

Table I. A Comparison of the Hexosamine Content of Liver Nuclei and Mitochondria from Malathion-Treated vs. Untreated Rats^a

Malathion fed, mg/kg rat	Hexosamine concentration	
	Nuclei, mg/mg N	Mitochondria, mg/mg N
0	0.016 ± 0.001	0.034 ± 0.003
250	0.016 ± 0.001	0.026 ± 0.003
Difference	0	0.008
Significance	$p > 0.1$	$0.01 > p > 0.001$

^a Each of four replications includes pooled livers of five male rats.

Table II. A Comparison of ³⁵S₄²⁻ Uptake and Swelling of Liver Mitochondria from Malathion-Treated vs. Untreated Rats^a

Malathion fed, mg/kg rat	³⁵ S Sulfate uptake, cpm/mg N	Swelling, % decrease in absorbance
0	2462 ± 91	53 ± 1
250	1437 ± 233	49 ± 1
Difference	1025	4
Significance	$0.02 > p > 0.01$	$0.02 > p > 0.01$

^a Data are averages ± SE of values obtained from five female rats.

The apparent reversal of the malathion effect on specific activity and hexosamine content which has been reported when whole mitochondria are compared with mitochondrial membranes may be explained by assuming a loss in membrane nitrogen. Based on the nitrogen content of the whole mitochondria, there is a 25% decrease in hexosamine content, but based on the nitrogen content of the membrane, there is a 10% increase in hexosamine content as a result of malathion intoxication. Therefore, in order to obtain these data, the mitochondria would have to lose 25% of the mucopolysaccharide and 35% of the nitrogen in their membranes. It can be argued that the apparent loss of membrane nitrogen and hexosamine is an artifact of the extraction procedure. However, the ³⁵S specific activity of the mucopolysaccharide in the malathion-fed and corn oil-fed mitochondrial membranes is 8.0×10^5 cpm and 8.5×10^5 cpm per mg of hexosamine, respectively. Since this difference is only 6%, preparation artifacts could not explain the differences observed. Thus,

Table III. A Comparison of ³⁵SO₄²⁻ Uptake and Hexosamine Content of Salt-Extracted Liver Mitochondria from Malathion-Treated vs. Untreated Rats^a

Malathion fed, mg/kg rat	³⁵ S Sulfate uptake, cpm/mg N	Hexosamine concentration, mg/mg N
0	2290	0.029
250	2729	0.032
Difference	439	0.003

^a These data were obtained from the pooled livers of 15 female rats.

the apparent loss of membrane nitrogen, mucopolysaccharide, and a decrease in the swelling of mitochondria isolated from the livers of malathion-fed rats indicate that malathion intoxication damages mitochondria and impairs their function.

ACKNOWLEDGMENT

The authors are indebted to the American Cyanamid Company, Princeton, N. J., for the donation of the malathion. This paper is published by the permission of the Dean, Tennessee Agricultural Experiment Station.

LITERATURE CITED

- Albert, A., "Selective Toxicity," Wiley, New York, N. Y., 1965, p 280.
 Bigley, W. S., Plapp, F. W., Jr., *J. Insect. Physiol.*, **8**, 545 (1962).
 Boas, N. F., *J. Biol. Chem.*, **204**, 553 (1953).
 Disney, G. W., Smith, J. T., *Fed. Proc.*, **26**, 427 (1967).
 Disney, G. W., Smith, J. T., *J. Agr. Food Chem.*, **18**, 541 (1970).
 Fulton, S. F., Smith, J. T., *J. Nutr.*, **100**, 525 (1970).
 Hogeboom, G. H., *Methods Enzymol.*, **1**, 16 (1955).
 Levin, E., Thomas, L. E., *Exp. Cell Res.*, **22**, 363 (1961).
 Mahin, D. T., Lofberg, R. T., *Anal. Biochem.*, **16**, 500 (1966).
 Smith, J. T., Funckes, A. J., Barak, A. J., Thomas, L. E., *Exp. Cell Res.*, **13**, 96 (1957).
 Stavinoha, W. B., Rieger, J. R., Jr., Ryan, L. C., Smith, P. W., *Advan. Chem. Ser.*, **60**, 79 (1966).
 Tedeschi, H., Harris, D. L., *Arch. Biochem. Biophys.*, **58**, 52 (1955).
 Willets, C. O., Ogg, C. L., *J. Ass. Offic. Agr. Chem.*, **33**, 179 (1950).

