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

R. G. KRISHNAMURTHY[2] and STEPHEN S. CHANG,
Department of Food Science, Rutgers, The State University, New Brunswick, New Jersey

Abstract

A total of 45 compounds were identified and an additional 20 compounds were tentatively identified in the nonacidic volatile decomposition products produced by corn oil under conditions simulating commercial deep fat frying. The 65 compounds consisted of 11 hydrocarbons, 7 alcohols, 2 esters, 6 lactones, 21 aldehydes, 9 ketones, and 9 aromatic compounds. Including the 30 acidic compounds reported in a previous paper, a total of 95 compounds have been identified as volatile decomposition products of corn oil.

The chemical structure of the identified compounds and the postulated mechanisms of their formation revealed some of the chemical reactions involved in the deep fat frying of foods. Many of the identified compounds had interesting odor characteristics. It is concluded that their effect on human health when inhaled or ingested should be investigated.

THE IMPORTANCE of the systematic identification of the volatile decomposition products (VDP) produced by fats and oils during deep fat frying and literature in this field were reviewed previously (1). The present paper reports the characterization of the nonacidic VDP produced by corn oil under simulated restaurant conditions of deep fat frying. It is a continuation of the previous paper (1) which described the systematic identification of acidic VDP.

Experimental

Collection of Nonacidic Volatile Decomposition Products

Corn oil was heated at 185C for 30 hr with moist cotton balls fried in it periodically. Fresh corn oil was used to replenish the oil at suitable intervals to compensate for the loss of oil due to evaporation, decomposition and adsorption by the cotton balls. The VDP thus produced in 30 hr were separated into acidic and nonacidic compounds. The latter were used for the present investigation. Detailed procedure has been reported in a previous paper (1).

Fractionation by Gas Chromatography

The isolated nonacidic VDP of corn oil were first separated into five broad fractions by preparative gas chromatography using a 10 ft × $\frac{3}{8}$ in. I.D. column of 20% Methyl Silicone SE-30 on 60/80 mesh silanized Chromosorb W. (Wilkens Instrument & Research Inc., Walnut Creek, Calif.). The gas chromatogram obtained from a Wilkens A-90-P Aerograph is shown in Fig. 1. The amount of 0.4 ml of the ethyl ether solution of the nonacidic volatile decompositoin products was injected each time. The gas chromatography was repeated 18 times. Each of the six broad fractions was accumulatively collected in one cold trap with the aid of a fraction collector described by Deck, Thompson and Chang (2). These fractions were rechromatographed separately with an 8 ft × $\frac{1}{4}$ in. I.D. column packed with 15% Ucon Polar 50 HB 280 X on 80/100 mesh Chromosorb W-HMDS (Microtek Instruments, Inc., Baton Rouge, La.). The gas chromatogram of the rechromatography of Fraction No. 4 as obtained from a Wilkens

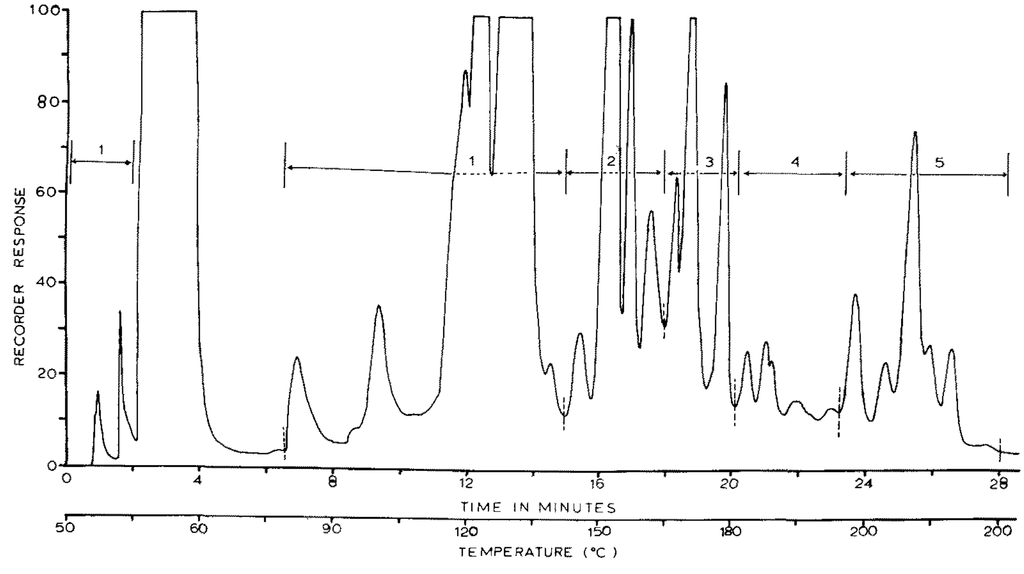

FIG. 1. Gas chromatogram of nonacidic volatile decomposition products of corn oil with a preparative column.

