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The odor of matcha (Japanese powdered green tea) as the base note of green tea leaves

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Abstract: We previously reported the group of aroma constituents that characterize the odor of sencha (green tea made from leaves) which is similar to but distinct from the odor of commercially available matcha (Japanese green tea made from powder).This study, investigated whether the group of aroma compounds contributing to this matcha-like odor is present in all green tea cultivars and products. Crude sencha teas made from the 'Yabukita', 'Sayamakaori', 'Samidori', and 'Ujimidori' cultivars, and teas prepared by different processes (hojicha and unkacha), were investigated. These green tea leaves had a common matcha-like odor originating from a group of identical constituents. Commercially available matcha were studied as the source of the standard odor. The extracts obtained from matcha were separated into groups with different odors by fractional distillation. Chemical and analytical methods showed that the group of key compounds producing the matcha-like odor included a minute quantity of several aliphatic aldehydes. Many aldehyde proton signals were observed by ^{1}H NMR and some aldehydes were detected by mass spectroscopy. It was concluded that a matcha-like odor that contained some aliphatic aldehydes was the base note of green tea leaves, indicating the importance of the matcha-like odor to green tea's odor character.

Keywords: Matcha, green tea leaves, matcha-like odor, base note, aldehyde

Running title: MATCHA ODOR AS BASE NOTE IN GREEN TEA LEAVES

Introduction

Green tea is a popular beverage in everyday life. Recently, green tea leaves have been used as additives to impart green tea odor to many kinds of foods, such as ice cream and cakes. The odor of crude green teas (sencha) is not very strong, and is not often used to flavor foods, but Japanese powdered green tea (matcha) has a strong and characteristic green tea odor, and is therefore widely used to add green tea flavor and odor into many kinds of foods. Matcha is obtained from tencha, a type of tea leaf specially manufactured for use as flavoring, which a is different source than that of sencha. Thus, there are two typical green tea odors encountered. Over 600 volatile compounds from green tea leaves have been reported in green tea beverages.[1] Although new constituents have been added to the list of known volatile components in green tea leaves,[2] those specific constituents responsible for green tea odor have not been identified. Matcha-like odor is an important odor of green tea leaves and is due to a group of organic compounds.[3]

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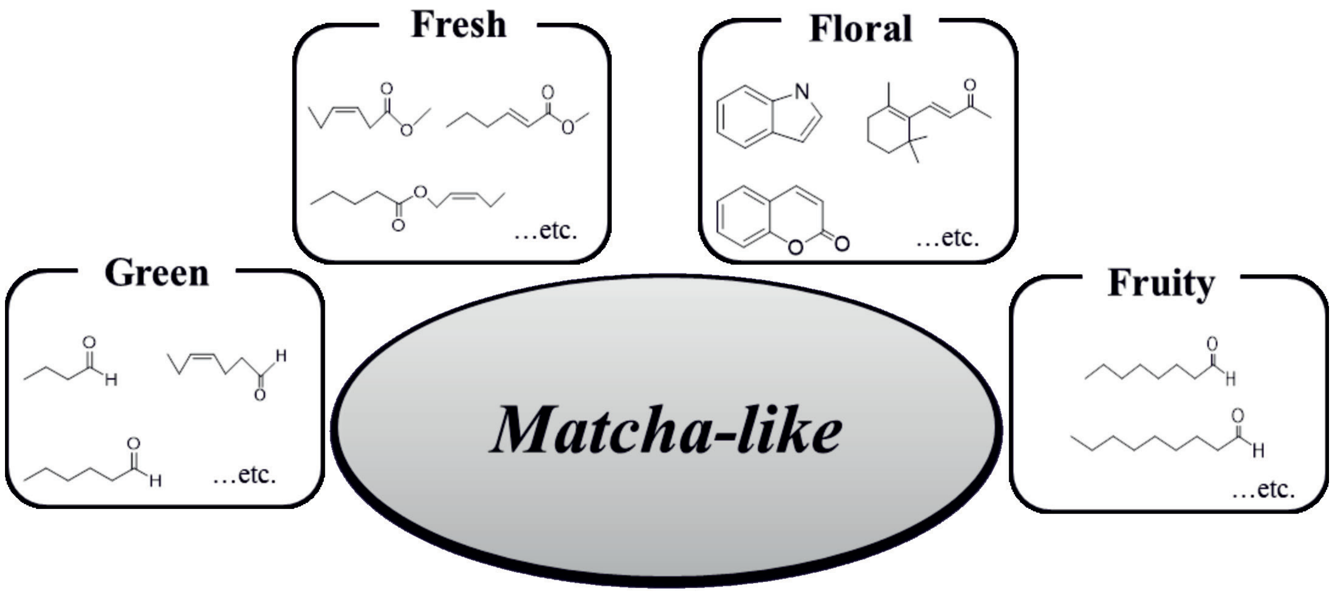


