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Inclusion of Acaricides by Complexation with β-Cyclodextrin*

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Abstract. Many synthetic pesticides (herbicides, insecticides, fungicides etc.) can be complexed with cyclodextrins. The inclusion complexes of acaricides such as Fenson, Chlorfenson and Genite were prepared. The formation of inclusion complexes was established by UV and X-ray diffraction techniques. The host-to-guest ratio was determined by UV spectral and GLC methods.

Key words: β-Cyclodextrin (β-CD), acaricide, dimethylformamide (DMF), spectrophotometry, X-ray diffraction, GLC.

1. Introduction

Pesticides can be complexed with cyclodextrins just as drug molecules or food flavours [1]. This 'molecular encapsulation' frequently results in advantageous modifications of the properties of complexed substances [2, 3]. However, in continuation of our study on encapsulation of organic molecules with β-CD [4], a few acaricides were subjected to inclusion studies. Inclusion is expected to lend stability to such degradable and sensitive (to light, heat, oxygen etc.) pesticides [5–10].

2. Experimental

2.1. Materials and Methods

β-CD (Fluka) was used for this study. Fenson (*p*-chlorophenyl benzenesulfonate) (**I**), Chlorfenson (4-chlorophenyl-4-chlorobenzenesulfonate) (**II**), and Genite (2,4 dichlorophenyl benzenesulfonate) (**III**) were synthesised in the laboratory using the Hinsberg method [11] and characterized fully prior to inclusion studies.

Melting points were taken on a Gallenkamp melting point apparatus after drying the inclusion complex to a constant weight. Benzene was used as a mobile phase for TLC. A Shimadzu Graphicord UV-240 spectrophotometer was used for spectrophotometric studies. UV spectra of inclusion complexes were obtained by dissolving 10 mg of complex in 10 mL of spectral grade DMF. X-ray pow-

* This paper is dedicated to Professor A.B. Kulkarni on his 75th birthday.
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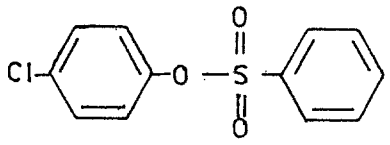
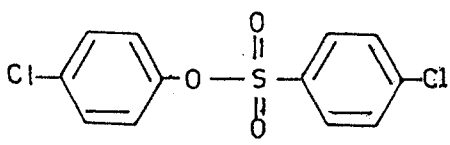


(I)



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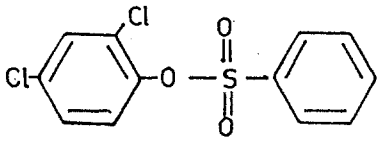

(III)

Chart 1.

der diffractograms were recorded on a Rigaku Geigerflex D/max-B series X-ray diffractometer. Samples were prepared in the form of cakes after being ground to 200 mesh and were scanned in the range of 5°–45° 2θ. Gas liquid chromatographic analysis was done on a Netel Omega-QC gas chromatograph. For GLC dibutyl phthalate was used as an internal standard and DMF was used for declathration prior to the analysis.

Operating conditions for GLC:

Column	3% OV-17 on chromosorb WHP,60/100 mesh, 2 m, 1/8″O.D., S.S.
Injector/Detector (FID) temperature	250 °C
Column temperature	230 °C
Carrier gas flow	Nitrogen 40 mL/min.

2.2. Preparation of Inclusion Complexes

β-CD was dissolved in the minimum amount of distilled water (slight heating was necessary) and to this solution were added the pesticides shown in Chart 1, such as Fenson (**I**), Chlorfenson (**II**) and Genite (**III**) in 1 : 4 mole proportions at 80 °C to obtain a homogeneous solution. The contents on further mixing at 15 °C for 2 h left a residue, which was cooled and kept overnight to settle. The inclusion complex so formed was filtered, washed with acetone to remove the untrapped feed and was dried in an oven at 100 °C.

