Chemical Reactions Involved in the Deep-Fat Frying of Foods[1]

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ABSTRACT

Deep-fat frying is one of the most commonly used procedures for the preparation and manufacture of foods in the world. During deep-fat frying, oxidative and thermal decompositions may take place with the formation of volatile and nonvolatile decomposition products, some of which in excessive amounts are harmful to human health. A limited survey of frying fats used in commercial operations indicated that some were maintained at good quality and others were overused or abused. The volatile decomposition products produced by corn oil, hydrogenated cottonseed oil, trilinolein, and triolein, under simulated commercial frying conditions, were collected, fractionated, and identified. A total of 211 compounds were identified. The nonvolatile decomposition products produced by trilinolein, triolein, and tristearin under simulated commercial frying conditions were collected and characterized. After being treated under deep-fat frying conditions at 185 C for 74 hr, trilinolein yielded 26.3% non-urea-adduct-forming esters, triolein yielded 10.8%, and tristearin also yielded 4.2%.

INTRODUCTION

Deep-fat frying is one of the most commonly used procedures for the preparation and manufacture of foods in the world. The fast food restaurants which have been growing rapidly in recent years further increase the consumption of fried foods, especially fried chicken, fish and chips, and french fries. Evidently, a major portion of the ten billion pounds of edible fats and oils consumed each year in the United States are used in fried foods. For example, an estimated 500 million pounds of fats and oils are used each year for the manufacture of potato chips and another 200 million pounds in 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. The latter can be isolated from fats and oils which have been used for deep-fat frying as a brownish, transparent, viscous liquid (Fig. 1). They also cause foaming when moist foods are deep-fat fried in the oil (Fig. 2). The foaming is often regarded by restauranteurs and food processors as an indication that the frying oil must be discarded. However, at that time, there is already a considerable amount of decomposition products in the oil. Foods fried in such oils during the period prior to the foaming may contain a sufficient amount of decomposition products to cause adverse effects to the safety, flavor, flavor stability, color, and texture of the fried food. For example, foods fried in oils with a foaming tendency are often greasy and less crispy. In addition, such decomposition products, both volatile and nonvolatile, may effect human health.

Various symptoms of toxicity, including irritation of the digestive tract, organ enlargement, growth depression, and even death have been observed when highly abused (oxidized and heated) fats were fed to laboratory animals. Kaunitz et al. (1) autoxidized lard and cottonseed oil at 100 C for 210 hr and found growth depression, diarrhea, and rapid death when the product was fed to Albino rats. Crampton et al. (2) heated polymerized linseed oil at 275 C for 12 hr under carbon dioxide and found toxic materials which are believed to be monomeric cyclic acids. Perkins and Kummerow (3) reported significant growth depression after feeding rats corn oil that had been heated at 200 C for 48 hr while being aerated with a stream of oxygen. The

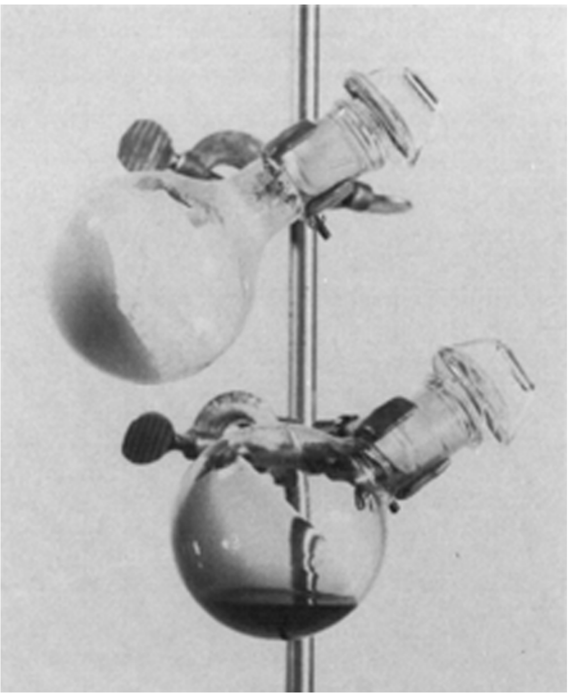

FIG. 1. Thermally oxidized materials (top) isolated from commercial shortening (bottom) after being used for simulated deep-fat frying.

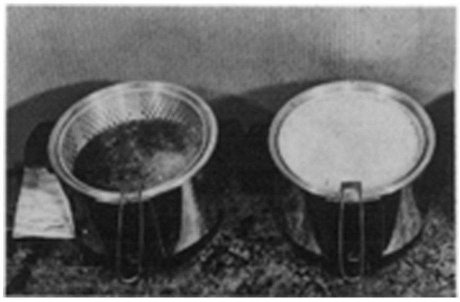

FIG. 2. When potato slices were deep-fat fried in fresh corn oil (left) and in corn oil which had been heated at 185 C for 72 hr (right).

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elucidation of the chemical structure of such decomposition products and their possible toxicity were reviewed by Artman (4).

Furthermore, there is some evidence that highly oxidized and heated fat may have carcinogenic properties. As early as 1944, Roffo (5) suggested that heated fat might cause cancer. He found that sunflower and olive oils oxidized by heating to 250-350 C had carcinogenic potential when fed to rats. Peacock and Beck (6) reported that long term feeding of heated oil to mice raised the incidence of squamous carcinomas. Sugai et al. (7) claimed that the non-urea-adduct-forming fraction isolated from heated corn oil acted in synergism with 2-acetylaminofluorene and enhanced its carcinogenic activity. Among the volatile decomposition products, Dickens and Jones (8) reported the carcinogenic properties of some unsaturated lactones.

