

Identification and Sensory Characterization of Volatile Flavor Compounds in Sesame Seed Oil

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Volatile flavor compounds in sesame seed oil were investigated. Commercially processed sesame seed oil was steam distilled under reduced pressure, and volatiles from the distillate were separated by an adsorptive column method. Among 171 individual peaks detected, 134 peaks were definitely or tentatively identified by analysis of mass spectra and modified Kovats indices. To elucidate the compounds directly contributing to the characteristic flavor, the odor concentrate was fractionated by silica gel thin-layer chromatography and preparative gas chromatography. As a result, 1-(5-methyl-2-furanyl)-1-propanone, 3-formylthiophene, 2-propyl-4-methylthiazole, 2-ethyl-4-methyl-1H-pyrrole, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 4,5-dimethylisothiazole, 4,5-dimethylthiazole, 2,6-diethylpyrazine, 2-ethyl-2,5-dimethylpyrazine, 1-(2-pyridinyl)ethanone, and 1-(1-methyl-1H-pyrrol-2-yl)ethanone were considered to be principal contributors of sesame seed oil flavor.

Keywords: Volatiles; flavor compounds; sesame seed oil

INTRODUCTION

Sesame seed oil produced from roasted sesame seeds has a distinctive flavor and is widely used in both Chinese and Japanese foods.

Extensive studies have been carried out concerning the nutritional value and chemical composition of sesame seeds and some have focused on flavor components of the sesame seed oil (Kinoshita and Yamanishi, 1973; Manley et al., 1974; Soliman et al., 1975, 1985, 1986). However, there has been limited research with respect to volatile flavor constituents of sesame seed oil. This paper deals with identification and quantification of volatile flavor compounds in sesame seed oil followed by identification of principal contributors to the flavor.

MATERIALS AND METHODS

Materials. The commercially roasted sesame seed oil was obtained from Ajinomoto Company, Ltd. (Tokyo, Japan). Diethyl ether and anhydrous sodium sulfate were from Nakarai Tesque, Inc. (Kyoto, Japan). 3-Phenyl-1-propanol was from Tokyo Kasei Kogyo Company, Ltd. (Tokyo, Japan). The silica gel 60 F254 plate for thin-layer chromatography (TLC) of the odor concentrate was from E. Merck (Darmstadt, Germany) and Porapak type Q (50–80 mesh) resin was from Millipore Corp. (Milford, MA).

Isolation of Volatile Flavor Compounds. Three hundred milliliters of deionized water were added to the sesame seed oil (100 mL). Volatiles were separated from the dispersion by a combination of steam distillation under reduced pressure (~90 mmHg) and column concentration (Shiratsuchi et al., 1993). The adsorptive column (10 × 2 cm i.d.) was prepared by packing 10 mL of Porapak Q resin. Adsorbed volatiles were eluted with 60 mL of diethyl ether, and 10 μ L of 1% 3-phenyl-1-propanol in diethyl ether was added as an

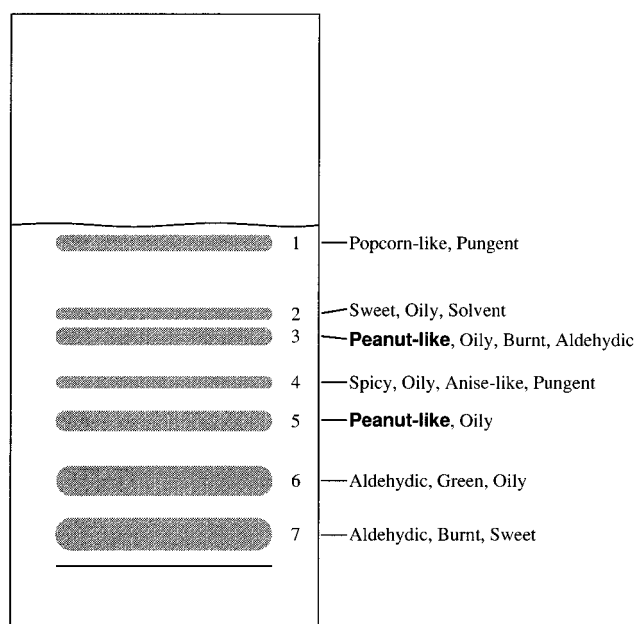


Figure 1. Thin-layer chromatogram of odor concentrate from sesame seed oil.

internal standard. Then, the extract was dried over anhydrous sodium sulfate for 3 h and concentrated to ~200 μ L by evaporating ethyl ether constantly with boiling glass beads in a water bath at 40 °C.

