

Volatile Components of Chinese Quince (*Pseudocydonia sinensis* Schneid)

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Chinese quince (*Pseudocydonia sinensis* Schneid; *Chaenomeles sinensis* Koehne; *Cydonia sinensis* Thouin, karin in Japanese) oils from the peel and the flesh were analyzed by gas chromatography and gas chromatography-mass spectrometry. A total of 111 compounds were identified. In the Chinese quince, 84 compounds consisting of 4 hydrocarbons, 50 esters, 6 alcohols, 6 aldehydes, 3 ketones, 3 acids, 3 lactones, 6 acetals, and 3 miscellaneous compounds were identified from the oil in the peel. Of these compounds, the alkyl and alkenyl esters of ω -alkenoic acids and the 5-hexenyl esters of the aliphatic acids, which have been previously unreported in any essential oil except ethyl 9-decenoate, were recognized to be an important contributor to the typical Chinese quince flavor. From the flesh 42 compounds were identified. The flavor concentrate from the peel was thought to be more important to the Chinese quince aroma than that from the flesh.

Chinese quince (*Pseudocydonia sinensis* Schneid; *Chaenomeles sinensis* Koehne; *Cydonia sinensis* Thouin, karin in Japanese) is a dark yellow, hard, oval or egg-shaped fruit (ca. 10 cm in diameter) of a high tree of the rose family. It is not edible due to its very hard consistency and strong acid taste. They were often used for preparing candied fruits and fruit liqueur, which were used as an effective cough medicine and diuretic. Chinese quince, when ripe, imparts a more powerful flavor than quince (*Cydonia oblonga* Mill.; *Cydonia vulgaris* Pers., marmelo in Japanese). The volatile components of quince have already been reported by Spanyol et al. (1965), Shimizu and Yoshihara (1977), Schreyen et al. (1979), Tsuneya et al. (1983), and Umano et al. (1986). However, the aromatic substances of Chinese quince have received little attention (Hashimoto et al., 1983). The very powerful flavor of Chinese quince made study of these volatile compounds interesting, looking for characteristic flavor compounds in relation to quince.

EXPERIMENTAL SECTION

Materials. Fresh Chinese quinces harvested in Nagano Prefecture in Nov 1982 were used.

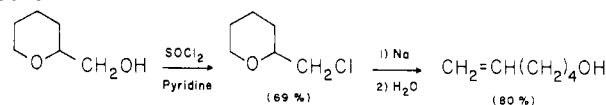
Methods. (1) *Collection of Volatile Flavor Compounds.*

(a) *From the Peel.* Portions of 10 kg of Chinese quinces were used. Each fruit was peeled, cut into quarters, and cored to give 7.8 kg of flesh and 1.9 kg of peel. The peel was crushed by a food processor and immersed in the 2.2 kg of 85% aqueous ethanol for 8 days. The mixture was filtered, and the filtrate (2.5 kg) was extracted with 250 mL of isopentane. The solvent was removed by distillation to give 0.5 g of extract. The extract was distilled under reduced pressure [120 °C (2 mmHg)]. The resulting distillate (30 mg) had the typical Chinese quince odor; yield 0.0016%.

(b) *From the Flesh.* After 7.8 kg of flesh was ground, 5.5 kg of brine was added and the mixture was filtered, resulting in 9.1 kg of filtrate. The juice was extracted with ether and treated in the same manner as the peel, yielding 47 mg of flavor concentrate (0.0006%).

(2) *GC Conditions.* A Hewlett-Packard Model 5710A gas chromatograph with a flame ionization detector (FID) modified for capillary analyses was used (Shibamoto, 1982). The gas chromatograph was fitted with an all-glass injector splitter of our own design to avoid any contact with metal

Scheme I



surfaces to avoid artifacts and was operated with an injector split ratio of 50:1. A 50 m \times 0.22 mm (i.d.) fused silica capillary column (coated with Carbowax 20M) prepared in our laboratory was used in the experiments. The column temperature was programmed from 80 to 200 °C at a rate of 3 °C/min, and the flow rate of the nitrogen carrier gas was 0.67 mL/min.

(3) *GC/MS Conditions.* A Hitachi Model M-80 mass spectrometer was used under the following conditions: ionizing voltage, 70 eV; accelerating voltage, 3100V; ion source temperature, 200 °C; carrier gas, helium. The gas chromatographic column and oven conditions were as described for the Hewlett-Packard gas chromatograph. Identification of all the peaks was made by comparison of their mass spectra and Kovat's indices to those of authentic compounds. For some compounds, standard samples were not available to confirm positive identification. If the mass spectrum matched precisely that of published data and the retention could be estimated from the published data, the compound was listed as tentatively identified.

(4) *Instrumental Analysis.* Infrared spectra were obtained with a Jasco IR-S. NMR spectra were measured in CDCl_3 with a JNM-PMX 60 using tetramethylsilane as the internal standard.

