not as great as that achieved by steeping, but nonetheless was significant. This method of treatment is being studied further in order to increase its effectiveness.

Acknowledgment

The authors are indebted to C. L. Brooke of Merck and Co., Rahway, N. J., for the potassium gibberellate used in this study.

Literature Cited

(1) Bawden, R. F., Dahlstrom, R. F., Sfat, M. R., *Am. Soc. Brewing Chemists Proc.* **1959,** 137–41.
(2) Fleming, J. R., Johnson, J. A., Miller, B. S., *Cereal Chem.* **37,** 363–70 (1960).
(3) Hayashi, T., *J. Agr. Chem. Soc. Japan* **16,** 386–8 (1940).
(4) Kavanagh, F., Kuzel, N. R., J. AGR. FOOD CHEM. **6,** 459–63 (1958).
(5) Kneen, E., Sandstedt, R. M., *Cereal Chem.* **18,** 237–52 (1941).
(6) Mastovsky, J., Karel, V., Kahler, M., *Kvasny pruniple* **5,** 81–6 (1959); *Chem. Abst.* **53,** 10657.
(7) Miller, B. S., Johnson, J. A., *Arch. Biochem. Biophys.* **32,** 200–6 (1951).
(8) Morris, E. O., *Chem. & Ind. (London)* **1958,** 97.
(9) Munekata, H., Kato, S., *Bull. Brewing Sci. (Japan)* **3,** 1–10 (1957).
(10) Owades, J. L., Chiano, G., *Am. Brewer* **91,** 39 (1958).
(11) Peck, H. M., McKinney, S. E., Tytell, A., Byham, B. B., *Science* **126,** 1064 (1957).
(12) Pollock, J. R. A., *Chem. & Ind. (London)* **1957,** 387–8.
(13) Sandegren, E., Beling, H., *Braueri Wiss. Beil.* **11,** 231–5 (1958).
(14) Sandstedt, R. M., Kneen, E., Blish, M. J., *Cereal Chem.* **16,** 712–23 (1939).

Received for review May 31, 1960. Accepted October 26, 1960. Contribution No. 332, Department of Flour and Feed Milling Industries, Kansas Agricultural Experiment Station, Manhattan, Kan. Work done under contract with U.S. Department of Agriculture; authorized by Research and Marketing Act of 1946, and supervised by Northern Utilization Research and Development Division of the Agricultural Research Service. Report taken in part from a thesis submitted by the senior author in partial fulfillment of requirements for a Master of Science degree from Kansas State University.

TRANSLOCATION OF HERBICIDES

Fate of 2,2-Dichloropropionic Acid (Dalapon) in the Cotton Plant

GRANT N. SMITH and DENZEL L. DYER[1]

Agricultural Chemical Research, The Dow Chemical Co., Midland, Mich.

2,2-Dichloropropionic acid (dalapon) is readily absorbed from the soil by the cotton plant and accumulates in the actively growing tissues. As the tissues mature, the dalapon is retranslocated to more actively growing areas. No indications were obtained that any significant amount was metabolized or synthesized into natural products. The herbicide appears to be present in the tissues as a free acid or salt, which can readily be leached from the tissues by simple water extraction.

IN COTTON-GROWING AREAS, 2,2-dichloropropionic acid (dalapon) is used to control established clumps of Johnson grass in cotton fields. Although the herbicide is applied as a directed spray (*7, 8, 10, 12, 13, 17, 18*), there is always the possibility that it will come in contact with the cotton plants either directly or via the soil. Once this happens, it will probably be absorbed and translocated throughout the plant.

In considering the use of a new herbicide it is necessary to determine whether the compound will accumulate in portions of the plant which may be used for feed or food products, or be metabolized into products which would remain as an undesirable residue in the plant.

To investigate the fate of dalapon within the cotton plant it was necessary to develop chemical or radiochemical procedures for determining the herbicide and its possible biological degradation products.

A review of the chemistry of dalapon indicated that the most likely degradation steps would involve dehalogenation, hydration, and decarboxylation reactions with the formation of pyruvic acid, acetic acid, and carbon dioxide. Satisfactory chemical methods are available for the determination of these compounds (*1, 5–7, 12*). Unfortunately, however, all of the compounds occur naturally in plants and it would be impossible to distinguish by chemical means the naturally occurring compounds from the biological degradation products of dalapon.

To ascertain the fate of each portion of the dalapon molecule, radiochemical techniques were employed using labeled dalapon-2-C^{14} (*3*), to obtain residue information on the fate of dalapon in the cotton plant.

