Determination of Volatile Lipid Oxidation Products by Dynamic Headspace–Capillary Gas Chromatographic Analysis with Application to Milk-Based Nutritional Products

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A dynamic headspace–capillary gas chromatographic analysis technique with cryofocusing was investigated for the quantitation of volatile lipid oxidation products. Alkanals, *t*-2-alkenals, *t*,*t*-2,4-alkadienals, and 1-pentanol were purged, trapped onto Tenax TA, and then back-flushed into a gas chromatograph by thermal desorption. Back-flushed compounds were reconcentrated at −150 °C and then injected into a capillary column by rapid heating, resulting in a satisfactory separation with no band broadening. Volatile compounds were transferred quantitatively during thermal desorption. Recoveries of volatile compounds were greatly affected by purge temperature, suggesting that purge recovery in addition to detector response be considered in quantitative analysis. Procedures for the quantitation of volatile lipid oxidation compounds in milk-based nutritional products are described. Hexanal, although predominant, was present at sub-ppm levels.

INTRODUCTION

Lipid oxidation is a detrimental process causing the loss of food quality through flavor deterioration and nutrient destruction as well. Various analytical methods have been developed to evaluate the extent of lipid oxidation on the basis of peroxide value, thiobarbituric acid number, anisidine value, carbonyl value, conjugated diene, Kreis absorbance, oxygen uptake, etc. (Gray, 1978; Nawar, 1985). However, these methods failed to provide an unequivocal answer in evaluating flavor changes associated with lipid oxidation (Scholz and Ptak, 1966; Jackson, 1981; Min and Kim, 1985; Pongracz, 1986). In contrast, headspace analysis by gas chromatography has been the analytical approach of considerable interest because volatile lipid oxidation products (VLOP) determined by headspace analysis were highly correlated to flavor deterioration (Depuy et al., 1977; Fritch and Gale, 1977; Warner et al., 1978; Min, 1981; Rho et al., 1986; Robards et al., 1988).

VLOP in the headspace can be analyzed by either static or dynamic headspace analysis. In static headspace analysis, VLOP are allowed to equilibrate between the sample and the gas phases in a sealed vial, and then an aliquot of headspace is injected into a gas chromatograph for analysis (Ioffe and Vitenberg, 1984; Robards et al., 1988); samples are usually heated to enrich VLOP in the headspace; however, heating may form artifacts failing to reveal aromas as they were. This lack of sensitivity is easily overcome in dynamic headspace (DHS) analysis, also known as purge-and-trap analysis (Westendorf, 1985); volatiles are purged continuously out of the sample, simultaneously concentrated on a solid adsorbent trap, and then desorbed thermally prior to gas chromatographic (GC) separation.

In order to inject thermally desorbed VLOP as a narrow band into the capillary columns, VLOP back-flushed from the trap were reconcentrated with on-column trapping by dipping one or more loops of a column in cryogenic coolant prior to separation (Hsieh et al., 1989; Lin et al., 1990). In other cases the entire GC oven was cooled for on-column trapping which also enabled temperature programming from subambient temperatures (Leland et al., 1987; Hall, 1989; Selke and Frankel, 1987; Snyder et al., 1988). Another development used only a short segment of a column (a few centimeters) as a cryotrap in which back-flushed volatiles were trapped with liquid nitrogen, the injection being implemented by rapid heating of the cryotrap (Westendorf, 1985; Hall, 1989). This technique is advantageous to the previous two approaches in terms of either automation or reduced coolant consumption and more precise, rapid oven temperature manipulation.

Only a few studies have used the DHS–GC analysis technique for the determination of VLOP (Selke and Frankel, 1987; Snyder et al., 1988; Hsieh et al., 1989). However, these studies did not use the above-described cryofocusing technique and also reported VLOP in terms of area counts. The objectives of the present study were to evaluate a DHS–GC analysis technique with cryofocusing for the quantitation of VLOP and to describe DHS–GC procedures applicable to milk-based nutritional products.

