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### Flavour and off-flavour compounds of Swiss Gruyère cheese. Evaluation of potent odorants

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#### Abstract

The flavour of a typical sample of Gruyère cheese and that of a Gruyère exhibiting a potato-like off-flavour was examined by instrumental and sensory analyses. Based on the results of dynamic headspace gas chromatography-mass spectrometry (DHGC/MS), aroma extract dilution analysis (AEDA) and gas chromatography-olfactometry of static headspace samples (GCO-H), 2-/3-methylbutanal, methional, dimethyltrisulphide, phenylacetaldehyde, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, methanethiol, as well as butyric, 2-/3-methylbutyric and phenylacetic acid form the typical flavour of Gruyère cheese. The potato-like character of the sample showing an aroma defect, however, could not be attributed definitively to one of these compounds. Considering the results of DHGC/MS and AEDA, 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine could be the possible causes of the off-flavour. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Aroma extract dilution analysis; Flavour; Gruyère cheese; Off-flavour

#### 1. Introduction

Swiss Gruyère cheese is a hard cheese exhibiting a characteristic flavour that is described as rancid, sulphury and animal-like (Muir, Hunter, Banks, & Horne, 1995). Some years ago, a Swiss village cheese factory reported that a lot of Gruyère loaves had to be discarded because they showed a potato-like off-flavour.

A perusal of the literature indicated two reports of similar flavour defects in cheeses. The first was detected in a French Comté cheese by Dumont, Roger, and Adda (1975), who attributed it tentatively to 3-methoxy-2propylpyrazine. As no systematic sensory studies were performed, the contribution of this compound to the flavour defect could not be confirmed. The second study dealt with a smear coated Munster cheese, whose flavour compounds were assessed by gas chromatography coupled to olfactometry and to mass spectrometry (Dumont, Mourgues, & Adda, 1983). In the alkaline fraction, 2-methoxy-3-isopropylpyrazine produced a potato-like odour and was therefore held responsible for the off-flavour.

The flavour composition of typical Gruyère cheese has been the subject of several recent studies. Liardon, Bosset, and Blanc (1982), Bosset and Liardon (1984, 1985) and Bosset, Collomb, and Sieber (1993) followed the concentration changes of alkaline, neutral and acidic volatiles during ripening. More recently, Engels and Visser (1994) examined the water-soluble fraction of different cheeses and considered butyric acid to be a potent odorant of Gruyère cheese.

However, as there has been no systematic approach to screen for important flavour contributors, the true composition of Gruyère flavour has so far remained a matter of speculation. The purpose of the present study was therefore (i) to investigate potent odorants of Gruyère cheese and (ii) to determine those substances responsible for the above-mentioned potato-like offflavour. In a similar way, as we reported the flavour of Swiss Emmentaler cheese (Preininger, Rychlik, & Grosch, 1994; Preininger, Warmke, & Grosch, 1996; Preininger & Grosch, 1994), the aim of the first part of this study was to conduct an aroma extract dilution analysis (AEDA) and to undertake several assays in order to characterise the headspace volatiles. After

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screening for potent odorants, quantification of these compounds as well as identifications of those which are responsible for the off-flavour were performed in the second part (Rychlik & Bosset, 2002).

#### 2. Materials and methods

#### 2.1. Cheeses

For a period of several months, a Swiss village factory had serious problems due to the production of Gruyère cheese loaves exhibiting a potato-like off-flavour. One of them was used for the current study (PG = potato-like Gruyère). A Reference Gruyère cheese (RG) without this flavour defect was obtained from a neighbouring village manufacture.

#### 2.2. Chemicals

Diethylether, *n*-pentane and dichloromethane were purified as previously reported (Schieberle & Grosch, 1983).

The pure reference compounds listed in the various tables were purchased: No. 1((S)-(+)-2-methylbutanal), 2–5, 7, 9, 10, 12, 14–17, 19–21, 26 ((S)-(+)-2-methylbutyric acid), 27, 29, 30-34, 37, 38 (Aldrich, Steinheim, Germany); 34, (Merck, Darmstadt, Germany); 23–25, 28, 35, 36 (Fluka, Buchs, Switzerland). The following compounds were gifts: 2-acetyl-1-pyrroline (8), dimethyltetrasulphide (18), (Z)-6-dodecen- $\gamma$ -lactone (22), 2-ethyl-3,5-dimethylpyrazine (11), (Z)-2-nonenal (13) from Prof. Grosch (formerly Deutsche Forschungsanstalt für Lebensmittelchemie, Garching, Germany) and (Z)-4-heptenal (6) from Haarmann & Reimer (Holzminden, Germany).

