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The Improvement of the Flavor of Canned Satsuma Mandarin

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The flavor of the canned Satsuma mandarin (juice sacs and syrup) is poorer than that of the commercially extracted Satsuma mandarin juice. The study aims to improve of the flavor of canned Satsuma mandarin. We added cold-pressed oil to the canned Satsuma mandarin. Satsuma mandarin and Valencia orange were used for preparing the cold-pressed oil. The cold-pressed oil was extracted from the peel. The volatile compounds of fresh juice sacs and canned Satsuma mandarin were isolated by simultaneous distillation and extraction under reduced pressure, and analyzed by a GC-MS. Predominant aroma compounds in the canned Satsuma mandarin were limonene and linalool. The concentration of limonene, linalool and hexanal decreased by canning. Limonene, linalool and hexanal were remained more abundantly with the canned containing cold-pressed oil. In the sense evaluation, the canned Satsuma mandarin containing the cold-pressed oil of Valencia orange was liked more than the canned Satsuma mandarin containing the cold-pressed oil of Satsuma mandarin. It is not clear why it was liked at the time of the present.

Key words : aroma, canned fruit, cold-pressed oil, flavor, GC-MS, Satsuma mandarin, volatile compounds.

Introduction

We have already evidenced that there is a limonene of predominant aroma compounds and a linalool in the canned Satsuma mandarin (juice sacs and syrup) (1). The concentration of limonene, linalool and hexanal decreased by canning. The flavor of the canned Satsuma mandarin is poorer than that of the commercially extracted Satsuma mandarin juice, because the canned Satsuma mandarin has little peel oil. Some peel oil is mechanically transferred to the commercially extracted fruits juice during the extraction of unpeeled fruits (2). Peeled Satsuma mandarin was used for preparing the canned Satsuma mandarin. Flavoring is done with the canned drink (3). Since flavoring is hardly done with the canned Satsuma mandarin, we try to process the canned Satsuma mandarin which contains cold-pressed oil. The purpose is the manufacture of the canned Satsuma mandarin further favorable by the people. The volatile compounds of fresh juice sacs and those canned were isolated by simultaneous distillation and extraction under reduced pressure (RSDE), and analyzed by a GC-MS. Those canned fruits were evaluated the sense in the paired preference test.

注　本論文は *Applied Biological Science*, 6 (2000) 67－73 掲載論文を転載したものである.

MATERIALS AND METHODS

Materials

The Satsuma mandarin (*Citrus unshiu* MARC. cv. Miyagawa-wase) produced in Kumamoto prefecture were purchased from a fruit market. The concentration of soluble solids and citric acid were 9.5 °Brix and 0.7%, respectively, in the fresh Satsuma mandarin. Cold-pressed oil of the Satsuma mandarin and the Valencia orange were obtained from Shionokoryo Ltd. The dichloromethane purchased from Wako Jyunnyaku Kougyo Ltd. was especially grade. The high purity helium gas (Zero-U) of the Sumitomoseika Ltd. was used for the GC-MS measurement. The ultra pure water which treated with high purity water system (Elgastat UHQ: Elga Ltd., Lane End, U.K.) was used.

Sample Preparation

(1) The preparation of fresh Satsuma mandarin juice sacs

Satsuma mandarin were immersed in 90℃ hot water for one minute in order to soften the outer peel. The outer peel was removed by hand. After removal of the peel, the fruit was separated into segments by hand. The segments soaked 0.7% hydrochloric acid solution at 40℃ for 60min with stirring occasionally. The weight ratio of 0.7% hydrochloric acid solution to segments was 4 to 3. They were washed by running water and soaked 0.3% sodium hydroxide solution at 40℃ for 20min with stirring. The weight ratio of 0.3% sodium hydroxide solution to segments was 4 to 3. After chemical treatment, they were fully washed with water and then they were washed with running water for 60min. The segment membranes were dissolved by chemical treatment to get fresh juice sacs. The concentration of soluble solids, pH and citric acid of fresh juice sacs were 8.8 °Brix, 3.3 and 0.6%, respectively. The volatile compounds of fresh juice sacs were isolated by RSDE.

