

## Volatile Constituents of Litchi (*Litchi chinensis* Sonn.)

Judy C. Johnston,\* Ronald C. Welch, and G. L. K. Hunter

The volatile constituents of litchi have been investigated by the combined technique of gas chromatography-mass spectrometry with 42 components identified and confirmed. Of these,  $\beta$ -phenethyl alcohol, its derivatives, and terpenoids comprised the major portion of the volatiles. An additional compound with a mass spectral pattern typical of organosilicon compounds was detected but not identified.

The fruit of the litchi (lychee) (*Litchi chinensis* Sonn.) has a white, juicy aril which is surrounded by a reddish, prickly leather-like skin and contains a shiny brown, usually large seed. A popular fruit throughout much of southeast Asia, the litchi is indigenous to southern China but can be grown in a few warm subtropical areas such as Florida (Campbell and Malo, 1968). This exotic fruit has an unusual warm-floral and sweet citrus flavor, which unfortunately begins to change as soon as the fruit is picked from the tree. In particular, the warm sulfuraceous taste is quite fleeting. For this reason only those who reside in the areas where the litchi is grown are familiar with the flavor of the fresh fruit. The more commonly known flavor is that of the canned juice, which is quite different from the taste of the fresh fruit.

The litchi has been examined for its nonvolatile acids (Chan and Kwok, 1974), amino acids (Farooqi and Kaul, 1964), sugar (Mathew and Pushpa, 1964), and mineral content (Singh, 1952) and the effect of  $\gamma$  irradiation upon it (Beyers et al., 1979). No work, however, has been reported on the fruit volatiles. This paper presents an analysis of the volatile components of the litchi fruit.

### EXPERIMENTAL SECTION

**Isolation of Volatiles.** The fresh litchi fruit used in this analysis was obtained from the Florida Lychee Growers Association. The skin and seeds were removed from about 180 whole litchi, leaving 2597 g of the white, slippery fruit, which was subsequently pulverized in a Waring blender for 1 min. The resulting juice and pulp mixture (2384 mL) was vacuum distilled [20-23 °C (1 mmHg)] on a Büchi Rotovaporator R until the residue had no detectable odor. Two hundred milliliters of distillate was collected in a dry ice/acetone cold trap, thawed, and extracted with three 60-mL portions of high-pressure LC grade methylene chloride. The extracts were combined and dried over anhydrous sodium sulfate.

To insure complete removal of the volatile material, 50 mL more of distillate was collected [30 °C (1 mmHg)] in a dry ice/acetone cold trap, thawed, and extracted with three 25-mL portions of methylene chloride. Again the organic extracts were combined and dried over anhydrous sodium sulfate. Twenty-five milliliters of each distillate was concentrated through a 15-cm Vigreux column to ca. 0.06 mL for comparative GC analysis, which indicated that essentially all of the volatile material was contained in the first distillate. The second distillate showed only trace amounts of the same material. An additional 150 mL of the first distillate was therefore concentrated to 0.5 mL and used for all other analyses.

**Combined Gas Chromatography-Mass Spectrometry.** The volatile components were separated on a Varian Aerograph Series 1200 gas chromatograph fitted with a flame ionization detector and a 3 m  $\times$  2 mm (i.d.) silanized glass column packed with 5% Carbowax 20M on 100/120

mesh Chromosorb W AW DMCS. The oven temperature was operated at a programmed rate of 2 °C/min from 70 to 220 °C. The injector and detector temperatures were 220 and 240 °C, respectively. The He carrier gas flow rate was 25 mL/min. The retention indices ( $I_E$ ) were determined, using a mixture of ethyl esters ( $C_1-C_{18}$ ) as standards, according to the method of van den Dool and Kratz (1963). A small fraction of the column effluent was bypassed through a fine metering valve and a Ryhage single-stage glass jet separator into the ion source of a Hitachi RMU-6L single-focusing, low-resolution, magnetic sector mass spectrometer. Both the separator and valve were maintained at 200 °C with a convection-circulated air oven. All mass spectra were obtained at 90 eV and 80  $\mu$ A with an ion source temperature of 200 °C.