Results of investigations from laboratories using commercial frying fats and oils, on the other hand, generally indicated that such decomposition products have no deleterious effect upon human health. Melnick et al. (9) concluded that the oils used in the production of potato chips are free of thermal polymers and that there is no reason to question the wholesomeness of the oil being absorbed by the chip. Keanne et al. (10) reported that hydrogenated cottonseed oil used in a commercial deep fryer under actual production conditions for as long as 24 days had no toxic effect on rats when fed at levels as high as 20% of the diet. Rice et al. (11) claimed that fats are not nutritionally damaged when handled by normally accepted good practice in present day food preparation.

Very recently, Billek and Guhr (12) isolated a large amount of the thermally oxidized materials from oils used commercially for production of fish-fingers which were taken at the end of a production period when the oil was usually discarded, according to the practice of this company. The oil contained only 6.5% of polymeric materials which, based upon their quality assessment work of commercial frying oil, could still be considered to be of good quality. They reported that when the thermally oxidized materials were fed to rats at 20% by weight in the diet over a period of one and a half years, growth retardation, increased weight of liver and kidney, increased SGPT and SGOT activities were observed.

It is, therefore, evident that fried foods prepared with fresh oils or fats under good food preparation practices are delicious in flavor and have no adverse effect upon human health. However, if the frying oil or fat is overused or abused in the frying process, the triglycerides may produce thermal oxidative materials harmful to human health.

SURVEY OF COMMERCIALLY USED FRYING FAT

A limited survey was conducted in 1967 with 21 sets of samples of fats and oils commercially used for deep-fat frying in restaurants, food processing plants, and institutions (13). Each set consisted of two samples: one was the fresh oil before it was used for frying; the other was the same batch of oil after it had been used for deep-fat frying until it was ready to be discarded in the batch process or until it had reached a state of equilibrium in continuous process. The results clearly demonstrated that some of the fats and oils commercially used for deep-fat frying were maintained at good quality and others were overused or abused to a higher degree of deterioration. This could be observed even visually. The sample of cottonseed oil used commercially for the manufacture of potato chips (Fig. 3, left top) was evidently not abused, while that used commercially for the manufacture of another food product (Fig. 3, left bottom) was badly damaged. The same wide range of deterioration was observed in more saturated hydrogenated shortenings. The sample collected from the dining hall of a university (Fig. 3, right top) was of good quality, while that collected from a large chain restaurant was highly deteriorated (Fig. 3, right bottom).

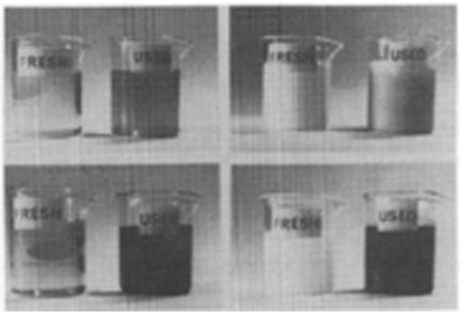

FIG. 3. Comparison of two sets each of cottonseed oils (left) and hydrogenated shortenings (right) before and after being commercially used for deep-fat frying.

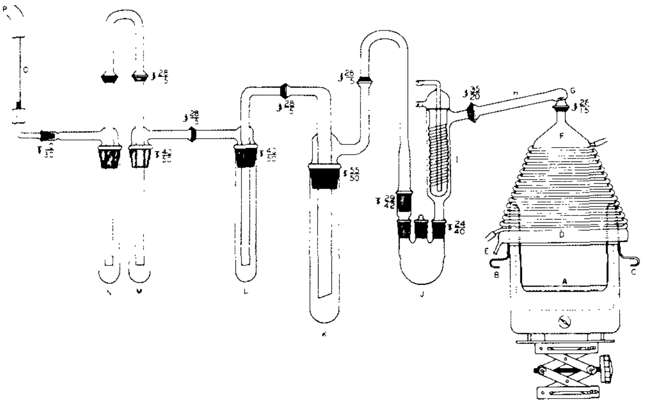

FIG. 4. Laboratory apparatus for deep-fat frying under simulated restaurant conditions.

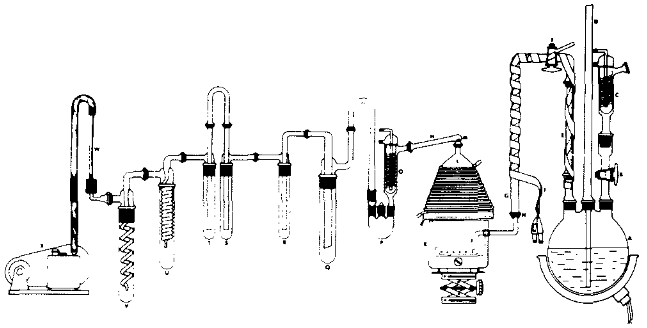

FIG. 5. Apparatus used for treating pure triglycerides under simulated deep-fat frying conditions.

Chemical and physical analyses of the fats and oils commercially used for deep-fat frying (13) indicated that the degree of deterioration was independent of their degree of unsaturation, but rather depended upon how they were used. Of the two analyzed sets of cottonseed oil samples, the used Sample 2, had a minor decrease in iodine value and linoleic acid content along with a minor increase in viscosity and non-urea-adduct-forming esters. On the other hand, the used Sample 1 had a much larger decrease in iodine value, and linoleic acid content, and a much larger increase in viscosity and non-urea-adduct-forming esters. These changes indicated a significant degree of thermal oxidation. The same type of conclusion may be drawn from an examination of the two sets of hydrogenated shortenings.

