Emilsson, B.; Gustafsson, N. *Acta Agric. Scand.* **1956**, *6*, 369.
Kenworth, A. L., presented at the annual meeting of American Society for Horticulture Science, Stillwater, OK, 1960.
Kozlowska, A. *Eur. Potato J.* **1963**, *6* (3), 1943.
Kozlowska, A. *Acta Biol. Cracov., Ser. Bot.* **1964**, *7*, 55.
Mondy, N. I.; Chandra, S.; Cukierski, M. A. *Am. Potato J.* **1980**, *57*, 131.
Mondy, N. I.; Koch, R. L. *J. Food Sci.* **1978**, *43*, 703.
Panjar, E. *Acta Agrobot.* **1960**, *9* (2), 131.
Singh, R.; Mall, T. P. *Curr. Sci.* 1973, *42* (21), 764.
Slusarek, S. *Proc. Conf. Pol. Plant Virol., 1968* **1971**.
Smith, O. "Potatoes: Production, Storing, Processing", 2nd ed.; Avi Publishing Co.: Westport, CT, 1977; Chapter 17, p 525.
True, R. H.; Hogan, J. M.; Augustin, J.; Johnson, S. R.; Teitzel, C.; Toma, R. B.; Orr, P. *Am. Potato J.* **1979**, *56*, 339.
True, R. H.; Hogan, J. M.; Augustin, J.; Johnson, S. R.; Teitzel, C.; Toma, R. B.; Shaw, R. L. *Am. Potato J.* **1978**, *55*, 511.
Wright, N. S. *Am. Potato J.* **1970**, *47*, 475.
Wright, N. S. *Am. Potato J.* **1977**, *54*, 147.
Wynd, F. L. *Bot. Rev.* **1943**, *9* (7), 395.

Received for review September 11, 1980. Revised February 23, 1981. Accepted April 17, 1981.

α-Chaconine and α-Solanine Content of Potato Products and Their Stability during Several Modes of Cooking

Rodney J. Bushway* and Rathy Ponnampalam

Several commercial potato products were analyzed for their α-chaconine and α-solanine content by using high-performance liquid chromatography (HPLC). The α-chaconine content ranged from 0.04 to 97.9 mg/100 g of product while the quantity of α-solanine varied from 0.04 to 48.0 mg/100 g of product. Percent recoveries for α-chaconine ranged from 98 to 101% while those for α-solanine were 93–98%. Glycoalkaloid stability during four cooking procedures—frying, baking, microwaving, and boiling—was investigated, and it was determined that they were stable for all except frying where a slight loss of glycoalkaloids was shown. α-Chaconine and α-solanine were confirmed as the major glycoalkaloids in each product by thin-layer chromatography (TLC).

Potatoes contain glycoalkaloids, a class of naturally occurring toxicants, of which α-chaconine and α-solanine are the most prevalent in commercial tuber varieties. These two compounds are comprised of a steroidal-like alkaloid, solanidine, to which three monosaccharides are attached. α-Chaconine contains the sugars rhamnose (two moieties) and glucose, whereas α-solanine has the monosaccharides glucose, galactose, and rhamnose.

Several investigators have reported on the toxicological effects of the glycoalkaloids when consumed by humans. Poisoning and in a few cases death have occurred when potatoes with high total glycoalkaloid (TGA) content were consumed (Hanson, 1925; Willimott, 1933; Wilson, 1959). Teratogenic effects in various animal species have been described (Mun et al., 1975., Keeler et al., 1976; Allen et al., 1977). But epidemiological investigations attempting to correlate potato consumption and abnormalities in humans have produced conflicting results (Renwick, 1972; Emanuel and Sever, 1973). As a safety precaution though, a guideline of 20 mg of TGA/100 g of potatoes has been established as the maximum TGA content allowed in commercial tuber varieties.

Although 57% of all potatoes consumed in the United States today are in some processed form (Thornton and Sieczka, 1980), very little information has been collected on total glycoalkaloid content of processed potato products and none on individual glycoalkaloids to see if they are changed, decreased, or remain the same. Alvarado (1977) attempted to determine TGA values of some commercial products but had difficulty with the method employed. Sizer et al. (1980) and Maga (1980) investigated the TGA content of potato chips and potato flakes, respectively. Also, there is little information as to the stability of these compounds during various home cooking processes except for one report (Sizer et al., 1980) on TGA content during frying of potato chips.