Matcha has a characteristic laver-like odor, which was distinct from that of the matcha-like odor in other green tea leaves.[4] This investigation attempted to establish the odor of matcha as the standard odor in green tea leaves.

Methodology

Experimental setup

All dehydrated solvents and reagents used for synthesis were purchased from Wako Pure Chemical Industries, Ltd., Japan. The 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were measured on an Avance 400 NMR system (Bruker, Karlsruhe, Germany). The 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra were measured on an Avance 500 NMR system (Bruker). Chemical shifts are expressed in ppm relative to the signal of tetramethylsilane as an internal standard (^{1}H and ^{13}C data). Gas chromatography-mass spectrometry (GC-MS) analysis was performed by a SCION SQ 456-GC/MS System (Bruker Daltonics, Leipzig, Germany). The column was an InertCap Pure-WAX (GL Science Inc., 30 m × 0.25 mm i.d.) with a film thickness of 0.25 µm. The column temperature program was as follows: 40 °C (5 min) to 250 °C (30 min) at a rate of 4 °C / min. Helium was used as carrier gas at flow rate of 1 mL/min, and the split ratio was 1:50. The injection and detection temperature was 250 °C.

Plant materials

Commercially available matcha was obtained from Marukyu Koyamaen Co., Ltd., Japan. The tea leaves of *Camellia sinensis L.* cultivars Yabukita and Sayamakaori and of unkacha (tea leaves derived from insect-damaged Yabukita green tea leaves, and which have a characteristic sweet odor) were collected at a tea plantation at the Green Tea Laboratory, Saitama Prefectural Agriculture and Forestry Research Center, Japan. The tea leaves of two cultivars, Samidori and Ujimidori, were collected at a tea plantation at the Green Tea Laboratory, Kyoto Prefectural Agriculture, Forestry and Fisheries Technology Center Tea Industry Research Division, Japan. Several kinds of crude green teas (sencha) were made from these cultivars. Hojicha (tea leaves prepared by roasting, with a characteristic roasted odor) was manufactured from Yabukita at the Green Tea Laboratory, Saitama Prefectural Agriculture and Forestry Research Center, Japan.

