyl/mole	0.04	0.28	0.13	0.16	Nil	Nil	Nil	Nil	Nil
Peroxide value, meq/kg	100	50	84	83	89	121	149	155	43.8
Peroxide/mole	0.03	0.02	0.05	0.06	0.07	0.11	0.9	0.13	0.04
Conjugated diene, %	2.3	21.3	14.4	11.6	9.3	9.3	10.2	11.4	8.7
Oxirane oxygen, %	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Dehydrogenation	—	+	—	—	—	—	—	—	—

TABLE III

Distribution of Oxygen among Functional Groups in Fractions of NAF Esters Obtained from Trilinolein after Being Used for Simulated Deep Fat Frying

Functional groups	Fractions of NAF esters							
	1B	2B	3B	4B	5B	6B	7A	7B
Hydroxyl	0.22	0.61	0.49	0.91	0.96	2.35	0.97	2.80
Ester	3.12	4.16	4.54	4.90	6.22	6.26	5.60	6.16
Carbonyl	0.28	0.13	0.16	Nil	Nil	Nil	Nil	Nil
Peroxide	0.04	0.10	0.12	0.14	0.22	0.18	0.26	0.08
Epoxy	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Total	3.66	5.00	5.31	5.95	7.40	8.79	6.83	9.04
Unaccounted	0.10	0.54	1.97	2.03	2.26	1.52	0.62	4.31

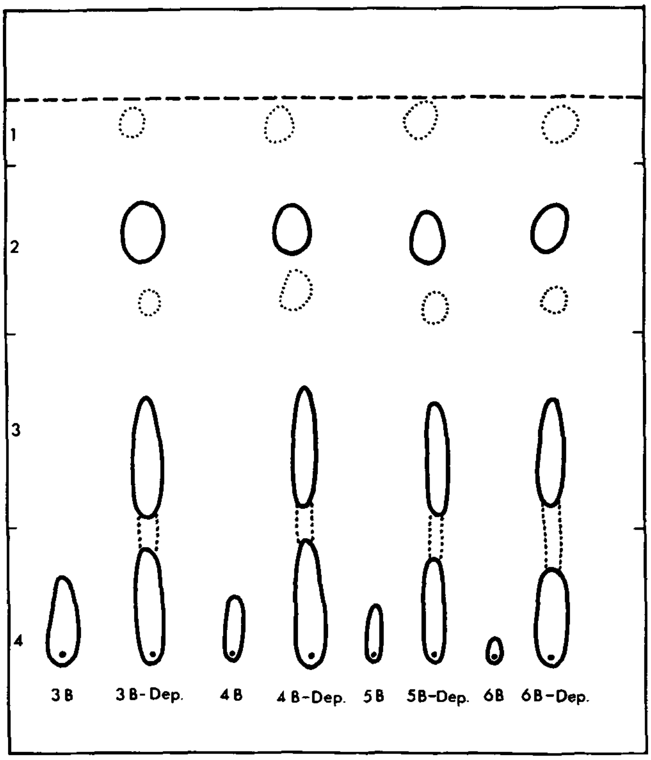

FIG. 4. Thin layer chromatograms of fraction 3B-6B before and after depolymerization.

26.3% NAF esters, which were considered nonvolatile decomposition products. The AF esters were analyzed by gas chromatography at 180 C using a 150 ft capillary column coated with polyphenyl ether. It consisted of more than 99% *cis*-9-*cis*-12-octadecadienoic acid with trace amounts of *trans*-9-*cis*-12, *trans*-9-*trans*-12 and *cis*-9-*trans*-12 isomers. No higher unsaturated fatty esters due to dehydrogenation nor shorter chain fatty esters due to chain breaking were noticed. This indicated that 73.7% linoleic acid remained unchanged after the trilinolein was used for simulated deep fat frying for 74 hr.

Characterization of Liquid Chromatographic Fractions

The eight fractions of NAF esters obtained from silicic acid column chromatography (Fig. 2) were evidently not pure compounds. However they could not be further fractionated by liquid column chromatography. Sephadex LH 20, Florisil and silicic acid impregnated with silver nitrate were tried separately without any success. Therefore they were analyzed to yield a general idea of the chemical nature of nonvolatile decomposition products produced during deep fat frying (Table II).

