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Volatile Constituents of Used Frying Oils

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The volatile constituents of used frying oils obtained from a local food-processing plant were isolated by simultaneous distillation–extraction and fractionated by silica gel column chromatography. The isolates were analyzed by capillary gas chromatography and combined capillary gas chromatography–mass spectrometry, resulting in the identification of 140 compounds. The major constituents identified were 1-pentanol, hexanal, furfuryl alcohol, (*E*)-2-heptenal, 5-methylfurfural, 1-octen-3-ol, octanal, 2-pentylfuran, (*E*)-2-octenal, nonanal, (*E*)-2-nonenal, and hexadecanoic acid.

Keywords: *Frying oil; volatiles; simultaneous steam distillation–extraction; deep-fat frying*

INTRODUCTION

Deep-fat frying is a widely used procedure for the preparation of food. During deep-fat frying, fats and oils are continuously or repeatedly heated at high temperatures (up to 190 °C) for prolonged periods of time in the presence of air. Under these conditions both thermal and oxidative reactions of the oils occur, leading to the formation of volatile and nonvolatile decomposition products (Chang et al., 1978). During the frying of foods there is the possibility of interaction of proteins and carbohydrates with oil decomposition products. The production of volatiles from interactions of Maillard reaction products and lipids has been reviewed by Whitfield (1992). The frying oil decomposition products as well as products formed from reactions between food components (proteins, carbohydrates) and oil constituents may adversely affect the flavor, color, nutritive value, and safety of the fried food. There have been numerous studies questioning the safety of thermally oxidized frying oils. Feeding experiments with laboratory animals have shown that consumption of oxidized fats or isolated fractions exerts adverse effects such as weight loss, growth suppression, increased liver and kidney weights, and cellular damage to liver, thymus, epididymides, and testes (Andia and Street, 1975; Billek, 1976; Alexander, 1981; Alexander et al., 1987; Clark and Serbia, 1991, and references cited therein). Studies on the genotoxic potential of heated fats and fried foods using the Ames assay are less conclusive. Used frying fats obtained from commercial German establishments showed no mutagenic activity (Scheutwinkel-Reich et al., 1980). In their study of fried foods Taylor et al. (1982) found weak mutagenic activity in the basic methylene chloride extract from 10 of 30 samples. Taylor et al. (1983) found no mutagenic activity in frying oil after repetitive frying of potatoes, onion rings, or fish fillets. These workers reported that fried foods possess only low levels of mutagenic activity and that severely abusive frying conditions must be used to obtain appreciable levels of mutagenic activity. Six commonly used frying oils showed no mutagenic activity with strains TA98 and TA100 after heating at 180 °C for 24 h (Van Gastel et al., 1984). In their study of 100 samples of used cottonseed frying oil obtained

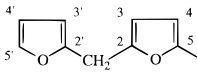
from restaurants, Saleh et al. (1986) found significant mutagenic activity in only six samples. Hageman et al. (1988) showed that repeatedly used frying fats obtained from restaurants and snack bars possessed mutagenic activity, with the majority of activity residing in the polar fraction of the fat. They observed a positive correlation between mutagenicity in strain TA97 and thiobarbituric acid-reactive substances (TBA-RS), which may indicate the involvement of lipid oxidation products in mutagen formation during frying. The differences in mutagenicity assays may be the result of different frying, fractionation, and mutagenicity screening procedures. Taylor et al. (1982, 1983) utilized the *Salmonella* tester strain TA98 with S-9 mix to examine the oil fractions, while Hageman et al. (1988, 1990) found that strain TA97 without S-9 mix most sensitively detected mutagenic activity of the oil fractions. Various lipid oxidation products such as hydroperoxides and carbonyls have been shown to be weakly mutagenic in the Ames assay (MacGregor et al., 1985; Marnett et al., 1984; Yamaguchi and Yamashita, 1980).

Chang et al. (1978) performed pioneering studies on the volatile products formed from corn oil, hydrogenated cottonseed oil, trilinolein, and triolein during simulated deep-fat frying. Other researchers have also studied the volatile constituents resulting from the thermal treatment of vegetable oils (Chung et al., 1993; Wu and Chen, 1992; Macku and Shibamoto, 1991a; Snyder et al., 1985). This study was undertaken to identify oxidative and other degradative volatiles formed in large-scale commercial meat and poultry processing operations to assess possible health risks from the chronic consumption of fried foods. An elucidation of the formation mechanisms of these volatiles will help us to understand reactions occurring during frying.

EXPERIMENTAL PROCEDURES

Simultaneous Steam Distillation–Extraction (SDE).

Used frying oil (250 mL) was placed in a 2-L round-bottom flask along with 250 mL of Milli-Q water (Millipore, Bedford, MA). The mixture was subjected to SDE at atmospheric pressure for 2 h with 100 mL of pentane–diethyl ether (1:1 v/v) using the SDE head described by Schultz et al. (1977). The extract was dried overnight with anhydrous sodium

Table 1. ¹H NMR Spectral Data of 2-(2-Furanylmethyl)-5-methylfuran (400 MHz, CDCl₃, δ Relative to TMS)


| atom | δ ^a | signal ^b | <i>J</i> | CH ₃ | CH ₂ | 3 | 4 | 3' | 4' | 5' |
|-----------------|----------------|-------------------------|-----------------|-----------------|-----------------|-----|---|-----|-----|----|
| CH ₃ | 2.25 | 3H, ddt (1.1, 0.4, 0.4) | CH ₃ | | | | | | | |
| CH ₂ | 3.94 | 2H, br s | CH ₂ | 0.4 | | | | | | |
| HC3 | 5.95 | 1H, dtq (3.0, 0.9, 0.4) | 3 | 0.4 | 0.9 | | | | | |
| HC4 | 5.87 | 1H, dqt (3.0, 1.1, 0.3) | 4 | 1.1 | 0.3 | 3.0 | | | | |
| HC3' | 6.08 | 1H, ddt (3.2, 0.9, 0.9) | 3' | 0 | 0.9 | * | | | | |
| HC4' | 6.30 | 1H, ddt (3.2, 1.9, 0.3) | 4' | 0 | 0.3 | * | * | 3.2 | | |
| HC5' | 7.32 | 1H, ddt (1.9, 0.9, 0.2) | 5' | 0 | 0.2 | * | * | 0.9 | 1.9 | |

^a Assignments and couplings were determined using the homonuclear correlation experiment COSY and homonuclear decoupling. The COSY experiment assigned the signals for HC3', HC4', and HC5' and for HC3 and HC4. However, expansion of the 1d spectrum showed more couplings than could be explained by COSY cross-peaks, raising the possibility that the assignments for HC3 and HC4 could be reversed. Irradiation of CH₂ and of CH₃ in homonuclear decoupling experiments clarified and confirmed their assignments. By irradiation it was clear that the CH₂ is coupled to all other protons including the CH₃. The size of the coupling to the adjacent ring protons, 0.9 Hz, is larger than the more distant couplings, 0.2–0.3 Hz. On this basis the proton adjacent to the CH₃ is assigned to the proton at δ 5.87.

