residual water peak relative to the solute peaks increases. Nonetheless we have easily detected glucose in human cerebrospinal fluid (normal concentration of glucose 64 mg/100 g or 3.5 mM) and at higher concentrations in other body fluids (Eads et al., 1986). Thus, the method is applicable to more dilute systems. In addition aqueous slurries and semisolids may be studied to advantage with this method, as has been shown with spin–echo spectra of minced and whole brain tissue (Eads et al., 1986) and in other tissues and cells (Rabenstein, 1984) whose natural water proton T_2 may sometimes be short enough that a paramagnetic reagent need not be added.

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Selective Removal of Bitter Compounds from Grapefruit Juice and from Aqueous Solution with Cyclodextrin Polymers and with Amberlite XAD-4

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Several polymers were prepared from α-, β-, and γ-cyclodextrin with various cross-linking agents and evaluated for capacities to remove bitter compounds. Naringin and limonin removal was tested in grapefruit juice, as well as removal of these plus caffeine in aqueous solution. They were compared with Amberlite XAD-4 for capacity to remove these compounds from aqueous solution. None of the cyclodextrin polymers removed caffeine. The capacity of cyclodextrin monomer to form inclusion compounds with naringin and limonin was determined with a YM2 membrane and with undissolved cyclodextrin which did not remove any of either compound. The polymers appeared to have about 10 times the capacity of the monomer for formation of inclusion complexes with these bitter components. Of nine media tested, two commercially prepared β-cyclodextrin polymers showed the greatest capacities to remove limonin and naringin combined.

Some processed citrus juices have excessive bitterness that adversely affects the flavor and therefore the marketability of products made from these juices. In California, bitterness occurs mainly in processed navel orange juice; 60 million gallons were processed during the 1982–1983 season (Citrus Fruit Industry Statistical Bulletin, 1984), and about half of that was bitter enough for its flavor to be adversely affected. In Florida, excessive bitterness is a major problem in early-season grapefruit juice, potentially affecting about 6.4 million gallons of single-strength juice. Bitter juices are often blended with less bitter juice so that an even larger portion of the processed juice products are affected by these bitter juices (Shaw, 1985). A process is needed to decrease the bitterness of these juices that does not add anything to the juice or remove desirable juice components.

Several methods have been developed recently to remove the bitter components naringin, limonin, and nomilin from citrus juice by treatment of the juice with insoluble polymers (Johnson and Chandler, 1982; Puri, 1984; Shaw and Wilson, 1983) or immobilized dead bacteria (Hasegawa et al., 1985). None of these processes are currently being used commerically to debitter citrus juices, although some of the insoluble polymers have been approved for food use in the United States.

In earlier studies, we found polymers made from β-cyclodextrin to be effective in removing limonin and nomilin from navel orange juice and in removing these bitter compounds as well as naringin from grapefruit juice (Shaw, 1985; Shaw and Wilson, 1983; 1985; Shaw et al., 1984). Before studies are carried out on pilot plant scale with grapefruit juice, the most effective of several possible polymers of cyclodextrin at debittering citrus juices needs

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to be determined. The relative capacities to form inclusion compounds for cyclodextrin monomer and polymers made from it need to be determined also. From this information, the efficiencies of the polymers that have been prepared can be determined. This report presents necessary information to answer these questions so that larger scale studies can be carried out efficiently.

EXPERIMENTAL SECTION

Samples. Single-strength grapefruit juice (10° Brix and 6% sinking pulp) was prepared by reconstitution of 55° Brix frozen concentrated grapefruit juice containing no added flavor fractions (evaporator "pumpout") with 5.67 volumes of water. Clarified juice was prepared for gravity flow experiments by removing pulp by centrifugation at 1600 rpm for 10 min. Aqueous solutions of naringin up to 1200 ppm were prepared by dissolving the appropriate weighed amount of naringin in deionized water. Limonin solutions up to 20 ppm were prepared by dissolving limonin crystals in 1 mL of HPLC-grade acetonitrile and diluting to 500 mL with water. Limonin solutions were used the same day they were prepared because significant decomposition usually occurred on standing overnight.