Capillary Gas Chromatography (GC). Capillary GC analysis was carried out on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector (FID) and connected to a Shimadzu Chromatopak C-R5A integrator. Separation was achieved on a 60 m × 0.25 mm i.d. fused silica capillary column that was coated with cross-linked 20M poly(ethylene glycol) (PEG 20M) to a film thickness of 0.25 μ m (DB-Wax; J&W Scientific, Folsom, CA). The oven temperature was programmed from 50 to 230 °C at 2 °C/min (60-min hold). The injector and detector temperatures were 230 °C. The helium carrier gas flow rate was 22 cm/s, with an injection splitter at a split ratio of 30:1. Retention indices were estimated by a modified Kovats method (Van den Dool and Kratz, 1963).

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Table 1. Volatile Flavor Compounds Identified in Sesame Seed Oil

peak	compound	Kovats index ^a	content, ppb	peak	compound	Kovats index ^a	content, ppb
1	ethyl formate	832	12.1	77	2-ethenyl-5-methylpyrazine ^b	1493	5.7
2	ethyl acetate	891	45.0	78	2,3-diethyl-5-methylpyrazine	1494	21.5
3	3-ethoxy-1-propene ^b	919	52.1	79	3,5-diethyl-2-methylpyrazine	1496	92.4
4	ethanol	932	38.7	80	1-(1 <i>H</i> -pyrazol-4-yl)ethanone ^b	1499	tr
5	3-methyl-2-butanone	936	tr	81	1 <i>H</i> -pyrrole	1505	69.7
6	pentanal	984	35.7	82	benzaldehyde	1512	240.1
7	toluene	1042	20.2	83	unknown	1516	20.7
8	dimethyl disulfide	1078	12.2	84	2-furanmethyl acetate	1521	74.7
9	hexanal	1086	262.9	85	(<i>E</i>)-2-nonenal	1528	48.1
10	2-methyl-2-butenal	1095	31.4	86	2-methyl-6-(1-propenyl)pyrazine ^b	1535	47.4
11	3-methylthiophene	1121	6.5	87	unknown	1539	39.4
12	ethylbenzene	1138	10.3	88	pyrazine derivative	1543	47.9
13	1-methyl-1 <i>H</i> -pyrrole	1142	11.1	89	unknown	1559	39.1
14	1,3-dimethylbenzene	1149	5.6	90	1-octanol	1562	25.5
15	4,5-dimethylloxazole	1152	6.2	91	3-methyl-1 <i>H</i> -pyrrole	1569	25.5
16	5-methylpyridinamine ^b	1158	tr	92	5-methyl-2-furfural	1574	219.4
17	1-ethyl-1 <i>H</i> -pyrrole	1178	tr	93	pyrazine derivative	1578	176.5
18	2-ethyl-1 <i>H</i> -pyrrole	1183	18.7	94	unknown	1584	21.5
19	2-heptanone	1185	30.9	95	1-methyl-1 <i>H</i> -pyrrole-2-acetonitrile ^b	1598	40.3
20	heptanal	1186	30.0	96	1-(2-pyridinyl)ethanone ^b	1603	15.7
21	trimethylloxazole	1190	8.0	97	1-ethyl-1 <i>H</i> -pyrrole-2-carboxyaldehyde ^b	1610	29.0
22	<i>α</i> -limonene	1194	26.6	98	3,5,5-trimethyl-2-cyclopenten-1-one	1617	37.3
23	unknown	1198	6.1	99	unknown	1627	54.5
24	2,3,4-trimethyl-1 <i>H</i> -pyrrole	1205	9.5	100	2-acetylpyrazine	1627	177.9
25	propylbenzene	1207	11.2	101	unknown	1636	25.4
26	(<i>E</i>)-2-hexenal	1209	7.5	102	4-pyridinyl acetate ^b	1643	67.2
27	2-methylpyridine	1216	9.3	103	2,3-dihydro-1 <i>H</i> -indole	1647	37.4
28	1-ethyl-2-methylbenzene	1222	10.9	104	1-phenylethanone	1651	141.7
29	1-ethyl-3-methylbenzene	1225	13.6	105	1-(1-methyl-1 <i>H</i> -pyrrol-2-yl)ethanone	1657	21.5
30	2-pentylfuran	1228	50.1	106	furfuryl alcohol	1664	316.1
31	unknown	1243	17.8	107	(<i>E</i>)-2-methyl-6-(1-propenyl)pyrazine ^b	1671	51.2