General procedure for hexane extraction

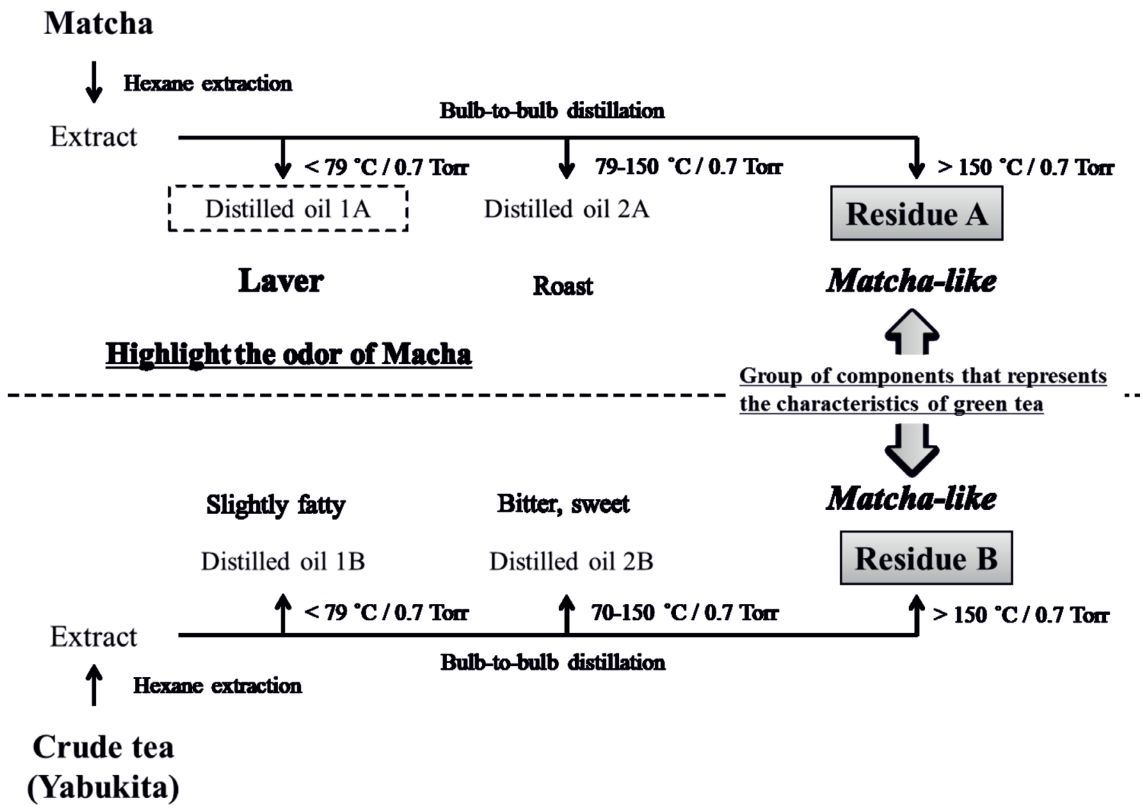
Tea (20–100 g) was added to flasks with hexane (1 L), and stirred at room temperature for 24 h. Removal of the solvent under reduced pressure afforded an oily residue. Extractabilities were 4.2 % (matcha), 0.6 % (Yabukita green tea), 0.8 % (Sayamakaori green tea), 1.3 % (Samidori green tea), 1.1 % (Ujimidori), 1.0% (unkacha), and 0.9 % (hojicha).

General procedure for reducing the oil with a matcha-like odor

$LiAlH_4$ (95.8 mg) and absolute diethyl ether (3.0 mL) were added to a flask purged with nitrogen. A solution of the matcha residue (60.2 mg) in ether (3.0 mL) was added to the flask. The reaction was monitored by thin layer chromatography (SiO_2, CH_2Cl_2). Diethyl ether (3.0 mL), water (6.0 mL), 15 % NaOH aq. (1.0 mL) were added slowly to the reaction mixture. The organic layer was separated, washed with brine (3.0 mL × 2), and dried over magnesium sulfate. Removal of the solvent gave the crude compounds as a greenish oil (5.1 mg).

