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Article

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Structure-Odor Relationships of (*Z*)-3-Alken-1-ols, (*Z*)-3-Alkenals, and (*Z*)-3-Alkenoic acids

Katja Lorber[†‡], Gina Zeh[†], Johanna Regler[†], Andrea Buettner[†‡*]

[†]*Professorship of Aroma Research, Department of Chemistry and Pharmacy, Emil Fischer Center, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Henkestr. 9, 91054 Erlangen, Germany, andrea.buettner@fau.de*

[‡]*Department of Sensory Analytics, Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Str. 35, 85354 Freising, Germany, andrea.buettner@ivv.fraunhofer.de*

*Address for correspondence

Phone +49-9131-85-22739

E-mail andrea.buettner@fau.de

Abstract

(*Z*)-3-Unsaturated volatile acids, alcohols, and aldehydes are commonly found in foods and other natural sources, playing a vital role in the attractiveness of foods but also as compounds with chemo-communicative function in entomology. However, a systematic investigation of their smell properties, especially regarding humans, has not been carried out until today. To close this gap, the odor thresholds in air and odor qualities of homologous series of (*Z*)-3-alken-1-ols, (*Z*)-3-alkenals, and (*Z*)-3-alkenoic acids were determined by gas chromatography-olfactometry. It was found that the odor qualities in the series of the (*Z*)-3-alken-1-ols and (*Z*)-3-alkenals changed, with increasing chain length, from grassy, green to an overall fatty and citrus-like, soapy character. On the other hand, the odor qualities of the (*Z*)-3-alkenoic acids changed successively from cheesy, sweaty via plastic-like to waxy in their homologous series. With regard to their odor potencies, the lowest thresholds in air were found for (*Z*)-3-hexenal, (*Z*)-3-octenoic acid, and (*Z*)-3-octenal.

Keywords

gas chromatography-olfactometry; odor threshold in air; odorant; chemo-communicative; retention index; odor activity; odor intensity

Introduction

From the vast number of odor-active compounds, a number of fatty acid-derived odorants are formed as products during lipid oxidation, mostly autoxidation or enzymatic oxidation of linoleic or linolenic acid, but also by other biosynthetic pathways.[1, 2] Corresponding to the (*E*)-3-alkenoic acids, (*E*)-3-alken-1-ols, and (*E*)-3-alkenals that have been described in our previous study,[3] the corresponding (*Z*)-3-alkenoic acids, (*Z*)-3-alken-1-ols, and (*Z*)-3-alkenals are commonly found as odorants or chemo-communicative substances for humans and other species in diverse foods and other natural sources. (*Z*)-3-Heptenoic acid, (*Z*)-3-octenoic acid, (*Z*)-3-nonenoic acid, (*Z*)-3-decenoic acid, (*Z*)-3-undecenoic acid, and (*Z*)-3-dodecenoic acid are volatile decomposition products of various triglycerides like trilinolein and triolein, or oils (corn oil, hydrogenated cottonseed oil) built during thermal oxidization by (simulated) deep-fat frying.[4, 5] Further, (*Z*)-3-hexen-1-ol is a bioconversion product of (*E*)-3-hexenoic acid, and (*Z*)-3-octen-1-ol of (*E*)-3-octenoic acid by the highly metabolically active fungus *Botrytis cinerea*.[6] In previous studies, the odor of (*Z*)-3-hexen-1-ol has been described as *herbal/green*[7], *green/cut grass*[8], or *green leaves-like*[9], while (*Z*)-3-octen-1-ol has been reported to elicit *toasted nut/smoky/dusty*[7] or *pungent/rancid*[10] odor qualities. A number of the compounds investigated in this study have previously been identified in diverse food materials, often playing a vital role in their attractiveness: (*Z*)-3-penten-1-ol has been detected in black tea[11] and lamb's lettuce[12]. (*Z*)-3-Hexen-1-ol was, among others, identified in lamb's lettuce[12], different melon types[13, 14], and oyster leaf[8]. (*Z*)-3-Octen-1-ol is, for example, part of the aroma profiles of banana[10] and chili pepper[15]. With the exception of (*Z*)-3-undecen-1-ol and (*Z*)-3-dodecen-1-ol, all compounds in the

homologous series of the (*Z*)-3-alken-1-ols have been identified in food. The same holds true for the series of (*Z*)-3-alkenals whereas (*Z*)-3-undecenal and (*Z*)-3-dodecenal have not yet been reported as food constituents. Just a few examples of the (Z)-3-alkenals reported so far are highlighted here: (*Z*)-3-pentenal was identified in black tea[16], (*Z*)-3-hexenal in lamb's lettuce[12], and oyster leaf[8], in all cases accompanied by (*Z*)-3-hexen-1-ol. Moreover, (*Z*)-3-hexenal could be identified as important odorant in fresh squeezed citrus juices,[17, 18] but also as constituent of an off-odor in German rainbow trout.[19] (*Z*)-3-Heptenal, (*Z*)-3-octenal, (*Z*)-3-nonenal, and (*Z*)-3-decenal have been detected in peanut butter oil.[20] Most of the (*Z*)-3-alkenoic acids have also been reported before but not in such a large variety of foods as the (*Z*)-3-alken-1-ols and (*Z*)-3-alkenals. For instance, (*Z*)-3-hexenoic acid has shown to be part of the volatile spectrum of different types of tea.[21, 22] These are just a few examples of the occurrence of these structurally related compounds in food. For the interested reader, these and several more examples together with their reported odor qualities and odor threshold values are given in the supporting information.

Apart from that, two of the acids have been identified in non-food matrices: (Z)-3-pentenoic acid is a volatile in cigarette smoke[23], and (*Z*)-3-hexenoic acid in the absolute of *Gardenia jasminoides Ellis*[24].

It is possible, maybe even likely, that compounds from these homologous series exist in nature even if they have not yet been reported. Their current lack of detection might be due to their potentially low concentrations, instability, or the difficulty of extraction, even if they might be highly potent odorants.

Besides their occurrence in food, consumables or plants, some of these compounds also play a role in entomology, comparable to the corresponding (*E*)-3-alkene compounds as we reported in our previous study.[3] (*Z*)-3-Hexen-1-ol and (*Z*)-3-hexenal are part of the defensive secretion from male Florida woods cockroaches, *Eurycotis floridana*,[25] and the secretion of the ventral glands in *Nematus* sawfly larvae, as protection from predation.[26] (*Z*)-3-Hexenal is a plant attractant that stimulates the antennae of male fall webworm moths, *Hyphantria cunea*.[27] (*Z*)-3-Octenal was also detected in the already mentioned ventral glands of *Nematus* sawfly larvae[26] and, likewise, in the ventral glands of the *Cladius, Priophorus and Trichiocampus* sawfly larvae.[28] (*Z*)-3-Decenoic acid is one compound of the anal secretion from different species of idolothripine thrips acting as a repellent.[29] Further, it has been reported as sex pheromone in the furniture carpet beetle, *Anthrenus flavipes* LECONTE.[30]

Despite the fact that various compounds from the homologous series of (*Z*)-3-alken-1-ols, (*Z*)-3-alkenals, and (*Z*)-3-alkenoic acids have been identified in foods, plants, or insects, there has been no systematic investigation of their odor properties in terms of their odor thresholds and smell qualities. In view of these important analytical parameters, only a few data have been published so far (**Table 1 A-C** and **Table 2 A-C**). Therefore, the aim of this work was to provide comprehensive sensory and analytical data on these compounds to support future research on these important substance classes. Further, odor qualities and odor properties of the corresponding saturated compounds were determined, to provide a comprehensive understanding of the impact of the characteristic (*Z*)-3-moiety on relation to the chain length and oxidation status of the target substances, and to establish a comprehensive substance library

87 comprising their analytical and sensory characteristics. This offers the possibility to
88 compare the previously published data related to the (*E*)-3-alkene compounds,[3] with
89 data on the (*Z*)-3-alkene compounds and their saturated analoga of the present
90 investigation.