32	unknown	1250	103.7	108	2,3-dimethyl-5-isopentylpyrazine ^b	1680	27.7
33	unknown	1252	12.6	109	1-(5-methyl-2-furanyl)-1-propanone ^b	1686	69.6
34	ethenylbenzene	1255	18.3	110	3-formylthiophene	1693	37.7
35	unknown	1260	14.1	111	2-propyl-4-methylthiazole	1695	123.1
36	2-methylpyrazine	1271	778.9	112	(<i>E,E</i>)-2,4-nonadienal	1706	31.7
37	2-methylpyrazine	1271	778.9	113	2-ethyl-4-methyl-1 <i>H</i> -pyrrole	1711	14.4
38	4-ethylthiazole	1281	34.6	114	unknown	1720	49.7
39	1,3,5-trimethylbenzene	1283	18.6	115	unknown	1726	132.0
40	2,4-dimethylthiazole	1285	58.0	116	2-butyl-5-methylthiazole ^b	1738	45.1
41	octanal	1291	26.2	117	?-dodecenal ^b	1752	19.1
42	5-methylisothiazole	1299	16.4	118	(<i>E,Z</i>)-2,4-decadienal	1766	35.0
43	4-octen-3-one ^b	1303	10.1	119	unknown	1770	73.6
44	1,2-diethylbenzene	1305	8.4	120	methyl 4-pyridinecarboxylate ^b	1782	54.9
45	unknown	1324	18.5	121	unknown	1789	11.5
46	2,5-dimethylthiazole	1326	115.4	122	unknown	1793	10.9
47	2,5-dimethylpyrazine	1329	735.2	123	4-(methylthio)pyridine ^b	1796	14.0
48	2,6-dimethylpyrazine	1334	382.6	124	(2-propynyloxy)benzene ^b	1800	27.3
49	ethylpyrazine	1338	152.5	125	2-furanmethanethiol ^b	1802	40.2
50	2,3-dimethylpyrazine	1352	101.4	126	(<i>E,E</i>)-2,4-decadienal	1811	153.6
51	<i>n</i> -hexanol	1354	79.0	127	unknown	1816	15.5
52	unknown	1361	19.1	128	1-(2-furanylmethyl)-1 <i>H</i> -pyrrole ^b	1822	7.8
53	unknown	1374	12.5	129	1-(3,4-dimethylphenyl)ethanone	1828	22.8
54	unknown	1379	14.7	130	5,6,7,8-tetrahydroquinoline	1832	23.7
55	unknown	1385	12.0	131	hexanoic acid	1834	32.1
56	2-ethyl-6-methylpyrazine	1390	236.6	132	α -methyl- α -vinyl-2-furanacetaldehyde ^b	1837	25.1
57	2-nonanone	1393	62.1	133	4-methyl-1,2-benzoquinone	1842	14.3
58	2-ethyl-5-methylpyrazine	1397	212.0	134	guaiaicol	1846	320.6
59	4,5-dimethylisothiazole	1400	39.4	135	2,5-diethylthiophene	1857	17.3
60	4,5-dimethylthiazole	1409	109.6	136	1-(2,4-dimethylphenyl)ethanone	1861	423.9
61	trimethylpyrazine	1410	345.8	137	benzenmethanol	1868	69.2
62	4-nonyne ^b	1418	24.4	138	3-pyridincarbonitrile ^b	1875	22.4
63	(<i>E</i>)-2-heptenal	1430	81.8	139	4-(2-furanyl)-3-buten-2-one ^b	1879	22.1
64	ethenylpyrazine	1438	45.9	140	benzopyrazine	1886	22.3
65	2,6-diethylpyrazine	1440	8.3	141	benzenethanol	1893	46.6
66	acetic acid	1445	tr	142	α -ethylidenbenzeneacetaldehyde	1922	46.9
67	3-ethyl-2,5-dimethylpyrazine	1449	541.6	143	3-(2-furanyl)-3-penten-2-one ^b	1933	10.7
68	2-furfural	1456	51.2	144	heptanoic acid	1953	31.9
69	2-ethyl-5,6-dimethylpyrazine ^b	1460	5.2	145	benzothiazole	1958	22.5
70	2-ethyl-3,5-dimethylpyrazine ^b	1462	153.8	146	1-(1 <i>H</i> -pyrrol-2-yl)ethanone	1970	71.2
71	2-(2-methylpropyl)pyrazine ^b	1465	106.1	147	<i>n</i> -dodecanol	1977	68.8
72	4-methyl-5-ethylthiazole	1467	22.8	148	1 <i>H</i> -imidazole	1992	10.7
73	2-propylpyridine	1472	7.0	149	unknown	1998	64.8
74	2-(1-methylpropyl)pyrazine	1479	22.6	150	unknown	2010	52.8
75	2-ethyl-5-methylthiazole	1486	28.2	151	unknown	2022	53.2
76	2-ethenyl-6-methylpyrazine ^b	1490	55.3	152	1 <i>H</i> -pyrrole-2-carboxaldehyde	2030	126.8

