ELSEVIER

0144-8617(95)00036-4

Carbohydrate Polymers **27** (1995) 1–4

0144-8617/95/$09.50+.00

Extraction of citrus glucosides

S.A. El-Nawawi

Chemical Engineering Department, National Research Centre, Dokki, Cairo, Egypt

(Received 6 January 1995; revised version received 8 March 1995; accepted 17 March 1995)

Hesperidin and naringin were extracted from orange peel and grapefruit peel, respectively, by treating the peel with $Ca(OH)_2$. The effect of maturity of the peel and recycling of the extracting liquor upon the yield of glucoside were investigated. The highest yields of hesperidin were obtained from orange peel extracted at the early season, increase in maturity led to a decrease in yield of hesperidin extracted and a decrease of its purity. Recycling of the extracting liquor led to an increase of the yield of both extracted hesperidin and naringin. The highest yield of hesperidin was 15·5 g/2 kg peel, and the highest yield of naringin was 12 g/2 kg peel.

A hot water leach was used to recover naringin and pectin successively from grapefuit peel. The highest yields of naringin were obtained using a 1:3 ratio of peel to leach water at 88–90°C for 5 min. A three-fold concentration of leach water increased the yield of isolated naringin by more than 25%. 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 4·1 to 10·4 g per 2 g of wet peel. After the hot water leach, pectin was extracted from the leached grapefruit peel using hydrochloric acid and an alcohol precipitation. The jelly units ranged from 67·3 to 91.

INTRODUCTION

Pectin and glucosides have long been recognised as valuable speciality products of citrus (Mcready & Owens, 1954; Poore, 1925). Neohesperidin dihydrochalcone, a sugar substitute made from naringin, is 15,000 times sweeter than sucrose. The principal glucosides of oranges and grapefruits are hesperidin and naringin, respectively. The proportion of hesperidin in the component parts of a mature orange were: 32–50% in the rag and pulp, 30–50% in the albedo, 12–23% in the flavedo and 1·5–6% in the juice (Hendrickson & Kesterson, 1955). The distribution of naringin on a percentage basis in the component parts of a mature grapefruit was 50–60% in the albedo, 30–40% in the rag, 5–10% in the flavedo, and 1–3% in the juice (Kesterson & Hendrickson, 1953). Possible uses for naringin as a fine organic chemical include in the preparation of acid azo dyes and wood stains, citrin, and rhamnose. It is also used to enhance the piquant flavor of confections and beverages (Hendrickson & Kesterson, 1965). Glucosides are recovered in most commercial procedures by treating the peel with $Ca(OH)_2$, pressing and then crystallizing them from the press liquor after pH adjustment. This process renders the pectin in the peel nonrecoverable because it has been precipitated as calcium pectate. In commercial operations, pectin is normally extracted by heating in a mineral acid solution after first leaching the peel with room temperature water to remove the soluble solids (mostly sugars). If the glucosides are not leached from the peel, they will be destroyed by the heat and mineral acids used to extract the pectin (Poore, 1934). A possible procedure for the recovery of both pectin and glucoside would involve leaching the peel with hot (90°C) water to remove soluble solids, solubilize glucosides, and inactivate enzymes. Then glucosides could be recovered from the hot leach water as a speciality product of pectin manufacture.

EXPERIMENTAL

Hesperidin extraction (Hendrickson & Kesterson, 1964)

A 2000 g sample of the finely chopped peel was stirred mechanically with 3000 g of water over a period of 90 min, while increments of calcium hydroxide were added to maintain the pH at approximately 11. The alkaline peel slurry was stained through cheesecloth and additional liquor recovered by pressing the remaining peel hydraulically at pressures of 300 lb/sq. inch. After combining both liquids, the turbid solution was adjusted to pH 4·7 with concentrated hydrochloric acid and heated to 55–60°C. After stirring the extract for 90 min to aid crystallization, it was allowed to stand overnight. The crude hesperidin was filtered, dried at 80°C, weighed and an aliquot analyzed. The filtrate was separately analyzed. The modified Davies method (Hendrickson & Kesterson, 1957) was used for analysis and the Hendrickson (Hendrickson & Kesterson, 1955) method for purification.

