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Volatile Profiles in Cold-Pressed Peel Oil from Korean and Japanese Shiranui (*Citrus unshiu* Marcov. × *C. sinensis* Osbeck × *C. reticulata* Blanco)

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A comparison of the volatile profiles between Korean and Japanese Shiranui cold-pressed peel oil was performed by GC and GC–MS. Limonene was the most abundant in the Japanese (91.8%) and Korean (86.4%) oil. Alcohols accounted for 1.8% in the Korean oil, and 0.2% in the Japanese oil, in which the respective linalool levels were 1.2% and 0.1%. The level of aldehydes was also higher in the Korean oil (1.6%) than in the Japanese oil (0.7%).

Key words: Shiranui; Hallabong; Dekopon; volatile component; citrus essential oil

Shiranui, a hybrid variety, was bred by crossing between Kiyomi (*Citrus unshiu* Marcov. × *C. sinensis* Osbeck) and Nakano No. 3' Ponkan (*Citrus reticulata* Blanco) at Kunchinotsu Branch of the Fruit Tree Research Station in Nagasaki Prefecture (Japan) in 1972.[1)] Shiranui (called Dekopon in Japan), a sweet citrus fruit like orange, was recently brought from Japan to Korea and then named Hallabong in 1998, as its round shape with a folded neck looks like Mt. Halla with its crater in Korea.[2)] There are several research reports about Hallabong and Dekopon: character impact odorants of citrus Hallabong,[3)] headspace-SPME analysis of Hallabong,[4)] volatile compounds identified in extracts from Dekopon,[1)] and quality changes of Hallabong during storage by chitosan and calcium treatment.[5)] There are many *Citrus* species, including *Citrus* hybrids, throughout the world, and these citrus fruits are regarded as important products. Among the many kinds of citrus fruits, Satsuma mandarin (*Citrus unshiu*), Yuzu (*Citrus junos*), and Shiranui are the major *Citrus* varieties cultivated and produced in Korea and Japan. Differences in the essential oil compositions have been reported between Korean and Japanese *C. unshiu* and *C. junos*.[6,7)] However, there has been no study on a comparison of the volatile profile of Korean Shiranui with that of Japanese Shiranui, although they are both popular fruits in each country. This study investigates the difference in volatile profiles between Korean and Japanese Shiranui cold-pressed peel oil.

Mature Hallabong fruit harvested in January 2004 was obtained from National Institute of Subtropical Agriculture in Jeju (Korea). Mature Dekopon fruit harvested in December 2003 was provided by Kochi Fruit Experimental Station in Kochi (Japan). These producing regions are located at a similar latitude between 33.3° and 34° north. Authentic standard chemicals were purchased from Tokyo Kasei Kogyo (Tokyo, Japan), Nacalai Tesque (Kyoto, Japan), Aldrich Chemical Co. (USA) and Fluka Fine Chemicals (Switzerland) for identification of the oil components. Preparation of the cold-pressed oil (CPO) was performed according to the method described in a previous report.[7)]

GC and GC/MS analyses were respectively carried out with a Shimadzu GC-17A gas chromatograph equipped with flame ionization detector (FID), and with a Shimadzu QP-5050A coupled with the GC-17A instrument under the same conditions as those described previously.[8)] Two types of column, DB-Wax (polar) of 60 m × 0.25 mm i.d. with a film thickness of 0.25 µm and DB-1 (non-polar) of 60 m × 0.25 mm i.d. with a film thickness of 0.25 µm (both from J & W Scientific, Folsom, CA, USA), were used. Quantitative GC analyses were performed with two internal standards, *n*-heptanol and methyl myristate.[7)] The quantity ratios of the two internal standards and an oil sample were 1:1:150, respectively. The percentage weight of each compound in an oil sample was calculated from the FID response factors.[7–9)]

Table 1 shows the individual volatile components present in Korean and Japanese Shiranui CPO, and a classification based on functional groups is summarized in Table 2. *β*-Cubebene, *β*-elemene, decyl acetate and geranyl acetate were only detected in Japanese Shiranui CPO. Such components as octanol, (*E*)-limonene-1,2-epoxide, *l*-menthol, neral, (*E*)-carveol and perillyl

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Abbreviation: CPO, cold-pressed oil

Table 1. Volatile Components of Cold-Pressed Peel Oil from Korean and Japanese Shiranui