^b Coupling constants (*J* in Hz) in parentheses. Asterisks indicate that homonuclear decoupling experiments were not performed as all observed couplings were accounted for.

sulfate and concentrated with a Vigreux column to a final volume of 0.3–0.4 mL. Three batches of used frying oil (total volume of 750 mL) were sampled in this manner. The extracts were combined and fractionated by column chromatography.

Preseparation by Adsorption Chromatography. The combined extracts were fractionated on a silica gel column [220 mm × 22 mm (i.d.); 230–400 mesh, grade 60, Merck]. For samples obtained by SDE the following stepwise elution was performed: 100 mL of pentane (fraction 1), 100 mL of 10:90 diethyl ether–pentane (v/v, fraction 2), 100 mL of 20:80 diethyl ether–pentane (v/v, fraction 3), 100 mL of 40:60 diethyl ether–pentane (v/v, fraction 4), 100 mL of 60:40 diethyl ether–pentane (v/v, fraction 5), and 100 mL of diethyl ether (fraction 6).

Capillary Gas Chromatography. A HP 5890 Series II gas chromatograph equipped with a flame ionization detector (FID) was used. A DB-1 fused silica column (60 m × 0.32 mm i.d.; *d_f* = 0.25 μm; J&W Scientific, Folsom, CA) was used. Split injection was employed (1:24). The oven temperature was programmed from 30 °C (4 min isothermal) to 220 °C at 2 °C/min. The injector and detector temperatures were 190 and 300 °C, respectively.

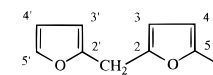
Capillary Gas Chromatography–Mass Spectrometry (GC–MS). A HP 5890 gas chromatograph equipped with a split/splitless injector was coupled to a HP 5970B mass selective detector (capillary direct interface). A 60 m × 0.25 mm i.d. (*d_f* = 0.25 μm) DB-1 fused silica capillary column was used with the following temperature program: 30 °C (4 min isothermal) to 220 °C at 2 °C/min. Split injection was employed (1:22). The injector temperature was 190 °C, and the transfer line temperature was 230 °C.

Capillary Gas Chromatography–Fourier Transform Infrared Spectroscopy (GC–FTIR). A HP 5965B infrared detector was interfaced with a HP 5890 Series II gas chromatograph and controlled by a HP G1034A MS/IR ChemStation. A DB-1 fused silica capillary column (25 m × 0.32 mm i.d.; *d_f* = 0.52 μm) was used. Splitless injection was employed (purge delay time was 45 s). The oven temperature was programmed from 30 °C (4 min isothermal) to 180 °C at 2 °C/min. Light pipe and transfer line temperatures were 190 °C. Vapor-phase spectra were recorded from 550 to 4000 cm^{−1} with a resolution of 8 cm^{−1}.

Reference Compounds. Reference compounds were obtained commercially or synthesized according to established methods. (*E*)-2-Octene had the following mass spectrum: 112 (37), 97 (4), 84 (10), 83 (20), 71 (6), 70 (55), 69 (31), 68 (6), 67 (9), 57 (19), 56 (64), 55 (100), 54 (11), 53 (11), 43 (10), 42 (34), 41 (81), 39 (34); FTIR (vapor phase, *v*, cm^{−1}) 2933, 2870, 1458, 965. (*Z*)-2-Octene had the following mass spectrum: 112 (42), 97 (3), 84 (15), 83 (25), 71 (6), 70 (65), 69 (31), 68 (6), 67 (7), 57 (23), 56 (67), 55 (100), 54 (10), 53 (12), 43 (11), 42 (37), 41 (82), 39 (39); FTIR (vapor phase, *v*, cm^{−1}) 3022, 2963, 2934, 2873,

1460, 1405, 693. 2,4-Nonanedione was obtained from Lancaster Synthesis (Windham, NH). 6-Undecanol was prepared by the reduction of 6-undecanone (Aldrich Chemical Co., Milwaukee, WI) with LiAlH₄. It had the following mass spectrum: 154 (3), 101 (35), 84 (7), 83 (100), 71 (9), 57 (13), 55 (81), 43 (23), 41 (34); Kovats index (DB-1) 1275. Myristicin, isolated by preparative GC from parsley seed oil, had the following mass spectrum: 193 (13), 192 (100), 191 (14), 177 (8), 165 (25), 161 (20), 147 (19), 133 (19), 131 (22), 119 (27), 103 (16), 91 (37), 79 (20), 77 (22), 65 (25), 63 (15), 53 (14), 51 (14), 39 (15). 2-Heptylfuran was prepared in two steps. The first step involved a Friedel–Crafts acylation following the procedure of Gilman and Calloway (1933) to form 2-heptanoyl-furan. This compound was subsequently reduced by the Huang–Minlon modification of the Wolff–Kishner reduction (Furniss et al., 1989). 2-Heptylfuran had the following mass spectrum: 166 (17), 123 (9), 109 (8), 95 (17), 94 (8), 82 (25), 81 (100), 67 (7), 53 (21), 43 (7), 41 (15). 2-Octylfuran, prepared in an analogous way, had the following mass spectrum: 180 (16), 151 (3), 137 (5), 123 (10), 109 (2), 95 (30), 82 (37), 81 (100), 67 (6), 53 (13), 41 (11). 1-Furfurylpyrrole (Aldrich) had the following mass spectrum: 147 (M⁺, 52), 117 (2), 81 (100), 53 (24), 39 (8). 2,2'-Methylenebis(furan) was prepared by the acid-catalyzed condensation of furfuryl alcohol with furan according to the procedure of Brown and Sawatzky (1956). It had the following spectral properties: mass spectrum (*m/z*, %) 148 (M⁺, 100), 147 (18), 120 (19), 119 (15), 94 (14), 91 (94), 81 (11), 65 (19), 53 (15), 39 (21); ¹H NMR (400 MHz, CDCl₃) δ 4.00 (2H, s, CH₂), 6.09 (2H, dd, *J* = 3.4, 1.0 Hz, HC3), 6.31 (2H, dd, *J* = 3.4, 2.0 Hz, HC4), 7.33 (2H, dd, *J* = 2.0, 1.0 Hz, HC5); ¹³C NMR (100 MHz, CDCl₃) δ 27.4 (CH₂), 106.4 (C3), 110.4 (C4), 141.6 (C5), 151.6 (C2). 2-(2-Furanylmethyl)-5-methylfuran was prepared by the acid-catalyzed condensation of furfuryl alcohol and 2-methylfuran according to the same procedure used for 2,2'-methylenebis(furan). It had the following spectral properties: mass spectrum (*m/z*, %) 162 (M⁺, 100), 161 (21), 147 (23), 133 (8), 119 (20), 108 (8), 105 (10), 95 (9), 91 (53), 81 (11), 65 (10), 53 (16), 51 (16), 43 (34). Its ¹H and ¹³C NMR spectra are shown in Tables 1 and 2, respectively. (*Z*)-3-Dodecene (Aldrich) had the following spectral properties: mass spectrum (*m/z*, %) 168 (26), 125 (4), 112 (6), 111 (15), 98 (12), 97 (26), 84 (27), 83 (41), 82 (13), 71 (15), 70 (62), 69 (76), 68 (12), 67 (19), 57 (48), 56 (65), 55 (88), 43 (50), 41 (100); FTIR (vapor phase, *v*, cm^{−1}) 3011, 2967, 2933, 2865, 1463, 1305, 715. Hexylbenzene (Aldrich) had the following mass spectrum: 162 (M⁺, 32), 133 (7), 119 (3), 105 (10), 93 (7), 92 (99), 91 (100), 78 (7), 77 (6), 65 (12), 43 (11). Heptylbenzene (Aldrich) had the following mass spectrum: 176 (M⁺, 27), 133 (7), 119 (3), 105 (9), 104 (4), 92 (100), 91 (90), 78 (6), 77 (6), 65 (13), 51 (5), 43 (16), 41 (12).

