Volatile Fatty Acids in Flavors of Potatoes Deep-Fried in a Beef Blend

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The volatile free fatty acids were analyzed in commercial french-fried potatoes that had been deep-fried in beef tallow-hydrogenated vegetable oil shortening. The results showed that many of the volatile fatty acids present in beef tallow were transferred to the potatoes. Of the fatty acids derived from beef tallow, butanoic, 2-methylbutanoic, 3-methylbutanoic, heptanoic, 4-methyltanoic, and nonanoic acids were present in concentrations above their respective thresholds, and should contribute to tallow-like flavors. Several unsaturated volatile fatty acids also were identified, and they should contribute to the general deep-fried potato flavor.

KEY WORDS: **Beef tallow, branched-chain fatty acids, flavors, french-fried potatoes, volatile free fatty acids.**

American consumers have become conditioned to prefer the flavor of french-fried potatoes that have been deep-fried in beef tallow over those fried in vegetable oil. However, because of consumer resistance to saturated animal fats containing cholesterol, many fast-food establishments have commenced using beef fat-vegetable oil blends (1) which apparently provide beef-like flavor notes to french-fried potatoes. Some (1) have suggested that consumers may eventually demand the use of all-vegetable fats for fast-food deep frying. However, vegetable fats are not able to provide the characteristic desirable flavor of beef tallow, and the use of vegetable fats could lead to significant losses in consumer appeal for french-fried potatoes. Thus, to prevent this from occurring, a demand exists for naturally-derived beef tallow flavors for use in deep frying fats of vegetable origin.

Deep frying in polyunsaturated vegetable oils often produces various intensities of the green flavor notes that are contributed by unsaturated aldehydes or related compounds originating from lipid oxidation. Commercial vegetable frying oils are usually partially hydrogenated which lessens their tendency to oxidize during frying. However, even though vegetable oils are hydrogenated to simulate beef tallow in the degree of saturation of fatty acids, they lack the characteristic of contributing beef-like flavors to fried foods. This indicates that beef tallow contains some compounds that contribute either directly or indirectly to the desirable flavors in deep-fried foods.

More than one-hundred compounds have been identified from heated beef tallow, including aldehydes, n-alkanes, n-alkenes, free fatty acids, ketones, alcohols, lactones, and nitrogen-containing compounds (2–5). Of these compounds, lactones and methyl ketones are unique in their occurrence in beef and other animal fats (2, 6–8). However, species-related characterizing flavors in meats and fats have been extremely difficult to chemically define.

Haumann (1) has recently stated that the pleasant flavor of foods deep-fried in beef tallow does not originate in fatty acids per se, but rather reflects contributions of minor flavor constituents contained in the tallow. Carlin (9) identified 427 volatile compounds from french-fried potatoes, and the compounds were postulated to form primarily through the nonenzymatic browning reactions, degradation of sugars, thermal and oxidative decomposition of lipids, and lipid-protein interactions. However, a large number of compounds from the study remain unidentified (10).

Recently, we have observed that several minor fatty acids contribute unique species-related flavors to red meats, including beef (J. Kim Ha, and R.C. Lindsay, submitted for publication). While volatile fatty acids ($< C_{10}$) are not generally recognized as components of beef tallow, significant concentrations from a flavor perspective occur as esterified components of the acylglycerols of tallow. Because the conditions of deep frying potatoes promote hydrolysis of fats, release of flavorful volatile fatty acids from beef tallow should provide unique flavor compounds to foods fried in this medium. Therefore, the purpose of this investigation was to quantitatively analyze the minor volatile free fatty acids (FFAs) in commercial french-fried potatoes cooked in a beef tallow-vegetable fat blend. It was further a goal to investigate relationships between volatile fatty acids occurring in beef tallow and deep-fried potatoes.

MATERIALS AND METHODS

Samples. French-fried potatoes were obtained from a national retail fast-food establishment, and were of the usual quality provided by the firm. These potatoes were deep-fried in a commercial beef tallow-hydrogenated vegetable oil-blended shortening. Commercial fractionated pourable beef tallow oil shortening for deep-fat frying (1), and choice grade steer beef tallow (perinephric fat) were obtained from distributors.

