Changes of Volatile Compounds during Heating of Bacuri Pulp

R. Boulanger and J. Crouzet*

Laboratoire de Génie Biologique et Sciences des Aliments, Université de Montpellier II, Unité de Microbiologie et de Biochimie Industrielles Associée à l'INRA, 34095 Montpellier Cedex 05, France

The formation of volatile compounds from precursors or through chemical rearrangement during heat treatment of bacuri pulp at fruit natural pH were studied using simultaneous distillation/extraction (SDE) technique. An increase of the quantities of oxygenated and hydrocarbon terpenes and, to a lesser degree, aldehydes, was observed after SDE at pH 3, relative to the other extraction methods used, SDE at neutral pH and solid phase extraction (SPE). More particularly, linalool, linalool furanoxides, α-terpineol, hotrienol, nerol oxide, nerol, and geraniol were isolated in more important quantities after the first treatment than after the others. These results can be partially explained by the hydrolysis of glycosidically bound compounds previously identified in bacuri. Other pathways such as polyol rearrangements were also involved. The formation of linalool and α-terpineol was probably the result of the rearrangement of 2,6-dimethyloct-1-ene-3,7-diol. Moreover, it was assumed that oxidation reactions occurred during SDE at pH 3; more particularly, linalool pyranoxides partially resulted from nonenzymatic oxidation of linalool. When SDE was performed at pH 3, an increase of furfural and 4-methoxy-2,5-dimethyl-3(2*H*)-furanone was noticed. The modifications of the concentration of aliphatic aldehydes, known as lipid oxidation compounds, and of fatty acid esters were in good agreement with the observed decrease of palmitic and linoleic acid concentrations during this treatment. Moreover, important amounts of 2-acetyl-1-pyrroline were found in the SDE extract recovered at pH 7.

Keywords: *Bacuri; heat treatment; aroma compounds; precursors; hydrolysis; rearrangement; oxidation*

INTRODUCTION

Free volatile compounds, extensively studied over the past 30 years, were also present in plants as glycosidically bound components. To date, glycoconjugates have been detected in almost 170 plants belonging to 50 families (*1*−*3*).

Seven glycosides and three rutinosides were recently identified in bacuri fruit by GC-MS of their trifluoroacetylated (TFA) derivatives in agreement with quantitative data obtained for enzymatically released aglycons and saccharidic moieties structure (*4*).

Hydrolysis of glycosidically bound compounds was previously reported during thermal treatment in acidic conditions of passion fruit, apricot, and mango pulp (*5*−*8*). The volatile compounds formed will give information on the amount of glycosidically bound compounds (*5*, *9*, *10*). However, some glycoconjugates were found to be more stable at the natural pH of fruits than aglycons; in fact, the reaction temperature affected the relative proportion of the hydrolysis products (*11*).

During thermal treatment of fruit juices, rearrangement reactions of volatile and nonvolatile compounds were also reported (*7*, *12*−*16*).

The aim of the present work was the study of volatile compound modifications occurring during heat processing of bacuri pulp. This fruit is generally used as canned pulp, purée, and jams. In agreement with the work of Takeoka et al. (*17*), the simultaneous distillation/extraction (SDE) technique performed at pH 3 and 7 can simulate the composition of volatiles generated during pulp processing. Moreover, the results concerning the volatile compounds released by acid hydrolysis of the glycosidic extract were compared to those obtained by enzymatic hydrolysis of this extract (*4*) in order to precisely determine the contribution of the glycoside hydrolysis and of the other precursors to aroma compound modifications during thermal treatment.

EXPERIMENTAL PROCEDURES

Reagents. Solvents, *n*-pentane, dichloromethane, and methanol, were of pure grade (purity > 97.7%) from Carlo Erba (Rodano, Italy) and were distilled before use.

n-Paraffins C_8−C_{32}, purity > 95.5%, were obtained from Sigma (St. Quentin Fallavier, France).

Amberlite XAD-2 (20−60 mesh), obtained from Röhm and Haas (Philadelphia, PA), was treated according to the procedure of Günata et al. (*18*).

Reference volatile compounds were obtained from commercial firms or received as gifts.