SIMULATED DEEP-FAT FRYING

In order to elucidate the chemical structures of the volatile and nonvolatile decomposition products which were formed by the triglycerides during deep-fat frying, without the complication and interference of the food fried, an inert material must be found to substitute for the food. After trying with various materials, it was found that moist cotton balls containing 75% by weight of water were a good simulation of an inert piece of potato. They were used for simulated deep-fat frying in the apparatus as shown in Figure 4, which was designed to produce nonvolatile decomposition products, as well as to collect the volatile decomposition products produced during the deep-fat frying (14). The aluminum frying basket (A) was held in position by clamping at (B) and (C). The top of the Sunbeam deep-fat fryer was fitted with an Alembic-type cone (F) made of stainless steel. The cone was 10 in. high and had a top diameter of 5 in.; bottom diameter, 11 in. It was cooled with running water through aluminum coils wrapped around the outside of the cone. A glass connector (H) with an Alembic-shaped head (G) was used to join the cone to the condenser (I).

For frying, the deep-fat fryer containing 2300 ml of corn oil maintained at 185 C was lowered until the aluminum basket was out of the oil. Ten moist cottonballs, each containing 75% by weight of water, were placed in the aluminum basket. A vacuum pump connected to the end of the flowmeter (P) was turned on to draw a current of air through the top of the fryer and then through the train of traps at a rate of 7.2 liters/min as indicated by the flowmeter (O). The fryer was then raised until the cotton balls were immersed in the oil and fried.

The volatile decomposition products and steam thus produced were drawn by the current of air flowing through the apparatus into the stainless steel cone and then the condenser and the train of traps (K through N). The condensate collected on the inside of the cone could not drip back into the fryer because it was trapped by the Alembic edge (D). Excessive amounts of volatile decomposition products and steam condensed in the cone would flow out from the exit (E) and could be collected with a suitable container. Those which were not condensed in the cone were collected in the flask (J) and traps (K through N). Those condensed in the head of the connector tube (H) also could not drip back into the fryer because of the Alembic head (G).

Ten moist cotton balls containing ca. 16 g of water were fried every 30 min. Thirteen frying operations were done each day in 6 hr. After each 12 hr of frying, 800 ml of fresh corn oil were added into the fryer to replenish the oil absorbed by the cotton balls. After each 6 hr of frying, the oil was allowed to cool to room temperature. The apparatus was disassembled and all the condensates were washed out with distilled water and ethyl ether.

Difficulty arose when pure synthetic triglycerides were used for simulated deep-fat frying so that the nonvolatile decomposition products could be more easily characterized than mixed triglycerides. The cotton balls would absorb too much of the expensive pure triglycerides and would make the experiment financially impossible. The apparatus was therefore modified as shown in Figure 5 so that steam could be periodically injected into the heated pure triglycerides to simulate frying (15).

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 inside 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 bottom 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 pure triglycerides 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 connected to the train of cold traps in the same manner as described previously.

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 of water, was bubbled through the triglycerides 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 triglycerides were cooled to room temperature and allowed to stand overnight. Total time of simulated frying was 74 hr.

VOLATILE DECOMPOSITION PRODUCTS

Systematic chemical identification of the volatile decomposition products (VDP) of fats and oils produced during deep-fat frying is important in at least three aspects. First, the mechanisms of the formation of these compounds may lead us to an understanding of the chemical reactions which take place during deep-fat frying. Since nonvolatile decomposition products (NVDP) are simultaneously produced, the chemical structures of the volatile ones may be of use in the elucidation of those of the nonvolatiles.

Second, the VDP are inhaled by the operators of deep-fat frying, particularly restaurant cooks. Furthermore, it has been shown by our investigation that a portion of the VDP remains in the frying oil and thus enters the consumer's diet. An understanding of their chemical identities may facilitate the investigation of their effect upon human health.

Last, the flavor of deep-fat fried foods is partly due to the VDP. A knowledge of their chemical composition may make possible the manufacture of a synthetic flavor which can be used to enhance the flavor of deep-fat fried foods or to manufacture foods having deep-fat fried flavor without the necessity of the frying process.

The VDP produced by corn oil (16,17), hydrogenated cottonseed oil (18,19), trilinolein (20), and triolein (21), respectively, under simulated deep-fat frying conditions, were collected, separated into acidic and nonacidic compounds, fractionated by repeated gas chromatography with columns of a polar and a nonpolar stationary phase consecutively, and the pure gas chromatographic fractions were then identified by a combination of retention time and infrared and mass spectrometry. The identifications were finally confirmed with authentic compounds. If they were not available commercially, they were synthesized in the laboratory.

A total of 220 compounds were identified as VDP produced during deep-fat frying (Table I). Their amount was mostly in ppm. However, many of them were of known toxic properties.

