mixing required to obtain a representative portion from a small sample.

Acetone and chloroform were effective extracting solvents for trifluralin and diphenamid in soils and sediments. However, the high boiling points of these solvents (56.6° and 61°) caused trifluralin losses as great as 70% during evaporation. Methylene chloride with a boiling point of 40° effectively extracted trifluralin and diphenamid but not paraquat from the soil. Sample concentration and final solvent evaporation procedures did not result in trifluralin loss.

These data were determined using Cecil soil and sediment samples. Extraction efficiencies can vary for other soil types, particularly those of high organic content, and longer extraction periods may be required for efficient pesticide recovery.

The use of the Coulson detector in the nitrogen mode, while not as responsive to trifluralin as the electron capture detector, permitted simultaneous detection of both trifluralin and diphenamid. Time-consuming cleanup procedures were eliminated because the Coulson detector was not as responsive to extraneous extracted material as were the electron capture and flame ionization detectors.

Although two separate instruments are used for the final determinations, the method integrates separation and extraction techniques so that all three herbicides may be measured in the same sediment or soil sample. This is especially important for runoff samples from cropped areas, since sediment load usually decreases as the crop canopy increases.

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Received for review May 21, 1973. Accepted October 9, 1973. Use of trade names does not imply endorsement by the Environmental Protection Agency or by the Southeast Environmental Research Laboratory.

Herbicide Residues in Air-Cured Burley Tobacco

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Mature cured leaves from three stalk positions of tobacco (*Nicotiana tabacum*, cv. Ky 14) treated in the field with *N*-butyl-*N*-ethyl-α,α,α-trifluoro-2,6-dinitro-*p*-toluidine (benefin), *N,N*-dimethyl-2,2-diphenylacetamide (diphenamid), or *S*-propylbutylethylthiocarbamate (pebulate) were analyzed for herbicide residues using glc. Benefin was detected in trace amounts (2 to 4 ng/g of dry wt) in the upper leaves from treated plants. Slightly higher amounts occurred in leaves from the bottom of the plant. Diphenamid was detected in amounts as high as 0.16 μg/g of dry wt. The highest levels were from leaves taken from the middle portion of treated plants. Two peaks consistently appeared in chromatographs from treated plants that were not present in the chromatographic record of untreated (control) plants. One of the peaks was tentatively identified as *N*-methyl-2,2-diphenylacetamide. Pebulate was not present in the leaves from treated plants at the lower limit of detection (0.02 μg/g of dry wt).

N-Butyl-*N*-ethyl-α,α,α-trifluoro-2,6-dinitro-*p*-toluidine (benefin), *N,N*-dimethyl-2,2-diphenylacetamide (diphenamid), and *S*-propylbutylethylthiocarbamate (pebulate) are three herbicides registered for use on burley (*Nicotiana tabacum* L.) tobacco. They are applied at planting and are persistent in the soil throughout the growing season, probably remaining available for continued uptake by the tobacco plant. Both diphenamid and pebulate are readily absorbed by many of the crops in which they are used (Bingham and Shaver, 1971; Fang and Fallin, 1965). While residues of these herbicides are not found in significant amounts in the fruits or edible portions of most crops (Fang and Fallin, 1965; Golab *et al.*, 1970; Lemin, 1966), they may be retained in some nonedible portions (*e.g.*, leaves, roots). The present study was initiated to determine if residues were present in mature, air-cured leaves of tobacco plants grown in soils treated with the above-mentioned herbicides.

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MATERIALS AND METHODS

Plant Material and Treatment. Burley tobacco (*Nicotiana tabacum* L. cv. Ky 14) was planted June 7, 1971, in rows 96.5 cm apart in soil fertilized with 165 kg/ha of N. Herbicide treatments were 1.65 and 3.3 kg/ha of benefin and 4.4 and 8.8 kg/ha of pebulate applied preplant and incorporated into the soil approximately 5 cm deep. Diphenamid at 6.6 and 13.2 kg/ha was applied immediately after transplanting tobacco seedlings to the field. The lower rate is the recommended rate of application for each of the three herbicides. Tobacco was also transplanted into untreated soil. Experimental design was randomized complete block with four replications.

