

Determination of Heavy Metals and Pesticides in Ginseng Products

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Medicinal plants may carry residuals of environmentally persistent pesticides or assimilate heavy metals in varying degrees. Several factors may influence contaminant accumulation, including species, level and duration of contaminant exposure, and topography. As part of a program for assessment of the quality of herbal medicines, we have analyzed 21 over-the-counter ginseng (*Panax ginseng*) products in various dosage forms. Chromium, mercury, and arsenic were undetectable above their limits of detection in both liquid and solid samples; while cadmium, lead, and nickel were present in the majority of samples. The chlorinated pesticide levels varied widely. In most samples, the total concentration of pesticides was below 100 ppb; while in 5 samples the total concentration exceeded 100 ppb.

At present, more than 30% of the U.S. households use botanical products, mainly as health enhancers. The growing popularity of herbal products in the United States is reflected in a market revenue that grew to \$4 billion in 1998 (1). Although most vitamin and mineral supplements pose no threat to individuals, botanicals and herbal products are still under investigation (2). In spite of this, more than 65% of the U.S. users of botanical products believe that they are safe (1).

While many investigations of their medicinal values are being reported in current literature, less emphasis has been made on the purity of herbal products. With metals as com-

mon contaminants in such products, toxicity, primarily due to lead, arsenic, and mercury, has been manifested in the form of anorexia, constipation, and abdominal pain (3–5). It has been suggested that the maximum allowable level of cadmium and lead in herbal products should not exceed 0.5 and 10 mg/kg, respectively. These values were based on statistical percentiles of observed concentrations in herbal samples (6).

Because the presence of environmental contaminants in a variety of foods is well documented (7, 8), the U.S. Food and Drug Administration (FDA) routinely monitors food products to minimize risk to consumers. Medicinal herbs, which are classified as dietary supplements, are not subjected to the same monitoring process; that is, they are not regulated as drugs by the FDA. Instead, they are regulated under the Dietary Supplement Health and Education Act (DSHEA). Under DSHEA, companies are allowed to make claims about the benefit of their products in maintaining normal health (2, 9). However, standard quality control procedures for ensuring safety and efficacy, as well as purity, are not necessarily enforced (10).

In this preliminary study, measurable levels of metals and chlorinated pesticides were found in the botanical dietary supplement ginseng (*Panax ginseng*). Our results, although qualitative in nature, serve to identify the problem of environmental contamination of dietary supplements and to draw attention to the necessity for developing validated quantitative methods for the analysis of such contaminants in the various herbal products available at present.

Experimental

Samples

Ginseng samples were purchased from the United States, Europe, and Asia and analyzed for metals (chromium, nickel, lead, arsenic, cadmium, mercury) and chlorinated pesticides.

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Samples consisted of both solid (tablet, capsule) and liquid (tincture) formulations.

Metal Analysis

For the determination of chromium, nickel, lead, arsenic, and cadmium, ginseng samples (0.5–3.0 g) were weighed into Teflon-lined microwave digestion vessels (CEM Corp., Matthews, NC). To each vessel, 3 mL concentrated trace metal grade nitric acid, 2 mL concentrated trace metal grade HCl, 2 mL concentrated trace metal grade sulfuric acid, and 5 mL Nanopure filtered deionized water were added. Each vessel was sealed and microwave digested (CEM Corp., Model MDS-2100) for 40 min at a maximum temperature of 120°C and pressure of 130 psi. Following digestion, samples were cooled to ambient temperature and pressure vented. Samples were then quantitatively transferred to 100 mL volumetric flasks following a triple rinse with deionized water and made to volume with deionized water. Each sample was subsequently transferred to a 125 mL high-density polyethylene (HDPE) bottle for storage. Graphite furnace and flame atomic absorption spectrophotometry were utilized for analysis of metals. The detection limits for liquid samples were 0.1 mg/L for chromium, 0.5 mg/L for nickel, 0.1 mg/L for lead, 0.5 mg/L for arsenic, and 0.2 mg/L for cadmium. The detec-

tion limits for nickel, lead, arsenic, and cadmium in solid samples were 0.5, 1.0, 0.5, 1.0, and 0.5 ng/g, respectively.