Beth Feland
John T. Smith*

Department of Nutrition
University of Tennessee
Knoxville, Tennessee 37916

Received for review March 14, 1972. Accepted July 24, 1972.

A Pesticide Residue Data Information Retrieval System

The retrieval of laboratory, residue, and field data necessary for the formulation of safe and effective pest control programs is accomplished by a computer search of previously coded data collected from various locations. The retrieval program uses up to 16 search keys, including chemical, crop, and

analytical method used. A printed report is prepared which contains 24 field and laboratory parameters, sample identification number, and residue found. The program is designed to run on a small computer using disk storage for all data.

The obvious culmination of any pesticide research program is the publication and interpretation of data and the intergration of all data available into practical recommendations for the safe and effective utilization of the chemical under study.

The data amassed by many investigators in countless controlled experiments, ranging over field and orchard, domestic

and laboratory animals, and extending over a period of many years, present a difficult problem in information retrieval when recommendations for a particular pesticide are finally contemplated. Numerous retrieval systems were studied, including the notched edge cards (Elias and Warren, 1962). This method, however, becomes cumbersome as the data collection grows. The technique used by the pharmaceutical

PESTICIDE RESIDUE ANALYSIS
REQUEST
FIELD DATA

INVESTIGATOR Taschenberg 01177 APPLICATION RATE 1.5 013
 CROP Grapes 040 APPLICATION RATE UNITS lbs/A 08
 PESTICIDE Torak 00011 NUMBER APPLICATIONS 3 03
 CLASS Insecticide 05 DATE LAST APPLICATION 240 0410
 YEAR 1968 058 PLANTING DATE Not Known 00
 FORMULATION Wettable Powder 078 SOIL TYPE Not Known 00
 SOURCE Hercules 044 TOTAL RAINFALL 25 inches 025
 ACTIVE INGREDIENTS 50% 050 FIELD COMMENTS None
 APPLICATION METHOD High Pressure 045 APPLICATION TYPE Foliage 05
 APPLICATION TYPE Foliage 05 HARVEST DATE 282 0282
 FACTOR STUDIED Weathering 049 OTHER PESTICIDES APPLIED None

LAB DATA

ANALYTICAL METHOD G.C. 010 EXTRACTION METHOD Reynolds 030
 SAMPLING METHOD _____ STORAGE Frozen
 INSTRUMENT Microtrac CLEANUP None
 COLUMN SIZE 6 ft WAVE LENGTH Not applicable
 SUBSTRATE 3% OV-1 STD. CURVE (MCG.) Not applicable
 SUPPORT Gas Chrom. Q TEMP. COLUMN 220°C
 CARRIER GAS N₂ TEMP. DETECTOR 150°C
 RETENTION TIME 7.95 cm TEMP. INJECTOR 240°C
 DETECTOR Flame Photometer STANDARD ADDED To Blender
 ANALYST S. D. Gibbs 0298 RECOVERY 100%
 LAB COMMENTS Samples Frozen 030

Field sample no.	Lab sample no.	Date sampled	Date Extd.	Date Anal.	mmg sample	sample wt.	ppm	Notes
3A	1526	210	11/4	11/5	360	100g	5.60	
3B	1527	240	11/4	11/5	470	100g	4.20	

Figure 1. Request for pesticide residue analysis

(Geer and Howard, 1962) and pesticide (Wieman, 1964) industries based on the retrieval of the location of the data requested was rejected because of the large number of experimental stations and laboratories located throughout the state submitting samples. A more advanced system, reported by Waldo *et al.* (1964), indicated the coding and storing of all field trial data. The requirements of the Cornell Pesticide Residue Laboratories and Extension service, however, mandated the inclusion of laboratory analysis and residue, as well as field data. It was for this reason that the development of a computer-based system into which all residue and field data could be introduced was undertaken. This information is now readily available for recall when needed by laboratory or extension personnel, and by state, federal, or commercial scientists involved in toxicological evaluations prior to possible public use clearance. Over 20,000 of the samples submitted to the laboratories since 1956 have been recorded.