(5) *Quantitative Assessment.* Samples were prepared in such a manner that a known aliquot of the fruit sample was analyzed. Quantitative data were then derived from the FID trace during routine GC. Known amounts of a selection of identified compounds (acetic acid, isobutyric acid, octanoic acid, 2-methylpropanol, hexanol, (Z)-3-hexenol, acetone, β -ionone, (E)-2-hexenal, decanal, ethyl butyrate, ethyl octanoate, hexyl acetate, hexyl octanoate, theaspirane, acetaldehyde diethyl acetal, limonene) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the essence.

(6) *Sensory Evaluation.* The odor description for each compound was carried out at the level of 1 ppm in syrup composed of sucrose (10 g) and water (90 mL) by three flavorists.

(7) *Synthesis of Authentic Compounds.* (a) *5-Hexenol.* This compound was prepared by the method described by Brooks and Snyder (1955) using tetrahydropyran-2-

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methanol (46 g, 0.40 mol) as a starting material: yield 22.0 g (55%); bp 62–63 °C (20 mmHg) [lit. bp 57–58 °C (15 mmHg); Lyle et al. (1956)] (Scheme I); IR (ν_{\max} , cm^{-1} ; neat) 3330, 2920, 1640, 1440, 1060, 910; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 1.2–1.8 (4 H, m), 1.8–2.3 (3 H, m), 3.60 (2 H, t, $J = 6$ Hz), 4.8–5.3 (2 H, m), 5.5–6.3 (1 H, m); MS, m/z 82 ($\text{M}^+ - 18$, 50%), 67 (100), 57 (83), 55 (48), 54 (98), 42 (73), 41 (87), 39 (25).

(b) *5-Hexenyl Acetate, Butyrate, Hexanoate, and Octanoate*. These compounds were synthesized from 5-hexenol (0.7 g, 0.007 mol), aliphatic acids (acetic acid, butyric acid, hexanoic acid, octanoic acid; 0.007 mol), and catalytic amounts of *p*-toluenesulfonic acid in toluene by standard methods.

5-Hexenyl acetate: IR (ν_{\max} , cm^{-1} ; neat) 3080, 2930, 1740, 1645, 1370, 1245, 1040, 920; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 1.2–1.8 (4 H, m), 1.8–2.2 (2 H, m), 2.03 (3 H, s), 4.06 (2 H, t, $J = 7$ Hz), 4.8–5.2 (2 H, m), 5.5–6.2 (1 H, m); MS, m/z 112 ($\text{M}^+ - 30$, 8%), 100 (10), 82 (46), 67 (73), 55 (50), 54 (87), 43 (100), 41 (45). These data indicate the compound to be 5-hexenyl acetate synthesized by Gol'mov (1952).

5-Hexenyl butyrate: IR (ν_{\max} , cm^{-1} ; neat) 3080, 2940, 1730, 1640, 1460, 1180, 1095, 995, 910, 750; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 0.95 (3 H, t, $J = 7$ Hz), 1.3–1.8 (6 H, m), 1.9–2.4 (4 H, m), 4.09 (2 H, t, $J = 6$ Hz), 4.8–5.2 (2 H, m), 5.4–6.2 (1 H, m); MS, m/z 127 ($\text{M}^+ - 43$, 6%), 89 (35), 82 (58), 71 (89), 67 (85), 55 (63), 54 (100), 43 (83), 41 (41).

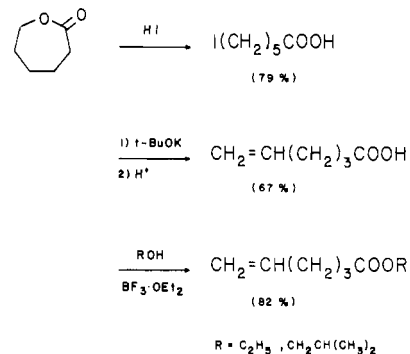
5-Hexenyl hexanoate: IR (ν_{\max} , cm^{-1} ; neat) 3070, 2920, 1730, 1640, 1460, 1170, 1100, 1000, 910, 740; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 0.88 (3 H, t, $J = 6$ Hz), 1.1–1.4 (6 H, m), 1.4–1.8 (4 H, m), 1.8–2.4 (4 H, m), 4.08 (2 H, t, $J = 7$ Hz), 4.8–5.2 (2 H, m), 5.5–6.2 (1 H, m); MS, m/z 157 ($\text{M}^+ - 41$, 18%), 117 (30), 100 (26), 99 (68), 83 (35), 82 (61), 71 (57), 67 (84), 54 (100), 43 (75), 41 (37).

5-Hexenyl octanoate: IR (ν_{\max} , cm^{-1} ; neat) 3070, 2900, 1730, 1640, 1460, 1160, 1100, 910, 725; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 0.88 (3 H, t, $J = 6$ Hz), 1.1–1.4 (10 H, m), 1.5–1.8 (4 H, m), 1.8–2.4 (4 H, m), 4.06 (2 H, t, $J = 6$ Hz), 4.8–5.2 (2 H, m), 5.4–6.1 (1 H, m); MS, m/z 185 ($\text{M}^+ - 41$, 4%), 145 (25), 127 (54), 83 (43), 82 (72), 67 (80), 57 (87), 55 (72), 54 (100), 43 (25).

