Importance of Some Lactones and 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone to Mango (*Mangifera indica* L.) Aroma

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Sensory panels were used to assess the contributions to mango aroma by a mixture of seven lactones in amounts present in Alphonso and Baladi mangoes, two lactones in amounts present in Keitt mango, and 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone by using a bland puree from Tommy Atkins mango. The mixture of lactones added to Tommy Atkins puree in concentrations reported for Alphonso mango was significantly preferred to Tommy Atkins puree alone and to a mixture of lactones added to puree at the higher concentrations reported for Baladi mangoes. Aroma panelists significantly preferred the lactone mixture added to Tommy Atkins puree in concentration reported for Alphonso mangoes over Tommy Atkins, Haden, and Kent mango purees. 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone did not make a positive contribution to mango aroma or flavor, and some panelists suggested its presence caused an overripe aroma and flavor.

Mango is one of the most important commercial tropical fruits consumed worldwide and is cultivated mostly for fresh market consumption (MacLeod and De Troconis, 1982; MacLeod and Pieris, 1984). World production estimates for 1982 exceeded 13.6 million metric tons (Vasquez-Salinas and Lakshminarayana, 1985).

Widespread use of gas chromatography–mass spectrometry (GC–MS) combinations with capillary column resolution has enabled researchers to identify and quantify many volatile flavor components in mango (Engel and Tressl, 1983; MacLeod and Pieris, 1984; MacLeod and Snyder, 1985; Idstein and Schreier, 1985; Sakho et al., 1985). Since flavor characteristics among the many different cultivars vary widely, only a few components have been identified that are known to be important contributors to mango flavor and aroma.

Flavor studies, based on subjective evaluations and on quantitative amounts of flavor components present, have suggested that certain monoterpene hydrocarbons are important to mango flavor (MacLeod and De Troconis, 1982; Engel and Tressl, 1983). Esters and other carbonyls impart a fruity note, and lactones and some fatty acids are also considered important to mango flavor (MacLeod and De Troconis, 1982; MacLeod and Pieris, 1984; MacLeod and Snyder, 1985; Engel and Tressl, 1983; Hunter et al., 1974). However, few definitive studies have been carried out to assess the importance of these compounds to mango flavor (Hunter et al., 1974). Reports suggest that because of the complexity of components in mango there can be no typical flavor component or flavor formulation for mangoes (MacLeod and Snyder, 1985; Engel and Tressl, 1983; Hunter et al., 1974).

Several mango cultivars possess a peach-like flavor and aroma (Bautista et al., 1982; Lakshminarayana, 1980). Investigations on peach and nectarine flavors reported the identity of several lactones that are important contributors to the flavor and aroma of these fruits (Do et al., 1969; Sevenants and Jennings, 1966; Spencer et al., 1978; Engel et al., 1988). Many of the lactones reported in peaches and nectarines have also been found in mango. The identity of 14 lactones was reported for Alphonso mangoes; this number is greater than those reported in nectarine, peach, apricot, or coconut, where similar lactones are important contributors to flavor (Idstein and Schreier, 1985). Because of the peach-like flavor character of some mango cultivars, it is probable that certain lactones make a positive contribution to mango flavor.

Some mango cultivars exhibit a pineapple-like flavor and aroma. 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone (furanone 1, Figure 1) contributes to pineapple flavor and has been reported in several other fruits and processed foods. It imparts a caramel-like or burnt sugar flavor note at high concentration but is herbal, sweet, fruity, or strawberry-like at lower concentrations (Pickenhagen et al., 1981; Pyysalo et al., 1977). Thus, furanone 1 might be responsible for some of the flavor attributes of mango cultivars that have pineapple-like flavor and aroma.

In this study the presence of some lactones and 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone in mango was related organoleptically to mango aroma.

