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Identification and Formation of Volatile Components Responsible for the Characteristic Aroma of Mat Rush (Igusa)

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An aroma concentrate of the mat rush (igusa) was prepared by combining solvent extraction with the solvent-assisted flavor evaporation (SAFE) technique. An aroma extract dilution analysis (AEDA) applied to the volatile fraction revealed 51 odor-active peaks with FD factors between 4^3 and 4^7. Among the perceived odorants, twelve peaks with the higher FD factors ($\geq 4^6$) were proved to be the most important components of the characteristic aroma in mat rush. Eleven odorants were identified or tentatively identified from the twelve peaks as methional, (*E*,*Z*)-2,6-nonadienal, (*E*)-2-nonenal, (*E*,*E*)-2,4-nonadienal, (*E*,*E*,*Z*)-2,4,6-nonatrienal, *trans*-4,5-epoxy-(*E*)-2-decenal, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone, isovaleric acid, methyl anthranirate, and vanillin. The FD factors of the odor-active peaks in dried mat rush were observed to be much higher than those in raw mat rush. This finding suggests that the drying process during manufacturing of the mat rush is one of the most important factors for the formation of the characteristic mat rush aroma.

Key words: mat rush; igusa; odorant; aroma; aroma extract dilution analysis (AEDA)

Tatami, which is enshrined in Japanese culture and grows naturally in Japan's climate, is a significant part of such traditions as flower arrangement and the tea ceremony, and is closely involved with the Japanese lifestyle. Tatami, which is prepared from igusa (mat rush) as the main raw material, is the original Japanese flooring material. Many Japanese consider a room floored with the tatami as a space providing peace of mind. The tatami has such characteristics as purification of the air, thermal insulation, humidity adjustment, acoustic absorption, elasticity, and aroma,1) and it is said that these characteristics influence the peace of mind feeling. The characteristic and comfortable aroma in particular makes the mat rush extremely popular with the Japanese, and it has recently been suggested that the mat rush aroma has a relaxation effect.2) Interest in the odorants producing the mat rush aroma is therefore high.3–5)

Investigations to elucidate the odorants in the mat rush have already been reported,3–5) and many volatile components have been identified, mainly by gas chromatographic (GC) and GC-mass spectrometric (GC-MS) measurements. However, there were some problems with these investigations. For instance, many of the authors gave no details about the importance of the recognized compounds, because the GC analysis was not coupled with a GC-olfactometry (GC-O) technique such as an aroma extract dilution analysis (AEDA).6) Many of the previous investigations chose steam distillation to prepare the analytical samples, and it is known that this method makes it difficult to obtain the original aroma of the analytical samples.7) The actual significance of the odorants in the mat rush aroma is therefore still mostly unclear.

The harvested raw mat rush is generally processed into tatami products, in which the processing steps involved include soaking in clay mud, which is called sendo, drying, and weaving by a machine. The raw mat rush aroma is quite different from that of the dried mat rush that is used in the tatami products. It can therefore be expected that the manufacturing process is closely connected with the formation of the characteristic aroma of the mat rush.

The objective of the present investigation was to elucidate the potent odorants in the original mat rush aroma by AEDA. Furthermore, in order to clarify the generation of the characteristic aroma of the mat rush during manufacture, a comparison was made of the dried (muddied and non-muddied) mat rush and raw mat rush.

Materials and Methods

Mat rush (igusa). The mad rush (*Juncus effusus* L. var. *decipiems* Buchen.) samples were dried (muddied and non-muddied) and raw. These samples were produced in Kumamoto Prefecture (Japan) in 2008 and 2009, and presented by the Kumamoto Prefectural Agricultural Research Center (Kumamoto, Japan).

Chemicals. The following compounds were synthesized according to the literature procedures: 2-acetyl-1-pyrroline,8) (*Z*)-1,5-octadien-3-one,9) 3-mercapto-1-hexanol,10) and *cis*- and *trans*-4,5-epoxy-(*E*)-2-decenals.11) Compound nos. 1, 7–11, 13, 15, 19–23, 25–28, 31, 33, 37, 43, 45, 46, 49, and 51 were obtained from Tokyo Chemical Industry Co., (Tokyo, Japan); nos. 2–4, 12, 16, and 41 were obtained from Sigma-Aldrich Japan (Tokyo, Japan); nos. 18 and 50 were obtained from Wako Pure Chemical Industries (Osaka, Japan); no. 29 was obtained from Nihon Firmenich (Tokyo, Japan); and no. 36 was obtained from Acrōs Organics (Geel, Belgium) (Table 1).

