

ARTICLES

Volatile Constituents of Used Frying Oils

Gary Takeoka,* Charles Perrino, Jr., and Ron Buttery

Western Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture,
800 Buchanan Street, Albany, California 94710

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

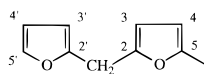
Deep-fat frying is a widely used procedure for the preparation of food. During deep-fat frying, fats and oils are continuously or repeatedly heated at high temperatures (up to 190 °C) for prolonged periods of time in the presence of air. Under these conditions both thermal and oxidative reactions of 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 filets. 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, dtq (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.

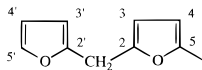
Capillary Gas Chromatography–Mass Spectrometry (GC–MS). A HP 5890 gas chromatograph equipped with a split/splitless injector was coupled to a HP 5970B mass selective detector (capillary direct interface). A 60 m × 0.25 mm i.d. (*d_f* = 0.25 μm) DB-1 fused silica capillary column was used with the following 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-heptanoylfuran. 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 Bochmann, 1987), xylose-lysine (Ames and Apriyanton, 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	J^{DB-1}				constituent	J^{DB-1}			
	exptl	ref	fraction ^a	rel amt ^b		exptl	ref	fraction ^a	rel amt ^b
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-acetylfuran ^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-decanone	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.

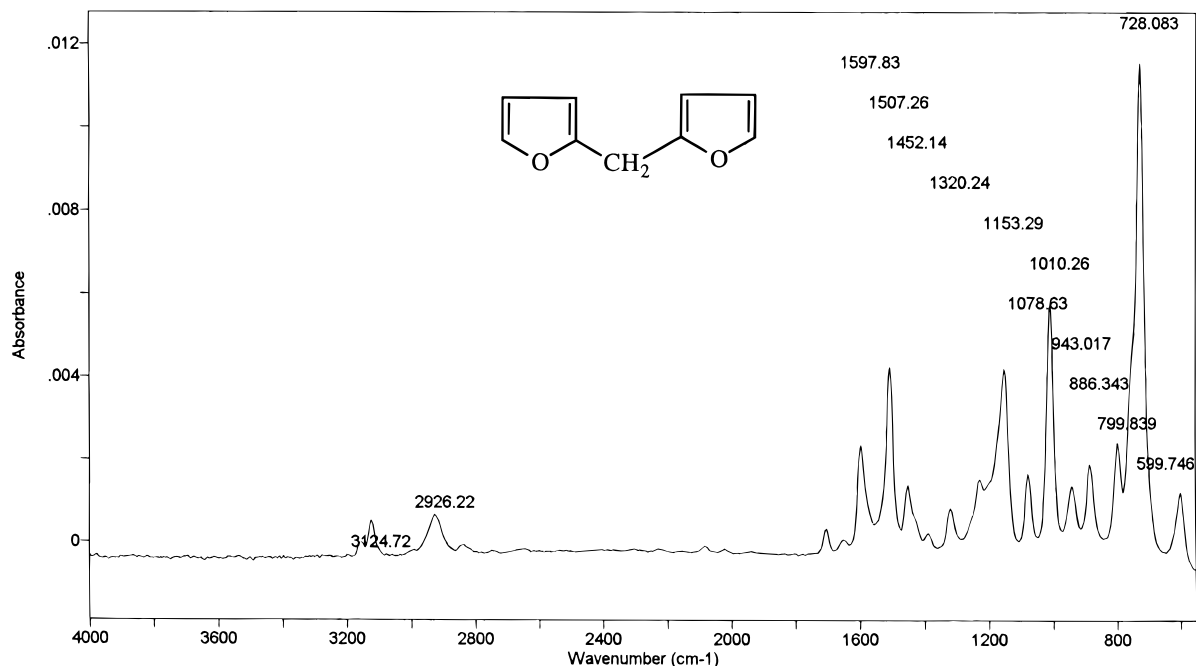


Figure 1. Vapor-phase FTIR spectrum of 2,2'-methylenebis(furan).

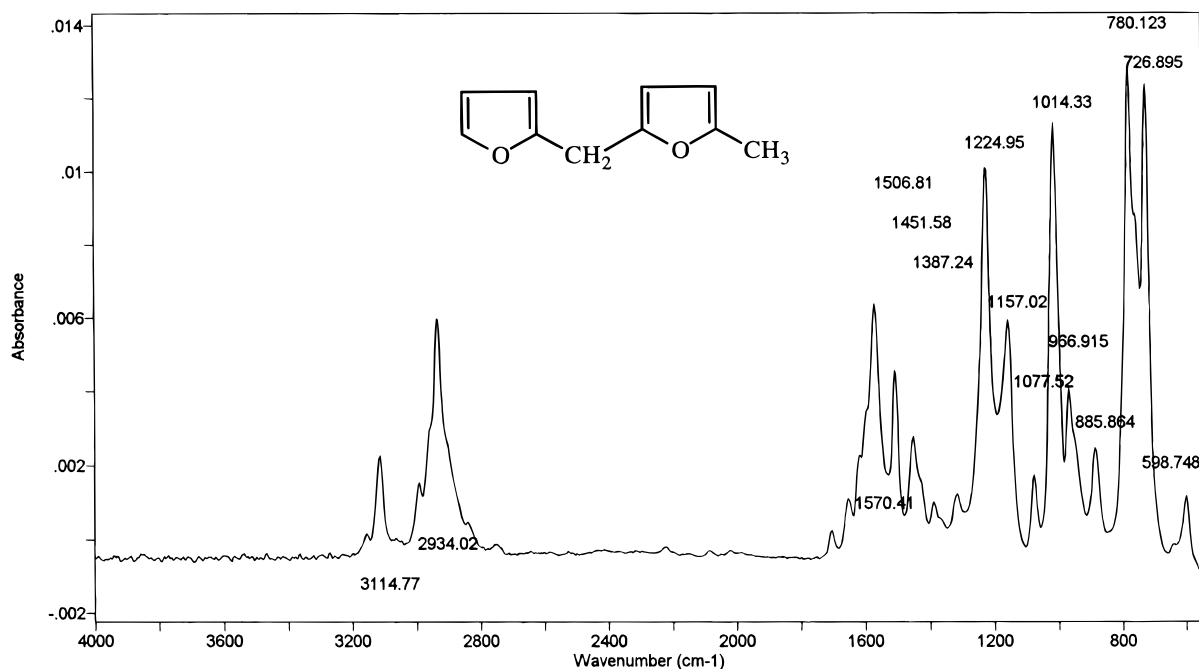


Figure 2. Vapor-phase FTIR spectrum of 2-(2-furanylmethyl)-5-methylfuran.

(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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