Plant Material. Bacuri fruits at commercial maturity stage were purchased at Belém market and transported to France by plane. After seed separation, the pulp was frozen and stored at −18 °C until used. The thawed pulp was homogenized in a Waring blender in the presence of distilled water (1:1, w/v), liquefied using a mixture of cellulase (5 g/L), Pectinol D5 S (2 g/L), and PVP (0.2 g/L) at 25 °C for 90 min, as indicated by Salles et al. (*19*), and centrifuged (30 min, 10000*g*) at 4 °C. The precipitate was diluted in distilled water (1:1, w/v), and the solution was centrifuged in the same conditions. The two clear supernatants were pooled and used in the next separation steps. Freezing and thawing processes can modify the free volatile composition; however, aroma precursors were not

* Author to whom correspondence should be addressed (fax 467 14 42 92; e-mail crouzet@arpb.univ-montp2.fr).

10.1021/jf010894m CCC: $20.00
Published on Web 11/20/2001

affected by this treatment. All of the assays were conducted using frozen samples, and the relative results obtained were compared.

Glycoside Extraction. Clear juice (100 mL) was poured onto a 9 × 1 cm i.d. column filled with solvent-washed XAD-2 at 1.5 mL min^{-1}. The column was rinsed with 50 mL of distilled water, and the free volatile compounds were eluted with 50 mL of pentane/dichloromethane (2:1, v/v) (*18*). Then, the glycosides were eluted from the XAD-2 column using 50 mL of methanol. The methanol phase was dried, filtered, and concentrated to dryness under vacuum at 45 °C. The residue constituted the crude glycosidically bound fraction.

Simultaneous Distillation/Extraction. For SDE at pH 3 100 g of clarified bacuri pulp was diluted with 500 mL of distilled water; the final pH was 3. The equivalent of 20 mL of glycosidic fraction was diluted with 100 mL of distilled water, and the pH was adjusted to 3 by the addition of 0.1 N HCl.

For SDE at pH 7 100 g of clarified bacuri pulp was diluted with 500 mL of 0.2 M phosphate buffer, pH 7.

In all cases, 10 μL of nonan-4-ol (3.2 g/L in absolute ethanol) used as internal standard was added. The extraction was performed for 2 h by means of SDE at atmospheric pressure in a Likens−Nickerson apparatus using dichloromethane as solvent. The organic extract was dried over anhydrous sodium sulfate and concentrated to a final volume of 300 μL by microdistillation at 29 °C (*20*).

Volatile Compounds Analysis. A Varian 3300 (Walnut Creek, CA) chromatograph equipped with a split injector (1/10) and a flame ionization detector was used for GC analysis. Two fused silica capillary columns (J&W Scientific, Folsom, CA) were employed: (a) a DB-Wax and (b) a DB-5MS (30 m × 0.25 mm i.d., film thickness = 0.25 μm). The temperature programs were as follows: (a) 3 min isothermal at 60 °C, increased at 2 °C/min to 220 °C and then from 220 to 250 °C at 5 °C/min and maintained for 15 min; (b) 5 min isothermal at 40 °C, increased from 40 to 200 °C at 2 °C/min and then from 200 to 250 °C at 5 °C/min, and maintained for 15 min. In the two cases, the carrier gas was H_2 at 1.8 mL/min, N_2 at 30 mL/min was used for the makeup gas. The injector temperature was maintained at 250 °C, and the detector temperature was (a) 250 °C or (b) 300 °C.

GC-MS Analysis. EI mass spectra were recorded by coupling a Varian 3400 gas chromatograph equipped with a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d.; 0.25 μm bonded phase, J&W Scientific) to an Automass 020 (Unicam, Argenteuil, France) mass spectrometer. Injections were of 1 μL with a split ratio of 1/10. The transfer line and the injector temperature were maintained at 250 °C. The column temperature was programmed as previously indicated for GC analysis. He at 2 mL/ min was the carrier gas. Source temperature was 150 °C, and mass spectra were scanned at 70 eV in the *m*/*z* range from 40 to 250 at 1.0 s/decade.

Identification and Quantification. Identification of aroma compounds was based on the comparison of retention indices and mass spectral data with those of reference compounds, using litterature data or data bank (Wiley Mass Spectral Data). Three analyses, extractions, and measurements were carried out on each sample. Nonan-4-ol was used as internal standard for quantification; it was assumed that the response factor was equal to 1 for all of the compounds. Retention indices were calculated using *n*-paraffin standard (*21*). The standard deviation was determined for each compound identified.

