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

KOSAKU YASUDA,[2] B. R. REDDY and S. S. CHANG,
Department of Food Science, Rutgers, The State University, New Brunswick, New Jersey 08903

Abstract

The acidic volatile decomposition products (VDP) produced by a 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 38 acidic compounds were identified. They consisted of 13 saturated acids, 11 unsaturated acids, five aldehydo acids, two hydroxy acids, two keto acids, and five dicarboxylic acids. The similarities and differences between the acidic VDP produced by a more unsaturated corn oil and a more saturated hydrogenated cottonseed oil under simulated commercial deep fat frying conditions are discussed.

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). Recently, 95 compounds have been identified as the acidic and nonacidic VDP of corn oil produced under simulated conditions of commercial deep fat frying (1,2). However, hydrogenated fat of less unsaturation than corn oil is also often used in deep fat frying. The present paper reports the characterization of the acidic VDP produced by hydrogenated cottonseed oil under conditions which simulate deep fat frying in restaurants.

Experimental

Collection of Acidic Volatile Decomposition Products. Deodorized hydrogenated cottonseed oil, 2,300 ml, was heated to 185C in a Sunbeam household deep fat fryer. Ten moist cotton balls containing 16 g of water were deep fat fried every 30 min (3). After 3 min of frying, the cotton balls were removed from the oil. The fried cotton balls contained approximately 4.1% moisture and 83.5% 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 approximately 600 ml of fresh hydrogenated cottonseed oil after every 12 hr of operation. The VDP thus produced and evaporated with the steam were collected by the use of the apparatus described previously (3). They were separated into acidic and nonacidic VDP by being dissolved in ethyl ether and then extracted with 10% aqueous sodium carbonate solution. Since they were contaminated with some entrained oil, the acidic VDP were molecularly distilled at 50–175C for 5 hr under 2 μ of vacuum with an apparatus described previously (4). The nonacidic VDP were similarly distilled at 50–165C. The distillates were considered as the collected VDP and were subjected to gas chromatographic analyses and fractionations.

The acidic VDP collected during 0–3, 3–6, 6–12, 12–30, 30–60, 60–90, 90–120, and 120–150 hr of frying were analyzed separately by gas chromatography. They were then combined for fractionation and characterization. In order to obtain enough VDP for this purpose, the experiment was repeated once by starting with 2,300 ml of fresh hydrogenated cottonseed oil. The acidic VDP from the two batches of operation were combined.

In a separate experiment, one batch of 2,300 ml of the hydrogenated cottonseed oil was heated continuously at 185C for 120 hr without frying. The VDP produced were not collected in this case.

Analysis by Gas Chromatography. The acidic VDP collected during different intervals of time of frying were converted into their methyl esters with the use of diazomethane (5). It has been reported previously that the diazomethane has no side reaction with double bond, keto and hydroxy groups under the conditions used (6). The esters were then analyzed by an Aerograph 1520 gas chromatograph with a 6 ft × ¼ in. I.D. aluminum column packed with 20% DEGS on 70/80 mesh Anakrom ABS. The flow rate of the helium carrier gas was 60 ml per min and the temperature was linearly programmed from 60 to 200C at 10C per min.

Preliminary Fractionation by Column Chromatography. Since the methyl esters of the acidic VDP contained mostly the fatty acids which were originally present in the hydrogenated cottonseed oil, they were fractionated first into four fractions according to their polarity by column chromatography. The 2.2 cm × 40 cm column was packed with 50 g of silicic acid deactivated with 6.25 g of water. The column was successively eluted with pentane, pentane containing 10%, 20%, and 50% ethyl ether, ethyl ether, and methanol. Each of the four fractions was then fractionated by gas chromatography.

Fractionation by Gas Chromatography and Identification by Infrared and Mass Spectrometry. The procedures for the fractionation and identification of the acidic VDP were essentially the same as those reported previously (1,7).

