Fragrance profiles of cooked and raw rice using PAL SPME Arrow and Agilent GC7890-MS7000

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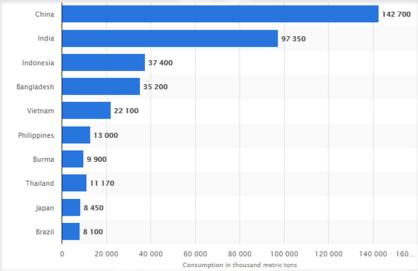
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Introduction

- Rice is the seed of plant Oryza sativa which is the main carbohydrate source especially for East Asian
- Aroma of rice is a key factor to attract consumer, so the production of fragrance rice has increased.

Rice consumption 2018 in 1,000 metric tons



- The Thai Fragrant rice price could always be traded 2-3x higher price, when certified as Thai Hom Mali rice.
- Counterfeit rice issue occurred in Hong Kong, by mixing 90% of low quality rice with 10% Thai Hom Mali rice.

Customs seize 15,000kg of counterfeit rice from company that supplied to almost 100 restaurants in Hong Kong

Supplier would make mix of 10 per cent real rice and 90 per cent low-quality rice and could make a profit of HK\$100 per bag, customs head said



- Thai Hom Mali rice, is a preferred choice as "Thai Fragrance Rice" because of its "pandan" like smell
- Some fragrances are formed through Maillard reaction.¹
- The rice could only be produced in the northern part of Thailand, which provides the optimum climate to grow the rice and so, resulted in the higher trading value
- From chemical prospective, the Thai Hom Mali rice contains more 2-acetyl-1-pyrroline.

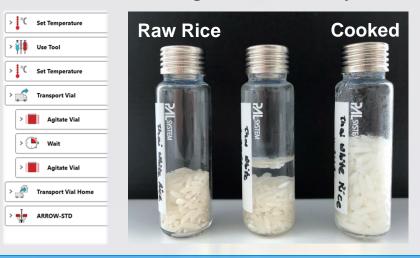


Compound Name: 2-Acetyl-1-pyrroline

Method

- Traditional rice analysis is done by transfer from the rice cooker and transfer into sample vial for analysis. However, during this transfer the volatiles might get lost.
- In this study, the rice was automatically cooked by the PAL autosampler, so fragrances are released inside the vial.
- Some fragrances are formed during the cooking process through the Maillard reaction.
- High sensitivity of PAL SPME Arrow allows to create aroma profiles even from trace compounds.
- PAL Method Composer software was used to create the Method, including Cooking and SPME Arrow Extraction

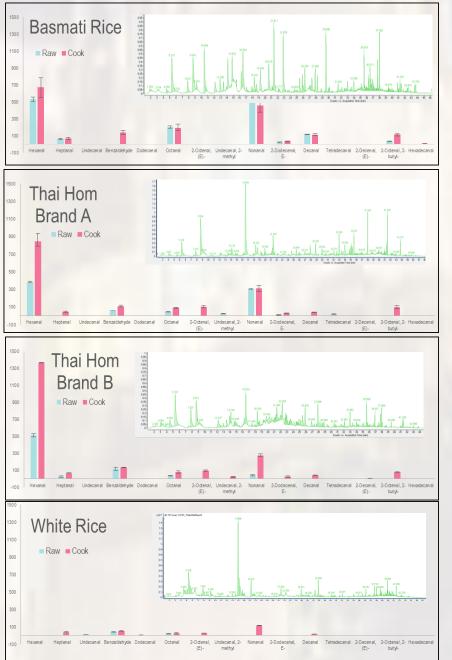
PAL Method Composer steps (left) were used tor automated cooking of rice and analysis.



Fragrance Profiles

- Full Aroma Profiles were created by simple SPME Arrow extractions
- The profiles allows to select from Alkanes, Alkenes, Ketones, Alcohols and Aldehydes as target compounds.

Full Aroma Profiles (TIC, green), and comparison of Aldehyde content in raw an coocked Rice.



Results and Discussion

 Fragrance compounds are presented in following comparisons of the different rice seeds

Aldehydes

Basmati Rice			Thai Hom Mali Rice – Brand A			Thai Hom Mali Rice – Brand B			White Rice		
Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice
fexanal	~	~	Hexanal	~	~	Hexanal	~	~	Heptanal		~
leptanal	~	~	Heptanal		× 1	Heptanal	× .	×	Undecanal	×	
Benzaldehyde		~	Benzaldehyde	×	×	Benzaldehyde	1	×	Benzaldehyde	×	1
Octanal	~	~	Octanal	~	× .	Octanal	×	× 1	Dodecanal	~	
lonanal	1	1	2-Octenal, (E)-		1	2-Octenal, (E)-		×	Octanal	×	1
-Dodecenal, E-	~	~	Undecanal, 2-methyl	×		Undecanal, 2-methyl	1	×	2-Octenal, (E)-		×
Decanal	~	~	Nonanal	~	×	Nonanal	×	×	Nonanal		1
-Octenal, 2-butyl-	~	~	2-Dodecenal, E-	×	×	2-Dodecenal, E-		×	Decanal		1
lexadecanal		~	Decanal		×	Decanal		×			
			Tetradecanal	1		2-Decenal, (E)-		~			
			2-Octenal, 2-butyl-		× .	2-Octenal, 2-butyl-		× .			