**Sulfur Analysis.** For the purpose of selective detection of sulfur compounds, a 2- $\mu$ L sample of the litchi volatile concentrate was injected in a Perkin Elmer F30 gas chromatograph equipped with a flame ionization detector and a 6.5 m  $\times$  5 mm (i.d.) stainless steel column packed with 5% Carbowax 20M on 80/100 mesh Chromosorb W AW DMCS operated under the same conditions as those for GC/MS. A portion of the column effluent was bypassed via a T-valve to a Tracor 700 Hall electrolytic conductivity detector with a furnace temperature of 700 °C, using an empty quartz reaction tube, 50% aqueous isopropyl alcohol as conductivity solvent, and air as the reaction gas at a flow of 3 cm<sup>3</sup>/min.

### RESULTS AND DISCUSSION

A typical chromatogram of the concentrated methylene chloride extract of the first distillate from the litchi fruit is shown in Figure 1. Peak identification was accomplished on the basis of mass spectral and retention time data. Table I lists 48 compounds with their retention indices ( $I_E$ ) and observed mass spectral data.

The litchi owes its citrus note to the presence of limonene, geranial, and neral, while its floral character is undoubtedly due mainly to  $\beta$ -phenethyl alcohol and its derivatives. Although the warm flavor of freshly picked litchi is strongly suggestive of sulfur compounds, only one such compound, benzothiazole, was found, using the mass spectrometer and the electrolytic conductivity detector. With its rubber-like odor, benzothiazole could hardly be responsible for the hint of sulfur compounds in the litchi flavor. Presumably the suspected sulfides are quite volatile and escaped during the period of time from harvesting to analyzing the fruit. Experiments in this laboratory have demonstrated that less volatile sulfur compounds are stable under conditions of analysis and can be detected if present in reasonable concentration (100 ppm in concentrated extract).

Compound 20 showed an unusual mass spectral pattern (Figure 2), which was exemplary of others which appeared several times as shoulders of other peaks. The  $m/e$  73, 147 pattern is peculiar to organosilicon compounds, which are normally not found naturally occurring in plants. The entire isolation procedure was repeated with scrupulous

Corporate Research and Development Department, The Coca-Cola Company, Atlanta, Georgia 30301.