TABLE I
Fatty Acid Composition of the Hydrogenated Cottonseed Oil

Fatty acids	Fresh	After frying for 150 hr	After continuously heated for 120 hr
C_{14}	0.6	0.8	0.9
C_{16}	23.0	24.5	24.4
C_{18}	7.4	8.3	8.1
$C_{18:1}$ =	56.4	54.9	56.2
$C_{18:2}$ =	12.6	11.5	10.5
Trans Isomers	48.5	48.9	46.6

[1] Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers, The State University.
[2] Present address: Nisshin Oil Mills, Yokohama, Japan.

TABLE II

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 (40C)	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, 37.7C)	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

Analytical Methods. Fatty acid composition was analyzed by the method as reported by Thompson et al. (8). Free fatty acid, peroxide number, iodine value and trans isomer content were determined according to the Official Methods of the American Oil Chemists' Society. Foaming, viscosity, and color were analyzed in the same manner as reported previously (3).

Peak Size

The area of each peak during one run of the first gas chromatography was calculated. This peak area was divided into the peaks obtained during the second chromatography according to the ratio of their areas. This was repeated for the third chromatography. If more than one fraction after the third chromatography was identified as the same compound, the areas of these fractions were combined. The peak size was considered as extra large if the total peak area was more than 500 units; large if 250–500 units; medium, if 100–250 units; small, if 25–100 units; and extra small, if less than 25 units.

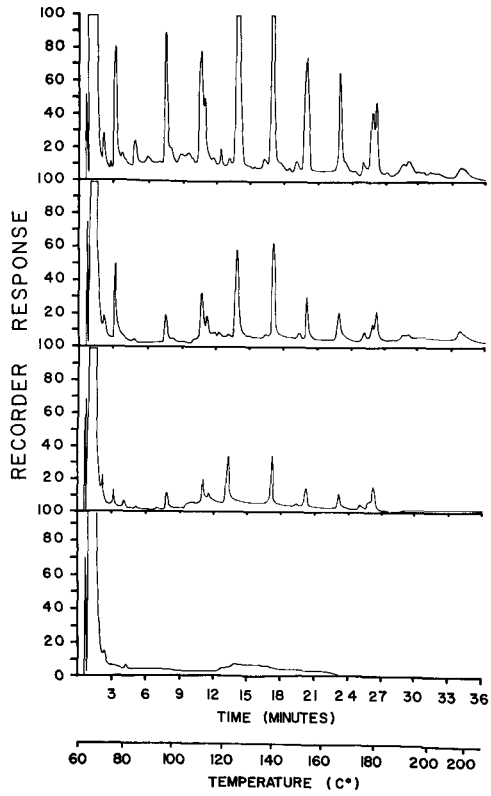

FIG. 1. Gas Chromatogram of Methyl Esters of Acidic VDP Collected During Deep Fat Frying with Hydrogenated Cottonseed Oil at 3–6 hr (bottom curve), 12–30 hr (lower center curve), 60–90 hr (upper center curve), and 120–150 hr (top curve).

Results and Discussion

The hydrogenated cottonseed oil used in this investigation was deodorized before it was used for the frying experiment. It had an iodine value of

TABLE III

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

Peak No.	Identified as	Size of peak
I. Saturated acids		
I– I	Methyl pentanoate	Small
A– 2– 2	Methyl hexanoate	Small
A– 2– 3	Methyl heptanoate	Small
A– 2– 4	Methyl octanoate	Small
A– 2– 6	Methyl nonanoate	Small
A– 2– 8	Methyl decanoate	Small
A– 3– 1– 4	Methyl undecanoate	Extra small
A– 3– 1– 6	Methyl laurate	Small
A– 2–14	Methyl myristate	Medium
A– 3– 3	Methyl pentadecanoate	Extra small
A– 2–15	Methyl palmitate	Extra large
A– 3– 5	Methyl heptadecanoate	Extra small
A– 3– 6	Methyl stearate	Large
II. Unsaturated acids		
A– 3– 7	Methyl oleate	Extra large
A– 3– 8	Methyl linoleate	Large
A– 3– 9	Methyl linolenate	Extra small
B– 9– 1	Methyl palmitoleate	Extra small
5– 1	Methyl 2-heptenoate	Extra small
A– 2– 2	Methyl 2t-octenoate	Extra small
A– 2– 5– 4	Methyl 2t-nonenoate	Extra small
A– 2–10	Methyl 3-decenoate	Small
4– 2	Methyl 6-heptenoate	Extra small
6– 2	Methyl 7-octenoate	Small
A– 2–11– 2	Methyl 10-undecenoate	Extra small
III. Aldehydo acids		
C– 5– 3	Methyl suberate semialdehyde	Extra small
C–10– 4	Methyl azelate semialdehyde	Extra small
C–11– 6	Methyl sebacate semialdehyde	Extra small
C–11– 8	Methyl undecanedioate semialdehyde	Extra small
D– 5– 3	Methyl tetradecanedioate semialdehyde	Extra small
IV. Hydroxy acids		
B– 9– 5	δ-Hydroxy-methyl-octanoate[a]	Extra small
B– 9– 6	δ-Hydroxy-methyl-decanoate[a]	Extra small
V . Keto acids		
B– 6– 2	Methyl 4-oxononanoate[a]	Extra small
B– 9– 3	γ-Keto-methyl-heptanoate[a]	Extra small
VI. Dicarboxylic acids		
B– 7– 1	Dimethyl pimelate	Extra small
B– 7– 2	Dimethyl suberate	Extra small
C–10– 5	Dimethyl azelate	Extra small
C–10– 7	Dimethyl sebacate	Extra small
C–11– 9	Dimethyl undecandioate	Extra small

