

# PRELIMINARY FORENSIC ANALYSIS OF THE WILDLIFE CONTENT OF PATENTED ASIAN MEDICINES

by

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The Chinese Herbal Medicine Materia Medica (Bensky and Gamble 1986) identifies 392 substances that have pharmaceutical uses. A survey of this publication reveals that 88 percent of the ingredients are plants, 9.4 percent of the ingredients are minerals or nonendangered animal products, and only 2.6 percent are from endangered animal taxa. Endangered animal taxa identified include antelope, bear, macaque monkey, musk deer, pangolin, rhinoceros, sea turtle, seal, tiger, and tortoise. A research goal at NFWFL is to identify and analyze oriental medicines that purport to contain endangered species products, specifically materials from bear, rhinoceros, tiger, musk deer, and seal. The following discussion will concentrate on these taxa only.

## Bear

Gallbladders from 289 members of the bear family, Ursidae, were analyzed using the method of Espinoza *et al.* (1993). Species represented include grizzly bear (*Ursus arctos*), North American black bear (*U. americanus*), polar bear (*Thalarctos [Ursus] maritimus*), farmed bears (suspected to be *U. thibetanus* and *U. arctos* [Mills and Servheen 1991]). Additionally, Hagey *et al.* (1993) investigated the bile acid composition of sun bears (*Helarctos malayanus*), sloth bears (*Melursus ursinus*), and spectacled bears (*Tremarctos ornatus*).

The main Ursidae bile acids consist of ursodeoxycholyl-aurine, chenodeoxycholyl taurine, and cholyl-aurine as well as minor components (Hagey 1992). Therefore, it can be inferred that the combination of these bile acids is an Ursidae family characteristic; no other species among 600 analyzed (Hagey 1992) share this unique bile acid profile. The main bile acids of farmed bears consist of ursodeoxycholyl-aurine and chenodeoxycholyl taurine, with little or no cholyl-aurine (Guanlin and Guanzhu 1988, Espinoza *et al.* 1993). The absence of the characteristic Ursidae species bile acids are indicative that the source of the bile does not belong to the Ursidae family.

Bile salts and gallbladders received as evidence from Asia (Hong Kong,

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Taiwan, and Malaysia), Canada, and the United States were analyzed. Analysis showed that of the samples from Asia (sample size was 137), 3 gallbladders (2 percent) were from the Ursidae family and 25 (18 percent) were from farmed bears. The probable source of the majority (109) of the bile salts and gallbladder samples was domestic pigs. Samples seized in the United States (sample size was 468) showed that 106 gallbladders (23 percent) were from the Ursidae family and 77 percent were from pigs. Gallbladders seized in Canada (sample size was 300) revealed that 255 (85 percent) were from the Ursidae family. The substitution of pig gallbladders for those of bear and the fraudulent nature of the trade in gallbladders and bile salts was documented by Namba *et al.* (1982).

### Musk Deer

Investigations on musk-containing patented medicines have focused on only the musk-tiger Bone plaster preparations. Male musk deer produce an odoriferous substance called Muscone that is secreted from a ventral gland. Natural muscone is *laevo*-Muscone. Synthetic muscone is *racemic*- or *di*-muscone (Nelson and Mash 1986).

Natural and synthetic muscones have unique, distinctive mass spectra that allow for identification by gas chromatography-mass spectrometer (GC-MS). Examination of the musk-tiger bone plaster preparations in Table 16 by GC-MS did not detect the presence of Muscone.

### Tiger

Investigations of tiger-containing patented medicines has focused only on musk-tiger bone plaster. Research has branched into two areas: (1) confirmation of the presence of bone by Fourier transform infrared spectroscopy (FTIR) and (2) elemental analysis of the plaster by x-ray fluorescence spectroscopy (XRF). If bone is detected, immunodiffusion techniques (e.g., ouchterlony) may be used to identify the taxonomic family (not species).

