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Degradation and Residues of Dimefuron in Pineapple

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ABSTRACT

Dimefuron-^{14}C (1,1-dimethyl-3-(3-chloro-4-(2-*t*-butyl-5-oxo-1,3,4-oxadiazolin-4-yl) phenylurea) was applied to Smooth Cayenne pineapple plants (grown from tillers and crowns), at the rate of approximately 2.5 kg ai/ha, at 3 days, 4 and 9 months after planting. Plants were harvested after 16 months and the ^{14}C-residues were analysed by extraction with acetone, methanol and 0.1 N. HCl/90% methanol respectively. The extracts and bound residues were assayed by liquid scintillation counting and a combustion technique respectively. The results showed that dimefuron and/or its metabolites were absorbed via the roots and/or shoots and transported to the fruits, which developed after application. At harvest the radioisotope was found in all parts of the treated plants. The ^{14}C-residues expressed as dimefuron equivalents in flesh, peel, crown, stem and leaves were 0.045, 0.049, 0.087, 0.288 and 0.822 μ g/g (fresh weight) for the pineapples grown from crowns and 0.064, 0.058, 0.0128, 0.405 and 1.235 μ g/g (fresh weight) for the pineapples grown from tillers respectively. In the pineapple flesh 81.3 to 97.8% of the residue was found in acetone and methanol, 0.0 to 12.5% in 0.1 N. HCl/90% methanol and 2.2 to 6.3% as a bound residue.

INTRODUCTION

Pineapple crops are sensitive to weed competition. Hand weeding would have to be done many times during the growing season, which is not practical due to the spiny leaves, furthermore it would certainly damage the plants which are grown at high density. Various selective and high efficacy herbicides such as ametryn, atrazine, bromacil, diuron and simazine have been accepted for use in pineapple crops for many years. Recently dimefuron, a selective herbicide, has been used. However, the metabolism and residues of dimefuron in pineapple had not been determined. This study was designed to provide this information.

Dimefuron is from the phenylurea family of herbicides and it can be applied either pre or post-emergence. It is selective for the control of many grasses and broadleaf weeds in cotton, sunflowers, beans, peas, oil palm and peanuts and is used commercially in oil seed rape and pea (Hisada and Imanura, 1986).

Other workers have shown that when dimefuron was applied at a low rate (0.33 kg/ha) it was detectable in soil for up to 7 weeks, but at a higher rate it was still detectable in soil after 38 weeks (Richardson and Parker, 1977). Under tropical and high light intensity conditions the phytotoxicity of other urea herbicides such as diuron, monuron and fenuron is reduced by sunlight particularly ultra-violet radiation (Comes and Timmons, 1965). In addition, the degradation rate of diuron in soil under waterlogged condition was slower than under field capacity condition (Wang *et al.*, 1978). Dimefuron can therefore be viewed as a compound of moderate persistence.

Selectivity of urea herbicides is based on retention, translocation and metabolism. The chloroplasts of pea are more sensitive to dimefuron than chloroplasts from field bean. However field bean plants are more sensitive to dimefuron than pea plants when dimefuron is applied as a planting solution. Autoradiography has indicated that dimefuron translocates to leaves and stems in

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field bean at a higher rate than in pea. The tolerance of pea to dimefuron occurred because the compound accumulated in the root. However the tolerance in field bean to dimefuron when applied at pre-emergence was attributed to the depth of the root (Glasgow and Dick, 1980). In cotton, accumulation of fluometuron in root (lysigenous glands) and the high degradation rate reduced the phytotoxicity of the herbicide (Rogers and Funderburk, 1968). The distribution of diuron-^{14}C in soybean and cotton plants were similar but the rate of degradation in cotton was higher (Smith and Sheets, 1967). Under field condition the translocation and metabolism of urea herbicides depend on the plant species. The metabolism of fast translocated ureas such as monuron and monolinuron occurred in leaves but the metabolism of slow translocated ureas such as chloroxuron occurred in the roots (Geissbuhler, 1968). All plant parts, leaves, root, hypocotyl and stem can metabolise the urea herbicides, they do not have to be located in photosynthetic tissue (Geissbuhler *et al.*, 1975).