---

[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, The State University.

[2] Present address, Corn Products Co., Bayonne, N.J.

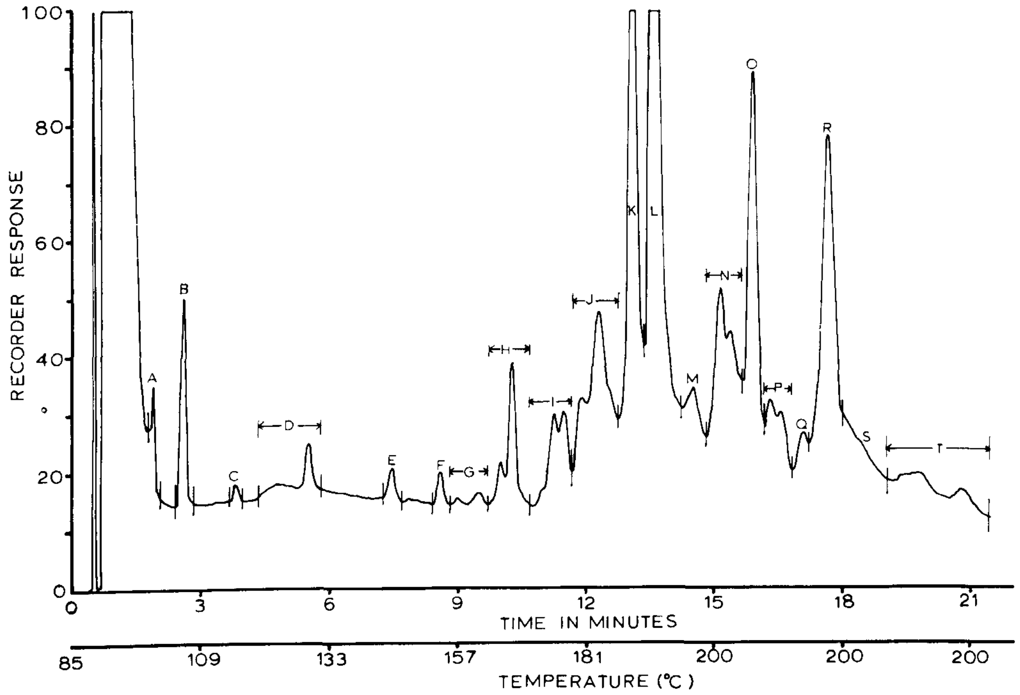

Fig. 2. Gas chromatogram of the rechromatography of the broad fraction No. 4 of nonacidic volatile decomposition products of corn oil.

202 Aerograph Gas Chromatograph is shown in Fig. 2 as an example of the 92 fractions thus obtained. These were collected individually with either the cold trap as described by Deck, Thompson and Chang (2) or that described by Smouse and Chang (3). Each of the rechromatographed fractions was again chromatographed with an 8 ft × ¼ in. I.D. column of 20% Methyl Silicone SE-30 on 70/80 mesh Anakrom ABS. The second rechromatography yielded 370 gas chromatographic fractions which were each collected in a cold trap.

Identification of Gas Chromatographic Fractions

The techniques reported by Kawada, Mookherjee and Chang (4) were used for the determination of IR and mass spectra of the gas chromatographic fractions. The identification of a gas chromatographic fraction by the combined use of IR and mass spectra and retention times has been reported in the previous paper (1).

Peak Size

The area of the peak during the second rechromatography with Methyl Silicone SE-30 as stationary phase was standardized to an attenuation of 2 by multiplying the peak area by the necessary factor. Since the chromatography was repeated a number of times and each peak was accumulatively collected in one cold trap, the standardized peak area was multiplied by the number of injections to obtain the total peak area of the fraction. The peak size was considered as extra large if the total peak area was more than 1000 units; large, if 500–1000 units; medium, if 200–500 units; and small, if 25–500 units.

