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Processing Effects during Commercial Debittering of California Navel Orange Juice

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The advent of commercial debittering of citrus juices in the United States has resulted in concern regarding the compositional and nutritional changes that occur with the use of adsorbents. Such a commercial system was recently built by Dow Chemical at California Citrus Producers, Inc., Lindsay, CA. Treated and untreated lots of California Washington navel orange concentrate were analyzed by four professional laboratories and the laboratories at CCPI for 27 general citrus juice components (including those required for nutritional labeling), 10 minerals, and 20 amino acids. Significant changes included a reduction of limonin, the bitter component of citrus juices and the object of the debittering, and a reduction in essential oils and pulp that can be replenished without violation of the standards of identity for frozen concentrated orange juice or concentrated orange juice for manufacturing. Mineral increases were found to result from the use of mineral-laden water in reconstituting navel concentrate prior to treatment and not from the use of the adsorbent itself.

Excessive bitterness in citrus juices processed from early and mid season Washington navel oranges [*Citrus sinensis* (L.) Osbeck] results from the development of limonin from its precursor, limonoate A-ring lactone, found primarily in the membrane tissues of the fruit. When these membranes are ruptured during processing, the limonoate A-ring lactone comes into contact with the acid environment of the juice, which precipitates the slow conversion to the bitter limonin (Maier and Beverly, 1968). This delayed bitter development has resulted in the sale of bitter juices at reduced prices. High limonin juices, such as early and mid season navel juice, generally cannot be blended into commercial orange juices due to the penetrating flavor of the limonin bitterness. The fresh-market value of Washington navel oranges places them second in popularity among citrus varieties in the world. Limonin does not have time to develop when the fruit is consumed fresh and thus does not affect the fresh-market quality. Limonin bitterness is primarily a problem for the processor of navel juice from fresh-market culls. Debittering of navel orange juice opens up the possibility of blending early and mid season navel concentrates into consumer products without affecting the juice qual-

ity or consumer acceptance.

Methods to commercially reduce the limonin bitterness in processed citrus juices have been investigated for decades (Dekker, 1988). Most methods constitute a lack of economic feasibility or violate federal standards of identity for frozen concentrated orange juice (FCOJ) or concentrated orange juice for manufacturing (COJFM). The use of polymeric adsorbents to selectively remove limonoids from citrus juices has proved to be the preferred method for commercial processors (Johnson and Chandler, 1986; Konno et al., 1982; Maeda et al., 1984; Nisperos and Robertson, 1982; Shaw and Buslig, 1986). Such systems have been used commercially in other parts of the world outside the United States.

With the advent of commercial debittering, questions have arisen concerning the nutritional and compositional changes that take place during debittering. Recently a study was reported that gave preliminary findings on the effects of debittering navel orange juice (Kimball and Norman, 1990). In this study a wider variety of effects were explored to determine if significant nutritional changes occurred that may be of concern to the consumer. Also, significant compositional changes that might

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take place during debittering were investigated to determine if a change in the federal standards of identity is warranted.

MATERIALS AND METHODS

Recently Dow Chemical entered into a joint venture with California Citrus Producers, Inc. (CCPI), a major processor of navel orange juice, providing the first commercial debittering system in the United States. The system consisted of a commercial vacuum distiller used to remove excess oil from freshly extracted juice, two parallel centrifuges to remove excess pulp that may clog the adsorbent, and two columns containing the adsorbent that can be used alternatively for treatment and regeneration in a continuous process that can process juice at about 190 L/min (50 gal/min). Each of the commercial columns contained 1.4 m³ of proprietary Dow hydrophilic adsorbent. Deoiled, depulped, and freshly extracted (or reconstituted) California navel orange juice was processed in 13 000-gal batches and combined into 1000-gal lots of 60–65° Brix concentrate. The adsorbent has an affinity for the oil and requires vacuum deoiling of freshly extracted juice prior to debittering to avoid oil saturation and fouling of the adsorbent. Deoiling is a common practice among the processors of chilled or pasteurized orange juices. Deoiling also occurs during evaporation when processing juice into FCOJ or COJFM. Freshly extracted juices contain as high as 0.180% v/v oil on an 11.8° Brix basis while reconstituted juices contain 0.003–0.010% v/v oil. Commercial juices contain 0.015–0.030% v/v oil. Deoiling below commercial levels was performed prior to debittering. Pulp removed during centrifugation was added back to the debittered juice prior to concentration.