Alcohols

Basmat	i Rice		Thai Hom Mali R	lice – Bra	and A	Thai Hom Mali R	Thai Hom Mali Rice – Brand B			White Rice		
Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	
S)-(+)-3-Methyl-1-pentanol	~		1-Nonanol	~		(S)-(+)-3-Methyl-1-pentanol	~		1-Octanol, 2,7-dimethyl-	~	~	
I-Nonanol	×	~	1-Octen-3-ol		1	1-Nonanol	~	× 1	1-Decanol, 2-ethyl-	×	×	
I-Octen-3-ol	~	~	Bicyclo(3.1.1)heptane-2,3-diol, 2.6.6-trimethyl-	~	~	1-Octen-3-ol	~	×	Cycloheptanol, 2-methylene	~		
Bicyclo(3.1.1)heptane-2,3-diol, 2,6,6-trimethyl-	~	~	1-Hexanol, 2-ethyl-		~	Bicyclo(3.1.1)heptane-2,3-diol, 2,6,6-trimethyl-	~	~	1-Octen-3-ol	~	×	
1-Octyn-3-ol, 4-ethyl-		~	2-Propyl-1-pentanol	×		1-Octanol, 2-butyl-	~		2-Nonen-1-ol		×	
2-Propyl-1-pentanol	×		3,5-Octadien-2-ol		1	1-Hexanol, 2-ethyl-	~		1-Octyn-3-ol, 4-ethyl-	1		
3,5-Octadien-2-ol	×	~	2-Nonen-1-ol	~	~	Cyclohexanol, 2-methyl-3-(1- methylethenyl)-, (1.alpha2.alpha3.alpha.)-		~	1-Octanol, 2-butyl-	~		
2-Nonen-1-ol	×		1-Decanol	~	1	3,5-Octadien-2-ol		×	1-Decanol		1	
1-Octanol, 2-butyl-	~		1-Decanol, 2-methyl-	~		2-Nonen-1-ol	~	×	Cyclohexanol, 1-methyl-4-(1- methylethyl)-, cis-		1	
1-Decanol, 2-ethyl-	×	~	Benzenemethanol, alphaalphadimethyl-	~		1-Decanol, 2-methyl-	~		1-Tetradecanol		1	
1-Decanol	· ·	1	1-Octanol, 2-butyl-	~		1-Decanol	~	1				
p-Menth-8(10)-ene-2,9-diol	×	~	2-Isopropyl-5-methyl-1-heptanol	~		2-Isopropyl-5-methyl-1-heptanol	~					
Cyclohexanol, 1-methyl-4-(1- methylethyl)-, cis-	~	~	1-Decanol, 2-ethyl-	~		Cyclohexanol, 1-methyl-4-(1- methylethyl)-, cis-		×				
3-Dodecanol, 3,7,11-trimethyl-	× .	~	Cyclohexanol, 1-methyl-4-(1- methylethyl)-, cis-		~	3-Dodecanol, 3,7,11-trimethyl-	~					
1-Decanol, 2-hexyl-	×	~	3-Dodecanol, 3,7,11-trimethyl-	~	1	Isopulegol		×				
1-Tetradecanol	×	~	Isopulegol	~	×	1-Decanol, 2-hexyl-	~	×				
			1-Decanol, 2-hexyl-		×							
		1	Decord 2 ochd			1			1	1		

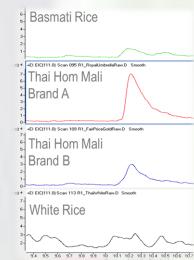
Ketones

Basmati Rice			Thai Hom Mali Rice – Brand A			Thai Hom Mali Rice – Brand B			White Rice		
Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice
Oxacyclododecan-2-one	~	~	1,13-Tetradecadien-3-one	~	~	Cyclohexanone, 3-butyl		~	1,13-Tetradecadien-3-one		~
2(3H)-Furanone, 5- heptyldihydro-	~		Cyclohexanone, 3-butyl	~	~	1,13-Tetradecadien-3-one			1-Penten-3-one, 1-(2,6,6- rimethyl-1-cyclohexen-1-yl)-		~
1,4-Cyclododecanedione		~	2-Piperidinone, N-[4-bromo-n- butyl]-		~	1,4-Cyclododecanedione		~			
2(3H)-Furanone, dihydro-5- pentyl-	~		1,4-Cyclododecanedione	×		1-Penten-3-one, 1-(2,6,6- trimethyl-1-cyclohexen-1-yl)-	1				
			1-Penten-3-one, 1-(2,6,6- trimethyl-1-cyclohexen-1-yl)-	×	·						