This investigation was conducted to obtain the α-chaconine and α-solanine content of numerous commercial processed potato products and the effect of four cooking modes—boiling, baking, frying, and mircowaving—upon each glycoalkaloid.

EXPERIMENTAL SECTION

Materials. Glycoalkaloids were obtained from potato blossoms by using the method of Bushway et al. (1980). These glycoalkaloids were separated into individual components for standards by HPLC (Bushway et al., 1979). Solvents used in extracting and partitioning were A.C.S. grade of the Fisher Scientific Co. (Pittsburgh, PA). HPLC-grade solvents (Fisher) were used for the HPLC analyses of glycoalkaloids and to dissolve the glycoalkaloid ammonium precipitate.

Processed potato products were purchased from several local stores, and several different brands of the same processed product were analyzed. Russet Burbank potatoes, which were used in the cooking studies, were obtained from the Aroostook State Farm, University of Maine, Presque Isle, ME.

Extraction, Cleanup, and Quantitation of Process Products. A 200–300-g sample (frozen commercial products were thawed first) was blended in a king-size Waring Blendor (3.8-L capacity) with 550 mL of methanol–chloroform (2:1) for 10 min at 18300 rpm, followed by vacuum filtration using a Buchner funnel fitted with Whatman No. 1 filter paper. The filtrate was brought to a final volume of 1 L. A 300-mL aliquot (a total of three

Department of Food Science, University of Maine at Orono, Orono, Maine 04469.

0021-8561/81/1429-0814$01.25/0

Table I. Glycoalkaloid Content of Various Commercial Products

type of product	no.[a] analyzed	range of mg of glycoalkaloids/100 g of product α-chaconine	α-solanine	α-chaconine and α-solanine
(1) chips	4	1.61-2.46	1.06-1.41	2.67-3.83
(2) chips	4	10.2-10.9	4.57-5.18	14.8-16.2
(3) chips	4	3.86-4.88	1.97-2.22	5.83-7.06
(4) chips	2	1.55-2.03	1.26-1.66	2.81-3.69
(5) frozen steak fries	2	1.57-2.97	1.66-2.87	3.06-5.78
(6) frozen french fries	2	1.18-1.43	0.95-1.43	2.13-2.92
(7) frozen fried potato balls	2	0.73-1.10	0.78-1.24	1.54-2.34
(8) frozen french fries	3	0.16-0.31	0.17-0.31	0.33-0.62
(9) frozen french fries	6	0.39-1.23	0.43-1.43	0.82-2.72
(10) frozen crinkle cut fries	5	0.50-1.17	0.49-1.16	0.99-2.33
(11) frozen fried potato balls	2	0.76-1.21	0.63-1.10	1.39-2.29
(12) frozen mashed potatoes	3	0.13-0.28	0.07-0.13	0.20-0.46
(13) frozen baked potatoes	2	4.77-7.20	3.25-5.11	8.02-12.3
(14) frozen fried potatoes	5	0.19-0.35	0.20-0.48	0.43-0.84
(15) dehydrated potato flour	2	3.38-3.98	3.12-3.65	6.50-7.51
(16) dehydrated potato flakes	2	0.97-1.46	0.52-0.82	1.49-2.28
(17) canned sliced white potatoes	2	0.06-0.13	0.06-0.12	0.12-0.25
(18) canned peeled whole potatoes	2	0.04-0.08	0.04-0.06	0.09-0.15
(19) canned home fries	2	0.06-0.09	0.05-0.07	0.11-0.15
(20) fried peels	2	93.1-97.9	46.1-48.0	139-145

[a] Each analysis was done in triplicate.