Samples of early to mid season California Washington navel concentrates (60–65° Brix) both debittered and untreated at CCPI were analyzed by four professional laboratories as well as by laboratories at CCPI. Treated and untreated sample pairs were taken from lots processed the same day to minimize differences due to fruit maturity and processing conditions. Each sample represented an independent and separate lot, and thus the results of one laboratory should not be compared directly with another. CCPI analyzed 10 treated and 10 untreated lots for the percent acid as citric acid, Brix/acid ratio, vitamin C, percent oil v/v, and percent pulp v/v according to methods commonly used in the industry (Praschan, 1976). Limonin was determined by using HPLC with a Perkin-Elmer Series 10 HPLC pump set at 1.5 mL/min, a 25 cm × 4.6 mm Du Pont Zorbax CN column and a 5 cm × 4.6 mm Du Pont Zorbax CN precolumn with a mobile phase consisting of ethylene glycol monomethyl ether, 2-propanol, and *n*-heptane in the ratio 10:15:25, a Perkin-Elmer LC-75 variable-wavelength UV detector set at 220 nm, and a Perkin-Elmer Model R100 chart recorder with a speed of 5 mm/min. Sample preparation for the limonin determination consisted of mixing 10 mL of the reconstituted juice with about 60 mL of diatomaceous earth (amorphous diatomaceous silica and crystalline silica). Some diatomaceous earths proved unsuitable for the extraction, especially those obtained from laboratory supply houses. Diatomaceous earth obtained from a local swimming pool supplies vendor proved to be the best. The cake was vacuum extracted with five 60-mL portions of chloroform into a rotary evaporator. The limonin concentrate in the rotary evaporator, along with chloroform rinsings, was filtered through a 2-μm syringe filter, and transferred to a sealed test tube (about 10 mL) and used directly for the HPLC analysis.

The Gesellschaft für Lebensmittel-Forschung mbH (GfL) (Berlin, FRG) performed an adulteration screening commonly used in Europe (RSK) on three treated and three untreated navel lots processed at CCPI. The screening consisted of determinations of total sugars, percent sucrose, percent glucose, percent fructose, percent acid as citric acid, percent citric acid, percent L-malic acid, percent isocitric acid, Brix/acid ratio, sodium, potassium, calcium, magnesium, phosphate, chloride, nitrate, sugar-free extract, formol number, ammonia, 20 amino acids, ethanolamine, hesperidin, water-, oxalate-, and alkaline-soluble pectins, percent carotenoids, and percent cryptoxanthin ester and xanthophyll ester of the carotenoids using standard procedures (Association of the German Fruit Juice Industry, 1987).

General Physics (Columbia, MD) performed a standard adulteration screening consisting of the measurements of percent total sugars, percent sucrose, percent glucose, percent fructose, percent isocitric acid, sodium, potassium, calcium, and magnesium for two treated and two untreated lots using methods commonly used in the United States (Brause et al., 1984).

Medallion Laboratories (Minneapolis, MN) analyzed for percent total sugars, vitamins C, B₁, B₆, and A, percent protein, percent fat, calories, sodium, potassium, calcium, phosphorus, iron, copper, and zinc for five treated and five untreated lots by using methods commonly used in determining nutritional labeling values (AOAC, 1984).

Pent-A-Vate Laboratories (Lindsay, CA) used flame photometry to determine the sodium and calcium levels in two treated and two untreated navel concentrate lots from freshly extracted juice and similar concentrate samples made from reconstituting navel concentrate prior to debittering and reconcentrating (Chapman and Pratt, 1961).

RESULTS AND DISCUSSION

A comparison of laboratory analyses for treated and untreated lots appears in Table I. As can be seen, limonin levels were reduced to below the generally accepted 7 ppm taste threshold (Guadagni et al., 1973). A two-way analysis of variance of all constituents herein reported was performed, resulting in a significant reduction occurring in only four components. Limonin was one of these components, showing a significant variance at the 0.001 level. Limonin levels as high as 30 ppm in early season navel juice are common and have been reduced below the accepted 7 ppm level.