Analysis of volatile free fatty acids (VFFAs) in french-fried potatoes. VFFAs were analyzed according to the method of Ha and Lindsay (11). Five grams of french-fried potatoes plus 6.5 μg of 2-ethylnonanoic acid as an internal standard (I.S.), diethylether (15 mL), and 5.5 N H_2SO_4 (0.5 mL) were blended with a high-speed probe homogenizer (Brinkmann Instruments Co., Westbury, NY). Hexane (20 mL) and anhydrous Na_2SO_4 (12.5 g) were then added and mixed thoroughly to extract lipid materials. The fatty acids in this extract were adsorbed on 5 g of deactivated neutral alumina contained in a glass column. After washing the alumina column twice with 10 mL portions of hexane:diethyl ether (1:1, v/v) to remove neutral lipids, fatty acids were desorbed with 5 mL of formic acid (6%, v/v) in diisopropyl ether.

After removal of excess organic solvent by evaporation, volatile fatty acids were dissolved in an aqueous solution which had been acidified with 0.25 mL of 5.5 N H_2SO_4. The samples were then simultaneously distilled and extracted (SDE) for 20 min with diethyl ether

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using a micro-SDE apparatus (Chrompack Inc., Bridgewater, NY). Diethyl ether extracts containing volatile fatty acids were brought to near dryness using nitrogen, and butyl esters were prepared using BF_3/butanol (0.5 mL, 14%).

Butyl esters were extracted into pentane, and were separated using a Supelcowax 10 (60 m × 0.32 mm i.d., 0.25 μm coating thickness) capillary column (Supelco Inc., Bellefonte, PA) with a Varian model 3700 Gas Chromatograph (Varian, Palo Alto, CA) equipped with a flame ionization detector (temperature, 250°C; hydrogen, 30 mL/min; air, 300 mL/min). Helium was used for the carrier gas (2 mL/min) and make-up gas (30 mL/min). The column oven temperature was programmed from 50°C to 230°C at 2°C/min after a 15 min hold at 50°C, and the on-column injection system employed a temperature program from 50°C to 250°C at 100°C/min after injection.

Quantification of fatty acids was performed by comparing the peak area of each butyl ester peak with that of the internal standard (2-ethylnonanoic acid), and employing method correction factor for each fatty acid. The identity of branched-chain fatty acids (BCFAs) was verified by mass spectral analysis as described previously (12).

Analysis of volatile total fatty acids (VTFAs) in pourable beef tallow oil. VTFAs in the commercial pourable beef tallow oil were analyzed in a manner similar to that used for VFFAs except that one gram of frying oil with 6.5 μg of 2-ethylnonanoic acid (I.S.) was employed. The sample was hydrolyzed by heating with 2 mL of aqueous 1 N NaOH in a glass-stoppered flask for 10 min in boiling water. After transferring the hydrolysate into a screw-capped test tube, diethyl ether (15 mL) and 5.5 N H_2SO_4 (0.5 mL) were added. The mixture was blended with a high-speed probe homogenizer (Brinkman Instruments Co.). Hexane (20 mL) and anhydrous Na_2SO_4 (12.5 g) were then added, and the fatty acids in this extract were adsorbed on 5 g of deactivated neutral alumina column. The remaining steps were the same as in the analysis for the VFFAs.

Aroma assessments of fatty acids. Aroma properties for authentic unsaturated fatty acids were assessed by the authors as they eluted from a packed gas chromatograph column through a effluent splitter and a heated exit port. Aroma properties for authentic n-chain and branched-chain fatty acids have been reported elsewhere (13).

RESULTS AND DISCUSSION

A gas chromatographic separation of the butyl esters of volatile fatty acids in the french-fried potatoes is presented in Figure 1. Volatile free fatty acids were transferred to the potatoes from the frying medium. The lipids in the potatoes (14–16) are comprised of long-chain fatty acids from plant origin, and could contribute some of the unsaturated fatty acids through lipid oxidation reactions. However, the odd-numbered n-chain saturated and branched-chain fatty acids found in the fried potatoes likely have their origin in the beef tallow component of the frying medium. The results of the analysis for VFFAs in the commercial french-fried potatoes are summarized in Table 1 along with data for the VTFAs in raw beef tallow (perinephric fat) and a commercial pourable tallow oil.

