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Monitoring of Residual Pesticides in Herbal Drug Materials of Korea and China

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Abstract The information of the pesticide residues in herbal drug materials (HDMs) is not sufficient to support the scientific risk management so far. Therefore, 30 types of HDMs such as the herba of *Artemisia montana* were analyzed for 47 different pesticides. Among 292 samples, eight Chinese and one Korean HDMs were contaminated with five pesticides such as methoxychlor, DDT, γ-BHC, endosulfan, and procymidone (0.044–0.501 mg/kg). The detection rate of pesticides in the tested HDMs was determined as 3.1%. On critical observation of the detected amount of procymidone (0.501 mg/kg) and methoxychlor (0.382 and 0.312 mg/kg), further intensive monitoring of the pesticides might be necessary for HDMs.

Keywords Herbal drug materials · Pesticides · Monitoring · Gas chromatography

Among 520 registered herbal drug materials (HDMs) in Korea Pharmacopeia (KP) and Korean Herbal Pharmacopeia (KHP), more than 418 HDMs are originated from plants that are mostly under cultivation like agricultural crops. Consumers could be exposed to the residual pesticides via foods plus HDMs simultaneously. However, from the regulatory point of view, uniform criteria on a world-wide level regarding the safety assessment of pesticides in HDMs do not currently exist. Recently Korea Food & Drug Administration (KFDA) commissioned a project for establishing a method to determine the maximum residue limits (MRLs) for pesticides in HDMs. This project aims to develop a scientific method to reduce the potent risk posed by residual pesticides in HDMs that are widely circulated in the market (CTOMC 2007). According to the report, most herbal medicinal plants are minor crops which are lack of registered pesticide products where the costs involved in generating data for registration. This is the one of the reason why it is hard to establish pesticide MRLs for HDMs by the traditional method. Moreover, Korea imports a large quantity of HDMs from China. Therefore, other scientific background, such as residual pesticide monitoring data, should be considered to establish the MRLs of HDMs (CTOMC 2007). Unfortunately the information of the pesticide residues in HDMs is not sufficient to support the scientific risk management so far. Previously the author reported the residual pesticide monitoring results of the 229 HDM samples (36 types of HDMs) in that eight pesticides were quantitatively detected in seven imported and two domestic HDMs (Oh 2007a). In this study, which is a continuation of the previous research, 292 samples of 30 types of HDMs were analyzed for the presence of 47 different pesticides. A matrix attributing problems encountered during the sample preparation of some HDMs are reported with the monitoring result too.

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Materials and Methods

The 292 HDM samples used in this study were different from those used in the previous study (Oh 2007a). Immediately after the HDMs were sampled, they were identified by an herbal medicine expert. Ten samples were collected for each HDM as possible as the sample is commercially available. Because some HDMs such as Ganghwal, Gwakhyang, Bangpoong, Aeyeup, Injinho, Jisil, and Jinpi, were identified as two or three different plant species, there were found to be a total of 40 HDM varieties and 30 HDM types (expressed as different Korean names) (Table 1). Two samples for each HDM were purchased at the HDMs market in Hébĕi Shĕng, China. These Chinese HDMs were cultivated in Hébĕi Shĕng, Guăngdōng Shĕng, and Sìchuān Shĕng in China. And the rest of the imported HDMs were purchased in Kyoungdong market that is the largest herbal drug market in Korea. Domestically produced HDMs were purchased at large herbal drug wholesale markets located in Daegu, Geumsan, and Yeongcheon from March to October 2002.

Fifty-five pesticide standards (47 kinds of pesticides) above the purity 95% were purchased from ChemService, Inc. (West Chester, PA, USA), Dr Ehrenstorfer (Augsburg, Germany), and Waco pure chemical Industries (Osaka, Japan) (Table 2).

The modified pesticides MRM No. 83 of Korea Food Code (KFDA 2002) was applied to the HDMs. Fifty-six target pesticide standards were divided into four groups including chlordane for gas chromatography-micro electron capture detection (GC-μECD) and one group for GC-nitrogen phosphorus detector (GC-NPD) analysis in which all peaks belong to each group were non-overlapping on a HP-5 GC capillary column. For validating the efficiencies of the method, the recovery tests were performed with Sansa, Injin, and Hwangjung after spiking the above pesticide group mixtures at two concentration levels (0.05 and 0.1 mg/kg). The sample preparation methods were the same as those used in the previous study (Oh 2007a). However for Ganghwal, Baekji, Mokhyang, and Hyangbuza, the different amount of each sample (5 g) was used. This is one-fourth of the sample amount (20 g) used in the previous study. To compensate for the loss of sensitivity due to the reduced sample amount, the final solution volumes of the four HDMs were reduced to 0.5 mL each. This volume is one-fourth of the final volume of the samples used in the modified pesticide multi-residual analysis method (MRM) No. 83 (Oh 2007a).

