The Industrial Solution to Citrus Juice Bitterness

by Dan A. Kimball, California Citrus Producers, Inc., Lindsay, California

The Washington navel orange is the best eating orange in the world. This is because it is less juicy and therefore less messy to eat, it is seedless, and it has excellent flavor. It is second in popularity of any fruit, second only to the Valencia orange.

This is remarkable considering that the Valencia orange grows under a wide range of climate and soil conditions. The Washington navel, however, can grow only in Mediterranean climates such as Australia, South Africa, around the Mediterranean basin, and in California.

In Florida, where twice the citrus is grown as in California, navel oranges do not grow well. Florida, due to its climate, has centered its citrus industry around juice products with about 90 percent of its citrus going to citrus proccessors.

In California, about 70-80 percent of the oranges are marketed fresh. Marketing fresh fruit is approximately ten times more profitable than marketing juice or other byproducts.

About two-thirds of the oranges in California are navel oranges with the remainder being of the Valencia variety. These two varieties provide a back-to-back year-round season with fresh fruit citrus being available essentially at any time of the year.

The navel orange does have one defect. In the membrane of the juice cells is a tasteless compound called limonate A-ring lactone. When the membrane of the fruit is ruptured, such as during processing, this compound comes into contact with the acid environment of the juice and slowly is converted into the highly bitter compound limonin.

This conversion is slow enough not to affect the eating quality of the fresh fruit. However, if early or mid-season navel juice is stored for any length of time, limonin is sure to develop at levels above the generally accepted taste threshold of about 6-7ppm.

Early and mid-season navel juice constitutes about half of the navel juice produced in a season in California and represents approximately 3-5 percent of the orange juice supply in the United States. Other citrus juice varieties that are important commercial products such as grapefruit, certain mandarin varieties and hybrids grown in the orient, and certain blood oranges grown in the Mediterranean basin exhibit similar bitterness problems.

Even though some bitterness is considered desirable in certain products—such as grapefruit juice—generally, consumer acceptability is inversely proportional to limonin content and bitterness. Limonin bitterness is difficult to mask in blending and excessively bitter juices are generally sold at a lower price to the manufacturers of drinks that contain low levels of juice.

Reducing limonin content

Various preharvest and postharvest techniques for reducing this bitterness have been proposed (Kefford and Chandler, 1961) (Maier et al. 1973) (Hasegawa et al. 1977) (Sakamoto et al. 1985) (Orme and Hasegawa, 1987). However, these methods

 0272-2666/90/0003-4101$04.00/00—

either do not reduce the limonin levels sufficiently or are too costly or cumbersome to the navel grower who receives the bulk of his profits from the fresh fruit market.

The addition of taste suppressers, such as neodiosmin (Guadagni et al. 1976), would violate federal standards of identity for 100 percent orange juices. The use of immobilized enzymes or bacteria that degrade limonin (Hasegawa et al. 1985) has proved difficult to scale up to commercial levels. The use of supercritical carbon dioxide (Kimball, 1987) has proved to be effective but too costly for commercialization.

The use of ion exchange or adsorption resins in debittering citrus juices was first investigated by Chandler (1968). Chandler found that cellulose acetate effectively removed limonin from citrus juices but did not hold up to the rigors of caustic clean-up, necessary in the use of any citrus processing equipment. The resin would break down into a fine powder with regeneration or clean-up.

About a decade later, more durable ion exchange resins were reported to be effective in linonin removal (Kitagawa et al. 1983) (Maeda et al. 1984). Ion exchange resins have since been used to deacidify citrus juices with the emergence of a new standard of identity for reduced acid juices.

The acid tartness combined with the sweetness of the sugars produces the major portion of the flavor characteristic of citrus juices. The removal of the limonin bitterness without significantly affecting this acid tartness has been the goal of navel orange juice processors during the past decade. The acids from early and mid-season navel juice are generally needed to blend with the acid deficient late season navel juice.

The first adsorbent that was reported as being effective in removing limonin was β-cyclodextrin (Konno et al. 1982). Cyclodextrin, however, has yet to achieve FDA approval for use in food processing. Private resin manufacturers have since developed highly stable proprietary polystyrene polymeric adsorbents that are FDA approved and that have been shown to be very effective in limonin removal under commercial and industrial conditions.

