June 2007 *Volume 2 Issue 2*

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 2(2), 2007 [48-52]

Polarographic Determination Of Bioresmethrin

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Received: 27th December, 2006
Accepted: 2nd January, 2007

Web Publication Date : 5th June, 2007

ABSTRACT

The electrochemical characteristics of bioresmethrin have been determined by means of electrochemical techniques such as cyclic voltammetry and differential pulse polargraphy over a wide range of pH from 2.0-12.0. The title compound exhibits a single well defined peak due to the reduction of the -C=C- mookety present in bioresmethrin. The variation of half-wave potential with the pH, concentration of the title compound, and other experimental conditions is described. The overall reduction process is diffusion-controlled and adsorption free in nature. A possible mechanism for the reduction is suggested. The number of electrons involved in the electrode reduction is two. Investigation was also undertaken for the determination of bioresmethrin in vegetables and in storage bags of rice and wheat under FCI's storage system.

KEYWORDS

Bioresmethrin;
Polarography;
Vegetables;
Storage bags;
Wheat;
Rice.

INTRODUCTION

Bioresmethrin 5-benzyl-3-furylmethyl(1R,3R)-2-2-dimethyl-3-(2-methylprop-1-enyl) cyclopropanecarboxylate(I) is a systemic, granular pyrethroid insecticide for the control of pests of rice, sorghum, barley, maize, cotton, vegetables, fruits etc. Today it is widely used because of its low persistence and high effectiveness. Its wide-spread use as an effective pesticide has created a demand for a quick, easy, and reliable method for its determination.

Analysis of bioresmethrin by Bhuller method[1]. A genetic analysis of resistance to location of permethrin and bioresmethrin in adults[2].

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Quantitation of bioresmethrin, a synthetic pyrethroid grain protectant by enzyme-immunoassay[3]. Determination and extraction, clean-up and chromatographic determination of organophosphate, pyrethroid and carbamate insecticides in grain and grain products[4] pilot usage of the grain protectants chloropyrifos methyl plus bioresmethrin, fenitrothion plus d-phenothrin, methacrifos and pirimiphos.methyl plus carbaryl[5] predicted and observed residues of bioresmethrin, carbaryl, dichlorovos fenitrothion, d-phenothrin, methacrifos and pirimiphos methyl on rice and barley after storage and losses of these insecticides during processing[6] residue analysis of bioresmethrin with several other pesticides were studied[7]

The purpose of the present investigation was to elucidate the electrochemical reduction mechanism and electrode kinetics by employing advanced electrochemical techniques and to develop analytical procedures for the quantitative estimation of bioresmethrin in vegetables and in storage bags of wheat and rice. In comparison with spectrometry and chromatographic techniques, DPP technique employed in this study is cheaper, fast and easier to carry out. Reviewing the literature revealed that, up to the present time nothing has been published concerning their determination in vegetables and in storage bags of wheat and rice and formulations using differential pulse polarography

EXPERIMENTAL

A detailed description of the instrumentation and experimental conditions has been reported earlier[8]. All the experiments were performed at 25±1^{0}C. pH measurements were carried out with a Elico digital pH meter. Dissolved air was removed from the solution by degassing with oxygen-free nitrogen for 10-15min. Prior to each run.

Bioresmethrin was supplied by 'Hoechst Schering Agr Evo', Mumbai. The purity of the compound was tested by boiling point and by TLC experiments. A stock solution was prepared by dissolution of the required amount of pesticide in dimethyl formamide. Universal buffers of pH 2.0-12.0 were prepared from 0.2M boric acid, 0.05M citric acid, and 0.1M trisodium orthophosphate[9]. All the chemicals used were of analar grade.

RESULTS AND DISCUSSION

The electrochemical behavior of bioresmethrin was examined over the pH range 2.0-12.0. Typical polarogram are given in figures 1 and 2. In all the cases, a single well defined peak is observed at a potential around -0.7V. In the case of cyclic voltammetry, no anodic peak is observed in the reverse scan.

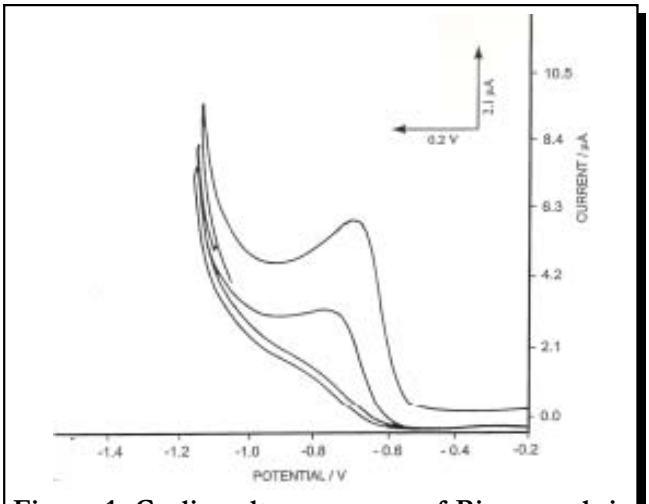

Figure 1: Cyclic voltammogram of Bioresmethrin at pH 2.0. Concentration, 0.5mM; drop time, 2Sec, scan rate, 40mV s^{-1}.