MATERIALS AND METHODS

Materials. The following compounds were selected based on their presence among VLOP (Depuy et al., 1985; Frankel, 1980; Snyder et al., 1988; Ullrich and Grosch, 1988): pentane, pentanal, heptanal, octanal, nonanal, decanal, *t*-2-heptenal, *t*,*t*-2,4-heptadienal, and *t*,*t*-2,4-decadienal from Aldrich Chemical Co., Inc. (Milwaukee, WI), and hexanal, *t*-2-hexenal, and 1-pentanol from Sigma Chemical Co. (St. Louis, MO). 4-Methyl-2-pentanone (same as methyl isobutyl ketone, MIBK) and 4-heptanone from Aldrich and Sigma Chemical Co., respectively, were used as an internal standard (IS) for quantitation and a secondary reference to check the analysis system stability, respectively. Methanol (HPLC grade) and casein were from Fisher Scientific Co. (St. Louis, MO). Distilled water (DW) in this study represents Milli-Q water (Millipore Corp., Milford, MA) which was further filtered each day through an activated charcoal column (32 cm × 5-cm i.d., Tekmar Co., Cincinnati, OH). Three brands of milk-based nutritional products were purchased from a local supermarket. At the time of analysis, samples were approximately 16 months from expiration.

Volatile Standard Solution. Aliquots (5–7 μL unless otherwise stated) of each standard were diluted to 100 mL with methanol, 1 mL of which was further diluted to 10 mL with DW

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to prepare a working solution of standard mixture (5 ng/μL). Sample solution for purge-and-trap was made by adding 6 μL of a working solution into 5 mL of DW in a purge vessel giving a final concentration of 6 ppb for each standard.

Concentration of VLOP. A purge-and-trap concentrator (Model LSC2000, Tekmar) equipped with a built-in pocket heater and a capillary interface for cryofocusing was connected to a gas chromatograph. Volatiles of the sample solution (5 mL) were purged with helium at 40 mL/min and swept into a porous polymer adsorbent, Tenax TA (60/80 mesh, 0.29 g, 30 cm × 0.32-cm i.d., Tekmar), kept below 35 °C. Volatiles were then thermally desorbed by heating the trap at 180 °C and back-flushed through the sample transfer line kept at 150 °C (an empty fused silica tubing, 0.53 mm × 90 cm) to the capillary interface sitting above a gas chromatograph injector. Back-flushed volatiles were cryofocused at −150 °C using liquid nitrogen and then rapidly heated to 200 °C over a 0.75-min span for injection into a gas chromatograph. The analytical column was connected to the capillary interface using an empty fused silica tubing (0.53 mm × 25 cm) passing through a gas chromatograph injector.

The following were operational parameters in the order of automation sequence: prepurge, 1 min at 23 °C, if used; preheat, 2 min at 30–70 °C with no helium flow; purge (see below for time and temperature); dry purge, 2 min; desorption preheat, to 175 °C with no helium flow; desorption, at 180 °C (see below); bake, 8 min at 225 °C.

Preliminary experiments in which 5 mL of DW (blank) was purged at 23 °C for 5 min immediately after the sample run revealed that the carryover from the previous run ranged from 3 to 12%. Since the carryover was not detected (<1%) in the second consecutive blank run, a blank run was made between analyses.

Thermal Desorption. The standard mixture was purged at 23 °C for 10 min, and then peak area responses after desorption times of 1–6 min were compared. In another experiment the purge step was skipped, and standard mixtures (5–200 ng) were directly placed using a syringe into the trap after detaching its top end from the concentrator. Following the direct injection the detector response factor (RF) was calculated from the formula, RF = (amount injected)/(area response) and the relative RF (RRF) to IS was from the formula, RRF = (RF of a volatile compound)/(RF of MIBK).

Purge. The standard mixture was purged at 23 °C for 10–90 min, and peak area responses were compared. In the second experiment the standard mixture was purged for 20 min at various temperatures up to 70 °C, and the purge recovery was obtained by dividing peak area responses observed after purge by those observed from the direct injection into the trap.

Gas Chromatography. A Hewlett-Packard 5890A gas chromatograph equipped with a flame ionization detector was used with a fused silica capillary column, DB-5 (30 m × 0.32 mm, 1.0-μm film thickness) from J&W Scientific (Rancho Cordova, CA). The injector and detector were at 250 and 300 °C, respectively. Helium was the carrier gas according to the previous study (Park, 1992) and set at 10 psi. The make-up gas was nitrogen. The oven temperature was programmed from 40 °C after initial hold for 3 min to 180 °C at a 5 °C/min rise and then to 250 °C at a 25 °C/min rise. Chromatograms were recorded with a Hewlett-Packard 3392A computing integrator at a chart speed of 0.5 cm/min.

