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High-quality Italian rice cultivars: Chemical indices of ageing and aroma quality

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1-Butanol, 2-methyl- (PubChem CID: 8723)
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ABSTRACT

The volatile fractions of six Italian high-quality rice cultivars were investigated by HS-SPME–GC–MS to define fingerprinting and identify chemical markers and/or indices of ageing and aroma quality. In particular, four non-aromatic (Carnaroli, Carnise, Cerere and Antares) and two aromatic (Apollo and Venere) rices, harvested in 2010 and 2011, were monitored over 12 months.

Twenty-five aroma components were considered and, despite considerable inter-annual variability, some of them showed similar trends over time, including 2-(*E*)-octenal as a marker of ageing for all cultivars, and heptanal, octanal and 2-ethyl hexanol as cultivar-specific indicators. The area ratios 2-acetyl-1-pyrroline/1-octen-3-ol, for Venere, and 3-methyl-1-butanol/2-methyl-1-butanol, for Apollo, were also found to act as ageing indices.

Additional information on release of key-aroma compounds was also obtained from quantitation and its dependence on grain shape and chemical composition. Heptanal/1-octen-3-ol and heptanal/octanal ratios were also defined as characterising the aroma quality indices of the six Italian rice cultivars investigated.

1. Introduction

Rice (*Oryza sativa* L.) is one of the most widely cultivated cereals in the world. It is a staple food for about half the world's population, in particular for Asian, South-American and African countries (Food and Agriculture Organization of the United Nations (FAOSTAT), United States Department of Agricultural (USDA)). Italy is the largest rice producer in the European Union, producing approximately 50% of the total EU-27 harvest. Although Italy accounts for less than 1% of world production, it is currently the fourth-largest rice-exporting country, after Thailand, United States, and India (counting intra-EU trade). Rice cultivation in Italy is mainly located in the northern regions (Piedmont, Lombardy and Veneto).

Rice cultivars can be classified into two major groups: the ecotype "*indica*", which is characterised by long grains, and the ecotype "*japonica*", with short grains. Several cultivars are cultivated in Italy, around 70% of them belonging to the "*indica*" variety (Ariete-Drago, Arborio, Baldo, S. Andrea, Carnaroli) (Istituto di Ricerche Economiche e Sociali per il Piemonte (IRES)). The EU characterises specific qualities of specific products, through a series of

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labels (Protected Designation of Origin – PDO, Protected Geographical Indication – PGI, and Traditional Specialty Guaranteed – TSG), that give them a further added value related to their origins, and to the manufacturing and/or processing practices employed (European Commission, Agricultural and Rural Development). The quality of rice grains has great economic interest, characteristics such as yield, shape and defects being important in marketing, while the aroma of the cooked product, in particular when prepared in the Asiatic mode, has a big impact on consumers. The aroma of both aromatic and non-aromatic rice cultivars consists of a complex mixture of odor-active compounds. Several authors have studied the composition of the cooked rice volatile fraction, identifying a large number of components and defining several key-aroma compounds (Champagne, 2008; Jezussek, Juliano, & Schieberle, 2002; Widjaja, Craske, & Wootton, 1996a; Yang, Lee, Jeong, Kim, & Kays, 2008; Yang, Shewfelt, Lee, & Keys, 2008; Zeng, Zhang, Chen, Zhang, & Matsunaga, 2008). These include saturated and unsaturated aldehydes, alcohols, and cyclic compounds; in particular, hexanal, 1-octen-3-ol and 2-pentylfuran are markers of both quality and ageing, while 2-acetyl pyrroline (2-AP) is one of the aroma quality markers for aromatic rice (Buttery, Turnbaugh, & Ling, 1988; Champagne, 2008; Grimm, Bergman, Delgado, & Bryant, 2001; Laguerre, Mestres, Davrieux, Ringuet, & Boulanger, 2007; Mahatheeranont, Keawsa-Ard, & Dumri, 2001; Widjaja et al., 1996a). It has a characteristic popcorn-like aroma that, together with its low odor threshold, gives aromatic rice a characteristic flavour, whose accumulation is favored by their genetic characteristics (Bradbury, Henry, Qingsheng, Reinke, & Waters, 2005; Fitzgerald, McCouch, & Hall, 2009; Kovacha, Calingacionb, Fitzgerald, & McCouch, 2009).

Rice is a seasonal product, harvested during a limited period of a few weeks, but consumed throughout the year. Rice in the field is never uniform, changing at each crop, therefore processing and storage after harvesting have a big impact on yield and quality of the final product (Champagne 2008). During storage, the rice aroma can change, mainly because of oxidation and losses over time.

