Registry No. 2,4-D, 94-75-7; GA_3, 77-06-5.

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Volatile Constituents of Mountain Papaya (*Carica candamarcensis*, syn. *C. pubescens* Lenne et Koch) Fruit

Heinz Idstein, Theresia Keller, and Peter Schreier*

The volatiles of fresh mountain papaya (*Carica candamarcensis*, syn. *C. pubescens* Lenne et Koch) were separated from the fruit pulp by high-vacuum distillation and subsequent solvent extraction (pentane–dichloromethane, 2:1). In three fractions obtained by preseparation of the concentrated extract with adsorption chromatography on silica gel (pentane–diethyl ether gradient) the volatiles were analyzed by capillary gas chromatography and combined capillary gas chromatography–mass spectrometry. From 199 volatiles identified by these methods 103 compounds showed structures of esters, among them some uncommon substances such as, e.g., ethyl 3-mercaptopropanoate, ethyl 4-hydroxy- and 4-acetoxybutanoate, methyl (*E*)-2- and (*E*)-3-octenoate, butyl and hexyl (*E*)-2-butenoate, and butyl 2-furoate and butyl nicotinoate were found.

The mountain papaya (*Carica candamarcensis*, syn. *C. pubescens* Lenne et Koch) originates in Colombia and Ecuador where it grows at elevations about 2400–2800 m (Brücher, 1977). As the fruit ripens its skin color changes from dark green to lemon yellow. The ripe fruit has an outer layer of firm pale orange to white translucent flesh, and a cavity filled with seeds and soft pulp. Its strong aromatic flavor and attractive color are both stable to heating or prolonged storage. Mountain papayas are grown commercially as a processing crop in Chile where the fruits are mostly canned as peeled pieces in syrup. In New Zealand, the fruits are used for homemade preserves, jams, and chutneys; recently, they have been recommended for commercial production of nectars, canned fruit slices, and fruit leather (MacKenzie and Strachan, 1980). Nonvolatile fruit constituents such as sugars and acids have been already investigated (Heatherbell, 1974), but the volatile components have not been studied as yet.

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EXPERIMENTAL SECTION

Sample Preparation. Fresh ripe mountain papayas (*C. candamarcensis*, syn. *C. pubescens* Lenne et Koch) were obtained from the fruit market in Santiago, Chile (Dec, 1983; Jan, 1984), transported by air freight, and analyzed the day after arrival. After removal of the kernels, crushing by a Waring blender, and separation by a hydraulic press (Hafico) 2.6 kg of fresh fruit pulp was

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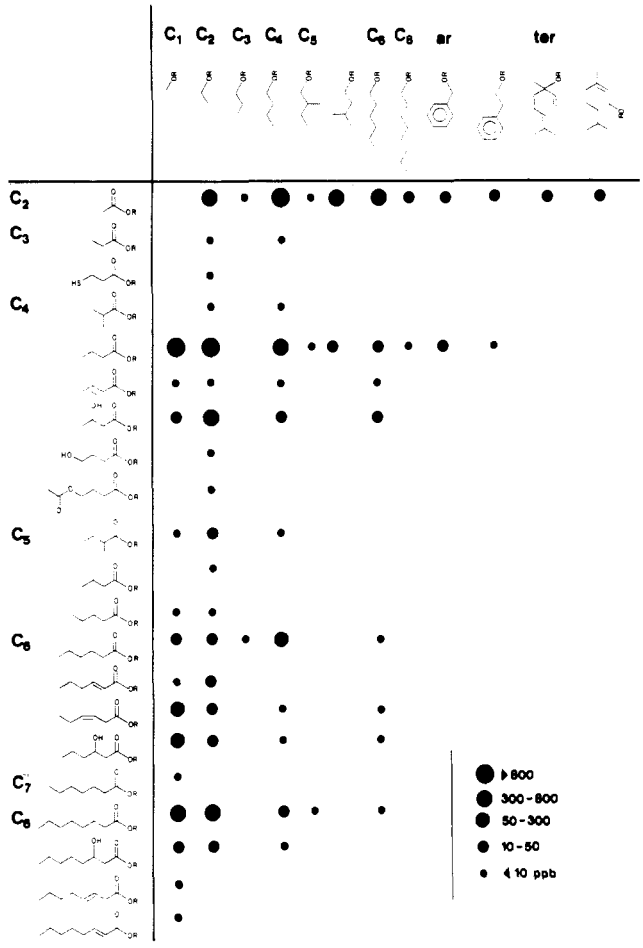

Figure 1. Composition of esters among mountain papaya volatiles. Moieties arranged according to their chain lengths; alcohols from left to right, acids (C2-C8) from top to bottom.

