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Characteristic odor components of essential oil from *Caesalpinia decapetala*

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The components of the essential oil from *Caesalpinia decapetala* (Roth) Alston (jaketsuibara) were analyzed by gas chromatography–mass spectrometry (GC–MS). Seventy-two components, representing 99.6% of the total oil were identified by GC–MS. The main components of the oil were β-caryophyllene (17.2%), followed by β-myrcene (16.6%), (*E*)-β-ocimene (12.4%), limonene (10.4%), and caryophyllene oxide (9.6%). Monoterpenoids and sesquiterpenoids accounted for about 90% of the essential oil. With regard to odor components from essential oil of *C. decapetala*, it was revealed that β-myrcene and β-caryophyllene affect spicy-odor of the oil, while, (*Z*)-β-ocimene and (*E*)-β-ocimene contributed to the sweet odor through gas choromatography olfactometry (GC–O) and aroma extraction dilution analysis (AEDA). On the basis of flavor dilution (FD)-factors and odor activity values (OAVs), monoterpenoids and sesquiterpenoids influence the aroma of this plant and participated in the characteristic odor of *C. decapetala*.

Keywords: *Caesalpinia decapetala*; aroma extraction dilution analysis (AEDA); GC–MS; GC–O; odor activity values (OAVs)

Introduction

Caesalpinia decapetala (Roth) Alston (jaketsuibara) belongs to the *Caesalpinia* genus of Fabaceae family. This plant is a deciduous twisted tree growing on the riversides and in forests in Japan. The dried seed and root of *C. decapetala* have been reported as a Chinese traditional medicine (1), in addition, the leaves are used to treat burns and biliousness. The leaves of *C. decapetala* contain cassane diterpenoid, caesaldecan, spathulenol, 4,5-epoxy-8(14)-caryophyllene (2). Some compounds were isolated and elucidated as lupeol, oleanoic acid, phytosterols (3), in addition, a new cassane diterpenoid, caesaljapin, was isolated form *C. decapetala* (4). In the studies on essential oil of the genus *Caesalpinia*, β-caryophyllene, spathulenol and germacrene D were identified as the main components in the essential oil from the leaves of *C. violacea* (5), α-phellandrene, *p*-cymene and γ-terpinene have been reported as the major compounds of the essential oil from flowers of *C. pulcherrima* (6). However, there is no report on the essential oil from *C. decapetala*. In this study, we investigated the characteristic aroma components of essential oil from *C. decapetala* by aroma extract dilution analysis (AEDA) method and odor activity values (OAVs). In flavor analysis, gas choromatography olfactometry (GC–O) is the most used method for evaluation of odorant, in particular, GC–O including AEDA have been useful methods for estimating the contribution of the most odor-active compounds (7), however, these methods do not permit a study on the influence of the food matrix on odorant binding when matching the overall odor impression of the food (8). Thus, OAV is the ratio of concentration to the odor threshold of the compound, it is well-accepted that compounds with high OAV contribute more to the aroma of food (9).

The aim of this study is to investigate the characteristic odor components of *Caesalpinia decapetala* by a sensory evaluation and by using the concept of odor activity values.

Experimental

Plant materials

Fresh field-grown plant twigs during the flowering period were collected from Fukushima in Japan in May 2010. Identification of the plant was performed in the biotechnology laboratory at Kinki University. A voucher specimen (BT 0522) was deposited at the biotechnology laboratory of Kinki University of Osaka, Japan.

Fresh twigs were separately submitted for hydrodistillation in a Likenes-Nikerson type apparatus for two hours. At the end of each distillation the oil was collected, dried with anhydrous sodium sulfate (Na_2SO_4), measured, and transferred to glass flasks that were filled to the top and kept at a temperature of –30°C for further analysis.

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Chemicals

Myrcene, linalool, nonanal, geraniol, and β-caryophyllene were purchased from Wako Pure Chemical Industries. (Osaka, Japan). α-Phellandrene, limonene, ocimene, α-humulene were purchased from Sigma Aldrich Japan (Tokyo, Japan).

Analysis of the essential oil

Oil sample analysis was performed on an Agilent Technologies-6890N gas chromatograph with a flame ionization detector (FID) equipped with HP-5MS (fused silica capillary column composed of 5% phenylmethylpolysiloxane) 30 m × 0.25 mm × 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA, USA). Temperature programmed as follows: 40–260°C at 4°C/minute, ending with 5 minutes at 260°C. The carrier gas was helium (He) at a flow of 1.8 mL/minute; injector port and detector temperature were 270°C and 280°C, respectively. Sample was injected by splitting and the split ratio was 1:10. One microliter of oil was injected, and the split ratio was 1:10.

