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Identification of 8-Nonenal as an Important Contributor to "Plastic" Off-Odor in Polyethylene Packaging

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Food and beverage products stored in polyethylene (PE) containers may absorb some of PE's volatile minor components and become tainted by its characteristic "plastic" odor. High-density PE containers that had imparted "plastic" odor to an experimental corn chip product were analyzed by simultaneous distillation/extraction to remove the volatile components, by gas chromatography/olfactometry (GC/O) to locate the offending components and by 2-D GC/mass spectrometry (MS) to identify the major "plastic" odor contributor (8-nonenal). The identification was made using high-resolution electron ionization and chemical ionization MS data to narrow the possibilities to two isomers of nonenal, followed by retrieval of reference spectra and confirmatory synthesis. By monitoring 8-nonenal in HDPE containers and corn chips it was demonstrated that 8-nonenal tracks with "plastic" aroma observed in containers and with "plastic" flavor observed in corn chips stored in the containers.

KEYWORDS: Polyethylene volatiles; HDPE; 8-nonenal; plastic off-odor; plastic off-flavor; packaging off-odor

INTRODUCTION

Food packaging can contribute undesirable off-flavors to the foods stored in them (*1*). Off-flavors imparted to foods or beverages by polyolefin packaging material may be caused by minor components (indigenous components that survive refining or additives such as plasticizers or antioxidants) in the resins (*2*), or off-flavors may result from oxidation of polyolefin during polymerization or during subsequent thermal processing (*3*–*6*), such as extrusion to form films, sheets, or containers. In the case of polyethylene, many compounds (*5*) have been identified in the volatiles of thermally oxidized material, including eight compounds known to be odor-active through application of the GC/O technique of CharmAnalysis (*6*). In the latter work Bravo, et al. (*6*) obtained GC/O, mass spectral, and retention index data for several oxidized PE volatiles that eluded identification efforts, including the one (RI = 1073 on cross-linked methyl silicone) that CharmAnalysis pinpointed as the most odor-active oxidation product. From the data generated in the current work it is likely that their RI = 1073 peak is the same compound as the "plastic" peak identified here, consistent with their conclusion that it is an unsaturated carbonyl compound with the greatest odor impact of all the oxidized polyethylene volatile components.

The current work was undertaken to address the specific problem of an off-flavor induced in an experimental corn chip product by storage in HDPE containers at typical stability test temperatures of 21, 29, and 38 °C for times varying from 2 weeks to 8 months. Because the most common descriptor ascribed to the off-flavor by expert sensory panelists was "plastic", the HDPE container became the early focus of analytical efforts to understand the problem. The goals were to identify the actual odorant, predict the chemistry that might have produced the odorant, track the odorant in an experimental protocol based on the predicted chemistry, and recommend an acceptable remediation procedure. This paper focuses primarily on the identification effort.

MATERIALS AND METHODS

Chemicals. Reagents for simultaneous distillation/extraction: water (MilliQ, deionized), methylene chloride (Burdick & Jackson 300-4).

Resins and Canisters. HDPE canisters were made from resins of medium molecular weight homopolymer with density greater than 0.96 g/cm^3. An example is Paxon AD60−007 (Exxon Mobil), but three comparable resins from other suppliers were tested with similar results. Canisters made internally at P&G were made by a shuttle station continuous-extrusion blow-molding process, while canisters used for plant production food products were made by a rotary continuous-extrusion multilayer blow-molding process.

Sample Preparation. Food products were cut, ground, or chopped to small pieces with a characteristic length of 2−4 mm and thickness of 1−2 mm. A food processor, mortar and pestle, or compression through a funnel was used to achieve the desired particle size. Plastic materials were reduced to a fine, granular powder that passed through a number 12 U.S. Sieve Size. The plastic was cut into small pieces

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about 6 mm square and then cooled with dry ice for about 10 min. Grinding to the desired particle size was achieved with a Model RT commercial food processor made by Robot Coupe Corp. (Ridgeland, MS).