TABLE I

Volatile Decomposition Products Produced by
Various Triglycerides during Simulated Deep-fat Frying[a]

Compound	Relative amount of compound			
	Corn oil	Hydrogenated cottonseed oil	Trilinolein	Triolein
I. Acidic VDP				
A. Saturated acids				
Acetic	S	— — —	— — —	— — —
Propanoic	S	— — —	M	— — —
Butanoic	S	— — —	S	M
Pentanoic	L	S	M	L
Hexanoic	XL	S	XL	L
Heptanoic	L	S	L	M
Octanoic	L	S	M	XL
Nonanoic	L	S	M	XL
Decanoic	S	S	M	L
Undecanoic	S	XS	— — —	M
Dodecanoic	S	S	— — —	M
Tridecanoic	— — —	L	— — —	S
Tetradecanoic	— — —	M	— — —	S
Pentadecanoic	— — —	XS	— — —	— — —
Hexadecanoic	— — —	XL	— — —	— — —
Heptadecanoic	— — —	XS	— — —	— — —
Octadecanoic	— — —	L	— — —	— — —
B. Unsaturated acids				
trans-2-Butenoic	— — —	— — —	S	— — —
trans-2-Pentenoic	— — —	— — —	L	— — —
trans-2-Hexenoic	S	— — —	— — —	— — —
trans-2-Heptenoic	— — —	S	XL	— — —
trans-2-Octenoic	M	S	S	M
trans-2-Noneonic	M	XS	XL	M
trans-2-Decenoic	— — —	— — —	XL	M
trans-2-Undecenoic	S	— — —	— — —	L
trans-2-Dodecenoic	— — —	— — —	— — —	S
trans-2-Tridecenoic	— — —	— — —	— — —	S
cis-2-Heptenoic	— — —	— — —	S	— — —
cis-2-Nonenoic	— — —	— — —	L	— — —
cis-2-Decenoic	— — —	— — —	S	— — —
trans-3-Pentenoic	— — —	— — —	M	— — —
trans-3-Nonenoic	— — —	— — —	L	— — —
trans-3-Decenoic	S	S	— — —	XS
cis-3-Heptenoic	— — —	— — —	S	— — —
cis-3-Octenoic	— — —	— — —	S	M
cis-3-Nonenoic	— — —	— — —	S	S
cis-3-Decenoic	L	M	S	XS
cis-3-Undecenoic	— — —	— — —	S(tent.)	— — —
cis-3-Dodecenoic	— — —	— — —	— — —	M
cis-4-Nonenoic	— — —	— — —	S(tent.)	— — —
5-Hexenoic	— — —	— — —	S	L
6-Heptenoic	— — —	XS	L	L
7-Octenoic	— — —	S	S	L
10-Undecenoic	— — —	XS	— — —	— — —
Palmitoleic	— — —	XS	— — —	— — —
Elaidic	— — —	S	— — —	M
Oleic	— — —	XL	— — —	— — —
Linoleic	— — —	L	— — —	— — —
Linolenic	— — —	XS	— — —	— — —
cis-2-*trans*-4-Octadienoic	— — —	— — —	M	S(tent.)
trans-2-*cis*-4-Decadienoic	— — —	— — —	M	— — —
trans-2-*trans*-4-Decadienoic	— — —	— — —	M	— — —
C. Hydroxy acids				
3-Hydroxyhexanoic	S	— — —	S	— — —
2-Hydroxyheptanoic	S	— — —	M	— — —
2-Hydroxyoctanoic	— — —	— — —	S	— — —
3-Hydroxyoctanoic	— — —	— — —	S(tent.)	— — —
5-Hydroxyoctanoic	— — —	XS(tent.)	— — —	— — —
5-Hydroxydecanoic	— — —	XS(tent.)	— — —	— — —
10-Hydroxy-*cis*-8-hexadecenoic	— — —	— — —	— — —	XS(tent.)
D. Aldehydo acids				
Octanedioic acid semialdehyde	— — —	XS	— — —	S
Nonanedioic acid semialdehyde	— — —	XS	— — —	— — —
Decanedioic acid semialdehyde	— — —	XS	— — —	— — —
Undecanedioic acid semialdehyde	— — —	XS	— — —	— — —
Tetradecanedioic acid semialdehyde	— — —	XS	— — —	— — —
E. Keto acids				
4-Oxohexanoic	M(tent.)	— — —	— — —	— — —
4-Oxoheptanoic	S(tent.)	XS(tent.)	S(tent.)	— — —
4-Oxooctanoic	S(tent.)	— — —	— — —	— — —
4-Oxononanoic	— — —	XS(tent.)	— — —	— — —
4-Oxo-*trans*-2-octenoic	— — —	— — —	— — —	L
4-Oxo-*trans*-2-nonenoic	— — —	— — —	— — —	M
4-Oxo-*trans*-2-undecenoic	— — —	— — —	— — —	S
4-Oxo-*cis*-2-dodecenoic	— — —	— — —	— — —	XS(tent.)

TABLE I

Volatile Decomposition Products Produced by Various Triglycerides during Simulated Deep-fat Frying[a]

