Comparison of aroma active and sulfur volatiles in three fragrant rice cultivars using GC–Olfactometry and GC–PFPD

Kanjana Mahattanatawee a,*, Russell L. Rouseff b

a Department of Food Technology, Faculty of Science, Siam University, 38 Petchkasem Road, Phasi-Charoen, Bangkok 10160, Thailand
b Institute of Food and Agricultural Sciences, Citrus Research and Education Center, University of Florida, 700 Experiment Station Road, Lake Alfred, FL 33850, USA

A R T I C L E   I N F O

Article history:
Received 13 October 2013
Received in revised form 21 December 2013
Accepted 30 December 2013
Available online 8 January 2014

Keywords:
PCA
Cooked rice
Headspace SPME

A B S T R A C T

Aroma volatiles from three cooked fragrant rice types (Jasmine, Basmati and Jasmati) were characterised and identified using SPME GC–O, GC–PFPD and confirmed using GC–MS. A total of 26, 23, and 22 aroma active volatiles were observed in Jasmine, Basmati and Jasmati cooked rice samples. 2-Acetyl-1-pyrroline was aroma active in all three rice types, but the sulphur-based, cooked rice character impact volatile, 2-acetyl-2-thiazoline was aroma active only in Jasmine rice. Five additional sulphur volatiles were found to have aroma activity: dimethyl sulphide, 3-methyl-2-butene-1-thiol, 2-methyl-3-furanthiol, dimethyl trisulphide, and methional. Other newly-reported aroma active rice volatiles were geranyl acetate, β-damascone, β-damascenone, and α-ionone, contributing nutty, sweet floral attributes to the aroma of cooked aromatic rice. The first two principal components from the principal component analysis of sulphur volatiles explained 60% of the variance. PC1 separated Basmati from the other two cultivars and PC2 completely separated Jasmine from Jasmati cultivars.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Rice (Oryza sativa L.) is a major human dietary component in many countries. Fragrant rice cultivars are considered more desirable and of higher quality, primarily due to their pleasing aroma. 2-Acetyl-1-pyrroline (2-AP) is widely acknowledged as the character impact volatile in fragrant rice and has been described as producing a “popcorn-like” or “pandan-like” odour (Buttery, Ling, & Juliano, 1982; Paule & Powers, 1989). 2-AP is also responsible for the characteristic aroma of white bread, pandan (Pandanus amaryllifolius) leaves and bread flowers (Vallais glabra) (Wongporchawai, Sriseadka, & Choovisase, 2003). Although 2-AP is found in non-aromatic rice, the concentration is at trace levels (Buttery, Ling, & Mon, 1986; Mahatheeranont, Keawsa-ard, & Dumri, 2001; Maraval et al., 2008). An alternative hypothesis is that 2-AP is present in a starch-bound form in non-fragrant cultivars (Yoshihashi, 2001; Maraval et al., 2008). 2-Acetyl-1-pyrroline was aroma active in all three rice types, but the sulphur-based, cooked rice character impact volatile, 2-acetyl-2-thiazoline was aroma active only in Jasmine rice. Five additional sulphur volatiles were found to have aroma activity: dimethyl sulphide, 3-methyl-2-butene-1-thiol, 2-methyl-3-furanthiol, dimethyl trisulphide, and methional. Other newly-reported aroma active rice volatiles were geranyl acetate, β-damascone, β-damascenone, and α-ionone, contributing nutty, sweet floral attributes to the aroma of cooked aromatic rice. The first two principal components from the principal component analysis of sulphur volatiles explained 60% of the variance. PC1 separated Basmati from the other two cultivars and PC2 completely separated Jasmine from Jasmati cultivars.

2. Materials and methods

2.1. Rice samples

Jasmine rice (Khao Dawk Mali 105) was obtained from a producer in Surin province located in the eastern part of Thailand. The sample was put in a laminated aluminium bag, purged with nitrogen, then vacuum sealed and kept at 4°C until analysed.
Basmati (Indian fragrance rice) and Jasmati (RiceSelect™, American grown Jasmine-style long grain rice) were obtained from a super-market in the United States and were packed in a glass bottle with a screw-top lid, purged with nitrogen and kept at 4 °C until analysed. In an effort to cook the rice samples in the form they would normally be prepared for consumption, 5 g of rice and 5 g of distilled water was added into a 40-mL glass vial, the headspace purged with nitrogen gas and loosely sealed with a Teflon-coated septum screw cap and placed into the bottom of a rice cooker (Black & Decker, Model No. RC3406) at ~100 °C, for 18 min.