[a] Tentatively identified.

Letters indicate the number of fractions obtained by preliminary column chromatography.

Numerals indicate the number of peaks when gas chromatographed. Second and third numerals indicate the number of peaks when rechromatographed for the second and third time respectively.

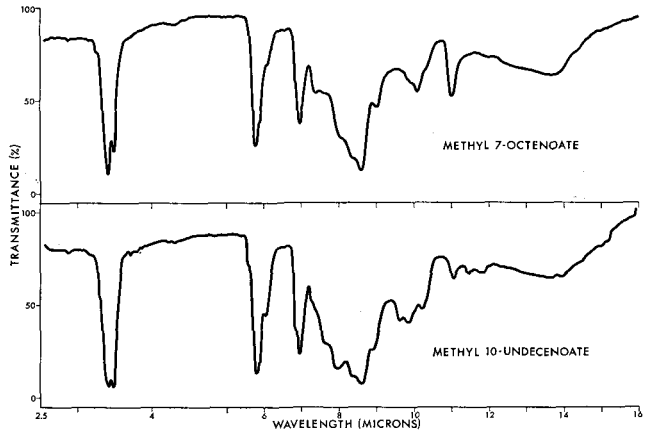

FIG. 2. Infrared Spectra of Methyl 7–Octenoate and Methyl 10–Undecenoate.

69.2 and is one of the more saturated fats commonly used for commercial deep fat frying. Its fatty acid composition before and after being used for frying is shown in Table I.

The deterioration of the hydrogenated cottonseed oil during the frying period as measured by its physical and chemical constants is shown in Table II. For purpose of comparison, a sample of the same oil which had been continuously heated for 120 hr was also analyzed. The hydrogenated cottonseed oil used for frying had a higher free fatty acid content and iodine value and lower viscosity than the continuously heated oil. The high free fatty acid content may have an effect upon the metabolism of cholesterol. Kritchevsky (9) has reported that rabbits fed with cholesterol suspended in corn oil had higher atheromata when the free fatty acid content was increased to 0.5%. It is interesting to note that the free fatty acid contents of the hydrogenated cottonseed oil during deep fat frying are higher than those of a corn oil used for frying under the same conditions (3). This seems to substantiate the previous report (10) that saturated triglycerides are more susceptible to hydrolysis than unsaturated triglycerides.

In commercial practice, an oil is discarded when it begins to foam during frying. Since the hydrogenated cottonseed oil used for the present investigation 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 (3).