	Relative amount of compound			
Compound	Corn oil	Hydrogenated cottonseed oil	Trilinolein	Triolein
F. Dibasic acids				
Hexanedioic	S	– – –	S	– – –
Heptanedioic	S	XS	XS	– – –
Octanedioic	M	XS	S	S
Nonanedioic	L	XS	– – –	M
Decanedioic	– – –	XS	– – –	– – –
Undecanedioic	– – –	XS	– – –	– – –
4-Oxoheptanedioic	– – –	– – –	XS(tent.)	– – –
II. Nonacidic VDP				
A. Saturated hydrocarbons				
Hexane	– – –	– – –	– – –	XS
Heptane	S	– – –	– – –	M
Octane	S	S	– – –	S
Nonane	M	– – –	S	XL
Decane	L	M	M	M
Undecane	M	M	– – –	S
Dodecane	S	S	– – –	L
Tridecane	S	XS	– – –	– – –
Tetradecane	S	S	S	– – –
Pentadecane	– – –	S	XS	– – –
Hexadecane	– – –	S	XS	– – –
Heptadecane	– – –	S	– – –	– – –
Octadecane	– – –	XS	– – –	– – –
B. Unsaturated hydrocarbons				
1-Octene	– – –	– – –	S	M
1-Nonene	– – –	– – –	S	M
1-Decene	– – –	– – –	– – –	S
1-Undecene	– – –	XS	– – –	– – –
trans-2-Octene	– – –	S	S	– – –
cis-2-Octene	– – –	– – –	S	– – –
trans-Undecene	– – –	– – –	S	– – –
trans-Dodecene	M	XS	S	– – –
trans-Tridecene	XS	S	– – –	– – –
trans-Tetradecene	S	XS	– – –	– – –
trans-Hexadecene	– – –	S	– – –	– – –
trans-Heptadecene	– – –	S(tent.)	– – –	– – –
trans-1,3-Octadiene	– – –	– – –	S(tent.)	– – –
trans-1,3-Nonadiene	– – –	– – –	S(tent.)	– – –
trans, trans-Tetradecadiene	– – –	– – –	S(tent.)	– – –
trans, cis-Tetradecadiene	– – –	– – –	S(tent.)	– – –
C. Alcohols				
Ethanol	– – –	– – –	M	– – –
1-Propanol	– – –	– – –	– – –	L
1-Butanol	S	M	L	M
1-Pentanol	XL	L	XL	– – –
1-Hexanol	S	M	S	L
1-Heptanol	– – –	L	S	L
1-Octanol	XL	M	L	L
1-Decanol	– – –	S	– – –	– – –
1-Undecanol	– – –	– – –	M	– – –
1-Dodecanol	– – –	– – –	S	– – –
2-Hexanol	– – –	XS(tent.)	– – –	– – –
2-Octanol	– – –	– – –	M	– – –
3-Octanol	XL	– – –	S	– – –
1-Penten-3-ol	L	– – –	– – –	– – –
1-Octen-3-ol	XL	L	XL	– – –
D. Saturated aldehydes				
Propanal	– – –	– – –	– – –	L
Butanal	– – –	– – –	S	M
Pentanal	XL	M	XL	– – –
Hexanal	XL	L	XL	M
Heptanal	XL	L	XL	L
Octanal	M	XL	M	XL
Nonanal	XL	XL	S	XL
Decanal	M	M	M	M
Undecanal	– – –	S	– – –	L
Dodecanal	– – –	XS	XS	M
Tridecanal	– – –	XS	– – –	– – –
Tetradecanal	– – –	XS	– – –	– – –
Pentadecanal	– – –	XS	– – –	– – –
3,4,5-Trimethylheptanal	L(tent.)	– – –	M(tent.)	– – –
4-Methoxy-3,3-dimethyl-butanal	S(tent.)	– – –	S(tent.)	– – –
E. Unsaturated aldehydes				
trans-2-Hexenal	M	M	M	S
trans-2-Heptenal	XL	XL	XL	M
trans-2-Octenal	XL	XL	XL	M
trans-2-Nonenal	XL	XL	M	L
trans-2-Decenal	XL	XS	M	XL