When the plants reached maturity they were harvested, cured, stripped, and graded. Leaf samples were collected from the top, middle, and bottom stalk position on the plant. The leaf samples were dried at 43° for 96 hr and

ground in a Wiley mill to pass a 40-mesh screen. Portions of the powdered samples were used for gas chromatographic determination of herbicide residues.

Benefin Extraction. The extraction procedure for benefin as supplied by Eli Lilly and Co. (General Procedure 5801230) was modified only as necessary to accommodate the dried leaf material. A 25-g sample of tissue was homogenized in 200 ml of 90% methanol for 5 min at high speed in a Sorvall omnimixer. The homogenate was filtered through Whatman No. 1 filter paper and the residue was washed twice with 25-ml portions of 90% methanol. The extract was transferred to a 1-l. separatory funnel and 500 ml of 5% NaCl was added to it. This solution was extracted three times with 50-ml portions of methylene chloride. The combined methylene chloride phases were drained through anhydrous Na_2SO_4 into a 300-ml round-bottomed flask and evaporated just to dryness on a rotary evaporator at 50°.

The contents of the flask were dissolved in 20 ml of *n*-hexane and layered on a Florisil column. The clean-up column was prepared by placing 20 g of partially deactivated (6% H_2O, w/w) 60–200 mesh Florisil in a 25 × 400 mm column and topping it with 15 g of anhydrous Na_2SO_4. The column was eluted with 350 ml of *n*-hexane, the first 100 ml of which was discarded. The following 250 ml was collected (predetermined to be the benefin-containing fraction) and evaporated as before with a rotary evaporator.

The residue from the Florisil column cleanup was dissolved in 2.0 ml of benzene and transferred to a small vial. Two microliters of this solution was injected into the glc for analysis. Recovery of benefin with this procedure was in the range of 96 to 104% as determined by quantitation of gas chromatographic output and by liquid scintillation detection of benefin-^{14}C recovered from spiked control samples.

Diphenamid Extraction. The extraction of diphenamid from cured tobacco leaf was a modification of the procedure of Boyack *et al.* (1966) and Tepe *et al.* (1967). A 25-g portion of ground leaf material was extracted on a wrist-action shaker with 400 ml of benzene for 30 min. The extract was filtered through Whatman No. 1 filter paper and the filtrate was evaporated with a rotary evaporator at 50°.

The residue was dissolved in 100 ml of acetonitrile and extracted with four 100-ml portions of *n*-hexane in a 500-ml separatory funnel. The *n*-hexane extracts were discarded and the acetonitrile fraction was evaporated just to dryness on a rotary evaporator as before. The residue was dissolved in 10 ml of methylene chloride.

The column chromatography cleanup was accomplished by passage of the sample through a Florisil column, followed by a column of partially activated alumina. The sample was eluted from the Florisil column with 400 ml of 1% methanol in methylene chloride, the first 200 ml of which was discarded. The remaining 200 ml was collected in a 300-ml round-bottomed flask, concentrated by rotary evaporation, and layered onto the alumina column. The sample was eluted from the alumina column with 0.5% methanol in methylene chloride. The first 75 ml eluted from the column was discarded and then 150 ml of eluate was collected and evaporated just to dryness with a rotary evaporator. The residue was taken up in 10 ml of *n*-hexane, transferred to a 1-l. separatory funnel, and extracted twice with 400 ml of water. The combined aqueous phases were subsequently extracted with three 50-ml portions of methylene chloride. The methylene chloride extracts were filtered through anhydrous Na_2SO_4 and combined in a 300-ml round-bottomed flask and evaporated just to dryness. The residues were quantitatively transferred to a small vial with two 3-ml rinses of methylene chloride. The methylene chloride was then evaporated with a stream of dry air and the residue was dissolved in 0.2 ml of chloroform. One microliter of this solution was analyzed by glc. This procedure rendered the sample sufficiently free of contaminants to detect and quantitate as little as 0.02 μg/g of dry wt of diphenamid.

