

## Flavor Analysis of Quince

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Quince (*Cydonia vulgaris*) essential oils were obtained by steam distillation and by headspace condensation and studied by a combination of capillary gas chromatography and mass spectrometry. In the quince oil obtained by steam distillation and subsequent continuous ether extraction, 79 components were identified. The essential oil, obtained by headspace condensation had a pleasant natural quince flavor and showed a much simpler composition. Aromagrams indicated a lot of organoleptic important esters to be the base of the fruity flavor, and ethyl 2-methyl-2-butenate was recognized to be an important contributor to the typical quince flavor.

In the last decade much attention has been paid to the analysis of volatile components in fruits by flavor chemists all over the world. Economically important fruits such as apples, pineapples, oranges, and grapefruit were the subject of many papers (Gierschner and Baumann, 1966; Teranishi, 1966; Wagner, 1966). Fundamental investigation on the overall composition of flavor mixtures is one option one can take in flavor research, searching specific contributory compounds is another possibility. Further points of interest and characterization of off-flavors, preparation of nature identical flavors, study of the changes in flavor complexes during ripening and processing, quality control, and labeling of fruits.

Exploration in fruit flavor complexes has advanced very quickly. The important classes of products and special flavor contributing components are in some cases well known. Although a lot of contributory compounds and noncontributory components have also been identified, in many cases important minor compounds still remain unidentified, due to concentration or separation problems.

Among apples, Red Delicious is the most studied object in flavor research (Schultz et al., 1967; Flath et al., 1967; Brown et al., 1966). Some important and revealing papers on pear flavor have been published (Drawert, 1962; Phan-Chou-Ton, 1965), especially on Bartlett pears by Jennings et al. (Heinz et al., 1964, 1965; Heinz and Jennings, 1966; Jennings, 1961; Jennings and Creveling, 1963; Jennings and Sevenant, 1964; Jennings et al., 1960, 1964; Creveling and Jennings, 1970). To the author's knowledge only one paper has been published dealing with quinces (Spanyar et al., 1964).

Quinces (*Cydonia vulgaris*), when ripe, impart an agreeable, long-lasting, and powerful flavor. As they are not edible due to their very hard, tough, and fibrous consistency they were often used in the kitchen for preparing jam. Nowadays one can hardly find quinces, as quince trees are used as an understem for vegetative production of other pear trees. The very powerful flavor of quinces made it interesting to study this flavor complex, looking for characteristic flavor components in relation to the classical pear flavor.

### EXPERIMENTAL SECTION

**Isolation Procedure.** Isolation and concentration of the volatile components was performed by two different methods. In a first experiment, about 30 kg of fresh ripe quinces were submitted to steam distillation, followed by a continuous ether extraction of the obtained distillate. Method and material are identical with that used for

isolation of leek volatiles as described earlier in this journal (Schreyen et al., 1976a). The yield was about 3 mL of yellow, extremely aromatic etherous extract containing more than 90% of enriched flavor components.

In a second experiment, quince volatiles were isolated and collected by headspace condensation, the method being also already described (Schreyen et al., 1976b). The headspace condensate was further extracted with dichloromethane and concentrated to a final volume of 100  $\mu$ L, prior to gas chromatographic analysis.

**Gas Chromatography.** Volatile components were analyzed on a Varian 2400 FID gas chromatograph, equipped with a subambient temperature programmer. Open tubular glass columns of 600-ft length and 0.03 in. i.d. were used, statically coated with OV<sub>1</sub> at a loading of 6 mg of OV<sub>1</sub>/mL of solvent. Operating conditions are as follows: carrier gas, nitrogen, 4 mL/min with make-up gas to 20 mL/min; hydrogen, 30 mL/min; air, 300 mL/min; injector and detector temperature, 225 °C. The steam-distillate extract (0.6  $\mu$ L) was injected together with a 1% solution of *n*-alkanes C<sub>8</sub>-C<sub>17</sub> in carbon disulfide (0.7  $\mu$ L) for calculation of Kovats indices; temperature programming from 0 to 230 °C at 1 °C/min.

The headspace condensation extract (2  $\mu$ L) was injected isothermally at 35 °C and temperature programmed directly after elution of the solvent peak to 220 °C at 1 °C/min.

