vom Adsorbens und Laufmittel durch die zunehmende Zahl an Hydroxylgruppen erheblich vergrössert. Methoxylgruppen können die R_F-Werte sowohl verringern als auch erhöhen, führen jedoch bei hydroxylhaltigen Verbindungen in *o*- und *p*-Stellung zur Ketonhydrazongruppierung stets zu einer Abnahme der Adsorption. C-Methylgruppen sind ohne wesentlichen Einfluss auf das chromatographische Verhalten. Nitroguanylhydrazone von Aldehyden zeigen gegenüber denen von Ketonen eine grössere Adsorptionsaffinität. Der Austausch der am Benzolkern substituierten Aldehydfunktion gegen die O=CH—CH=CH— Gruppierung führt zu grösseren R_F-Werten.

Methodik

Für die Herstellung der Dünnschichtplatten (20 × 20 cm) werden Aluminiumoxid D (Chemiewerk Greiz-Döhlau) bzw. Magnesiumsilikat "Woelm" benutzt. Bei Verwendung von Kieselgel als Adsorbens sind die Trenneffekte gering. Die Platten beschichtet man manuell mit 12 g Aluminiumoxid in 14 ml Wasser oder 5 g Magnesiumsilikat in 15 ml Wasser nach der von LEES UND DE MURIA[6] angegebenen Methode und aktiviert anschliessend 30 Min. bei 120°. Die Nitroguanylhydrazone werden in 0.1-proz. dimethylformamidhaltiger Lösung aufgetragen und bei Kammersättigung bis zu einer Laufhöhe von 13 cm chromatographiert. Zur Detektion verwendet man Rhodamin B[7] im U.V.-Licht. Falls die ursprünglichen Carbonylverbindungen säurestabil sind, können die Platten mit 20-proz. HCl intensiv besprüht und anschliessend 20 Min. auf 120° erhitzt werden. Dabei erfolgt hydrolytische Spaltung unter Rückbildung der Ausgangsverbindungen, die sich mit 2,4-Dinitrophenylhydrazin anfärben lassen.

Institut für Organische Chemie an der Bergakademie Freiberg/Sa. (Deutschland)

WOLFGANG WILDENHAIN
GÜNTER HENSEKE

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Eingegangen den 3. November 1966

The detection of thiram by thin layer chromatography

During work involving the wheat coleoptile straight growth bioassay, it was found necessary to test the wheat seed for the presence of the fungicide Thiram, bis(dimethylthiocarbamoyl) disulphide. Chloroform washings of the seed and Thiram standards in chloroform were spotted on to thin layers of Silica Gel G, developed in methanol–water (1:1) in an S chamber[1] and sprayed with a sodium azide and iodine solution (3 g sodium azide in 100 ml 0.1 *N* iodine)[2]. The decolorization of the spray by spots containing Thiram was temporary but clear enough to warrant further investigations of sensitivity.

It was found that solvents containing considerable amounts of water could not be used to develop spots containing 5 μg or more of Thiram without severe streaking. A solvent comprising chloroform–carbon tetrachloride (3:1) saturated with water was most convenient, enabling adequate loading and producing well defined spots after a short development time, on thin layers air dried overnight at 35°. Although the sodium azide and iodine spray is very sensitive for Thiram on silica gel, the background colour fades so rapidly that spots with < 1 μg become invisible in seconds. Immediate subsequent spraying with a 2% starch solution stabilizes the remaining colour. Much more sensitive detection with more permanent colour and higher contrast can be obtained by spraying the thin layers first with starch solution until they are opalescent and then with the sodium azide and iodine solution[3]. This procedure immediately shows up Thiram as white spots on a blue-black background, although 15–30 min may be required before spots containing less than 1 μg are fully developed. The blue-black background fades to light brown in several hours but may be darkened again by simply spraying with water if maximal contrast is needed for photographic recording.

Provided care is exercised in limiting the size of the spot to *ca.* 1 mm diameter during application, as little as 0.01 μg may be detected with this system. R_F values measured from the spot centre vary little over a thousand-fold concentration range—from 0.190 for 0.01 μg to 0.196 for 10 μg samples. The spots expand during migration, and the spot diameter, if initially limited to 1 mm, may be used for visual estimation of unknown amounts of Thiram with an accuracy of $\pm$ 0.5 μg, by comparison with a range of concentration standards.

A commercial preparation of 75% Thiram applied to wheat and barley seed at the rate of *ca.* 1 part per 500 (2 ounces to the bushel) could be detected clearly in 1 g samples of whole or finely ground seed. By washing the seed for 1 min in 10 ml chloroform and preparing chromatograms of the washing as described above, spots corresponding to Thiram were observed. Untreated samples produced no spot. The chromatograms prepared from the barley sample, which had been stored for several months after treatment, also showed faint bands indicative of some chemical change or degradation in Thiram induced by prolonged contact with the seed. Complex formation of Thiram with amino acids is suggested in recent work[4,5].

Treated and untreated *Brassica* seed samples were also tested after Thiram had been applied at the rate of 1 part per 5,000. Although this seed had a high content of sulphur compounds which could possibly interfere with the test and the rate of application was some ten-fold less than that commonly used in agricultural practice, only one spot, corresponding to Thiram, was detected.

Plant Chemistry Division, D.S.I.R.,
Lincoln (New Zealand)

N. G. PORTER

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Received December 28th, 1966