EXPERIMENTAL PROCEDURES

Sample Preparation. The mango cultivars Alfonso, Carabad, Haden, Keitt, Mulgoba, Tommy Atkins, Turpentine, and Haden x Carabad were obtained from the U.S. Subtropical Horticultural Research Station, Miami, FL, and held at 21 °C to uniform ripeness. Kent mangoes were purchased at a local market and ripened as above. Fruits of individual cultivars (2–3 fruit of each sample) were peeled, deseeded, and blended with equal weights of deionized water in a high-speed blender to afford 0.2–1.0 kg of puree. A 100-g sample of puree was used for each extraction to determine the amount of furanone 1 present (see below).

Extractions for Quantification of Furanone 1. Most of the volatile materials were removed from the liquefied puree by distillation on a rotary evaporator at 40 °C and 20 mmHg pressure. The puree residue was transferred to a separatory funnel and successively extracted four times with 50-mL portions of freshly distilled methylene chloride and then HPLC-grade diethyl ether. The combined extracts were dried over sodium sul-

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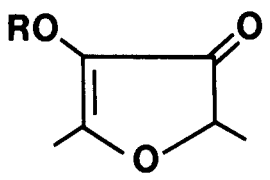

1, R=H

2, R=CH_3

Figure 1. Dimethyl furanones in mango.

fate and concentrated to a final volume of ca. 0.5 mL on a rotary evaporator at 30 °C and 20 mmHg pressure and then stored in 1-mL screw-capped vials under nitrogen at 4 °C until used. A second extract from 100 g of Tommy Atkins cultivar was prepared to be certain that furanone 1 (Figure 1) was not present in that sample.

Extractions for Quantification of Two γ-Lactones. Duplicate 50-g samples of Keitt mango puree were also extracted (omitting the distillation step to remove volatile materials) to estimate amounts of γ-heptalactone and γ-dodecalactone present.

GC Analyses. *Furanone 1.* Mango extracts were analyzed for furanone 1 on a Hewlett-Packard Model 5840 GC equipped with a 30 m × 0.32 mm DB-5 fused silica capillary column of 1-μm film thickness (J & W Scientific, Rancho Cordova, CA). The temperature program was 70 °C for 10 min, increased at 2 °C/min to 225 °C. A glass-lined capillary injection port was used with a split ratio of 100:1. The injection port and flame ionization detector temperatures were 250 and 350 °C, respectively. The carrier gas flow rate (H_2) was 38 cm/s at 70 °C. Retention times for furanone 1 and its methyl ether 2 (Figure 1) were determined by using 0.02–0.1% solutions of authentic compounds in diethyl ether. Quantitative estimations of furanone 1 were obtained by comparison of area percentages from 0.1-μL injections of standard solution prepared in ethanol versus mango extracts. Authentic samples of lactones were obtained from Aldrich Chemical Co. (Milwaukee, WI) ICN Pharmaceutical, Inc. (Plainview, NY), and Pfaltz & Bauer (Waterbury, CT); furanone 1 was a gift from Firmenich (New York). The methyl ether of furanone 1 was synthesized from 1 by treatment with diazomethane. Identity of furanone 1 in mango puree was determined by GC–MS comparison with the authentic sample above on a Finnigan Model 4021 GC–MS operated in the electron impact mode at 70 eV. Mass units of 40–300 were monitored. The GC column was a 60 m × 0.25 mm DB-5 fused silica capillary column with a flow rate of 1 mL/min. Injection port temperature and oven programming were as described above. Mass spectral identifications were made by comparison with spectra published for authentic compounds (Heller and Milne, 1978), except for furanone 1 discussed above.

γ-Lactones. Quantitative estimations of γ-heptalactone and γ-dodecalactone were performed in triplicate on duplicate extracts from Keitt mango. Chromatographic analyses were performed on a Hewlett-Packard Model 5750 GC fitted with a fused silica megabore column (30 m × 0.53 mm, DWX-3, J & W Scientific, Rancho Cordova, CA). The temperature program was 50 °C for 5 min, increased at 4 °C/min to 225 °C with a 10-min hold at 225 °C. Helium at 10 mL/min was the carrier gas, and the injection port and detector temperatures were 200 and 350 °C, respectively. Quantitative values were obtained by comparison of peak area percentages for 0.1-μL injections of standard solutions prepared in ethanol versus those from mango extracts.

