

Aroma Constituents of the Fruit of the Mountain Papaya (*Carica pubescens*) from Colombia

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The volatile components of papayuela (a tropical fruit, collected for this study at the Bogotá high plateau) were isolated by simultaneous steam microdistillation-extraction using CH_2Cl_2 as solvent and concentrated until obtaining an essence of characteristics similar to those of fresh fruit. Analysis by GC and GC-MS showed at least 53 components (total 110 mg/kg of fruit), of which 45 were positively identified (about 99.3% of the total volatiles), 6 partially characterized (about 0.5% of the total volatiles), and only 2 unidentified. Esters afforded the most abundant group of compounds (63% of the extract), followed by alcohols (30% of the extract). The major aroma compounds were ethyl butyrate, butanol, ethyl acetate, methyl butyrate, and butyl acetate.

Mountain papaya (*Carica pubescens*) is a native of tropical America and very popular on the Cundinamarca and Boyaca high plateaus of Colombia, due to its medicinal properties (antitussive, wound healing) and to the strong and pleasant aroma of its fruit (in Spanish, the same word, papayuela, is used for the tree and its fruit). The fruit is light yellow, oblong, and elliptic, truncate at the base, pointed at the apex (8-11-cm length and 5-6-cm diameter), and weighs up to 200 g (Garcia, 1975). It is covered by a thin skin and shows five very pronounced ridges. Inside the fruit, a yellow firm flesh makes up about 60% of the fruit weight. Normally the flesh is not consumed as such, but it is widely used to prepare delicious and delicately flavored homemade preserves. Very numerous seeds are found within the central cavity of the fruit, covered by a sweet, transparent, and gelatinous membrane.

A study on the nature of the volatile components that may contribute to the unique flavor of this fruit has recently been carried out by Idstein et al. (1985). They used mountain papaya grown in Chile. We report our results because our data show that there are significant differences in the composition of the mixture of volatile components of fruits cultivated in different geographical locations.

EXPERIMENTAL SECTION

Fully ripe papayuela fruits (*Carica pubescens*) showing desirable color, texture, and flavor qualities were obtained from a local grower, at the Bogotá high plateau.

Aroma Isolation. Flesh of the fruit (50 g) separated from the seeds was blended and extracted for 1 h by means of simultaneous steam microdistillation-extraction (Godefroot et al., 1981) using 2 mL of CH_2Cl_2 as solvent. The extraction was repeated three more times, each time using 50 g of fresh fruit but maintaining the same solvent. The aroma extract was dried over Na_2SO_4 and concentrated to a volume of 0.1 mL by using a Vigreux column. The resultant essence possessed a strong aroma, characteristic of the fresh papayuela fruit.

Gas Chromatography. Capillary GLC was carried out on a Hewlett-Packard 5700 A chromatograph equipped with flame ionization detector and a 25 m \times 0.31 mm (i.d.) fused capillary column cross-linked with methyl silicone OV-101. Helium carrier gas was used (0.75 mL/min), and the temperature column was programmed from 60 to 200 °C at 2 °C/min. The retention indices were estimated according to Kováts method (Kováts, 1958) using normal paraffins (C_6 - C_{19}) as standards.

Gas Chromatography-Mass Spectrometry. Combined GC-MS was performed on a Shimadzu 9020 DF spectrometer using the same GC conditions as described above. Mass spectra were obtained in both the electron impact and chemical ionization modes (reagent gas isobutane).

Quantitative Assessment. Quantitative data were obtained both from the trace of TIC monitor during GC-MS and from the FID trace during GC analysis. Relative percentages of individual components were calculated in the extract based on GLC peak areas. Known amounts of internal standards were added to the fruit pulp before aroma isolation, to assess the recovery of the procedure and the response factors of the detectors for the calculation of absolute amounts of the major identified compounds.

RESULTS AND DISCUSSION

Genuine aroma extract of papayuela fruit was obtained by means of simultaneous steam microdistillation-extraction method (Godefroot et al., 1981), and its constituents were identified by using GC data (comparison of the experimental retention indices with those reported by Jennings and Shibamoto (1980)) and GC-MS data (mass spectra), initially based on a careful analysis of the spectral data but ultimately by comparisons with the EPA/NIH mass spectral library and with other published spectra (Jennings and Shibamoto, 1980; MacLeod and Pieris, 1981b). MS of sample components agreed with those of literature spectra, considering normal variability. Chemical ionization mass spectrometry was particularly useful to determine the molecular weights of most components, thus rendering the interpretation of conventional electron impact mass spectra easier. Table I lists the volatile flavor components of the papayuela together with GC retention data (retention indices found experimentally for the aroma components of the papayuela and those found in the literature for reference compounds) and quantitative data (relative percentages and absolute amounts of the individual components). Among the 53 isolated compounds, 45 were positively identified (comprising about 99.3% of the sample), 6 partially characterized (comprising 0.5% of the sample), and only 2 (0.3%) unidentified.

