Fate of Dieldrin in Radishes

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[^{14}C]Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene) was applied in a commercial dieldrin formulation to the roots and surrounding soil of early mature radishes, maintained in environmental growth chambers, at rates of 1.1 and 11.1 kg/ha. Edible portions of the radishes were sampled 1, 7, 14, and 21 days postapplication. ^{14}C residues (as dieldrin equivalents) present in the 1.1 kg/ha treatment ranged from 0.4 to 2.1 ppm and in the 11.1 kg/ha treatment from 4.0 to 8.5 ppm. Extractable ^{14}C was primarily dieldrin (77–94%) and photodieldrin (2.7–10.4%). The concentration of unextractable ^{14}C increased with time for both treatments (0.11–0.96 ppm). Much of the bound ^{14}C was released by acid hydrolysis of the solvent-extracted tissue. Radiocarbon associated with lignin remained relatively constant for the 1, 7, and 14 day postapplication periods (approximately 0.02 ppm), but a large increase occurred between 14 and 21 days (approximately 0.27 ppm).

Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene) is a chlorinated hydrocarbon insecticide that was registered for use in the United States as an insecticide. It is considered to be relatively persistent in the environment and is not metabolized extensively by plants or animal enzyme systems.

Major mechanisms for plants to contain dieldrin residues are root absorbed translocation from soil and absorption through the leaves (either from direct application or volatilization from the soil). Translocation of root absorbed dieldrin occurs in red mangrove seedlings (Walsh et al., 1974), corn (Beestman et al., 1969), and grass plants (Voerman and Besemer, 1975). Aerial contamination by absorption through the leaves is more pronounced when field-grown corn is compared to greenhouse-grown corn that had been protected from aerial contamination (Barrows et al., 1969). Volatilization of dieldrin from soil over a growing season and absorption through the leaves of corn, combined with root absorption, results in residues up to 1.33 ppm (Taylor et al., 1976). The availability of dieldrin for absorption by plants is increased by increasing the water content of the soil (Saha et al., 1971) and decreasing the soil organic content (Saha et al., 1971; Wheeler et al., 1967b; Harris and Sans, 1972; Nash et al., 1970). Wheeler et al. (1967b) observed 2–6 times higher levels of dieldrin in forage plants grown in sand than in plants grown in soil. Quantitative extraction of absorbed dieldrin from forage plants was achieved by using chloroform–methanol (1:1) (Wheeler et al., 1967a). Photodieldrin is the major metabolite detected (5–10%) in cabbage, spinach, and carrots (Weisgerber et al., 1970).

Nonextractable (or bound) pesticide residues are defined as chemical species originating from pesticide usage that cannot be extracted by methods commonly used in residue analyses and metabolism studies. This definition was formulated by the First FAO/IAEA Research Coordination Meeting on isotopic tracer aided studies of bound pesticide residues in soil, plants, and food. Generally, chlorinated hydrocarbon insecticides are not often reported to form bound residues in plant substrates. In one instance, however, Nash et al. (1970) reported for soybeans grown in soil containing [^{14}C]dieldrin that as much as 40% of the ^{14}C in the beans and 9% in the hay was unextractable by using chloroform–methanol as the extracting solvent. Wheeler and Thompson (1981) have noted the presence of bound ^{14}C when radiolabeled dieldrin was applied in a commercial formulation to the roots and surrounding soil of early mature radishes. Twenty to thirty percent of the ^{14}C could not be extracted by blending with either acetone, acetonitrile, or methanol. This phenomenon noted with dieldrin resulted in efforts to determine (1) uptake and metabolism of dieldrin at various application rates, (2) extractability of the adsorbed dieldrin, (3) levels and percentages bound, and (4) some characteristics of the bound material.

