Determination of Pesticide Residue in Vegetable Juice, Fruit Juice and Green Tea Solution in Closed Package

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ABSTRACT

Determination of pesticide residue in 25 closed-package samples of vegetable juice, fruit juice and green tea solution revealed pesticide residue in 20 samples. Pesticides that were frequently found were heptachlor and lindane. We found heptachlor 0.025-0.060 ppm in green tea and the amounts from 2 of 5 samples were over the permissible level. Lindane was also found at 0.005-0.014 ppm. Lindane is a nonpermitted pesticide. In apple juice, we found hepatachlor 0.040 ppm, lindane 0.007 ppm, aldrin 0.010 ppm which were within the allowable limit. In foreign carrot juice samples, we found heptachlor 0.030 ppm, o,p'-DDD 0.600 ppm and B-endosulphan 0.240 ppm. The amount of o,p'-DDD in foreign carrot juice was over the limit and B-endesulphan is a nonpermitted pesticide. We found that the Thai carrot juice consisted of heptachlor 0.020 ppm and G-chlordane 0.400 ppm. G-chlordan is also a nonpermitted pesticide. We found pesticide residue in grape juice that might be abamectin. We did not find any pesticide residue in orange juice. These results from our investigations should stimulate the Ministry of Public Health to be interested in controlling the use of pesticides in packaged juices and teas.

Key words: Pesticide residue, Vegetable juice, Fruit juice, Green tea solution.

INTRODUCTION

In 1985, we found organochlorine and organophosphate pesticide residues in fruits, vegetables, oil plants, animal food and eggs in more than 2000 samples of the 3000 samples from Thailand. (http://wbc.msu.ac.th/ge/0299101/tarapron/tarapron 0.5-3.R.html).

In 1982-1985, Thai Ministry of Public Health found DDT in 39% and dieldrin in 15% of 663 samples. In 1993 National Environment Board of Thailand found pesticide residues in 86% of water samples, 32% of fruits and 25% of vegetables. The amount found was 8 times higher than the limit value, this was the result of insect resistance.

In 1990, USFDA found pesticide residues in 900 samples of baby food which were beononyl-thiabendazole (fungicide), daminazide, ethylenethiourea (ETU,

fungicide), aldicarb, organochlorine compounds and also found beononyl-thiabendazole in apple sauce, banana, orange and pear. Daminazide was found in apple, grape juice, apple sauce and canned pear. ETU was also found in banana, orange and orange juice. The amount of aldicarb found was under the limit.

In 1990-2000, the Environment Protective Agency of USA declared limit use of organophosphate, e.g., the limit use of azinphos methyl, chlorpyrifos and methyl paraben.

In 1994, Thai government found heptachlor, DDT and methyl bromide in rice and also found monochlortophos, methonyl, cypermethrin and organochlorine such as BHC, dieldrin and DDT in vegetables. Organochlorine such as BHC, heptachlor, lindane and DDT were found in other products. The amounts of pesticide residues found were not over Maximum Residue Limit (MRL). (http://www.consumerthai.ag/data/ chemicals/chemical_01.htm#1).

In 1992-2001, US Department of Agriculture (USDA) found that 34 types of organophosphates were used. The amounts found were less than the amounts used before. Contaminated samples were 19-29%. Much pesticide residue was found in the years 1996-1997, and lesser amounts were found in 2001.

In 1997, Pesticide Data Program (PDP) of USA determined pesticide residues in 8,177 fruit samples. Pesticidue residues were found in 409 samples. The amounts found were under the government limit and more than 1 type of pesticide was found. (http://virtualorchard.net/glfgn/april199/pdprepot.html).

Total Diet Study of US. FDA found pesticide residues in 1,030 types of food in the year 2002. The pesticides that were much used were DDT, chlorpyrifos-methyl, malathion, endosulfan and dieldrin.

In 2000, Government of England determined pesticide residues in vegetables and fruits. They found that dicofol was used in strawberry. They also found pesticide residues in grape and plants at the amount higher than the limit. They found lindane in mushroom and tomatoes and aldicarb was found in potatoes.

Nowadays, Thai people drink vegetable juice, fruit juice and green tea in closed package although these foods are expensive and do not think about pesticide residues in them. If people drink these foods containing a high amount of pesticide for a long time, they could become sick. (Hardman and Limbird, 2001). We thought about this risk, so we will identify and determine types and amounts of pesticide in these samples.

MATERIALS AND METHODS

Preparation of samples

Sample of 100 ml. was mixed with acetonitrile 100 ml and celite 545 10 gm. It was blended with high speed for 2 minutes and filtered. The filtrate was extracted with petroleum ether 100 ml. for 2 minutes and then a saturated solution of sodium chloride 10 ml was added and distilled water 3000 ml. was added and extracted for

30 seconds. The aqueous layer was discarded. Petroleum ether layer was washed with distilled water 100 ml., 2 times. Anhydrous sodium sulfate 15 gm. was added, mixed and filtered. The filtrate was evaporated to dryness under vacuum.