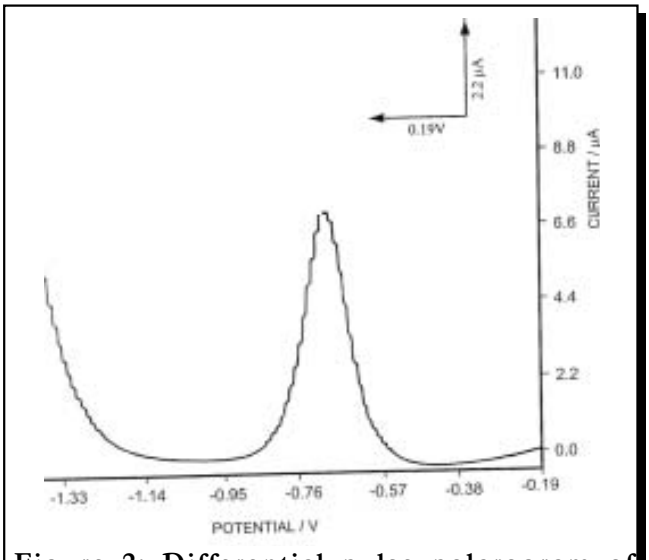

Figure 2: Differential pulse polarogram of Bioresmethrin at pH 4.0. Concentration, 0.5mM; drop time, 2Sec; pulse amplitude, 50mV.

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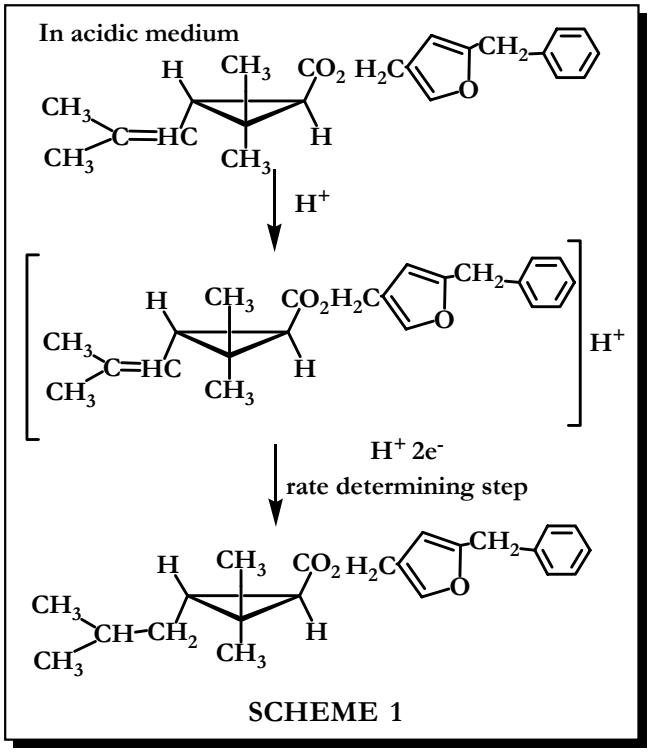
From the polarogram, it was concluded that the peak current increases as the concentration increases. The above facts suggest that the electrochemical reduction is irreversible and involves diffusion-controlled electron transfer. Irreversibility is also indicated by the variation of peak potential(E_p) with scan rate in cyclic voltammetry.

The number of electrons was determined by millicoulometry at -0.65V. The n value was found to be two. On the basis of the above results, the following mechanism may be proposed(SCHEME 1, 1a). Controlled potential electrolysis(CPE) was carried out at pH 4.0 at -0.82V vs. SCE to identify the product, and it was further confirmed by I.R. spectral studies.

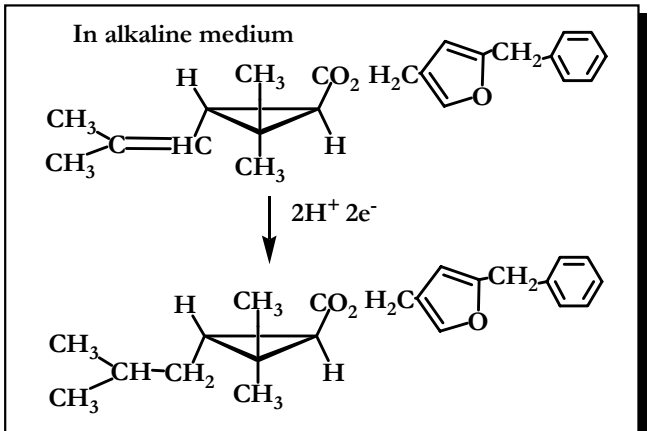
Kinetic data obtained with different techniques are summarized in TABLE 1. The diffusion coefficient values evaluated from all techniques are in good agreement. This is particularly evident because no adsorption complications are involved in the electrode process. The slight decrease in D-values with an increase in pH may be attributed to the lower availability of protons with an increase in pH 2.