2.2. Headspace sampling, SPME optimisation conditions

Five solid phase microextraction (SPME) fibre types: PDMS, CAR/DVB, PDMS/DVB, CAR/PDMS and DVB/CAR/PDMS (Supelco, Bellefonte, PA) were evaluated for their ability to extract and concentrate the headspace volatiles of cooked rice. Equilibrium temperatures of 30, 40, 50 and 60 °C, equilibrium times of 15, 30, 45, and 75 min., and exposure times of 5, 15, 30, 45, and 60 min. were evaluated to determine the optimal conditions to extract rice volatiles using each SPME fibre type. As the result of optimisation, DVB/CAR/PDMS was employed to extract and concentrate the headspace volatiles of cooked rice. Cooked rice samples were placed in a water bath at 30 °C and equilibrated for 15 min. before sampling. The SPME fibre was inserted into the headspace of the rice sample and exposed for 30 min. Subsequently, the fibre was thermally desorbed in the GC injector port for 5 min. (220 °C).

2.3. Gas chromatography–FID/olfactometry

Chromatography was performed using an Agilent 6890N GC (Agilent Technologies, Santa Clara, CA) equipped with a sniffing port and FID (flame ionisation detector). Samples were separated and evaluated using a polar DB-wax column (J&W Scientific, Folsom, CA; 30 m × 0.32 mm i.d. × 0.5 μm film thickness) and a non-polar ZB-5 column (5% phenyl, 95% dimethyl-polysiloxane, 30 m × 0.32 mm i.d. × 0.5 μm film thickness; Phenomenex, Torrance, CA). The oven temperature was programmed from 40 to 240 °C at 7 °C/min. Helium was the carrier gas at flow rate of 2.0 mL/min. Injector and detector temperature were 220 °C and 275 °C, respectively. Injections were splitless and a 0.75-mm injector liner was employed to improve peak shape and chromatographic efficiency. The column effluent was split, 1/3rd of the flow was conducted to the FID and the other 2/3rds to the olfactory port for sniffing, previously mixed with warm humid air. Two assessors, trained as described by Bazemore and co-workers (Bazemore, Goodner, & Rouseff, 1999) evaluated each sample in duplicate on both ZB-5 and DB-Wax columns. Odour descriptors and retention times were recorded for each sample. Assessors rated odour intensity continuously throughout the chromatographic separation process using a linear potentiometer as previously described (Bazemore et al., 1999). Intensities of odour-active compounds of each GC–O run were normalised so the highest intensity from each assessor was given a score of 10 (Mahattanatawee, Ruiz Perez-Cacho, Davenport, & Rouseff, 2007). The normalised intensities of all runs were averaged. A peak was considered odour-active only if at least half of the panel responses found a similar odour quality at the same retention time. Olfactory assessor and FID responses were separately recorded and integrated using two channels and ChromPerfect software version 5.0 (Justin Innovations, Inc., Palo Alto, CA).

2.4. Mass spectrometry

GC–MS was employed to confirm the identities of the odour-active volatile identified in the GC–O experiments. Volatiles were separated using an RTX-5 capillary column (column length 60 m, inner diameter 0.25 mm, film thickness 0.50 μm; Restek, Bellefonte, PA) and identified using a Perkin–Elmer Clarus 500 quadrupole mass spectrometer equipped with Turbo Mass software (Perkin–Elmer, Shelton, CT). Helium was used as the carrier gas at 2 mL/min. The oven temperature program consisted of a linear gradient from 40 to 240 °C at 7 °C/min. with a 2 min. initial hold and a 7.5 min. final hold. The source was kept at 200 °C, and the transfer line was maintained at 260 °C and injector at 220 °C. Electron impact ionisation in the positive ion mode was used (70 eV), either scanning a mass range from m/z 25 to 300 or acquiring data in the selected ion mode at specific m/z values. Mass spectra matches were made by comparison with NIST 2005 version 2.0 standard spectra (NIST, Gaithersburg, MD). Only those compounds with spectral fit values > 800 were considered positive identifications. Authentic standards obtained from Sigma–Aldrich Co. LLC, (except 2-acetyl-1-pyrridine) were used to establish retention values and confirm spectral identifications.

