

solution, bitterness was decreased by the X-B component.

The taste phenomena described in this paper produced the following assumptions. A sweet substance has tri-functional sweet units AH-X-B. Among them, AH-X corresponds to bitterness production units. Further, a taste receptor is able to recognize both sweet and bitter tastes. The receptor has three sites as described in Figure 1. Sweet and bitter tastes are easily discriminated by the difference of combination of functional units between AH-X-B and AH-X in the receptor. Therefore, bitterness (AH-X) was changed to sweetness (AH-X-B) with the addition of B on the tongue, and bitterness (AH-X) was eliminated by X-B. In addition, the result in which tasteless hexamethylenetetramine participated in both sweetness and bitterness production by the suitable combination mentioned in type d supports our assumption.

One of the authors, Okai, previously reported that the production of bitterness in peptides arose when bifunctional units (one of which is a basic or bulky side chain amino acid unit and the other is a hydrophobic amino acid unit) were brought within 3-5 Å (Okai, 1977). These units just correspond to the AH-X component of aspartame. From our point of view, aspartame is regarded as one of bitter peptides. The bitterness production in aspartame isomers (Mazur et al., 1969) conveniently supports our identifying the sweet and bitter receptors.

Registry No. 1L, 40298-89-3; 1D, 97336-13-5; 2L, 16227-24-0; 2D, 97372-81-1; 3L, 97336-14-6; 3D, 97336-15-7; 4L, 97336-16-8; 4D, 97336-17-9; AcOH, 64-19-7; (CO₂H)CH₂C(OH)(CO₂H)CH₂(CO₂H), 77-92-9; NH₃, 7664-41-7; NEt₃, 121-44-8; BzNHCH₂CO₂H, 495-69-2; BzNH(CH₂)₂CO₂H, 3440-28-6; BzNH(CH₂)CO₂H, 956-09-2; HGlyH, 56-40-6; β-HAlaH, 107-95-9; CO₂HCH₂CH₂CH₂NH₂, 56-12-2; PhCH₂OH, 100-51-6; hexamethylenetetraamine, 100-97-0;

cyclohexylamine, 108-91-8; brucine, 357-57-3; phenylthiourea, 103-85-5; caffeine, 58-08-2; strychnine, 57-24-9; benzoyl-(E)-aminocaproic acid, 956-09-2; aspartame, 22839-47-0.

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Volatile Flavor Components of Babaco Fruit (*Carica pentagona*, Heilborn)

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The volatile flavor components of babaco fruit were isolated by low temperature high vacuum steam distillation and diethyl ether extraction. Analysis of the concentrate by capillary gas chromatography and gas chromatography-mass spectrometry led to the identification of 32 components. Preliminary sensory evaluation experiments suggest that ethyl butanoate and ethyl hexanoate are important contributors to the unique volatile flavor in this fruit.

INTRODUCTION

Carica pentagona Heilborn, better known as "babaco", is a hybrid between "mountain papaya" (*Carica pubescens* Lenné and Koch) and *Carica stipulata* Badillo. The plant was introduced into New Zealand from Ecuador where it thrives in high mountainous regions at 2000 and 3000 meters (Endt, 1981). Before 1973 babaco was only grown as a fresh crop in Ecuador (Bollard, 1981) and only for the domestic market. However since that time commercial interest in the New Zealand grown fruit has resulted in a rapid growth in domestic production for local and international markets. Presently about 70% of production is consumed as fresh fruit with another 15% exported and

the balance processed into canned fruit products (Endt, 1984).

The large (0.5-1.0 kg), virtually seedless fruit have a pleasant "fruity" flavor quite distinct from that found in *Carica pubescens* Lenné and Koch. To date there have been no reports characterizing the volatile flavor components of fresh babaco fruit. This paper describes the isolation and characterization of babaco aroma and highlights those components thought to be important contributors to babaco flavor quality.

