Chemical Reactions Involved in the Deep Fat Frying of Foods: V. Identification of Nonacidic Volatile Decomposition Products of Hydrogenated Cottonseed Oil.[1]

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Abstract

The nonacidic volatile decomposition products (VDP) produced by a deodorized hydrogenated cottonseed oil maintained at 185C with periodic frying of moist cotton balls and with periodic addition of fresh fat to replenish the fat lost due to evaporation, decomposition, and adsorption by the cotton balls were collected, fractionated and characterized. A total of 61 compounds were identified. They consisted of 17 hydrocarbons, eight alcohols, two esters, three lactones, 22 aldehydes, seven ketones, and two aromatic compounds.

Introduction

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 a deodorized hydrogenated cottonseed oil under conditions which simulate commercial deep fat frying. It is a continuation of the previous paper (2) which described the systematic identification of acidic VDP.

Experimental

Collection of Nonacidic Volatile Decomposition Products

The detailed procedure for the collection of nonacidic VDP produced by a deodorized hydrogenated cottonseed oil under simulated commercial conditions of deep fat frying has been reported in a previous paper (2). The fatty acid composition of the hydrogenated cottonseed oil and its chemical and physical constants have also been published previously (2).

The VDP remaining in the frying oil at the end of the experiment were isolated by vacuum steam distillation at 150C for 2 hr under a vacuum of 5 μ. The amount of steam used was 2% by weight of the oil. The distillate thus collected was treated in the same manner as described previously (2).

Analysis by Gas Chromatography

The nonacidic VDP collected during 0–3, 3–6, 6–12, 12–30, 30–60, 60–90, 90–120, and 120–150 hr of frying and those remaining in the oil at the end of the frying experiment were analyzed separately by an Aerograph Model 1520 gas chromatograph. A 6 ft × ¼ in. I.D. aluminum column packed with 15% by weight of Ucon Polar 50 HB 280 X on Chromosorb W HMDS (Microtek Instruments, Inc., Baton Rouge, La.) was used. The temperature was programmed from 60–200C at 4C per min. The helium flow rate was 75 ml/min.

Fractionation by Gas Chromatography

The total combined nonacidic VDP from two batches of the deep fat frying experiment with hydrogenated cottonseed oil was first separated into 14 broad fractions by preparative gas chromatography using a 10 ft × ⅜ in. I.D. aluminum column packed with 20% methyl silicone SE-30 on 60/80 mesh silanized chromosorb W (Varian Aerograph, Walnut Creek, Calif.). The gas chromatogram obtained from an Aerograph Model A-90-P gas chromatograph is shown in Fig. 1. The temperature was non-linearly programmed from 60 to 200C in 22 min and then held at that temperature for the remaining period of the gas chromatography. The process was repeated 14 times. Each of the 14 broad fractions was accumulatively collected in one trap with the aid of a fraction collector as described by Deck, et al. (3). Each of these fractions were rechromatographed with an 8 ft × ¼ in. I.D. aluminum column packed with 15% Ucon Polar 50 HB 280 X on 70/80 mesh Anakrom ABS (Analabs Inc., Hamden, Conn.). The gas chromatogram of the rechromatography of Fraction No. 6 as obtained from an Aerograph Model 202 gas chromatograph is shown in Fig. 2 as an example. A total of 150 fractions was thus collected. Each of these fractions was again rechromatographed with an 8 ft × ¼ in. I.D. aluminum column packed with 20% methyl silicone SE-30 on 70/80 mesh Anakrom ABS. The second rechromatography yielded 308 gas chromatographic fractions, each of which was collected and studied.

Identification of Gas Chromatographic Fractions

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

Peak Size

The calculation of the size of gas chromatographic fractions is the same as reported previously (2).

