

the synthetic mixture, although not identical, was very similar to the natural honeymelon juice as far as humans are concerned.

Studies with insects are incomplete but preliminary results indicate that *Drosophila* spp. have an overwhelming preference for the natural honeydew melon aroma compared to that of the synthetic mixture. It is probable that the insects respond quite differently than humans to the honeydew melon volatile components. It is interesting that Jacobson et al. (1971) found synthetic (*E*)-6-nonenyl acetate to be a strong attractant for the female melon fly (*Dacus cucurbitae*).

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Headspace Components of Passion Fruit Juice

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Volatile components of three varieties of passion fruit (*Passiflora edulis* Sims., *Passiflora edulis* forma *flavicarpa*, and their commercial hybrid) were collected from the headspace of passion fruit juice by using Tenax-GC as the adsorbing material. Individual components were identified by mass spectrometry and their retention indices. About 60 volatile components have been identified in one single chromatograph, including esters, alcohols, aldehydes, ketones, terpene compounds, and other miscellaneous compounds. The comparison of the flavor of three varieties of passion fruits indicated that the hybrid passion fruit would be the best for the manufacturing of passion fruit juice.

Passion fruit is a tropical fruit native to tropical America but now grown in most of the tropical and subtropical countries of the world. At present, there are three varieties of passion fruit grown in Taiwan, the purple passion fruit (*Passiflora edulis* Sims.), the yellow passion fruit (*Passiflora edulis* forma *flavicarpa*), and the hybrid passion fruit originated from the crossbreeding of yellow and purple passion fruit (δ yellow \times η purple, F_1), each with a different harvesting period during late March to early December. The harvesting period of purple passion fruit begins in late March and ends in early August, the yellow passion fruit period begins in late July and ends in early December, and the hybrid passion fruit period begins in early June and ends in late November. The purple passion fruit is purple skinned with an average weight about 35 g and grew uncultivated in the mountainous areas not exceeding 3000 ft above sea level of this island; pollination is done by the insects. The yellow passion fruit is yellow skinned with an average weight about 82 g and is commercially cultivated in the middle part of Taiwan but is unable to do the

pollination itself. The hybrid passion fruit is purple skinned and self-pollination is possible. It has fruit size larger than that of the purple passion fruit but smaller than that of the yellow passion fruit (ca. 63 g). The cultivation of hybrid passion fruit is well established in the eastern region of Taiwan and may economically become an important agricultural product in the near future. Due to their exotic flavor, the passion fruit juice is now widely used in beverages and cordials. For the purpose of mass production of canned juice or concentrated juice, the understanding of the flavor components of passion fruit cultivated in this island becomes necessary. The studies of volatile components of purple and yellow passion fruit had been done separately in the past decade (Murray et al., 1972; Parliment, 1972; Winter and Klöti, 1972; Huet, 1973; Murray, 1977; Chan, 1980; Casimir et al., 1981) but the volatile components of hybrid passion fruit is still unknown, and the comparison of three varieties of passion fruit has not been done yet.

In recent years, adsorption polymers have been used for collection, concentration, and subsequent GC analyses in a wide variety of applications (Zlatkis et al., 1973; Murray, 1977; Charalambous, 1978; Buckholz et al., 1980). In this paper, we describe the use of Tenax-GC (a polymer of *p*-2,6-diphenylene oxide) as the adsorbing material to analyze and compare the headspace components of passion fruit juice.

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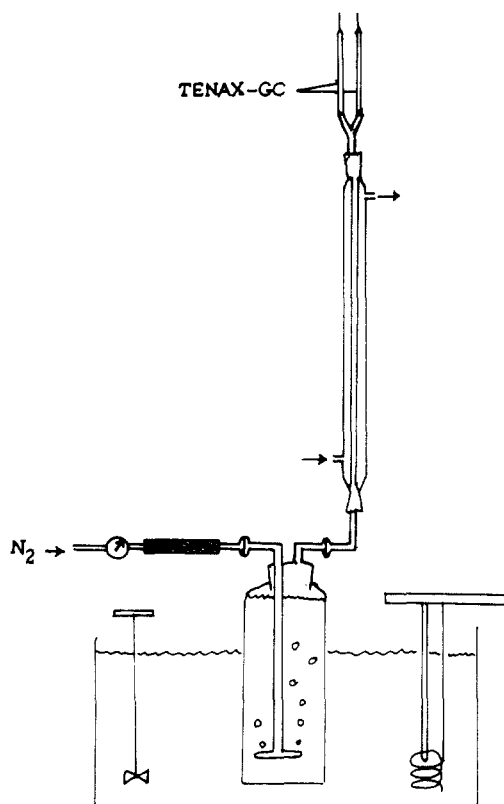


Figure 1. Illustration of the collection apparatus. The temperature of the water bath was kept at 40 °C, the nitrogen gas flow rate was 60 mL/min, the collection time was 4 h, and the sample was 85 g of passion fruit juice diluted to 850 g with distilled water.