For mercury determination, ginseng samples were weighed (0.5–5.0 g) into biochemical oxygen demand (BOD) bottles (Fisher Scientific, Pittsburgh, PA). To each bottle, 5 mL concentrated trace metal grade nitric and hydrochloric acids were added. Samples were allowed to digest for a minimum of 6 h. Following digestion, 15 mL of a 5% (w/v) potassium permanganate and 10 mL of a 5% (w/v) potassium persulfate solution in deionized water were added to each bottle. The resulting reaction was allowed to occur for a minimum of 30 min. Next, 60 mL deionized water, 100 mL Baxter Antifoam agent "B," and 5 mL NaCl and hydroxylamine hydrochloride (each 12% w/v) solution, in deionized water, were added to each sample vessel. The samples were immediately analyzed using a Varian Spectra AA 20 (Palo Alto, CA) atomic absorption spectrophotometer with a Varian VGA-76 cold vapor generation accessory. Detection limits for liquid and solid ginseng samples were estimated to be 50.0 and 100.0 ng/L, respectively.

Chlorinated Pesticides Analysis

The ginseng samples were analyzed by the method routinely used in-house for chlorinated pesticides (11). Samples were accurately weighed (3.00–5.00 g) into 40 mL glass centrifuge tubes and spiked with internal standards PCBs 103 and 198 (50.0 µL). Twenty milliliters acetonitrile (liquids) or a 65% acetonitrile–water solution (solids) was added and samples subsequently sonicated with a micro-probe fitted, 650 watt sonicator for a minimum of 2 min. Each sample was then centrifuged (IEC clinical centrifuge, setting 4), at room temperature, for 5 min. Samples were decanted into 125 mL borosilicate glass bottles containing 70 mL pentane-ashed deionized water, and saturated with 2% sodium sulfate. Following centrifugation, 20 mL pesticide grade pentane was added to each bottle. The bottles were sealed with a Teflon-lined cap and shaken for a minimum of 2 min. The aqueous layer was allowed to separate from the solvent layer. Following separation, the solvent layer was removed using a glass pipet and transferred to an Erlenmeyer flask containing 15 g anhydrous sodium sulfate. Each sample was reduced to 10 mL using a nitrogen evaporator (Organomation N-EVAP, Berlin, MA) under heat (40°–45°C). Impurities were removed by running samples through a Florisil chromatography column (10 × 300 mm length, 5 g heated Florisil, 1.5 g sodium sulfate). Columns were eluted with 25% ethyl ether–pentane (v/v), 10% methylene chloride–pentane (v/v), and pentane, respectively, and the eluates collected in 150 mL Erlenmeyer flasks. Sample volume was reduced to 20 mL using nitrogen evaporation, quantitatively transferred to 25 mL concentrator tubes, and further reduced to a final volume of 1 mL. Samples were transferred to auto-sampler vials and analyzed by a Hewlett-Packard (Santa Clarita, CA) 5980 Series II gas chromatograph (GC) with data station. The GC was also equipped with dual injectors, dual electron capture detectors, auto-sampler, and J&W Scientific (Agilent Technologies, Palo Alto, CA) dual DB-5 columns (60 m × 0.25 mm ×

Table 1. Heavy metal levels (ppb) detected in ginseng products

Sample	Ni	Pb	Cd
S1	1.8	— ^a	35.9
S2	4.3	—	39.4
S3	4.7	7.9	38.7
S4	5.6	4.1	44.0
S5	2.4	14.5	41.0
S6	1.4	9.2	54.1
S7	—	20.6	49.6
S8	4.7	12.0	52.2
S9	3.0	26.7	63.1
S10	3.0	15.6	60.4
S11	2.4	17.0	42.9
S12	5.8	19.1	53.4
S13	10.4	14.9	120.8
L1	—	19.2	9.5
L2	20.0	8.3	9.4
L3	6.0	62.2	9.4
L4	18.0	—	9.1
L5	12.0	23.2	8.5
L6	—	26.1	8.4
L7	10.0	12.9	9.9
L8	—	14.3	8.8

^a Undetectable levels.