Bone is mineralized connective tissue that consists of organic components (cells and matrix) and an inorganic component consisting mainly of the mineral hydroxyapatite [ $CA_{10}(PO_4)_6(CO_3)H_2O$ ]. Hydroxyapatite has a unique, distinctive spectra by FTIR analysis, and samples that contain detectable levels of bone can be identified by this signature.

Seven patented tiger bone plaster preparations were analyzed by FTIR. The corresponding results are shown in Table 16. These results reveal that none of the patented Musk-Tiger Bone Plasters contain detectable amounts of bone.

The main element detected by XRF analysis of the musk-tiger bone plaster was zinc (Zn). A possible source of zinc in plasters is the mineral Smithsonite ("Smithsonitum" in TCM pharmacopeia), which is zinc carbonate ( $ZnCO_3$ ) of the calcite group found in limestone areas (Frye 1981).

Additionally, current investigations are underway to determine the occurrences of the practice of modifying the dried genitals of domestic animals, such as cattle, to resemble the barbed penises of tiger (*Panthera tigris*). Bulls lack the os penis, a heterotopic bone embedded in the penis, and the male tiger has a reduced baculum that may be obscured by an X-ray. Therefore, it is necessary to rehydrate the organ and dissect the penis to retrieve and identify the baculum if present. Under magnification, traces of delicate v-shaped incisions may be visible on the surface of the glans penis of cattle, made before the organ was completely dried and subsequently curling toward the tip to form false barbs.

### Rhinoceros

Research on rhinoceros has branched into two areas: (1) the search for unique keratin proteins found in the rhinoceros horn and (2) the analysis of other substances found in patented oriental medicine rhino horn preparations.

**Rhinoceros Horn Keratin Research** - Initial research involving the characterization of keratin proteins in rhinoceros horn has followed the work of Carracedo et al. (1987) by identifying unique isoelectric focusing (IEF) patterns of the horn keratin. The presence of such proteins in patented oriental medicines will indicate the use of rhinoceros horn in the preparations. Preliminary analysis by a NFWFL scientist (K.A. Oakes, unpubl.) indicated that in three rhinoceros horn tea ball patented medicines no keratin proteins were detected that were consistent with known rhinoceros horn samples. Possible explanations for the absence of rhinoceros keratin from the rhino horn tea balls include fraud; the quantity of rhino horn in the medicine is below the sensitivity of the method (2 percent); or in processing the sample. Limitations of the IEF method resulted in shifting the research emphasis to characterizing rhinoceros horn keratin by size exclusion chromatography and FTIR. These approaches are currently in the development stage.

**Elemental Analysis of Rhinoceros Horn Tea Balls** - Multiple samples were analyzed from 10 different preparations of rhino horn tea balls using XRF and atomic absorption spectroscopy (AA) (Table 17). The following are the results of the elemental analysis of 9 patented medicines listing rhino as an ingredient

Table 16. Chemical analysis of patented oriental medicines generically known as musk-tiger bone plasters

PATENTED MEDICINE	NAME OF MANUFACTURER/LOCATION	SUMMARY OF TEST RESULTS DETECTED		
		HYDROXYAPATITE?	MUSK?	MAJOR ELEMENTS
NATURAL MUSK & TIGER-BONE PLASTER	Fifth Chengdu Pharmaceutical Factory Sichuan, China	NO	NO	Zinc
NATURAL MUSK & TIGER-BONE PLASTER	Aba Prefecture Pharmaceutical Factory Sichuan, China	NO	NO	Zinc
MUSK AND TIGER-BONE PLASTER	Changzhen Pharmaceutical Factory Huangshi, Hubei, China	NO	NO	Zinc
MUSK TIGER BONE PLASTER	White Plume Hubei, China	NO	NO	Zinc
ZhiTongGao MUSK & TIGER-BONE ANALGESIC PLASTER	[Not Available] Guangchow, China	NO	NO	Zinc
MUSK MEDICATED PLASTER	Zhanjiang Hygienic Materials Manufactory Kwangtung, China	NO	NO	Zinc
MUSK RHEUMATIC PLASTER	TopTez Pharmaceutical Co. Ltd. Guangdong, China	NO	NO	Zinc

