Chemical Reactions Involved in the Deep Fat Frying of Foods. II. Identification of Acidic Volatile Decomposition Products of Corn Oil[1]

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Abstract

Chemical identification of the volatile decomposition products (VDP) produced by fats and oils under conditions of deep fat frying is important for the elucidation of the mechanisms of thermal oxidation, for the study of their effects upon human nutrition, and for their contribution to the deep fat fried flavor of foods. The acidic VDP produced by corn oil maintained at 185C for 30 hr with periodic frying of moist cotton balls and with addition of fresh oil to replenish the oil lost due to evaporation, decomposition, and adsorption by the cotton balls were fractionated by repeated gas chromatography. The gas chromatographic fractions were identified by IR and mass spectrometry. A total of 30 acids were characterized. They consisted of 12 n-aliphatic saturated acids, seven 2-enoic acids, one 3-enoic acid, three keto acids, two hydroxy acids, four dicarboxylic acid and one aromatic acid. It is suggested that the effects of some of these acids upon human nutrition be studied.

Introduction

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 are simultaneously produced, the chemical structures of the volatile ones may be of use in the elucidation of those of the nonvolatile decomposition products.

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.

Lastly, 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 chemical characterization of the VDP produced during deep fat frying has not been extensively studied. Endres et al. (1) analyzed the volatile decomposition products produced by bubbling air through synthetic triglycerides at 200C. Crossley et al. (2) studied the effect of heat on tricaprin and 2-oleodipalmitin both in the absence and in the presence of oxygen. They demonstrated that even a pure saturated triglyceride may be thermally oixdized, although as expected, unsaturated glycerides are more readily degraded. The volatile carbonyl compounds formed during the deep fat frying of potato in different fat were analyzed by Wishner and Keeney (3) and those evolved from heated cottonseed oil at various levels of moisture by Dornseifer et al. (4).

The volatile thermal oxidation products of soybean oil were analyzed by Ota et al. (5) by the use of retention time on gas chromatography. Recently, Lea and Swoboda (6) studied the VDP of highly autoxidized sunflower oil at 200C.

None of the previous investigators used conditions which are similar to those of commercial deep fat frying. The present paper reports systematic chemical characterization of the acidic VDP produced by corn oil under simulated restaurant conditions of deep fat frying. A subsequent paper will report the identification of nonacidic VDP.

Experimental

Collection of Acidic Volatile Decomposition Products

Corn oil, 2,300 ml, was heated to 185C in a Sunbeam household deep fat fryer. Ten moist cotton balls, each weighing 2 g and containing 75% by weight of water, were fried in the oil every 30 min. After 3 min of deep fat frying, the cotton balls were removed from the oil. The fried cotton balls contained approximately 1.8% moisture and 82% oil. After each 6 hr of heating at 185C, the oil was allowed to cool to room temperature and to stand overnight. The fryer was replenished with 800 ml of fresh corn oil after every 12 hr of operation. The VDP thus produced and evaporated with the steam during 30 hr of heating and frying were collected by the apparatus described previously (7). In order to obtain enough VDP for fractionation and characterization, the experiment was repeated eight times, each time starting with 2,300 ml fresh corn oil. The VDP from the eight batches of operation were combined. Since they were contaminated with some entrained oil, they were molecularly distilled at 150C and under 1 μ of vacuum for 6 hr (7). The distillate was separated into acidic and nonacidic VDP by being dissolved in ethyl ether and then extracted with 10% aqueous sodium carbonate solution.

The residue of molecular distillation was dissolved in ethyl ether and the remaining acidic compounds isolated by extraction with 10% aqueous sodium carbonate solution. These acidic compounds were again molecularly distilled at 150C under 1 μ of vacuum for 6 hr. This distillate was also used as volatile

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acidic decomposition products. Further molecular distillation at 185C did not yield a significant amount of volatile compounds.

In two additional separate experiments, one batch of corn oil was used for heating and frying for a period of 90 hr while the other batch was used for 120 hr. The acidic VDP produced in these two experiments were prepared separately by the same means described above.