The papayuela aroma extract's main constituents were carboxylic esters (63% of the total extract), dominated by the ethyl and butyl esters of the C_2 - C_8 saturated-chain carboxylic acids, with the exception of C_5 . Saturated normal-chain C_4 , C_6 , C_7 , and C_8 methyl esters were also found, as well as other saturated aliphatic and aromatic esters. Some unsaturated esters were also detected: ethyl but-2-enoate, *n*-butyl but-2-enoate, ethyl oct-2-enoate, and *n*-butyl oct-2-enoate together with two β -hydroxy esters:

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Table I. Volatile Flavor Components of Papayuela Fruit

item	component	M ⁺ , m/z	retention index		rel, %	mg/kg of fruit
			exptl	lit.		
1	acetaldehyde	44	363	363	tr ^a	
2	ethanol	46	495	500	tr	
3	acetone	58	525	530	6.0	2.59
4	3-buten-2-one	70	ND		tr	
5	ethyl acetate	88	600	595	7.2	29.26
6	2-butenal	70	630		tr	
7	unknown		642		tr	
8	butanol	74	647	655	25.7	20.56
9	pentan-2-ol	88	688	685	tr	
10	ethyl <i>n</i> -propionate	102	706	691	tr	
11	methyl <i>n</i> -butyrate	102	710	705	4.0	6.62
12	ethyl <i>n</i> -butyrate	116	790	784	32.5	32.04
13	<i>n</i> -butyl acetate	116	800	793	11.9	8.23
14	ethyl <i>trans</i> -but-2-enoate	114	833	823	0.2	
15	ethyl 2-methylbutyrate	130	844	837	tr	
16	hexanol	102	859	858	3.4	0.77
17	aliphatic ether ^b	130	871		tr	
18	2-heptanone	114	878	872	0.2	
19	<i>n</i> -propyl <i>n</i> -butyrate	130	892	881	tr	
20	<i>n</i> -butyl <i>n</i> -propionate	130	900	889	tr	
21	methyl <i>n</i> -hexanoate	130	913	906	0.1	1.52
22	ethyl 3-hydroxybutyrate	132	920		tr	
23	1-octen-3-one	126	966		tr	
24	<i>n</i> -butyl <i>n</i> -butyrate	144	985	979	0.6	1.52
25	ethyl <i>n</i> -hexanoate	144	988	983	0.6	4.29
26	<i>n</i> -hexyl acetate	144	1002	1012	0.1	
27	benzyl alcohol	108	1007	1007	0.1	
28	methyl <i>n</i> -heptanoate	144	1007	1006	tr	
29	1,8-cineole	154	1026	1027	0.5	
30	<i>n</i> -butyl <i>trans</i> -but-2-enoate	142	1027	1023	tr	
31	aliphatic ether ^b	158	1047		tr	
32	octanol	130	1063	1061	0.2	
33	<i>trans</i> -linalool oxide	170	1079	1068	tr	
34	ethyl <i>n</i> -heptanoate	158	1089	1082		tr
35	<i>n</i> -butyl 3-hydroxybutyrate	160	1111		tr	
36	methyl <i>n</i> -octanoate	158	1111	1107	0.5	
37	ethyl benzoate	150	1149	1154	tr	
38	<i>n</i> -butyl <i>n</i> -hexanoate	172	1181	1177	2.4	1.43
39	ethyl <i>n</i> -octanoate	172	1186	1180	0.7	
40	<i>n</i> -octyl acetate	172	1199	1193	tr	
41	ethyl oct-2-enoate	170	1231		tr	
42	ethyl salicylate	166	1256	1257	tr	
43	4-methylbenzaldehyde <i>O</i> -methyloxime ^b	149	1320		0.3	
44	<i>n</i> -butyl benzoate	178	1351	1354	tr	
45	unknown		1355		tr	
46	<i>n</i> -butyl <i>n</i> -octanoate	200	1378	1373	2.1	1.43
47	<i>n</i> -butyl oct-2-enoate	198	1404		tr	
48	<i>n</i> -butyl salicylate	194	1426	1436	tr	
49	alkyl cyclohexene carboxylate ^b		1532		tr	
50	C ₁₆ H ₂₄ ^b	204	1552		tr	
51	alkyl cyclohexene carboxylate ^b		1562		tr	
52	<i>n</i> -hexyl <i>n</i> -octanoate	228	1572	1564	tr	
53	<i>n</i> -butyl <i>n</i> -decanoate	228	1575	1575	tr	

^a tr = trace (<0.1%). ^b Compounds only partially characterized. ND = not determined.