The molecular weight of these fractions ranged from 485 to 833, indicating the presence of monomers to trimers. Recently, Michael and coworkers (14) obtained polymers with molecular weights up to 1122, on heating methyl linoleate diluted with methyl laurate at 200 C for 200 hr. Polymers obtained by Perkins and Kummerow (15) from corn oil heated at 200 C with air bubbled through had a molecular weight range of 692-1600. Similarly, Firestone and coworkers (16) obtained polymers from cottonseed oil heated at 205 C for 40 days with a molecular weight as high as 1790. This seemed to indicate that the degree of polymerization under simulated deep fat frying conditions was not nearly as high as that which occurred during the simple heating of the fatty esters under air or during the bubbling of air through heated triglycerides. Consequently, simulated deep fat frying conditions, such as those used in this investigation, probably produce products more closely resembling the reactions taking place during actual deep fat frying.

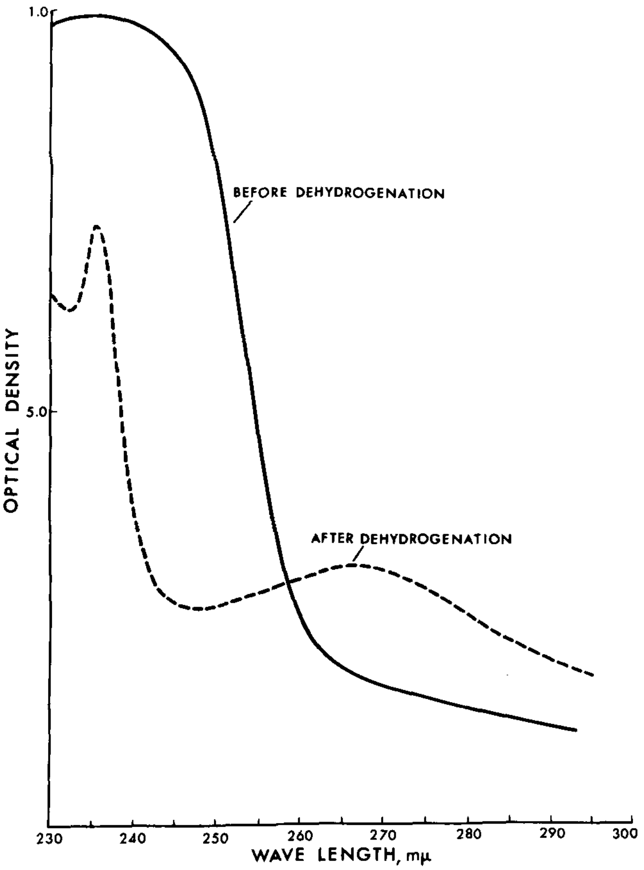

FIG. 5. UV absorption spectra of fraction 1B2 before and after dehydrogenation.

NAF esters from the used trilinolein, on the other hand, were quite polar and rich in oxygen content. For example, their hydroxyl values were considerably higher than those obtained by Michael et al. (14) from heated methyl linoleate (Table II). This might be important, because it has been reported that the polar fractions of heated fats and oils were the ones that showed signs of toxicity (14, 15).

Polarity and oxygen content of the eight fractions increased with polarity of the solvent used for elution, while amount of unsaturation and conjugated diene decreased. Peroxide value of these fractions indicated that some autoxidation did take place during fractionation and analysis.

It is interesting to note that only fraction 1B contained cyclic compounds later identified as carbon to carbon linked dimers. No cyclic monomer was found in the trilinolein treated under simulated deep fat frying conditions. However Michael et al. (14) reported identification of cyclic monomers in heated methyl linoleate. This might be important, because cyclic monomers were reported toxic by both Michael et al. (14) and Firestone et al. (16).

TABLE IV

Analysis of Isolated Cyclic (1B2) and Noncyclic Dimers (2B1B)

Characteristic	Fraction 1B2	Fraction 2B1B
Molecular weight	577	601
Carbon, %	77.28	74.00
Hydrogen, %	11.35	10.54
Oxygen, % (by difference)	11.37	15.46
Iodine value	91.1	98.1
Double bond/mole	2.07	2.32
Saponification value	189.4	185.4
Ester/mole	1.95	1.99
Hydroxyl value	0	165.0
Hydroxyl/mole	0	1.77

TABLE V

Thin Layer Chromatographic Fractionation of Products Obtained by Depolymerization of Polar Polymers[a]

