Purification of Citrus Peel Juice and Molasses

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Citrus peel juice and molasses are extremely bitter and unpalatable byproducts of orange and grapefruit juice production. Major components of interest are soluble sugars, glucose, fructose, and sucrose, which account for 60−70% of the dry solids. Analyses indicate that the remaining components are suspended tissue fragments, proteins, organic acids, mineral ions, phenolic compounds, and polyols. A purification sequence that removed a majority of bitter limonoids and phenolic compounds by adsorption on nonionic, macroporous resins was tested. Residual phenolic compounds were removed by adsorption on activated carbon or anion-exchange resin, which also removed anions of organic and inorganic acids. Taste panel results suggested that debittered products could be acceptable for food uses.

Keywords: *Citrus molasses; orange peel; bitterness; adsorption; macroporous resins*

INTRODUCTION

Production of orange and other citrus juices generates vast quantities of processing byproducts, mainly peel, cores, and segment membranes (Agricultural Research Service, 1962; Kesterson and Braddock, 1976). Approximately 2×10^6 dry tons of these residues are generated annually in two major citrus-processing countries, the United States and Brazil (Grohmann and Bothast, 1994). These processing residues are usually dried and sold as a citrus cattle feed by U.S. processors, because the former practice of dumping the residues on pastures was banned more than 40 years ago. Because citrus-processing byproducts have a very high moisture content, their drying consumes a large amount of energy. Energy savings are achieved by liming and pressing the peel to produce peel juice. The resulting peel juice is evaporated in multiple effect evaporators heated by stack gases from peel dryers (Kesterson and Braddock, 1976). D-Limonene is obtained as a valuable byproduct from overhead vapors of these evaporators. The evaporated citrus molasses, concentrated to ∼50−70 °Brix, are usually blended back with the peel and also dried to citrus cattle feed. Minor amounts of molasses are sold to the outside market.

The orange peel molasses contain edible sugars, glucose, sucrose, and fructose, accompanied by minor amounts of organic acids, phenolic compounds, and other unidentified components (Agricultural Research Service, 1962; Kesterson and Braddock, 1976). Soluble sugars account for 60−70% of the total dry solids, making them by far the most abundant component. The composition of orange peel juice varies with maturity in the same fashion as the composition of the orange juice; that is, as the fruit matures, total sugar content and sugar-to-acid ratio both increase (Ting and Deszyck, 1961; Clements, 1964a,b). The wider utilization of peel juice and molasses is hampered by their dark color and the presence of bitter and astringent compounds, which make these byproducts unpalatable to humans and farm animals with the exception of ruminants (Kesterson and Braddock, 1976). Any upgrading of citrus peel juice and molasses for human consumption thus requires removal of colored, bitter, and other objectionable components and possibly salts of citric and other organic acids. The resulting clarified syrup could then be used as a sweet base for soft drinks or juice-based beverages.

Investigations of debittering and deacidification methods using food grade resins are described in this paper. Our research utilized previous results of other investigators on debittering and deacidification of grapefruit and navel orange juices (Johnson and Chandler, 1985, 1988; Shaw and Buslig, 1986; La Flamme and Weinand, 1993; Milnes and Agmon, 1995).

MATERIALS AND METHODS

Samples. Samples of peel juice and citrus molasses from evaporator outlets and storage tanks were obtained from local citrus-processing plants during middle (winter) and late (spring) seasons. Most samples contained pure peel juice and molasses from orange (chiefly Valencia and Hamlin) varieties, but some samples from storage tanks also contained grapefruit peel juice due to coprocessing of oranges and grapefruits during parts of each season. Control (laboratory made) peel juice and molasses were prepared by peeling local Valencia orange fruit, separating membranes from the peel, grinding the peel to coarse (2−3 mm) particles in a meat grinder, and pressing the ground peel in a fruit press. The resulting peel juice was then evaporated in a rotary evaporator at ∼40 °C and reduced pressure to minimize thermal degradation of peel juice components. Samples of peel juice and molasses were stored at 2−4 °C and were preserved by the addition of 15% (v/v) ethanol or 0.2% (w/v) sodium azide.

Resins and Other Chemicals. Commercial macroporous neutral resins (Amberlite XAD-4, -7, and -16) and weak anion exchangers (Amberlite IRA-93 and -95) manufactured by Rohm and Haas Corp. were purchased in dry form from Sigma Chemical Co., St. Louis, MO. The adsorbents were washed with deionized water until the conductivity of the wash water decreased below 100 $\mu\Omega^{-1}$. The initial wash was performed

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under vacuum in a suction flask where the bead suspension was evacuated until air bubbles ceased forming and beads settled to the bottom. Beads were then filtered and stored in a wet form in a closed jar. The bulk density of the beads was obtained by drying washed beads to constant weight at 70 °C and determining the weight of the known volume of beads settled in a graduated cylinder. A sample of granular activated carbon CPG 12 X 40 was a kind gift of Calgon Carbon Corp., Pittsburgh, PA, and the sample of extruded activated carbon NORIT ROX 0.8 was kindly provided by NORIT America Inc., Atlanta, GA. A macroporous cation exchanging resin (Dowex MSC-1) was purchased from Sigma Chemical Co.

Clarification and Ultrafiltration of Peel Juice and Molasses. The citrus peel juices or molasses diluted to 25−30 °Brix were centrifuged at room temperature in a superspeed centrifuge (Sorvall Instruments, Newtown, CT) at relative centrifugal force of 14000*g* for 20 min. A small floating layer was removed with a spoon, and the supernatant was poured off from the bulky pellet at the bottom of the centrifuge bottle. Supernatants were then pooled and clarified by ultrafiltration through hollow fiber units. Smaller volumes (<2 L) were ultrafiltered at room temperature using A/G Technology (Needham, MA) module UFP-10-E−5A (10000 NMW cutoff). Larger volumes (2−15 L) were ultrafiltered using a larger Romicon, Inc. (Woburn, MA), cartridge HF1.0-43-PM30 (30000 NMW cutoff). Approximately 90−95% of the supernatant volume was ultrafiltered without membrane fouling or increased inlet pressure.