RESULTS

The quantities of the main classes of aroma compounds isolated by SDE of bacuri pulp at pH 3 and 7 are reported Table 1. These results show that the quantities of aliphatic alcohols, esters, aromatic compounds, and ketones isolated at these two pH were similar. The quantities of oxygenated and terpene hydrocarbons and, to a a lesser degree, aldehydes obtained by SDE at the native pH of the fruit were higher than those extracted by SDE at pH 7 and by SPE (*4*). In contrast, an increase of miscellaneous compounds was found when SDE was processed at pH 7 relative to pH 3. According to these preliminary results, only modifications of terpene compounds, fatty acid esters, aldehydes, and miscellaneous compounds are discussed.

Table 1. Main Classes of Aroma Compounds Extracted from Bacuri Pulp Using SDE at pH 3 and 7 and SPE (Expressed in Milligrams per Kilogram of Fresh Pulp)

aroma compound class	SDE, pH 3	SDE, pH 7	SPE[a]
aliphatic alcohols	1.07	1.13	0.80
aromatic compounds	0.40	0.25	0.32
terpenes	1.58	0.75	0.82
oxygenated terpenes	35.57	14.67	16.05
acids	10.04	3.32	33.16
esters	8.07	7.02	0.38
ketones	2.96	2.24	0.91
aldehydes	2.47	1.03	0.61
miscellaneous	0.73	1.75	0.05

[a] Boulanger et al. (*4*).

The concentrations of the most abundant oxygenated terpenes extracted by SDE from bacuri pulp at neutral and natural acid pH and from bacuri glycosidic extract at pH 3 are given Table 2. The previously reported data (*4*) concerning free volatile compounds obtained by solid phase extraction and aglycons enzymatically released from the heterosidic fraction were added to this table. The quantities of linalool and its furanoxides and those of hotrienol, α-terpineol, nerol, and geraniol, obtained by SDE extraction of bacuri pulp at pH 3, were greater than the quantities obtained by SPE. For these compounds, the results obtained using SDE at pH 7 were comparable to those obtained by SPE. Conversely, 2,6-dimethylocta-3,7-diene-2,6-diol and (*Z*)-2,6-dimethylocta-2,7-diene-1,6-diol were present in the SPE extract and in the aglycon fraction obtained by enzymatic hydrolysis of glycosides. The quantities of linalool pyranoxides were approximatly the same in SPE and in SDE at pH 3 and 7 extracts. Finally, compounds such as nerol oxide and 2,6-dimethylocta-3,5,7-trien-2-ol appeared to be characteristic of the extract obtained at pH 3.

The concentrations of individual terpene hydrocarbons recovered by extraction of bacuri pulp at pH 3 and 7 are listed in Table 3; these compounds were not found in bound form, so only the results previously obtained for free compounds by SPE (*4*) are listed. Some compounds not previously detected or found in trace amount in the SPE extract, β-myrcene, (*E*)-ocimene, 1,3,8-*p*-menthatriene, 1,5,8-*p*-menthatriene, and bergamotene, were identified in low amount in the SDE extract at pH 3 and 7. For (*Z*)-ocimene and terpinolene, the amounts recovered by SDE were 3.5−8-fold more important at pH 3 and 7, respectively, than those obtained by SPE. Conversely, limonene was in less important concentration after SDE at the two pH values used than after SPE.

The results concerning fatty acid esters (Table 4) indicated that the same compounds were isolated by SDE at pH 3 and 7. However, an increase of long-chain fatty acid concentrations relative to SPE was noticed. The augmentation was more important when ethyl tetradecanoate, hexadecanoate, and octadecanoate were considered. These results must be compared with those obtained for long-chain fatty acids indicating a decrease of the concentration of these compounds during SDE relative to SPE (Table 5). However in this case, more

