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Effects of debittering on red grapefruit juice concentrate

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Abstract

Clarified, debittered grapefruit juice concentrate (64.2 °Bx) was produced by membrane filtration, debittering, and an evaporation process. Debittering by an XAD-16 adsorption column removed more than 78% of bitterness in grapefruit juice, based on naringin content. Also, some of the non-bitter flavonoids, such as narirutin and hesperidin, were nearly completely removed. Other values, such as vitamin C, and total phenolics, based on absorbance at 325 nm, were also reduced ($P<0.05$) after debittering. The vitamin C loss can probably be attributed to juice handling during processing. Absorption spectra in the 200–450 nm region showed characteristic absorption maxima around 280 and 322 nm in the control but no spectral fine structure in debittered concentrate. Besides differences in flavonoid profile, there was a slight difference in colour. Debittered concentrate had less chroma (CIE C^*) and more lightness (CIE L^*) than the control. Thus, the colour of debittered concentrate could be described as slightly paler than that of the control.

Keywords: Clear grapefruit juice concentrate; Vitamin C; Color; Debitter

1. Introduction

Unlike sweet oranges, grapefruit contains bitter flavanone glycosides, such as naringin, neohesperidin, and poncirin (Rouseff, 1980). Naringin is by far the most dominant flavonoid bitter principle in grapefruit (Hagen, Dunlop, & Wender, 1966). As in all citrus, the grapefruit also contains the bitter limonoid, limonin (Maier & Dreyer, 1965). Naringin and limonin impart a bitter and objectionable taste to grapefruit juice, and excessive bitterness of the juice was considered as an important economic problem in commercial grapefruit juice production (Manlan et al., 1990).

Several commercial debittering processes, using polystyrene divinylbenzene adsorbents, have been successfully applied in the citrus industry around the world (Wethern, 1991). This process is designed to treat fruit juice that had problems with bitterness, such as juice extracted from Navel orange or by-products such as pulp-washed juice. Further, the combined technology of ultrafiltration and the debittering system were evaluated for grapefruit juice and pulp wash by Hernandez, Couture, Rouseff, Chen, and Barros (1992), and for various citrus products, including grapefruit juice (Milnes & Agmon, 1995). Recently, Stinson and Barros (1997) pointed out that possible opportunities exist for improving grapefruit juice quality by removal of excessive bitterness or acidic compounds. Since the excessive bitterness in grapefruit juice has limited its consumption, debittered grapefruit juice was considered as a solution to increase the consumption of grapefruit solids through further utilization, such as a sweetening base for fruit beverage formulation and in new product development.

Since debittered grapefruit juice concentrate produced by the combined ultrafiltration and adsorption process is a new type of product, we desired to evaluate the influence of debittering on some chemical compositions of red grapefruit juice.

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2. Materials and methods

2.1. Clarified grapefruit juice concentrate

Debittered membrane-clarified juice concentrate from Ruby Red grapefruit was processed in the pilot plant at the Citrus Research & Education Center, University of Florida, Lake Alfred, FL. For the preparation of membrane-clarified juice concentrate, single-strength grapefruit juice was processed in a pilot plant ultrafiltration-debittering system (Koch Membrane System, Inc., Wilmington, MA), as described previously by Hernandez et al. (1992). It consisted of an ultrafiltration step with three hollow fibre polysulfone ultrafiltration cartridges arranged in parallel (500 KDa molecular weight cutoff, Romicon Inc., Woburn, MA). The debittering column was equipped with 25 l of non-ionic, hydrophobic, cross-linked polystyrene divinylbenzene resin, Amberlite XAD-16 (Rohm & Haas, Philadelphia, PA). A pilot plant scale TASTE evaporator (Gulf Machinery Co., Clearwater, FL) was used for concentration, and the strengths of both concentrates were adjusted to 64.2 °Bx.

2.2. Sample analyses

Each duplicated sample was diluted with water to 25 ml in a volumetric flask before analysis. Analysis of vitamin C was carried out according to the HPLC procedure of Lee and Coates (1987). The chromatographic system consisted of a Waters model 510 pump, a Rheodyne injector, a Spectra Physics model 200 programmable wavelength UV detector and a Zorbax ODS column with 5 μm packing (250×4.6 mm). The ascorbic acid was eluted isocratically with a mobile phase of 2% KH_2PO_4 (pH 2.4) at a flow rate 0.5 ml/min elution. The eluant was monitored at 245 nm.

