Pineapple Shell as a Source of Dietary Fiber with Associated Polyphenols

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Some properties of a high dietary fiber powder prepared from pineapple fruit shell were evaluated and compared to those of several commercial fruit fibers. Total dietary fiber (TDF) content (70.6%) was similar to some commercial dietary fibers from apple and citrus fruits; however, its sensory properties (neutral color and flavor) were better than those from commercial fibers above mentioned. The insoluble dietary fiber fraction amounted to 99% of the TDF. Major neutral sugars in soluble and insoluble dietary fiber were, respectively, xylose (36% of total sugar) and glucose (43% of total sugar). Total uronic acids (5.1%) and Klason lignin (11.2%) were also measured. Antioxidant activity (AA), a new property derived from the bioactive compounds associated with dietary fiber, was evaluated. At the concentration of 0.5 g of powdered sample/100 mL in the assay mixture, pineapple fiber showed a higher AA (86.7%) than orange peel fiber (34.6%), while commercial lemon and apple fibers did not exhibit any activity. Myricetin was the major polyphenol identified in pineapple fiber, which could be responsible for the AA shown. The AA together with its sensory properties, which would not interfere with those from the food to be added, make pineapple shell a suitable source of dietary fiber.

Keywords: *Pineapple byproducts; dietary fiber; antioxidant activity; polyphenols*

INTRODUCTION

The dietary fiber market is highly competitive, with cereals providing the major source for commercial products. Nevertheless, it is well-known that dietary fibers from fruits, with a higher proportion of soluble dietary fiber and bioactive associated compounds, have a better quality than those from cereals (Spiller, 1986).

There is increasing interest to find new sources of dietary fibers (such as mango fruit, passion fruit, algae) with specific bioactive constituents that may add new healthy properties to the traditionally commercialized products (Larrauri *et al*., 1996a; Baquera and Bermúdez, 1996; Bobin-Dubigean *et al*., 1996).

Pineapple is one of the most important fruits in the world, and most of its production is used in processing. Pineapple is consumed as canned slices, chunks, dice, or fruit salads and in the preparation of juices, concentrates, and jams (Salvi and Rajput, 1995). Frozen storage of slices is also an alternative method for pineapple preservation (Bartolomé *et al*., 1995a). Byproducts obtained from industrial processing represent 25−35% of the fruit, and the shell is the major constituent. They have been used to produce alcohol, citric acid, vinegar, bromelain, wine, sugar syrup, wax, sterols, and cattle feed (Joseph and Mahadeviah, 1988; Salvi and Rajput, 1995).

The dietary fiber content and composition of pineapple flesh has been reported by different authors (Lund and Smoot, 1982; Bartolomé and Rupérez, 1995). Thus, Voragen *et al*. (1983) extracted the different polysaccharide fractions from the ethanol-insoluble residue of pineapple, and Bartolomé *et al*. (1995b) reported on the partial characterization of the hemicellulosic fraction from pineapple fruit cell wall.

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Nevertheless, there are few composition data in the literature on the waste products (ends, shell, core, etc.) obtained from the pineapple fruit processing industry (Larrauri *et al*., 1994), and no research on dietary fiber preparation from these byproducts has been found.

Any characterization based on physicochemical and physiological parameters derived from the typical constituents of dietary fiber (lignin, uronic acids, neutral sugars) cannot be regarded as a novelty. In the selection of a new source, some additional property, such as antioxidant activity, related to minor constituents (polyphenols, flavonoids, carotenoids, etc.) should also be included (Larrauri *et al*., 1996b). On this basis, the aim of this work was to characterize pineapple shell as a new source of dietary fiber with associated polyphenols and to compare it to several commercial fruit fibers.

MATERIALS AND METHODS

Raw Material. The pineapple fruits (*Ananas comosus* L. Merr. cv. Red Spanish) were collected from an experimental field in Cuba. Shells were obtained as a byproduct from the pilot plant production of slices in syrup at the Instituto de Investigaciones para la Industria Alimenticia (La Habana, Cuba).

The procedure followed to obtain high dietary fiber powders from pineapple shells was previously described by Larrauri *et al*. (1994). In brief, shells were washed, pressed, dried, milled to a particle size of <0.5 mm, and packed in multiwall paper bags.

Commercial lemon and apple fibers were obtained from Indulérida, S.A. (Lleida, Spain).

Chemical Analysis. Residual moisture content was determined by drying to a constant weight at 105 °C.

Dietary Fiber (DF). The enzymatic−gravimetric AOAC method (Prosky *et al*., 1988) was followed, but the incubation with α-amylase and amyloglucosidase was ommitted because the samples did not contain starch. Dialysis was used instead of ethanolic precipitation to avoid losses of the soluble dietary fiber (SDF), as reported by Mañas and Saura-Calixto (1993).

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Due to the low content of SDF in the dialysate, an aliquot (30 mL) was concentrated by freeze-drying, and then it was hydrolyzed with 1 M sulfuric acid (100 °C, 1.5 h). Neutral sugars (NS) were determined by gas−liquid chromatography (GLC), and uronic acid (UA) was quantified in the hydrolysates according to the Scott (1979) method with galacturonic acid as standard and 3,5-dimethylphenol as reagent.

