

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*-nitroresol, one of the degradation products of Sumithion. In the treated cocoa beans *p*-nitroresol was also detected, but the amount was less than 0.06ppm.

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

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 African 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*-nitroresol 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*-nitroresol, 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

Kelthane, an alcoholic type compound, and DBP, a ketonic type compound of DDT derivatives, were also discovered in several species of insects by Tsukamoto^{1,2,3)} and by Perry and Miller⁴⁾ respectively. It is concluded that, in general, the metabolic pathways of DDT are now considered to be two; one to DDE by the dehydrochlorination and the other to Kelthane or DBP by the oxidative metabolisms in insects.

The dehydrochlorination of DDT to DDE by chemical method is also very easy. In fact, DDE is obtainable by simply treating DDT with alcoholic alkaline solution without any difficulty. On the other hand, it is not so simple to prepare Kelthane from DDT by the chemical conversion. No method has been demonstrated to convert DDT to Kelthane in a single step. It is necessary to dehydrochlorinate DDT to DDE, then chlorinate DDE to Cl-DDT, acetoxylation Cl-DDT to Acetoxy-DDT, and finally hydrolyse Acetoxy-DDT to Kelthane⁵⁾.

The purpose of this investigation is to synthesize some different derivatives of DDT by chemical conversion from DDT or TDE as the starting material and to clear up the chemical relationship among these compounds. It is of interest to compare the relationship between the chemical conversion and metabolic pathways known in insects and animals.

Twenty compounds were prepared and thirty-eight pathways of chemical conversion were identified in this investigation. These pathways are shown in Fig. 1, together with that of the study of metabolic fate of DDT in insects as shown in Fig. 2. The results of experiments and analytical data are tabulated in Table 1.

The chemical names of compounds and the abbreviation used in this paper are given below:

1. Cl-DDT : 1, 1-bis (*p*-chlorophenyl)-1, 2, 2, 2-tetrachloroethane.
2. Acetoxy-DDT : 1, 1-bis (*p*-chlorophenyl)-1-acetoxy-2, 2, 2-trichloroethane.
3. DBP : 4, 4'-dichlorobenzophenone.
4. DDA : bis (*p*-chlorophenyl)-acetic acid.
5. DDE : 1, 1-bis (*p*-chlorophenyl)-2, 2-dichloroethylene.
6. DDT : 1, 1-bis (*p*-chlorophenyl)-2, 2, 2-trichloroethane.
7. Kelthane : 1, 1-bis (*p*-chlorophenyl)-2, 2, 2-trichloroethanol.
8. *iso*-DDT : 1, 1-bis (*p*-chlorophenyl)-1, 2, 2-trichloroethane.
9. TDEE : 1, 1-bis (*p*-chlorophenyl)-2-chloroethylene.
10. TDE : 1, 1-bis (*p*-chlorophenyl)-2, 2-dichloroethane.
11. FW-152 : 1, 1-bis (*p*-chlorophenyl)-2, 2-dichloroethanol.
12. Acetoxy-TDE : 1, 1-bis (*p*-chlorophenyl)-1-acetoxy-2, 2-dichloroethane.
13. DME : 1, 1-bis (*p*-chlorophenyl)-ethylene.
14. DDM : 1, 1-bis (*p*-chlorophenyl)-2-chloroethane.
15. DDA-Me-Ester : methyl di-(*p*-chlorophenyl)acetate.
16. *iso*-DMC : 2, 2-bis (*p*-chlorophenyl)-ethanol.
17. K-3926 : 1, 1-bis (*p*-chlorophenyl)-ethane.
18. DMC : 1, 1-bis (*p*-chlorophenyl)-ethanol.
19. DDA-Et-Ester : ethyl di-(*p*-chlorophenyl)acetate.
20. *iso*-Acetoxy-K-3926 : 1, 1-bis (*p*-chlorophenyl)-2-acetoxyethane.
21. DCPM : bis (*p*-chlorophenyl)-methane.
22. DBH : bis (*p*-chlorophenyl)-methanol.
23. DCMC : 1, 1-bis (*p*-chlorophenyl)-2-chloroethanol.
24. *iso*-Kelthane : 2, 2-bis (*p*-chlorophenyl)-1, 1, 2-trichloroethanol.
25. *iso*-TDE : 1, 1-bis (*p*-chlorophenyl)-1, 2-dichloroethane.
26. *iso*-FW-152 : 2, 2-bis (*p*-chlorophenyl)-1, 2-dichloroethanol.
27. *iso*-DDM : 1, 1-bis (*p*-chlorophenyl)-1-chloroethane.
28. *iso*-DCMC : 2, 2-bis (*p*-chlorophenyl)-2-chloroethanol.
29. Acetoxy-K-3926 : 1, 1-bis (*p*-chlorophenyl)-1-acetoxyethane.