Headspace solid phase microextraction (HS-SPME) is a well-established and popular technique for headspace sampling, that is used in several fields, (Belliardo et al., 2006), including rice. Because of its flexibility and sensitivity, HS-SPME with a DVB/CAR/PCMS fibre has also been used to monitor the evolution of volatiles directly during storage (Bryant & McClung, 2011; Grimm et al., 2001; Laguerre et al., 2007; Zeng et al., 2008).

This study aimed to analyse the volatile fractions of six high-quality Italian rice cultivars, by a fully-automated HS-SPME–GC–MS method, so as to define volatiles characterising fingerprints and to identify reliable chemical markers and indices of ageing and aroma quality. In particular, the study comprised four main parts: (i) the first part focused on validating the method of analysis; (ii) the second part dealt with the effects of storage and temperature on the composition of the volatile fraction (aroma fingerprinting) of the investigated cultivars, seeking markers or indices correlated with ageing, independently of the inter-annual variability; (iii) the third part comprised quantitation of the identified key-aroma compounds and the influence of the physico-chemical characteristics of the grain of the cultivars investigated on the release of the aroma components; (iv) the final part concerns the identification of indices to describe the aroma quality of rice.

In particular, four non-aromatic (Carnaroli, Carnise, Cerere and Antares) and two aromatic (Apollo and Venere) rice cultivars, harvested in 2010 and 2011, were investigated over a period of 12 months.

2. Materials and methods

2.1. Reference compounds and solvents

Pure reference compounds for analyte identity confirmation, and n-alkanes (n-C5 to n-C25) for linear retention index (I^T) determination, were from Sigma–Aldrich (Milan, Italy), 2-acetyl-2-pyrroline was from BOC Sciences (Shirley, NY, USA). A standard stock solution of n-heptadecane (C17) at 63 mg/L was prepared in dibutyl phthalate (Sigma–Aldrich, Milan, Italy) and stored in a sealed vial at −18 °C. C17 was used as Internal Standard for peak response normalisation (ISTD). Solvents (cyclohexane) were HPLC-grade from Riedel-de Haen (Seelze, Germany).

2.2. Samples

Rice (*O. sativa* L.) samples, of six high-quality Italian cultivars, were harvested in 2010 and in 2011: four cultivars (Carnaroli, Carnise, Cerere and Antares) were non-aromatic, and two (Apollo and Venere) were aromatic; all were supplied by SA.PI.SE. (Vercelli – Italy). Carnaroli is a high-quality non-aromatic rice that is PDO-labelled as "Riso di Baraggia Biellese e Vercellese" (IT/PDO/0005/0337) and PGI-registered as "Riso del delta del Po" (IT/PGI/0005/0712); Carnise is an agronomically-improved cultivar of Carnaroli, with enhanced ability to absorb condiments, maintaining its texture after cooking. Venere is a patented semi-whole pigmented black aromatic rice produced by SA.PI.SE (EU4481/1999) that has recently been introduced into Italy (2008), after adaptation to the climatic conditions by crossbreeding an Asiatic pigmented rice with a local cultivar, which contains lower relative amounts of key-odor compounds than does Apollo. Table 1 reports the list of rice cultivars and their characteristics. Rice samples were stored as paddy at different controlled temperatures (i.e. at the conventional temperatures of 25 °C and 5 °C in air) and times (0–6–12 months), under 13% relative humidity.

A set of commercial Thai rice samples and a standard solution of methyl isobutyl ketone (80 mg/L), carvone (4.75 mg/L), 3-hexanol (40 mg/L), linalool (4.35 mg/L), 1-butanol-3-methyl acetate (17 mg/L), and eucalyptol (3.68 mg/L) in water (EXTD) were stored at −18 °C and used as references to standardize the HS-SPME system performance over time (see Section 2.5).

2.3. Headspace solid phase microextraction (HS-SPME) sampling and optimisation

The SPME device and fibres were from Supelco (Bellefonte, PA, USA). A Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) d_f 50/30 μm, 2 cm length fibre was chosen, and conditioned before use as recommended by the manufacturer.

Volatiles were sampled by automated headspace solid phase microextraction (auto-HS-SPME) using a Combi-PAL AOC 5000 (Shimadzu, Milan, Italy) on-line integrated with a Shimadzu QP2010 GC–MS system provided with a Shimadzu GC–MS Solution 2.51 software (Shimadzu, Milan, Italy).

The HS-SPME sampling conditions were optimised on a group of characteristic components of the rice volatile fraction of a milled Thai sample, i.e. 3-methyl-butanal, pentanal, hexanal, 3-methyl-1-butanol, 2-pentyl furan, hexanol, and nonanal at three temperatures (40 °C, 60 °C, 80 °C) and times (15, 30, 60 min). The adopted HS-SPME fibre (2 cm, DVB/CAR/PDMS) and conditions (60 °C for 60 min) were a compromise to maximise recovery and repeatability throughout the 2 years of the project (Fig. 1 SD – Supplementary data).