Besides GC analysis of the total extract obtained after steam distillation, the largest quantity of this extract was submitted to preparative gas chromatography with a thermal conductivity detector on a polar packed column. Operating conditions: column, 10 ft  $\times$  1/4 in. o.d.; coated with Carbowax 20M 10% w/v on Chrom W 80/100 AW-DCMS; injector 215 °C; detector and collector 225 °C; filament current 180 mA; gas flow 50 mL/min hydrogen; oven temperature, isothermal at 70 °C until elution of peak 4 and programming at 4 °C/min to 210 °C; isothermal at 210 °C; sample volume 50  $\mu$ L.

More than 50 samples were injected, separated on CW 20M, and collected in 22 fractions according to Figure 1.

The fractions were trapped at the collector end in a U-shaped tube, i.d. 2 mm, cooled by liquid nitrogen and stored at -20 °C in a freezer prior to analysis.

Each of these 22 fractions was analyzed on the 600-ft glass capillary column for retention indices; when possible preparative capillary gas chromatography was used to obtain pure components. Sample volumes of 3-4  $\mu$ L were injected on a 300-ft capillary column OV<sub>1</sub> i.d. 0.03 in., temperature programmed from 40-230 °C at 2 °C/min.

**Gas Chromatography-Mass Spectrometry.** The GC-MS apparatus consisted of a Varian 1200 gas chromatograph linked to a MS 30 double-beam mass spectrometer (A.E.I., Manchester) via a membrane separator.

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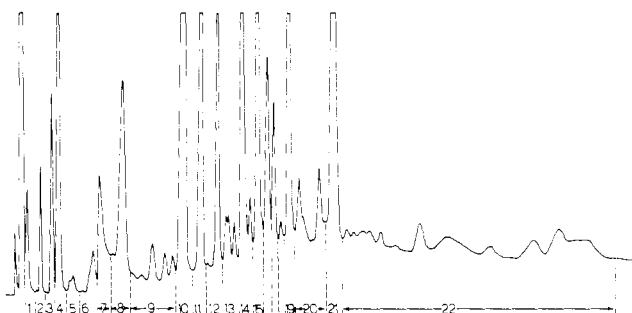


Figure 1. Preparative gas chromatography of quince essential oil.

Operating conditions for GC-MS were: 600 ft  $\times$  0.03 in. i.d. glass capillary coated with OV<sub>1</sub>, linear temperature programming from 0 to 230 °C at 1 °C/min; carrier gas He, 6 mL/min and make-up to 20 mL/min; temperatures: injector, 220 °C; separator oven and interconnecting lines, 200 °C; ion source, 200 °C; ion source pressure  $10^{-5}$  mmHg; trap current, 300  $\mu$ A; filament voltage 70 eV; scan speed, 3 s/decade.

**Infrared Spectroscopy.** Infrared spectra were determined on a Perkin Elmer spectrophotometer Model 256, fitted with a beam condenser. Spectra were taken in a microcavity cell (inner volume 2  $\mu$ L).

**NMR Spectroscopy.** Nuclear magnetic resonance spectra were determined on a Varian T 60, with Me<sub>4</sub>Si as internal standard and deuteriochloroform as a solvent.

## RESULTS AND DISCUSSION

**Quince Oil Obtained by Steam Distillation.** As a result of the present investigation on quince flavor, some 79 components were identified in the essential oil, obtained by steam distillation and subsequent continuous ether extraction. Nearly all of them have not earlier been reported in quince since only one paper was found in literature (Spanyar et al., 1964) in which four components were identified: ethanol, 1-pentanol, ethyl acetate, and pentyl acetate. This paper in fact dates from a period in which capillary columns and GC-MS coupling were uncommon.

In the present paper most identifications have been done by mass spectral analysis of the GC-MS coupled total quince oil and or the different preparative fractions. The obtained mass spectra were compared to file and literature spectra. Wherever possible retention indices, comparison with authentic products, infrared and NMR spectra are used to provide more certainty.

A typical gas chromatograph of steam distilled quince oil is shown in Figure 2. The components identified are presented in Table I and their peak numbers correspond to the numbers of Figure 2.

