Residues in Potato Tubers Following Haulm Desiccation with ^{14}C-Diquat

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Diquat, as the dibromide, is the active constituent of 'Reglone' (1) herbicide and is approved, in the United Kingdom, for the desiccation of potato haulms prior to harvesting the tubers. Residues of diquat in the potato tubers, following such treatment, have been shown to be less than 0.05 p.p.m. (2,3). The chemical determination of diquat is specific for that ion, thus residue data can yield no information concerning the presence of any degradation products.

It has already been established that diquat (I) is not metabolically degraded in certain plants (4), but,

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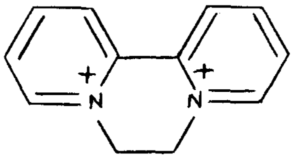
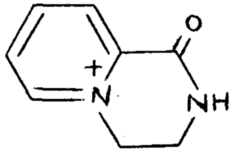
the chemical can undergo photochemical breakdown, and the photochemical decomposition product (II) has been isolated and identified (5). However it is unlikely that this material, or any others formed during the photochemical degradation, will be translocated into the tubers since this breakdown takes place largely on dead, or rapidly dying leaves. It has been shown (6) that no translocation of the photochemical degradation products of the related bipyridyl herbicide paraquat occurs from dead leaves. Furthermore, paraquat salts have been used as potato haulm desiccants but no breakdown products have been detected in the tubers (6).

The work described here was carried out to assess conclusively whether degradation products of diquat do in fact appear in potato tubers. Potato plants, grown under field conditions, were sprayed with ^{14}C-ethylene-bridge-labelled diquat at a rate roughly equivalent to $1\frac{1}{2}$ lb. ion per acre. After harvesting, the total radioactivity in the tubers from each treated plant was measured and converted into "diquat ion equivalents". The quantity of diquat ion present in the tubers was also assayed chemically (7) and compared with the value obtained radiochemically.



$2Br^-$ I



Br^- II

METHODS AND MATERIALS

Six potato plants Solanum tuberosum (var. Majestic) grown under field conditions in a trial plot were each sprayed with 15 ml. solution containing 0.3% (w/v) ^{14}C-ethylene-bridge-labelled diquat ion in 0.1% 'Lissapol' NX. It had been calculated that this rate of application was roughly equivalent to $1\frac{1}{2}$ lb. diquat ion per acre of potato tops. The ^{14}C-diquat used had a specific activity of 4.13 mc/mM. and was obtained from the Radiochemical Centre (Amersham, England) with a radiochemical purity greater than 99%. After two weeks the tubers were harvested, washed to remove adhering soil, dried and weighed. 250 gm. random samples from each of the six batches of tubers were treated according to the procedure for the determination of diquat residues in potato tubers (7). Prior to percolation through the cation-exchange resin the volume of each extract was adjusted to 1000 ml. with distilled water and the radioactivity in the individual extracts determined, using a Tri-Carb liquid scintillation counter (Model 574), by removing 2 x 1.0 ml. aliquots and adding 20 ml. scintillator (1.6% Butyl P.B.D., 17% naphthalene in dioxan). In this way the average radioactivity in each case could be determined and converted to "diquat ion equivalents". The remainder of the extracts (998 ml.) were passed through cation-exchange resin columns which were then washed with 150 ml. 2.5% aqueous ammonium chloride ; 2 x 1.0 ml. aliquots from the washings were checked for radioactivity.

The resin was finally eluted with saturated aqueous ammonium chloride and the diquat ion present in the effluent measured colorimetrically in the usual way (7).

Separate experiments were carried out in which a standard amount of ^{14}C-diquat bromide (9 μgm. ion ; 0.036 p.p.m.) was added to untreated potato tubers (250 gm.), which were then subjected to the above radiochemical and analytical procedures.