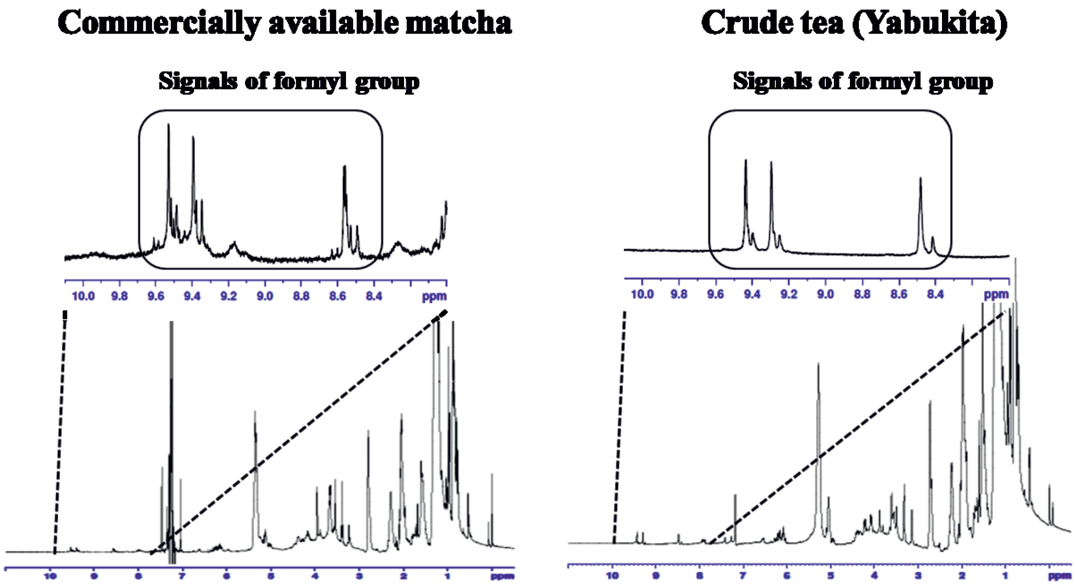
Results

The hexane extract obtained from green tea leaves, except for commercially available matcha, were obtained via bulb-to-bulb distillation under reduced pressure (96–135 °C, 0.08–0.6 Torr) to afford oil residues. The fractions obtained at lower boiling temperatures (distilled oil 1B and in Figure 2) had slightly fatty, bitter, and sweet odors. The residue (higher boiling point fraction) had a matcha-like odor. The extraction of matcha and the bulb-to-bulb distillation of the hexane extract were carried out using the same procedure. The obtained residue had similar matcha-like odor and the low-boiling fraction (distilled oil 1A in Figure 2) gave a laver-like odor, which is due to the characteristic matcha odor. Previously, the residue obtained from the hexane extract of matcha had a laver odor,[4] but further experiments gave the results shown in Figure 2, where the residue had a matcha-like odor.