300-mL aliquots were taken) was placed in a 500-mL round-bottom flask and concentrated to 25 mL by using a rotary evaporator. Two milliliters of glacial acetic acid was added to the concentrate, followed by sonication for 5 min in an ultrasonic cleaner. The flask was rinsed twice with 5 mL of 2 N acetic acid after which the concentrate was centrifuged at 38000*g* at 6 °C for 10 min. The supernatant was transferred to a 125-mL separatory funnel containing 50 mL of petroleum ether. The mixture was shaken for 2 min and centrifuged for 5 min at 15000*g* to break the emulsion. Once centrifuged, the sample was poured gently into another 125-mL separatory funnel, and the lower layer was drained into a 125-mL Erylenmeyer flask to which 25 mL of concentrated ammonium hydroxide was added to precipitate the glycoalkaloids. The basic solution was placed in a 70 °C water bath for 50 min and refrigerated overnight. The precipitate was collected by centrifugation at 38000*g* for 10 min at 6 °C. The pellet was washed once with a 2% solution of ammonium hydroxide. Once the ammonia vapors had dissipated (overnight at room temperature), the pellet was dissolved in 5 mL of tetrahydrofuran–water–acetonitrile (50:30:20). This mixture was centrifuged at 12000*g* for 5 min. A 1-mL aliquot was removed for analysis of α-chaconine and α-solanine by HPLC (Bushway et al., 1979).

Cooking Studies. Four cooking procedures—microwaving, frying, baking, and boiling—were investigated. Six whole unpeeled tubers of approximately the same size were used for each type of cooking, and each study was performed twice. Cooking conditions were as follows: baking, 425 °F for 1 h; boiling, 25 min; microwaving, Menumaster systems 70/80 Litton microwave oven (Minneapolis, MN), full power (2000 W), 8 min total for six tubers, 4 min on each side; deep fat frying, Dormeyer Fri-Well (with corn oil), 350 °F (temperature measured with a thermometer), 3–4 min. The extraction, cleanup, and quantitation were the same as for the processed products except the fried sample was the only sample that needed to undergo partitioning with petroleum ether. Also for these analyses three 100-mL aliquots were removed from a 1-L sample instead of three 300-mL aliquots.

Recovery Studies. Percent recovery studies were preformed by adding 0.24 mg of α-chaconine and 0.93 mg of α-solanine to two different commercial products. One was a frozen french fried product and the other fried potato balls. Each product and each spiking level were done 3 times. For determination of the glycoalkaloid values of each product before spiking, three subsamples were removed and extracted.

Reproducibility Studies. Four commercial products (three potato chip products and a frozen mashed potato product) were extracted, cleaned up, and quantified by using the same procedures as described above except the weight of the sample and the volume of the extracting solvent were doubled to permit the analysis of five to six replications.

Thin-Layer Chromatography. Thin-layer chromatography (TLC) using Whatman high-performance TLC plates, 10 × 10 cm, 200-μm thickness silica gel plates (Whatman, Inc., Clifton, NJ), was performed on each commercial and cooked product. The solvent system employed was 100:100:50 methanol–chloroform–1% aqueous ammonium hydroxide. Three microliters of each extract was spotted.

RESULTS AND DISCUSSION

The glycoalkaloid content of 20 commercial potato products is given in Table I. These products were analyzed for their α-chaconine and α-solanine content. The deep fat fried peels contained the highest amounts of α-chaconine and α-solanine, 93.1–97.9 mg/100 g of product and 46.1–48.0 mg/100 g of product, respectively, while a canned boiled potato product had the lowest quantity of these glycoalkaloids, 0.04–0.08 mg of α-chaconine/100 g of product and 0.04–0.06 mg of α-solanine/100 g of product. The low glycoalkaloid value for boiled canned potatoes was most likely due to the absence of peels and the absence of glycoalkaloid concentration because of moisture loss. The levels of α-chaconine and α-solanine were approximately equal for the majority of the products, although a few had substantially greater amounts of α-chaconine than α-solanine. A typical HPLC chromatogram for a processed product is shown in Figure 1.