(c) *5-Hexenoic Acid*. A mixture of ϵ -caprolactone (34 g, 0.30 mol) and 56% hydriodic acid (93 g, 0.41 mol) was heated at 125 °C for 2 h. After the mixture was cooled to room temperature, toluene (70 g) was added and the mixture was washed with brine. After solvent removal in vacuo, the residue was recrystallized from a 1:5 benzene-hexane solution to give 6-iodohexanoic acid [57 g (79% yield from ϵ -caprolactone)] as pale red needles, mp 43.5–44.0 °C [lit. mp 43.0–43.5 °C; Pattison et al. (1956)].

6-Iodoohexanoic acid (57 g, 0.24 mol) was refluxed with potassium *tert*-butoxide (65 g, 0.58 mol) in *tert*-butyl alcohol (600 g) for 1 h. The reaction mixture was acidified with 10% H_2SO_4 (164 g) and water added (600 g). The product was then extracted with toluene. The organic layer was concentrated to 50 mL and extracted with 10% sodium hydroxide solution (140 g). The alkaline solution was washed with toluene, acidified with 6 N hydrochloric acid solution, and then extracted with toluene. The toluene extracts were washed with brine (200 mL) and dried over anhydrous MgSO_4 . Distillation gave 5-hexenoic acid: 18 g (67% yield from 6-iodohexanoic acid); bp 71–73 °C (3 mmHg) [lit. bp 107 °C (17 mmHg); LaForge et al. (1948)] (Scheme II); IR (ν_{\max} , cm^{-1} ; neat) 2940, 1710, 1640, 1415, 1250, 920; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 1.6–2.6 (6 H, m), 4.8–5.3 (2 H, m), 5.5–6.2 (1 H, m), 11.40 (1 H, br s); MS, m/z 114 (M^+ , 25%), 96 (35), 73 (57), 69 (56), 68 (78), 60 (100), 55 (97), 54 (53), 42 (63), 41 (75).

Scheme II



(d) *Ethyl 5-Hexenoate*. A solution of 5-hexenoic acid (17.1 g) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (20 mL) in dry 1:1 ethanol-ether (40 g) was stirred for 8 h at 34 °C. To this solution was added water (350 mL), and the resultant mixture was neutralized with 10% sodium hydroxide solution. The organic layer was extracted with ether. The extract was washed with water, dried over MgSO_4 , and evaporated. The residue was distilled to give ethyl 5-hexenoate: 17.5 g (82%); bp 69–70 °C (25 mmHg) [lit. bp 58–60 °C (15 mmHg); Ogibin et al. (1974)] (Scheme II); IR (ν_{\max} , cm^{-1} ; neat) 3090, 2980, 1735, 1640, 1450, 1380, 1180, 1110, 1000, 920, 860; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 1.21 (3 H, t, $J = 7$ Hz), 1.5–2.5 (6 H, m), 4.13 (2 H, q, $J = 7$ Hz), 4.8–5.2 (2 H, m), 5.5–6.2 (1 H, m); MS, m/z 142 (M^+ , 3%), 114 (5), 97 (44), 88 (77), 70 (42), 69 (65), 68 (100), 61 (65), 60 (88), 55 (53), 41 (55).

(e) *Isobutyl 5-Hexenoate*. By the same procedure for the synthesis of ethyl 5-hexenoate, isobutyl 5-hexenoate was synthesized (Scheme II) as a colorless liquid: 21.1 g (83%); bp 62–63 °C (5 mmHg); IR (ν_{\max} , cm^{-1} ; neat) 3060, 2950, 1735, 1640, 1460, 1380, 1180, 1000, 910; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 0.92 (6 H, d, $J = 7$ Hz), 1.5–2.5 (7 H, m), 3.84 (2 H, d, $J = 7$ Hz), 4.8–5.2 (2 H, m), 5.5–6.2 (1 H, m); MS, m/z 155 ($\text{M}^+ - 15$, 2%), 114 (47), 97 (70), 96 (45), 73 (40), 69 (63), 68 (73), 60 (50), 57 (100), 56 (59), 55 (71), 41 (79).

(f) *7-Octenoic Acid*. To a solution of 5-hexenol (18 g, 0.18 mol) in dry carbon tetrachloride (300 mL) was added triphenylphosphine (55 g, 0.21 mol). The reaction mixture was stirred and refluxed for 1 h. After the usual workup, the reaction products were distilled to give 5-hexenyl chloride: 15.2 g (71%); bp 72 °C (100 mmHg).

Sodium metal (4 g, 0.174 mol) was dissolved in dry ethanol (100 mL) to which was added ethyl malonate (20 g, 0.125 mol). To this solution was added 5-hexenyl chloride (14 g, 0.118 mol) gradually. The reaction mixture was refluxed for 2 h. Evaporation of the solvent and subsequent distillation gave ethyl 5-hexenylmalonate: 23.2 g (81%); bp 115–116 °C (3 mmHg).