Gas chromatography–mass spectrometry (GC–MS) analysis was performed on Agilent Technologies-5973N-MSD apparatus using a HP-5MS 30 m × 0.25 mm × 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA, USA). Temperature programmed as earlier. The carrier gas was He at a flow rate of 1.8 mL/minute. After 4 mg of oil was diluted with 500 μL of diethylether, 1 μL of the dilution was injected, and the split ratio was 1:10.

The injection port was set at 270°C. Significant quadrupole mass spectrometry (MS) operating parameters: interface temperature 230°C; electron impact ionization at 70 eV with scan mass range of 40 to 450 *m/z* at a sampling rate of 2.4 scan/seconds. Compounds were identified by using digital library (Mass Finder 4 and NIST02) and Aroma Office version 3.0 (Nishikawa Keisoku Co. Ltd., Tokyo, Japan), which includes 72,120 entries of retention index (RI) of aroma compounds and literature sources, and by comparison of their retention indexes and authentic mass spectra (10), relative to C_5-C_{28} *n*-alkane series (11) in a temperature-programmed run.

Quantification of aroma compounds

The quantification of aroma active compounds was performed on the basis of calibration curves for myrcene (peak 4), α-phellandrene (peak 6), limonene (peak 9), (*Z*)-β-ocimene (peak 10), (*E*)-β-ocimene (peak 12), linalool (peak 14), nonanal (peak 15), geraniol (peak 27), β-caryophyllene (peak 34), α-humulene (peak 37) within the concentration range 0.5–1000 μg/mL.

Gas chromatography olfactometry (GC–O)

GC–O was carried out using an Agilent Technologies-6890N gas chromatograph equipped with Agilent 5973 MSD mass spectrometer and sniffing port ODP2 (Olfactory Detector Port 2, Gerstel, Tokyo, Japan). The gas chromatography (GC) was equipped with a HP-5MS 30 m × 0.25 mm × 0.25 μm film thickness (Agilent Technologies, Santa Clara, CA, USA). The sample was injected into the GC in splitless mode. The GC effluent from the capillary column was split 1:1 (v/v) between the MS and the sniffing port. The oven conditions, injector and detector temperatures, the carrier gas, flow rate, and inonization mode were the same as for GC-MS described earlier.

Aroma extract dilution analysis (AEDA)

The highest sample concentration (10 mg/mL) was assigned a flavor dilution (FD)-factor of one. The volatile oil was stepwise diluted with diethylether (1 + 1 by volume), and aliquots of the dilutions (1 μL) were evaluated. The process stopped when no aromas were detected by assessors. The result was expressed as the FD-factor, which is the ratio of the concentration of the odorant in the initial volatile oil to its concentration in the most diluted volatile oil in which the odor is still detectable by GC–O.

Results and discussion

The oil of *Caesalpinia decapetala* was light yellow with a spicy-sweet odor. The yield was of 0.065% (w/w). Gas chromatogram of essential oil was shown in Figure 1. Table 1 shows the results of the qualitative and quantitative oil analysis listed in order of elution in the HP-5MS column. In total, seventy-two compounds were identified, accounting for 99.6% of volatile compounds. Their composition was based on monoterpene hydrocarbons (40.2%), such as β-myrcene, limonene and (*E*)-β-ocimene. As characteristic components, sesquiterpenes with caryophyllane skeltone accounted for 28.4% of the total oil. Caryophyllen oxide and spathulenol that are chemical components of the leaves of *C. decapetala*, were detected in this oil, however, cassane diterpenoids were not confirmed.

As the minor components, khusimone (peak 53) and junenol (peak 56) were detected for the first time in the genus *Caesalpinia.*

The oil of *Caesalpinia decapetala* was subjected to odor evaluation by AEDA and GC–O. The results are shown in Table 2.

A total of 13 aroma-active components were detected by the sniffing test. Among aroma components, β-myrcene and β-caryophyllene with a spicy odor occupied the highest FD-factor of 64, and had the characteristic aroma of *Caesalpinia decapetala*. The

