Odour-active compounds in an inflatable PVC beach ball

Isabella Märkl, Klaas Reglitz and MARTIN STEINHAUS
Leibniz-Institute for Food Systems Biology at the Technical University of Munich, Lise-Meitner-Straße 34, 85354 Freising, Germany

Abstract

Application of an aroma extract dilution analysis to an inflatable beach ball made of PVC revealed 38 odour-active compounds with flavour dilution (FD) factors of 1 to 4096 among which 13 compounds showed FD factors >128. The most potent odorants were sweet, plastic-like smelling 2-ethylhexanal (FD 4096), fatty smelling (2*E*,4*E*)-nona-2,4-dienal (FD 4096), mushroom-like smelling non-1-en-3-one (FD 2048), plastic-like smelling 2-ethylhexyl 4-methylbenzoate (FD 2048), fatty smelling (2*Z*)-non-2-enal (FD 1024), solvent-like smelling γ-butyrolactone (FD 1024), plastic-like smelling hexan-3-ol (FD 512), green, fatty smelling (2*E*)-hept-2-enal (FD 512), and fruity smelling hexyl hexanoate (FD 512). (2*E*,4*E*)-Nona-2,4-dienal, 2-ethylhexyl 4-methylbenzoate, and (2*E*)-hept-2-enal were previously unknown in PVC material. Structures suggested that autoxidation of unsaturated fatty acids and degradation of di(2-ethylhexyl) terephthalate (DEHT) used as plasticizer were the most important sources of odour-active compounds.

Introduction

Inflatable beach toys such as beach balls and pool floats are typically manufactured from polyvinyl chloride (PVC). Particularly when new, these PVC toys often exhibit an intense and characteristic "plastic-like" odour. To date, little is known on the molecular background of this odour [1,2]. The aim of the current study was to extract the volatiles from a typical PVC beach toy with a characteristic smell and screen them for odour-active compounds by gas chromatography-olfactometry (GC-O) and aroma extract dilution analysis (AEDA) [3].

Experimental

Materials

Numerous PVC beach toys including pool floats in different sizes and shapes as well as beach balls were obtained from local shops in Freising, Germany and from German e-tailers. All materials were orthonasally evaluated by a sensory panel using free choice profiling. In open discussion, a beach ball was finally selected for the further investigations, because it showed an intense and highly characteristic smell.

Reference odorants

2-Ethylhexanal (**1**), (2*E*,4*E*)-nona-2,4-dienal (**2**), γ-butyrolactone (**6**), hexan-3-ol (**7**), and (2*E*)-hept-2-enal (**8**) were purchased from Sigma-Aldrich (Taufkirchen, Germany). Oct-1-en-3-one (**10**) was obtained from Alfa Aesar (Karlsruhe, Germany). Non-1-en-3-one (**3**) was synthesized by oxidation of non-1-en-3-ol (Alfa Aesar) with Dess-Martin periodinane (Sigma-Aldrich) [4]. Hexyl hexanoate (**9**) was obtained from hexan-1-ol and hexanoic acid (both Sigma-Aldrich) using the general approach detailed in [5].

The same approach was used to synthesize 2-ethylhexyl 4-methylbenzoate (**4**) from 2-ethylhexan-1-ol and 4-methylbenzoic acid (both Sigma-Aldrich). **4** was obtained as a colourless oil. RI (FFAP) 2300. MS (EI, 70 eV), m/z (%) 41 (35), 55 (26), 65 (20), 70 (90), 83 (20), 91 (45), 112 (30), 119 (100), 137 (20). ^{1}H-NMR ($CDCl_3$, 400.13 MHz, 298

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K), δ (ppm) 0.90-0.95 (m, 3H), 0.97 (t, 3H), 1.29-1.39 (m, 2H), 1.39-1.46 (m, 4H), 1.46-1.54 (m, 2H), 1.69-1.77 (m, 1H), 2.43 (s, 3H), 4.21-4.29 (m, 2H), 7.25-7.27 (m, 2H), 7.94-7.97 (m, 2H). ^{13}C-NMR ($CDCl_3$, 100.62 MHz, 298 K): δ (ppm) 11.1 (CH_3), 14.0 (CH_3), 21.6 (CH_3), 23.0 (CH_2), 24.0 (CH_2), 29.0 (CH_2), 30.6 (CH_2), 38.9 (CH), 67.1 (CH_2), 127.8 (C), 129.0 (CH), 129.5 (CH), 143.4 (C), 166.8 (C).