		Relative amount of compound			
	Compound	Corn oil	Hydrogenated cottonseed oil	Trilinolein	Triolein
	trans-2-Undecenal	S	S	– – –	XL
	cis-2-Heptenal	– – –	– – –	S	– – –
	cis-2-Octenal	– – –	– – –	S	– – –
	cis-2-Nonenal	– – –	– – –	XS	– – –
	cis-3-Hexenal	– – –	– – –	M(tent.)	– – –
	trans-4-Hexenal	S	– – –	S(tent.)	– – –
	trans-3-Decenal	S	– – –	– – –	M
	5-Hexenal	– – –	– – –	– – –	M
	6-Heptenal	– – –	– – –	– – –	M
	7-Octenal	– – –	– – –	– – –	L
	5-Methyl-4-hexenal	S(tent.)	– – –	– – –	– – –
	4-Oxo-*trans*-2-octenal	– – –	– – –	– – –	L(tent.)
	trans-2-*cis*-4-Heptadienal	– – –	– – –	M	– – –
	trans-2-*cis*-4-Nonadienal	S	L	M	M
	trans-2-*trans*-4-Nonadienal	L	M	XL	– – –
	trans-2-*trans*-6-Nonadienal	XL	– – –	– – –	– – –
	trans-2-*cis*-4-Decadienal	S	L	XS	– – –
	trans-2-*trans*-4-Decadienal	XL	L	XL	– – –
F.	Ketones				
	2-Heptanone	S	– – –	L	S
	2-Octanone	S	– – –	M	– – –
	2-Nonanone	– – –	XS	S	M
	2-Decanone	S	S	– – –	L
	2-Undecanone	– – –	– – –	M	– – –
	2-Dodecanone	– – –	S	XS	– – –
	3-Heptanone	– – –	– – –	S	S
	3-Octanone	– – –	XS	S	S
	3-Nonanone	– – –	– – –	S	S
	3-Decanone	– – –	– – –	M	– – –
	3-Dodecanone	– – –	– – –	XS(tent.)	– – –
	4-Octanone	– – –	– – –	– – –	M
	4-Undecanone	M	XS	– – –	– – –
	4-Dodecanone	S	– – –	– – –	– – –
	1-Octen-3-one	S(tent.)	– – –	– – –	– – –
	2-Methyl-3-octen-5-one	S(tent.)	– – –	S(tent.)	– – –
	trans-3-Nonen-2-one	XL	– – –	S(tent.)	– – –
	trans-3-Undecen-2-one	– – –	– – –	S(tent.)	– – –
	Noneone	– – –	XS(tent.)	– – –	XS(tent.)
	Dodecenone	– – –	– – –	– – –	XS(tent.)
	1-Methoxy-3-hexanone	M(tent.)	– – –	L(tent.)	– – –
G.	Esters				
	Ethyl acetate	XL	XL	XL	XL
	Butyl acetate	– – –	S	S	– – –
	Hexyl formate	– – –	– – –	XS	L
	Ethyl hexanoate	S	– – –	– – –	– – –
	Octyl formate	S	– – –	– – –	L
	Methyl nonanoate	– – –	– – –	S	– – –
	Ethyl octanoate	– – –	– – –	– – –	S
	Methyl dodecanoate	– – –	– – –	XS	– – –
	trans-2-Octenyl formate	– – –	– – –	– – –	S
	Ethyl *cis*-2-dodecenoate	– – –	– – –	– – –	S(tent.)
H.	Lactones				
	4-Hydroxypentanoic	S	– – –	M	– – –
	4-Hydroxylhexanoic	L	– – –	S	– – –
	4-Hydroxyheptanoic	S	XS	– – –	XS
	4-Hydroxyoctanoic	L	– – –	M	S
	4-Hydroxynonanoic	– – –	S	S	M
	4-Hydroxydecanoic	– – –	S	S	S
	5-Hydroxyhexanoic	– – –	– – –	S(tent.)	– – –
	5-Hydroxydecanoic	– – –	– – –	S	– – –
	6-Hydroxyhexanoic	– – –	– – –	S	– – –
	4-Hydroxy-2-hexenoic	– – –	– – –	M	XS(tent.)
	4-Hydroxy-2-heptenoic	S	– – –	XS	– – –
	4-Hydroxy-2-octenoic	– – –	– – –	XS	M
	4-Hydroxy-2-nonenoic	L	– – –	XL	– – –
	4-Hydroxy-2-decenoic	– – –	– – –	S	– – –
	4-Hydroxy-3-octenoic	– – –	– – –	– – –	S(tent.)
	4-Hydroxy-3-nonenoic	– – –	– – –	XL(tent.)	– – –
	5-Hydroxy-2-nonenoic	– – –	– – –	M(tent.)	– – –
I.	Aromatic compounds				
	Toluene	S	– – –	– – –	– – –
	Butylbenzene	– – –	– – –	S	– – –
	Isobutylbenzene	M	– – –	– – –	– – –
	Hexylbenzene	S	– – –	S	– – –
	Phenol	L	– – –	– – –	– – –
	Benzaldehyde	S	XS	M	– – –
	Acetophenone	S(tent.)	– – –	– – –	– – –
	4-Phenylbutanal	M(tent.)	– – –	XS	– – –
	5-Phenylpentanal	S(tent.)	– – –	S	– – –
J.	Miscellaneous compounds				
	2-Pentylfuran	XL	L	XL	– – –
	1,4-Dioxane	– – –	– – –	L	– – –

[a] XS indicates extra small gas chromatographic peaks; S, small; M, medium; L, large; XL, extra large.

TABLE II

Physical and Chemical Changes of Corn Oil during Deep-fat Frying and during Continuous Heating

	Oil used for frying (hr)							Oil continuously heated (hr)
	0	3	6	12	30	60	90	90
Free fatty acid (% oleic acid)	0.12	0.13	0.13	0.17	0.30	0.88	1.37	0.32
Peroxide number (meq/kg)	1.34	1.53	1.63	2.75	1.92	2.41	2.94	2.20
Iodine value (Wijs)	128	128	127	126	126	123	124	122
Refractive index (40 C)	1.4625	1.4675	1.4680	1.4681	1.4681	1.4681	1.4681	1.4681
Color (photometric)	2.86	3.26	3.92	4.58	5.26	8.04	8.56	12.47
Viscosity (centistokes) 37.7 C	39.7	40.0	40.3	43.2	42.3	44.9	43.9	50.4
Foaming (ml)	None	None	None	None	None	None	None	200

TABLE III

Physical and Chemical Changes of Hydrogenated Cottonseed Oil during Deep-fat Frying and Continuous Heating

	Oil used for frying (hr)									Oil continuously heated (hr)
	0	3	6	12	30	60	90	120	150	120
Free fatty acid (% oleic acid)	0.07	0.14	0.20	0.37	0.71	1.83	2.99	5.07	5.20	0.34
Peroxide number (meq/kg)	1.15	1.65	1.80	1.90	1.70	1.15	1.60	1.60	1.65	2.10
Iodine value (Wijs)	69.2	69.2	69.0	68.6	68.3	68.1	67.7	67.2	66.9	64.5
Refractive index (40 C)	1.4603	1.4604	1.4604	1.4606	1.4608	1.4607	1.4608	1.4609	1.4607	1.4620
Color (photometric)	1.4	1.9	2.4	2.7	3.5	6.6	8.6	13.3	15.0	9.2
Viscosity (centistokes, 37.7 C)	10.2	10.4	10.4	10.4	10.5	10.7	10.7	10.8	10.8	13.2
Foaming (ml)	0	0	0	0	0	0	0	0	0	10

TABLE IV

Physical and Chemical Changes of Triglycerides during Simulated Deep-fat Frying

	Trilinolein ($C_{18:2=}$)		Triolein ($C_{18:1=}$)		Tristearin ($C_{18:0=}$)	
	Before treatment	After frying	Before treatment	After frying	Before treatment	After frying
Color (photometric)	3.55	76.00	5.8	62.5	1.26	12.04
Free fatty acid content (%)	0.04	2.6	Nil	3.9	Nil	4.0
Iodine value (Wijs)	176.0	155.4	85.0	78.1	0.0	0.5
Peroxide value (meq/kg)	25.8	4.7	0.9	3.4	0.0	3.2
Viscosity[a] (centistokes, 30 C)	36.2	200.6	56.2	101.8	16.0	21.1
Refractive index[a] (40 C)	1.4728	1.4793	1.4632	1.4655	1.4402	1.4420
NAF esters (%)	----	26.3	----	10.8	----	4.2

[a]Note: Viscosity and refractive index of tristearin were measured at 80 C.

