Odour qualities and odour thresholds of halogenated, alkylated, alkenylated and methoxylated guaiacol-derived odorants

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Abstract

In the present study, we compare the odour qualities and odour thresholds of guaiacols with different structural moieties with special focus on the impact of halogenation on their sensory properties. Thereby, a series of substances, which were not commercially available, was synthesized. All compounds were systematically analysed regarding their retention indices, odour qualities and odour thresholds.

Odour qualities of alkylated, alkenylated and methoxylated guaiacols were mainly smoky, clove-like and vanilla-like. Halogenated derivatives also exhibited smoky, sweet and vanilla-like odours, but also medicinal and plaster-like smells. Odour thresholds in air were very low, namely between 0.00018 and 111 ng/L for all compounds. Huge inter-individual differences were found for odour thresholds, whereas the perceived odour qualities were quite comparable between different individuals.

The analytical and sensory data library created in this study will aid future analytical discovery of this interesting substance class. Parts of this work are also published in [1] and [2].

Introduction

Guaiacol-derived odorants are commonly found in nature. Guaiacols are produced by various plants as well as by animals, and widely used in food and perfume industry. They are employed inter alia as antiseptic and anesthetic agents [3, 4]. Guaiacol derivatives have been found in smoked foods like smoked ham [5], in wheat beers [6] and brandy amongst a row of other foods. Halogenated guaiacols are, however, up to now mainly found in nature due to human intervention. Halogenated guaiacols are for example present in waste water of pulp mills and therefore responsible for some off-odours in fish [7, 8]. However, comprehensive data on sensory characteristics of guaiacol derivatives and the impact of halogenation have not been reported until now.

Experimental

Gas chromatography

GC-FID and GC-olfactometry (GC-O) were carried out with a Trace CT Ultra using a DB-5 and FFAP capillary. Helium at a flow rate of 2.5 mL/min was used as carrier gas. Samples were injected at 40 °C, 40 °C was kept for 2 minutes, then the oven temperature was raised at 10 °C/min to 200 °C or at 6 °C/min to 250 °C, then raised at 20 °C/min or 40 °C/min to 300 °C (DB-5), or at 8 °C/min to 240 °C (FFAP), respectively, and held for 5 or 10 minutes. GC-MS analyses were performed with an Agilent MSD 5975C using the same temperature programs and types of capillaries as described above. Mass spectra

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were generated in the electron impact mode (EI) at 70 eV. Retention indices were determined according to the method of Van den Dool and Kratz [9].

Odour thresholds and odour qualities

Panellists were trained assessors form the University of Erlangen. Odour thresholds in air were determined according to the method described by Ulrich & Grosch [10] using *(E)*-2-decenal as internal standard. 2 µL were injected of every dilution. Odour thresholds were determined by 8 assessors for all compounds. Odour qualities were determined during GC-O and panellists were asked to freely choose odour quality descriptors.

Syntheses

Compounds, which were not commercially available, were synthesized according to the literature procedures named in [1] and [2].

Results and discussion

Figure 1 gives an overview of odour thresholds of all investigated compounds.