Naringin recovery

Naringin can be recovered by methods similar to those used for hesperidin. When alkali is used to solubilize the naringin, a lower pH is needed than when recovering hesperidin. Lime was added to maintain an extraction pH of 9·2, the extraction was partially neutralized prior to processing and finally adjusted to a pH of 4·0 for crystallization and the naringin was isolated by filtration after 18 h of storage time without any prior heating. The analytical technique for naringin recovery resembles that for hesperidin. Crude naringin was purified by the method of Hendrickson and Kesterson (1956).

Recovery of naringin and pectin from grapefruit peel

Samples of grapefruit peel were divided in halves and half 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 (Hendrickson & Kesterson, 1954). Yield and grade of the pectin extracted from the experimentally leached peel were also determined.

Experimental hot water leach (Crandall & Kesterson, 1976)

2000 g of wet peel were added to 6000 ml of boiling water (1:3 ratio), and this first leach was carried out at 88–90°C for 5 min. The leached peel was then pressed at 300 psi. The hot water leachate, removed by this pressing was saved from naringin recovery. Following this, the pressed peel was cooled to a temperature of below 60°C, to avoid destroying the pectin (Poore, 1925). The press cake was rapidly cooled by dropping into 4000 ml cold water (1:2 ratio) and quickly stirred. This cold water leach constituted the second leaching of the peel. A 30 mesh screen was used to separate the peel and the majority of the leach water prior to the second pressing of the peel. The hot water leachate from the first leach was further processed to enable the recovery of naringin. Lime ($Ca(OH)_2$) was added 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 during filtration and later concentration. HCl was then used to adjust the pH to 4 to facilitate the precipitation of the naringin. This solution was divided into halves, and half was put into cold storage at 0°C for 48 h for precipitation of naringin. The second half of the solution was concentrated three-fold under vacuum at (49°C) before precipitation of the naringin at 0°C for 48 h. After precipitation, the naringin from both halves was separated by filtration from the cold solution and then the naringin was dried at 80°C. The dried naringin was finely ground and assayed for purity by a modification of the Davies test (Hendrickson & Kesterson, 1957). Pectin was extracted from the leached peel after the hot water leach. The extraction was carried out according to the method previously investigated (El-Nawawi & Shehata, 1987). The jelly grade of the pectin was determined by the 1959 Institute of Food Technologists' method (Institute of Food Technologists, 1959).

Commercial caustic leach for naringin recovery

In this procedure, 2000 g of wet peel were added to 3000 ml of water at 27°C. Lime ($Ca(OH)_2$) was added to adjust the pH of the mixture between 8·8 and 9·0 and it was maintained at this pH for 1 h. The pH was then adjusted between 7·5 and 8 with HCl, which reduced the consistency of the naringin solution prior to pressing at 300 psi. The naringin solution was recovered from the caustic leached peel 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 0°C for the precipitation of naringin, as in the hot water leach procedure. All experiments and analysis were carried out in duplicate.

RESULTS AND DISCUSSION

Hesperidin extraction

Effect of maturity of fruit upon yield

To study the effect of maturity upon the yield of hesperidin, peel samples from October to April 1970 were investigated. The results shown in Table 1 indicate

Table 1. Effect of fruit maturity upon yield and purity of extracted hesperidin and the loss of hesperidin-like material in the isolation filtrate

Month of season	Hesperidin per 2 kg peel in cake (g)	Purity (%)	Hesperidin per 2 kg peel in filtrate (g)
October	15·5	65	7·5
November	14·5	63	8·5
December	13	61	9·0
January	12	54	8·0
February	10·5	49	8·0
March	9·0	46	9·0
April	8·0	40	9·0

