IMPACT FLAVOUR COMPOUNDS IN COOKED RICE CULTIVARS FROM THE CAMARGUE AREA (FRANCE)

I. Maraval¹, C. Mestres¹, K. Pernin²-⁴, F. Ribeyre¹, R. Boulanger¹, E. Guichard²-⁴, Z. GUNATA⁵

¹ UMR Qualisud, CIRAD, 73 Rue J.F. Breton, Montpellier F-34398 France
² INRA, UMR1129 FLAVIC, F-21000 Dijon, France
³ ENESAD, UMR1129 FLAVIC, F-21000 Dijon, France
⁴ Université de Bourgogne, UMR1129 FLAVIC, F-21000 Dijon, France
⁵ UMR Qualisud, Université de Montpellier II, place E. Bataillon, 34095 Montpellier Cedex 5, France

Abstract

Rice from two scented (Aychade, Fidji) and one nonscented (Ruille) cultivars from Camargue area (France) together with one Asian scented rice (Thai) were cooked and volatile compounds were extracted by dichloromethane/pentane (1:2, v/v) solvent mixture. 40 odorous compounds were noticed during GC-O analysis of the organic extracts, amongst which oct-1-en-3-one and 2-acetyl-1-pyrroline were almost constantly perceived. Hierarchical cluster analysis (HCA) of perceived odours enabled to distinguish the groups of rice cultivars. 60 compounds were identified and quantified by GC-MS. New odour-active components of cooked rice were detected for the first time including oct-3-en-2-one, 2-methylpropanoic acid, γ-decalactone and δ-decalactone. A principal component analysis (PCA) differentiated scented cultivars from a non-scented one and scented rice cultivars from Camargue from Thai sample.

Introduction

Scented rice is highly appreciated in Asian diet by its specific aroma. Its consumption has tendency to increase in North America and Europe including France. New scented cultivars suitable to temperate climate have been developed in the Camargue, a traditional rice cultivation area in the south of France [1]. 2-acetyl-1-pyrroline (2AP) developing a roasty popcorn-like odour, was reported as an important contributor to the scented character of cooked rice [2-5]. However, other volatile compounds, such as aldehydes, volatile phenols, and sulphur- and nitrogen-based compounds were considered as contributors to the overall cooked aroma of scented rice [6,7]. In the present study the flavour compounds of cooked rice from two scented (Aychade and Fidji) rice cultivars from the Camargue area were compared with those of a well-known Asian scented rice cultivar (Thai) through GC-O and GC-MS analyses [8,9]. Additionally one non-scented rice cultivar (Ruille) from the Camargue area has been subject of the study.

Experimental

Rice Samples. Aychade, Fidji and Ruille were harvested in 2006 in the Camargue area. Thai was purchased as milled grain in a French supermarket.

Extraction of flavour compounds and representativeness of the organic extracts. Rice (5 g) was cooked with mineral water (10 mL) in open steam for 20 min. After
resting for 10 min, the freshly cooked rice was frozen under liquid nitrogen followed by the addition of 30 g of anhydrous sodium sulphate. The ensemble was ground to flour under liquid nitrogen and extracted with 100 mL of organic solvent or organic solvent mixtures: dichloromethane, dichloromethane/pentane (1:2, v/v), ether, and ether/pentane (1:1, v/v). The organic extracts were concentrated to ca. 0.5 mL through a Vigreux column and a Kuderna-Danish concentrator fitted with a Snyder column (Jezussek et al. [6]). The representativeness of the organic extracts was estimated by sensory analysis. Panellists were asked to note the similarity between the odour of the organic extracts and the freshly cooked rice. More details are reported elsewhere [10].

**GC-O and GC-MS Analysis.** The dichloromethane/pentane (1:2, v/v) organic extracts from four cooked rice were analysed by GC-O with odour detection frequency method. Semi-quantification of volatiles were performed by GC-MS analysis using 2,4,6-trimethylpyridine as internal standard [10].

**Statistical treatment.** HCA was performed with XL-STAT Prov.7 (Addinsoft), PCA with Statistica v.7.1 (StatSoft).

**Results and discussion**

**Representativeness of the Organic Extracts.** Higher similarity values with the reference (cooked rice) were obtained with dichloromethane and dichloromethane/pentane (1:2, v/v) extracts. Dichloromethane/pentane (1:2, v/v) mixture was chosen for further work because of its lower temperature for the evaporation.

**GC-O results.** 40 odorous compounds have been detected by GC-O, among which 2 showed high detection frequency in the 4 cultivars: 2-Acetyl-1-pyrroline (2AP, cooked rice attribute) and oct-1-en-3-one (mushroom attribute).

Hierarchical cluster analysis (HCA) of odorous compounds enabled to distinguish the groups of rice cultivars. Class (A) includes odours detected at similar frequency of detection for the 4 rice. Class (B) reports odours detected by frequency of detection which differed between cultivars (Figure 1).