Table I. Identity of Volatile Components of Litchi

peak no. <sup>a</sup>	compound	retention <sup>b</sup> index ( <i>I<sub>R</sub></i> ) CBW 20M	characteristic MS data, <sup>c</sup> <i>m/e</i> (rel intensity)
1	pentane		solvent
2	acetone		solvent
3	methylene chloride		solvent
4	chloroform		solvent
5	$\alpha$ -pinene	4.00	M <sup>+</sup> 136, 93 (100), 92 (69), 91 (60), 77 (48), 79 (40), 121 (23), 105 (19), 136 (18)
6	camphene	4.51	M <sup>+</sup> 136, 93 (100), 121 (75), 79 (35), 67 (30), 107 (30), 136 (25)
7	isoamyl acetate	4.86	M <sup>+</sup> 130, 43 (100), 70 (80), 55 (62), 73 (60), 41 (50), 42 (43), 57 (33), 72 (27)
8 <sup>d</sup>	$\beta$ -pinene	4.93	M <sup>+</sup> 136, 93 (100), 41 (75), 69 (70), 79 (39), 91 (37), 77 (36), 80 (23), 121 (21), 136 (20)
9	sabinene	5.10	M <sup>+</sup> 136, 93 (100), 77 (28), 91 (25), 41 (19), 79 (19), 136 (18)
10	myrcene	5.32	M <sup>+</sup> 136, 93 (100), 41 (83), 69 (81), 91 (20), 39 (18), 79 (15), 77 (15), 92 (15), 71 (12), 136 (10)
11	$\alpha$ -terpinene	5.60	M <sup>+</sup> 136, 121 (100), 93 (82), 136 (45), 91 (42), 79 (26)
12 <sup>d</sup>	limonene	5.79	M <sup>+</sup> 136, 68 (100), 67 (56), 93 (52), 79 (24), 94 (19), 136 (19), 53 (19), 121 (17)
13	$\gamma$ -terpinene	6.23	M <sup>+</sup> 136, 93 (100), 136 (41), 121 (30), 92 (25), 91 (22), 43 (19), 77 (17), 79 (15)
14	$p$ -cymene	6.48	M <sup>+</sup> 134, 119 (100), 134 (25), 91 (17), 120 (10), 117 (9), 77 (6), 41 (5)
15	acetoin	6.54	M <sup>+</sup> 88, 45 (100), 43 (63), 88 (6)
16	terpinolene	6.63	M <sup>+</sup> 136, 93 (100), 121 (98), 136 (74), 39 (50), 41 (43), 79 (42), 91 (41)
17	2-methylbut-2-en-1-ol	6.80	M <sup>+</sup> 86, 71 (100), 41 (69), 43 (48), 53 (37), 39 (35), 68 (26), 86 (24)
18	hexanol	7.00	M <sup>+</sup> 102, 56 (100), 43 (92), 69 (78), 55 (77), 41 (68), 42 (46), 29 (46)
19	1-hepten-3-ol	7.20	M <sup>+</sup> 114, 57 (100), 55 (50), 41 (45), 81 (41), 67 (35), 39 (22), 96 (6)
20	unknown	7.70	M <sup>+</sup> 206 (?), 73 (100), 147 (31), 57 (18), 29 (17), 43 (14), 71 (9), 85 (6), 206 (2)
21 <sup>e</sup>	thujone	7.80	M <sup>+</sup> 152, 81 (100), 69 (50), 41 (20)
22	1-octen-3-ol	7.97	M <sup>+</sup> 128, 57 (100), 43 (27), 41 (26), 29 (19), 72 (17), 67 (12), 81 (8)
23	<i>cis</i> -linalool oxide (furanoid)	8.19	M <sup>+</sup> 154, 59 (100), 55 (53), 43 (53), 94 (40), 68 (40), 111 (24)
24	methyl $\beta$ -phenethyl ether	8.59	M <sup>+</sup> 136, 45 (100), 91 (42), 136 (30), 104 (15), 65 (9), 77 (7), 51 (7), 39 (6)
25	benzaldehyde	8.71	M <sup>+</sup> 106, 106 (100), 105 (99), 77 (96), 50 (52), 52 (27), 107 (20), 74 (17), 49 (6)
26	linalool	8.97	M <sup>+</sup> 154, 71 (100), 41 (76), 93 (69), 55 (59), 43 (49), 69 (48), 80 (30), 67 (20), 121 (17), 136 (9)
27	$\beta$ -fenchyl alcohol	9.44	M <sup>+</sup> 154, 81 (100), 41 (63), 80 (54), 43 (52), 69 (46), 55 (44), 57 (30), 71 (29), 111 (17)
28	terpinen-4-ol	9.61	M <sup>+</sup> 154, 71 (100), 43 (85), 57 (82), 41 (62), 55 (47), 69 (46), 111 (39)
29	hexadecane	9.72	M <sup>+</sup> 226, 57 (100), 71 (88), 43 (87), 85 (75), 41 (55), 55 (30), 99 (23)
30	menthol	10.00	M <sup>+</sup> 156, 71 (100), 81 (90), 95 (65), 41 (44), 55 (43), 82 (34), 43 (33), 69 (31)
31	1,2-dimethoxy-1-phenylethane	10.20	M <sup>+</sup> 166, 121 (100), 77 (53), 91 (38), 122 (24), 105 (12)
32	neral	10.47	M <sup>+</sup> 152, 41 (100), 69 (83), 39 (22), 84 (21), 94 (16), 27 (15), 29 (14), 67 (13)
33 <sup>d</sup>	$\alpha$ -terpineol	10.54	M <sup>+</sup> 154, 59 (100), 93 (65), 121 (44), 136 (27), 81 (35), 43 (35), 68 (28), 67 (24)
34	zingiberene	10.82	M <sup>+</sup> 204, 93 (100), 119 (90), 41 (73), 69 (60), 204 (30), 55 (28)
35	geranial	10.95	M <sup>+</sup> 152, 41 (100), 69 (99), 84 (34), 94 (24), 39 (21), 109 (15), 83 (15), 27 (13)
36	citronellol	11.09	M <sup>+</sup> 156, 41 (100), 69 (69), 55 (41), 67 (38), 82 (29), 68 (22), 43 (22)
37	nerol	11.46	M <sup>+</sup> 154, 69 (100), 41 (44), 93 (43), 68 (25), 80 (16), 121 (13), 67 (13), 111 (9), 154 (2)
38	$\beta$ -phenethyl formate	11.51	M <sup>+</sup> 150, 104 (100), 91 (41), 39 (33), 65 (29), 51 (27)
39	$\beta$ -phenethyl acetate	11.77	M <sup>+</sup> 164, 43 (100), 104 (90), 91 (23), 105 (18), 77 (14)
40	geraniol	11.85	M <sup>+</sup> 154, 41 (100), 69 (65), 39 (29), 93 (26), 27 (23), 29 (20), 68 (11)
41	benzyl acetoacetate	12.05	M <sup>+</sup> 192, 79 (100), 108 (95), 107 (89), 77 (83), 51 (62), 91 (58), 39 (49), 78 (48), 50 (47)
42	$\beta$ -phenethyl alcohol	12.55	M <sup>+</sup> 122, 91 (100), 92 (61), 122 (25), 65 (18), 57 (11), 39 (9)