Table 2. Effect of recycling the extraction mother liquor upon the yield of hesperidin from orange peel

Month of season	Hesperidin per 2 kg peel isolated (g)	Hesperidin per 2 kg peel in filtrate (g)	Hesperidin per 2 kg peel with recycle (g)	Hesperidin per 2 kg peel in filtrate after recycle (g)
October	15·5	7·5	17	9·5
November	14·5	8·5	16	10·0
December	13·0	9·0	15	10·5
January	12·0	8·0	13·25	9·5
February	10·5	8·0	12	9·5
March	9·0	9·0	10	9·8
April	8·0	9·0	9	9·5

that the best yields of hesperidin were obtained by processing oranges at the early season. These data show a decrease in the yield of hesperidin with increasing maturity. A further greater fruit maturity was accompanied by a noticeable decrease in the purity of the isolated hesperidin. The isolated hesperidin samples were about 65% actual hesperidin in the early season, with the ballast material increasing with maturity until the samples in the last season were about 40% hesperidin.

Effect of recycling hesperidin extracting liquor

Noticeable in Table 1 is the high concentration of hesperidin in the filtrate of the hesperidin isolation procedure. It was reasoned that this filtrate would serve as an excellent extracting medium for subsequent runs since it was already saturated with hesperidin and thus would reduce the extraction loss in the new batch of peel. A further advantage in using the filtrate rather than water would be a reduction in the volume handled and the maintenance of higher sugar concentration, thus simplifying later use or disposal of the liquid. The quantity of hesperidin lost in each isolation filtrate is shown in Tables 1 and 2. There is a constant amount ranging from 7·5 to 9 g per 2 kg of hesperidin that was lost in each run.

Each extraction of orange peel was repeated under identical conditions except that the filtrate from one hesperidin isolation was used to replace the make-up water of the next extraction. The overall effect of recycling the extracting liquor was an increase in yield from 10 to 15% as shown in Table 2. The increased yield was attributed to the fact that the concentration of hesperidin in the isolation filtrate increased only slightly when recycled. In actual practice the industry uses citrus press liquor from the feed mill as the extracting liquid.

Naringin recovery

Effect of maturity of the fruit upon yield

Table 3 shows the effect of maturity upon the yield of naringin recovered from grapefruit peel. The results of this investigation can be summarized as follows: the maximum yield of 12 g of naringin per 2 kg of grapefruit peel extracted was obtained early in the season. The purity was nearly 46%; this can be increased to 95% by purification.

Effect of recycling naringin extracting liquor

Table 4 shows the effect of recycling the extracting liquor. From the data in this table, there is an advantage

Table 3. Effect of fruit maturity upon yield and purity of extracted naringin and the loss of naringin-like material in the isolation filtrate

Month of season	Naringin per 2 kg peel in cake (g)	Purity (%)	Naringin per 2 kg peel in filtrate (g)
October	12·0	48	8·0
November	12·0	49	7·0
December	11·0	47	5·5
January	9·5	46	5·0
February	9·0	46	6·0
March	8·0	42	6·5
April	6·5	40	7·5

Table 4. Effect of recycling the extraction mother–liquor upon the yield of naringin from grapefruit

Month of season	Naringin per 2 kg peel isolated (g)	Naringin per 2 kg peel in filtrate (g)	Naringin per 2 kg peel with recycle (g)	Naringin per 2 kg peel in filtrate after recycle (g)
October	12·0	8·0	13	9·0
November	12·0	7·0	13·5	7·5
December	11·0	5·5	12·5	6·5
January	9·5	5·0	10·5	6·0
February	9·0	6·0	9·8	6·7
March	8·0	6·5	8·5	7·2
April	6·5	7·5	7·0	7·8

in recycling the mother liquor at certain times of the year.