Materials and Methods

Chemicals. Lindlar's catalyst, quinoline, n-butyl lithium solution (2.7 M in THF), ethylene oxide, hexamethylphosphoramide (HMPA), nonyne, decyne, 3-dodecyn-1-ol, calcium carbonate, chromium trioxide, periodic acid, hydrochloric acid, diethyl ether, sodium sulfate dibasic, sodium bisulfite, sodium chlorite, magnesium sulfate, Dess-Martin periodinane, sodium bicarbonate, acetonitrile, toluene, tetrahydrofurane anhydrous, and sodium thiosulfate were purchased from Sigma-Aldrich (Steinheim, Germany). Silica gel (Normasil 60, 40 – 63 µm), sodium chloride, dichloromethane, n-hexane, and ethyl acetate were purchased from VWR International GmbH (Darmstadt, Germany). (*Z*)-3-Penten-1-ol was purchased from abcr (Karlsruhe, Germany), (*Z*)-3-hexen-1-ol, (*Z*)-3-hepten-1-ol and (*Z*)-3-nonen-1-ol were from Sigma-Aldrich (Steinheim, Germany), and (*Z*)-3-octen-1-ol from TCI Europe (Zwijndrecht, Belgium). All chemicals were used without further purification.

Nuclear Magnetic Resonance (NMR) Spectra. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on an Avance 360 spectrometer, 360 MHz, and an Avance 600 spectrometer, 600 MHz (Bruker Biospin, Rheinstetten, Germany), at room temperature operated at 360 or 600 MHz (^{1}H) and 90 or 150 MHz (^{13}C), with tetramethylsilane (TMS) as internal standard.

Preparative High-Performance Liquid Chromatography (Prep-HPLC). The preparative HPLC separation (AS 2057plus autosampler, two PU 2087plus gradient pumps, a mixing chamber, DG 98050 degasser, and UV 2077plus UV/vis detector, all by JASCO, Gross-Umstadt, Germany) was performed using a C18-material preparative

column (Nucleodur 100-5 C18ec, 10 × 250 mm, 5 µm particle size, with inline-filter, Macherey-Nagel, Düren, Germany) with gradient elution program (A: acetonitrile, B: water; flow rate 3 mL/min, gradient A/B: 20:80 to 100:0 in 60 min) and detection by UV at 254, 280, and 300 nm. Fractions from several runs containing the target compound were collected manually, combined, dried over $MgSO_4$, and evaporated.

GC-FID, GC-Olfactrometry (GC-O) and GC-Electron Impact-Mass Spectrometry (GC-EI-MS). GC-FID and GC-O analyses were performed with a Trace GC Ultra (Thermo Fisher Scientific GmbH, Dreieich, Germany) by using the following capillaries: FFAP (30 m x 0.32 mm i.d. fused silica capillary, free fatty acid phase FFAP, 0.25 µm; Chrompack, Mühlheim, Germany) and DB5 (30 m x 0.32 mm i.d. fused silica capillary DB-5, 0.25 µm; J & W Scientific, Fisons Instruments). The samples were applied by the cool-on-column injection technique at 40 °C. After 2 minutes, the temperature of the oven was raised at 10 °C/min to 240 °C, then raised at 40 °C/min to 280 °C (DB5), or at 10 °C/min to 240 °C (FFAP), respectively, and held for 5 minutes. The flow rate of the carrier gas helium was 2.5 mL/min. At the end of the capillary, the effluent was split in a ratio 1:1 (by volume) into an FID and a sniffing port using two deactivated but uncoated fused silica capillaries (50 cm x 0.32 mm). The FID and the sniffing port were held at 250 °C, respectively. GC-EI-MS analyses were performed with an Agilent MSD 5975C (Agilent Technologies, Waldbronn, Germany) and a Thermo ITQ 900 (Thermo Fisher Scientific, Dreieich, Germany) with the capillaries described above, using the same temperature programs as for the GC-FID and GC-O measurements, with a flow rate of the carrier gas helium of 1.0 mL/min. Mass spectra in the electron impact mode (EI-MS) were generated at 70 eV.

Retention indices (RI). Retention indices were determined according to the method previously described by Van den Dool and Kratz (1963).[31]

Panelists. Panelists were trained volunteers from the University of Erlangen-Nürnberg (Erlangen, Germany), exhibiting no known illness at the time of examination and with audited olfactory function. In preceding weekly training sessions, the assessors were trained for at least half a year in recognizing orthonasally about 150 selected known odorants at different concentrations according to their odor qualities, and in naming these according to an in-house developed flavor language. Furthermore, the panel was trained every two weeks on specific attributes with the help of specifically developed sniffing sticks; in the course of this training, all panelists also had to fill the same questionnaire (hedonic, intensity) to obtain insights into their specific sensitivities or insensitivities which were systematically recorded. Based on these tests, panelists were regularly tested if they complied with the established flavor language.

Odor threshold values. Thresholds in air were determined by GC-O with (*E*)-2-decenal as internal standard.[1, 32, 33] Of every dilution, 2 µL were applied for injection into the GC system. The thresholds were determined by five panelists (one male, four female), with each experiment being conducted once. GC analyses were performed on capillary FFAP as described above. The purity of all commercially available and synthesized compounds was taken into account in the GC-O experiments. All synthesized compounds were further checked for potential olfactorily active impurities by sniffing each single substance on both capillaries of different polarity, to exclude any interferences.

Odor quality determination. The odor qualities, determined during GC-O evaluation, were related in comparison to odor qualities of commercially available reference compounds. Thereby, panelists were asked to freely choose the respective odor quality descriptors based on the in-house developed flavor language that is related to these references (cf. panelists). No additional descriptors were supplied to the panelists. The panelists determined the qualities during sniffing of the solution corresponding to FD 1 (injection of 2 µL). The panelists were instructed to record any changes in odor qualities in all following dilutions.

Syntheses, general procedures:

3-Alkyn-1-ols (Figure 1 A). n-Buthyllithium (2.7 M in hexane, 1 eq) was injected into a cooled solution (≤ 0 °C) of the corresponding 1-alkyne (1 eq) in dry THF (approx. 10 mL/12 mmol alkyne) under nitrogen atmosphere. Ethylene oxide (1.2 eq) was injected from a precooled syringe, and then HMPA (ca. 2 eq) was injected. The resulting mixture was stirred over night at room temperature and then worked up by dilution with water and extraction with hexane. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, eluent: hexane/EtOAc = 4/1) to give the pure 3-alkyn-1-ol as a colorless to pale yellow oily liquid.[34, 35]

(*Z*)-3-Alken-1-ols (6 to 8, Figure 1 B). 3-Alkyn-1-ol was added to a slurry of Lindlar's catalyst (5% Pd on $CaCO_3$ poisoned with Pb) in pentane and quinoline at room temperature. The reaction flask was swept with H_2 gas, evacuated three times and stirred under H_2 atmosphere overnight. The reaction mixture was filtered through a plug of $CaCO_3$ and rinsed with Et_2O twice. The filtrate was partitioned against 1.0 M HCl

saturated with NaCl, washed with saturated brine and dried over $MgSO_4$. After filtration and evaporation of the solvent the crude product was purified by column chromatography (silica gel, eluent: hexane/EtOAc = 4/1) to give the pure (*Z*)-3-alken-1-ol as a colorless oily liquid.[35]