Methods

Individual cotton plants (*Gossypium hirsutum* var. Cokers 100 Wilt Resistant) were grown in crocks in a greenhouse. The crocks were approximately $8\frac{1}{2}$ inches in diameter with a capacity of 2 gallons and were filled to within 1 inch of the top with potting soil consisting of an equal mixture of sand, peat moss, and sandy loam. The crocks were arranged in such a manner that the plants could be surface-irrigated and the excess moisture drained through a hole in the bottom into a glass tray.

When the plants had reached the early blossom stage, 12 were selected for uniformity and treated by irrigating each crock with 500 ml. of a dalapon solution containing approximately 71 p.p.m. of dalapon-2-C^{14} having a specific activity of 0.014 mc. per mmole. This solution was neutralized and applied as the sodium salt.

The plants were surface-irrigated daily with 500 ml. of water and the excess was allowed to drain from the bottom of the crock. They were grown 12 weeks in the greenhouse, using artificial lights to supplement the sunlight when necessary. At harvest, many of the bolls had matured, and the cotton was ready for picking.

[1] Present address, Glenn L. Martin Co., Denver, Colo.

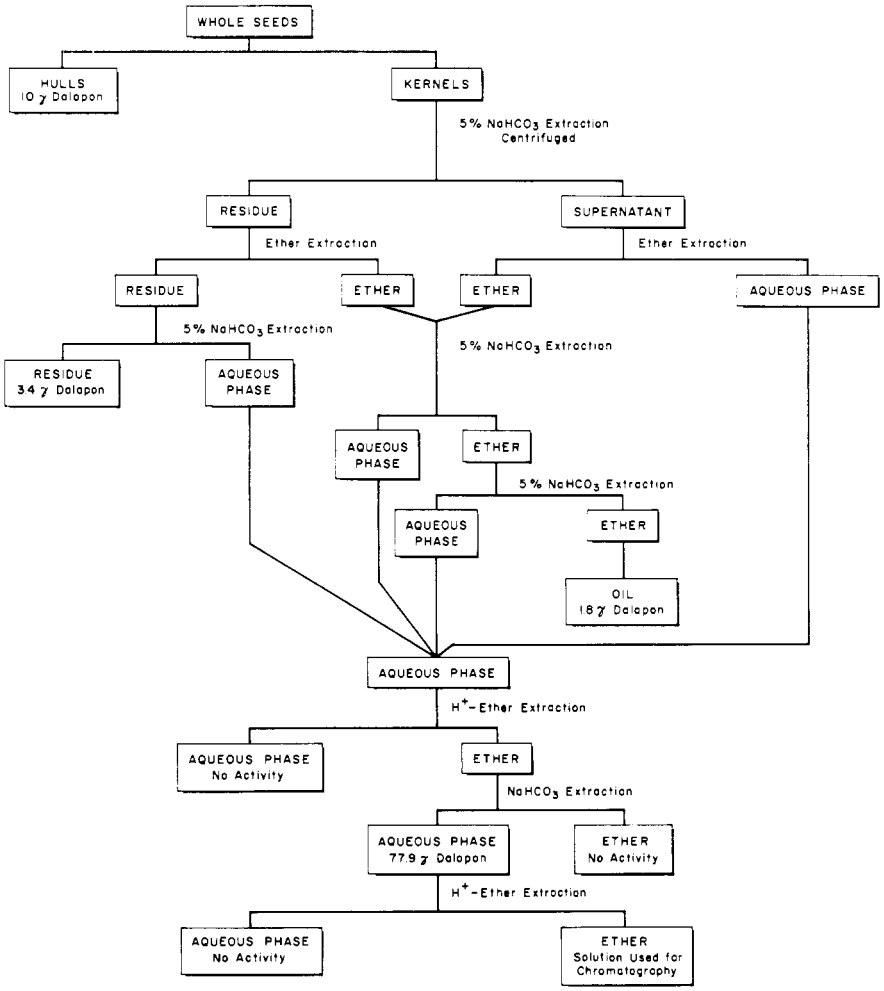

Figure 1. Extraction procedure for isolation of radioactive dalapon from cottonseeds

Table I. Solvent Systems Used to Separate Dalapon and Related Compounds

Solvent System	Ml.	R_f[a] × 100 Monochloropropionate	Dichloropropionate	Trichloropropionate	Pyruvate	Acetate
1-Butanol	100	51	78	80	31	23
Diethylamine	15					
Water	10					
1-Butanol	100	40	62	72	17	8
1.5*N* NH_4OH	100					
Chloroform	100	33	66	74	2	0
1-Butanol	100					
Diethylamine	30					
Water	10					

[a] Average of six or more determinations.

At the time of harvest, three plants were dried in plant presses and the specimens saved for radioautographs. The floral parts and immature bolls were sectioned and individual sections dried and radioautographed. To ascertain the distribution of radioactivity in the whole plant, it was necessary to divide it into sections and prepare radioautographs of each section. These were made by exposing the specimens to Eastman no-screen x-ray film for several months.

