Aroma profile of a red berries yoghurt drink by HS-SPME-GC-MS-O and influence of matrix texture on volatile aroma compound release of flavoured dairy products

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Introduction

Headspace-solid-phase microextraction (HS-SPME) sampling followed by gas chromatography (GC) separation is widely employed for the analysis of volatile odorant compounds in dairy products (1, 2). In a previous study, the odour representativeness of HS-SPME extracts of a commercial red berries yoghurt drink was investigated by direct-GC-Olfactometry (D-GC-O), i.e. without chromatographical separation. The odour of the product was best represented by the DVB/CAR/PDMS 50/30 µm fibre (3).

Objectives

Here we report on the volatile chemical composition and odour-impact compounds of an odour representative HS-SPME-extract of the yoghurt drink by GC-MS/FID-O with the described fibre. As flavour release in dairy products is known to be influenced by multiple interactions with the matrix (4, 5), possible influence of product texture on volatile compound release was investigated.

Experiment setup

1. Chemical composition and odour-impact compounds: 2W-GC-MS/FID-O-analyses with a DVB/CAR/PDMS 50/30 µm 1 cm-fibre on two stationary phases (DB-5ms/VF-WAXms, trained panel *n*= 8). Odour-impact of constituents was evaluated by multiplying the detection frequency (*DF*, percentage of panellists having perceived an odour) with the mean intensity (scale: 1 to 3)
2. Matrix texture and flavour release: GC-MS/FID-analyses of dairy matrices differing in texture spiked with a simple red berries model aroma and an internal standard (*IS*)

Model aroma

1. Ethyl 2-methylbutanoate (57.39 µg resp. 57.16 µg) / methyl hexanoate (131.74 µg resp. 131.70 µg): ratio 1:2.3; based on analyses of the original product and GC-MS-O results
2. Methyl octanoate as *IS* (addition of 16.82 µg resp. 17.00 µg to samples, resulting in 2–7 % of the total volatile profile depending on the matrix)

Volatile chemical composition and odour-impact compounds of the tested red berries yoghurt drink

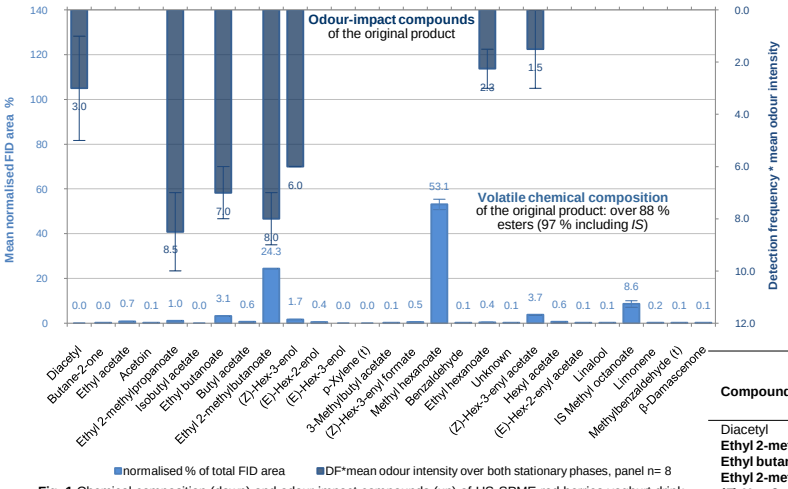

Fig. 1 Chemical composition (down) and odour-impact compounds (up) of HS-SPME red berries yoghurt drink extract. Only odorant compounds perceived by either 75 % of the panel (*n*= 8) on one column or by 50 % on both columns are listed. t= tentatively identified without reference compound injection.

Fruity odour zones were **dominant** and the **main odour-impact compounds** were **three ethyl esters** and **one alcohol** (Table 1).

Despite being the main component, **methyl hexanoate (~53%) was not perceived** by the panel: as for the *IS* **methyl octanoate** (200 ppb in water), its **odour threshold is relatively high** (70–84 ppb in water) compared to the odour thresholds of the main odour-impact compounds (6).
(*Z*)-Hex-3-enol, however, although showing a similar odour threshold, was determined to be an odour-impact compound (6).