Recovery of naringin and pectin from grapefruit peel
Recovery of the pure naringin from the hot water leach averaged 6·1 g per 2000 g of wet peel for the single strength leach water (Table 5). When the leach water was concentrated three-fold, the yield of naringin was increased by more than 25%. This increase is apparently due to the removal of two-thirds of the water that 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 5). Concentrating the caustic leach water increased the naringin yield, but the average increase for the caustic leach was less than that recovered by the concentrated hot water leach. The concentrated hot water leach gave the highest yields of pure naringin, 10·4 g per 2000 g of wet peel, 10·4 lb/ton (5·2 kg/metric ton). This amount is slightly higher than the 4·7 kg/ton found by Crandall and Kesterson (1976). The results of pectin extraction are shown in Table 6. The data show that a pectin of high yield and good quality can be obtained from hot water leached grapefruit peel.

The concentrated hot water leach seems to be a feasible method for recovering naringin. It reduces the volume of the waste load by two-thirds 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 decreases the required holding capacity of a plant as well as the time needed for crystallization.

Table 5. Naringin extracted from grapefruit peel with a hot water or caustic leach

Date	Hot water leach		Caustic leach	
	Single strength g/2 kg peel	Concn (3/1)	Single strength g/2 kg peel	Concn (3/1)
December	8·2	10·4	9·6	10·0
January	7·0	9·0	8·2	8·5
February	6·2	7·9	7·1	7·4
March	5·1	6·4	5·8	6·0
April	4·1	5·2	4·3	4·8

Table 6. Yield and quality of pectin recovered from grapefruit peel after a hot water leach for naringin

Date	% Yield	Jelly grate	Jelly units	Purity as % AGA	% ash
December	33·7	270	91·0	88·4	0·79
January	32·6	262	85·4	87·8	0·81
February	31·0	253	78·43	86·5	0·84
March	29·3	246	72·1	84·1	0·83
April	28·4	237	67·31	81·0	0·85

REFERENCES

Crandall, P.G. & Kesterson, J.W. (1976). Recovery of naringin and pectin from grapefruit albedo. *Proc. Fla. State. Hort. Soc.*, **89,** 189–91.

El-Nawawi, S.A. & Shehata, F.R. (1987). Extraction of pectin from Egyptian orange peel. Factors affecting the extraction. *Biol. Wastes*, **20,** 281–90.

Hendrickson, R. & Kesterson, J.W. (1954). Recovery of citrus glucosides. *Proc. Fla. State Hort. Soc.*, **67,** 199 203.

Hendrickson, R. & Kesterson, J.W. (1955). Hesperidin in Florida oranges. *Fla-Agr. Exp. State Tech. Bull.*, **684,** 121–4.

Hendrickson, R. & Kesterson, J.W. (11956). Purification of naringin. *Proc. Fla. State Hort. Soc.*, **69,** 149–52.

Hendrickson, R. & Kesterson, J.W. (1957). Chemical analysis of citrus bioflavenoids. *Proc. Fla. State Hort. Soc.*, **70,** 196–203.

Hendrickson, R. & Kesterson, J.W. (1964). Hesperidin in Florida oranges. Univ. of Florida, Agr. Exp. State Tech Bull, 684.

Hendrickson, R. & Kesterson, J.W. (1965). By products of Florida citrus. *Agr. Exp. State Inst. of Food and Agri.*, Soc., Univ. of Fla. Bull., 698, 76 pp.

Institute of Food Technologists, Committee on Pectin Standardization (1959). Final Report. *Food Technol.*, **13,** 496–500.

Kesterson, J.W. & Hendrickson, R. (1953). Naringin a bitter princile of grapefruit. *Fla. Exp. State. Tech. Bull.*, **511,** 5–35.

Mcready, R.M. & Dwens, H.S. (1954). Pectin—a product of citrus waste. *Economic Botany*, **8,** 29–47.

Poore, H.D. (1925). Citrus pectin. U.S. Dept. Agr. Dept. Bull. 1323, 19 pp.

Poore, H.D. (1934). Recovery of naringin and pectin from grapefruit residue. *Ind. Eng. Chem.*, **26,** 637–9.