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ASSESSMENT OF FLAVOR VOLATILES OF MODIFIED IRANIAN RICE CULTIVARS DURING THE GELATINIZATION PROCESS

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A combined GC-MS with the headspace solid-phase microextraction (SPME) method has been employed for the analysis of the flavor volatiles of two modified Iranian rice cultivars during gelatinization. In order to optimize the different experimental parameters, the effect of fiber composition, water content of the rice samples, and equilibrium time were investigated. As a result, while gelatinization progresses, the amount of volatile compounds would increase as well. Therefore, a broad range of the flavor volatiles of rice could be extracted, concentrated, and identified. Altogether, 54 and 66 components were identified for HD5 and HD6 rice samples, respectively, of which 33 unique compounds were not detected previously. The identified volatile components in the modified cultivars belong to the chemical classes of aldehydes, ketones, alcohols, and heterocyclic compounds, phenolic compounds, and hydrocarbons.

Keywords: *Oryza sativa* L. (rice), flavor volatile components, solid-phase microextraction (SPME), gas chromatography (GC), mass spectrometry (MS).

Oryza sativa L. (rice) is the main product of people′s diet in many countries, which consists of 21% of the calorific intake in the daily needs of the whole population. In this regard, one of the most significant factors in the marketing and pricing of rice is the aroma of fragrant rices. This is a trait which distinguishes it from ordinary rice [1, 2].

There are many different volatile components in cooked rice grains, including those which are the result of biochemically distinct pathways, and these are very rich sources of hydrocarbons, organic acids, alcohols, aldehydes, ketones, esters, and phenols. In some cases, there are chemically synthesized components that are stored during the process of rice development. However, there are some other compounds that are extracted as a result of chemical breakdown. Among the latter, fatty acids are good samples [3].

The aroma can have both positive and negative influence on people′s tastes. The former can be flavor and fragrance components such as 2AP and the aromatic alcohols, and the latter can be the off-flavors of hexanal and 2-pentylfuran [4].

Among those aromatic compounds that have been identified in many studies, 2-acetyl-1-pyrroline (2AP) is known to be the most important key flavor component of rice aroma [5–8]. Its structure consists of a five-carbon *N*-heterocyclic ring that was first determined in cooked rice and the volatile oil of freeze-dried Pandan leaf, with a threshold value of 0.1 nl/L water, which was very low compared with other components [9–11].

The concentration was high, up to 0.09 mg/kg, which was 10 times more than that of nonfragrant rice (< 0.006–0.008 mg/kg). This amount was identified in all parts of fragrant rice, but not in roots [5].

In order to provide sample preparation methods and analytical techniques, solid-phase microextraction (SPME) is introduced as a rapid, sensitive, and reliable technique for the extraction and concentration of volatile compounds from different sample matrices. SPME consists of two separate steps. The first step deals with partitioning the target analytes between sample matrix and fiber surface, whereas the second step deals with the direct desorption of absorbed analytes into the injection port by means of chromatographic techniques [12].

This technique has many advantages, including less time needed for extraction, ease of use, no loss of analytes, and field sampling with a portable field sampler [13, 14].

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TABLE 1. HD5 Rice Samples

Cooking time, min	Number of gelatinized grains for each of 5 samples					Average of gelatinized grains, %	First equalization of values, %	Second equalization of values, %
	1	2	3	4	5			
16	**2**	**1**	**2**	**1**	**2**	**16.0**		
							22.0	
17	3	3	3	2	3	28.0		29.5
							37.0	
18	5	4	5	4	5	46.0		46.0
							55.0	
19	7	6	6	6	7	64.0		65.0
							75.0	
20	9	8	8	9	9	86.0		83.0
							91.0	
21	10	10	10	9	9	96.0		94.0
							97.0	
22	**10**	**10**	**10**	**10**	**9**	**98.0**		