*Synthesis of (*E,E,E*)-2,4,6-nonatrienal.* The target compound was prepared from (*E*,*E*)-2,4-heptadienal as the starting material by Horner-Wadsworth-Emmons olefination, DIBAL reduction and final Dess-Martin oxidation. Ethyl (*E*,*E*,*E*)-2,4,6-nonatrienoate was first synthesized by using diethylphosphonoacetate. To a solution of ethyl diethylphosphonoacetate (8.97 g, 40.0 mmol) in THF (100 ml) in an

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argon atmosphere was added sodium hydride (a 60% suspension in oil, 1.60 g, 40.0 mmol) at −70 °C, and 30 min later, to this mixture was added a solution of (*E*,*E*)-2,4-heptadienal (purity >95%, 2.53 g, 23.0 mmol; Tokyo Chemical Industry Co., Tokyo, Japan). The mixture was stirred for 1 h at −35 °C and then quenched with a saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with a mixture of *n*-hexane and ethyl acetate (5/1, v/v). The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel (silica gel 60N; Kanto Chemical Co., Tokyo, Japan), using 9–3% ethyl acetate in *n*-hexane, into a yellow oil of ethyl (*E*,*E*,*E*)-2,4,6-nonatrienoate (3.91 g, 94% yield). This ethyl (*E*,*E*,*E*)-2,4,6-nonatrienoate was reduced to the corresponding alcohol. To a solution of ethyl (*E*,*E*,*E*)-2,4,6-nonatrienoate (3.78 g, 21.0 mmol) in THF (140 ml) was added DIBAL (63.0 ml of a 1.0 mol/l *n*-hexane solution) at 0 °C in an argon atmosphere. After stirring for 1 h at the same temperature, the reaction was quenched with water. To the mixture was added a saturated potassium sodium tartrate solution, and stirring was continued for an additional 30 min. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The extract was washed with brine and dried (Na_2SO_4), and then the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, 9–50% ethyl acetate in *n*-hexane) to give 2.78 g (96% yield) of (*E*,*E*,*E*)-2,4,6-nonatrienol as an amorphous solid. In the final step, the target compound, (*E*,*E*,*E*)-2,4,6-nonatrienal, was synthesized from the corresponding alcohol by selective oxidation with Dess-Martin periodinane. To a solution of (*E*,*E*,*E*)-2,4,6-nonatrienol (1.37 g, 9.88 mmol) in methylene chloride (66 ml) was added Dess-Martin periodinane (37 ml of a 15 wt% methylene chloride solution, 18 mmol) at 0 °C in an argon atmosphere. After stirring for 1 h, the reaction mixture was quenched with a saturated Na_2CO_3 solution and extracted with a mixture of *n*-hexane and ethyl acetate (1/1, v/v). The combined extracts were successively washed with a saturated $Na_2S_2O_3$ solution and brine, dried (Na_2SO_4), and concentrated under vacuum. The residue was purified by column chromatography (silica gel, 17–50% ethyl acetate in *n*-hexane) to give 0.92 g (68% yield) of (*E*,*E*,*E*)-2,4,6-nonatrienal as a yellow oil (purity >98%). This structure was confirmed by mass spectrometry (electron impact [EI] mode) and nuclear magnetic resonance (^{1}H and ^{13}C). ^{1}H-NMR characterization of (*E*,*E*,*E*)-2,4,6-nonatrienal afforded data for δ (multiplicity, coupling constant [in hertz], and relevant H at carbon [numbering refers to Fig. 1]). MS/EI m/z (%): 136 (10, [M^+]), 121 (4), 107 (6), 91 (7), 79 (12), 66 (3), 53 (3), 39 (4); ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 1.05 (3H, t, $J = 7.6$ Hz, C9), 2.21 (2H, dt, $J = 7.6$, 7.6 Hz, C8), 6.04–6.22 (3H, m, C2, 6, 7), 6.35 (1H, dd, $J = 15.2$, 11.2 Hz, C4), 6.65 (1H, dd, $J = 15.2$, 10.4 Hz, C5), 7.12 (1H, dd, $J = 15.2$, 11.2 Hz, C3), 9.57 (1H, d, $J = 7.6$ Hz, C1); ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 13.7, 26.7, 128.4, 129.4, 131.3, 143.9, 144.5, 153.0, 194.2.