Isolation of the volatile compounds

The PVC beach ball skin was cut into small pieces (1 cm × 1 cm). The mouthpiece was discarded. The pieces (500 g) were stirred with dichloromethane (1 L, 20 h). The extract was filtered and non-volatiles were removed by solvent-assisted flavour evaporation (SAFE) [6] at 40 °C in high vacuum.

Odorant screening

The SAFE distillate was concentrated (1 mL) using a Vigreux column (60 cm × 1 cm). An aliquot of the concentrate (1 µL) was analysed by GC-O using an FFAP column (30 m × 0.32 mm i.d. × 0.2 µm film thickness). The GC eluate was split 1:1 between an FID and a heated exit serving as sniffing port [7]. Following the concept of an AEDA [3], the initial concentrate was stepwise diluted 1:2 and each diluted sample was also analysed by GC-O. Each odour-active compound was assigned an FD factor representing the dilution factor of the highest diluted sample in which the odorant was detected by any of three trained panellists.

Structure assignment of odorants

Preliminary structure assignments were achieved by comparing odour and retention indices of the PVC beach ball odorants as obtained by GC-O using the FFAP column detailed above and a DB-5 column (30 m × 0.32 mm i.d. × 0.2 µm film thickness) as well as mass spectra as obtained by GC-MS with data compiled in databases. Preliminary structure assignments were then confirmed by GC-O and GC-MS analysis of authentic reference substances analysed in parallel to the PVC ball volatile isolates. To avoid coelution problems during MS analysis, the PVC ball volatiles were previously separated into a fraction containing the acidic volatiles and a fraction containing the neutral and basic volatiles. The latter was further fractionated into five fractions of different polarity by silica gel chromatography as detailed in [7]. Before the fractions were subjected to GC-MS, the PVC beach ball odorants were localized in the fractions by GC-O.

Results and discussion

The AEDA resulted in a total of 38 odour-active compounds covering an FD factor range of 1 to 4096 (data not shown). Thirteen compounds exhibited FD factors >128 (Figure 1). Among them, sweet, plastic-like smelling 2-ethylhexanal (**1**) and fatty smelling (2*E*,4*E*)-nona-2,4-dienal (**2**) were the most potent (FD 4096), followed by mushroom-like smelling non-1-en-3-one (**3**, FD 2048), plastic-like smelling 2-ethylhexyl 4-methylbenzoate (**4**, FD 2048), fatty smelling (2*Z*)-non-2-enal (**5**, FD 1024), solvent-like smelling γ-butyrolactone (**6**, FD 1024), plastic-like smelling hexan-3-ol (**7**, FD 512), green, fatty smelling (2*E*)-hept-2-enal (**8**, FD 512), fruity smelling hexyl hexanoate (**9**, FD 512), mushroom-like smelling oct-1-en-3-one (**10**, FD 256), plastic-like smelling hex-1-en-3-one (**11**, FD 128), solvent-like smelling cyclohexanone (**12**, FD 128), and plastic-like smelling 2-ethylhexan-1-ol (**13**, FD 128).