Insoluble dietary fiber (IDF) residues obtained after enzymatic treatment and centrifugation were hydrolyzed with 12 M sulfuric acid (room temperature, 1 h) and 1 M sulfuric acid (100 °C, 1.5 h). The insoluble material was dried (105 °C, overnight) and quantified as Klason lignin (KL). NS and UA were determined following the same techniques as in SDF analysis. IDF was calculated as NS and UA plus KL. Total dietary fiber (TDF) was calculated as the sum of SDF plus IDF.

GLC. NS released from SDF and IDF, hydrolyzed as described above, were analyzed by GLC as alditol acetates (Rupérez and Leal, 1986). A Hewlett-Packard gas chromatograph and a fused silica capillary column SP-2330 (30 m × 0.32 mm i.d., 0.2 μm film thickness) were used. The oven, injector, and detector temperatures were 230 °C (isothermal), 270 °C, and 270 °C, respectively. The split ratio was 1:120, and the carrier gas (nitrogen) pressure was 9 psi. NS were identified and quantified by comparison with known standards.

Antioxidant Activity. *Preparation of the Sample Extracts.* Powdered samples (500 mg) were extracted sequentially with 40 mL of methanol/water (50:50 v/v) and 40 mL of acetone/water (70:30 v/v) at room temperature for 60 min, in each case. After centrifugation at 2500*g* for 15 min, the supernatants from the previous extractions were combined and the extracts were concentrated in a vacuum rotatory evaporator at 50 °C, freeze-dried, and dissolved in absolute ethanol (10 mL).

Antioxidant Activity Assay. The ferric thiocyanate (FTC) method reported by Kikuzaki and Nakatani (1993) and modified in our laboratory (Larrauri *et al.*, 1996b) was followed. In brief, a mixture containing the sample extract in absolute ethanol (0.5 mL), linoleic acid in ethanol (0.5 mL), sodium phosphate buffer (1 mL), and distilled water (0.5 mL) was placed in an oven at 40 °C in the dark. A control without sample extract was used. An aliquot of this mixture was added to the ferric thiocyanate method reagent, and the absorbance was measured against a reagent blank at 500 nm. The oxidation index (OI) and antioxidant activity (AA) were calculated as

$$\mathrm{OI} = \frac{\text{absorbance}_t}{\text{absorbance}_{t=0}} \times 100$$

$$\mathrm{AA} = 100 - \left[\frac{\text{product extract oxidation index}_{96\text{h}}}{\text{control oxidation index}_{96\text{h}}} \times 100\right]$$

Polyphenols Analysis by High-Performance Liquid Chromatography (HPLC). Prior to HPLC determination, an aliquot of the sample extracts was filtered through 0.5 μm filter units (Millex-SR Millipore, France). The procedure followed to determine polyphenols in the sample extracts has been previously reported (Larrauri *et al.*, 1996c). In brief, the column used was a Nucleosil 120 C_{18} (250 × 4.6 mm, 5 μm particle size) with a flow rate of 1.0 mL/min, with a four-step gradient of methanol and 0.01 M phosphoric acid from an initial ratio of 20:80 (v/v) to a final ratio of 100:0 (v/v) in 25 min at 40 °C. A diode array detector (DAD) was set at 280 and 350 nm. Ultraviolet−visible spectra were recorded over the range 200−400 nm at 1 nm/s. Polyphenols were identified by comparison of UV spectra and retention times with those of known standards. Quantification was made according to the area method at the wavelength where the highest response was obtained.

Standard polyphenols were purchased from Sigma Chemical Co. (St. Louis, MO): caffeic, ellagic, salicylic, tannic, *trans*-cinnamic, *p*-coumaric, and ferulic acids and naringin, hesperidin, myricetin, quercitin, and kaempferol. The standard solutions were kept frozen in the dark.

Table 1. Dietary Fiber Constituents of Pineapple Shell (Percent Dry Sample)[a]

component	soluble dietary fiber	insoluble dietary fiber
neutral sugars		
arabinose	0.06 ± 0.00	7.38 ± 0.83
xylose	0.10 ± 0.00	12.84 ± 0.35
mannose	0.05 ± 0.00	7.93 ± 0.99
galactose	0.03 ± 0.00	2.64 ± 0.30
glucose	0.04 ± 0.00	23.22 ± 0.90
uronic acid	0.23 ± 0.01	4.90 ± 0.30
Klason lignin	−[b]	11.20 ± 0.40
total	0.51 ± 0.04	70.10 ± 1.50

[a] Mean value ± standard deviation. [b] −, not determined.

Sensory Evaluation. Eight trained assessors performed a descriptive test for color and flavor of the powdered samples contained in Petri dishes in a sensory laboratory conforming to UNE (1976) norms.

All analyses were performed in triplicate from at least two different batches of the fiber products, and means (X) and standard deviation (s) were calculated.