(2) Processing procedures for the canned Satsuma mandarin

Fresh juice sacs (275g) were filled into steel can, which is made from plain electrolytic plate and recommended for canned Satsuma mandarin, by hand. The concentration of the sugar syrup was determined based on the sugar content of fresh juice sacs. The canned fruits were stood two weeks to equalize the syrup to the desired Brix degree. We desired around 14 °Brix degree. The sugar syrup of 22.1 °Brix degree (165g/can) was filled to get 14 °Brix degree. The sugar syrup was added at a temperature of 90℃. The total weight of contents was 440g. Cold-pressed oil was not added to the control. We used the cold-pressed oil of the Satsuma mandarin and the Valencia orange. The cans were closed by 5M vacuum sealers. The gauge of chamber vacuum was fitted to -62kPa. The canned Satsuma mandarin were subjected to low temperature pasteurization by a rotary sterilizer at a bath temperature of 80℃ for 10min at the rate of 5rpm. Immediately after pasteurization, the cans were cooled until the average temperature of the contents reached to 40℃ by a water cooling bath. The cans stored at room temperature (15~25℃) by the use for analysis.

(3) Processing procedures for the canned Satsuma mandarin containing the cold-pressed oil

We produced the canned Satsuma mandarin contains the cold-pressed oil of Satsuma mandarin (SMO). Processing procedures are as follows: Fresh juice sacs

(275g) were filled into can by hand and then added 880mg of 50% of Satsuma mandarin cold-pressed oil ethanol solution. The total weight of contents was 440g by the addition of the sugar syrup as described above. The cans were closed, pasteurized and cooled in the same way as the control cans, and stored at the room temperature. We produced the canned Satsuma mandarin contains the cold-pressed oil of Valencia orange (VO). Fresh juice sacs (275g) were filled into can by hand and then added 880mg of 50% of Valencia orange cold-pressed oil ethanol solution. The total weight of contents was 440g by the addition of the sugar syrup as described above. The cans were closed, pasteurized and cooled in the same way as the control cans, and stored at the room temperature.

(4) The extraction and concentration of the volatile compounds

We prepared the apparatus called simultaneous distillation and extraction (SDE) head as it was shown in the figure that was in the paper (4). The SDE system is used for isolating volatiles from agricultural products. The volatile compounds from fresh juice sacs and canned Satsuma mandarin were isolated by the method of RSDE with the SDE system. Samples were taken in a 2L flask. The 2L flask was joined to the left-hand riser of the SDE head, and a 100mL flask containing 50mL of high purity dichloromethane was connected to the other riser. When temperature of the 2L flask reached to 65℃, a reducing valve was closed to start distillation it for 2 hours at constant pressure. Cyclohexanol of 1mg was dissolved in dichloromethane of 1mL. This cyclohexanol solution of 200 μL was added to the extracted solution as an internal standard. The solution was dehydrated by shaking with sodium sulfate anhydrous. The solution was concentrated to 500 μL by the Kuderna-Danish apparatus, then to 100 μL by blowing nitrogen in a freezing mixture with sodium chloride and ice. The volatile compounds concentration of each sample was measured. Each sample prepared for the RSDE as follows. Fresh juice sacs of 550g were put in the 2L flask, and the syrup of 330g was added. On the other hand, preparing "the fresh juice sacs added with the cold-pressed oil of Satsuma Mandarin", fresh juice sacs of 550g were put in the 2L flask, and the 50% cold-pressed oil (Satsuma mandarin) ethanol solution of 1760mg was added and the syrup was added to weigh 880g. Fresh juice sacs (550g), the 50% cold-pressed oil (Valencia orange) ethanol solution of 1760mg, and the syrup were used for "the fresh juice sacs added with the cold-pressed oil of Valencia orange", "SMO" and "VO" used two canned fruits. Volatile compounds were determined by the extraction from these samples (880g). Volumes of 3 μL were injected to determine with GC-MS.