The Florisil clean-up column was prepared by placing 10 g of anhydrous Na_2SO_4 at the bottom of a 25 × 400 mm glass column equipped with a stopcock. Fifty grams of a mixture of three parts 60–100 mesh:two parts 100–200 mesh (w/w) Florisil was placed in the column in methylene chloride with constant vibration being applied to the column, followed by another 10 g of anhydrous Na_2SO_4. The alumina column was made up of a 10-g layer of anhydrous Na_2SO_4, a 30-g layer of alumina (80–200 mesh, Alcoa F-20), and another 10-g layer of anhydrous Na_2SO_4.

Pebulate Extraction. The following procedure is primarily that of Barney and Schwab (1970) with some modification to permit the extraction of cured leaf tissue. A 25-g sample of leaf tissue was homogenized in 1.5 l. of distilled water in a Waring blender. The macerate was transferred to a 4-l. Erlenmeyer flask. The total volume was made up to 3 l. with water and the pH was adjusted to 4.5 with concentrated HCl. The solution was then steam distilled in a modified Friedrichs apparatus until 400 ml of distillate had accumulated in a 500-ml separatory funnel.

The distillate was acidified with 5 drops of concentrated HCl and extracted once with 8 ml of isooctane. The isooctane extract was evaporated just to dryness on a rotary evaporator at 35°. This residue was dissolved in 5 ml of 10% diethyl ether in *n*-hexane for cleanup on an alumina column. After the sample and three 5-ml rinses were layered on the column, the column was eluted with 250 ml of 10% diethyl ether in *n*-hexane (the first 100 ml was discarded, the following 150 ml was collected in a 300-ml round-bottomed flask).

The eluate was evaporated just to dryness on a rotary evaporator as before and the residue was dissolved in 5 ml of 5% diethyl ether in *n*-hexane for chromatography on a silica gel column.

The sample and two 5-ml rinses were pipetted onto the column and the column was eluted with 70 ml of 5% diethyl ether in *n*-hexane, the first 20 ml of which was discarded and the following 50 ml retained. A positive air pressure was required to expel the eluent.

This fraction, predetermined to contain pebulate, was evaporated just to dryness on a rotary evaporator (35°) and the residue was dissolved in 0.5 ml of isooctane. A 2-μl portion of this was injected into the gas chromatograph for analysis.

The alumina clean-up column was prepared by placing 10 g of anhydrous Na_2SO_4 in the bottom of a 25 × 400 ml glass column fitted with stopcock. A slurry containing 25 g of alumina (80–200 mesh, Alcoa F-20) in *n*-hexane was poured on the column, followed by another 10 g of Na_2SO_4. A silica gel clean-up column was prepared by pouring a slurry containing 5 g of silica gel H (tlc grade) in 40 ml of *n*-hexane into a 11 × 450 mm chromatography tube. A 1-cm cap of anhydrous Na_2SO_4 was placed on the column after the silica gel settled.

Gas–Liquid Chromatography. The instrument employed was a Varian-Aerograph Model 2740 equipped with flame ionization (FID) and ^{63}Ni electron capture (ec) detectors. Quantitation of the peaks was achieved with a Varian-Aerograph Model 480 electronic digital integrator.

The analysis of benefin residues was achieved, using the ec detector coupled to a 6 ft × ¼ in. glass column packed with 3% XE-60 (w/w) on 60–80 mesh Chromosorb W; electrometer, 10^{-9} mV/A; injector temperature, 232°; column temperature, 170°; detector temperature, 234°; N_2 carrier gas flow, 39 ml/min at 21 psi.