RESULTS AND DISCUSSION

The powder obtained from pineapple shell had a high amount of TDF (Table 1), the insoluble fraction being its main constituent (99% of TDF). TDF from pineapple shell (70.6%) was similar to data reported for some commercial dietary fibers (Indulérida, S.A., Spain), such as apple (55−65%) and citrus fibers (50−70%) using the same dietary fiber methodology (Technical Bulletin, 1995).

NS were the main components of this fraction, accounting for 77% of IDF. No data were found on the composition of pineapple fruit waste; consequently, further comparison focused on the fresh fruit.

Major NS in SDF and IDF were, respectively, xylose (36% of total sugar) and glucose (43% of total sugar). These were also reported as the main sugars in the ethanol-insoluble residue of fresh pineapple (Voragen *et al.*, 1983), and they were also associated with the hemicellulose and cellulose fractions, respectively (Huber, 1983). These fractions were reported as the major constituents in the fiber composition of fresh pineapple (Lund and Smoot, 1982; Bartolomé *et al.*, 1995b).

The concentration of arabinose and galactose, commonly associated with UA, was low, in agreement with the results shown in Table 1. Erythrose, rhamnose, and fucose were not detected.

Total UA concentration (5.13%) was similar to that reported in the fruit flesh [6.5% (Voragen *et al.*, 1983)].

Klason lignin content (11.2%) was higher than that reported by Voragen *et al.* (1983) (8.5%) for the fresh fruit, which may be related to the different structures in the mass fraction and the fruit shell.

AA is a health-promoting property derived from the bioactive compounds associated with dietary fiber (Larrauri *et al.*, 1996b). The OI of pineapple fiber and those from some commercial fibers are shown in Figure 1. The higher the OI, the lower the AA of the samples. The comparison of OI was performed when the control reached a maximun oxidation (96 h). Commercial lemon and apple fibers did not exhibit any activity because their OI were not lower than the control. The AA of pineapple fiber (86.7%) was higher than that of orange (34.6%) at the concentration studied (0.5 g/100 mL). This property may add new uses of pineapple fiber as a better food ingredient than the commercial fibers previously mentioned, which did not exhibit any activ-

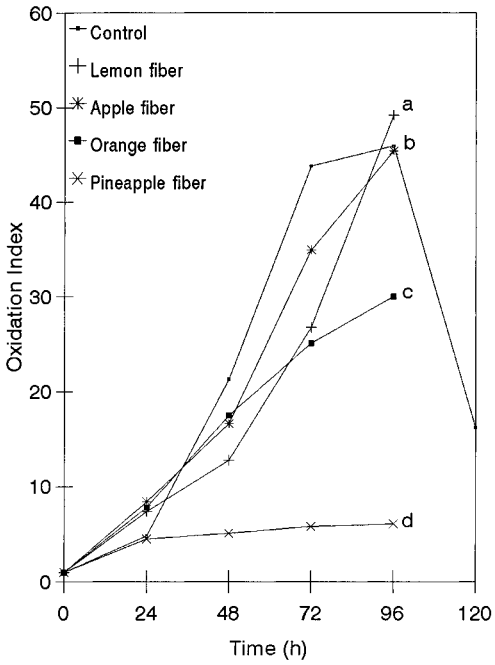

Figure 1. OI of various high dietary fiber products at a concentration of 0.5 g of powdered sample/100 mL in the assay mixture. Different letters indicate significant differences ($p \leq 0.05$).

Table 2. Phenolics Identified in a High Dietary Fiber Powder from Pineapple Shell

constituent	concn (μg/g of dry matter)
myricetin	1576.0
salicylic acid	656.8
tannic acid	404.0
trans-cinnamic acid	19.8
p-coumaric acid	13.4

ity. Other high dietary fiber products obtained from mango and lime possess a powerful antioxidant capacity at a lower concentration [0.05% (Larrauri *et al*., 1996b,c).

Myricetin (59% of the polyphenols identified) and salicylic, tannic, *trans*-cinnamic, and *p*-coumaric acids were found in the high dietary fiber powder from pineapple shell (Table 2). The highest response for myricetin and salicylic acid was obtained at 350 nm and for the other phenolics at 280 nm, as inferred from both DAD spectra and chromatogram report (data not shown). The high antioxidant capacity reported for myricetin (Shahidi and Wanasundara, 1992; Vinson *et al*., 1995) could explain the AA of the pineapple shell previously discussed in Figure 1.

Neutral color and flavor described by the sensory panelists may be another advantage of pineapple fiber because they would not interfere with the sensory properties of the food to which the fiber will be added. On the contrary , the bitter acid taste of citrus fibers prevents them from being added in high amounts to food (usually <3%).

To get a balanced fiber composition, pineapple fiber could be mixed with another dietary fiber product having a high soluble dietary fiber fraction.

In summary, pineapple shell is a promising source of dietary fiber containing associated polyphenols that exhibit antioxidant activity. This property together with the neutral color and flavor makes it a suitable fiber for a wide range of applications as a food ingredient.

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