## 2.3. Steam distillation of cheeses and dynamic headspace gas chromatography-mass spectrometry

After addition of boiled (15 min) Milli-Q water (100 mL), the cheese samples (50 g) were grated and homogenised for 2 min by means of a Polytron dispersion aggregate PT-DA 3020/2 with rotor 30/2 M (Kinematica, Littau/Luzern, Switzerland) and adjusted to pH 8.5 using aqueous sodium hydroxide (5 mol  $L^{-1}$ , 1 mL). The suspension was then distilled at 60°C into a flask containing sulphuric acid (30%, 10 mL) using the modified rotavapour equipment reported by Imhof and Bosset (1989). After concentrating in a rotavapour, the distillate was adjusted to pH 11 by the addition of sodium hydroxide and subjected to dynamic headspace GC/MS, as detailed previously (Bosset, Bütikofer, Gauch, & Sieber, 1997).

## 2.4. Isolation of the volatile fraction for AEDA; separation into neutral/alkaline and acidic volatiles

Each cheese sample (200 g) was frozen in liquid nitrogen, then broken into smaller pieces and ground in a Waring blender (Privileg, Quelle, Fürth, Germany). The powder was then suspended in diethyl ether (500 mL), stirred for 4 h, and the suspension was filtered. The filtrate was dried over anhydrous sodium sulphate and concentrated to about 150 mL by distilling off the solvent under a Vigreux column ( $60 \times 1 \text{ cm}^2$ , Bahr, Manching, Germany). The solution of the volatiles was distilled off from the non-volatile materials under high vacuum (5-6 mPa) in an apparatus described earlier (Jung, Sen, & Grosch, 1992). When a pressure of 5-6 mPa was reached, the extract was slowly allowed to drop over 1.5 h into the distillation flask, which was heated to 40°C. Then, the distillation was continued for 90 min at 60°C. The trapped condensate was extracted twice with aqueous sodium carbonate (total volume 200 mL,  $0.5 \text{ mol L}^{-1}$ ) and washed with a saturated aqueous solution of sodium chloride (200 mL). Then, the etheral solution containing the neutral and alkaline components was dried over anhydrous sodium sulphate and finally concentrated to 0.2 mL under a Vigreux column  $(40 \times 1 \text{ cm}^2)$  and by microdistillation (Bemelmans, 1979).

To isolate the acidic volatiles, the aqueous alkaline solution was acidified to pH 3 with concentrated hydrochloric acid and extracted with diethylether  $(2 \times 100 \text{ mL})$ . The ether solution was washed with a saturated aqueous solution of sodium chloride (200 mL), then dried over anhydrous sodium sulphate and finally concentrated to 0.2 mL.

# 2.5. Separation of the alkaline volatiles and column chromatography (CC) of the neutral volatiles for identification experiments

The neutral/alkaline fraction (NAF) was separated into fractions containing neutral or alkaline compounds by extraction with aqueous hydrochloric acid (0.1 mol L<sup>-1</sup>, 2 × 50 mL). The pH of the aqueous extract containing the alkaline compounds was adjusted to 12 by the addition of sodium hydroxide (20%), and the mixture was then extracted with diethyl ether (3 × 50 mL). After concentration to 0.2 mL, the alkaline volatiles in the etheral extract were analysed by high resolution gas chromatography coupled to mass spectrometry (HRGC/MS).

The remaining organic layer after extracting NAF with hydrochloric acid contained neutral compounds and was furthermore fractionated at  $10-12^{\circ}$ C on a water-cooled column ( $30 \times 2 \text{ cm}^2$ ), packed with a slurry of silica gel 60 (Merck, Darmstadt, Germany, purified as described by Esterbauer (1968)) in pentane/

diethylether (95+5, vol+vol). Stepwise elution for each column was performed with the following pentane/diethylether mixtures: 25 mL (95+5, vol+vol,fraction 1), 50 mL (85+15, vol+vol, fraction 2), 45 mL (7+3, vol+vol, fraction 3), 75 mL (2+8,vol+vol, fraction 4) and finally 50 mL pure diethylether (fraction 5).