EXPERIMENTAL SECTION

Sample Preparation. Only those passion fruit that have fallen to the ground can be picked up as raw material, and the pick-up process must be practiced every day during the harvesting period to obtain good flavor quality. Purple passion fruit (*P. edulis* Sims.), yellow passion fruit (*P. edulis* forma *flavicarpa*), and hybrid passion fruit (♂ yellow × ♀ purple, F₁), each variety at their harvesting period with average size and full colored, were purchased from Wu-Fong, Pu-Li, and Tai-Tung of Taiwan, respectively. The fruits were washed and cut into halves; the pulp was manually scooped into a beaker and then stirred for a few seconds in a commercial blender; then by use of a nylon cloth to remove the seeds, the juice (ca. 30–35% yield) was transferred quickly to a freezer for further use.

Two Pyrex glass adsorbing tubes (70 mm × 6 mm i.d.) with one end having a thin neck (30 mm × 2 mm i.d.), each containing 200 mg of Tenax-GC (60–80 mesh, Alltech Associates), were plugged at both ends with silanized glass wool. Before adsorption, the tubes containing Tenax-GC were activated at 260 °C overnight while being flushed with filtered nitrogen at a flow rate of 60 mL/min.

Adsorption on Tenax-GC. Passion fruit juice (85 g) was thawed, diluted to 850 g with distilled water, and then transferred to an apparatus as described in Figure 1. The juice was kept at 40 °C while being bubbled with filtered nitrogen gas (flow rate 60 mL/min) for 4 h, and components from about 14.4 L of headspace gases were thus adsorbed by Tenax-GC. After adsorption, the tubes were back-flushed with helium gas (flow rate 50 mL/min) for 20 min to remove the moisture. The tubes were sealed quickly with paraffin paper and placed in a cold and dry place for further use. One of the two tubes was used for GC analysis; the other tube was used for GC-MS analysis.

Desorption and Transfer to GC Capillary Column.

The adsorbed tubes were installed at the injection port of the gas chromatograph. One end of the tube was connected to a helium source; the other end was connected to a specially made luer lock and a needle (Lin, 1976). The needle was punched through the injection septum and the outside helium flow was turned on. The first 10-cm section of the stainless steel capillary column was bent as a U loop. The oven fan of GC was turned off and liquid nitrogen was poured into a Dewar flask to cool the U loop. The Tenax-GC tube was desorbed at 215 ± 10 °C with a helium flow rate of 10 mL/min for 25 min. At the end of desorption, the needle was pulled out from the injector and the oven fan was turned on to accelerate the evaporation of the liquid nitrogen left. Once the liquid nitrogen was evaporated completely, the oven cover was closed and the helium flow to the column was turned on. The GC analysis was carried out with temperature programming.

GC and GC-MS Analyses. Analyses and identifications of the samples were accomplished by using Hewlett-Packard Model 5985B gas chromatography-mass spectrometry system equipped with a flame ionization detector. The analyses were performed on a 5 ft × 0.02 in. stainless steel column coated with Carbowax 20M (SCOT, Perkin-Elmer). The injector port temperature was held at 250 °C. The oven was held isothermally at 50 °C for 10 min and then programmed from 50 to 160 °C at 1 °C/min. The flow rate of the helium carrier gas was 2 mL/min. The peak area reported by the flame ionization detector was integrated through a built-in integrator in this system (Hewlett-Packard 5840A gas chromatograph). The linear retention indices were calculated according to the modified Kovat's method proposed by Von Den Dool and Kratz (1963) and Majlát et al. (1974), using normal paraffin (C₅–C₂₀, Alltech Associates) as the standard.

The ion source temperature of the mass spectrometer was held at 200 °C and the ion current monitor operated at 70 eV. The accelerating voltage was held at 1800 V. The GC and GC-MS data were combined to obtain both qualitative and quantitative analyses.