Table 2. Main Oxygenated Terpenes Recovered from Bacuri Fruit in Different Extraction Conditions (Expressed in Milligrams per Kilogram of Fresh Pulp)

aroma compound	SDE of glycosidic extract, pH 3	enzymatic hydrolysis of glycosidic extract[a]	SDE of pulp, pH 3	SDE of pulp, pH 7	SPE[a]
1,8-cineole			0.107 ± 0.021	0.095 ± 0.019	0.059 ± 0.004
(*Z*)-linalool furanoxide	0.352 ± 0.007	0.076 ± 0.002	4.822 ± 0.145	1.938 ± 0.097	2.171 ± 0.043
(*E*)-linalool furanoxide	0.215 ± 0.009	0.017 ± 0.001	2.698 ± 0.054	0.459 ± 0.018	0.417 ± 0.020
linalool	0.317 ± 0.013	0.607 ± 0.019	13.817 ± 0.276	9.682 ± 0.194	6.091 ± 0.107
hotrienol	0.239 ± 0.007	0.014 ± 0.001	7.767 ± 0.155	0.264 ± 0.018	0.231 ± 0.006
nerol oxide	0.022 ± 0.002		0.503 ± 0.040		
(*Z*)-linalool pyranoxide	0.019 ± 0.001	0.089 ± 0.004	0.615 ± 0.062	0.473 ± 0.071	0.714 ± 0.011
(*E*)-linalool pyranoxide	tr[b]	tr	0.138 ± 0.014	0.064 ± 0.006	0.169 ± 0.052
α-terpineol	0.096 ± 0.010	0.057 ± 0.016	1.475 ± 0.074	0.190 ± 0.017	0.252 ± 0.005
2,6-dimethylocta-3,7-diene-2,6-diol (isomer 2)	0.006 ± 0.001	0.390 ± 0.036	0.046 ± 0.004	0.078 ± 0.004	5.121 ± 0.404
2,6-dimethyl-octa-3,5,7-trien-2-ol			0.207 ± 0.031	0.098 ± 0.005	
nerol	0.021 ± 0.002	0.012 ± 0.001	0.442 ± 0.027		
geraniol	0.059 ± 0.005	0.079 ± 0.006	2.029 ± 0.061	0.808 ± 0.081	0.341 ± 0.003
(*Z*)-2,6-dimethylocta-2,7-diene-1,6-diol		0.317 ± 0.002	tr	tr	0.194 ± 0.029

[a] Boulanger et al. (*4*). [b] Trace.

Table 3. Main Terpene Hydrocarbons Recovered from Bacuri Pulp after SDE at pH 3 and 7 and SPE (Expressed in Milligrams per Kilogram of Fresh Pulp)

aroma compound	SDE, pH 3	SDE, pH 7	SPE[a]
β-myrcene	0.096 ± 0.014	0.085 ± 0.013	tr[b]
p-cymene	0.082 ± 0.011	0.066 ± 0.010	0.055 ± 0.001
limonene	0.249 ± 0.007	0.182 ± 0.004	0.487 ± 0.020
(*Z*)-ocimene	0.236 ± 0.009	0.155 ± 0.008	0.031 ± 0.004
(*E*)-ocimene	0.136 ± 0.019	0.053 ± 0.008	tr
γ-terpinene	0.030 ± 0.002		0.045 ± 0.001
terpinolene	0.146 ± 0.013	0.069 ± 0.007	0.024 ± 0.001
1,3,8-*p*-menthatriene	0.345 ± 0.062		
1,5,8-*p*-menthatriene	0.221 ± 0.033	0.103 ± 0.012	
bergamotene	0.046 ± 0.008	0.038 ± 0.006	tr

[a] Boulanger et al. (*4*). [b] Trace.

Table 4. Main Esters Recovered from Bacuri Pulp after SDE at pH 3 and 7 and SPE

aroma compound	SDE, pH 3	SDE, pH 7	SPE[a]
ethyl octanoate	0.029 ± 0.005	0.079 ± 0.012	0.040 ± 0.001
neryl acetate			0.031 ± 0.011
methyl dodecanoate	0.325 ± 0.039	0.279 ± 0.042	
ethyl dodecanoate	0.143 ± 0.003	0.112 ± 0.003	tr[b]
methyl tetradecanoate	0.300 ± 0.030	0.250 ± 0.020	tr
ethyl tetradecanoate	1.617 ± 0.146	1.415 ± 0.113	0.030 ± 0.002
methyl hexadecanoate	0.631 ± 0.013	0.518 ± 0.010	0.095 ± 0.006
ethyl hexadecanoate	4.620 ± 0.092	4.020 ± 0.121	0.150 ± 0.032
methyl octadecanoate	0.057 ± 0.014	0.036 ± 0.011	tr
ethyl octadecanoate	0.352 ± 0.042	0.313 ± 0.031	

[a] Boulanger et al. (*4*). [b] Trace.