Debittering and Deacidification in Batch Operation. Debittering and deacidification were conducted in batches by adding preweighed aliquots of washed resins to a predetermined volume of diluted, ultrafiltered peel juice or molasses. The mixtures were mixed at room temperature by a magnetic stirrer to keep the beads in suspension. A contact time for each aliquot of nonionic macroporous beads was ∼1 h except for kinetic experiments. In these cases the ultrafiltered peel juice or diluted molasses were stirred with excess of beads at room temperature and samples of liquid with a small portion of beads were taken at predetermined time intervals, usually every 15 min. Samples were then filtered through a 0.45 μm membrane filter, and their absorbance was measured at 280 and 320 nm using a UV−vis diode array spectrophotometer (model 8452A, Hewlett-Packard Corp., Wilmington, DE).

The debittered (Amberlite XAD-4, -7, or -16 treated) bead slurry was filtered through a 1.2 μm glass fiber filter (Cole-Parmer Instrument Co., Vernon Hills, IL), and the beads were washed with 10 volumes of deionized water. Electrical conductivity, pH, and absorbance at 280 and 320 nm were measured for pooled filtrate and washes. Cations were removed from this solution by a batch treatment with strongly acidic, macroporous polystyrene sulfonate resin beads (Dowex MSC-1, Dow Chemical Co., Midland, MI) until the pH of the solution decreased to 2.0. The acidified solution was then deionized by batch treatment with washed weakly basic macroreticular anion-exchange resin beads (Amberlite IRA-93 or -95, Rohm & Haas Co., Philadelphia, PA) until the pH of the solution reached 5.5 and conductivity decreased to ∼200 $\mu\Omega^{-1}$. Residual phenolic compounds were removed from some Amberlite XAD treated samples by additional treatment with granulated activated carbon. These batches were evacuated in the presence of activated carbon to aid penetration of liquid into the pores and then stirred for 1 h between treatments with additional portions of activated carbon. The nonionic Amberlite XAD-16 resin was regenerated by washing with 10 volumes of 0.5% (w/v) sodium hydroxide solution in water, followed by 10 volumes of deionized water, 2 volumes of 0.3% hydrogen peroxide, and a final rinse with 10 volumes of deionized water. The Amberlite IRA-93 resin was regenerated by washing with 1% NaOH solution followed by a rinse with 10 volumes of deionized water.

Analytical Procedures. Total dry solids content was determined by drying aliquots of citrus peel juice or molasses to a constant weight at 70 °C. Ash content was determined by a slow combustion of dry solids at 600 °C according to AOAC Method 942.05 (AOAC, 1990). The content of suspended solids was determined by filtration of preweighed aliquots of citrus peel juice or molasses through a preweighed 1.2 μm glass fiber filter, washing of the filter cake with deionized water, and drying at 70 °C to a constant weight. The content of nondialyzable soluble solids was determined by dialysis of centrifuged samples against deionized water using Spectra/Por 1 dialysis tubing (MW cutoff 6000−8000, Spectrum Corp., Houston, TX) and drying the contents of dialysis bags at 70 °C as described above. Protein was estimated as 6.25 × nitrogen content determined using the Kjeldahl method. Sugars, polyols, and uronic acids were separated and determined by ion-exchange chromatography using dilute sodium hydroxide and sodium hydroxide/sodium acetate solutions as eluants (Lee, 1990; Clarke et al., 1991) with a pulsed amperometric detector (Dionex Corp., Sunnyvale, CA). The procedure described by Clarke et al. (1991) was followed. The pulsed amperometric detector was operated at $E_1 = 0.05$, $E_2 = 0.60$, and $E_3 = -0.60$V and applied pulse times of 480, 120, and 6 ms, respectively, as recommended by the manufacturer. 2-Deoxy-D-galactose (Sigma Chemical Co.) was used as an internal standard, and the detector response was calibrated for each individual sugar. Polyols were also separated and determined by ion-moderated partition chromatography as described below.

The carboxylic acids were separated and determined either by ion-moderated partition chromatography and refractive index detection (Pecina et al., 1984) or by ion-exchange chromatography and conductometric detection (Dionex Corp.). Sodium trifluoroacetate was used as internal standard. The monocarboxylic and some dicarboxylic acids were separated on a polystyrene−divinylbenzene sulfonate (H^+ form) column operated at 60 °C (Bio-Rad Laboratories, Richmond, CA) using dilute (0.01 N) sulfuric acid as an eluant and a Perkin-Elmer (Norwalk, CT) LC-30 refractive index detector. 2-Propanol was used as the internal standard. The sugars and polyols were removed from these samples by absorption of cations using Dowex MSC-1 resin and absorption of carboxylic acids on Amberlite IRA-93. Sugars and polyols did not absorb on either of these resins. The IRA-93 resin was packed into a small column, washed with deionized water, and organic acids were eluted with 5% (v/v) sulfuric acid and analyzed as described above. It must be noted that citric and phosphoric acids did not elute completely from the IRA-93 resin unless 10% (v/v) H_2SO_4 solution was used as an eluent.

Although some polyols could also be separated by ion-exchange chromatography and pulsed amperometric detection, a better separation could be obtained by ion-moderated chromatography using polystyrene−DVB sulfonate resin in the Pb^{2+} form (Bio-Rad Laboratories) and refractive index detection. The column was operated at 80 °C using deionized water as an eluent, and the samples were deionized by treatment with ion-exchange resins.

Di- and tricarboxylic acids were separated and determined by ion-exchange chromatography and conductometric detection as recommended by the manufacturer (Dionex Corp., Sunnyvale, CA). A high-capacity (Dionex Ion-Pac AS11-HC) column was used in series with two suppressors, a self-regenerating autosuppressor model ASRS-1 manufactured by Dionex Corp. and an ERIS 1000 autosuppressor manufactured by Alltech Corp., Deerfield, IL. Dionex pulsed electrochemical detector operated in conductometric mode was used for the detection of anions. Eluent A was 10% (v/v) methanol in deionized water, and eluent B was 43.4 mM sodium hydroxide in 15% v/v methanol. Flow was maintained at 1.5 mL/min, and the following gradient was used for elution of organic and inorganic anions: 2% solution B for 15 min, 2−90% solution B linear gradient for 25 min, and 90% solution B for 20 min.