The diphenamid residue analysis was carried out using FID with a 6 ft × ¼ in. borosilicate glass column containing 5% XE-60 (w/w) on 80–100 mesh Gas Chrom Q; electrometer, 10^{-11} mV/A; injector temperature, 235°; col-

Table I. Benefin Recovery from Cured Mature Burley Tobacco Foliage, ng/g of Dry Wt

Stalk position	1.65 kg/ha	3.3 kg/ha
Top	2.51[a] ± 0.84	2.22 ± 1.22
Middle	1.59 ± 0.36	2.34 ± 2.12
Bottom	7.64 ± 3.23	4.36 ± 2.57

[a] Mean of four reps with standard deviation.

Table II. Recovery of Diphenamid and Metabolites from Mature Cured Tobacco Foliage

Application, kg/ha	Position	Diphenamid	Unknown[a] no. 1	Unknown[a] no. 2
6.6	Top	[b]	0.19 ± 0.14	0.06 ± 0.06
	Middle	[b]	0.37 ± 0.26	0.44 ± 0.46
	Bottom	0.03 ± 0.01[c]	0.22 ± 0.16	0.42 ± 0.41
13.2	Top	0.03 ± 0.01	0.32 ± 0.10	[b]
	Middle	0.16 ± 0.09	0.94 ± 0.81	1.63 ± 0.63
	Bottom	0.04 ± 0.02	0.56 ± 0.29	0.54 ± 0.30

[a] Values for unknowns no. 1 and no. 2 are based on MDA and DA, respectively. [b] Only trace amounts detected. [c] Mean of four reps with standard deviation values of μg/g of wt.

umn temperature, 214°; detector temperature, 262°; air, 340 ml/min; H_2, 34 ml/min; N_2, 30 ml/min at 27 psi.

FID detector was also utilized in the analysis of pebulate residues. The column was 6 ft × ¼ in. borosilicate glass packed with 10% OV-17 (w/w) on 80–100 mesh Gas Chrom Q; electrometer, 10^{-11} mV/A; injector temperature, 228°; column temperature, 149°; detector temperature, 270°; air, 380 ml/min; H_2, 37 ml/min; N_2, 38 ml/min at 24 psi.

RESULTS AND DISCUSSION

Benefin Residues. Benefin was recovered from mature, air-cured tobacco leaves and detected in trace amounts (Table I). The levels of benefin recovered from the top and middle stalk position are essentially the same at both the recommended rates and at twice the recommended rates of herbicide application. The levels found in the leaves from the bottom stalk position, however, were significantly higher than those from leaves at the other two positions. This might be due to translocation of benefin which was limited primarily to the lower portion of the shoot or, more plausibly, the higher levels of benefin in the lower leaves were the result of contact between the soil (probably rain-splashed soil) and the lower leaves.

These data are consistent with the information on accumulation of the dinitroaniline herbicides in seedlings and fresh green plants. Golab *et al.* (1970) recovered only trace amounts of benefin in the foliage of peanuts and alfalfa grown in benefin-treated soil. They also reported the presence of trace amounts of derivatives of benefin in the foliage of peanuts and alfalfa.

The chromatograms did not provide any indications of derivatives or metabolites of benefin in cured tobacco leaves (Figure 1). However, the use of a relatively nonpolar elution solvent (hexane) during the Florisil cleanup may have precluded the appearance of any polar derivatives of benefin.

Diphenamid Residues. It is evident from Table II that only very small amounts of diphenamid remain in air-cured tobacco leaves. The lowest levels of diphenamid occurred in leaves from plants grown in soil treated at the recommended rate and slightly greater amounts were recovered from plants treated with twice the recommended rate of diphenamid, particularly in the lower leaves. Two peaks consistently occurred in the glc chromatography of extracts from leaves of treated plants that did not appear in the glc chromatography of untreated (control) plants.