The flowers, bolls, and seeds from the remaining plants were harvested and divided into various types of tissues for radiochemical analyses. The samples were analyzed by burning them, using a modification of the Van Slyke combustion procedure (*15*, *16*). The radioactive carbon dioxide liberated during the combustion was trapped as barium carbonate (*2*). Infinitely thick plates of barium carbonate were prepared using Tracerlab filter tower apparatus No. E-29. The filter paper and layer of barium carbonate were mounted in a Tracerlab No. E-7B ring and disk. The precipitate was dried and counted in a Nuclear-Chicago Model C-110 automatic sample changer using a D-47 gas flow counter with a Micromil window in connection with a D-181 scaler and C-111-B printing timer. The scaler was set for a predetermined count of 10,000. Triplicate samples of each tissue were analyzed for radioactivity, using duplicate plates of barium carbonate from each combustion to ensure adequate counting of the samples.

To determine the distribution of radioactivity in the cottonseeds, they were separated from the cotton and delinted by a standard acid delinting process (*4*). The seeds were dehulled and the kernels extracted to remove the oil. The extraction procedure employed to separate the oil from the water-soluble components and insoluble residue is outlined in Figure 1.

Typical Extraction. The kernels were homogenized in 25 ml. of 5% sodium bicarbonate solution in a glass homogenizer until a uniform suspension was obtained. The suspension was centrifuged at high speeds to separate the insoluble material from the aqueous phase. The residue was again extracted with 10 ml. of 5% sodium bicarbonate solution. The aqueous phases from both extractions were combined, placed in a continuous liquid-liquid extractor, and extracted 24 hours with ethyl ether (*12*). The residue was transferred to a micro-Soxhlet extractor and extracted overnight with ether.

The resulting ether extracts from both extractions were combined and washed twice with 10-ml. portions of a saturated sodium bicarbonate solution. The washings were then combined with the sodium bicarbonate solution in the continuous liquid-liquid extractor.

The defatted residue was again extracted with 30 ml. of 5% sodium bicarbonate solution by stirring the suspension slowly for 5 hours. The suspension was centrifuged and the residue washed twice with water. The residue was then analyzed for radioactivity and discarded. The aqueous supernatant and washings were combined with the sodium bicarbonate solution in the continuous extractor. The aqueous solution was acidified with phosphoric acid (acid to Congo red paper), saturated with sodium sulfate, and extracted with ether. After 24 hours of continuous extraction the aqueous phase contained no detectable amount of radioactivity and was, therefore, discarded.

The radioactive material in the ether was passed back and forth through the ether-bicarbonate extraction procedure twice more to purify the sample for chromatography. The resulting ether solution was assayed for radioactivity and chromatographed.

The ether solution was spotted on Whatman No. 4 filter paper strips 2.5 × 50 cm. Approximately 0.1 ml. of the radioactive solution was applied, 5 cm.

from one end of the filter paper in such a manner that the area covered by the solvent did not exceed 0.5 cm. in diameter. The strips containing the ether extract were then chromatographed with strips containing reference standards of dalapon-2-C^{14}, 2-monochloropropionic acid-2-C^{14}, pyruvic acid-1-C^{14}, and acetic acid-1-C^{14} using the ascending method (*11*). After the solvent had run 35 to 40 cm., the strips were removed from the chromatographic chamber, the solvent front was marked, and the strips were air-dried at room temperature. They were then scanned in a Nuclear-Chicago Actograph strip assembly consisting of an Actograph strip feeder No. 100 with a D-47 gas flow counter, Model 1615 B rate meter, and a Houston laboratory chart recorder. A Micromil window was used with the D-47 flow counter.

The three chromatographic systems shown in Table I were used to identify the radioactive compound. The R_f values obtained with the tissue extracts were compared with those from the reference standards run at the same time. The extracts were also cochromatographed with the reference standards as an additional check on the identity of the radioactive compound.

Radioautographs of the strips were prepared by exposing them to Eastman no-screen x-ray film for several months. This procedure may detect areas of activity missed by the continuous scanning technique.

Results and Discussion

When dalapon is applied to the soil surrounding a cotton plant, it is gradually leached down through the soil. During the leaching process, the herbicide comes in contact with the roots and is probably absorbed and translocated into the cotton plant.

The amount of herbicide absorbed depends on the amount of compound initially added to the soil and the period of time it is in contact with the roots. The soil type, condition, flora, and rate of leaching determine the length of time the herbicide is in contact with the soil.