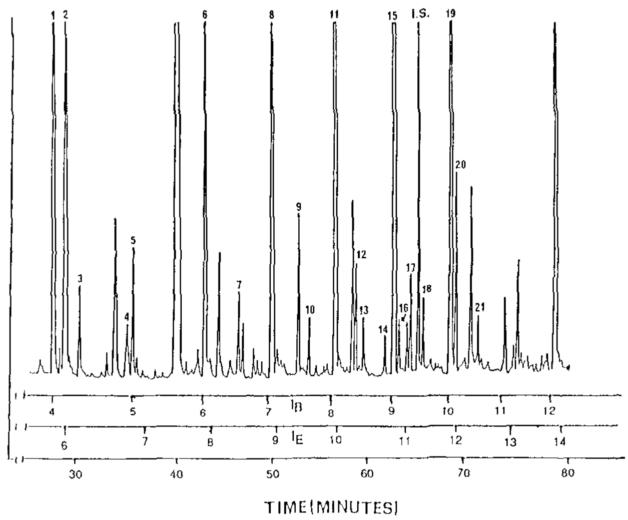

FIG. 1. Gas chromatogram of volatile free fatty acids in french-fried potatoes separated on a Supelcowax 10 capillary column (60 m × 0.32 mm i.d.).

Taken individually, relatively few of the fatty acids appear to be present above threshold concentrations (13), but subthreshold flavor interactions among the fatty acids (17) probably occur, and result in contributions to the flavor of french-fried potatoes. Since french-fried potatoes are normally served hot, the elevated temperature would also promote volatilization of fatty acids compared to room temperature. Thus greater aroma and flavor impacts may be expressed by a given concentration of fatty acids in french fries than would be encountered under the ambient conditions usually employed for threshold determinations.

Of the fatty acids for which aroma or flavor thresholds have been reported (13), butanoic, 2-methylbutanoic, 3-methylbutanoic, 4-methyloctanoic, heptanoic, and nonanoic acids occurred in the french-fried potatoes at concentrations above their respective aroma thresholds (Table 1). The aroma quality of each of these fatty acids appears to lack a recognizable beef-like note although 4-methyloctanoic acid is peculiarly associated with the milk and depot fats of ruminants, including cattle. 4-Methyloctanoic acid has been observed to exhibit a waxy, mutton-goaty aroma quality (13). In other studies on characterizing species-related flavors in meats, it has been observed that the fatty acids noted here as well as others appear to contribute flavor notes to beef as well as other meats (Ha, and Lindsay, submitted for publication). Although they were not measured in the current study, the flavors of some alkylphenols (18,19) which apparently are derived from ruminant fermentations synergistically interact with those of the fatty acids to provide species-related flavor notes (18).

A sample of the beef tallow-hydrogenated vegetable oil shortening employed in the frying of the potatoes could not be obtained for analysis. However, a sample of commercial fractionated pourable beef tallow oil shortening was analyzed. The VTFAs in this sample

TABLE 1

Concentrations of Volatile Free Fatty Acids (VFFAs) as Butyl Esters in Commercial French-Fried Potatoes and Volatile Total Fatty Acids (VTFAs) as Butyl Esters in a Commercial Pourable Beef Tallow Oil Shortening and Raw Beef Tallow

Peak no.	I_B[a]	Compounds	VFFAs	VTFAs	
			Commercial french-fried potatoes	Commercial pourable beef tallow oil	Raw beef tallow
			ppm, whole sample basis		
1	4.00	Butanoic acid	11.41	74.31	100
2	4.15	2-Methylutanoic acid	9.83	118.00	179
3	4.35	3-Methylbutanoic acid	0.95	0.39	4
4	4.66	2-Ethylbutanoic acid	0.12	31.17	ND[b]
5	5.00	Pentanoic acid	0.52	11.84	2
6	6.00	Hexanoic acid	3.99	11.81	144
7	6.57	2-Ethylhexanoic acid	ND	3.21	ND
8	7.00	Heptanoic acid	2.20	2.39	9
9	7.50	*cis*-4-Heptanoic acid	0.53	ND	ND
10	7.71	6-Methylheptanoic acid	0.06	1.97	ND
11	8.00	Octanoic acid	3.67	9.93	345
12	8.41	4-Methylaoctanoic acid	0.04	4.16	trace
13	8.48	An octenoic acid[c]	0.12	ND	ND
14	8.85	7-Methyloctanoic acid	0.06	0.09	ND
15	9.00	Nonanoic acid	2.33	1.53	16
16	9.03	*cis*-2-Octenoic acid	0.03	ND	ND
17	9.20	*trans*-2-Octenoic acid	0.11	ND	ND
18	9.37	4-Methylnonanoic acid	ND	3.25	3
19	9.52	8-Methylnonanoic acid	0.09	ND	ND
20	10.00	Decanoic acid	1.57	31.43	682
21	10.07	*trans*-2-Nonenoic acid	0.35	ND	ND
22	10.52	9-Decenoic acid	0.22	2.19	ND