RESULTS AND DISCUSSION

TABLE 1

Radiochemical Recovery of 9.0 μgm. ^{14}C-Diquat Ion from 250 gm. Potato Tubers

Sample	Total Activity Recovered		^{14}C not Retained by Resin		^{14}C Eluted by 2.5% NH$_4$Cl		Total ^{14}C not Retained by Resin	
	μgm. Ion	%	μgm. ion	%	μgm. ion	%	μgm. ion	%
1	10.75	119	2.32	21.6	0.02	0.2	2.34	21.8
2	8.78	98	2.88	32.8	0.04	0.5	2.92	33.3
3	7.46	84	1.02	13.7	0.09	1.2	1.11	14.9
4	8.10	90	0.13	1.6	0.05	0.6	0.18	2.2
5	7.63	85	0.64	8.4	0.06	0.8	0.70	9.2
6	6.65	73	0.61	9.2	0.06	0.9	0.67	10.1
Mean	8.23	92	1.27	14.6	0.05	0.7	1.32	15.3

TABLE 2

Chemical Recovery of 9.0 μgm. ^{14}C-Diquat Ion from 259 gm. Potato Tubers

Sample	μgm. Eluted	% Recovery
1	7.50	83
2	5.73	64
3	6.77	75
4	7.81	87
5	7.81	87
6	7.50	83
Mean	7.19	80

The results of the control experiments (Tables 1 and 2), in which known amounts (0.036 p.p.m) of ^{14}C-diquat were added to diced potato tubers indicate that the recoveries of diquat, as determined colorimetrically (Table 2), ranged from 64% to 87%, with a mean value of 80%. The mean radioactivity present in the neutralised tuber hydrolysate was observed (Table 1) to be 92% of the amount added, indicating a loss of approximately 8% at the hydrolysis and filtration stage. A further variable loss of diquat (2% to 33% with a mean of 15%) occurred during percolation of the extracts through the resin and subsequent washing of the resin column prior to elution. It has been suggested (8) that this loss may be due to incomplete retention of the diquat ion on the cationic-exchange resin in the presence of a large excess of naturally occurring cationic substances, which possibly compete with diquat for negative sites on the resin.

In the actual field experiments the total radioactivity in each 1000 ml. of extract was corrected for 92% recovery, while the total diquat, determined chemically in the saturated ammonium chloride effluent, was adjusted for 80% recovery.

The results obtained are shown in Table 3 and indicate that the mean residue of diquat as determined chemically (0.023 p.p.m) is in very good agreement with the total radioactivity present in the tubers (0.021 p.p.m.) calculated as "diquat ion equivalents". Thus all the radioactivity can be accounted for as diquat, confirming the absence of significant amounts of any degradation products.

TABLE 3

Radiochemical and Chemical Determination of ^{14}C-Diquat Ion from the Tubers of Treated Potato Plants.

Sample	Radiochem. Det.^{m} of Diquat Total Activity of Ion. *		Chemical Det.^{m} of Diquat Ion +	
	μgm.	p.p.m.	μgm.	p.p.m.
1	11.85	0.047	11.72	0.046
2	41.0	0.016	4.30	0.018
3	3.38	0.014	4.30	0.018
4	2.97	0.012	4.88	0.020
5	4.29	0.017	6.10	0.025
6	4.29	0.017	2.44	0.010
Mean	5.13	0.021	5.62	0.023

* Corrected for 92% recovery

\+ Corrected for 80% recovery

The diquat photochemical degradation product (II) being much less polar than diquat (I) can be eluted from the cation-exchange resin with 2.5% aqueous ammonium chloride. Negligible activity was found in the ammonium chloride wash and this is taken as further evidence for the absence of decomposition products in the tubers of potato plants desiccated with diquat.

CONCLUSIONS

When potato haulms are desiccated with ^{14}C-diquat at a rate roughly equivalent to 1½ lb. diquat ion per acre, no degradation products of the chemical appear in the harvested tubers.

ACKNOWLEDGEMENTS

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REFERENCES

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