Isolation of the volatiles from mat rush. The crushed mat rush (dried, 25 g; raw, 20.8 g) was added to 1% water that contained diethyl ether (500 ml), the mixture then being stirred and extracted at room temperature. The water content of the raw mat rush is generally about 70%,[12] so the dry weight of this raw mat rush was equivalent to 1/4 of the weight of the dried mat rush. After standing for 2 h, the residual substances were removed by passing through filter paper. The filtrate (the aroma extract, approximately 350 ml) was dried over anhydrous Na_2SO_4, and then concentrated to a volume of approximately 50 ml by rotary evaporation (35 °C at 550 mm of Hg). To remove the non-volatile material, the aroma extract from the mat rush was distilled under reduced pressure (40 °C at 5×10^{-3} Pa) by the solvent assisted flavor evaporation (SAFE) method.[13] The distillate was dried over anhydrous Na_2SO_4, and the solvent was then removed by rotary evaporation (35 °C at 550 mm of Hg) to approximately 5 ml. Further concentration to approximately 150 µl was achieved in a nitrogen stream. The resulting concentrate was used as the sample for the AEDA and GC-MS analyses.

Enrichment of the odorants for identification. The identification experiments were conducted on the mat rush volatiles that had been isolated from the crushed mat rush by combining solvent extraction with the SAFE technique as already described. These procedures were repeated, and all the volatile fractions were combined (total 500 g of mat rush) and concentrated to approximately 2 ml. Part of the concentrated volatile fraction (150 µl) was applied to a glass column (10×0.7 cm i.d.) filled with silica gel in *n*-pentane. Elution was performed with the following solvents: *n*-pentane (20 ml, fraction I), *n*-pentane/diethyl ether (20 ml, 10 + 1, v/v, fraction II), *n*-pentane/diethyl ether (20 ml, 1 + 1, v/v, fraction III), and diethyl ether (20 ml, fraction IV). The solution was concentrated to approximately 150 µl as already described. The basic and weakly acidic volatiles were isolated by treating the other part of the concentrated volatile fraction (200 µl) dissolved in about 10 ml of diethyl ether. The basic volatiles were extracted with 1 M hydrochloric acid (2×5 ml). The combined acid extract was then washed with diethyl ether (1×5 ml), and the washed acid extract was neutralized with aqueous sodium hydroxide and then extracted with diethyl ether (2×5 ml). This extract was washed with brine (2×5 ml), dried over anhydrous Na_2SO_4 and finally concentrated to 50 µl (B, the basic fraction). The organic phase, which removed the basic volatiles, was extracted with 1 M-NaOH (2×5 ml), after extracting with a saturated solution of $NaHCO_3$ (2×5 ml). The combined extract with 1 M-NaOH was then washed with diethyl ether (1×5 ml). The washed 1 M-NaOH extract was neutralized with hydrochloric acid and then extracted with diethyl ether (2×5 ml). This extract was washed with brine (2×5 ml), dried over anhydrous Na_2SO_4 and finally concentrated to 50 µl (WA, the weakly acidic fraction).

Gas chromatography-olfactometry (GC-O). An Agilent 6850 series gas chromatograph equipped with a thermal conductivity detector (TCD) (Agilent Technologies, Palo Alto, USA) and fused silica column (30 m × 0.25 mm i.d., coated with a 0.25 25-µm film of DB-Wax; J & W Scientific, Folsom, USA) were was used in the splitless injection mode (splitless time: 1 min). The column temperature was programmed from 40 °C to 210 °C at the rate of 5 °C/min for all runs. The respective injector and detector temperatures were 250 °C and 230 °C, helium being used as the carrier gas at the flow rate of 1 ml/min. A glass sniffing port was connected to the outlet of the TCD and heated by a ribbon heater, with moist air being pumped into the sniffing port at about 100 ml/min to quickly remove the odorant from the sniffing port that had been eluted from the TCD.