To the ethyl 5-hexenylmalonate (11 g, 0.046 mol) was added 10% potassium hydroxide aqueous solution (35 mL) dropwise for 4 h, and the mixture was allowed to stand overnight. Sulfuric acid solution (3%; 14 mL) was then added, and the resulting mixture was refluxed for 5 h. The cooled reaction mixture was extracted with ether, washed with water, dried over anhydrous Na_2SO_4 , and evaporated. The residue was distilled to give 7-octenoic acid: 5.1 g (79%); bp 110–112 °C (5 mmHg) [lit. bp 126 °C (12 mmHg); Colonge and Lasfargues (1962)] (Scheme III); IR (ν_{\max} , cm^{-1} ; neat) 2900, 1705, 1640, 1410, 1280, 995, 910; $^1\text{H NMR}$ (δ , CDCl_3 , Me_4Si) 1.1–1.8 (6 H, m), 1.8–2.6 (4 H, m), 4.8–5.2 (2 H, m), 5.5–6.2 (1 H, m), 11.23 (1 H, br s); MS, m/z 142 (M^+ , 0.1%), 124 (40), 96 (50), 74 (46), 73 (40), 69 (47), 68 (50), 60 (55), 55 (100), 43 (57), 41 (58).

(g) *Ethyl 7-Octenoate*. An ethanol solution (20 mL) of 7-octenoic acid (1.8 g, 0.0127 mol) and *p*-toluenesulfonic

Table I. Volatile Compounds Identified in Chinese Quince Oil from the Peel

peak no. ^a	compound	Kovat's index		% rel abund	mg/kg of peel	peak no. ^a	compound	Kovat's index		% rel abund	mg/kg of peel
		I _u ^b	I _k ^c					I _u ^b	I _k ^c		
Hydrocarbons											
20	limonene	1204	1206	0.1	0.02	92	sesquiterpene (tentative)	1709		0.1	0.02
69	sesquiterpene (tentative)	1572		0.3	0.05	93	(<i>E,E</i>)- α -farnesene	1734	1729	19.5	3.07
Alcohols											
33	hexanol	1327	1330	2.4	0.38	41	(<i>E</i>)-2-hexenol	1380	1383	0.2	0.03
36	diacetone alcohol	1340	1343	0.2	0.03	62	octanol	1516	1519	0.4	0.06
38	(<i>Z</i>)-3-hexenol	1358	1360	1.4	0.22	118	β -dihydroionol	1926	1915	tr ^e	tr
Aldehydes											
14	hexanal	1081	1082	0.4	0.06	31 ^d	(<i>E</i>)-2-heptenal	1313	1315	0.3	0.05
18	heptanal	1180	1181	0.2	0.03	42	nonanal	1382	1382	0.2	0.03
21	(<i>E</i>)-2-hexenal	1211	1216	0.2	0.03	97	(<i>E,E</i>)-2,4-decadienal	1769	1771	0.1	0.02
Ketones											
8	isobutyl methyl ketone	1007	1000	0.1	0.02	117	β -ionone	1906	1909	0.1	0.02
107	α -ionone	1825	1833	tr	tr						
Acids											
44	acetic acid	1403	1413	1.2	0.19	124	octanoic acid	2000	2011	0.1	0.02
98	hexanoic acid	1778	1782	0.1	0.02						
Esters											
6	ethyl isobutyrate	968	956	0.3	0.05	60	propyl octanoate	1507	1510	0.7	0.11
9	ethyl butyrate	1035	1037	0.1	0.02	61	<i>sec</i> -butyl octanoate	1510	1506	0.4	0.06
10	ethyl 2-methylbutyrate	1050	1058	0.1	0.02	64	ethyl nonanoate	1529	1527	0.3	0.05
15	isobutyl isobutyrate	1090	1091	0.1	0.02	66	isobutyl octanoate	1545	1537	12.9	2.04
17	isobutyl butyrate	1156	1152	tr	tr	68	propyl 7-octenoate	1558	1556	0.4	0.06
22 ^d	ethyl hexanoate	1227	1223	0.7	0.11	70	isobutyl 5-octenoate	1575	1576	1.4	0.22
24	hexyl acetate	1264	1265	1.4	0.22	74	isobutyl 7-octenoate	1591	1592	5.1	0.81
25	ethyl 5-hexenoate	1269	1271	0.6	0.10	76	hexyl hexanoate	1600	1600	4.2	0.66
29	ethyl (<i>Z</i>)-4-hexenoate	1289	1284	0.1	0.02	77	butyl octanoate	1603	1604	3.5	0.55
30	(<i>Z</i>)-3-hexenyl acetate	1305	1307	2.7	0.43	79	ethyl decanoate	1626	1626	0.6	0.10
31 ^d	5-hexenyl acetate	1313	1313	0.4	0.06	81	butyl 5-octenoate	1637	1641	0.4	0.06
32	(<i>E</i>)-2-hexenyl acetate	1322	1325	0.6	0.10	82	hexyl 5-hexenoate	1643	1644	2.2	0.35
35	hexyl isobutyrate	1336	1339	0.4	0.06	83	butyl 7-octenoate	1650	1651	3.5	0.55
37	isobutyl hexanoate	1346	1350	0.9	0.14	84	5-hexenyl hexanoate	1652	1657	2.2	0.35
40	(<i>Z</i>)-3-hexenyl isobutyrate	1378	1381	0.8	0.13	86	ethyl 9-decenoate	1673	1675	0.9	0.14
43	isobutyl 5-hexenoate	1386	1394	0.6	0.10	87	(<i>Z</i>)-3-hexenyl 5-hexenoate	1684	1686	0.1	0.02
45	hexyl butyrate	1405	1406	0.8	0.13	88	5-hexenyl 5-hexenoate	1691	1695	1.4	0.22
49	ethyl octanoate	1425	1429	5.6	0.88	89	pentyl octanoate	1696	1700	0.3	0.05
51	isobutyl heptanoate	1443	1448	0.4	0.06	96	<i>sec</i> -butyl 9-decenoate	1762	1764	0.8	0.13
53	(<i>Z</i>)-3-hexenyl butyrate	1448	1453	0.4	0.06	99	isobutyl 9-decenoate	1788	1792	0.1	0.02
54	5-hexenyl butyrate	1456	1462	0.6	0.10	100	hexyl octanoate	1793	1795	0.6	0.10
55	ethyl 5-octenoate	1460	1452	0.6	0.10	106	ethyl dodecanoate	1822	1820	0.1	0.02
57	ethyl 7-octenoate	1471	1478	1.8	0.28	108	hexyl 7-octenoate	1829	1838	0.1	0.02
59 ^d	hexyl pentanoate	1500	1498	0.3	0.05	110	5-hexenyl octanoate	1845	1851	0.4	0.06
59 ^d	pentyl hexanoate	1500	1502			116	5-hexenyl 7-octenoate	1895	1887	0.1	0.02
Lactones											
125	marmelo lactone (tentative)	2094		0.3	0.05	127	dihydroactinidiolide (tentative)	2263		0.1	0.02
126	marmelo lactone (tentative)	2118		0.1	0.02						
Acetals											
2	acetaldehyde diethyl acetal	890	890	0.8	0.13	22 ^d	hexanal diethyl acetal	1227	1229	2.5	0.40
7	isobutanal diethyl acetal (tentative)	977		0.1	0.02	26	(<i>Z</i>)-3-hexenal diethyl acetal	1272	1269	0.1	0.02
16	isopentanal diethyl acetal (tentative)	1133		0.1	0.02	28	(<i>E</i>)-2-hexenal diethyl acetal	1287	1285	tr	tr
Miscellaneous											
58	<i>trans</i> -theaspirane	1498	1491	0.2	0.03	121	methyl eugenol	1970	1979	0.4	0.06
63	<i>cis</i> -theaspirane	1524	1524	tr	tr						

