Summary

Storage of 42° Brix Pineapple and Valencia orange concentrates at 40° F. resulted in increased gelation, clarification, and apparent pulp content, whereas pectin decreased. Total glycosides, as hesperidin, remained constant in these products during storage. The experimental packs heated at 1- and 2-fold were more stable than those heated at 3- and 4-fold; also all of the Valencia concentrates, control and heat-treated, were more stable than the Pineapple packs.

Literature Cited


Purification of Naringin

R. Hendrickson and J. W. Kesterson
Florida Citrus Experiment Station
Lake Alfred

The pharmaceutical usefulness and physiological importance of naringin has long been overlooked, even though its characteristic bitterness is a nostalgic reminder of early medicines. Prime interest has been centered on the tasteless glucoside of sweet oranges, hesperidin, which has been closely associated with all vitamin P investigations. Circumstantial evidence has pointed to the fact that naringin may have an even greater pharmacological activity as previously shown by Armentano (1) and recent work on antiviral activity (4). Sufficient evidence has been accumulated to encourage the pharmaceutical industry to objectively re-evaluate naringin. An investigation was therefore undertaken to find an improved naringin purification procedure for preparing a high purity product.

As with many products, naringin has a much higher solubility in hot water than in cold and is the basis for an extraction and purification technique reported by Poore (7). According to this method, crude naringin is extracted from chopped grapefruit peel by adding four parts of water and heating to 90° C. The water extract is filtered off after five minutes and the clear extract concentrated to approximately one-ninth the original volume. The concentrated extract is allowed to crystallize for two days in a cool place and then filtered. The isolated naringin crystals are then purified by the following technique. First dissolved in a small amount of hot water containing 20 percent alcohol, impurities are precipitated by adding an excess of neutral lead acetate with the excess lead eliminated by passing hydrogen sulfide through the solution. After filtering, naringin is crystallized by concentrating the solution and allowing it to stand in a cool place. The naringin is further purified by dissolving it in small amounts of hot water, from which it will recrystallize upon cooling. The pronounced solubility of naringin in water above 50° C. has been shown by Pulley (8) who plotted its solubility at numerous temperatures. The simplicity of recrystallizing naringin from water can readily be seen from his plotted solubility curve which shows naringin to be more than 10 percent soluble at 75° C. and less than 0.02 percent soluble at 6°C. This decreased solubility of naringin at low temperatures may at times cause the precipitation of this substance in canned grapefruit sections and juice.

Naringin may also be recrystallized from water by adding an alkali, which greatly increases its solubility followed by acidification, and is the basis of another extraction technique.
The addition of acid forces the recrystallization of naringin, but the compound thus obtained is yellow. It was found difficult to remove this color even when activated carbon is used.

The need for an even better method of purifying naringin became evident in the over-all investigation on the recovery of citrus glycosides. Some of the results have been reported previously by the authors (6), but the optimum methods of purifying crude naringin required further study.

**Extraction Technique and Discussion**

In the following investigation three different samples of crude naringin were employed. Two samples used were purchased and analyzed 81 and 86 percent pure by the Davis test (5) while the third sample was only 29 percent pure. This last sample was typical of the crude naringin obtained in the alkaline extraction of grapefruit peel by the Baier process (3). About 50 percent of the impurities in this product is a filter-aid which is added to facilitate the final extraction.

All naringin samples and extracts were analyzed by the Davis test (5).

The first hopeful sign of a new method to purify naringin occurred when an attempt was made to dissolve and filter a hot, highly concentrated solution of naringin in 99 percent isopropyl alcohol. Before the filtration was more than one-third complete the entire mass had become granular, stiff, and finally solidified. The product was crystalline, with the minute crystals being needle-shaped.

Upon stirring 30 g. of a purchased naringin sample (86 percent pure) in 150 ml. of boiling isopropyl alcohol, a solution was obtained that filtered readily leaving a residue of 2.5 g. of which 0.5 g. was found to be naringin. The clear filtrate, when boiled, quickly seeded itself and within five minutes had crystallized into a solid mass. After diluting with 150 ml. more of isopropyl alcohol and stirring to a thin slurry, the naringin was filtered and dried at 85° C. There was an 87 percent recovery of a very white product which analyzed as being 95 percent naringin. The filtrate was found to have 1.0 percent naringin still in solution. When this trial was repeated with a few modifications, such as stirring the initial solution longer, permitting the naringin to crystallize over a longer period of time, and washing the final product with more isopropyl alcohol, even better results were obtained. Recovery was improved to 89 percent; the final product was exceedingly white and analyzed as being a 100 percent pure product by the Davis test.