TABLE 2. HD6 Rice Samples

Cooking time, min	Number of gelatinized grains for each of 5 samples					Average of gelatinized grains, %	First equalization of values, %	Second equalization of values, %
	1	2	3	4	5			
16	**2**	**2**	**2**	**2**	**3**	**22.0**		
							30.0	
17	4	4	4	3	4	38.0		36.5
							43.0	
18	5	6	5	4	4	48.0		49.5
							56.0	
19	6	7	6	6	7	64.0		63.0
							70.0	
20	7	8	7	8	8	76.0		75.5
							81.0	
21	8	9	8	9	9	86.0		86.0
							91.0	
22	9	10	9	10	10	96.0		94.0
							97.0	
23	10	10	10	10	10	98.0		97.7
							98.5	
24	**10**	**10**	**10**	**10**	**10**	**99.0**		

This technique has great sensitivity, particularly in identifying flavor indicators of rice, since the extracted fraction on the fiber is statistically introduced into the gas chromatograph (GC) by thermal desorption [15, 16]. For instance, Laguerre et al. [17] suggested an analytical technique for analysis of the volatile fraction using SPME-MS.

In our current study, our main purpose is to use the HS-SPME/GC-MS device as a reliable system for effective trapping and screening of a wide range of volatile flavor compounds in the headspace of Iranian rice samples during the gelatinization process.

The cooking time of rice is determined by the temperature at which the crystalline structure of the starch begins to melt. This is called the gelatinization temperature (GT). In rice samples, GT ranges from 55–85°C. Rice grains with high GT require more time to cook. Lowering the GT of the modified rice grains (HD5, HD6) could decrease average cooking time.

Regarding Tables 1 and 2, and Fig. 1, gelatinization time for 0%, 50%, 90%, and 100% of the whole grains is identified and, during this time, SPME fiber is injected. The whole process was divided into four stages: I, 15′; II, 18′:12″; III, 20′:28″; IV, 22′:38″. These were assigned to HD5 rice samples leading to 0, 50, 90, and 100% gelatinization of rice grains. Furthermore, for the HD6 variety, cooking stages I, 15′; II, 18′:38″; III, 21′:28″; IV, 24′:18″ lead to 0, 50, 90, and 100% gelatinization of rice grains.

Flavor Volatiles in the Two Iranian Rice Cultivars. Using the headspace SPME method, flavor volatiles in the two modified Iranian rice cultivars were extracted during gelatinization and analyzed by GC-MS. These compounds were determined by comparing their mass spectra and RI values with an authentic compound, whereas others were identified by their corresponding mass spectra (Adams Mass Spectra Libraries) and RI values, when RI values on the HP-5MS capillary column were available in the literature [18–20]. A whole range of 54 and 66 components was identified for HD5 and HD6, respectively. For HD5, 23, 11, 23, and 36 specific compounds were identified at stages I, II, III, and IV, respectively. For HD6, 14, 19, 47, and 32 specific compounds were identified at the same stages as HD5.