Fractionation by Gas Chromatography

The acidic VDP were converted into their methyl esters by the use of diazomethane (8). The methyl esters were then gas chromatographed with an Aerograph A-90-P using a 6 ft × 1/4 in. I.D. aluminum column packed with 20% stabilized DEGS on 70/80 Anakrom. The temperature was nonlinearly programmed from 60–200C in 18 min and then maintained at the latter temperature for the rest of the period. The gas chromatography was repeated 35 times. Each gas chromatographic fraction was accumulatively collected in one trap with the fraction collector reported by Deck et al. (9).

Each of the collected gas chromatographic fractions was rechromatographed with the same instrument using a 6 ft × 1/4 in. I.D. aluminum column packed with 20% methyl silicone gum SE-30 on 70/80 mesh Anakrom ABS. The temperature was nonlinearly programmed from 60–200C in 18 min and then held at the latter temperature for the remaining period. Each of the gas chromatographic fractions was again collected for identification.

Identification of Gas Chromatographic Fractions

The techniques for the determination of IR and mass spectra of gas chromatographic fractions have been reported previously (10). The chemical structure postulated for a gas chromatographic fraction by the interpretation of its IR and mass spectra was considered as tentative. If the postulated structure was confirmed by comparing its retention times on two different stationary phases with those of the authentic compound, then the gas chromatographic fraction was considered as identified. Where the authentic compound of a particular carbon number was not available, homologous plots of log retention time against carbon number were prepared on two different stationary phases using available compounds of the same homologous series. The carbon number of the fraction was then determined from the homologous plots.

TABLE I

Compounds Identified as Volatile Decomposition Products of Corn Oil during Deep Fat Frying For 30 Hr

Peak No.	Identified as	Size of peak
Saturated acids		
0-A	Methyl formate	....
1-A	Methyl acetate	Small
2-B	Methyl propanoate	Small
3-B	Methyl butanoate	Small
4-B	Methyl pentanoate	Large
5-B	Methyl hexanoate	Extra large
6-B	Methyl heptanoate	Large
8-B	Methyl octanoate	Large
10-C	Methyl nonanoate	Large
12-C	Methyl decanoate	Small
13-E	Methyl undecanoate	Small
18-B	Methyl laurate	Small
Unsaturated acids		
7-A	Methyl 2-hexenoate	Small
9-B	Methyl 2-octenoate	Medium
11-A	Methyl 2-nonenoate	Medium
13-C	Methyl 2-decenoate	Small
14-A	Methyl 2-undecenoate	Small
17-E	Methyl 2-dodecenoate	Small
13-D	Methyl 3-decenoate[a]	Large
Keto acids		
16-A	γ-keto-methyl-hexanoate[a]	Medium
17-C	γ-keto-methyl-heptanoate[a]	Small
19-C	γ-keto-methyl-octanoate[a]	Small
Hydroxy acids		
15-A	β-Hydroxy-methyl-hexanoate[a]	Small
15-C	α-Hydroxy-methyl-heptanoate[a]	Small
Dicarboxylic acids		
17-B	Dimethyl adipate	Small
20, 21-B	Dimethyl pimelate	Small
22-A	Dimethyl suberate	Medium
24-C	Dimethyl azelate	Large
Aromatic acid		
15-B	Methyl benzoate	Small

[a] Tentatively identified.

Numerals indicate the number of gas chromatographic peaks with DEGS as stationary phase (Same as numbers in Fig. 1).

Letters indicate the number of gas chromatographic peaks when rechromatographed with SE-30 as stationary phase.

Analysis of Fatty Acid Composition

The fatty acid composition of the corn oil before and after being used for deep fat frying was analyzed by gas chromatography according to the method described previously (11).

Results and Discussion

A total of 30 acidic compounds were identified in the VDP of corn oil during deep fat frying under simulated restaurant conditions for 30 hr (Table I). These compounds consisted of normal saturated aliphatic fatty acids from C_1 to C_{12}, 2-ene acids from C_6 to C_{12}, one 3-ene acid, three keto acids, two hydroxy acids, four dicarboxylic acids, and one aromatic acid. The IR and mass spectra of some of the acids identified are not available in the literature. They are therefore shown in Fig. 1 and 2, respectively.