[a]Retention indices based on butyl esters on Supelcowax-10 capillary column (Butyl butanoate, $I_B = 4$; Butyl decanoate, $I_B = 10$).
[b]Not detected (ND).
[c]Tentative identification based on mass spectral data (8).

were present in generally higher concentrations than the VFFAs in the potatoes, but the concentrations of fatty acids were quite low. In fact, it would have required hydrolysis and transfer of significant portions of the VTFAs in this cooking oil to have equaled the VFFAs found in the french-fried potatoes. It is possible that the fractionation procedure used to obtain this liquid shortening excluded some acylglycerols that contained higher concentrations of notable fatty acids, or they were distilled during the refining process.

Data from the analysis of raw, nonrendered beef tallow (perinephric fat) are also included in Table 1, and it can be noted that the beef tallow provided a larger pool of some of the flavorful free fatty acids than the fractionated beef tallow oil. Another factor in the differences noted between the fractionated beef tallow oil and the raw beef tallow is the distribution of volatile branched-chain fatty acids in various tissues in carcasses (C.P. Brennand, and R.C. Lindsay, submitted for publication). Perinephric fat which was employed in this study contains lower concentrations of these fatty acids than other locations on carcasses of ruminants. Over 95% of the volatile fatty acids in unheated meat depot fats are esterified to the acylglycerols, and adequate concentrations of some fatty acids may be present in raw fats to contribute a characteristic aroma (data not shown). However, thermally-mediated hydrolysis of acylglycerols would be expected to provide the bulk of the volatile fatty acids found in the french-fried potatoes. This continual release of VFFAs from the reservoir of triacylglycerol-bound fatty acids would be compatible with observations that cooking tallows require an initial heat-conditioning for flavor development, and that beef-like flavors are not readily distilled during frying.

Many of the volatile fatty acids found in french-fried potatoes appeared in the fractionated and raw beef tallow, and thus their primary origin appeared to be established. However, some of the n-chain saturated fatty acids may have also been formed as a result of thermal oxidations during frying (20,21). For example, heptanoic acid has been identified as a minor volatile compound in autoxidized methyl linoleate (22), and trilinolein (23), and nonanoic acid each has been found in heated triolein (24) and oleic acid (25).

Several volatile unsaturated fatty acids were found in the french-fried potatoes that were not present in beef tallow samples (Table 1). It has not been possible as yet to evaluate the thresholds or the aroma properties of various dilutions of these fatty acids because of the limited availability of authentic compounds. However, the odor qualities for authentic compounds were observed as they eluted from packed column gas chromatographic separations.

It seems probable that the volatile unsaturated fatty acids in the french-fried potatoes were derived from oxidation of corresponding aldehydes which were derived initially from long-chain unsaturated fatty acids in either the potatoes or the frying medium. Thus, it appears probable also that unique beef fat-like flavors would not be derived from unsaturated fatty acids because they could be derived from vegetable oils as well as from the frying medium. Further unsaturated lipids in potatoes would also serve as precursors for their formation.

cis-4-Heptenoic acid which would be expected to be derived from linoleic acid (Fig. 2) exhibited a unique aroma that was described as a complex sensation of slight goaty, dried anchovy-like, and green notes. Josephson and Lindsay (26) found recently that *cis*-4-heptenal was an important compound contributing to the aroma of boiled potatoes. Lipoxygenase activity on linoleic acid in injured potato tissue yields *trans*-2-*cis*-6-nonadienal (14,15) which is then converted to *cis*-4-heptenal by a retro-aldol condensation reaction (16). Under the conditions of deep-fat frying, *cis*-4-heptenal could be converted to the corresponding acid via a peracid mediated oxidation (27–30). Thus, *cis*-4-heptenoic acid may provide unique flavors to deep-fried potatoes and fish because *cis*-4-heptenal occurs notably in each (26,31,32).

Linoleic acid should serve as the precursor of *cis*- and *trans*-2-octenoic acids as well as *trans*-2-nonenoic acid (Fig. 3). The *cis*-2-octenoic acid would be derived from *trans*-2-*cis*-4-decadienal while the *trans*-2-octenoic acid could be derived from the *trans*-*cis* isomerization as shown in Figure 3, or directly from *trans*-2, *trans*-4-decadienal. 2,4-Decadienal is one of the major aldehydes expected from linoleate autoxidation (33), and 2-octenal is produced via retro-aldol related degradations of 2,4-decadienal (34). An insufficient amount of the *cis*-2-octenoic acid precluded aroma characterization of this acid, but *trans*-2-octenoic acid exhibited complex fresh nut, oatmeal, handsoap notes with a slight citrus overtone aroma. *trans*-2-Nonenoic acid exhibited green, fatty, and soapy aroma notes. Again, it would be expected that the contributions of these unsaturated fatty acids would be general contributions to overall fried-food flavor properties.