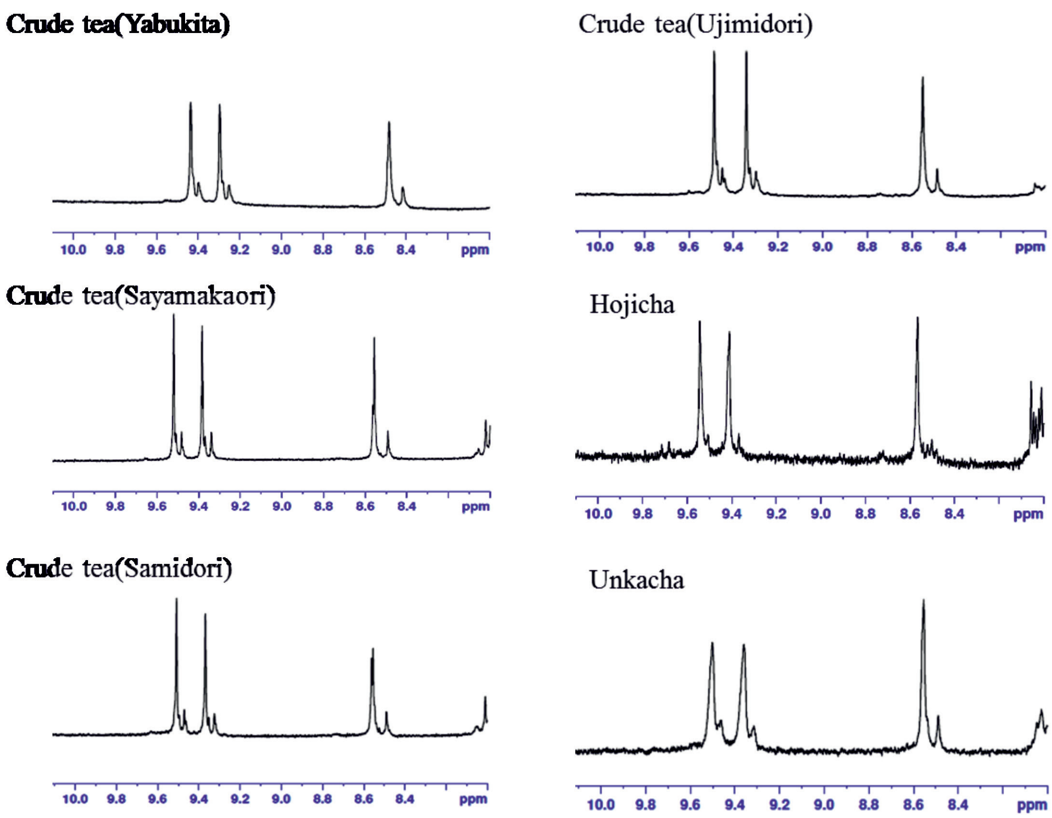


Discussion

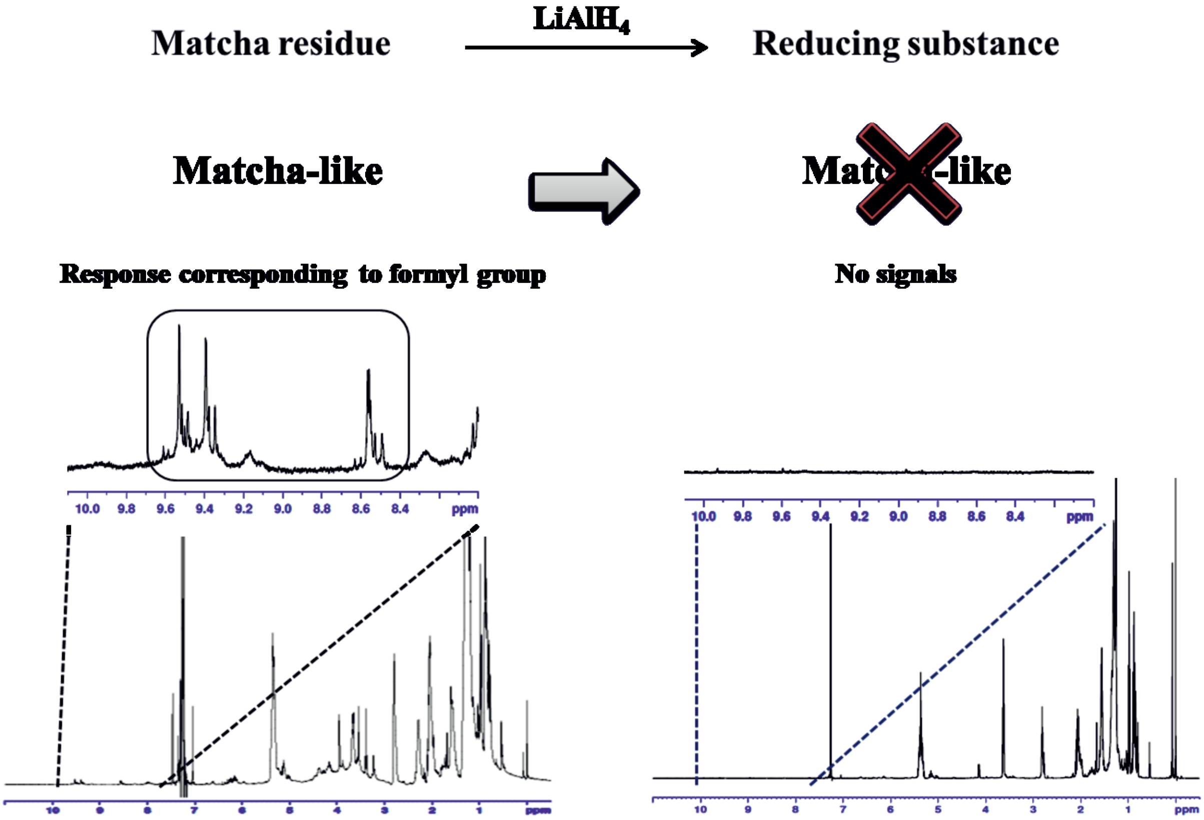
The signals of formyl groups in the obtained NMR spectra indicated that both Yabukita green tea and matcha had similar aldehyde constituents. In a commercially available matcha there were matcha-like odors that were composed of similar aldehydes.



It was investigated whether every green tea cultivar and differently prepared teas have common aldehydes by H-1 NMR analysis. Figure 4 shows that all teas have the same responses for a formyl group, and the results indicated the existence of similar aldehydes contributing to the matcha-like odor.



The importance of aldehydes in the matcha-like odor by the previous reported chemical method (the reduction of the residue)[4] were investigated. The results shown in Figure 5 were obtained.