The oil concentrations were significantly reduced during treatment with a significant variance at the 0.001 level. Even though this decrease in oil during debittering is significant, commercial addition of oil to citrus concentrates is a common practice and does not violate standards of identity for FCOJ or COJFM (U.S. Government, 1964).

Pulp also decreased with a significant variance at the 0.001 level. Even though pulp removed in centrifugation prior to treatment was added back after treatment, some pulp became entrapped in the adsorbent and was removed and discarded during regeneration. However, the levels of pulp in our debittered juices are well within the commercially normal range of 8–12%. Pulp addition or removal does not violate existing standards of identity for FCOJ or COJFM (U.S. Government, 1964). Analyses of the limonin content of treated juice with and without pulp addition resulted in an increase of only 0.6 ppm limonin with pulp addition.

Vitamin C, as determined by CCPI, decreased 9% with a significant variance at the 0.001 level. This is partially, at least, attributed to the added heat applied to the juice during debittering. The inbound juice must be at least 120 °F for the adsorbent to remove the limonin. Heat is known to degrade vitamin C in citrus juices (Marcy et al., 1989). The Medallion and RSK vitamin C determinations resulted in no significant variance. However, since a 6-oz serving of treated and untreated orange juice contains more than 100% of the U.S. Recommended Daily Allowance (USRDA) of vitamin C, the slight reduction of this nutrient that may occur during debittering can be considered nutritionally insignificant.

There has been some concern that adsorbent treatment of citrus juices will significantly reduce the nutritious trace minerals and/or increase the levels of detrimental minerals such as sodium (Stutsman, 1988). The effects on mineral composition during debittering are depicted in Table II. By use of a two-way analysis of variance four mineral levels underwent significant increases

Table I. Comparison of General Juice Characteristics of Treated (after) and Untreated (before) Samples of Navel Orange Concentrate Reported on a 11.8° Brix Basis Using Dow's Commercial Debittering Unit

parameter	CCPI[a]		Medallion[b]		RSK[c]		General Physics[d]	
	before	after	before	after	before	after	before	after
limonin, ppm	17.2 ± 1.3	4.9 ± 0.8						
% total sugars			7.93 ± 0.07	7.87 ± 0.06	8.90 ± 0.14	8.94 ± 0.36	9.27 ± 0.45	10.28 ± 0.19
% sucrose					4.22 ± 0.06	4.19 ± 0.27	4.38 ± 0.37	4.88 ± 0.09
% glucose					2.33 ± 0.07	2.37 ± 0.06	2.31 ± 0	2.61 ± 0.07
% fructose					2.35 ± 0.06	2.38 ± 0.04	2.56 ± 0.09	2.79 ± 0.04
% acid as citric	0.98 ± 0.05	0.93 ± 0.05			0.72 ± 0.05	0.67 ± 0.03		
% citric acid					0.79 ± 0.05	0.73 ± 0.03		
% L-malic acid					0.07 ± 0.01	0.07 ± 0.01		
% isocitric acid					0.011 ± 0.001	0.010 ± 0	0.013 ± 0	0.013 ± 0.001
Brix/acid ratio	12.1 ± 0.6	12.7 ± 0.7			16.4 ± 1.1	17.7 ± 0.8		
% oil	0.007 ± 0	0.005 ± 0.002						
% pulp	11.0 ± 0.2	9.6 ± 0.7						
vitamin C, mg/100 g	58.4 ± 2.0	53.1 ± 2.1	46.6 ± 1.1	44.2 ± 2.1	37.8 ± 9.2	37.7 ± 6.0		
vitamin B$_1$, mg/100 g			0.04 ± 0	0.04 ± 0				
vitamin B$_6$, mg/100 g			0.06 ± 0.04	0.10 ± 0.05				
vitamin A, IU/100 g			<50	<50				
% protein			0.57 ± 0.01	0.57 ± 0.01				
% fat			0.50 ± 0.07	0.51 ± 0.04				
calories/100 g			38.5 ± 0.5	38.4 ± 0.2				
hesperidin, mg/L					593 ± 116	441 ± 30		
water-soluble pectin, ppm					270 ± 11	269 ± 18		
oxalate-soluble pectin, ppm					133 ± 7	142 ± 24		
alkaline-soluble pectin, ppm					257 ± 13	247 ± 20		
total carotenoids, ppm					6 ± 1	6 + 0		
% β-carotene of carotenoids					2.5 ± 0.6	2.2 ± 0.1		
% cryptoxanthin ester of carotenoids					19.1 ± 1.1	19.0 ± 0.2		
% xanthophyll ester of carotenoids					7.1 ± 0.7	7.2 ± 0.8		

