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LOW-TEMPERATURE THIN-LAYER CHROMATOGRAPHY FOR DETECTION OF POLYBUTENE CONTAMINATION IN VOLATILE OILS

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SUMMARY

A method for the detection of polybutene contamination in volatile oils is described. The procedure involves low-temperature thin-layer chromatography followed by detection with a chromogenic reagent. The method gave qualitative detection of 2 μg of polybutene in eight of nine oils investigated. The procedure could be used in conjunction with thin-layer densitometry for quantitative assay of polybutene residues in six of the nine oils studied.

INTRODUCTION

Polybutenes are butylene polymers consisting of high-molecular-weight monoolefins (85–98 %), the balance being isoparaffins. They are stable, non-drying sticky viscous liquids and have been shown to possess insecticidal and fungicidal properties[1]. Polybutene emulsions have been used as pest control agents, but the primary utilization of these polymers in pesticides has been as additives to conventional spray formulations, where they function as stickers.

Polybutene residues are extremely persistent[2], and it was considered that they could provide a problem on crops which were to be solvent extracted or steam distilled. The presence of polybutenes in a volatile oil would reduce its commercial value, and the increased use of polybutenes suggested that a method was needed for their detection and assay in volatile oils.

Polybutene residues can be assayed by thin-layer densitometry[3], but difficulty was experienced in obtaining systems for the discrete isolation of polybutenes from the components of many volatile oils. Such a separation is essential for densitometric or gravimetric determinations and is also needed for qualitative assessment. Low-temperature thin-layer chromatography (TLC) was shown to improve separations, and provided a method suitable for detection and assay of polybutenes in several volatile oils.

EXPERIMENTAL

Materials

The polybutenes used in this study were from the Indopol range (Amoco

Chemical, Chicago, Ill., U.S.A.). The following compounds were selected (average molecular weight in brackets): L-10 (320), L-50 (420), H-50 (750), and H-300 (1290). The polymers were applied to plates as solutions in analytical grade *n*-hexane.

The volatile oils used were commercial samples obtained from Penick (Chicago, Ill., U.S.A.), Bush, Boake and Allen (Quebec, Canada), and Fritsche (Toronto, Canada). Samples were also obtained by steam distillation of peppermint plants which previously had been sprayed with polybutene emulsions.

Silica gel GF_{254} (Brinkmann, Rexdale, Ontario, Canada) was used as TLC adsorbent, with *n*-hexane as the running solvent. A 1% (w/v) solution of vanillin in concentrated sulphuric acid was used as the chromogenic reagent.

General procedure

TLC plates (20 × 20 cm) were coated with silica gel GF_{254}, 250 μm thick, using a Quickfit applicator and a slurry containing 25 g of adsorbent in 50 ml of distilled water. The plates were air dried at room temperature for 16 h prior to use. Stock solutions of the oils (10%, v/v) and the polybutenes (1%, w/v) were prepared in *n*-hexane.

For chromatographic separation, the solutions were applied using Hamilton micropipettes. The air-dried plates were spotted before equilibration with the *n*-hexane developing solvent at −20° for 2 h. Following equilibration, the plates were chromatographed at −20° using the supersaturated method of Stahl[4]. The solvent front was allowed to advance 15 cm from the origin, after which the plates were removed from the tank and air dried for 10 min. The plates were sprayed with 1% vanillin in concentrated sulphuric acid and then heated at 110° for 10 min. They were then examined in daylight and in a Chromato-Vue Cabinet (Canlab, Montreal, Canada) with ultraviolet light.

The oils examined were coriander, eucalyptus, geranium, lavender, lemon, orange, peppermint, rose, and spearmint. The limits of detection of polybutenes in these oils were determined by applying a range of weights of the polymers, from 1 to 10 μg, mixed with oil or oil solution up to the equivalent of 20 μl of pure oil. After low-temperature TLC, the plates were assessed to determine whether polybutene contaminants of these oils could be detected qualitatively or assayed by thin-layer densitometry.

Oil was obtained from glasshouse-grown peppermint plants which had been sprayed on several occasions with 2% (w/v) polybutene emulsions[5]. Oil samples were also obtained from coriander and spearmint which had been field grown and sprayed twice with 2% (w/v) polybutene emulsions. After steam distillation, low-temperature TLC was used to detect the presence of polybutenes in the oil samples.

RESULTS

Typical chromatograms of the separation of polybutene L-50 from the various oils are shown in Fig. 1. Similar results were obtained with the other polybutenes, although the higher polymers tended to produce more elongated spots. Results for the limits of detection of polybutene in samples of oil spiked with polybutenes are given in Table I.