MATERIALS AND METHODS

Chemicals. Uniformly ring labeled [^{14}C]dieldrin (Amersham Corp., 85 mCi/mmol) was used to fortify a Shell emulsifiable concentrate (EC) containing 18% technical dieldrin. Three application rates were used: 1.1, 11.1, and 111 kg/ha. The 111 kg/ha treatment solution was prepared by mixing 16.39 g (3.06 g of technical dieldrin) of the formulation with 6.72 mg of [^{14}C]dieldrin in acetone (1.5 mCi) and diluting to 300 mL with H_2O for a final specific activity of 0.19 mCi/mmol. Dilutions of this solution were made to prepare the 1.1 and 11.1 kg/ha stock solutions. All solvents used were pesticide grade. Dieldrin (99.7%) and photodieldrin (98%) analytical standards were obtained from the Environmental Protection Agency (Research Triangle, NC). *trans*-Aldrin diol was synthesized by the H_2SO_4 hydrolysis of dieldrin (Korte and Arent, 1965) with the addition of 1,4-dioxane to enhance the yield (Mckinney et al., 1971). Pepsin powder from porcine stomach mucosa with an activity of 1200–2000 units/mg of protein was used as received (Sigma).

Chromatographic and Radioassay Procedures. Thin-layer chromatography (TLC), carried out by using silica gel 60 F-254 chromatoplates (0.25 × 20 cm, E. Merck), employed two solvent systems: methylene chloride and *n*-heptane–acetone (80:20). Gas chromatography (GC) was done on a Hewlett-Packard Model 5840 fitted with a ^{63}Ni electron capture detector (ECD) and a flame ionization detector (FID). Argon–methane (5:95) was the carrier gas for ECD with a flow rate of 60 mL/min. Nitrogen was the carrier gas for FID and had a flow rate of 30 mL/min. The air and hydrogen flows for FID were 300 and 30 mL/min, respectively. The injector and detector temperatures were 225 and 350 °C, respectively. Glass columns (1.8 m × 2.0 mm i.d.) were packed with 3% QF-1, 1.5% OV-17 plus 1.95% QF-1 (on 100–120-mesh Gas-Chrom Q), and 2% SP 2330 (on 100–120 Chromosorb) and were operated between 180 and 210 °C. Electron impact GC mass spectrometry (MS) was performed on a Finnigan 4021 GC–MS, fitted with a 1.8 m × 2.0 mm i.d. glass column packed with 3% QF-1 (on 100–120-mesh Gas-

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Chrom Q) and operated at isothermal and programmed temperatures between 155 and 220 °C. GC–MS was done to authenticate the reference compounds.

Radish tissues remaining after extraction and the hydrolytic treatments were dried at 105 °C for 24 h. Radiocarbon determinations in all tissues were made by combustion on a Packard Tri-Carb Sample Oxidizer B 306. All liquid scintillation counting (LSC) was done on a Searle Analytic 92 liquid scintillation counter utilizing Aquasol II plus 10% water. The cpm were converted to dpm by using quench curves.

Treatment and Analysis of Plants. Red Globe radish seeds were germinated in flats containing soil and then transplanted to 14.6-cm pots (four per pot) containing sand at 1.5–2 weeks of age. The flats and pots were maintained in an environmental growth chamber (Scherer-Gillet Model CEL 512-37), with 10-h light periods and 14 h of dark. Light and dark temperatures were 27 and 16 °C, respectively; light and dark relative humidities were 80% and 60%, respectively. The radishes were treated at 5–6 weeks after germination by pipetting 5 mL of the ^{14}C-fortified formulated dieldrin onto the roots and surrounding soil of each radish (total of 20 mL/pot) at rates of 1.1, 11.1, and 111 kg/ha. An untreated control was maintained in the same growth chamber. The sand was covered with paraffin shavings immediately after dieldrin application to reduce volatilization of the insecticide.

The radishes were harvested 1, 7, 14, and 21 days postapplication by pulling them from the sand, rinsing them with water to remove adhering sand, and removing the tops. They were immediately weighed and then chopped with a hand-operated food chopper to particles of 0.5–1.0 mm in size prior to analysis. The radish weights from the various treatments were analyzed statistically by a one-way analysis of variance. Dunnett's procedure was used to compare means of treatment groups to controls and Tukey's procedure was used to compare treatment means.

The chopped radish tissues were extracted in a Soxhlet extractor for 24 h (an average of two cycles per h) with chloroform–methanol (2:1). The solvent-extracted radish tissues were dried; the extracts were transferred to separatory funnels, 100 mL of distilled water was added, and the funnels were shaken. After separation of the aqueous and organic phases, the aqueous phases were repartitioned with 50 mL of chloroform, which was then combined with the first chloroform phase. Both the aqueous and organic phases were assayed for ^{14}C by LSC. The organic phases were then concentrated on a rotory evaporator for another ^{14}C determination and evaluation of ^{14}C components by TLC. Benzene–ethanol (2:1) was also used to extract portions of the chopped radish tissue as the initial step in the Association of Official Analytical Chemists (AOAC) indirect lignin analysis (1970).