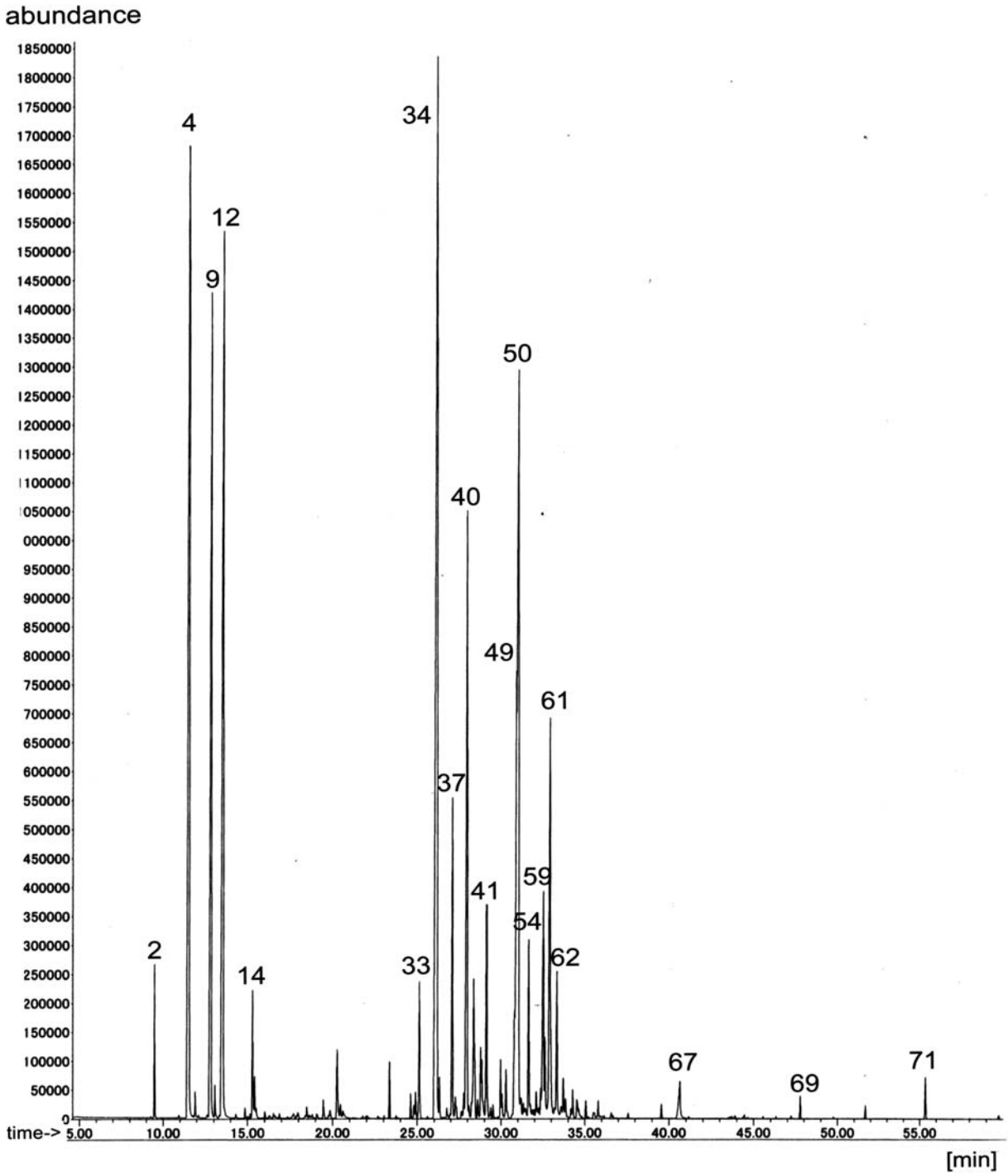

Figure 1. Gas chromatogram of essential oil from twigs of *Caesalpinia decapetala*; HP-5MS (30 m × 0.25 mm; 0.25 μm film); flow rate of carrier gas (He), 1.8 mL/min; oven temperature, 40–260°C at 4°C/min and held at 260°C for five minutes.

high FD-factors of β-myrcene and β-caryophyllene might be owing to their high content in the essential oil. (*Z*)-β-Ocimene (FD-factor = 16, sweet) and (*E*)-β-ocimene (FD-factor = 32, sweet, herb) contributed to the sweet odor of the oil, moreover, monoterpenes, such as α-phellandrene, limonene, linalool and geraniol participated in aroma of the essential oil. As the other compound, nonanal with citrus and green odor also affected the odor of the oil.

In order to determine the relative contribution of each compounds to the aroma of *Caesalpinia decapetala*, OAVs have been employed. OAVs were obtained by taking into account the concentration and odor threshold of each compound. The results were shown in

Table 1. Components of the essential oil from *Caesalpinia decapetala*.