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR spectra were taken on a Bruker ARX 400 spectrometer (400 MHz).

Table 2. ^{13}C NMR Spectral Data of 2-(2-Furanylmethyl)-5-methylfuran (100 MHz, Broad Band Decoupled, CDCl_3)


| atom | δ^a | atom | δ^a |
|---------------|------------|------|------------|
| CH_3 | 13.5 | C5 | 149.6* |
| CH_2 | 27.5 | C2' | 151.9* |
| C2 | 151.1* | C3' | 106.2 |
| C3 | 107.1 | C4' | 110.3 |
| C4 | 106.1 | C5' | 141.4 |

^a Chemical shifts were assigned on the basis of H,H correlation and H,C correlation experiments. Asterisks indicate interchangeable values.

Determination of Polar Compounds in Frying Oils.

This was done according to AOCS Official Method Cd 20-91 (revised 1993; reapproved 1993).

RESULTS AND DISCUSSION

Used frying oil samples (soybean or cottonseed oil) were collected from a local processing plant that fried various beef, veal, and chicken products. Volatiles were isolated by SDE. The volatiles were subsequently fractionated by silica gel chromatography and analyzed by capillary GC and combined capillary GC-MS. Sample components were identified by comparison of the compound's Kovats index, *I* (Kovats, 1958), and mass spectrum with that of a reference standard. Used frying oil samples were collected on three separate occasions. The first used oil sample collected was cottonseed oil; the plant subsequently switched to using exclusively soybean oil, and the latter two samples were this oil. All of the oils possessed similar qualitative profiles, and only the results for the soybean oils are presented. The two used oils had compositions of 12.0% and 12.4% polar compounds as measured by AOCS Official Method Cd 20-91. Table 3 shows the used frying oil constituents isolated by SDE. The major volatiles found in used frying oil included 1-pentanol, hexanal, furfuryl alcohol, (*E*)-2-heptenal, 5-methylfurfural, 1-octen-3-ol, octanal, 2-pentylfuran, (*E*)-2-octenal, nonanal, (*E*)-2-nonenal, and hexadecanoic acid.

Nonpolar Constituents. Henderson et al. (1980) studied the effect of heating conditions on the decomposition of linoleates and reported that higher temperatures and longer heating times produced a large number of cyclic hydrocarbons which were not detected with the milder heat treatments (250 °C for 5 h vs 180 °C for 1 h). Alencar et al. (1983) found that *n*-alkanes and 1-alkenes were the main products resulting from the pyrolysis (300–500 °C) of tropical vegetable oils. They also detected low levels of a variety of cyclic hydrocarbons (alkylcyclopentanes, alkylcyclopentenones, alkylcyclohexanes, and alkylcyclohexenes) as pyrolysis products. Five *n*-alkylbenzenes were previously reported in heated peanut oil (Chung et al., 1993). These constituents along with two additional *n*-alkylbenzenes, hexylbenzene and heptylbenzene, were identified in the used frying oil samples. Hexylbenzene was already reported in heated corn oil and heated trilinolein (Chang et al., 1978). The alkylcycloalkanes, propylcyclohexane and butylcyclopentane, were previously found in heated corn oil (Macku and Shibamoto, 1991a,b). The terpene hydrocarbons, limonene, β -phellandrene, and caryophyllene, probably originate from spices such as black pepper used to season the food products, although

camphane and limonene have been reported in heated peanut oil (Chung et al., 1993). A series of alkylfurans ranging from 2-propylfuran to 2-octylfuran were also identified. 2-Heptylfuran, which induces increased activity of the detoxifying enzyme glutathione *S*-transferase, has been shown to inhibit tumorigenesis in mice. Lam et al. (1994) have reported that 2-heptylfuran reduces benzo[a]pyrene-induced forestomach tumors and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone-induced lung tumors in A/J mice.