Results and Discussion

A total of 58 compounds were identified and an additional three compounds were tentatively identified as being among the nonacidic VDP produced by a hydrogenated cottonseed oil under conditions simulating commercial deep fat frying. The oil had an iodine value of 69.2 and was deodorized before it was used for the frying experiment. The 61 compounds consisted of 17 hydrocarbons, eight alcohols, two esters, three lactones, 22 aldehydes, seven ketones, and two aromatic compounds (Table I). The postulated mechanisms for the formation of these compounds have been discussed previously

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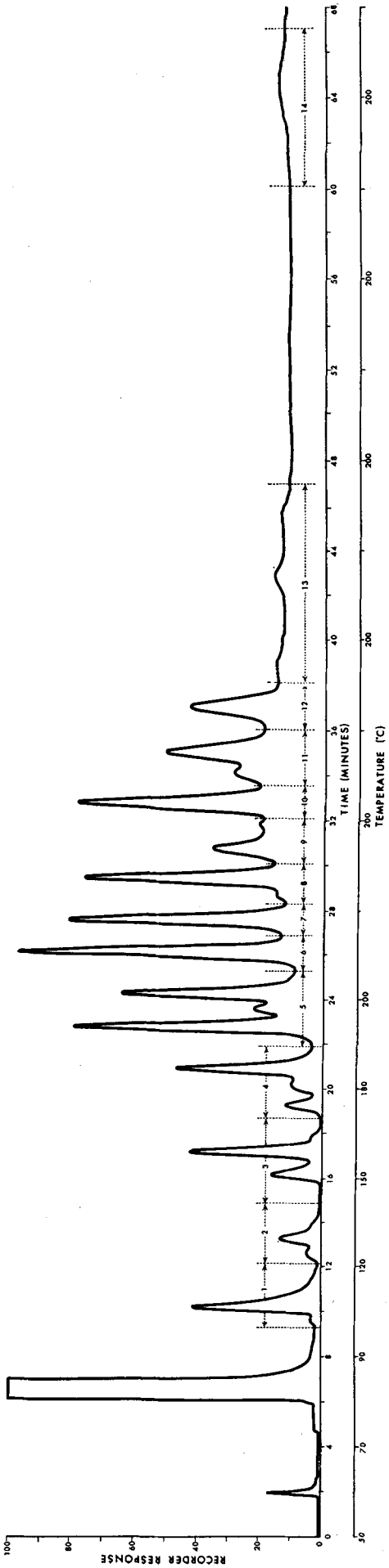

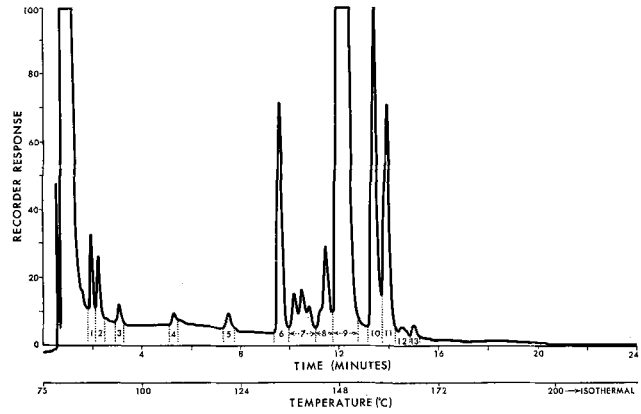

FIG. 2. Gas chromatogram of the rechromatography of the broad fraction No. 6 of the nonacidic volatile decomposition products of hydrogenated cottonseed oil.

(5). Including the 38 acidic compounds reported in a previous paper (2), 102 compounds have been identified as the VDP produced by a hydrogenated cottonseed oil by periodic frying of moist cotton balls at 185C. Fresh hydrogenated cottonseed oil was used to replenish the oil every 12 hr in order to compensate for the loss of oil resulting from evaporation, decomposition, and adsorption by the cotton balls.

In commercial practice, an oil is discarded when it begins to foam during frying. Since the hydrogenated cottonseed oil did not foam at the end of the experiment, it would still be considered good and re-usable by commercial standards. The VDP identified may therefore possibly be present in the fried foods of our diet (6).