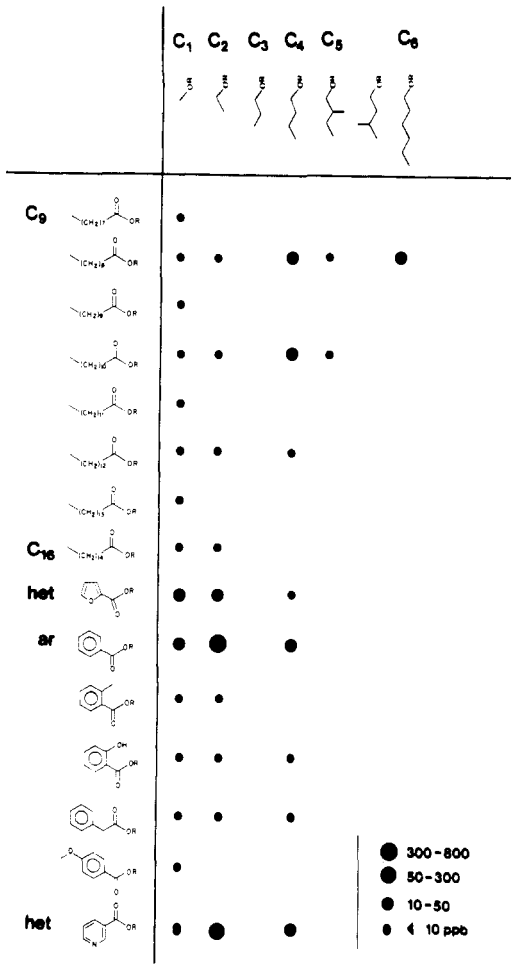

Figure 2. Composition of esters among mountain papaya volatiles. Moieties arranged according to their chain lengths; alcohols from left to right, acids (C9-aromatic and heterocyclic acids) from top to bottom.

obtained from 4 kg of total fruit. After dilution with 1 L of distilled water internal standards were added (butylbenzene, 220 μg/L; methylpropyl octanoate 180 μg/kg; 1-undecanol, 260 μg/kg), and high-vacuum distillation (40–50 °C (0.1 bar)) with subsequent solvent extraction (pentane–dichloromethane, 2:1) was carried out as previously described (Idstein et al., 1984). The distillation residue was studied by direct liquid–liquid extraction. After prefractionation of the carefully concentrated distillation extract by liquid chromatography on silica gel with a pentane–diethyl ether gradient in three fractions (fraction I, pentane; fraction II, pentane–diethyl ether, 9:1; fraction III, diethyl ether) (Idstein et al., 1984) the eluates were concentrated to 0.5 mL for HRGC and HRGC–MS study.

HRGC. A Carlo Erba Fractovap 4160 gas chromatograph with FID equipped with a Macherey & Nagel 25 m × 0.31 mm fused silica CW 20 M-CB capillary column (df = 0.15 μm) connected to a 2-m uncoated fused silica capillary ("retention gap") (Grob and Müller, 1982) was used. On-column injection with an air-cooled injection system was employed. The temperature program was 50–240 °C at 5 °C min. The flow rates for the carrier gas were 2.5 mL/min of He, for the makeup gas 30 mL/min of N_2, and for the detector gases 30 mL/min of H_2 and 300 mL/min of air, respectively. The detector temperature was 220 °C. Volumes of 0.2 μL were injected.

Results of qualitative analyses were ensured by comparison of HRGC retention and mass spectral data (cf. below) with those of authentic reference substances. Quantitative determinations were carried out by standard controlled calculations with a Hewlett Packard 3388 A laboratory data system without consideration of distillation and extraction yields and HRGC response (i.e., calibration factors $F = 1.00$ for all compounds).

HRGC–MS. A Varian Aerograph 1440 gas chromatograph coupled by an open-split interface to a Finnigan MAT 44 mass spectrometer was used. The system was equipped with a water-cooled on-column injector and with a 30-m × 0.31 mm J & W CW 20 M fused silica capillary column (df = 0.15 μm) connected to a 2-m uncoated fused silica capillary (Grob and Müller, 1982). The operation conditions were as follows: temperature program, 2 min isothermal at 60 °C, 60–240 °C, 5 °C/min; carrier gas, 1.0 mL/min of He; temperature of ion source and connection parts, 200 °C; electron energy, 70 eV; cathodic current, 0.8 mV; injection volumes, 0.5 μL.