#### 2.6. High resolution gas chromatography (HRGC)

The high resolution gas chromatography (HRGC) was performed on a type 5300 gas chromatograph (Carlo Erba, Hofheim, Germany) using the following fused silica capillary columns due to their different resolution efficiencies towards different classes of compounds: capillary DB-5 ( $30 \text{ m} \times 0.32 \text{ mm}$ ,  $d_f = 0.25 \mu\text{m}$ ), capillary DB-1701 ( $30 \text{ m} \times 0.32 \text{ mm}$ ,  $d_f = 0.25 \mu\text{m}$ ), and capillary DB-FFAP ( $30 \text{ m} \times 0.32 \text{ mm}$ ,  $d_f = 0.25 \mu\text{m}$ ). The three capillary columns were supplied by Fisons Instruments, Mainz, Germany.

The samples were applied by the cold on-column technique at 35°C. Two min after injecting  $0.5 \,\mu\text{L}$  of the sample the temperature of the oven was raised to 60°C (50°C for DB-1701) at a rate of 40°C min<sup>-1</sup>, held for 2 min isothermally and then raised at 4°C min<sup>-1</sup> (5°C min<sup>-1</sup> for DB-FFAP) to 240°C. The flow rate of the carrier gas, helium, was 2 mL min<sup>-1</sup>.

#### 2.7. Aroma extract dilution analysis (AEDA)

The FD (flavour dilution)-values and odour descriptions of the compounds in the neutral/alkaline and the acidic fractions of the cheeses were determined by AEDA (Ullrich & Grosch, 1987). An aliquot of the respective fraction was stepwise diluted with diethyl ether (1+1, vol+vol) and the diluted solutions (0.5  $\mu$ L) were separated on the capillary columns DB-5, DB-1701, and DB-FFAP. The effluent was split into a flame ionization detector (FID) and a sniffing port (1+1, vol+vol) and evaluated by two assessors. Retention data of the compounds are presented as retention indices (RI) calculated according to Van den Dool and Kratz (1963).

## 2.8. HRGC/olfactometry (HRGC/O) and HRGC/mass spectrometry (HRGC/MS) of static headspace samples

Static headspace analysis was performed with a CP-9001 gas chromatograph interfaced to the purge and trap system TC/PTI 4001 (Chrompack, Frankfurt, Germany), as previously reported (Rychlik & Grosch, 1996). The glass tube in the desorption heating block of the purge and trap facility was empty and deactivated.

A ground sample of frozen cheese (5 g) was filled in a water-jacket vessel (250 mL) sealed with a septum. After

tempering for 30 min at 25°C, headspace samples (0.625–25 mL) were drawn by a gastight syringe and injected with a velocity of  $3 \,\mathrm{mL}\,\mathrm{min}^{-1}$  into the purge system which operated in the desorption mode for 10 min at 250°C. The carrier gas, helium (flow  $20 \,\mathrm{mL\,min^{-1}}$ ), swept these headspace samples into the trap  $(40 \text{ cm} \times 0.53 \text{ mm} \text{ fused silica capillary coated with})$ CP-sil 8 CP,  $d_f = 5 \,\mu m$ ; Chrompack, Frankfurt, Germany) which was precooled with liquid nitrogen to  $-110^{\circ}$ C for 5 min. The trap was heated up very rapidly to 200°C to start HRGC/O. This temperature was held for 1 min and the sample was flushed by the helium (flow rate  $3 \,\mathrm{mL}\,\mathrm{min}^{-1}$ ) into the gas chromatograph. The thin film capillary used for static headspace GC/O was RTX-5 (30 m × 0.53 mm fused silica capillary,  $d_f = 1.5 \,\mu\text{m}$ , Amchro, Sulzbach/Taunus, Germany). The temperature of the oven was held at 0°C for 0 min and then programmed at a rate of 6°C min<sup>-1</sup> to 230°C. At the exit of the capillary, the effluent was split 1+1(vol+vol) into an FID and the sniffing port using deactivated fused silica capillaries  $(30 \text{ cm} \times 0.15 \text{ mm})$ . The FID and the sniffing port were held at 250°C. Nitrogen  $(20 \,\mathrm{mL\,min^{-1}})$  was used as the make-up gas for the FID. After each GC/O run the purge system was automatically cleaned (clean-up flow,  $50 \,\mathrm{mL}\,\mathrm{min}^{-1}$ helium; clean-up temperature, 275°C).

