Glycoalkaloid Content and *in Vitro* Glycoalkaloid Solubility of Extruded Potato Peels

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Potato peelings from French fry production are a potential source of dietary fiber, but the presence of naturally occurring glycoalkaloids could limit their use as a food additive. Potato peels were twin-screw extruded at 110 or 150 °C and 30 or 35% feed moisture to potentially reduce levels of glycoalkaloids. Individual glycoalkaloids were measured by HPLC. Neither α-chaconine nor α-solanine decreased on a dry weight basis from nonextruded peels (3.9 and 8.0 mg/10g, respectively). Extrusion did not change α-chaconine/α-solanine ratios. Only 3–5% of total glycoalkaloids were solubilized during *in vitro* digestion.

Keywords: *Glycoalkaloids; potatoes; extrusion; potato peels*

INTRODUCTION

In the United States most potatoes are peeled before processing. French fry production yielded nearly 2 million metric tons of potato peels (PP) as a byproduct. Although PP have some value as cattle feed, production outpaces demand, thus most PP are discarded. In Maine, as in other potato-processing states, waste disposal fees are increasing while available landfill declines. Potato processors are examining the feasibility of processing PP as a concentrated source of dietary fiber since PP contain about 45% total dietary fiber on a dry weight basis (Camire et al., 1993).

One potential problem with this use is the presence of glycoalkaloids in PP. Glycoalkaloids have been studied extensively as a natural toxicant (Morris and Lee, 1984; Jadhav et al., 1991) with symptoms similar to gastroenteritis (McMillan and Thompson, 1979), although some fatalities have been reported (Morris and Lee, 1984). A maximum level of 20 mg of glycoalkaloids/100 g of potato (fresh weight) has been recommended for safety and flavor reasons (Sinden and Deahl, 1976; Morgan and Coxon, 1987). Glycoalkaloids are not readily destroyed under typical food processing conditions (Sizer et al., 1980; Bushway and Ponnampalam, 1981; Mondy and Gosselin, 1988; Friedman and Dao, 1992). Maga (1980), however, reported reductions of total glycoalkaloids (TGA) in potato flakes extruded in a small single-screw extruder under a wide range of barrel temperatures and moisture contents. Extrusion also removes volatiles by steam-stripping, and previous research on PP as a food ingredient showed that odor was a limiting factor in product development using PP (Orr et al., 1982).

Our primary objective was to learn which extrusion conditions could reduce glycoalkaloids in PP using a laboratory-scale twin-screw extruder. In addition, advances in analytical methods now permit detection of individual glycoalkaloids, which was not possible with the titration method used by Maga (1980). Since α-chaconine is more toxic than α-solanine (Friedman et al., 1991, 1992), knowledge of extrusion effects on each of these compounds, which account for over 98% of TGA, is essential. Furthermore, *in vitro* solubility of TGA must be determined because the toxicity of these compounds may be dependent on their solubility *in vivo* (Blankemeyer et al., 1992).

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MATERIALS AND METHODS

PP were obtained from Basic American Foods, Blackfoot, ID. USDA Grade A Russett Burbank potatoes were steam-peeled and dried in a fluidized bed drier under typical industry conditions and then ground at the processing plant. Peels were further ground in a Thomas-Wiley mill (Model 4, Philadelphia, PA) to pass a 1 mm screen. Moisture content was determined by loss in weight after 16 h at 105 °C. Glycoalkaloid standards of α-solanine and α-chaconine (95% pure) were purchased from Sigma (St. Louis, MO). Tetrahydrofuran (THF) and acetonitrile used in extraction were of ACS grade; water and solvents for HPLC analysis were of HPLC grade, and all solvents were obtained from Fisher Scientific Co. (Fair Lawn, NJ).