[a] Averages with standard deviations of 10 lots. [b] Averages with standard deviations of five lots. [c] Averages with standard deviations of three lots. [d] Averages with standard deviations of two lots.

Table II. Comparison of Mineral Levels in Treated (after) and Untreated (before) Samples of Navel Orange Concentrate Reported on a 11.8° Brix Basis Using Dow's Commerical Debittering Unit

parameter	RSK[a]		Medallion[b]		General Physics[c]	
	before	after	before	after	before	after
sodium, ppm	3 ± 2	3 ± 3	10 ± 3	17 ± 3	30 ± 4	85 ± 67
potassium, ppm	1600 ± 10	1607 ± 86	1471 ± 174	1579 ± 100	1711 ± 117	1719 ± 179
calcium, ppm	75 ± 2	78 ± 6	73 ± 25	92 ± 15	104 ± 21	126 ± 52
magnesium, ppm	86 ± 6	93 ± 6			123 ± 6	139 ± 30
phosphorus, ppm			139 ± 49	165 ± 25		
phosphate, ppm	466 ± 30	458 ± 39				
chloride, ppm	64 ± 2	62 ± 8				
nitrate, ppm	2 ± 3	2 ± 2				
iron, ppm			0.71 ± 0.27	0.65 ± 0.22		
copper, ppm			0.11 ± 0.06	0.23 ± 0.12		
zinc, ppm			0.32 ± 0.19	0.55 ± 0.21		

[a] Averages and standard deviations of three lots. [b] Averages and standard deviations of five lots. [c] Averages and standard deviations of two lots.

but only in determinations performed by Medallion. Sodium, potassium, calcium, and copper increased significantly at the 0.025 level. The analysis of variance for the General Physics data showed no significant difference even though differences seem apparent. This is due to the small number of General Physics samples analyzed. These mineral increases were attributed to the use of water in reconstituting concentrate prior to treatment that contained minerals at levels that vary widely. Water addition does not violate the standards of identity for FCOJ or COJFM, and the reconstituting and reprocessing of citrus concentrates is a common though generally undesirable commercial practice. This practice is especially common in juice debittering, where concentrates are transported to the debittering plant, reconstituted, debittered, and then reevaporated. To illustrate the effect of the water on the mineral content of the juice, treated and untreated freshly extracted lots were analyzed for sodium and calcium, common minerals in hard

Table III. Comparison of Sodium and Calcium Levels in Treated and Untreated Lots Using City Water To Reconstitute Concentrate Prior to Treatment and Freshly Extracted Juice without City Water Addition[a]

type of juice processed	sodium,[b] ppm	calcium,[b] ppm
untreated freshly extracted	34.3 ± 4.1	70.5 ± 16.8
untreated reconstituted	404.4 ± 15.1	156.3 ± 3.4
treated freshly extracted	51.1 ± 12.3	75.0 ± 0.3
treated reconstituted	229.6 ± 125.5	143.2 ± 6.7

[a] Pent-A-Vate data are reported on a 11.8° Brix basis. [b] Represents averages and standard deviations of two lots.

water, and compared to treated and untreated reconstituted concentrates. The results are illustrated in Table III. As can be seen in the table, the reconstituted lots contained higher mineral levels than those with no water addition. From these data, it appears that the mineral content of the water used in the debittering process has such a large effect on the mineral content of the juice