Fatty acids, which were major components of the corn oil used (Table II) were not identified in the VDP produced during 30 hr of frying. They were, however, identified in those produced during 90 hr

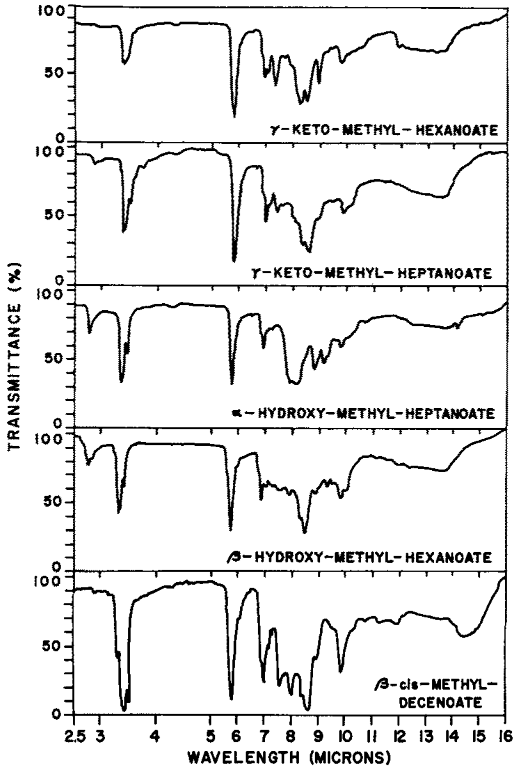


FIG. 1. Infrared Spectra of gas chromatographic fractions identified as compounds given.

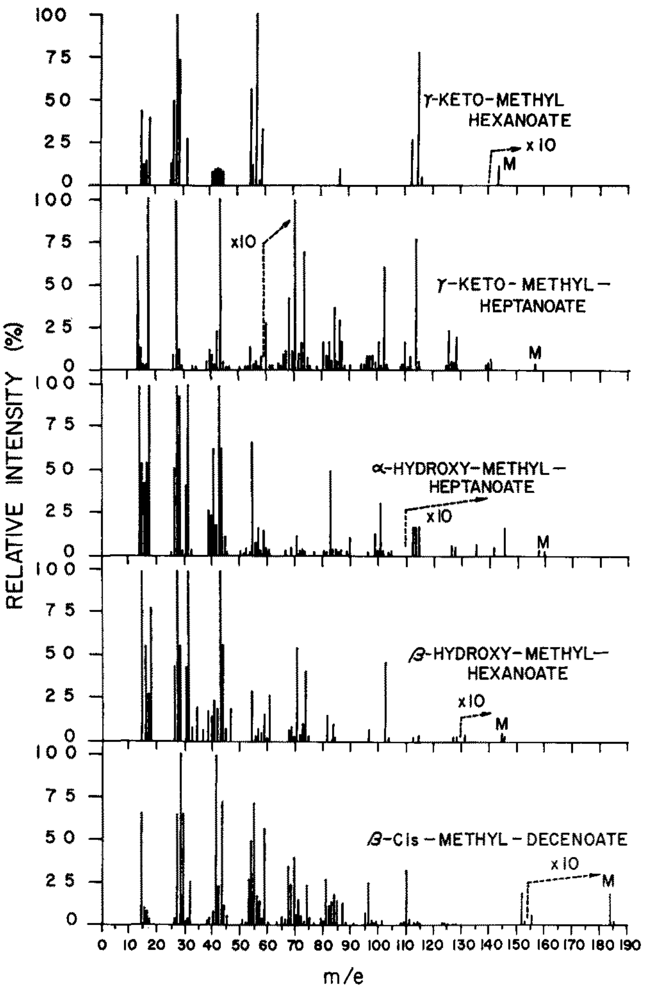


FIG. 2. Mass Spectra of gas chromatographic fractions identified as compounds given.

of frying (Table III). The minor component, myristic acid, was identified in only those produced during 120 hr of frying. These fatty acids eluted on gas chromatography as large peaks at positions approximately the same as peaks 22, 24, 25, and 26 in Fig. 3. However, the peaks at these positions during the gas chromatography of VDP produced in 30 hr of frying did not represent these fatty acids. The order of the peak areas of these acids were linoleate > oleate > palmitate > stearate, which was the same as the proportions of these acids in corn oil. These observations confirmed our previous conclusion that during the early stage of frying, acidic decomposition products are predominantly produced by the breakage of carbon chains through oxidation and that during the later stage of frying, acidic decomposition products are predominantly produced by hydrolysis of triglycerides (7).