(*Z*)-3-Alkenals (9 to 16, Figure 1 C). A solution of (*Z*)-3-alken-1-ol (1 eq) in CH_2Cl_2 (1 mL/mmol alcohol) was added dropwise to a suspension of Dess-Martin periodinane (1.1 eq) in CH_2Cl_2 (2 mL/mmol Dess-Martin periodinane). After a few minutes, in some cases the reaction mixture started to boil and was allowed to do so for about five minutes. The obtained suspension was stirred for three hours at room temperature. It was then filtered through a glass frit and the filtrate was washed with saturated aqueous $NaHCO_3$ solution containing $Na_2S_2O_3$ (25%) (3.5 mL/mmol alcohol). The resulting clear solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to give the corresponding (*Z*)-3-alkenal as a colorless to pale yellow oily liquid.[36] (*Z*)-3-Decenal and (*Z*)-3 dodecenal were purified by preparative HPLC.

(*Z*)-3-Alkenoic acids (17, 22 to 24, Figure 1 D). By dissolving H_5IO_6 (11.4 g, 50 mmol), and CrO_3 (23 mg, 1.2 mol %) in wet MeCN (0.75 v % water) to a volume of 114 mL a stock solution of H_5IO_6/CrO_3 was prepared (complete dissolution took 1 – 2 hours). The H_5IO_6/CrO_3 solution (11.4 mL) was added to a solution of the (*Z*)-3-alken-1-ol **1**, **6**, **7** or **8** (2.0 mmol) in wet MeCN (10 mL, 0.75 v % water) over 30 to 60 minutes while maintaining the reaction temperature at 0-5 °C. The mixture was aged at 0 °C for 30 minutes and quenched by adding an aqueous solution of Na_2HPO_4 (0.6 g in 10 mL H_2O). Toluene (15 mL) was added, the organic layer was separated, washed with 10 mL of a 1/1 brine/water mixture twice, then with 5 mL of an aqueous $NaHSO_3$ (0.22 mg

in 5 mL water) once, and finally with 5 mL of brine once. The solvent was removed under reduced pressure to give the corresponding (*Z*)-3-alkenoic acid **17**, **22**, **23** or **24** as a colorless oily liquid or solid.[37]

(*Z*)-3-Alkenoic acids (18 to 21, Figure 1 D). To a solution of (*Z*)-3-alkenal (1 eq) in DMSO (5 eq) an aqueous solution of $NaClO_2$ (1.1 to 1.2. eq) with a pH of 4.3 (set with NaH_2PO_4) was added in portions and stirred over night at room temperature. The two layers were extracted with EtOAc thrice, and the combined organic layers were washed with brine. The resulting clear solution was dried over anhydrous $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography (silica gel, eluent: hexane/EtOAc = 4/1) to give the pure (*Z*)-3-alkenoic acid as a colorless oily liquid.[38-40]

Results and Discussion

The 3-alkyn-1-ols that were required as intermediates for the subsequent synthetic steps were successfully obtained following to the method reported by Heath et al. 1988 and Argenti et al. 2006.[34, 35] The (*Z*)-3-alken-1-ols were generated therefrom by selective hydrogenation of the corresponding 3-alkyn-1-ol with poisoned Lindlar's catalyst, and the corresponding (*Z*)-3-alkenals were obtained via mild oxidation of the corresponding (*Z*)-3-alken-1-ols with Dess-Martin periodinane as oxidizing agent.[35, 36] The respective (*Z*)-3-alkenoic acids were synthesized following two different methods. Compounds 17 and 22 to 24 were obtained by oxidation with H_5IO_6/CrO_3 in wet MeCN according to Zhao et al. 1998,[37] whereas compounds 18 to 21 were synthesized applying a Pinnick oxidation reaction (**Figure 1 A-C**).[38-40]

The synthesized compounds were then used to determine their retention indices, and their mass spectrometric and NMR data, thereby unambiguously confirming their chemical identity. Following the analytical characterization, the individual odor threshold values in air were determined by a panel using GC-O, thereby yielding the median odor threshold of the panel as well as the odor threshold distribution amongst the group, and the main odor qualities of the homologous (*Z*)-3-alken-1-ols, (*Z*)-3-alkenals, and (*Z*)-3-alkenoic acids; all data are compiled in **Table 1** and **Figure 2**.

As in our previously published study on the structure–odor relationships of the related (*E*)-3-alkenoic acids, (*E*)-3-alken-1-ols, and (*E*)-3-alkenals, the geometric mean values are given in addition to the median odor threshold values reported in **Table 3**.[3] In the following, however, only the median values will be discussed. In view of this it is important to note that strong deviations between the single values would influence the

geometric mean more significantly than the median. However, when comparing the median and geometric mean values, it becomes evident that both values showed the same tendencies in the present study, and that the differences between both values were generally low, if any.

When evaluating the odor qualities of the investigated compounds it was found that the main odor quality in the series of (*Z*)-3-alken-1-ols was *grassy-green* for (*Z*)-3-penten-1-ol, (*Z*)-3-hexen-1-ol and (*Z*)-3-hepten-1-ol, then changing to *fatty* for (*Z*)-3-octen-1-ol, (*Z*)-3-nonen-1-ol and (*Z*)-3-decen-1-ol, and finally to *soapy, citrus-like* for (*Z*)-3-undecen-1-ol and (*Z*)-3-dodecen-1-ol (**Table 1 A-C**).

The (*Z*)-3-alkenals revealed very similar main odor qualities and the smell changes followed a comparable pattern with increasing chain length: starting with *grassy, green* for (*Z*)-3-pentenal and (*Z*)-3-hexenal, changing to *fatty* for (*Z*)-3-heptenal, (*Z*)-3-octenal, (*Z*)-3-nonenal and (*Z*)-3-decenal, and finally reaching *citrus-like, soapy* impressions for (*Z*)-3-undecenal and (*Z*)-3-dodecenal.

In contrast to this, the (*Z*)-3-alkenoic acids were associated with odor qualities that are typical for fatty acids: (*Z*)-3-pentenoic acid, (*Z*)-3-hexenoic acid and (*Z*)-3-heptenoic acid were found to mainly elicit a *sweaty* odor impression. With increasing chain length, a *plastic-like* note developed for (*Z*)-3-octenoic acid and (*Z*)-3-nonenoic acid, whereas (*Z*)-3-decenoic acid, (*Z*)-3-undecenoic acid and (*Z*)-3-dodecenoic acid were primarily described as smelling *waxy* and *acidic*.

Nevertheless, some variations were observed in the individual naming of odor attributes between panelists (**Table 2 A-C**). (*Z*)-3-dodecen-1-ol, for example, was described as *citrus-like* and *soapy*, but also *musty* and *earthy*, *metallic*, or *pungent, tangy*. This

variance in selection of descriptors was especially pronounced in the group of (*Z*)-3-alcohols with smell attributes ranging from *grassy*, *citrus-like* to *waxy*, *metallic*, or *pungent*.

In contrast to the alcohols, the selected odor qualities of the (*Z*)-3-alkenals were much more consistent as most panelists reported the terms *grassy, green* for (*Z*)-3-pentenal and (*Z*)-3-hexenal, *fatty* for (*Z*)-3-heptenal and (*Z*)-3-octenal, and *fatty, citrus-like* for (*Z*)-3-nonenal. However, the attributes named for (*Z*)-3-decenal, (*Z*)-3-undecenal and (*Z*)-3-dodecenal differed to some extent. These compounds were reported as smelling *citrus-like, soapy, fresh* but also *metallic-waxy*.

