Phosdrin acid is the first step in the degradation of Phosdrin in plants, followed by subsequent cleavage to dimethyl phosphate. The results shown in Figure 1 might support this hypothesis. However, those in Figure 2 cast doubt on the single pathway. If Phosdrin acid were an essential step in Phosdrin degradation in the plant, desmethyl Phosdrin acid should have been isolated in Phosdrin degradation and been present in the same proportion to dimethyl phosphate as indicated in Figure 2. Since none was detected, there are at least two pathways for Phosdrin degradation, the main one being directly to dimethyl phosphate and the other via Phosdrin acid.

Monodealkylation of organophosphorus insecticides by plants had not been reported until recently. Under conditions of alkaline hydrolysis some occurred with *cis*-Phosdrin (*8*), while in the plant some was shown with Dimethoate (*4*). Although no desmethyl Phosdrin was found in this study, some monodealkylation was shown with the identification of desmethyl Phosdrin acid (IV) from the metabolism of Phosdrin acid as shown in Figure 2.

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HERBICIDE UPTAKE FROM SOILS

Uptake of Radioactive Ethyl-*N,N*-di-*n*-propylthio carbamate (EPTC-S^{35}) and Translocation of Sulfur-35 in Various Crops

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A study of the absorption of radioactive EPTC by crops in pre-emergence application indicated an uptake of this chemical from soil. By use of radioautographic technique the differences in accumulation patterns of sulfur-35 from EPTC-S^{35} among crops were demonstrated; above-ground portions of beans, peas, and corn contained slightly more sulfur-35 than the roots, while above-ground portions of radishes, carrots, and other plants contained 70 to 94% of the sulfur-35 from the absorbed EPTC-S^{35}. Total absorption by individual crops at various stages of growth was determined. Generally, an increase in applied EPTC-S^{35} increased absorption, but not in proportion to the increase in rate of application.

An earlier study (*1*) showed that less than 3% of the ethyl-*N,N*-di-*n*-propylthiolcarbamate (EPTC) absorbed from soils was left as a residue in a variety of plant tissues. This investigation has been extended to include the total uptake of radioactive EPTC and the distribution of sulfur-35 by various crops, when a pre-emergence application of EPTC-S^{35} is made to soil.

Experimental

The crops used were kidney beans, sweet corn, garden peas, radishes, carrots, cabbage, mustard, swiss chard, table beets, Mung beans, and cucumbers. Beans, peas, and corn were planted in

Table I. Absorption of EPTC-S^{35} from Soil and Translocation of Sulfur-35 by Kidney Bean Plants

Appl. Rate, Lb./Acre	Interval,[a] Days	No. of Plants	Accumulation of S^{35}, %: Root	Stem	First leaf	Trifoliate	Flower and pod	Total EPTC-S^{35} Absorption, γ/Plant
1	10	5	48	26	26	..	..	5.0
	17	5	33	32	35	..	..	7.2
	24	5	53	22	16	8	..	11.6
	38	5	48	22	19	8	3	15.7
	52	5	42	14	14	19	11	22.4
4	10	5	35	33	32	..	..	18.8
	17	5	33	40	27	..	..	16.7
	24	5	38	32	30	..	..	33.2
	38	5	39	29	26	4	3	40.7

[a] Interval between treatment and harvest.

separate flats. A total of 72 seeds from each crop was sown. The others were planted two crops per flat in three rows each. Newberg sandy loam was used throughout this experiment. One day after the seeds were planted, all flats received a pre-emergence application of EPTC-S^{35} at a rate of either 1 or 4 pounds per acre (*1*).

The plants were harvested at various intervals after treatment, as indicated in the tables. One plant from each crop was used for making a radioautograph in order to study the accumulation pattern of sulfur-35 at various stages of growth. The other plant samples were dried immediately in a vacuum oven at 60° C. and were ground. The radioactivity of a weighed sample was determined and corrected for self-absorption as well as for half life of sulfur-35. The total absorption of EPTC-S^{35} by the plant was then evaluated from the total radioactivity of the plant tissue and the activity of a known amount of EPTC-S^{35}, after impregnation into a sample of weighed ground tissue (*2*).