α-Cyclodextrin was purchased from Sigma Chemical Co., St. Louis, MO, and β-cyclodextrin from Chemical Dynamics Corp., South Plainfield, NJ. Samples of β- and γ-cyclodextrin were provided by Toyomenka (America) Inc., New York, NY, and research quantities of β-cyclodextrin polymer by American Maize-Products Co., Hammond, IN, and by Toshin Chemical Co., Ltd., Tokyo, Japan.

Analytical Methods. Quantities of limonin and caffeine were determined by HPLC. A 4.6 mm × 10 cm 5-μm Brownlee C-18 column and 4.6 mm × 3 cm guard column containing the same packing material were used. A Perkin-Elmer Model Series 2 pump and Model LC-85B variable-wavelength detector and a Hewlett-Packard 3390A integrator and a 20-μL injection loop were used for all analyses. Limonin in aqueous solution was eluted with a solvent mixture of 50:50 acetonitrile–water at 0.5 mL/min and detected at 207 nm. Limonin in grapefruit juice was determined by an HPLC method reported earlier (Shaw and Wilson, 1984). Caffeine values were determined at 214 nm with a solvent mixture of 15:85 acetonitrile–water at 1 mL/min. Naringin values were determined by using the Davis test (Praschan, 1975) and by the HPLC method of Fisher and Wheaton (1976).

Solubility of β-Cyclodextrin Monomer in Water. A 1.00-g portion of β-cyclodextrin was stirred magnetically in 25 mL of water for 60 min at room temperature. The mixture was filtered through a sintered-glass funnel and the undissolved β-cyclodextrin precipitate dried at 55 °C in a vacuum oven for 2 h to give 0.30 g of recovered cyclodextrin. Thus, the solubility of β-cyclodextrin was 28 mg/1 mL of water at 25 °C. A Davis test on this saturated solution was negative (Davis value 0).

Formation of Inclusion Compounds with Undissolved β-Cyclodextrin Monomer. *Limonin.* A 25-mL sample of 10.2 ppm limonin in water was stirred with 1.7 g of β-cyclodextrin monomer for 60 min at room temperature. At 10-min intervals a 1-mL portion of the mixture was withdrawn, filtered through a 0.45-μm filter, and analyzed for limonin by HPLC. No change in limonin content was found during the sampling period. At the end of the 60-min reaction period the mixture was filtered and the solid precipitate dried, as above, to give 0.92 g of undissolved cyclodextrin monomer.

A 25-mL sample of 10.2 ppm limonin was heated to 80 °C, and 3.0 g of β-cyclodextrin monomer was added. A clear solution was formed in 2 min. The solution was cooled to 4 °C and filtered, and the precipitate was dried, as above, to afford 2.1 g of cyclodextrin monomer. The filtrate contained the same amount of limonin by HPLC (10 ppm) as did the starting solution that was similarly heated to 80 °C for 2 min and cooled prior to use as the standard for HPLC analysis.

Naringin. A solution of 800 ppm naringin in water (25 mL) was stirred with 1.70 g of β-cyclodextrin monomer for 60 min at room temperature. The undissolved cyclodextrin monomer was removed by filtration through a sintered-glass funnel. The filtrate contained 780 ppm naringin by the Davis test and 813 ppm by HPLC and thus contained the same amounts as the starting solution. The precipitate was dried for 1.5 h at 55 °C in a vacuum oven to give 1.0 g of undissolved cyclodextrin.

Grapefruit Juice. A 25-mL portion of centrifuged grapefruit juice was similarly treated with 1.7 g of β-cyclodextrin monomer at room temperature. Neither the naringin (Davis value 960) nor the limonin (8.3 ppm by HPLC) contents were changed by treatment with cyclodextrin monomer.

Membrane Separation of Inclusion Compounds with β-Cyclodextrin Monomer. Fifty-milliliter aqueous solutions of naringin or limonin with or without 1.0 g of added β-cyclodextrin monomer were prepared. When cyclodextrin was added, the mixture was stirred for 15 min. Each mixture was circulated in an Amicon Model TCF 10 ultrafiltration system with a YM2 membrane (molecular weight cutoff 1000–2000). Flow rate through the membrane was 0.33–0.40 mL/min without added cyclodextrin and 0.16–0.17 mL/min with added cyclodextrin at equivalent circulation rates (80 mL/min). Separation was continued each time until 17.5 mL of liquid had passed through the membrane. Permeate samples were analyzed for naringin, limonin, and cyclodextrin as appropriate.