EXPERIMENTAL SECTION

Chemical Standards. Methyl acetate was prepared by reaction of acetic acid with diazomethane. Esters, (a) ethyl butanoate, ethyl crotonate, ethyl hexanoate, ethyl benzoate, (b) *n*-butyl butanoate, *n*-butyl hexanoate, (c) *n*-hexyl butanoate, *n*-hexyl hexanoate, (d) *n*-heptyl butanoate, and

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(e) *n*-octyl butanoate were all prepared by direct esterification of the corresponding acid with either (a) ethanol, (b) *n*-butanol, (c) *n*-hexanol, (d) *n*-heptanol, and (e) *n*-octanol. All other chemical standards were obtained from commercial sources.

Sample Preparation. Babaco fruit were obtained from a local fruit wholesale outlet. Six fruit (3.2 kg) that were free from apparent skin damage were selected for analysis. The unpeeled fruit were macerated with 0.5 L of glass distilled water with a Waring blender and then subjected to low temperature (30–35 °C) high vacuum steam distillation. The essence (670 mL) was collected over 3 h in a 2-L round-bottom flask cooled with solid carbon dioxide/isopropyl alcohol and then continuously extracted with glass distilled diethyl ether for 3 h. The extract was dried over anhydrous sodium sulfate for 15 h and then concentrated with a low holdup Vigreux column to a final volume of 3–4 mL. The concentrate was held at –10 °C until required.

Gas Chromatography. The babaco extract was analyzed by gas chromatography with a Hewlett-Packard 5840A instrument fitted with flame ionization detection. Two columns were used throughout this investigation: (a) 50 m × 0.2 mm i.d. glass WCOT capillary column coated with Carbowax 20M and (b) 25 m × 0.2 mm i.d. vitreous silica WCOT capillary column coated with OV 101. Each column was temperature programmed from 50 to 200 °C at 5 °C/min with a nitrogen carrier gas linear velocity of 23 cm/s; injector temperature 250 °C; detector temperature 260 °C.

Gas Chromatography–Mass Spectrometry. Low resolution electron impact (70 eV) GC–MS analyses were carried out with the following: (a) A double beam Kratos MS30 mass spectrometer interfaced to a Pye 104 GC via an all-glass single stage jet separator. The GC was equipped with a 2.5 m × 4 mm i.d. glass column, packed with 3% Carbowax 20 M or 5% OV101 on 100–120 mesh Gas Chrom Q and programmed from 50–180 °C at 4 °C/min., with a He carrier gas flow rate of 30 mL/min; injector temperature 250 °C; interface temperature 230 °C. (b) A Hewlett-Packard 5885A quadrupole mass spectrometer directly coupled to a Hewlett-Packard 5840A GC equipped with a 25 m × 0.2 mm i.d. vitreous silica OV101 WCOT capillary column. The column was temperature programmed from 50 to 200 °C at 3 °C/min with a He carrier gas flow of 25 cm/s.

Mass spectral assignments were made primarily by comparison with published compilations of mass spectra (Heller and Milne, 1978; Kennett et al., 1977; Stenhagen et al., 1974). In those cases where comparisons were not possible, because the molecular ion was either absent (i.e., unknown molecular weight) or where the identity of this ion was in doubt, a computer search was undertaken against one of the mass spectral compilations (Heller and Milne, 1978) with a satellite link to the host computer (Chemical Information Systems, Inc.). Structural assignments were verified on the basis of GC peak enhancement analysis by coinjection of authentic chemical standards with the volatile flavor concentrate.

Volatile Odor Assessment. The aroma of individual GC peaks was monitored at the aroma evaluation port of a modified Hewlett-Packard 5670A gas chromatograph. Separations were carried out on a 2.5 × 4 mm i.d. glass column packed with 3% Carbowax 20 M on 100–120 mesh Chromosorb Q. The column was temperature programmed from 50 to 180 °C at 4 °C/min. Injector and detector temperatures were held at 250 °C and 270 °C respectively. Nitrogen carrier gas flow rate was 40 mL/min. 90% of the