TABLE 3. Flavor Volatiles Identified in Headspace of HD5 Rice Cultivar, %

Compound	RI	Odor description	I	II	III	IV
n-Hexanal	801	Green, grass-like	62.3	56.7	38.9	22.2
n-Octane	809		0.7			
n-Hexanol	869	Herbaceous				1.1
n-Heptanal	899	Fruity, fatty	1.9			3.3
2-Acetyl-1-pyrroline	915		1.4			
Anizole	917		1.8	3.3	3.5	3.9
Ethanol	920	Sweet	0.9			
Benzaldehyde	974	Nutty, bitter	0.9			
6-Methyl-5-hepten-2-ol	982		1.0			
2-Pentylfuran	985	Nutty, bean	4.0	11.2	3.3	4.3
1-Octen-3-ol	989	Raw mushroom				2.4
1,3,5-Trimethylbenzene	990		0.8	4.8		
n-Octanal	993	Green, citrus-like	2.6		2.7	4.4
n-Decane	1009				1.6	1.7
D-Limonene	1022				6.2	
Undecane	1091		0.6			
n-Nonanal	1100	Soapy, citrus-like	6.1	7.6	8.8	11.7
Octyl formate	1140					1.9
(*E*)-2-Nonenal	1157	Fatty, tallowy				1.4
1,3-Dimethoxybenzene	1178		1.2			
Dodecane	1200		2.5	1.6	0.5	1.1
Tridecane	1297		0.4	3.2	1.7	2.4
E-2-Heptenal	1320	Herbaceous				1.4
Hexyl furan	1322					2.1
2,6-Dimethoxyphenol	1340					3.5
2-Methyl-undecanal	1366					0.9
n-Undecanol	1372					0.8
N.d.	1379				0.9	
N.d.	1379					0.7
Tetradecane	1391			4.0	4.1	3.0
(*E*)-2-Octenal	1432	Green, fatty				2.6
2,6-Dimethylnaphthalene	1442					1.3
Geranyl acetone	1463	Magnolia, green				1.6
1-Heptanol	1466	Green, fatty			1.6	
N.d.	1469					1.7
N.d.	1491		0.4			
Pentadecane	1500			3.6	6.3	3.6
Butylated hydroxytoluene	1524					1.5
1-Octanol	1560	Fruity, floral	0.6		1.0	
Hexadecane	1600			2.2	4.8	2.1
1-Nonanol	1670	Floral, citrus-like				1.1
n-Tetradecanol	1670					1.0
Heptadecane	1700				0.6	1.0
Phthalic acid	1703		3.4			
Farnesol	1710		2.2			
1-Octadecene	1799					0.6
n-Nonadecane	1905					0.7
n-Nonadecane	1907				4.1	
n-Eicosane	1995		0.3		2.0	
n-Heneicosane	2101			1.9	0.7	1.2
Docosane	2209		0.5		0.7	3.5
n-Tricosane	2291				2.0	
Tetracosane	2411		0.6		2.2	0.6
Pentacosane	2510				1.8	1.3
Total			97.0	100.0	99.9	99.3

N.d.: not detected.

TABLE 4. Flavor Volatiles Identified in the Headspace of HD6 Rice Cultivar, %

Compound	RI	Odor description	I	II	III	IV
Pentanal	710	Woody, fruity			1.5	
Octane	801				1.4	
n-Hexanal	802	Green, grass-like	49.0	42.2	14.2	36.3
n-Heptanal	900	Fruity, fatty	3.0	2.2		2.2
2-Acetylfuran	911					1.8
Anisole	919		5.3	7.1	5.2	2.5
α-Pinene	935					1.5
Camphene	951					1.1
Benzaldehyde	960	Nutty, bitter			2.0	1.2
2-Pentylfuran	981	Nutty, bean	6.6	4.4	3.8	5.3
1-Octen-3-ol	982	Raw mushroom	1.9	2.0	2.2	1.3
Octanal	990	Green, citrus-like		4.7	2.3	
1,3,5-Trimethylbenzene	992		4.0			2.8
D-Limonene	1020					2.6
Undecane	1091				2.7	
n-Nonanal	1095	Soapy, citrus-like	10.9	17.4	10.0	6.1
Octyl formate	1139			1.7		0.9
(*E*)-2-Nonenal	1152	Fatty, tallowy		0.9		0.5
1,3-Dimethoxybenzene	1175				0.4	1.1
Naphthalene	1187				1.0	
Dodecane	1200				0.3	
n-Octyl-1-iodo-octane	1250			2.6		
(*E*)-2-Decenal	1260	Waxy			1.2	
(*E,Z*)-2,4-Decadienal	1299	Fatty, green			1.3	
Tridecane	1300		1.4	1.1	1.4	0.9
Undecanal	1312	Fresh, lemon-like		0.6	0.3	
(*E*)-2-Heptenal	1316	Herbaceous			0.8	0.7
2,6-Dimethoxyphenol	1357		0.9	1.8	4.6	
2-Butyl-2-octenal	1383			0.7	1.0	
Biphenyl	1385				0.6	
Tetradecane	1400		2.2	2.3	2.1	1.6
2,6,10,14-Tetramethylhexadecane	1421					3.0
(*E*)-2-Octenal	1433	Green, fatty		1.4	1.7	1.7
2,6-Dimethylnaphthalene	1437				1.2	
1-Methoxynaphthalene	1440				1.2	
Neryl acetone	1441			2.1	1.0	1.0
2-Hydroxy, 2-methylbenzoic acid	1449					2.3
(2*Z*,6*E*)-Dodecadiene-1-al	1455				0.5	
2-Pentadecanone	1459				7.5	
Geranyl acetone	1460	Magnolia, green	1.4		2.2	
1,2-Benzenedicarboxylic acid	1469		2.4			
Pentadecane	1500		2.1	2.6	2.7	1.3
6-Isopropylquinoline	1519					0.9
N.d.	1539				0.6	
N.d.	1553					2.7
1-Octanol	1570	Fruity, floral			1.3	
N.d.	1573				0.6	
N.d.	1595					2.0
1-Hexadecene	1599				0.7	
Hexadecane	1600		2.1	2.4	4.4	4.0
2-Acetylnaphthalene	1602				1.6	
N.d.	1612				0.8	
Tetradecanal	1617				0.6	
N.d.	1658				0.7	
N.d.	1673				0.6	