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Table 1. Pathways of *p,p'*-DDT by chemical conversion

Path-way	Starting material	Product	M. P. (°C)	Yield (%)	Empirical formula	Analysis (%)		Reference
						Calcd.(Cl)	Found(Cl)	
1	DDE	Cl-DDT	91	70	C ₁₄ H ₈ Cl ₆	54.70	54.21	5)8)
2	Kelthane	Cl-DDT	91~92	66	C ₁₄ H ₈ Cl ₆	54.70	54.54	
3	Cl-DDT	Acetoxy-DDT	124~125	82	C ₁₆ H ₁₁ O ₂ Cl ₅	42.97	42.55	5)
4	Kelthane	Acetoxy-DDT	124~125	55	C ₁₆ H ₁₁ O ₂ Cl ₅	42.97	42.70	
5	DDA	DBP	145~146	96	C ₁₃ H ₈ OC ₂	28.24	28.21	
6	Acetoxy-DDT	DBP	145~146	80	C ₁₃ H ₈ OC ₂	28.24	28.54	
7	Kelthane	DBP	145	60	C ₁₃ H ₈ OC ₂	28.24	28.55	
8	DDE	DBP	145	62	C ₁₃ H ₈ OC ₂	28.24	28.27	
9	DDT	DDA	165~166	74	C ₁₄ H ₁₀ O ₂ Cl ₂	25.23	25.84	6)
10	DDE	DDA	164~166	71	C ₁₄ H ₁₀ O ₂ Cl ₂	25.23	25.63	6)
11	Cl-DDT	DDE	87~88	88	C ₁₄ H ₈ Cl ₄	44.60	44.10	7)
12	<i>iso</i> -DDT	DDE	87~88	75	C ₁₄ H ₈ Cl ₄	44.60	44.13	
13	FW-152	DDE	87~88	60	C ₁₄ H ₈ Cl ₄	44.60	45.01	
14	DDT	DDE	87~88	98	C ₁₄ H ₈ Cl ₄	44.60	44.88	8)
15	Acetoxy-DDT	Kelthane	(crude)	100	C ₁₄ H ₈ OC ₂	47.85	46.92	5)
16	FW-152	<i>iso</i> -DDT	(crude)	96	C ₁₄ H ₈ Cl ₄	50.01	49.37	
17	TDEE	<i>is-o</i> DDT	(crude)	100	C ₁₄ H ₈ Cl ₄	50.01	49.13	8)9)
18	<i>iso</i> -DDT	TDEE	62~64	81	C ₁₄ H ₈ Cl ₄	37.51	37.81	
19	TDE	TDEE	66	93	C ₁₄ H ₈ Cl ₄	37.51	37.35	8)
20	Acetoxy-TDE	FW-152	107~108	93	C ₁₄ H ₁₀ OC ₂	42.21	42.07	
21	<i>iso</i> -DDT	Acetoxy-TDE	125~127	77	C ₁₆ H ₁₂ O ₂ Cl ₄	37.51	37.35	
22	FW-152	Acetoxy-TDE	129~131	42	C ₁₆ H ₁₂ O ₂ Cl ₄	37.51	38.04	
23	<i>iso</i> -Acetoxy-K-3926	DME	84~85	80	C ₁₄ H ₁₀ Cl ₂	28.46	28.11	
24	DMC	DME	84~85	80	C ₁₄ H ₁₀ Cl ₂	28.46	28.63	10)
25	DDM	DME	85~86	94	C ₁₄ H ₁₀ Cl ₂	28.46	28.31	
26	<i>iso</i> -DMC	DDM	51~53	84	C ₁₄ H ₁₁ Cl ₃	37.25	37.25	
27	DDA	DDA-Me-Ester	38~40	67	C ₁₆ H ₁₂ O ₂ Cl ₂	24.03	24.16	11)
28	DDA	<i>iso</i> -DMC	99	83	C ₁₄ H ₁₂ OC ₂	26.54	26.52	
29	DDA-Et-Ester	<i>iso</i> -DMC	97~98	81	C ₁₄ H ₁₂ OC ₂	26.54	26.83	
30	<i>iso</i> -Acetoxy-K-3926	<i>iso</i> -DMC	98~99	91	C ₁₄ H ₁₂ OC ₂	26.54	26.55	
31	DDT	K-3926	53~54	52	C ₁₄ H ₁₂ Cl ₂	28.23	28.62	
32	DBP	DMC	68~69	66	C ₁₄ H ₁₂ OC ₂	26.54	26.69	10)
33	DDA	DDA-Et-Ester	86~87	95	C ₁₆ H ₁₄ O ₂ Cl ₂	22.94	22.74	
34	<i>iso</i> -DMC	<i>iso</i> -Acetoxy-K-3926	67~68	70	C ₁₆ H ₁₄ O ₂ Cl ₂	22.94	22.69	
35	DDA	DCPM	53~54	78	C ₁₃ H ₁₀ Cl ₂	29.91	30.02	
36	DBP	DCPM	53~54	25	C ₁₃ H ₁₀ Cl ₂	29.91	30.06	
37	DBH	DCPM	53.5~54.5	63	C ₁₃ H ₁₀ Cl ₂	29.91	29.55	
38	DBP	DBH	92~93	90	C ₁₃ H ₁₀ OC ₂	28.02	28.40	

