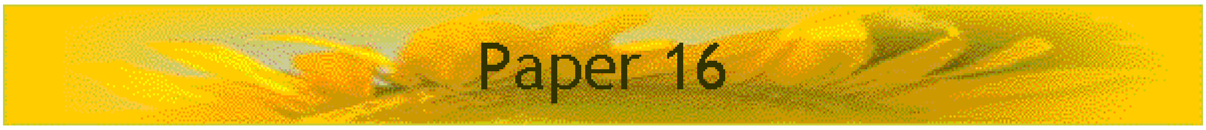


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# Volatile Constituents of cooked Rice (Oryza Sativa L.)

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## Abstract

Since 1994 some aromatic varieties and Basmati cultivated in Italy have been studied taking into account their agronomical traits and chemical properties related to the so-called "popcorn"-like aroma.

After agronomical and chemical evaluations, some lines were selected and considered for further more detailed analysis. For all the selected lines a quantification of 2-acetyl-1-pyrroline was performed and with one of the richest lines in aroma all the compounds were investigated and quantified in detail. 2-acetyl-1-pyrroline content ranged from 0.52 to 2.75 ppm.

Aroma components were studied during cooking and isolated by the Tenax Trapping method. Sixtysix constituents have been identified: 18 hydrocarbons, 16 aldehydes, 13 alcohols, 7 ketones, 4 eterocyclic, 4 terpenes, 3 acids and 1 disulphide.

Soil texture seems to affect milled rice pyrrolina content which was generally higher where rice was grown in the lighter soils.

## Keywords

- Aroma composition; cooked rice quality; Oryza sativa L., headspace
- Italy

# Introduction

From an economic point of view, aromatic rice occupies a special place in the international markets due to its pronounced, pleasant fragrance. Currently the rice consumption is increasing in the world with very active competition by rice producers stimulated by the renewed interest in improving the grain quality of modern rice varieties to meet the increasingly discriminating demand of consumers everywhere. Consumers in fact have become very discriminating and sensory quality has become very important. As a result, most plant breeding programs now incorporate sensory evaluation of the product into their objectives.

The European import of aromatic rices (Basmati) is dramatically increasing probably due to the ethnic market and to the European consumer looking for new tastes. EU imports of Basmati-like rices will probably reach 70.000 t per year in the near future, thanks to the new European law that reduces tariffs on imports (UE report 1503/96 and 2131/96).

Research on new agrotechniques for these special purpose crops could be carried out even with the aim to detect the possible influence of the pedoclimatic characteristic on the aroma content.

After having evaluated many cv. and lines based on their 2-acetyl-1-pyrroline content comparing to Basmati (Bocchi et al., 1995) the richest one was selected for this research.

The present study was undertaken in order to evaluate :
a) the different content of 2-acetyl-1-pyrroline in brown, milled and white rice grown in different environments;
b) the total flavour composition of this new line produced in Italy

.

# Materials and Methods

In 1994 and 1995, a line selected from cv. A301 was cultivated in 18 and 13 farms respectively located in Pavia Province, one of the most important and typical Italian rice producing areas. The soil features are reported in table 1. The agrotechnique adopted was the standard for the area able to prevent any stress to the crop during the growing season. From each field before the harvest rice samples were collected and dried under the same conditions and prepared for further chemical analysis. Samples of hulls, brown rice and milled rice have been used for chemical evaluation.

Two-acetyl-1-pyrroline content was determined through extraction of volatiles by steam distillation (Buttery et al. 1983). Total volatiles were determined by using Purge and Trap method as described in Tava and Bocchi (1997a). Analysis of volatiles was carried out by GC and GC/MS. Components identification was achieved with authentic reference compounds obtained from commercial sources, library research and experimental literature (McLafferty and Stauffer, 1980; Adams, 1995). 2-acetyl-1-pyrroline was synthesised according to the previously reported method (Buttery et al. 1983). Quantitative evaluation was carried out by GC using the internal standard method.

# Results and Discussion

Table 2 shows the 2-acetyl-1-pyrroline content in the different brown rice samples. The variability of the 2-acetyl-1-pyrroline is quite high. In 1994, the content was higher than the one obtained in average in 1995

(0.8 vs 0.6 ppm with standard deviation of 0.47and 0.38 respectively). During the first year in two farms, the 2-acetyl-1-pyrroline values were higher than 2 ppm. The frequency class with the highest value was 0.5 - 1 ppm in 1994 and the class with value < 0.5 in 1995. These results indicated that the 2-acetyl-1-pyrroline content in the samples was generally quite high if compared with the Basmati.