ethyl 3-hydroxybutyrate and *n*-butyl 3-hydroxybutyrate. These compounds (2-enoates and β -hydroxy esters) although reported infrequent as aroma constituents seem to be highly characteristic to aroma fruit of the tropics (MacLeod and Pieris, 1981b). Alcohols were the other group of important components observed in the papayuela fruit, representing 30% of the total extract. As was to be expected, we found ethanol, butanol, hexanol, and octanol corresponding to the alcohol part of the identified esters. 2-Pentanol and benzyl alcohol were also detected together with four ketones, two aldehydes, and two terpene compounds. Two aliphatic ethers, two cyclohexenoates, one

nitrogen compound, and one hydrocarbon having a C₁₅H₂₄ formula were partially identified.

The total papayuela aroma extract obtained from fresh fruit was 110 mg/kg, a relatively high value, consistent with the intense and permanent odor of this delicately flavored fruit. This value is comparable to that reported by MacLeod and Pieris (1981a) for wood apple (80 mg/kg) but much higher than that found for other tropical fruits such as papaya (0.097 mg/kg) (MacLeod and Pieris, 1983), soursop (1.2 mg/kg) (MacLeod and Pieris, 1981b), guava (0.2 mg/kg) (MacLeod and de Troconis, 1982). However, it is to be noted that we used a different extraction method.

The major components of the papayuela aroma extract were found to be butanol (20.56 mg/kg), ethyl acetate (29.26 mg/kg), ethyl *n*-butyrate (32.04 mg/kg), methyl *n*-butyrate (6.62 mg/kg), and *n*-butyl acetate (8.23 mg/kg). An artificial aroma extract, composed of these components, provided an aroma very similar to that of fresh fruit, consistent with our findings that these compounds are major contributors to the aroma of fresh papayuela fruit.

It is very interesting to note that the composition of the aroma of fruit obtained in Santiago, Chile (Idstein et al., 1985), is different from the aroma of the fruit from Bogotá high plateau used in this study. In the Colombian papayuela, the major components found were, among others, ethyl acetate and butanol, in similar concentrations, while these compounds in the Chile-grown papayuela were reported in lesser proportion, the ethyl acetate being approximately 10 times higher than the butanol. Furthermore, we were unable to detect several of the main volatile components of the Chilean fruit in our Colombian fruit; examples are methyl *cis*-hex-3-enoate, isopentyl acetate, methyl 3-hydroxyhexanoate, as ethyl nicotinoate, whereas others such as hexyl acetate, ethyl 3-hydroxybutyrate, ethyl benzoate, and methyl octanoate were detected only as trace components in the Colombian fruit. It is also worth noting the presence of more volatile compounds in the Colombian papayuela such as acetaldehyde, ethanol, 3-buten-2-one, acetone, and butanol.

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Registry No. Acetaldehyde, 75-07-0; ethanol, 64-17-5; acetone, 67-64-1; 3-buten-2-one, 78-94-4; ethyl acetate, 141-78-6; 2-butenal, 4170-30-3; butanol, 71-36-3; pentan-2-ol, 6032-29-7; ethyl propionate, 105-37-3; methyl butyrate, 623-42-7; ethyl butyrate, 105-54-4; butyl acetate, 123-86-4; ethyl *trans*-but-2-enoate, 623-70-1; ethyl 2-methylbutyrate, 7452-79-1; hexanol, 111-27-3; 2-heptanone, 110-43-0; propyl butyrate, 105-66-8; butyl propionate, 590-01-2; methyl hexanoate, 106-70-7; ethyl 3-hydroxybutyrate, 5405-41-4; 1-octen-3-one, 4312-99-6; butyl butyrate, 109-21-7; ethyl hexanoate, 123-66-0; hexyl acetate, 142-92-7; benzyl alcohol, 100-51-6; methyl heptanoate, 106-73-0; 1,8-cineole, 470-82-6; butyl *trans*-but-2-enoate, 591-63-9; octanol, 111-87-5; *trans*-linalool oxide, 11063-78-8; ethyl heptanoate, 106-30-9; butyl 3-hydroxybutyrate, 53605-94-0; methyl octanoate, 111-11-5; ethyl benzoate, 93-89-0; butyl hexanoate, 626-82-4; ethyl octanoate, 106-32-1; octyl acetate, 112-14-1; ethyl oct-2-enoate, 2351-90-8; ethyl salicylate, 118-61-6; 4-methylbenzaldehyde *O*-methyloxime, 33499-39-7; butyl benzoate, 136-60-7; butyl octanoate, 589-75-3; butyl oct-2-enoate, 57403-32-4; butyl salicylate, 2052-14-4; hexyl octanoate, 1117-55-1; butyl decanoate, 30673-36-0.