Portions of the extracted dry tissue were subjected individually to the various hydrolytic treatments shown in Table I. After the AOAC indirect lignin analysis, only lignin and ash remained. The soluble fractions from the hydrolytic treatments were partitioned with methylene chloride. They were then neutralized with sodium hydroxide and again partitioned with methylene chloride, and finally they were made alkaline with sodium hydroxide and again partitioned with methylene chloride. The radiocarbon in the methylene chloride fractions and that remaining in the aqueous hydrolysate were determined.

Identification of Conversion Products. The organic phase concentrates were streaked on TLC plates and developed to 10 cm. Areas of ^{14}C were detected by placing the plates in contact with Kodak No-Screen X-ray film for autoradiography. The separated zones were scraped, eluted with Aquasol II plus 10% H_2O scintillation cocktail, and counted to determine the percentage distribution of ^{14}C. Also, ^{14}C zones from TLC were eluted with acetone, methanol, or methylene chloride for GC and GC–MS analysis. The chromatographic behavior of reference compounds was compared to the ^{14}C zones.

Table I. Hydrolytic Treatment Conditions

0.1 N HCl, 40 °C, 24 h
0.1 N HCl plus 1% pepsin, 40 °C, 24 h
0.1 N HCl, 100 °C, 2 h
AOAC indirect lignin analysis[a]
0.1 N HCl plus 1% pepsin, 40 °C, 24 h
5% H_2SO_4, 100 °C, 1 h
75% H_2SO_4, 20 °C, 2 h
3% H_2SO_4, 100 °C, 1 h

[a] Performed on benzene-ethanol (2:1) extracted tissue.

RESULTS AND DISCUSSION

Radish Physical Parameters. In an effort to detect effects of dieldrin on radish physiology, the weights of the roots were measured. The mean radish weight 1 day postapplication was 4.6 g (all statistically equivalent at the 0.01 confidence level) for all application rates and the untreated control. The mean weight of radishes treated at the 1.1 and 11.1 kg/ha rates, including the control, increased to 25.9 g (0.01 confidence level) by 21 days postapplication at a nearly linear rate. Radishes treated at the 11.1 kg/ha rate averaged 5 g less than the control and 1.1 kg/ha treatments through the 7- and 14-day harvests, but they had attained an equivalent mean weight by 21 days postapplication. The 111 kg/ha radishes did not grow or increase in weight, remaining at 5 g for all harvest periods. Due to the inhibition of growth and obvious visual signs of toxicity as a result of this treatment rate, the data for the 111 kg/ha treated radishes will not be discussed.

Other physical parameters of the radishes that were measured were percentage H_2O, extracted dry weight, volume to weight ratio, and lignin content at the various harvest intervals. The percentage H_2O remained constant through treatment rates and harvest intervals, ranging from 92 to 95%. The percentage of tissue residue remaining after extraction also remained constant over treatment rates and harvest intervals, ranging between 3.0 and 4.0%. The volume to weight ratio of the radishes at the 1-, 7-, and 14-day harvest periods (4–6 weeks postgermination) was approximately 1.00 and increased to 1.29 at 21 days. Amounts of lignin present (mg of lignin/g wet weight) again were relatively constant for the 1-, 7-, and 14-day harvest intervals at approximately 8.3 mg/g but had increased to 11.8 mg/g at 21 days postapplication. The 22% increase in the volume to weight ratio between 14 and 21 days corresponded to higher amounts of lignin and visual signs of plant senescence.