Commercial debittering

Recently, Dow Chemical (Midland, MI) and California Citrus Producers, Inc. (Lindsay, CA) produced the first commercial citrus juice debittering system in the United States. The system consists of a commercial deoiler to reduce the essential oil level, up to 0.180 percent of freshly extracted juices, down to below levels of about 0.015 percent. Unless removed, this oil can be adsorbed by the resin and reduce the limonin removal efficiency.

The juice then is depulped down to levels of about 1 percent using commercial centrifuges. Pulp can become entrapped in the resin and clog the column. Pulp removed during centrifugation is generally added back after resin treatment in order to restore the character of the juice.

Small but significant amounts of oil and pulp are removed during resin treatment (Kimball and Norman, 1989). However, oil and pulp can be removed or added to 100 percent orange juice products without violation of federal standards of identity.

The Dow debittering system consists of two columns, each containing about 2.8 m^3 of Dow hydrophilic adsorbent. The two columns can be used alternatively for debittering and regeneration to provide for a continuous system that can process juice at the rate of about 50 gallons per minute.

Without the advent of commercial navel orange juice debittering in the United States come the questions as to how this new technology affects juice composition. The first concern is one involving the standards of identity for 100 percent orange juice products.

Existing standards of identity do not mention the use of adsorption or ion exchange resins except for the standard of identity for reduced-acid orange juice. Reduced-acid orange juice must use ion exchange technology. However, other standards of identity do not specifically exclude resin treatment.

The validity of modifying the standards of identity for 100 percent orange juice products to describe legal use of ion exchange resins becomes a matter of degree. Some juices, such as apple, white grape, and pear, are sometimes processed with ion exchange resins to the degree that the only remaining authentic components are sugar and water. The dramatic compositional change would clearly justify a change in the standards of identity.

On the other hand, debittered navel juice undergoes very light treatment with the only significant compositional change being the loss of as much as 25 ppm of the highly bitter limonin (Kimball and Norman, 1989). This recent study by Kimball and Norman found no justification for modifying the standards of identity for debittered navel orange juice.

When considering the dramatic compositional changes that occur during evaporation, deoiling, centrifuging, oil and pulp addition, water addition, and blending of up to 10 percent tangerine or tangerine hybrids (all legal methods for producing frozen concentrated orange juice or concentrated orange juice for manufacturing), debittering becomes essentially a non-process in regards to orange juice composition.

The other concern regarding orange juice debittering is whether or not special labeling requirements should be imposed. Again, the matter of orange juice compositional changes during debittering arises and, again, no significant compositional changes have been found that would indicate that debittered orange juice is not the same as commercial orange juice.

Consumers that have special sensitivities to specific compositional changes in orange juice have a right to have such changes declared on the label. However, the work of Kimball and Norman (1989) again revealed that no significant compositional changes in minerals, organic acids, amino acids, carbohydrates, nutrients, carotenoids, or flavonoids occured during the debittering of navel orange juice.

It should also be noted that debittering represents approximately a 20 percent increase in the monetary value of navel juice. Any feasible debittering method must fall within this relatively narrow profit margin.

Since navel orange juice constitutes only about three to five percent of the orange juice supply in the United States, any labeling requirements would render the process unfeasible. The reason for this is that if the purchasers of products containing debittered navel juice were required to declare the debittering, they would simply purchase other juices instead of debittered navel juice.

Implications of debittering technology

Debittering of navel orange juice has many side benefits. Since many people are especially sensitive to limonin bitterness (down as low as 1 ppm), a reduction of limonin levels in the industry may mean an increase in overall citrus juice consumption. This increased consumption would also mean an increase in the consumption of the nutrients inherent in the juice and thus better health for the consumer.

Debittering has already reduced the amount of imported concentrate needed to make commercial blends, which has in turn reduced the trade deficit that is crippling the country's economy. Additionally, navel orange juice and grapefruit juice processors will be able to blend their products into more profitable commodities.

The development of debittering technology goes beyond the solving of one of the most difficult problems ever to face the citrus industry. The commercial removal of limonin opens up many doors.

First, there is no commercial source of limonin. Limonin is important in the development and calibration of limonin detection methods used in citrus quality control. It has been shown to be an effective and ecologically safe antifeedant for a number of agricultural pests (Klocke and Kubo, 1982) (Alford and Bentley, 1986) (Bilton et al. 1985). Since limonin is nontoxic to humans it becomes an attractive alternative to pesticides.