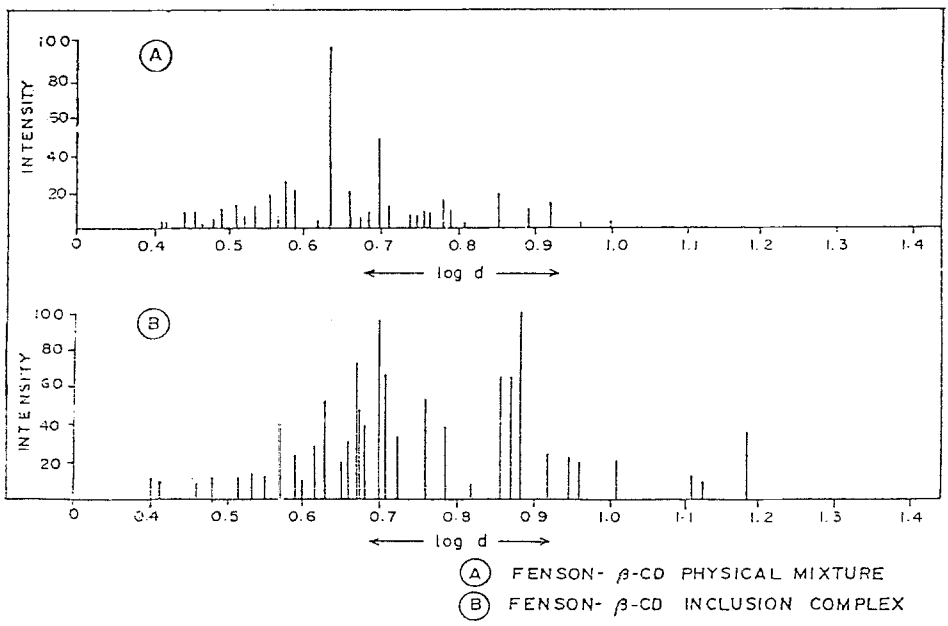

Fig. 1. X-ray Powder diffraction pattern (line diagram).

TABLE I. Melting point data of the inclusion complexes of pesticides with β-CD.

Pesticide	Melting points °C	
	Inclusion Complex of pesticide with β-CD	Physical mixture of pesticide and β-CD
Fenson	286–88	268–70
Chlorfenson	282–86	244–48
Genite	270–76	236–40

3. Results and Discussion

3.1. Detection of Inclusion

Complex formation was confirmed by melting point (Table I), TLC analysis, UV spectra and X-ray diffraction techniques.

β-CD inclusion complexes of pesticides decomposed in a particular range, with liberation of included guest. Results were compared with a physical mixture of pesticide with β-CD having the same composition as the inclusion complex. The temperature range in which the inclusion complex decomposed was found to be different from that of the physical mixture (Table I).

TLC analysis of declathrated inclusion complexes showed a spot corresponding to the pesticide used for inclusion. β-CD does not move in benzene and shows a spot due to the adduct formation with iodine.

TABLE II. Data for percentage content of included pesticide.

Technique	Fenson	Chlorfenson	Genite
UV spectral method	8.02%	8.81%	8.4%
GLC method	8.33%	8.44%	8.39%

The UV spectrum of declatharated inclusion complexes showed λ_{max} 267 nm and 273 nm which corresponds to the λ_{max} of included guests.

The X-ray diffraction pattern for the inclusion complex and the physical mixture were compared. A typical diffraction pattern line diagram of Fenson-β-CD inclusion complex illustrates the entry of the guest in the β-CD moeity (Figure 1).

3.2. Determination of Percentage Content of Included Pesticides

For this purpose the following methods were used:

a. UV spectral method.

b. GLC method.

UV spectra were recorded for a known concentration (0.2 mg/mL) of standard pesticide solution and the corresponding inclusion complex solution (2 mg/mL) in DMF. The absorbance at 273 nm and 267 nm were used to obtain the percentage content of included guest.

The solutions of standard pesticides and inclusion complexes used for the UV spectral method were also used for the GLC method. The detection response was calculated and used to obtain the percentage content of pesticide from the respective inclusion complex.

4. Conclusion

Degradable pesticides such as Fenson, Chlorfenson and Genite can form inclusion complexes with β-cyclodextrin. UV spectral and GLC methods showed 8–9% inclusion of these pesticides in β-CD.

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