Table 5. Main Acids Recovered from Bacuri Pulp after SDE at pH 3 and 7 and SPE

aroma compound	SDE, pH 3	SDE, pH 7	SPE
nonanoic acid			tr
dodecanoic acid	0.259 ± 0.010	0.036 ± 0.004	tr
tetradecanoic acid	2.161 ± 0.216	0.314 ± 0.019	0.742 ± 0.022
hexadecanoic acid	6.124 ± 0.674	1.977 ± 0.257	15.317 ± 0.766
oleic acid	1.500 ± 0.225	1.000 ± 0.200	17.098 ± 0.855

important effects were detected when SDE was realized at neutral pH value.

The augmentation of total aldehyde content in the extract obtained by SDE at pH 3 relative to the other pulp extracts is due to aliphatic aldehydes and furfural. The aliphatic aldehyde content increased from 0.26 mg/kg when SPE was used to 0.81 and 2.05 mg/kg when the extraction was processed by SDE at pH 7 and 3, respectively. Furfural detected in trace amount in the SPE extract was present at 0.15 and 0.43 mg/kg of pulp, respectively, after SDE at pH 7 and 3. The use of SDE resulted also in the increase of the quantity of 4-methoxy-2,5-dimethyl-3(2*H*)-furanone, 0.95 and 1.49 mg/kg of pulp at pH 7 and 3, respectively, versus 0.70 mg/kg of pulp in the SPE extract (*4*).

Moreover, an important amount of 2-acetyl-1-pyrroline, 1.5 mg/kg of pulp, was found in the SDE extract obtained at pH 7, whereas a less important concentration was found at pH 3, 0.4 mg/kg of pulp. This compound was not detected in the SPE extract (*4*).

DISCUSSION

The increase of the concentration of oxygenated terpenes, such as linalool, (*Z*)- and (*E*)-linalool furanoxides, nerol, geraniol, hotrienol, or α-terpineol, noticed after SDE of bacuri pulp at pH 3 relative to SDE at pH 7 or SPE (Table 2) can be explained by acid hydrolysis of glycoconjugate compounds previously identified in this fruit (*4*). However, the quantities of oxygenated terpenes released by acid or enzymatic hydrolysis of the bacuri heterosidic extract were much less important than the quantities of these compounds released after heating of bacuri pulp at pH 3. This finding indicated that other pathways can be involved in their formation: a first possibility was the formation of terpene alcohols by acid-catalyzed rearrangement of polyols (*5*, *13*, *22*−*24*). For example, previously published data (*22*) indicated that hotrienol and nerol oxide were produced by nonenzymatic rearrangement of 2,6-dimethylocta-3,7-diene-2,6-diol in acid model medium. Moreover, 2,6-dimethylocta-3,7-diene-2,6-diol, (*Z*)- and (*E*)-2,6-dimethylocta-2,7-diene-1,6-diol, and 2,6-dimethylocta-1,7-diene-3,6-diol were previously reported in bacuri (*4*). Except for the two first compounds present in small amount in all of the extracts, the other diols were not detected after SDE. The presence of hotrienol and nerol oxide after SDE at pH 3 and acid hydrolysis of the heterosidic extract showed that the diol, in free or glycoconjugate form, can be considered as their precursor. Moreover, it was shown (*23*) that 2,6-dimethylocta-3,7-diene-2,6-diol 6-*O*-β-D-glucopyranoside is the natural precursor of hotrienol from lulo fruit. However, (*E*)- and (*Z*)-anhydrolinalool oxides described by Williams et al. (*22*) as resulting from the acidic rearrangement of 2,6-dimethylocta-1,7-diene-3,6-diol were not detected in the present work.

The oxygenated terpene compound formation can be explained by a second pathway—the oxidation of hydro-

carbon terpenes as previously described during mango pulp heating (*7*). However, the increase of the concentration of terpenes such as myrcene (Table 3) in SDE extracts, relative to its concentration after SPE extraction, indicated that these compounds were probably not oxidized. The observed increase of terpene hydrocarbons can be explained from previously reported results (*24*) showing that hydrolysis of terpenyl glucosides, in a model system at pH 3.2, produced several hydrocarbons: limonene, terpinolene, (*E*)- and (*Z*)-ocimene, α- and γ-terpinene, and myrcene.