Moderately Polar Constituents. 2,4-Nonanedione and 3-methylnonane-2,4-dione were previously reported in reverted soybean oil (Guth and Grosch, 1989). On the basis of its low odor threshold (0.01 ng/L of air) and the result of an aroma dilution extract analysis, the researchers concluded that the latter compound is an important contributor to the reversion odor of soybean oil. We could not identify it in our samples; however, if present, it would have coeluted with 4-oxononanal. *trans*-4,5-Epoxy-(*E*)-2-decenal was previously identified as a volatile produced in the thermal decomposition of trilinolein (Selke et al., 1980). Guth and Grosch (1990) have shown that this compound with its low threshold of 0.5 pg/L of air contributes to the green, haylike odor in soybean oil stored in the dark. This odorant has also been identified in stored beef (Konopka and Grosch, 1991), wheat bread crumb (Schieberle and Grosch, 1991), popcorn (Schieberle, 1991), tomato (Buttery and Ling, 1993), roasted sesame seeds (Schieberle, 1993), and puff pastries (Gassenmaier and Schieberle, 1994a). Volatile epoxyalkenals of this type were first identified as products from lipid oxidation by Swoboda and Peers (1978), who discovered *trans*-4,5-epoxy-(*E*)-2-heptenal in oxidized butterfat. Model studies by Gardner et al. (1978) have shown that this epoxydecenal is formed during thermal degradation of methyl 12,13-epoxy-9-hydroperoxy-10-octadecenoate. Other model experiments have revealed that the epoxydecenal is formed during the thermal degradation of the linoleic acid peroxidation products, 13-hydroperoxy-9,11-octadecadienoic acid and 9-hydroperoxy-10,12-octadecadienoic acid (Gassenmaier and Schieberle, 1994b). These researchers also established that 2,4-decadienal and 12,13-epoxy-9-hydroperoxy-10-octadecenoic acid are key intermediates in the thermal generation of the epoxydecenal. 2-Pentylpyridine was reported as the major constituent in the basic fraction from roasted lamb fat (Buttery et al., 1977). The authors postulated that the compound might be formed from the reaction of the lipid breakdown product, 2,4-decadienal, with ammonia, which is generated from the thermal degradation of free or bound amino acids. Schieberle (1993) corroborated this postulate, showing that 2,4-decadienal is an important intermediate in the formation of 2-pentylpyridine. 2-Ethylpyridine was also identified, which was probably formed by an analogous reaction of 2,4-heptadienal with ammonia. 2,2'-Methylenebis(furan) has been reported in coffee (Stoll et al., 1967) as well as in various model browning systems such as lactose-casein (Ferretti et al., 1970), furfural- H_2S - NH_3 (Shibamoto, 1977), serine-sucrose (Baltes and Boehmann, 1987), xylose-lysine (Ames and Apriyantono, 1993), and xylose-tryptophan (Baltes and Knoch, 1993). Its mass spectral fragmentation mechanisms have been discussed in detail by Loughran et al. (1972). Its FTIR spectrum is shown in Figure 1. Similarly, 2-(2-furanylmethyl)-5-methylfuran has also been found in coffee

Table 3. Volatile Constituents of Used Frying Oil Samples Isolated by Atmospheric SDE