Preparation of Polymers. α-, β-, and γ-cyclodextrin polymers cross-linked with epichlorohydrin were prepared under carefully controlled conditions by a modification of the procedure of Solms and Egli (1965). Thus, a mixture of 25 g of cyclodextrin monomer and 11 mL of water in a 500-mL three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel was stirred as a hot (80 °C) solution of 13.5 g of sodium hydroxide in 13.5 mL of water was added in one portion. Then, 50 mg of sodium borohydride was added (optional) and the mixture was stirred for 2 min. At that point, most of the solid was in solution. A 25-mL portion of epichlorohydrin (Fisher Chemical Co., Fair Lawn, NJ) was added rapidly dropwise over a 2-min interval. The viscous, mostly solid mixture was stirred until it spontaneously heated to 50-60 °C for 30 min. The product was purified as described earlier (34 g) by Shaw et al. (1984). In the polymerization of γ-cyclodextrin, where only 5 g of monomer was used, the reaction mixture was kept in an oil bath at 50 °C during addition of all reagents using one-fifth the above listed amounts. Failure to follow the above procedure exactly often afforded a viscous, liquid, water-soluble polymer.

A polymer cross-linked with diisocyanatohexane (Aldrich Chemical Co., Milwaukee, WI) was prepared from 10.0 g of β-cyclodextrin following the procedure of Mizobuchi et al. (1980) for preparation of their B-HDI-P5.5-A polymer.

A tricarbanilate ester with phenyl isocyanate and β-cyclodextrin was prepared by the procedure of Wolff and Rist (1948).

Debittering Procedures. Standardized procedures were used for treating aqueous solutions of naringin and

Table I. Membrane Separation of Cyclodextrin Complexes with Naringin and Limonin

concn, ppm	concn through membrane: alone ppm	alone %	with cyclo ppm	with cyclo %	cyclodextrin through membrane[a] %	cyclodextrin through membrane[a] wt, g
			Naringin			
400	252	63	136	34	0.53	0.093
800	408	51	246	31	0.50	0.090
1200	571	48	546	46	0.54	0.095
			Limonin			
5	3.0	60	2.0	40	ND[b]	
10	5.4	54	3.5	35	ND	
20	8.4	42	7.8	39	ND	

[a] No naringin or limonin present. [b] ND = not determined.

limonin with various cyclodextrin polymers, and Amberlite XAD-4 polymer (Baker Chemical Co., Phillipsburg, NJ). Thus, either 25 mL of 800 ppm naringin in water was treated with 0.50 g of polymer, or 15 mL of 10 ppm limonin in water was treated with 0.30 g of polymer. Each solution was stirred for 30 min with a magnetic stirrer and then filtered through a 0.45-μm filter prior to analysis.

Clarified grapefruit juice was debittered in small-scale batch processes using these polymers. A 25-mL sample of juice was stirred with 1.0 g of polymer for 60 min by a magnetic stirrer. Portions (1-mL each) were removed at 10-min intervals and filtered through a 5.0-μm filter prior to analysis by the Davis test. Limonin content was determined after 60 min by HPLC.

RESULTS AND DISCUSSION

β-Cyclodextrin Monomer. Experiments were conducted to determine the capacity of β-cyclodextrin to form inclusion compounds with the bitter citrus juice components naringin and limonin (Konno et al., 1982). An earlier study (Shaw and Wilson, 1983) showed that inclusion complexes between naringin or limonin and β-cyclodextrin in solution did not change the apparent concentrations of naringin or limonin as determined by analyses. The solubility of β-cyclodextrin in water at 25 °C was 28 mg/mL and at 80 °C was 120 mg/mL. Addition of excess β-cyclodextrin to an aqueous solution of either naringin or limonin at 25 °C to provide undissolved cyclodextrin (40 mg/mL) for possible removal of naringin or limonin from the solution caused no change in the concentration of either compound after removal of undissolved monomer by filtration. Similarly, addition of excess β-cyclodextrin to grapefruit juice caused no change in naringin or limonin concentrations after removal of the undissolved cyclodextrin monomer. Sufficient cyclodextrin was added at 80 °C to a solution of 10.2 ppm of limonin in water to raise the dissolved cyclodextrin level to 120 mg/mL. When the solution was then cooled to precipitate 70% of the dissolved cyclodextrin, the level of limonin remaining in the solution was unchanged. Apparently, the complex does not precipitate from solution under these conditions.