(5) Analysis of the volatile compounds

Mass spectra were obtained on a Hewlett-Packard 6890 GC/MSD system containing a fused silica polar capillary column coated with DB-WAX (J & W Scientific, Inc., 0.25mm i.d.×60m, film thickness 0.25 μm). The operating conditions were as follows: helium (Zero-U) carrier, rate of line (25cm/sec) ; a split ratio of 20:1; the injector temperature 260℃. The column temperature was held at 40℃ for 5 min, then programmed to 200℃ at 3℃/min, and held there for 30 min. The transfer line temperature was 250℃. Mass spectra were obtained from

electron ionization energy at 70eV and within the mass range of m/z 10 ~ 300. We used the Hewlett Packard Chemistation System for the analysis of the data and searched the library database of the National Bureau of Standards. Results of qualitative analysis were verified by comparison of mass spectral data and Kováts index with those of authentic reference substances. Eight compounds were identified referring to retention indices which were reported by Sakamoto (5). The internal standard used for the experiments was cyclohexanol. Concentrations were calculated from total ion intensity by internal standard method without response correction. The weight of the total juice sacs of two cans was 550g. We calculated, therefore, concentration of the volatile compounds as a weight of the sample is 550g.

(6) The paired preference test

Twenty persons were used as a sensory panel. Of these, nine were young men (M = 19 years), six were elderly men (M = 48 years) and five were females (M = 30 years). For the paired preference test, each member was given two canned samples, one with the cold-pressed oil of Satsuma mandarin and the other with the cold-pressed oil of Valencia orange. They indicated on a card which one they preferred.

RESULTS & DISCUSSION

The volatile compounds isolated from samples are listed in Table 1. These retention indices and concentration data are also shown in this table. The limonene concentration of the fresh juice sacs was 1226.8 ppb. The limonene concentration of the canned Satsuma mandarin was 425.5 ppb. The limonene concentration of the canned SMO and the canned VO was 540 ppm and 669 ppm, respectively. The linalool concentration was the amount of trace in the fresh juice sacs. The linalool concentration of the canned Satsuma Mandarin orange was 1.25 ppb. The linalool concentration of the canned SMO and the canned VO was 5.7 ppm and 7.1 ppm, respectively. Limonene and linalool left more abundantly with the canned fruits contained cold-pressed oil. In the case of the sample that terpenoids existed in a large quantity, some of the alcohols were impossible to be identified because alcohols and terpenoids overlap each other in some peaks. Citral did not exist in the canned SMO. (*Z*)-citral and (*E*)-citral existed in the canned VO. The total of (*Z*)-citral and (*E*)-citral was 2.6 ppm. Though cold-pressed oil was added, (*Z*)-3-hexenal was not remained. Canned fruits were evaluated sensually. Table 2 shows result of the paired preference test. The canned VO was more liked than the canned SMO significantly at the 5% level. It is not clear why it was liked at the present.

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Table 1 Volatile compounds of the fresh juice sacs and the canned Satsuma mandarin (*Citrus unshiu* MARC. cv. Miyagawa-wase) which contained cold-pressed oil