Table 1 (Continued)

peak	compound	Kovats index ^a	content, ppb	peak	compound	Kovats index ^a	content, ppb
153	4-ethylguaiacol	2032	11.2	160	unknown	2122	11.5
154	dihydro-5-pentyl-2(3 <i>H</i>)-furanone ^b	2037	18.0	161	1-naphthalenethiol ^b	2131	9.1
155	methyl pyrrole-2-carboxylate ^b	2058	32.7	162	(<i>E</i>)-2-methoxy-5-(1-propenyl)phenol ^b	2169	32.9
156	octanoic acid	2062	86.4	163	nonanoic acid	2176	68.9
157	unknown	2084	49.7	164	1-(3-methoxyphenyl)ethanone	2200	176.9
158	unknown	2097	37.4	165	unknown	2275	30.4
159	2-pyridinemethanol ^b	2110	57.5	166	unknown	2328	55.8
total							11586.2

^a Modified Kovats indices calculated for DB-Wax capillary column on the GC system. ^b Tentative identification by mass spectrum alone.

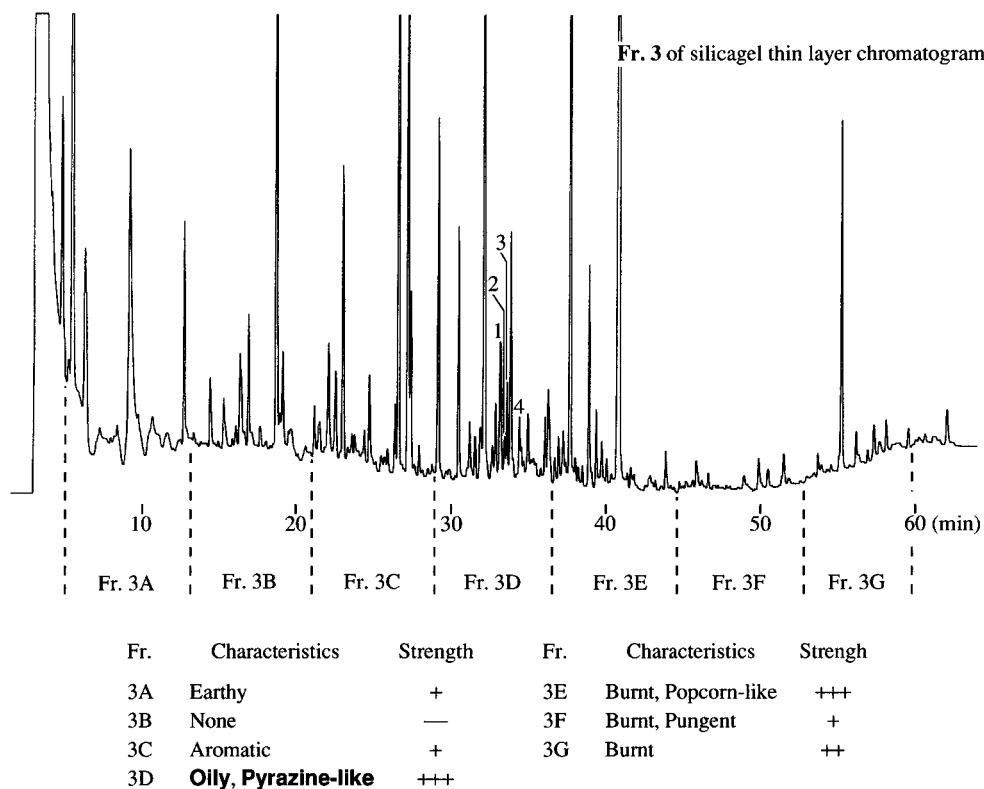


Figure 2. Sniffing of the fractions obtained by preparative gas chromatography on fraction 3 of the thin-layer chromatogram. For more information, see Materials and Methods.

Capillary Gas Chromatography–Mass Spectrometry (GC–MS). Electron-impact mass spectrometric data were collected on a JEOL Automass 50 mass spectrometer interfaced to a Hewlett-Packard 5890 Series II gas chromatograph. The column and chromatographic conditions were the same as described for GC analysis. The mass spectrometer was operated at an ionization voltage of 70 eV and ion source temperature of 200 °C. The scanning rate was 1 scan/s. The mass spectra of the unknown compounds were compared with those in the NIST data base of Automass 50 system and other published spectra (*Eight Peak Index of Mass Spectra*, 1983; *Wiley/NBS Registry of Mass Spectral Data*, 1989).