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Table IV. Comparison of the Change of Amino Acids and Other Nitrogenous Compounds in Treated (after) and Untreated (before) Samples of Navel Orange Juice Concentrate Reported on a 11.8° Brix Basis[a]

parameter	before[a]	after[a]	RSK range[b]
sugar-free extract	2.97 ± 0.14	2.93 ± 0.36	
formol number (mL of 0.1 N OH)	23.2 ± 0.6	22.2 ± 1.2	
ammonia	0.41 ± 0.08	0.50 ± 0.18	<1.5
aspartic acid	1.51 ± 0.04	1.61 ± 0.33	1.7–3.0
threonine	0.14 ± 0.01	0.16 ± 0.03	0.10–0.30
serine	1.62 ± 0.07	1.83 ± 0.26	1.0–1.8
asparagine	3.90 ± 0.30	4.57 ± 0.49	1.7–4.5
glutamic acid	0.75 ± 0.01	0.61 ± 0.56	0.5–1.1
glutamine	0.40 ± 0.04	0.37 ± 0.18	0–0.5
proline	18.00 ± 3.83	17.97 ± 2.55	3.9–11.3
glycine	0.24 ± 0.01	0.28 ± 0.04	0.15–0.30
alanine	1.36 ± 0.09	1.47 ± 0.15	0.7–1.5
valine	0.15 ± 0.01	0.17 ± 0.04	0.07–0.23
methionine	0.02 ± 0.02	0.01 ± 0.02	trace–0.03
isoleucine	0.04 ± 0.01	0.05 ± 0.01	0.025–0.060
leucine	0.04 ± 0.03	0.02 ± 0.04	0.020–0.060
tyrosine	0.06 ± 0.05	0.02 ± 0.01	0.025–0.10
phenylalanine	0.11 ± 0	0.10 ± 0.01	0.08–0.30
γ-aminobutyric acid	2.53 ± 0.05	2.87 ± 0.44	1.7–3.5
ethanolamine	0.19 ± 0.04	0.20 ± 0.03	<0.6
ornithine	0.07 ± 0.02	0.13 ± 0.02	0.025–0.10
lysine	0.25 ± 0.03	0.32 ± 0.04	0.15–0.40
histidine	0.06 ± 0.01	0.09 ± 0.01	0.03–0.12
arginine	4.11 ± 0.04	4.84 ± 0.67	2.5–6.0

[a] Values represent RSK averages and standard deviations of three lots in millimoles per liter unless otherwise noted. [b] Authentic RSK ranges (Association of the German Fruit Juice Industry, 1987).

Table V. Authenticity Ranges Established by General Physics and by the GfL (RSK) for Parameters Included in Their Analyses on a 11.8° Brix Basis[a]

	RSK range	General Physics range
% total sugars		7.2–10.8
% sucrose	<4.8	3–5.5
% glucose	>2.0	2–3
% fructose	>2.2	2–3
% citric acid	0.77–1.16	
% L-malic acid	0.11–0.29	
% isocitric acid	0.007–0.013	>0.004
% vitamin C	>20.2	
hesperidin, mg/L	<1000	
water-soluble pectins, ppm	<506	
oxalate-soluble pectins, ppm	<202	
alkaline-soluble pectins, ppm	<303	
total carotenoids, ppm	<15	
% β-carotene of total carotenoids	<5	
% cryptoxanthin ester of total carotenoids	<15	
sodium, ppm	<30	<50
potassium, ppm	1415–2325	>1400
calcium, ppm	61–121	65–120
magnesium, ppm	71–152	95–170
phosphorus, ppm		120–310
phosphate, ppm	354–607	
chloride, ppm	<61	
nitrate, ppm	<10	

[a] Analytical results that fall within these ranges are classified as describing authentic orange juice.

that minor deviations due strictly to the adsorbent treatment were undetectable and therefore insignificant. Also, federal nutritional labeling regulations require minerals to be present at levels of at least 10% of the USRDA to be considered significant nutritionally (U.S. Government, 1988). None of the minerals found in citrus juices approach this level. Thus, according to federal definitions, the mineral content of citrus juices, diminished or not, during any type of citrus processing is not nutritionally significant.