Extrusion. Dried, ground PP were extruded in a Werner-Pfleiderer (Ramsey, NJ) ZSK-20 twin-screw extruder with heating gradually increased in seven individually controlled zones from the feed end to the die end of the barrel. Barrel temperature profiles were approximately 27–38–54–93–104–110–110 °C or 27–49–88–110–130–150–150 °C, based on experimental treatments of two final zone barrel temperatures (110 or 150 °C) and two feed moisture levels (30 and 35%). A K-Tron volumetric feeder (K-Tron Corp., Pitman, NJ) was used to control feed rate at 11.4 kg/h. Screw speed was 300 rpm. The screw configuration was recommended by the manufacturer for cornmeal; screw specifications have been previously reported (Arora et al., 1993). A single 4 mm die hole was used. Melt temperature (temperature of material within the extruder), torque, and die pressure were read directly from the extruder control panel. Duplicate samples were collected for each set of extrusion conditions. Peels were dried postextrusion at 93 °C to ca. 5% moisture, ground as before to pass a 0.131 mm (no. 80) mesh without raising sample temperature, and stored in Ziplock bags at room temperature for 4 months.

Glycoalkaloid Extraction. The extraction procedure was modified from that of Bushway et al. (1986), and each extrusion duplicate sample and nonextruded peels were extracted in triplicate. During preliminary analyses it was apparent that dried peels were not easily wetted and that incomplete extraction occurred. Peels that were not extruded were either mixed with extraction solution and Polytroned immediately or soaked first for 1 h in extraction solution. Longer soaking periods from 2 to 16 h were unsuitable because

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additional compounds other than glycoalkaloids were solubilized, resulting in too many interfering peaks in the chromatograms. Two gram samples were soaked in 45 mL of extraction solution (THF, water, acetonitrile, and glacial acetic acid; 50:29:20:1) for 1 h in a 50 mL polyethylene centrifuge tube. After 2 min of extraction by the Polytron (Kinematica Model CH-6010) set at medium speed, samples were centrifuged at 6842*g* for 10 min in a Beckman tabletop centrifuge. Twenty milliliters of supernatant from each tube was transferred to a 250 mL round-bottom flask and rotary-evaporated to a volume less than 10 mL to remove THF. After addition of 10 mL of 0.2 N HCl, the samples were sonicated, transferred to another tube, and centrifuged at 27216*g* for 10 min in the same Beckman model. The supernatant was removed for cleanup.

Cleanup. A nonextruded peel sample and extruded (150 °C, 30% moisture) peel sample were extracted similarly and then passed through a C_{18} Sep-Pak (Bushway et al., 1986) or precipitated using the method of Bushway and Ponnampalam (1981) as modified by Friedman and Dao (1992). After comparison of TGA recovery by HPLC, the precipitation method was selected for the remainder of the study.

The supernatant from extraction was adjusted to pH 10–11 with concentrated ammonium hydroxide. Samples were then transferred to a 70 °C water bath for 30 min and then cooled in ice water for 1 h to permit precipitation. Following centrifugation at 27216*g*, the solid residue was washed with 5 mL of 1% ammonium hydroxide and centrifuged again. The resulting pellet was air-dried, dissolved in 20 mL of methanol, sonicated, and boiled for 10 min. The suspension was filtered hot through a Gelman nylon Acrodisc 13 mm 0.45 μm filter, and the filtrate was evaporated to 2 mL under air with gentle heating. Four milliliters of 60% aqueous acetonitrile was mixed with the residue.

HPLC. Quantitative HPLC analysis of glycoalkaloids was performed using a Shimadzu (Kyoto, Japan) LC-6A pump, a Waters (Milford MA) Model 450 variable-wavelength detector, a Valco Instrument Co., Inc. (Houston, TX), injector, and a Hewlett-Packard (Wilmington, DE) 3396A integrator. Separation of α-solanine and α-chaconine was achieved with a Phenomenex Ultramex 3 μ 3C8 150 × 4.6 mm i.d. column and a flow rate of 1.0 mL/min. The mobile phase was a mixture of 300 mL of water, 350 mL of acetonitrile, 10 mL of THF, 0.2 mL of phosphoric acid, and 0.2 mL of monoethylamine. A 5 μL injection volume was used. The UV detector was set at 205 nm with a sensitivity of 0.04 AUFS. The external standard, 0.108 mg/mL α-solanine plus 0.188 mg/mL α-chaconine, was injected after each sample. Peak height was used for quantification. TGA content was calculated as the sum of α-chaconine and α-solanine.