Table I shows that esters, alcohols, alkanals, ketones, and terpenes are the most important volatile components in quince essential oil. Among them, the 15 alcohols represent 47% of the total solvent-free extract. Important concentrations of 2-methylpropanol, a nonresolved doublet of 2- and 3-methylbutanol and tiglyl alcohol (7.96%) are present together with two terpene alcohols, linalol, and  $\alpha$ -terpineol.  $\Delta^3$ -Carene is probably a dehydration product of *trans*-2-caranol.

More important for flavor contribution are the esters with some 31 representatives in a total concentration of about 19% of the total extract. Remarkable is the large concentration of ethyl tiglate (10.17%), beside ethyl hexanoate (1.7%), ethyl 3-methylbutyrate (1.13%), and ethyl 2-methylbutyrate (1.09%). Some of the acetate esters seem to decompose during fractionation on the

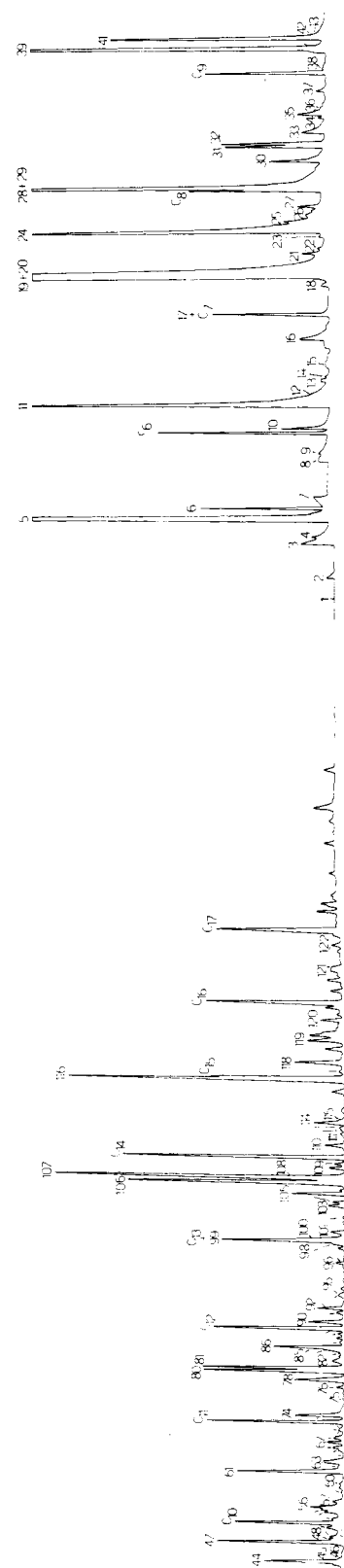


Figure 2. Gas chromatogram of steam-distilled quince oil.

carbowax column since fraction 14 of the preparative separation was nearly pure acetic acid. Methyl and ethyl esters of *trans*-2-*cis*-4-decadienoic acid, which are reported in literature to possess a strong pear flavor (Heinz and Jennings, 1966) could not be identified.

Eight alkanals, with furfural (10.14%) and benzaldehyde (3.28%) as largest concentrations, represent about 14% of the total extract. Citral, tigraldehyde, 2- and 3-methylbutanal, and 2,6-dimethylhept-2-enal also play an

Table I. Volatile Compounds Identified in Quince Essential Oil, Isolated by Steam Distillation-Extraction

