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RECOVERY OF NARINGIN AND PECTIN FROM GRAPEFRUIT ALBEDO[1]

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Abstract. **Samples of 'Duncan' grapefruit albedo were obtained at 2-month intervals from October through April from commercial plants which use the Automatic Machinery Corporation Shaver. A hot water leach was used to remove the soluble solids and naringin from the albedo prior to the pectin extraction. Highest yields of naringin were obtained using a 1:3 ratio of albedo to leach water at 190-194°F (88-90°C) for 5 min. A threefold concn of leach water increased the yield of isolated naringin by approx 33%. In 5 out of 6 tests, the hot water leach resulted in as great or greater recoveries of naringin than did the control, a caustic leach similar to commercial practice. Pure naringin recovery ranged from 4.9-10.6 g per 2,000 g of wet albedo.**

After the hot water leach, pectin was extracted from the leached grapefruit albedo using nitric acid and an alcohol preciptation. The jelly units ranged from 88.1-79.9 for the albedo.

There are 2 major economic advantages of using a hot water leach for pectin. It permits the recovery of naringin and allows reuse of the distilled water recovered during the concn of the naringin leach water.

Pectin and naringin have long been recognized as valuable specialty products of citrus (12, 13). Grapefruit albedo contains both pectin and naringin, but presently neither is recovered in Florida. Demands for naringin may significantly increase if the Food and Drug Administration approves the use of neohesperidin dihydrochalcone. This sugar substitute, made from naringin is 1,500 times sweeter than sucrose (1, 20).

Florida produces more than ½ of the world supply of grapefruit (3), and therefore has the potential of becoming a major supplier of naringin. However, the currently accepted commercial naringin extraction procedure has a disadvantage in that it does not permit subsequent extraction of pectin, and pectin could become a major specialty product from Florida grapefruit. Commercially, naringin is usually extracted from the peel with lime ($Ca(OH)_2$) which precipitates the pectin in the peel as calcium pectate. The naringin is then pressed from this treated peel. Unfortunately, the formation of calcium pectate precludes later extraction of the pectin, which is currently a more lucrative product than naringin.

In addition, the commercial procedure for pectin recovery usually uses ambient temp leach water. It was not known if the water leach at this temp would be effective in solubilizing the naringin from the peel. However, the ambient temp leach water is known to be able to remove the soluble solids (mostly sugars) from the peel. If the soluble solids are not removed, they would caramelize and turn the resulting pectin brown. If the naringin is not removed from the peel, then it will be destroyed by the heat and mineral acids used to extract the pectin from the leached peel (14).

Thus, industry is faced with a dilemma. If they extract naringin, they are unable to extract pectin and vice versa. Ideally, industry needs a single process that would permit the extraction of both naringin and pectin from the same peel. A possible procedure for the recovery of both pectin and naringin would involve leaching the peel with hot (194°F, 90°C) water to remove soluble solids, solubilize naringin, and inactivate enzymes. Then naringin could be recovered from the hot leach water as a specialty product of pectin manufacture.

It was the purpose of this study to test the feasibility of using a process designed to recover both pectin and naringin.

Materials and Methods

Samples of commercially shaved 'Duncan' grapefruit albedo were obtained from 2 plants using the Automatic Machinery Corporation Shaver. Commercially shaved grapefruit albedo was evaluated because it more closely resembles that which could be used in actual commercial practice. Previous studies (4, 11) have shown that laboratory prepared samples of shaved grapefruit albedo were a good source of naringin. Other earlier studies (14, 16, 19) disagree regarding the amount of pectin that can be recovered from laboratory prepared grapefruit albedo.

The shaved albedo sample was divided in half and ½ was processed using (a) an experimental hot water leach and the other half was processed using (b) a caustic leach similar to the commercial methods. The hot water leach was used to recover both naringin and pectin. The amount of naringin recovered by this experimental method was compared with the amount recovered by a caustic leach method (5). Yield and grade of the pectin extracted from the experimentally leached albedo were also determined. It was hypothesized from earlier work (15) that commercial pectin extraction procedures using ambient temp leach water would not extract naringin. This hypothesis was tested on 1 sample.

Experimental Hot Water Leach

In this leach 2,000 g of wet albedo and 6,000 ml of water (1:3 ratio) were used. The albedo was added to boiling water and this first leach was conducted between 190-194°F (88-90°C) for 5 min. The leached albedo was immediately pressed at 1,000 psi (70 kg/sq cm). The hot water leachate, removed by this pressing, was saved for naringin recovery. Then the pressed albedo was quickly cooled to a temp below 140°F (60°C), because temps above this point have been found to be injurious to pectin (13). The press cake was rapidly cooled by dropping into 4,000 ml cold water (1:2 ratio) and quickly stirred. This cold water leach constituted a 2nd leaching of the albedo. A 30-mesh screen was used to separate the albedo and a majority of the leach water prior to a 2nd pressing of the albedo.