The nonacidic compounds identified as the VDP of hydrogenated cottonseed oil (Table I) are quite similar to those of corn oil (5). Aldehydes were predominant not only in numbers but also in the size of gas chromatographic peaks representing them. Although the number of hydrocarbons identified is relatively large, all of them except one were represented by small or extra small peaks. Alcohols were more predominant, and three of them were represented by large peaks. As with corn oil, methyl ketones were present in relatively very small amounts.

There are, however, six significant differences between the VDP of the more unsaturated corn oil (5) and those of the more saturated hydrogenated cottonseed oil (Table I). First, hydrogenated cottonseed oil yielded more higher members of the homologous series of saturated hydrocarbons, unsaturated hydrocarbons, lactones, and saturated aldehydes. This indicated that breakage of the fatty acid chains occurred less in hydrogenated cottonseed oil than in corn oil under the conditions of deep fat frying. Second, less aromatic compounds were produced by hydrogenated cottonseed oil. Third, less branch chain compounds were produced by hydrogenated cottonseed oil. Fourth, two unsaturated alcohols, 1-pentene-3-ol and 1-octene-3-ol were found as large and extra large components of VDP of corn oil while only the latter was found as a large component of those of hydrogenated cottonseed oil. Fifth, fewer

FIG. 1. Gas chromatogram of nonacidic volatile decomposition products of hydrogenated cottonseed oil obtained with a preparative column.

TABLE I

Compounds Identified as Nonacidic Volatile Decomposition Products of Hydrogenated Cottonseed Oil During Deep Fat Frying

Peak number[a]	Identified as	Peak size
I. Saturated hydrocarbons		
3– 1– 1	n-Octane	Small
6– 6– 3	n-Decane	Medium
7– 4– 3	n-Undecane	Small
9– 5– 2	n-Dodecane	Small
10– 5– 1	n-Tridecane	Small
13– 4– 3	n-Tetradecane	Extra small
13– 7– 5	n-Pentadecane	Small
14–11– 3	n-Hexadecane	Small
14–11– 5	n-Heptadecane	Small
14–12– 5	n-Octadecane	Extra small
II. Unsaturated hydrocarbons		
7– 4– 2	Undecene	Extra small
9– 5– 1	Dodecene	Extra small
10– 6– 2	Tridecene	Small
13– 4– 2	Tetradecene	Extra small
13– 7– 4	Pentadecene	Small
14–10– 5	Hexadecene	Small
14–11– 4	Heptadecene	Small
III. Alcohols		
2– 4– 1	n-Butanol	Medium
3– 6– 1	n-Pentanol	Large
4– 4– 1	n-Hexanol	Medium
4– 2– 3	n-Heptanol	Large
7–12– 1	n-Octanol	Medium
8– 7– 3	n-Decanol	Small
5–12– 3	1-Octene-3-ol	Large
3– 6– 2	2-Hexenol[a]	Extra small
IV. Esters		
1– 1– 1	Ethyl Acetate	Extra large
6– 9– 2	Butyl Acetate	Small
V. Lactones		
8–10– 1	4-Hydroxy heptanoic acid, lactone	Extra small
12–10– 2	4-Hydroxy nonanoic acid, lactone	Small
13–14– 1	4-Hydroxy decanoic acid, lactone	Small
VI. Saturated aldehydes		
2– 3– 1	n-Pentanal	Medium
3– 3– 1	n-Hexanal	Large
5– 6– 1	n-Heptanal	Large
7– 9– 1	n-Octanal	Extra large
7– 9– 4	n-Nonanal	Extra large
9– 8– 3	n-Decanal	Medium
11– 9– 3	n-Undecanal	Small
13– 9– 3	n-Dodecanal	Extra small
13– 9– 4	n-Tridecanal	Extra small
13–16– 6	n-Tetradecanal	Extra small
14–12– 3	n-Pentadecanal	Extra small
VII. Unsaturated aldehydes		
4– 2– 2	2t-Hexenal	Large
5–11– 2	2t-Heptenal	Extra large
6– 8– 5	2t-Octenal	Extra large
11–15– 3	2c-Octenal	Extra small
8– 7– 4	2t-Nonenal	Extra large
13–11– 3	2t-Decenal	Small
13–11– 5	2t-Undecenal	Small
9– 9– 4	2t, 4t-Nonadienal	Medium
11–11– 3	2t, 4c-Nonadienal	Large
11–12– 5	2t, 4t-Decadienal	Large
12– 8– 4	2t, 4c-Decadienal	Large
VIII. Ketones		
5– 9– 2	3-Octanone	Extra small
7– 9– 5	2-Nonanone	Extra small
11– 9– 2	2-Decanone	Small
10– 8– 3	4-Undecanone	Extra small
13–10– 5	2-Dodecanone	Small
8– 4– 6	Nonenone[b]	Extra small
8– 6– 2	5 Keto-3,6-Nonadiene[b]	Extra small
IX. Aromatic compounds		
5–13– 1	Benzaldehyde	Extra small
5– 8– 2	2-Pentyl Furan	Large