Quantitation. VLOP were quantified using MIBK as an IS after purging the sample solution at 60 °C for 20 min. To compensate for the difference in purgibility a correction factor (CF) for the DHS–GC analysis was calculated using the same formula for RRF but after the calibration run in which the working solution of 6 ppb was purged at 60 °C for 20 min. The concentration was calculated using the following formula

$$\text{concentration} = \frac{(\text{area of compound})(\text{IS amount})(\text{CF})}{(\text{area of MIBK})(\text{sample amount})}$$

To check for recovery of volatiles from a proteinaceous liquid, volatiles were spiked to 5 mL of casein solution (mg/mL, pH 7.0) at 6 and 20 ppb and then quantified by the DHS–GC analysis. The percent recovery was obtained by dividing the volatile content found experimentally by their known added amount. For milk-based nutritional products, a 500-μL aliquot was diluted to 5 mL with DW in a purge vessel. After the addition of MIBK and 4-heptanone, the sample solution was analyzed by the DHS–GC analysis.

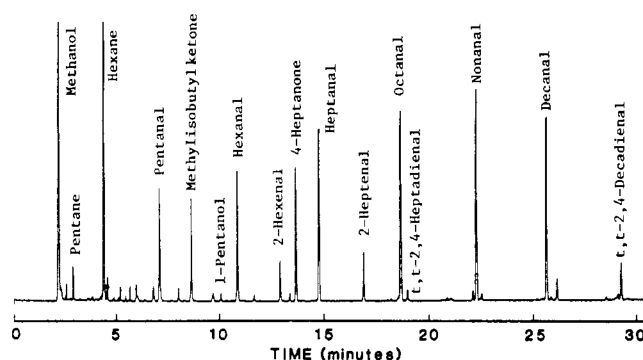

Figure 1. Gas chromatogram obtained with DHS–GC analysis of volatiles standard (30 ng/5 mL). After purging volatiles out of distilled water at 23 °C for 10 min, volatiles trapped on the Tenax TA were thermally desorbed at 180 °C for 4 min, cryofocused at −150 °C, and then injected by raising the temperature to 200 °C over 0.75 min (see Materials and Methods for details). The capillary column was a DB-5 (0.32 mm × 30 m, 1.0 μm). Oven temperature was held at 40 °C for 3 min and then programmed to 180 °C at 5 °C/min rise and then to 250 °C at 25 °C/min rise.

Statistical Analysis. All data represent a mean value of at least duplicate analyses. Linear regressions and correlation coefficients (*r*) were calculated by the least squares method (Snedecor and Cochran, 1978).

RESULTS AND DISCUSSION

From the standpoint of functional purposes, the DHS–GC analysis system may be broken into the following components: purge and trap, desorption, cryofocusing, and chromatographic separation. Therefore, the performance of each component was evaluated with a view to optimizing variables for VLOP quantitation.

GC Separation. After a series of injections, conditions of oven temperature programming were optimized as described in Materials and Methods, and all compounds studied were resolved completely. When VLOP were introduced into a gas chromatograph through the ancillary concentrator, a virtually identical chromatogram resulted (Figure 1). Although VLOP were injected via the capillary interface after cryofocusing followed by rapid heating, their peak shapes looked comparable to those by means of a syringe injection, indicating no noticeable broadening of peak width.

Thermal Desorption. For a reproducible analysis with high sensitivity it is required that the volatiles trapped on an adsorbent be desorbed quantitatively and as thoroughly as possible. On the basis of the combined volume of the trap (assuming empty) and the sample transfer line the minimum gas volume for the desorption was estimated to be approximately 2.7 mL. Since the gas flow is switched from the purge gas (40 mL/min) to the carrier gas (3.7 mL/min) at the onset of desorption, a 1–6-min desorption time was evaluated. The peak response was similar during such desorption times for most VLOP except unsaturated aldehydes which showed a slightly greater response with prolonged desorption (partially presented in Table I). In view of the recovery, analysis time and coolant consumption, 4 min was chosen for desorption time. The coefficient of variation of the desorption performance was below 2%.

When varying aliquots of standard solution were placed directly into the trap and then thermally desorbed, increased peak area correlated strongly with increased

Table I. Effect of Desorption Time on Peak Area Response[a,b]

compound	desorption time, min		
	2	4	6
MIBK	1.02	1.04	1.05
1-pentanol*	1.17	1.17	1.16
hexanal	1.01	1.04	1.04
4-heptanone	1.03	1.06	1.05
t,*t*-2,4-decadienal*	1.06	1.10	1.16

[a] Standard mixture of 6 ppb (except asterisked (*) compounds, 60 ppb) was purged for 10 min at 23 °C. [b] Peak area response was referenced to that of 1-min desorption.