Naringin recovery from the hot water leachate. The hot water leachate from the first leach was further processed to enable the recovery of naringin. Lime ($Ca(OH)_2$) was used to adjust the solution to pH 9 and it was held for 20 min to precipitate the low grade water soluble pectin as calcium pectate. Unless removed, this pectin would undesirably increase the consistency of the naringin solution

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during later concn. HCl was then used to adjust the pH to 4 to facilitate the precipitation of the naringin. This solution was divided into halves, and ½ was put into cold storage at 32°F (0°C) for 48 hr for precipitation of naringin. The 2nd ½ of the solution was concd threefold under vacuum at 120°F (49°C) before precipitation of the naringin at 32°F (0°C) for 48 hr. After precipitation, the naringin from both halves was separated by filtration from the cold solution and then the naringin was dried at approx 175°F (80°C). The dried naringin was finely ground and assayed for purity by a modification of the Davis test (7).

Pectin extraction from hot water leached albedo. Pectin was extracted from the leached albedo after the hot water leach. These extractions used 1,190 ml of distilled water, 17 g of dry albedo (70:1 ratio) heated to a temp of 194°F (90°C) for 0.75 hr, and sufficient 1.0 N HNO_3 acid to give a pH of 1.6 ± 0.05. Optimum temp and pH for pectin extraction were previously determined to give some of the best jelly units (17).

After extraction of pectin from the albedo, the mixture was quickly cooled and centrifuged, then the supernatant containing most of the pectin was poured off. The semisolids were resuspended in water and stirred for 5 min, which constituted a 2nd extraction. This mixture was centrifuged again, and the supernatants from both extractions were combined. The pectin was precipitated by diluting the supernatant (1:2 vol:vol) with isopropyl alcohol. The resulting pectin was washed with 70% isopropanol to remove any residual acid prior to vacuum drying and grinding. The jelly grade of the pectin was determined by the 1959 Institute of Food Technologists' method (9).

Commercial Caustic Leach for Naringin Recovery

In the caustic naringin leach, which served as a control, 2,000 g of wet albedo and 3,000 ml of water at 80°F (27°C), a 2:3 ratio, were used. Lime ($Ca(OH)_2$) was used to adjust the mixture to a pH between 8.8-9.0 and it was maintained at this pH for 1 hr. This procedure, similar to the one used by industry to recover naringin, precipitates almost all of the pectin in the albedo as calcium pectate. The pH was then adjusted between 7.5-8.0 with HCl, which reduced the consistency of the naringin solution prior to pressing at 1,000 psi (70 kg/sq cm). The naringin solution was recovered from the caustic leached albedo by pressing. Then the pH of the naringin solution was adjusted to 4, and this solution was divided into halves. Both halves were held at 32°F (0°C) for the precipitation of naringin as in the hot water leach procedure.

Results and Discussion

When we tested the hypothesis that room temp leach water would recover an appreciable quantity of naringin from grapefruit albedo, we found very little naringin recovered. This agrees with the earlier work on solubility of pure naringin in distilled water (15).

Naringin Recovery

Recovery of pure naringin from the hot water leach averaged 6.7 g per 2,000 g of wet albedo for the single strength leach water (Table 1). When the leach water was concd threefold, yields of naringin were increased by more than 33%. This increase is apparently due to the removal of 2/3 of the water that otherwise holds naringin in solution.

The average for the single strength caustic leaches was slightly higher than the average for the single strength hot water leaches (Table 1). Concentrating the caustic leach water increased the naringin yield, but the average increase for the caustic was less than that recovered by the concd hot water leach.

Table 1. Naringin extracted from 'Duncan' grapefruit albedo with a hot water or caustic leach.

Date	Hot water: Single strength[z]	Hot water: Concn[z] (3/1)	Caustic: Single strength[z]	Caustic: Concn[z] (3/1)
Oct.	7.5[y]	—[x]	7.1	—[x]
Dec.	8.2	10.6	7.3	—[x]
Feb.	4.9	9.3	8.4	9.3
April	6.1	8.7	4.5	6.4

[z]Single strength denotes the naringin solution after pressing while concn denotes a threefold concn of this solution.
[y]Values are expressed as g of pure naringin isolated per 2,000 g of shaved albedo which is equivalent to pounds of pure naringin isolated per ton of shaved albedo (wet wt).
[x]Data not determined.

The concd hot water leach gave highest yields of pure naringin; 9.5 g per 2,000 g of wet albedo, 9.5 lb/ton (4.7 kg/metric ton). This amount is similar to the 4-8 lb. found by Hendrickson and Kesterson (8). The 9.5 lb. is approx ½ of the theoretical amount of naringin found in the whole albedo as determined by the modified Davis procedure (7). Kesterson and Hendrickson (11) also showed a similar theoretical value of 19.6 lb. of naringin per ton of albedo. Thus, the concd hot water leach seems to be a feasible method for recovering naringin.