Synthesis of 8-Nonenal. 8-Nonenal was prepared according to the procedure described by Farquhar et al. (*7*). [Note that there is a typographical error in the experimental procedure on p 969 (compound **8e**): in method A: "*N*-methylmorpholine *N*-oxide (1.22 g....)" should read 12.2 g.] ^{1}H and ^{13}C NMR spectra were obtained to confirm the structure, and gas chromatography indicated a purity of approximately 97%.

Volatiles Extraction Method. Qualitative application of simulta-neous distillation/extraction for the purpose of locating and identifying off-odors used tetramethylpyrazine as an internal standard and a 75 g sample of HDPE prepared as described above. The sample was steam-distilled at atmospheric pressure, and the distillate was methylene-chloride-extracted at the same time (*8*). In the quantitative application of this procedure 150 ng of *cis*-6-nonenal (internal standard) was added to 30 g of ground sample prior to distillation/extraction. To the sample and internal standard was added 700 mL of distilled, deionized water. Distillation/extraction was carried out for 90 min using 100 mL of methylene chloride as the extracting solvent. The methylene chloride extract was concentrated to 300 (plastic materials) or 100 μL (food products) under a gentle stream of nitrogen.

2-D GC/MS. The methylene chloride extract from simultaneous distillation/extraction was injected into the injection port of a 2-D GC (Siemens SiChromat 2) with the following columns:

Column 1 = 30 M × 0.32 mm, 1.0 μm film thickness, DB-1701;

Column 2 = 30 M × 0.32 mm, 0.25 μm film thickness, DB-5;

Oven 1 = 40 (5 min hold) to 225 °C at 7 °C/min;

Oven 2 = 40 (25.5 min hold) to 225 °C at 2 °C/min.

The flow rate on each column was approximately 1 mL/min (He), and the effluent from each column was split approximately 50:50 to GC/O ports using Restek Universal "Y" Press Tight connectors. Conditions were found on column 1 in which a single 30 s heart cut (25.4−25.9 min.) diverted both 8-nonenal and *cis*-6-nonenal to the second column. Detection of the effluent from column 2 was done using high-resolution mass spectrometry with a Finnigan MAT95 Q mass spectrometer. For purposes of identifying off-odors, full-scan mode at a resolution of ∼1000 was used in positive-ion electron and chemical ionization (isobutane reagent gas) modes. To produce accurate mass data for determining fragment formulas the mass resolution was increased to 3000, and perfluorokerosene was introduced continuously to the ion source for mass calibration. For purposes of quantifying 8-nonenal in plastic and food products, the MAT95 Q was operated in selected-ion monitoring mode using the following conditions:

ionization = electron ionization (70 eV);

resolution (10% valley) = 3000;

quantitation masses = 98.073 and 81.070

For plastic and food samples *m/z* 98 was used to measure the internal standard (*cis*-6-nonenal). For plastic samples *m/z* 98 was also used to measure 8-nonenal. For food samples *m/z* 81 was used to measure 8-nonenal as this *m/z* is less susceptible to interferences.

Determination of Retention Indices. The following gas chromato-graphic columns were utilized in an Agilent 6890 GC for the purpose of determining retention indices: Stabilwax (Restek) 30 M × 0.32 mm, 0.25 μm film thickness; HP-1 (Hewlett-Packard) 30 M × 0.32 mm, 0.25 μm film thickness; and DB-1701 (Agilent) 30 M × 0.32 mm, 0.25 μm film thickness. For all columns the GC conditions were 40 °C (1 min hold), 7 °C/min to 240 °C (10 min hold).