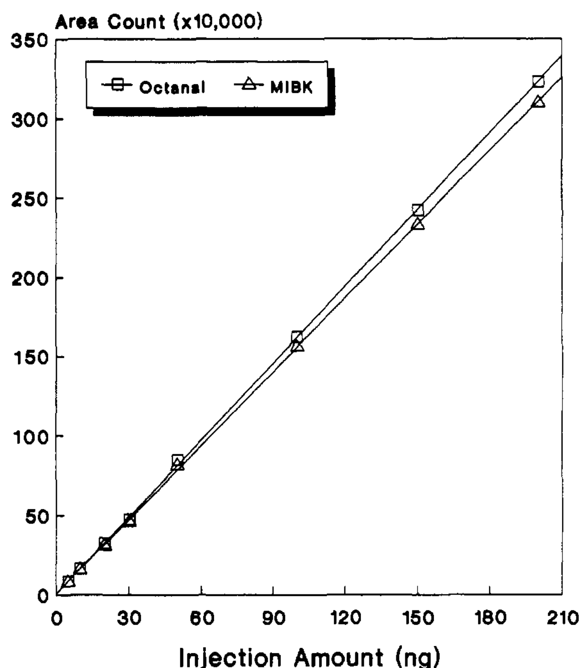

Figure 2. Illustration of linear response of volatile compounds released from the trap by thermal desorption. The DHS-GC conditions were the same as in Figure 1 except for no purge. Volatiles standards were thermally desorbed from the Tenax TA trap at 180 °C after being placed directly into the trap.

Table II. Effect of Purge Time on Peak Area Response[a,b]

compound	purge time, min			
	20	30	60	90
MIBK	1.6	1.9	2.4	2.5
1-pentanol*	2.0	2.8	5.4	7.4
hexanal	1.6	1.8	2.0	2.1
4-heptanone	1.5	1.7	2.0	2.0
t,*t*-2,4-decadienal*	2.9	3.9	6.1	6.4

[a] Standard mixture of 6 ppb (except asterisked (*) compounds, 60 ppb) was purged at 23 °C. [b] Peak area response was referenced to that after 10-min purge.

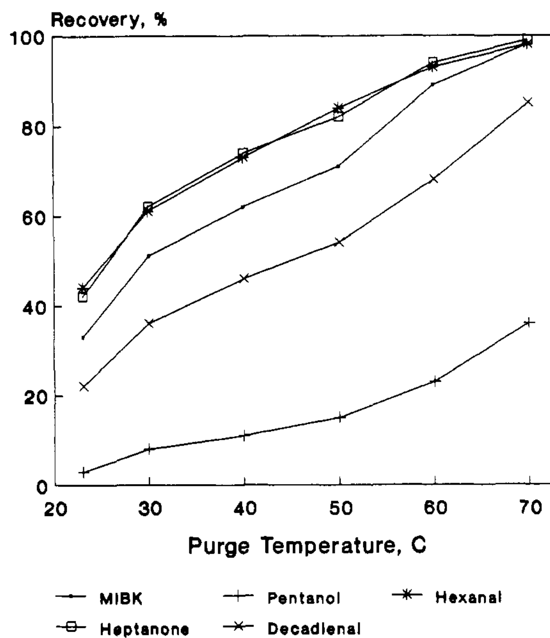

Figure 3. Effect of purge temperature on the recovery of volatile compounds. Standard mixture of 6 ppb was purged at each temperature for 20 min following prepurge for 1 min and preheat for 2 min to the purge temperature. Other DHS-GC conditions were the same as in Figure 1. Recovery percent was obtained by dividing peak area response of volatile standard purged at each temperature by that of volatile standard directly placed into the trap and desorbed.

amount of standards ($r^2 = 0.99$ as illustrated in Figure 2), implying that thermal desorption did not cause VLOP loss due to incomplete desorption or destruction. These results established the RF of each compound which was irrelevant to the purge and thus a base for the calculation of the recovery through purge at different temperatures (to be discussed later). Using MIBK as an IS, RRFs (in parentheses) of VLOP were estimated as follows: pentanal (1.10), 1-pentanol (1.09), hexanal (1.02), *t*-2-hexenal (1.01), 4-heptanone (0.92), heptanal (0.97), *t*-2-heptenal (1.11), octanal (0.96), *t*,*t*-heptadienal (1.13), nonanal (0.99), decanal (1.17), and *t*,*t*-2,4-decadienal (1.31). Due to the difficulty of keeping pentane in standard mixtures, pentane was excluded from the RRF estimation and the remaining quantitative studies.