SENSORY EVALUATIONS

In all sensory detection tests an experienced 12-member panel was used. Each panel member received two presentations in a paired comparison test for 24 total judgements (Larmond, 1967).

Furanone 1. The aroma and flavor detection thresholds of furanone 1 in water and in mango puree (Tommy Atkins) were determined. The aroma and flavor threshold values in water were determined by dissolving 9.3 mg of furanone in 50 mL of deionized water and diluting the mixture to give five test concentrations (0.465, 0.93, 1.86, 9.3, and 18.6 mg/1000 g) for the aroma panel and four test concentrations (0.093, 0.279, 0.465, and 1.86 mg/1000 g) for the flavor panel. For the aroma threshold value in mango, 0.5-mL portions of varying concentrations of furanone 1 were added to 10 g of mango puree to yield four concentrations (100, 125, 150, and 200 mg/1000 g) for aroma panel evaluation. For the flavor threshold value, 33-mL portions of varying concentrations of furanone 1 in 50 mL of deionized water were added to 600 g of mango puree to yield five concentrations (20.0, 100.1, 126.5, 139.0, and 152.1 mg/1000 g) for flavor threshold values in Table I. An equal proportion of water was added to mango puree as the control sample in each test. Panel members were asked to indicate the sample that contained added flavor compound. Mathematical line fitting was used for log of concentration versus percent-above-chance to determine the threshold value (50% above chance score) and confidence limits (Harrison and Elder, 1950). To determine a flavor preference, the furanone was added to mango puree at a level of 67% above chance (143 ppm) in a paired comparison test versus control mango puree. Panel members were asked to select the sample they preferred (Krum, 1955).

Table I. Aroma and Flavor Thresholds of Furanone 1 in Water and in Mango

	threshold, ppm		confidence limits,[a] ppm	
medium	aroma	flavor	aroma	flavor
water	1.7	0.46	3.9	1.9
mango puree[b]	173	101	1.3	8.0

[a] Calculated for 95% confidence level (Harrison and Elder, 1950). [b] Tommy Atkins variety.

Table II. Concentration and Flavor Threshold of Specific Flavor Components Evaluated in Mango

	concn, ppb, in puree from			threshold, ppm in water,	
compd	Alphonso[a]	Baladi[a]	Keitt[b]	aroma[c]	flavor[d]
γ-butyrolactone	50	50			200
γ-valerolactone	20	20			
γ-hexalactone	50	40		1.6	8.0
γ-heptalactone			20	0.4	3.4
γ-octalactone	150	500		0.007	3.0
δ-octalactone[e]	30	50			
γ-nonalactone	30	40			2.4
δ-nonalactone[e]	50	40			
γ-decalactone	50	40		0.011	0.14–1.4
δ-decalactone	20	40		0.1	1.0
γ-dodecalactone			50	0.007	

[a] Engel and Tressl (1983); Idstein and Schreier (1985). [b] Quantitative values determined for Keitt mango by GC at this laboratory. [c] Engel et al. (1988), except where noted. [d] Fazzalari (1978). [e] Quantities for these lactones were reported, but authentic samples were not available for use in aroma evaluation.

Mixtures of Lactones and Furanone 1. All lactones used in the aroma solutions except valerolactone (95% pure) were better than 99% pure by GC analysis. Solutions of seven of the nine lactones whose concentrations in Alphonso and Baladi mango were reported by Engel and Tressl (1983; see Table II, footnote *e*) and the two lactones quantified in Keitt mango (Table II) were added to Tommy Atkins mango puree in parts per billion (ppb) concentration for aroma testing. Individual compounds were successively dissolved in 20 mL of 95% ethanol and then added slowly with stirring to deionized water; the final volume was adjusted to 100

Table III. Aroma Comparisons of Mango Purees with and without Added Lactones and Furanone 1

samples compared	confidence limit	samples compared	confidence limit
puree A[a,b] vs Tommy Atkins puree	99.9	puree A vs Kent puree	95.0
puree A vs puree B[c]	NS[d]	puree A vs puree D[f]	99.9
puree A[b] vs puree C[e]	95.0	puree A vs puree E[g]	NS
puree A vs Haden puree	95.0	puree A vs puree F[h]	NS