Fractions 1 and 2 and the residue of matcha extract (Figure 2) were analysed by GC/MS. The obtained results are shown in Tables 1–3.

Table 1: GC-MS analysis of the distilled oil 1A

Compounds	Retention time (min)	Retention index
(*Z*)-2-Heptyl-4-phenyl-1,3-dioxolane	9.65	1033
Unknown	10.44	1109
Unknown	11.19	1129
1.8-Nonadien-3-ol	11.45	1136
1,2,3,4-Tetrahydro-5-methyl-1-[2-hydroxymethyl-3-dimethylamino] tetrahydrofur-5-yl pyrimidin-2,4-dione	12.50	1161
Unknown	12.65	1164
Unknown	15.32	1228
2-Pyrrolidinecarboxylic acid	16.24	1251
N-[4-Aminobutyl]aziridine	17.60	1284
Unknown	18.91	1317
Unknown	19.02	1320
2-Ethyl-1-hexanethiol	19.23	1326
3-Methoxy-3-methylbutanol	20.11	1350
2-Ethyl-1-hexanol	22.33	1407
3-Methylthiononanal	22.50	1412
3,5-Octadien-2-one	22.97	1426
2-Methyl-6-hepten-1-ol	25.34	1493

10-Undecenoic acid octylester	25.92	1509
Unknown	26.08	1514
Unknown	28.49	1585
2-Propanoicacid, 1-ethyldodecylester	29.16	1605
Estragole	31.84	1695
Benzylalcohol	33.12	1736
3-Bromobenzaldehyde	34.02	1764
ar-Tumerone	42.40	2041
7-Methyl-(*Z*)-tetradecen-1-ol acetate	43.71	2090
2-Trifluoroacetoxydodecane	48.46	2270
1-Gala-1-ido-octose	48.64	2277
3-Hydroxydodecanoic acid	50.29	2343
2-Propenoic acid 1-methylundecylester	50.48	2351
4-[*N*–(2-Hydroxyethyl)-N-nitro]amino-1,2,4-triazole	51.66	2397
Total	-	-

Table 2: GC-MS analysis of the distilled oil 2A

Compounds	Retention time (min)	Retention index	Peak area (%)
3-Methoxy-3-methylbutanol	19.89	1352	0.67
2-Hexadecanol	26.02	1520	0.67
1,1-Oxybisoctane	29.03	1600	0.48
Octacosane	31.82	1695	0.96
2-Methyl-5-(1-methylethyl)-(1α, 2α, 5α)-bicyclo[3.1.0]hexan-2-ol	32.48	1716	0.29
Benzylalcohol	33.12	1736	0.86
2-Octylcyclopropanetetradecanoic acid methylester	33.60	1751	0.38
2-Methyl-1-hexadecanol	34.51	1778	0.29
(*E*)- *β*-Ionone	34.78	1786	0.48
10-Octadecenal	35.13	1797	0.48
1,5,5-Trimethyl-6-acetylmethylcyclohexene	36.07	1829	1.05
(*E*)-3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	37.76	1887	3.83
(*E*)-2-Decen-l-ol	37.98	1894	0.57
2,10-Dimethyl-9-undecenol	39.88	1955	3.83
Cyclohexanebutanoic acid	40.56	1976	2.39
(*E*)-2-Undecylcyclopropanepentanoic acid methylester	42.03	2027	0.24
Unknown	42.25	2036	0.19
2-Oxa-6-azatricyclo[3.3.1.1(3.7)]decane	42.59	2048	1.15
7-Methyl-(*Z*)-tetradecen-1-ol acetate	42.92	2061	0.38
(*R*)-5,6,7,7α-Tetrahydro-4,4,7α-trimrethyl-2(4H)-benzofuranone	43.67	2089	8.90
Unknown	44.08	2104	0.77
2-Ethylidene-6-methyl-3,5-heptadienal	44.68	2126	0.96
12,15-Octadecadiynoic acid methylester	44.70	2127	0.77
3-Ethenyl-4-methyl-1*H*-pyrrole-2,5-dione	45.57	2158	0.77
Acetic acid 2-methyl-6-oxo-heptylester	45.73	2163	1.34
3-Hydroxy-dodecanoic acid	46.12	2177	0.38
Unknown	46.55	2192	0.34
3-Acetoxydodecane	48.51	2272	0.34
3,7,11-Trimethyl-1-dodecanol	48.62	2276	0.48