Potential acceptance of debittered or debittered and deionized products for human consumption was examined by acceptance test (Meilgaard et al., 1991) using 13 panelists. A nine-point verbal hedonic scale was used (1 = dislike extremely, 5 = neither like nor dislike, 9 = like extremely), and the results were evaluated by one-way analysis of variance. Two sets of samples were evaluated. The first set consisted of commercially made and laboratory made molasses either debittered by a treatment with XAD-16 resin and charcoal or

Table 1. Composition of Peel Juice and Molasses[a]

	peel juice[b]	fresh molasses[b]	stored molasses[c]	exptl molasses[d]
suspended solids	4.6−7.7	3.4−7.9	3.80−4.4	Tr[e]
nondialyzable solids	4.7−7.0	4.1−6.6	4.7−5.3	4.7−5.2
ash	3.1−4.7	3.5−4.7	3.3−5.0	3.9−4.2
protein	4.9−6.0	5.0−5.6	4.7−4.9	7.2−7.7

[a] Expressed in wt % of total dry solids. [b] From Valencia or Hamlin orange peel. [c] Orange peel molasses containing variable amounts of grapefruit peel molasses. [d] From Valencia orange peel. [e] Tr, trace.

Table 2. Content of Sugars and Polyols in Ultrafiltered Peel Juice and Molasses[a]

	peel juice	fresh molasses	stored molasses	exptl molasses
glucose	22.6−32.8	19.2−26.2	23.1−28.7	19.5−21.7
fructose	24.3−24.6	19.5−24.4	21.7−25.4	19.4−20.7
sucrose	20.9−21.5	21.5−26.2	20.7−25.1	30.5−33.8
galactose	0.4−0.5	0.3−0.4	0.4−0.5	0.5−0.6
myo-inositol	3.20−3.3	2.7−4.4	3.2−3.5	2.8−3.5
D-inositol	0.6−1.3	0.8−1.1	1.0−1.2	1.3−1.9
mannitol	0.3−1.5	0.2−1.3	1.0−1.9	0.0−0.1
total sugars	70.7−80.1	70.2−77.9	76.5−79.6	75.3−81.0

[a] Expressed in wt % of total dry solids.

subjected to additional deionizing treatment with Dowex MSC-1 and Amberlite IRA-93 resins. The approximate pH of all these samples was 5.8. The second set consisted of two samples (commercial and laboratory) of debittered molasses that were adjusted to pH 3.5 by a treatment with Dowex MSC-1 resin. A paired comparison test (Larmond, 1967) was also employed to determine preference between commercially made and laboratory made molasses that were first debittered by treatment with XAD-16 resin and charcoal and then acidified to pH 3.5 by treatment with Dowex MSC-1 resin.

RESULTS AND DISCUSSION

Composition. Because citrus (mainly orange) peel juice and molasses are low-value byproducts of juice production, only scant attention has been paid to analyses of their composition (Agricultural Research Service, 1962; Kesterson and Braddock, 1976). The analyses are also complicated by blending of molasses from different varieties of oranges and by addition of grapefruit molasses to storage tanks during the processing season. The main components of citrus molasses are the soluble sugars, glucose, fructose, and sucrose, which after inversion account for 60−70% of total dry solids (Kesterson and Braddock, 1976, Table 2). The remaining components, such as ash, crude protein, and fat, account for ∼10% of total solids (Kesterson and Braddock, 1976), leaving a significant portion (∼15−25%) of total solids unidentified. Therefore, we extended prior analyses of total solids in molasses to improve the mass balance and obtain additional information on low molecular weight components that can interfere with the purification of sugars. The results are summarized in Tables 1−3. All commercial samples of peel juice and molasses contain ∼4−8% of finely divided suspended solids (see Table 1). These solids appear to be produced by abrasion of peel during grinding, blending with lime, and dewatering in screw presses. Larger particles are screened from the juice, but abundant fine particles are carried through the evaporators and into stored citrus molasses. Particles from both flavedo and albedo of citrus fruit are present, as shown by different densities and colors of pellet layers after centrifugal sedimentation. The water

Table 3. Content of Anions in Peel Juice and Molasses[a]

	peel juice	fresh molasses	stored molasses	exptl molasses
quinate	0.31−0.87	0.45−0.92	0.57−0.85	0.63−1.33
lactate	0.53−4.20	0.42−4.15	0.32−4.73	0.03−0.13
acetate	0.11−0.21	0.10−0.32	0.11−0.32	0.16−0.52
chloride	0.15−0.27	0.19−0.25	0.19−0.25	0.14−0.20
nitrate	0.05−0.06	0.05−0.07	0.03−0.04	0.06−0.08
malate	0.76−1.37	1.01−1.54	1.05−1.13	1.74−2.43
succinate	Tr[b]−0.22	Tr−0.11	Tr	Tr−0.03
malonate	0.35−0.47	0.35−0.54	0.51−0.56	0.14−0.24
sulfate	0.21−0.24	0.19−0.24	0.18−0.20	0.21−0.22
oxalate	0.06−0.22	0.05−0.23	0.05−0.07	0.09−0.24
phosphate	0.02−0.11	0.01−0.06	0.02−0.10	0.50−0.61
citrate	1.07−1.36	0.87−1.02	0.67−0.87	1.56−2.16
total	3.62−9.60	3.69−9.50	3.70−9.07	5.26−8.19

[a] Expressed in wt % of total dry solids. [b] Tr, trace.

soluble polymeric components (nondialyzable solids in Table 1) are also present at 4−7% of total solids. The bulk of these components appears to be proteins, because nondialyzable nitrogeneous material is a large portion of total nondialyzable solids (see Table 1). We estimated pectin in peel juice and molasses by enzymatic hydrolysis of these substrates with a commercial pectinase preparation (Pectinex Ultra SP/L, Novo Nordisk Biochem North America, Franklinton, NC) followed by determination of galacturonic acid by ion-exchange chromatography and pulsed amperometric detection, but we observed only traces of this major peel component. The low concentration of water soluble pectin in peel juice and molasses can be caused by precipitation of pectin during treatment of peel with lime, which precedes the peel pressing step (Agricultural Research Service, 1962; Kesterson and Braddock, 1976). We estimated the content of phenolic compounds (*p*-hydroxycinnamic acid derivatives, flavonoids, and other unidentified compounds) as ∼3 wt % of total dry solids from UV spectra of phenolic components separated by reverse phase chromatography. We also determined a residual limonene content in several samples of commercial molasses by bromate titration (Scott and Veldhuis, 1966) and found a range of 61−4610 ppm, indicating that some evaporator units do not efficiently remove D-limonene from the peel juice.

