Effects of Plant Growth Regulators on Levels of Phorate and Aldicarb in Soybeans

A series of plant growth regulators was applied to the foliage of soybeans in combination with a soil drench of the systemic insecticides phorate and aldicarb. No significant differences were found in the uptake or degradative metabolism of either insecticide due to the individual plant growth regulators.

Mixtures of herbicides and plant growth regulators with other pesticides are becoming increasingly important in crop production. Whether the chemicals are applied as physical mixtures or used consecutively, it is reasonable to expect that more than one chemical will exist in the plant simultaneously. Thus, an opportunity exists for interaction among the chemicals applied.

Interactions in terms of plant response have been noted for herbicide–insecticide mixtures (Bowling and Hudgins, 1966; Hacskaylo *et al.*, 1964). A number of *in vitro* studies have indicated that several herbicide–insecticide combinations show metabolic interactions (Chang *et al.*, 1971a,b). Little is known about the influence of plant growth regulators on systemic insecticides when these chemicals are present together in the plant.

This study was initiated to determine the effects of a wide range of plant growth regulators on the uptake and metabolism of phorate and aldicarb in soybeans under greenhouse conditions.

METHODS AND MATERIALS

Soybean plants (*Glycine max* L., var. "Harosoy") were grown in a 1:3 mixture of peat and autoclaved silt loam in a greenhouse. When the plants (2½-cm plastic pot) completed development of the 1st trifoliate leaves and the 2nd trifoliate cluster was just beginning to unfold, the plants were sprayed to runoff with the various plant growth regulators at 10, 100, and 1000 ppm. When severe phytotoxicity occurred, the dosage was decreased by factors of 10 until there was little or no phytotoxicity. Technical and formulated materials were dissolved or suspended in 1 ml of acetone containing 1% Triton X-100 which was diluted to 100 ml with water.

One week after growth regulator treatment, the soil in each pot was drenched with 50 ml of water containing either 9 mg of phorate diluted from a 67.1% EC-Thimet 600 or 3 mg of aldicarb diluted from an 8% acetone solution containing 6% Triton X-100. Three two-plant replicates of each insecticide–plant growth regulator combination and a plant growth regulator free control were harvested 3, 10, and 20 days following phorate treatment and 10 and 20 days following aldicarb treatment. All trifoliate leaves were combined from each treatment and stored at −15° until analyzed. All tests were performed in the greenhouse.

Chemicals. The following plant growth regulators were tested with aldicarb and phorate: (1) *N*-dimethylaminosuccinamic acid (Alar, Naugatuck Chemical Co.); (2) naphthalenacetamide (Amid Thin W, Amchem Products, Inc.); (3) 2-chlorofluorene–carbonic acid-(9)–methyl ester (Bayer 102613, E. Merck); (4) 2-chloroethyltrimethylammonium chloride (Cycocel, Cyanamid); (5) propargyl *n*-octyl sulfide (D 459, Uniroyal Chemical); (6) α-cyclopropyl-α-methoxyphenyl-5-pyrimidenemethanol (EL 531, Eli Lilly & Co.); (7) 2-chloroethylphosphonic acid (Ethrel, Amchem Products, Inc.); (8) pyrrolidinosuccinic acid (F 529, Uniroyal); (9) 2-(*m*-chlorophenoxy)propionamide (Fruitone CPA, Amchem Products, Inc.); (10) ethyl hydrogen 1-propylphosphonate (NIA 10637, FMC Corp.); (11) methyl esters of fatty acids (Off Shoot, Procter & Gamble Co.,); (12) 2,4-dichlorobenzyltributylphosphonium chloride (Phosfon, Mobil Chemical Co.); (13) monodimethylcocoamine succinate (TD 692, Pennwalt Corp.); (14) 3,4-dichloroisothiazole 5-carboxylic acid (TD 1123, Pennwalt Corp.); (15) 2,3,4-triiodobenzoic acid (TIBA, Amchem Products, Inc.); (16) gibberellic acid; (17) kinetin riboside; (18) maleic acid hydrazide; (19) *m*-coumaric acid; (20) 2,6-dimethyl-2,5-heptadiene; (21) 4-hydroxy-5-isopropyl-2-methylphenyltrimethylammonium chloride 1-piperidinecarboxylate; (22) indole-3-acetic acid; and (23) 2,4,5-trichlorophenoxyacetic acid.