^a Refers to peaks numbered in Figure 1. ^b Kovat's index of unknown. ^c Kovat's index of authentic sample. ^d More than two compounds in one peak. ^e tr = trace.

m), 3.85 (2 H, d, $J = 7$ Hz), 4.9–5.1 (2 H, m), 5.7–5.9 (1 H, m); MS, m/z 226 (M^+ , 0.3%), 152 (28), 135 (40), 119 (27), 108 (26), 101 (20), 96 (34), 84 (41), 69 (41), 68 (38), 60 (36), 57 (100), 56 (68), 55 (47), 43 (18), 42 (46).

RESULTS AND DISCUSSION

The flavor concentrate from the peel was thought to be more important to Chinese quince aroma than from the flesh, judging from their odors.

Chinese Quince Oil from the Peel. Since the peel of Chinese quince was very hard and had much wax on its surface, it was immersed in aqueous ethanol solution for 8 days. In order to avoid chemical reactions during the immersion, the variation of each component in the extract with the time was monitored by the use of GC and sensory evaluation.

As a result of this investigation of Chinese quince flavor, 84 compounds were identified in the essential oil from the

Table II. Odor Descriptions of Esters

(a) Alkyl and Alkenyl Esters of ω -Alkenoic Acids	
ethyl 5-hexenoate	sweet, fruity, tropical fruit-like, strong, diffusive
isobutyl 5-hexenoate	pineapple-like, sweet, strong
hexyl 5-hexenoate	sweet, fruity, mild
5-hexenyl 5-hexenoate	dry fruit-like, sour
(Z)-3-hexenyl 5-hexenoate	fatty, green, apple-like, fruity
ethyl 7-octenoate	chinese quince-like, cognac-like, sweet, strong
propyl 7-octenoate	chinese quince-like, fatty
butyl 7-octenoate	sweet, tropical fruit-like, fatty, liquor-like
isobutyl 7-octenoate	sweet, sour, fruity
hexyl 7-octenoate	fatty, mild, chinese quince-like
5-hexenyl 7-octenoate	fatty, fruity, chinese quince-like
ethyl 9-decenoate	dry, woody, peel of chinese quince-like, strong, diffusive
sec-butyl 9-decenoate	woody, fatty, chinese quince-like
isobutyl 9-decenoate	woody, green, strong, fatty
(b) 5-Hexenyl Esters of Aliphatic Acids	
5-hexenyl acetate	sweet, sour, fruity
5-hexenyl butyrate	fruity, pineapple-like
5-hexenyl hexanoate	sweet, fatty
5-hexenyl octanoate	mild, sweet, fatty