Therefore, it can be postulated that the formation of linalool and α-terpineol resulted from the rearrangement of 2,6-dimethyloct-1-ene-3,7-diol. However, the pathway involving limonene oxidation cannot be discarded, as indicated by the decrease of this compound during extraction processes involving a heat treatment.

The quantities of (*Z*)- and (*E*)-linalool furanoxides were approximatively the same after SPE and SDE at pH 7. An increase of furanoxides was observed when SDE was performed at pH 3; conversely, the content in linalool pyranoxides remained more or less constant independent of the extraction procedure used. These results can be explained by previously reported data showing that only linalool furanoxides were generated during acid thermal treatment (*22*, *25*). In the present work, one other possibility to explain the results reported was the presence in bacuri pulp of 3,7-dimethyloct-1-ene-3,6,7-triol, not detected in the present work, according to the extraction methods used. Indeed, this compound was described as a precursor of linalool furanoxides through acid rearrangement (*22*).

Moreover, the formation of 2,6-dimethylocta-3,5,7-trien-2-ol following SDE of bacuri pulp can be the result of a dehydration of 2,6-dimethylocta-3,7-diene-2,6-diol. This phenomenon was previously described (*5*) for the formation of three unsaturated alcohols: 2-methylbut-3-en-1-ol, 3-methylbut-3-en-1-ol, and 3-methylbut-2-en-1-ol from 3-methylbutane-1,3-diol heated in acid medium. A structural isomer of the trienol found in the present work, 2,6-dimethylocta-1,3,7-trien-6-ol, was previously described as an important flavor compound of mature baelfruit (*26*).

The augmentation of total aldehydes content in the extract obtained by SDE at pH 3 relative to the other extracts resulted from the increase of the aliphatic aldehydes, known as resulting from lipid oxidation, such as hexanal, heptanal, octanal, undecanal, and (*E*)-dec-2-enal. These results, as well as the observed increase of fatty acid esters, were in good agreement with the observed decrease of hexadecanoic (palmitic) and linoleic acid concentration during this treatment.

Furfural and 4-methoxy-2,5-dimethyl-3(2*H*)-furanone were known as compounds produced during heat treatment of fruits or fruit juices.

Moreover, 2-acetyl-1-pyrroline, having a typical bread, popcorn, corn chip flavor, was previously reported in several heat-treated food products such as rice, bread, popcorn, honey, corn tortilla, and pearl millet (*27*−*29*). The formation of this compound was reported during boiling of a 2-oxopropanol−proline solution and during dry heating of a fructose−proline mixture (*30*). This compound was also described as a volatile constituent of chempedak fruit isolated after SDE (*31*) and was produced during extraction of cupuacu pulp at pH 9 (*32*).

However, it was also shown that this compound was produced by several *Bacillus cereus* strains isolated from cocao fermentation boxes, incubated for 2 days on standard count plate agar (*33*). 2-Acetyl-1-pyrroline was recently reported as a compound produced by mold growing at the surface of Mediterranean dried sausages (*34*).

Therefore, several pathways can be involved in the formation of 2-acetyl-1-pyrroline. However, the results reported in the present work, showing that its formation occurred during heating of bacuri pulp in neutral medium, indicated that this compound is likely the result of a Maillard reaction.

ACKNOWLEDGMENT

We are indebted to Pr. P. Winterhalter, Der Technischen Universität Carolo-Wilhelmina, Braunschweig, and Dr. R. Baumes, Institut des Produits de la Vigne, INRA, Montpellier, for the gift of reference compounds.

LITERATURE CITED

(1) Stahl-Biskup, E.; Intert, F.; Holthuijzen, J.; Stengele, M.; Schultz, G. Glycosidically bound volatiles—a review 1986−1991. *Flavour Fragrance J*. **1993**, *8*, 61−80.

(2) Winterhalter, P.; Skouroumounis, G. Glycoconjugated aroma compounds: occurrence, role and biotechnological transformation. In *Advances in Biochemical Engineering/Biotechnology: Biotechnology of Aroma, Special Vol. 55*; Berger, R. G., Ed.; Springer-Verlag: Berlin, Germany, 1997; pp 73−105.