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Fresh Tomato Aroma Volatiles: A Quantitative Study

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A method for the quantitative analysis of major C₅-C₉ fresh tomato volatiles was developed using Tenax trapping and CaCl₂ enzyme deactivation. Information was obtained on the concentrations of (*Z*)-3-hexenal, hexanal, 1-penten-3-one, 2-isobutyl cyanide, 2- and 3-methylbutanols, (*E*)-2-hexenal, (*E*)-2-heptenal, 6-methyl-5-hepten-2-one, (*Z*)-3-hexenol, 2-isobutylthiazole, and 6-methyl-5-hepten-2-ol in fresh ripe tomatoes. The identities of components were confirmed by GC-MS methods. Refrigerator storage (2 °C) of fresh ripe tomatoes was found to lead to a lowering of the concentration of (*Z*)-3-hexenal and other volatiles in the macerated tomato. This provides a scientific basis for the informal subjective observation that such cold storage is deleterious to fresh tomato flavor. It is also of interest in regard to the generally expressed belief that there is a lack of flavor in fresh market tomatoes.

It seems generally accepted that ripe tomatoes, purchased in supermarkets in the United States, lack the desirable aroma and flavor associated with ripe tomatoes picked directly from the plant in the field. There have been a large number of studies carried out on the identification of the volatile flavor components of fresh tomatoes, which have been reviewed (Buttery et al., 1971; Dirinck et al., 1976; Stevens et al., 1977; Wright and Harris, 1985). Despite these (largely qualitative) studies there are some questions unanswered particularly regarding the actual quantitative concentrations of the identified volatile components. Such quantitative data are necessary for the full understanding of the role of the individual components in fresh tomato flavor. One major problem with quantitative analysis has been that some of the enzyme-produced volatile flavor components are themselves degraded by other tomato enzymes before or during the volatile isolation by conventional methods. This was first pointed out by Kazeniak and Hall (1970) who showed that (*Z*)-3-hexenal was largely rearranged to (*E*)-2-hexenal by the tomato medium in about the same order of time needed to isolate the volatiles by the faster conventional methods (ca. 20-60 min).

In the present study we set out to first develop a workable quantitative method for the analysis of the major volatile flavor components of fresh tomatoes and then to apply it to the various forms of fresh tomatoes.

A number of important studies on the nonvolatile flavor (or taste) components of fresh tomatoes have been carried out in recent years (Buesher, 1975; Kader et al., 1978; Stevens et al., 1977).

EXPERIMENTAL SECTION

Materials. Vine-ripened tomato samples were grown on experimental fields in Davis and Albany, CA, during 1985 and 1986. These included the following varieties:

Ace, Rutgers, Patio, FM785, Severianin, Oregon II, Ace yellow, and High beta. Fresh market table tomatoes were obtained from local supermarkets. The supermarket varieties were not accurately known but were probably Sunny, Contessa, or related varieties. Unless otherwise stated, tomato samples were stored at room temperature (25 °C) until used.

Authentic reference chemical compounds were obtained from reliable commercial sources or synthesized by established methods. (*Z*)-3-Hexenal was obtained by the CrO₃-pyridine oxidation of (*Z*)-3-hexenol in CH₂Cl₂ following the procedure of Kajiwara et al. (1975). All compounds were purified by gas-liquid chromatography (GLC) separation. This was particularly important for the internal standards 2-octanone and 3-pentanone because small concentrations of impurities in these could interface with the analysis. Ethyl antioxidant 330 (ca. 0.01%) was added to the purified aldehydes, which were stored at freezer temperatures and used within a few hours. Saturated CaCl₂ solution was made by adding an excess of CaCl₂ to water and then boiling the solution in an open Erlenmeyer flask for 1 h to remove volatile impurities. Diethyl ether (anhydrous) was distilled, and a trace (ca. 0.001%) of Ethyl antioxidant 330 added. It was stored in the dark and used within a few days.

Isolation of Volatile Concentrate from Tomatoes. The tomato sample (100 g at 25 °C) of ca. equal pieces cut from three different tomatoes (of the same lot) was blended (blender blades rotating at 13670 rev/min) for 30 s. The blended mixture was allowed to stand for 180 s longer, and then saturated CaCl₂ solution (100 mL at 25 °C) was added all at once and the mixture blended for 10 s. Five milliliters of a water solution containing 50.0 ppm 2-octanone and 50.0 ppm 3-pentanone was then added and the mixture blended for 10 s. The mixture was then placed in a 1-L flask containing an efficient magnetic stirrer. Purified air (3 L/min drawn from outside the laboratory and passed through activated charcoal) was led into the flask via a Teflon tube and passed over the vigorously stirred mixture and out of the flask through a Tenax trap

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