TABLE II

Fatty Acid Composition of Corn Oil Used for Deep Fat Frying

	Fresh corn oil %
Myristic acid	Trace
Palmitic acid	11.70
Stearic acid	1.49
Oleic acid	28.59
Linoleic acid	57.92
Linolenic acid	Trace

TABLE III

Additional Compounds Identified as Volatile Decomposition Products of Corn Oil During Deep Fat Frying for 90 and 120 Hours

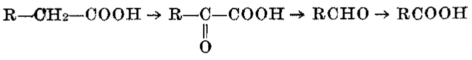
Peak No.	Identified as	Size of peak
22-A	Methyl palmitate	Large
24-B	Methyl stearate	Large
25-A	Methyl oleate	Large
26-B	Methyl linoleate	Large
19-E[a]	Methyl myristate	Small

[a] In products of 120 hr of frying only.

Acidic volatile decomposition products may be produced from triglycerides of corn oil during deep fat frying through the following schemes:

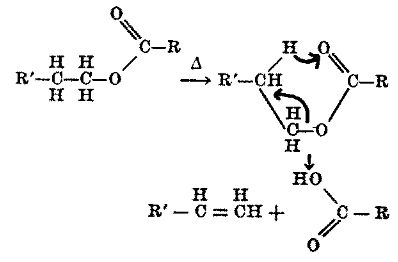
1) Hydrolysis of the ester linkages.

2) Oxidation of fatty acids of longer chain length (14).

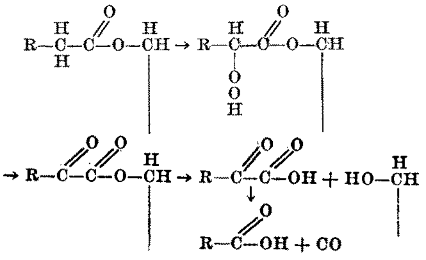


$$R{-}CH_2{-}COOH \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}COOH \rightarrow RCHO \rightarrow RCOOH$$

3) Thermal degradation of esters (15).

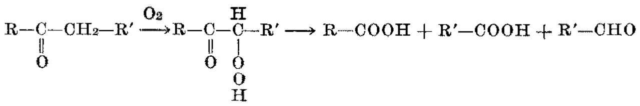


4) Thermal Oxidation of an α-carbon atom of the acids in triglycerides (2).



5) Autoxidation of aldehydes (12).

6) Autoxidation of ketones (13).



$$R{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}R' \xrightarrow{O_2} R{-}\underset{\underset{O}{\|}}{C}{-}\overset{H}{\underset{\underset{\underset{H}{O}}{\overset{|}{O}}}{C}}{-}R' \longrightarrow R{-}COOH + R'{-}COOH + R'{-}CHO$$

The aldehydes and ketones required in the last two mechanisms may be formed either from saturated or unsaturated fatty acids in triglycerides under the conditoins of deep fat frying. Crossley et al. (2) postulated that for saturated fatty esters, the dominant attack during thermal oxidation was on the α-carbon atom. The attack on β-carbon atoms with the formation of ketones was less frequent. He also postulated that for unsaturated fatty esters, oxidation took place in vicinity of double bonds in preference to attack in the proximity of the carboxyl function with the formation of aldehydes.

That some of the identified fatty acids were the autoxidation products of corresponding aldehydes