The herbicide residues in plants are found in 3 forms, firstly the free residues which are easily extracted, secondly the conjugated residues which and be extracted and thirdly the residues which can not be extracted (Khan, 1982). The amount of bound residues was governed by plant species and the time after herbicide application (Geissbuhler *et al.*, 1975). The residues of monolinuron in redroot pigweed were hydroxymonolinuron, *N*-(4-chlorophenyl)-*N*-methoxyurea, 4-chlorophenylurea and two glucoside derivatives (Schuphan and Ebing, 1978). Chlortoluron degradation in wheat and barley occurred by *N*-demethylation and ring-methyl oxidation (Ryan *et al.*, 1981). The residues of diuron in corn were 3,4-dichloronitrobenzene, 3-(3,4-dichlorophenyl)-1-methylurea, 3-(3,4-dichlorophenyl) urea and 3,4-dichloroaniline (Onley *et al.*, 1968) Sixty days after linuron application at 1.1 or 1.7 kg/ha to cotton and cereal, less than 0.55 ppm linuron and 0.03 ppm of 3,4-dichloroaniline were found in cotton seeds. Futhermore <0.20 ppm of linuron, <0.1 ppm of 3,4-dichloroaniline and <0.13 ppm of 4-chloroaniline were found in grain, however 3 times more residue was found in straw. Moreover, approximately 15 to 25 percent of the absorbed herbicide was found as bound residue (Maier-Bode and Hartel, 1981).

The objective of this study was to determine the quantity and nature of radiolabelled residues of dimefuron in a pineapple crop.

MATERIALS AND METHODS

Smooth Cayenne pineapple both tillers and crowns were planted in cement pots. The pot size was $0.65\times0.75\times0.75$ m. with a drainage hole at the bottom. Sandyloam soil was sieved into the pot to a volume of $0.65\times0.75\times0.5$ m. and 2 plants were placed in each pot. All pots were forced to flowering 11 months after planting using ethephon in combination with urea.

Dimefuron (a commercial product), molecular weight of 338.5 was mixed with dimefuron -^{14}C to make a specific activity of 0.16 mCi/m mole. Dimefuron-^{14}C was applied at 3 days, 4 and 9 months after planting. The soil moistures were 13.5%, 12.4% and 15.2% at each application respectively.

The concentration of dimefuron in the spray solution was determined by HPLC from which the application rate was calculated. The HPLC was Hewlett - Packard 3392A with LDC spectromonitor III detector and spherisorb 5 ODS-16 column. The amount of radioisotope in the spray solution was determined by radioassay of samples taken prior to application in each pot. Immediately after application, extra plants both tiller and crown were harvested. The plants were washed with acetone and the solution was assayed for radioactivity. The plants were homogenised with acetone followed by 0.1 N. HCl/90% methanol. The solution were concentrated and then assayed for radioactivity. After extraction, the remaining plant tissues were combusted and assayed for radioactivity.

At harvesting, each plant was separated into leaves, stump and fruit (the fruit was separated into crown, peel and flesh). Fruit,

leaves and stump were washed with acetone, followed by methanol and the washing solutions were assayed for radioactivity. For each plant part, 30 g fresh weight was randomly taken in triplicate and homogenised in acetone (150 ml), methanol (150 ml) and 0.1 N HCl/90% methanol (150 ml) and aliquots assayed for radioactivity. The solid residue was then assayed by combustion followed by liquid scintillation counting. Attempts were made to identify dimefuron and its metabolites by autoradiography of TLC plates. The TLC plate was developed using ethyl acetate/ dichloromethane (1:1 by volume). The quantity of dimefuron-^{14}C and its metabolites were measured by combustion of the scraped absorbant. Unfortunately, the radiolabelled residue was at a very low level so that it was not possible to identify the metabolites.