The following plant growth regulators were tested with phorate only: (24) 2-chloro-9-hydroxyfluorenecarbonic acid-(9)-*p*-chlorophenoxy ethyl ester (Bayer 102612, E. Merck); (25) 2,7-dichloro-9-hydroxyfluorenecarbonic acid (Bayer 102614, E. Merck); (26) *N,N*-dinitroethylenediamine disodium salt (EDNA, Dow Chemical Co.); (27) diethanolamine salt of 6-hydroxy-3-(2*H*)-pyridazinone (Slo Grow, Uniroyal Chemical); (28) *N*-benzyladenine (SD 4901, Shell Development Co.); (29) 2-cyclohexene-1-penta-2,4-dienoic acid, 1-hydroxy-β,2,6-tetramethyl-4-oxo,*cis*-2,*trans*-4 (abscisic acid, Shell Development Co.); (30) β-naphthoxyacetic acid; (31) β-2-furylacrylic acid; (32) ethyl-3-indole acetate; (33) 3-indolebutyric acid; (34) *o*-coumaric acid; (35) *N*-6-benzyladenine; (36) *N*-nitrosomorpholine; (37) naphthaleneacetic acid; (38) *o*-chlorophenoxyacetic acid; (39) *p*-chlorophenoxyacetic acid; (40) 2,4-dichlorophenoxyacetic acid; (41) 2,4,5-trichlorophenoxyacetic acid; (42) α-*p*-chlorophenoxypropionic acid; (43) 2,4,5-trichlorophenoxypropionic acid; (44) 3-indolepropionic acid; and (45) α-*o*-chlorophenoxypropionic acid.

Compounds 9, 21, and 28 were tested at 1, 10, and 100 ppm. Compound 41 was tested at 0.1, 1, and 10 ppm. Compounds 16 and 39 were tested at 0.01, 0.1, and 1 ppm.

Phorate Extraction and Analysis. Soybean leaf samples were extracted by homogenizing in a Waring blender for 6 min with 100 ml of a 9:1 chloroform–methanol mixture. Extracts were filtered through glass wool into a flask containing 0.3 g of neutral carbon (Fisher Scientific Co.) and 13 g of anhydrous sodium sulfate, and stirred with a magnetic bar for 5 min. Next, the extract was filtered through Whatman no. 40 filter paper and flash evaporated at 40° to 5 ml. Eight λ were used for gas chromatographic analysis.

Samples of phorate, phorate sulfoxide (PSO), phorate sulfone (PSO_2), phorate oxygen analog (POA), phorate oxygen analog sulfoxide (POASO), and phorate oxygen analog sulfone ($POASO_2$) were obtained from American Cyanamid Co., Princeton, N. J.

Quantitative measurements of phorate and each of its five oxidative analogs were obtained with a Packard model 871 gas chromatograph equipped with a flame photometric detector (Tracor, Inc.). The glass chromatographic column (2.2 m × 4.2 mm i.d.) was packed with 10% DC 200 on 60–80 mesh Gas Chrom Q. Operating parameters were: column temperature, 190°; carrier gas N_2, 67 ml/min, O_2, 20 ml/min, air, 80 ml/min, and H_2, 180 ml/min. At an electrometer setting of 16×10^3 we observed a 33, 24, 4.2, and 8.3% scale deflection in 5, 6, 11, and 15 min, respectively, with 0.01 μg of POA, phorate, PSO + PSO_2, and POASO + $POASO_2$.

Aldicarb Extraction and Analysis. Extraction and analysis of aldicarb and its oxidative metabolites were es-

Table I. Typical Residues of Phorate and Aldicarb in Soybean Leaves

Days posttreatment	Aldicarb, ppm	Phorate, ppm
3		24–113
10	50–150	70–257
20	35–143	81–265

sentially the same as described by Lindquist *et al.* (1972). Analytical standards of aldicarb, aldicarb sulfoxide, and aldicarb sulfone were supplied by Union Carbide Corp., South Charleston, W. Va.

