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Comparative Study of Monocarbonyl Compounds Formed During Deep Frying in Different Fats¹

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Abstract

Fresh commercial corn oil, fresh commercial lard, and hydrogenated vegetable shortening were analyzed for carbonyl compounds before and after deep frying. The frying was carried out in an apparatus with a capacity for 2000 g of oil designed to quantitatively trap the volatile materials evolved during frying and which would ordinarily escape into the atmosphere. The trapped distillate was also subjected to carbonyl analysis.

Analysis of the fats and distillates showed a carbonyl pattern in essential agreement with the classical autoxidation mechanism for the different fats, i.e., the typical alkanals, alk-2-enals, and alk-2,4-dienals. The pattern correlated generally with the fatty acid composition of the fats. Comparison of the concentrations of the monocarbonyl compounds in the fats before and after frying, and in their distillates, indicated that the deodorization process which accompanies frying is effective in preventing the accumulation of the more volatile compounds formed. The less volatile products, mainly deca-2,4-dienal, were not efficiently removed. Accordingly, it was observed that the oils containing higher proportions of linoleic acid contained more residual monocarbonyl compounds after frying.

CONSIDERABLE INTEREST has been stimulated by the possibility of toxic chemical alterations in fats during cooking. Thermal oxidation of unsaturated fats at 200C for 24 hr has been reported to produce substances toxic to rats (1). The efficacy of extrapolating from extreme laboratory conditions of heating and oxidation to the milder conditions of practical cooking has been vigorously questioned by Melnick (2,3,4) and Kaunitz (5). With the exception of the surveys made in the potato chip industry by Melnick, (2,3,4), there have been no definitive chemical studies of actual frying operations. The present work was designed to study the production of carbonyl compounds during the frying of potatoes under controlled laboratory conditions which would simulate good cooking practice. Carbonyl compounds were

chosen for study because of the availability of reliable analytical methods and the belief that as an important class of oxidation products, their study could provide information on the extent and type of oxidation. Knowledge of this type is necessary to help settle the controversy over the biological significance of heated fats.

Experimental

Potato Frying Operation. In order to quantitatively trap the vapor evolved during the frying process, the apparatus illustrated in Figure 1 was designed. Vessel No. 1 was a 3 liter resin kettle adapted to a still-head. The kettle was heated with an electric mantle connected to a variable transformer. The opening at B was vented to a nitrogen source. Instead of a thermometer at D, a stainless steel wire entering the apparatus around a rubber stopper was used to suspend the stainless steel basket containing the potatoes. This basket could be lowered and raised without removing the stopper. The distillate was collected in three low-temperature traps 2, 3, and 4. Trap No. 2 (2 liters) was mounted under a cold-water condenser, and was cooled by an ice-water bath. The major portion of the distillate was retained at this point. Traps 3 and 4 were mounted under cold-finger condensers charged with an ethanol-dry ice mixture. They were also cooled by ice-water baths. Trap No 5, containing 300 ml of 3 M phosphoric acid saturated with 2,4-dinitrophenylhydrazine, was used only when the system was under

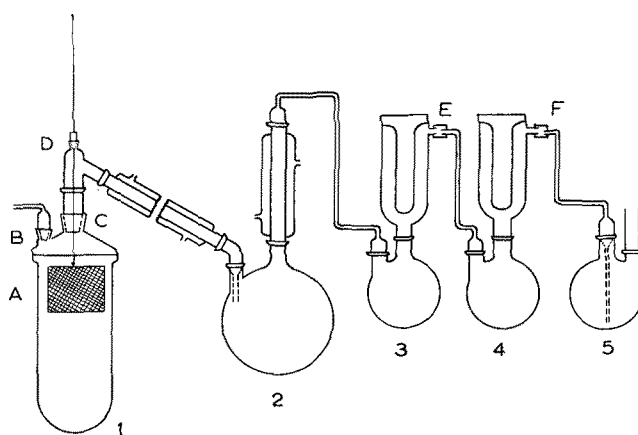


FIG. 1

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TABLE I
Data Pertaining to the Frying Operation^a

	Corn oil	Lard	Hydrogenated vegetable oil
Weight of fat before frying	2000 g	2000 g	2000 g
Weight of fat after frying	1863 g	1835 g	1844 g
Volume of distillate	1575 ml	1600 ml	1730 ml
Color of oil after frying	Dark	Very dark	Light

^a The amount of 3400 g raw potatoes was fried in 10 batches. Total heating time 240 min; frying time, 100 min.

positive nitrogen pressure.