No.	Component	Retention index		Peak % (w/w)		Identification
		DB-wax	DB-1	Korean Shiranui	Japanese Shiranui	
1	α-pinene	1029	933	0.63	0.70	RI,MS,Co–GC
2	camphene	1075		tr	tr	RI,MS,Co–GC
3	β-pinene	1117	973	0.18*	0.08	RI,MS,Co–GC
4	sabinene	1127	968	3.62*	1.65	RI,MS,Co–GC
5	myrcene	1162	982	2.41	2.55	RI,MS,Co–GC
6	α-phellandrene	1170	997	0.03	0.04	RI,MS,Co–GC
7	limonene	1214	1033	86.36	91.82*	RI,MS,Co–GC
8	β-phellandrene	1220		0.48	0.56	RI,MS,Co–GC
9	(*Z*)-β-ocimene	1234	1040	0.03	0.01	RI,MS,Co–GC
10	(*E*)-β-ocimene	1252		0.98*	0.35	RI,MS,Co–GC
11	terpinolene	1286		0.01	0.01	RI,MS,Co–GC
12	octanal	1289	980	0.52*	0.08	RI,MS,Co–GC
13	nonanal	1392	1082	0.04	0.02	RI,MS,Co–GC
14	(*Z*)-limonene oxide	1450		0.02	tr	RI,MS,Co–GC
15	(*E*)-limonene oxide	1462	1120	0.02	0.04	RI,MS,Co–GC
16	(*E*)-sabinene hydrate	1466	1056	0.08*	0.01	RI,MS,Co–GC
17	δ-elemene	1471	1334	tr	0.03	RI,MS,Co–GC
18	octyl acetate	1474		tr	tr	RI,MS,Co–GC
19	citronellal	1477	1132	0.17*	0.10	RI,MS,Co–GC
20	decanal	1495	1184	0.51*	0.33	RI,MS,Co–GC
21	β-cubebene	1539		—	tr	RI,MS,Co–GC
22	linalool	1545	1084	1.16*	0.14	RI,MS,Co–GC
23	octanol	1557		0.01	—	RI,MS,Co–GC
24	(*E*)-limonene-1,2-epoxide	1553		0.01		RI,MS
25	β-elemene	1588		—	0.01	RI,MS,Co–GC
26	undecanal	1600	1285	0.02	0.02	RI,MS,Co–GC
27	*l*-menthol	1628		0.05	—	RI,MS
28	(*E*)-2-decenal	1641		0.02	0.02	RI,MS,Co–GC
29	citronellyl acetate	1658	1333	0.03	0.08*	RI,MS,Co–GC
30	α-humulene	1671		0.05	0.01	RI,MS,Co–GC
31	decyl acetate	1676		—	tr	RI,MS,Co–GC
32	neral	1685		0.02	—	RI,MS,Co–GC
33	α-terpineol	1695	1173	0.16*	0.02	RI,MS,Co–GC
34	dodecanal	1705	1387	0.09	0.09	RI,MS,Co–GC
35	germacrene D	1708	1475	0.02	0.05	RI,MS,Co–GC
36	valencene	1718	1486	tr	0.12*	RI,MS,Co–GC
37	neryl acetate	1721	1342	0.08	0.01	RI,MS,Co–GC
38	bicyclogermacrene	1734	1489	0.07	0.03	RI,MS,Co–GC
39	α-farnesene	1744	1495	1.28*	0.74	RI,MS,Co–GC
40	geranyl acetate	1752		—	0.03	RI,MS
41	δ-cadinene	1756	1513	0.01	0.06	RI,MS,Co–GC
42	β-citronellol	1763	1208	0.17*	0.07	RI,MS,Co–GC
43	perillaldehyde	1783		0.21*	0.02	RI,MS,Co–GC
44	2,4-decadienal	1805	1287	0.03	tr	RI,MS,Co–GC
45	(*E*)-carveol	1833		0.05	—	RI,MS,Co–GC
46	unknown	1839		0.02	—	RI,MS
47	perillyl alcohol	1992		0.02	—	RI,MS,Co–GC
48	nerolidol	2034		0.13*	0.01	RI,MS,Co–GC
49	unknown	2050		0.16	—	RI,MS
50	unknown	2240		—	0.03	RI,MS
51	nootkatone	2526	1774	0.04	0.08*	RI,MS,Co–GC

Tr, Peak weight quantified as less than 0.005%.
—, not detected.
*, Significantly different peak percentage between Korean and Japanese Shiranui CPO.
RI, Identification based on retention index.
MS, Identification based on comparison of mass spectra.
Co–GC, Identification based on co-injection with authentic standards.

alcohol, on the other hand, were only detected in Korean CPO. Although these 10 components were not major in either oil, these results suggest a difference in the volatile profiles between Korean and Japanese Shiranui oil.