No.	RI[a] HP-5MS	RI[a] Literature values	Compound[b]	Peak area (%)	Identification[c]
1	925	930	α-thujene	tr	RI, MS
2	932	939	α-pinene	1.2 ± 0.4	RI, MS
3	974	979	β-pinene	tr	RI, MS
4	993	990	β-myrcene	16.6 ± 2.1	RI, MS
5	1000	1002	δ-2-carene	tr	RI, MS
6	1003	1002	α-phellandrene	0.2 ± 0.1	RI, MS
7	1008	1011	δ-3-carene	tr	RI, MS
8	1023	1024	*p*-cymene	tr	RI, MS
9	1029	1029	limonene	10.4 ± 1.7	RI, MS
10	1036	1037	(*Z*)-β-ocimene	0.3 ± 0.2	RI, MS
11	1043	1042	phenyl acetaldehyde	tr	RI, MS
12	1049	1050	(*E*)-β-ocimene	12.4 ± 1.2	RI, MS
13	1090	1092	(6,7)-epoxymyrcene	tr	RI, MS
14	1098	1096	linalool	0.9 ± 0.3	RI, MS
15	1100	1110	nonanal	0.3 ± 0.1	RI, MS
16	1119	1122	*trans*-mentha-2,8-dien-1-ol	tr	RI, MS
17	1126	1132	(4*E*,6*Z*)-*allo*-cimene	tr	RI, MS
18	1135	1136	*trans* -limonene oxide	tr	RI, MS
19	1143	1141	verbenol	tr	RI, MS
20	1165	1170	*p*-mentha-1,5-dien-8-ol	tr	RI, MS
21	1167	1174	*cis*-linalool oxide	tr	RI, MS
22	1172	1176	*trans*-linalool oxide	tr	RI, MS
23	1189	1188	α-terpineol	0.1 ± 0.2	RI, MS
24	1193	1191	methyl salicylate	tr	RI, MS
25	1207	1205	verbenone	tr	RI, MS
26	1217	1216	*trans*-carveol	0.2 ± 0.3	RI, MS
27	1251	1252	geraniol	0.1 ± 0.2	RI, MS
28	1334	1338	δ-elemene	0.4 ± 0.3	RI, MS
29	1347	1348	α-cubebene	tr	RI, MS
30	1373	1376	α-copaene	0.2 ± 0.2	RI, MS
31	1379	1381	geranyl acetate	0.1 ± 0.3	RI, MS
32	1383	1388	β-bourbonene	0.2 ± 0.2	RI, MS
33	1390	1390	β-elemene	0.9 ± 0.5	RI, MS
34	1424	1419	β-caryophyllene	17.2 ± 1.9	RI, MS
35	1428	1432	β-copaene	0.3 ± 0.1	RI, MS
36	1449	1453	*trans*-muurola-3,5-diene	tr	
37	1454	1454	α-humulene	2.2 ± 0.4	RI, MS
38	1460	1460	aromadendrene	0.2 ± 0.1	RI, MS
39	1462	1466	*cis*-muurola-4-(14), 5diene	0.1 ± 0.1	RI, MS
40	1485	1483	germacrene D	5.2 ± 0.1	RI, MS
41	1496	1500	bicyclogermacrene	0.9 ± 0.6	RI, MS
42	1498	1500	α-muurolene	0.5 ± 0.2	RI, MS
43	1503	1505	*(E,E)*-α-farnesene	0.2 ± 0.1	RI, MS
44	1512	1513	γ-cadinene	0.3 ± 0.2	RI, MS
45	1522	1523	δ-cadinene	0.5 ± 0.4	RI, MS
46	1530	1534	*trans*-cadina-1,4-diene	0.1 ± 0.1	RI, MS
47	1535	1538	α-cadinene	0.1 ± 0.3	RI, MS
48	1563	1563	(*E*)-nerolidol	0.4 ± 0.2	RI, MS
49	1584	1578	spathulenol	4.0 ± 0.3	RI, MS
50	1589	1583	caryophyllene oxide	9.6 ± 0.5	RI, MS
51	1593	1592	viridiflorol	0.1 ± 0.1	RI, MS
52	1594	1594	salvia-4(14)-en-1-one	0.1 ± 0.2	RI, MS
53	1603	1604	khusimone	0.2 ± 0.1	RI, MS
54	1610	1608	humulene epoxide	1.4 ± 0.5	RI, MS
55	1614	1619	1,10-di-*epi*-cubenol	0.1 ± 0.2	RI, MS
56	1619	1619	junenol	0.1 ± 0.1	RI, MS
57	1627	1628	1-*epi*-cubenol	0.2 ± 0.3	RI, MS
58	1636	1640	caryophylla-4(12),8(13)-dien-5-ol[e]	0.3 ± 0.1	RI, MS
59	1643	1642	*epi*-α-muurolol	2.6 ± 0.2	RI, MS

(*Continued*)

Table 1. (*Continued*)