peel. Nearly all of them have not been reported in the literature as being found in Chinese quince (Hashimoto et al., 1983). Six compounds were identified as ethyl hexanoate, ethyl octanoate, benzaldehyde, ethyl nonanoate, ethyl decanoate, and ethyl dodecanoate. A typical gas chromatograph of Chinese quince oil is shown in Figure 1. The compounds identified are presented in Table I, and their peak numbers correspond to the numbers in Figure 1. Table I shows that esters, alcohols, aldehydes, and ketones are the most important volatile components in Chinese quince oil. Among them, the 50 esters represent 63.0% of the total solvent-free extract. The large concentration of alkyl and alkenyl esters of ω -alkenoic acids and the 5-hexenyl esters of aliphatic acids is remarkable. Ethyl 9-decenoate has been reported as a component in apple brandy (Schreier et al., 1978) and grape brandy (Schreier et al., 1979). Other alkyl and alkenyl esters of ω -alkenoic acids and 5-hexenyl esters of aliphatic acids have been previously unreported in any essential oil. Six alcohols, with hexanol (2.4%) and (Z)-3-hexenol (1.4%) as the largest concentrations, represent about 5% of the total extract. Six aldehydes represent about 1% of the total extract. Hexanal, heptanal, (E)-2-hexenal, (E)-2-heptenal, nonanal, and (E,E)-2,4-decadienal also play an important role since aldehydes are generally powerful flavor contributors.

Four terpene hydrocarbons, with (E,E)- α -farnesene (19.5%) as the largest concentration, represent 20.0% of the total extract. Some of the six aldehyde diethyl acetals probably were derived from the reaction of corresponding aldehydes contained in Chinese quince with ethanol during the isolation and identification procedures. Five ionone series such as α - and β -ionone, *trans*- and *cis*-theaspriane, and dihydroactinidiolide were identified. They are assumed to be carotenoid metabolites (Ohloff, 1978). α - and β -ionone have a particularly high aroma value due to their characteristic odor qualities and their threshold values (α -ionone, 0.4 ppb in water; β -ionone, 0.007). *trans*- and *cis*-theaspriane have been found in raspberry, yellow passion fruit, and tea. Small amounts of *trans*- and *cis*-marmelo lactone, which have been isolated from quince fruit (marmelo in Japanese) as the main aroma, were also identified in this oil. Indeed, comparison of the composition of the Chinese quince essential oil with that of quince essential oil as described in the literature (Spanyar et al.,

Table III. Volatile Compounds Identified in Chinese Quince Oil from the Flesh

compound	Kovat's index		% rel abund	mg/kg of flesh
	I_a^a	I_k^b		
Alcohols				
propanol	996	990	0.3	0.02
2-methylpropanol	1063	1060	10.9	0.66
butanol	1113	1113	0.9	0.05
1-penten-3-ol	1127	1130	0.2	0.01
3-methylbutanol	1179	1180	1.0	0.06
pentanol	1223	1224	0.3	0.02
acetoin	1264	1268	1.9	0.12
cyclopentanol	1289	1292	0.2	0.01
hexanol	1327	1330	17.0	1.03
(Z)-3-hexenol	1358	1360	20.7	1.25
(E)-2-hexenol	1380	1383	7.6	0.46
ethyl 3-hydroxybutyrate	1515	1516	1.5	0.09
benzyl alcohol	1841	1844	0.5	0.03
2-phenylethyl alcohol	1865	1865	0.2	0.01
Aldehydes				
(E)-2-hexenal	1211	1216	1.2	0.07
benzaldehyde	1530	1532	0.1	0.01
Ketones				
acetone	822	810	2.9	0.18
diisopropyl ketone	1011	1007	tr ^c	tr
carvone	1748	1750	tr	tr
β -ionone	1906	1909	0.2	0.01
Acids				
acetic acid	1403	1413	5.4	0.33
isobutyric acid	1560	1570	8.1	0.49
2-methylbutyric acid	1673	1685	0.7	0.04
Esters				
ethyl acetate	880	872	0.7	0.04
ethyl isobutyrate	968	956	0.3	0.02
ethyl butyrate	1035	1037	0.5	0.03
ethyl crotonate	1153	1161	0.4	0.02
ethyl hexanoate	1227	1223	0.4	0.02
hexyl acetate	1264	1265	0.4	0.02
ethyl 3-hexenoate	1289	1283	0.1	0.01
(Z)-3-hexenyl acetate	1305	1307	0.5	0.03
diethyl succinate	1689	1689	0.1	0.01
ethyl benzoate	1694	1693	0.1	0.01
ethyl phenylacetate	1818	1823	0.1	0.01
Lactones				
γ -butyrolactone	1637	1640	0.1	0.01
γ -hexalactone	1710	1715	0.2	0.01
marmelo lactone (tentative)	2094		0.4	0.02
	2118		0.4	0.02
dihydroactinidiolide (tentative)	2265		1.0	0.06
Miscellaneous				
<i>cis</i> -linalool oxide (furanoid)	1443	1435	0.6	0.04
<i>trans</i> -linalool oxide (furanoid)	1465	1464	0.2	0.01
methyl eugenol	1970	1979	0.1	0.01

^a Kovat's index of unknown. ^b Kovat's index of authentic sample. ^c tr = trace.