Presented also in Table I is the sum of the α-chaconine and α-solanine content for every product. This value according to previously published work on potato tubers (Sinden and Webb, 1974) should represent at least 95% of the total glycoalkaloid content of these products. For

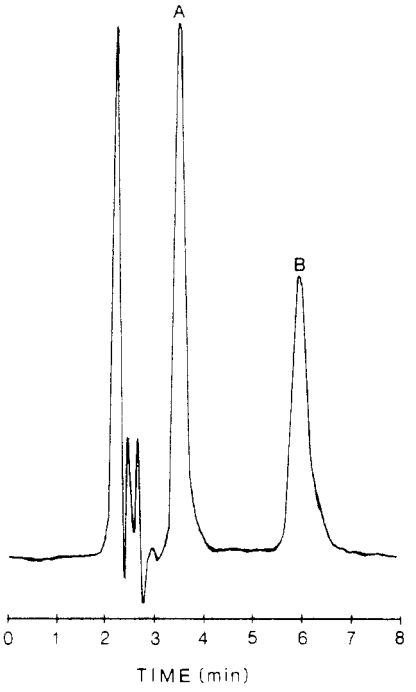

Figure 1. HPLC chromatogram of glycoalkaloids from an extract of potato chips. Solvent system, tetrahydrofuran–water–acetonitrile (56:14:30); flow rate, 1 mL/min; detector sensitivity, 0.04 aufs; wavelength, 215 nm; chart speed, 0.4 in./min. Peaks: A = α-chaconine; B = α-solanine.

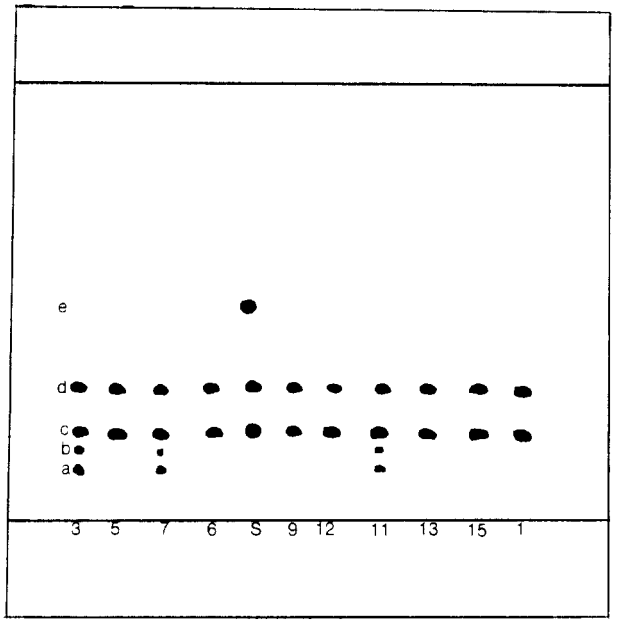

Figure 2. TLC chromatogram of several commercial products and the standard. Plate, Whatman HP-KF; solvent system, methanol–chloroform–1% aqueous ammonium hydroxide (100:100:50). Spots: a = unknown; b = unknown; c = α-solanine; d = α-chaconine; e = β-chaconine.

confirmation of this, each item was analyzed by using TLC. The results demonstrated that the major glycoalkaloids in all 20 commercial products were α-chaconine and α-solanine. Five of the products 3, 7, 8, 11, and 17 also contained two faint spots below α-solanine, none of which have been identified. Thus, the sum of the α-chaconine and α-solanine values should be a good representation of the TGA content of these products. A typical TLC chromatogram is shown in Figure 2.

All products except fried peels had their glycoalkaloid content below the critical 20 mg of glycoalkaloids/100 g of potato which is used as the upper limit when screening new potato varieties for human consumption. Most products had a glycoalkaloid content between 1 and 6 mg/100 g of potato which would be expected since most commercial products are peeled. Because of the high levels of glycoalkaloids in fried potato peels and the possible toxicity of glycoalkaloids, one should exercise moderation when eating potato peels.