TABLE V

Functional Group Analysis of NAF Esters from Trilinolein, Triolein, and Tristearin Used for Simulated Deep-fat Frying

	Trilinolein NAF esters	Triolein NAF esters	Tristearin NAF esters
Double bonds/mole	1.53 - 2.57	1.18 - 1.72	0.11 - 0.93
Hydroxyl groups/mole	0.22 - 2.80	Nil - 2.10	Nil - 1.57
Ester groups/mole	1.56 - 3.13	1.62 - 2.98	1.37 - 2.80
Carbonyl groups/mole	Nil - 0.28	Nil - 0.45	Nil - 0.11
Peroxide/mole	Nil - 0.9	Nil - 0.06	Nil - 0.1
Epoxide/mole	Nil	Nil	Nil

Among the VDP identified, the unsaturated lactones are of particular interest. The γ-lactones with unsaturation at the 2- or 3-position, viz., 4-hydroxy-2-nonenoic acid, lactone and 4-hydroxy-3-nonenoic acid, lactone, impart a characteristic deep-fat fried flavor to cottonseed oil when added at 2.5 ppm (22). The responses of the panel to the description of the cottonseed oil, plus 4-hydroxy-2-nonenoic acid, lactone, included nutty, fried fat notes, plus a butter-like note.

This observation explains well some previously published results. 4-Hydroxy-2-nonenoic acid, lactone was found by Krishnamurthy and Chang (17) in corn oil after it was simulatedly deep-fat fried. However, such lactones were not found by Reddy et al. (19) in hydrogenated cottonseed oil after it was simulatedly deep-fat fried under identical conditions. Since such lactones are now ascertained to play an important role in deep-fat fried flavor, they might be the reason why Blumenthal et al. (23) found that vegetable oils, such as corn oil, had a more desirable flavor than hydrogenated fat, such as hydrogenated soybean oil, after both were subject to simulated deep-fat frying under identical conditions.

More recently, Thompson et al. (20) isolated, fractionated, and identified the volatile flavor compounds produced by trilinolein, and May et al. (21) identified those by triolein when each was subjected to simulated deep-fat frying, separately. They found more unsaturated lactones in the decomposition products of trilinolein, but less in those of triolein; both in number and in amount. This may indicate that some linoleic acid is necessary in frying fat if the characteristic deep-fat fried flavor is desired.

Organoleptic evaluation also showed that 4-hydroxy-2-nonenoic acid, lactone and 4-hydroxy-2-octenoic acid, lactone had an adverse effect upon the flavor of margarine. However, addition of 2.5 ppm of 4-hydroxy-3-nonenoic acid, lactone and 4-hydroxy-3-octenoic acid, lactone improved the flavor of margarine. The former could also improve the flavor of a snack food.

NONVOLATILE DECOMPOSITION PRODUCTS

The NVDP produced under simulated deep-fat frying with corn oil (14), hydrogenated cottonseed oil (18), and pure triglycerides of the three major fatty acids of the commonly used frying fats and oils, viz., trilinolein (15), triolein (24), and tristearin (25), were studied by Chang and his associates.

The change in physical and chemical properties of corn oil before and after the simulated deep-fat frying and continuous heating are shown in Table II and those of the hydrogenated cottonseed oil in Table III. The hydrogenated cottonseed oil had an iodine value of 69.2 and contained 0.6% of C_{14}, 23.0% of C_{16}, 7.4% of C_{18}, 56.4%, of $C_{18:1=}$ and 12.6% of $C_{18:2=}$ fatty acids. The *trans* isomer content of the fatty acids was 48.5%. Evidently, it had a better thermal oxidative stability than the corn oil. Both oils showed a higher free fatty acid content, iodine value, and color, but lower viscosity when used for simulated deep-fat frying than for continuous heating for the same length of time. This indicated that chemical reactions which take place during deep-fat frying were different from those during continuous heating. Therefore, studies conducted with oils heated under air, with or without agitation, might not be used to represent those of frying oils.

The change of physical and chemical properties of the three pure triglycerides, when fresh and after being treated under deep-fat frying conditions at 185 C for 74 hr, are shown in Table IV.