The crude naringin from the hot water leach was found to have an average purity of approx 46%. With naringin purification procedures (6), it is possible to increase the purity to better than 95%.

Pectin Recovery

The results of pectin extractions on 2 different sampling dates are shown in Table 2. The jelly grades of 271 and 258 for February and April are similar to the 263 and 245 reported for the whole peel of the same cultivar (17). However, caution must be exercised in comparing recovery values reported for a cultivar or method of extraction to other cultivars and methods. These and other variables may affect the values for the pectins actually recovered.

Table 2. Yield and quality of pectin recovered from 'Duncan' grapefruit albedo following a hot water leach for naringin.

Date	% yield[z]	Jelly grade	Jelly units	Purity as % AGA[y]	% ash[x]
Feb.	32.5	271	88.1	87.4	0.84
April	31.0	258	79.9	87.8	0.83

[z]On dry leached peel basis.
[y]Anhydrogalacturonic acid.
[x]On dry wt basis.

Using various extraction procedures, some researchers (19) have shown the albedo to be a richer source of pectin than an equivalent wt of whole peel. Thus, it may be advantageous to use the albedo for pectin recovery because it involves handling fewer pounds of raw product per amount of pectin obtained. In addition, if the albedo is leached with hot water (194°F, 90°C), the pectin destroying enzyme, pectin methylesterase (PE), will be inactivated (10). This will prevent later degradation of the pectin and give more flexibility to a pectin operation in which the leached peel can be stored a few hours prior to extraction or drying.

Discussion

The use of the albedo for the manufacture of specialty products offers economic advantages as well as flexibility. More pounds of naringin can be produced from shaved albedo than from whole peel. Grapefruit peel is approx 70-75% albedo, but according to Kesterson and Hendrickson (11), the albedo contains approx 55% of the total naringin, 25% more than the same wt of whole peel.

There are advantages to leaching grapefruit peel for naringin with hot water and subsequently recovering pectin. Not only does the hot water inactivate the PE, allowing for a more flexible pectin processing operation, but the recovery of naringin as a specialty product would be an additional source of income.

Additionally, a threefold concn of the hot water leach from the pectin operation offers several advantages: it reduces the vol of the waste load by 2/3 which may be further treated by drying, it produces distilled water that may be used in the pectin operation without costly water treatment to remove harmful cations, it increases the naringin recovery, and it decreases the needed holding capacity of a plant as well as the time needed for crystallization.

The potential for Florida to manufacture naringin and pectin can be calculated, assuming the yields found in our laboratory would be representative of commercial production. During the 1974-1975 processing season, approx 25.8 million boxes (approx 1.1 million short tons) of grapefruit were processed in Florida (2). The 85 lb. box of grapefruit contains approx 45 lb. of peel which will provide 31.5 lb. of shaved albedo. Thus, Florida has the potential to produce 406,350 tons of shaved albedo. If a commercial procedure similar to our hot water leach with concn is used, we would assume the yield to be approx 9.5 lb. of pure naringin per ton of wet albedo. Thus, based on the 1974-1975 processing season, Florida could have potentially produced 3.86 million pounds of pure naringin (0.15 lb. per box). This could have returned millions of dollars to the Florida processor and grower.

As for the pectin, on the basis of a 4.7% average yield of 150 grade pectin (wet wt) from grapefruit albedo, Florida could potentially produce 38 million lb. of 150 grade pectin annually (1.5 lb. per box). This could have resulted in returns of millions of dollars through the use of a method of recovering both naringin and pectin from the same commercially shaved grapefruit peel. Due to the promise of this work, we are currently planning additional investigations.

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NEW GRAPEFRUIT PRODUCT: DEBITTERIZING ALBEDO IN SITU

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Abstract. **The skeletal membranes and rind of grapefruit, consisting of 50% of the fruit weight, are discarded as inedible. We have developed a method of debitterizing the albedo portion of grapefruit rind so that it can be consumed with the sections. The method consists of removing the flavedo to expose the albedo. A solution containing the enzyme naringinase, nutrients, colorants, flavor substances, and preservatives was vacuum infused into the albedo and gas filled cavities of the fruit. Treating a medium sized grapefruit with 350 U/l of pectinase-free naringinase at 50°C for 60 minutes lowered the naringin content of albedo juice 81%. A panel of six tasters judged the enzyme-treated albedo to be less bitter. The significance of this development is that grapefruit can be processed to contain food fiber, proteins, vitamins, and minerals and still be attractive and tasty.**

The consumers discard as inedible about one-half of the fresh grapefruit they buy for the table. This inedible portion consisting of 50% of the fruit by weight, includes the albedo and section membranes, which are sources of food fiber, a recognized dietary essential for good health.

[1]One of the laboratories of the Southern Region, U.S. Department of Agriculture, Agricultural Research Service.
Mention of a brand name is for identification only and does not imply endorsement by the U. S. Department of Agriculture.