GC-μECD, GC-NPD, and GC-mass spectrometric detector (MSD) were utilized for the instrumental analysis of prepared samples. The instrumental conditions are same to former research (Oh 2007a).

Results and Discussion

The limit of detection (LOD) for the fifty-four pesticide standards ranged from 0.001 to 0.05 μg/mL. Dicofol indicated the highest LOD of 0.05 μg/mL. In order to determine the amount of pesticides recovered, Sansa (fructus), Injin (herba), and Hwangjung (radix) were selected from the 30 types of HDMs. Three preparations of each sample were analyzed, the results were averaged, and the percentage relative standard deviation (%RSD) was calculated for each pesticide. The percentage recovery of 54 pesticides ranged from 66% to 117%. Iprodione and bifenthrin had comparatively low recoveries of 66% and 68%, respectively. The %RSDs were 10% and 9% for iprodione and bifenthrin, respectively. The percentage recovery of the remaining pesticides from the three HDM samples was more than 70%.

During the extraction step performed using acetonitrile, three root samples (Ganghwal, Baekji, Mokhyang, and Hyangbuza) coagulated. This problem was occurred when 20 g of sample and 100 mL of acetonitrile was used. No coagulation was observed when the sample amount was reduced to 5 g. The similar problem was encountered with dried tea leaves in other study (Oh 2007b).

Among the thirty different HDMs, seven HDMs were consisted with two or three different species. Two samples of Wiyoo collected in Korea were confirmed as Uin (*Prinsepia uniflora* BATAL). Furthermore one Korean and five Chinese Hwangjung were confirmed as Wiyoo (*Polygonatum odoratum* Druce var. pluriflorum Ohwi). This was due to a shortage in the supply of authentic HDMs and also because the Chinese characters used to express the names of HDMs can be interpreted differently (Choi et al. 2002).

Among 292 samples, eight Chinese and one Korean HDMs were contaminated with five pesticides (Table 3). The pesticides, not detected in the previous study (Oh 2007a) were methoxychlor and DDT. Methoxychlor was detected at concentrations of 0.382 and 0.312 mg/kg in two different Chinese Jinpi which is the pericarp of the ripe fruit of *Citrus retecalata*. It appears in many traditional stomach medicines (KPTA 2003). These values are below the Korean MRL of the pesticide in Jinpi (1 mg/kg). Methoxychlor is one of a few organochlorine pesticides that have seen an increase in use since the ban on DDT in 1972. It is quite similar in structure to DDT, but has relatively low toxicity and relatively short persistence in biological systems (EXTOXNET 1996). It is also the one of the regulatory contaminants of drinking water in USA. Based on the maximum contaminant level goals (MCLG), EPA has set an enforceable standard, maximum contaminant level (MCL) as 40 ppb for drinking water (US EPA 2003). Even though it is not registered in Korea, there are 38 Korean MRL values (1.0–14.0 mg/kg) of methoxychlor for 36 agricultural products and one group MRL (for Mushrooms) (KFDA 2008). The ratio of theoretical maximum daily intake (TMDI) to the acceptable daily intake (ADI) of methoxychlor is approximately 62% (%TMDI) in Korea. The %TMDI is based on only the MRLs of pesticides in the agricultural products. KFDA has estimated that agricultural food contributes 80% of all exposure to pesticide residues over a lifetime, and the remainder (20%) is contributed by animal products, water and residential use of pesticides