The sugar and polyol contents of ultrafiltered peel juice and molasses are shown in Table 2. Besides glucose, fructose, and sucrose, we detected traces of galactose, but no other monomeric or dimeric sugars (see Figure 1a). We detected several unknown components in a few samples of molasses that had been stored for long periods (see Figure 1b), but these compounds were absent from fresh samples of laboratory or commercial peel juice or molasses (see Figure 1a). Because these components copurified with neutral sugars and polyols and samples containing them had a lower sugar content, they may be condensation or decomposition products derived from sugars in citrus molasses during extended storage.

The sugars are accompanied by two isomers of inositol, and in all commercial samples of peel juice and molasses by mannitol and sometimes by traces of glycerol. The presence of *myo*-inositol in citrus peel has been known for a long time (Baier and Manchester, 1949; Krehl and Cowgill, 1950; Wolford, 1958), and citrus fruit is one of the richest sources of this sweet polyol (Krehl and Cowgill, 1950; Wolford, 1958). The identity of the second isomer of inositol is less clear. Two

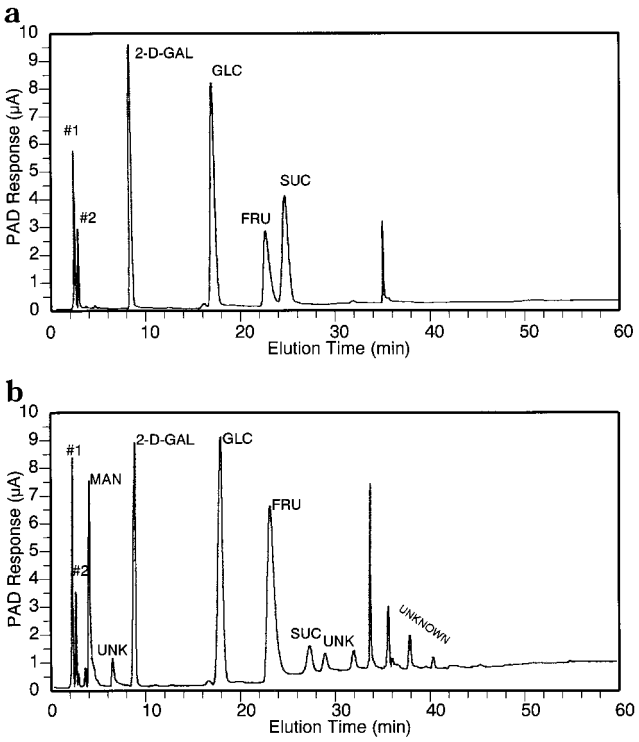

Figure 1. (a) Ion-exchange chromatogram of sugars and polyols in fresh citrus peel juice and molasses. Peaks: 1, *myo*-inositol; 2, *chiro*-inositol; 2-D-GAL, 2-deoxy-D-galactose (internal standard); GLC, D-glucose; FRU, D-fructose; SUC, sucrose. (b) Ion-exchange chromatogram of sugars, polyols, and unknown compounds in citrus molasses stored for long periods of time. Peaks: MAN, mannitol; UNK, unknown compounds; other peaks are labeled as in (a).

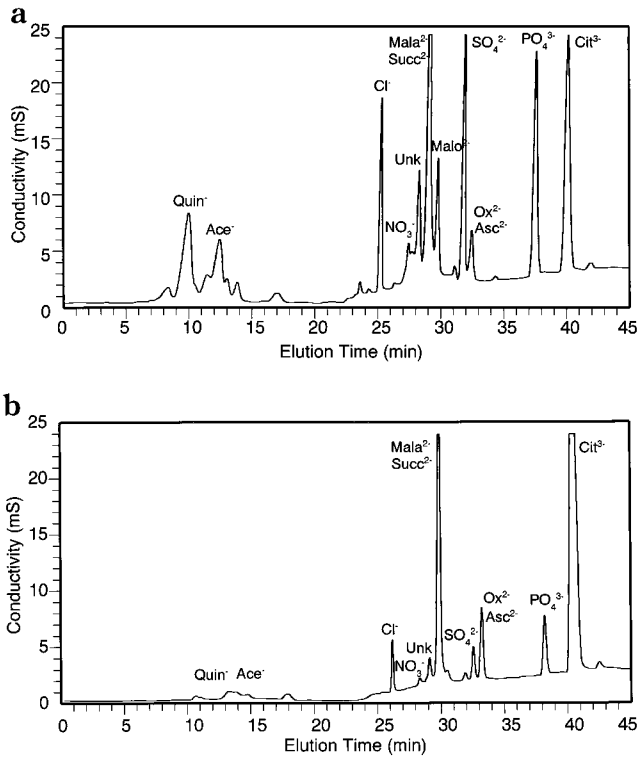

Figure 2. (a) Ion chromatogram of organic and inorganic anions in orange peel juice and molasses. Peaks: $Quin^-$, quinate; Ace^-, acetate; Cl^-, chloride; NO_3^-, nitrate; Unk, unknown; $Mala^{2-}$, malate; $Succ^{2-}$, succinate; $Malo^{2-}$, malonate; SO_4^{2-}, sulfate; Ox^{2-}, oxalate; Asc^{2-}, ascorbate; PO_4^{3-}, phosphate; Cit^{3-}, citrate. (b) Ion chromatogram of organic and inorganic anions in orange juice. The peaks are labeled as in (a).

independent groups of investigators identified the second isomer as either *chiro*-inositol (Dowd et al., 1994) or *epi*-inositol (Cancalon and Parish, 1995). Our chromatographic separations ruled out *epi*-inositol as the second isomer, but we could not confirm the presence of *chiro*-inositol, due to a lack of appropriate standard. (+)-*chiro*-Inositol was also identified (Ohsugi et al., 1991) in the leaves of Satsuma mandarin (*Citrus unshiu*). Mannitol was not present in any sample we prepared in the laboratory from fresh orange peel. Mannitol is a relatively common byproduct of microbial fermentation of fructose (Spencer and Spencer, 1978); therefore, its presence is a strong indication of microbial fermentation of peel, peel juice, or molasses.