MS-analyses were performed with an INCOS XL (Finnigan MAT, Bremen, Germany) in tandem with capillary RTX-5. Mass spectra in the electron impact mode (MS-EI) were generated at 70 eV and in the chemical ionization mode (MS-CI) at 115 eV with isobutane as the reactant gas.

Table 1

Comparison of dynamic headspace gas chromatography-mass spectrometry of alkaline extracts from Gruyère cheeses with a potato-like offflavour (PG) and without an off-flavour (RG)

| Compound <sup>a</sup>        | Ratio PG/RG <sup>b</sup> |  |  |
|------------------------------|--------------------------|--|--|
| Pyridine                     | 3                        |  |  |
| 1-Methyl-[1H]-pyrrole        | 11                       |  |  |
| 2-Methylpyridine             | 4                        |  |  |
| 3-Methylpyridine             | 3                        |  |  |
| 2,4-Dimethylpyridine         | 3                        |  |  |
| 2,6-Dimethylpyrazine         | 10                       |  |  |
| Dimethylpyridine             | 3                        |  |  |
| 2-Ethyl-6-methylpyrazine     | 2                        |  |  |
| Trimethylpyrazine            | 2                        |  |  |
| 5-Ethyl-2-methylthiazole     | 4                        |  |  |
| 5-Ethyl-2-methylpyridine     | 8                        |  |  |
| 5-Ethenyl-2-methylpyridine   | 4                        |  |  |
| 2-Ethyl-3,5-dimethylpyrazine | 4                        |  |  |
| Tetramethylpyrazine          | 12                       |  |  |
| 3-Ethyl-2,6-dimethylpyridine | 7                        |  |  |

<sup>a</sup> The compounds were identified by comparing their mass spectra with those of reference substances.

<sup>b</sup>Ratio of peakheights in the extract of PG to that of RG.

## 2.9. High resolution gas chromatography/mass spectrometry (HRGC/MS) of extracts

For identification of the odorants, MS-analyses were performed with a MAT 95 S (Finnigan, Bremen, Germany) in tandem with the capillaries DB-5, DB-1701, and DB-FFAP. Mass spectra in the electron impact mode (MS-EI) were generated at 70 eV and in the chemical ionization mode (MS-CI) at 115 eV with isobutane as reagent gas.

#### 3. Results and discussion

High grade Swiss Gruyère cheese exhibits a slightly milky (smear, rind), vegetable- and animal-like (meat broth), and spicy (pepper) flavour with a white vinegar note (Lavanchy & Bütikofer, 1999). In contrast to the odour of cheese loaves of a high quality RG, the tainted Gruyère (PG) produced by a Swiss village cheese factory smelled intensively sweaty and cooked potato-like.

In order to get the first insight into the nature of the defect, dynamic headspace GC/MS (DHSGC/MS) analyses of alkaline extracts (obtained with the enriched off-flavour components) of the two cheese samples were performed. The results in Table 1 indicate that the cheese with the potato-like off-flavour had much higher concentrations of tetramethylpyrazine, 2,6-dimethylpyrazine, 1-methyl-[1H]-pyrrole, 5-ethyl-2-methylpyridine. As the odour of pyrazines is described as potato-like (Rychlik, Schieberle, & Grosch, 1998), these compounds were at first suspected of causing the off-flavour.

As DHSGC-MS does not provide any sensory information, the cheeses were then subjected to AEDA. This method has been shown to be a powerful means for evaluating the potent odorants in cheeses, e.g. in Swiss

Table 2

Neutral/alkaline odorants of Gruyère cheeses with a potato-like off-flavour (PG) and without an off-flavour as reference (RG)<sup>a</sup>