The 2-acetyl-1-pyrroline content in the dehulled rice resulted correlated (r= 0.9) with the milled rice one with higher values detected in the former (+ 13 %). The correlation analysis performed between the soil parameters and the 2-acetyl-1-pyrroline content provided some interesting information.

A relation between the soil texture and 2-acetyl-1-pyrroline content was observed in both years. The lighter the soil, the higher the 2-acetyl-1-pyrroline content. Future research will be necessary to shed light on this issue.

For a better understanding of the aromatic pattern which gives the characteristic behaviour of one of the rices studied, total volatile components were isolated using headspace trapping. The GC and GC/MS analyses allowed to identify and quantify several constituents that are reported in Table 3. These components, amounting to 82.49% of the total, are indicated as chemical classes. The most abundant constituents were found to be hexanal, representing the 13.16% of the total volatiles, followed by nonanal (6.37%), decanal (4.45%), pentanal (3.70%), octanol (3.33%), 1-octen-3-ol (3.23%), heptanal (3.09%) and 2-acetyl-1-pyrroline (3.03%).

Aldehydes made up the most abundant class in terms of quantitative presence in the aroma. The higher levels of these compounds probably resulted from enzymatic activity on rice lipids during storage. In fact, Aisaka (1977) reported that carbonyl compounds in the stored rice accounted for 30% of total aroma which was 10 times more than in fresh rice. Additionally Tsugita et al. (1983) compared the cooked flavour of rice stored at 4°C to that stored at 40°C for 60 days. The major compound found at both temperatures was hexanal which increased with storage temperature.

Alcohols represents 15.80% of the extract followed by hydrocarbons (13.67 %), terpenes (3.71 %), ketones (3.20) and acids (0.58). All these components were previously reported by several authors, as reviewed by Maga (1978).

Eterocyclic compounds were also detected in the extract. 2-Acetyl-1-pyrroline is the most abundant component of this chemical class and has been quantified as 3.03% of the total extract corresponding to 2.25 ppm in the variety of rice under study. The same quantitative data have been obtained for this compound comparing results from flavour extracted by steam distillation (Tava and Bocchi, 1997b). This last procedure is normally used by several authors to quantify 2-acetyl-1-pyrroline considered as responsible for the "popcorn"-like aroma of cooked rice (Buttery et al., 1983; Buttery et al., 1986; Paule and Powers, 1989; Lin et al., 1990; Tanchotikul and Hsieh, 1991; Laksanalamai and Ilangantileke, 1993; Bocchi et al, 1995; Bocchi et al., 1997).

# Conclusions

After some experiments carried out in Italy - both in field and in laboratory - on aromatic rice, we obtain rice lines with high pyrroline content especially when rice was cultivated in light soil. Pirr content

The quantitative determination of pyrroline is accurate using the two methods : GC after extraction with steam distillation, and Purge and Trap.

Pyrroline was detected to be responsible for the so called popcorn-like aroma, but many other components could contribute to the global flavour bouquet of aromatic rices.