2.5. Gas chromatography–FPFPD

Sulphur-compounds were detected using a pulsed flame photometric detector (FPFPD) in the square root mode (Model 5380, OI Analytical Co., College Station, TX) installed on an Agilent 6890N GC. Separations were accomplished using two different capillary columns as described above in the GC–FID and GC–O sections. The oven temperature program used was the same as that employed for the GC–O studies. Injector temperature was 200 °C (to minimise possible thermal degradations) and the detector temperature was set at 250 °C. Odour-active sulphur-containing compounds were confirmed by comparison with authentic standards on both columns and LRI value matching.

2.6. Multivariate statistics

The sulphur volatile data set included integrated FPFPD peak area values (ChromPerfect software version 5.0) from the three rice types. Principal component analysis (PCA) was carried out using Unscrambler version 10 from Camo (Woodbridge, NJ). In order not to overemphasise the larger peaks, the data from all peaks were normalised by setting mean values to zero and scaling on the basis of one standard deviation.

3. Results and discussion

3.1. Cooked rice aroma active volatiles by gas chromatography–olfactometry

Plant volatiles are secondary metabolites which are under genetic control. Different cultivars will have different genetics and thus can be expected to have different volatile profiles. Conversely, plants with very similar genetics would be expected to have very similar volatile profiles. Cooked rice aroma active volatiles of Jasmine rice, Basmati rice and Jasmati rice were analysed by GC–FID and GC–O. Shown in Fig. 1 is the FID chromatogram and inverted olfactory arogram from Jasmine rice. A total of 26, 23, and 22 aroma active volatiles were detected in Jasmine, Basmati, and Jasmati rice, respectively (Table 1). Three prior GC–O studies on cooked rice have reported 39, 41 and 36 aroma active volatiles (Jezussek, Juliano, & Schieberle, 2002; Maraval et al., 2008; Yang, Shewfelt, Lee, & Kays, 2008). (Maraval et al., 2008) employed solvent extraction and frequency of detection to determine the aroma active volatiles in four cooked rice cultivars. (Jezussek et al., 2002) used solvent extraction and AEDA GC–O to examine aroma-active volatiles in four brown rice cultivars. (Yang, Shewfelt, et al., 2008) employed dynamic headspace with Tenax trapping to
Fig. 1. GC–FID and GC–O (inverted) chromatograms of cooked Jasmine rice. Numbers correspond to the compounds listed in Table 1.

Examine the aroma active volatiles in five aromatic and one non-aromatic rice samples. The cooked rice character impact volatile, 2-acetyl-1-pyrroline, was one of the more pronounced odorants in all studies. Even though the total number of aroma active volatiles was about the same for all studies, only seven aroma-active volatiles were common to all three. Common aroma active volatiles in the three previous GC–O studies were hexanal, octanal, 2-acetyl-1-pyrroline, (E,E)-2,4-nonenal, (E)-2- nonenal, 4-vinyl-2-methoxyphenol and indole. Five of these volatiles are also listed in Table 1.

Two volatiles in Table 1 were described as “cooked Jasmine rice”. One was the well-known 2-acetyl-1-pyrroline (2-AP, popcorn-like) (Buttery et al., 1982) observed at a ZB-5 alkane index (Linear Retention Index, LRI) value of 924. The second cooked rice character impact volatile, 2-acetyl-2-thiazoline (2-AT) was observed at a ZB-5 LRI value of 1112. There was also a sulphur peak (using GC–PFPD) at this identical retention time. Authentic 2-AT also produced a peak at this standardized retention value. Identification of 2-AT was confirmed from the GC–MS TIC chromatographic standard retention value match and further confirmed by matching the mass spectrum from a 2-AT standard with that from the rice sample (Mahattanatawee & Rouseff, 2008).