In Vitro Solubility of Glycoalkaloids. Solubility of TGA is a limiting step for absorption by the small intestine and subsequent toxic effects *in vivo*. Therefore, we measured the solubility of α-chaconine and α-solanine under simulated digestion conditions as an indication of possible glycoalkaloid bioavailability. Steamed peels that had or had not been extruded were evaluated in triplicate. Two gram samples were added to 45 mL polyethylene centrifuge tubes with 15 mL of 0.01 N HCl and incubated in a water bath for 2 h at 37 °C with shaking to simulate mixing in the stomach. Samples were then neutralized with 1 N NaOH to *ca.* pH 7, followed by addition of 10 mL (10 mg/mL) of porcine pancreatin (5× USP, ICN Biochemicals) in 0.01 M, pH 7.0, phosphate buffer. Centrifuge tubes were capped and incubated as before for 16 h. Tubes were then centrifuged for 10 min at 3491*g* in a Beckman tabletop centrifuge without braking, and supernatants were removed for cleanup. The precipitation procedure used previously was modified in that the final volume after evaporation was only 1 mL and the HPLC injection volume was 10 μL. Although the same HPLC system was used as in the first part of the study, the detector was set at 200 nm to increase sensitivity. The mobile phase was a mixture of 300 mL of acetonitrile, 330 mL of water, 10 mL of THF, 0.2 mL of phosphoric acid, and 0.1 mL of monoethylamine. The external standard was 0.0376 mg/mL α-chaconine plus 0.0216 mg/mL α-solanine. Peak height was used for quantification. A flow chart of the *in vitro* procedure is presented in Figure 1.

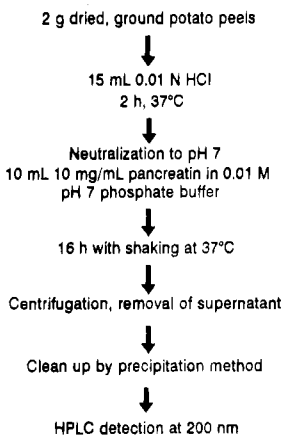

Figure 1. *In vitro* glycoalkaloid solubility assay.

Table 1. Extrusion Conditions and Potato Peel Moisture Content after Extrusion[a]

barrel temp,[b] °C	feed moisture, %	melt temp, °C	torque,[c] %	die pressure, kPa	peel moisture,[d] %
110	30	126	30	898.3	26.3
110	35	122	23	689.5	31.9
150	30	150	23	482.6	22.5
150	35	146	17	482.6	28.7

[a] Average of duplicates. [b] Final barrel temperature. [c] Reading during extrusion minus torque (14%) when barrel was empty at screw speed of 300 rpm. [d] Average of two readings per duplicate without additional drying.

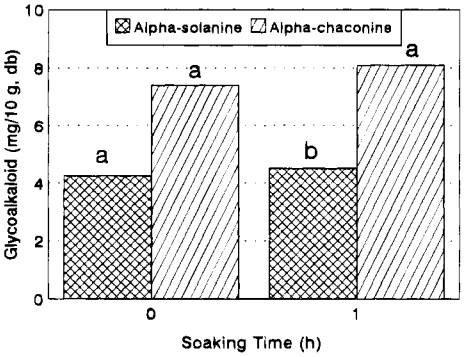

Figure 2. Recovery of individual glycoalkaloids from potato peels immediately after addition of extraction solution or 1 h after addition. Means ($n = 2$) with different letters are significantly different (Tukey's honest significant difference test, $p \leq 0.05$).

Statistical Analysis. Barrel temperature and feed moisture effects on α-chaconine, α-solanine, TGA, and the α-chaconine/α-solanine ratio were treated as a two-factor design and analyzed using the multivariate general linear hypothesis (MGLH) ANOVA program (SYSTAT, Evanston, IL). Each of the four extrusion treatments was compared with the nonextruded peels using a one-way ANOVA design. Differences among means were tested with Tukey's honest significant difference (HSD) test at $p \leq 0.05$.

RESULTS AND DISCUSSION

Extrusion. Average melt temperatures, torque, and die pressures during extrusion are shown in Table 1. The higher feed moisture decreased all three parameters. Little radial expansion was observed as peels exited the die. Moisture contents of peels extruded at 150 °C were lower than those of peels extruded at 110 °C.