out with the support of a grant-in-aid from the National Council on Science Development. DDT and TDE (Rhothane) used in this experiment were furnished by the Agricultural Chemical Works, Kaohsiung, and Elephant TradingCo., Ltd.,

Taipei, Taiwan, respectively, to which thanks are due.

Experimental

DDT used in this experiment was recrystallized

twice with ethanol from the technical grade produced by the Agricultural Chemical Works, Kaohsiung, Taiwan. The recrystallized product showed mp. 107~108°. TDE was extracted from the commercial product of Rhothane WP-50, the product of Rohm and Haas Co., U.S. A., and recrystallized from ethanol, showing mp. 110~111°. Both compounds were proved to be paper chromatographically pure.

Pathways 1 and 17 : Prepared from DDE or TDEE according to the method of Bergmann and Kaluszyner,⁵⁾

Pathways 2 and 16 : Kelthane or FW-152 was refluxed for 3 hrs. with an excess of thionylchloride in a dry benzene solution.

Pathways 3 and 21 : Cl-DDT or *iso*-DDT was refluxed with mercuric acetate in an acetic acid solution for 90 minutes. The mp. of Acetoxy-TDE was reported to be 129~131°.¹²⁾

Pathway 4 : Crude Kelthane was refluxed with acetic anhydride and few drops of conc. sulfuric acid for 3 hrs.

Pathways 5 and 8 : Oxidized from DDA or DDE with potassium dichromate and conc. sulfuric acid in an acetic acid solution. The mp. of DBP was reported to be 146~147°.⁶⁾

Pathways 6 and 7 : The product was obtained by treating Acetoxy-DDT or Kelthane with alcoholic potassium hydroxide solution.

Pathways 9 and 10 : DDA was prepared from DDT or DDE by the method of Grumitt *et al.*⁶⁾

Pathways 11 and 18 : Cl-DDT or *iso*-DDT was reduced with zinc granule and conc. hydrochloric acid in an ethanol solution.⁷⁾

Pathways 12, 14, 19, and 25 : Dehydrochlorination was carried out with alcoholic potassium hydroxide solution in an usual manner.

Pathways 13 and 24 : Dehydration was carried out by the method of Grumitt *et al.*¹⁰⁾

Pathways 15 and 20 : Acetoxy-derivative was refluxed with sulfuric acid in an acetic acid solution as the method described by Bergmann and Kaluszyner⁵⁾. But Kelthane was obtained only in a state of a viscous oil. Since the compound was reported to be a solid with mp. 77~78°, attempts were made to crystallize from several kinds of organic solvents. But the crystallization was not successful.