The foundation of the system is a directory composed of 16 "indices." Each index contains all the codes and associated key words by which the user may select particular classes of information. There is for instance an index of investigators with their associated code numbers, an index of pesticide names which utilizes Caswell numbers as codes, an index of application methods, soil types, factors studies, etc.

The field scientist requesting chemical analysis submits to the laboratory both his samples and an analysis request form (Figure 1) containing all pertinent field information. Laboratory parameters and analytical results are added to the form, and the directory number is inserted in the appropriate boxes. Additional results may be continued on a second page; thus the page number and total number of pages in the data set are recorded on the upper right-hand corner. When the forms are completed, the coded data found in the boxes is transferred to an 80-column punch card. The format for these data is shown in Figure 2. Columns 1-53 of the first card are reserved for Experimental Conditions. Residue

Table I. Pesticide Residue Information Retrieval Search Procedure

Possible select keys	Key words of interest	Card column	Directory number
Pesticide	Torak	1-5	10014
Crop	Grape	6-10	140
Application type	Foliage	11-15	5
Application method	Ground spray, high pressure	16-20	45
Formulation		21-25	
Factor studied	Weathering	26-30	45
Pesticide class		31-35	
Soil type			36-40
Investigator			41-45
Source		46-50	
Application rate		51-55	
Field comments		56-60	
Analytical method	Gas chromatography	61-65	20
Extraction method	Reynolds	66-70	30
Analyst		71-75	
Lab comment		76-80	

data for the first sample are placed in columns 54-69, and if the Experimental Conditions represent only this one residue determination, an "end of data" mark (asterisk) is placed by column 72. If more samples are represented by the conditions, then no "end of data" mark is used on the first card. Additional residue data are placed on additional cards, as shown on Additional Data Card (Figure 2). As many additional cards may be used as required, and the last card need not be completely filled. An "end of data" mark, however, must be placed in column 72 of the last card containing residue data. A complete data set for the example given in Table I is reproduced on Figure 2.

Columns 73-80 of all cards are reserved for a short code to be used in returning cards to their proper data set in the event they become rearranged. Columns 74-78 are used for the data set number (usually starting with 00001, with increments of 1 for each new data set), right justified. Columns 79-80 are reserved for the card number within the data set starting with 01, with increments to 99 in steps of 1. Within our laboratories, column 73 is used to designate which laboratory originated the data (*i.e.*, 0 for Geneva and 1 for Ithaca). In the example given, the zero in column 73 signifies that the data were collected at Geneva. The digits 00003 in columns 74-78 represent the number of a data set described by a given set of field conditions, and the final two digits indicate the sequence of cards within the set.

The information on these data cards is then reorganized by a computer program for efficiency in generating reports and written on a disk cartridge, where it forms a master file of all the pesticide residue information which has been sampled in Geneva and Ithaca. Information from current and future projects on new and familiar compounds will continuously update the system and make possible contemporary and instantaneous retrieval.

The master file and a single card into which the user punches 1 to 16 codes representing the index key words to be searched comprises the input to the Select program. Increasing the number of codes by which the program selects the information results in a narrower range of information being retrieved. A typical input card to search the indicated keywords is shown in Table I. The result of using the keywords given in the example resulted in the recovery of experimental data, shown in Figure 3. Additional data contained on the master file and defined by these keywords were also recovered.

PESTICIDE RESIDUE INFORMATION RETRIEVAL INPUT DATA SET

(Example)

