Aroma compounds generation in brown and polished rice during extrusion

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Abstract

The effect of mechanic extrusion on aroma compounds in brown and polished rice was studied by gas chromatography-olfactometry (GC-O). Aroma compounds were isolated using solvent extraction followed by solvent-assisted flavor evaporation. Aroma extract dilution analysis (AEDA) was performed on both brown rice and polished rice before and after the extrusion process. A total of 71 odorants were identified. On the basis of flavor dilution (FD) factors, the most important aroma compounds in extruded rice could be hexanal, heptanal, 2-acetylpyrroline, 1-octen-3-ol, octanal, (*E*)-2-octenal, nonanal, decanal and (*E*, *E*),2,4-nonadienal. The aroma compounds were similar in all rice samples but FD factors were different. The FD factors of 2-acetylpyrroline, 1-octen-3-ol in brown rice were much higher than in polished rice. The extrusion process greatly increased the FD factors of most aroma compounds, particularly aldehydes in brown rice.

Introduction

The aroma and volatile profile of cooked rice can be affected by postharvest processes (harvesting, drying, milling and storage) and cooking processes (boiling, puffing or extrusion) [1]. Extrusion is a high-temperature/short-time cooking process, producing breakfast cereals and other snack food products [2]. Extrusion conditions such as temperature and screw speed can affect product quality such as expansion, bulk density, and texture. Those conditions are also critical for the development, retention, and degradation of flavor components in the finished products [3].

In brown rice, the bran and germ are present while in milled rice, they are partly or totally removed[1]. Rice bran contains amino acid, lipids, minerals and antioxidants. Milled rice has a different chemical composition according to the degree of milling, and therefore could lead to differences on the formation of rice aroma during cooking [4][5].

In this work, the aroma compounds in brown and polished rice powder were analyzed by gas chromatography-mass spectrometry/olfactometry (GC-MS/O). Aroma extract dilution analysis (AEDA) was used to study the generation of aroma compounds in brown and polished rice before and after the extrusion process.

Experimental

Materials

‘Huanghuazhan’ rice cultivar was used in this study because it is one of the main commercial cultivars in South China. The rice was grown in the Experimental Station of the Rice Research Institute of Guangdong Academy of Agricultural Sciences on a sandy loam soil in 2016. They were sown in late March and harvested in mid-July. The rice grains were then air-dried to a moisture content of approximately 13% and stored at room temperature for 3 months. The rice samples were milled to separate the husk from the brown rice. The brown rice was then polished using a rice milling machine (Satake Co. Hiroshima, Japan) to obtain approximately 90% (w/w) polished rice. The brown rice and

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polished rice samples were sieved by passing through a 60-mesh sieve using a Cyclone Sample Mill (UDY Corporation, Fort Collins, CO, U.S.A.) for further process.

Extrusion

Extrusion was performed using a twin-screw extruder (Continua 37, Werner and Pfleiderer, Stuttgart, Germany) system with co-rotating. The screw diameter was 37 mm, overall L/D ratio was 27, and the diameter of extrusion die was 6 mm. The feed rate (25 kg/h) and screw speed (200 rpm) were kept constant. The extrusion was carried out at 120°C with the temperature of different barrel zones set at 60, 100 and 120°C. The feed moisture was conditioned to 12–17%. The extrudates were cooled to room temperature, packed in polyethylene bags and milled later to flour using a grinder (Sujata, India) to a particle size < 250 µm and stored at -20°C until further analysis. All samples, including raw polished rice (RPR); extruded polished rice (EPR), raw brown rice (RBR), and extruded brown rice (EBR), were kept in a refrigerator at 4 °C until analysis.

Rice aroma isolation with Solvent-Assisted Flavor Evaporation (SAFE)

The aroma compounds from four rice samples were extracted using organic solvent. For each variety, 200 g of sample was mixed with amylase (0.2% w/w) and Milli-Q water (1:1, v/v) and shaked for 1 hour. Then 100 mL of pentane/diethyl ether mix (2:1, v/v) was added to the rice mixture. The mixture was shaken vigorously for 1 hour at room temperature in a Teflon centrifuge bottle. The organic phases were separated by centrifugation at 5000 rpm for 15 min at 5 °C. The organic phase was saved and the sample was extracted two more times. The organic phases from three extractions were combined and distilled using solvent assisted flavor evaporation (SAFE) (Glasblaserei Bahr, Manching, Germany) technique to remove the nonvolatile constituents at 50 °C under high vacuum. After distillation, the receiving part of SAFE in the system was carefully rinsed with 5 mL of pentane/diethyl ether mix, and combined with the distillates in the volatile-receiving flask. The final distillates were dried over anhydrous sodium sulfate overnight and concentrated to about 1 mL at 40 °C using a Vigreux column, then concentrated to 0.1 mL using a stream of gentle nitrogen flow for further analysis.

Gas Chromatography/Olfactometry-Mass Spectrometry (GC/O-MS)

The GC-O and GC-MS analysis were performed using an Agilent 6890 GC with an Agilent 5973N mass selective detector (MSD, Willmington, DE, U.S.A.), and a Gerstel olfactory detection port (ODP series 2, Baltimore, MD, U.S.A.). All samples were analyzed on a DB-Wax column (30 m, 0.25 mm ID, 0.5 µm film thickness). One microliter of sample was injected into the GC in splitless mode. The oven temperature was programmed initially at 40 °C for 4 min, then increased to 230 °C at a rate of 4 °C/min with 20 min holding. The column carrier gas was helium at a flow rate of 2.5 mL/min. The flow was split between MS and ODP to provide one stream for MS identification and another stream the sniffing port for odor detection simultaneously. Six experienced panelists (2 males and 4 females) performed the GC-O analysis on the original extracts. Each sample was sniffed by each panelist in duplicates. Compounds' identification was achieved by comparing mass spectral data from the database and confirmed by comparing Kovats retention indices (RI) of standards obtained under the same conditions in the lab, in addition to odor description.