Aroma extract dilution analysis (AEDA). The original odor concentrate of the mat rush was stepwise diluted with methylene chloride to 4^n (n = 3–8), and aliquots (1 µl) of each fraction were analyzed by capillary GC in a DB-Wax column. The odorants were then detected by GC eluate sniffing (GC-O). The flavor dilution (FD) factors of the odorants were determined by AEDA.[6] The FD factor of the original odor concentrate of the raw mat rush was converted into dry weight and is defined as 4^1. Before measuring the FD factor, two panelists repeatedly checked the retention time and odor quality of the odorants by using each diluted sample (1:16), and then the FD factor of each odorant was determined by being detected at the dilution step by both panelists.

Gas chromatography-mass spectrometry (GC-MS). An Agilent 7890 N gas chromatograph coupled to an Agilent 5975C inert XL series mass spectrometer (Agilent Technologies, Palo Alto, USA) was used. The column was a 60 m × 0.25 mm i.d. DB-Wax fused silica capillary type (J & W Scientific, Folsom, USA) with a film thickness of 0.25 µm. The column temperature was programmed from 80 °C to 210 °C or from 40 °C to 210 °C at the rate of 3 °C/min. The injector temperature was 250 °C, and the flow rate of the helium carrier gas was 1 ml/min. An injection volume of 1 µl or 0.2 µl was applied, using the split (the split ratio was 1:30) or splitless technique. The mass spectrometer was used with an ionization voltage of 70 eV (EI) and ion source temperature of 150 °C.

Identification of the components. Each component was identified by comparing its Kovats GC retention index (RI), mass spectrum and odor quality with those of the authentic compound.

Proton and carbon magnetic resonance spectrometry (^{1}H- and ^{13}C-NMR). The ^{1}H- and ^{13}C-NMR spectra were recorded in a $CDCl_3$ solution with a Bruker AVANCE 400 spectrometer operated at 400 MHz or 100 MHz. Tetramethylsilane was the internal standard for the ^{1}H-NMR measurements.

Table 1. Potent Odorants with FD factors ($\geq 4^3$) in the Mat Rush (igusa)

No.	RI[a]	Fraction[b]	Compound[c]	Odor quality[h]	$\log_4$ (FD factor)
1	1090		hexanal[e]	green	5
2	1137		(*Z*)-3-hexenal[de]	green	3
3	1237	II	(*Z*)-4-heptenal[e]	metallic, hay-like	3
4	1298	II	1-octen-3-one[e]	metallic, mushroom-like	4
5	1338	B	2-acetyl-1-pyrroline[e]	roasty	4
6	1370		(*Z*)-1,5-octadien-3-one[de]	metallic	5
7	1378		dimethyl trisulfide[e]	roasty, putrid	5
8	1378		(*Z*)-3-hexenol[e]	green	4
9	1427	II	(*E*)-2-octenal	green, fatty	3
10	1439		acetic acid	sour	4
11	1451		methional[e]	green, potato-like	6
12	1464	B	2,6-dimethyl-3-ethylpyrazine[e]	roasty, nutty	4
13	1493	B	2,3-diethyl-5-methylpyrazine[e]	roasty, nutty	3
14	1501	II	(*Z*)-2-nonenal[ef]	green, earthy	4
15	1535	II	(*E*)-2-nonenal	sweet, fatty	6
16	1565	II	(*E*,*E*)-2,6-nonadienal[e]	green, earthy	5
17	1578		unknown	green, earthy	6
18	1582		(*E*,*Z*)-2,6-nonadienal[e]	green	7
19	1621		butyric acid	sour	4
20	1648		phenylacetaldehyde	sweet, honey-like	3
21	1665	III	isovaleric acid	sour	7
22	1701		(*E*,*E*)-2,4-nonadienal[e]	sweet, fatty	6
23	1719	III	(*Z*)-6-nonenol[e]	green	3
24	1724		unknown	sweet	4
25	1733		pentanoic acid	sour	4
26	1766	III	(*E*,*Z*)-2,6-nonadienol[e]	green	3
27	1775		methyl salicylate[e]	green, minty	3
28	1813		(*E*,*E*)-2,4-decadienal	sweet, fatty	5
29	1823	II	*β*-damascenone	sweet, honey-like	3
30	1832		unknown	spicy, sweet	3
31	1842		hexanoic acid	green	3
32	1847		3-mercapto-1-hexanol[de]	fruity, grapefruit-like	3
33	1857	II	2-methoxyphenol	spicy, burnt	5
34	1876	II	(*E*,*E*,*Z*)-2,4,6-nonatrienal[ef]	sweet	6
35	1895	II	(*E*,*E*,*E*)-2,4,6-nonatrienal[e]	sweet	4
36	1936	II	(*Z*)-3-hexenoic acid[e]	green	3
37	1951		(*E*)-2-hexenoic acid[e]	green	3
38	1966		unknown	sweet	3
39	1986	III	*cis*-4,5-epoxy-(*E*)-2-decenal[eg]	sweet	3
40	2001	III	*trans*-4,5-epoxy-(*E*)-2-decenal[eg]	sweet	6
41	2028		4-hydroxy-2,5-dimethyl-3(2*H*)-furanone[de]	sweet, caramel-like	7
42	2075		unknown	spicy, phenolic	3
43	2167	WA	eugenol	spicy	4
44	2178		unknown	spicy	3
45	2195		3-hydroxy-4,5-dimethyl-2(5*H*)-furanone[de]	sweet, burnt sugar-like	7
46	2236	B	methyl anthranilate[e]	fruity, grape-like	7
47	2253		unknown	spicy, phenolic	3
48	2271		unknown	spicy, metallic	4
49	2456		coumarin[e]	sweet	3
50	2553	III	phenylacetic acid[e]	sweet	4
51	2565		vanillin	sweet, vanilla-like	7