TABLE 4. (continued)

Compound	RI	Odor description	I	II	III	IV
ar-Turmerone	1675				1.7	
1-Nonanol	1681	Floral, citrus-like			0.7	
Heptadecane	1700					0.9
(*E*)-2-Undecenal	1759	Fatty, sweet			0.9	
Octadecane	1809					3.1
2-Ethylhexyl salicylate	1811				1.8	
Tridecanal	1830					0.7
Isopropyl tetradecanoate	1839				1.3	2.1
Hexadecanoic acid	2006					2.7
2-Methoxy-4-vinylphenol	2191	Spicy, clove-like			1.0	
Docosane	2209				1.0	
Total			93	100	92.3	98.7

N.d.: not detected.

Altogether, the volatile compounds in the two Iranian rice samples during gelatinization belong to the chemical classes of aldehydes, ketones, hydrocarbons, esters, phenols, etc. These chemical classes correspond to those previously mentioned in non-Iranian rice using various methods of extraction.

Tables 3 and 4 show all compounds detected in the collected rice samples. The compounds listed in Tables 3 and 4 were mentioned before in rice. However, 33 new unique compounds were detected (docosane, 2-methylundecanal, phthalic acid, tetracosane, 1,3-dimethoxybenzene, anisole, pentacosane, heneicosane, tricosane, octane, octyl formate, 2,6-dimethoxyphenol, neryl acetone, tetradecanal, 1-methoxynaphthalene, 2-acetylnaphthalene, naphthalene, 1-hexadecene, *ar*-turmerone, 2-ethylhexyl salicylate, 1,3-dimethoxybenzene, biphenyl, isopropyl tetradecanoate, (2*Z*,6*E*)-dodecadien-1-al, α-pinene, camphene, 6-isopropylquinoline, 2-acetylfuran, 1,2-benzenedicarboxylic acid, *n*-octyl-1-iodo-octane, 2-butyl-2-octenal, 2,6,10,14-tetramethylhexadecane, and 2-hydroxy-2-methylbenzoic acid), which were not reported in the previous studies [8, 10, 21, 22].

Variation in Flavor Volatiles of Rice during Four Different Cooking Stages. Significant differences were investigated in the volatiles of rice during the four different gelatinization stages.

Two major compounds were detected at stage I for HD5 and HD6 rice cultivars, known as nonanal and hexanal. The latter is known as an important lipid oxidation product in rice. However, there are other components that have been identified only at stage I for HD5, such as ethanol, which were apparently lost by steam vaporization at later cooking stages during the cooking process. In contrast, hexadecanoic acid, which was identified as a predominant compound at stage IV for HD6, as well as pentacosane, were detected at stages III and IV for HD5. The variation in the volatile components of rice cultivars during cooking showed the same tendency for those flavor volatiles with a higher volatility (for instance ethanol) and a lower volatility (such as hexadecanoic acid).

Primary heating of rice at gelatinization stages I and II resulted in the evaporation of aldehydes in rice and fatty acids in steam distillation. But excess steam and heat have a destructive influence on the extraction of low-boiling-point volatiles. Thus, further heating at stages III and IV increased the rate of evaporation of a broad range of the flavor volatiles of rice.

Similarities and Differences among the Two Different Iranian Rice Cultivars. By comparing the volatile components in Tables 3 and 4, one can see the similarities and differences in the two Iranian rice samples. These samples were examined under the same conditions.