| Odorant <sup>b</sup>                               | Odour quality <sup>c</sup> | Sub-fraction <sup>d</sup> | RI <sup>e</sup>   |                      | $FD^{f}$ |     |
|--|----------------------------|---------------------------|-------------------|----------------------|----------|-----|
|  |                            |                           | DB-5 <sup>g</sup> | DB-1701 <sup>g</sup> | PG       | RG  |
| 2-/3-Methylbutanal (1/2)                           | Malty                      | 2                         | 649               | 724                  | 128      | 64  |
| Methyl 2-methylbutanoate (3)                       | Sweet                      | 1                         | 777               | 841                  | 1        | 16  |
| Ethyl 2-methylbutanoate (4)                        | Sweet                      | 1                         | 848               | 903                  | 4        | 64  |
| 2-Heptanone (5)                                    | Green                      | 2                         | 884               | 976                  | 16       | 64  |
| (Z)-4-Heptenal <sup>h</sup> (6)                    | Biscuit-like               | 2                         | 897               | 986                  | _        | 32  |
| Methional (7)                                      | Boiled potato              | 3                         | 905               | 1035                 | 512      | 512 |
| 2-Acetyl-1-pyrroline <sup>h</sup> (8)              | Roasty                     | AL                        | 921               | 1010                 | 16       | 32  |
| Dimethyltrisulphide (9)                            | Cabbage-like               | 1                         | 964               | 1030                 | 64       | 128 |
| Unknown  | Fatty                      | 2                         | 1024              |                      | 32       | 32  |
| Phenylacetaldehyde (10)                            | Honey-like                 | 2                         | 1041              | 1169                 | 64       | 128 |
| 2-Ethyl-3,5-dimethyl-pyrazine (11)                 | Earthy                     | AL                        | 1082              | 1148                 | 256      | 32  |
| Unknown  | Sweet                      | 1                         | 1091              | 1192                 | 8        | 16  |
| 2-Phenylethanol (12)                               | Honey-like                 | 2                         | 1114              | 1267                 | 32       | _   |
| (Z)-2-Nonenal (13)                                 | Green                      | 2                         | 1150              | 1254                 | 8        | 32  |
| 2,3-Diethyl-5-methylpyrazine (14)                  | Earthy                     | AL                        | 1159              | 1211                 | 64       | 16  |
| (E)-2-Nonenal (15)                                 | Green                      | 2                         | 1161              | 1269                 | 8        | 128 |
| Unknown  | Seasoning-like             | 1                         | 1172              | 1249                 | 64       | 32  |
| Ethyl octanoate (16)                               | Fatty, fruity              | 1                         | 1199              | 1259                 | 2        | 32  |
| (E,E)-2,4-Nonadienal <sup>h</sup> (17)             | Deep-fried                 | 2                         | 1212              | 1340                 | _        | 32  |
| Dimethyltetrasulphide (18)                         | Cabbage-like               | 1                         | 1209              | 1297                 | 64       | 128 |
| Indole (19)  | Mothball-like              | 3                         | 1293              | 1540                 | 32       | 16  |
| (E,E)-2,4-Decadienal (20)                          | Deep-fried                 | 2                         | 1313              | 1445                 | _        | 16  |
| Unknown  | Sweet, honey-like          | 1                         | 1349              | 1495                 | 128      | 32  |
| Unknown  | Raspberry-like             | 1                         | 1472              | 1589                 | _        | 32  |
| $\delta$ -Decalactone (21)                         | Sweet, coconut-like        | 3                         | 1494              | 1713                 | 64       | 64  |
| (Z)-6-Dodecen- $\gamma$ -lactone <sup>h</sup> (22) | Sweet                      | 3                         | 1657              | 1878                 | 64       | 32  |

<sup>a</sup>The numbers indicated in brackets refer to those listed under Section 2.2.

<sup>b</sup>The compound was identified by comparing it with the reference compound on the basis of the following criteria: RI on the two capillaries detailed in the Table, odour quality at the sniffing port, and mass spectra in the electron impact mode and the chemical ionization mode. <sup>c</sup>Odour description perceived at the sniffing port.

<sup>d</sup> Fractions in which the compound was identified; AL alkaline fraction; No.: fraction of column chromatography (see Section 2.5).

<sup>e</sup>Retention index.

<sup>f</sup>Flavour dilution factor.

<sup>g</sup>Different capillary columns (see Section 2.6).

<sup>h</sup> The mass spectra were too weak for an unequivocal interpretation. The compound was tentatively identified on the basis of the resting criteria detailed in footnote<sup>b</sup>.

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Emmentaler (Preininger et al., 1994), Camembert (Kubickova & Grosch, 1997), or Cheddar cheese (Milo & Reineccius, 1997). Moreover, AEDA is suitable for identifying the substances responsible for off-flavours, as Heiler and Schieberle (1996) reported for buttermilk. Therefore, PG and RG were both extracted with diethylether and the extracts distilled under vacuum to obtain the volatile fraction. The volatiles were then separated into neutral/alkaline (NAF) and acidic (AF) fractions, which were both subjected to AEDA. Gas chromatography-olfactometry of NAF revealed 21 and 25 odorous compounds in PG and RG, respectively (Table 2). The overwhelming majority of odorants were identified by mass spectrometry, after NAF was cleaned up by extracting the alkaline volatiles, and by column chromatography. Of these, the potato-like smelling methional showed the highest flavour dilution (FD) factor of 512 in both cheeses. In PG, the next lower FD factors were found for 2-ethyl-3,5-dimethylpyrazine (EDMP), 2-/3-methylbutanal and an unknown compound with a sweet odour quality. In contrast to this, AEDA of RG revealed dimethyltrisulphide, phenylacetaldehyde, (E)-2-nonenal and dimethyltetrasulphide to be further important odorants in this sample with FDfactors exceeding 128.