Trilinolein, after the simulated deep-fat frying, formed 26.3% of non-urea-adduct-forming (NAF) esters (15). The amount of NAF esters was decreased to 10.8% when triolein was similarly treated (24). It was surprising to find that tristearin with a melting point of 73 C also produced

TABLE VI

Analysis of Isolated Cyclic and Noncyclic Dimers from Thermally Oxidized Trilinolein

Characteristic	Cyclic dimer	Noncyclic dimer
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 VII

Analysis of Isolated Dimers from Thermally Oxidized Triolein

	Noncyclic dimer	Noncyclic carbonyl dimer
Molecular weight	581	589
Carbon, %	76.81	75.06
Hydrogen, %	11.95	11.56
Oxygen, % (by difference)	11.24	13.38
Iodine value	89.3	84.5
Double bond/mole	2.04	1.96
Saponification value	189.4	194.1
Ester/mole	1.96	2.04
Carbonyl value	Nil	1654
Carbonyl/mole	Nil	0.97

TABLE VIII

Estimated Composition of Oxidized and Polymerized Materials Formed during Simulated Deep-fat Frying at 185 C for 74 Hours

	Trilinolein (%)	Triolein (%)	Tristearin (%)
Cyclic dimers joined by carbon-to-carbon linkages	4.9	0.0	0.0
Noncyclic dimers joined by carbon-to-carbon linkages	2.8	3.4	0.70
Trimers joined by two carbon-to-carbon linkages	8.4	0.3	0.36
Dimers and trimers joined wholly or partly by carbon-to-oxygen linkages	4.9	6.2	1.2
Others			

4.2% of NAF esters, which were clear, brownish, viscous liquids at room temperature.

The iodine value of trilinolein and triolein decreased during the simulated deep-fat frying (Table IV) due to the consumption of double bonds by oxidation and polymerization. However, the iodine value of tristearin increased from 0.0 to 0.5 meq/kg, indicating that dehydrogenation of long chain fatty acids could take place during deep-fat frying. Since double bonds are consumed by oxidation and polymerization, the actual degree of dehydrogenation should be higher than that indicated by the increase in iodine value.

After being used for simulated deep-fat frying at 185 C for 74 hr, 73.7% of the fatty acids in trilinolein remained as $C_{18:2=}$; while 89.2% of the fatty acids in triolein remained as $C_{18:1=}$ and 95.8% of the acids in tristearin remained as $C_{18:0=}$ under identical conditions.

The NAF esters of trilinolein, triolein, and tristearin formed during the simulated deep-fat frying were fractionated by liquid chromatography with the use of silicic acid and stepwise gradient elution into eight to nine fractions. Analysis of these fractions indicated that their average molecular weight ranged from 485 to 832 for those from trilinolein, 464 to 742 for those from triolein, and 426 to 742 for those from tristearin. Therefore, whether the fatty acid was polyunsaturated, monounsaturated, or saturated, the polymers formed during deep-fat frying were essentially dimers and trimers. However, only trilinolein yielded a fraction which was characterized as cyclic dimers. No cyclic polymers were found in the fractions from triolein and tristearin, according to UV analysis of the dehydrogenated esters.

The functional group analysis of the NAF esters from trilinolein, triolein, and tristearin, after they had been used for simulated deep-fat frying, are shown in Table V. The oxygen atoms in all the functional groups analyzed could not account for the percentage of oxygen as determined by elemental analysis. Therefore, some oxygen atoms might be present in the bridges between the monomeric units or in some functional groups which were not analyzed.

Two relatively pure dimers were obtained from the NAF esters of trilinolein by repeated TLC which was followed by GC (Table VI). Physical and chemical analysis, together with IR, UV, and NMR spectrometric analysis, indicated one was a cyclic carbon-to-carbon linked dimer which amounted to 4.9% of the treated trilinolein; the other was a noncyclic dimer formed through carbon-to-carbon linkage and containing two hydroxyl groups. The noncyclic dimer constituted 2.8% of the treated trilinolein.

Triolein also yielded two dimers joined by carbon-to-carbon linkages under simulated deep-fat frying conditions (Table VII). However, both of them were noncyclic. One was a dimer of methyl oleate which constituted 1.36% of the thermally oxidized triolein. The other constituted 1.36% of the treated olein and was also a dimer of methyl oleate, but it contained one carbonyl group per molecule.

The liquid chromatogrphic fractions of the NAF esters from trilinolein, triolein, and tristearin, respectively, could not be depolymerized by refluxing with 2.5 N dry hydrochloric acid in anhydrous methanol. This indicated that the polymers formed during deep-fat frying were different from those formed by bubbling oxygen into methyl linoleate at 63 C which, according to Chang and Kummerow (26), could be easily depolymerized by this treatment. However, the fractions of NAF esters could be partially depolymerized by hydrochloric acid indicating that the polymers formed during deep-fat frying were partially joined by carbon-to-carbon linkages and partially by carbon-to-oxygen linkages.

The depolymerized product from each of the NAF ester fractions showed three major spots on Silica Gel G thin layer plates corresponding to R_f values of monomers, dimers, and trimers. From the molecular weight and amount of each of the NAF esters fractions and those of each of the TLC spots after the depolymerization of each fraction, the composition of the oxidized and polymerized materials in trilinolein, triolein, and tristearin after each had been treated under simulated deep-fat frying conditions were estimated and shown in Table VIII.

FRYING FAT AND HUMAN HEALTH

There is no doubt that overused or highly abused frying oil contains oxidized and polymerized materials which are harmful to human health. There is also no doubt that the volatile decomposition products which are produced during deep-fat frying contain chemical compounds which are known to be toxic. Since huge amounts of oils and fats are used for deep-fat frying, not only in this country but all over the world, and deep-fat fried foods are a major item of human diets, it is absolutely essential for the research institutions, commercial and industrial operators, and government agencies to join forces to ascertain the extent to which a frying oil can be used without producing enough oxidized and polymerized materials to cause an adverse effect in human metabolism. A quick, simple, and dependable test must be developed to allow those who conduct deep-fat frying to determine the point at which a batch of frying oil must be discarded.

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