Journal of Chromatography, 100 (1974) 247–248

CHROM. 7675

Note

Sodium azide–iodine reagent for the detection of 1,4-oxathiin derivatives by thin-layer chromatography

F. I. ONUSKA and M. E. COMBA

Analytical Methods Research Subdivision, Canada Centre for Inland Waters, Water Quality Branch, P.O. Box 5050, 867 Lakeshore Road, Burlington, Ontario, L7R 4A6 (Canada)

(Received May 2nd, 1974)

A new group of systemic fungicides (1,4-oxathiins) are becoming commercially important for seed pre-treatment of forage crops of soya bean, groundnut, oats, barley, wheat plants, cotton, potatoes and sugar beets.

Vitavax (Uniroyal Canada Ltd.), 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide (I), and its analogues such as 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxamide (II), 5,6-dihydro-2-methyl-1,4-oxathiin-3-N-methyl carboxamide (III) and 5,6-dihydro-2-methyl-1,4-oxathiin-3-*p*-methylcarboxanilide (IV) were studied by thin-layer chromatography (TLC). The chemical structures of the above compounds are given in Fig. 1.

Prior to conducting photodegradation studies of the oxathiin derivatives, it was necessary to investigate their purity and chromatographic behaviour. Optimum separation of oxathiin derivatives was obtained by TLC in two solvent systems. The compounds were detected as white or yellowish spots on a blue background when the developed sheet was sprayed with sodium azide–iodine reagent. This reagent gave a more sensitive detection limit than that described by Tripathi and Bhaktavatsalam[1].

The compounds employed were prepared in our laboratory according to the procedure outlined by Kulka *et al.*[2].

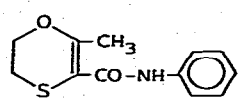
EXPERIMENTAL

Thin-layer sheets, pre-coated with a 100-μm layer of silica gel with a fluorescent indicator (Eastman Chromatogram Sheet 6060) were used throughout the study.

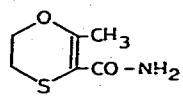
One microlitre of each compound was spotted, separately or together, 3 cm from the bottom of the sheet and developed for 10 cm in a saturated chamber using the solvent systems listed in Table I. The chromatogram was dried at room temperature in a forced-air hood and sprayed with sodium azide–iodine reagent (3 g of sodium azide in 100 ml of 0.1 *M* iodine solution)[3]. A more sensitive detection and higher contrast was obtained by spraying the sheet first with starch solution.

RESULTS AND DISCUSSION

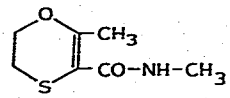
Table I gives the $R_F \times 100$ values for 1,4-oxathiin derivatives in two different



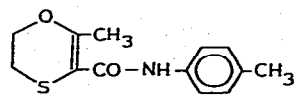
(I)



(II)



(III)

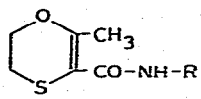


(IV)

Fig. 1. Chemical structures of 1,4-oxathiin derivatives.

TABLE I

$R_F \times 100$ VALUES OF THE 1,4-OXATHIIN DERIVATIVES



R	*Benzene–ethyl acetate (9:1)*		*Benzene–acetonitrile (8:2)*	
	$R_F \times 100$	*Standard deviation (%)*	*$R_F \times 100$*	*Standard deviation (%)*
H	7	2.0	20	1.5
CH_3	21	1.7	36	3.5
C_6H_5	42	1.7	57	1.5
p-Me-C_6H_4	44	1.9	59	2.5

solvent systems. These results are average values for eight replicates. The spots were easily identified (except for pair I and IV) and gave good reproducibility.

From Table I it would appear that several systems would separate the compounds; however, when considering the time involved and the desire to have all compounds move from the start, benzene–acetonitrile (8:2) was chosen as the optimum solvent for use in photodegradation and clean-up studies. This solvent system gave a good separation in approximately 35 min.

The utilization of Feigl's reagent for the detection of 1,4-oxathiins was based on the ability of bivalent sulphur to catalyze the reaction between iodine and azide ion, forming colourless iodide and evolving nitrogen.

The lower limit of detection for these compounds, under the experimental conditions used, was about 200 ng. In comparison with silver nitrate–bromophenol blue reagent[1], the sensitivity was at least one order of magnitude better in favour of the sodium azide–iodine reagent.

REFERENCES

1 R. K. Tripathi and G. Bhaktavatsalam, *J. Chromatogr.*, 87 (1973) 283.
2 M. Kulka, D. S. Thiara and W. A. Harrison, *U.S. Pat. 3,393,206*, 1968.
3 F. Feigl, *Qualitative Analysis by Spot Tests*, Elsevier, New York, 1966, p. 608.