by Mr. M. Endo, to whom we are much obliged.

Summary

1. Metabolic fate of Sumithion was studied in rice plant after the emulsion of this insecticide labeled with phosphorus-32 had been sprayed on the plant at the preheading stage.

Sumithion penetrated into the tissues was decomposed rather rapidly to desmethylsumithion, dimethylphosphrothioic acid and phosphorothionic acid. Presence of the oxygen analog (Sumioxon) was also demonstrated.

2. Residual amount of Sumithion and its metabolites in rice grains of several varieties of rice plant applied with Sumithion under the various conditions were determined. Sumithion and Sumioxon were hardly detectable. Only minute amount of such degradation products as dimethylphosphorothioic acid, phosphorothionic acid and free *p*-nitrocresol was identified.

From the results it can be concluded that the residual amount of Sumithion as well as of its metabolic products in rice grains lies within the permissible limit from the view-point of public health.

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Determination of Insecticide Residue in Animal and Plant Tissues. III. Determination of Residual Amount of Sumithion in Cocoa Beans grown in Nigeria. Junshi Miyamoto, Yoshishige Sato and Katsutoshi Fujikawa (Agricultural Chemical Research Department, Osaka Works, Sumitomo Chemical Co., Ltd. Kasugade-cho, Konohana-ku, Osaka, Japan) Received April. 26, 1965. *Botyu-kagaku*, 30, 1965.

10. 動植物組織中における残留殺虫剤の定量 3. ナイジエリヤ産ココア豆におけるミスチオン残留量の測定 宮本純之・佐藤香重・藤川勝利（住友化学工業株式会社 大阪製造所 農薬研究部 大阪市此花区春日出町）40. 4. 26 受理

ココアの害虫防除に用いられたスミチオンのココア豆中における残留量を測定した．

スミチオン散布後2週間で，豆中のスミチオンは最大に達し，以後次第に減少するが，最大含量は 0.12 ppm と推定される．またスミチオンの分解物たる 3—メチル—4—ニトロフェノールの含量は 0.06 ppm もしくはそれ以下であつた．

これらの量は，公衆衛生的見地よりみて，問題とするに足りず，人体には全く無害であると考えられる．

Introduction

In cocoa producing countries such as Nigeria and Ghana, benzene hexachloride (γ-BHC) has mainly been used for the control of mirids, *Distantiella theobroma* and *Sahlbergella singularis*, the most noxious insects to the plant. Recently, however, these insects have become more and more resistant against the insecticide and much effort is now being exerted in search of alternative compounds. Sumithion, or 0, 0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate, has proved to be very effective against the mirids[1,2] and it is now under study for practical application. One of the most pivotal points is to establish whether or not the residue of Sumithion in cocoa beans remains within the permissible limit from the medical view-point.

In this report we determined residual amount of Sumithion as well as 3-methyl-4-nitrophenol (abbreviated as *p*-nitrocresol) in cocoa beans which had been applied with Sumithion.

Materials and Methods

Samples of Sumithion-treated cocoa beans as well as control ones were kindly supplied by West African Cocoa Research Institute (W. A. C. R. I.), Ibadan, Nigeria. According to the information from W. A. C. R. I., conditions of application of Sumithion and date of reaping of beans were as follows.

Date of the insecticidal application was 1st July 13, 2nd August 10, and 3rd September 7, 1964.

Beans were harvested on 1st September 8, 2nd September 15, 3rd September 22, 4th September 29, and 5th October 7, 1964.

Three control samples were harvested on around 21st of October, 1964. These harvested beans, after dried and fermented as usual, were transported by air to Japan. Seed coat (epidermis) was removed from the beans and 250 g of dried seeds were soaked in water overnight in a refrigerator. The swollen seeds were homogenized with about 500 ml of distilled water, and the homogenate, after acidified with 10% of cold perchloric acid (the final concentration, 2%), was extracted twice with chloroform. Combined chloroform layers (about 1,400ml) were dehydrated with anhydrous sodium sulfate. Subsequently sodium sulfate was discarded by filtration, and chloroform was evaporated at 40~45°C under gentle stream of air. Residue obtained was suspended in 100 ml of liquid paraffin and shaken three times with acetonitrile. Combined acetonitrile layers were evaporated in vacuo at 40~45°C to a volume of approximately 10 ml. The acetonitrile concentrate, after washed with 5 ml of *n*-hexane, was poured on the silica gel column (2×20 cm). The column was further washed with 50 ml of acetonitrile and approximately 60ml of acetonitrile eluate was collected. Acetonitrile was evaporated in vacuo to dryness at 40~45°C. Residue was dissolved in a small volume of chloroform. Sumithion and / or *p*-nitrocresol therein was separated by thin-layer chromatography and determined colorimetrically, as described in the previous paper.[3]

These procedures are satisfactorily applicable for the separation and analysis of a minute amount of Sumithion and/or *p*-nitrocresol in samples grossly contaminated with organic matters, especially with lipid substances like beans or fatty tissues of animals[4].