[a] Puree A picked as most mango-like in all tests (except where NS is noted). [b] Tommy Atkins puree with lactones added at levels reported for Alphonso and Keitt Mango (Table II). [c] Tommy Atkins puree and lactone mixture with 5 ppb of γ-nonalactone. [d] NS indicates "not significant". [e] Tommy Atkins puree with lactone concentration doubled. [f] Tommy Atkins puree with lactones added at levels reported for Baladi and Keitt mango (Table II). [g] Tommy Atkins puree and lactone mixture with 400 ppb of furanone 1. [h] Tommy Atkins puree and lactone mixture with 2000 ppb of furanone 1.

mL with deionized water. A blank solution containing 20% ethanol in deionized water was prepared for addition to control samples. Samples of mango puree for aroma panels with lactones (Table II) and furanone 1 (400–2000 ppb when added) in the concentration range reported for mangoes were prepared by vigorously mixing 0.1 mL of the above aroma solutions with 100 g of puree. The aroma solution and puree mixtures were allowed to equilibrate for at least 30 min before presentation to aroma panels. The control and test mixtures (10 g) were placed in 30-mL amber-colored bottles for presentation to the panel. Tommy Atkins purees with and without aroma solutions were compared, and Tommy Atkins puree with aroma solution added was evaluated against both Haden and Kent mangoes.

RESULTS AND DISCUSSION

Sensory evaluation studies were conducted to assess the importance of selected lactones to mango aroma and of furanone 1 (Figure 1) to mango aroma and flavor. Aroma and flavor panels were conducted with Tommy Atkins mango because of its mild mango aroma and flavor and lack of measurable amounts of furanone 1.

Tommy Atkins puree with seven lactones added in amounts reported in Alphonso and two lactones added in amounts found in Keitt mango (Table II) was designated puree A in Table III. Comparison of puree A with Tommy Atkins puree showed a significant preference for puree A at the 99.9% confidence level. The coconut-like aroma from γ-nonalactone was objectionable to some panel members. Thus, its concentration was reduced from 30 to 5 ppb with concentrations of other lactones (Table II) remaining the same (puree B Table III). When puree B was compared with puree A, no significant preference for either puree was noted. Panelists who originally objected to the coconut-like aroma still found it equally objectionable at the lower concentration.

The aroma panel also could distinguish between two samples of Tommy Atkins puree containing different concentrations of added lactone mixtures (Table III). In tests with a mixture of seven lactones added in concentrations reported in Table II as present in Alphonso mango plus two lactones in concentrations present in Keitt mango (puree A) and these nine lactones added at twice this level (puree C), the panel selected the puree with the lower lactone concentration as the sample with the better mango aroma (Table II) at the 95% confidence level.

Mango puree A was compared to purees from Haden and Kent mangoes as well (Table III). Both cultivars are considered to have good mango aroma and flavor. In both cases puree A was determined to have a better mango aroma at the 95% confidence level (Table II). Results from aroma panels suggest that the mixture of nine lactones used in this study contributes significantly to mango aroma.

Aroma panels assessed two seven-lactone mixtures in Tommy Atkins puree which were prepared in concentrations reported for Alphonso mango (puree A) and Baladi mango (puree D, Table III) as listed in Table II. The two lactones quantified in Keitt mango were added at equal levels in both puree samples. In comparison of puree A with puree D, the aroma panel preferred the mixture from Alphonso mangoes (puree A) at the 99.9% confidence level (Table III).

The aroma thresholds in water for six of the nine lactones evaluated have been reported (Table II). Three of these, γ-octa-, γ-deca-, and γ-dodecalactones, have the lowest aroma thresholds. All six lactones have aroma thresholds considerably lower than their quantities found in mangoes. In each case where a flavor threshold was reported also, the aroma threshold was the lower value by a factor of 5 or more.