Pathways 22 and 34 : FW-152 or *iso*-DMC was refluxed for 3 hrs. with acetic anhydride, a small quantity of pyridine and sodium acetate.

Pathways 23 and 38 : *iso*-Acetoxy-K-3926 or DBP was treated with metallic sodium in a boiling solution of absolute ethanol. The mp. of DBH was reported to be 92.8~93.3°.¹³⁾

Pathway 26 : *iso*-DMC was treated with thionylchloride and pyridine at room temperature. The mp. of DDM was reported to be 51~53°.¹⁴⁾

Pathways 27 and 33 : Synthesized from DDA, methanol or ethanol and a small quantity of conc. sulfuric acid. Reaction was carried out at reflux for several hours.¹¹⁾ The mp. of ethyl ester was reported to be 87.5~88°.¹⁵⁾

Pathways 28 and 29 : Attempts to reduce DDA or its ester with metallic sodium or with zinc and acid were not successful. These were finally obtained by the reduction with lithium aluminum hydride¹⁶⁾. The mp. of *iso*-DMC was reported to be 98.5~99.5°.¹⁷⁾

Pathway 30 : *iso*-Acetoxy-K-3926 was refluxed for 2 hrs. alcoholic potassium hydroxide solution.

Pathway 31 : DDT was reduced with zinc granule and conc. hydrochloric acid in a solution of ethanol or acetic acid. The mp. of K-3926 was reported to be 54~55°.¹⁰⁾ Besides K-3926, some by-products with higher melting points were obtained. But these were not further investigated.

Pathway 32 : Prepared by the Grignard reaction from methyl iodide, metallic magnesium, and DBP according to the method of Grumitt *et al.*¹⁰⁾

Pathway 35 : DDA was treated with barium hydroxide in an ethylene glycol at above 190° according to the method of Cristol and Haller.¹⁸⁾

Pathway 36 : DBP was reduced with zinc granule and conc. hydrochloric acid by refluxing for about 10 hrs. in a solution of acetic acid. It was also prepared by the Clemmensen reduction¹⁹⁾. Besides DCPM, a higher melting product (mp. 213~215°) was obtained in 13~20% yield from both methods. The compound was identified to be 4,4',4'',4'''-tetrachlorobenzopinacol (Analysis, Calcd. for $C_{26}H_{18}O_2Cl_4$: Cl, 28.13% found : Cl, 27.88%, 28.37%)

Pathway 37 : DBH was reduced with zinc granule

and conc. hydrochloric acid by refluxing for 8 hrs. in an acetic acid solution.

Discussion

Besides several metabolic pathways identified by Tsukamoto³⁾, (Fig. 2. pathways a~g) and by Perry and Miller,⁴⁾ (Fig. 2. pathways h~i), possible metabolic pathways in insects were added by the authors (Fig. 2. pathways j~q). Although the pathway from *iso*-DDT to *iso*-Kelthane (Fig. 2. pathway K) was already proposed by Tsukamoto³⁾, it seems to be possible to metabolize to DDE (Fig. 2. pathway j) simultaneously.

Owing to the lack of facilities, several important reactions such the catalytic hydrogenation under the high pressure still could not be performed in this investigation. Moreover, many possible chemical pathways were not successful in this experiment, such as the chlorination of DME to *iso*-TDE, DMC to *iso*-DDM, acetoxylation of DMC to Acetoxy-K-3926, and reduction of TDE or DDM to K-3926 etc. Further studies are still needed to complete this investigation.

Many compounds were prepared in this investigation. But only one compound, *iso*-Acetoxy-K-3926, seems to be a new compound.

DDA, Acetoxy-DDT, Kelthane, and DDE were easily converted to DBP by chemical methods. But DDT itself could not be oxidized to DBP with potassium dichromate. The result is well agreed with that of the metabolic pathway in insect.⁴⁾

It is very interesting to compare the chemical pathways with that of the metabolic pathways in insects, and the results obtained are seemed to be very helpful in the future study of metabolic fate of DDT or related compounds in insects and animals.