Effect of Recycling Alcohol. — In repeated trials where attempts were made to conserve alcohol and improve the over-all recovery by re-using the filtrate of one run as the solvent for the second, the following results were obtained. Initial recovery was 88 percent with the product being 99.5 percent pure; the following trial using the previous filtrate improved the recovery to 95 percent with purity of the product dropping to 98 percent. Reusing the filtrate a second time decreased the recovery to 91 percent and the product purity to 95 percent. The concentration of naringin in the filtrates continually increased to 2.4 percent and failed to crystallize further during an extended holding time.

Effect of Concentration. — The possibility of a critical concentration ratio of solvent to naringin in this purification procedure was then investigated. Crude naringin of 86 percent purity was dissolved in boiling isopropyl alcohol at four concentration levels; 30 g. per 600 ml., 30 g. per 300 ml., 30 g. per 150 ml., and 30 g. per 100 ml. These levels of concentration are respectively equivalent to 4.3, 8.6, 17.2 and 25.8 g. of pure naringin per 100 ml. of isopropyl alcohol. Each sample was stirred for two minutes, filtered, and the filtrate heated to its boiling point to initiate crystallization. As soon as each sample began to crystallize, it was allowed to cool and was filtered subsequently and washed. The sample with the lowest naringin concentration was an exception in that it failed to crystallize promptly and was allowed to cool to room temperature and stand overnight. By the next day the sample appeared to have crystallized as well as the others. Isolated similarly, it was found to be the equal of the other three trials, each of which yielded an 89-90 percent recovery of naringin having 98-99.5 percent purity. The trial having a concentration of 8.6 g. of naringin per 100 ml. of isopropyl alcohol appeared to be the more suitable for a large scale operation. At higher concentrations, it is conceivable that recrystallization could begin before the initial filtration was
complete. There is the further disadvantage at higher concentrations that the voluminous character of the recrystallized naringin will so stiffen the mixture as to make handling too difficult. At lower concentrations, the higher cost of solvent and longer time required for recrystallization would preclude its industrial use.

In a trial where crude naringin of 29 percent purity was purified by this procedure using a ten to one solvent to naringin ratio, a product of 98 percent purity was obtained. The recovery of available naringin was not as efficient as with samples of higher initial purity, being only 60 percent. The filtrate and washings contained 26 percent of unrecoverable naringin and constituted the greatest loss. The 14 percent naringin remaining in the extracted crude residue could be recovered with more efficient washing of this residue. A better recovery of purified naringin is possible when the crude naringin samples have a higher initial purity. It is quite possible in this case that the crude naringin recovered by the Baier process (3) could be isolated using smaller quantities of filter-aid which would improve the purity of the crude product. Upon using purchased naringin of 86 percent purity under similar conditions, there was a 92 percent recovery of a 99.5 percent pure product. Only 5.5 percent naringin was lost in the filtrate and washings, with another 1.9 percent lost in the extracted residue. In another trial with a purchased product of 81 percent purity, 85 percent was recovered with 11.4 percent naringin being lost in the filtrate and 3 percent in the residue.

Critical Effect of Water. — Another important consideration in the purification of naringin is water. For example, naringin will crystallize from water as an octa-hydrate molecule having eight waters of crystallization, which product melts at 83° C. (2). When crystallized from certain other solvents, such as isopropyl alcohol, naringin has two waters of crystallization and melts at 171° C. (2). The physical appearance of the products under the microscope is very similar, crystallizing as needles which are usually found agglomerated in a rosette pattern. The drying of purified naringin is considerably simplified when the dihydrate molecule is formed and is a distinct advantage of this process over the others previously mentioned, since the naringin can be dried more readily and at higher temperatures. The octa-hydrate product must be carefully dried at approximately 60° C., after which the temperature can be raised slowly to over 100° C., whereupon an equivalent dihydrate product will be obtained.

In preparing a highly purified product, it is also important to consider the hygroscopic property of naringin. An exceedingly dry sample of naringin dihydrate, dried at 105-110° C. for two hours, was found to increase approximately six percent in weight in less than two hours when exposed to average room temperature conditions. The uptake of water is exceedingly rapid initially, and especially so with a small sample having a large surface exposed.