There were no significant differences in the profiles of flavor volatiles; however, less volatile compounds were identified in HD5 rice samples compared to HD6 rice samples. For instance, some components such as phthalic acid, farnesol, ethanol, and 2-acetyl-1-pyrroline were detected in HD5 modified samples, whereas HD6′s major compounds were α-pinene and camphene.

A broad range of the flavor volatiles of rice during gelatinization could be extracted and identified in a single headspace SPME/GC-MS, in which naphthalene compounds and benzene compounds were liberated widely and predominantly from different rice samples. These components have not been previously reported in rice.

From more than 300 rice volatiles identified by many research groups, 2-acetyl-1-pyrroline (2AP) is the principal aroma compound. We were able to detect 2-acetyl-1-pyrroline in the HD5 rice samples at gelatinization stage I, but we were unable to detect any 2-acetyl-1-pyrroline in the HD6 modified rice samples.

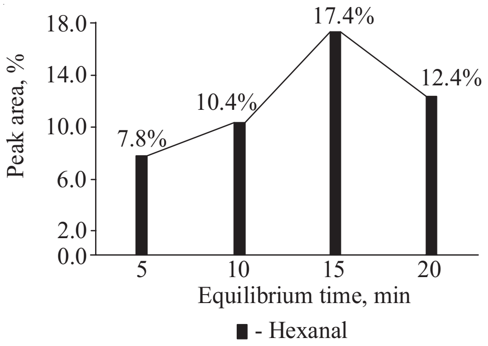

Fig. 1. Equilibrium time profile.

The aroma of rice can be directly linked to consumer preference in both positive terms (such as 2AP) and negative terms, of which hexanal and 2-pentylfuran were detected in the headspace of different rice samples.

In HD5 cultivar the amount of hexanal decreased with increasing gelatinization. The amount of 2-pentylfuran increased significantly at gelatinization stage II and decreased at stage III, and then increased slightly at stage IV.

In HD6 cultivar the amount of hexanal decreased with increasing gelatinization stage I, II, and III, and then increased significantly at gelatinization stage IV. Similar results were observed for 2-pentylfuran.

Optimization of Different Experimental Parameters. In order to optimize the conditions of presence of flavor compounds, the hexanal target was investigated.

Initially, three types of commercial fibers (PDMS, CAR/PDMS, and DVB/CAR/PDMS) were selected in order to extract volatiles from the headspace above the rice samples at the beginning of the experiment. The last is known as the most effective compound (12.4%) in the extraction of flavor volatiles, followed by PDMS (7.5%) and CAR/PDMS (5%). The DVB/CAR/PDMS fiber was used in all applications.

In order to estimate the effect of water content of rice samples on the SPME of target analytes, different volumes of water were added to 150 g rice sample, and SPME experiments were performed. The results indicate that increasing the water content to 300, 350, 400, 450, and 500 mL corresponded to increasing the extraction efficiency of hexanal to 9%, 12, 15, 13, and 10%, respectively. However, addition of greater than 400 mL water led to a large decrease in extraction efficiency, since this would result in producing an adhesive mixture that was not easily agitated and made the diffusion of analytes more difficult. On the other hand, addition of less than 400 mL water was not enough to cook the rice. Therefore, 400 mL water was selected as a suitable amount of water for the rest of the experiment.

For the investigation of the effect of equilibrium time on the target analytes, the rice samples were extracted 5–30 min. As Fig. 1 shows, with increase in equilibrium time, the extracted amounts of hexanal increased to a maximum after 30 min of extraction. As a whole, the optimum equilibrium time for hexanal was considered as 30 min (Fig. 1).

Contact Allergens Identified in the Headspace of Different Rice Cultivars. Farnesol is one of the most frequent contact allergens in perfumes. As a fragrance allergen, farnesol has to be mentioned by name in cosmetics within the EU (contact dermatitis).

D-Limonene is contained in citrus species such as citrus, orange, mandarin orange, and bergamot. The presence of D-limonene has to be mentioned by name in cosmetics of the EU (contact dermatitis).