The (*Z*)-3-alkenoic acids were perceived as *acidic*, *sweaty* or *cheesy* in case of the short-chain (*Z*)-3-alkenoic acids changing to *sweaty*, *plastic-like* or *waxy* with increasing chain length. Interestingly, panelist 3 consistently reported *fatty* impressions for all acids, accompanied by *soapy* for (*Z*)-3-pentenoic, (*Z*)-3-octenoic, (*Z*)-3-decenoic and (*Z*)-3-undecenoic acid, or *green* for (*Z*)-3-heptenoic, (*Z*)-3-octenoic and (*Z*)-3-dodecenoic acid.

When regarding the odor thresholds, the lowest median value was determined for (*Z*)-3-hexenal with 0.27 ng/L_{air}, followed by (*Z*)-3-octenoic acid with 0.42 ng/L_{air}, (*Z*)-3-octenal with 0.93 ng/L_{air}, and (*Z*)-3-heptenoic acid with 0.94 ng/L_{air}. Overall, comparison of all three homologous series shows, that the (Z)-3-alkenals were the compounds with the lowest median odor threshold values, ranging between 0.27 and 2.32 ng/L_{air}. However, for the alcohol and acid derivatives, ranging between 9.5 and 191 ng/L_{air}, or 0.42 and 77 ng/L_{air}, respectively, no clear trend is observable: for the compounds containing five carbon atoms, (*Z*)-3-pentenoic acid (median OT 21 ng/L_{air}) showed a lower value by a

factor of about 3 than (*Z*)-3-penten-1-ol (median OT 57 ng/L_{air}), whereas it was the other way around for the C6-derivatives. On the other hand, (*Z*)-3-heptenoic acid (median OT 0.94 ng/L_{air}) and (*Z*)-3-octenoic acid (median OT 0.42 ng/L_{air}) showed significantly lower median values than the corresponding (*Z*)-3-alken-1-ols, and somewhat lower median OTs than the related aldehydes (*Z*)-3-heptenal (1.08 ng/L_{air}) and (*Z*)-3-octenal (0.93 ng/L_{air}).

Regarding the individual odor threshold values, the extent of the spreading of the individual OT values was inconsistent for substances of the same substance class: as an example, the OT ranges of (*Z*)-3-penten-1-ol and (*Z*)-3-hexen-1-ol were notably narrower with a factor of 16 between their minimum and maximum threshold values of both substances than those of the related (*Z*)-3-hepten-1-ol or (*Z*)-3-octen-1-ol comprising a factor of 64 (**Table 1 A, Table 3 A** and **Figure 2 A**). For (*Z*)-3-hexen-1-ol, it is especially interesting to note that the individual odor threshold values were distributed in a relatively narrow range in comparison to all other compounds of the homologous series of (*Z*)-3-alken-1-ols (lowest individual odor threshold value for four of five panelists), potentially indicating a somewhat exceptional biological meaning of this substance. This observation might be related to the fact that this compound is commonly produced in the course of lipid oxidation processes, for example when plant tissue is disrupted. Likewise, a second narrow distribution of the individual threshold values was observed for (*Z*)-3-nonen-1-ol, which is potentially also linked to its preferential formation in nature. Further, regarding the quotient of highest and lowest value, (*Z*)-3-hepten-1-ol and (*Z*)-3-octen-1-ol showed the highest factor of 64 (cf. **Table**

3 A), thus the broadest variance in individual threshold levels, followed by (*Z*)-3-undecen-1-ol and (*Z*)-3-decen-1-ol with factors of 33 and 32, respectively.

In contrast to that, much more consistent data were obtained for the individual panelists when regarding the (*Z*)-3-alkenals with a variance that was commonly only in the range of approximately a factor 8 to 16 between extremes (**Table 1 B** and **Figure 2 B**). Nevertheless, the spreading of the values followed a comparable pattern, albeit in a narrower range than for the corresponding alcohols. Highly reproducible values could be observed for the individual OT values of (*Z*)-3-hexenal, with a factor of only 4 between minimum and maximum value. Further, (*Z*)-3-dodecenal showed a threshold range from 0.03 ng/L_{air} to 1.06 ng/L_{air} which corresponds to a factor of 35 (**Table 3 B**), spanning two orders of magnitude.

While the single values of the (*Z*)-3-alkenals from all panelists were quite reproducible, single values of some of the (*Z*)-3-alkenoic acids varied to a higher extent between the lowest and the highest individual threshold value (**Table 1 C, Table 3 C** and **Figure 2 C)**. In case of (*Z*)-3-heptenoic acid and (*Z*)-3-octenoic acid, the minimum and maximum values even spanned 6 and 5 orders of magnitude, respectively. Neither the (*Z*)-3-alken-1-ols, nor the (*Z*)-3-alkenals showed such high variation in threshold levels. Nevertheless, despite these differences, the ranking of the OTs of the individual panelists of a specific homologous series was comparable (cf. **Table 3 A-C**). For instance, the lowest individual odor threshold of the (*Z*)-3-alken-1-ols was that of (*Z*)-3-hexen-1-ol for four out of five panelists as discussed above.

Further, we did not observe any correlation between the individual odor descriptors and the individual odor threshold values.

The variations in odor thresholds between panelists appear, at first sight, as being huge, especially when being compared to other studies: in the odor threshold determination study of Czerny et al.[33], for example, a maximum factor of 8 has been reported. However, the number of panelists was commonly comparatively lower in other studies with e.g. only two panelists in the study of Czerny et al. and only aromatic compounds having been investigated but no open-chained substances. Accordingly, data are only comparable to a limited extent.

There may be several reasons for inter-individual variance in odor thresholds and odor qualities. First, the receptor repertoire might be different between individuals as has been reported in several studies on receptor expression in humans.[41, 42] Second, it is known that a large number of odorants activate not only one but often a number of different receptors whereas one receptor can be activated by a range of different compounds, obviously resulting in a complex coding of smell.[43, 44] The potential variation in this code between individuals is not yet resolved. Third, odorants may be bio-transformed during their passage through the nasal cavity, for example by cytochrome P450 metabolization; such processes are also termed *peri-receptor events*.[45-50] This can modify the structure and quantity of a substance, and might, accordingly, lead to differences in odor threshold and quality. In view of this it is especially interesting to note that the (Z)-3-compounds investigated in this study might be prone to e.g. oxidative attack potentially leading to epoxides and a series of other derivatives as described previously.[45, 49, 50]

To translate the data of the present study into a comparison with other structurally related odorants, we listed the median values of the OTs of the (*Z*)-3-alkene

compounds, (*E*)-3-alkene compounds, and the corresponding saturated compounds in **Table 4 A-C** for direct comparison. Overall, the investigated (*Z*)-3-compounds showed lower odor thresholds in air than the corresponding saturated compounds, followed by the (*E*)-3-analoga. Accordingly, the (*Z*)-3-configuration obviously represents an important stereo-chemical feature in these substance groups.

Our study demonstrates that the investigated compounds of the series of the (*Z*)-3-alken-1-ols, (*Z*)-3-alkenals and (*Z*)-3-alkenoic acids show a broad variance of odor qualities, and partially very low odor thresholds corresponding to high odor potencies. This study is important insofar as it not only provides data on the smell properties of these substances, but as it also highlights the at times relatively high variance in olfactory perception between individuals; this latter aspect is, in our opinion, not sufficiently regarded in odorant research. More detailed studies would be required but the laborious and time consuming analyses as applied in this study are commonly just executed by one or two panelists only in other investigations in this field.