[a] The first, second, and third numerals 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.
[b] Tentatively identified.

unsaturated ketones were present in the VDP of hydrogenated cottonseed oil. Sixth, unsaturated lactones were found in the VDP of corn oil but not in those of hydrogenated cottonseed oil. It should be noted that a lactone ring having double bonds at the 2 or 4 position has been claimed as possibly having carcinogenic activity (7).

Gas chromatograms of the nonacidic VDP produced by hydrogenated cottonseed oil during different intervals of the deep fat frying operation (Fig. 3)

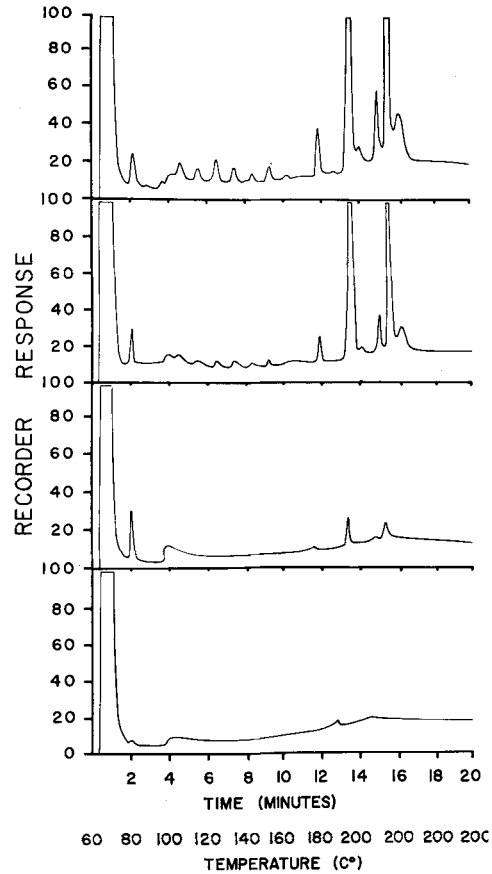

FIG. 3. Gas chromatograms of nonacidic volatile decomposition products produced by hydrogenated cottonseed oil during deep frying for 3–6 hr (bottom curve), 12–30 hr (lower center curve), 60–90 hr (upper center curve), and 120–150 hr (top curve).

are quite different from those of corn oil (6). They indicated that considerably less VDP were produced by hydrogenated cottonseed oil than corn oil during equal intervals of deep fat frying under simulated commercial conditions. However, the VDP produced by corn oil at the end of 30 hr of frying were similar to those produced by hydrogenated cottonseed oil at the end of 150 hr of frying.

The gas chromatogram of the VDP remaining in the hydrogenated cottonseed oil at the end of the frying experiment has the same general pattern as that of the VDP evaporated from the oil during the frying operation. The only difference is that the latter yielded larger gas chromatographic peaks which represent the more volatile decomposition products. The 99 acidic and nonacidic compounds identified in this investigation are therefore not only inhaled by the operators of deep fat frying but also are present in the deep fat fried foods.

ACKNOWLEDGMENT

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