RESULTS AND DISCUSSION

Table I shows typical residues of aldicarb and phorate. Aldicarb and its toxic oxidation products are expressed as aldicarb sulfone. The phorate results are represented as the total of phorate and the five oxidation products. A typical breakdown of the phorate data would be as follows: 0.28 ppm of POA, 1.4 ppm of phorate, 92 ppm of PSO + PSO_2, and 14 ppm of POASO + $POASO_2$. None of the plant growth regulators tested changed this metabolic pattern to any great extent. Under the conditions used in this experiment, there were no significant differences in the uptake or degradative metabolism of either phorate or aldicarb when used in combination with plant growth regulators. Inasmuch as the chromatographic procedures used in this study did not separate the aldicarb oxidation products or the several phorate oxidation products, we were not able to determine whether the various plant growth regulators had any effect on that portion of the aldicarb or phorate metabolic pattern.

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Identification of Compounds Responsible for Baked Potato Flavor

The volatile flavor compounds in baked Idaho Russet Burbank potatoes were isolated and separated into acidic, neutral, and basic fractions. The basic and neutral fractions had odors reminiscent of that of baked potato. They were each fractionated by repeated gas chromatography. The odor of each of the gas chromatographic fractions was evaluated by organoleptic means and those fractions with interesting odors were collected and identified by infrared and mass spectrometry. Among the compounds identified, it was believed that a combination of 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine had an odor closer in character to baked potato aroma than did any single compound.

Baked potato flavor has not been extensively studied. Very recently, Buttery *et al.* (1973) reported the identification of 45 compounds, mostly pyrazines and aliphatic aldehydes, as voltatile flavor components of Washington Russet Burbank potatoes. The authors consider the following compounds to be the most important to baked potato aroma: 2-ethyl-3,6-dimethylpyrazine, methional, deca-*trans,trans*-2,4-dienal, and possibly 2-ethyl-3,5-dimethylpyrazine. It is interesting to note that these compounds have been previously identified by Deck *et al.* (1973) as components of potato chip aroma.

We have also studied the flavor of baked potatoes using Idaho Russet Burbank potatoes. The volatile flavor compounds were isolated from a water slurry made from 68 kg of freshly baked potatoes by flash evaporation and vaporization from a continuous thin heated film using the apparatus of Herz and Chang (1966). The isolated volatile flavor compounds did have the characteristic baked potato aroma. They were separated into acidic, neutral, and basic fractions. The neutral fraction was separated into broad fractions by gas chromatography with a Carbowax 20M column. The chromatography was repeated many times and each fraction was cumulatively collected in one trap. The odor of each collected broad fraction was evaluated by an organoleptic evaluation panel.

The broad fractions which had an odor related to the baked potato aroma were further gas chromatographed into subfractions by using a Silicone SE-30 column. The odor of each subfraction was again assessed organoleptically. When necessary, subfractions were gas chromatographed a third time to obtain pure fractions. Finally, the pure gas chromatographic fractions were identified by infrared and mass spectrometry. A similar procedure was used for the basic group except that a Silicone SE-30 column was used first, followed by a Carbowax 20M column. The acidic fraction possessed odors reminiscent of those of lower fatty acids. It was not further studied.

Among the compounds identified are those listed in Table I. Eight other pyrazines were tentatively identified. They were 2-ethyl-3,5,6-trimethylpyrazine, isoamylmethlypyrazine, trimethylisobutylpyrazine, a diethylmethylpyrazine, two alkylpyrazines of mol wt 164, a tetra-substituted alkylpyrazine of mol wt 178, and olefinic pyrazines of mol wt 148 and 178.

Our organoleptic data confirm the assertion of Buttery *et al.* that 2-ethyl-3,6-dimethylpyrazine is one of the most important odorants in baked potato flavor. However, we have found that 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine, taken as a mixture, have an odor closer in character to