An alternative method for measuring amount of inclusion complex involved use of a semipermeable membrane with a molecular weight cutoff of 1000–2000. With this membrane, limonin (MW 402) and naringin (MW 580) should mostly pass through the membrane, while their complexes with β-cyclodextrin (MW 1536 and 1714, respectively) should be largely retained by the membrane. The results of studies with aqueous solutions of β-cyclodextrin, limonin, naringin, and complexes of the latter two compounds with β-cyclodextrin are shown in Table I.

With 2% aqueous solutions of β-cyclodextrin (1 g/50 mL, or 0.88 mmol) about 0.09 g (0.07 mmol) consistently passed through the membrane under the conditions used (Table I). Thus, 0.81 mmol of β-cyclodextrin/32.5 mL of retained solution was available for inclusion complex formation with limonin or naringin. At 400 ppm initial concentration of naringin, a 116 ppm difference in the 17.5-mL portions that passes through the membrane gave an excess of 2.03 mg of naringin retained by the membrane in the presence of cyclodextrin. This represents 0.0035 mmol of inclusion complex/32.5 mL of solution, or 1 molecule of inclusion complex/230 molecules of cyclodextrin. Similar calculations at 800 ppm naringin from data in Table I afforded 1 molecule of inclusion complex/165 molecules of cyclodextrin.

Table II. Relative Capacities of Polymers To Remove Bitter Components from Aqueous Solution

polymer	cross-linking agent[a]	% redn in caffeine (500)[d]	% redn in naringin (800)	% redn in limonin (10)
cyclodextrin				
β-A[b]		0	88	95
β-B[b]			81	85
β-C	ECH	0	61[c]	84
β-D	ECH		51	82
β-E	DIC	0	70	95
β-F	PIC		0	17
α-	ECH	0	42	71
γ-	ECH	0	23	86
polystyrene XAD-4[b]	DVB	81	36	100

[a] Cross-linking agents: ECH = epichlorohydrin; DIC = diisocyanatohexane; PIC = phenyl isocyanate; DVB = divinylbenzene. [b] Commercially prepared polymer. [c] At 400 naringin a 79% reduction was obtained. [d] Control values given in ppm in parentheses.

Data from Table II were used to calculate the capacity of β-cyclodextrin polymer to form the inclusion complexes. In experiments with 1 g of β-cyclodextrin polymer (74% cyclodextrin + 26% cross-linking agent)/50 mL of aqueous naringin solution (400 or 800 ppm) the ratios of molecules of inclusion complex to molecules of cyclodextrin monomeric units were 1:24 and 1:16, respectively. Because of assumptions made above concerning passage through the membrane of the complex formed with cyclodextrin monomer, the relative ratios of complex to cyclodextrin monomeric units are approximations only. These data do show, however, that the insoluble polymer seems about 10-fold more efficient at forming a stable inclusion compound with naringin than is the soluble monomer.

With regard to complex formation with limonin, calculations from data in Table I show ratios of inclusion complex to cyclodextrin monomeric units for 5 ppm limonin of 1:18 000 and for 10 ppm limonin of 1:9800. Treatment of 10 ppm limonin with β-cyclodextrin polymer (data on β-C in Table II) gave a ratio for 10 ppm limonin of 1:635. The polymer is about 15-fold more efficient at forming an inclusion complex with limonin than is the monomer. The possibility also exists that the cross-linking agent complexes with the bitter substances and, thus, increases the capacity of the polymer to remove them from solution.