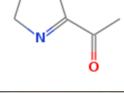
Alkenes

Basmati Rice			Thai Hom Mali Rice – Brand A			Thai Hom Mali Rice – Brand B			White Rice		
Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice	Compounds	Raw Rice	Cooked Rice
Styrene	~	~	Ethylbenzene	~	~	Ethylbenzene	~		1-Undecene, 7-methyl-	~	
5-Tridecene, (Z)-		~	p-Xylene		~	Styrene	~	~	1-Decene, 3,4-dimethyl-	1	
1-Heptadecene	×	~	Styrene	×	~	D-Limonene	~	~	2-Octene, 2,6-dimethyl-	×	
1-Nonadecene	×	~	3-Carene	· ·		2-Undecene, 9-methyl-, (E)-	1		6-Tridecene, (Z)-	×	
			Benzene, propyl-	× 1		1-Heptadecene	~		Pentadecane, 7-methyl-	×	
			Benzene, (1-methylethyl)-	× 1		1-Pentadecene	~		5-Tridecene, (Z)-	×	
			D-Limonene	×	~	4-Nonene, 5-butyl-		~			
			5-Eicosene, (E)-	· ·		Tetradecane, 4-methyl-		~			
			4-Nonene, 5-butyl- Naphthaliene, 1,2,3,4- tetrahydro-2,7-dimethyl- Naphthaliene, 5-ethyl-1,2,3,4- tetrahydro-	*	*						

Fragrance indicator 2-Acetyl-1-Pyrroline



2-Acetyl-1-Pyrroline can be used as target to distinguish different rice qualities. The extraction by PAL SPME Arrow reveals low levels in Basmati and White Rice. This compound can clearly distinguish the higher grade Thai Hom Mali Rice, with highest level in Brand A.

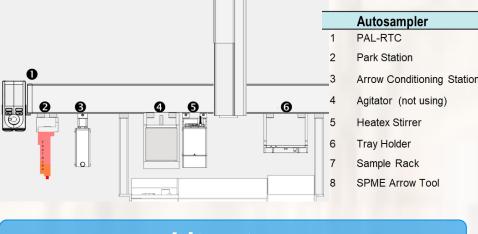


Molecular weight: 111.1418 CAS No.: 85213-22-5 Aroma : popcorn³, pandan³, nut³, walnut⁴, bread⁴ Aroma threshold: 0.007 ug/kg (in water)⁵

PAL SPME Arrow was used in this study as a simple extraction method to create full fragrance profiles in various rice seeds, and to detect 2-Acetyl-1-pyrroline in Thai Hom Mali Rice.

Equipment

- Traditional rice analysis was done by transfer from the rice cooker, but during this transfer the volatiles might get lost.
- In this study, the rice was automatically cooked with the PAL autosampler, so fragrances remain inside the vial.
- The Modular design of the Autosampler allows ful control by the Agilent Mass Hunter Sample List.
- Agilent GC 7890 MS 7000 with HP5MS Column was used as analytic system.



Literature

 Detection was based on the algorithm of Agilent MassHunter Workstation Software, based on the library database of National Institute of Standards and Technology (NIST, ver 14) with the matching score more than 80. Peaks that possess low matching score would be classified as "Unidentified".

Frangrance Peaks - Standard deviation

2-Acer in Thai		/rroline	Data	Retention Time (min)	Peak Area
III IIIa		NICE	1	10.222	636543
* 10.222	10,214	10.210	2	10.214	726184
			3	10.210	776907
			Average	10.218	681364
			Std Dev.	0.006	63386
			%RSD	0.06%	9%
L					

Conclusions

- Different rice seeds show different GCMS profiling.
- White Rice contains very little Aldehydes compounds as compared to other rice which have distinctive fragrance, such as the Basmati and Hom Mali rice.
- D-Limonene was detected in both brands of Hom Mali rice, but not other types of rices
- By cooking the rice, aromatic profiling has changed as well, showing that chemical reactions have occurred during the cooking.
- By using the PAL Autosampler for rice cooking, all the volatile compounds could be preserved inside the enclosed headspace vial for well controlled and senstitive extractions by PAL SPME Arrow.
- R.J. Bryant, Food Chemistry 124 (2011) 501-513. Volatile profiles of aromatic and non-aromatic rice cultivars using SPME/GC-MS
- S. Mahatheeranont et. al., Journal of Agr. and Food Chemistry, 2003, 51(2): 457-62. Identification and Quantitation of the Rice Aroma Compound, 2-Acetyl-1-pyrooline, in Bread Flowers