Total Uptake of Dieldrin. Concentrations of ^{14}C, calculated as dieldrin equivalents, detected in the radishes at the time of harvest for the 1.1 and 11.1 kg/ha rates are presented in Table II. Control radishes contained between 0.5 and 1.0 ppm, which may have been caused by cross contamination through volatilization of dieldrin and subsequent absorption through the leaves. These levels were used to normalize the 1.1 and 11.1 kg/ha treatment rate data. Levels at the 1.1-kg rate ranged from 0.4 to 2.1 ppm and at the 11.1-kg rate from 4.0 to 8.5 ppm. Reductions in ppm as time increased postapplication were caused by radish growth. Even though the ppm levels present decreased or remained relatively constant over the 21-day

Table II. Concentration of ^{14}C as Dieldrin Equivalents at Time of Harvest (ppm)

	1.1 kg/h				11.1 kg/h			
	1[a]	7	14	21	1	7	14	21
extractable	1.92	1.09	0.29	0.85	8.27	7.10	3.88	3.12
unextractable[b]	0.15	0.31	0.11	0.54	0.23	0.23	0.56	0.96
total[b]	2.10	1.40	0.40	1.39	8.50	7.33	4.44	4.08

[a] Days postapplication. [b] Average of two combustion analyses.

Table III. Percentage Recovery of Applied Radiocarbon from Radish Roots for the 1.1 and 11.1 kg/ha Treatment Rates at 1, 7, 14, and 21 Days

treatment rate, kg/ha	days postapplication			
	1	7	14	21
1.1	1.6	3.6	2.2	7.6
11.1	0.6	1.2	1.4	2.3

interval, the absolute amount of dieldrin residues increased. The recovery of applied radiocarbon from the plants (edible portion of the roots) at the various harvest intervals as a percentage of applied dose increased for both the 1.1 and 11.1 kg/ha rates (see Table III).

Extractable Radiocarbon. The total ppm extractable radiocarbon expressed as dieldrin equivalents, for the 1.1 and 11.1 kg/ha rates at 1, 7, 14, and 21 days are shown in Table II. At the 1.1 kg/ha rate 60–90% of the ^{14}C was extractable and at the 11.1 kg/ha rate 76–97% was extractable.

The percentage distribution of dieldrin and conversion products in the extractable fraction (organic phase) are shown in Table IV (there was no detectable ^{14}C in the aqueous phase). Dieldrin ranged from 78 to 94% at 1.1 kg/ha and 76 to 93% at 11.1 kg/ha. Photodieldrin and *trans*-aldrin diol were the major and minor conversion products identified, respectively. The chromatographic behavior of these two products matched the behavior of the reference standards. Three other minor conversion products were detected: products A, B, and C. There were not sufficient quantities of any of the three to obtain a direct mass spectral analysis. Product A migrated between aldrin and dieldrin with the *n*-heptane–acetone (80:20) solvent system (R_f = 0.64), behavior which is similar to metabolite X reported by Klein et al. (1973). Product B migrated in a manner similar to metabolite C-1 of Matthews and Matsumura (1969) when developed in methylene chloride (R_f = 0.19) and *n*-heptane–acetone (80:20) (R_f = 0.34). These authors reported their metabolite C-1 to be a hydroxy photodieldrin metabolite. Product C migrated between *trans*-aldrin diol and photodieldrin in *n*-heptane–acetone (80:20) (R_f = 0.18) and had a 0.05R_f in methylene chloride. Polar materials remaining at the origin comprised 2–5% of the ^{14}C and were not identified.

The dieldrin EC formulation contained many impurities that were chlorinated and structurally similar to dieldrin. Many of the chlorinated impurities were absorbed by the plants along with dieldrin and were detected in the cleanup procedure as nonradioactive entities. The major impurity was chlorohydrin dieldrin.

Unextractable Radiocarbon. Amounts of unextractable ^{14}C residues, calculated as dieldrin equivalents, are shown in Table II for the 1.1 and 11.1 kg/ha rates. Trends were toward increasing ppm bound over time. The percentages of recovered ^{14}C (extractable plus unextractable) that were bound also increased with time and were slightly higher from the 1.1 kg/ha rate than from the 11.1 kg/ha rate.

The bound ^{14}C residues were comprised of those releasable by hydrolytic treatments and those remaining lignin bound. Both total bound and lignin-bound residues increased slowly postapplication through 14 days but increased rapidly between 14 and 21 days. The lignin-bound ^{14}C ranged between 0.02 and 0.07 ppm for both the 1.1 and 11.1 kg/ha treatment rates at the 1-, 7-, and 14-day harvest periods. Between the 14- and 21-day harvest interval the lignin-bound ^{14}C increased from 0.02 to 0.18 ppm for the 1.1 kg/ha rate and 0.07 to 0.27 ppm for the 11.1 kg/ha rate. An increase in lignin was also observed between 14 and 21 days.