Aroma Extract Dilution Analysis (AEDA)

The aroma extracts were diluted stepwise with 1:1 (v/v) distilled pentane/ ether mix (1:1, v/v). Analyses were performed on the same instrument as described previously on a DB-5 column (30 m, 0.25 mm ID, 0.5 µm film thickness). One microliter of sample was injected into the GC in splitless mode. Determination of the flavor dilution (FD) factors was then done by two panelists, and each dilution was evaluated by each panelist in duplicates.

Results and discussion

GC/Olfactometry analysis of the four rice extract revealed 71 odor-active areas in the gas chromatogram (*data not shown*). AEDA revealed 28 compounds with FD factors ranging from 1 to 2048 (Table 1). Although the aroma-active compounds identified were similar among all the samples, their FD factors varied in different samples, demonstrating the flavor differences among the products.

Table 1: Aroma -active compounds in polished and brown rice, before and after extrusion

Compounds	*Odor*	*RI*	*ID*	*FD factor*			
				RPR	*EPR*	*RBR*	*EBR*
Dimethyl sulfide	cabbage	723	RI, A	8	8	8	8
Butan-2,3-dione	buttery	736	RI, A	2	8	8	8
3-Methylbutanal	malty	761	MS,RI,A	Na	na	2	1
Hexanal	green	819	MS,RI,A	32	64	32	256
Methional	potato	898	MS,RI,A	16	64	8	256
4-Mercapto-4-methylpentan-2-one (4MMP)	Grapefruit	912	RI, A	8	32	16	8
2-Acetylpyrroline	popcorn	917	MS,RI,A	16	64	512	2048
Pentanoic acid	sweaty	941	MS,RI,A	8	8	8	16
1-Octen-3-ol	mushroom	972	MS,RI,A	32	64	1024	1024
Octanal	oily	996	MS,RI,A	1	16	32	1024
Hexanoic acid	sour	1032	MS,RI,A	16	2	2	8
(*E*)-2-Octenal	oily	1057	MS,RI,A	16	32	32	64
Linalool oxide	floral	1080	MS,RI,A	Na	na	2	16
Nonanal	oily	1098	MS,RI,A	16	64	2	128
Ethyl hexanoate	fruity	1127	MS,RI,A	Na	na	8	8
(*E*)-2-Nonenal	oily, green	1130	MS,RI,A	2	na	2	32
Decanal	waxy	1195	MS,RI,A	2	64	8	128
(*E*,*E*)-2,4-Nonadienal	oily	1207	MS,RI,A	4	8	16	64
4-Vinylphenol	woody	1227	MS,RI,A	2	na	32	64
Octanoic acid	sour	1281	MS,	na	na	16	16
4-Vinylguaiacol	woody	1312	MS,RI,A	2	8	2	64
Vanillin	vanilla	1376	MS,RI,A	2	na	8	na

ID representes identification method. RI: compounds were identified by retention indices compared with pure compound standard; A: compounds were identified by the aroma descriptors; MS: compounds were identified by the MS spectra.

Among all the compounds identified, 2-acetylpyrroline, 1-octen-3-ol, hexanal, octanal, nonanal and decanal had relatively high FD factors, suggested their potentially higher aroma contribution. 2-Acetylpyrroline is a well-known character compound for rice products, whereas 1-octen-3-ol, hexanal, octanal, nonanal and decanal are generated from lipid oxidation of unsaturated fatty acids. 4-Mercapto-4-methylpentan-2-one (4-MMP) was also identified as a key odor-active compound.

Compared with the raw polished rice, the raw brown rice had higher FD factors for 2-acetylpyrroline, 1-octen-3-ol, octanal, and 4-vinylphenol, suggesting these compounds were associated with the bran and germ of the rice. The reason that the brown rice had higher FD factors for 1-octen-3-ol and octanal could be due to the fact that brown rice is more susceptible to off-flavor development, mainly due to oxidation of rice oil catalyzed by enzymes such as lipase and lipoxygenase and autooxidation. It is interesting to notice that the brown rice also showed a higher FD factor for 2-acetylpyrroline.

Extrusion changed the FD factors of many compounds. Extrusion increased the FD factors of 4-mercapto-4-methylpentan-2-one, 2-acetylpyrroline, and some lipid derived compounds (i.e. octanal, nonanal) in polished rice, and the increases were much more pronounced for brown rice, especially for lipid derived compounds including hexanal, heptanal, octanal, nonanal, decanal. During the extrusion process, thermal processing of the raw ingredients occurs under high temperature and shear, with limited moisture conditions. This process causes decomposition, degradation, denaturation, cross-linking, and various chemical reactions such as oxidation, polymerization, hydrolysis and other reactions in the extruded material. Thermal oxidation will generate straight-chained aldehydes. Linalool oxide was only detected in brown rice, and the extrusion process greatly increased its FD factor. 3-Methylbutanal, ethyl hexanoate and octanoic acid were also detected only in brown rice, however their FD factors were not greatly influenced by extrusion process.

In conclusion, brown rice had higher FD factors than polished rice for most of aroma-active compounds. The extrusion process greatly increased the FD factors of most aroma compounds, particularly aldehydes in brown rice.

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