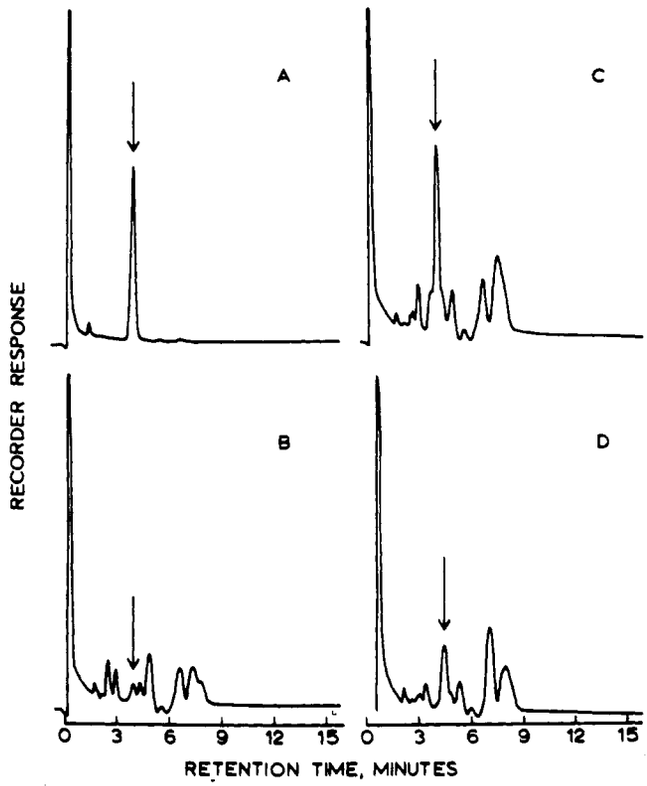

Figure 1. Typical chromatograms from analysis of benefin residues. A. Benefin, 1.0 ng injected. B. Untreated control plant. C. Control plant fortified with 20 ng/g of dry wt of benefin. D. Field-treated plant, 3.3 kg/ha of benefin.

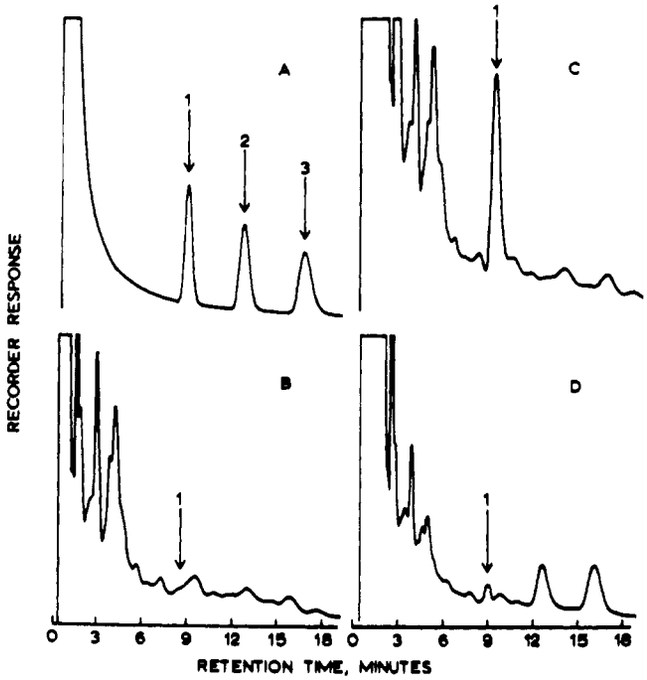

Figure 2. Typical chromatograms from analysis of diphenamid residues. A. (1) *N,N*-dimethyl-2,2-diphenylacetamide (diphenamid), 25.0 ng. (2) *N*-methyl-2,2-diphenylacetamide, 25.0 ng. (3) 2,2-diphenylacetamide, 25.0 ng. B. Untreated control plant. C. Control plant fortified with 0.1 μg/g of dry wt of diphenamid. D. Field-treated plant, 13.2 kg/ha of diphenamid.