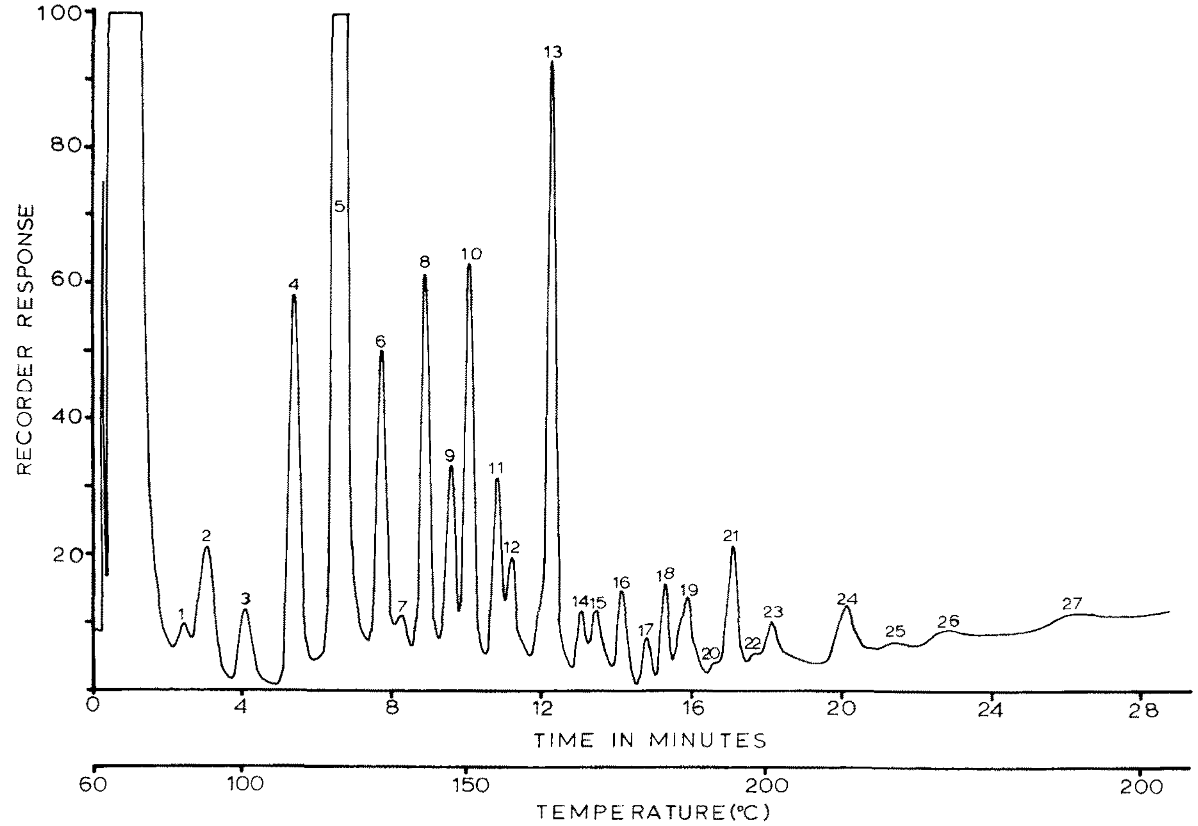


FIG. 3. Gas chromatogram of acidic volatile decomposition products produced by corn oil during deep fat frying.

was supported by the compounds identified in the nonacidic fraction of the VDP produced by corn oil (16). Among the n-aliphatic saturated fatty acids identified, C_6 was represented by the largest gas chromatographic peak, while C_5, C_7, C_8, and C_9 were large peaks. The same order was found for the corresponding normal aliphatic saturated aldehydes. However, not all the corresponding aldehydes of the complete homologous series of n-aliphatic saturated fatty acids from C_1 to C_{12} (Table I) were identified in the nonacidic fraction. It therefore appeared that some or portions of some of these fatty acids were produced by the consecutive shortening of the fatty acid chain according to the mechanism proposed by Endres et al. (14). The starting fatty acid may be produced either by hydrolysis of the triglyceride or by the thermal oxidation of the α-carbon atom of the triglyceride as postulated by Crossley et al. (2).