In the present investigation, a soil was selected which would permit rapid leaching of the dalapon through the soil and would require several weeks before the soil flora could adapt itself to the metabolism of the herbicide (*14*). To check the rate of leaching of dalapon through the soil under the conditions used, the excess water which drained from the crock was collected daily and monitored for radioactivity. Typical results obtained are shown in Figure 2. At the completion of the leaching process, the soil was monitored for radioactivity by taking samples at various depths and counting them in the flow counter. After the leaching was completed, no significant amount of radioactivity could be detected in the soil.

During the growing period, the plants were scanned with a Geiger counter to determine if radioactive materials were entering the plant. Spot checks indicated that radioactivity was present in the young leaves and growing tips within 24 hours after treatment.

Table II shows the typical distribution of radioactivity in a young cotton plant in the early blossom stage 5 days after treatment with dalapon-2-C^{14}.

In general, the concentration of radioactivity tended to increase from the base of the plant to the top, being concentrated primarily in the young leaves and growing tips. In the individual leaves the activity increased from the midvein toward the margin of the leaf. The roots of these plants were still in contact with the dalapon in the soil and radioactivity could be detected throughout the plant. In mature plants no significant amount of radioactivity could be observed in the roots or lower portions of the plant. In this case a 12-week period had elapsed between the time the plants had been treated with radioactive dalapon and the time of harvest. In this case the radioactivity was accumulated in the growing tissues, the terminal leaves, and flowers (see Figures 3 and 4).

From the results obtained by direct counting of the living plants with a GM tube indications were obtained that the radioactivity accumulated in the young leaves. As the plant continued to grow and the leaves matured, there appeared to be a retranslocation of the dalapon from the mature leaves to younger tissues. It was not possible to ascertain the exact degree of this relocation of the dalapon because of the difficulties involved in counting carbon-14 in living tissues. In present investigation, it was possible to detect significant amounts of radioactivity initially in the young leaves with a GM probe and ratemeter, but none could be detected in those same leaves when they had matured. The radioactivity in the matured leaves was checked by the radioautography and combustion techniques, which could detect much lower amounts of radioactivity than the GM probe.

It can easily be demonstrated under the proper environmental conditions that radioactivity applied to a leaf can be absorbed and translocated to other parts of the plant. If the plant is grown in a nutrient solution, radioactivity can be detected in the nutrient solution, showing that the dalapon has been translocated into the roots and out into the nutrient solution. The amount of dalapon translocated downward into the roots and out into the nutrient solution is determined by light conditions and other environmental factors. These factors are now being investigated.

Radioautographs and radiochemical analyses of the floral parts (Table III) indicated a tendency for the radioactivity to concentrate in these tissues. The petals and bracts were both high in radioactive materials.

Radioautographs of the boll showed an accumulation of radioactivity in the seeds and woody portions of the pod (Figure 5). The radioactivity was largely concentrated in the seeds (94 p.p.m. expressed as radioactive dalapon). The activity found in the cotton (20 p.p.m.) apparently was not chemically bound. It was initially observed that in immature bolls, where the cotton still contained a large amount of moisture, the liquid which could easily be pressed from the cotton contained radioactive materials. With mature cotton the radioactivity could be largely removed by simple extraction with water in a Soxhlet

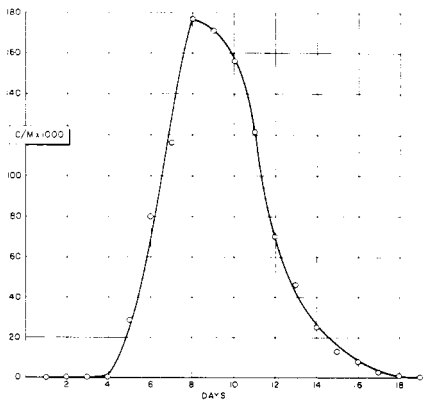

Figure 2. Leaching of radioactive dalapon-C^{14} from soil

Table II. Distribution of Radioactivity in the Cotton Plant 5 Days after Soil Treatment with Radioactive Dalapon-2-C^{14}

Plant Sample	Net [a] C.P.M.	Total D.P.M.	Dalapon, P.P.M.
Three top leaves	2250 ± 20	39,240	2.58
Leaf 5 cm. from top	300 ± 3	5,232	0.34
17 cm. from top	175 ± 3	3,052	0.20
23 cm. from top	125 ± 2	2,180	0.14
45 cm. from top	125 ± 2	2,180	0.14
73 cm. from top	100 ± 2	1,744	0.12
Roots	125 ± 2	2,180	0.14
Flower	1075 ± 10	18,748	1.23
	1200 ± 12	20,928	1.38

[a] Count per 100 mg. of dry tissue corrected for background.

extractor. Because of the low count obtained after extraction, <1 count per minute above background, it was impossible to ascertain if any significant amount of radioactivity were still present or if the observed count were due to variations in sample preparation, counting error, etc. The results obtained indicated that the radioactivity in the liquid was deposited on the cotton fibers when the boll opened and the cotton dried out.