[a] Retention index in the DB-Wax column (30 m × 0.25 mm i.d.; coated with a 0.25-µm film) observed for GC-O.

[b] Fraction in which most of the compound appeared after column chromatography on silica gel of the aroma concentrate (I–III) or after separating in to the basic (B) and weakly acidic (WA) fractions.

[c] The compound was identified by comparing with the reference substance on the basis of the following criteria: retention index (RI) of stationary phases given in the DB-Wax column, mass spectrum, and odor quality.

[d] The MS signals were too weak for unequivocal interpretation. The compound was tentatively identified by comparing with the reference substance on the basis of the following criteria: retention index (RI) of stationary phases given in the DB-Wax column and odor quality.

[e] Newly identified compounds in mat rush.

[f] The *cis-trans* isomer was tentatively identified by matching its mass spectrum, and retention index of the polar stationary phase with those of literature data.14,15)

[g] The stereochemistry was not determined.

[h] Odor quality assigned during AEDA.

Results and Discussion

Potent odorants in mat rush

The aroma concentrate of the mat rush was prepared by combining solvent extraction with the SAFE technique. The solvents used for aroma extraction from the crushed mat rush had a favorable polarity range, and diethyl ether was comparatively better for extraction than *n*-hexane or ethyl acetate. However, the aroma intensity of the diethyl ether extract was weak, and it could not reproduce the original aroma quality of the mat rush. A small amount of distilled water was then added to the