peak no.	component	Ip <sup>a</sup>	mol. wt	ID <sup>b</sup>	concn <sup>c</sup>
1	methanol		32	MS	<0.01
2	ethanal		44	MS	0.17
3	ethanol		46	MS, Fr5	1.23
4	acetone		58	MS	0.08
5	diethyl ether		74	MS	(solvent)
6	dichloromethane		84	MS	(solvent impurity)
7	carbon disulfide		76	MS	(solvent for hydrocarbons)
8	1-propanol		60	MS, Fr6	0.49
9	2-butanone		72	MS, Fr4	0.06
10	ethyl acetate	603	88	MS, Fr3	0.59
11	2-methylpropanol	622	74	MS, IR, Fr8	7.73
12	3-methylbutanal	633	86	MS, Fr4	0.02
13	2-methylbutanal	644	86	MS, Fr4	0.16
14	benzene	648	78	MS	0.05
15	1-butanol	657	74	MS, IR, Fr9	0.28
16	unknown	678	86	MS, Fr9	0.8
17	ethyl propionate	700	102	MS	0.16
18	2-methyl-2-butenal (tiglaldehyde)	722	84	MS, Fr9	0.20
19	3-methylbutanol	731	88	MS, IR, NMR	27.8
20	2-methylbutanol	731	88	Fr10	
21	ethyl 2-methylpropionate	749	116	MS	0.25
22	toluene	753	92	MS	0.05
23	1-pentanol	762	88	MS, Fr11	0.06
24	2-methyl-2-buten-1-ol	766	86	MS, Fr12, IR, NMR	7.96
25	3-methylbutyl formiate	773	116	MS, Fr8	0.51
26	hexanal	779	100	MS, Fr8	0.30
27	ethyl butyrate	787	116	MS	0.24
28	butyl acetate	800	116	MS, Fr8	Tr
29	furfural	801	96	MS, IR, NMR	10.14
30	ethyl crotonate	825	114	MS	0.62
31	ethyl 2-methylbutyrate	837	130	MS, Fr8	1.09
32	ethyl 3-methylbutyrate	839	130	MS, Fr8	1.13
33	cis-3-hexen-1-ol	848	100	MS, Fr13	0.68
34	3-methylbutyl acetate	860	130	MS, Fr9	0.05
35	1-hexanol	862	102	MS, Fr13	0.77
36	2-heptanone	870	114	MS, Fr10	0.02
37	2-acetylfuran	882	110	MS, Fr8	0.12
38	methyl hexanoate	906	130	MS, Fr11	0.02
39	ethyl 2-methyl-2-butenate	921	128	MS, IR, NMR	10.17
40	unknown	920-925		MS, Fr16	Tr
41	benzaldehyde	930	106	MS, Fr17	3.28
42	5-methylfurfural	932	110	MS, Fr18	Tr
43	unknown	935		MS, Fr9	Tr
44	2-methyl-2-hepten-6-one	962	126	MS, Fr13	0.95
45	unknown	965		MS	0.10
46	2-octanone	970	128	MS, Fr12	Tr
47	ethyl hexanoate	982	144	MS, IR, NMR	1.70
48	ethyl 3-hexenoate	984	142	MS, Fr12	0.12
49	cis-3-hexenyl acetate	986	142	MS, Fr13	0.18
50	unknown	987		MS, Fr17	Tr
51	unknown	990		MS, Fr13	Tr
52	hexyl acetate	998	144	MS, Fr12	0.13
53	unknown	1002	152	MS, Fr11	0.06
54	unknown + trimethylbenzene	1008	120	MS	0.26
55	propyl 2-methyl-2-butenate	1010	142	MS, Fr13	0.31
56	benzyl alcohol	1012	108	MS	0.40
57	ethyl 2-hexenoate	1018	142	MS, Fr13	
58	2,6-dimethyl-2-heptenal	1020	140	MS	0.10
59	limonene	1024	154	MS, Fr11	0.02
60	$\Delta^3$ -carene	1038	136	MS, Fr11	0.05
61	unknown	1049		MS, Fr16	1.66
62	5-nonanone	1053	142	MS, Fr13	0.08
63	1-octanol	1057	130	MS	0.32
64	hydroquinone monoacetate	1062	152	MS, Fr15	Tr
65	unknown	1069	156	MS, Fr13	0.06
66	2-nonanone	1072	142	MS	0.16
67	ethyl heptanoate	1078	158	MS, Fr13	0.23
68	unknown	1082	124	MS, Fr18	0.20
69	linalol	1084	154	MS, Fr16	0.20
70	3-methylbutyl 3-methylbutyrate	1088	172	MS, Fr18	
71	heptyl acetate	1090	158	MS, Fr13	0.10
72	2-methylbutyl 3-methylbutyrate	1092	172	MS, Fr12	
73	unknown	1105			0.8