A. Fraction 3B

Fraction	R_f	%	Mol wt.
Before D	—	—	656
After D			
Total	—	—	555
3B1	0.97	0.7	—
3B2	0.77	11.4	298
3B3	0.37	25.0	570
3B4	0.09	62.9	753

B. Fraction 4B

Fraction	R_f	%	Mol wt
Before D	—	—	752
After D			
Total	—	—	548
4B1	0.97	0.6	—
4B2	0.77	12.2	289
4B3	0.37	22.4	570
4B4	0.09	64.8	780

C. Fraction 5B

Fraction	R_f	%	Mol wt
Before D	—	—	832
After D			
Total	—	—	563
5B1	0.97	0.7	—
5B2	0.77	13.1	289
5B3	0.37	21.0	548
5B4	0.09	65.2	902

D. Fraction 6B

Fraction	R_f	%	Mol wt
Before D	—	—	818
After D			
Total	—	—	535
6B1	0.97	0.7	—
6B2	0.77	22.8	327
6B3	0.37	19.2	555
6B4	0.09	57.3	858

[a] D indicates depolymerization.

Another interesting observation was that the number of oxygen atoms per molecule distributed among the functional groups analyzed, did not total the number of oxygen atoms per molecule determined by elemental analysis (Table III). The only possible exceptions were fractions 1B, 2B and 7A. Fraction 7B, for example, contained as many as four oxygen atoms per molecule that could not be accounted for. Such oxygen atoms may be present in the molecule, either in some unusual functional groups or as linkages joining the monomeric units.

IR spectra of all seven fractions were similar to those of long chain fatty methyl esters. Fractions 1B and 2B were the only ones that showed strong bands at 10.15μ, suggesting the presence of *trans-trans* conjugated diene. The band at 5.75μ was shifted toward 5.80μ with the increase in polarity. The hydroxyl group band at 2.9μ was weak in fractions 1B and 2B, but strong in all other fractions. This band was shifted to 2.92 and 2.95μ, respectively, in fractions 7A and 7B.

UV spectra of all the fractions showed absorption maximum due to conjugated diene. However maximum absorption of fraction 1B was at 236-237 mμ, while that of all the others was at 233 mμ. After dehydrogenation, fraction 1B showed absorption maxima at 264-265, and 236-237 mμ. The former was probably due to an aromatic ring, and the latter was originally present. On the other hand, all the other fractions lost their maximum at 233 mμ by the dehydrogenation process. These fractions also showed the absence of *trans-trans* conjugated unsaturation at 10.15μ in the IR spectra. This indicated that cyclic compounds were present only in fraction 1B (15,16), which constituted 7.6% of the used trilinolein.

Identification of Cyclic Dimer

Fraction 1B was separated into three fractions (1B1, 1B2 and 1B3) by TLC. Fraction 1B1 constituted 24% of fraction 1B, and this is equivalent to 1.8% of the used trilinolein. Dehydrogenation analysis showed that this fraction was not cyclic in nature. Further separation by gas chromatography on a 6 ft x 1/4 in. column, packed with 15% diethylene glycol succinate on 70/80 mesh Anakrom ABS, yielded one major and three small peaks. The IR spectrum and retention time of the major peak agreed with those of methyl linoleate. IR spectra of the three minor peaks was similar to that of a fatty acid methyl ester with a *trans* double bond. These monomers were present in the dimer fraction, due to incomplete separation by the urea adduct formation method.

Fraction 1B2 constituted 65.0% of fraction 1B which corresponded to 4.9% of the used trilinolein. Attemps were made to further purify this fraction by TLC on Silica Gel G plates with different solvent systems, including benzene, benzene-ethyl ether-acetic acid 90:10:1, and iso-octane-ethyl acetate 9:1, as well as on Silica Gel G impregnated with silver nitrate using benzene-hexane-acetic acid 70:30:1 as a developing solvent. All methods produced only one peak. Attempts were also made to gas chromatograph this fraction on 1 ft x 1/4 in. columns packed with 1% methyl silicone OV-1 and Versamid on 60/80 mesh Chromosorb G, respectively. Further fractionation was not achieved, due to observation of signs of decomposition.

Chemical and physical analysis of fraction 1B2 indicate; that it was a cyclic dimer with two ester groups and two double bonds—one of the double bonds in the ring and the other in the side chain. Such monocyclic dimers can be formed by Diels-Alder reaction and had been reported previously in oils heated under air (8,14,16). The molecular weight and elemental analysis of this fraction (Table IV) agreed with those of a cyclic dimer of methyl linoleate, which should have a theoretical molecular weight of 588, a theoretical C% of 77.6 and a theoretical H% of 11.7. The analysis also showed that this fraction had two ester groups and two double bonds per molecule.