Another relevant aspect of our study is the fact that several of the 24 investigated substances have already been identified in foods or generally in nature; accordingly, some of the remaining substances may be also promising candidates to be discovered as natural compounds in future studies. The analytical data compiled in this study, such as retention indices, mass spectra, odor threshold data in air and odor qualities are intended to aid their future discovery. Moreover, this study aims at raising attention to this substance class not only in terms of some of the compounds being potentially important odorants in food but also with regard to other biological meaning, for example as compounds with chemo-communicatory function, like pheromones, attractants or

repellents in the research field of entomology. Substance libraries as generated in the present study will support their future discovery and systematic investigation.

Abbreviations

GC-O	Gas Chromatography - Olfactometry

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Associated content

Supporting Information

Spectroscopic data (MS-EI, NMR), yield and purity of all synthesized compounds as well as a table including the entry numbers and structures of all investigated (Z)-3-compounds, a table of foods / consumables the substances have been identified in, besides tables of literature data on odor qualities and odor threshold values, and a table comprising the concentrations of the FD1 solutions of the respective odorants and retention indices of the investigated saturated compounds are given in the supplementary material, together with figures visualizing the individual odor thresholds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure captions

Figure 1 A: General synthetic route leading to the 3-alkyn-1-ols

Figure 1 B: General synthetic route leading to the (*Z*)-3-alken-1-ols (compounds 6 to 8)

Figure 1 C: General synthetic route leading to the (*Z*)-3-alkenals (compounds 9 to 16)

Figure 1 D: General synthetic route leading to the (*Z*)-3-alkenoic acids (left: compounds 17, 22 to 24; right: compounds 18 to 21)

Figure 2 A: Influence of the chain length on the odor thresholds of the (*Z*)-3-alken-1-ols. Mean value (± SD), markers at minimum and maximum OT, box perc. 25-75%.

Figure 2 B: Influence of the chain length on the odor thresholds of the (*Z*)-3-alkenals. Mean value (± SD), markers at minimum and maximum OT, box perc. 25-75%.

Figure 2 C: Influence of the chain length on the odor thresholds of the (*Z*)-3-alkenoic acids. Mean value (± SD), markers at minimum and maximum OT, box perc. 25-75%.

Table 1 A. Retention Indices (RI), Odor Thresholds (OT) and Odor Qualities of (*Z*)-3-Alken-1-ols

Compound	Odorant	RI[a]		OT [ng/L_{air}][b]		Odor qualities[c,d]
		DB5	FFAP	median	range	
1	(*Z*)-3-Penten-1-ol	768	1304	57	28 – 455	fresh cut grass, fatty, green
2	(*Z*)-3-Hexen-1-ol	857	1385	9.5	2.38 – 38	grassy, **green**, fatty
3	(*Z*)-3-Hepten-1-ol	959	1480	45	5.7 – 361	grassy, clover, green, fatty, soapy
4	(*Z*)-3-Octen-1-ol	1057	1577	40	5 – 319	**fatty**, citrus, fresh
5	(*Z*)-3-Nonen-1-ol	1157	1678	40	10 – 160	**fatty**, green
6	(*Z*)-3-Decen-1-ol	1256	1780	191	12 – 382	**fatty**
7	(*Z*)-3-Undecen-1-ol	1357	1892	107	13 – 426	citrus, **soapy**
8	(*Z*)-3-Dodecen-1-ol	1459	1985	71	35 – 564	citrus, **soapy**, musty

[a] Retention indices were determined as described by Van den Dool and Kratz (1963).[31]

[b] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[c] Odor qualities as perceived at the sniffing port.

[d] Attributes given in bold are the main odor qualities. These were named by the majority of the panel.

Table 1 B. Retention Indices (RI), Odor Thresholds (OT) and Odor Qualities of (*Z*)-3-Alkenals

Compound	Odorant	RI[a]		OT [ng/L_{air}][c]		Odor qualities[c,d]
		DB5	FFAP	median	range	
9	(*Z*)-3-Pentenal	712	1096	1.68	0.42 – 3.35	grassy, **green**, clover
10	(*Z*)-3-Hexenal	801	1133	0.27	0.14 – 0.54	grassy, **green**
11	(*Z*)-3-Heptenal	899	1227	1.08	0.27 – 4.34	clover, fatty
12	(*Z*)-3-Octenal	997	1323	0.93	0.47 – 3.73	**fatty**, green
13	(*Z*)-3-Nonenal	1096	1421	1.33	0.66 – 2.66	**fatty**, cucumber, **citrus**
14	(*Z*)-3-Decenal	1193	1518	2.32	0.58 – 4.63	fatty, fresh
15	(*Z*)-3-Undecenal	1297	1618	1.93	0.21 – 3.87	**citrus**, soapy
16	(*Z*)-3-Dodecenal	1398	1753	1.06	0.03 – 1.06	soapy, citrus

[a] Retention indices were determined as described by Van den Dool and Kratz (1963).[31]

[b] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[c] Odor qualities as perceived at the sniffing port.

[d] Attributes given in bold are the main odor qualities. These were named by the majority of the panel.

Table 1 C. Retention Indices (RI), Odor Thresholds (OT) and Odor Qualities of (*Z*)-3-Alkenoic acids

Compound	Odorant	RI[a]		OT [ng/L_{air}][b]		Odor qualities[c,d]
		DB5	FFAP	median	range	
17	(*Z*)-3-Pentenoic acid	911	1849	21	11 – 85	acidic, **cheesy**, **sweaty**
18	(*Z*)-3-Hexenoic acid	1016	1936	17	0.27 – 549	sweaty
19	(*Z*)-3-Heptenoic acid	1101	2036	0.94	0.0074 – 1933	**sweaty**, pungent
20	(*Z*)-3-Octenoic acid	1193	2139	0.42	0.0065 – 858	plastic, sweaty, acidic
21	(*Z*)-3-Nonenoic acid	1276	2240	48	12 – 387	**sweaty**, fatty, plastic
22	(*Z*)-3-Decenoic acid	1370	2348	18	9 – 72	musty, waxy, acidic, fatty
23	(*Z*)-3-Undecenoic acid	1464	2467	42	2.63 – 84	sweaty, acidic, pungent, waxy
24	(*Z*)-3-Dodecenoic acid	1562	2571	77	2.4 – 153	waxy, plastic, fatty

[a] Retention indices were determined as described by Van den Dool and Kratz (1963).[31]

[b] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[c] Odor qualities as perceived at the sniffing port.

[d] Attributes given in bold are the main odor qualities. These were named by the majority of the panel.