TGA Recovery. Soaking peels for 1 h in extraction solution significantly increased recovery of α-solanine ($p \leq 0.05$) but not recovery of α-chaconine (Figure 2).

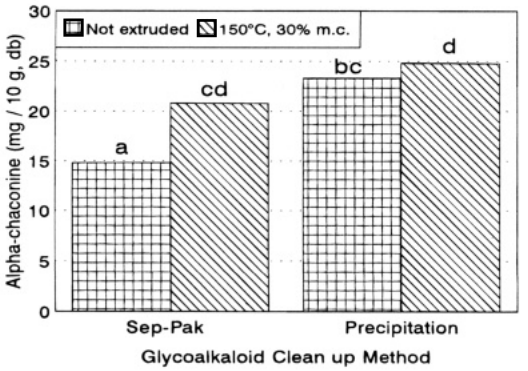

Figure 3. Recovery of α-chaconine by Sep-Pak and ammonium hydroxide precipitation cleanup methods for nonextruded or extruded (150 °C, 30% moisture) potato peels. Means ($n = 2$) with different letters are significantly different (Tukey's honest significant difference test, $p \leq 0.05$).

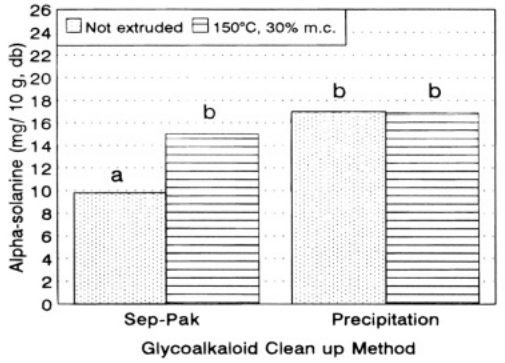

Figure 4. Recovery of α-solanine by Sep-Pak and ammonium hydroxide precipitation cleanup methods for nonextruded or extruded (150 °C, 30% moisture) potato peels. Means ($n = 2$) with different letters are significantly different (Tukey's honest significant difference test, $p \leq 0.05$).

The precipitation cleanup procedure resulted in significantly higher recovery of both α-solanine (Figure 3) and α-chaconine (Figure 4).

Peel Glycoalkaloids. Moisture was higher in nonextruded peels than in dried, ground extrudates; therefore, all glycoalkaloid levels were expressed on a dry weight basis. Extrusion cooking did not result in lower levels of either glycoalkaloid (Table 2). A slightly higher level of α-chaconine was found for peels extruded at 110 °C and 35% moisture, which was significantly different ($p \leq 0.05$) only from the peels extruded at 110 °C and 30% moisture. No difference was found for the ratio of α-chaconine to α-solanine.

These findings do not totally agree with those reported for potato flakes by Maga (1980). In that study, TGA, as measured by titration, were significantly lower in flakes extruded at 25% moisture over a range of barrel temperatures. The lower feed moisture increased viscosity within the extruder, resulting in increased residence time. We also found an effect of feed moisture for α-chaconine and TGA ($p \leq 0.05$). Barrel temperature and interaction between temperature and feed moisture had no effect on either glycoalkaloid.

Several possible explanations exist for the disagreement between studies. The potato flakes had initial TGA levels that were 7 times lower than the levels found in potato peels used in this study. Statistically significant differences are smaller with small measurements. The Brabender single-screw extruder may have produced more shear over its short barrel compared with the twin-screw extruder, which has more efficient mixing and transport elements. Finally, the titration assay for glycoalkaloids used by Maga (1980) is less sensitive to changes in TGA, or compounds formed during extrusion may have interfered with or altered color development.

Glycoalkaloid Solubility. Greater amounts of both glycoalkaloids were solubilized from extruded peels processed at 110 °C under *in vitro* digestion conditions (Table 3). Peels extruded at the higher temperature were not significantly different from nonextruded peels. Both main effects and the interaction of temperature and moisture significantly ($p \leq 0.05$) influenced glycoalkaloid solubility. A previous study found smaller mean particle sizes for extruded peels compared with nonextruded peels (Arora et al., 1993), and the glycoalkaloids may have been easier to extract from the smaller peel particles.