Recently limonin and related limonoids have been reported to show anticarcinogenic activity (Miller et al. 1989). Such applications would be futile without a commercial source of the compound. Commercial debittering provides a linonin-rich waste stream that shows promise as a commercial source of limonin and other limonoids.

Commercial application of adsorption technology opens up the possibility of its use removing undesirable components in other foods and beverages such as caffeine, bitter components in beer, undesirable colors, and perhaps even macromolecules such as cholesterol. Also, adsorbents could easily be used in the extraction of flavors, aromas, and other desirable components from raw materials or other foods and beverages.

On a more romantic note, citrus juice debittering represents a major step forward by man, who is gaining more and more control over nature herself, specifically over the foods and beverages she gives him to consume.

Debittering literally has become a winning technology for everyone.

References

Address correspondence to A. Kimball, California Citrus Producers, Inc., 525 E. Livermore Ave., Lindsay, CA 93247 USA.

A R Alford and M D Bentley, Citrus limonoids as potential antifeedants for the spruce budworm *(Lepidoptera: Tortricidae)*, *J Econ Entomol* **79**, 35-38 (1986)

N J Bilton, H B Broughton, S V Ley, Z Lidert, E D Morgan, H S Rzepa and R N Sheppard, Structural reappraisal of the limonoid insect antifeedant azadirachtin, *J Chem Soc Chem Commun* (14) 968-71 (1985)

B V Chandler, J F Kefford and G Ziemelis, Removal of limonin from bitter orange juice, *J Sci Food Agric* **19**, 83-86 (1968)

D G Guadagni, V P Maier and J G Turnbaugh, Effect of neodiosmin on threshold and bitterness of limonin in water and orange juice, *J Food Sci* **41**, 681-684 (1976)

S Hasegawa, H Yokoyama and J E Hoagland, Inhibition of limonoid biosynthesis in leaves of *Citrus limon.* by triethylamine derivatives, *Phytochemistry* **16**, 1083-1085 (1977)

S Hasegawa, C E Vanercook, G Y Choi, Z Herman and P Ou, Limonoid debittering of citrus juice sera by immobilized cells of *Corynebacterium facians*, *J Food Sci* **50**, 330-332 (1985)

J F Kefford and B V Chandler, Influence of rootstocks on the composition of oranges with special reference to the bitter principles, *Aust J Agric Res* **12**, 56-68 (1961)

D A Kimball, Debittering of citrus juices using supercritical carbon dioxide, *J Food Sci* **52**, 481-482 (1987)

D A Kimball and S I Norman, Processing effects during commercial debittering of California navel orange juice, presented to the American Chemical Society, Miami, FL (September 12, 1989)

H Kitagawa, S Kamei and K Kawada, Reduction of acidity in Satsuma mandarin juice with ion exchange resins, *J Japan Soc Hort Sci* **52**, 189-195 (1983)

J A Klocke and I Kubo, Citrus limonoid by-products as insect control agents, *Ent Exp and Appl* **32**, 299 (1982)

A Konno, M Misaki, J Toda, T Wada and K Yasumatsu, Bitterness reduction of naringin and limonin by β-cyclodextrin, *Agric Biol Chem* **46**, 2203-2208 (1982)

H Maeda, Y Takahashi, M Miyake and Y Ifuku, Studies on the quality improvement of citrus juices and utilization of peels with ion exchange resins. 1. Removal of bitterness and reduction of acidity in Hassaku *(C. Hassaku Hort. Ex. Tanaka)* juice with ion exchange resins and adsorbents, *Nippon Shokuhin Kogyo Gakkaishi* **31**, 413-420 (1984)

V P Maier, L C Brewster and A C Hsu, Ethylene-accelerated limonoid metabolism in citrus fruits: a process for reducing juice bitterness, *J Agric Food Chem* **21**, 490-495 (1973)

E G Miller, R Fanous, F Rivera-Hidalgo, W H Binnie, S Hasegawa and K T Lam, The effect of citrus limonoids on hamster buccal pouch carcinogenesis, *Carcinogenesis* **10**, 1535-1537 (1989)

E D Orme and S Hasegawa, Inhibition of nomilin accumulation in *Citrus limon* fruit by naphthaleneacetic acid, *J Ag and Food Chem* **35**, 512-513 (1987)

K Sakamoto, A Inoue and M Iyama, Effect of high temperature storage on the contents of limonin and nomilin in navel orange and Hassaku *(Citrus Hassaku)*, *Bull Hiroshima Prefectural Food Tech Res Center*, (17) 41-44 (1985)