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Note

Improved determination of dalapon residues in plant tissues and natural water by derivatization and electron capture gas chromatography

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The sodium salt of dalapon (2,2-dichloropropionic acid) is a growth regulator which is used to control undesirable grasses. It is actively absorbed and translocated by both foliage and roots.

Residues of dalapon in various substrates can be determined by gas–liquid chromatography (GLC) with an electron capture detector. Determination of the free acid by GLC is possible, but special conditions are required such as stainless-steel plugs in the column and injection of an acidic "chaser". GLC of derivatives, *e.g.*, the methyl ester[2] or the 1-butyl ester[3], seems easier to carry out. The methyl ester is very volatile, however, and is therefore susceptible to interferences by co-extractives which often also appear in the early sections of the chromatogram. The 1-butyl ester is an improvement in this respect, but is in our view still rather volatile. (Column temperature and retention time reported by Cotterill[3] are 100° and 95 sec, respectively.)

We have studied the GLC determination of dalapon as the hexyl, nonyl, 2-chloroethyl, benzyl, 2-phenylethyl and 3-phenylpropyl ester. The last derivative was found to be the most appropriate, giving the highest retention times and good sensitivity. It can be determined on columns and at temperatures normally used in pesticide residue analysis. A procedure for determining dalapon residues in plants via the ester of 3-phenylpropanol-1 is reported.

EXPERIMENTAL

Gas–liquid chromatography

A Micro Tek MT 222 gas chromatograph with two ^{63}Ni electron capture detectors was used. The detectors were operated in the pulse mode at 50 V. The electrometer attenuation was $10^2 \times 8$ (corresponding to $8 \cdot 10^{-10}$ A at full recorder scale deflection). Two columns (A, 1.8 m × 4 mm ID; B, 0.90 m × 4 mm I.D.), both glass, were used to determine the ester: Column A was packed with 3% OV-210 on Gas-Chrom Q (80–100 mesh), column B with 1.8% OV-1 and 2.7% OV-210 on Gas-Chrom Q (80–100 mesh). Carrier gas: nitrogen; flow-rate; 70 ml/min on both columns The temperatures of the column oven, injectors and detectors were 160, 205 and 275° respectively.

Reagents and materials

3-Phenylpropanol-1 was obtained from E. Merck (Darmstadt, G.F.R.) Art. No. 7014. 85% Ortho-phosphoric acid, diluted 1:1 with distilled water, was purified by extraction with diethyl ether (three times). The 3-phenylpropyl ester of dalapon (b.p. 116° at 0.2 mm Hg) was prepared in our laboratory. Standard solutions in hexane are stable for at least 1 year.

Silica gel 60 (0.05–0.2 mm, 70–270 mesh) (ASTM) for column chromatography was obtained from Macherey, Nagel & Co. Düren, G.F.R.). It was heated overnight in an oven at 130°. After cooling, 95.0 g of the silica gel was de-activated with 5.00 g water. The mixture was then homogenized and allowed to equilibrate overnight in a tightly stoppered bottle before use.

All other chemicals were of reagent grade quality and were checked for the absence of interfering impurities by means of blank determinations. The sodium salt of dalapon (98% purity) was used as a standard. The plant tissues were macerated in an Ultra Turrax mixer with solvent. Evaporations were carried out in a rotary evaporator (water-bath, *ca.* 35°).

A chromatographic tube (350 × 6 mm) with reservoir (200 ml) was used to separate the derivative from impurities. The esterification procedure was performed with a reagent tube (40 ml) with ground-glass joint and micro-Snyder condenser (10 cm).

Procedures

Extraction of plant tissues. A 100-ml volume of water, 6 ml ortho phosphoric acid dilute solution and 6 ml 25% phosphotungstic acid solution were added to 50 g ground and homogenized sample. The mixture was blended for 5 min and allowed to stand for 30 min. Then 10–15 g Celite 545 were added and the mixture was filtered by suction through a thin pad of Celite on a büchner funnel. The filter cake was pressed dry and subsequently washed twice with 20 ml water. Water was added to the combined filtrate and washings to make a total of 200 ml (4 ml ≡ 1 g sample). A 100-ml volume of the aqueous extract was saturated with 34 g sodium chloride and then extracted wity 50, 25 and 25 ml diethyl ether respectively. The combined diethyl ether extracts were dried over anhydrous sodium sulphate.

Extraction of natural water. A 500-ml volume of water was acidified with 30 ml ortho phosphoric acid (dilute solution). After standing for 15 min the mixture was filtered on a büchner funnel by suction. The filter was washed twice with 20 ml water. The aqueous extract was saturated with 185 g sodium chloride and then extracted with 100, 50 and 50 ml diethyl ether respectively. The combined diethyl ether extracts were dried over anhydrous sodium sulphate.

Esterification. After adding 1.0 ml 3-phenylpropanol-1 to the ether extract, the latter was evaporated to *ca.* 5 ml. The concentrate was transferred to a reagent tube and further evaporated until no diethyl ether was left. The residue was saturated with dry hydrogen chloride gas (5 min). A micro-Snyder condenser was put on top of the tube which was then placed in a steam-bath for 5 min. After cooling, 25 ml hexane were pipetted through the condenser into the tube which was stoppered and shaken vigorously for 1 min. Then the mixture was transferred to a separating funnel. Subsequently, 20 ml water were added to the tube. It was stoppered, shaken vigorously and the mixture was again transferred to the separating funnel. The funnel was

TABLE I

RECOVERY OF KNOWN AMOUNTS OF DALAPON SODIUM SALT FROM CROPS BY THE GAS CHROMATOGRAPHIC PROCEDURE DESCRIBED

Sample	*Dalapon sodium salt added (mg/kg)*	*Recovery (%)*
Potatoes	0.05	94
	0.16	96
Grasses	0.05	103
	0.16	86
Apples	0.05	98
	0.16	100
Natural water	0.004	95
	0.008	100

stoppered and shaken. After separation of the phases the water layer was discarded. The hexane layer was extracted twice more with 20 ml water and then filtered over anhydrous sodium sulphate.