Table I. (Continued)

peak no.	component	Ip <sup>a</sup>	mol. wt	ID <sup>b</sup>	concn <sup>c</sup>
74	methyl octanoate	1106	158	MS, Fr13	Tr
75	unknown	1125			
76	unknown	1136			0.1
77	2-methylpropyl hexanoate	1140		MS, Fr13	Tr
78	unknown	1144	172	Fr17	0.70
79	ethyl benzoate	1147	150		Tr
80	oxygenated monoterpene	1153	152	MS, Fr16	1.58
81	oxygenated monoterpene	1157	152	MS, Fr16	1.52
82	citral	1165	152	MS	0.22
83	unknown	1171	154		0.02
84	2-decanone	1176	156	MS, Fr16	
85	unknown	1178			
86	ethyl octanoate	1180	172	MS, Fr15	0.26
87	$\alpha$ -terpineol	1184		MS	0.83
88	unknown	1193		MS, Fr15	0.04
89	benzothiazole	1196	135	MS, Fr12	0.06
90	unknown	1207			Tr
91	unknown	1219		Fr18	0.46
92	$\gamma$ -caprolactone	1224		Fr16	0.12
93	unknown	1224		Fr17	Tr
94	unknown	1234		Fr15	0.29
95	unknown	1237		Fr15	0.16
96	$\beta$ -decalone	1275	152	MS, Fr18	Tr
97	ethyl nonanoate	1279	186	MS, Fr16	0.10
98	unknown	1298	138	MS, Fr17	0.14
99	unknown	1300			
100	unknown	1302			0.50
101	unknown	1310	138	Fr17	0.15
102	unknown	1331		Fr17	0.02
103	unknown	1334		Fr17	0.20
104	unknown	1335			0.18
105	unknown	1354	178	Fr19	0.63
106	unknown	1371	166	Fr19	3.11
107	unknown	1377	166	Fr19	4.13
108	ethyl decanoate	1378	200	MS	Tr
109	unknown	1389	192	MS	0.15
110	3-methylbutyl benzoate	1414	192	MS	0.25
111	unknown	1429		MS	
112	ethyl cinnamate	1433		MS	0.03
113	unknown	1436		MS	0.04
114	unknown	1441		MS	0.40
115	<i>trans</i> - $\beta$ -farnesene	1448	204	MS, Fr19	0.04
116	unknown sesquiterpene	1494		MS	2.77
117	unknown	1508			0.07
118	unknown	1519			0.65
119	unknown sesquiterpene	1548	204	MS	0.50
120	ethyl dodecanoate	1577	228	MS	
121	unknown	1648			
122	2-pentadecanone	1679	226	MS	0.10

<sup>a</sup> Retention index on OV<sub>1</sub> between C<sub>6</sub> and C<sub>17</sub> with linear temperature programming (Rasquinho, 1965). <sup>b</sup> MS, identification by mass spectrometry in the GC-MS coupled total quince oil; NMR, identification by nuclear magnetic resonance spectroscopy; IR, identification by infrared spectroscopy; Frx, identification by mass spectrometry in preparative fraction x. <sup>c</sup> Relative concentration of each component in percent, the total mixture without solvent being 100% (internal normalization method).

important role since alkanals are generally powerful flavor contributors. Ketones represent only 1.5% of the overall extract with 2-methyl-2-hepten-6-one (0.95%) as largest representative. Besides three furan derivatives, furfural, 5-methylfurfural and acetylfuran, six terpenes could also be identified: citral,  $\alpha$ -terpineol, linalol, *trans*- $\beta$ -farnesene,  $\Delta^3$ -carene, and limonene.

Among the unidentified components there are some quantitative important ones such as peak 80 (1.58%), 81 (1.52%), 106 (3.11%), 107 (4.13%), and 116 (2.77%). Identification of these compounds from which no reference spectra could be found in literature was not feasible by mass spectral analysis alone. Indeed, comparison of the composition of the quince essential oil with the composition of the Bartlett pear essential oil as described in literature (Jennings, 1972) showed important differences.

In order to find out which components are flavor contributing and important, aromagrams were taken by

sniffing the eluting product from the column at the collector exit of a microthermal conductivity cell. A lot of fruity, estery odors were observed all over the chromatogram and could be related to the volatile esters. As for other apple and pear species a complex mixture of volatile esters forms a base for the fruity flavor. The different aromagrams also indicated that ethyl 2-methyl-2-butenolate, which relative concentration is over 10% of the total essential oil should play an important role in quince flavor as it imparts a strong and characteristic note to its overall flavor.