| constituent | μ B-1 | | fraction ^a | rel amt ^b | constituent | μ B-1 | | fraction ^a | rel amt ^b |
|--------------------------------------|-----------|------|-----------------------|----------------------|---|-----------|------|-----------------------|----------------------|
| | exptl | ref | | | | exptl | ref | | |
| 1-butanol | 657 | 654 | 5 | + | decane | 1001 | 1000 | 1 | + |
| 1-penten-3-ol | 674 | 671 | 4, 5 | ++ | phenylacetaldehyde | 1008 | 1007 | 3 | + |
| pentanal | 679 | 676 | 3, 4 | ++ | 3-octen-2-one | 1013 | 1013 | 3 | + |
| 3-hydroxy-2-butanone | 682 | 680 | 5 | + | β -phellandrene | 1017 | 1018 | 1 | + |
| 3-pentanol | 688 | 687 | 4 | + | limonene | 1019 | 1020 | 1 | + |
| 2-pentanol | 688 | 687 | 5 | + | (<i>E</i>)-2-octenal | 1041 | 1030 | 3 | +++ |
| 1-heptene | 691 | 689 | 1 | + | butylbenzene | 1042 | 1040 | 1 | + |
| 2-ethylfuran | 692 | 691 | 1 | + | 2-methoxyphenol | 1059 | 1059 | 4 | + |
| 2,5-dimethylfuran | 697 | 695 | 1, 2 | + | octanol | 1060 | 1053 | 5 | + |
| heptane | 701 | 700 | 1 | ++ | 2,2'-methylenebis(furan) | 1061 | 1063 | 2 | + |
| pyrazine | 704 | 706 | 6 | + | 3,5-octadien-2-one | 1068 | 1063 | 4 | + |
| 2-heptene | 705 | 710 | 1 | + | 2-hexylfuran | 1081 | 1080 | 1 | + |
| 3-penten-2-one | 715 | 711 | 4 | + | heptanoic acid | 1083 | 1065 | 6 | + |
| pyridine | 719 | 717 | 6 | + | nonanal | 1087 | 1082 | 2, 3 | +++ |
| <i>N</i> -methylpyrrole | 719 | 717 | 2 | + | (5-undecene) | 1090 | | 1 | + |
| dimethyl disulfide | 729 | 722 | 2 | + | 4-oxooctanal | 1100 | 1099 | 5 | + |
| (<i>E</i>)-2-pentenal | 730 | 723 | 3 | + | γ -heptalactone | 1100 | 1103 | 5 | + |
| (ethylcyclopentane) ^c | 733 | | 1 | + | undecane | 1101 | 1100 | 1 | + |
| 2-methylpentanal | 745 | 736 | 2 | + | 3-nonen-2-one | 1116 | 1114 | 3, 4 | + |
| toluene | 755 | 748 | 1 | + | (<i>E</i>)-2-nonenal | 1142 | 1134 | 3 | +++ |
| cyclopentanone | 759 | 752 | 4 | + | pentylbenzene | 1143 | 1142 | 1 | + |
| 1-pentanol | 763 | 758 | 5 | +++ | 1-(2-furanylmethyl)-1 <i>H</i> -pyrrole | 1148 | 1149 | 2 | + |
| 1-hexen-3-ol | 769 | 756 | 4 | + | 2,4-nonanedione | 1152 | 1152 | 5 | + |
| 2-hexanone | 770 | 761 | 3 | + | 5-decanone | 1155 | 1155 | 2 | + |
| 2-methyltetrahydrofuran-3-one | 777 | 776 | 4 | + | 2-(2-furanylmethyl)-5-methylfuran | 1156 | 1157 | 2 | + |
| hexanal | 780 | 778 | 2, 3 | +++ | (2,4-nonadienal) | 1169 | | 3 | + |
| 2-propylfuran | 781 | 781 | 1 | + | 2-pentylpyridine | 1175 | 1173 | 4 | + |
| 1-octene | 790 | 785 | 1 | + | 2-heptylfuran | 1182 | 1181 | 1 | + |
| 2-cyclopenten-1-one | 793 | 793 | 5 | + | decanal | 1186 | 1184 | 2 | + |
| methylpyrazine | 794 | 796 | 6 | + | (<i>E,E</i>)-2,4-nonadienal | 1187 | 1184 | 3 | + |
| octane | 801 | 800 | 1 | ++ | octanoic acid | 1194 | 1165 | 6 | + |
| furfural | 805 | 800 | 4 | ++ | (<i>Z</i>)-3-dodecene | 1195 | 1195 | 1 | + |
| (<i>E</i>)-2-octene | 805 | 805 | 1 | + | dodecane | 1201 | 1200 | 1 | + |
| (<i>Z</i>)-2-octene | 814 | 814 | 1 | + | 4-oxononanal | 1203 | 1200 | 4, 5 | ++ |
| 4-hydroxy-4-methyl-2-pentanone | 814 | 811 | 6 | + | γ -octalactone | 1211 | 1210 | 5 | + |
| (3-hexen-2-one) | 819 | | 4 | + | (2,4-decadienal) | 1243 | 1286 | 3 | + |
| (3-cyclohepten-1-one) | 821 | | 1 | + | hexylbenzene | 1245 | 1245 | 1 | + |
| 2-methylcyclopentanol | 828 | 825 | 4, 5 | + | (2,2'-methylenebis(5-methylfuran)) | 1249 | | 2 | + |
| (<i>E</i>)-2-hexenal | 831 | 822 | 3 | ++ | 6-undecanone | 1255 | 1253 | 2 | + |
| 5-methyl-2(3 <i>H</i>)-furanone | 836 | 835 | 4 | + | 2-pentyl-2-cyclopenten-1-one | 1260 | 1259 | 4 | + |
| furfuryl alcohol | 844 | 827 | 5 | +++ | nonanoic acid | 1272 | 1260 | 6 | + |
| ethylbenzene | 848 | 844 | 1 | + | (<i>E,E</i>)-2,4-decadienal | 1289 | 1286 | 3, 4 | ++ |
| γ -butyrolactone | 857 | 855 | 6 | + | 2-octylfuran | 1282 | 1281 | 1 | + |
| hexanol | 862 | 848 | 5 | + | undecanal | 1287 | 1286 | 2 | + |
| 2-heptanone | 873 | 865 | 3 | + | (6-tridecene) | 1287 | | 1 | + |
| styrene | 873 | 871 | 1 | + | tridecane | 1300 | 1300 | 1 | + |
| heptanal ^d | 881 | 876 | 2, 3 | ++ | 4-oxodecanal | 1304 | 1303 | 5 | + |
| 2-ethylpyridine ^d | 881 | 881 | 5 | + | γ -nonalactone | 1312 | 1315 | 5 | + |
| 2-acetylthiophene ^d | 882 | 876 | 4 | ++ | 2-undecenal | 1346 | 1339 | 3 | +++ |
| 2-butylfuran | 882 | 881 | 1 | + | heptylbenzene | 1348 | 1348 | 1 | + |
| 2,6-dimethylpyrazine | 885 | 882 | 6 | + | 6-dodecanone | 1355 | 1353 | 2 | + |
| 2-heptanol | 888 | 882 | 5 | + | decanoic acid | 1365 | 1335 | 6 | + |
| 2,3-dimethylpyrazine | 890 | 890 | 6 | + | dodecanal | 1388 | 1388 | 2 | + |
| nonane | 900 | 900 | 1 | + | tetradecane | 1400 | 1400 | 1 | + |
| γ -pentalactone | 898 | 902 | 6 | + | caryophyllene | 1410 | 1415 | 1 | + |
| 4-oxohexanal | 911 | 909 | 5 | + | γ -decalactone | 1419 | 1423 | 5 | + |
| (1,2-nonadiene) | 920 | | 1 | + | 1-phenyl-1-hexanone | 1428 | 1426 | 2 | + |
| 3-methyl-2-cyclopenten-1-one | 923 | 923 | 6 | + | dodecanol | 1459 | 1457 | 5 | + |
| benzaldehyde | 925 | 926 | 2 | + | pentyl octanoate | 1469 | 1468 | 2 | + |
| propylcyclohexane | 926 | 925 | 1 | + | myristicin | 1484 | 1482 | 2 | + |
| (<i>N</i> -butylpyrrole) | 928 | | 2 | + | tridecanal | 1490 | 1489 | 2 | + |
| (<i>E</i>)-2-heptenal ^d | 929 | 927 | 3 | +++ | pentadecane | 1500 | 1500 | 1 | + |
| butylcyclopentane ^d | 932 | 931 | 1 | + | dodecanoic acid | 1554 | 1547 | 6 | + |
| 5-methylfurfural ^d | 938 | 926 | 4 | +++ | tetradecanal | 1592 | 1592 | 2 | + |
| propylbenzene | 940 | 938 | 1 | + | (tributyl phosphate) | 1619 | | 6 | + |
| 1-octen-3-one | 961 | 953 | 3 | + | γ -dodecalactone | 1633 | 1636 | 5 | + |
| 2,3-octanedione | 967 | 959 | 2 | + | 2-pentadecanone | 1679 | 1679 | 2 | + |
| 3-octanone | 969 | 964 | 2, 3 | + | heptadecane | 1700 | 1700 | 1 | + |
| (2,4-heptadienal) | 975 | 980 | 3 | + | tetradecanoic acid | 1750 | 1740 | 6 | + |
| 1-octen-3-ol | 976 | 968 | 4 | +++ | octadecane | 1800 | 1800 | 1 | + |
| 2,3,5-trimethylpyrazine | 976 | 974 | 6 | + | (neophytadiene) | 1837 | | 1 | + |
| 4-octanol | 979 | 977 | 4 | + | pentadecanoic acid | 1843 | 1840 | 6 | + |
| hexanoic acid | 981 | 975 | 6 | + | (2-heptadecanone) | 1882 | | 2 | + |
| octanal ^d | 983 | 979 | 2 | +++ | heptadecanal | 1898 | 1897 | 2 | + |
| 2-pentylfuran ^d | 984 | 977 | 1, 2 | +++ | methyl hexadecanoate | 1909 | 1909 | 2 | + |
| (5-ethyl-2(5 <i>H</i>)-furanone) | 984 | | 6 | + | hexadecanoic acid | 1960 | 1940 | 6 | +++ |
| (<i>E,E</i>)-2,4-heptadienal | 987 | 980 | 3, 4 | ++ | ethyl hexadecanoate | 1978 | 1978 | 2 | + |
| γ -hexalactone | 999 | 1003 | 5, 6 | + | | | | | |

^a Fraction number from silica gel column chromatography; refer to Experimental Procedures for details. ^b Relative amount in unfractionated SDE sample; +++ represents >2%, ++ represents 0.5–2.0%, and + represents <0.5% of the total peak area, respectively.

^c Tentative identifications are enclosed in parentheses. ^d Components were not resolved in the unfractionated sample.