An interesting observation was made that may suggest differences in extractability based on the mode of exposure, root absorption vs. absorption through the leaves. If one

Table IV. Percentage Distribution of ^{14}C in the Extractable Fraction as Dieldrin and Conversion Products

	1.1 kg/ha				11.1 kg/ha			
	1	7	14	21	1	7	14	21
dieldrin	93.8	89.6	78.2	80.4	93.4	88.9	76.5	78.9
photodieldrin	3.3	5.0	7.4	8.0	2.7	5.0	10.4	9.3
trans-aldrin diol	0.0	0.0	3.4	1.0	0.0	0.0	1.8	1.2
A[a]	0.0	1.0	1.0	1.0	0.0	1.0	2.0	2.0
B[a]	0.0	0.5	1.2	1.2	0.0	1.5	2.0	2.0
C[a]	0.0	2.0	3.0	4.0	0.0	0.5	2.3	2.0
polar[b]	2.7	1.9	5.8	4.4	3.9	3.1	5.0	4.6

[a] Unknown conversion products; see Extractable Radiocarbon for chromatographic behavior. [b] Radiocarbon remaining at the origin.

Table V. Percentage Radiocarbon Released from the Solvent-Extracted Dry Tissue by the Hydrolytic Treatments

	1.1 kg/ha				11.1 kg/ha			
	1[a]	7	14	21	1	7	14	21
0.1 N HCl, 40 °C[c]	–[b]	–	19.2	11.8	–	–	17.1	20.6
0.1 N HCl plus 1% pepsin, 40 °C[c]	–	–	32.4	34.4	–	–	36.5	33.6
0.1 N HCl, 100 °C[c]	–	–	64.2	76.7	–	–	75.9	84.1
lignin analysis[d]	88.1	86.3	80.7	66.5	92.9	92.5	86.7	71.8

[a] Days postapplication. [b] These treatments were not performed on the 1- and 7-day tissues. [c] Average of duplicate determinations. [d] Average of triplicate determinations.

compares data for the control and 11.1 kg/ha application rate, there were large differences in the percentage [^{14}C]dieldrin that was unextractable. The control possessed 24–31% unextractable materials in the roots while the 11.1 kg/ha treatment contained 3–24% unextractable ^{14}C. If one assumes that the control samples received the [^{14}C]dieldrin predominantly as a leaf application resulting from volatilization of the insecticide (probably from the 111 kg/ha application), and if one further assumes that the 11.1 kg/ha rate received its dosage primarily as a root application, then differences in extractability appear to exist between the modes of exposure (or application). This cross-contamination assumption seems valid since the level of ^{14}C per gram of radish in the control was 10–20% of the ^{14}C levels in the 11.1 kg/ha treatment.

The percentages of radiocarbon released from the extracted dry radish tissue by the various hydrolytic treatments are shown in Table V. The AOAC lignin analysis and 0.1 N HCl reflux released approximately the same amount of ^{14}C. This was approximately 2 times the amount released by the 0.1 N HCl plus 1% pepsin digest at 40 °C and approximately 3 times the amount released by 0.1 N HCl at 40 °C alone. These values were obtained by combusting the extracted dry tissue before and after treatment.

The stability and extractability of dieldrin in 0.1 N HCl were evaluated to determine possible effects of the hydrolytic treatment on dieldrin residues. Technical dieldrin was spiked with [^{14}C]dieldrin, and the mixture was purified by TLC and added to 0.1 N HCl. One hundred percent of the ^{14}C would partition into methylene chloride both before and after refluxing. The methylene chloride fractions were then subjected to TLC and autoradiography. Before the fractions were refluxed, all the ^{14}C was dieldrin, and after they were refluxed, there were 12% conversion products.

The unextractable ^{14}C had several interesting characteristics. Seventy percent of the ^{14}C released from extracted tissue residue by the hydrolytic treatments remained in the aqueous phase when partitioned with methylene chloride whether the aqueous phase was acidic, neutral, or basic. This polar ^{14}C material probably did not form as a result of the hydrolytic treatment since preliminary experiments using dieldrin as the starting material showed it to partition into methylene chloride even after refluxing in 0.1 N HCl. The fact that adding pepsin to 0.1 N HCl increased the amount of ^{14}C released suggests the involvement of protein in some of the bound ^{14}C.