Flavanone glycosides (naringin, narirutin, hesperidin, and neohesperidin) were analyzed by a gradient HPLC method (Kirksey, Schwartz, Hutfilz, Gudat, & Wade, 1995) with a slight modification. The HPLC used a Supelcosil LC-18 (150×4.6 mm, 3 μm) column and was eluted with a binary gradient of a 10 mM KH_2PO_4 pH 3.1 (eluent A) and 70% acetonitrile/water (eluent B), using 0–3 min, 0% B; 3–38 min, 42% B; 38–40 min, 100% B; and 40–50 min, 100% B. Detection was conducted at 280 nm. The sample was prepared by dilution with 40% acetonitrile (1:1), centrifuged (6500 rpm for 5 min), and filtered through a cellulose acetate membrane filter, 0.45 μm. Limonin was analyzed by an isocratic HPLC method with a Supelco CN column (250×4.6 mm, 5 μm), acetonitrile/water (68:32), and detection at 214 nm (Widmer, 1991).

Colour values (CIE L^*, a^*, b^*) were measured in transmittance mode by a Macbeth colour-eye 3001 spectrophotometer (Macbeth Division of Kollmorgen Instruments Corp., Newburgh, NY). Chroma $[(a^{*2}+b^{*2})^{1/2}]$, and hue angle (tan $^{-1}$ b^*/a^*) were calculated from tristimulus values CIE L^*, a^*, and b^* (Lee & Chen, 1998).

The °brix, pH, titratable acidity (as% citric acid) and formol value were analyzed according to methods commonly used in the citrus industry (Kimball, 1991). The polyphenolic content was estimated as the spectral absorbance of the alcohol-diluted sample at 325 nm, as described by Petrus and Dougherty (1973).

The data were analyzed using SigmaStat software from SPSS Inc. (Chicago, IL) with significance at $P<0.05$. The results were submitted to analysis of variance (ANOVA), and t-test.

3. Results and discussion

3.1. Effects of debittering on juice quality

In Table 1, major differences in juice composition between debittered concentrate, which was processed through an ultrafiltration system to separate the pulp and further processed through a debittering unit to remove the bitterness, and control (non-debittered concentrate) are listed. Since the debittering process, using polystyrene divinylbenzene adsorbents (PSDVB), is known to remove the bitter compounds (Manlan et al., 1990), some differences in chemical compositions between the two concentrates were expected.

Naringin, which is a major bitter compound, was 575 mg kg^{-1} in control, and less than 3 was found in the debittered concentrate. Also, some of the non-bitter flavonoids, such as narirutin and hesperidin, were nearly

Table 1
The characteristics of clear red grapefruit juice concentrate before and after debittering[a]

Parameters	Control	Debittered
°Brix	64.2	64.2*
PH	3.3	3.3*
Titratable acidity	5.9	5.6*
Vitamin C (mg/100 ml)	33.3	24.6
Formol values (meq AA/100 ml)	3.0	2.9*
Polyphenolics (@ 325 nm)	2.0	0.2
Naringin (mg kg^{-1})	576	2.7
Narirutin (mg kg^{-1})	163.0	0.9
Hesperidin (mg kg^{-1})	13.2	0.0
Neohesperidin (mg kg^{-1})	6.4	0.0
Limonin (mg kg^{-1})	6.4	0.0
CIE colour parameters		
L^*	97.1	97.9*
a^*	−3.4	−1.1
b^*	9.6	5.5
Hue (H^*)	109	101
Chroma (C^*)	10.2	5.6

[a] Measurements are mean values and based on 10 °Brix.
* Not significant ($P>0.05$).

completely removed (Table 1). Limonin, which is the predominant factor in the perception of bitterness in grapefruit juice, was also completely removed from the debittered concentrate (Table 1) as demonstrated previously with XAD-16 resin by Couture and Rouseff (1992). Naringin and limonin are essentially neutral molecules, but it has been known that polymeric adsorbents are relatively more selective for limonin than for naringin (Manlan et al., 1990). Debittering treatment removed more than 78% of bitterness in grapefruit juice, based on naringin content.

Other values, such as vitamin C, and total phenolics, based on absorbance at 325 nm, were also reduced after debittering. The vitamin C loss can probably be attributed to juice handling during processing. The effect of adsorbent resin treatment of citrus juices on the vitamin C content has been reported by a number of researchers, from no measurable loss up to 33% loss, depending on the types of adsorbents used in the debittering process (Matthews, Rouseff, Manlan, & Norman, 1990). However, it should be noted that there were no significant differences ($P > 0.05$) in °brix, acidity, and total amino acid content as previously reported for orange juice by Kimball and Norman (1990).

Previously, a two-step treatment of juice, through both cation and anion exchange resins, had been successfully used to reduce bitterness to acceptable levels in grapefruit juice, and improvement in colour stability, due to removal of compounds that promote browning, was indicated (Onayemi & Bruemmer, 1984). Ion exchange resins were very effective in removing the amino acids and ascorbic acid reactants in the juice (Onayemi & Bruemmer, 1984), which are known to affect the discoloration of stored juice and concentrate, in large part (Nagy, Rouseff, & Lee, 1989). However, debittered juice, using a polymeric adsorbent, such as the XAD-16 used for this study, does not seem to effectively remove the colour-destabilizing compounds from clear grapefruit juice, as shown in Table 1.