RESULTS AND DISCUSSION

Identification of the Compound Responsible for "Plastic" Off-Odor in HDPE. A GC/MS chromatogram resulting from 1-D GC/MS analysis of a simultaneous distillation/extract of an HDPE container (30 g) is shown in **Figure 1**. The primary "plastic" aroma was detected by GC/O immediately following the large 1-dodecene peak. Extensive efforts, including the use of deconvolution techniques, failed to produce a "clean"
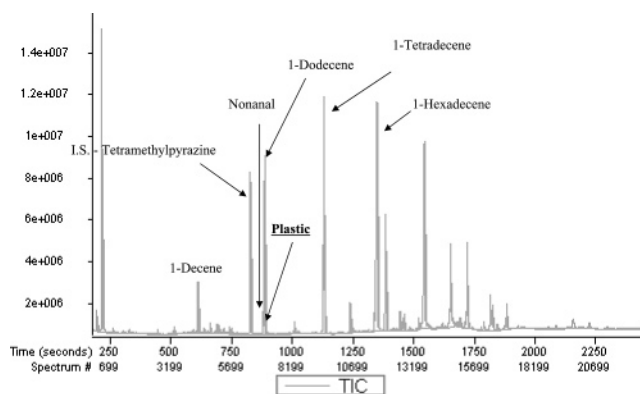
Figure 1.
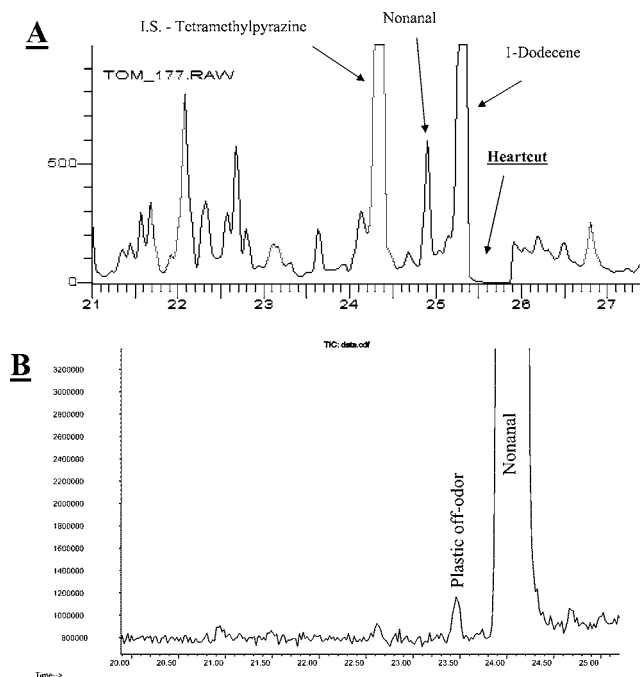
Figure 2.

spectrum of any component with the appropriate odor character or threshold because all spectra were dominated by unsaturated hydrocarbon ions. It became clear that the component respon-sible for the "plastic" odor was either below the GC/MS detection limit or too similar to the complex mixture of hydrocarbons to be detected. The situation was similar on three columns of different stationary phase, including carbowax and methyl silicone, so 2-D GC/MS was chosen as the most promising way to achieve high-resolution isolation of the "plastic" aroma while being able to track it by GC/O. The 2-D GC/MS results in **Figure 2** correspond to a sample size of 75 g because initial results with a 30 g sample produced no detectable peak tracking the "plastic" aroma on the second column. **Figure 2A** is an expanded view of the GC/flame ionization detector chromatogram encompassing the elution region of the "plastic" aroma, now shown as the region that has been heart cut to the second column. Note the nonanal peak eluting immediately ahead of the 1-dodecene peak so that its presence in the heart-cut region is only the minute amount of the tail extending beyond the 1-dodecene peak. **Figure 2B** shows the result of GC/MS analysis of that heart-cut portion on the second column, in the region where the same "plastic" aroma was detected by GC/O. **Figure 2B** has been expanded 80× on the vertical axis in order to observe a peak in the total ion current

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Figure 3.