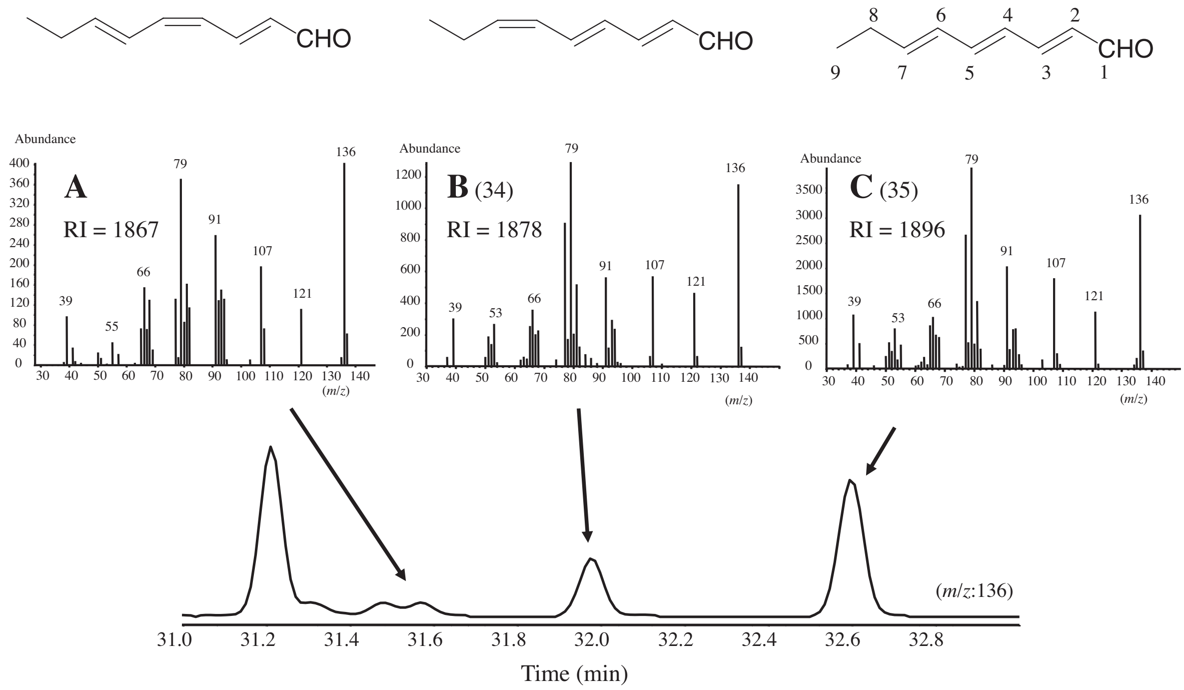


Fig. 1. Mass Chromatogram of the Volatile Concentrate of the Mat Rush Showing the Extracted Ion (*m/z*: 136), and Mass Spectra of Geometric Isomers of 2,4,6-Nonatrienal in the Mat Rush.

diethyl ether, and the intensity and quality of the aroma extract were markedly improved. In particular, the best aroma extract was provided when distilled water was added to diethyl ether in the range from 1% to 5%. Based on this result, the preparation method of for the volatile fraction was determined for to identification of the potent odorants in the mat rush was determined. This involved extracting the aroma extract from the crushed mat rush with 1% water-containing diethyl ether, and then the volatile fraction was prepared by a SAFE treatment to remove the non-volatiles from the aroma extract. The obtained volatile concentrate well-reproduced the characteristic aroma of the mat rush, and was regarded as the most preferable analytical sample for screening the potent odorants by the GC-O technique.

The AEDA technique that was applied to the volatile concentrate, which had been prepared from the crushed mat rush, revealed 51 odor-active peaks with FD factors between 4^3 and 4^7, and it was confirmed that the aroma of the mat rush consisted of many potent odorants (Table 1). After enriching the volatile fraction by column chromatography or solvent separation, thirty eight of these odorants could be identified by the GC-MS and GC-O analysis. Among the perceived odorants, two unknown compounds (nos. 34 and 35), which had similar mass spectra, were assumed to be geometric isomers of 2,4,6-nonatrienal by comparing the mass spectra to the literature data.[14] The mass chromatogram of the volatile concentrate of the mat rush in Fig. 1 shows the extracted ion with *m/z* 136, and at least three kinds of compound (A, B and C), which gave similar mass spectra, were contained in the mat rush. When considering the retention indices, nos. 34 and 35 may be considered to respectively correspond to B and C. (*E*,*E*,*E*)-2,4,6-nonatrienal was synthesized to confirm the structures of nos. 34 and 35, and its retention index was compared to the peaks of the volatile concentrate of the mat rush. The result showed that the retention index of synthesized (*E*,*E*,*E*)-2,4,6-nonatrienal closely agreed with that of compound C, enabling no. 35 in the mat rush to be confirmed as (*E*,*E*,*E*)-2,4,6-nonatrienal. The three kinds of 2,4,6-nonatorienals in the mat rush have also been found[14] in oat flakes, and their retention indices on the polar stationary phase were in good agreement with the observed values for the mat rush. Accordingly, based on the retention index of (*E*,*E*,*E*)-2,4,6-nonatrienal, compounds A and B were assigned as the *E*,*Z*,*E* and *E*,*E*,*Z* isomers, while the structure of no. 34, which gave a high FD factor for the mat rush aroma, was tentatively identified as (*E*,*E*,*Z*)-2,4,6-nonatrienal. The mass spectral signals of the remaining odorants were too weak for any unequivocal interpretation; these odorants were therefore tentatively identified by matching their retention indices and odor quality to those of the standard compounds from GC-O (DB-Wax). The result showed that, in addition to the 38 previously identified odorants, another five compounds could be added as tentatively identified odorants.