Table I (Continued)

peak no. <sup>a</sup>	compound	retention <sup>b</sup> index ( $I_E$ ) CBW 20M	characteristic MS data, <sup>c</sup> $m/e$ (rel intensity)
43	benzothiazole	13.20	$M^+$ 135, 135 (100), 108 (35), 69 (27), 63 (13), 45 (12), 82 (12), 136 (9), 54 (9), 91 (8)
44	eicosane	13.73	$M^+$ 282, 57 (100), 43 (76), 71 (59), 41 (42), 55 (37), 85 (36), 83 (19), 97 (16), 95 (11), 111 (10)
45	cinnamaldehyde	13.86	$M^+$ 132, 131 (100), 132 (74), 103 (55), 77 (48), 51 (43), 78 (30), 104 (25)
46	ethyl myristate	14.00	$M^+$ 256, 88 (100), 101 (83), 43 (68), 41 (63), 55 (63), 70 (61), 57 (59), 73 (59), 157 (58), 211 (26), 213 (22)
47	cinnamyl acetate	14.87	$M^+$ 176, 43 (100), 115 (44), 134 (25), 105 (24), 116 (23), 117 (23), 176 (16), 133 (16)
48	docosane	15.49	$M^+$ 310, 57 (100), 43 (68), 71 (64), 85 (40), 41 (33), 55 (31), 69 (22), 83 (16)

<sup>a</sup> Refers to peak in Figure 1. <sup>b</sup> Authentic  $I_E$  values were determined on packed columns (van den Dool and Kratz, 1963). <sup>c</sup> Determined with a Hitachi-RMU 6L. <sup>d</sup> The major component where overlapping occurred. <sup>e</sup> Tentatively assigned.