Table 1 Odour-impact compounds of HS-SPME red berries yoghurt drink extract

Compound	Odour threshold (6) (ppb in water)	Mean (*DF* * Intensity)	Odour descriptors given by the panellists
Diacetyl	2.3–6.5	3.0 ± 2.0	buttery, creamy, sweet
Ethyl 2-methylpropanoate	0.1	8.5 ± 1.5	fruity, pineapple, red berries, sweet
Ethyl butanoate	1.0	7.0 ± 1.0	fruity, soapy, banana/pineapple, buttery, sweet, artificial
Ethyl 2-methylbutanoate	0.1–0.3	8.0 ± 1.0	fruity, sweet, strawberry, pineapple, chewing-gum
(*Z*)-Hex-3-enol	70	6.0 ± 0.0	cut grass, green, fruity, flowery, sour
Ethyl hexanoate	1	2.3 ± 0.8	chemical, fruity, solvent
(*Z*)-Hex-3-enyl acetate	-	1.5 ± 1.5	flowery, green, rancid

Four panellists smelled the sample on each column. Only odorant compounds perceived by either 75 % of the panel on one column or by 50 % on both columns are listed.

Interaction between matrix and aroma release: Addition of a simple model aroma to different dairy matrices

Ethyl 2-methylbutanoate / methyl hexanoate and methyl octanoate as *IS* added to milk, yoghurt drink, plain yoghurt, and curd

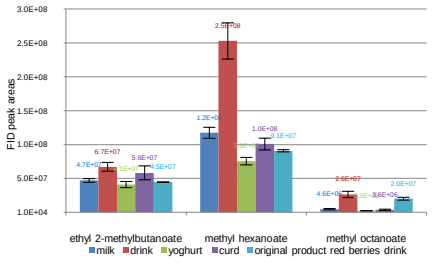

Fig. 2 Absolute FID areas of target compounds in the four chosen dairy matrices compared to the original red berries drink

- sum of added compounds ≥ 93 % for all matrices, but shift in percentage was observed
- highest deviations of peak areas (%) found in curd: less homogenous distribution?
- influence of compound volatility? Higher peak area variations for methyl octanoate and most similar absolute peak areas for ethyl 2-methylbutanoate
- highest absolute peak areas for methyl hexanoate and octanoate in the yoghurt drink

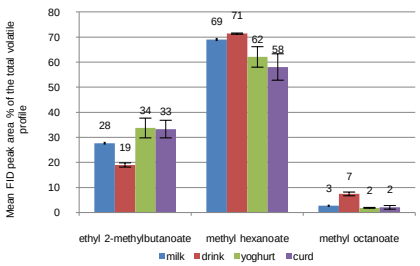

Fig. 3 FID area percentage in the total volatile profile of target compounds in the four chosen dairy matrices

Conclusion

GC-O analyses revealed seven odour-active zones which were reliably perceived by the panel. The main odour-impact compounds were ethyl 2-methylpropanoate (described by the panellists as fruity, red berries, pineapple; present at ~1 %), ethyl 2-methylbutanoate (fruity, strawberry, pineapple; ~24 %), ethyl butanoate (fruity, banana, pineapple, soapy; ~3 %), and (*Z*)-hex-3-enol (grassy, fruity; ~2 %). Methyl hexanoate (~53 %) and octanoate (*IS*) were not perceived.

For the model aroma composed of ethyl 2-methylbutanoate, methyl hexanoate, and methyl octanoate as *IS*, the sum of these three compounds constituted ≥ 93 % of the total GC/FID-profile for all four matrices i.e. milk, yoghurt drink, plain yoghurt, and curd. Repetitions of analysis (*n*= 3) revealed deviations among their peak areas in all matrices. Curd showed the highest deviations which might be due to a less homogeneous distribution and release of the compounds compared to more liquid matrices. Compound volatility might be another factor influencing deviations as methyl octanoate area deviations were found to be the highest in most cases. Ethyl 2-methylbutanoate showed similar absolute FID-areas in all matrices, whereas methyl hexanoate and octanoate areas varied. In complex food matrices, additional factors such as the presence of other volatile compounds, differences in *pH*, texture, and chemical composition can strongly influence flavour release and these matrix effects cannot be neglected when analysing foods. Especially for quantitative analyses, it is highly advisable to employ suitable internal standards and, if necessary, model matrices as similar as possible to the original product.

Literature 1. Arthur C.L.; Pawliszyn J. *Anal. Chem.* **1990**, *62*, 2145−2148, 2. Lehotay S.J.; Hajslova J. *Trends Anal. Chem.*, **2002**, *21*, 686−697, 3. Breme K. *et al. Proceedings: 9th Wartburg Symposium on Flavor Chemistry and Biology* **2011**, in press, 4. Paçi Kora E. *et al. J. Agric. Food Chem.* **2004**, *52*, 3048−3056, 5. Saint-Eve A. *et al. J. Agric. Food Chem.* **2006**, *54*, 3997−4004, 6. Leffingwell *et al.* Services for the perfume, flavor, food, and beverage industry – odor thresholds, 01/09/2011, http://www.leffingwell.com/odorthre.htm

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