**Table 1. Fisical-chemical features of the soils**

**Table 1. Fisical-chemical features of the soils**

| 1994 | schel | om | s | fs | vfs | s tot | si | fsi | C |
|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % | % |
| 1 | 0,2 | 1,52 | 36,26 | 15,98 | 14,09 | 66,33 | 9,39 | 13,66 | 10,61 |
| 2 | 4,14 | 2,28 | 4,43 | 5,74 | 13,74 | 23,91 | 21,44 | 37,1 | 17,55 |
| 3 | 2,3 | 2,48 | 34,91 | 13,67 | 19,17 | 67,75 | 13,74 | 11,74 | 6,77 |
| 4 | 0,05 | 1,31 | 50,76 | 23,07 | 12,34 | 86,17 | 3,5 | 6,59 | 3,75 |
| 5 | 16,25 | 2,55 | 41,55 | 10,54 | 10,61 | 62,7 | 9,65 | 14,01 | 13,65 |
| 6 | 6,44 | 2,55 | 29,78 | 8,24 | 15,44 | 53,46 | 15,14 | 19,09 | 12,31 |
| 7 | 0,19 | 1,86 | 26,55 | 13,92 | 23,56 | 64,03 | 13,86 | 14,16 | 7,95 |
| 8 | 3,79 | 1,8 | 28,27 | 18,85 | 16,99 | 64,11 | 7,13 | 17,21 | 11,56 |
| 9 | 1,16 | 2,14 | 34,12 | 11,81 | 12,73 | 58,66 | 11,24 | 17,17 | 12,93 |
| 10 | 8,37 | 3,24 | 32,29 | 10,17 | 12,69 | 55,15 | 9,97 | 21,19 | 13,69 |
| 11 | 21,27 | 4,27 | 56,58 | 10,78 | 4,65 | 72,01 | 7,83 | 11,18 | 8,98 |
| 12 | 0,58 | 3,22 | 27,89 | 13,21 | 12,77 | 53,87 | 13,12 | 22,47 | 10,54 |
| 13 | 0,47 | 3,5 | 39,34 | 17,88 | 6,88 | 64,1 | 11,4 | 15,49 | 9,02 |
| 14 | 4,1 | 1,82 | 37,81 | 12,15 | 11,23 | 61,19 | 11,87 | 15,63 | 11,31 |
| 15 | 0,98 | 2,17 | 20,03 | 13,9 | 17,51 | 51,44 | 12,88 | 20,55 | 15,13 |
| 16 | 0,61 | 1,4 | 31,89 | 17,06 | 15,15 | 64,1 | 11,92 | 12,93 | 11,05 |
| 17 | 1,02 | 2,24 | 15,32 | 8,65 | 17,36 | 41,33 | 17,29 | 24,86 | 16,52 |
| 18 | 0,56 | 2,18 | 4,08 | 6,24 | 12,25 | 22,57 | 20,14 | 39,87 | 17,43 |
| **1995** | | | | | | | | | |
| 1 | 3,8 | 1,8 | 28,27 | 18,85 | 16,99 | 64,11 | 7,13 | 17,21 | 11,56 |
| 2 | 0,98 | 2,17 | 20,03 | 13,9 | 17,51 | 51,44 | 12,88 | 20,55 | 15,13 |
| 3 | 15,4 | | 39,12 | 11,2 | 15,08 | 65,4 | 7,6 | 14,5 | 12,5 |
| 4 | 12,8 | | 30,09 | 8,83 | 9,63 | 48,55 | 17,95 | 19,55 | 13,95 |
| 5 | 8,37 | 3,24 | 32,29 | 10,17 | 12,69 | 55,15 | 9,97 | 21,19 | 13,69 |
| 6 | 1,16 | 2,14 | 34,12 | 11,81 | 12,73 | 58,66 | 11,24 | 17,17 | 12,93 |
| 7 | | | 40 | 4 | 7 | 51 | 12 | 19 | 14,84 |
| 8 | 0,3 | | 12,31 | 9,82 | 21,57 | 43,7 | 11,5 | 27,35 | 17,45 |
| 9 | 13 | | 23,54 | 9,19 | 17,77 | 50,5 | 16,35 | 19,9 | 13,25 |
| 10 | 31,9 | | 39,08 | 8,48 | 13,85 | 61,41 | 8,75 | 15,85 | 13,88 |
| 11 | 0 | | 28,38 | 18,39 | 21,48 | 68,25 | 11,3 | 11,65 | 8,8 |
| 12 | 0,5 | | 21,72 | 9,46 | 19,32 | 50,5 | 16,7 | 21,45 | 11,35 |
| 13 | 1,8 | | 39,33 | 12,14 | 19,13 | 70,6 | 12,3 | 11,8 | 5,3 |

om =organic matter; s = sand; fs=fine sand; vfs=very fine sand; si=silt; fsi=fine silt; c=clay

**Table 2. Pyrroline content (ppb) in the rice samples (brown and milled)**

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| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 95 | mil | 691 | 100 | 2606 | 707 | 1254 | 514 | 2247 | 100 | 507 | 636 | 1072 | 1545 | 648 | 600 | 870 | 803 | 688 |
| 95 | bro | 346 | 382 | 1328 | 577 | 668 | 1342 | 1876 | 397 | 1129 | 712 | 184 | 212 | 557 | | | | |
| 95 | mil | 400 | 239 | 1082 | 618 | 930 | 1250 | 1219 | 212 | 1015 | 442 | 155 | 146 | 760 | | | | |

**Table 3. Headspace components of cooked rice detected by purge and trap method.**

**Table 3. Headspace components of cooked rice detected by purge and trap method.**

| compoud | RA (%) | ppb[a] |
|---|---|---|
| Aldeyides | 41.79 | 8343 |
| Alcohols | 15.80 | 3154 |
| Eterocyclic | 13.68 | 2731 |
| Hydrocarbons | 13.67 | 2729 |
| Terpens | 3.71 | 741 |
| Ketones | 3.20 | 639 |
| Acids | 0.58 | 116 |
| Disulphyde | 0.19 | 38 |
| **Total** | **92.62** | **18491** |

RA: relative abundance (%). [a] referred to collidine as Internal Standard. [b]<0.01%

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