Thus, 94.3% and 86.7% out of 75μg and 50μg of Sumithion respectively or 98.5% out of 25μg of *p*-nitrocresol added to the chloroform extract from 250g of dried seeds were recovered.

Results and Discussions

Contents of Sumithion and *p*-nitrocresol in 5 lots of the cocoa beans treated with Sumithion of the (corresponding to 1st to 5th harvest) and 3 control beans are indicated in Table 1.

As faint yellow color was also developed in the control runs, ppm values (parts per million) subtracted (mean of 3 control beans, Sumithion, 0.026ppm, and *p*-nitrocresol, 0.054ppm), are shown in Table 2.

Table 1. Contents of Sumithion and *p*-nitrocresol in Sumithion-treated and control beans. (mean of 3 replications, expressed as μg equivalent/250g of dried seeds.)

		Sumithion	*p*-nitrocresol
Control	1	6.2	13.6
	2	5.8	13.6
	3	7.4	13.1
Treated	1	19.1	11.4
	2	23.5	23.0
	3	32.0	28.1
	4	14.5	13.6
	5	10.8	18.0

Table 2. Contents of Sumithion and *p*-nitrocresol in Sumithion-treated cocoa beans. (expressed as pp m value)

		Sumithion	*p*-nitrocresol
Treated	1	0.050	—
	2	0.068	0.038
	3	0.100	0.058
	4	0.032	—
	5	0.017	0.018

As is clear from the results, the content of Sumithion is largest in the cocoa beans harvested two weeks after the last application. The residual amount of Sumithion found was less than 0.1 ppm. If the recovery of Sumithion in the

preliminary test is taken account of, remaining Sumithion is calculated to be less than 0.12ppm. Thereafter Sumithion decreased rather rapidly. The time lag between the final application and the maximal content of Sumithion might indicate that Sumithion sprayed to a canopy of cocoa tree transferred gradually into the beans.

The determination of metabolic products resulting from the use of Sumithion is potentially so important from the view-point of public health. However, such methods have not yet been devised except for *p*-nitrocresol, one of the degradation products of Sumithion. In the treated cocoa beans *p*-nitrocresol was also detected, but the amount was less than 0.06ppm.

These contents of Sumithion as well as *p*-nitrocresol seem to be quite negligible and completely harmless to human body from the medical viewpoint.

Acknowledgment : We wish to express our sincere thanks to Dr. L. K. Opeke, Ag. Director, and Mr. P. F. Entwistle, former Ag. Deputy Director, of West Arfican Cocoa Research Institute for arranging the spray programs and supplying the samples of the cocoa beans. We are also grateful to Sumitomo Chemical Co., Ltd. for permission to publish this work.

Summary

The contents of Sumithion and *p*-nitrocresol in cocoa beans were determined after the plant had been sprayed with Sumithion.

Sumithion remaining in the beans was approximately 0.1ppm and the content of *p*-nitrocresol, one of the degradation products of Sumithion, was less than 0.06 ppm.

These contents are considered to be too small to exhibit any harmful effects to human body from the view-point of public health.

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Studies on the Pathways of DDT by Chemical Conversion. I. Pathways of *p, p'*-DDT. Yuh-Lin Chen and Hong-Ming Cheng (Pesticide Chemistry Laboratory, Department of Agricultural Chemistry, College of Agriculture, National Taiwan University, Taipei, Taiwan). Received March 1, 1965. *Botyu-Kagaku*, 30, , 1965.

11. DDTの化学変化経路に関する研究 I. *p, p'*-DDT の経路について 陳玉麟・鄭弘命 (国立台湾大学 農学院 農業化学系 農薬化学研究室) 40. 3. 1 受理

DDT は昆虫体内では酵素 DDT-dehydrochlorinase の作用で脱塩酸されて DDE になることは一般に良く知られているが，最近になつてから或る種の昆虫では酸化的代謝が起り，Kelthane や DBP となることがわかつた．化学的にも DDT を DDE に変える脱塩酸反応は容易に行われ得るが，DDT を Kelthane へ酸化することは簡単には行われない．著者等は DDT 或は TDE を原料として化学的に種々の誘導体を合成し，これら化合物間の相互関係を明らかにして，昆虫或は動物体内での代謝研究の結果との比較に便ならしめた．本研究においては20種の *p, p'*-DDT の誘導体を合成し，38個の化学的変化の経路を明らかにしたが，これら化合物は *iso*-Acetoxy-K-3926 を除いては何れも今迄に知られているものである (Fig. 1)．実験及び分析の結果は表に示した (Table 1)．

著者等は更に今迄に知られている昆虫での代謝経路の外に昆虫で起り得る新しい代謝経路8個を推測した (Fig. 2)．この種の研究は今後の DDT 或は DDT 誘導体の昆虫或は動物における代謝の研究に役に立つもので，化学的変化の経路を昆虫における代謝のそれと比較することは極めて興味深いものと思われる．

It is well known that DDT is easily dehydrochlorinated by the action of an enzyme, DDT-dehydrochlorinase, to yield DDE in the insect body. Recently, the other metabolic products