The retention times of unknown no. 1 (Figure 2) coincided with the retention time (R_t) of commercially supplied *N*-methyl-2,2-diphenylacetamide (MDA) and the R_t of unknown no. 2 was the same as that of 2,2-diphenylacetamide (DA). Cochromatography of samples enriched with

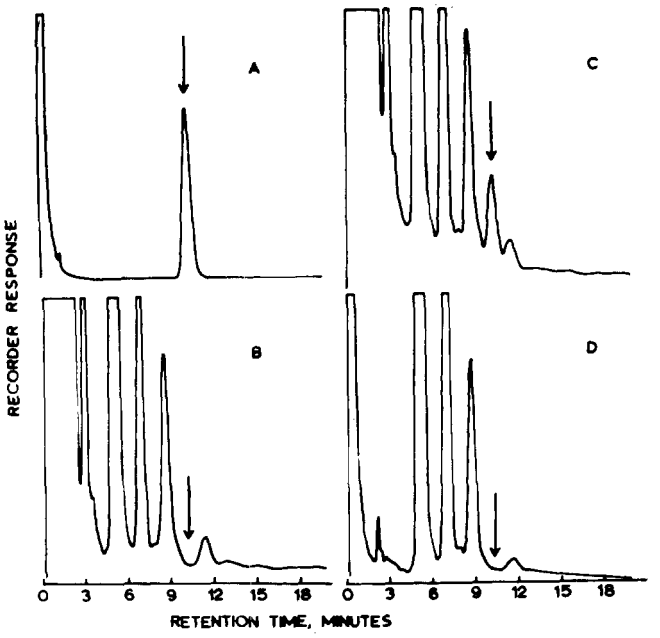

Figure 3. Typical chromatograms from analysis of pebulate residues. A. Pebulate, 0.2 μg. B. Untreated control plant. C. Control plant fortified with 0.1 μg/g of dry wt of pebulate. D. Field-treated plant, 8.8 kg/ha of pebulate.

standards of the two derivatives did not alter the R_t of unknown no. 1 but a shoulder appeared in the second peak, suggesting that unknown no. 2 was not authentic DA. Both compounds occurred at low levels in the leaves from the top of plants treated with recommended rates of diphenamid and at significantly higher levels in the leaves from the middle and lower stalk positions. The trend was for the highest accumulations of the two compounds to occur in leaves of the middle stalk position and at twice the recommended treatment rate. Diphenamid, also, was recovered in slightly greater quantities from leaves of the middle stalk position at the higher treatment rate.

The relatively high variability expressed in Table II seemed to accompany the multistep procedure employed for the extraction of diphenamid. Although the variability between samples was somewhat high, the efficiency of the extraction procedure was good (Table III).

It is not surprising that diphenamid and one of its metabolites were recovered from tobacco leaf tissue since the accumulation of diphenamid has been demonstrated in leaves of other crop plants. Lemin (1966) reported that when tomato seedlings were incubated in nutrient or soil containing diphenamid-^{14}C, the radioactivity was associated primarily with the monomethyl derivative and lesser amounts in the desmethyl derivative of diphenamid. Bingham and Shaver (1971) also reported that *N*-methyl-2,2-diphenylacetamide was the most persistent metabolite of diphenamid in tomato. Strawberries tended to accumulate unaltered diphenamid in leaves and fruits from treated soil (Golab *et al.*, 1966). The *N*-methyl-2,2-diphenylacetamide derivative accumulated in the strawberry plants to a lesser extent.

It appears that the monomethyl and another unidentified metabolite of diphenamid (unknown no. 2) were persistent in tobacco throughout the growing season and the curing process.