Purge Efficiency. For a given sample, purge time and temperature would be most critical to the recovery of volatile compounds affecting the detection limit. The effect of purge time on the recovery of VLOP was examined by varying the purge duration. In general, the longer the purge time, the greater the peak area response of the sample solution (partially presented in Table II). After a 20-min purge, the further increase in peak area response was regarded as marginal for alkanals and ketones, although it was still pronounced for alkenals. Since the response increase was nonlinear and slowed down with the increasing time, purge times longer than 20 min were not considered to be an effective means of improving the purge efficiency.

As the purge temperature was elevated, the volatiles recovery increased in almost a linear fashion (partially illustrated in Figure 3), indicating that temperature is more effective than time in improving the purge efficiency. The recovery was higher in alkanals than alkenals and also higher in longer chain alkanals (C7–C9) than shorter chain alkanals (C5 and C6). This difference in purge recovery suggests that the observed peak area count be corrected for the purge recovery in addition to the detector response (i.e., RRF) for quantitative analysis (see below). For quantitation of 2,4-alkadienals and alcohols the purge must be conducted at elevated temperatures due to their low recoveries. It should, however, be pointed out that the purge at the elevated temperature will cause higher transfer of water vapor into the trap, which may cause faster deterioration of the trap and extinguishment of the flame in the detector with insufficient dry purge. Based on the above observations it was concluded that purging at elevated temperatures, such as 60 °C, would be necessary when the sensitive detection is desirable. Otherwise, purging at lower temperatures such as 23 °C would be a reasonable choice because it is advantageous in terms of analysis speed and reduced transfer of water vapor into the analysis system.

Table III. Correction Factor (CF)[a] and Percent Recovery of Volatiles Spiked[b]

compound	CF	concentration spiked, ppb	
		6	20
pentanal	1.18	100.8 ± 2.4[c]	100.4 ± 2.6
1-pentanol	2.31	93.1 ± 11.6	93.6 ± 8.5
hexanal	1.04	99.0 ± 4.1	100.3 ± 4.2
t-2-hexenal	1.25	100.2 ± 4.8	98.6 ± 2.4
4-heptanone	0.94	102.8 ± 4.1	102.2 ± 1.2
heptanal	0.98	105.0 ± 3.7	105.0 ± 2.8
t-2-heptenal	1.17	103.3 ± 4.5	98.6 ± 3.7
octanal	1.04	97.2 ± 3.4	98.2 ± 2.6
t,*t*-2,4-heptadienal	2.05	98.9 ± 3.9	97.1 ± 1.6
nonanal	1.07	101.8 ± 3.3	98.0 ± 4.5
decanal	1.34	108.7 ± 7.5	102.2 ± 4.3
t,*t*-2,4-decadienal	1.35	98.3 ± 9.1	91.0 ± 7.5

[a] Combined RRF with purge recovery. Evaluated by running standard mixture of 6 ppb with the purge at 60 °C for 20 min. [b] Volatile compounds were spiked to 5 mL of casein solution (mg/mL, pH 7). [c] Mean ± SD (n = 3).

Table IV. Volatile Lipid Oxidation Products in Milk-Based Nutritional Products by Dynamic Headspace–Gas Chromatographic Analysis[a]

compound	content, ppb		
	product A	product B	product C
pentane	NQ[b]	NQ	NQ
pentanal	99 ± 15[c]	81 ± 3	92 ± 10
1-pentanol	23 ± 2	19 ± 7	15 ± 1
hexanal	240 ± 15	294 ± 3	282 ± 20
t-2-hexenal	ND[d]	ND	ND
heptanal	27 ± 2	27 ± 1	28 ± 1
t-2-heptenal	93 ± 4	104 ± 3	99 ± 4
octanal	46 ± 6	54 ± 3	50 ± 3
t,*t*-2,4-heptadienal	ND	ND	ND
nonanal	96 ± 19	82 ± 11	78 ± 9
decanal	42 ± 8	51 ± 8	65 ± 8
t,*t*-2,4-decadienal	ND	ND	ND

[a] Sample solutions were purged for 20 min at 60 °C (see Materials and Methods). [b] Not quantified. [c] Mean ± SD (n = 3). [d] Not detected.