No.	RI[a] HP-5MS	RI[a] Literature values	Compound[b]	Peak area (%)	Identification[c]
60	1646	1646	α-muurolol	0.7 ± 0.3	RI, MS
61	1657	1654	α-cadinol	4.4 ± 1.2	RI, MS
62	1672	1669	14-hydroxy-9-*epi*-β-caryophyllene	1.3 ± 0.1	RI, MS
63	1686	1688	eudesma-4(15),7-dien-1-ol[e]	0.3 ± 0.2	RI, MS
64	1716	1715	(2*E*, 6*Z*)-farnesol	0.2 ± 0.1	RI, MS
65	1798	1803	14-hydroxy-δ-cadinene	tr	RI, MS
66	1915	1921	methyl palmitate	0.1 ± 0.1	RI, MS
67	1961	1960	palmitic acid	0.3 ± 0.2	RI, MS
68	2180	2184	sandaracopimarinal	tr	RI, MS
69	2300	2300	tricosane	0.2 ± 0.1	RI, MS
70	2500	2500	pentacosane	0.1 ± 0.2	RI, MS
71	2700	2700	heptacosane	0.4 ± 0.2	RI, MS
72	2900	2900	nonacosane	tr	RI, MS
			monoterpene hydrocarbons	41.1	
			monoterpene alcohols	1.3	
			sesquiterpene hydrocarbons	29.9	
			sesquiterpene alcohols	14.7	
			miscellaneous sesquiterpene	11.1	
			other compounds	1.5	
			total	99.6	

Notes: [a]RI, retention indexes HP-5MS column or literature values. [b]Compounds are listed in order of their elution time from a HP-5-MS column. [c]Percentages of each compound were calculated from FID data. Data represents means ± standard deviation of triplicate samples (tr, trace, i.e. < 0.1%). [d]Indentification methods: RI, retention index; MS, mass spectroscopy. [e]Correct isomer not identified.

Table 2. Aroma compounds of *Caesalpinia decapetala.*

No.	RI [a]	Compound	Odor description[b]	FD-factor[c]
2	932	α-pinene	pine,turpentine	2
4	993	β-myrcene	spicy	64
6	1003	α-phellandrene	mint	8
9	1029	limonene	lemon, orange	16
10	1036	(*Z*)-β-ocimene	sweet	16
12	1049	(*E*)-β-ocimene	sweet, herb	32
14	1098	linalol	floral	16
15	1100	nonanal	citrus, green	32
23	1189	α-terpineol	mint, anise	2
27	1251	geraniol	rose, geranium	4
34	1424	β-caryophyllene	spicy, woody	64
37	1454	α-humelene	woody	4
48	1563	(*E*)-nerolidol	green	2

Notes: [a]RI, retention index on HP-5MS column. [b]Odor description perceived through the sniffing port. [c]FD-factor, flavour dilution factor in the HP-5MS column, the sample concentration (10 mg/mL) was assigned a FD-factor of one.

Table 3. β-Myrcene showed high OAV (7149), followed by nonanal (1938), β-caryophyllene (1736). These compounds had high FD-factors and high OAVs, thus, we considered these compounds as main aroma components of the oil from *C. decapetala.* As the other aroma components, monoterpenoids, such as, linalool (969), and limonene (336) effected odor of the oil. In conclusion, with regard to aroma of *C. decapetala*, it was revealed that monoterpenoids and sesquiterpenoids contribute to characteristic aroma. Nonanal with high FD-factor and high OAV made citrus and green odor of the oil, however, this compound was not regarded as the characteristic odor of *C. decapetala* by the sniffing test.

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Table 3. Quantifications and OAVs of aroma active compounds (FD-factor ≥ 4) from *Caesalpinia decapetala.*

No.	Compound	Concentration (ppb)[a]	Odor threshold (ppb) in water	OAV[b]
4	β-myrcene	107236	15[c]	7149
6	α-phellandrene	10498	40[c]	32
9	limonene	67184	200[d]	336
10	(*Z*)-β-ocimene	1938	34[d]	57
12	(*E*)-β-ocimene	80104	NA	ND
14	linanool	5814	6[c]	969
15	nonanal	1938	1[c]	1938
27	geraniol	1938	40[c]	16
34	β-caryophyllene	173613	64[e]	1736
37	α-humulene	10498	160[c]	105

Notes: [a]The concentrations of aroma active compounds (FD-factor > 4) was obtained by the calibration curve of each compound. [b]The OAV was obtained by dividing the concentrations of odorants by their reported thresholds in water. [c]According to reference 12. [d]According to reference 13. [e]According to reference 14. NA, data not available; ND, not determined.

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