Constituents of Essential Oil from the Dried Fruits and Stems of *Akebia quinata* (THUNB.) DECNE.

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Abstract: The compositions of the essential oil from *AKEBIAE FRUCTUS* and *AKEBIAE CAULIS*, the dried fruits and stems of *Akebia quinata* (THUNB.) DECNE. (Lardizabalaceae), have been investigated by GC and GC/MS. As a result, the fruits oil was revealed the presence of 86 components, representing 98.4% of the total oil. The major compounds of the fruits oil were limonene, eugenol, octanal and *p*-cymene. The monoterpenoids and saturated short-chain aldehyde (C6~C10) were main volatile fractions of the oil. Ninety components accounting for 90.5% of constituents of stems oil were identified, and the main compounds of the oil were hexanoic acid, palmitic acid, (2*E*, 4*E*)-decadienal and hexanol. The oil had high content of saturated fatty acids (C6~C16), and unsaturated short-chain aldehyde (C6~C10).

Key words: *Akebia quinata* (THUNB.) DECNE., *AKEBIAE FRUCTUS*, *AKEBIAE CAULIS*, Lardizabalaceae, essential oil

1 INTRODUCTION

Lardizabalaceae consist of 7 genes with about 35 species of woody plants, which were found eastern Asia, from the Himalayan to Japan. Most investigatory species of the family, *Akebia quinata* (THUNB.) DECNE. ('akebi' in Japanese) commonly referred to as chocolate vine, grow naturally in Japan and China (Kiangsu, Honan, Hupeh and Szechwan). The plant possesses a stem growing up 3 m in height on which can be found violent flowers in April-May. In August, the natural ripe fruits are eaten by human and birds. The fruits and stem of *A. quinata* have been used as Chinese folk medicines¹⁾. The dried fruits, *AKEBIAE FRUCTUS* (known as 'yochishi' in Japanese) has been long used to an antiphlogistic, a diuretic and an antidote. On the other hand, the dried stem, *AKEBIAE CAULIS* (known as 'mokutsu' in Japanese) is also used as a diuretic and an antiphlogistic.

In previous reports, various triterpenoid saponins have been isolated and detected in the plant²⁻⁸⁾. As newly saponins, the eleven akebosides were isolated by Fujita *et al.*^{2,3)}. Choi *et al.* also reported the antinociceptive and anti-inflammatory properties of the stem could be attributed to the sapogenins oleanolic acid and hederagenin⁷⁾. However there is no report of volatile components in this plant. In this report, the components of essential oil from

AKEBIAE FRUCTUS and *AKEBIAE CAULIS*, the dried fruits and stems of *A. quinata*, were investigated using GC and GC/MS.

2 EXPERIMENTAL

2.1 Material plant

Commercially available air-dried fruits and stems of *A. quinata* (*AKEBIAE FRUCTUS* and *AKEBIAE CAULIS* from Tokushima, Japan), were obtained from Takasago Yakugyoku Co., Ltd. Osaka.

2.2 Isolation of the essential oil

The essential oils were obtained by steam distillation for 2 h with a Likens-Nickerson-type apparatus using diethyl ether, and the oils were dried over anhydrous sodium sulphate prior to analyses.

2.3 Gas chromatography (GC)

GC was carried out using a Hewlett Packard 6890 equipped with a flame ionization detector (FID) on a capillary column, DB-5 (30 m × 0.25 mm, film thickness 0.25 μm). The column temperature was programmed from 60-240 °C at a rate of 4 °C/min and held at 240 °C for 5 min.

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The injector and detector temperature were 240 °C and 280 °C, respectively. The flow rate of the carrier gas (He) was 0.679 mL/min.

2.4 Gas chromatography/mass spectrometry (GC/MS)

The GC/MS analysis was carried out using a Hewlett Packard model 6890 GC with a Hewlett Packard 5973A MS. The capillary column was a capillary column HP-5MS (30 m × 0.25 mm, film thickness 0.25 µm). The oven temperature was programmed from 40–240 °C at a rate of 4 °C/min and held at 240 °C for 5 min. The flow rate of the carrier gas (He) was 1.8 mL/min. The injector and the detector temperature were 270 °C and 280 °C, respectively, with the actual temperature in the MS source reaching approximately 230 °C and the ionization voltage of 70 eV.

2.5 Identification of constituents

The components of the oil were identified by direct comparison of their mass spectral patterns and retention indices (RI) with our previous reports^{9–11} and those published in the literature¹².