These findings identified forty-three potent odorants involved in the characteristic aroma of mat rash. Since thirty were newly identify compounds in the mat rush, the major portion of the potent odorants of mat rush can be assumed to be too low and thus difficult to clarify.

Formation of the potent odorants in mat rush

Raw mat rushes, which are generally harvested in the early summer (from June to the end of July), are processed into igusa seat products (so-called tatami omote). The steps involved in processing tatami omote involve soaking in clay mud, which is called sendo, drying at a comparatively low temperature for a long time (approximately 50–70 °C for more than 10 h), and finally machine weaving. The muddied and dried mat rush was found to have the characteristic aroma, despite the raw

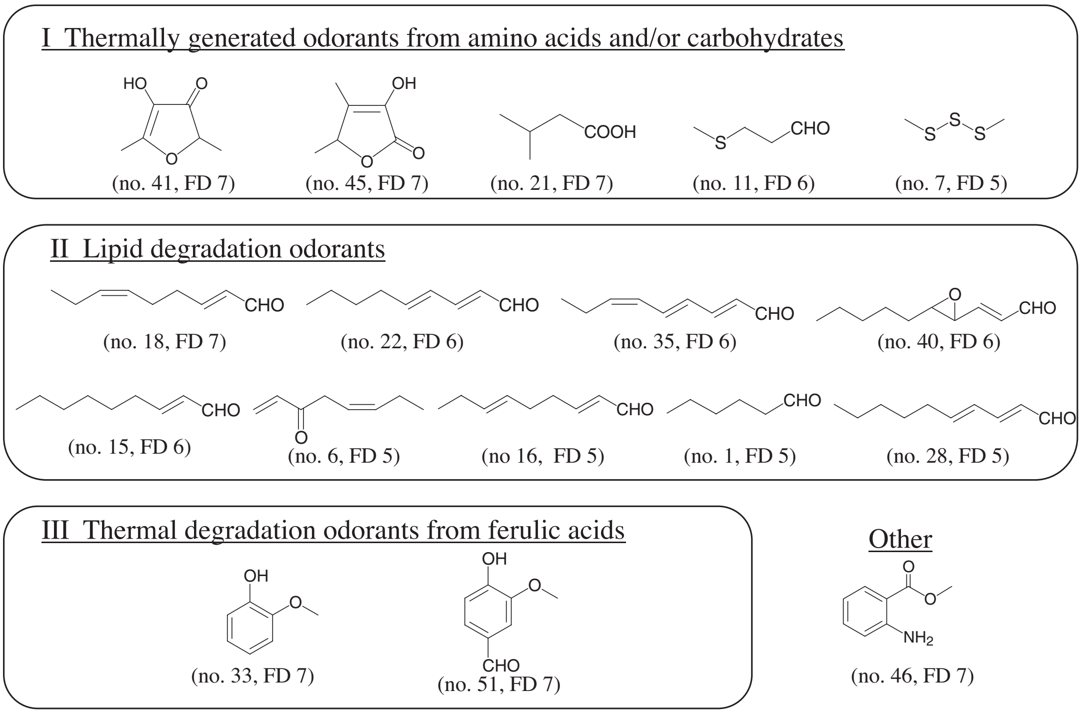
Table 2. Comparison of the Potent Odorants Showing High FD-Factors ($\geq 4^4$) in the Dried (muddied and non-muddied) and Raw Mat Rush Samples