The presence of furanone 1 (Figure 1) in mango has been established by several workers (Pickenhagen et al., 1981; Engel and Tressl, 1983; Idstein and Schreier, 1985). Since it does not steam distill, it must be extracted from pulp with an organic solvent for identification. It is sensitive to gas chromatographic conditions and can be lost during chromatographic analysis (Pickenhagen et al., 1981). Quantitative values for furanone 1 reported for Israeli and Alphonso mangos ranged from 0.4 to 2.0 ppm (Pickenhagen et al., 1981; Engel and Tressl, 1983). We estimated quantities of furanone 1 in seven Florida mango cultivars using capillary GC of extracts from mango pulp. Estimated amounts of furanone 1 for the Florida cultivars Haden, Alphonso, Turpentine, and Mulgoba were 2.0, 1.5, 1.0, and 0.2 ppm, respectively. Trace amounts were found in Carabad and Haden x Carabad mangos, but furanone 1 was not detected in Tommy Atkins mango. We found flavor thresholds of 0.46 and 101 ppm for the furanone in water and mango puree, respectively (Table I). Thus, the quantitative amounts of the furanone in four mango cultivars were from 50 to 500 times less than the flavor threshold in mango puree.

The aroma thresholds for furanone 1 that we determined in water (1.7 ppm) and in mango puree (173 ppm) were of the same order of magnitude as the flavor thresholds (Table I). Pyysalo et al. (1977) had reported an aroma threshold for furanone 1 in water of only 4×10^{-5} ppm, a value almost 10^5 times lower than the value we determined in water. On the basis of the aroma threshold in mango puree determined in the current study, the quantities of the furanone in four mango cultivars were about 90–900 times lower than the aroma threshold in mango puree.

A possible synergistic effect of furanone 1 on mango aroma was assessed by adding it in combination with the above lactones to Tommy Atkins puree. Aroma tests with the Alphonso lactone mixture (Table II) and furanone 1 at 400 ppb in Tommy Atkins puree (puree E, Table III) compared to puree A showed no significant difference between samples. Some panelists indicated overripe or burnt sugar aroma attributes in mango with added furanone 1. When puree E was compared to puree with 2000 ppb of furanone 1, there was no significant preference for either sample. Results of the flavor thresholds and aroma comparison studies suggest that furanone 1 does not make

a significant contribution to mango aroma and flavor in the cultivars studied. Because of its importance in pineapple aroma (Pickenhagen et al., 1981), furanone 1 could contribute to the aroma of mango cultivars that possess pineapple-like aromas.

The methyl ether of furanone 1 (compound 2 in Figure 1) also has been identified in mango volatiles (Hunter et al., 1974). It was present in all of the Florida mangoes studied except for the Carabad and Haden x Carabad cultivars. Since the methyl ether is steam volatile, amounts for this compound could not be estimated by the extraction method used in this study. Its aroma threshold was reported to be 0.03 ppb in water (Pyysalo et al., 1977). Furanone 1 has a more pervasive, penetrating aroma than does the methyl ether.

CONCLUSION

Studies on mango aroma indicate the importance of a mixture of nine volatile lactones to good mango aroma. The mixture of lactones added to Tommy Atkins puree in concentrations reported for Alphonso (+Keitt) mangoes was significantly preferred to a mixture of lactones added to puree at the higher concentration reported for Baladi (+Keitt) mangoes. Amounts of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (furanone 1, Figure 1) in extracts of distilled mango purees for several Florida mango cultivars were in the range of amounts reported for other mangoes. Furanone 1 does not seem to contribute significantly to good mango aroma and flavor. Since mango aroma and flavor vary widely among cultivars, there is no one typical formulation of flavor components for this fruit.

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Registry No. 1, 3658-77-3; γ-butyrolactone, 96-48-0; γ-valerolactone, 108-29-2; γ-hexalactone, 695-06-7; γ-heptalactone, 105-21-5; γ-octalactone, 104-50-7; γ-nonalactone, 104-61-0; γ-decalactone, 706-14-9; δ-decalactone, 705-86-2; γ-dodecalactone, 2305-05-7.