Results and Discussion

A total of 45 compounds were identified and an additional 20 compounds were tentatively identified as being among the nonacidic VDP produced by corn oil under conditions simulating commercial deep fat frying. The 65 compounds consisted of 11 hydrocarbons, 7 alcohols, 2 esters, 6 lactones, 21 aldehydes, 9 ketones, and 9 aromatic compounds (Table I). These results demonstrated the complexity of the chemical reactions involved in deep fat frying. Including the 30 acidic compounds reported in a previous paper (1), a total of 95 compounds have been identified as the VDP of corn oil. The IR and mass spectra of these compounds which have not been previously published in literature are shown in Figs. 3, 3a, 4, and 4a, respectively.

It should be noted that the large number of compounds were not produced under abnormal drastic laboratory conditions such as by bubbling air through an oil at elevated temperatures. They were produced under simulated restaurant conditions of deep fat frying. The corn oil was heated to only 185C for 30 hr with moist cotton balls fried in it every 30 min. Furthermore, fresh corn oil was added to the fryer every 12 hr to replenish the loss of oil due to evaporation, decomposition, and adsorption by the cotton balls. At the end of the present experiment, the corn oil did not foam during frying and it had a free fatty acid content of only 0.30% (5). Since in commercial practice, an oil is discarded when it begins to foam during frying or when its free fatty acid content is high, such as over 0.7% in the case of doughnut frying or 0.44–0.55% in the case of potato chip frying, the corn oil used for the present experiment would still be considered as good and reusable by commercial standards. Therefore, the 95 compounds identified may evolve during normal commercial deep fat frying and may well be present in the fried foods of our diet (5).

Hydrocarbons were not the major components of the thermal oxidative decomposition products of corn oil. Although 11 hydrocarbons were identified, none of them was represented by an extra large gas chromatographic peak and only one was represented by a large peak (Table I). Alcohols were more predominant; three of these were represented by extra large and one by large gas chromatographic peaks. The most predominant group of compounds was the

TABLE I
Compounds Identified as Nonacidic Volatile Decomposition Products of Corn Oil during Deep Fat Frying for 30 Hours

Peak number	Identified as	Peak size
I. Saturated hydrocarbons		
1-A-a	n-Heptane	Small
1-C-b	n-Octane	Small
1-E-a	n-Nonane	Medium
1-I-d	n-Decane	Large
3-D-c	n-Undecane	Medium
4-H-b	n-Dodecane	Small
5-I-d	n-Tridecane	Small
5-L-k	n-Tetradecane	Small
II. Unsaturated hydrocarbons		
4-H-a	t-Dodecene	Medium
5-1-c	t-Tridecene	Small
5-L-j	t-Tetradecene	Small
III. Alcohols		
1-G-a	n-Butanol	Small
1-K-b	n-Pentanol	Extra large
1-N-b	n-Hexanol	Small
3-M-d	n-Octanol	....
2-P-e	4-Octanol[a]	Extra large
1-H-a	1-Pentene-3-ol	Large
2-O-b	1-Octene-3-ol	Extra large
IV. Esters		
2-A-a	Ethyl acetate	Extra large
4-J-c	5-Octenyl formate[a]	Small
V. Lactones		
2-Q-c	4-Hydroxy pentanoic acid, lactone	Small
3-O-a	4-Hydroxy hexanoic acid, lactone	Large
4-P-b	4-Hydroxy heptanoic acid, lactone	Small
5-Q-c	4-Hydroxy octanoic acid, lactone	Large
4-Q-b	4-Hydroxy-2-heptenoic acid, lactone*	Small
5-S-c	4-Hydroxy-2-nonenoic acid, lactone*	Large
VI. Saturated aldehydes		
1-D-a	n-Pentanal	Extra large
1-H-b	n-Hexanal	Extra large
2-H-c	n-Heptanal	Extra large
2-M-e	n-Octanal	Small
3-J-f	n-Nonanal	Extra large
4-L-f	n-Decanal	Medium
4-S-e	3,4,5-Trimethyl heptanal[a]	Large
VII. Unsaturated aldehydes		
1-K-d	2-Hexenal	Medium
2-M-b	2-Heptenal	Extra large
3-J-e	2-Octenal	Extra large
3-M-g	2-Nonenal	Large
5-M-d	2-Decenal	Extra large
5-O-g	2-Undecenal	Small
2-K-a	4-Hexenal[a]	Small
2-K-a	5-Methyl-4-hexenal[a]	Small
2-P-a	4-Methoxy-2,3-dimethyl butyraldehyde[a]	Small
4-O-d	2t, 4t-Nonadienal	Large
5-P-k	2t, 4t-Decadienal	Extra large
5-P-e	2t, 4c-Decadienal	Small
4-L-d	2t, 6t-Nonadienal[a]	Extra large
4-N-e	2t, 4c-Nonadienal[a]	Small
VIII. Ketones		
1-K-e	2-Heptanone	Small
2-M-d	2-Octanone	Small
4-K-e	2-Decanone	Small
5-L-e	4-Undecanone[a]	Medium
5-N-e	4-Dodecanone[a]	Small
3-O-b	1-Methoxy-hexan-3-one[a]	Medium
4-K-c	5-Keto-3,6-nonadiene[a]	Extra large
4-K-c	4-Keto-7, methyl-5-octene[a]	Extra large
2-P-e	Vinyl amyl ketone[a]	Extra large
IX. Aromatic compounds		
1-F-a	Toluene	Small
2-P-b	Benzaldehyde	Small
2-U-a	Phenol	Large
2-K-e	2-Pentyl-furan	Extra large
4-N-C	Phenyl ethyl ketone[a]	Small
5-L-e	5-Phenyl-3-pentanone[a]	Medium
5-N-e	6-Phenyl-3-hexanone[a]	Small
3-H-c	3-Phenyl propionaldehyde[a]	Medium
4-J-e	4-Phenyl butyraldehyde[a]	Medium