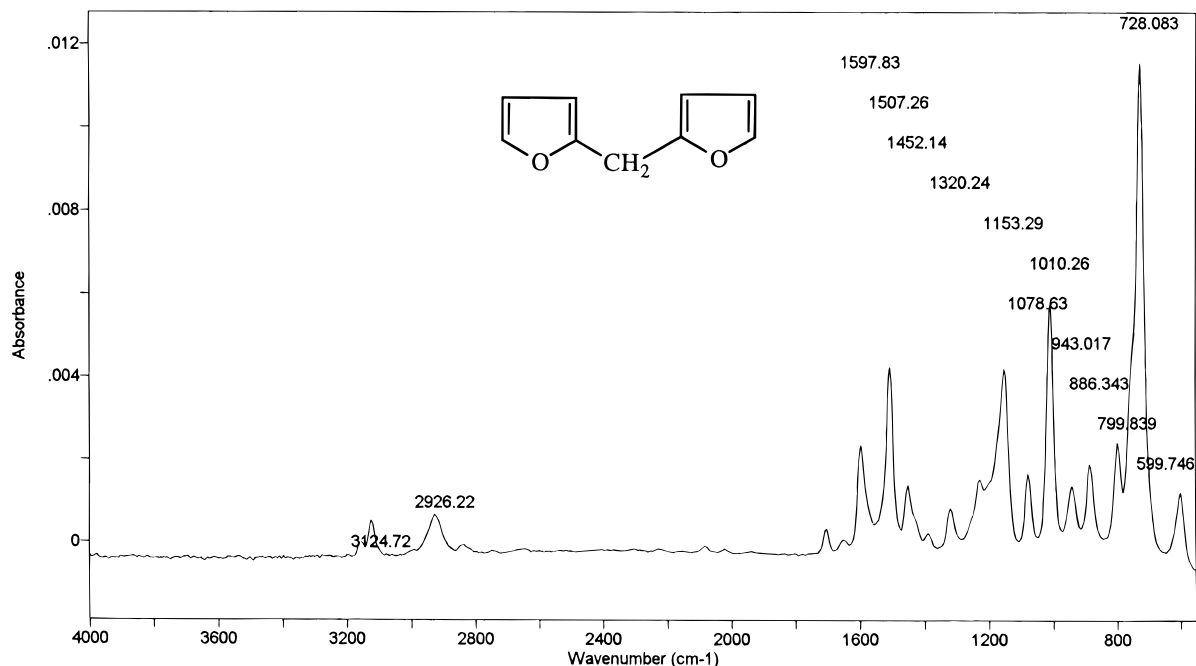


Figure 1. Vapor-phase FTIR spectrum of 2,2'-methylenebis(furan).

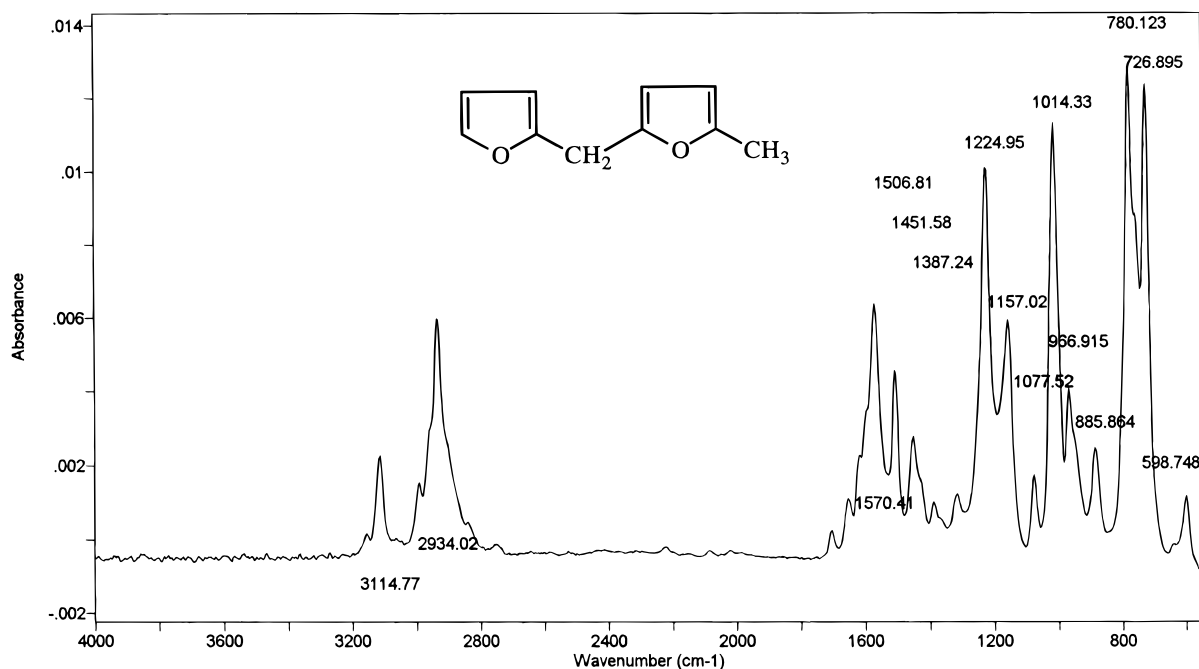


Figure 2. Vapor-phase FTIR spectrum of 2-(2-furanylmethyl)-5-methylfuran.

(Stoll et al., 1967) as well as in different model browning systems such as lactose–casein (Ferretti et al., 1970), serine–threonine–sucrose (Baltes and Bochmann, 1987), and glucose–tryptophan (Baltes and Knoch, 1993). Its FTIR spectrum is shown in Figure 2, while its ^1H and ^{13}C NMR spectral data are displayed in Tables 1 and 2, respectively. The formation pathway of the difuryl-methanes is not clear. Ferretti and Flanagan (1971) proposed a condensation reaction of formaldehyde with furans to form difurfuryl-methanes, while Baltes and Knoch (1993) postulated that this condensation could also occur by an attack of 2-furymethanol on another furan molecule. Myristicin is a mild hallucinogen that occurs in a variety of spices (van Straten and Maarse, 1983) as well as carrots (Buttery et al., 1968), parsley leaf oil (Shaath et al., 1986), dill seed herb oil (Huo-

palahti and Linko, 1983), and celery seed oil (Formacek and Kubeczka, 1982). Myristicin has been shown to induce increased activity of the detoxifying enzyme system glutathione *S*-transferase in several samples of mouse tissue selected from various targeted organs (Zheng et al., 1992a). Due to this biological activity, myristicin may be considered a potential cancer chemopreventative agent (Zheng et al., 1992b).