Results and Discussion

Table I presents the per cent accumulation of sulfur-35 in the various plant parts of the kidney bean, and the total absorption of EPTC in bean plants at various stages of growth. The growth of bean plants which had been treated with 1 pound per acre of EPTC-S^{35} appeared to be normal but growth was slightly inhibited in those treated with 4 pounds per acre. Individual plants, which received the 4-pound-per-acre treatment, absorbed from two to four times more EPTC than those treated with 1 pound per acre.

EPTC-S^{35} was readily absorbed from the soil and translocated throughout the entire plant. This is indicated also in Figure 1, *A*, which is the radioautograph of a bean plant harvested 10 days after application. Absorption of EPTC-S^{35} was continuous throughout the 52-day experimental period. The accumulation of sulfur-35 was highest in the roots at any stage of growth.

Five bean plants treated with 1 pound per acre of EPTC-S^{35} were allowed to grow for 66 days, and the pods were harvested. Determination of radioactivity in both shells and seeds indicated the presence of sulfur-35 in a concentration equivalent to 1.1 and 1.0 γ per 100-mg. dry weight of shells and seeds, respectively. However, these samples were submitted to radiochemical determination (*1*) and were shown to contain no EPTC-S^{35} residue.

The total absorption of EPTC-S^{35} by various crops at various stages of growth is presented in Table II as well as the per cent accumulation of sulfur-35 in the roots and tops. EPTC-S^{35} was translocated readily in all plants. In the pea plant, the sulfur-35 concentration was slightly higher in the tops than in the roots at any stage of growth. The early growth of pea plants was definitely inhibited by treatment with this chemical.