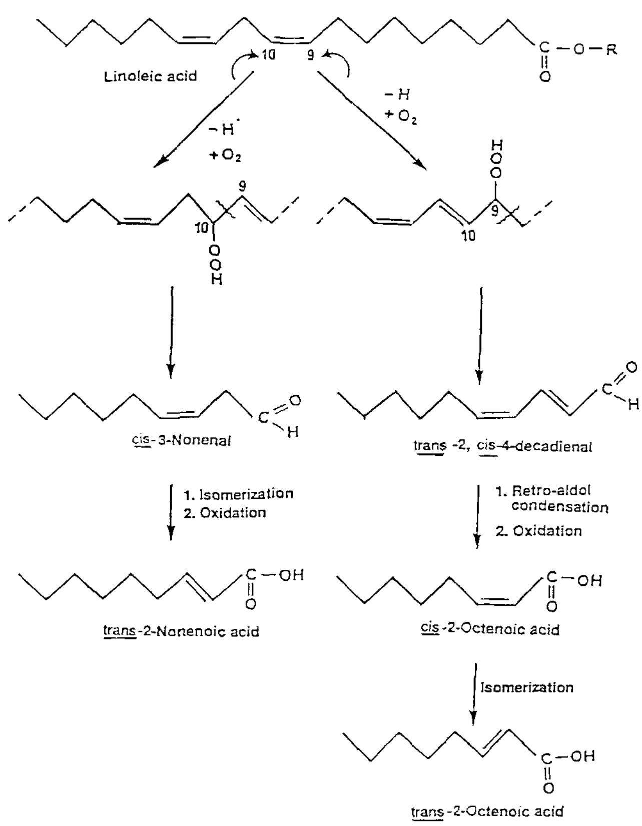

FIG. 3. Proposed mechanisms for the formation of *cis*-2-octenoic, *trans*-2-octenoic, and *trans*-2-nonenoic acids from linoleic acid.

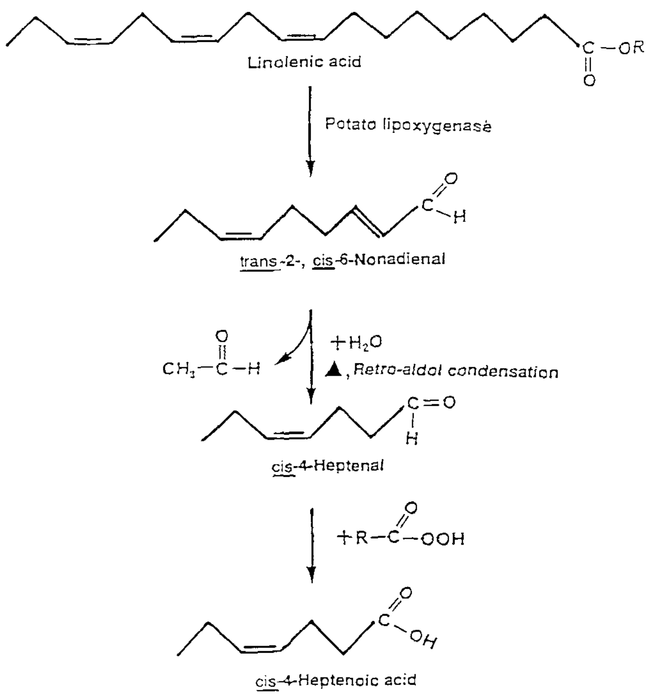

FIG. 2. Proposed mechanism for the formation of *cis*-4-heptenoic acid from linolenic acid.

Analysis of commercial french-fried potatoes that had been deep-fried in a beef tallow-hydrogenated vegetable oil blend contained a number of minor fatty acids that were also found in a fractionated beef tallow shortening. Several of the volatile fatty acids occurred at above-threshold concentrations. It is proposed that volatile fatty acids from beef tallow contribute to a beef-like flavor in french-fried potatoes cooked in this medium. Further research is needed to more clearly define these flavors and to devise means to recover natural beef-like flavor concentrates from nonrefined beef tallow.

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