Table II. Reproducibility of Glycoalkaloid Determination in Four Commercial Potato Products

product	no. of samples	mg of glycoalkaloid/100 g of product: α-chaconine	mg of glycoalkaloid/100 g of product: α-solanine	α-chaconine coeff of var, %	α-solanine coeff of var, %
1	5	0.26	0.27	11.0	8.79
2	6	10.4	4.72	3.44	5.93
3	5	2.46	1.36	2.15	5.88
4	6	4.63	2.13	8.42	5.16

Table III. Stability of Glycoalkaloids during Cooking

product	no.[a] analyzed	mg of glycoalkaloids/100 g of product[b]: α-chaconine	α-solanine	α-chaconine and α-solanine
raw potatoes	2	6.49-9.84	3.84-6.30	10.3-16.1
baked potatoes	2	5.97-6.95	3.92-4.34	9.89-11.3
boiled potatoes	2	6.24-7.05	3.78-4.40	10.0-11.5
microwaved potatoes	2	7.56-8.04	4.82-5.30	12.4-13.3
raw peel	2	43.6-49.8	24.2-26.5	67.8-76.3
fried peel	2	37.9-39.9	18.8-19.5	56.7-59.4

[a] Each analysis was done in triplicate. [b] All values are corrected for moisture loss and fat absorption.

There seems to be much variation in the glycoalkaloid content between similar products from different manufacturers. For example, the analysis of four brands of potato chips demonstrated a glycoalkaloid content that varied from 2.67 to 16.2 mg of glycoalkaloids (α-chaconine plus α-solanine)/100 g of chips, and eight french fried items ranged in glycoalkaloid content from 0.43 to 5.78 mg/100 g of fried potatoes. The chips with the high concentration of glycoalkaloids still had some peel remaining. The only type of products that do not seem to vary from processor to processor are the canned items. For the products showing a large variation in glycoalkaloid content, the differences are most likely due to potato varieties, storage conditions, and processing techniques.

A recovery study of both α-chaconine and α-solanine was performed on two different processed products. Percent recoveries for α-chaconine were 98–101%, and for α-solanine they were 93–98%. These values indicate that this HPLC method can quantitatively recover both glycoalkaloids in varied sample matrices.

For determination of the reproducibility of this method for a wide variety of commercial products, four different products were analyzed several times. The results are given in Table II. The coefficients of variation for all values ranged from 2.15 to 11.0% with all but one below 9.0%, thus indicating the method is reproducible.

The results of the examination of the stability of glycoalkaloids during four types of cooking are shown in Table III. All glycoalkaloid values have been corrected for moisture loss and fat absorption during cooking. Of the four treatments, only frying appears to significantly de-

crease glycoalkaloid content.

LITERATURE CITED

Allen, R. J.; Marlar, R. J.; Chesney, G. F.; Helgeson, J. P.; Kelman, A.; Weckel, K. G.; Traisman, E.; White, J. W., Jr. *Teratology* **1977**, *15*, 17.
Alvarado, R. M.S. Thesis, University of Massachusetts, Amherst, MA, 1977.
Bushway, R. J.; Barden, E. S.; Bushway, A. W.; Bushway, A. A. *J. Chromatogr.* **1979**, *178*, 533.
Bushway, R. J.; Barden, E. S.; Bushway, A. W.; Bushway, A. A. *Am. Potato J.* **1980**, *57*, 175.
Emanuel, I.; Sever, L. E. *Teratology* **1973**, *8*, 325.
Hanson, A. A. *Science (Washington, D.C.)* **1925**, *61*, 340.
Keeler, R. F.; Brown, D.; Douglas, D. R.; Stallknecht, G. F.; Young, S. *Bull. Environ. Contam. Toxicol.* **1976**, *15*, 522.
Maga, J. A. *J. Food Process. Preserv.* **1980**, *4*, 50.
Mun, A. M.; Barden, E. S.; Wilson, J. M.; Hogan, J. M. *Teratology* **1975**, *11*, 73.
Renwick, J. H. *Br. J. Prev. Soc. Med.* **1972**, *26*, 67.
Sinden, S. L.; Webb, R. E. *U.S., Dep. Agric., Tech. Bull.* **1974**, *No. 1492*.
Sizer, C. E.; Maga, J. A.; Craven, C. J. *J. Agric. Food Chem.* **1980**, *28*, 578.
Thornton, R. E.; Sieczka, J. B., Eds. "Commercial Potato Production in North America"; Potato Association of America: Orono, ME, 1980.
Willimott, S. G. *Analyst (London)* **1933**, *58*, 431.
Wilson, G. S. *Mon. Bull. Minist. Health Public Health Lab. Serv. (G.B.)* **1959**, *18*, 207.