The content of the other set of important components of citrus peel juice and molasses, anions of organic and inorganic acids, is shown in Table 3. The majority of anions was separated by ion-exchange chromatography and detected by conductivity detector (see Figure 2a) as described under Materials and Methods. Although we found that this system separated many anions very well, some anions, notably malate and succinate or ascorbate and oxalate, coeluted in single peaks. The separation of anions of monocarboxylic acids was also rather poor. These anions were separated by ion-moderated partition chromatography using polystyrene–divinylbenzene sulfonate resin beads in acidic form and a refractive index detector (Pecina et al., 1984). A chromatogram of a sample of commercial orange juice is shown in Figure 2b. A preliminary comparison of these samples indicates that peel juice and molasses have lower amounts of citric, malic, and succinic acids than orange juice but are enriched in monocarboxylic acids and malonate. The major monocarboxylic acids in experimental peel juice and molasses are quinic and acetic, with trace amounts of lactic and glycolic acids. Fermented commercial samples usually show an increase in lactic acid (see Table 3). We have separated an unknown acid, which may also have been observed in orange fruit extracts by previous investigators (Ting and Vines, 1966; Clements, 1964a,b). The unknown acid comigrates with an authentic sample of glutaric acid on ion-exchange column, but additional analyses are needed for determination of its structure.

Analyses of peel juice and molasses indicate that a bulk of previously unaccounted for dry matter is composed of suspended and polymeric (nondialyzable) solids. The suspended solids are peel tissue fragments, and the nondialyzable solids contain nitrogen and are probably water soluble proteins. The dialyzable solids contain sugars, anions of organic and inorganic acids, inorganic cations (ash components), polyols, and phenolic compounds. Citrus peel juice and molasses also contain extremely bitter limonoids and nonbitter limonoid glucosides (Fong et al., 1992; Hasegawa et al., 1996), but these compounds are present in very low concentrations (<1 wt % of dry solids) and have a minor impact on composition. However, their removal has to be addressed in any upgrading scheme, because limonoids and phenolic compounds are responsible for the unpalatable nature of citrus peel juice and molasses. We have concentrated on removal of objectionable components according to a generalized flowchart outlined in Figure 3.

Removal of Suspended Solids and Water Soluble Polymers. Commercial peel juice and molasses contain

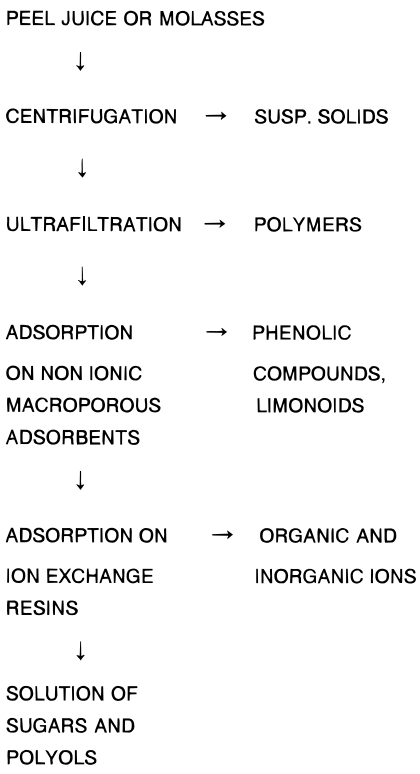

Figure 3. Outline of the purification sequence for upgrading of peel juice or molasses to a sweet product. Components removed at each step are shown on the right side.

significant levels of very fine suspended solids (see Table 1), some of which do not settle even after weeks of storage. Attempts to remove these solids by filtration through filter paper or 1.2 μm glass fiber filter resulted in rapid plugging of all filters. We did not investigate addition of filter aids, because the suspended solids would probably be blended with cattle feed and filter aids could potentially interfere with this application. Therefore, we conducted a preliminary investigation of the removal of suspended solids by centrifugation. Most of the solids in peel juice and molasses diluted to 40 °Brix or less pellet when centrifuged, but even then the supernatants contain a small amount of suspended solids which seem to have the same density as the liquid phase. Two distinct pellets, one floating on the top of the liquid and the other one settled on the bottom, form during centrifugation of molasses at 40−60 °Brix of dissolved solids. The floating pellet is bright yellow in color and waxy or oily in appearance and seems to be derived from the flavedo of the fruit. Since previous investigators (La Flamme and Weinand, 1993) reported severe fouling of the adsorption resin beds by particulate and water soluble polymeric materials, we ultrafiltered the clarified peel juice or molasses through 10000 or 30000 MW cutoff membranes.

Because exceptional fouling of hollow fiber membranes was not observed and ultrafiltration of similar materials was evaluated by other investigators (Hernandez et al., 1992; La Flamme and Weinand, 1993; Milnes and Agmon, 1995), we did not pursue extensive investigations of the ultrafiltration step and concentrated on debittering of ultrafiltered peel juice and molasses.

Evaluation of Macroporous Adsorbents. The initial experiment addressed kinetic aspects of the uptake of phenolic compounds by XAD-16 beads. Removal of phenolic compounds was followed by a decrease in absorbance at 280 and 320 nm, at which flavonoids and *p*-hydroxycinnamic acids show absorption maxima (Macheix et al., 1990). The data summarized in Figure 4 show that ∼80% of the phenolic compounds are adsorbed in 30−60 min and this relatively rapid phase is followed by slow adsorption of an additional 5−10% of phenolic compounds. Removal of phenolic compounds from peel juice and molasses prepared in the laboratory (lower curve) was slightly better than removal from commercial samples. The improved removal from laboratory samples may be ascribed to the lower oxidation and polymerization in these samples, which were much lighter in color than the commercial ones. It must be pointed out that the pH of molasses and peel juice was not adjusted in this and the subsequent set of experiments. The pH of commercial molasses ranged from 4.3 to 6.5, which reflects the extent of liming of the peel prior to the pressing operation. The pH of laboratory peel juice, prepared by pressing unlimed juice, was in the range of 4.6−4.8.

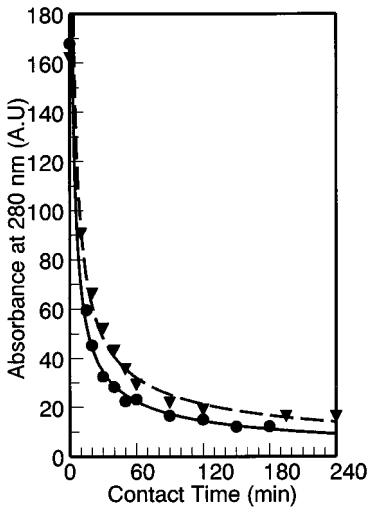

Figure 4. Rate of adsorption of phenolic compounds from orange peel juice (solid line) and commercial citrus molasses (dashed line) by Amberlite XAD-16. Total phenolic compounds were measured by absorbance at 280 mm.

