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A note on the determination of dichlorophen and hexachlorophene in mixtures

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Dichlorophen and hexachlorophene can be separated and estimated rapidly. Separation was achieved on thin-layer chromatograms using ethyl acetate containing 10% v/v of methanol and silica gel, the appropriate areas for each compound being collected and eluted with methanol. The absorbances of these solutions at 286 and 299 nm respectively were measured and compared with standard curves. Application of the method to several commercial formulations was successful.

The separation from mixtures of dichlorophen and of hexachlorophene has been attempted by Clements & Newburger (1954) who isolated and purified the compounds from a commercial product by extractions and estimated them by ultraviolet absorption. Derry, Holden & Newburger (1961) separated mixtures of *p*-hydroxybenzoates, dichlorophen and hexachlorophene by partition chromatography followed by spectrophotometric determination. Bravo & Hernandez (1962) claimed to have separated mixtures of dichlorophen and hexachlorophene by thin-layer chromatography using silicic acid and n-heptane saturated with glacial acetic acid. After elution from the plates the isolated compounds were assayed by ultraviolet spectrophotometry. We were unable to reproduce the method of Bravo & Hernandez (1962) so a new chromatographic procedure was devised.

EXPERIMENTAL

Materials

Dichlorophen (May & Baker, Dagenham) was crystallized once from aqueous methanol and twice from toluene: m.p. 177–8°, E (1%, 1 cm) at 286 nm in methanol solution, 200·0.

Hexachlorophene (R. A. Cripps & Son, Brighton) was crystallized twice from aqueous ethanol and three times from benzene: m.p. 167°, E (1%, 1 cm) at 299 nm in methanol solution, 150·0.

Methanol and ethyl acetate were redistilled.

Procedure

Glass plates (8 × 15 cm) were coated with a Merck silica gel PF_{254} layer, 500 μm thick, according to Stahl (1956). A known amount (40–100 mg) of dichlorophen and hexachlorophene was dissolved in 10 ml of methanol and 100 μl of this solution applied to an activated plate (110° for 30 min) as a streak 1·5 cm from the bottom and sides of the plate using a Hamilton Repeating Dispenser microsyringe.

The chromatogram was run at room temperature (about 22°) using ethyl acetate containing 10% v/v methanol in a glass tank presaturated with the developing solvent until the solvent front was 1 cm from the top of the plate.

The plate was then removed from the tank and dried at 60° for 10 min, and subsequently examined under a short wave ultraviolet lamp, when the substances appeared as dark blue–purple areas against a bright green fluorescent background giving Rf values for dichlorophen of 0·93 and for hexachlorophene of 0·51.

The appropriate areas were scraped off and collected in a 'thimble' using a Quickfit T.L.C. Spot Remover and extracted with methanol (40 ml) in a Soxhlet apparatus for 30 min. The resulting methanol solution was cooled to room temperature and adjusted to 50 ml.

The absorbance of the dichlorophen extract was measured at 286 nm and the hexachlorophene extract at 299 nm using a Hilger and Watts Uvispek spectrophotometer, and the values obtained were interpolated in the standard curves.

The reference solution for use in the spectrophotometer was prepared analogously, using silica gel from the same plate.

Assay of commercial preparations

Product 1 was an aerosol spray containing dichlorophen 0·25%, hexachlorophene 0·25%, undecenoic acid 2·5%. For this assay, a known amount of the aerosol was collected and the propellant allowed to evaporate, methanol was added and the volume adjusted to give an approximately 1% w/v solution. The sample volume used was 100 μl.

Product 2 was a foot powder containing dichlorophen 0·2%, hexachlorophene 0·5%, sodium polymetaphosphate 4%, light kaolin 20%. Approximately 10 g of the powder was extracted with methanol for 1 h in a Bolton-Revis apparatus, sufficient dichlorophen and hexachlorophene was added and the volume adjusted to give 50 ml of an approximately 1% solution of each component. Sample volume used was 100 μl.

Product 3 was a shampoo containing γ-hexachlorocyclohexane 0·2% and hexachlorophene 1·0%. 100 μl of the shampoo was applied directly to an activated plate.

RESULTS

Ten mixtures containing 5 to 11 mg/ml of dichlorophen and hexachlorophene were assayed and the deviation % of theoretical was $\pm$1·17% for the dichlorophen and $\pm$1·15% for the hexachlorophene. The assay procedure applied to an aerosol, a foot powder, and a shampoo gave 99·4 and 99·7% of the stated amount of dichlorophen in the aerosol and powder respectively and 101·5, 99·6 and 99·5% for hexachlorophen in the three products.

DISCUSSION

Bravo & Hernandez (1962) used a solvent system consisting of n-heptane saturated with glacial acetic acid, since these are completely miscible, no idea of the composition of their developing solvent could be deduced. Saturation of the n-heptane with acetic acid B.P. did not lead to the separation of the dichlorophen and hexachlorophene, in fact, the spots hardly moved off the baseline.

Separation was achieved on plates coated with Merck silica gel PF_{254} using eight solvent systems, most having some disadvantage compared with that chosen: ethyl acetate containing 10% v/v of methanol. Systems containing benzene (95) or toluene (90) with acetic acid (to 100) were held tenaciously on the silica gel after

development and consequently interfered with the subsequent absorption measurements. On drying the plates after development with those systems and another containing acetic acid 1% v/v, the spots or streaks quickly turned a dark yellow. The system ethyl acetate–methanol 90:10 was the most suitable since both solvents can be obtained pure, are readily volatile and cause no discolouration of the compounds over short periods of time.

Both compounds were determined at their maxima, this being 286 nm for dichlorophen and 299 nm for hexachlorophene in methanol solution, whereas Bravo & Hernandez (1962) determined both compounds at 290 nm.

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