It was found that air drying the plates and adequate equilibration at low

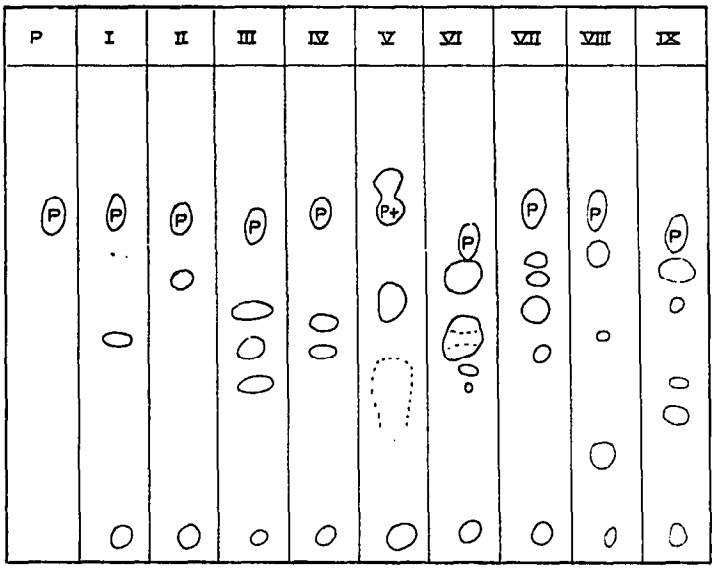

Fig. 1. Thin-layer chromatogram of polybutene L-50 in volatile oils. Adsorbent, silica gel GF_{254}: mobile solvent, *n*-hexane. Development at −20°. Samples I–V: coriander, eucalyptus, lemon, orange, rose, respectively, each 5 μl; samples VI–IX: geranium, lavender, peppermint, spearmint, respectively, each 1.25 μl. Each sample contains 5 μg polybutene L-50 (P). P+ = polybutene plus compounds from oil. Chromogenic reagent: vanillin (1%) in conc. sulphuric acid, heated at 110°.

temperature prior to development of the chromatogram were essential for production of satisfactory separations of the polybutenes from other oil constituents. The techniques described provided separations which were satisfactory for the densitometric assay of polybutenes in oils of coriander, eucalyptus, lemon, and orange. Difficulty was experienced in obtaining a good baseline for the assay of lavender and peppermint, due to the proximity of the polybutene spot to one of the oil components. Separation was inadequate for the assay of polybutenes in rose, geranium and spearmint, although the compound could be detected qualitatively in the latter two oils.

TABLE I

LIMITS OF DETECTION FOR POLYBUTENE IN OILS

No.	*Oil*	*Lowest concentration of polybutene detectable in oil**
I	Coriander	2 μg/20 μl
II	Eucalyptus	2 μg/15 μl
III	Lemon	2 μg/15 μl
IV	Orange	2 μg/15 μl
V	Rose	Incomplete separation
VI	Geranium	2 μg/2.5 μl
VII	Lavender	2 μg/10 μl
VIII	Peppermint	2 μg/5 μl
IX	Spearmint	2 μg/2.5 μl

* Higher volumes of oil cause streaking or incomplete separation.

Polybutenes were present in all the oil samples obtained from sprayed plants, and were detected by the low-temperature TLC technique.

DISCUSSION

The increased use of polybutenes in pesticide formulations has resulted in the need for improved assay procedures for residues. Polybutenes can be assayed by thin-layer densitometry, but difficulties may be experienced in obtaining satisfactory separations from other compounds on a TLC plate. This problem was particularly apparent in the detection and assay of polybutene residues in volatile oils. The results show that low-temperature TLC provides a marked improvement over separations obtained at room temperature. A further advantage was that the polybutenes produced more compact spots in low-temperature TLC, which was useful in cases where densitometric assay was to be used.

Equilibration of the tank was found to be essential in obtaining consistent results and temperature equilibration of the plate was important, as shown by Stahl[6].

The R_F values obtained for the components of the volatile oils were found to be reduced in low-temperature TLC, but the reduction was not as great with the polybutenes. Rose oil was an exception among the oils tested, and the method proved unsatisfactory for separation of polybutenes from the highest R_F component of this oil.

Many polybutenes are extremely sticky, and are undesirable as contaminants in a volatile oil. Qualitative detection in an oil would be sufficient in many cases, and the techniques described in this paper were satisfactory for this purpose in the majority of oils examined. Quantitative determination by densitometric methods requires a good separation of compounds on a plate. This was readily achieved with coriander, eucalyptus, lemon, and orange oils. Modification of the temperature and changes in the solvent did not improve the separations obtained with lavender and peppermint oils, and difficulty was experienced in densitometric assay of polybutene in these oils. The chromatographic conditions were satisfactory for qualitative detection of polybutenes in geranium and spearmint oils, but no conditions were found which would provide for quantitative TLC determination in either of these products.

Insecticide residue investigations on volatile oils have been reported[7,8], but these have not included polymeric materials of the polybutene type. The results obtained with low-temperature TLC showed that polybutene residues on sprayed crops were persistent, and that polybutenes can be detected in the oil obtained by steam distillation of such crops.

The method would also be applicable to other situations, such as the detection of polymeric contaminants of solvents, which can cause interference in spectrophotometric assays[9].

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REFERENCES

1 Amoco Chemical Corporation, *Indopol Polybutenes, 12F* (1967).
2 R. W. Downing and K. Williams, *Can. J. Plant Sci.*, 43 (1963) 416.
3 C. J. Briggs and S. B. Challen, *J. Sci. Food Agr.*, 18 (1967) 602.
4 E. Stahl, *Arch. Pharm.*, 292 (1959) 411.
5 C. J. Briggs, *Planta Med.*, 24 (1973) 120.
6 E. Stahl, *Angew. Chem., Int. Ed. Engl.*, 3 (1964) 784.
7 H. Starr, U. Kiigemagi and C. C. Terriere, *J. Agr. Food Chem.*, (1963) 482.
8 H. Beitz, F. Seefeld and F. Park, *Pharmazie*, 28 (1973) 270.
9 B. M. Cumpelick, *Drug Cosmet. Ind.*, 113 (1973) 44.