RESULTS AND DISCUSSION

The volatiles of fresh ripe mountain papayas were separated from the pulp by high-vacuum distillation and subsequent solvent extraction with a pentane–dichloromethane (2:1) mixture. Internal standards had been added before distillation. After careful concentration of the extract the volatiles were prefractionated by liquid adsorption chromatography on silica gel. When a pentane–diethyl ether gradient (Idstein et al., 1984) was used three fractions were eluted and after concentration by distilling off the solvent analyzed by fused silica capillary gas chromatography (HRGC) and coupled capillary gas chromatography–mass spectrometry (HRGC–MS). The concentrated extract obtained by direct solvent extraction

Table I. Volatile Components[a] Identified by HRGC and HRGC–MS in Mountain Papaya (*Carica candamarcensis*, syn. *C. pubescens* Lenne et Koch) Fruit

compound	fraction[b]	concn, ppb <10	10–50	50–300
Hydrocarbons				
alkanes C12–C22	I	+		
alkenes C13,15,17,19,21,23	I	+		
o-, *m*-, *p*-xylenes	I	+		
ethylbenzene	I	+		
1,2,3-trimethylbenzene	I	+		
propenylbenzene	I	+		
1,2,4,5-tetramethylbenzene	I	+		
naphthalene	I	+		
2-methylnaphthalene	I	+		
Δ-3-carene	I	+		
β-farnesene	I	+		
Aldehydes				
2-butenal	III		+	
2-methyl-(*E*)-2-butenal	III		+	
(*E*)-2-pentenal	III		+	
decanal	II	+		
dodecanal	II	+		
tetradecanal	II	+		
benzaldehyde	II	+		
4-methylbenzaldehyde	II	+		
phenylacetaldehyde	II	+		
furfural	III	+		
Ketones				
2,3-butandione	III	+		
3-hydroxy-2-butanone	III			+
3-acetoxy-2-butanone	III			+
2-cyclohexanone	II	+		
2-hexanone	II	+		
2-heptanone	II	+		
6-methyl-5-hepten-2-one	II	+		
2-octanone	II	+		
1-octen-3-one	III	+		
2-nonanone	II	+		
2-decanone	II	+		
2-tridecanone	II	+		
2-tetradecanone	II	+		
2-hexadecanone	II	+		
acetophenone	II	+		
3-methylacetophenone	II	+		
2-hydroxyacetophenone	III	+		
benzophenone	II	+		
fenchone	II	+		
β-damascone	II	+		
β-ionone	II	+		

compound	fraction[b]	concn, ppb <10	10–50	50–300
Alcohols				
1-butanol	III			+
3-methyl-1-butanol	III	+		
1-pentanol	III	+		
1-hexanol	III		+	
1-octanol	III		+	
1-octen-3-ol	III	+		
1-decanol	III	+		
benzyl alcohol	III		+	
2-phenethanol	III	+		
linalool	II/III			+
α-terpineol	III	+		
4-terpinenol	III	+		
farnesol	III		+	
(*Z*)-linalool oxide, furanoid	III	+		
(*E*)-linalool oxide, furanoid	III	+		
Lactones				
γ-hexalactone	III	+		
γ-heptalactone	III	+		
δ-heptalactone	III	+		
γ-octalactone	III	+		
δ-octalactone	III	+		
γ-nonalactone	III	+		
δ-nonalactone	III	+		
γ-undecalactone	III	+		
Miscellaneous				
2-methylthiophene	II	+		
3-methylthiophene	II	+		
2,5-dimethylthiophene	II	+		
1,8-cineol	II	+		
phenylacetonitrile	II/III		+	
benzyl isothiocyanate	III			+
2-phenethyl isothiocyanate	III		+	
acetic acid	III	+		
butanoic acid	III	+		
hexanoic acid	III	+		
octanoic acid	III	+		
decanoic acid	III	+		

[a] Esters are not included. [b] The fraction in which the compound was identified.

from the residue of high-vacuum distillation was also studied by these techniques, but nondistillable aroma components were not found.

The results of HRGC and HRGC–MS identifications are outlined in Figures 1 and 2 as well as Table I. The figures show the structures of 103 esters identified in silica gel fractions II and III and their concentration ranges determined in the pulps of two samples (cf. Experimental Section). The remaining volatiles characterized by the above-mentioned techniques comprised 11 hydrocarbons (alkanes and alkenes not considered), 30 carbonyls, 14 alcohols, 8 lactones, and 12 components of miscellaneous structures, respectively; they are all listed in Table I.