The ^{14}C remaining in the lignin fraction is probably covalently incorporated since it was not released or destroyed by the rigorous AOAC indirect procedure. This has been observed by other investigators for a variety of other pesticides in plants (Chin et al., 1973; Honeycutt and Adler, 1975; Forbes, et al., 1980; Balba et al., 1979; Still et al., 1981; Khan, 1980; Stratton et al., 1981). The nature of this complex is not known for dieldrin. However, studies with chloroaniline suggest covalent incorporation of the parent, or a structurally similar metabolite, into the lignin polymer (Still et al., 1981). Dieldrin does contain a reactive epoxide functional group that could be involved in an ether or ester covalent linkage.

More research is needed to identify the materials that can be released, to determine the structure of the "lignin–dieldrin" complex, and to assess the toxicological significance of such unextractable residues.

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LITERATURE CITED

Association of Official Analytical Chemists "Official Methods of Analysis", 11th ed.; AOAC: Washington, DC, 1970; p 51.
Balba, H. M.; Still, G. G.; Mansager, E. R. *J. Assoc. Off. Anal. Chem.* **1979**, *62*, 237.
Barrows, H. L.; Caro, J. H.; Armiger, W. H.; Edwards, W. M. *Environ. Sci. Technol.* **1969**, *3*, 261.
Beestman, G. B.; Keeney, D. R.; Chesters, G. *Agron. J.* **1969**, *61*, 390.
Chin, W. T.; Kucharczyk, N.; Smith, A. E. *J. Agric. Food Chem.* **1973**, *21*, 507.
Forbes, D. H.; Wheeler, W. B.; Littell, R. C. "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980; American Chemical Society: Washington, DC, 1980; PEST 111.
Harris, C. R.; Sans, W. W. *J. Econ. Entomol.* **1972**, *65*, 333.
Honeycutt, R. C.; Adler, I. L. *J. Agric. Food Chem.* **1975**, *23*, 1097.
Khan, S. U. *J. Agric. Food Chem.* **1980**, *28*, 1096.
Klein, W.; Kohli, J.; Weisgerber, I.; Korte, F. *J. Agric. Food Chem.* **1973**, *21*, 152.
Korte, F.; Arent, H. *Life Sci.* **1965**, *4*, 2017.
Matthews, H. B.; Matsumura, F. *J. Agric. Food Chem.* **1969**, *17*, 845.
McKinney, J. D.; Keith, L. H.; Alford, A.; Fletcher, C. E. *Can. J. Chem.* **1971**, *49*, 1993.
Nash, R. G.; Beall, M. L.; Woolson, E. A. *Agron. J.* **1970**, *62*, 369.
Saha, J. G.; Karapally, J. C.; Janzen, W. K. *J. Agric. Food Chem.* **1971**, *19*, 842.
Still, G. G.; Balba, H. M.; Mansager, E. R. *J. Agric. Food Chem.* **1981**, *29*, 739.
Stratton, G. D.; Wheeler, W. B.; Carlson, D. A. "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, Aug 1981; American Chemical Society: Washington, DC, 1981; PEST 75.
Taylor, A. W.; Glotfelty, D. E.; Glass, B. L.; Freeman, H. P.; Edwards, W. M. *J. Agric. Food Chem.* **1976**, *24*, 625.
Voerman, S.; Besemer, A. F. H. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 501.
Walsh, G. E.; Hollistor, T. A.; Forester, J. *Bull. Environ. Contam. Toxicol.* **1974**, *12*, 129.
Weisgerber, I.; Klein, W.; Korte, F. *Tetrahedron* **1970**, *26*, 779.
Wheeler, W. B.; Frear, D. E. H.; Mumma, R. O.; Hamilton, R. H.; Cotner, R. C. *J. Agric. Food Chem.* **1967a**, *15*, 227.
Wheeler, W. B.; Frear, D. E. H.; Mumma, R. O.; Hamilton, R. H.; Cotner, R. C. *J. Agric. Food Chem.* **1967b**, *15*, 231.
Wheeler, W. B.; Thompson, N. P. DHEW, FDA Contract No. 223-76-2220, Final Report, 1981.

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