Comparison of Polymers for Debittering. Polymers were prepared from α-, β-, and γ-cyclodextrin with epichlorohydrin as the cross-linking agent and from β-cyclodextrin with other cross-linking agents (Table II). Standardized conditions were used in a batch process with aqueous solutions of naringin and limonin so that a direct comparison of the capacities of these polymers to form inclusion compounds with other bitter grapefruit juice components could be determined. Another bitter food component, caffeine, was included in this study. Since styrene polymers cross-linked with divinylbenzene are

Table III. Comparison of Capacities and Rates for Polymers To Debitter Grapefruit Juice

polymer	cross-linking agent[a]	% redn in[b] naringin 10 min	20 min	30 min	40 min	50 min	60 min	limonin (60 min)
cyclodextrin								
β-A		73	75	76	76	76	74	91
β-B		69	76	76	77	79	78	73
β-C	ECH	29	42	45	49	52	59	75
β-E	DIC	48	57	60	65	65		73
β-F	PIC	0	0	0	0	0	0	47
α-	ECH	42	49	51	48	52	53	77
γ-	ECH	25	33	34	38	40	42	73
polystyrene								
XAD-4	DVB	0	24	30	40	42	47	79

[a] Cross-linking agents as in Table II. [b] Starting grapefruit juice contained 900 ppm naringin and 8.3 ppm limonin.

capable of decreasing naringin and limonin contents in citrus juices (Johnson and Chandler, 1982), we included one of these polymers, Amberlite XAD-4, in the study for comparison.

The two β-cyclodextrin polymers prepared by commercial firms (β-A and β-B in Table II) were the most effective polymers at removing both bitter compounds, naringin and limonin, from solutions. The cross-linking agents for these polymers were unspecified by the manufacturers. The remaining cyclodextrin polymers were prepared in our laboratory. The polymer (β-E) using diisocyanatohexane as the cross-linking agent was most effective at removing limonin and naringin combined. The least effective polymer (β-F) was prepared by esterifying β-cyclodextrin with phenyl isocyanate to form a tricarbanilate. The physical characteristics of this polymer gave it poor "wettability" properties with water and probably accounted for its poor performance. The polystyrene–divinylbenzene polymer completely removed all limonin from solution and thus was superior to any of the cyclodextrin polymers in this respect. However, it was less effective in removing naringin from aqueous solution. Johnson and Chandler (1985) recently reported similar results with this polymer.

Ability of most polymers to remove the important bitter compound, caffeine, was included in this study. None of the cyclodextrin polymers showed any capacity to remove caffeine from aqueous solution at the approximate level present in hot tea (500 ppm). In contrast, the styrene polymer removed most of this compound from solution.

Capacities of most of these polymers to remove naringin and limonin from grapefruit juice were studied also (Table III). Again, standard conditions were used so that direct comparison of polymer capacities could be measured. The two commercially prepared polymers of β-cyclodextrin were the most effective at removing naringin and were both effective at removing limonin from grapefruit juice. The other polymers evaluated were all less effective at removing naringin, but only β-F, the polymer esterified with phenyl isocyanate, was relatively ineffective at removing limonin. These results generally parallel those found with aqueous solutions of naringin and limonin (Table II).

By following the progress of naringin removal at 10-min intervals, the minimum contact time for each polymer was determined. All of the polymers reached virtually full absorption capacity in 10-20 min except for Amberlite XAD-4 and γ-cyclodextrin, the two least effective polymers (excluding the inactive polymer with phenyl isocyanate). This information, as well as capacity to remove bitter compounds, is important in preparation for scaling up the process for larger capacity pilot plant studies.

In conclusion, two commercially prepared polymers of β-cyclodextrin and a β-cyclodextrin polymer cross-linked with diisocyanatohexane showed the greatest total capacities for removing the major bitter components from grapefruit juice. Polymers from the more expensive α-, and γ-cyclodextrins were less effective. Amberlite XAD-4 had a greater capacity to remove limonin (and caffeine) from aqueous solution than did any of the cyclodextrin polymers but was less effective than most cyclodextrin polymers in removing naringin. For future larger scale studies involving debittering of grapefruit juices, either of the commercially prepared β-cyclodextrin polymers seems best. The polymers appeared to have a greater capacity to form inclusion compounds with limonin or naringin than did β-cyclodextrin monomer.

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