From a residue standpoint, the radioactivity found in the seeds was of prime importance. The seeds exhibited approximately 94 p.p.m. of radioactivity when calculated in terms of parts per million of radioactive dalapon. In all radiochemical analyses the results were calculated in terms of parts per million of dalapon for comparison purposes. This does not necessarily mean that all the radioactivity was present as radioactive dalapon.

In commercial operations the seeds are separated into the hulls and kernels. The kernels are then processed to obtain the oil. It was, therefore, desirable to determine the nature of the dalapon residue in the seed and its fate in processing of the seed for commercial products (see Table IV).

Since the majority of the radioactivity in the seed was confined to the kernel (83.2 p.p.m.), major effort was devoted to ascertaining in what chemical form the radioactivity was present. In order to do this, it was necessary to separate the radioactive components from the other cell constituents. In the extraction procedure described above, the kernel was divided into the water-soluble components, the insoluble residue, and the oil as shown in Figure 1. The water-soluble components included the organic acids such as dalapon, pyruvic acid, and acetic acid. The insoluble residue was largely protein in nature.

In carrying out the extraction procedure, great care was exercised to obtain complete extraction and separation of the various components. Under these conditions most of the radioactivity originally present in the kernel was found in the water-soluble components after the fractionation procedure. This fact suggested the possibility that the radioactivity was still present as the original compound.

The radioactivity present in the insoluble residue appeared to be occluded in the residue and not chemically bound to the protein. Continuous water extraction of the residue gradually decreased the amount of radioactivity per unit weight of the sample. Similarly, the radioactivity in the oil could be decreased by continuous extraction. When the oil was dissolved in ether and repeatedly extracted with a 1% sodium bicarbonate solution, the activity in the oil gradually decreased. The concentration of radioactivity, expressed as dalapon, in the oil was reduced from 1.8 to 0.12 p.p.m. by six extractions with 1% sodium bicarbonate solution. The oil sample was shaken with the bicarbonate solution 4 hours each time it was extracted.

The fact that the specific radioactivity in the oil could be decreased by repeated extractions precludes the possibility that the dalapon or one of its degradation products had been synthesized into an ester or triglyceride. Even though the extraction was carried out under slightly alkaline conditions, the conditions were

Table III. Distribution of Radioactivity in Floral Parts of Cotton Plant

Floral Part	Calcd. Concn. of Radioactivity, P.P.M. Dalapon
Boll (excluding seeds and cotton)	37
Seeds	94
Cotton	20
Petals	219
Sepals	8
Bracts	235

Table IV. Distribution of Radioactivity in Cottonseed

Tissue	Calculated Radioactivity, P.P.M. Dalapon				
	1	2	3	4	Av.
Hulls	9.0	9.6	10.5	10.9	10.0
Kernel					
Residue	4.0	2.9	3.5	..	3.5
Oil	1.7	2.2	1.7	..	1.9
Fatty acids (dalapon)	80.4	80.4	72.8	..	77.9

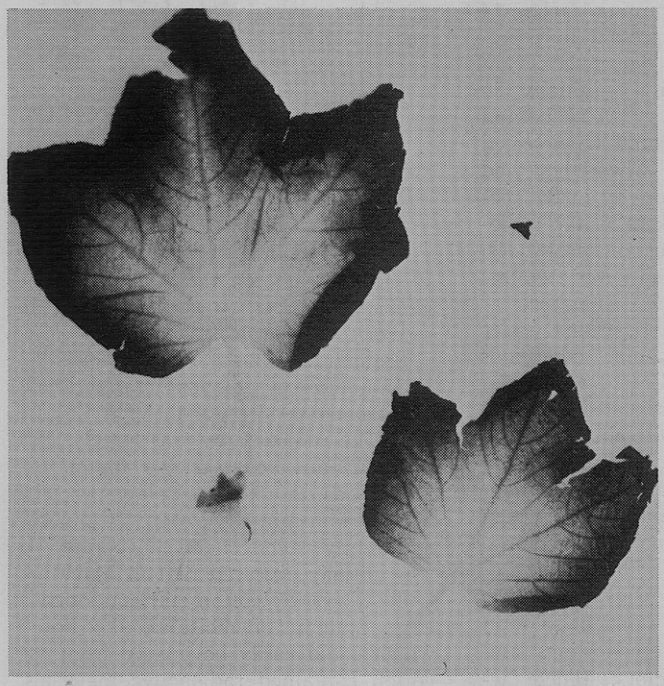

Figure 3. Accumulation of radioactive dalapon-C^{14} in terminal leaves of cotton 3 months after single soil application