Fractionation of Odor Concentrates. The odor concentrate from 600 mL of the sesame seed oil was fractionated by silica gel TLC (solvent, diethyl ether/*n*-pentane, 30:70). Two polar fractions with oily and roasted-peanut-like odors, which seemed to contribute directly to the characteristic flavor of sesame seed oil, were eluted from the silica gel support and further fractionated by preparative GC (Shimoda et al., 1993). For preparative GC, a Shimadzu GC-8A gas chromatograph equipped with a 60 m × 0.75 mm i.d. cross-linked PEG 20M (film thickness, 1 μm) megabore open tubular glass column (Supelcowax 10; Supelco, Bellefonte, PA) and FID was used. The oven temperature was programmed from 50 to 230 °C at 2 °C/min. The helium carrier gas flow rate was 25 cm/s, with a splitless injection. Short capillaries (25 cm × 0.53 mm i.d.)

with a chemically bonded PEG 20M film were used for trapping separated fractions or components with a split ratio of 20:1. The separation port was specifically designed so that a large negative temperature gradient could be produced in the middle of the capillary, and the capillary could be exchanged in a very short time. The separated compounds were eluted with a drop of ethyl ether on a filter paper, so that their odors could be sniffed, or in a small glass tube (2 × 0.8 cm i.d.) for splitless injection into a GC–MS.

RESULTS AND DISCUSSION

The yield of total volatiles was 0.0012% (w/w, relative to the sesame seed oil used). Of a total of 171 peaks detected, 147 peaks were definitely or tentatively identified (Table 1). The area of these 134 peaks represented ~91% of the chromatogram surface (excluding solvent and 3-phenyl-1-propanol). The compounds identified included 25 pyrazines, 1 pyridinamine, 8 pyridines, 14 pyrroles, 3 thiophenes, 11 thiazoles, 2 thiols, 1 disulfide, 11 furans and furanone, 11 hydrocarbons, 2 esters, 14 aldehydes, 9 ketones, 6 alcohols, 3 phenols, 5 fatty acids, and 8 miscellaneous compounds.