RESULTS AND DISCUSSION

The trapping of volatile compounds on a very small amount of Tenax-GC followed by heat desorption is a very simple and extremely effective method. Very large volume of the headspace vapor over the juice could thus be concentrated. The results of GC analyses of the headspace of three varieties of passion fruit juice are shown in Figure 2 and Table I. The identifications were accomplished by comparing the mass spectra of the compounds with the published mass spectral data and their linear retention indices (Parliament, 1972; Whitfield et al., 1973; MSDC, 1974; Winter et al., 1979; Jennings and Shibamoto, 1980; De Brauw et al., 1981). There are about 60 compounds identified in this study; over half the compounds are esters—ethyl acetate, ethyl butanoate, ethyl hexanoate, hexyl butanoate, and hexyl hexanoate are among the major esters identified—and the other half are alcohols, aldehydes, ketones, terpene compounds, and some miscellaneous compounds.

Some components, such as edulan I, edulan II (only a trace in the MS analyses), ethyl 4,7-octadienoate, and β-ionone, although their concentration is low, are noted for the characteristic "roselike" aroma of passion fruit as indicated by the previous report (Whitfield et al., 1973; Winter et al., 1979; Parliament, 1972) and also can be found in this study.

The isomer of 6-but-2-enylidene-1,5,5-trimethylcyclohex-1-ene, stated by Whitfield et al. (1977) and Whitfield

Table I. Volatile Compounds Identified from 14.4-Liter Headspace of Passion Fruit Juice

peak ^b no.	compounds	10 ⁻⁶ g ^a			linear retention index ^d
		purple passion fruit	yellow passion fruit	hybrid passion fruit	
Alcohols					
6	ethanol	0.84	0.38	0.38	908
15	2-methyl-1-propanol	5.06	0.00	1.13	1068
17	2-pentanol	3.38	3.28	0.00	1116
33	2-heptanol	7.13	0.84	14.71	1290
36	1-hexanol	0.84	0.84	10.13	1314
47	2-nonanol	2.81	0.00	0.00	1485
51	1-octanol	0.19	trace ^c	7.13	1526
Aldehydes					
13	hexanal	0.00	2.53	0.00	1063
44	benzaldehyde	26.63	9.84	4.13	1465
Ketones					
4a	acetone	trace	trace	trace	816
8	2-pentanone	21.84	1.13	1.50	971
21	cyclopentanone	0.00	2.06	0.00	1166
22	2-heptanone	25.78	25.88	29.01	1174
37	2-nonanone	11.34	3.94	8.25	1370
Esters					
4b	methyl acetate	0.19	trace	4.60	817
5	ethyl acetate	137.81	96.94	110.26	881
7	ethyl propanoate	3.84	0.38	1.97	951
9	methyl butanoate	9.19	1.97	15.09	977
10	isobutyl acetate	2.53	1.03	0.38	1012
11	ethyl butanoate	307.59	205.41	2156.25	1025
12	butyl acetate	4.78	2.72	6.84	1058
14	3-methyl-2-butyl acetate	11.72	0.00	0.56	1064
16	propyl butanoate	3.28	trace	2.63	1110
18	ethyl pentanoate	2.16	0.47	1.78	1120
19	ethyl 2-butenate	5.06	0.38	27.46	1152
23	methyl hexanoate	trace	trace	2.43	1184
25	butyl butanoate	1.03	1.22	2.44	1201
26	ethyl hexanoate	220.50	267.66	812.50	1224
28a	2-heptyl acetate	13.59	1.22	20.53	1255
28b	hexyl acetate	28.22	15.00	60.19	1257
30	ethyl 3-hexenoate	4.59	0.66	6.94	1269
31	cis-3-hexenyl acetate	53.34	7.59	23.16	1275
34	propyl hexanoate	0.28	0.00	0.00	1297
35	ethyl-2-hexenoate	6.66	trace	12.09	1305
38	2-heptyl butanoate	35.44	0.66	26.44	1390
39	butyl hexanoate	0.00	71.53	0.00	1400
40	hexyl butanoate	132.47	64.50	754.46	1414
41	ethyl octanoate	50.53	37.78	21.47	1430
42	cis-3-hexenyl butanoate	2.72	7.03	29.34	1447
43	ethyl cis-3-octenoate	5.06	6.75	1.78	1460
45	pentyl hexanoate	0.00	1.88	0.00	1471
48	ethyl 4,7-octadienoate	8.44	3.37	9.09	1490
52	2-heptyl hexanoate	165.19	2.72	40.31	1599
53	hexyl hexanoate	90.47	159.56	446.87	1608
55	cis-3-hexenylhexanoate	13.31	20.34	22.88	1626
56	ethyl 3-hydroxyhexanoate	2.16	2.53	5.91	1664
58	benzyl acetate	0.66	0.75	1.13	1706
Terpene Compounds					
20	myrcene	0.56	42.56	trace	1162
24	limonene	1.22	trace	trace	1196
27	cis-ocimene	107.06	32.34	18.00	1247
29	terpinolene	1.41	1.03	0.38	1261
49	linalool	5.81	5.25	2.25	1500
57	α-terpineol	4.41	0.90	2.53	1638
Miscellaneous					
1	pentane	1.41	0.38	3.84	500
2	ether	1.41	0.75	1.97	596
3	heptane	1.13	3.28	3.47	700
54	edulan I	6.19	4.13	56.11	1620
59	β-ionone	0.66	0.38	0.75	1910
Unidentified					
32	unknown 1 (150/69)	1.59	0.75	8.16	1282
46	unknown 2 (138/138)	3.00	10.22	4.13	1474
50	unknown 3 (138/138)	2.25	9.38	9.00	1510