It was not surprising that methional exhibits such a high FD-factor in PG, because of its potato-like odour. But this odorant had the same high FD in RG, which did not have a potato-like off-flavour; hence, AEDA could not prove the impact of methional on this offflavour. However, methional is not essential for a potato-like flavour, e.g. in French fries (Wagner & Grosch, 1998) or in boiled potatoes (Mutti, 2000). Both of the latter studies attributed this odour quality to a combination of methanethiol and pyrazines. As highly volatile compounds such as the former are underestimated in AEDA because of losses during distilling steps, gas chromatography-olfactometry of static headspace samples (GCO-H) was subsequently performed. As is apparent from Table 3, methanethiol in RG showed the highest FD-factor of 32 corresponding to a minimal headspace volume of 0.6 mL. Further, important odorants in the headspace of RG were dimethylsulphide, dimethyltrisulphide and ethyl 2-methylbutanoate. By contrast, in PG dimethylsulphide had the highest FD of 16 followed by methanethiol, 3-methylbutanal and dimethyltrisulphide. Since the FD of methanethiol in PG was lower than in RG, this compound seemed not to be responsible for the flavour defect.

In the acidic phases of both cheeses, the 12 compounds listed in Table 4 showed FD-factors higher than 4. In both samples, the sweaty smelling mixture of 2- and 3-methylbutyric acid had the highest FD-factor followed by phenylacetic acid and butyric acid.

In summary, methanethiol as well as the neutral compounds methional, EDMP, 2-/3-methylbutanal, dimethyltrisulphide, phenylacetaldehyde, (E)-2-nonenal, dimethyltetrasulphide as well as the acidic volatiles 2- and 3-methylbutyric, phenylacetic and butyric acids were found to be potent odorants in Swiss Gruyère cheese. Of these compounds, butyric and isovaleric acids have already been previously suggested as being contributors to the Gruyère flavour (Bosset et al., 1993; Engels & Visser, 1994). Similarly, our results

Table 3

Results of the static headspace analysis of Gruyère cheeses with a potato-like off-flavour (PG) and without an off-flavour as reference (RG)<sup>a</sup>

| Odorant <sup>b</sup>                     | Odour quality <sup>c</sup> | RI (RTX-5) <sup>d</sup> | FD-factor <sup>e</sup> |    |  |
|--|----------------------------|-------------------------|------------------------|----|--|
|  |                            |                         | PG                     | RG |  |
| Acetaldehyde ( <b>34</b> )               | Green                      | < 500                   | 2                      | 2  |  |
| Methanethiol (35)                        | Sulphurous                 | < 500                   | 8                      | 32 |  |
| Dimethylsulphide (36)                    | Sulphurous                 | 505                     | 16                     | 16 |  |
| 2-Methylpropanal (37)                    | Malty                      | 556                     | 2                      | 1  |  |
| 3-Methylbutanal (2)                      | Malty                      | 654                     | 8                      | 8  |  |
| 2-Methylbutanal (1)                      | Malty                      | 664                     | 4                      | 1  |  |
| Methyl 2-methylbutanoate (3)             | Sweet                      | 777                     | 1                      | 1  |  |
| Dimethyldisulphide (38)                  | Sulphurous                 | 741                     | 1                      | 2  |  |
| Ethyl 2-methylbutanoate <sup>f</sup> (4) | Sweet                      | 848                     | 4                      | 8  |  |
| Methional <sup>f</sup> (7)               | Boiled potato              | 909                     | 1                      | 1  |  |
| Dimethyltrisulphide (9)                  | Cabbage-like, sulphurous   | 968                     | 8                      | 16 |  |

<sup>a</sup>The numbers indicated in brackets refer to those listed under Section 2.2.