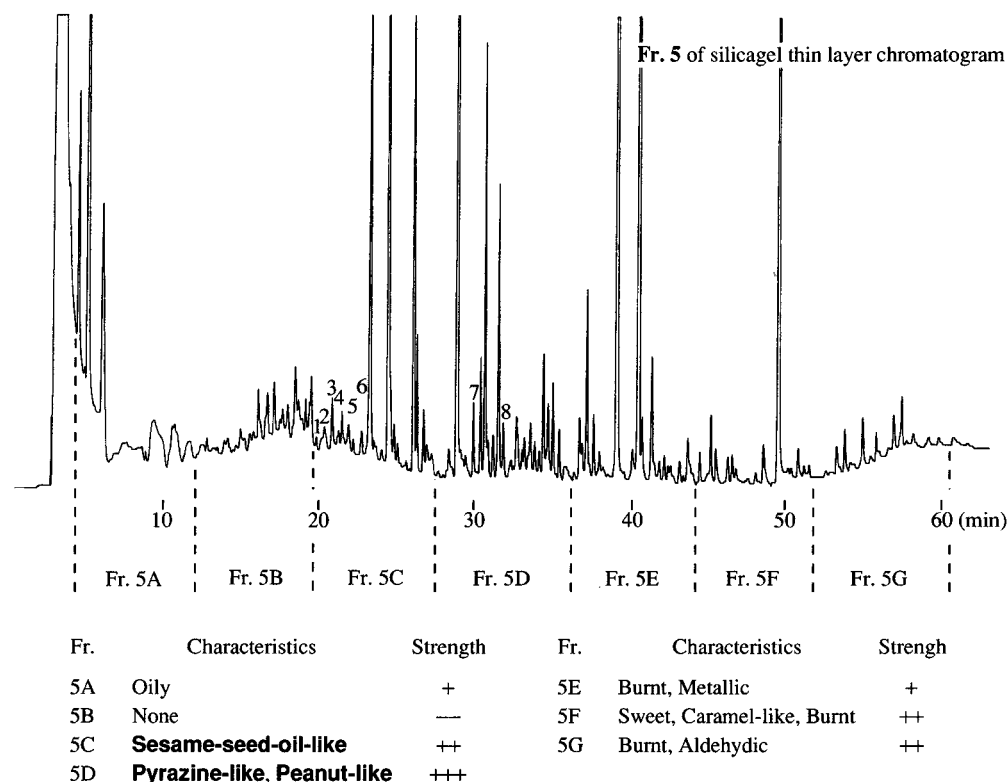


Figure 3. Sniffing of the fractions obtained by preparative gas chromatography on fraction 5 of the thin-layer chromatogram. For more information, see Materials and Methods.

To clarify the compounds that directly contribute to the characteristic flavor of sesame seed oil, the odor concentrate was fractionated by TLC. The chromatogram of the odor concentrate from sesame seed oil is shown in Figure 1. Among these fractions, fractions 3 and 5 had peanut-like odor, which is the most important flavor attribute of sesame seed oil. Therefore, further fractionation was carried out by preparative GC. At first, fraction 3 was separated into eight subfractions (Figure 2). As shown in this figure, fraction 3D had oily and pyrazine-like odors. Because it was considered that the character-impact compounds of sesame seed oil flavor were included in this fraction, fraction 3D was further separated, and the odors were sniffed. The region from 1665 to 1715 (Kovats indices) had strong sesame-seed-oil-like and aromatic odors. As a result of sniffing of every peak, peak 1 [1-(5-methyl-2-furyl)-1-propanone], peak 2 (3-formylthiophene), peak 3 (2-propyl-4-methylthiazole), and peak 4 (2-ethyl-4-methyl-1H-pyrrole) were considered to be the principal contributors to the flavor of sesame seed oil. On the other hand, fraction 5 was separated into eight subfractions by preparative GC (Figure 3). Fraction 5C had sesame-seed-oil-like odor, and fraction 5D had pyrazine-like and peanut-like odors. In addition, the character-impact compounds of sesame seed oil flavor were thought to be included in these fractions. These fractions were further separated, and the regions from 1380 to 1460 and 1600 to 1660 had strong sesame-seed-oil-like, aromatic, and burnt odors. As a result of sniffing, peak 1 (2-ethyl-6-methylpyrazine), peak 2 (2-ethyl-5-methylpyrazine), peak 3 (4,5-dimethylisothiazole), peak 4 (4,5-dimethylthiazole), peak 5 (2,6-diethylpyrazine), peak 6 [2-ethyl-3,5-dimethylpyrazine (former region)], peak 7 [1-(2-pyridinyl)ethanone], and peak 8 [1-(1-methyl-1H-pyrrol-2-yl)ethanone (latter region)] had some sesame-like flavor characteristics.

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