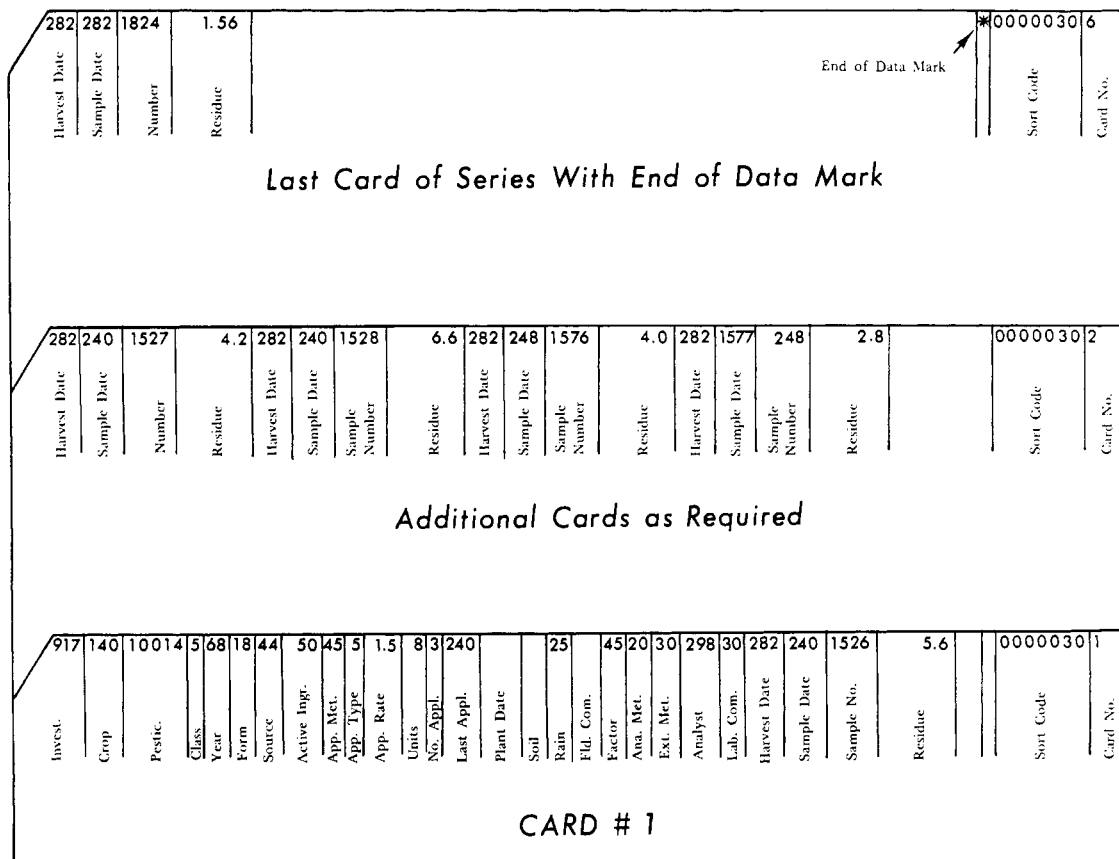


Figure 2. A data set as punched which shows the coded input of the data listed in Figure 1

PESTICIDE RESIDUE INFORMATION RETRIEVAL REPORT
 NEW YORK STATE AGRICULTURAL EXPERIMENT STATION, GENEVA, N.Y.
 CORNELL UNIVERSITY, ITHACA, N.Y.

PESTICIDE	TORAK
CROP	GRAPES
APPLICATION TYPE	FOLIAGE
APPLICATION METHOD	GRD.HIGH PRESSRE
FORMULATION	WETT POWDER
FACTOR STUDIED	WEATHERING
CHEMICAL CLASS	INSECTICIDE
SOIL TYPE	NOT REPORTED
INVESTIGATOR	TASCHENBERG, E.
CHEMICAL SOURCE	HERCULES
APPLICATION RATE	1.50 LBS/ACRE
ANALYTICAL METHOD	GCFPO
EXTRACTION METHOD	REYNOLDS
ANALYST	GIBBS, S.
LAB COMMENTS	SAMPLES FROZEN
FIELD COMMENTS	NOT REPORTED
YEAR	68
RAINFALL	25 INCH
ACTIVE INGREDIENT	50 PERCENT
NUMBER APPLICATIONS	3
DAY LAST APPL.	240
PLANTING DATA	NOT REPORTED