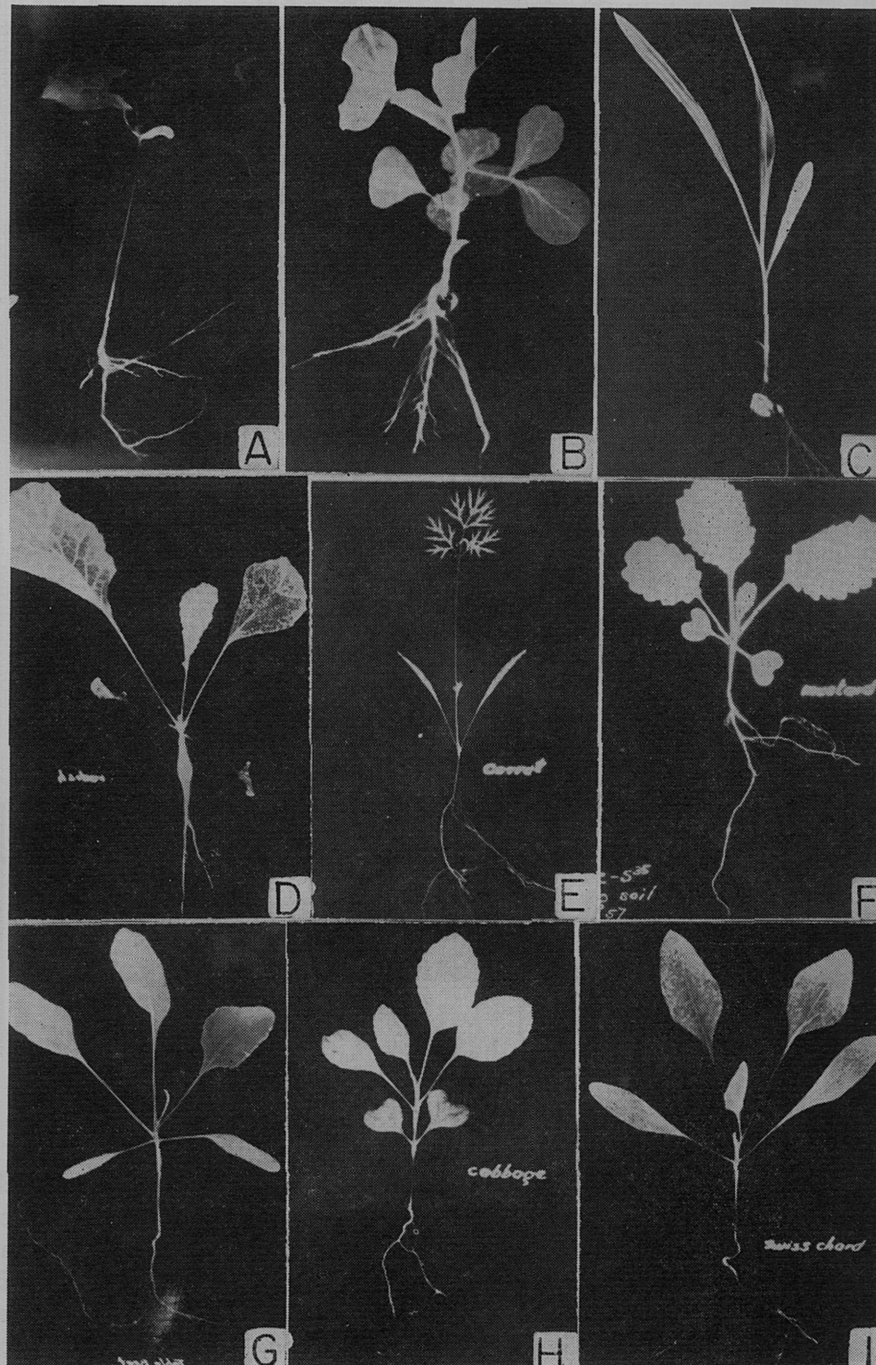

Figure 1. Autoradiograms of plants showing accumulation pattern of sulfur-35 after pre-emergence treatment of EPTC-S^{35} in soil at a rate of 1 pound per acre

A. Kidney bean plant, 10 days old
B. Pea plant, 17 days old
C. Corn plant, 17 days old
D. Radish plant, 24 days old
E. Carrot plant, 24 days old
F. Mustard plant, 24 days old
G. Table beet plant, 38 days old
H. Cabbage plant, 24 days old
I. Swiss chard plant, 24 days old

During the first 24 days, pea plants seemed to absorb EPTC-S^{35} continuously from the soil at either rate of treatment. In the last 14-day period, no significant additional amount was taken up from the soil, although a considerable increase in weight of the tops of pea plants was noted. This phenomenon was very different from that observed in bean plants and may reflect the degree of sensitivity of these two crops to EPTC treatment. The detailed accumulation pattern of sulfur-35 from EPTC-S^{35}–treated pea plants is shown in Figure 1, *B*.

The higher rate of EPTC-S^{35} application (4 pounds per acre) did not cause a decrease in the germination or growth rates of corn plants. On the contrary, the

Table II. Absorption of EPTC-S^{35} from Soil and Translocation of Sulfur-35 by Various Crops