Soluble α-chaconine/α-solanine ratios were lower than the ratios shown in Table 2. Some extruded peels had significantly higher ($p \leq 0.05$) soluble ratios than did nonextruded peels (Table 3). These findings suggest that α-chaconine is more soluble than α-solanine under simulated digestion conditions. If α-chaconine is indeed more toxic than α-solanine, then extrusion of peels may be undesirable. However, soluble levels are very low, and *in vivo* feeding studies may be able to determine

Table 2. Glycoalkaloid Content of Extruded and Nonextruded Potato Peels[a]

barrel temp,[b] °C	feed moisture,[c] %	α-chaconine, mg/10 g	α-solanine, mg/10 g	TGA,[d] mg/10 g	ratio[e]
110	30	7.82 ± 0.18a	3.70 ± 0.09 a	11.52 ± 0.26 a	2.11 ± 0.02 a
110	35	8.40 ± 0.26 b	3.90 ± 0.26 a	12.30 ± 0.36 b	2.15 ± 0.02 a
150	30	8.00 ± 0.27 ab	3.79 ± 0.13 a	11.79 ± 0.38 ab	2.11 ± 0.05 a
150	35	8.24 ± 0.12 ab	3.79 ± 0.05 a	12.03 ± 0.16 ab	2.18 ± 0.03 a
nonextruded		8.00 ± 0.08 ab	3.90 ± 0.17 a	11.90 ± 0.20 ab	2.05 ± 0.10 a

[a] Average of three analyses per extrusion duplicate on a dry weight basis. Different letters following values within a column indicate significant differences using Tukey's honest significant difference test at $p \leq 0.05$. Dry weight basis. [b] Final barrel temperature before die. [c] Percentage prior to extrusion. [d] Sum of α-chaconine and α-solanine. [e] Ratio of α-chaconine to α-solanine.

Table 3. Solubility of Glycoalkaloids under Simulated Digestion Conditions[a]

barrel temp, °C	feed moisture, %	α-chaconine, mg/10 g	α-solanine, mg/10 g	TGA,[b] mg/10 g	ratio[c]
110	30	0.319 ± 0.027 b	0.165 ± 0.008 b	0.484 ± 0.034 c	1.93 ± 0.09 b
110	35	0.407 ± 0.027 c	0.216 ± 0.015 c	0.626 ± 0.037 d	1.89 ± 0.06 b
150	30	0.254 ± 0.023 ab	0.136 ± 0.005 ab	0.389 ± 0.023 ab	1.86 ± 0.18 b
150	35	0.271 ± 0.032 ab	0.153 ± 0.012 ab	0.423 ± 0.042 ac	1.77 ± 0.10 ab
nonextruded		0.221 ± 0.019 a	0.137 ± 0.015 a	0.358 ± 0.033 a	1.61 ± 0.09 a

[a] Average of three analyses per extrusion duplicate on a dry weight basis. Different letters following values within a column indicate significant differences using Tukey's honest significant difference test at $p \leq 0.05$. [b] Sum of α-chaconine plus α-solanine. [c] Ratio of α-chaconine to α-solanine.

the amounts of soluble glycoalkaloids that are absorbed by the intestine and subsequent toxic effects. Another possible explanation for these findings is the cleavage of sugar moieties from glycoalkaloids during the simulated gastric step (Friedman et al., 1993), which may have resulted in compounds that were not detected with the HPLC system used.

Extrusion cooking under the conditions used in this study did not significantly reduce glycoalkaloids in potato peels. *In vitro* solubility of glycoalkaloids was enhanced at low extrusion temperature. Lower feed moisture in combination with increased residence times should be studied to determine whether any reduction is possible. Addition of chemicals during extrusion may further reduce TGA availability by formation of insoluble byproducts. Steamed peels may be incorporated into food products at a level of 18 g/100 g of final product without exceeding the recommended limit of 20 mg/100 g, but this level may result in an unacceptably dark and dense food product. Animal feeding studies should be conducted first to guarantee the safety of this food additive.

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