HARVEST DATE	282	SAMPLING DATE	240	SAMPLE NO.	1526	RESIDUE	5.6000	PPM
HARVEST DATE	282	SAMPLING DATE	240	SAMPLE NO.	1527	RESIDUE	4.2000	PPM
HARVEST DATE	282	SAMPLING DATE	240	SAMPLE NO.	1528	RESIDUE	6.6000	PPM
HARVEST DATE	282	SAMPLING DATE	248	SAMPLE NO.	1576	RESIDUE	4.0000	PPM
HARVEST DATE	282	SAMPLING DATE	248	SAMPLE NO.	1577	RESIDUE	4.8000	PPM
HARVEST DATE	282	SAMPLING DATE	248	SAMPLE NO.	1578	RESIDUE	3.0000	PPM
HARVEST DATE	282	SAMPLING DATE	257	SAMPLE NO.	1621	RESIDUE	2.4200	PPM
HARVEST DATE	282	SAMPLING DATE	257	SAMPLE NO.	1622	RESIDUE	1.4200	PPM
HARVEST DATE	282	SAMPLING DATE	257	SAMPLE NO.	1623	RESIDUE	1.5800	PPM
HARVEST DATE	282	SAMPLING DATE	261	SAMPLE NO.	1675	RESIDUE	3.0000	PPM
HARVEST DATE	282	SAMPLING DATE	261	SAMPLE NO.	1676	RESIDUE	2.7500	PPM
HARVEST DATE	282	SAMPLING DATE	261	SAMPLE NO.	1677	RESIDUE	2.8200	PPM
HARVEST DATE	282	SAMPLING DATE	268	SAMPLE NO.	1712	RESIDUE	1.9400	PPM
HARVEST DATE	282	SAMPLING DATE	268	SAMPLE NO.	1713	RESIDUE	1.8100	PPM
HARVEST DATE	282	SAMPLING DATE	268	SAMPLE NO.	1714	RESIDUE	2.3800	PPM
HARVEST DATE	282	SAMPLING DATE	282	SAMPLE NO.	1822	RESIDUE	2.0600	PPM
HARVEST DATE	282	SAMPLING DATE	282	SAMPLE NO.	1823	RESIDUE	1.3100	PPM
HARVEST DATE	282	SAMPLING DATE	282	SAMPLE NO.	1824	RESIDUE	1.5600	PPM
HARVEST DATE	0	SAMPLING DATE	0	SAMPLE NO.		RESIDUE	0.0000	PPM
HARVEST DATE	0	SAMPLING DATE	0	SAMPLE NO.		RESIDUE	0.0000	PPM
HARVEST DATE	0	SAMPLING DATE	0	SAMPLE NO.		RESIDUE	0.0000	PPM

Figure 3. Actual output of recovered data

The entire retrieval system is written in Fortran IV and designed to run on the IBM system 1800 or 1130. The system, which has been operational for about 2 years, is relatively easy to use and maintain, and experimental data or directory terms may be added as required. The inclusion of the investigators and analysts' names, as well as sample number, give the user a source for additional field and lab data which may not be in the master file.

In practice, the user either prepares a punch card containing the search parameters and initiates a batch processing program or enters his parameters through a typewriter keyboard as a time-sharing program. In the latter case, when processing on the IBM 1800, his program will directly enter the background processing queue for execution on a time-sharing basis with laboratory monitoring.

ACKNOWLEDGMENT

The authors wish to acknowledge the use of field data collected by E. F. Taschenberg, Vineyard Laboratory, New York State Agricultural Experiment Station, Fredonia, N. Y. 14063.

LITERATURE CITED

- Elias, A. W., Warren, M. R., *J. Chem. Doc.* **2**, 185 (1962).
 Geer, H. A., Howard, C. C., *J. Chem. Doc.* **2**, 51 (1962).
 Waldo, W. H., Hamm, P. C., Hannah, L. H., Dunn, P. V., Billman, R. C., *J. Chem. Doc.* **4**, 218 (1964).
 Wieman, J. A., *J. Chem. Doc.* **4**, 209 (1964).

John B. Bourke*
 Gloria Loftus
 Donald J. Lisk¹

Pesticide Residue Research Laboratories
 New York State Agricultural Experiment Station
 Geneva, New York 14456

¹ Cornell Agricultural Experiment Station
 Cornell University
 Ithaca, New York 14850

Received for review April 17, 1972. Accepted August 16, 1972.
 Approved by the Director of the New York State Agricultural Experiment Station as Journal Paper No. 1800, April 17, 1971.
 This work was supported in part by the Regional Research Program, NE-36.