The experiment was designed as a randomized complete block with 3 replications.

RESULTS AND DISCUSSION

Dimefuron-^{14}C at the rate of 2.8, 2.2 and 2.2 kg ai/ha was applied to pineapple plants at 3 days, 4 and 9 months after planting respectively (Table 1). The average amounts of radioisotope inside and outside the plants are tabulated in Table 2. Plants grown from tillers retained a greater amount of radioisotope than those grown from crowns (Table 2) probably because the plants were larger at treatment. The amount of radioisotope was highest in plants harvested after the third application which was derived from all applications.

Off the spray applied a significant proportion would inevitably reach the soil, during the original spraying or by rain wash off. It has been reported that dimefuron is absorbed by leaves and roots followed by translocation in the xylem to other parts of the plants (Glasgrow and Dick, 1980; Hisada and Imanura, 1986). Moreover, dimefuron is detectable in soil 12 months after treatment (Crowley, 1977 ; Kirby, 1977 ; Richardson and Parker,1977). It is therefore conceivable that dimefuron-^{14}C and its metabolites will be absorbed by roots and translocated to aerial plant parts after application.

Table 1 The average amount of dimefuron in combination with dimefuron-^{14} C applied to pineapple plants.

Time of application	dimefuron - ^{14} C/ dimefuron	Total dimefuron
	(μg/g)	(kg/ha)
Crowns		
3 Days after planting	3,089	2.8
4 Months after planting	5,572	2.2
9 Months after planting	5,480	2.2
Tillers		
3 Days after planting	2,789	2.8
4 Months after planting	5,049	2.2
9 Months after planting	5,240	2.2

Table 2 The average total amount of radioisotope on pineapple plants after washing, extracting and radioassay by liquid scintillation counting.

Pineapple plants	Time of application		
	3 Days after planting[1]	4 Months after planting[1]	9 Months after planting[2]
	(dpm)		
Crows	2,600,810	13,755,478	19,103,179
Tillers	7,941,340	16,044,860	30,328,081

[1] from 1 plant.
[2] the average of 6 plants.

The distribution of radioisotope found in the plants is tabulated in Table 3. The amount of radioisotope found in leaves was more than 80% of the total found in the plants grown from both crowns and tillers. (Table 3). The stumps grown from both crowns and tillers showed approximately 11% of total radioisotope found in the plants. The lowest level of residue (6%) was found in the fruits. Although the fruit did not receive dimefuron directly, it is believed that dimefuron can translocate from the root, stump and leaves to the fruit via acropetal movement. This was suggested by Glasgow and Dicks (1980) who reported the mechanism in field bean and pea after treatment with dimefuron. Furthermore urea herbicides have been reported to accumulate in adventitious root and expanded leaves where strong water movement occurs (Geissbuhler *et al.*, 1975).

The concentrations of radioisotope expressed as dimefuron equivalents in each part of the pineapple plants are tabulated in Table 4. The dimefuron equivalent in the flesh, peel, crown, stem and leaves were 0.045 ± 0.013, 0.049 ± 0.008, 0.087 ± 0.013, 0.288 ± 0.065 and 0.822 ± 0.278 μg/g (fresh weight) for pineapple grown from crown and 0.064 ± 0.034, 0.058 ± 0.013, 0.128 ± 0.027, 0.405 ± 0.131 and 1.236 ± 0.498 μg/g (fresh weight) for pineapple grown from tiller respectively.

Although metabolites of dimefuron in pineapple were not identified in this study, it is believed that degradation of dimefuron might occur via *N*-demethylation as observed for other urea herbicides (Geissbuhler *et al.*, 1975). The residues of dimefuron equivalent in the flesh of pineapple were found in 3 forms (Table 3), firstly the free residue that could be extracted by acetone and methanol (81.3 to 97.8%). Secondly, the conjugated residue which could be extracted by 0.1 N. HCl/90% methanol (0 to 12.5%) and thirdly, the bound residue (2.2 to 6.3%) which could not be extracted, using the procedure employed.

