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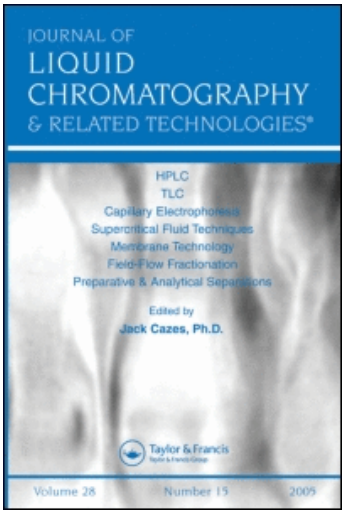

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STRUCTURE AND TLC MOBILITY RELATIONSHIPS FOR TEBUTHIURON AND RELATED THIADIAZOLES

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ABSTRACT

Tebuthiuron and structurally-related thiadiazoles are separated by thin-layer chromatography on silica gel plates in two developing solvent systems. Relationships between chemical constitution and chromatographic mobility are discussed.

INTRODUCTION

The 5-substituted 1,3,4-thiadiazole ureas are of interest as possible herbicides (1). Tebuthiuron, 1-(5-t-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea, is an herbicide developed in these laboratories. Also known as GRASLAN®, SPIKE®, or PERFLAN®, the compound is effective for broad spectrum weed control. It has been found useful in forests and rangeland (2), in crops (3, 4) and is effective for control of woody plants (5, 6).

An organic synthesis of tebuthiuron has been described (1) as has been an improved synthesis of 1,3,4-thiadiazoles in general (7). However, little chromatographic work with tebuthiuron and related substances has been reported. HPLC of selected herbicides including tebuthiuron has been discussed (8) as well as GC analysis of the latter with its metabolites in grass and sugarcane (9). In a toxicology study of tebuthiuron metabolism

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in some animals, TLC of the herbicide and metabolites was reported (10).

In this work, separation of tebuthiuron from some structurally related thiadiazoles by TLC is reported. Mobilities of the spots are discussed with reference to structural features. With the exception of this work and (10), no reports of TLC behavior of thiadiazoles are known to exist.

EXPERIMENTAL

Apparatus

Thin-layer plates were precoated silica gel F_{254}, 20 cm x 20 cm with 0.25 mm adsorbent layer (E. Merck, available from Brinkmann Instruments, Inc., Westbury, N. Y.). Spotting pipets were disposable (Drummond type, distr. by Ace Glass Co., Louisville, Ky.). Rectangular, heavy-wall glass tanks 30 cm x 10 cm x 28 cm (Brinkmann) were used as developing chambers. The plates were viewed (after development and drying) under short-wave UV (254 nm) light using a Chromato-Vu (Ultra-Violet Products, Inc., San Gabriel, Ca.).

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Reagents

Reagent grade solvents were used in these experiments. Methyl alcohol was used to dissolve the samples while 30 ml/75 ml acetone-chloroform (System A) or 70 ml/30 ml diethyl ether-acetonitrile (System B) were used to charge the developing tanks at each use. All test samples were from in-house sources.

Thin-Layer Chromatography

The adsorbent layer of each TLC plate was scored 15 cm above the starting line which was 2.5 cm from the bottom of the plate. One hundred micrograms of each compound was spotted in

adjacent lanes across the plates. Developing solvents were charged into the glass chambers lined on the sides and back with Whatman No. 1 filter paper, and 30 minutes equilibration time was allowed before use. Plates were developed at room temperature until the solvent reached the scored line. Plates were removed, allowed to dry at room temperature, and were viewed under 254 nm light.

RESULTS AND DISCUSSION

In Table 1, all compounds with the exception of VI have the general formula shown. Compound IV and the triazoline VI (structure shown complete in Table 1) are isomers.

While IV and V (tebuthiuron) contain t-butyl substituents as R_1, R_2 in IV is a secondary amine and in V is more tertiary-amine-like. The greater mobility of V may be explained by the low polarity (11) and adsorption capacity (12) of tertiary vs secondary amines. Mobilities of amines are also increased as chain length on the amino group increases (12) and with aliphatic substitution on the chain (13). Similar results were reported for some thiadiazole ureas and their metabolites (10).

Note that R_f values are very low for compounds I - III in System A while System B starts to differentiate III from the others. Low R_f's may be due to solubility considerations, but III is more mobile as expected for reducing the amino character of the molecule (14).

In Compounds III and V, substituent R_2 is constant but R_1 is varied. The aliphatic t-butyl group has the effect of lowering the polarity and thus increasing the mobility of the spot (14). The same argument applies to II and V. V is much more mobile than II because V is more aliphatic.

Triazoline Compound VI has a much greater mobility than its isomer IV which may be accounted for by two facts. VI lacks a conjugated double-bond system (15) and a secondary amine group at the 5-position on the ring.

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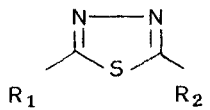
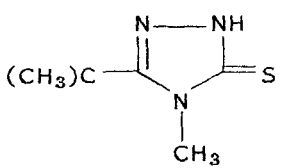
TABLE I.

STRUCTURES AND TLC R_f VALUES FOR TEBUTHIURON AND RELATED THIADIAZOLES



Cmpd.	Substituent R_1	Substituent R_2	Rf in System A	Rf in System B
I	$-NHCH_3$	$-NHCH_3$	0.03	0.04
II	$-NHCH_3$	$-(NCH_3)CO(NHCH_3)$	0.03	0.07
III	$-(NCH_3)CO(NHCH_3)$	$-(NCH_3)CO(NHCH_3)$	0.07	0.15
IV	$-C(CH_3)_3$	$-NHCH_3$	0.18	0.35
V	$-C(CH_3)_3$	$-(NCH_3)CO(NHCH_3)$	0.30	0.55
VI			0.51	0.85

In addition to the related materials described in Table I, all starting materials and intermediates from the synthesis of tebuthiuron may be separated from the latter in either of the TLC systems.

ACKNOWLEDGEMENTS

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