No.	RI[a]	Compound	Odor quality[b]	$\log_4$ (FD factor)		
				Dried (muddied)	Dried (non-muddied)	Raw[c]
1	1090	hexanal	green	5	4	<4
4	1298	1-octen-3-one	mushroom-like	4	4	<4
5	1338	2-acetyl-1-pyrroline	roasty	4	<4	<4
6	1370	(*Z*)-1,5-octadien-3-one	metallic	5	5	<4
7	1378	dimethyl trisulfide	roasty, putrid	5	4	<4
8	1378	(*Z*)-3-hexenol	green	4	<4	<4
10	1439	acetic acid	sour	4	4	<4
11	1451	methional	green, potato-like	6	5	<4
12	1464	2,6-dimethyl-3-ethylpyrazine	roasty, nutty	4	4	<4
14	1501	(*Z*)-2-nonenal	green, earthy	4	<4	<4
15	1535	(*E*)-2-nonenal	sweet, fatty	6	5	4
16	1565	(*E*,*E*)-2,6-nonadienal	green, earthy	5	5	<4
17	1578	unknown	green, earthy	6	5	<4
18	1582	(*E*,*Z*)-2,6-nonadienal	green	7	6	5
19	1621	butyric acid	sour	4	4	<4
21	1665	isovaleric acid	sour	7	6	<4
22	1701	(*E*,*E*)-2,4-nonadienal	sweet, fatty	6	5	<4
24	1724	unknown	sweet	4	4	<4
25	1733	pentanoic acid	sour	4	4	<4
28	1813	(*E*,*E*)-2,4-decadienal	sweet, fatty	5	4	<4
33	1857	2-methoxyphenol	spicy, burnt	5	4	<4
34	1876	(*E*,*E*,*Z*)-2,4,6-nonatrienal	sweet	6	5	<4
35	1895	(*E*,*E*,*E*)-2,4,6-nonatrienal	sweet	4	<4	<4
40	2001	*trans*-4,5-epoxy-(*E*)-2-decenal	sweet	6	6	4
41	2028	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	sweet, caramel-like	7	6	<4
43	2167	eugenol	spicy	4	<4	<4
45	2195	3-hydroxy-4,5-dimethyl-2(5*H*)-furanone	sweet, burnt sugar-like	7	6	<4
46	2236	methyl anthranilate	fruity, grape-like	7	6	<4
48	2271	unknown	spicy, metallic	4	3	<4
50	2553	phenylacetic acid	sweet	4	4	<4
51	2565	vanillin	sweet, vanilla-like	7	7	5

[a] Retention index in the DB-Wax column (30 m × 0.25 mm i.d.; coated with a 0.25-µm film) observed for GC-O.

[b] Odor quality assigned during AEDA.

[c] The FD factor of the original odor concentrate of the raw mat rush was converted into the dry weight equivalent and is defined as 4^1 (See the Materials and Methods section).



I Thermally generated odorants from amino acids and/or carbohydrates

II Lipid degradation odorants

III Thermal degradation odorants from ferulic acids

Other

Fig. 2. Classification of Most Contributed Odorants (FD $\geq 4^5$) by Hypothetical Precursors.

mat rush just after harvesting hardly presenting any aroma. The sendo used in the muddying process is clay powder, and it is believed to be important for enhancing homogeneous drying and producing the characteristic color, luster, and aroma of the mat rush.[12] The potent odorants contained in the dried mat rush (muddied and non-muddied) were compared to those of the raw mat rush (Table 2). On the basis of this result, a marked difference in the FD factors was observed between the dried and raw mat rush samples, despite the FD factors and composition of the potent odorants in the dried mat rush (between the muddied and non-muddied) being similar. It is therefore assumed that the drying process is the most important factor for forming the characteristic aroma of the mat rush, and that the mud had little effect on the formation of this characteristic aroma.

Since the mat rush aroma was mainly generated during the drying process, it is considered that the formation of the potent odorants would be strongly affected by the heating. It therefore seems that many of the most contributive odorants ($\mathrm{FD} \geq 4^5$) could be classified by the hypothetical precursors into the three groups (I, II and III) (Fig. 2). Group I contains the so-called thermally generated odorants,[7] which were generated by the reaction of amino acids with carbohydrates or themselves, the furanones (nos. 41 and 45), isovaleric acid (no. 21), methional (no. 11) and dimethyl trisulfide (no. 7) also falling into group I. Group II contains the lipid degradation odorants,[11,14,16] which are known to be generated by both heating and by light and enzyme reactions, with hexanal (no. 1), the unsaturated aldehydes (nos. 15, 16, 18, 22, 28, 35 and 40) and a ketone (no. 6) also falling into group II. Finally, the odorants in group III are derived from ferulic acid,[7,17] with 2-methoxyphenol (no. 33) and vanillin (no. 51) that are formed by thermal degradation accompanied by decarboxylation and oxidation also falling into group III. It is therefore considered that the characteristic odorants in mat rush have the corresponding precursors. These hypothetical precursors are generally non-volatile compounds included in a variety of foodstuffs, although there have been few detailed studies concerning the chemical composition of the mat rush. It will be important to understand the formation mechanism of the mat rush odorants and their precursors in the future to improve the aroma quality of tatami products.

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