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Review

Evaluation of 2-acetyl-1-pyrroline in foods, with an emphasis on rice flavour

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ABSTRACT

The popcorn-like aroma compound 2-acetyl-1-pyrroline (2-AP) is a key contributor to the desirable aroma of fragrant rice and is also important in the aroma of other foods, such as pandan leaf, popcorn and Mediterranean sausage. It can be formed enzymatically in the rice grain as it grows and is also formed, as part of the Maillard reaction, when rice is heated. This review examines the formation of 2-AP in rice and other foods, particularly its formation during cooking, focusing on the importance of the Maillard reaction between reducing sugar breakdown products and 1-pyrroline derived from the amino acids proline and ornithine. The synthesis of 2-AP is discussed alongside the attempts that have been made to stabilise this relatively unstable compound. The analysis of 2-AP by instrumental techniques, particularly gas chromatography-mass spectrometry and gas chromatography-olfactometry, alongside the use of sensory studies, is also discussed.

Contents

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1. Introduction

The IUPAC name of 2-acetyl-1-pyrroline (2-AP) is 1-(3,4-dihydro-2*H*-pyrrol-5-yl)ethanone, its CAS number is 85213-22-5 and its FEMA (Flavour and Extract Manufacturers Association) number is 4249. 2-AP was first identified in rice by Buttery, Ling, and Juliano (1982), and is regarded as the most important aroma compound in rice, especially fragrant rice (Buttery, Ling, Juliano, & Turnbaugh, 1983). In that study, 0.05 ppm 2-AP was described as popcorn-like and its odour threshold in water was measured as 0.1 nL/L, while its odour threshold in air was reported by Schieberle (1991) as 0.02 ng/L; this very low threshold makes it an important contributor to a food's aroma when present. As well as rice, it is also a key flavour compound in many cereal products, as well as some vegetable and animal products (Adams & De Kimpe, 2006; Wakte et al., 2017).

Bioformation of 2-acetyl-1-pyrroline in both plants and microorganisms has been studied and several types of bacteria are able to form this compound (see Part 3 of this review). 2-Acetyl-1-pyrroline has also been shown to form in the Maillard reaction; it can be formed from the reaction between proline and reducing sugars/sugar degradation products upon heating (Schieberle, 1989).

Although there is a high commercial interest in 2-AP because of its desirable sensory attributes, the instability of this compound is a significant problem for its commercial application. Pure 2-AP will turn red and degrade within 10 min at room temperature (Fang & Cadwallader, 2014), and there is significant short-term reduction of 2-AP concentration in food products, such as popcorn (Schieberle, 1995) and raw fragrant rice (Widjaja, Craske, & Wootton, 1996a).

The occurrence of 2-acetyl-1-pyrroline in food products, its bioformation and thermal formation, synthesis, stabilisation, analysis and sensory evaluation will be reviewed in this paper, with particular emphasis on the role of 2-AP in fragrant rice aroma.

2. Food sources of 2-acetyl-1-pyrroline

2.1. Rice

Non-fragrant rice (long and medium grain *indicas* and short grain *japonicas*), mainly grown in USA, Vietnam, Thailand and Australia, constitutes around 80% of the world rice trade (Singh, Singh, & Khush, 2000). Major producers of fragrant rice are India, Pakistan and Thailand. Most of the fragrant rice exported from India and Pakistan is basmati, while fragrant jasmine rice is a major export of Thailand (Singh et al., 2000). In 2010, Thailand was the biggest exporter of fragrant rice: 2.65 million tonnes of jasmine rice were exported, followed by India (1.80 million tonnes basmati) and Pakistan (1.05 million tonnes basmati) (Slayton & Muniroth, 2015).

The price of fragrant rice is much higher than that of non-fragrant rice. For example, high-quality fragrant basmati rice has a three times higher price than high quality non-fragrant rice. The commercial value of fragrant rice is higher than that of non-fragrant rice, partly because fragrant rice varieties are relatively low yielding. Fragrant rice is less resistant to disease and insect pests and is prone to high shedding, leading to losses in yield (Berner & Hoff, 1986; Golam et al., 2011). It has been shown that higher quality grains with stronger aromas are generated in crops grown in drought and saline conditions (Yoshihashi, Nguyen, & Kabaki, 2004). These adverse conditions do not favour high yields.

2-AP is the key discriminator between fragrant and non-fragrant rice and many studies have focused on the concentration of 2-AP in different rice cultivars. 2-AP concentrations in different fragrant cultivars vary substantially (Table 1). For example, 2-AP was present in milled Fowler Gourmet Aromatic rice (a US-grown aromatic rice) at 999 μg/kg, while, in a set of five basmati samples, levels of 2-AP from 19 μg/kg to 342 μg/kg were measured (Bergman et al., 2000).

Milled rice (commonly referred to as white rice) is obtained from the milling of brown rice to remove the outer bran layer. Whole rice grains are dehulled; then the dehulled (brown) rice is milled twice. Generally, 20–22% of the rice grain is hull, and another 8–10% is bran and embryo; therefore, the yield of milled rice is around 70% (Singh et al., 2000). As can be seen in Table 1, in most cases more 2-AP is present in brown rice compared to milled rice.

Table 1
2-AP concentrations in fragrant and non-fragrant rice.

Rice variety	2-AP concentration (μg/kg)	
	Milled	Brown
Fragrant rice		
Basmati	60[a]	170[a]
	87[d]	610[b]
	588[g]	119[h]
	19–342[h]	
	434[k]	
Khao Dawk Mali 105	70[a]	200[a]
	87–532[i]	
Malagkit Sungsong	90[a]	200[a]
		760[b]
Milagross	70[a]	
Seratus Malam	60[a]	
Azucena	40[a]	160[a]
Hieri	40[a]	100[a]
Ir841-76-1	70[a]	200[a]
		560[b]
Jasmine	156[d]	550[h]
	810[h]	
Della	76[d]	
Goolarah	691[e]	
Yrf9	670[e]	344[f]
B5-3	2746[g]	
Amber Aromatic (Lundberg)		345[h]
Aromatic (Fowler Gourmet)	999[h]	
Black Thai (Bulk)		259[h]
Jasmati (Rice Tec)	526[h]	
Kasmati (Rice Tec)	496[h]	
Texmati (Rice Tec)	266[h]	
Aychade	575–638[j]	
Fidji	45–475[j]	
Giano	28–336[j]	
Kala Bhat	920[k]	
Kali Kumud	732[k]	
Amritbhog	787[k]	
Non-fragrant rice		
Calrose	<6[a]	
California Long-Grain	0.6[c]	
Pelde	15[e]	
Texas Long Grain	<8[a]	
	6[b]	
Ariette	10.6[j]	
Ruille	24.7[j]	
Sonsali	72[k]	
Kolamb	125[k]	

Data are from the following references:
[a] Buttery et al. (1983).
[b] Buttery et al. (1986).
[c] Buttery et al. (1988).
[d] Tanchotikul and Hsieh (1991).
[e] Widjaja et al. (1996a).
[f] Widjaja et al. (1996b).
[g] Tava and Bocchi (1999).
[h] Bergman et al. (2000).
[i] Yoshihashi et al. (2004).
[j] Maraval et al. (2010).
[k] Mathure et al. (2014).