Dehydrogenation analysis clearly demonstrated that Fraction 1B2 was a cyclic compound. UV absorption spectra of this fraction before and after dehydrogenation were shown in Figure 5. Absorption maxima developed at 264-268 mμ by dehydrogenation indicated the formation of a benzene ring. Absorption at 233-238 mμ indicated the presence of some conjugated double bonds.

The NMR spectrum of fraction 1B2 showed the following proton signals: 4.0-4.8τ (double bond on the ring and side chain), 6.4τ (methyl ester), around 7.8τ (methylene group adjacent to ester group), 8.65τ (methylene group) around 9.0τ (terminal methyl group).

The IR absorption spectrum of fraction 1B2 was similar to that of a fatty acid methyl ester. A band at 10.15μ was due to *trans-trans* conjugation. After dehydrogenation, all the *trans* unsaturation absorption disappeared, and a new absorption at 12.25μ, due to the polysubstituted benzene ring, was developed. Similar observation was reported previously on dehydrogenation of cyclic dimers by Paschke et al. (8).

Identification of Noncyclic Dimer

Fraction 2B1B constituted 2.8% of the used trilinolein (88% of 2B1 and 75% of 2B). Further gas chromatography of this fraction, using a column packed with 10% methyl

TABLE VI

Analysis of the Dimers and Trimers Obtained by Thin Layer Chromatographic Fractionation of Depolymerized Polar Polymers

	Dimers				Trimers			
Characteristics	3B3	4B3	5B3	6B3	3B4	4B4	5B4	6B4
Molecular weight	570	570	548	555	753	780	902	858
Carbon, %	75.47	76.47	75.17	77.27	73.82	73.57	74.10	73.29
Hydrogen, %	11.78	12.14	11.76	12.54	11.18	11.08	11.08	10.82
Oxygen, % (by difference)	12.75	11.39	13.07	10.19	15.00	15.35	14.82	15.89
Iodine value	54.0	54.7	49.2	55.9	50.5	52.0	54.8	51.0
Double bonds/mole	1.21	1.23	1.06	1.22	1.50	1.60	1.95	1.74
Saponification value	186.7	197.3	193.0	189.5	212.6	201.5	205.0	208.4
Ester/mole	1.90	2.04	1.89	1.88	2.85	2.87	3.29	3.19
Hydroxyl value	0.00	0.00	0.00	0.00	25.8	36.8	37.6	40.8
Hydroxyl/mole	0.00	0.00	0.00	0.00	0.34	0.51	0.60	0.64
Peroxide value, meq/kg	17.5	16.5	14.0	14.1	14.4	20.3	28.6	30.6
Peroxide/mole	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.03

TABLE VII

Distribution of Oxygen among Functional Groups in Dimers and Trimers Obtained by Thin Layer Chromatography Fractionation of Depolymerized Polar Polymers

	Distribution of oxygen atoms							
Functional groups	Dimers				Trimers			
	3B3	4B3	5B3	6B3	3B4	4B4	5B4	6B4
Ester	3.80	4.08	3.78	3.76	5.70	5.74	6.58	6.28
Hydroxyl	0.00	0.00	0.00	0.00	0.34	0.51	0.61	0.64
Peroxide	0.02	0.02	0.02	0.02	0.02	0.03	0.05	0.05
Total oxygen atoms	3.82	4.10	3.80	3.78	6.06	6.28	7.23	6.97
Oxygen atoms calculated from elemental analysis	4.53	4.06	4.48	3.54	7.06	7.48	8.40	8.52
Difference	+0.71	−0.04	+0.68	−0.24	−1.00	+1.20	+1.17	+1.55

silicone OV-1 and 2% Versamid 900, respectively, on 60/80 mesh Chromosorb G, yielded only one peak. Chemical and physical analysis of this fraction indicated that it was a noncyclic dimer with approximately two ester groups, two hydroxyl groups and two double bonds (Table IV). That the analyses did not yield whole numbers was clear evidence that this fraction was not homogeneous, even though it appeared as one peak during gas chromatography. The molecular weight and elemental analysis of this fraction were close, but not equal to the theoretical values of a noncyclic dimer of methyl linoleate (mol wt, 622; C%, 73:38; H%, 11.34).