3 RESULT AND DISCUSSION

The yields of essential oils obtained by steam distillation from the dried fruits and stems of *A. quinata* were 0.034% and 0.016% (w/w), respectively. The characteristic odor of fruits oil was powerful spicy and sour with earthy odor. The stems oil gave off a very pungent green odor with faint sweet odor. The oils were analyzed using GC and GC/MS, of which the total ion chromatograms (TIC) were shown in Fig. 1. The chromatograms of fruits oil and stems oil showed presence of 93 and 103 volatile compounds, respectively. The percentage compositions of the oils were listed in Table 1. The fruits oil was revealed the presence of 86 components, representing 98.4% of the total oil. The major compounds of the fruits oil were limonene (35.5%), eugenol (14.3%), octanal (4.4%) and *p*-cymene (2.9%). The monoterpenoids, aromatic compounds and saturated short-chain aldehyde (C6~C10) were main volatile fractions of the fruits oil. It was presumed that powerful spicy odor of eugenol contributes to the characteristic odor of fruits oil. On the other hands, 90 components accounting for 90.5% of constituents of the stems oil were identified, and the major

Fig. 1 The Total Ion Chromatograms (TIC) of Essential Oil from the Dried Fruits and Stems of *Akebia quinata*. **A:** fruits oil; **B:** stems oil

Table 1 The Compositions of Essential Oils from the Dried Fruits and Stems of *Akebia quinata*.

No	RI	compound	peak area (%)		No	RI	compound	peak area (%)	
			fruits	stems				fruits	stems
1	801	pentanol	0.5	1.7	70	1217	decanoic acid		1.2
2	808	(2Z)-pentenol		0.1	71	1219	(2E,4E)-nonadienal		0.8
3	821	hexanal	1.4	2.9	72	1224	4-methylene isophorone		0.5
4	832	ethyl acetate	0.7	0.9	73	1225	methyl pelargonate	1.0	
5	845	furfural	2.6	0.7	74	1228	trans-carveol		0.6
6	854	pentanoic acid	0.3		75	1234	nerol	0.4	
7	862	(2E)-hexenal		0.1	76	1240	cis-carveol		0.5
8	863	furfryl alcohol	0.6		77	1242	cumin aldehyde	0.1	0.5
9	875	hexanol	0.5	3.1	78	1246	carvone	0.3	1.1
10	892	2-heptenone	tr	0.3	79	1259	γ -octalactone	0.7	
11	902	heptanal	0.3	0.2	80	1260	p-anis aldehyde		0.4
12	911	2-acetyl furan	tr		81	1266	(2E)-decenal		0.4
13	914	pentyl acetate	0.2		82	1276	(E)-cinnamaldehyde + 2-hexyl thiophene		1.4
14	924	methyl caproate	0.4		83	1280	pelargonic acid	1.4	
15	933	α -pinene	0.2		84	1288	(E)-anethole	0.3	2.7
16	954	(2E)-heptenal	tr	0.3	85	1297	indole	0.4	
17	958	benzaldehyde	tr	0.4	86	1298	2-undecanone + (2E,4Z)-decadienal		2.4
18	961	5-methyl furfural	1.8		87	1305	carveol	0.4	
19	968	heptanol	0.4	0.3	88	1309	carvacrol		0.2
20	975	β -pinene	0.3		89	1317	4-vinyl-o-guaiacol	0.2	
21	977	2-propyl thiophene		0.2	90	1323	(2E,4E)-decadienal	0.2	3.7
22	980	1-octen-3-ol		0.6	91	1362	eugenol	14.3	0.4
23	983	3-octanone		0.3	92	1368	γ -nonalactone		0.8
24	986	6-methyl-5-hepten-2-one		0.2	93	1380	α -copaene	0.1	
25	989	myrcene	0.7		94	1387	lauric acid		0.5
26	991	2-pentylfuran	0.9	1.7	95	1387	(E)- β -damascenone	0.4	0.3
27	1000	octanal	4.4	0.2	96	1395	β -elemene	0.2	
28	1010	(2E,4E)-heptadienal		0.6	97	1406	methyl eugenol	1.1	
29	1015	α -terpinene	0.3		98	1407	2-dodecanone + methyl eugenol		0.3
30	1023	p-cymene	2.9	0.1	99	1424	β -caryophyllene	0.4	
31	1029	limonene	35.5	0.3	100	1446	paeonol		0.2
32	1031	(3Z,5Z)-octadien-2-one + 1,8-cineole		0.2	101	1456	geranyl acetone		0.6
33	1037	lavendor lactone	0.4	0.4	102	1458	α -humulene	tr	
34	1043	benzeneacetaldehyde	0.3	1.4	103	1472	γ -decalactone		0.2
35	1053	γ -hexalactone	tr		104	1486	ar-curcumene	0.1	0.2