(3) Crouzet, J.; Chassagne, D. Glycosidically bound volatiles in plants. In *Naturally Occurring Glycosides*; Ikan, R., Ed.; Wiley: Chichester, U.K., 1999; pp 225−274.

(4) Boulanger, R.; Chassagne, D.; Crouzet, J. Free and bound flavour components of amazonian fruits. 1: Bacuri. *Flavour Fragrance J*. **1999**, *14*, 303−311.

(5) Engel, K. H.; Tressl, R. Formation of aroma components from nonvolatile precursors in passion fruit. *J. Agric. Food Chem*. **1983**, *31*, 998−1002.

(6) Crouzet, J.; Chairote, G.; Rodriguez, F.; Seck, S. Volatile components modifications during heat treatment of fruit juices. In *Instrumental Analysis of Foods*; Charalambous, G., Inglett, G. Eds.; Academic Press: New York, 1983; Vol. 2, pp 119−135.

(7) Sakho, M.; Crouzet, J.; Seck, S. Evolution des composés volatils de la mangue au cours du chauffage. *Lebensm. Wiss. Technol*. **1985**, *18*, 89−93.

(8) Nitz, S.; Kollmannsberger, H. Z. Changes in flavour composition during thermal concentration of apricot purée. *Z. Lebensm. Unters. Forsch*. **1993**, *197*, 541−545.

(9) Koulibaly, A.; Sakho, M.; Crouzet, J. Variability of free and bound volatile terpenic compounds in mango. *Lebensm. Wiss. Technol*. **1992**, *25*, 374−379.

(10) Herderich, M.; Neubert, C.; Winterhalter, P.; Schreier, P. Identification of C_{13}-norisoprenoid flavour precursors in starfruit (*Averrhoa carambola* L.). *Flavour Fragrance J*. **1992**, *7*, 179−185.

(11) Skouroumounis, G.; Sefton, M. Acid-catalyzed hydrolysis of alcohols and their β-glucopyranosides. *J. Agric. Food Chem*. **2000**, *48*, 2033−2039.

(12) Williams, P. J. Hydrolytic flavor release in fruit and wines through hydrolysis of nonvolatile precursors. In *Flavor Sciences—Sensible Principles and Techniques*; Acree, T., Teranishi, R., Eds.; American Chemical Society: Washington, DC, 1993; pp 287−308.

(13) von Sydow, E.; Karlsson, G. The aroma of black currants IV. The influence of heat measured by instrumental methods. *Lebensm. Wiss. Technol*. **1971**, *4*, 54−58.

(14) Shimoda, M.; Shigematsu, H.; Shiratsuchi, H.; Osajima, Y. Comparison of the odor concentrates by SDE and adsorptive column method for green tea infusion. *J. Agric. Food Chem*. **1995**, *38*, 1616−1620.