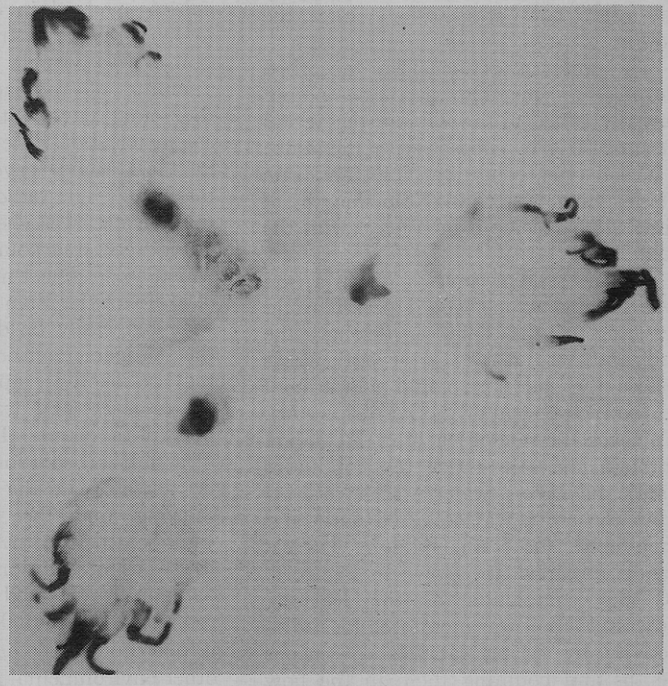

Figure 4. Distribution of radioactive dalapon-C^{14} in floral parts of cotton 3 months after single soil application

so mild that the triglyceride of dalapon would not be hydrolyzed. The mono-, di-, and triglyceride esters of dalapon and naturally occurring fatty acids were prepared and their rates of hydrolysis were studied to be sure that hydrolysis would not occur during the conditions used in the extraction procedure.

The fact that the radioactive material could be readily extracted from the seeds and other plant tissues by water extraction suggests the possibility that the radioactive carbon was still present as a free aliphatic acid and not chemically bound to the cell components. The distribution of the radioactivity between the acidified water phase and ethyl ether phase also supports this conclusion, since aliphatic acids would pass into the organic phase under these conditions.

To identify the chemical nature of the radioactivity, the paper partition chromatography procedure was resorted to.

The ether extract containing the radioactivity was concentrated and chromatographed by the ascending method (*11*). The extract was run individually with the reference standards and also cochromatographed with each standard. The position of the individual compounds was determined by continuous scanning with the Nuclear-Chicago Actograph. This procedure will detect the major spots of radioactivity but may miss some of the minor spots. To detect minor components the paper strips were exposed to Eastman no-screen x-ray film for approximately 3 months. Typical scans are shown in Figure 6, together with a radioautograph of the strip containing the plant extract.

The scans indicated that radioactivity isolated from the kernels was associated with the dalapon molecule. Similar results were obtained with extracts prepared from the hulls, leaves, and floral parts. It appeared that dalapon was readily absorbed by the plant and translocated to the actively growing tissues. As the tissues mature, the dalapon appears to be translocated to younger tissues. From the ease of extraction it appears likely that the dalapon remained as a free acid or salt in the tissue and was not chemically bound to the cell components. Dalapon could be readily extracted from the tissues by a simple water extraction. No indications were obtained that the dalapon could be incorporated into the glyceride of the cottonseed.

Apparently dalapon is not metabolized in the cotton plant to any significant extent and remains intact during the life of the plant. Occasionally radioautographs of the chromatographic strips showed possible minor traces of other areas of radioactivity besides radioactive dalapon. These areas would have represented a very small percentage of the total radioactivity of the strip

These secondary areas of radioactivity were generally associated with those areas containing a visible amount of tissue components. The ether extracts used in the chromatographic determination contained traces of the tissue components which had been carried through the extraction procedure. When the ether extract was concentrated on the paper strips, the area containing the tissue components could be observed by viewing the strips under an ultraviolet light. These tissue components migrate to some extent in the various solvent systems employed. It appeared likely that the radioactivity associated with them was dalapon which had not been completely extracted from these materials by the chromatographic solvent. In order to check this possibility, radioactive dalapon was added to a blank tissue extract and the sample chromato-