No	RI	compound	peak area (%)		No	RI	compound	peak area (%)	
			fruits	stems				fruits	stems
36	1058	γ -terpinene	1.4		105	1489	(<i>E</i>)-b-ionone	tr	0.3
37	1061	(2 <i>E</i>)-octenal		1.0	106	1491	β -selinene	0.2	
38	1065	vinyl caproate		0.8	107	1498	2-tridecanone		0.4
39	1073	<i>trans</i> -linalool oxide	1.5	0.1	108	1500	α -selinene	0.1	
40	1074	(3 <i>E</i> ,5 <i>Z</i>)-octadien-2-one		0.1	109	1522	δ -cadinene	0.1	
41	1081	hexanoic acid		22.7	110	1549	α -calacorene		0.2
42	1089	<i>cis</i> -linalool oxide	2.3	0.5	111	1556	elemol		0.2
43	1098	(3 <i>E</i> ,5 <i>E</i>)-octadien-2-one		0.9	112	1583	ar-turmerol	tr	2.2
44	1101	linalool	2.0	1.0	113	1589	caryophyllene oxide	0.2	
45	1105	nonanal	1.8	0.6	114	1616	humulene epoxide II	tr	
46	1113	(2 <i>E</i> ,4 <i>E</i>)-octadienal		0.3	115	1635	1-epi-cubenol	0.2	
47	1117	phenylethylalcohol	0.8		116	1647	hinesol		0.4
48	1122	<i>trans</i> - <i>p</i> -mentha-2,8-dien-1-ol	0.3		117	1648	epi- α -muurolol	0.1	
49	1126	methyl caplylate	0.6		118	1659	β -eudesmol		0.9
50	1127	heptanoic acid		2.0	119	1661	neointermederol	0.3	
51	1132	limona ketone	0.1		120	1662	α -cadinol		0.2
52	1137	<i>cis</i> - <i>p</i> -mentha-2,8-dien-1-ol	tr		121	1669	ar-turmerone	0.2	0.3
53	1143	(3 <i>E</i>)-nonen-2-one		0.4	122	1678	(3 <i>Z</i>)-butylidene phthalide	0.1	
54	1147	camphor	0.1		123	1682	cadalene		0.2
55	1150	(<i>E</i>)-5-ethyl-6-methyl-3-hepten-2-one		0.6	124	1740	(<i>Z</i>)-ligustilide	tr	
56	1153	lilac aldehyde	0.2		125	1771	myrstic acid		0.2
57	1158	menthone		0.3	126	1847	6,10,14-trimethyl pentadecan-2-one	tr	0.1
58	1160	(2 <i>E</i>)-nonenal	0.1	0.7	127	1927	methyl palmitate	0.4	0.2
59	1172	<i>cis</i> -linalyl oxide	0.1		128	1966	palmitic acid	0.2	8.0
60	1177	borneol + 2-pentyl thiophene		0.4	129	2096	methyl linoleate	0.2	
61	1179	terpinen-4-ol	1.3		130	2102	methyl oleate	0.6	
62	1182	menthol		2.0	131	2108	methyl phytol		0.4
63	1188	octanoic acid	2.3		132	2128	methyl stearate	tr	
64	1193	α -terpineol	1.2	0.7	133	2140	ethyl phytol		0.3
65	1194	<i>p</i> -cymen-8-ol		0.6	134	2152	linoleic acid		0.7
66	1198	methyl salicylate		0.9	135	2700	heptacosane	0.2	
67	1200	dodecane	0.3						
68	1206	decanal	0.6	1.4					
69	1212	octyl acetate	0.1				total	98.4	90.5

RI: Retention Index on a DB-5 column; peak area (%) was related to total detected compounds by GC; tr: trace<0.1.

compounds of the oil were hexanoic acid (22.7%), palmitic acid (8.0%), (2*E*, 4*E*)-decadienal (3.7%), and hexanol (3.1%). The stems oil had high content of saturated fatty acids (C6~C16), and unsaturated short-chain aldehyde (C6~C10). The pungent green odor of the unsaturated short-chain aldehyde, such as (2*E*)-hexenal, seemed to play an important role in the characteristic aroma of stems oil. Hexanal and linalool were detected as common main compounds (peak area>1.0%) to two oils, however there was hardly a similarity between fruits oil and stems oil.

To the best of our knowledge, the essential oil of *Lardizabalaceae* has not been the subject of previous studies. Thus this study is the first report on the volatile composition of this family.

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