[a] Tentatively identified.

Numerals, capital letters, and letters indicate the number of gas chromatographic fractions collected with the preparative column, with the Ucon Polar column for first rechromatography and with the Methyl Silicone column for second rechromatography, respectively.

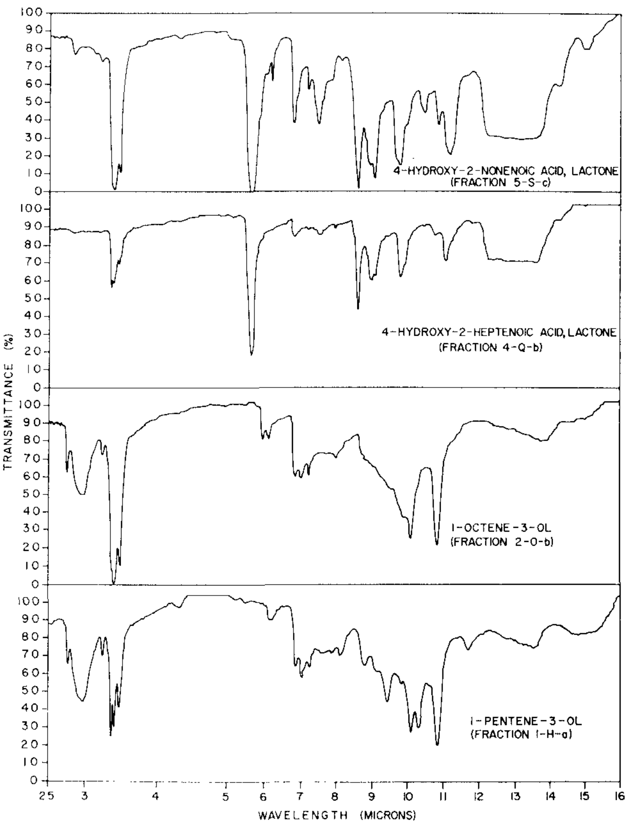

FIG. 3. Infrared spectra of the gas chromatographic fractions identified as the chemical names given.