The capacity of three commercial macroporous resins, Amberlite XAD-4, -7, and -16, was evaluated in the next set of experiments, summarized in Figure 5. The three resins were selected on the basis of prior investigations (Hernandez et al., 1992; Shaw and Buslig, 1986; Johnson and Chandler, 1985, 1988) because they have a high capacity for adsorption of bitter principles in citrus juices and are approved for food use. Amberlite XAD-4 and -16 are based on a polystyrene−divinylbenzene matrix, and Amberlite XAD-7 is a cross-linked polyacrylate resin (Johnson and Chandler, 1988). The batch adsorption experiments, in which contact time for each aliquot of the resin was maintained at 1 h, indicated that XAD-16 resin had the highest capacity for phenolic compounds and removed 80−90% of these components from the peel juice or molasses. XAD-7 resin had slightly lower capacity but could still remove ∼70−80% of the phenolic compounds, whereas XAD-4 required 2−3 times more resin for similar extent of removal. Smaller average pore diameter (Johnson and Chandler, 1988) and smaller surface area may account for the lower capacity of XAD-4 resin. Because Amberlite XAD-16 resin was clearly superior to the other two resins, we performed additional experiments using only this resin

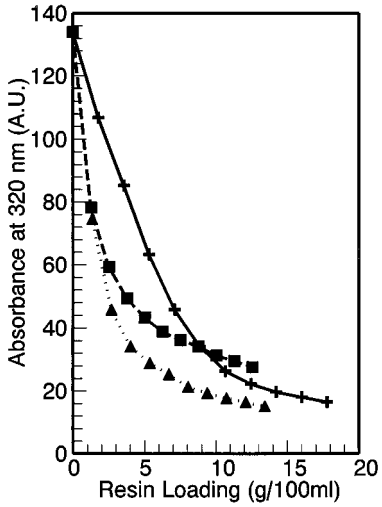

Figure 5. Resin consumption (loading) for removal of phenolic compounds from citrus peel molasses. Resins: (+) Amberlite XAD-4; (■) Amberlite XAD-7; (▲) Amberlite XAD-16.

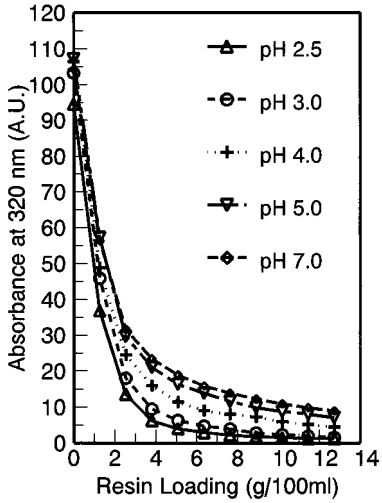

Figure 6. Effects of pH on adsorption of phenolic compounds by Amberlite XAD-16.

as an adsorbent. Results of a study of the effects of pH on adsorption of phenolic compounds from peel juice and molasses are summarized in Figure 6. Decreasing pH of the peel juice increased removal of phenolic compounds by XAD-16 resin from ~90% at pH 5−7 to 98−99% at pH 2−3. pH of peel juice or molasses was adjusted either by replacement of cations by hydronium ions using strongly acidic cation-exchange resin Dowex MSC-1 or by adding dilute sulfuric acid. There did not seem to be any difference in adsorption results between the two methods of pH adjustment (data not shown). The batch adsorption results were verified by adsorption of phenolic compounds at pH 3.0 and 5.8 using adsorption on columns packed with XAD-16 resin. The results summarized in Figure 7 show that at pH 3.0 the column removed all phenolic compounds until ~7−8 bed volumes of peel juice passed through the column, whereas adsorption was incomplete after passage of only 1−2 bed volumes at pH 5.8. Removal of phenolic compounds renders the product colorless, because these components are responsible for the yellow to dark brown color of eluted fractions referred to as "yellow water" by some investigators (Milnes and Agmon, 1995; La Flamme and Weinand, 1993). We performed all adsorption experiments at room temperature (~23 °C) and did not

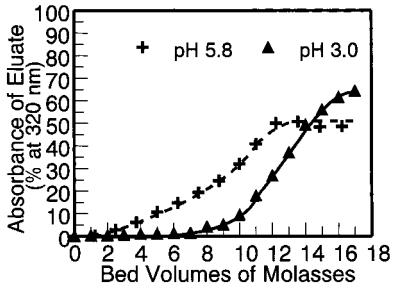

Figure 7. Adsorption of phenolic compounds from peel juice by XAD-16 column at two different pH values.

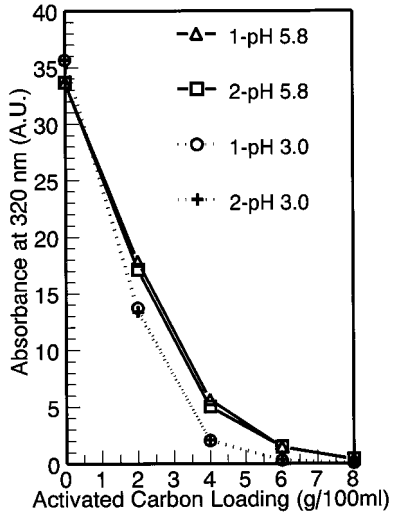

Figure 8. Adsorption of residual phenolic compounds from citrus molasses by activated carbon pellets. Bulk of phenolic compounds was removed by prior adsorption using XAD-16 resin. "1" and "2" refer to two samples of activated carbon.

investigate effects of temperature on the adsorption of phenolic compounds, because prior investigations with grapefruit pulp wash (Hernandez et al., 1992) indicated that these effects would not be important at the dilution (10 °Brix) we were using.

Removal of Residual UV-Absorbing Compounds and Deacidification. The product from the adsorption of phenolic compounds is often yellow in color and sometimes retains traces of bitterness, which would limit its potential applications. The macroporous nonionic adsorbents do not remove polar organic and inorganic ions (Johnson and Chandler, 1985, 1988). The presence of salts of organic and inorganic acids affects the taste of partially purified product as will be discussed below. We have investigated removal of residual phenolic compounds by two methods. The first one, which would not influence the content of polar ions, involved additional treatment with food grade activated carbon. Two commercial samples of pelletized carbon were obtained and tested in the batch adsorption mode using partially purified samples of peel juice and molasses from which most phenolic compounds were removed by adsorption with XAD-16 resin.