Purified petroleum ether extract by column chromatography using activated florisil as the adsorbent (florisil was activated at 130°C for 5 hours, activated florisil that was kept in dessiccator could be used within 3 days) and eluted with 6% and 15% diethyl ether in petroleum ether each 200 ml. Each eluent was evaporated to dryness under vacuum.

Identification and determination of pesticide residues

The samples were identified by using thin layer and gas chromatography. Alumina was used as the adsorbent for thin layer chromatogram with a thickness 0.25 mm. Developing solvents for organochlorine and organophosphate were n-heptane for 6% fraction and 2% acetone in n-heptane for 15% fraction except grape juice which also used cyclohexane as another developing solvent because the suspected pesticide was abamectin. (Horwitz, 2000)

We also identified and determined pesticide residues by gas chromatography. The column used for identification and determination was RTX-CLP (capillary column coated with fused silica, Restek Company) and HP-5 column (5% phenylmethyl polysiloxane, J.W. Scientific Company) was used for confirmation test. GC conditions were : GC oven 100°C, increasing 20°C /min until 175°C and increasing 8°C/min until 250°C., GC injection port was 210°C and GC μ electron capture detector was 300°C., carrier gas was nitrogen. Injection volume for RTX-CLP was 2 μl and for HP-5 was 1 μl.

Preparation of standard abamectin

We have no pure standard abamectin, therefore we prepared it from marketed abamectin pesticide by extraction and purification by the same method like the samples.

RESULTS

Pesticide residues in green tea solution samples were heptachlor and lindane, the amounts are shown in Table 1.

Table 1. The amounts of pesticide residues in green tea solution samples.

Descriptions	Heptachlor (ppm)	Lindane (ppm)
1st Sample	0.060	0.014
2nd Sample	0.040	0.010
3rd Sample	0.030	0.007
4th Sample	0.025	0.005
5th Sample	0.006	0.010

Pesticide residues in 5th apple juice sample were heptachlor 0.040 ppm, aldrin 0.010 ppm. and lindane 0.007 ppm. We found heptachlor 0.030 ppm, o,p'-DDD 0.600 ppm and B-endosulphan 0.240 ppm in carrot juice sample made from foreign country and 4th carrot juice sample made in Thailand was found to contain heptachlor 0.020 ppm and G-chlordane 0.400 ppm

Pesticide residue in 1st grape juice sample might be abamectin. We found no pesticide residue in all orange juice samples.

DISCUSSION AND CONCLUSION

From TLC and GC, we found that 5 green tea sample solutions consisted of heptachlor and lindane as shown in Table 1. In 1st and 5th sample, we found heptachlor 0.060 ppm which were over the permissible limit. The Thai Food Act of 2005 declared that in vegetable, fruit juice and green tea solution in closed package, the amount of heptachlor can not exceed 0.050 ppm and lindane is not permitted to be used.

From TLC and GC, 5 apple juice samples consisted of heptachlor, lindane and aldrin, so we only determined the amount of pesticide in 5th sample which (from TLC) consisted of large spots of pesticide. In this sample, there were heptachlor 0.040 ppm, lindane 0.007 ppm and aldrin 0.010 ppm, and lindane is not permitted to be used according to the Thai Food Act of 2005.

We found that foreign carrot juice sample consisted of heptachlor 0.030 ppm, o,p'-DDD 0.600 ppm and B-endosulphan 0.240 ppm. The amount of o,p'-DDD was higher than the permissible limit which is 0.010 ppm and B-endosulphan is an unpermitted pesticide. Four Thai carrot juice samples (2nd -5th samples) consisted of heptachlor and G-chlordane and we chose to determine the amount of residue in 4th sample, which from TLC, consisted of the largest spot of pesticide. 4th sample consisted of heptachlor 0.020 ppm and G-chlordane 0.400 ppm which is an unpermitted residue.

In 5 grape juice samples, we did not find organochlorine. Abamectin was the preferred pesticide used in grapes, so we turned to detect abamectin. We used prepared standard abamectin from marketed pesticide and compared the Rf-value from TLC using three developing solvents which were n-heptane, 2% acetone in n-heptane, and cyclohexane. 2nd –5th samples gave the unclear results. 1st sample gave the Rf-value in n-Heptane and cyclohexane the same as and near the prepared standard abamectin, so the pesticide in 1st sample might be abamectin. We could not confirm and determine the amount of abamectin because we did not have pure standard abamectin.

In 5 orange juice samples, we did not find organochlorine and organo-phosphate. We identified by TLC using two developing solvents which were n-heptane and 2% acetone in n-heptane. The 5 orange juice samples did not contain carbamate because carbamate was not the pesticide used in orange.

From this investigation, we found that the preferred organochlorine were heptachlor and lindane. In some green tea sample solutions it was found that the amounts of heptachlor were higher than the permitted limit. In foreign and Thai carrot juice samples, the amounts of pesticide were over the permitted limit and some contained unpermitted pesticide. Pesticide found in grape juice sample might be abamectin which is the fungus toxin, so it could be harmful. (O' Neil et al, 2001). These results should encourage the Ministry of Public Health to concentrate on the use of pesticides in green tea solution, vegetable and fruit juice in closed package.

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