Received for review January 2, 1981. Accepted April 30, 1981.

Effect of Phenolic Compound Removal on in Vitro Forage Digestibility

Hans-Joachim G. Jung and George C. Fahey, Jr.*

The effect of phenolic compounds on in vitro digestion of forages was studied by using polyvinylpolypyrrolidone (PVP) to remove forage phenolics prior to digestion. Phenolic removal appeared to increase cellulose and protein digestibilities of alfalfa (*Medicago sativa*) but not crown vetch (*Coronilla varia*). Total organic matter disappearance was not significantly affected. The digestion process resulted in an increase in McDougall's buffer soluble phenolic compounds in the PVP-treated samples. The apparent source of this material was insoluble material prior to digestion. Lignin did not appear to be responsible for the increase in concentration of soluble phenolic compounds.

Phenolic compounds are ubiquitous in their distribution among vascular plants and are well-known for their ability to complex with protein (Van Sumere et al., 1975). The polymerized phenolics known as "tannins" are particularly well-known for this phenomenon (Loomis and Battaile, 1966; Feeny and Bostock, 1968) and are often blamed for the poor performance of animals fed tanniferous plants (Hawkins, 1955; Tamir and Alumot, 1970; Marquardt and Ward, 1979; Griffiths and Moseley, 1980). Monomeric phenolics are also capable of complexing with proteins and reducing proteolysis (Loomis and Battaile, 1966; Rhoades, 1977).

Since many agriculturally important legumes contain tannins and other phenolics (Sarkar et al., 1976; Milic, 1972), and since tannins depress digestibility of cellulose and protein in in vitro rumen fermentations (Tagari et al., 1965; Smart et al., 1961; Lyford et al., 1967), the nutritional effects of forage phenolics on ruminant digestion may be significant. In this study, we have examined the effect of removal of phenolic material from a high-quality forage, alfalfa (*Medicago sativa*), and a forage of disputed quality, crown vetch (*Coronilla varia*) (Hawkins, 1955; Reynolds et al., 1969; Burns et al., 1972), on in vitro nutrient digestibilities. It was expected that removal of phenolic compounds from these forages would result in increases in digestibilities of total organic matter, cellulose, and protein. The concentration of phenolic material was monitored in both the soluble and insoluble fractions of the digestion to determine if removal of phenolics from the soluble fraction affected insoluble forms of phenolic compounds.

Department of Animal Science, Animal Sciences Laboratory, University of Illinois, Urbana, Illinois 61801.

Table I. Composition of McDougall's Buffer Solution

constituent	mM/L
sodium bicarbonate	117
sodium phosphate dibasic	26
potassium chloride	8
sodium chloride	8
magnesium sulfate	0.3
calcium chloride	0.2

MATERIALS AND METHODS

Plant Material. The alfalfa was first-cut, early bloom material preserved as hay. The crown vetch was collected at Dixon Springs Agricultural Center, Simpson, IL, in late Nov 1979 and was lyophilized before grinding. Both forages were ground to pass a 2-mm screen and dried again at 45 °C. No information on varieties of the forages was available.

Removal of Forage Phenolics. Prior to in vitro digestion experiments, both forages were extracted for 24 h on a metabolic shaker, in the dark, with 30 mL of McDougall's (1948) buffer (pH 6.8) per g of plant material. The buffer composition is given in Table I. Forage phenolics were removed from a portion of each extract (after filtration) by using 1 g of polyvinylpolypyrrolidone (PVP) per 30 mL of extract and shaking for 1 h. Phenolics bind preferentially to PVP (Loomis and Battaile, 1966; Anderson and Sowers, 1968). The insoluble PVP was then removed by filtration and the PVP extraction was repeated 5 times. The change in phenolic concentration was monitored by the Folin–Denis assay (Swain and Hillis, 1959). The PVP was washed twice with 95% ethanol, 3 times with

0021-8561/81/1429-0817$01.25/0