Both activated carbon samples reduced residual absorbance at 280 and 320 nm from 30 AU to 0 at the loading of 8 g of activated carbon/100 mL of partially purified peel juice or molasses (Figure 8). Although both adsorbents removed residual phenolic compounds with equal ease, adsorption at lower pH (3.0) again improved the capacity of both adsorbents.

The second method we have investigated involved a treatment with strongly acidic Dowex MSC-1 resin,

which removed cations and decreased the pH of peel juice and molasses to 2.0 but did not remove phenolic compounds. This treatment was followed by adsorption of anions and residual phenolic compounds using weakly basic macroporous anion exchanger Amberlite IRA-93, currently being replaced by the manufacturer with Amberlite IRA-95. Control experiments to deionize and debitter peel juice and molasses using only Dowex MSC-1 and Amberlite IRA-93 resins also removed high levels of phenolic compounds. Approximately 6−7 g of dry IRA-93 or IRA-95 resin/100 mL of 10 °Brix peel juice or molasses (treated first with MSC-1 resin) was required to increase the pH from 2 to 4. This treatment removed 74 and 84% of absorbance at 280 and 320 mm, respectively. Approximately 19 g of dry IRA-93 resin/100 mL of 10 °Brix molasses was needed to increase the pH of the samples from pH 2 to 6, but this treatment removed 95% of respective absorbance at both 280 and 320 mm. The sequential treatment with anion-exchange resins thus effectively removed both polar ions and phenolic compounds. Our results are more positive than those reported by Johnson and Chandler (1988), who observed only weak to moderate capacity of IRA-93 resin for removal of naringin and limonin from citrus juices. These authors did not remove inorganic cations from citrus juices prior to treatment with IRA-93 resin, and the cations probably interfered with adsorption of phenolic compounds by the anion exchanger.

The use of anion-exchange resins for simultaneous removal of phenolic compounds and polar anions suffers, however, from certain drawbacks summarized below. Only 50−60% of UV-absorbing compounds eluted from IRA-93 resin during regeneration with dilute (1% w/v) sodium hydroxide. Some organic acids, for example, malic and citric, are valuable and may need to be retained in the debittered stream. Recovery of these acids from IRA-93 resin would be complicated by the presence of phenolic compounds coeluting with anions of these acids. Therefore, we have separately investigated removal of polar organic and inorganic ions from peel juice and molasses pretreated with XAD-16 resin and in some cases also by activated carbon. The consumption of Dowex MSC-1 resin for removal of cations and adjustment of pH to 2.0 ranged from 4.5 to 6.0 g of dry resin/100 mL of 10 °Brix peel juice or molasses, depending on initial pH and cation content. The addition of 3−6 g of dry IRA-93 or IRA-95 resin/100 mL of pretreated 10 °Brix peel juice and molasses brought the pH to the 3−4 range, removed approximately 85 and 95% of residual absorbance at 280 and 320 mm, respectively, and decreased conductivity of the treated sample by 90−95%. Additional treatment with IRA-93 or -95 resins to a pH range of 4.1−6.0 had a minor effect on the removal of phenolic compounds and practically no effect on residual conductivity (data not shown). Because the increase of the pH from 4 to 6 requires a ∼3-fold increase in resin consumption and provides minor benefits, the deionization and removal of residual phenolic compounds at lower pH (3−4) values appears to be most efficient. The resulting deionized product is a colorless sugar solution, containing minor amounts of two isomers of inositol and, in the case of partially fermented peel juice or molasses, also mannitol and sometimes traces of glycerol (see Figure 1a). Because these polyols are sweet and do not interfere with the taste or aroma of the deionized product, their removal may not be important for potential applications in the food industry. However, unlike treatment with neutral adsorbents, the deionizing step also removes lactic and other odorous organic acids from partially fermented peel juice or molasses and improves the taste of these products.

Regeneration of Amberlite XAD-16 Resin. The macroporous adsorbent resins are relatively expensive materials, which have to be reused many times for debittering to be economically viable. Because the most common eluent for phenolic compounds adsorbed from pulp wash or grapefruit juice is dilute sodium hydroxide (La Flamme and Weinand, 1993; Milnes and Agmon, 1995), we concentrated our investigations on this reagent. We used a protocol suggested by scientists from Koch Membrane Systems, Inc. (Milnes and Agmon, 1995; D. Greenlaw, Koch Membrane Systems, Inc., Wilmington, MA, personal communication, 1997) as a basis of our investigations, except we omitted the final rinse with dilute phosphoric acid because acidified molasses (pH 3.0) had sufficient buffering capacity. The chromatographic columns were packed with XAD-16 beads saturated with phenolic compounds from citrus peel juice or molasses. The resin beds were eluted at different temperatures, first with 10 bed volumes (BV) of 0.5% (w/v) sodium hydroxide followed by 10 BV of deionized water. The absorbance of combined eluate and wash was measured at 280 and 320 nm, respectively. The results indicated that ∼59% of absorbance at both wavelengths was recovered at room temperature (25 °C); the recovery increased to 66−68% at 40 and 60 °C and to 68−71% at 80 °C. Therefore, we have chosen the highest temperature (80 °C) for all subsequent elution experiments. The effects of sodium hydroxide concentration were investigated in the next series of experiments. The results indicate that at 10 BV of eluant the concentration of NaOH can be safely decreased to 0.1 wt % (data not shown). We have also investigated addition of sodium sulfite (0.1% w/v), sodium metaborate (0.5% w/v), ethylenediaminetetraacetic acid (EDTA) tetrasodium salt (0.1% w/v), or tetrasodium pyrophosphate (0.2% w/v) to 0.5% sodium hydroxide eluent as a means to increase recovery of UV-absorbing compounds from XAD-16 beads. The only additive with apparent positive effect was EDTA·Na_4, which increased recovery at 280 nm to 84 ± 1.5% and at 320 nm to 88.5 ± 2.6% of initial absorbance, respectively. The chelating action of EDTA may aid release of additional phenolic compounds from XAD-16 resin by sequestering polyvalent cations that can form insoluble complexes with phenolic compounds.