Table I. Volatile Flavor Components of Babaco Fruit

peak ^a no.	component	identn ^b	t _R , min		rel ^c abund, %
			OV101	CW20M	
1	diethyl ether (solvent)		6.82	4.96	
2	acetaldehyde	RT, MS	6.29	5.22	0.9
3	methyl acetate	RT	7.00	6.18	0.1
4	ethyl acetate	RT, MS	7.84	6.93	0.5
5	propan-2-ol	RT, MS	6.48	7.44	1.1
6	ethanol	RT, MS	6.48	7.58	6.3
7	propan-1-ol	RT, MS	7.22	9.65	0.6
8	ethyl butanoate	RT, MS	11.91	9.81	8.4
9	2-methylpropan-1-ol	RT	8.11	10.67	0.2
10	butan-1-ol	RT, MS	8.84	12.49	46.3
11	ethyl crotonate	RT, MS	13.12	13.22	0.2
12	3-methylbutan-1-ol	RT, MS	7.55	14.50	0.2
13	butyl butanoate	RT, MS	18.40	14.72	1.2
14	1,8-cineole	RT, MS	20.28	14.72	0.2
15	(<i>E</i>)-hex-2-en-1-al	RT	13.30	14.87	0.1
16	ethyl hexanoate	RT, MS	18.53	15.18	5.3
17	pentan-1-ol	RT	10.93	15.34	0.1
18	octan-2-one	RT	18.18	16.83	0.1
19	hexan-1-ol	RT, MS	14.15	18.47	11.7
20	(<i>Z</i>)-hex-3-en-1-ol	RT	13.63	19.44	0.1
21	(<i>E</i>)-hex-2-en-1-ol	RT	13.92	20.00	0.1
22	hexyl butanoate	RT, MS	25.11	20.47	0.3
22	butyl hexanoate	RT, MS	25.17	20.47	0.4
23	heptyl butanoate	RT	28.62	23.45	0.1
24	linalool	RT, MS	22.24	23.99	0.7
25	octan-1-ol	RT, MS	21.16	24.38	8.2
26	hexyl hexanoate	RT, MS	31.29	26.00	0.7
27	octyl hexanoate	RT, MS	31.40	26.23	0.2
28	nonan-1-ol	RT	24.57	27.58	<0.1
29	ethyl benzoate	RT, MS	24.36	27.89	0.2
30	α-terpineol	RT, MS	25.53	28.38	3.0
31	decan-1-ol	RT, MS	27.88	29.78	0.4
32	tridecan-2-one	RT, MS	35.02	31.36	0.1
33	geraniol	RT, MS	27.21	37.04	0.5

^a Numbers correspond to those in Figure 1. ^b MS = mass spectra; RT = GC retention times were verified by GC peak enhancement analysis. ^c FID response factors were not determined.

GC effluent was passed to the aroma evaluation port via an all glass splitter, with the remainder going to an FID. Aroma descriptions were inscribed onto the GC recorder trace situated out of view of the assessment panelist (McGill et al., 1974). The comments of three staff members were compared in this investigation.

RESULTS AND DISCUSSION

When a combination of low temperature high vacuum steam distillation of freshly macerated babaco fruit was used, liquid–liquid extraction of the essence and subsequent concentration of the ether extract gave a concentrate with an aroma which was judged by the authors to be indistinguishable from that of the fresh fruit.

A typical Carbowax 20 M capillary gas chromatogram of this fraction is shown in Figure 1. Results are tabulated in Table I. For the nine components on which MS data were poor, structural assignments were made by comparing retention time data with those found for positively identified flavor volatile components from other fruits presently being analyzed in this laboratory.

Relative FID peak area percentages arise from electronic integration of GC peaks. These data should only be seen as giving a general indication as to the relative amounts of each component as detector response factors and extraction recoveries were not determined.

Table I shows that the 12 aliphatic alcohols, 12 esters, 4 carbonyl compounds, and 4 terpenoids identified comprised about 98 area % of the GC profile. Aliphatic alcohols were found to be the most abundant chemical class (75 area %) identified in the volatile flavor fraction, with