(15) Williams, P. J.; Sefton, M.; Wilson, B. Nonvolatile conjugates of secondary metabolites as precursors of varietal grape flavor components. In *Flavor Chemistry, Trends and Developments*; Teranishi, R., Buttery, R. G., Shaidi, F., Eds.; American Chemical Society: Washington, DC, 1989; pp 35−48.
(16) Honkanen, E.; Pyysalo, T. The aroma of cloudberries (*Rubus Chamaemorus* L.). *Z. Lebensm. Unters. Forsch.* **1976**, *160*, 393−400.
(17) Takeoka, G.; Flath, R. A.; Buttery, R. G.; Winterhalter, P.; Güntert, M.; Ramming, D. W.; Teranishi, R. Free and bound constituents of white-fleshed nectarines. In *Flavors Precursors. Thermal and Enzymatic Conversions*; Teranishi, R., Takeoka, G., Güntert, M., Eds.; American Chemical Society: Washington, DC, 1992; pp 116−138.
(18) Günata, Z.; Bayonove, C. L.; Baumes, R.; Cordonnier, R. The aroma of grapes I, Extraction and determination of free and glycosidically bound fractions of some grape aroma compounds. *J. Chromatogr.* **1985**, *331*, 83−90.
(19) Salles, C.; Jallageas, J. C.; Fournier, F.; Tabet, J. C.; Crouzet, J. Apricot glycosidically bound volatile components. *J. Agric. Food Chem.* **1991**, *39*, 1979−1983.
(20) Bemelmans, J. M. H. Review of isolation and concentration techniques. In *Progress in Flavour Research*; Land, D. G., Nursten, H. E., Eds.; Applied Science Publishers: London, U.K., 1979; pp 79−98.
(21) Van den Dool, H.; Kratz, P. D. A generalization of the retention time index system including linear temperature programmed gas−liquid partition chromatography. *J. Chromatogr.* **1963**, *11*, 463−471.
(22) Williams, P. J.; Strauss, C. R.; Wilson, B. Hydroxylated linalool derivative as precursors of volatiles monoterpenes of muscat grapes. *J. Agric. Food Chem.* **1980**, *28*, 766−771.
(23) Wintoch, H.; Morales, A.; Duque, C.; Schreier, P. (*R*)-(−)-(*E*)-Dimethyl-3,7-octadiene-2,6-diol 6-*O*-D-glucopyranoside: Natural precursor of hotrienol from lulo fruit (*Solanum vestissimum* D.) peelings. *J. Agric. Food Chem.* **1993**, *41*, 1311−1314.
(24) Williams P. J.; Strauss, C. R.; Wilson, B. J.; Massy-Westropp, R. A. Studies of the hydrolysis of *Vitis vinifera* monoterpene precursor compounds and model monoterpene β-D-glucosides rationalizing the monoterpene composition of grapes. *J. Agric. Food Chem.* **1995**, *43*, 1616−1620.
(25) Chen, S. H.; Huang, T. C.; Ho, C. T.; Tsai, P. J. Extraction, analysis and study on the volatiles in roselle tea. *J. Agric. Food Chem.* **1998**, *46*, 1101−1105.
(26) Tokitomo, Y.; Shimono, Y.; Kobayashi, A.; Yamanishi, T. Aroma components of baelfruit (*Aegle marmelos* Correa*). Agric. Biol. Chem.* **1982**, *46*, 1873−1877.
(27) Buttery, R. G.; Ling, L. C. 2-Acetyl-1-pyrroline: an important component of cooked rice. *Chem. Ind.* **1982**, 958−959.
(28) Seitz, L. M.; Wright, R. L.; Waniska, R. D.; Rooney, L. W. Contribution of 2-acetyl-1-pyrroline to odors from wetted ground pearl millet. *J. Agric. Food Chem.* **1993**, *41*, 955−958.
(29) Schieberle, P. Primary odorants in popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141−1144.
(30) Schieberle, P. Quantitation of important roast-smelling odorants in popcorn by stable isotope dilution assays and model studies on flavor formation during popping. *J. Agric. Food Chem.* **1995**, *43*, 2442−2448.
(31) Wong, K. C.; Lim, C. L.; Wong, L. L. Volatile flavor constituents of Chempedak (*Artocarpus polyphema* Pers.) fruit and Jackfruit (*Artocarpus heterophyllus* Lam.) from Malaysia. *Flavour Fragrance J.* **1992**, *7*, 307−311.
(32) Fisher, N.; Hammerschmidt, F. J.; Brunke, E. J. Analytical investigation of the flavor of cupuacu (*Theobroma grandiflorum* Spreng.). In *Fruit Flavors, Biogenesis, Characterization, and Authentification*; Rouseff, R. L., Leahy, M. M., Eds.; American Chemical Society: Washington, DC, 1995; pp 8−20.
(33) Romanczyk, L. J.; McClelland, C. A.; Post, L. S.; Aitken, V. M. Formation of 2-acetyl-1-pyrroline by several *Bacillus cereus* strains isolated from cocao fermentation boxes. *J. Agric. Food Chem.* **1995**, *43*, 469−475.
(34) Stahnke, L. H. 2-Acetyl-1-pyrroline—key aroma compound in mediterranean dried sausages. In *Frontiers of Flavour Science*; Schierbele, P., Engel, K. H., Eds.; Deutsche Forschungsanstalt für Lebensmittelchemie: Garching, Germany, 2000; pp 361−365.

Received for review July 11, 2001. Accepted September 28, 2001. This work was supported by the European Union, Contract STD ERB-TS3-CT94-0300, and R.B. received financial support from the Ministère de l'Education Nationale de la Recherche et de la Technologie.

JF010894M