Table 2 A. Odor Qualities (GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alken-1-ols

Odorant	Odor qualities				
	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Penten-1-ol	fresh cut grass, pungent	fresh cut grass	fatty, citrus	green, leaves, fatty	green
(*Z*)-3-Hexen-1-ol	grassy, fresh cut grass	grassy green	green, fatty	green, leaves fatty	green, fatty, grassy, green banana skin
(*Z*)-3-Hepten-1-ol	grassy, clover, sweet	clover, green	fatty, soapy	fatty, rubber	green, grassy, green banana skin
(*Z*)-3-Octen-1-ol	fatty	fatty, pungent	citrus, fresh, fatty	fatty, fresh, citrus	green, grassy, fresh,
(*Z*)-3-Nonen-1-ol	fatty, musty	fatty, green, pungent	green, fatty	fatty, waxy	green, fatty
(*Z*)-3-Decen-1-ol	fatty	fatty, sweet, tangy	fatty	fresh, waxy	fatty,
(*Z*)-3-Undecen-1-ol	citrus, soapy	citrus, soapy	fatty, soapy	metallic, sweet	soapy, coriander
(*Z*)-3-Dodecen-1-ol	citrus, soapy, musty	citrus, soapy, earthy, musty	fresh, soapy, fatty	soapy, waxy, metallic	pungent, tangy, herb, green banana skin

Table 2 B. Odor Qualities (GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alkenals

Odorant	Odor qualities				
	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Pentenal	grassy, green, clover	green, clover	citrus, soapy	Grassy, green fatty	green, grassy, clover
(*Z*)-3-Hexenal	grassy, green, fresh cut grass	green, clover	cucumber, fatty	Grassy, green, fresh cut grass, fatty	grassy, green, clover
(*Z*)-3-Heptenal	grassy, sweet, clover	clover, fatty	cucumber, fatty	green, fatty	grassy, green, clover, vinegar acidic
(*Z*)-3-Octenal	fatty, fresh	fatty, green	soapy, citrus	citrus, fatty	green, clover, acidic, floral
(*Z*)-3-Nonenal	fatty, cucumber	fatty	citrus, cucumber, soapy	waxy, citrus, fatty	green, clover, citrus
(*Z*)-3-Decenal	fatty, fresh	fatty, citrus	soapy, fresh	metallic, waxy, sweet	clover, soapy, citrus
(*Z*)-3-Undecenal	citrus, soapy	citrus, cleanser	soapy, citrus, fatty	metallic, waxy	soapy, citrus
(*Z*)-3-Dodecenal	soapy, citrus	citrus, cleanser, fatty	citrus, soapy	waxy, soapy	soapy, citrus

Table 2 C. Odor Qualities (GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alkenoic acids

Odorant	Odor qualities				
	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Pentenoic acid	acidic, pungent	cheesy, sweaty	fatty, soapy	sweaty, cheesy	vinegar acidic, cheesy, sweaty
(*Z*)-3-Hexenoic acid	green, fresh, sweet, cheesy	sweaty	fatty	sweaty	acidic, pungent, plastic, sweaty
(*Z*)-3-Heptenoic acid	musty, waxy, pungent, sweaty	sweaty, cardboard	fatty, green	sweaty	acidic, plastic, pungent
(*Z*)-3-Octenoic acid	plastic, musty, waxy	sweaty, pungent	fatty, green, soapy	sweaty	acidic, plastic, pungent
(*Z*)-3-Nonenoic acid	cheesy, waxy, sweaty, musty	fatty, sweaty, pungent	fatty, rancid	sweaty, plastic	acidic, plastic, rubber
(*Z*)-3-Decenoic acid	musty, waxy, acidic	fatty, sweaty	fatty, soapy	waxy	plastic, acidic, musty
(*Z*)-3-Undecenoic acid	sweaty, acidic, pungent, waxy	perfume, harsh	fatty, rancid, soapy	waxy, metallic	plastic, rubber, phenolic
(*Z*)-3-Dodecenoic acid	musty, waxy, plastic	floral, fatty	fatty, green	sweaty, sweet, waxy	plastic, pungent, rubber, acidic

Table 3 A. Odor Thresholds (OT, GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alken-1-ols

Odorant	OT in air (ng/L_{air})[a]						
	Geometric mean	Factor (Quotient high/low)	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Penten-1-ol	86	16	28	57	57	114	455
(*Z*)-3-Hexen-1-ol	8	16	2.38	19	2.38	9.51	38
(*Z*)-3-Hepten-1-ol	45	64	5.65	361	181	45	11
(*Z*)-3-Octen-1-ol	46	64	4.99	40	319	20	160
(*Z*)-3-Nonen-1-ol	46	16	10	80	40	40	160
(*Z*)-3-Decen-1-ol	96	32	12	48	191	382	191
(*Z*)-3-Undecen-1-ol	97	33	426	267	107	53	13
(*Z*)-3-Dodecen-1-ol	107	16	35	564	71	71	141

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

Table 3 B. Odor Thresholds (OT, GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alkenals

Odorant	OT in air (ng/L_{air})[a]						
	Geometric mean	Factor (Quotient high/low)	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Pentenal	1.27	8	0.84	1.68	3.35	0.42	1.68
(*Z*)-3-Hexenal	0.27	4	0.14	0.54	0.54	0.14	0.27
(*Z*)-3-Heptenal	1.08	16	0.27	4.34	2.17	1.08	0.54
(*Z*)-3-Octenal	1.23	8	0.47	3.73	3.73	0.93	0.47
(*Z*)-3-Nonenal	1.53	4	1.33	1.33	2.66	2.66	0.66
(*Z*)-3-Decenal	2.32	8	2.32	2.32	4.63	4.63	0.58
(*Z*)-3-Undecenal	0.94	18	3.87	0.48	0.97	1.93	0.21
(*Z*)-3-Dodecenal	0.19	35	1.06	0.03	0.26	1.06	0.03

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

Table 3 C. Odor Thresholds (OT, GC-O) of all five Panelists (P 1 to P 5) of (*Z*)-3-Alkenoic acids

Odorant	OT in air (ng/L_{air})[a]						
	Geometric mean	Factor (Quotient high/low)	P 1	P 2	P 3	P 4	P 5
(*Z*)-3-Pentenoic acid	28	8	85	21	43	11	21
(*Z*)-3-Hexenoic acid	7.49	2033	17	17	549	0.54	0.27
(*Z*)-3-Heptenoic acid	2.50	261216	0.94	60	1933	0.12	0.0074
(*Z*)-3-Octenoic acid	2.54	13200	0.42	107	858	0.42	0.0065
(*Z*)-3-Nonenoic acid	56	32	387	48	193	12	12
(*Z*)-3-Decenoic acid	24	8	72	18	72	9.05	9.05
(*Z*)-3-Undecenoic acid	21	32	84	42	42	2.63	11
(*Z*)-3-Dodecenoic acid	22	64	153	77	77	2.40	2.40

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

Table 4 A. Odor Thresholds in Air (OT in air) of (*Z*)-3-Alken-1-ols Compared to Odor Thresholds of (*E*)-3-Alken-1-ols and 1-Alkanols

Number carbon atoms	OT in air (ng/L_{air})[a]		
	(*Z*)-3-alken-1-ols[a,b]	(*E*)-3-alken-1-ols[a,c]	1-alkanols[a,b]
5	57	414	131
6	9.5	69	116
7	45	114	133
8	40	62	53
9	40	57	4.3
10	191	61	21
11	107	23	106
12	71	104	197

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[b] In this study determined median odor threshold values.

[c] In our previous study determined median odor threshold values (Lorber and Buettner 2015).[3]

Table 4 B. Odor Thresholds in Air (OT in air) of (*Z*)-3-Alkenals Compared to Odor Thresholds of (*E*)-3-Alkenals and 1-Alkanals

Number carbon atoms	OT in air (ng/L_{air})[a]		
	(*Z*)-3-alkenals[a,b]	(*E*)-3-alkenals[a,c]	1-alkanals[a,b]
5	1.68	3	21
6	0.27	5	4.3
7	1.08	14	30
8	0.93	12	6.7
9	1.33	12	24
10	2.32	9	9.1
11	0.97	11	11
12	0.26	8	4.8

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[b] In this study determined median odor threshold values.