α-Pinene is a major constituent of turpentine. Sensitization occurs mainly in painters, polishers, and varnishers, and those in the perfume and ceramics industries (contact dermatitis).

EXPERIMENTAL

Reagents and Standards. The alkane mixture, consisting of C8-C20 alkanes, was purchased from Fluka. The mixture was used for the calculation of retention indices (RI).

Headspace Solid-Phase Microextraction Sampling. For SPME, a sampling device was designed in order to collect the sample of flavor volatiles during the process of gelatinization. The flavor volatiles of rice during gelatinization were released through the first side arm, while the SPME fiber was located in the second side of the sampling device with a flexible septum. In all stages of gelatinization, the fiber was placed in the manually operated SPME holder, and the septum was covered with Teflon-coated silicone in order to prevent the release of volatile components in the septum. The fiber was lowered in the sampling port to adsorb flavor volatile components of the rice, and these were desorbed thermally in the injection port of the GC-MS instrument for 10 min at 250°C. Afterwards, the fiber was exposed to the SPME fiber conditioner at 250°C for 1 h for reconditioning before being subjected to the next volatile samples.

SPME fibers with PDMS (100 μm, nonbonded), CAR/PDMS (75 μm, bonded), and DVB/CAR/PDMS (65 μm, bonded) coating, provided by Supelco (Bellefonte, PA, USA), were used as commercial fibers and were preconditioned in an SPME fiber conditioner (GL Sciences) at 250°C for 1h before the first measurement.

Gas chromatographic separation was performed on an HP-6890 GC system (Hewlett-Packard, USA), coupled to a mass detector (HP-5973, USA) and equipped with a multi-channel detector. An HP-5MS (5% phenyldimethylsiloxane) column was used, with 30 m × 0.25 mm × 0.32 μm film thickness.

Analytes extracted onto the commercial fiber were injected using 9.5 mm Thermogreen LB-2 septa (Supelco).

The injector temperature was 250°C in this case. Helium purified to 99.99% was selected as a carrier gas at a flow rate of 1 mL/min. The temperature program was set at 60°C for 3 min, then increased at 220°C at a rate of 5°C/min and maintained at 220°C.

The mass selective detector was applied in an electron impact ionization mode at 70 eV.

The interface temperature was 230°C. The alkane mixture with C8-C20 alkane and concentration of 40 mg/mL in hexane was purchased from Fluka. The mixture was used to estimate retention indices (RI), and it was injected into the fiber by 5 min headspace extraction from a 10 mL SPME vial, including 1 mL HPLC-grade water spiked with 10 μL of the mixture.

The volatile components were positively identified by matching their mass spectra with the spectra of reference compounds in the Adams Mass Spectra Library (9th edition) and verified on the basis of mass spectra and RI values reported in the literature [18–20].

Rice Samples. Two new modified Iranian fragrant rice samples (HD5, HD6) were used in this study. These samples were collected from the Rice Research Institute. All samples were harvested in July 2009 and contained 20% moisture. Twenty-four hours after harvesting, the samples were sun-dried to about 12–13% moisture content, dehulled at the growing area, transported to the laboratory, stored in nylon bags, and placed in the refrigerator at 4°C until the time of experiment.

Gelatinization Process. First, some glass balls were poured into a glass containing 275 mL water, and the water was heated to the boiling point. Then 50 g of one of the tested sample was added to the boiling water and the whole stirred. After 7 min, we randomly chose 10 rice grains and put them on a glass plate at equal distance between them. Afterwards, the samples were covered with another plate and allowed to stand until gelatinized grains were observed, and then the number of gelatinized rice grains counted. After 8 min, we repeated the experiment every minute to determine all the ten gelatinized grains. This method is used for all samples in this study and was performed for the first time.

Rice Cooking. The traditional Iranian rice cooking method was used, employing a mixture of 150 g of white rice and 400 mL of distilled water. The whole process was divided into 4 stages, including all the steps from the beginning till the end of the gelatinization process. The cooking time of this process is determined by the temperature at which melting of the crystalline structure occurs. Rice with high GT requires more time to cook, whereas rice with low GT requires less time, usually up to 4 min. The former has unacceptable texture [1].

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