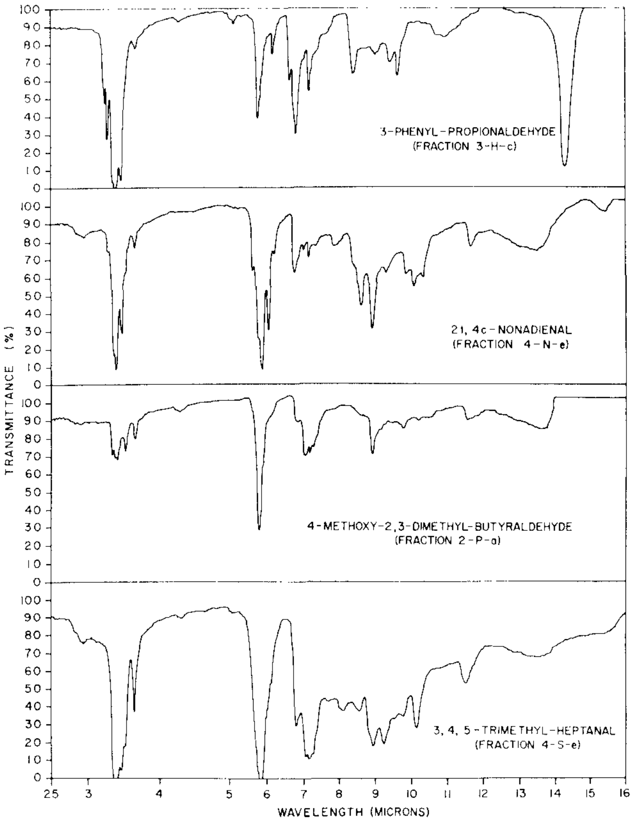

FIG. 3a. Infrared spectra of the gas chromatographic fractions identified as the chemical names given.

aldehydes. They were predominant not only in number but also in size of peaks.

It is interesting to note that methyl ketones were present in relatively very small amount, although three unusual ketones were represented by extra large peaks. This agrees with the study of Wishner and Keeney (6). They found no methyl ketone except a relatively small amount of acetone in the distillate collected during deep fat frying of potato in corn oil. However, in the study of the effect of heat on pure triglycerides, Crossley et al. found that methyl ketones were the major components of thermal degradation of 2-oleo-palmitin at 190C under air (7). This discrepancy might illustrate the difference

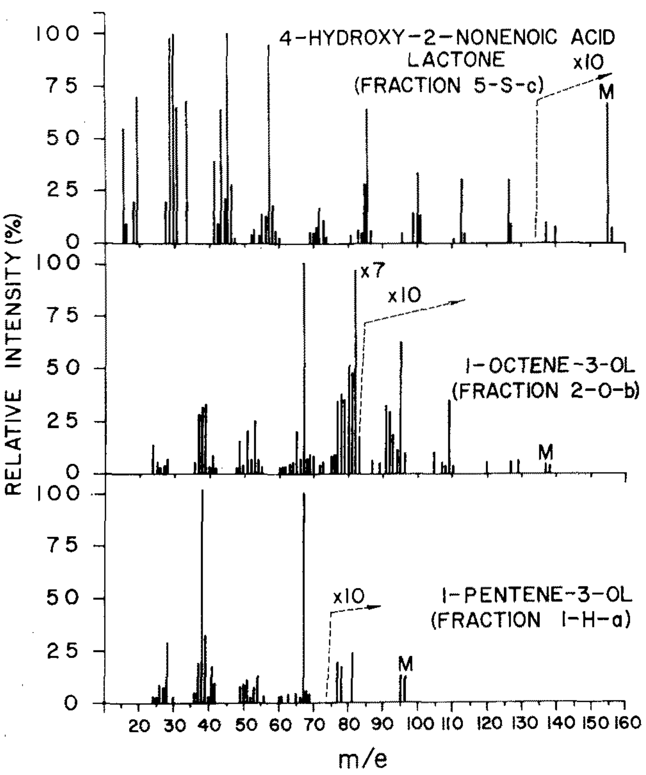

FIG. 4. Mass spectra of the gas chromatographic fractions identified as the chemical names given.