Though oxo acids were reported in heated trilinolein as early as 1978 (Chang et al., 1978), the identification of oxoaldehydes in used frying oils is relatively recent (Takeoka et al., 1995). These workers reported four oxoaldehydes, 4-oxohexanal, 4-oxooctanal, 4-oxononanal, and 4-oxodecanal, in used frying oils and in a model reaction found that the main product formed from refluxing 4-oxononanal in hexane was 3-octanone.

Polar Constituents. Various nitrogen-containing heterocyclic compounds such as pyrazine, methylpyrazine, 2,6-dimethylpyrazine, 2,3-dimethylpyrazine, and 2,3,5-trimethylpyrazine were found, indicating the occurrence of Maillard-type reactions. Discussion of the formation of these types of compounds has been covered in some reviews [e.g. Whitfield (1992)].

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LITERATURE CITED

- Alencar, J. W.; Alves, P. B.; Craveiro, A. A. Pyrolysis of tropical vegetable oils. *J. Agric. Food Chem.* **1983**, *31*, 1268–1270.
- Alexander, J. C. Chemical and biological properties related to toxicology of heated fats. *J. Toxicol. Environ. Health* **1981**, *7*, 125–138.
- Alexander, J. C.; Valli, V. E.; Chanin, R. E. Biological observations from feeding heated corn oil and heated peanut oil to rats. *J. Toxicol. Environ. Health* **1987**, *21*, 295–309.
- Ames, J. M.; Apriyatono, A. Volatile reaction products from a heated xylose-lysine model system. *Food Chem.* **1993**, *48*, 271–277.
- Andia, A. G.; Street, J. C. Dietary induction of hepatic microsomal enzymes by thermally oxidized fats. *J. Agric. Food Chem.* **1975**, *23*, 173–177.
- Baltes, W.; Bochemann, G. Model reactions on roast aroma formation. II. Mass spectrometric identification of furans and furanones from the reaction of serine and threonine with sucrose under the conditions of coffee roasting. *Z. Lebensm. Unters. Forsch.* **1987**, *184*, 179–186.
- Baltes, W.; Knoch, E. Model reactions on roast aroma formation. XIII. The formation of some uncommon N-heterocyclic compounds and furans after roasting of tryptophan with reducing sugars and sugar degradation products. *Food Chem.* **1993**, *46*, 343–349.
- Billek, G. Heated oils. Chemistry and nutritional aspects. *Nutr. Metab.* **1976**, *24*, 200–210.
- Brown, W. H.; Sawatzky, H. The condensation of furan and Sylvan with some carbonyl compounds. *Can. J. Chem.* **1956**, *34*, 1147–1153.
- Buttery, R. G.; Ling, L. C. Volatile components of tomato fruit and plant parts—relationship and biogenesis. In *Bioactive Volatile Compounds from Plants*; Teranishi, R., Buttery, R. G., Sugisawa, H., Eds.; ACS Symposium Series 525; American Chemical Society: Washington, DC, 1993; pp 23–34.
- Buttery, R. G.; Seifert, R. M.; Guadagni, D. G.; Black, D. R.; Ling, L. C. Characterization of some volatile constituents of carrots. *J. Agric. Food Chem.* **1968**, *16*, 1009–1015.
- Chang, S. S.; Peterson, R. J.; Ho, C. T. Chemical reactions involved in the deep-fat frying of foods. *J. Am. Oil Chem. Soc.* **1978**, *55*, 718–727.
- Chung, T. Y.; Eiserich, J. P.; Shibamoto, T. Volatile compounds identified in headspace samples of peanut oil heated under temperatures ranging from 50 to 200 °C. *J. Agric. Food Chem.* **1993**, *41*, 1467–1470.
- Clark, W. L.; Serbia, G. W. Safety aspects of frying fats and oils. *Food Technol.* **1991**, *45*, 84–89.
- Ferretti, A.; Flanagan, V. P. The lactose-casein (Maillard) browning system: volatile components. *J. Agric. Food Chem.* **1971**, *19*, 245–249.
- Ferretti, A.; Flanagan, V. P.; Ruth, J. M. Nonenzymatic browning in a lactose-casein model system. *J. Agric. Food Chem.* **1970**, *18*, 13–18.
- Formacek, V.; Kubeczka, K.-H. Celery seed oil. In *Essential Oil Analysis by Capillary Gas Chromatography and Carbon-13 NMR Spectroscopy*; Wiley: New York, 1982; pp 37–39.
- Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. In *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific & Technical: Essex, England, 1989; pp 827–828, 831.
- Gardner, H. W.; Selke, E. Volatiles from thermal decomposition of isomeric methyl (12*S*,13*S*)-(E)-12,13-epoxy-9-hydroperoxy-10-octadecenoates. *Lipids* **1984**, *19*, 375–380.
- Gassenmaier, K.; Schieberle, P. Comparison of important odorants in puff-pastries prepared with butter or margarine. *Lebensm. Wiss. Technol.* **1994a**, *27*, 282–288.
- Gassenmaier, K.; Schieberle, P. Formation of the intense flavor compound *trans*-4,5-epoxy-(E)-2-decenal in thermally treated fats. *J. Am. Oil Chem. Soc.* **1994b**, *71*, 1315–1319.
- Gilman, H.; Calloway, N. O. Super-aromatic properties of furan. II. The Friedel-Crafts reaction. *J. Am. Chem. Soc.* **1933**, *55*, 4197–4205.
- Guth, H.; Grosch, W. 3-Methylnonane-2,4-dione—an intense odour compound formed during flavour reversion of soya-bean oil. *Fat Sci. Technol.* **1989**, *91*, 225–230.
- Guth, H.; Grosch, W. Comparison of stored soya-bean and rapeseed oils by aroma extract dilution analysis. *Lebensm. Wiss. Technol.* **1990**, *23*, 59–65.
- Hageman, G.; Kikken, R.; Ten Hoor, F.; Kleinjans, J. Assessment of mutagenic activity of repeatedly used deep-frying fats. *Mutat. Res.* **1988**, *204*, 593–604.
- Henderson, S. K.; Witchwoot, A.; Nawar, W. W. The autoxidation of linoleates at elevated temperatures. *J. Am. Oil Chem. Soc.* **1980**, *57*, 409–413.
- Huopalahti, R.; Linko, R. R. Composition and content of aroma compounds in dill, *Anethum graveolens* L., at three different stages. *J. Agric. Food Chem.* **1983**, *31*, 331–333.
- Konopka, U. C.; Grosch, W. Potent odorants causing the warmed-over flavour in boiled beef. *Z. Lebensm. Unters. Forsch.* **1991**, *193*, 123–125.
- Kovats, E. sz. Gas-chromatographische charakterisierung organischer verbindungen teil 1: retentionindices aliphatischer halogenide, alcohole, aldehydeundketone. *Helv. Chim. Acta* **1958**, *41*, 1915–1932.
- Lam, L. K. T.; Zhang, J.; Zhang, F.; Zhang, B. Inhibition of chemically induced carcinogenesis by 2-*n*-heptylfuran and 2-*n*-butylthiophene from roast beef aroma. In *Sulfur Compounds in Foods*; Mussinan, C., Keelan, M. E., Eds.; ACS Symposium Series 564; American Chemical Society: Washington, DC, 1994; pp 278–291.
- Loughran, E. D.; Wewerka, E. M.; Hammons, G. J. A mass spectrometric study of substituted furfuryl compounds (I). *J. Heterocycl. Chem.* **1972**, *9*, 57–65.
- MacGregor, J. T.; Wilson, R. E.; Neff, W. E.; Frankel, E. N. Mutagenicity tests of lipid oxidation products in *Salmonella typhimurium*: monohydroperoxides and secondary oxidation products of methyl linoleate and methyl linolenate. *Food Chem. Toxicol.* **1985**, *23*, 1041–1047.
- Macku, C.; Shibamoto, T. Headspace volatile compounds formed from heated corn oil and corn oil with glycine. *J. Agric. Food Chem.* **1991a**, *39*, 1265–1269.
- Macku, C.; Shibamoto, T. Volatile sulfur-containing compounds generated from the thermal interaction of corn oil and cysteine. *J. Agric. Food Chem.* **1991b**, *39*, 1987–1989.
- Marnett, L. J.; Hurd, H. K.; Hollstein, M. C.; Levin, D. E.; Esterbauer, H.; Ames, B. N. Naturally occurring carbonyl compounds are mutagens in *Salmonella* tester strain TA104. *Mutat. Res.* **1984**, *148*, 25–34.
- Saleh, M. A.; Ahmed, K. A.; Sharaf, A. N.; Abdel-Latif, M. S. Mutagenicity of heated cottonseed frying oil. *J. Food Saf.* **1986**, *7*, 203–213.
- Schieberle, P. Primary odorants in popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141–1144.
- Schieberle, P. Studies on the flavour of roasted white sesame seeds. In *Progress in Flavour Precursor Studies*; Schreiber, P., Winterhalter, P., Eds.; Proceedings of the International Conference, Würzburg; Allured Publishing: Carol Stream, IL, 1993; pp 343–360.
- Schieberle, P.; Grosch, W. Potent odorants of the wheat bread crumb—Differences to the crust and effect of a longer dough fermentation. *Z. Lebensm. Unters. Forsch.* **1991**, *192*, 130–135.
- Schultz, T. H.; Flath, R. A.; Mon, T. R.; Eggling, S. B.; Teranishi, R. Isolation of volatile components from a model system. *J. Agric. Food Chem.* **1977**, *25*, 446–449.