**Figure 1.** HCA dendrogram of aroma attributes obtained from the four cooked rice cultivars (from A. Aychade, F. Fidji, T. Thai, R. Ruille, reprinted with permission from J. Agric. Food Chem, 2008, 56, 5291-5298. Copyright 2008 American Chemical Society).
GC-MS Analysis. 60 compounds have been identified and quantified by GC-MS analysis. 4 of them have been detected for the first time in cooked rice: oct-3-en-2-one, 2-methylpropanoic acid, \(\gamma\)-decalactone and \(\delta\)-decalactone. As expected, the level of 2AP was higher in the scented cultivars than in the non-scented one.

Principal component analysis (PCA) treatment enabled to separate Camargue cultivars from Thai sample and scented cultivars from non-scented one (Figure 2). Fatty acids and cinnamic acids derived volatile compounds, such as \((E,Z)\)-deca-2,4-dienal, hexanal and 4-vinylphenol, 2-methoxy-4-vinylphenol highly contributed to the discrimination of cultivars.

![Figure 2. Bi-plot of variables scores (A) and rice loadings (B) on the first two axes of the principal component analysis.](Reprinted with permission from J. Agric. Food Chem, 2008, 56, 5291-5298. Copyright 2008 American Chemical Society).

The odour active values (OAV) of the volatiles were calculated to have some view with regard to the contribution of volatiles to cooked rice flavour (Table 1).

<table>
<thead>
<tr>
<th>compounds</th>
<th>odor threshold (µg/L)</th>
<th>Aychade</th>
<th>Fidji</th>
<th>Thai</th>
<th>Ruille</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Acetyl-1-pyrroline</td>
<td>0.10</td>
<td>2150.00</td>
<td>2640.00</td>
<td>1860.00</td>
<td>nd</td>
</tr>
<tr>
<td>((E,Z))-Deca-2,4-dienal</td>
<td>0.07</td>
<td>2328.57</td>
<td>1671.43</td>
<td>357.14</td>
<td>257.14</td>
</tr>
<tr>
<td>2-Methoxy-4-vinylphenol</td>
<td>3.00</td>
<td>124.33</td>
<td>84.67</td>
<td>187.67</td>
<td>10.67</td>
</tr>
<tr>
<td>4-Vinyl-phenol</td>
<td>10.00</td>
<td>112.70</td>
<td>107.90</td>
<td>nd</td>
<td>96.20</td>
</tr>
<tr>
<td>((E,E))-Nona-2,4-dienal</td>
<td>0.09</td>
<td>74.43</td>
<td>33.21</td>
<td>19.23</td>
<td>38.52</td>
</tr>
<tr>
<td>Decanal</td>
<td>2.00</td>
<td>46.00</td>
<td>30.50</td>
<td>53.50</td>
<td>46.00</td>
</tr>
<tr>
<td>Hexanal</td>
<td>5.00</td>
<td>13.94</td>
<td>12.27</td>
<td>24.39</td>
<td>8.47</td>
</tr>
<tr>
<td>Vanillin</td>
<td>20.00</td>
<td>13.00</td>
<td>6.95</td>
<td>19.95</td>
<td>11.10</td>
</tr>
<tr>
<td>Oct-2-enal</td>
<td>3.00</td>
<td>16.00</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Indole</td>
<td>140.00</td>
<td>1.80</td>
<td>0.77</td>
<td>0.49</td>
<td>2.61</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>240.00</td>
<td>1.38</td>
<td>0.91</td>
<td>1.15</td>
<td>0.44</td>
</tr>
</tbody>
</table>

\(^a\) Odour threshold values in water obtained from the literature. \(^b\) The odour unit values were obtained by dividing the concentration of the odorant compound in the cooked rice by its odour threshold in water. nd: not determined since the concentration was below the detection limit of quantification (< 2 µg/L).
11 Compounds displayed OAVs greater than 1. The OAV for 2AP was very high in scented rice cultivars confirming its role in the flavour of these products. The second highest OAV was obtained with (E,Z)-deca-2,4-dienal. The scented cultivars from Camargue were distinguished by OAV of this compound in the same magnitude as the OAV of 2AP. Hence this aldehyde may play a significant role on the global aroma of scented Camargue cultivars. It is mainly formed upon auto-oxidation of linoleic acid. One can suppose the occurrence of the higher levels of linoleic acids in Camargue scented cultivars. The level of this acid in rice was supposed to correlate negatively with ripening temperature [11]. This may be reason of the lower levels of (E,Z)-deca-2,4-dienal in Thai cultivar. Two volatile phenols, 2-methoxy-4-vinylphenol and 4-vinilphenol showed high OAVs. Their formation from decarboxylation of putative cinnamic acid precursors is well documented [12,13]. Surprisingly 4-vinylphenol was not detected in Thai sample. This may be related to the compositional differences in cinnamic acids among rice cultivars [14].

In conclusion, organic extracts of cooked scented rice from Camargue cultivars (Aychade and Fidji), displayed aroma profile close to that of a well-known scented cultivar, Thai. However, quantitative differences were noticed for the levels of some flavour compounds, issued from the degradation of lipids and cinnamic acids, between scented Camargue cultivars and Thai one. Cultivar effect but also the growing and storage conditions could take part in these differences.

References