The kettle was charged with 2000 g of fat which was then heated to 200C. The temperature was observed by the periodical insertion of a thermometer at B. Potatoes (300-400 g), sliced uniformly with a wire grid to dimensions of 14 × 14 × 50 mm, were placed in the stainless steel basket suspended over the hot oil by means of the stainless steel wire and a hook (Fig. 1). After the kettle-head had been bolted down and the ball-joint clamps secured, the basket was lowered into the fat without removal of the stopper at D. The potatoes were fried for 10 min. The basket was then raised above the oil, trap No. 5 was connected, and nitrogen pressure was applied at B to sweep the volatiles remaining in the head space into the traps. The flow was maintained at a rate of about 500 ml per min for a period of 10 min, during which the oil temperature, which had fallen to 175C during frying, returned to 200C. The nitrogen pressure was then discontinued and trap No. 5 was disconnected. Some of the data concerning the frying operation are presented in Table I.

Analysis of the Oils and Distillates. After the completion of the frying process, the oil was allowed to cool to room temperature overnight and then stored in the freezer for not more than 24 hr. The distillate

TABLE II
Fatty Acid Composition of Fats Before and After Frying in Wt %

Fatty acid	Fat					
	Corn oil		Lard		Shortening	
	Fresh	Heated	Fresh	Heated	Fresh	Heated
12:0			Trace	Trace	3.65	3.45
14:0			1.24	1.32	1.42	1.52
16:0	14.1	13.6	30.1	29.5	21.4	22.3
16:1			1.74	2.04		
17:0			Trace	Trace		
18:0	2.00	2.30	16.3	16.7	10.6	10.3
18:1	28.6	30.8	42.0	42.3	49.3	47.8
18:2	55.0	53.7	8.56	8.18	13.7	14.7
18:3	Trace	Trace	Trace	Trace	Trace	Trace

fractions from the four traps were combined and thoroughly mixed with 400 ml of 8 M phosphoric acid saturated with 2,4-dinitrophenylhydrazine. After reacting overnight, this solution had lost its characteristic carbonyl odor and the oily material which had been floating on the surface had disappeared. The solution was then extracted with one liter of methylene chloride in 5 portions. The combined extracts were dried under reduced pressure in a rotary film evaporator and the residue was stored in the freezer.

The fatty acid compositions of the oils were determined before and after frying by the transesterification with HCl-methanol and gas-liquid chromatography. A column of 20% diethylene glycol succinate polyester on 60-80 mesh acid-washed celite was used in a conventional instrument equipped with an argon ionization detector containing a Sr⁹⁰ source. The column was operated at 188C. Fatty acid analysis is presented in Table II.

The carbonyl compounds were analyzed before and after frying according to the method of Schwartz, Haller, and Keeney (6). Briefly, carbonyls were converted to 2,4-dinitrophenylhydrazones in a fat-hexane solution on a celite-phosphoric acid-column, followed by separation of the fat on a magnesia column. The

TABLE III
Concentrations of Carbonyl Compounds Isolated from Fats Before and After Frying and from Their Distillates

Compound class, chain length	Micromoles of carbonyl compound per kg fat								
	Corn oil			Lard			Hydrogenated vegetable oil		
	Fresh	Heated	Distillate	Fresh	Heated	Distillate	Fresh	Heated	Distillate
Alkanones									
C ₃	49	55	8.2	9.1	5.0	18			25
C ₄	0.74					1.3			tr
C ₅	1.4	1.2			0.44	2.0			tr
C ₆	2.3	1.9			1.1	3.2			tr
C ₇	1.4	1.4				2.9			tr
C ₈	5.9	6.8		0.14		2.9			tr
C ₉				0.14		1.6			tr
C ₁₀				0.20		1.3		1.5	tr
C ₁₁	0.46	0.57							
Alkanals									
C ₁						50			36
C ₂			4.8			10			11
C ₃			3.3			8.1			
C ₄			31			36	1.5	1.9	26
C ₅	2.5		28	9.3		49	2.8	6.6	25
C ₆	3.8		41	13		61	0.64	2.5	25
C ₇			6.6	4.2		22	0.48	5.4	8.8
C ₈			1.7	5.8	1.9	16	0.64	2.9	4.9
C ₉			6.6	2.6		32	tr	tr	9.1
C ₁₀				5.7		4.9		3.9	2.4
C ₁₁				4.2		7.2			
Alk-2-enals									
C ₄						1.6			
C ₅						3.3			
C ₆			5.1			5.4		1.3	
C ₇			38	4.0	1.8	53		1.9	6.2
C ₈	1.3		12	2.4	1.4	28		7.9	26
C ₉	1.4		4.8	3.9	2.0	19		3.0	20
C ₁₀	0.72	0.79	11	5.2	8.6	53	tr	2.0	5.4
C ₁₁		1.5	7.1	5.5	18	29		6.2	12
C ₁₂		3.6		2.9	9.5	1.1		5.6	10
Alk-2,4-dienals									
C ₇				2.2		10			8.2
C ₈				0.88					
C ₉			15	4.4		1.8	0.28		
C ₁₀		160	70	15	28	87	1.4	9.0	44
C ₁₁				13	23		1.1	11	
Total volatile mono-carbonyls	70.9	234	294	114	101	622	8.84	72.6	306