The IR absorption spectrum of this fraction was similar to that of a hydroxy fatty acid methyl ester. A very weak absorption at 10.15μ could be due to the presence of *trans-trans* conjugation. Dehydrogenation of this fraction did not yield an absorption of the benzene ring in the UV region.

The NMR spectrum of this fraction showed the following proton signals: 4.65τ (double bond), 6.4τ (methyl ester), around 7.8τ (methylene group adjacent to ester group), 8.65τ (methylene group), around 9.0τ (terminal methyl group).

Formation of noncyclic carbon-to-carbon linked polymers had been reported by several previous workers (10,15,16,18). Such polymers could be formed by a free radical mechanism proposed by Rushman and Simpson (19).

Depolymerization Studies of Polar Polymers

Fractions 3B-6B could not be further fractionated by the methodologies available to us. Attempts made to further separate each of these four fractions by Florisil column, Sephadex LH-20 column and Silica Gel G thin layer plates, were all unsuccessful. They were therefore studied by depolymerization procedures, with the hope that the chemical nature of the simpler depolymerized product might aid the understanding of the structure of the original polymers.

Chang and Kummerow (9) reported previously that oxidative polymers formed by bubbling oxygen into methyl linoleate at 63 C could be easily depolymerized by refluxing with 2.5N dry hydrochloric acid in anhydrous methanol. For example, the molecular weight of a polar polymeric fraction was decresed from 699 to 412 by this treatment. However the polar polymeric fractions isolated from trilinolein, after it had been treated under deep fat frying conditions, could not be depolymerized by dry hydrochloric acid. The molecular weight of these fractions remained the same after the depolymerization treatment. This clearly indicated the chemical differences between polar polymers formed at 60 C, under air and those formed under deep fat frying conditions.

Hydroiodic acid was found to be capable of partially depolymerizing the polar polymeric fractions obtained from the used trilinolein. The molecular weights were decreased but not to the extent of monomers after the depolymerization procedure (Table V). This indicated that the polar polymers were joined both by carbon to oxygen and carbon to carbon linkages. The depolymerized products contained no halogen after dehalogenation. In addition, retreatment of the depolymerized product with hydroiodic acid did not further decrease the molecular weight, thus assuring the completeness of the reaction.

TLC of depolymerized products from fractions 3B-6B separately yielded five spots (Fig. 4). The three major spots corresponded to monomers, dimers and trimers, respectively (Table V). The fastest moving spots (3B1, 4B1, 5B1 and 6B1) were low molecular weight compounds, probably decomposition products. The first major spots (3B2, 4B2, 5B2 and 6B2) were monomers (Table V). Their gas chromatograms from a diethylene glycol succinate column showed that they were essentially methyl stearate. The minor spots between the first and second major spots were too small to be analyzed.

The results of the analyses of the dimer fractions (3B3, 4B3, 5B3 and 6B3) and trimer fractions (3B4, 4B4, 5B4 and 6B4) are shown in Table VI. The molecular weight and the number of ester groups of the dimers were close to theoretical values of a dimer of methyl linoleate. All the dimers had approximately one double bond per molecule. The molecular weight and the number of ester groups of two of the trimers (5B4 and 6B4) were also close to the theoretical values. However the molecular weights of the other two trimer fractions (3B4 and 4B4) were significantly lower than the theoretical value of trimers of methyl linoleate. They were probably constituted of partially decomposed linoleate fractions. The trimers had unsaturation ranging from 1.50 to 1.95 double bonds per molecule. Loss of hydroxyl groups was expected from the reaction with hydroiodic acid. It was found that all the monomers are saturated, whereas the dimers and trimers have some unsaturation (Table VI).

Distribution of oxygen atoms among functional groups in the dimer and trimer fractions obtained by depolymerization is shown in Table VII. Carbonyl and epoxy groups were absent. All the trimers and two of the dimers had oxygen atoms that still could not be accounted for by functional group analyses. Such oxygen atoms ranged from 0.68 to 1.55. The nature of these oxygen atoms was difficult to ascertain at the time.

Based upon the depolymerization study, it can be concluded that trilinolein, after having been treated under simulated deep fat frying conditions, contained 8.4% trimers with carbon to carbon linkages, and 4.9% dimers and trimers joined through carbon to carbon or carbon to oxygen linkages in the same molecule, and also trimers in which all three monomeric units were joined through carbon to oxygen linkages.

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