The maximum residue limits (MRL) of dimefuron in pineapple have not been reported. However, the low toxicity of dimefuron (LD_{50} of dimefuron in rat and mouse were 2,000 and 10,000 mg/kg respectively) (British Crop Protection Council 1987) together with the low residues, suggested by the results of this study, should not prevent its future use in pineapple crops.

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Table 3 The average total percentage of radioisotope detected in the different plant parts

Plant parts	Outside plant	Inside plant					Total
		Solvents			Combustion	Total	
		Acetone	Methanol	Acidified Methanol			
	(%)						
Crowns treated with dimefuron-^{14}C							
Flesh	-	0.10	1.86	0.00	0.04	2.00	
Peel	0.02 [3]	0.09	1.14	0.22	0.15	1.61	
Crown	-	0.84	0.44	0.09	0.38	1.71	
Stump	0.17	5.61	1.99	0.27	3.09	10.96	
Leaves	0.29	34.88	8.18	25.96	14.18	83.20	
Total	0.47	41.53	13.61	26.54	17.84	99.53	100.0 [1]
Tillers treated with dimefuron-^{14}C							
Flesh	-	0.20	1.55	0.24	0.17	2.15	
Peel	0.01 [3]	0.06	1.08	0.27	0.02	1.43	
Crown	-	0.53	0.60	0.24	0.14	1.51	
Stump	0.16	5.38	1.68	0.57	2.78	10.41	
Leaves	0.29	39.09	10.75	14.35	19.85	84.04	
Total	0.46	45.25	15.66	15.67	22.96	99.53	100.0 [2]

[1] 100% = 2,335,635.7 dpm
[2] 100% = 3,100,280.7 dpm
[3] Value for total fruit

Table 4 The average total amout of radioisotope expressed as dimefuron equivalent (ug) in pineapple tissue (g fresh weight) at harvest

Plant parts	Solvents			Combustion	Total
	Acetone	Methanol	Acidified methanol		
	(μg/g)				
Crowns					
Flesh	0.002 ± 0.003	0.042 ± 0.014	0.000 ± 0.000	0.001 ± 0.001	0.045 ± 0.013
Peel	0.003 ± 0.002	0.033 ± 0.008	0.009 ± 0.007	0.004 ± 0.004	0.049 ± 0.008
Crown	0.035 ± 0.012	0.025 ± 0.011	0.005 ± 0.009	0.022 ± 0.009	0.087 ± 0.013
Stump	0.147 ± 0.047	0.052 ± 0.021	0.007 ± 0.007	0.082 ± 0.016	0.288 ± 0.065
Leaves	0.342 ± 0.104	0.080 ± 0.037	0.263 ± 0.182	0.137 ± 0.057	0.822 ± 0.276
Total	0.529 ± 0.130	0.232 ± 0.054	0.284 ± 0.017	0.246 ± 0.060	1.291 ± 0.286
Tillers					
Flesh	0.006 ± 0.007	0.046 ± 0.018	0.008 ± 0.012	0.004 ± 0.005	0.064 ± 0.034
Peel	0.003 ± 0.002	0.045 ± 0.010	0.009 ± 0.006	0.001 ± 0.001	0.058 ± 0.013
Crown	0.044 ± 0.012	0.050 ± 0.004	0.016 ± 0.013	0.018 ± 0.017	0.128 ± 0.027
Stump	0.209 ± 0.085	0.065 ± 0.016	0.022 ± 0.012	0.109 ± 0.034	0.405 ± 0.131
Leaves	0.574 ± 0.265	0.157 ± 0.057	0.124 ± 0.114	0.291 ± 0.096	1.236 ± 0.498
Total	0.836 ± 0.340	0.363 ± 0.059	0.269 ± 0.131	0.423 ± 0.112	1.891 ± 0.604

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