Peak No.	Compounds	KI	Concentration, $\mu g\ kg^{-1}$ [a]					
			Control Without cold-pressed oil		With the cold-pressed oil of Satsuma mandarin		With the cold-pressed oil of Valencia orange	
			Fresh	Canned[b]	Fresh	Canned[b]	Fresh	Canned[b]
	Terpenoids							
4	α-Pinene	1020	–	–	8832.9	7255.5	6515.8	5887.6
5	α-Thujene	1026	–	–	5623.7	5511.3	–	–
10	β-Pinene	1106	tr	–	6911.6	7037.8	2841.3	3554.1
11	Sabinene	1121 [c]	–	–	529.7	378.7	–	–
16	Myrcene	1163	10.6	8.0	33138.4	24697.3	17807.1	20951.5
17	α-Terpinene	1179	tr	tr	–	–	–	–
19	Limonene	1197	1226.8	425.5	679394.7	540119.9	682821.5	668918.3
23	γ-Terpinene	1246	70.5	20.2	70424.9	72941.1	237.2	406.6
25	p-Cymene	1271	17.6	4.6	14270.8	15308.9	99.6	74.0
26	α-Terpinolene	1284	tr	0.8	5169.8	5561.2	70.1	23.8
40	δ-Elemene	1477 [c]	11.1	9.2	216.3	266.2	397.3	305.5
42	Copaene	1501 [c]	–	–	2922.3	2664.9	453.8	317.1
44	β-Cubebene	1547 [c]	–	–	1032.8	1660.7	470.6	310.5
48	β-Elemene	1600 [c]	14.0	–	23017.8	22627.4	377.8	617.7
49	β-Caryophyllene	1606	tr	3.4	2663.6	2093.9	726.6	440.8
54	α-Caryophyllene	1680	tr	8.4	4844.6	3824.3	103.2	80.9
60	GermacreneD	1722 [c]	38.5	4.8	3016.5	762.8	92.7	50.6
66	α-Farnesene	1754 [c]	tr	tr	20579.8	18560.0	406.3	402.5
68	γ-Cadinene	1768	tr	tr	4570.4	3818.7	1062.1	569.5
45	Linalool	1552	tr	1.2	5372.7	5739.3	12557.3	7070.0
50	Terpinen-4-ol	1611	tr	0.9	629.2	2582.9	4311.6	581.5
59	α-Terpineol	1707	12.8	2.1	3605.6	2168.2	2559.1	1083.6
69	Citronellol	1772	–	–	552.9	299.2	475.5	225.8
72	Nerol	1808	–	–	76.1	41.7	351.2	149.7
73	(*E*)-Carveol	1845	1.8	10.1	741.2	728.4	202.9	116.4
74	Geranaiol	1855	–	–	62.6	40.2	424.0	164.5
76	(Z)-Carveol	1876	–	–	66.7	66.8	77.1	47.1
84	β-Elemol	2090 [c]	–	–	507.3	191.6	665.6	160.1
41	Citronellal	1483	–	–	276.1	35.2	–	618.1
56	(Z)-Citral	1690	–	–	–	–	1201.3	920.6
64	(*E*)-Citral	1740	–	–	–	–	1672.2	1668.8
71	Perillaldehyde	1797	–	–	639.6	605.8	817.6	458.9
53	Citronellyl acetate	1666	–	–	538.9	526.8	252.1	121.5
67	Gerany acetate	1762	tr	6.2	2268.6	2228.4	127.9	77.8
47	UK(M+=204)	1587	–	–	1695.3	1509.7	–	–
51	UK(M+=204)	1647	–	–	999.9	819.7	–	–
58	UK(M+=204)	1702	14.8	2.3	1614.8	85.3	209.7	57.3
61	UK(M+=204)	1727	–	4.7	1255.8	762.8	–	–
62	UK(M+=204)	1731	46.1	51.0	1616.2	709.9	1415.2	871.4
63	UK(M+=204)	1737	1.3	4.0	867.0	379.3	203.3	97.0
65	UK(M+=204)	1747	–	–	642.2	567.8	550.2	309.7
70	UK(M+=204)	1776	1.7	1.8	–	–	168.9	102.2
			1467.6	569.2	911189.3	755179.6	742725.7	717813.0
	Alcohols							
2	Ethanal	937	24.3	16.6	–	tr	–	–
6	Propanal	1042	19.3	12.0	–	–	–	–
7	2-Methyl-3-buten-2-ol	1044	38.5	48.4	–	–	–	–
9	2-Methyl-1-propanol	1096	17.2	12.3	tr	tr	–	–
14	1-Butanol	1148	3.2	1.4	–	–	–	–
15	1-Penten-3-ol	1162	8.8	5.6	–	–	–	–
20	2-Methyl-1-butanol	1210	21.7	18.5	–	–	–	–
21	3-Methyl-1-butanol	1211	86.8	64.9	–	–	–	–
24	1-Pentanol	1255	2.4	1.6	–	–	–	–
29	(Z)-2-Penten-1-ol	1325	5.9	5.7	–	–	–	–
30	3-Methyl-2-buten-1-ol	1326	11.8	13.0	–	–	tr	tr
31	1-Hexanol	1358	4.6	3.2	–	–	–	–
32	(Z)-3-Hexen-1-ol	1389	11.5	9.3	tr	tr	12.3	20.9
36	1-Heptanol	1461	tr	–	41.7	52.4	33.1	19.5
46	1-Octanol	1563	–	–	172.3	143.2	1364.3	466.2
			256.0	212.5	214.0	195.6	1409.7	506.6