Table 1 Tested herbal drug materials confirmed to genuine with origin

Academic name	Korean name	Used part	Origin (number)	
			Imported	Domestic
Artemisia montana Pampani	Aeyeup	Herba		Yeongcheon, Cheongdo, Inje(2)
Artemisia princeps Pamp. var. orientlis Hara	Aeyeup	Herba	China(6)	
Angelica dahurica Bentham et Hooker	Baekji	Radix	China(6)	Yeongcheon(4)
Panax ginseng C. A. Meyer	Baeksam	Radix	China(2)	Geumsan(8)
Mentha arvensis L. var. *piperascens* Malinv.	Bakha	Herba	China(6)	Yeongcheon(2), Chungcheong(2)
Peucedanum japonicum Thunb.	Bangpoong	Radix		Uiseong, Andong, Jeonnam(2)
Saposhnikovia divaricata Schiskin	Bangpoong	Radix	China(6)	
Pinellia ternata Breitenbach	Banha	Tuber	N. Korea(2), China(6)	UN(2)*
Areca catechu Linne	Binrangja	Semen	China(10)	
Plantago asiatica Linne	Chajunja	Semen	China(9)	UN
Zizyphus jujuba Miller var. *inermis* Rehder	Daechoo	Fructus	China(6)	Yeongcheon(2), Nonsan(2)
Coix lacryma-jobi Linne var. ma-yuen Stapf	Euiin	Semen	China(6)	Hamyang(2), Imsil(2)
Am pubescens Maxim	Ganghwal	Radix	China	
Notopterygium incisum Ting	Ganghwal	Radix	China	
Ostericum koreanum (Max) Kitagawa	Ganghwal	Radix		Gyoungbook province, Samcheok, Kangwon(2), Imsil, UN(3)*
Dianthus sinensis Linne	Goomack	Herba		UN(3)
Dianthus superbus Linne	Goomack	Herba	China(7)	
Agastache rugosa O. Kuntze	Gwakhyang	Herba		UN(2)
Pogostemon cablin (B)Benth	Gwakhyang	Herba	China(7)	UN
Carthamus tinctorius Linne	Honghwa	Bloom	China(10)	
Magnolia officinalis Rehder et Wilson	Hoobak	Tuber	China(6)	Jeju(4)
Scutellaria baicalensis Georgi	Hwanggum	Radix	China(6)	Junnam province(4)
Polygonatum sibiricum Redoute	Hwangjung	Radix	China(2)	Jecheon(2)
Cyperus rotundus Linne	Hyangbuza	Rhizoma	China(6)	Chilgok, Goryoung(2), UN
Schizonepeta tenuifolia Briquet	Hyunggae	Spike	China(6)	Yeongju, Gyoungbook province, UN(2)
Artemisia capillaris Thunberg	Injinho	Herba	China(6)	
Artemisia iwayomogi KITAMURA	Injinho	Herba		Yeongcheon(2), Inje(2)
Citrus retecalata Blanco	Jinpi	Fructus (peel)	China(6)	
Citrus unshiu Markovich	Jinpi	Fructus (peel)		Jeju province(4)
Citrus aurantium Linne	Jisil	Fructus	China(6)	
Poncirus trifoliata Rafinesqul	Jisil	Fructus		Jeju province(2), Yeongcheon(2)
Hordeum vulgare Linne	Meaga	Fructus	USA, China(5)	UN(4)
Inula Helenium Linne	Mokhyang	Radix	China(6)	UN(4)
Crataegus pinnatifida Bunge var. typica Schneider	Sansa	Fuructus	China(6)	Gangwon provice(2), Samchuck(2)
Acorus gramineus Solander	Seokchangpo	Rhizoma	Cina(9)	UN(1)
Bupleurum falcatum Linne	Siho	Radix	China(6)	Uiseong, Yeongcheon(3)
Perilla frutescens Britton var. acuta Kudo	Soyeup	Herba	China(6)	Gyoungbook province, Yeongcheon(2), Junbook province
Alisma orientale Juzepczuk	Taeksa	Tuber	China(6)	Sanju, Junnam province, Poonggi(2)
Prinsepia uniflora BATAL	Uin	Semen		Jecheon(4), UN
Polygonatum odoratum Druce var. pluriflorum Ohwi	Wiyoo	Radix	China(8)	

* UN means there is no information of the domestic origin

Table 2 Target pesticides for herbal drug materials

Aldrin & Dieldrin	Diazinon	Iprodione	Procymidone
BHC (α, β, γ, δ)	Dichlofluanid	Malathion	Profenofos
Bifenthrin	Dicofol (Kelthane)	Methidathion	Prothiofos
Captan	Dieldrin	Methoxychlor	Pyrazophos
Chinomethionat	Endosulfan (α, β, Sulfate)	Methyl parathion	Quintozene
Chlordane	Endrin	Mevinphos	Tetradifon
Chlorfenapyr	EPN	Myclobutanil	Tolyfluanid
Chlorothalonil	Ethoprofos	Pendimethalrin	Triadimefon
Chlorpyrifos	Fenitrothion	Phenthoate	Triadimenol
Chlorpyrifos methyl	Fenpropathrin	Phosalone	Triazophos
Cypermethrin	Fenvalerate	Phospamidone	Vinclozolin
DDT (DDT, DDE, DDD)	Imazalil	Pirimiphos methyl	

Table 3 Pesticides monitoring results of the HDMs with MRLs of Korea and European pharmacopoeia 6.2