Limonene was the most prominent compound in Japanese (91.8%) and Korean (86.4%) CPO, and is well known to be a principal component in general citrus oil.[6,7,10] Limonene has also been reported as a characteristic odorant of Ponkan oil,[8] which is a parent of

Table 2. Constitution of Functional Groups in the Cold-Pressed Peel Oil of Korean and Japanese Shiranui

Functional group	Korean Shiranui		Japanese Shiranui	
	Total no. of components	Peak % (w/w)	Total no. of components	Peak % (w/w)
Monoterpene hydrocarbons	11	94.72	11	97.78
Sesquiterpene hydrocarbons	7	1.43	9	1.05
Alcohols	8	1.75	4	0.24
Aldehydes	10	1.63	9	0.66
Esters	4	0.20	6	0.13
Oxides	3	0.05	2	0.04
Ketones	1	0.04	1	0.08
Total	44	99.82	42	99.98

Shiranui. Among the abundant monoterpene hydrocarbons in both oils, sabinene and myrcene were determined as more than 1.6%. Apart from limonene, myrcene, α-phellandrene and β-phellandrene, however, monoterpene hydrocarbons were more abundant in Korean CPO than in Japanese CPO. Among these 7 monoterpene components, the individual proportions of sabinene, β-pinene and (E)-β-ocimene in Korean Shiranui oil were about 2 times higher than those in Japanese oil. Among the sesquiterpene hydrocarbons, α-farnesene accounted for the greatest percentage in both oils. Valenecene was relatively abundant in Japanese Shiranui oil (0.12%), but only encountered in a trace quantity in Korean oil. This is similar to the result that the content of valencene was higher in Japanese mandarin oil than in Korean.[6)]

The difference in the volatile profiles between Korean and Japanese Shiranui oil was significantly characterized by the identification and quantity of the alcohol group. The higher content of alcohols in Korean Shiranui oil resulted from the relative abundance of linalool (1.16%), β-citronellol (0.17%), α-terpineol (0.16%) and octanol (0.12%). Linalool in Japanese Shiranui CPO was as low as 0.14%. The proportion of aldehydes was also higher in Korean CPO (1.63%) than in Japanese (0.66%); however, in the case of Satsuma mandarin, a grandparent of Shiranui, it was significantly higher in Japanese oil than in Korean oil.[6)] Though esters were determined at a low level in both oils, citronellyl acetate, which has been suggested as a characteristic component of this *Citrus* hybrid,[3)] was more abundant in Japanese Shiranui CPO (0.08%) than in Korean CPO (0.03%). However, another characteristic odorant, citronellal,[3)] was at a higher level in Korean CPO (0.17%) than in Japanese CPO (0.10%). The total oxygenated compounds in Korean Shiranui oil accounted for 3.65% of the total volatiles, which is more than 3 times that in Japanese oil (1.07%). According to previous reports, the proportion of oxygenated compounds in Satsuma mandarin was higher in Japanese CPO than in Korean CPO, while in the case of *Citrus junos*, it was higher in CPO from Jeju (Korea) than in that from Kochi (Japan).[6,7)] Although the volatile profiles were different between Korean and Japanese Yuzu, Satsuma mandarin and Shiranui oils, it is difficult to clearly identify the characteristic differences in essential oil composition between Korean and Japanese citrus oil because the different volatile profiles between Korean and Japanese oil seem to depend on the kind of citrus.[6,7)]

To conclude, the characteristic volatile profile of Korean Shiranui oil seems to have been associated with a much higher proportion of oxygenated compounds such as alcohols and aldehydes, including linalool, octanal, decanal and citronellal. It is suggested, on the other hand, that the abundance of limonene, various terpene hydrocarbons and the relatively higher level of citronelly acetate are factors characterizing the volatile composition of Japanese Shiranui oil.

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