1965; Shimizu and Yoshihara, 1977; Schreyen et al., 1979; Tsuneya et al., 1983; Umano et al., 1986) showed important differences. (E,E)- α -Farnesene (19.5%), isobutyl octanoate (12.9%), ethyl octanoate (5.6%), isobutyl 7-octenoate (5.1%), hexyl hexanoate (4.2%), and butyl 7-octenoate (3.5%) were detected as the major components of Chinese quince oil obtained from the peel. (E,E)- α -Farnesene is also a major component in quince (Tsuneya et al., 1983). But, there is a considerable difference in the other compounds between Chinese quince and quince. Chinese quince oil has a sweet, fruity, and waxy odor of good tenacity with a somewhat slightly woody note. Table II shows the odor descriptions of the alkyl and alkenyl esters of ω -alkenoic acids and 5-hexenyl esters of aliphatic acids.

Table II indicated that the alkyl and alkenyl esters of ω -alkenoic acids and the 5-hexenyl esters of aliphatic acids should play an important role in Chinese quince flavor as they impart a strong and characteristic note to its overall flavor.

Chinese Quince Oil from the Flesh. A total of 42 compounds were identified in Chinese quince oil from the flesh (Table III). Tables I and III show that 111 compounds were identified in Chinese quince, and the essential oil from the flesh is completely different as compared to the composition of the essential oil from the peel. In contrast to the oil from the peel, where a pleasant natural quince flavor was obtained, the oil from the flesh had a green and sweet fruity odor with slightly acetoin-like fermented note. The major compounds in the oil from the flesh are (*Z*)-3-hexenol (20.7%), hexanol (17.0%), and 2-methylpropanol (10.9%). The 14 alcohols represent 63.2% of the total solvent-free extract. Hexanol, (*Z*)-3-hexenol, and (*E*)-2-hexenol are important aromatic constituents in the production of a green and fruity odor. More important for flavor are the esters, which represented only 3.6% of the overall extract. In addition, the alkyl and alkenyl esters of ω -alkenoic acids and the 5-hexenyl esters of aliphatic acids were not identified in Chinese quince oil from the flesh.

The difference in odor between the flavor concentrate from the flesh and that from the peel was thought to be due to the considerable differences in the volatile compounds. Of these compounds, the alkyl and alkenyl esters of ω -alkenoic acids and the 5-hexenyl esters of the aliphatic acids, which have been previously unreported in any essential oil except ethyl 9-decenoate, were recognized to be an important contributor to the typical Chinese quince flavor.

Registry No. $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Et}$, 67233-91-4; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$, 1577-22-6; $\text{HO}_2\text{C}(\text{CH}_2)_5\text{I}$, 4224-63-9; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Bu-}i$, 108058-74-8; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{H}$, 18719-24-9; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{OH}$, 821-41-0; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{Cl}$, 928-89-2; $(\text{EtO}_2\text{C})_2\text{CH}_2$, 105-53-3; $(\text{EtO}_2\text{C})_2\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 69298-59-5; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{Et}$, 35194-38-8; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$, 14436-32-9; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Bu-}s$, 108058-82-8; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Bu-}i$, 108058-53-9; $\text{Bu}(\text{CH}_2)_2\text{OH}$, 111-27-3; (*Z*)- $\text{HO}(\text{CH}_2)_2\text{CH}=\text{CHEt}$, 928-96-1; (*E*)- $\text{HOCH}_2\text{CH}=\text{CHPr}$, 928-95-0; $\text{Bu}(\text{CH}_2)_4\text{OH}$, 111-87-5; BuCH_2CHO , 66-25-1; $\text{Bu}(\text{CH}_2)_2\text{CHO}$, 111-71-7; (*E*)- $\text{OHCCH}=\text{CHPr}$, 6728-26-3; (*E*)- $\text{OHCCH}=\text{CHBu}$, 18829-55-5; $\text{OHC}(\text{CH}_2)_7\text{Me}$, 124-19-6; (*E,E*)- $\text{OHC}(\text{CH}=\text{CH})_2(\text{CH}_2)_7\text{Me}$, 25152-84-5; *i*- BuCOMe , 108-10-1; AcOH , 64-19-7; $\text{BuCH}_2\text{CO}_2\text{H}$, 142-62-1; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{H}$, 124-07-2; *i*- PrCO_2Et , 97-62-1; PrCO_2Et , 105-54-4; *s*- BuCO_2Et , 7452-79-1; *i*- $\text{PrCO}_2\text{Bu-}i$, 97-85-8; $\text{PrCO}_2\text{Bu-}i$, 539-90-2; $\text{BuCH}_2\text{CO}_2\text{Et}$, 123-66-0; $\text{AcO}(\text{CH}_2)_5\text{Me}$, 142-92-7; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Et}$, 54653-25-7; (*Z*)- $\text{MeCH}=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{Et}$, 34495-73-3; (*Z*)- $\text{EtCH}=\text{CH}(\text{CH}_2)_2\text{OAc}$, 3681-71-8; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{OAc}$, 5048-26-0; (*E*)- $\text{PrCH}=\text{CHCH}_2\text{OAc}$, 2497-18-9; *i*- $\text{PrCO}_2(\text{CH}_2)_5\text{Me}$, 2349-07-7; $\text{BuCH}_2\text{CO}_2\text{Bu-}i$, 105-79-3; (*Z*)-*i*- $\text{PrCO}_2(\text{CH}_2)_2\text{CH}=\text{CHEt}$, 41519-23-7; $\text{PrCO}_2(\text{CH}_2)_5\text{Me}$, 2639-63-6; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{Et}$, 106-32-1; $\text{Bu}(\text{CH}_2)_2\text{CO}_2\text{Bu-}i$, 7779-80-8; (*Z*)- $\text{PrCO}_2(\text{CH}_2)_2\text{CH}=\text{CHEt}$, 16491-36-4; $\text{PrCO}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 108058-75-9; $\text{EtCH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Et}$, 108058-76-0; $\text{BuCO}_2(\text{CH}_2)_5\text{Me}$, 1117-59-5; $\text{BuCH}_2\text{CO}_2(\text{CH}_2)_4\text{Me}$, 540-07-8; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{Pr}$, 624-13-5; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{Bu-}s$, 5458-61-7; $\text{Bu}(\text{CH}_2)_4\text{CO}_2\text{Et}$, 123-29-5; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{Bu-}i$, 5461-06-3; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{Pr}$, 108058-77-1; $\text{EtCH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Bu-}i$, 108058-78-2; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{Bu-}i$, 106917-25-3; $\text{BuCH}_2\text{CO}_2(\text{CH}_2)_5\text{Me}$, 6378-65-0; $\text{Bu}(\text{CH}_2)_3\text{CO}_2\text{Bu}$, 589-75-3; $\text{Bu}(\text{CH}_2)_5\text{CO}_2\text{Et}$, 110-38-3; $\text{EtCH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Bu}$,