#### Quince Oil Obtained by Headspace Condensation.

In order to isolate volatile components from quince in mild conditions a headspace condensation technique was used for isolation of the volatiles. This technique has been applied successfully for flavor quality evaluation of apples and tomatoes (Dirinck et al., 1975, 1976). In contrast to the steam-distillation essential oil, where a "cooked" quince

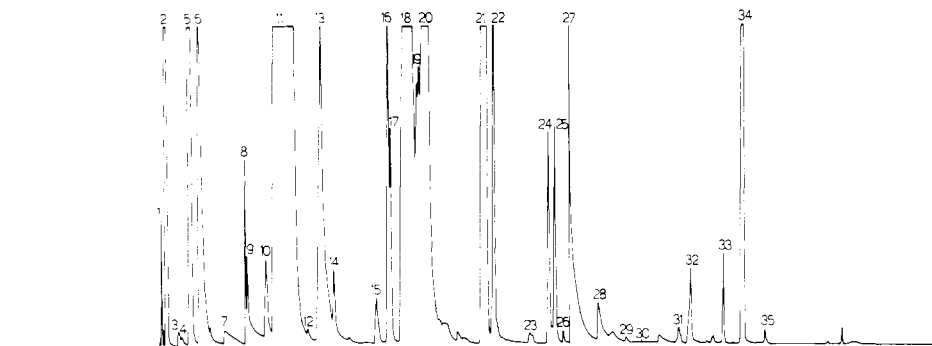


Figure 3. Gas chromatogram of essential quince oil obtained by headspace condensation.

Table II. Identification of Volatile Compounds in Quince Oil, Isolated by Headspace Condensation

1.	acetone
2.	dichloromethane (solvent)
3.	1-propanol
4.	2-butanone
5.	ethyl acetate
6.	2-methylpropanol
7.	1-butanol
8.	ethyl propionate
9.	propyl acetate
10.	2-methyl-2-butenal (tiglaldehyde)
11.	mixture: 2-methylbutanol + 3-methylbutanol
12.	ethyl 2-methylpropionate
13.	2-methyl-2-buten-1-ol (tiglyl alcohol)
14.	ethyl butyrate
15.	ethyl 2-butenate (ethyl crotonate)
16.	ethyl 2-methylbutyrate
17.	ethyl 3-methylbutyrate
18.	<i>cis</i> -3-hexen-1-ol
19.	3-methylbutyl acetate
20.	1-hexanol
21.	ethyl 2-methyl-2-butenate (ethyl tiglate)
22.	benzaldehyde
23.	2-methyl-2-hepten-6-one
24.	ethyl hexanoate
25.	<i>cis</i> -3-hexenyl acetate
26.	hexyl acetate
27.	benzyl alcohol
28.	unknown
29.	ethyl heptanoate
30.	2-phenylethanol
31.	benzyl acetate
32.	unknown MW 146
33.	ethyl octanoate
34.	dodecane (internal standard)
35.	$\gamma$ -caprolactone

flavor was obtained, the essential oil obtained by headspace condensation had a pleasant natural quince flavor. Also Figure 3 and the corresponding Table II show a completely different and much simpler composition as compared to the composition of the steam-distillation essential oil. The major components in the headspace condensation oil are: 2- and 3-methylbutanol, *cis*-3-hexenol, hexanol and ethyl 2-methyl-2-butenate (ethyl tiglate). Also quantitatively important are: ethyl acetate, 2-methyl-1-propanol, 2-methyl-2-butenol, ethyl 2-methylbutyrate, and benzaldehyde. Furthermore a lot of organoleptic important organic esters which form the base for the fruity flavor are present in minor quantities.

As described before, ethyl 2-methyl-2-butenate (ethyl tiglate) is an important contributor to the typical quince flavor. According to Fenaroli's Handbook of Flavor Ingredients (Furia and Bellanca, 1971) and to the lists of volatile compounds in foods (Van Straten et al., 1976),

ethyl tiglate has not yet been reported in nature. However, it is used in nonalcoholic beverages, ice cream, and baked goods as a contributory flavor agent. As nowadays in food legislations of several countries there is a tendency to allow only synthetic flavor components, which have already been found in nature, the determination of ethyl tiglate as a major component in quince might be important.

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