Summary

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 oxidative metabolic products Kelthane and DBP were also discovered in several species of insects. The dehydrochlorination of DDT to DDE by chemical method is also very easy. On the other hand, it is not so

simple to prepare Kelthane from DDT by the chemical conversion. The purpose of this investigation is to synthesize some different derivatives of DDT by chemical conversion from DDT or TDE as the starting material, and to compare the chemical relationship among results of metabolic studies in insects and animals. Twenty compounds were prepared and thirty-eight pathways of chemical conversion of *p, p'*-DDT were identified in this investigation (Fig. 1). But only one derivative, *iso*-Acetoxy-K-3926, seems to be a new compound. The results of experiment and analytical data are tabulated in Table 1. Besides nine metabolic pathways identified by the former investigators, eight possible metabolic pathways which might be occurred in insects were also proposed by the authors (Fig. 2).

It is very interesting to compare the chemical pathways with that of the metabolic pathways in insects, and the results obtained are seemed to be very helpful in the future study of metabolic fate of DDT or related compounds in insects and animals.

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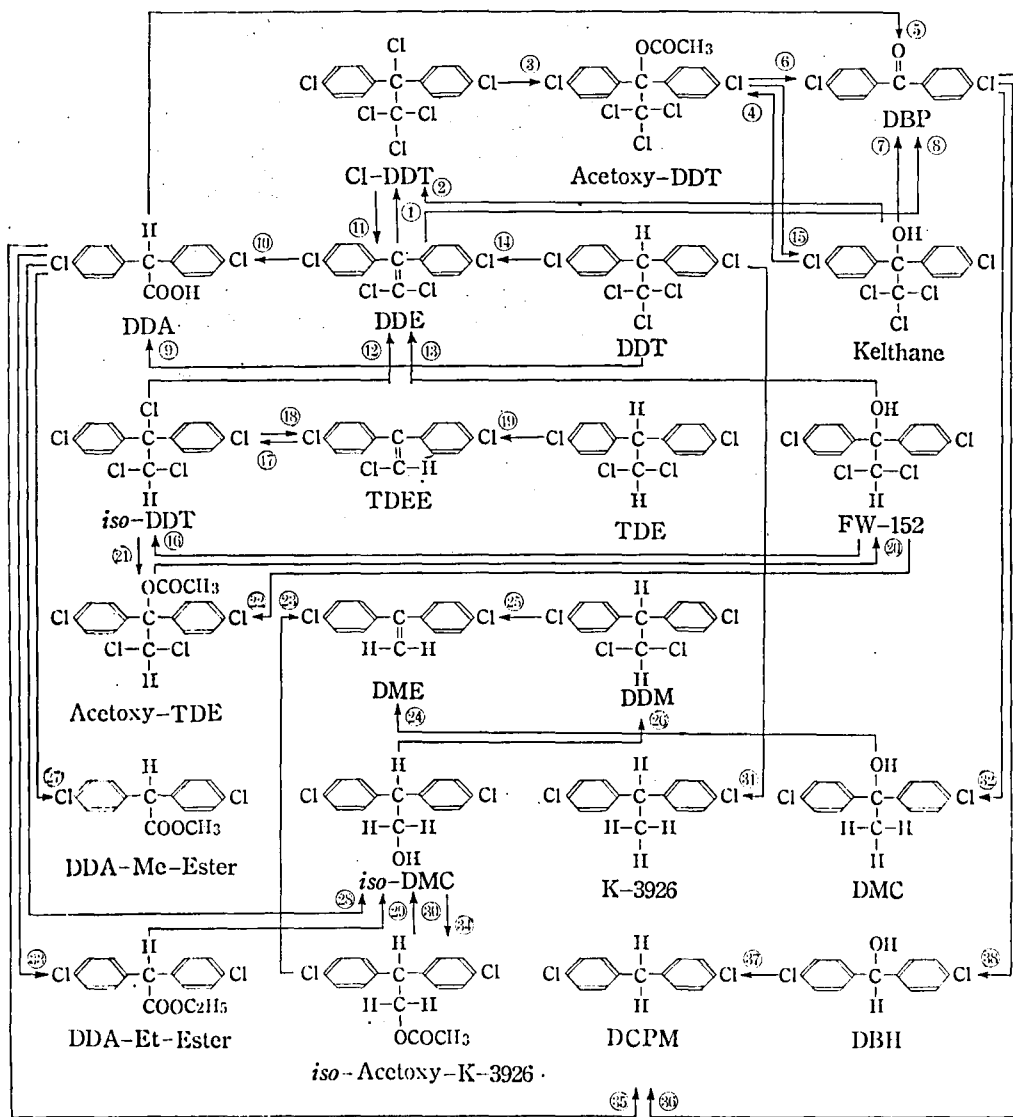