As seen from the average aroma intensity values in Table 1, the aroma intensity of 2-AT in cooked Jasmine rice was only about 1/2 that of the major character impact compound 2-AP. The aroma of 2-AT was first identified in beef broth and described as roasted and popcorn-like (Planck, Tonsbeek, & Copier, 1971). It has since been reported as an aroma impact compound in roasted beef (Cerny & Grosch, 1993) as well as other foods including chicken broth (Gasser & Grosch, 1990) and roasted white sesame seeds (Schieberle, 1993). In this study, 2-AT was observed as an additional character impact volatile in cooked Jasmine rice. As shown in Fig. 2, 2-AT was not detected in Basmati or Jasmati rice.

Thirty aroma active volatiles were detected, of which twenty-seven were identified (Table 1). Of the 30 volatiles detected five were novel: 3-methyl-2-buten-1-thiol, geranyl acetate, β-damascene, β-damascenone and α-ionone. 3-Methyl-2-buten-1-thiol contributed to the nutty, sulphury note detected only in Jasmine

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Odour descriptor</th>
<th>LRI DB-wax</th>
<th>LRI ZB-5</th>
<th>Odour intensity Jasmine</th>
<th>Odour intensity Basmati</th>
<th>Odour intensity Jasmati</th>
<th>Previously reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dimethyl sulphide</td>
<td>Cooked, sulphy</td>
<td>760</td>
<td>690</td>
<td>2.15</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Hexanal</td>
<td>Green</td>
<td>1086</td>
<td>799</td>
<td>8.00</td>
<td>9.96</td>
<td>9.85</td>
</tr>
<tr>
<td>3</td>
<td>3-Methyl-2-buten-1-thiol</td>
<td>Nutty, sulphy</td>
<td>1093</td>
<td>824</td>
<td>3.75</td>
<td>3.75</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Octanal</td>
<td>Citrusy</td>
<td>1290</td>
<td>999</td>
<td>7.97</td>
<td>9.38</td>
<td>9.98</td>
</tr>
<tr>
<td>5</td>
<td>1-Octen-3-one</td>
<td>Mushroom</td>
<td>1303</td>
<td>980</td>
<td>7.36</td>
<td>7.05</td>
<td>7.51</td>
</tr>
<tr>
<td>6</td>
<td>2-Methyl-3-furanthiol</td>
<td>Meaty</td>
<td>1313</td>
<td>873</td>
<td>5.45</td>
<td>5.57</td>
<td>4.40</td>
</tr>
<tr>
<td>7</td>
<td>2-Acetyl-1-pyrroline</td>
<td>Cooked jasmine rice</td>
<td>1342</td>
<td>924</td>
<td>9.93</td>
<td>9.88</td>
<td>9.50</td>
</tr>
<tr>
<td>8</td>
<td>Hexanal</td>
<td>Green</td>
<td>1376</td>
<td>869</td>
<td>6.28</td>
<td>5.87</td>
<td>5.53</td>
</tr>
<tr>
<td>9</td>
<td>Dimethyl trisulphide</td>
<td>Sulfur, cabbage-like</td>
<td>1384</td>
<td>979</td>
<td>8.68</td>
<td>10.00</td>
<td>9.82</td>
</tr>
<tr>
<td>10</td>
<td>Nonanal</td>
<td>Green, citrusy, soapy</td>
<td>1396</td>
<td>1106</td>
<td>4.95</td>
<td>3.53</td>
<td>3.57</td>
</tr>
<tr>
<td>11</td>
<td>(E)-2-Octenal</td>
<td>Green, nutty</td>
<td>1435</td>
<td>1062</td>
<td>3.63</td>
<td>7.31</td>
<td>3.07</td>
</tr>
<tr>
<td>12</td>