Table 1. Retention Indexes for 8-Nonenal on Different GC Columns

compound	HP-1	stabilwax	DB-1701
8-nonenal	1072	1454	1203
cis-6-nonenal	1079	1456	1207
nonanal	1083	1397	1198

Table 2. 8-Nonenal Levels in HDPE under Various Processing Conditions

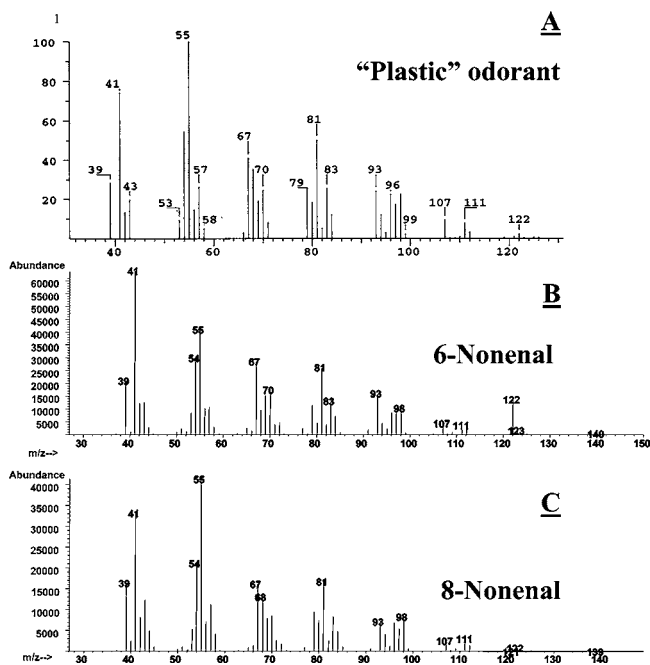| sample	8-nonenal Level (ppb)
starting resin	0.5
extrusion[a] 193 °C	0.8
extrusion[a] 216 °C	1.3
extrusion[a] 238 °C	5.4
virgin HDPE canister	1.0
canister (typical regrind level)	1.5
canister (high regrind level)	2.0
lump regrind material	2–4
AO[b] control canister	2.3
1% irgafos 168	0.95
1% irganox 1010	1.05
1% each	0.83

[a] Experimental canisters made at P&G. [b] AO = antioxidant.

which tracks the plastic aroma observed by GC/O on the second column. Nonanal is detected as an intense peak eluting immediately after the "plastic" off-odor was detected by GC/O (higher molecular weight components such as dodecene eluting later on the second column are not shown). The plastic peak was not observed on previous smaller (30 g) samples and represents a level at least an order of magnitude lower than the levels of peaks obscuring it in the 1-D GC/MS data. **Figure 3A** displays the EI mass spectrum of the "plastic" off-odor peak from **Figure 2B**. **Figure 3B** shows the mass spectrum of *cis*-6-nonenal, which was the best match retrieved by searching the NIST/Wiley reference library. Though qualitatively similar, many relative intensities are different from the "plastic" peak, including the important base (*m/z* 55) and water-loss (*m/z* 122) peaks. The *m/z* 122 intensity was so low in the "plastic" peak that accurate mass measurement attempts (which would have revealed the molecular formula once CI established the molecular weight) were unsuccessful. Accurate mass measurement did, however, confirm that several mass spectral fragments, including *m/z* 98, 84, 83, 70, and 44, contained a single oxygen atom, which indicated the likelihood of a PE oxidation product. Isobutane chemical ionization provided the missing data to propose an identification, providing not only the molecular weight (140) but also the following trend: protonated nonenal isomers show increasing proclivity to lose water (increasing *m/z* 123/141) as the carbon−carbon double bond moves further away from the terminal carbonyl. Following this pattern the correct nonenal isomer had to be either 7-nonenal (cis or trans) or 8-nonenal. With so few possibilities to focus on and due to the generous help of Dr. Thomas C. Hsieh (Givaudan Roure Flavors) a reference spectrum of 8-nonenal was quickly obtained. The quality of the match of the Givaudan reference spectrum led to a request for the synthesis of 8-nonenal, and the availability of this synthetic standard provided 2-D GC retention time and mass spectral confirmation (**Figure 3C**) of the identity. Subsequent addition of the standard to control product (a snack food product that had not been exposed to a plastic container) produced product with an off-flavor characteristic of those stored in heated HDPE containers. Having the synthetic standard also permitted the determination of 8-nonenal

retention indices on three different columns−displayed in **Table 1**−along with those of nonanal and *cis*-6-nonenal.