108058-79-3; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_5\text{Me}$, 106917-23-1; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{Bu}$, 108058-80-6; $\text{BuCH}_2\text{CO}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 108058-81-7; (*Z*)- $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_2\text{CH}=\text{CHEt}$, 106917-24-2; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 77131-17-0; $\text{Bu}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_4\text{Me}$, 638-25-5; $\text{Bu}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_5\text{Me}$, 1117-55-1; $\text{Bu}(\text{CH}_2)_7\text{CO}_2\text{Et}$, 106-33-2; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2(\text{CH}_2)_5\text{Me}$, 108058-84-0; $\text{Bu}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 108058-85-1; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, 108058-86-2; $\text{MeCH}(\text{OEt})_2$, 105-57-7; *i*- $\text{PrCH}(\text{OEt})_2$, 1741-41-9; *i*- $\text{PrCH}_2\text{CH}(\text{OEt})_2$, 3842-03-3; $\text{BuCH}_2\text{CH}(\text{OEt})_2$, 3658-93-3; (*Z*)- $\text{EtCH}=\text{CHCH}_2\text{CH}(\text{OEt})_2$, 73545-18-3; (*E*)- $\text{PrCH}=\text{CHCH}(\text{OEt})_2$, 67746-30-9; PrOH , 71-23-8; *i*- BuOH , 78-83-1; BuOH , 71-36-3; $\text{H}_2\text{C}=\text{CHCH}(\text{OH})\text{Et}$, 616-25-1; *i*- BuCH_2OH , 123-51-3; BuCH_2OH , 71-41-0; $\text{MeCH}(\text{OH})\text{CH}_2\text{CO}_2\text{Et}$, 5405-41-4; PhCH_2OH , 100-51-6; $\text{Ph}(\text{CH}_2)_2\text{OH}$, 60-12-8; PhCHO , 100-52-7; Me_2CO , 67-64-1; (*i*- Pr)- CO , 565-80-0; *i*- PrCO_2H , 79-31-2; *s*- BuCO_2H , 116-53-0; AcOEt , 141-78-6; $\text{MeCH}=\text{CHCO}_2\text{Et}$, 10544-63-5; $\text{EtCH}=\text{CHCH}_2\text{CO}_2\text{Et}$, 2396-83-0; $\text{EtO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{Et}$, 123-25-1; PhCO_2Et , 93-89-0; $\text{PhCH}_2\text{CO}_2\text{Et}$, 101-97-3; limonene, 138-86-3; (*E,E*)- α -farnesene, 502-61-4; diacetone alcohol, 123-42-2; β -dihydroionol, 3293-47-8; α -ionone, 127-41-3; β -ionone, 79-77-6; dihydroactinidiolide, 17092-92-1; *trans*-theaspirane, 66537-39-1; *cis*-theaspirane, 66537-40-4; methyl eugenol, 93-15-2; acetoin, 513-86-0; cyclopentanol, 96-41-3; carvone, 99-49-0; γ -butyrolactone, 96-48-0; γ -hexalactone, 695-06-7; *cis*-linalool oxide, 11063-77-7; *trans*-linalool oxide, 11063-78-8; ϵ -caprolactone, 502-44-3.

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