Fig. 1 Scheme of pathways of *p,p'*-DDT by chemical conversion

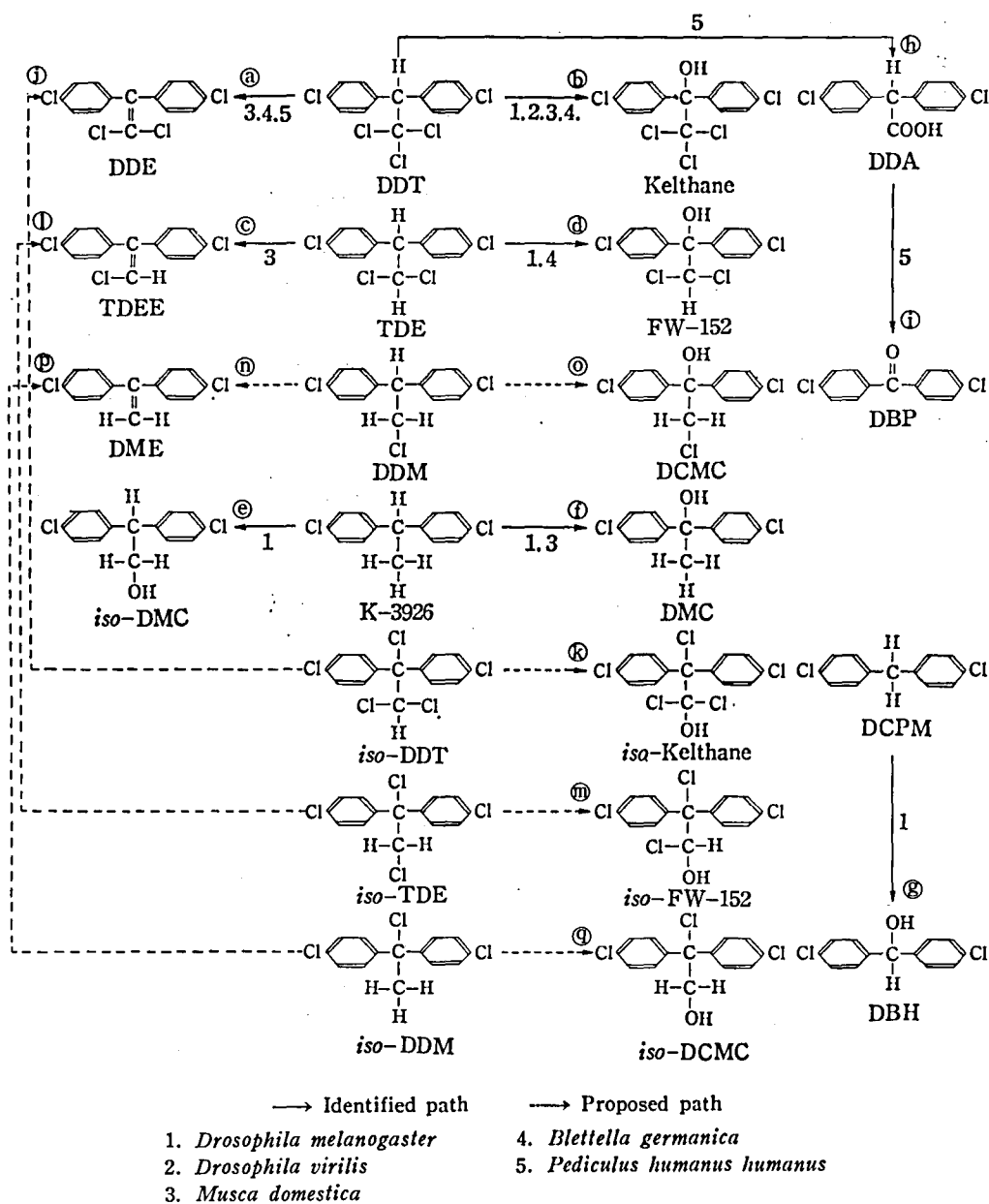


Fig. 2 Scheme of metabolic pathways of *p,p'*-DDT and its derivatives in insects

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Comparison of Synergistic Action of Anti-resistant DDT and DMC with DDT Against the Common House Fly Evaluated by the Impregnated Filter Paper Method. Studies on the Biological Assay of Insecticides. LIII. Sumio NAGASAWA and Michio SHIBU (Ihara Agricultural Chemicals Institute, Shimizu, Shizuoka). Received March 29, (1965). *Botyu-Kagaku*, 30, 1965. (with English Summary 61)

12. イエバエをもちいる濾紙法によつて評価した DDT に対する anti-resistant DDT と DMC の協力効果の比較 殺虫剤の生物試験に関する研究. 第53報. 長沢純夫・柴三千代 (イハラ農薬研究所) 40. 3. 29 受理

DDT に対する anti-resistant DDT の協力効果と DMC のそれを, イエバエをもちいる濾紙法によつて比較した結果, 致死を決定する要因として塗布薬量と曝露時間は, anti-resistant DDT の場合ほとんど同等の重要性を有するが, DMC の場合は塗布薬量より曝露時間の方がより重要で, また塗布薬量だけを考えた場合は, 両薬物においてほとんどひとしいことがたしかめられた. したがつて, 両薬物の相対協力効果をプロビット平面の垂直距離でしめすと, 曝露時間が短い間は anti-resistant DDT の DDT に対する協力効果は, DMC のそれより大きい, 曝露時間が長びくにつれてその相対値は小さくなり, 理論上曝露時間が312分になったとき, 両者同等の効果をしめすということが可能である.