[c] In our previous study determined median odor threshold values (Lorber and Buettner 2015).[3]

Table 4 C. Odor Thresholds in air (OT in air) of (*Z*)-3-Alkenoic Acids Compared to Odor Thresholds of (*E*)-3-Alkenoic acids and Saturated Carboxylic Acids

Number carbon atoms	OT in air (ng/L_{air})[a]		
	(*Z*)-3-alkenoic acids[a,b]	(*E*)-3-alkenoic acids[a,c]	saturated carboxylic acids[a,b]
5	21	28	2.7
6	17	4.13	69
7	0.94	3.60	30
8	0.42	34	27
9	48	68	48
10	18	66	9
11	42	24	11
12	77	34	19

[a] Odor thresholds in air were determined as described by Ullrich and Grosch (1987).[1]

[b] In this study determined median odor threshold values.

[c] In our previous study determined median odor threshold values (Lorber and Buettner 2015).[3]

Figure 1 A:

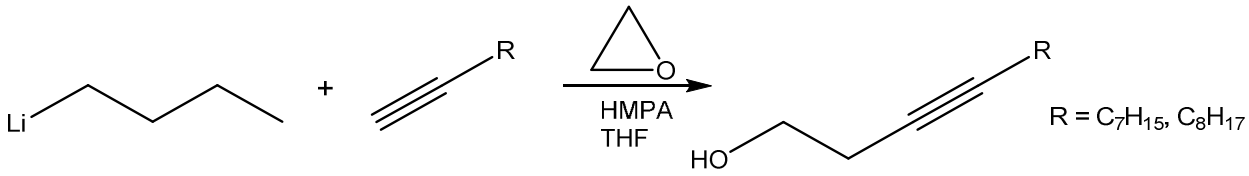


Figure 1 B:

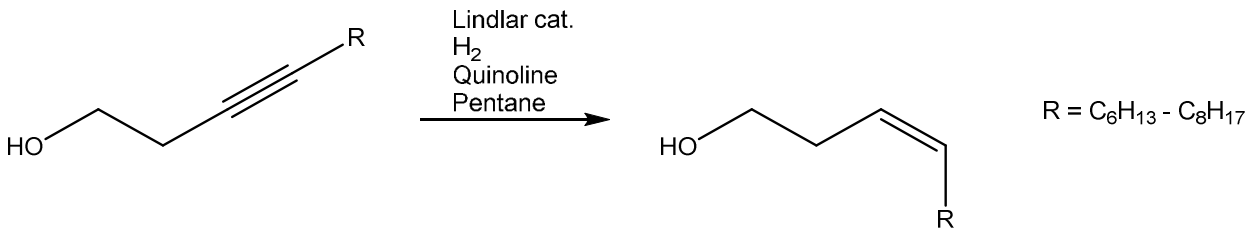


Figure 1 C:

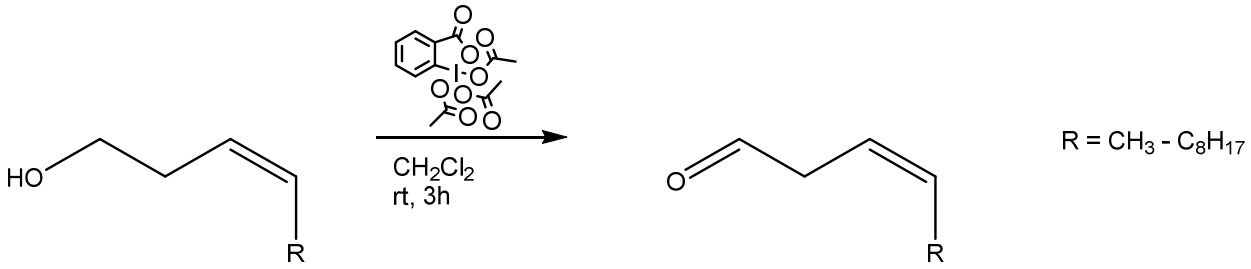


Figure 1 D:

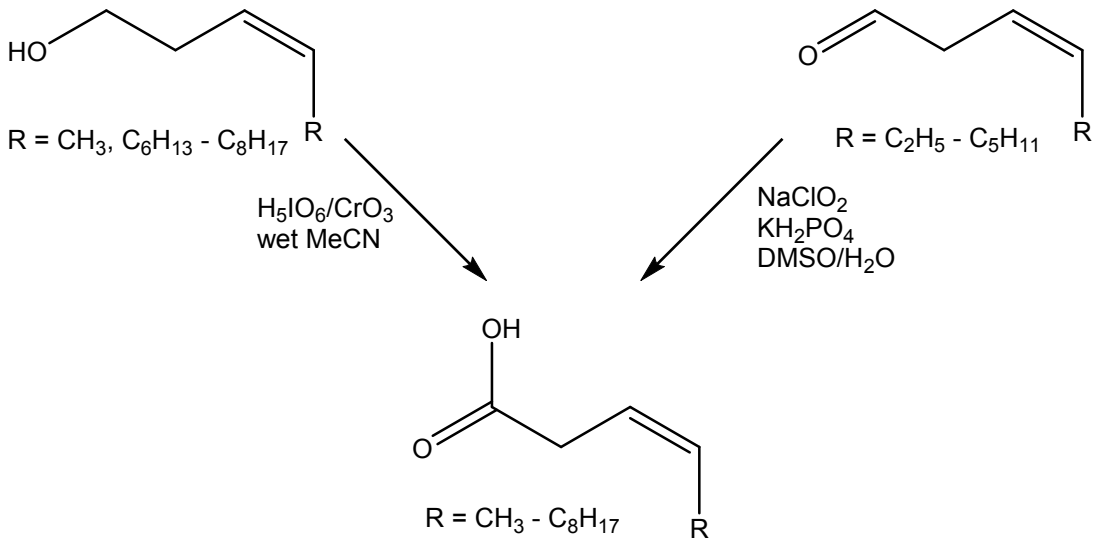

HO
R = CH3, C6H13 - C8H17
R
H5IO6/CrO3
wet MeCN
O
R = C2H5 - C5H11
R
NaClO2
KH2PO4
DMSO/H2O
OH
O
R = CH3 - C8H17
R

Figure 2 A

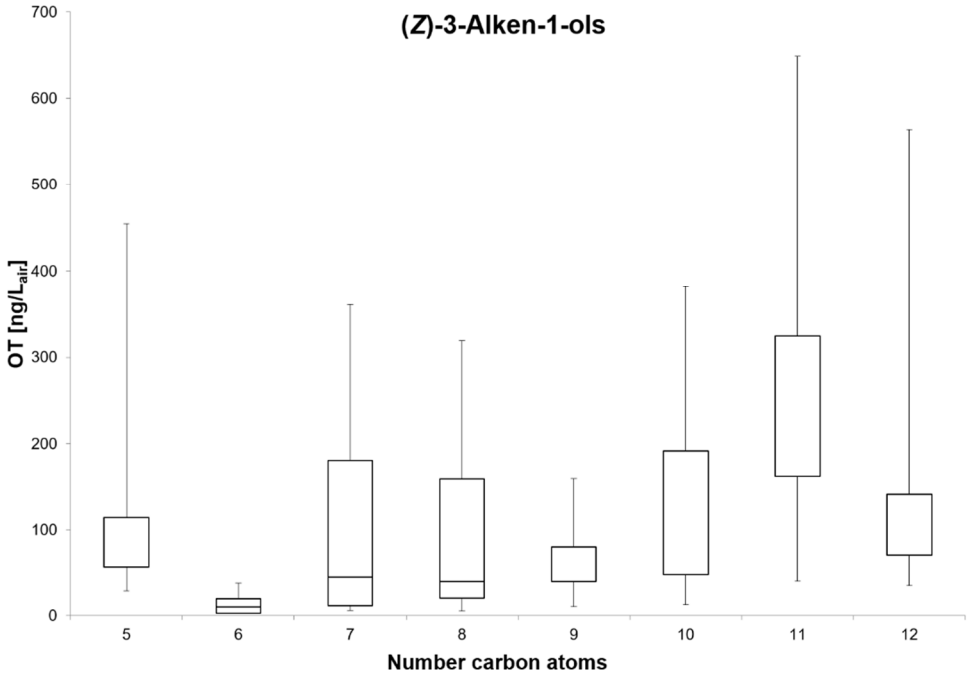

(Z)-3-Alken-1-ols
OT [ng/L$_{air}$]
700
600
500
400
300
200
100
0
5
6
7
8
9
10
11
12
Number carbon atoms

