Dodecylguanidine Acetate (Dodine) Residues on Apples

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The colorimetric method of Steller *et al.* was successfully used to analyze 73 samples of apples for dodine residues. Samples receiving no dodine showed an average apparent dodine residue of 0.10 p.p.m. Fifty-six samples of apples sprayed with Cyprex 65-W at rates of from 0.5 to 1.75 pounds per 100 gallons of water contained residues at harvest up to 1.29 p.p.m., with an average residue of 0.28 p.p.m. Disappearance studies showed residues after 33 days of 0.2, 0.4, and 0.6 p.p.m., respectively, from applications of 0.25, 0.50, and 0.75 pound of 65% dodine wettable powder formulation.

A COLORIMETRIC METHOD for the determination of *n*-dodecylguanidine acetate (dodine) in plant materials has been described by Steller *et al.* (*1*). During the 1958 season, the authors analyzed a considerable number of apple samples for dodine residues by this method and felt that the experience with the method and the results obtained would be of interest to others.

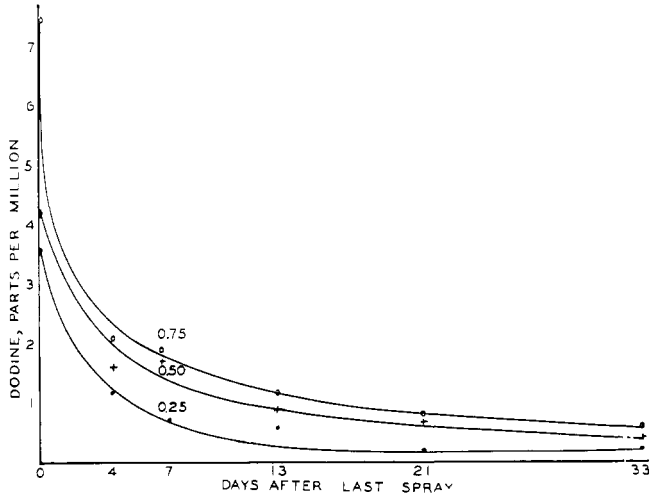
Results and Discussion

In general, the method has given excellent results when applied to apples. In all cases, 100-gram samples were macerated in a Waring Blendor; recoveries of dodine added to apple samples were from 70 to 115%, and were thus in the same range as reported by Steller *et al.* (*1*). Seventeen apple samples not sprayed with dodine were analyzed to establish blank values (Table I). These apples represented nine varieties from seven localities in the East. The maximum blank value was 0.20 p.p.m. and the minimum 0.05 p.p.m., with a mean of 0.10 p.p.m. There appeared to be no relation between variety and the apparent dodine found, and the earlier spray history of other fungicides (Captan, Ferbam, or Glyodin) did not affect the blank values.

As shown in Table II, 56 apple samples were analyzed for dodine residues at harvest. These were collected from experimentally sprayed orchards from Michigan to Maine and included 10 varieties. The complete spray history of every sample was known and is indicated in the table. Dodine was applied as Cyprex 65-W, a wettable powder formulation containing 65% dodine (American Cyanamid Co.). Rates of application varied from 0.5 to 1.75 pounds of Cyprex

Table I. Apparent Dodecylguanidine Acetate Residues on Harvest Samples of Apples Not Sprayed with Dodine

Variety	Location	Treatment	Apparent Dodine, P.P.M.
Cortland	Wooster, Ohio	No fungicide	0.07
	E. Lansing, Mich.	Captan, 2 lb.	0.05
	Geneva, N. Y.	Captan, 2 lb.	0.19
Golden Delicious	Urbana, Ill.	No fungicide	0.08
	Newark, Del.	No fungicide	0.15
Jonathan	Newark, Del.	No fungicide	0.20
	Urbana, Ill.	No fungicide	0.09
	Mich.	No fungicide	0.08
McIntosh	E. Lansing, Mich.	Captan, 2 lb.	0.12
	Geneva, N. Y.	Ferbam, 1.5 lb.	0.14
	Geneva, N. Y.	Ferbam, 1.5 lb.	0.15
Red Delicious	Newark, Del.	No fungicide	0.13
	Monroeville, N. J.	Unknown	0.08
	Staunton, Va.	Glyodin and Ferbam	0.04
Rome Beauty	Wooster, Ohio	No fungicide	0.05
Stayman	Mich.	No fungicide	0.05
York Imperial	Staunton, Va.	Glyodin and Ferbam	0.07
		Mean	0.102



Cyprex 65-W (containing 65% dodine) applied at 0.25, 0.50, and 0.75 pounds per 100 gallons. Date of last spray July 31, 1958

Figure 1. Disappearance curves for dodine on Golden Delicious apples in North Carolina