Appl. Rate, Lb./Acre	Interval,[a] Days	No. of Plants	Accumulation of S^{35}, % Roots	Tops	Total EPTC-S^{35} Absorption, γ/Plant
		Pea			
1	10	5	45	55	2.2
	17	5	43	57	4.2
	24	5	46	54	6.5
	38	4	39	61	6.1
4	10	5	37	63	5.4
	17	5	41	59	9.6
	24	5	51	49	15.6
	38	5	27	73	16.1
		Corn			
1	10	5	46	54	1.3
	17	5	45	55	3.3
	24	5	40	60	4.2
	38	4	28	72	11.7
4	10	5	43	57	4.4
	17	5	26	74	5.3
	24	5	37	63	6.8
	38	5	28	72	32.7
		Radish			
1	10	6	8	92	1.3
	17	6	..	..	1.3
	24	6	6	94	3.3
	38	6	21	79	6.7
	52	4	27	73	8.6
4	10	10	8	92	1.2
	17	12	8	92	1.3
	24	10	12	88	1.7
	38	10	8	92	2.5
		Carrot			
1	17	10	..	..	0.1
	24	10	..	..	0.2
	38	10	..	..	0.4
	52	6	11	89	0.9
4	17	24	19	81	0.2
	24	28	11	89	0.3
	38	40	13	87	0.9
	66	20	18	82	2.5
		Cabbage			
1	17	4	..	..	1.5
	24	4	11	89	4.4
	38	4	8	92	6.0
	52	4	12	88	5.9
		Mustard			
	17	4	..	..	0.5
	24	4	..	..	2.4
	38	4	..	..	2.1
	54	6	8	92	4.9
		Swiss Chard			
	38	4	20	80	3.0
	54	4	29	71	1.7
		Table Beets			
	54	6	..	..	1.4
4	38	9	28	72	4.0
		Cucumber			
	10	5	17	83	1.2
	17	5	14	86	2.2
	24	5	12	88	3.3
	38	5	10	90	5.0
		Mung Bean			
	10	10	18	82	5.6
	17	10	20	80	5.1

[a] Interval between treatment and harvest.

growth of plants receiving 4 pounds per acre of EPTC treatment was apparently slightly stimulated. With both rates of treatment, the absorption of EPTC-S^{35} was slow during the first 24-day period but increased immensely during the last two weeks of the experiment. The absorbed EPTC-S^{35} was translocated throughout the entire plants, the tops having a slightly higher percentage of sulfur-35 than the roots. Figure 1, *C*, is the radioautograph of an EPTC-S^{35}–treated corn plant showing the accumulation pattern of sulfur-35.

Two corn plants from the flat which received the 1-pound-per-acre treatment were allowed to grow to maturity. Two corn ears, weighing a total of 69 grams, were harvested after 114 days and tested for radioactivity as well as for EPTC-S^{35} residue. The kernel, the cob, the sheath, and the tassel contained amounts of radioactivity equivalent to 0.45, 0.41, and 0.47 γ of EPTC-S^{35} per 100-mg. dry weight, respectively. This suggested that the sulfur atom from EPTC was evenly distributed throughout the ears. Further determination for EPTC-S^{35} showed the absence of residue.

In radish plants, about 90% of the absorbed EPTC-S^{35} accumulated in the above-ground portion. This distribution differs distinctly from that noted in bean, pea, and corn plants. The absorption of this compound by radish plants which received the 4-pound-per-acre treatment was not greater than the absorption by those receiving a lower rate of treatment. The early growth of radishes in the 4-pound-per-acre flat appeared to be stunted by the EPTC treatment. It is not known at this stage of investigation whether or not the absorption system of radish roots is completely or temporarily impaired by higher concentrations of EPTC in soil. From the increased absorption observed in the 1-pound-per-acre flat, it is possible to assume that at higher concentrations the EPTC-S^{35} would have impaired the absorption system. However, if the plants had been allowed time to recover, further continual absorption might have taken place. Figure 1, *D*, is the radioautograph of a radish plant showing the accumulation pattern of sulfur-35. Two radish plants from the 4-pound-per-acre flat were allowed to grow to maturity. After 55 days, they were harvested and submitted to radiochemical analyses for EPTC residue. The results showed the absence of a detectable amount of EPTC-S^{35} in the roots and the presence of 0.51 γ of EPTC from 21.6 grams of fresh radish leaves.

The accumulation of sulfur-35 in the carrot plant was similar to that in the radish. Eighty to 90% of the absorbed sulfur-35 was found in the foliage rather than in the root system. The data suggest definitely that carrot plants absorb EPTC continuously from the soil, although the amount absorbed by each plant is rather small at the early stage. Figure 1, *E*, is the radioautograph of an EPTC-S^{35}–treated carrot plant, harvested 24 days after treatment, showing the detailed accumulation of radiochemical.