- (1) DA HUO LUO WAN (Guangzhou Chen Li Ji Pharmaceutical Factory) and BEIJING TSU HSUEH (Beijing Tong Jen Tang) revealed the presence of mercury;
- (2) NIU HUANG CHIANG YA WAN (Tianjin Drug Manufactory) and TA HUO LO TAN (Peking Tung Jen Tang) revealed the presence of arsenic;
- (3) NIU HUANG CHIANG HSIN WAN (Tientsin Manufactory), NIU HUANG CHING HSIN WAN (Beijing Tongren Tang), TSAI TSAO WAN (Peking Tung Jen Tang), and NANJING TJT (Tong Ten Tang Co) revealed the presence of arsenic and mercury; and
- (4) NIU HUANG CHING HSIN WAN (Peking Tung Jen Tang) revealed the presence of arsenic, mercury, and lead (Table 17).

Quantitative analysis by AA shows that some rhinoceros tea balls contain elevated levels of these toxic inorganic elements, which could lead to serious health problems in long-term users.

The most likely source of mercury in traditional oriental medicine is the mineral cinnabar. Cinnabar ("cinnabaris" in the TCM pharmacopeia) is a mercury sulfide  $HgS$  (Frye, 1981) that occurs naturally in volcanic areas (see Mineral Sources of Mercury, Arsenic, and Zinc, below). Only one of the nine tea ball preparations, DA HUO LUO WAN (Guangzhou Chen Li Ji), listed cinnabaris among its ingredients. Pyrite ("Pyritum" in TCM pharmacopeia) is a probable source of arsenic in oriental medicines (see Mineral Sources of Mercury, Arsenic, and Zinc, below). A common, naturally occurring ore of arsenic is arsenopyrite,  $FeAsS$  (Frye 1981). None of the examined tea ball preparations listed "pyritum" as an ingredient. Unlike the apparent intentional inclusion of mercury and arsenic, the presence of lead in 4 of the 22 NIU HUANG CHING HSIN WAN (Peking Tung Jen Tang) tea balls we examined could be accidental. Leaded cooking utensils, leaded paint flakes, or any number of other sources could produce contaminated lead in a factory or home environment.

### Seal

Investigations on medicines containing seal have focused only on seal penis items. The analysis to determine the origin of desiccated samples is as follows: Dried genitals are x-rayed to determine the presence or absence of the os penis or baculum, a heterotopic bone embedded in the penis (Kent 1969). The morphology of this bone can be used to distinguish pinnipeds from other mammals, especially dogs (Family Canidae). Canids have a rather wide groove down the ventral face for the urethra and corpus spongiosum (Ewer 1973). In pinnipeds, the groove is absent

Table 17. Analysis of patented oriental medicines known as "rhino horn tea balls"/preparations

PATENTED MEDICINE	NAME OF MANUFACTURER/LOCATION	SUMMARY OF TEST RESULTS	
		MAJOR ELEMENTS DETECTED	QUANTITATIVE DATA ( $\mu\text{g/g}$ )
DA HUO LUO WAN	Guangzhou Chen Li Ji Pharmaceutical Factory Guangzhou, China	Mercury (Hg)	Hg = 14,000
DA HUO LUO WAN	Guangzhou Chen Li Ji Pharmaceutical Factory Guangzhou, China	Mercury (Hg)	Hg = 12,900
DA HUO LUO WAN	Guangzhou Chen Li Ji Pharmaceutical Factory Guangzhou, China	Mercury (Hg)	Hg = 15,100
NIU HUANG CHIANG YA WAN	Tianjin Manufactory Tianjin, China	Arsenic (As)	As = 9,500
NIU HUANG CHIANG YA WAN	Tianjin Drug Manufactory Tianjin, China	Arsenic (As)	As = 8,900
NIU HUANG CHIANG YA WAN	Tianjin Drug Manufactory Tianjin, China	Arsenic (As)	As = 8,500
NIU HUANG CHIANG HSIN WAN	Tientsin Manufactory Tientsin, China	Mercury (Hg) Arsenic (As)	Hg = 24,500 As = 5,300
NIU HUANG CHIANG HSIN WAN	Tientsin Manufactory Tientsin, China	Mercury (Hg) Arsenic (As)	Hg = 25,300 As = 3,400
NIU HUANG CHIANG HSIN WAN	Tientsin Manufactory Tientsin, China	Mercury (Hg) Arsenic (As)	Hg = 30,300 As = 7,100
NIU HUANG CHIANG HSIN WAN	Peking Tung Jen Tang Peking, China	Mercury (Hg) Arsenic (As) Lead (Pb)	Pb = 1,450