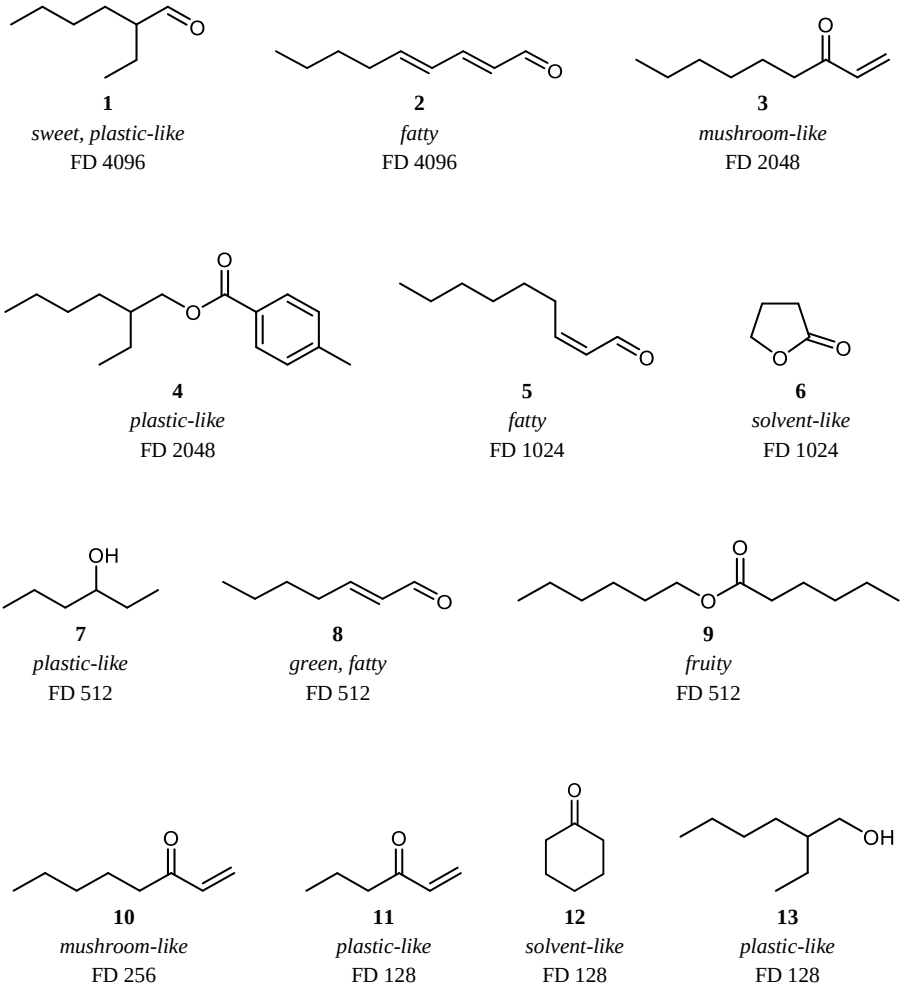

Figure 1: Structures, odour qualities, and FD factors of the most potent odorants identified in the beach ball

(2*E*,4*E*)-Nona-2,4-dienal (**2**), 2-ethylhexyl 4-methylbenzoate (**4**), (2*E*)-hept-2-enal (**8**), and γ-butyrolactone (**6**) were found for the first time in a PVC material.

Among the 13 most potent odorants in the PVC beach ball depicted in Figure 1 six were typical autoxidation products of unsaturated fatty acids, namely (2*E*,4*E*)-nona-2,4-dienal, non-1-en-3-one, (2*Z*)-non-2-enal, (2*E*)-hept-2-enal, oct-1-en-3-one, and hex-1-en-3-one [8]. Hex-1-en-3-one was previously identified as key odorant in a PVC-based automotive artificial leather [9].

Three compounds, namely 2-ethylhexanal (**1**), 2-ethylhexyl 4-methylbenzoate (**4**), and 2-ethylhexan-1-ol (**13**) were structurally related to common PVC plasticizers such as di(2-ethylhexyl) phthalate (DEHP) and di(2-ethylhexyl) terephthalate (DEHT) (Figure 2). It may therefore be assumed that **1**, **4**, and **13** are potential decomposition products and/or impurities of such plasticizers. GC-MS analysis of authentic reference

compounds of DEHP and DEHT in comparison with the PVC beach ball volatile isolate showed the presence of DEHT in the beach ball, whereas DEHP was absent. This was in particular also in agreement with the para-structure of **4**. For a long time, DEHP was the standard plasticizer in PVC materials, but today its use is restricted in most parts of the world and DEHT is used as a common substitute. DEHT shows similar plasticizing properties as DEHP, but is considered to be less toxic [10].

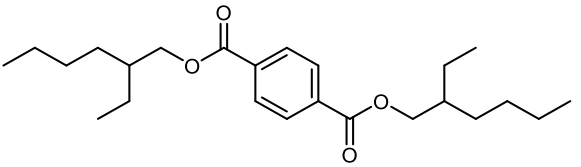

Figure 2: Structure of di(2-ethylhexyl) terephthalate (DEHT) used as plasticizer in the beach ball

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