Table II. Residues of *n*-Dodecylguanidine Acetate (Dodine) on Apples at Harvest

Variety	Location	Rate[a]	No. of Sprays	Insecticides	Interval[b]	Dodine,[c] P.P.M.
Grimes Golden	Delaware	0.5	13	Dieldrin	32	0.01
	Delaware	0.5	13	Systox, lead arsenate	32	0
Jonathan	Delaware	0.5	13	Dieldrin	32	0.08
	Delaware	0.5	13	Genite	32	0.08
	Delaware	0.5	13	Systox, lead arsenate	32	0.08
Red Delicious	Delaware	0.5	13	DDT	32	0.22
	Delaware	0.5	13	TDE, Kelthane	32	0.23
Rome Beauty	Delaware	0.5	13	Aramite	32	0.06
	Delaware	0.5	13	Parathion	32	0.12
McIntosh	Maine	0.5	15	Lead arsenate	32	0.10
	Maine	0.5	15	DDT	32	0.08
Cortland	New York	0.5	11	Aramite,	69	0.04
	New York	0.5	11	TDE, DDT,	69	0.08
	New York	0.5	11	TEPP, du	69	0.03
McIntosh	New York	0.5	11	Pont S. S.	58	0.19
	New York	0.5	11		58	0.19
	New York	0.5	11		58	0.12
Jonathan	Michigan	0.75	7	DDT, malathion	20	0.36
	Michigan	0.75	7	DDT, malathion	20	0.28
Stayman	Michigan	0.75	7	Systox, TDE	71	0.03
	Michigan	0.75	7	Systox, TDE	71	0.05
	Michigan	0.75	7	Systox, TDE	71	0.07
Rome Beauty	Virginia	0.75	9	Aramite,	42	0.52
	Virginia	0.75	9	TDE,	42	0.51
	Virginia	0.75	9	DDT,	42	0.55
	Virginia	0.75	9	dieldrin,	42	0.30
	Virginia	0.75	9	malathion	42	0.31
	Virginia	0.75	9		42	0.26
Red Delicious	New Jersey	0.75	[d]	Parathion, oil	12	0.46
	New Jersey	0.75	[d]	Parathion, oil	12	0.54
	New Jersey	0.75	[d]	Parathion, oil	12	0.55
	New Jersey	0.75	[d]	Parathion, oil	12	0.69
Cortland	Ohio	0.75	10	TDE, DDT,	55	1.23
	Ohio	0.75	10	lead arse-	55	1.29
	Ohio	0.75	10	nate	55	1.28
Rome Beauty	Virginia	1.0	9	Aramite,	42	0.52
	Virginia	1.0	9	TDE,	42	0.51
Stayman	Virginia	1.0	9[e]	DDT, dieldrin, malathion	43	1.08
Cortland	Michigan	1.0	12	Methoxy-	55	0.09
	Michigan	1.0	12	chlor, lead	55	0.10
McIntosh	Michigan	1.0	12	arsenate,	55	0.25
	Michigan	1.0	12	parathion	55	0.16
	Michigan	1.0	12		55	0.13
Golden Delicious	Illinois	1.0	9	Malathion	72	0
	Illinois	1.0	9	DDT	72	0.02
Jonathan	Illinois	1.0	9	Malathion	72	0.05
	Illinois	1.0	9	DDT	72	0.07
Rome Beauty	Ohio	1.5	9	Lead arsenate	55	0.09
	Ohio	1.5	9	TDE, DDT	55	0.05
Lowery	Virginia	1.75	10	TDE, EPN,	53	0.26
	Virginia	1.75	10	lead arse-	53	0.32
	Virginia	1.75	10	nate	53	0.27
Red Delicious	Virginia	1.75	10	Aramite,	53	0.18
	Virginia	1.75	10	DDT,	53	0.13
York Imperial	Virginia	1.75	10	Ferbam,	53	0.17
	Virginia	1.75	10	parathion	53	0.14

[a] In pounds of Cyprex 65-W (65% dodine) per 100 gallons.
[b] Days between last spray application and harvest.
[c] Corrected for blank values.
[d] Only final spray contained Cyprex.
[e] Plus methoxychlor.

65-W per 100 gallons, and the number and composition of spray mixtures applied followed closely the local recommendations.

Because of the rather wide variation in intervals between the final spray application and harvest, it was impossible to obtain a correlation between the amount of dodine applied and the residues at harvest. The residues varied from 0 to 1.29 p.p.m., with only four out of 56 samples higher than 1.0 p.p.m. The average of all 56 samples was 0.28 p.p.m.

Apple trees of the Golden Delicious variety in North Carolina were sprayed 10 times with mixtures containing 4 pounds of malathion wettable powder per 100 gallons plus Cyprex 65-W at 0.25, 0.50, and 0.75 pound per 100 gallons. The dates of spray applications were April 9, 18, and 30; May 13 and 23; June 4 and 18; and July 2, 16, and 31. Samples were collected at 0, 4, 7, 13, 21, and 33 days after the last application. During this 33-day period, 3.75 inches of rain fell. The samples were analyzed by the method of Steller *et al.*, and the results, corrected for appropriate blanks, are given in Figure 1.

Figure 1 shows that dodine residues of 7.5, 4.2, and 3.6 p.p.m. immediately after the last spray application were reduced to 0.6, 0.4, and 0.2 p.p.m., respectively, 33 days later. It should be noted that the slopes of the individual curves in Figure 1 are not as steep as those for certain other pesticides, indicating a good degree of retention.

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Literature Cited

(1) Steller, W. A., Klotsas, K., Kuchar, E. J., Norris, M. V., J. AGR. FOOD CHEM. **8**, 460 (1960).

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