DDT に対して anti-resistant DDT および DMC が高い協力効果を有することは, 早くから知られておりこれに関する報告も今日ですでにかなりの数におよんでいる. ここにのべようとするのは, 協力効果の比較算定をおこなうことを目的におこなわれた実験のひとつで, イエバエをもちいる濾紙法によつて, 塗布薬量とこれに曝露する時間の2要因を組合わせてえられた致死率との関係を, プロビット平面に描いて比較した結果である. 本文に入るに先立ち試料の提供を戴いた日本曹達株式会社生物研究所に謝意を表する. また供試昆虫の飼育に御尽力下さった伏見主子嬢に併せて感謝する次第である.

実験材料および方法

実験材料: この実験にもちいた *p, p'*-DDT は, メタノールで再結精製した m. p. 108°C の試料である. 以下単に DDT とする. その協力剤である anti-resistant DDT (N, N-di-*n*-butyl-*p*-chlorobenzen sulfonamide) および DMC (1, 1-bis-*p*-chlorophenyl methyl carbinol) は, 日本曹達株式会社生物研究所から提供を受けた research grade の試料である. イエ

バエは豆腐粕培基によつてその幼虫期を, 砂糖と水によつて成虫期を飼育した, いわゆる高槻系と称される累代飼育系統で, 実験には羽化後4~5日目の雌個体をもちいた. 本系統の滴下法による DDT の LD₅₀ は約 7μg/♀で, 欧米の標準の感受性系統にくらべるとその値はかなり高いようである.

実験方法: DDT と anti-resistant DDT あるいは DMC を等量混合し, アセトンでこの 12.5, 25, 50 および 100μg/mm³ の稀釈溶液をつくり, その1ccを直径9cmの濾紙(東洋濾紙 No. 2)上に一様に滴下し, 乾くのをまつて同じ直径のペトリ皿をかぶせ, これにイエバエ約40匹を導入, 所定の80, 100および126分間曝露した. 曝露後は直径9cm, 高さ5cmのガラス容器にうつし, 網蓋をかぶせた後その上から脱脂綿にひたした稀釈牛乳を餌としてあたえた. 曝露を終つた時からかぞえて, 24時間後にその死虫数をかぞえた. 別に対照区としてアセトンのみを1cc滴下して, 同様の実験をおこなつた. 処理区対照区とも実験は3~4回くりかえし, その結果を集計した. 飼育, 実験ともに25°C, 関係湿度約60%の環境条件下で施行した.