Because apparent recovery of UV-absorbing compounds from XAD-16 resin may be biased by unpredictable changes in specific absorbance caused by high reactivity of phenolic compounds under alkaline conditions, we also investigated adsorption of phenolic compounds from peel juice and molasses by regenerated XAD-16 resins. A sample of initial XAD-16 resin was used as a control. The results demonstrated that regenerated XAD-16 resin retained high capacity for adsorption of phenolic compounds. The resin beads washed with 10 BV of 0.25−1.0% NaOH solution and 10 BV of deionized water adsorbed on average 96.2 ± 1.23 and 95.2 ± 2.47% of UV absorbance at 280 and 320 nm, respectively, as fresh XAD-16 resin. The XAD-16 resin washed at 40−80 °C with 10 BV of 0.5% NaOH solution, then bleached at 60−80 °C with 2 BV of 0.3% hydrogen peroxide solution, and finally rinsed with 10

BV of deionized water removed 97.2 ± 0.52 and 97.5 ± 1.34% of absorbance at 280 and 320 nm, respectively, of the values obtained with fresh XAD-16 resin.

These results were confirmed by a recycle experiment using a column packed with XAD-16 beads. The regenerated XAD-16 resin removed on average 97.9 ± 2.77 and 96.4 ± 3.77% of absorbance at 280 and 320 nm, respectively, as the same resin during the previous cycle. No change was observed during five adsorption and regeneration cycles. The regeneration of XAD-16 resin by dilute NaOH solution thus appears to be very efficient and probably can be improved to nearly quantitative levels by additional treatment with dilute hydrogen peroxide or other oxidizing agents (Milnes and Agmon, 1995; Greenlaw, personal communication, 1997). We have not investigated regeneration of activated carbon because both manufacturers offer proprietary regeneration services.

Sensory Evaluation of Debittered Citrus Molasses. The acceptance of debittered molasses was evaluated at pH 5.8 and 3.5 as described under Materials and Methods. The acceptance of debittered and deionized samples was also evaluated at pH 5.8, which was the approximate final pH of these samples, but they were not tested at pH 3.5, because addition of any acid for pH adjustment would modify the taste of these products. The two deionized samples received the highest rating in the first (pH 5.8) set, with a mean rating of 5.53 ± 1.720. These samples formed a homogeneous group with debittered laboratory molasses with a mean rating of 4.88 ± 1.242 but were clearly superior to debittered commercial molasses with a mean rating of 3.60 ± 1.472. Some panelists described off-flavors in commercial molasses as rotten or overripe fruit. The difference between debittered commercial and laboratory molasses became even more pronounced in acidified samples. Nearly all panelists (at 0.1% level of significance) much to moderately preferred the acidified debittered laboratory sample over a similar commercial sample in a paired comparison test (Larmond, 1967). These results support the acceptance test using the same verbal hedonic scale as above. The rating means were 5.88 ± 1.315 and 3.56 ± 2.01, respectively, for acidified, debittered laboratory and commercial molasses. These means were significantly different from one another at the 0.1% rejection level. The acidified, debittered commercial molasses had pronounced fermented (rotten fruit and sour milk) off-flavors. These results indicate that debittered or debittered and deionized peel juice and molasses will be an acceptable base for drink products, but the mishandling leading to microbial contamination and fermentation of peel juice or molasses must be minimized. The off-flavors caused by microbial contamination can be removed by additional treatment with ion-exchange resins but at an additional cost.

CONCLUSIONS

Our study extended previous analyses of citrus (i.e., orange or mixed orange and grapefruit) peel juice and molasses to identification and determination of numerous components that are present in nonvolatile solids for these complex citrus processing byproducts. The results confirm that edible sugars, glucose, fructose, sucrose and traces of galactose, form the bulk (~60−70%) of the total solids. The remaining solids can be accounted for as suspended particles of fruit tissue, nondialyzable solids (mainly protein), polyols, anions of organic and inorganic acids, ash components, phenolic compounds, and other minor components, such as limonoids. The identified components account for >90% of the weight of dry total solids, and no other components have been detected in significant (>1 wt %) amounts. Detection of low concentrations of water soluble pectin in both peel juice and molasses was rather surprising, but it could be caused by precipitation of pectin during the treatment of peel with lime.

Because analytical results did not reveal the presence of unusual components, we devised and investigated two variants of a simple process for the removal of bitter and coloring components by adsorption on food grade macroporous resins. The samples of commercial peel juice and molasses were first clarified by centrifugation and ultrafiltration through 10000−30000 NMW cutoff hollow fiber membranes. Bitter and other objectionable low molecular weight components could then be readily removed by adsorption on macroporous resin beads without fouling or plugging problems.

Amberlite XAD-16 was the most efficient adsorbent from the three food grade nonionic macroporous resins we have investigated. Major improvement in adsorption of bitter and coloring compounds by Amberlite XAD-16 resin was accomplished by pH adjustment of peel juice or molasses to <4, either by treatment with sulfonated cation-exchange resin in H^+ form or by adding acid. The capacity of XAD-16 columns increased severalfold, and colorless effluent could be collected at these lower pH values. The XAD-16 columns can be efficiently regenerated by washing with hot (80 °C), dilute (0.1−0.5%) sodium hydroxide, followed by rinsing with deionized water and intermittent bleaching of the resin with 0.3% solution hydrogen peroxide in water. Approximately 95−98% of the adsorptive capacity of the resin has been recovered by these treatments, and the resin can be reused many times. The effluent from macroporous resin columns could then be polished by a treatment with food grade activated carbon or deionized and decolorized by a sequential treatment with cation- and anion-exchange resins. The adsorption of anions on weak anion exchangers Amberlite IRA-93 or -95 also removed the residual phenolic compounds and anions of volatile organic acids that can cause off-flavors in the purified product.

Sensory evaluations of debittered peel juice and molasses indicate that debittered and deionized product from commercial molasses and either debittered or debittered and deionized product from laboratory made peel juice will be acceptable for human consumption as a sweet base for food and beverage products. The debittered products from commercial molasses suffered from off-flavors caused by fermentation of peel and molasses during storage without refrigeration but could be upgraded by additional treatment with ion-exchange resins.

The results of this study demonstrate that citrus peel juice or molasses can be successfully debittered and decolorized by a treatment with macroporous adsorbent resins and thus upgraded for human consumption. The upgraded product can provide additional revenues for citrus-processing plants and improve utilization of citrus fruit during processing. A preliminary economic evaluation of the purification sequence (McAloon, 1999) indicates that the projected cost of purified product is ~24¢/lb of sugar in a syrup form.

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