^a Values obtained from the averages of four experiments; sample amount = 85 g. ^b The number refers to Figure 2.
^c Amount less than 0.10 × 10⁻⁶ g. ^d Calculated values, not authentic samples values.

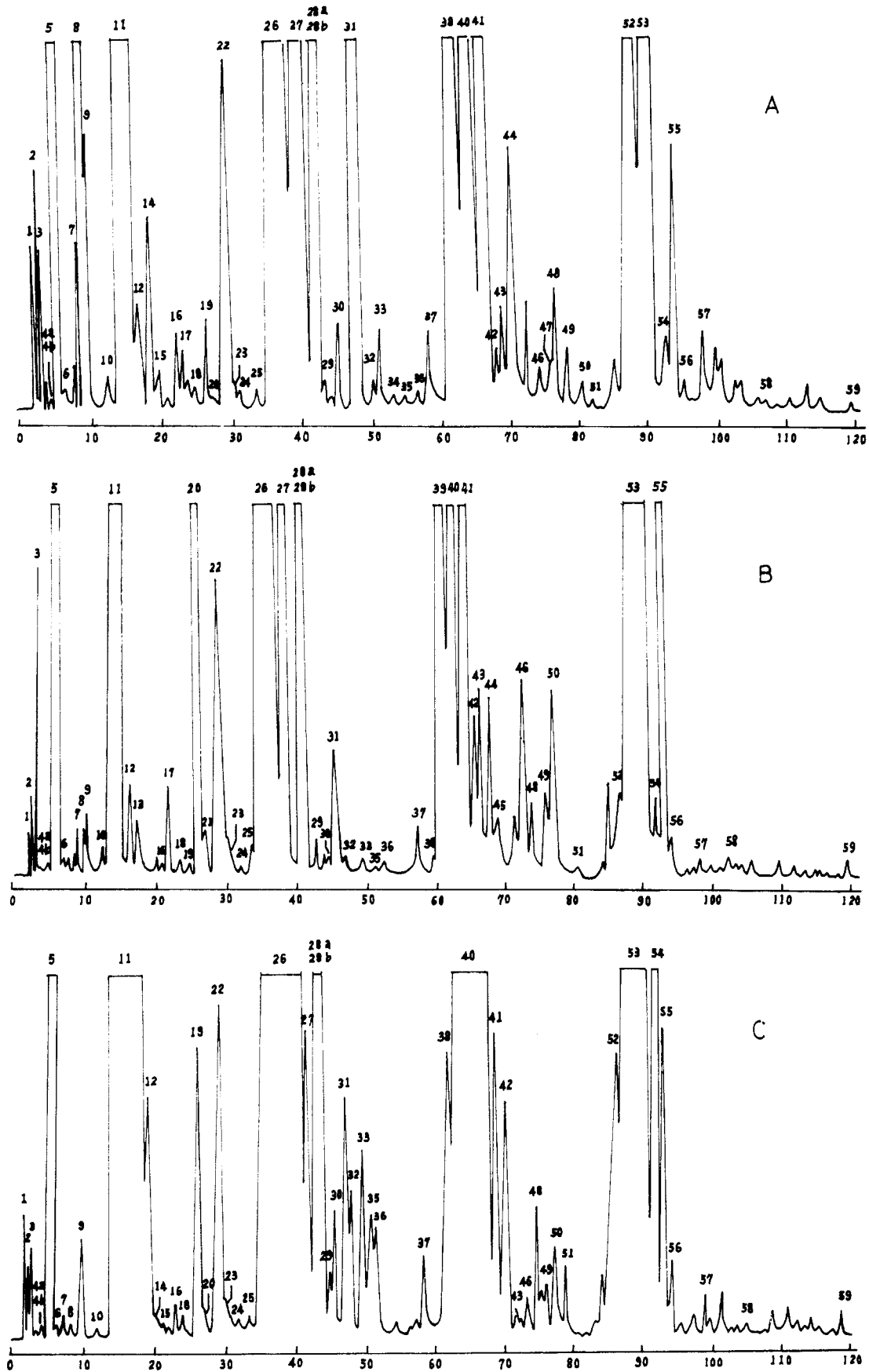


Figure 2. Gas chromatographic separation of headspace volatile components of three varieties of passion fruit juice. (A) Purple passion fruit; (B) yellow passion fruit; (C) hybrid passion fruit. Conditions: 50 ft \times 0.02 in. stainless steel capillary column coated with Carbowax 20M (SCOT, Perkin-Elmer Co.); carrier gas flow rate 2.0 mL/min of helium gas. Temperatures were as follows: 10 min, 50 $^{\circ}$ C; progression, 1 $^{\circ}$ C/min to 160 $^{\circ}$ C; injector, 250 $^{\circ}$ C; detector, 250 $^{\circ}$ C. Attenuation: (A and B) 2⁸; (C) 2¹¹.

and Sugowdz (1979) as important volatile constituents of purple passion fruit juice, cannot be found in this study. According to the above two reports, the isomer may be hidden in the larger peak of hexyl hexanoate of purple passion fruit in this study or the amount of the isomer may be too small.

Ethanol, which is a major component (ca. 100 ppm) identified in the previous report (Murray et al., 1972), is found only as a trace compound in this study, probably due to the poor retention ability of ethanol on Tenax-GC. However, another study of purple passion fruit flavor by this group indicated that ethanol was the major component identified from the headspace (>50%) when the adsorbent used was charcoal instead of Tenax-GC (Kuo, 1982).

From Table I it can be clearly seen that the hybrid passion fruit has the strongest flavor intensity among the three passion fruits. The sensory evaluation data also indicates that the hybrid passion fruit is retaining not only the highest flavor intensity but also the characteristic aroma of both yellow and purple passion fruit (Kuo, 1982). This is the main reason to choose the hybrid passion fruit as the raw material for the processing of passion fruit juice.