Identification of Photoaldrin Chlorohydrin as a Photoalteration Product of Dieldrin

A photoproduct produced by the thin film irradiation of dieldrin (I) with germicidal lamps has been isolated and identified. Based on glc, ir, nmr, ms, and melting point comparisons with independently

synthesized material, the product (IV) is considered to be a chlorohydrin derived from photodieldrin. The isolation and synthesis of the chlorohydrin is described.

Solid-state irradiation of thin films of dieldrin (I) produces photodieldrin (II) and several minor photoproducts (Benson, 1971; Harrison *et al.*, 1967; Rosen *et al.*, 1966). Benson reported that one minor product appeared to be a chlorohydrin (IV) derived from photodieldrin. We have investigated this chlorohydrin.

EXPERIMENTAL SECTION

Photoaldrin Chlorohydrin (IV) (1,1,2,3,3a,5(or 6),7a-heptachloro-6(or 5)-hydroxydecahydro-2,4,7-metheno-1H-cyclopenta[*a*]pentalene). Ten milliliters of concentrated HCl and 0.5 g of ZnCl₂ were added to a solution of 1.0 g (2.6 mmol) of 99+ % photodieldrin in 100 ml of absolute ethanol. (The samples of dieldrin and photodieldrin were prepared for use as reference standards in earlier work; their purities were determined by electron capture glc.) The solution was heated on a steam bath for 18 hr and then poured into 300 ml of water. The white precipitate was recrystallized once from acetone-hexane to give 0.8 g (1.9 mmol, 73%) of colorless crystalline product, mp 204.5–206.5°.

The mass spectrum showed a molecular ion at *m/e* 414 (calculated, 414) and an intense M - Cl peak at *m/e* 379. The chlorine isotopic ratio observed indicated that the compound contained 7 chlorine atoms. The ir (KBr) showed a nonbonded hydroxyl at 3600 cm⁻¹ and major bands at 1053 and 818 cm⁻¹. The nmr spectrum (100 MHz in DMSO-*d*₆) showed a singlet at δ 5.56, a doublet of doublets at δ 4.16 (*J* = 5.2 Hz), a doublet of doublets at δ 3.73 (*J* = 5.2 Hz), and the hydroxyl proton as a doublet at δ 5.76 (*J* = 5 Hz). Gas chromatographic retention times relative to aldrin on a 6-ft

10% DC-200 column and a mixed 10% DC-200 and 15% QF-1 column were 8.6 and 11.6, respectively. The operating parameters are described in the Pesticide Analytical Manual (1968).

Anal. C, calcd 34.54; found, 34.55, 34.56. H, calcd 2.28; found, 2.10, 2.11.

Aldrin chlorohydrin (III) was prepared in the same manner as IV in 84% yield, mp 150–152°. The mass spectrum showed a molecular ion at *m/e* 414 (calcd, 414) and a strong M - Cl peak at *m/e* 379. The observed chlorine isotopic ratio indicated a total of 7 chlorine atoms in the molecule. The ir (KBr) showed a hydrogen-bonded hydroxyl at 3240 cm⁻¹, the double bond at 1595 cm⁻¹, and major bands at 1054, 1037, 817, and 808 cm⁻¹. Its glc retention times relative to aldrin on the DC-200 and mixed columns were 3.6 and 4.0, respectively.

Photoaldrin Chlorohydrin (IV) from Irradiation of I. Thin films of 99.7% dieldrin (see above) (200 mg each, 2 g total) in five 0.5-in. petri dishes were exposed to two G.E. G30T8 germicidal lamps at a distance of 4.5 cm for 24 hr. The tan solids were combined and crystallized from 5 ml of hot absolute ethanol. The solid (photodieldrin) was filtered off and the mother liquor was found to be much richer in photoaldrin chlorohydrin (glc). Additional crystallization of photodieldrin occurred on standing; the filtrate contained approximately 50% of the desired component (by measurement of glc peak area) in addition to photodieldrin and unreacted dieldrin.

Evaporation of solvent from the filtrate gave a dark oil which was chromatographed on a silica gel column with benzene as eluting solvent. Several fractions rich in the desired component (glc) were obtained. Concentration of the com-