Pebulate Residues. Pebulate was not present in air-cured leaves of tobacco plants at levels that could be detected under the extraction and detection techniques employed in this study. (The limit of detection of pebulate under the extraction and detection techniques employed in this study was 0.02 μg/g of dry wt, including a 60% recovery value [Table IV].) No additional peaks suggestive of a derivative of pebulate were detected in the glc chromatographs of extracts from treated plants (Figure 3).

Table III. Recovery of Radioactivity from a Leaf Sample Fortified with Diphenamid-^{14}C

Step	% recovery[a]
Acetonitrile–hexane partition	93.7
Florisil cleanup	89.6
Alumina cleanup	90.4
Hexane–water partition	84.6
Final sample	78.4

[a] Percent of total radioactivity applied that was recovered after each step in the clean-up procedure.

Table IV. Recovery of Radioactivity from a Leaf Sample Fortified with Pebulate-^{14}C

Step	% recovery[a]
Steam distillation	72
Alumina cleanup	68
Silica gel cleanup	63
Final sample	60

[a] Percent of total radioactivity applied that was recovered after each step in the clean-up procedure.

The complete metabolism of thiocarbamate herbicides by resistant crop plants has been reported in several studies (Bourke and Fang, 1968; Fang and Fallin, 1965; Nalewaja *et al.*, 1964). When ^{14}C-labeled EPTC (*S*-ethyldipropylthiocarbamate) is supplied in the nutrient solution to alfalfa seedlings grown hydroponically, the label that was recovered from the plants after 2 or 5 days of treatment was associated primarily with several amino acids and sugars (Nalewaja *et al.*, 1964). They were unable to detect any ^{14}C-EPTC in the extracts from the alfalfa tissue. Pebulate was taken up in limited amounts from treated soil and was degraded within a relatively long period in foliage and fruits of tomato (Fang and Fallin, 1965). Pebulate was metabolized very rapidly after absorption from nutrient solution into tobacco seedlings (Long and Thompson, 1973). At 24 hr after treatment, only 5% of the extracted radioactivity was identified as pebulate. Bourke and Fang (1968) have also reported very rapid metabolism of vernolate-^{14}C applied to germinating soybean seeds. Although the rate of metabolism varies among species and herbicides, rates are usually rapid enough to metabolize all the herbicide by the time the plants mature. This seems to be the case in tobacco as well, since no pebulate was recovered from the mature, cured leaves.

Thus, of the three herbicides presently used in tobacco, only diphenamid, its monomethyl derivative, and a second unknown compound were recovered from the cured leaves in significant amounts. Pebulate was not present, and the presence of benefin was detected only because of the extreme sensitivity of the electron capture technique.

ACKNOWLEDGMENT

The authors are grateful for the able technical assistance provided by Jerry Ingram. We are indebted to Eli Lilly and Co., Indianapolis, Ind., for gifts of benefin, diphenamid, *N*-methyl 2,2-diphenylacetamide, and 2,2-diphenylacetamide and to Stauffer Chemical Co., Mountain View, Calif., for gifts of pebulate.

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Received for review March 21, 1973. Accepted August 22, 1973. The investigation reported in this paper (no. 73-3-11) is in connection with a project of the Kentucky Agricultural Experiment Station and is published with approval of the Director and this study was supported in part by KTRB Project Ky 024.

The Pyrolysis of Some Amine Salts of 2,4-Dichlorophenoxyacetic Acid

Shane S. Que Hee and Ronald G. Sutherland*

Amine salts of 2,4-dichlorophenoxyacetic acid (2,4-D) were pyrolyzed at various temperatures. Amide production was first observed at 80° by mass spectroscopy. The fastest rate of formation of the corresponding amide was between 140–150° for the methyl and *n*-butylamine salts, between 150–170° for the *n*-dodecyl and *n*-tetradecylamine salts, and above 160° for the dimethylamine salt. Beyond 160°, 2,4-dichlorophenol, imines, lactones, and other compounds were also formed. The amides appeared to decompose completely above 200°. The activation energy for amide formation was calculated by differential scanning calorimetry (DSC), utilizing a new manipulative technique involving the Boltzmann distribution. The activation energies were found to be (44 ± 1) and (38 ± 3) kcal mol^{-1} for the *n*-butyl and *n*-tetradecyl salts, respectively. The heats of fusion and stoichiometry of the salts were also determined.