Tracking the Formation of 8-Nonenal in HDPE Resins, Films, and Containers. **Table 2** shows the results of 8-nonenal level measurements in various PE samples. Experimental HDPE canisters from the same starting resin analyzed to have 0.5 ppb 8-nonenal showed a strong correlation between the extrusion temperature and level of 8-nonenal generated. Unfortunately, for a particular application lowering of the extrusion temperature is not always a practical remediation solution. The remaining data in **Table 2** are from canisters made by the rotary continuous-extrusion multilayer blow-molding process used for high-volume production. These data show that regrind (HDPE that has been extruded but not used on the first pass, so that it passes through the extruder multiple times) has increased levels of 8-nonenal compared to single-pass (or virgin) material. Lump regrind material (large chunks of heated plastic that are removed from the equipment during shutdowns and are possibly exposed to prolonged high temperatures once the liquid flow is stopped) can have levels of 8-nonenal as high as 4 ppb. Control of regrind level and elimination of lump regrind can result in reduced 8-nonenal levels in the final containers. **Table 2** also shows that antioxidants added prior to extrusion can significantly lower 8-nonenal levels in HDPE canisters. Reductions of 50% were achieved using Irgafos 168 or Irganox 1010 at the 1% level, compared to a control film (AO control) with no added antioxidant.

Tracking 8-Nonenal in Snack Food Products To Measure Migration from HDPE Containers with High 8-Nonenal Levels. **Table 3** displays data on experimental corn chips stored in containers made with high regrind levels so that the level of 8-nonenal in the container is approximately 2 ppb. Measurement of 8-nonenal levels in corn chips is a considerable challenge. Even after 2-D GC and high-resolution ion monitoring there are interferences at the sub-ppb levels relevant in these studies. **Table 3** shows that even snack foods that were not exposed to an HDPE container give a measurable 8-nonenal response (which could possibly be due to coeluting interferences). Because we were unable to achieve an acceptable corn chip blank at sub-ppb levels, 8-nonenal levels measured in corn chips were assigned arbitrary units (au) and are used to draw

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Table 3. 8-Nonenal Levels in Snack Foods Stored in HDPE Containers

sample	8-nonenal level (au)[a]
8 months at 38 °C	954
8 months at 29 °C	724
8 months at 21 °C	475
control chips (no HDPE)	233

[a] au = arbitrary unit.

conclusions from relative level measurements only under controlled conditions. It is clear from **Table 3** that migration of 8-nonenal from HDPE containers to the corn chips stored in them is facilitated by increased storage temperature. The corn chips of **Table 3** were evaluated sensorily by a panel of product development experts (seven scientists experienced in evaluating corn chip flavor in general), who had discovered the "plastic" flavor in products aged in HDPE containers. In the evaluation of the products in **Table 3** only one of the panelists noticed a slight "plastic off-flavor" in the 8 months at 21 °C product compared to control product that had never been in contact with the HDPE container. For the 8 months at 29 °C product five panelists detected a "plastic" off-flavor while the other two panelists described the product as having less overall flavor compared to the control. These and other sensory data indicate that some people distinguish product that has been aged in HDPE containers versus controls (in foil bags) by perceiving an absence of flavor instead of "plastic" off-flavor. Using Lickens−Nickerson extraction we measured the important odorants of this snack product (pentanedione, pyrazines, 2-acetyl-1-pyrroline, 2-acetyltetrahydropyrindine, methional, and lipid aldehydes) and found no difference between product stored in HDPE containers versus foil bags. These limited measurements and sensory data suggest that HDPE volatiles have the ability both to cause a characteristic "plastic" off-flavor in snack products and to mask other odorants resulting in the perceived decrease of flavor. Product stored for 8 months at 38 °C was found objectionable for "plastic" off-flavor by all panelists.