<td>Unknown</td>
<td>Musty</td>
<td>1439</td>
<td></td>
<td></td>
<td></td>
<td>2.95</td>
</tr>
<tr>
<td>13</td>
<td>Methional</td>
<td>Cooked potato</td>
<td>1456</td>
<td>910</td>
<td>8.95</td>
<td>9.98</td>
<td>8.82</td>
</tr>
<tr>
<td>14</td>
<td>Decanal</td>
<td>Fatty, citrusy</td>
<td>1506</td>
<td>1202</td>
<td>4.01</td>
<td>3.44</td>
<td>4.47</td>
</tr>
<tr>
<td>15</td>
<td>(E)-2-Nonenal</td>
<td>Metallic</td>
<td>1540</td>
<td>1161</td>
<td>10.00</td>
<td>9.96</td>
<td>10.00</td>
</tr>
<tr>
<td>16</td>
<td>1-Octanal</td>
<td>Fatty, metallic</td>
<td>1575</td>
<td>1062</td>
<td>3.31</td>
<td></td>
<td>3.75</td>
</tr>
<tr>
<td>17</td>
<td>(E,E)-2,6-Nonadienal</td>
<td>Green, metallic</td>
<td>1593</td>
<td>1157</td>
<td>5.11</td>
<td>5.10</td>
<td>3</td>
</tr>
<tr>
<td>18</td>
<td>Unknown</td>
<td>Roasted, nutty</td>
<td>1652</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(E)-2-Decenal</td>
<td>Green herbal geranium</td>
<td>1656</td>
<td>1275</td>
<td>8.28</td>
<td>7.72</td>
<td>4.54</td>
</tr>
<tr>
<td>20</td>
<td>(E,E)-2,4-Nonadienal</td>
<td>Fatty, metallic</td>
<td>1711</td>
<td>1218</td>
<td>4.84</td>
<td>4.18</td>
<td>4.30</td>
</tr>
<tr>
<td>21</td>
<td>Dodecanal</td>
<td>Minty, soapy</td>
<td>1727</td>
<td>1419</td>
<td>4.16</td>
<td>4.34</td>
<td>4.52</td>
</tr>
<tr>
<td>22</td>
<td>2-Acetyl-2-thiazoline</td>
<td>Cooked jasmine rice</td>
<td>1766</td>
<td>1112</td>
<td>5.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Geranyl acetate</td>
<td>Floral</td>
<td>1780</td>
<td>1382</td>
<td>7.55</td>
<td>7.04</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>(E,E)-2,4-Decadienal</td>
<td>Fatty, metallic</td>
<td>1820</td>
<td>1318</td>
<td>4.46</td>
<td>5.45</td>
<td>3.69</td>
</tr>
<tr>
<td>25</td>
<td>β-Damascone</td>
<td>Sweet honey</td>
<td>1828</td>
<td>1425</td>
<td>4.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>β-Damascenone</td>
<td>Sweet honey</td>
<td>1833</td>
<td>1395</td>
<td>6.50</td>
<td>4.64</td>
<td>5.44</td>
</tr>
<tr>
<td>27</td>
<td>α-ionone</td>
<td>Floral</td>
<td>1861</td>
<td>1459</td>
<td>9.80</td>
<td>8.11</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Unknown</td>
<td>Medicine</td>
<td>1867</td>
<td></td>
<td></td>
<td>4.60</td>
<td>4.65</td>
</tr>
<tr>
<td>29</td>
<td>2-Phenylethanol</td>
<td>Floral</td>
<td>1907</td>
<td>1106</td>
<td>3.23</td>
<td></td>
<td>2–3, 8</td>
</tr>
<tr>
<td>30</td>
<td>β-ionone</td>
<td>Raspberry, floral</td>
<td>1952</td>
<td>1496</td>
<td>8.75</td>
<td>6.23</td>
<td>3.06</td>
</tr>
</tbody>
</table>

*The volatile compounds have been identified by comparing their retention behaviour on DB-wax and ZB-5 columns, their aroma quality and their MS spectra. In addition sulphur volatile compounds were confirmed by PFPD response on both columns with authentic standards.  