Figure 2 B

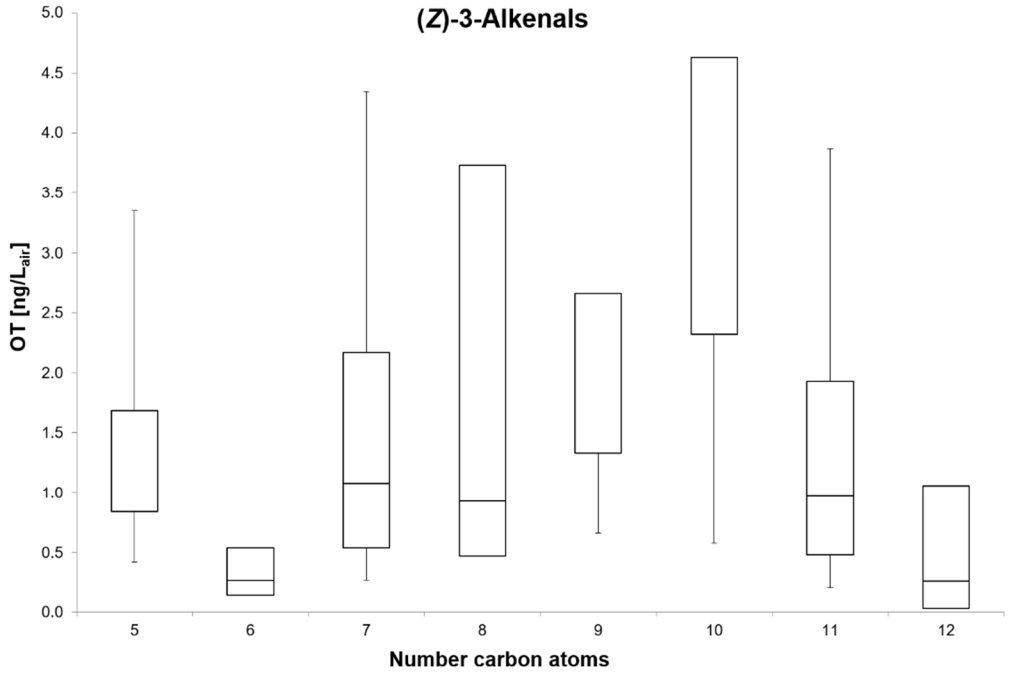
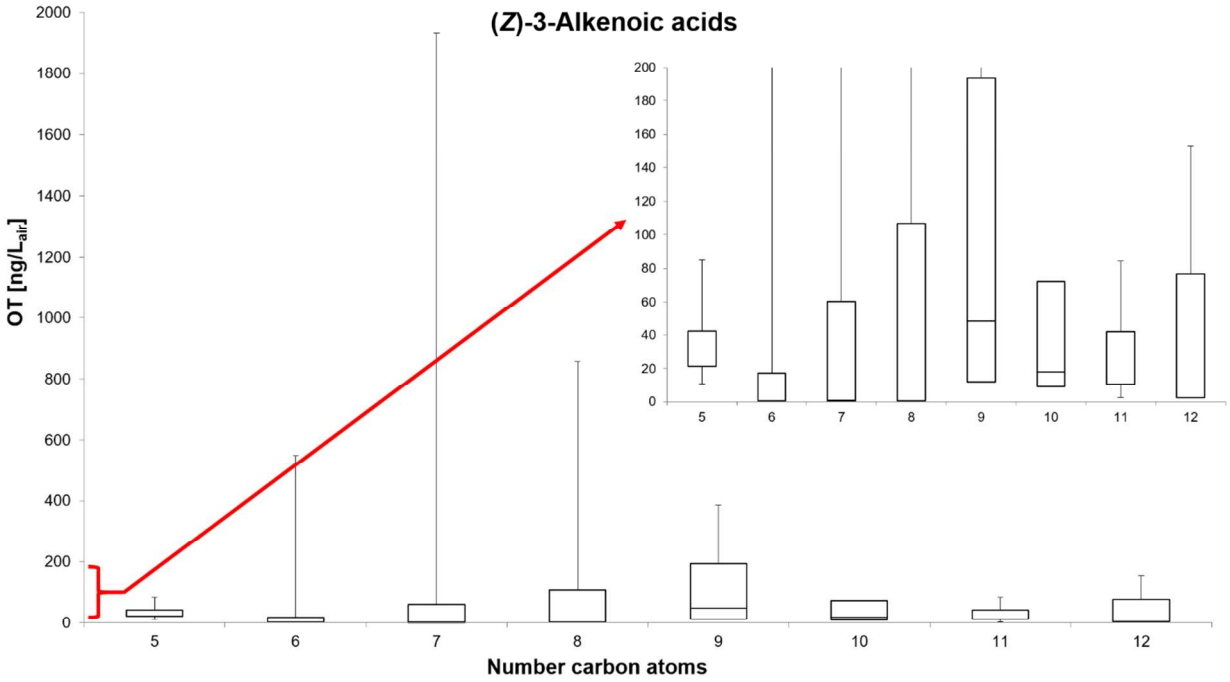
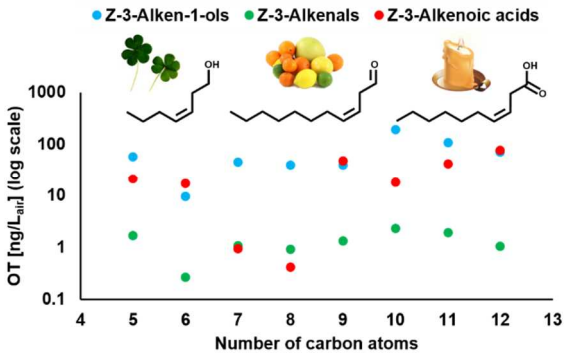

(Z)-3-Alkenals
OT [ng/L$_{air}$]
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5
6
7
8
9
10
11
12
Number carbon atoms

Figure 2 C


(Z)-3-Alkenoic acids
OT [ng/L$_{air}$]
Number carbon atoms
0
200
400
600
800
1000
1200
1400
1600
1800
2000
5
6
7
8
9
10
11
12
0
20
40
60
80
100
120
140
160
180
200

TOC graphic


Z-3-Alken-1-ols
Z-3-Alkenals
Z-3-Alkenoic acids
OH
O
OH
O
1000
100
10
1
0.1
OT [ng/L$_{air}$] (log scale)
4
5
6
7
8
9
10
11
12
13
Number of carbon atoms