monocarbonyl and carbonyl ester derivatives were then separated by chromatography on hydrated alumina. The carbonyl ester derivatives were not studied in detail. Separation of the monocarbonyl derivatives into classes of methyl ketones, saturated aldehydes, 2-enals, and 2,4-dienals was carried out on magnesia columns (7) followed by resolution of the classes on a hexane-acetonitrile column (8). This column was monitored by a Canaleo ultraviolet flow analyzer at 350 $m\mu$ to yield recorded chromatograms which were correlated with collected eluate fractions and which could reliably record less than 0.01 μ mole of derivative. The concentrations of the compounds isolated were determined spectrophotometrically and are presented in Table III. Identifications were made on the basis of partition chromatographic peak volumes, chromatographic mobilities, and ultraviolet spectra.

The distillate derivative residues were handled in a similar manner to the fats with the addition of two more steps. Excess reagent was removed from this residue by ion-exchange on Dowex-50 (9). Monocarbonyl and dicarbonyl derivatives were then separated on magnesia which had been deactivated with heat (10). This separation was necessary before class separation of the monocarbonyls. The concentrations of the compounds isolated from the distillates are shown in Table III.

Discussion

General Appearance of the Oils. The degree of darkening and the odor after frying was in proportion to the refinement of the oils. Before frying, all of the oils were fairly light in color and bland in odor. Lard was the darkest with its typical odor and the hydrogenated vegetable shortening was the lightest. Corn oil was darker after frying and gave a strong odor of deca-2,4-dienal. Hydrogenated vegetable oil developed very little odor. These general observations are consistent with the quantitative and qualitative monocarbonyl patterns shown in Table III.

Ketone Distribution. The demonstration of a homologous series of methyl ketones produced in the lard during frying represents a break with the tradition associating these compounds exclusively with heated milk fat. Evidence of this series in trace quantities was also obtained from the hydrogenated vegetable oil distillate and the unheated corn oil. Mechanisms for the production of ketones by thermal oxidation have been proposed by Crossley (11) and, for their production by low temperature oxidation, by Bell (12). However, the present data are insufficient to permit discussion of the relative merits of these. Crossley also proposed vinyl ketones as intermediates. The apparent absence of these, as well as alpha-beta unsaturated ketones in general, was studied carefully. Derivatives of synthetic alpha-beta un-

saturated ketones were subjected to chromatographic and spectral analysis and were found to conform to behavior which should have allowed their observation if they were present.

Aldehyde Distribution. The aldehyde patterns of all three fats are in general agreement with the observations on autoxidized fats made by Gaddis (13). This, along with the absence of unsaturated ketones and the small quantities of ketones in general, indicates that autoxidation is the principal degradative process occurring during frying. A supporting observation shows the apparent absence of acrolein from the fats and distillates. Acrolein is a typical product of the thermal degradation of fats.

Significance of Steam Evolution. A comparison of the total monocarbonyl content of each of the oils before and after frying and of their distillates shows that steam generation during frying is quite effective in removing some of the compounds. The residual compounds were identified as C_{11} and C_{12} enals and the C_{10} and C_{11} dienals which arise primarily from the degradation of hydroperoxides originating from linoleate. Corn oil, with 55% linoleic acid, contained 2 to 3 times as much residual monocarbonyls after frying than the other fats with only 8 to 14% linoleic acid. Sixty percent of this material was deca-2,4-dienal. It is apparent that the residual monocarbonyl content of the fats after frying depends largely upon the linoleate content of the fats.

Degree of Oxidation. An important point to be made from this work is that deep fat frying does not result in alarming degradation of fats. The total volatile monocarbonyl compound production ranged from 380 to 733 μ moles per kilogram for the three fats. There was no significant change in the fatty acid composition of the fats as a result of frying. It is doubtful that most frying operations, either commercial or in the home, would be more drastic than those used here.

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