rice and has been reported as a potent odorant of coffee brews prepared from roasted Arabica (Coffea arabica) (Semmelroch & Grosch, 1996). Geranyl acetate contributed to floral note and has been reported in honey (Serra Bonvehi & Ventura Coll, 2003). The potent carotenoid degradation volatiles (β-damascene, β-damascenone and α-ionone) were responsible for sweet honey and floral notes. Norisoprenoid volatiles are derived from enzymatic carotenoid cleavage (dioxygenase1) or thermal degradation of carotenoids (Ilg, Beyer, & Al-Babili, 2009; Kanasawud & Crouzet, 1990; Mahattanatawee et al., 2005). These potent volatiles have been detected in various foods, such as orange, tomato, black tea, coffee and honey (Mahattanatawee et al., 2005; Serra et al., 2003; Semmelroch et al., 1996).

The 27 identified aroma volatiles in Table 1 consist of 11 aldehydes, 5 ketones, 4 sulphur compounds, 3 alcohols, 3 heterocyclics and 1 ester. Numerically, the aldehydes comprised 41% of all aroma-active volatiles in cooked rice followed by ketones (18%), sulphur compounds (15%), alcohols (11%), heterocyclics (11%), and esters (4%). Other cooked rice volatile studies (Yang, Lee, Jeong, Kim, & Kays, 2008) also reported that aldehydes comprised most of the volatiles observed. Eleven aldehydes listed in Table 1 have been previously reported in rice and the sources of these reports are listed in the last column. Ten of the 11 aldehydes were found in all three types of cooked rice. These common aldehydes are hexanal, octanal, nonanal, (E)-2-octenal, decanal, (E)-2-nonenal, (E,E)-2,4-decadienal, (E,E,E)-2,4,6-nonatrienal, (E,E,E)-2,4-decadienal and (E,E,E,E)-2,4,6,8-tetradecadienal.

In order to get an estimation of how these aroma-active volatiles would contribute to overall aroma impression, all 30 aroma active volatiles were grouped in eight general aroma categories. The eight categories consisted of green, sweet/fruity/floral, minty/citrusy, cooked/mushroom/musty, roasted/nutty, fatty/metallic, sulphury/meaty, and medicine. The group membership consisted of: 1. green (hexanal, hexanol, (E)-2-decenal); 2. sweet/fruity/floral (geranyl acetate, β-damascene, β-damascenone, α-ionone, 2-phenylethanol, β-ionone); 3. minty/citrusy (octanal, nonanal); 4. cooked/mushroom/musty (1-octen-3-one, methional); 5. roasty/nutty (2-acetil-1-pyrroline, 2-acetyl-2-thiazoline); 6. fatty/metallic ([E]E-2-octenal, decanal, (E)-2-nonenal, 1-octanal, (E,E)-2,6-nonadienal, (E,E,E)-2,4-nonadienal, dodecanal, (E,E)-2,4-decadial); 7. sulphury/meaty (dimethyl sulphide, 3-methyl-2-buten-1-thiol, 2-methyl-3-furanthiol, dimethyl trisulfide) and 8. medicine (unknown wax LRI 1867). When the aroma intensities for each aroma group are summed, Jasmati contained 35% less roasty/nutty total aroma intensity than Jasmine rice and Basmati. The “medicine” aroma was not observed in Jasmine rice. Jasmine rice contained 35% more sweet/fruity/floral total intensity than Basmati and 79% more than Jasmati rice.

3.2. Separation of sulphur volatiles

As shown in Fig. 2, a total of 37 sulphur volatiles were detected in the three types of fragrant rice. Only 6 of the 37 sulphur peaks are labelled in Fig. 2 because they were the only ones associated with aroma activity. Three aroma active volatiles, 2-methyl-3-furanthiol, dimethyl trisulfide, and methional, were observed in all three fragrant rice types. Two new rice sulphur volatiles, 3-methyl-2-buten-1-thiol and 2-AT were only detected in Jasmine rice. 2-AT was only detected in cooked Jasmine rice. 2-AT has been reported as a key odorant of Maillard type reaction product in foods containing cysteine. Model studies indicate 2-[(1-hydroxyethyl)-4,5-dihydrothiazole (HDT) is a key intermediate in the thermal generation of 2-AT formed simply by heating for 10 min in water (Hofmann & Schieberle, 1995). Thus the rice cooking conditions (100 °C, 18 min) would be sufficient for the formation of 2-AT.