Fig. 1 shows the differences in absorption spectra, from as well as HPLC profiles recorded at 280 nm for both control and debittered clear grapefruit juice concentrates. These absorption spectra, in the 200–450 nm region, showed characteristic absorption maxima around 280 and 322 nm in the control but no spectral fine structure in debittered concentrate (Fig. 1). The visible portion of the spectrum is due mainly to the carotenoids present. The ultraviolet portion is due mainly to the total polyphenolics (325 nm), and total flavonoids (280 nm), as characterized by Petrus and Dougherty (1973). The debittering process apparently altered profiles of strong UV-absorbing compounds in the concentrate which provided initially lower absorption values and intensities compared to the control

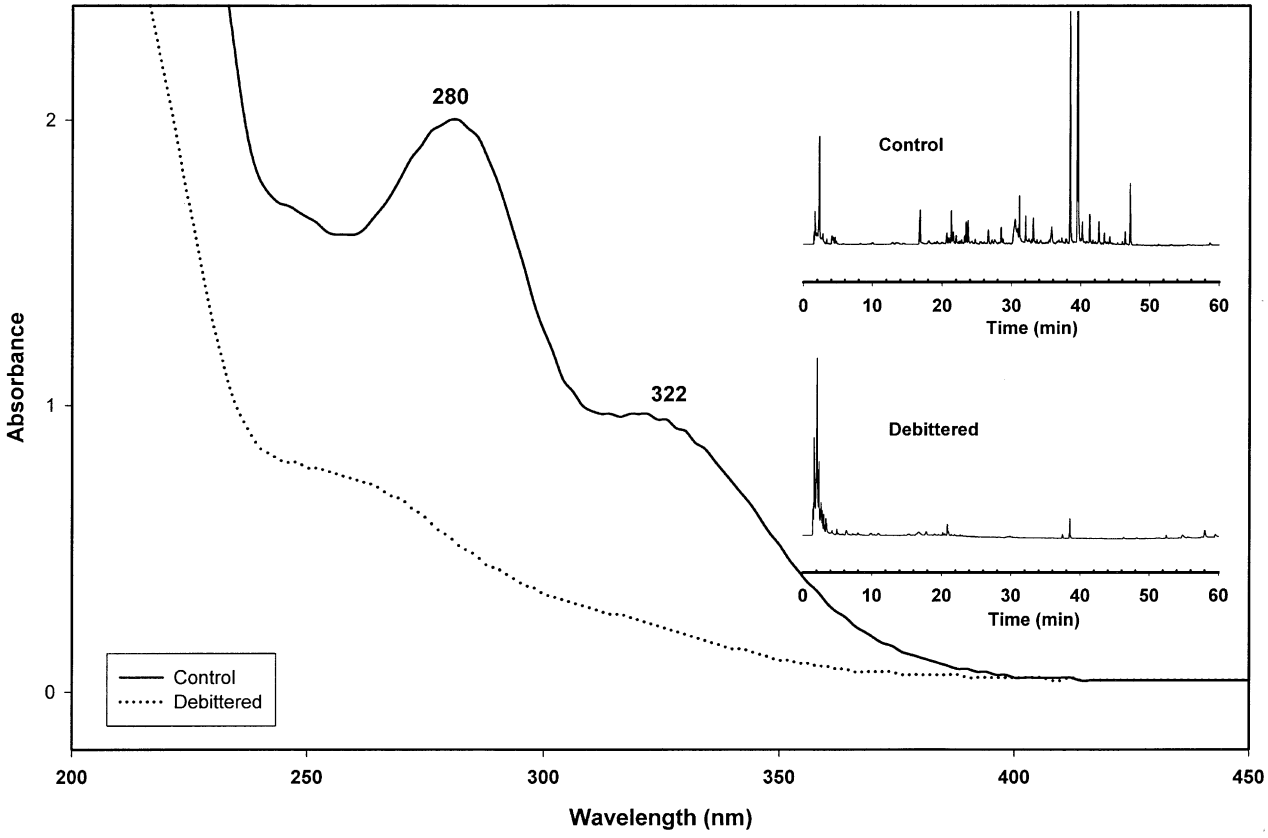

Fig. 1. Spectral characteristics and HPLC (at 280 nm) profiles for debittered clear grapefruit juice concentrates.

concentrate. The HPLC profiles, measured at 280 nm for both concentrates, showed the effectiveness of debittering more clearly, as presented in Fig. 1.

Besides differences in flavonoid profile, there was a slight difference in colour. Since there is no distinctive colour in clarified concentrates after ultrafiltration, the lightness (CIE L^*) and chroma (CIE C^*) values were used to describe any colour differences between control and debittered concentrates. Debittered concentrate had less chroma and more lightness than the control (Table 1). Thus, the colour of debittered concentrate could be described as slightly paler than that of the control.

In summary, a debittering process, utilizing polymeric adsorbent, selectively reduced the bitter compounds in grapefruit juice.

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