(*Z*)-2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol	49.08	2349	5.74
3-Hydroxy-7,8-dihydro-β-ionol	51.09	2375	2.39
1,5,5-Trimethyl-6-acetylmethylcyclohexene	51.94	2350	1.91
Caffeine	59.45	2584	53.61
Unknown	60.87	2628	2.11
Total	-	-	100.00

[a] t < 0.1 %

Table 3: GC-MS analysis of the residue A

Compounds	Retention time (min)	Retention index	Peak area[a] (%)
Octanal	14.16	1197	t
Hexanedioic acid, dioctylester	15.29	1227	t
Unknown	17.10	1272	t
Hexanedioic acid, dioctylester	17.61	1284	t
(*E*,*Z*)-2,6-Nonadienal	22.22	1404	t
(*E*)-2-Nonenal	24.10	1459	t
(*Z*)-2-Octen-1-ol	24.13	1460	t
Nonanal	24.39	1467	0.90
6-Azabicyclo[3,2,1]octane	25.18	1488	0.22
Unknown	26.60	1530	t
1-Decanol	28.75	1592	t
2-Ethyl-1-hexanamine	29.62	1621	0.90
Unknown	31.72	1691	0.22
Octan-2-yl propyl carbonate	32.44	1715	0.45
3,7,11,15-Tetramethyl-2-hexadecen-1-ol	35.16	1798	28.96
(*Z*)-2-(9-Octadecenyloxy)ethanol	35.88	1823	4.94
3,7,11,15-Tetramethyl-2-hexadecen-1-ol	36.55	1846	7.63
10-Ocatadecenal	38.35	1906	t
Unknown	43.43	2080	t
Unknown	43.60	2086	1.80
2-Hexadecanol	43.73	2091	0.22
(*Z*)-(13,14-Epoxy)tetradec-11-en-1-ol acetate	50.49	2351	8.08
3,7,11-Trimethyl-1-dodecanol	52.42	2365	1.80
Nonacosane	56.18	2482	2.69
(3β,5α)-2-Methylene-cholestan-3-ol	59.06	2572	0.90
Caffeine	59.31	2580	21.32
l-Acetyl-19,2l-epoxy-15,16-dimethoxy-aspidospermidin-17-ol	59.92	2599	t
3’,8,8’- Trimethoxy-3-piperidyl-2,2’-binaphthalene-1,l’,4,4’-tetrone	60.88	2629	2.02
1, l’-[1,2-Ethanediylbis(oxy)]bis-9-octadecene	69.17	2887	3.37
(*Z*,*Z*)-9-Octadecenyl-9-hexadecenoic acid	80.33	3234	13.47
Total	-	-	99.89

[a] t < 0.1 %

Some compounds, 2-pyrrolidinecarboxylic acid, 2-ethyl-1-hexanethiol, and 3-methylthiononanal were presumed to be the important constituents of laver-like odor by Table 1. The residue of matcha extract had the following aldehydes and aldehydes, octanal, (*E,Z*)-2,6-nonadienal, (*E*)-2-nonenal, (Z)-2-octen-1-ol, nonanal, and 1-decanol, which were almost the same as the reported results[3] as shown in Table 3. However, (*E,E*)-2,4-nonadienal and (*E,Z*)-2,4-decadienal were not detected.

In conclusion, it was clarified that matcha has a matcha-like odor as well as a laver-like odor. The matcha-like odor of matcha is the fundamental odor in the characteristic odor of green tea leaves.

Acknowledgement

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Figure captions

Figure 1. An overview of green tea aroma constituents

Figure 2. Separation of the hexane extracts of commercially available matcha and crude tea (Yabukita) by bulb-to-bulb distillation

Figure 3. Comparison of the NMR spectra of the hexane extracts of matcha and crude tea (Yabukita)

Figure 4. The NMR spectra (δ 10–8.2) of the hexane extracts of several crude teas and differently prepared teas.

Figure 5. Change in NMR spectra caused by the reduction of the residue obtained from matcha