Implications of 8-Nonenal Identification and Level Measurements. The data in **Table 2** and the identity (8-nonenal) of the "plastic" impact component detected by GC/O suggest strongly that this compound is a product of PE oxidation. By analogy with thoroughly studied lipid autoxidation processes (*9*), 8-nonenal could be explained as a logical secondary product of oxidation of an alkyl diene (e.g. 1,9-dodecadiene) proceeding through a dodecenyl hydroperoxide intermediate. Dodecene is one of the most abundant components of HDPE volatiles, and though no efforts were made in this study to look for the corresponding dienes, it would not be surprising to find the trace amounts necessary to generate low ppb levels of nonenals upon oxidation. The identification of a PE oxidation product is consistent with the findings of Bravo et al. (*6*), who concluded, via CharmAnalysis, that the most odor-active components of oxidized LDPE (50 000 molecular weight) are unsaturated carbonyl compounds. They also reported that an unidentified compound with retention index 1073 (methyl silicone column)

was attributed 32% of the odor impact (much higher than any other component) of oxidized polyethylene. **Table 1** shows that 8-nonenal has a virtually identical RI (1072, also on methyl silicone). These data support the likelihood that 8-nonenal and RI = 1073 (*6*) are the same compound. Thus, the current work not only provides the solution to a specific HDPE off-odor problem but also enhances the value of an earlier quantitative, odor-impact study by identifying the most odor-active component. In addition, its presence in the earlier study shows that 8-nonenal is the most important odor-impact component in both oxidized LDPE and oxidized HDPE.

ABBREVIATIONS USED

EI, electron ionization; 2-D GC, two-dimensional gas chromatography; HDPE, high-density polyethylene; MS, mass spectrometry; PE, polyethylene; O, olfactometry.

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LITERATURE CITED

(1) Reineccius, G. Off-flavors in foods. *Crit. Rev. Food Sci. Nutr.* **1991**, *29*, 381−402.

(2) Sanders, R. A.; Morsch, T. R. Ion profiling approach to detailed mixture comparison: Application to a polypropylene off-odor problem. *J. Chromatogr.* **1986**, *351*, 525−531.

(3) Brodie, V., III Taste testing as it relates to packaging resins. *Tappi J.* **1988**, *71*, 160−162.

(4) Koszinowski, J.; Piringer, O. Importance of oxidation products of unsaturated hydrocarbons in the sensorial properties of food packing. *Deutsche Lebensmittel-Rundschau* **1983**, *79*, 179−183.

(5) Bravo, A.; Hotchkiss, J. H. Identification of volatile compounds resulting from the thermal oxidation of polyethylene. *J. Appl. Polym. Sci.* **1993**, *47*, 1741−1748.

(6) Bravo, A.; Hotchkiss, J. H.; Acree, T. E. Identification of odor-active compounds resulting from thermal oxidation of polyethylene. *J. Agric. Food Chem.* **1992**, *40*, 1881−1885.

(7) Farquhar, D.; Cherif, A.; Bakina, E.; Nelson, J. A. Intensely potent doxorubicin analogues: structure−activity relationship. *J. Med. Chem.* **1998**, *41*, 965−972.

(8) Schultz, T. H.; Fath, R. A.; Mon, T. R.; Eggling, S. B.; Teranishi, R. Isolation of volatile compounds. *J. Agric. Food Chem.* **1977**, *25*, 446−449.

(9) Frankel, E. N. Chemistry of autoxidation: mechanism, products and flavor significance. In *Flavor Chemistry of Fats and Oils*; Min, D. B., Smouse, T. H., Eds.; American Oil Chemists' Society: 1985; AOCS Monograph 15, pp 1−37.