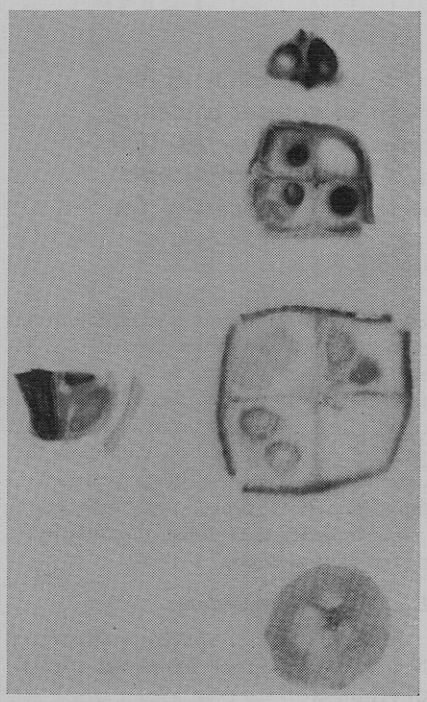

Figure 5. Distribution of radioactive dalapon-C^{14} in boll and seeds of cotton 3 months after single soil application

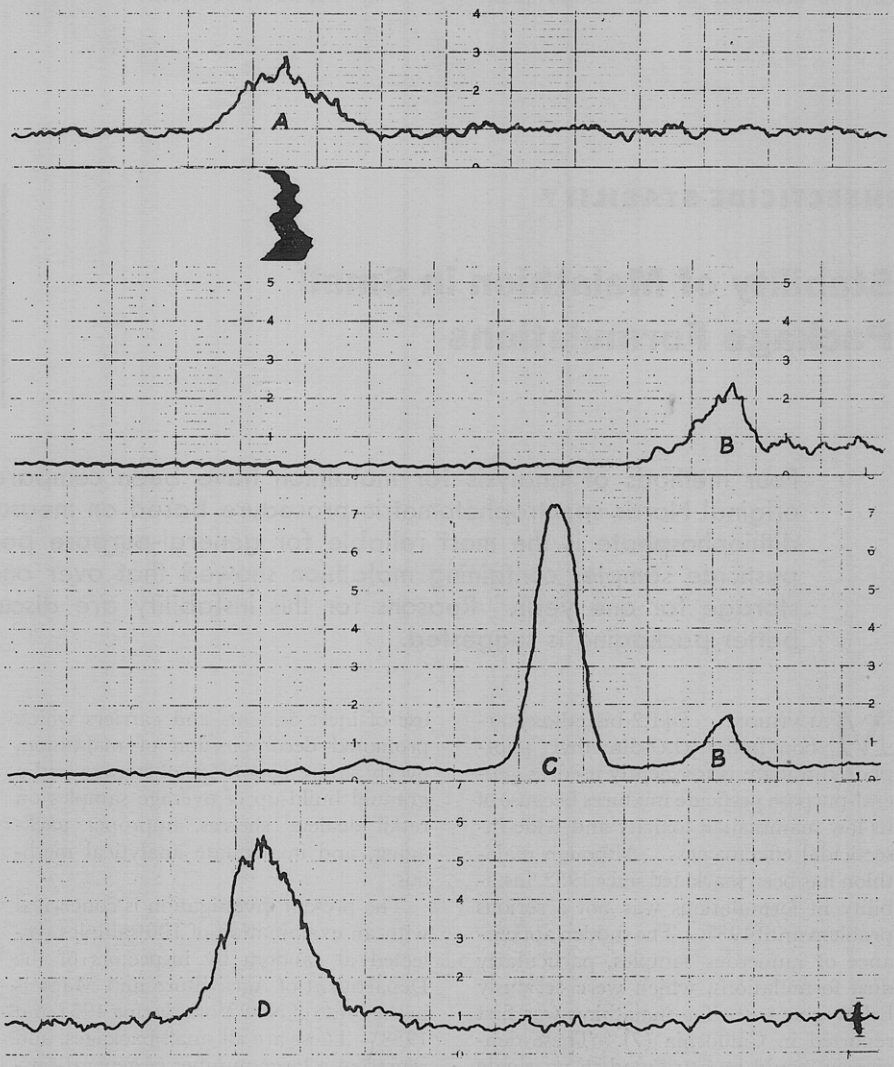

Figure 6. Chromatographic scans of plant extract and reference standards

A. Tissue extract
B. Acetic acid-C^{14}
C. Pyruvic acid-C^{14}
D. Dalapon-C^{14}

graphed in the usual manner. Radioactivity was found in the area of the tissue components in these chromatograms. It therefore appears likely that the secondary spots are due to dalapon occluded in the tissue components. In no case were the secondary spots associated with areas containing the reference standards.

In the commercial production of cottonseed oil, the oil is generally removed from the kernel by pressing or solvent extraction The resulting crude oil is then purified by a caustic extraction procedure. Under these conditions, some of the dalapon is carried over with the oil during extraction. The caustic treatment probably then removes the dalapon from the oil during the cleanup procedure. This was checked in the laboratory by adding radioactive dalapon to cottonseed oil and then processing the oil through the caustic cleanup procedure. Radiochemical analysis of the oil indicated that the dalapon could be removed by this procedure.