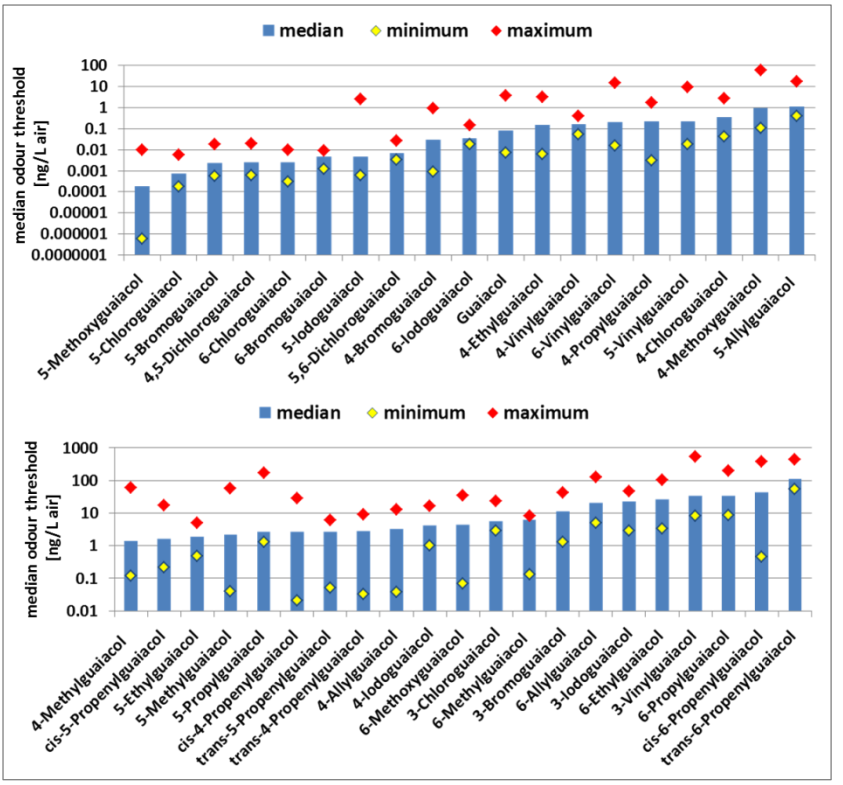

Figure 1: Odour thresholds of guaiacol derivatives

With the exception of 5-methoxyguaiacol, all compounds with lower odour thresholds than guaiacol itself were halogenated derivatives. The compound with the lowest odour threshold was 5-methoxyguaiacol with a median odour threshold about 500-times lower than that of guaiacol, namely 0.00018 ng/L. Halogenated compounds with an odour threshold lower than guaiacol were some chloro-, bromo-, and iodoguaiacols with the halogen in positon 4, 5, or 6. Additionally, two dichloroguaiacols were tested. Both had a lower odour threshold than guaiacol. Compounds with odour thresholds higher than

guaiacol were alkylated guaiacols as well as alkenylated guaiacols. Additionally, some halogenated compounds also exhibited odour thresholds higher than guaiacol. These were derivatives with halogens in position 3 or 4. The compounds with the highest odour thresholds of the investigated substances were cis- and trans- 6-propenylguaiacol with thresholds of 44 and 111 ng/L air, respectively. Of the halogenated compounds, the substances with halogens in position 3 showed the highest odour thresholds. These were 3-chloro-, 3-bromo- and 3-iodoguaiacol.

Inter-individual differences in odour thresholds were quite pronounced. The most prominent inter-individual differences were found for 5-methoxyguaiacol with a factor of about 17000 between the lowest and the highest individual odour threshold. Other compounds with high inter-individual differences in odour thresholds were 5-iodo-, 5-methyl-, cis-4-propenyl-, and 4-bromoguaiacol, all with factors over 1000 between highest and lowest individual odour thresholds. On the other hand, there were also compounds with small inter-individual variations, like 6-iodo-, 3-chloro-, 4,5-dichloro-, 4-vinyl-, 6-bromo-, and trans-6-propenylguaiacol, all with a factor of 8 between highest and lowest individual threshold.

Odour qualities were mainly smoky, clove-like and vanilla-like for alkylated, alkenylated and methoxylated guaiacols. Halogenated guaiacols also exhibited smoky, sweet and vanilla-like odour qualities. However, none of the halogenated compounds exhibited a clove-like odour. Conversely, some of the halogenated derivatives also showed medicinal and patch-like smells. Table 1 provides an overview of the odour qualities of the investigated compounds. The most frequently named attributes were smoky, vanilla-like and sweet. Several substances also exhibited a ham-like odour, but only one of them was a halogenated substance, namely 5-chloroguaiacol. All in all, odour impressions were quite consistent between individuals. Additionally, Table 1 shows odour thresholds in [pmol/L_{air}]. By giving odour thresholds in [pmol/L_{air}] (cf. Table 1) in addition to the values in [ng/L] (cf. Figure 1), one can also see the impact of the molecular weight on the odour threshold values.

These results form a basis for future analytical discovery of this substance class.