<sup>b</sup>The compound was identified by comparing it with the reference compound on the basis of RI on capillary RTX-5, odour quality at the sniffing port, and mass spectra in EI-Mode.

<sup>c</sup>Odour description perceived at the sniffing port.

<sup>d</sup>Retention index on capillary RTX-5.

<sup>e</sup>A headspace volume of 20 mL was equated to a flavour dilution (FD) factor of 1. The FD-factor values of the other odorants were calculated on this basis.

<sup>1</sup>The mass spectra were too weak for an unequivocal interpretation. The compound was tentatively identified on the basis of the resting criteria detailed in footnote<sup>b</sup>.

Table 4

| Odorant <sup>b</sup>                                    | Odour quality <sup>c</sup> | RI (DB-FFAP) <sup>d</sup> | FD <sup>e</sup> |     |  |
|---|----------------------------|---------------------------|-----------------|-----|--|
|   |                            |                           | PG              | RG  |  |
| Propionic acid (23)                                     | Fruity, pungent            | 1524                      | 4               | 16  |  |
| Methylpropionic acid (24)                               | Sweaty, rancid             | 1562                      | 32              | 8   |  |
| Butyric acid (25)                                       | Sweaty                     | 1622                      | 256             | 128 |  |
| 2- and 3-Methylbutyric acid (26/27)                     | Sweaty                     | 1662                      | 8196            | 512 |  |
| Unknown   | Sweet                      | 1802                      | 16              | 8   |  |
| Hexanoic acid (28)                                      | Goat-like                  | 1841                      | 32              | 16  |  |
| Unknown   | Sweet                      | 1912                      | 16              | 8   |  |
| 4-Hydroxy-2,5-dimethyl-3-(2H)furanone (29)              | Strawberry-like            | 2033                      | 64              | 32  |  |
| 2-Ethyl-4-hydroxy-5-methyl-3-(2H)furanone (30)          | Strawberry-like            | 2061                      | 32              | 32  |  |
| 3-Hydroxy-4,5-dimethyl-2-(5H)furanone <sup>f</sup> (31) | Seasoning-like             | 2199                      | 32              | 16  |  |
| Phenylacetic acid (32)                                  | Honey-like                 | 2569                      | 4096            | 512 |  |
| Phenylpropanoic acid (33)                               | Flowery                    | 2638                      | 256             | 128 |  |

<sup>a</sup>The numbers indicated in brackets refer to those listed under Section 2.2.

<sup>b</sup>The compound was identified by comparing it with the reference compound on the basis of the following criteria: retention index on capillary DB-FFAP, odour quality at the sniffing port, and mass spectra in the electron impact mode and the chemical ionisation mode.

<sup>c</sup>Odour description perceived at the sniffing port.

<sup>d</sup>Retention index on capillary DB-FFAP.

<sup>e</sup>Flavour dilution factor.

<sup>f</sup>The mass spectra were too weak for an unequivocal interpretation. The compound was tentatively identified on the basis of the resting criteria detailed in footnote<sup>b</sup>.

confirmed earlier reports that 3-methylbutanal (Bosset & Liardon, 1984; Engels, Dekker, de Jong, Neeter, & Visser, 1997) as well as dimethyltrisulphide (Engels et al., 1997) play an important role in the odour of this variety of cheese.

#### 4. Conclusions

Based on the results of AEDA of acidic volatiles, 2-/3methyl butyric and butyric acids seem to be responsible for the sweaty odour of PG. However, the cause of its potato-like taint is still not clear. Unlike in French fries (Wagner & Grosch, 1998) and in boiled potatoes (Mutti, 2000), GCO-H gives no indication that methanethiol is the causal substance. The results of AEDA, however, lead us to conclude that, due to their higher FD in PG, EDMP and 2,3-diethyl-5-methylpyrazine (DEMP) may evoke the defect. But both AEDA and GCO-H suffer from different limitations, the lack of precision and possible discriminations of these olfactory methods being the decisive ones (Grosch, 1993). Furthermore, the latter methods do not consider synergistic or suppressive effects of different odorants in a flavour mixture, since the compounds are evaluated separately after gas chromatography. The lacking precision and possible discriminations of the olfactory methods can be overcome by accurate quantifications. By subsequent sensory analyses of models simulating the cheeses with and without off-flavour, the interactions of the odorants can be considered, and those compounds can be identified, which are responsible for the flavour defect.

These investigations will be reported in the second part of this study (Rychlik & Bosset, 2002).

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