The solubility of naringin in isopropyl alcohol is influenced greatly by water of crystallization and extraneous water. The octa-hydrate form of naringin is more than 30 percent soluble in commercial (99 percent) isopropanol, while the dihydrate is soluble only to the extent of approximately 0.2 percent. The solubility of these same two naringin molecules in water is just the reverse, the dihydrate being the more soluble. In view of this information, the solubility of naringin dihydrate in isopropanol was investigated to determine the effect of extraneous water mixed with the alcohol. A series of isopropanol samples were made in which the water content was as follows: less than 1 percent, 2 percent, 3 percent, and 4 percent. After shaking each sample with an excess of naringin for 14 hours at 27° C., the solubility of the dihydrate in each was respectively as follows: 0.15, 0.28, 0.40, and 0.50 percent. When each of the four isopropanol samples was refluxed for 15 minutes at approximately 82° C. with an excess of naringin, the dihydrate crystals had the following solubility: 0.65, 1.1, 1.6, and 2.5 percent respectively. Relating this information back to the isopropanol purification procedure, it can be shown that maximum yield of purified naringin is obtained by cooling the crystallized naringin as close to room temperature as possible before filtering and by making every effort to keep the isopropanol as anhydrous as possible. In a number of repeated extraction trials, naringin recovery was improved one to three percent by thoroughly drying.
crude naringin samples just prior to extraction and keeping the isopropanol well enclosed at all times possible.

**Summary**

Commercial purification of crude naringin was shown to be possible by the following method: Sufficient well dried crude naringin is slurried for five to ten minutes with boiling hot anhydrous (or 99 percent) isopropanol, to yield an 8.5 to 10 percent naringin solution. The dissolved naringin is filtered quickly from the insolubles and heated further or seeded to initiate crystallization of the naringin dihydrate. The crystallized naringin and solution is allowed to cool to room temperature, whereupon it is filtered and the pure naringin further washed with isopropyl alcohol. The crystals are dried at 85° C, yielding a final product of 98 to 100 percent purity.

In establishing a new purification procedure, the effects of naringin concentration were measured and the necessity of keeping the process anhydrous as possible was shown. It was found that solvent costs can be reduced by recycling the extraction alcohol in subsequent purifications, but its effect was reflected in the final product purity. Solubility of naringin in isopropyl alcohol and mixtures of it and water were measured at two temperatures.

**LITERATURE CITED**


**SECTIONIZING MARSH SEEDLESS GRAPEFRUIT**

**Gray Singleton**

*Shirriff-Horsey Corporation, Ltd.*

*Plant City*

In the early days of grapefruit sectionizing the peeling was done with knives. Girls sliced off the stem, and stylar ends of the fruit, then the lateral peel was removed by strokes of the knife, from top to bottom. In peeling, a considerable slice was cut from each segment.

About 1929 the first canners started using lye to remove the carpellary membranes after the albedo had been stripped by hand. This saved that part of the fruit which had previously been lost in hand peeling.

When lye peeling was started, there was a great protest from the "green peel" canners who said that the lye would poison those who ate lye peel sections. But, when they found that lye peeling increased the yield about 30 per cent and decreased the cost of operation considerably, they decided that their fears about the toxicity of lye peeled fruit were unfounded, which, in fact, they were.

Lye peeled sections are usually not of as high quality as were those produced by hand peeling. At times the lye is too cool or too weak and fragments of membrane are not removed. Frequently, the lye is too hot or too strong and "cuts" into the sections making them soft and of poor appearance and texture.

During the period when hand peeling was in vogue, the marsh seedless variety of grapefruit was preferred. The sections were more uniform because no ragged pits were left where seed were removed.

When lye peeling came in, marsh seedless fruit went out. Seeded fruit became the standard for sections. This change was caused by the fact that seeded fruit has a solid core, while marsh seedless has a hollow core. Lye gets into this hollow core and destroys the membranes which bind the carpels together. When the sectionizing girls pick up a marsh seedless fruit that has been lye peeled, the segments fall apart in hand and she throws them on the garbage belt. The fruit must be firm if good sections are to be produced.

The shift from marsh to seeded fruit involved about four million boxes each year and