Table 1: Odour qualities and odour thresholds (OT) of all investigated guaiacol derivatives

Odourant[a,b]	*Odour qualities*	*OT [pmol/L_{air}] range*[c]
5-Methoxyguaiacol	sweet, clove, vanilla	0.000004 - 0.065
5-Chloroguaiacol	smoked, smoky, ham-like	0.0011 - 0.037
6-Chloroguaiacol	smoky, sweet	0.0020 - 0.063
5-Iodoguaiacol	sweet, smoked	0.0024 - 10
5-Bromoguaiacol	smoky, sweet	0.0028 - 0.089
4,5-Dichloroguaiacol	smoky, sweet, vanilla-like	0.0032 - 0.10
4-Bromoguaiacol	vanilla-like, sweet, smoky	0.0045 - 4.6
6-Bromoguaiacol	medical, smoky, patch-, plastic-like	0.0059 - 0.045
5,6-Dichloroguaiacol	smoky, medical, patch-like	0.018 - 0.14
4-Propylguaiacol	smoky, clove, sweet	0.018 - 10
4-Ethylguaiacol	clove, smoky	0.039 - 21
Guaiacol	smoky, vanilla, ham	0.056 - 30
6-Iodoguaiacol	medical	0.072 - 0.60
6-Vinylguaiacol	smoky, ham	0.11 - 100

Table 1. continued

Odourant[a,b]	*Odour qualities*	*OT [pmol/L_{air}] range*[c]
5-Vinylguaiacol	smoky, ham, clove, sweet, vanilla	0.12 - 63
cis-4-Propenylguaiacol	clove	0.13 - 177
trans-4-Propenylguaiacol	clove	0.20 - 55
4-Allylguaiacol	clove	0.23 - 79
4-Chloroguaiacol	sweet, vanilla-like	0.27 - 18
5-Methylguaiacol	vanilla, sweet, smoky	0.29 - 413
trans-5-Propenylguaiacol	vanilla, sweet	0.30 - 38
4-Vinylguaiacol	clove, smoky	0.35 - 2.7
6-Methoxyguaiacol	smoky, sweet	0.45 - 227
4-Methoxyguaiacol	clove, sweet, smoky, vanilla, ham	0.71 - 383
4-Methylguaiacol	vanilla, sweet, ham, smoky	0.87 - 441
6-Methylguaiacol	smoky, plastic, sweet, bacon	0.94 - 60
cis-5-Propenylguaiacol	smoky, clove, ham	1.3 - 104
5-Allylguaiacol	smoky, ham, clove, sweet	2.4 - 104
cis-6-Propenylguaiacol	smoky, ethereal, clove	2.8 - 2259
5-Ethylguaiacol	smoky, sweet, ham	3.1 - 33
4-Iodoguaiacol	vanilla-like, smoky, sweet	4.0 - 64
3-Bromoguaiacol	musty, old	6.4 - 212
5-Propylguaiacol	clove, vanilla	7.8 - 999
3-Iodoguaiacol	musty, moldy	12 - 184
3-Chloroguaiacol	smoky, medical	18 - 145
6-Ethylguaiacol	smoky	22 - 683
6-Allylguaiacol	plastic, clove, smoky	30 - 773
6-Propylguaiacol	plastic, sweet	51 - 1203
3-Vinylguaiacol	smoky, clove	55 - 3509
trans-6-Propenylguaiacol	ham, smoky	335 - 2698

[a] Odorants are displayed in the order of their minimum odour threshold.
[b] Retention indices of all compounds on DB-5 as well as on FFAP can be found in [1, 2].
[c] Odour thresholds were established according to the method described by Ullrich & Grosch [10].

References

1. Schranz, Lorber, Klos, Kerschbaumer, Buettner (2017). Food Chem., 232, 808-819.
2. Juhlke, Lorber, Wagenstaller, Buettner, (2017), Front. Chem., 5 (120), doi: 10.3389/fchem.2017.00120.
3. Hunnuis (1997). Hunnius pharmazeutisches Wörterbuch: De Gruyter.
4. Jadhav, Khandelwal, Ketkar, Pisal (2004). Drug Dev. Ind. Pharm., 30(2), 195-203.
5. Baloga, Reineccius, Miller (1990). J. Agr. Food Chem., 38(11), 2021-2026.
6. Langos, Schieberle (2013). J. Agr. Food Chem., 61 (47), 11303–11311.
7. Couillard, Nellis (1999). Environ. Toxicol. Chem., 18(11), 2545-2556.
8. Owens, Swanson, Birkholz (1994). Chemosphere, 29(1), 89-109.
9. Van den Dool, Kratz (1963). J. Chromatogr. A, 11, 463-471.
10. Ullrich, Grosch (1987), Z. Lebensm. Unters. For., 184(4), 277-282.