Table 17. Analysis of "rhino horn tea balls" (continued)

PATENTED MEDICINE	NAME OF MANUFACTURER/LOCATION	SUMMARY OF TEST RESULTS	
		MAJOR ELEMENTS DETECTED	QUANTITATIVE DATA ( $\mu\text{g/g}$ )
TA HUO LO TAN	Peking Tung Jen Tang Peking, China	Arsenic (As)	Not Done
TSAI TSAO WAN	Peking Tung Jen Tang Peking, China	Mercury (Hg) Arsenic (As)	Not Done
BEIJING TSU HSUEH	Beijing Tong Jen Tang Beijing, China	Mercury (Hg)	Not Done
NANJING TJJ	Tong Ten Tang Co [Not Available]	Mercury (Hg) Arsenic (As)	Not Done
DENDROBIUM MONILIFORME NIGHT SIGHT PILLS	Tientsin Drug Manufactory Tientsin, China	None Detected	Not Done
NIU HUANG CHING HSIN WAN	Beijing Tongren Tang Beijing, China	Mercury (Hg) Arsenic (As)	Not Done

or reduced, and with the otariids (eared seals), the apex of the baculum is distinctive to genus (Morejohn 1974). Analysis revealed that of 13 items examined, 10 were from the seal family, and the rest were from the Canid family.

## **MINERAL SOURCES OF MERCURY, ARSENIC, AND ZINC**

As discussed in the bear and tiger sections above, forensics tests detected in some medicines small amounts of mercury, arsenic, and zinc that were probably from the use of the minerals cinnabaris, pyritum, and smithsonitum, respectively. The following is a brief summary of the pharmacopeia of these.

### **Cinnabaris**

Cinnabaris, known as "Zhu Sha" in Mandarin, "Shusha" in Japanese, and "Chusa" in Korean, has properties of sweet, cool, and poisonous. Its known ingredients include mercuric sulfide and phosphates. It may be used for symptoms including restlessness, palpitations, insomnia, or convulsions, and it detoxifies poisons and prevents putrefaction. When combined with target ingredients such as Cornu Rhinoceri, it is used for high fever, loss of consciousness and convulsions; when combined with Radix Angelicae Sinensis and Semen Ziziphi Spinosae, it is used for irritability, insomnia, and palpitations. Cinnabaris should not be used in large amounts for long periods nor should it be heated to prevent mercury poisoning (Bensky and Gamble 1986).

### **Pyritum**

Pyritum, known as "Zi Ran Tong" in Mandarin, "Shizendo" in Japanese, and "Chayondong" in Korean, has properties of acrid, bitter, and neutral. It may be used for bone and sinew healing and treating swelling and pain from external injuries and fractures. Its known ingredients include ferrous disulfide, copper, nickel, and arsenic. (Bensky and Gamble 1986).

### **Smithsonitum**

Smithsonitum, known as "Lu Gan Shi" in Mandarin, "Rokanseki" in Japanese, and "Nogamsok" in Korean, has properties of sweet and neutral. Its known ingredients include zinc carbonate, calcium oxide, magnesium oxide, ferric oxide, and manganese oxide. It may be used for red and swollen eyes and visual obstructions or for draining pus and healing wounds. When combined with target ingredients, such as Fel Ursi and Borneol, it is used for redness, swelling, and ulceration of the eye. Contraindications include a caution not to use it internally and only as a powder refined by water. (Bensky and Gamble 1986).





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