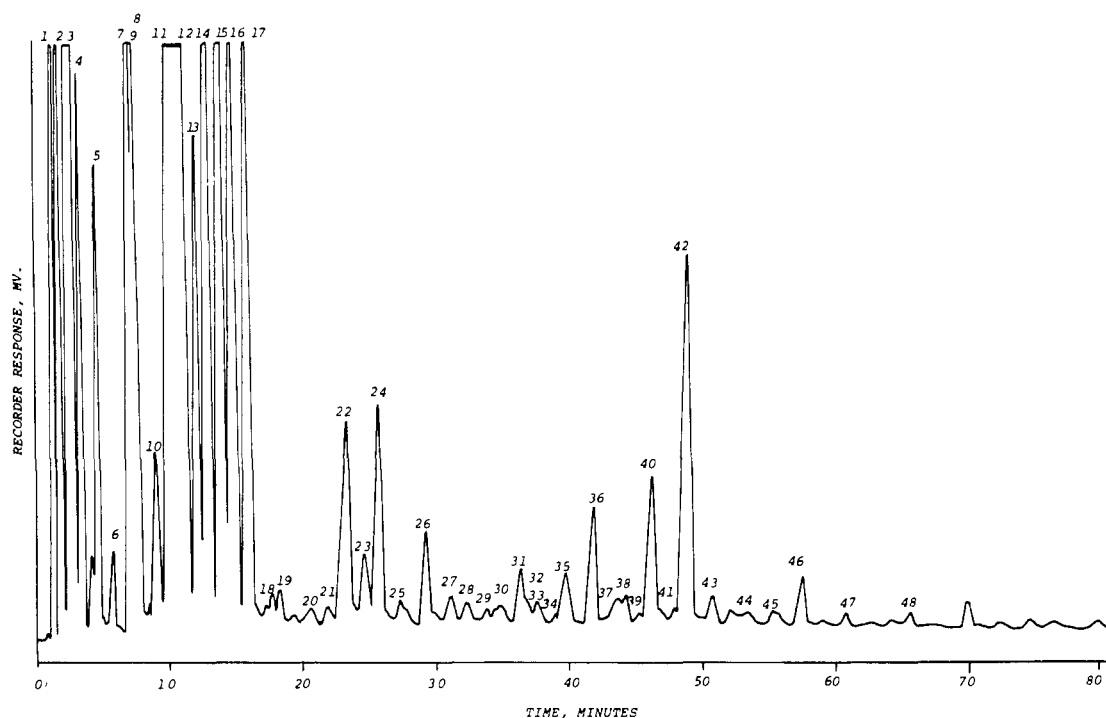


Figure 1. Typical gas chromatogram of concentrated litchi extract.

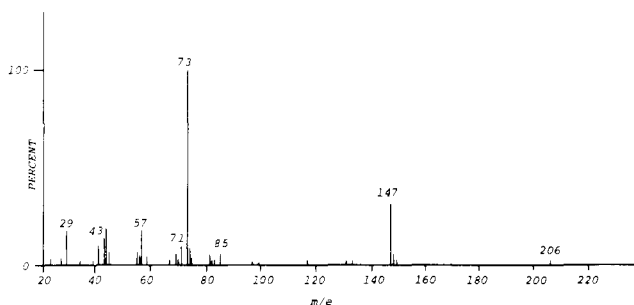


Figure 2. Mass spectrum of compound 20.

avoidance of silicon grease, but this resulted in no change in the GC/MS analysis. To determine whether compound 20 is an artifact of this work, the same isolation procedure and apparatus utilized for the litchi were used on a pure water sample. GC/MS analysis of the concentrated methylene chloride extract of the water blank showed no  $m/e$  73, 147 pattern, indicating that this unusual compound is derived from the litchi. Attempts to isolate compound 20 for further spectral analysis were unsuccessful.

In addition to compound 20 there remains a number of unidentified trace components whose contribution to the litchi flavor is unknown. It is possible that they are in part responsible for the uniqueness of the litchi flavor. However, it is well known by those who consume it that freshly picked litchi is very noticeably sulfurous and that this well recognized characteristic of the fruit rapidly diminishes on standing. It may be, therefore, that these and other flavor important components are either too volatile or unstable to survive the isolation and analysis procedure.

#### LITERATURE CITED

- Beyers, M., Thomas, A. C., Van Tonder, A. J., *J. Agric. Food Chem.* **27**, 37 (1979).  
 Campbell, C. W., Malo, S. E., "Fruit Crops Fact Sheet", No. 6, Florida Agricultural Extension Service, Oct 1968.  
 Chan, H. T., Kwok, S. C. M., *J. Food Sci.* **39**, 792 (1974).  
 Farooqi, M. I. H., Kaul, K. N., *Curr. Sci.* **33**(6), 183 (1964).  
 Mathew, A. G., Pushpa, M. C., *J. Food Sci. Technol.* **1**(4), 71 (1964).  
 Singh, M. P., *Indian J. Hort.* **9**, 53 (1952).  
 van den Dool, H., Kratz, P. D., *J. Chromatogr.* **11**, 463 (1963).

Received for review January 7, 1980. Accepted March 7, 1980.