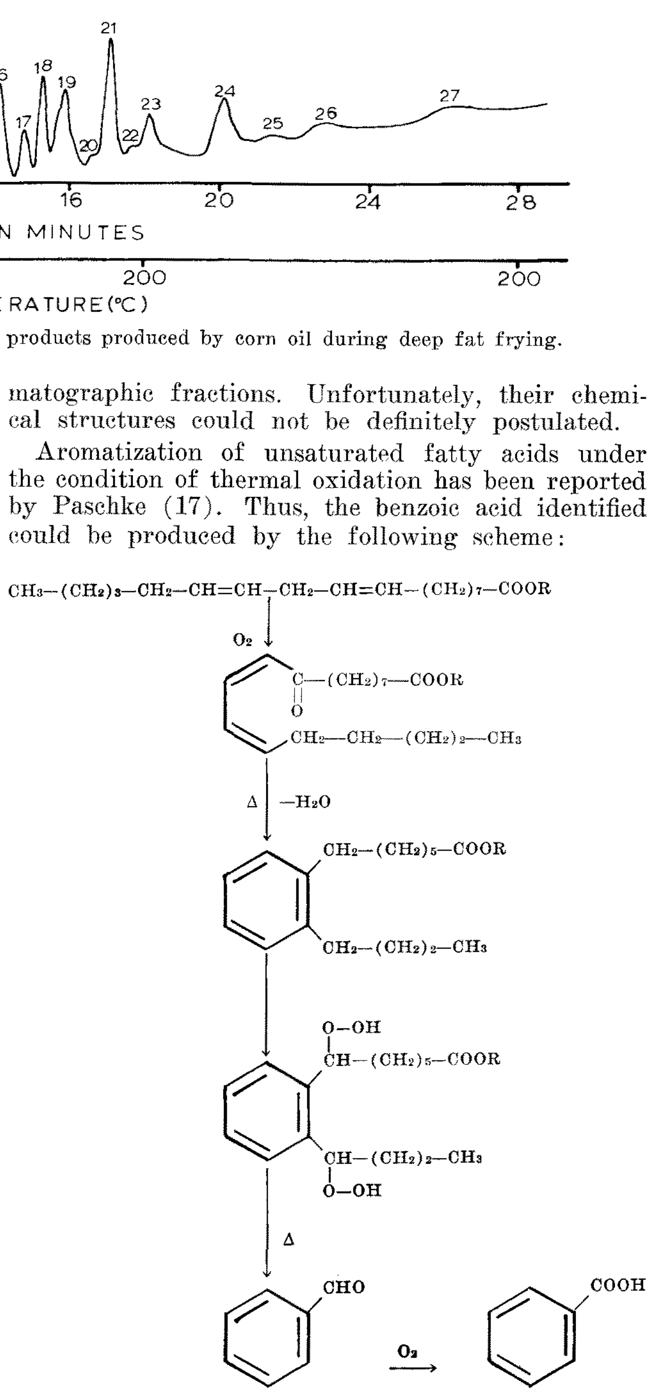
The mechanism of the formation of acids through the oxidation of ketones (13) was unlikely to occur during deep fat frying. Although a large number of fatty acids were identified in the acidic fraction of the VDP of corn oil during thermal oxidation, only a few corresponding ketones were identified in the nonacidic fraction.

The keto and hydroxy acids may be produced either by secondary oxidation of unsaturated fatty acids or by the attack of α-, β- or γ- carbon atom of saturated fatty acids through further oxidation (2). The dibasic acids could be produced by secondary oxidation of unsaturated fatty acids. For example,

$$R—CH = CH—(CH_2)_7—COOH \rightarrow R—CH_2—CHOOH—(CH_2)_7—COOH$$
$$\rightarrow OHC—(CH_2)_7—COOH \rightarrow HOOC—(CH_2)_7—COOH$$

The presence of the intermediates, aldehydo acids, was indicated by the IR spectra of several gas chromatographic fractions. Unfortunately, their chemical structures could not be definitely postulated.

Aromatization of unsaturated fatty acids under the condition of thermal oxidation has been reported by Paschke (17). Thus, the benzoic acid identified could be produced by the following scheme:



The conditions of thermal oxidation used in this investigation were simulated to those of commercial deep fat frying. The acidic compounds identified may well be present in the deep fat fried foods in our diet (7). The effects of the identified acids, particularly the keto, hydroxy, dicarboxylic and aromatic acids, upon human nutrition should therefore be studied.

ACKNOWLEDGMENTS

Frying experiments conducted by Mrs. Agnes S. Gibbons. Fatty acid composition of corn oils analyzed by B. R. Reddy. Determination and interpretation of mass spectra assisted by P. E. Funk and A. K. Bose, Department of Chemistry, Stevens Institute of Technology.

Supported in whole by Public Health Service Research Grant HE-07610 from the National Heart Institute.

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[Received September 9, 1966]