As shown in Figures 1 and 2 the major part of volatiles consisted of esters. Qualitatively, the ester composition was characterized by a number of various acetates as well as methyl, ethyl, and butyl esters. Among them structures were detected, which were rarely or not found in nature as yet. For instance, ethyl 3-mercaptopropanoate has been detected only in Concord grapes (Kolor, 1983), whereas the methyl esters of 2-methyl- and 4-methoxybenzoic acid have been found only in sapodilla fruit (MacLeod and Gonzales de Troconis, 1982), dried bonito (Yajima et al., 1983) and feijoa fruit, respectively (Hardy and Michael, 1970). Further examples are the methyl esters of (*E*)-2- and (*E*)-3-octenoic acid or the butyl and hexyl esters of 3-hydroxyhexanoic and -octanoic acid. The first mentioned volatiles have been identified in pineapple (Näf-Müller and Willhalm, 1971); the latter ones could be detected recently in mango fruit (Engel and Tressl, 1983; Idstein and Schreier, 1985a). According to the TNO lists of volatiles (Van Straten et al., 1983; Maarse and Viischer, 1984) the following esters (*m/e* (%)) were not described as yet as natural substances: butyl (*E*)-2-butenoate 69 (100), 41 (51), 87 (50), 56 (14); hexyl (*E*)-2-butenoate 69 (100), 84 (38), 41 (34), 43 (8); butyl 2-furoate 95 (100), 112 (48), 41 (40), 56 (32); ethyl 2-methylbenzoate 91 (100), 65 (29), 90 (27), 164 (22); butyl 2-hydroxybenzoate 120 (100), 92 (35), 65 (32), 138 (28); butyl nicotinoate 106 (100), 124 (90), 78 (80), 51 (73).

Quantitatively, butyl acetate and methyl and ethyl butanoate were determined in highest concentrations followed by lower amounts of ethyl, 3-methylbutyl and hexyl acetate, butyl butanoate, and benzoate as well as the ethyl

esters of 3-hydroxyhexanoic and 3-hydroxyoctanoic acid (cf. Figures 1 and 2).

With this complex ester composition the aroma distribution of mountain papaya is different from that of the common papaya fruit, *C. papaya*, in which a few esters represent only minor constituents (Idstein and Schreier, 1984, 1985b). As to the volatiles, the species are connected by the occurrence of benzyl isothiocyanate, a well-known and characteristic constituent of Caricaceae (Tang et al., 1972; Flath and Forrey, 1977; Idstein and Schreier, 1985b). In mountain papayas, additionally, 2-phenethyl isothiocyanate could be identified (cf. Table I).

As to the volatiles listed in Table I, the aroma composition does not show remarkable features; except for the thiophene derivatives, which have been found recently in different tropical fruit aromas (Idstein and Schreier, 1984), the substances often occur among plant volatiles.

Finally, it has to be pointed out that sensory tests during this study were only carried out checking the sample preparation steps. The concentrated distillation extract showed the typical sensory properties of fresh fruit, but they were destroyed after silica gel fractionation. Whereas fraction I was practically odorless, fraction II showed a fruity odor. Fraction III with its heavy, adherent floral–fruity odor was most likely to correspond to the original fruit odor.

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Registry No. Ethyl 3-mercaptopropanoate, 5466-06-8; butyl (*E*)-2-butenoate, 591-63-9; hexyl (*E*)-2-butenoate, 1617-25-0; butyl 2-furoate, 583-33-5; ethyl 2-methylbenzoate, 87-24-1; butyl 2-hydroxybenzoate, 2052-14-4; butyl nicotinoate, 6938-06-3; butyl acetate, 123-86-4; methyl butanoate, 623-42-7; ethyl butanoate, 105-54-4; ethyl acetate, 141-78-6; 3-methylbutyl acetate, 123-92-2; hexyl acetate, 142-92-7; butyl butanoate, 136-60-7; butyl benzoate, 136-60-7; ethyl 3-hydroxyhexanoate, 2305-25-1; ethyl 3-hydroxyoctanoate, 7367-90-0.

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Racemization Kinetics of Amino Acid Residues in Alkali-Treated Soybean Proteins

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Exposing soy proteins to alkaline conditions (pH 8–14), for various time periods (10–480 min) and temperatures (25–95 °C at 10 °C intervals), induced increasing racemization of L-amino acid residues to D isomers. Relative susceptibilities of most amino acids were correlated with a linear free energy relationship based on plots of the ratio of the logarithm of the rate of racemization of any amino acid to that of alanine vs. σ^*, a parameter that measures electron-donating inductive effects of amino acid side chains. Heats and entropies of activation for selected amino acids were obtained from Arrhenius plots. The values for protein-bound amino acids are compared to corresponding values for free amino acids. Mechanistic rationalizations are offered to account for the observed influence of these variables on racemization kinetics. The possible relevance of these findings to food processing and nutrition is also discussed.

INTRODUCTION

Processed proteins are increasingly used to meet human dietary needs. Alkali treatment of plant (corn, soy) and animal (casein) proteins brings about desirable changes in flavor, texture, and solubility. Such treatments also destroy toxins and trypsin inhibitors and are used to prepare protein isolates.

Treating food proteins with alkali and heat may produce undesirable, as well as desirable, changes in the constituent amino acids, however. Chemical changes that may be undesirable include cross-linking (Provanasal et al., 1975; Finot, 1983), degradation (Asquith and Otterburn, 1977; Sen et al., 1977), Maillard browning reactions, (Finot, 1982), and racemization (Masters and Friedman, 1979,

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