Miscellaneous Crops. Cabbage, mustard, Swiss chard, cucumber, table beet, and Mung bean analyses also indicated that EPTC-S^{35} was taken up readily from soil and translocated throughout the entire plant, with most of the sulfur-35 accumulating in the tops in all plants. The radioautographs of these vegetables are shown in Figure 1, *F* to *I*.

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HERBICIDAL ACTIVITY

Molecular Size *vs.* Herbicidal Activity of Anilides

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The search for better herbicides would be facilitated by some guiding principle. Molecular size was found to be very helpful. A number of the most effective herbicides were shown to have two common dimensions. Anilides were powerful foliage toxicants and the most active anilides possessed the two desired dimensions. Substitution of the phenyl ring also had a very marked effect on phytotoxicity. Maximum toxicity of anilides was associated with 3,4-chlorination of the phenyl ring. A chlorine atom in the 2 position greatly inhibited activity. Thioanilides were as active as anilides.

PREVIOUS INVESTIGATORS have made a number of attempts to correlate molecular size with physiological activity Success has been limited to a few which relate activity to a single dimension. Maximum hormonal activity of diethylstilbestrol and related compounds was associated with a specific long dimension (*7, 10, 16*). On a similar basis it has been postulated (*14*) that the high insecticidal activity of the gamma isomer of hexachlorocyclohexane is due to its being the only isomer small enough to enter an insect cell membrane interspace of 8.5 A.

A number of the most active herbicides known at the present time were found to have two common dimensions. This may be the first time that biological activity has been correlated with two dimensions of a number of molecules.

An excellent tabulation of structure *vs.* herbicidal activity was given by Shaw and Swanson (*17*). We measured the dimensions of Fisher-Hirschfelder-Taylor models of the compounds listed. Two dimensions were necessary for most carbamates to have high herbicidal activity: 13 and 10 A. A third dimension could not be found which could be correlated with herbicidal activity.

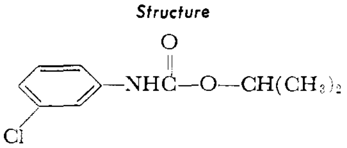
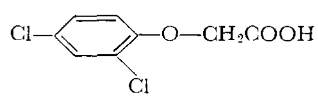
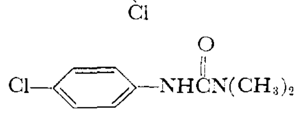
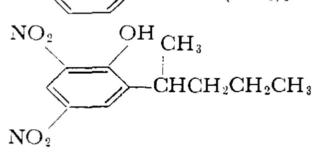
Measurement of models of several of the most active herbicides being marketed showed them to have about the same 13-A. extended dimension as the highly active carbamates. The collapsed dimension was 10 A. for carbamates and phenoxyacetic acids (*19*) and 11 A. for ureas and phenols. Table I records the structures and dimensions of models of these four herbicides. Each represents a different type of molecule, but all contain a phenyl group. It was assumed that esters of 2,4-D hydrolyze to the free acid; thus measurement of models of the various esters was not warranted.

Therefore the desired dimensions are: Extended 13 A. Collapsed 10 or 11 A.

Some active herbicides do not have the dimensions described. Several smaller compounds (about 10-A. maximum length) have high herbicidal activity. These include the α-chloroacetamides (*8*), 3-amino-1,2,4-triazole (*1*), and pentachlorophenol. Possibly different mechanisms of herbicidal action are operative with molecules which do not have the same dimensions.

The desired size concept was of value in the selection of the compounds to be synthesized. A preliminary seed-germination test had shown that most of the compounds with the desired dimensions

Table I. Molecular Dimensions of Active Herbicides

Designation	Structure	Extended A.	Collapsed A.
CIPC		13.2	9.8
2,4-D		12.9	10.2
CMU		13.1	10.8
DNAP		13.5	11.0

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