Column chromatography clean-up. A plug of glass wool was tamped into the bottom of a chromatographic tube. The tube was filled with *ca.* 10 ml hexane. Then 1.00 g silica gel (de-activated with 5% water) was slowly poured in and allowed to settle. The hexane was drained until the level reached the top of the silica gel. A 1-ml volume of the hexane extract was transferred to the column and allowed to sink in. The column was rinsed twice with 1 ml hexane, eluted with 50 ml hexane and the

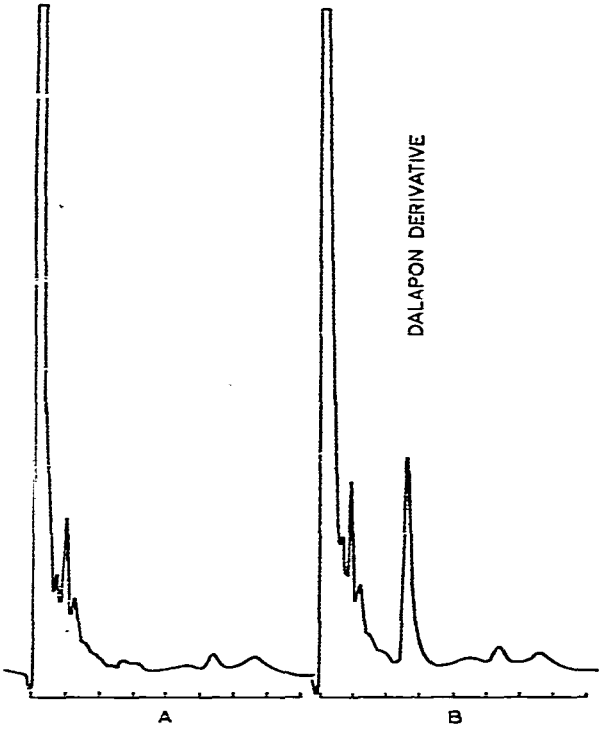

Fig. 1. Chromatogram on a column packed with 3% OV 210 on Gas-Chrom Q (80–100 mesh) of 5 mg potato (A) and 5 mg potato fortified with 0.05 mg/kg dalapon (B).

eluate discarded. Finally, the column was eluted with 70 ml hexane. This eluate was concentrated to *ca.* 5 ml and transferred to a graduated test-tube. The liquid was further concentrated to 1.0 ml, using a gentle stream of dry air. Then an aliquot was injected into the gas chromatograph.

RESULTS AND DISCUSSION

Recovery experiments were carried out by adding known amounts of the dalapon sodium salt to untreated samples prior to the extraction. The results are given in Table I.

The time required to complete the reaction between dalapon and 3-phenylpropanol-1 was determined experimentally by heating the compounds for different lengths of time under the conditions described above. It was found that a reaction time of 5 min or more was sufficient to obtain a quantitative yield of the ester. Therefore, a reaction time of 5 min was chosen in our procedure. After saturation of the 3-phenylpropanol-1, the alcohol contained *ca.* 20% hydrogen chloride gas.

The response of the detector was linear up to nanogram amounts of the 3-phenylpropyl ester of dalapon injected. As little as 0.02 mg dalapon per kg plant tissue and 0.001 mg dalapon per litre natural water can be detected by this method. In Fig. 1 and 2 typical chromatograms are shown of untreated fortified samples of potatoes and natural water, analysed with the method described.

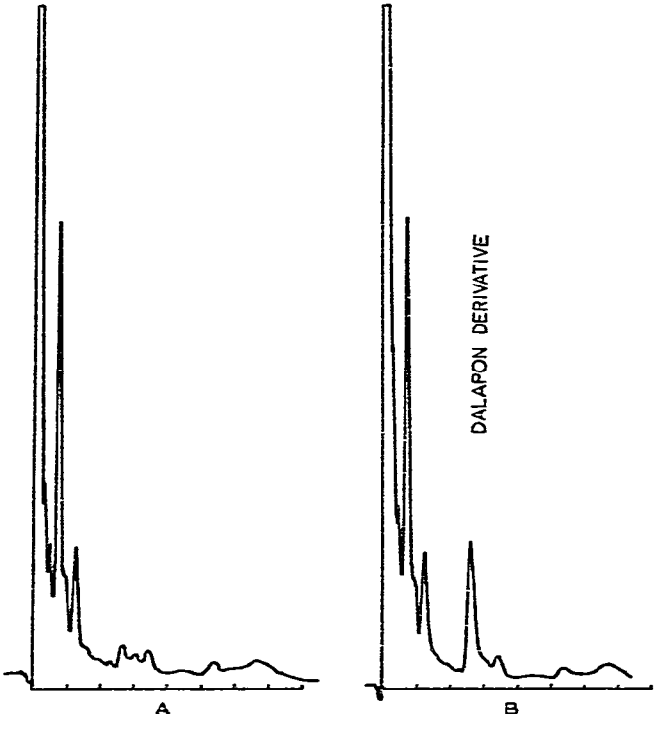

Fig. 2. Chromatogram on a column packed with 3% OV-210 on Gas-Chrom Q (80–100 mesh) of 100 μg natural water (A) and 100 μg natural water fortified with 0.001 mg/l dalapon (B).

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