Amine salts of 2,4-dichlorophenoxyacetic acid (2,4-D) are used widely for herbicidal applications. There is an extensive patent literature dealing with their synthesis (Dickson, 1952; Fischer, 1958; Harwood *et al.*, 1956). However, most of these patents often do not specify at what temperature the salt should be prepared or at what temperature amide production begins. In view of possible differences in biological effect between the salt and the corresponding amide, a detailed investigation of the rate of dehydration of the salts with respect to temperature was undertaken.

Reagents. Commercial solid *n*-tetradecyl- and *n*-dodecylamines (Aldrich) and liquid *n*-butylamine were purified by vacuum distillation. Reagent grade dimethylamine (Eastman) was used without further purification. A 20% aqueous solution of methylamine was used for the preparation of the methylamine salt. Commercial 2,4-D (Aldrich) was recrystallized from benzene until a constant melting point of 140.3 ± 0.5° was attained.

1:1 salts of 2,4-D were made by adding stoichiometric amounts of the amines dissolved in benzene–acetone solutions to solid 2,4-D at 10°. The solutions were shaken until all the 2,4-D had disappeared. The solvent was removed under vacuum at room temperature. The resultant salts were recrystallized from 1:1:1 ether–acetone–hexane until the melting points were constant.

EXPERIMENTAL SECTION

Pyrolysis Experiments. The solid salts were pyrolyzed in sealed Pyrex tubes covered with aluminum foil. Separate samples were pyrolyzed for 1 hr at temperatures from 30 to 200°. The tubes were then cooled before recording mass, infrared, and nuclear magnetic spin resonance spectra of the products.

Differential Scanning Calorimetry. Known amounts of salts were pyrolyzed in aluminum planchettes within the heating chamber of a Perkin-Elmer differential scanning calorimeter DSC-1B. The pyrolysis was carried out at a constant heating rate of 10°/min using range, slope, average, and differential settings of 16, 210, 405, and 470. The heating chamber was purged by a slow flow of nitrogen. Pure benzoic acid was used as a standard to compute the heats of fusion of the salts.

To obtain the activation energy for salt decomposition, weighed samples of the butyl- and tetradecylamine salts in the planchettes were pyrolyzed past the melting point to a temperature, the "prepyrolysis temperature," where the baseline became stable again. The planchettes were cooled immediately to ambient temperature and then repyrolyzed at the same heating rate to a higher temperature, approximately 10° above the initial prepyrolysis temperature. This higher temperature became the new "prepyrolysis temperature." This cooling and heating procedure was repeated until the heat of fusion peak at the melting point became negligible. As the heat of fusion is an extensive property, the area under the curve representing the heat of fusion is proportional to the mass of salt melted, providing eutectic or solid solution does not occur. Thus, the mass of salt which has not decomposed up to the preceding "prepyrolysis temperature" can be found, as long as negligible decomposition occurs at the melting point.

The mass of salt decomposed up to the "prepyrolysis temperature" can thus be found by subtraction from the known initial amount. During the pyrolyses, no solid solution formation occurred as the melting point of each salt remained constant until amide formation was complete. As the heat of fusion decreased smoothly as pyrolysis proceeded, the likelihood of pyrolysis products having the same melting point as the salt was assumed to be negligible. Mass spectral examination also verified that very little salt was present when the peak at the melting point disappeared.

The above approach was modified so that the Boltzmann distribution could be used.

$$N_i = N_o e^{-\epsilon_i/RT} \quad (1)$$

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