The amino acid content of juices has long been used as a fingerprint in identifying juices primarily in detecting adulteration (Kuneman et al., 1988). Each juice has a unique combination of amino acids, and even varieties of the same juice can often be differentiated by the amino acid composition. Some have suggested that debittered navel juice becomes something different from that described in the standards of identity for FCOJ or COJFM and should be identified as such (Stutsman, 1988). However, a close examination of Table IV will reveal that the amino acid composition of treated and untreated navel juice contains essentially the same amino acid profile with no significant statistical variance. Comparison of the measured values to the RSK authenticity ranges shows that only five amino acids fell outside these ranges. Aspartic acid concentrations, both treated an untreated, were below the RSK range. Proline concentrations, both treated and untreated, were above the RSK range. This variance is characteristic of California navel orange juice. The serine, asparagine, and ornithine concentrations for treated samples were slightly higher than the RSK range.

In Table V is a listing of RSK and General Physics authentic orange juice ranges for the compounds included in their analyses (Association of the German Fruit Juice Industry, 1987; Brause et al., 1984). Comparing Table V with Tables I and II will illustrate that most treated and untreated navel juice parameters fall within accepted authentic ranges. Exceptions include the acids, some min-

erals, and cryptoxanthin ester concentrations. Acid levels vary according to maturity, and untreated authentic juices often fall outside the RSK acid ranges. High mineral levels were explained previously as primarily coming from water addition. Slightly higher carotenoids, such as cryptoxanthin ester, are typical of highly colored California orange juice concentrates.

CONCLUSIONS

From this study, no significant changes were found that adversely affected the nutrition, quality, or composition of California Washington navel orange juice that can be ascribed strictly to the use of Dow's polymeric adsorbent. Those few components, other than limonin, that decreased with treatment can either be blended or replenished without violation of existing federal standards of identity. Overall juice composition resulted in only minor variations with treatment, much less than the changes that occur when existing acceptable processing methods such as evaporation, water addition, centrifuging, deoiling, and blending with other varieties are used. There exists no evidence from the amino acid data that navel juice has changed its identity during debittering. Comparison with accepted ranges for authentic citrus juices indicates that the concentration of debittered juice components either falls within the same authenticity parameters as untreated juice or increases slightly out of these authenticity ranges. Limonin removal was pronounced. Since some consumers have an especially high sensitivity to limonin bitterness, limonin reduction could mean greater consumer acceptance and increased nutritional intake inherent in citrus juices. Also, the new debittering process will mean increased profits for navel orange juice processors and potentially for those who process other citrus varieties that are considered bitter juices. These processors will be able to sell higher quality debittered products or blend debittered products into more profitable commodities.

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Limonoid Model Insect Antifeedants

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Two model insect antifeedants, 1α-(3'-furyl)-4β,4aβ-epoxy-5β,8aα-dimethyl-3-oxooctahydro-1H-2-benzopyran (IV) and 1β-(3'-furyl)-4α,4aα-epoxy-5β,8aα-dimethyl-3-oxooctahydro-1H-2-benzopyran (IX), based on the C and D rings of the citrus limonoid limonin have been prepared. Both were shown to have activity comparable to that of limonin as antifeedants against larvae of the Colorado potato beetle, *Leptinotarsa decemlineata* (Say), in no-choice laboratory assays.

The coevolution of insects and plants has resulted in a range of plant defense strategies with an associated array of phytochemical weapons affecting the growth and survival of herbivorous insects (Ehrlich and Raven, 1964). Prominent among these natural products are the insect antifeedants, or feeding deterrents, which depress or terminate insect feeding through mechanisms that may involve chemosensory-based food rejection, toxicity effects, or a combination of modes. Since the expression of these

effects may involve starvation of insects and suppression of growth, development, and reproduction, application of antifeedants as components of integrated pest management programs offers considerable promise. Other potential advantages not shared by many conventional insecticides may include high pest target specificity and facile biodegradation. On the other hand, many of the most potent insect antifeedants thus far isolated are of high structural complexity, and total synthesis of these compounds for agricultural applications will not likely be economically feasible (Menn, 1983). As an example, one of the most prominent antifeedants is azadirachtin

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