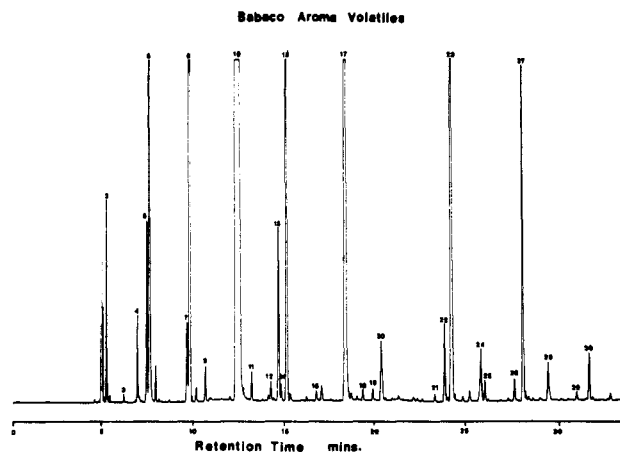


Figure 1. Capillary gas chromatogram (Carbowax 20 M) of volatile flavor components from babaco fruit.

the main components being a homologous series of even-carbon numbered primary alcohols ranging from ethanol to decan-1-ol. The most abundant component in New Zealand babaco was *n*-butan-1-ol which constituted 46 area % of the concentrate and clearly dominated the GC profile. Other saturated alcohols were present in relatively small amounts. Two unsaturated C₆ alcohols, (*Z*)-hex-3-en-1-ol and (*E*)-hex-2-en-1-ol known for their "green" sensory attributes, probably only make a minor contribution to the profile.

The diverse nature of the esters identified in volatile babaco flavor is in keeping with that found in other fruits (van Straten et al., 1983). Twelve esters constituting 18 area % were identified. Of these only ethyl butanoate, butyl butanoate, and ethyl hexanoate were found in concentrations greater than 1%. Under the GC conditions described hexyl butanoate and butyl hexanoate integrated as one peak on Carbowax 20 M (*t*_R 20.47 min) however partial resolution was obtained on OV101 (*t*_R 25.11 and 25.17 min, respectively). Identification of these two compounds was made by deconvolution of the mixed mass spectrum and confirmed by coinjection with authentic standards.

Four terpene alcohols were identified in this study. On Carbowax 20 M 1,8-cineole and butyl butanoate could not be resolved and so chemical characterization of these components were made on OV101. The co-occurrence of 1,8-cineole, linalool, α -terpineol, and geraniol suggests that in *Carica pentagona* Heilborn those components could be biosynthetically related (Charlwood and Banthorpe, 1977).

The carbonyl components were only found in small amounts, representing about 1% of the babaco concentrate. Except for acetaldehyde (0.9%), the others, (*E*)-hex-2-en-1-al, octan-2-one, and tridecan-2-one were only found at the 0.1% level.

To determine which volatile flavor components were organoleptically important in babaco preliminary sensory evaluation experiments were carried out. When the procedure of McGill et al. (1974) was used, ethyl butanoate and ethyl hexanoate were judged as being "babaco like" suggesting that these two components make an important contribution to the babaco flavor.

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Registry No. Diethyl ether, 60-29-7; acetaldehyde, 75-07-0; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; propan-2-ol, 67-63-0; ethanol, 64-17-5; propan-1-ol, 71-23-8; ethyl butanoate, 105-54-4; 2-methylpropan-1-ol, 78-83-1; butan-1-ol, 71-36-3; ethyl crotonate, 10544-63-5; 3-methylbutan-1-ol, 123-51-3; butyl butanoate, 109-21-7; 1,8-cineole, 470-82-6; (*E*)-hex-2-enal, 6728-26-3; ethyl hexanoate, 123-66-0; pentan-1-ol, 71-41-0; octan-2-one, 111-13-7; hexan-1-ol, 111-27-3; (*Z*)-hex-3-en-1-ol, 928-96-1; (*E*)-hex-2-en-1-ol, 928-95-0; hexyl butanoate, 2639-63-6; butyl hexanoate, 626-82-4; heptyl butanoate, 5870-93-9; linalool, 78-70-6; octan-1-ol, 111-87-5; hexyl hexanoate, 6378-65-0; octyl hexanoate, 4887-30-3; nonan-1-ol, 143-08-8; ethyl benzoate, 93-89-0; α -terpineol, 98-55-5; decan-1-ol, 112-30-1; tridecan-2-one, 593-08-8; geraniol, 106-24-1.

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