Table 1 continued

	Aldehydes							
8	Hexanal	1082	4.8	4.0	–	–	–	–
12	(*E*)-2-Pentenal	1129	2.0	0.9	–	–	–	–
13	(*Z*)-3-Hexenal	1143	2.3	–	–	–	–	–
18	Heptanal	1185	tr	–	–	–	–	–
22	(*E*)-2-Hexenal	1219	2.3	2.8	–	–	–	–
28	Octanal	1291	–	–	361.2	380.4	5376.9	3542.2
33	Nonanal	1399	–	–	350.0	367.9	905.1	1494.8
38	Furfural	1466	7.9	13.9	–	–	–	–
43	Decanal	1503	–	–	1375.5	1614.8	8381.6	5348.0
52	(*E*)-2-Decenal	1649	–	–	111.3	27.4	123.7	81.5
			19.3	21.6	2198.0	2390.5	14787.3	10466.5
	Acid							
94	Decanoic acid	2281	–	4.3	499.7	494.6	136.3	75.9
			0	4.3	499.7	494.6	136.3	75.9
	Paraffin Wax							
77	Nonadecane	1900	1.7	1.6	–	–	–	–
79	Eicosane	2000	20.1	18.9	–	–	–	–
82	Hydrocarbon	2051	55.9	49.6	81.0	75.4	480.9	441.8
85	Heneicosane	2100	126.7	131.0	180.5	174.2	231.5	207.5
86	Hydrocarbon	2149	40.5	36.9	61.5	49.0	77.5	56.8
87	Hydrocarbon	2164	35.8	31.8	261.5	282.3	149.2	91.0
89	Docosane	2200	102.2	122.1	298.1	231.5	197.3	213.9
92	Hydrocarbon	2253	440.5	425.8	655.7	679.8	722.2	649.3
95	Tricosane	2300	297.1	408.9	798.1	762.2	819.4	719.8
96	Hydrocarbon	2323	56.7	52.5	60.7	75.0	90.0	–
97	Hydrocarbon	2349	30.8	33.1	77.9	62.6	103.8	156.5
98	Hydrocarbon	2369	194.1	186.3	246.3	288.4	297.7	295.9
99	Tetracosane	2400	44.1	68.6	116.1	114.8	138.3	112.3
100	Hydrocarbon	2449	53.1	67.7	112.3	95.2	201.9	232.0
101	Pentacosane	2500	55.1	90.2	158.6	184.5	160.5	142.0
			1554.4	1725.0	3108.3	3074.9	3670.2	3318.8
	Others							
1	Acetone	813	13.6	44.0	–	–	–	–
3	Chloroform	1018	11.1	6.1	–	–	–	–
27	3-Hydroxy-2-butanone	1288	174.8	131.0	–	–	–	–
			199.5	181.1	0.0	0.0	0.0	0.0
	Unknowns							
34	UK	1440	–	–	258.0	290.2	–	–
35	UK	1443	–	–	63.6	76.7	–	–
37	UK	1465	–	–	194.6	84.3	75.2	129.0
39	UK	1475	–	–	3945.1	3911.6	19.8	20.2
55	UK	1685	–	–	541.3	439.4	92.8	45.9
57	UK	1698	–	2.3	255.9	156.3	109.8	117.8
75	UK	1866	–	–	691.3	745.7	438.2	250.6
78	UK	1951	–	–	178.2	51.5	–	–
80	UK	2006	–	–	260.6	131.5	290.2	331.7
81	UK	2018	–	–	1860.7	76.9	–	–
83	UK	2069	–	–	170.0	182.4	2332.4	1313.7
88	UK	2196	–	–	479.2	157.1	56.3	26.9
90	UK	2204	–	–	–	–	–	–
91	UK	2243	–	–	229.1	251.9	105.9	43.3
93	UK	2266	18.8	24.7	2595.8	2758.3	–	–
102	UK	2528	14.6	13.5	342.5	–	–	–
			33.4	40.5	12065.9	9313.8	3520.6	2279.1
			3530.2	2754.2	929275.2	770649.0	766249.8	734459.9

[a], Concentrations were calculated from total ion intensity by internal standard method (IS = cyclohexanol) without response correction;

[b], Concentrations based on the weight of canned vesicles;

[c], Sakamoto et al.(1997) [5]

tr, Trace;

–, Not detected.

Table 2 Preference of judges for canned Satsuma mandarin with the cold-pressed oil of Satsuma mandarin or the cold-pressed oil of Valencia orange by the paired preference test

Preference	Judges	
	Number	Percent
Canned Satsuma mandarin		
With the cold-pressed oil of Satsuma mandarin	5	25
Wtih the cold-pressed oil of Valencia orange	15*	75
Total	20	100

* Significantly difference at the 5% level.

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