Table 2. Chlorinated pesticide levels (ppb) detected in ginseng products

Pesticide	Sample														
	S1	S2	S3	S4	S5	S6	S9	S10	S13	L1	L2	L3	L4	L5	L7
HCB	39.30	— ^a	—	—	—	—	—	—	—	—	—	—	13.60	—	125.70
β-HCH	31.10	60.10	—	—	—	—	—	—	—	—	4.00	—	57.50	—	75.50
Lindane	21.00	20.30	—	—	—	—	—	—	—	2.50	—	—	24.00	—	104.70
PCNB	478.30	—	—	—	—	4.30	—	—	—	4.00	—	0.50	18.70	4.70	775.80
Chlorothalonil	—	192.90	—	—	—	—	—	—	—	—	—	2.00	17.90	—	—
Ronnel	219.50	—	15.20	—	—	—	—	—	3.90	—	—	—	—	—	23.90
Aldrin	—	—	28.10	—	—	—	—	—	9.60	—	—	—	8.00	—	—
Dicofol	207.90	—	115.30	—	—	—	—	—	—	—	—	—	9.00	—	76.20
Dacthal	42.70	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heptachlor	14.80	16.30	—	—	—	—	—	—	—	—	—	—	—	—	—
Heptachlor Epox	9.20	22.80	13.20	—	—	—	—	—	2.60	—	—	—	—	—	—
α-Chlordane	22.50	—	2.50	—	—	—	—	—	—	—	—	—	—	—	—
trans-Chlordane	—	94.20	—	—	—	—	—	—	—	—	—	5.20	9.00	—	—
o,p-DDT	—	—	21.90	—	—	—	—	—	—	—	—	—	—	—	—
p,p-DDT	—	—	14.90	45.10	—	—	4.30	3.80	—	—	—	—	—	—	44.10
o,p-DDD	12.60	—	—	—	—	—	—	—	—	—	—	—	—	—	—
p,p-DDD	—	—	58.60	—	27.20	—	—	—	—	—	—	—	0.70	—	—
o,p-DDE	63.30	6.30	13.30	—	—	—	—	—	—	—	—	—	—	—	—
p,p-DDE	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
trans-Nanochlor	—	—	—	—	—	—	—	—	—	—	—	—	1.40	—	—
Dieldrin	—	9.60	—	—	41.50	—	—	—	—	—	—	—	3.70	—	—
Endrin	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mirex	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

^a Undetectable levels. Samples S7, S8, S11, S12, L6, and L8 did not show detectable levels of any pesticide.

0.25 μm). Detection limits were 1.0 mg/L or 1.0 ng/g for all samples.

Results

Twenty-one samples (13 solid samples and 8 liquid samples) were evaluated. While concentrations of arsenic, mercury, and chromium were below the detection limit in all samples, cadmium (Table 1) was present in all samples. Nickel and lead were present in 81.0 and 85.7% of the samples, respectively. In general, cadmium concentrations were highest in solid samples, while concentration levels of nickel and lead were similar in liquid and solid samples.

Organochlorine compounds were detected in 75.0 and 69.2% of the liquid and solid samples, respectively (Table 2). In samples L4 and S1, there were more than 10 detected compounds. Individual compounds, such as quintozone (PCNB) and β -hexachlorocyclohexane (β -HCH) were detected in 33.0 and 23.8% of the samples, respectively. Dichlorodiphenyltrichloroethane (DDT) and its metabolites (42.8%), hexachlorobenzene (HCB; 19.0%), γ -hexachlorocyclohexane (lindane; 23.8%), heptachlor (9.5%), heptachlor epoxide (19.0%), aldrin (14.3%), α - and *trans*-chlordane (23.5%), and dieldrin (14.3%) were also detected.

Discussion

The analytical results obtained for all metals and most pesticides indicate that they were present within safety threshold limits (6).

Chlorinated pesticides were present in 3 solid samples (S1, S2, and S3) and in 2 liquid samples (L4 and L7), in total concentrations ranging from 163.5–1225.9 ppb. The presence of such relatively high levels (>100 ppb) of organochlorine pesticides may be due to their extensive use in specific locations, which is aggravated by their tendency to persist in the environment due to high binding affinities for soils and sediments.

To probe their significance, the current analytical results were utilized in standardized risk assessment procedures that

suggested that ingestion of pesticide-contaminated ginseng supplements might pose a carcinogenic risk to individuals consuming these products over their lifetime. The same study also showed that the doses of cadmium, lead, and nickel that are associated with ginseng, which would be ingested by an individual, would not drastically affect human health (12); however, risk assessment paradigms may underestimate the effects on children or adolescent who may be more susceptible to adverse effects of contaminants, especially metals.

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