The study of the flavor components from the skin of passion fruit indicated that compounds with "green-note" character such as hexanol, hexanal, and other similar aliphatic alcohols are richer in the skin than in the juice (Kuo, 1982). At present, the cold-press-type method is used for the production of passion fruit juice in industry; thus the flavor of the skin may contaminate the juice during processing. Since the skin of purple passion fruit has the strongest green note while the hybrid passion fruit has the lowest (Kuo, 1982), the hybrid passion fruit seems to have another reason to be chosen as the raw material for the processing of passion fruit juice.

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Photochemical Reactions of Eugenol and Related Compounds: Synthesis of New Flavor Chemicals

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Eugenol was irradiated in a methanol solution for various periods. The main photochemical product was 4-cyclopropyl-2-methoxyphenol (12–28%). In addition to the cyclopropyl derivative, three methanol solvent addition products, 2-methoxy-4-*n*-propylphenol (4–7%), 2-methoxy-4-(2-methoxypropyl)phenol (3–7%), and 2-methoxy-4-(1-methoxypropyl)phenol, were formed. The solvent addition products were not obtained when acetonitrile was used as a solvent. The eugenol-related compounds, safrol, methyleugenol, ethyleugenol, and estragole, also produced cyclopropyl derivatives (1-cyclopropyl-3,4-(methylenedioxy)benzene, 1-cyclopropyl-3,4-dimethoxyeugenol, 1-cyclopropyl-4-ethoxy-3-methoxybenzene, and 1-cyclopropyl-4-methoxybenzene, respectively) upon photochemical irradiation. The photochemical reaction mechanisms of eugenol are postulated to be di- π -methane rearrangement, disproportionation reaction, and addition reaction. The cyclopropyl derivatives possess an interesting floral, spicy odor.

It is well-known that sunlight degrades the main constituents of essential oils. Examples are the photochemical

degradation of *n*-decanal and (+)-limonene of sweet orange, (+)-limonene, dipentene, γ -terpinene, and citral of lemon oil, and *trans*-anethole of anis oil (Garnero and Roustan, 1979).

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Eugenol, a pale yellow or almost colorless liquid, is the main constituent of clove oil. Its powerful, warm-spicy odor has been used extensively in the perfumery industry. Eugenol and its structurally related compounds have been