Journal of Chromatography, 175 (1979) 222–223

CHROM. 11,827

Note

Thin-layer chromatographic detection of herbicidal thiocarbamates and their sulphoxide and sulphone metabolites

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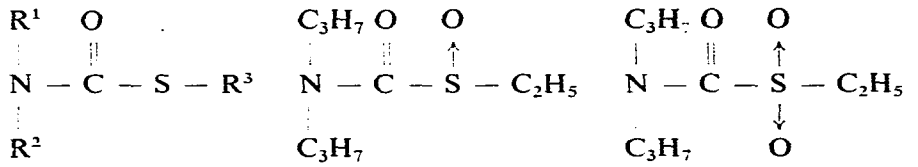
(First received December 6th, 1978; revised manuscript received February 27th, 1979)

For the elucidation of the mode of action of the herbicidal thiocarbamate EPTC (I: $R^1 = R^2 = Pr$; $R^3 = Et$), we followed its molecular fate in different weed species. Prior to conducting metabolic studies the chromatographic behaviour of EPTC and two of its metabolites (II and III) possibly responsible for phytotoxic action[1] was studied. The thermal instability of these compounds, however, greatly limits the applicability of gas–liquid chromatography[2], and with thin-layer chromatographic methods only 1–25 μg of thiocarbamate herbicides[3–6] and 2 μg of II and III can be detected[3].



I II III

The analysis described here permits the rapid separation of EPTC, II and III without interferences from plant co-extracts, and the sensitive detection of thiocarbamate herbicides, II (a member of a new class of herbicides)[2] and III on thin-layer plates.

EXPERIMENTAL

For each developing solvent system, 10-μl standards of I, II and III (1, 2.5, 5, 10 and 25 μg/ml in acetone) were spotted both separately and together at 2-cm intervals and 2.5 cm from the bottom edge of pre-coated silica gel sheets (Silufol; Kavalier, Sklárny, Czechoslovakia) and developed in a saturated chamber using acetone, acetonitrile, diethyl ether, ethyl acetate[3], acetone–*n*-hexane[3], diethyl ether–*n*-hexane,[3] ethyl methyl ketone–light petroleum (b.p. 80–90°)[7], acetone–acetonitrile–cyclohexane[7] and acetone–cyclohexane–ethanol[7] mixtures as solvent. After a 10-cm run, the sheets were removed from the chamber and dried at room temperature. The

dried sheets were sprayed with a 0.5% solution of 2,6-dibromo-N-chlorobenzoquinone imine or N,2,6-trichlorobenzoquinone imine (Gibbs reagents) in acetic acid, and heated in an oven for 10 min at 105–110°.

RESULTS AND DISCUSSION

After spraying with Gibbs reagents and heating, yellow spots of thiocarbamate herbicides and II and a pink spot of III emerged against a white background.

Solvent systems that resulted in adequate separations in 1 h or less were cyclohexane–acetone–acetonitrile (16:3:1) (R_F 0.56, 0.33 and 0.18 for EPTC, III and II, respectively) and light petroleum–ethyl methyl ketone (9:1) (R_F 0.72, 0.16 and 0.42 for EPTC, III and II, respectively). The limit of detection, determined after development, was 0.05 μg for EPTC, Pebulate (R^1 = Et, R^2 = Bu, R^3 = Pr), Molinate (R^1R^2 = hexamethylene, R^3 = Et), Butylate (R^1 = R^2 = *i*-Bu, R^3 = Et) and Cycloate (R^1 = cyclohexyl, R^2 = R^3 = Et), and 0.1 μg for II and III.

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