Quantitation. Since the difference in purgibility of volatile compounds required the correction in the peak area response, CF in which both the detector response and the purge recovery were combined was evaluated prior to quantitation. VLOP such as alcohol and unsaturated aldehydes that had purge recoveries lower than that of MIBK (as shown in Figure 3) showed a greater discrepancy between CF (Table III) and RRF. The mean recovery of VLOP spiked to a casein solution approached 100% while ranging from 91 to 109% (Table III). These results revealed that the presence of casein in the solution did not affect the recovery of VLOP and thus implied that proteins in nutritional products would not obstruct the VLOP quantitation by the DHS–GC analysis.

The DHS–GC method described in the present study was applied to quantifying VLOP in milk-based nutritional products. Hexanal was the most predominant species among VLOP detected and was estimated to be present at concentrations of 0.24–0.29 ppm (Table IV). Other VLOP were below 0.1 ppm, and 2,4-alkadienals were not detected. Although 2,4-decadienals were among the major VLOP in vegetable oils (Depuy et al., 1985; Snyder et al., 1988), they were not detected in the nutritional samples. This may be partly accounted for by the difference in sampling temperatures. The sampling of volatile compounds in the previous studies was conducted at 170–180 °C (Depuy et al., 1985; Snyder et al., 1988), whereas it was done at 60 °C in the present study. It was implied that the heating of linoleates at higher temperatures preferentially forms 2,4-decadienals over hexanal due to the cleavage of a carbon–carbon bond (adjacent to the hydroperoxide moiety) toward the carboxyl side rather than the methyl terminus (Lomanno and Nawar, 1982; Selke and Frankel, 1987). Worthy of mention is that the recovery of 4-heptanone added as a secondary reference was 96–103%, indicating the reasonably precise performance of the DHS–GC analysis.

Summary. A procedure based on the purge and trap of volatile compounds and the cryofocus technique prior to a capillary GC separation has been evaluated for the quantitation of volatile compounds resulting from lipid oxidation. The method has been applied to determining the VLOP concentration in liquid milk-based nutritional products. It had a good precision and its sensitivity was not a matter of concern, unlike equilibrium headspace analysis, thus offering a new approach to studying lipid oxidation in early stage and its implication in flavor deterioration. Nevertheless, it was frustrating that the carryover of nonanal and decanal was encountered frequently during analyses of nutritional products despite the careful operation to prevent liquid samples overflowing into the system. Moreover, nonanal and decanal peaks remained so persistently that blank water had to be run three or four times to ensure a clean background before the next sample analysis. This requirement for tedious washing to eliminate carryover for some VLOP can be a drawback for the present purge-and-trap analysis. Nonanal and decanal originate from oleates which oxidize at a slower rate than polyunsaturated fatty acids (Frankel, 1980; Nawar, 1985) and were found as minor aldehydes among VLOP in soybean oils (Selke and Frankel, 1987; Snyder et al., 1988) and in the present study as well. It would, therefore, be more practical to quantify VLOP sacrificing nonanal and decanal, if necessary, rather than sample throughput due to extensive washing of the analysis system. In that case, one could also modify purge variables in such a way that the purge would be done at lower temperatures for a shorter period as already discussed.

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Registry No. $CH_3(CH_2)_3CH_3$, 109-66-0; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_4OH$, 71-41-0; $CH_3(CH_2)_4CHO$, 66-25-1; (*E*)-$CH_3(CH_2)_2CH{=}CHCHO$, 6728-26-3; $CH_3(CH_2)_5CHO$, 111-71-7; (*E*)-$CH_3(CH_2)_3CH{=}CHCHO$, 18829-55-5; $CH_3(CH_2)_6CHO$, 124-13-0; (*E*,*E*)-$CH_3CH_2CH{=}CH\text{-}CH{=}CHCHO$, 4313-03-5; $CH_3(CH_2)_7CHO$, 124-19-6; $CH_3(CH_2)_8CHO$, 112-31-2; (*E*,*E*)-$CH_3(CH_2)_4CH{=}CH\text{-}CH{=}CHCHO$, 25152-84-5.