- Selke, E.; Rohwedder, W. K.; Dutton, H. J. Volatile components from trilinolein heated in air. *J. Am. Oil Chem. Soc.* **1980**, *57*, 25–30.
- Shaath, N. A.; Griffin, P.; Dedeian, S.; Paloympis, L. The chemical composition of Egyptian parsley seed, absolute and herb oil. In *Flavors and Fragrances: A World Perspective*; Lawrence, B. M., Mookherjee, B. D., Wills, B. J., Eds.; Proceedings of the 10th International Congress of Essential Oils, Fragrances and Flavors, Washington, DC; Elsevier Science Publishers: Amsterdam, 1986; pp 715–729.
- Shibamoto, T. Formation of sulfur- and nitrogen-containing compounds from the reaction of furfural with hydrogen sulfide and ammonia. *J. Agric. Food Chem.* **1977**, *25*, 206–208.
- Snyder, J. M.; Frankel, E. N.; Selke, E. Capillary gas chromatographic analysis of headspace volatiles from vegetable oils. *J. Am. Oil Chem. Soc.* **1985**, *62*, 1675–1679.
- Stoll, M.; Winter, M.; Gautschi, F.; Flament, I.; Willhalm, B. Recherches sur les arômes. Sur l'arôme de café. I. *Helv. Chim. Acta* **1967**, *50*, 628–694.
- Swoboda, P. A. T.; Peers, K. E. *trans*-4,5-Epoxyhept-*trans*-2-enal. The major volatile compound formed by the copper and α -tocopherol induced oxidation of butterfat. *J. Sci. Food Agric.* **1978**, *29*, 803–807.
- Takeoka, G. R.; Buttery, R. G.; Perrino, C. T., Jr. Synthesis and occurrence of oxoaldehydes in used frying oils. *J. Agric. Food Chem.* **1995**, *43*, 22–26.
- Taylor, S. L.; Berg, C. M.; Shoptaugh, N. H.; Scott, V. N. Lack of mutagens in deep-fat-fried foods obtained at the retail level. *Food Chem. Toxicol.* **1982**, *20*, 209–212.
- Taylor, S. L.; Berg, C. M.; Shoptaugh, N. H.; Traisman, E. Mutagen formation in deep-fat fried foods as a function of frying conditions. *J. Am. Oil Chem. Soc.* **1983**, *60*, 576–580.
- Van Gastel, A.; Mathur, R.; Roy, V. V.; Rukmini, C. Ames mutagenicity tests of repeatedly heated edible oils. *Food Chem. Toxicol.* **1984**, *22*, 403–405.
- van Straten, S.; Maarse, Eds. In *Volatile Compounds in Food Qualitative Data*; Division for Nutrition and Food Research, TNO: Zeist, The Netherlands, 1983.
- Whitfield, F. Volatiles from interactions of Maillard reactions and lipids. *Crit. Rev. Food Sci. Nutr.* **1992**, *31*, 1–58.
- Wu, C.-M.; Chen, S.-Y. Volatile compounds in oils after deep frying or stir frying and subsequent storage. *J. Am. Oil Chem. Soc.* **1992**, *69*, 858–865.
- Yamaguchi, T.; Yamashita, Y. Mutagenicity of hydroperoxides of fatty acids and some hydrocarbons. *Agric. Biol. Chem.* **1980**, *44*, 1675–1678.
- Zheng, G.-Q.; Kenney, P. M.; Lam, L. K. T. Myristicin: a potential cancer chemopreventative agent from parsley leaf oil. *J. Agric. Food Chem.* **1992a**, *40*, 107–110.
- Zheng, G.-Q.; Kenney, P. M.; Zhang, B.-L.; Lam, L. K. T. Inhibition of benzo[a]pyrene-induced tumorigenesis by myristicin, a volatile aroma constituent of parsley leaf oil. *Carcinogenesis* **1992b**, *13*, 1921–1923.

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