HDMs				Pesticides	Limit of detection (mg/kg)	Detected concentration (mg/kg)	Recovery (RSD%)	MRLs (mg/kg)	
Academic name	Korean name	Used part	Origin					For HDMs in Korea	European pharmaco-poeia 6.2
Dianthus sinensis Linne	Goomack	Herba	Domestic	Procymidone	0.006	0.501	83.4(14)	0.1	0.1
Dianthus superbus Linne	Goomack	Herba	China	γ-BHC	0.001	0.131	75.4(11)	0.2	0.6
Peucedanum japonicum Thunb.	Bangpoong	Radix	China	DDT	0.002	0.079	77.1(10)	0.1	1
Peucedanum japonicum Thunb.	Bangpoong	Radix	China	Endosulfan	0.001	0.044	70.9(10)	0.2	3
Acorus gramineus Solander	Seokchangpo	Rhizoma	China	Endosulfan	0.001	0.058	70.9(10)	0.2	3
Bupleurum falcatum Linne	Siho	Radix	China	DDT	0.002	0.108	77.1(10)	0.1	1
Citrus reticalata Blanco	Jinpi	Fructus (peel)	China	γ-BHC	0.001	0.206	75.4(11)	0.2	0.6
Citrus reticalata Blanco	Jinpi	Fructus (peel)	China	Methoxychlor	0.01	0.382	82.4(12)	1	0.05
Citrus reticalata Blanco	Jinpi	Fructus (peel)	China	Methoxychlor	0.01	0.312	82.4(12)	1	0.05

Korean MRL for BHC means the sum of α, β and γ-BHC

(CTOMC 2007). The %TMDI of methoxychlor (62%) may be close to the risk cup of 80% if the amount of HDM intake is considered. Another organochlorine pesticide detected in Jinpi was γ-BHC (0.206 mg/kg). γ-BHC was the most prominent of the BHC isomers in three types of Ayurvedic (herbal) formulations in India (Rai et al. 2007). It has also been detected in Chinese Goomack (herba of *Dianthus superbus*) (0.131 mg/kg). Korean MRL 0.2 mg/kg of BHC is the sum of isomers α, β, γ, and δ-BHC for HDMs. There is no separate MRL for γ-BHC in Korea. However, there is a separate MRL (0.6 mg/kg) for γ-BHC (Lindane) in European Pharmacopoeia 6.2 (EP6.2) (EDQM 2008). DDT, which has not been found in HDMs of previous study (Oh 2007a), was detected at concentrations of 0.079 and 0.108 mg/kg in the Bangpoong (radix of *Peucedanum japonicum*) and Siho (radix of *Bupleurum falcatum*), respectively. The type of DDT found in Bangpoong was $p.p'$-DDD ($p.p'$-TDE). DDT MRL in EP6.2 (1 mg/kg) is ten times higher than Korean's. Bangpoong is used in the treatment of migraine headaches, colds, and rheumatoid arthritis in Korea (NPRI 1998). Siho contains saikosides that is saponin-like substances have been shown to protect the liver from toxicity whilst also strengthening its function, even in people with immune system disorders (Chevallier 1996). Endosulfan is a inexpensive cyclodiene insecticide and acaricide used in agricultural and horticultural crops for the control of a variety of insects and mites. It was detected in Bangpoong and Seokchangpo (rhizome of *Acorus gramineus*) at concentrations of 0.044 and 0.058 mg/kg, respectively. These values were below the Korean MRL of 0.2 mg/kg and EP6.2 MRL of 3 mg/kg. There are 57 Korean MRL values (0.1–2.0 mg/kg) of endosulfan for 55 agricultural products and two group MRLs (for other citrus fruits and other cereal grains) (KFDA 2008). The detection and violation rates of endosulfan in 900 agricultural products (31 species) were 1.8% and 0.1%, respectively, according to the 2004 results of pesticide monitoring by Busan, Seoul, and Gyoungin regional FDA in Korea (2004). Endosulfan is registered for tobacco and mulberry tree in Korea (KCPA 2007). The detected amount of procymidone, i.e., 0.501 mg/kg, in Korean Goomack (herba of *Dianthus sinensis* or *D. chinensis*) was more than five times the Korean and EP6.2 MRL of 0.1 mg/kg (KFDA 2008; EDQM 2008). The whole plant of Goomack is a bitter tonic herb that stimulates the digestive and urinary systems and also the bowels (Bown 1995). Procymidone was previously detected at 0.57 and 0.58 mg/kg in the rhizoma of *Atractylodes japonica* and *A. lancea*, respectively, (Oh 2007a). Procymidone is a systemic fungicide with protective and curative properties. It absorbed through the roots, with translocation to leaves and flowers (BCPC 2006). Recently, KFDA established the additional MRL of procymidone (0.05 mg/kg) for the other agricultural products group (KFDA 2007). Therefore, the violation rate of procymidone residues in agricultural products has been increased recently. The present %TMDI for procymidone in agricultural products appears to be lower than the risk cup for procymidone in Korea. However, in Australia, the % acute reference dose of procymidone (ARfD; 0.03 mg/kg) for stone fruit is commonly observed to be exceeded in both children and in the general population (APVMA 2004).

In this study, the detection rate of pesticides in the tested HDMs was determined as 3.1%. This is lower than 3.9% obtained in the previous study (Oh 2007a). On critical observation of the detected amount of procymidone and methoxychlor, further intensive monitoring of the pesticides might be necessary for HDMs.

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