The gas chromatogram pattern of the methyl esters of the acidic VDP produced by hydrogenated cottonseed oil during different intervals of time (Fig. 1) is quite different from that of corn oil (3). In corn oil, it has been concluded that during the initial stage of frying, more acidic VDP are produced by chain breaking through autoxidation, and that during the later stage of frying more acidic VDP are produced by hydrolysis of the ester linkages of triglycerides. On the other hand, gas chromatograms of the methyl esters of acidic VDP collected from hydrogenated cottonseed oil during different intervals of frying indicated that the cleavage through hydrolysis predominates during the entire frying experiment. The size of the gas chromatographic peaks representing the fatty acids originally present in the hydrogenated cottonseed oil are relatively large during 30 hr of frying as well as during 150 hr of frying. This indicated that the

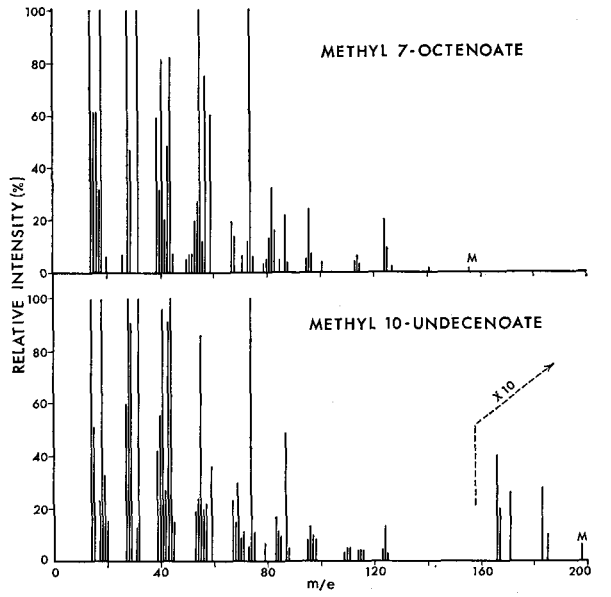

FIG. 3. Mass Spectra of Methyl 7–Octenoate and Methyl 10–Undecenoate.

hydrogenated cottonseed oil as expected is more stable than corn oil towards autoxidation under drying conditions. It also confirms the previous conclusion that hydrogenated fat is more susceptible to hydrolysis than unhydrogenated oil.

A total of 38 compounds were identified as the acidic VDP produced by hydrogenated cottonseed oils under simulated conditions of commercial deep fat frying (Table III). Infrared and mass spectra of some of the identified compounds are shown in Fig. 2 through 4. The mass spectrum of oxo fatty esters has been thoroughly discussed by Ryhage and Stenhagen (11).

The postulated mechanisms for the formation of these compounds have been discussed previously (1). The compounds identified were similar to the acidic VDP produced by corn oil under the same conditions. However, the frying with corn oil was continued for 30 hr while the experiment with hydrogenated cottonseed oil was continued for 150 hr.

There are nevertheless three major differences between the acidic VDP produced by the more unsaturated corn oil and the more saturated hydrogenated cottonseed oil. One, the unsaturated acids with double bond at vinyl position were found in

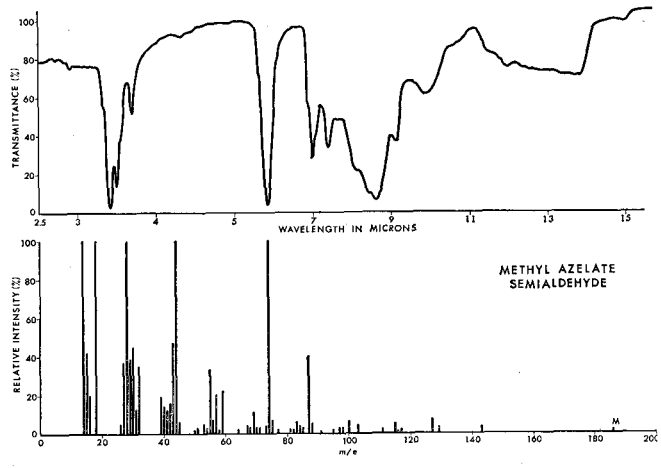

FIG. 4. Infrared and Mass Spectra of Methyl Azelate Semialdehyde.

the VDP of hydrogenated cottonseed oil but not in those of corn oil. Two, a homologous series of five aldehydo acids was identified as the VDP of hydrogenated cottonseed oils. These acids were not identified in the VDP of corn oil. Three, the aromatic acid benzoic acid identified in the VDP of corn oil was not found in those of the hydrogenated cottonseed oil.

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