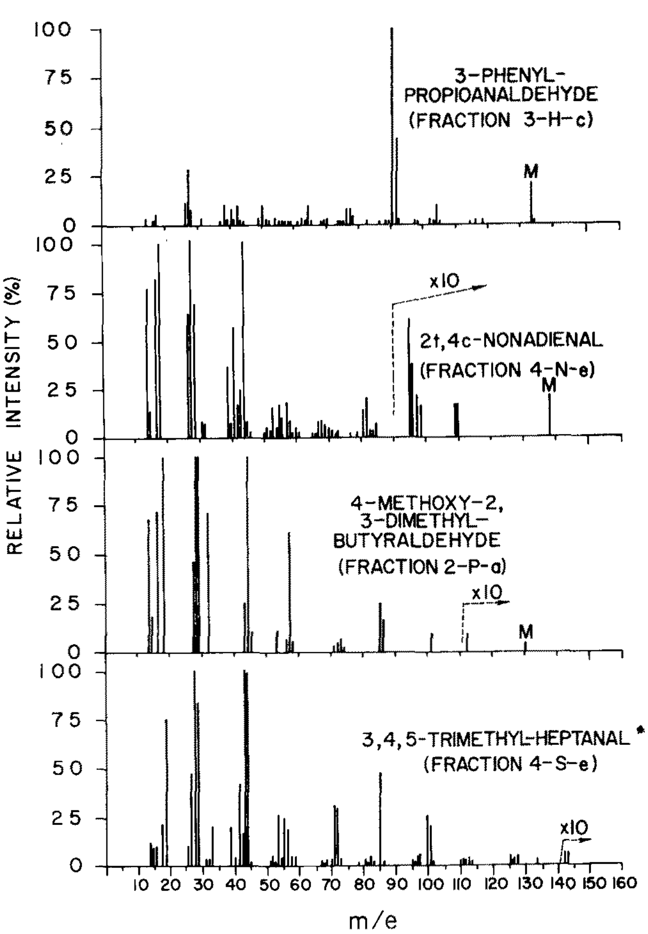

FIG. 4a. Mass spectra of the gas chromatographic fractions identified as the chemical names given.

in the thermal decomposition pattern of triglycerides under a current of dry air as used by Crossley and during the frying of potato and moist cotton balls as used by Wishner and Keeney and in the present investigation.

A comparison of the VDP of corn oil produced by thermal oxidation under conditions of deep fat frying with those of cottonseed (8) and soybean oils (9) produced respectively by slight autoxidation at room temperature revealed many interesting similarities and differences. In all cases, saturated aldehydes and 2-enals were found in relatively large numbers and as major components as determined by the sizes of the gas chromaotgraphic peaks. Pentanal, hexanal, 2-heptenal, and 2-octenal were found as extra large peaks in each case. However, 2-decenal was found as a major component only under conditions of deep fat frying. As for alcohols, pentanol and 1-octene-3-ol were found as extra large peaks in all cases. However, 2-pentene-1-ol was produced in large amounts by thermal oxidation of corn oil and slight autoxidation of soybean oil, but not by slight autoxidation of cottonseed oil. It should be noted that both 2-octenal and 1-octene-3-ol were represented by extra large gas chromatographic peaks in the volatile decomposition products of thermal oxidation of corn oil. This disagrees with the postulation of Hoffman (11) that the presence of large amounts of one is balanced by the presence of decreased amounts of the other.

The VDP produced by thermal oxidation of corn oil contained more lactones, more dienals, more aromatic compounds, and less methyl ketones than those produced by slight autoxidation of cottonseed and soybean oils at room temperature. It has been reported that during slight autoxidation at room temperature, the conditions are not drastic enough for ring formation (9). Therefore, the ring in the aromatic compounds identified in the VDP of autoxidation of cottonseed and soybean oils must be preformed in the oil during processing, such as during deodorization. Since more aromatic compounds in larger amounts were found in the VDP of thermal oxidation of corn oil, it is possible that ring formation could take place under the conditions of deep fat frying.

The compound 1-decyne has been reported as a major component of the VDP of slightly autoxidized cottonseed and soybean oils (11). However it was not identified in the VDP of thermal oxidation of corn oil. This compound with a triple bond might have been further oxidized under the more drastic conditions of deep fat frying.

The gas chromatographic fractions after having been rechromatographed twice with two different stationary phases as those used for identification in the present investigation were generally pure chemical compounds. However, some of them were still mixtures of two compounds such as 4-octanol and vinyl amyl ketone in fraction 2-P-e, 4-hexenal and 5-methyl-4-hexenal in fraction 2-k-a and 4-undecanone and 5-phenyl-3-pentanone in fraction 5-L-e. These compounds can only be considered as tentatively identified.

The mechanisms for the formation of hydrocarbons, alcohols, aldehydes, ketones, lactones, and aromatic compounds through the decomposition of the hydroperoxides of unsaturated fatty esters have been reviewed and postulated by Chang and his co-workers (1,4,9,12–15). The fatty acid composition of the corn oil before and after being used for the deep fat frying experiment has been reported previously (1).