Some aroma-active sulphur volatiles are extremely potent and although producing strong aroma notes, often produce only a small sulphur PFPD peak. An example is shown in Fig. 2 for 2-methyl-3-furanthiol at the normal attenuation this peak would generally be overlooked. It is only due to the fact that this compound produces a mid-level meaty aroma with GC–O at this retention value that further examination was warranted. Upon further expansion of

---

**Fig. 2.** Comparison sulphur chromatograms from Jasmine (top), Basmati (middle) and Jasmati (bottom) cooked rice.

**Fig. 3.** Score and load (bottom) Principal component analysis plots of the sulphur volatiles from the three types of fragrant rice samples.
the sulphur signal in this region (shown in the inset) the 2-methyl-3-furanthiol peak can be observed and even then it is not well resolved.

The primary sources for the sulphur-containing volatiles in rice are from the degradation of the sulphur-containing amino acids, methionine and cysteine, which have been reported in rice (Prippis-Nicou, De Revel, Bertrand, & Maujean, 2000; Saikusa, Horino, & Mori, 1994; Tressl, Helak, Martin, & Kersten, 1989). The relative levels of these amino acids in the different rice samples as well as possible chemical cofactors are probably responsible for the differences in the sulphur volatiles observed in Fig. 2.

3.3. Principal component analysis of cooked rice sulphur volatiles

Principal component analysis, PCA, is a multivariate pattern recognition procedure which was employed to determine if there were differences in the sulphur volatile patterns from the three rice types. Shown in Fig. 3 are the PCA score (upper) and load (bottom) plots from 37 integrated sulphur peaks from the three rice samples reported in triplicate. Since there were at least two orders of magnitude difference in the sulphur peak areas, the data for each sulphur peak was mean centred and scaled to one standard deviation. The grouping of the three triplicate rice samples indicates that the GC–5 chromatographic peak areas were fairly consistent. The first principal component separated the Basmati samples from the other two fragrant rice samples and PC2 separated the Jasmine from the Basmati samples. The first two principal components combined to describe 60% of the variance. The fact that the three groups did not overlap indicates that each of the three rice types had a unique sulphur peak pattern.

The load values indicate that PC1 is separated primarily by sulphur peak area values at 14.9 and 13.25 min in the positive half and by the values at 1.52 and 12.13 in the negative half. The PC2 axis is defined primarily by peak values at 10.71 and 1.43 (which was aroma active) and in the negative half by the values at 15.3 min. Therefore the Jasmine samples were characterised by higher values for the peaks at 12.13, 1.74 and 12.5 (the aroma active 2-AT). Correspondingly the values at 1.52 and 14.77 helped define the region for the Jasmati samples. The Basmati samples were characterised by numerous sulphur peaks, of which four were aroma-active.

4. Conclusion

Headspace SPME was employed to analyse aroma active volatiles in cooked Jasmine, Basmati and Jasmati rice. They can be distinguished by the pattern of sulphur volatiles via PCA analysis. The character impact compound, 2-AP was found in all three cultivars. A sulphur-containing “cooked rice” character impact compound, 2-AT was detected in cooked jasmine rice. There are five additional new aroma active volatiles, 3-methyl-2-buten-1-thiol, geranyl acetate, β-damascone, β-damascenone and α-ionone which contribute nutty, sweet floral character to the aroma of cooked aroatic rice. When all 30 aroma-active volatiles were grouped in eight general aroma categories and the aroma intensities for each aroma group were summed, Jasmati contained 35% less roasty/nutty total aroma intensity than Jasmine and Basmati rice. The “medicine” aroma was not observed in Jasmine rice. Jasmine rice contained 35% more sweet fruity/floral total intensity than Basmati and 79% more than Jasmati rice. The findings of this study as basic knowledge can be useful in breeding rice cultivars.

Acknowledgements

This study was supported by the Thailand Research Fund (TRF), Office of the Higher Education Commission (OHEC) Thailand, Siam University, Bangkok Thailand and the University of Florida, USA.

References