These studies indicate that dalapon can be absorbed by the cotton plant and will accumulate in the actively growing tissues. The dalapon does not appear to be metabolized to any significant extent in the plant but remains in the tissues in a form which can readily be removed by a simple water extraction. The material extracted from the plant can be identified as dalapon by paper chromatography and chemical analysis. In commercial production dalapon associated with the cottonseed oil will be removed during the cleanup procedure.

References

(1) Assoc. Offic. Agr. Chemists, Washington, D. C., "Methods of Analysis," 7th ed., p. 210, 1950.
(2) Beamer, W. H., Atchison, G. J., *Anal. Chem.* **22,** 303–6 (1950).
(3) Blanchard, F., Muelder, W., Smith, G. N., J. AGR. FOOD CHEM. **8,** 124–8 (1960).
(4) Cardozier, V. R., "Growing Cotton," pp. 68–71, McGraw-Hill, New York, 1957.
(5) Freedemann, T. E., Haugen, G. E., *J. Biol. Chem.* **147,** 415–41 (1943).
(6) Lichstein, H. C., Umbreit, W. W., *Ibid.*, **170,** 329–34 (1947).
(7) Loomis, W. E., Shull, C. A., "Methods in Plant Physiology," p. 151, McGraw-Hill, New York, 1937.
(8) Miller, J. H., Foy, C. L., *Proc. Southern Weed Conf.*, **1955,** 104–9.
(9) Rea, H. E., Agronomy Abstracts, Annual Meeting, Am. Soc. Agronomy, Aug. 15–19, 1955.
(10) Rea, H. E., *Proc. Southern Weed Conf.* **1955,** 394–6.
(11) Smith, G. N., *Down to Earth* **14,** No. 3–6 (1958).
(12) Smith, G. N., Getzendaner, M. E., Kutschinski, A. L., J. AGR. FOOD CHEM. **5,** 675–8 (1957).
(13) Swezey, A. W., Fisher, J. R., *Down to Earth* **11,** No. 1, 1–5 (1955).
(14) Thiegs, B. J., *Ibid.*, **11,** No. 2, 2–4 (1955).
(15) Van Slyke, D. D., Folch, J., *J. Biol. Chem.* **136,** 509–41 (1940).
(16) Van Slyke, D. D., Plazin, J., Weisiger, J. R., *Ibid.*, **191,** 299–304 (1951).
(17) Watson, A. J., *Down to Earth* **11,** No. 3, 2–3 (1955).
(18) Watson, A. J., *Proc. Southern Weed Conf.*, **1954,** 200–4.

Received for review July 17, 1959. Resubmitted June 29, 1960. Accepted October 30, 1960.

INSECTICIDE STABILITY

Stability of Malathion in Small Package Formulations

G. L. MACK

New York State Agricultural Experiment Station, Geneva, N. Y.

Four methods of analysis for malathion have been compared. A modification of the original Norris spectrophotometric procedure based on measurement of copper dimethyl dithiophosphate is the most reliable for general-purpose pesticides. A survey of 100 pesticide samples containing malathion showed that over one half were unstable upon storage for one year. Reasons for this instability are discussed and the necessity for better packaging is suggested.

MALATHION, *S*-[1,2-bis(ethoxycarbonyl)ethyl]*O,O*-dimethyl phosphorodithioate is frequently used in general-purpose pesticide mixtures because of its low mammalian toxicity and wide insecticidal effectiveness. Although malathion has been marketed since 1952, instability in formulations was not a serious problem until 1957. The sudden appearance of numerous samples, particularly dust formulations, which were seriously below guarantee for malathion was first reported in California (*7*). These deficiencies could be attributed to no single cause, but to a combination of independent factors. The more important factors were: improper methods of formulation and inadequate quality control, the use of inert diluents and carriers which promoted decomposition of malathion, overly severe conditions of storage and a gradual build-up of overage samples on retail dealers' shelves, improper packaging, and inadequate analytical methods.

The present investigation is concerned with an examination of 100 samples collected at random by inspectors of the Department of Agriculture and Markets in the State of New York during 1957 and 1958. These are all small packages, and represent a large number of general-purpose mixtures, so that the results reported here do not necessarily apply to bulk packages for commercial use. Among the uncontrolled variables were age, method of formulation, and composition of both inert and active ingredients, so that the conclusions as to the interrelation among packaging, formulation, and quality are developed from a pragmatic point of view. Because the validity of the chemical methods has been questioned, four analytical procedures were compared in order to establish the soundness of the test methods.

Experimental Procedures

Method 1. Spectrophotometric Method for Copper Dimethyl Dithiophosphate.

REAGENTS. Acetonitrile, anhydrous. Bromobenzene, technical grade, redistilled if not colorless.