Under the conditions of deep fat frying, saturated fatty esters may also be dehydrogenated to form unsaturation in the molecule (16). Furthermore, alkyl free radicals could be formed through decarboxylation of free fatty acids during thermal oxidation (17). The alkyl free radical could react with oxygen to yield a primary hydroperoxide. Under the conditions of deep fat frying, oxidative attack with the formation of hydroperoxides could also occur on the α- and β-carbon atoms of a saturated acyl radical (7). In addition to α- and β-oxidation, Crossley suggested that progressively diminishing oxidative attacks may occur further along the chain.

The n-nonanal and 2-decenal were represented by extra large gas chromatographic peaks which indicated a predominance of oxygen attack on the double bond of oleic acid under deep fat frying conditions. This hypothesis is further supported by the fact that only relatively small quantities of n-octanal and 2-undecenal were found. These two compounds were produced by oxygen attack on carbons 8 and 11 of oleic acid. However, in the case of linoleic acid, the pentadiene system and the methylene group on either side of the pentadiene system were probably equally attacked by oxygen. This was supported by the observation that pentanal, hexanal, 2-heptenal, 2-octenal, and 2,4-decadienal were all represented by extra large gas chromatographic peaks.

A few compounds with branch chain were identified. The mechanism of their formation cannot be postulated. It is possible that traces of branch chain fatty acids were originally present in the corn oil. Ordinary fatty acid analysis may not reveal unusual fatty acids present in trace amounts.

Many of the identified nonacidic VDP had interesting odor characteristics. The most outstanding ones were the dienals which had a deep fat fried odor. The lactones had a sweet coconut like odor reminiscent of heated butter and the unsaturated secondary alcohols had a mushroom like odor. 2-Pentyl furan was found to have a beany grassy flavor characteristic of that of the reversion flavor of soybean oil (15).

The 95 compounds identified in the VDP produced by corn oil during deep fat frying under simulated commercial conditions were of a wide range of chemical structures. The effect on human health of many of these compounds when inhaled or ingested have not been studied. Dickens and Jones (18) claimed that a lactone ring having double bonds at the 2 or 4 position may have carcinogenic activity. Two of such compounds 4-hydroxy-2-heptenoic acid, lactone, and 4-hydroxy-2-nonenoic acid, lactone, were tentatively identified. The nutritional effects of the 95 volatile decomposition products identified should therefore be thoroughly investigated.

ACKNOWLEDGMENT

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

REFERENCES

1. Kawada, T., B. D. Mookherjee and S. S. Chang, JAOCS, in press.
2. Deck, R. E., J. A. Thompson and S. S. Chang, J. Gas Chromatog. 392 (1965).
3. Smouse, T. H. and S. S. Chang, J. Chromatog. *13*, 244 (1964).
4. Kawada, T., B. D. Mookherjee and S. S. Chang, JAOCS *43*, 237 (1966).
5 .Krishnamurthy, R. G., T. Kawada and S. S. Chang, JAOCS *42*, 878 (1965).
6. Wishner, L. A. and M. Keeney, JAOCS *42*, 776 (1965).
7. Crossley, A., T. D. Heyes and B. J. F. Hudson, JAOCS *39*, 9 (1962).
8. Mookherjee, B. D., and S. S. Chang, reported at the AOCS Meeting, Cinncinati, Ohio, 1965.
9. Smouse, T. H., and S. S. Chang, reported at the AOCS Meeting, Houston, April 1965.
10. Hoffman, G., JAOCS *39*, 439 (1962).
11. Smouse, T. H., B. D. Mookherjee and S. S. Chang, Chem. and Ind. 1301 (1965).
12. Mookherjee, B. D., R. E. Deck and S. S. Chang, J. Agr. Food Chem. *13*, 131 (1965).
13. Silveira, A. Jr., Y. Masuda and S. S. Chang, JAOCS *42*, 85 (1965).
14. Mookherjee, B. D., and S. S. Chang, Ibid. *40*, 232 (1963).
15. Krishnamurthy, R. G., T. H. Smouse, B. D. Mookherjee, B. R. Reddy and S. S. Chang, Chem. & Ind. 1926 (1966).
16. Endres, J. G., V. R. Bhalerao and F. A. Kummerow, JAOCS *39*, 118 (1962).
17. Endres, J. G., V. R. Bhalerao and F. A. Kummerow, Ibid. *39*, 159 (1962).
18. Dickens, F. and H. E. H. Jones, Brit. J. Cancer *15*, 85 (1961).

[Received September 9, 1966]