The rate constants[$K^0_{f,h}$] obtained for the reduction of the $\rangle C = C \langle$ group are high in acidic media for all techniques, indicating that the rate of reaction is fast since in the acidic solutions proton involvement is high which makes the reduction process easier. But in basic media, the reduction process is not easily facilitated owing to the lower availability of protons. Hence, $E_{1/2}$ E_p, and E_m values in basic media are observed to shift to more negative potentials. Consequently, lower values are obtained for rate constants in basic media in contrast to acidic media.

The DPP wave obtained in the pH range from 2 to 6 is well resolved and is highly reproducible, and it was therefore chosen for the analysis of Bioresmethrin in vegetables and rice and wheat under FCI's storage system.



SCHEME 1



SCHEME 1a.

TABLE 1: Typical kinetic data of bioresmethrin, concentration: 0.5mM

Supporting electrolyte of pH	Cyclic voltammetry		Differential pulse polarography			
	$-E_p$ (V)	$D\times10^5$ (cm^2S^{-1})	$K^0_{f,h}$ cmS^{-1})	$-E_m$(V)	$D\times10^5$ (cm^2s^{-1})	$K^0_{f,h}$ (cm s^{-1})
2.0	0.67	6.41	7.98×10^{-9}	0.65	6.65	2.86×10^{-9}
4.0	0.73	6.35	2.31×10^{-11}	0.71	6.64	4.45×10^{-11}
6.0	0.89	5.91	6.81×10^{12}	0.81	6.31	8.56×10^{12}
8.0	1.20	5.95	2.21×10^{-16}	1.13	6.98	$4.10\times10^{1-16}$
10.0	1.22	5.88	8.98×10^{-18}	1.20	6.72	9.19×10^{-19}
12.0	1.31	5.61	2.11×10^{-20}	1.29	6.58	8.72×10^{-19}

Recommended analytical procedure

A stock solution(1.0×10^{-5}M) is prepared by dissolution of the appropriate amount of the electroactive species in dimethylformamide. Standard solution, 1ml, is transferred into a polarographic cell and diluted with 9ml of supporting electrolyte and then deoxygenated with nitrogen gas for 10min. After the polarogram is recorded, small increments (0.2ml) of standard solution are added and a polarogram is recorded after each addition under similar conditions. In the present study, the best precision was obtained at pH 4.0, with a drop time of 2s, pulse amplitude of 50mV, and an applied potential of -0.7V.

Analysis of formulations

The required quantity of formulation corresponding to a 1.0×10^{-3}M stock solution was accurately measured and transferred into a 50ml volumetric flask containing 50ml of dimethylformamide. A solution of approximately 1.0×10^{-5} M was prepared by dilution of this stock solution with universal buffer. Assay results for bioresmethrin in formulations at pH 4.0 are given in TABLE 2. Attempts were made to apply the proposed method to the determination of bioresmethrin in mixed formulation. The latter insecticide does not give a reduction wave and hence it was believed to be a non-interfering substance. Therefore, the proposed method has been employed for the assay of bioresmethrin in mixed formulations, and these results are incorporated in TABLE 2.

TABLE 2: Determination of bioresmethrin in formulations by differential pulse polarography at pH 4.0

Bioresmethrin formulation	Labelled amount (mg)	Average amount found (mg)[a]	Average recover
Chrysron	5.0	4.85	97.1
	10.0	9.63	96.3
Pynosect	5.0	4.79	95.9
	15.0	14.52	96.8
Mixed formulation (Bioresmethrin+ heptenophos)	10.0	9.72	97.2

Analysis of bioresmethrin in vegetables

In the present investigation, vegetables such as cabbage and tomato have been chosen for the analysis of bioresmethrin. Known amounts of bioresmethrin(Chrysron, pynosect) were sprayed on cabbage and tomato crops and left for 1-2h. The extracts were prepared by the treatment of a crushed sample with 100ml of acetone. Then the extract was allowed to dry. The residue of bioresmethrin was dissolved in DMF and transferred into a 50ml volumetric flask. Then the polarogram were recorded in the same manner as described earlier. The results obtained using the DPP method is shown in TABLE 3.

To ascertain the practical limit of determination of the method, 25g portions of potatoes were fortified at the 0.01mg kg^{-1} level for bioresmethrin. It could be determined at this level by the proposed DPP method. The levels detected are below the food and agricultural organization and World Health Organization maximum residue limit for bioresmethrin on cabbage and tomato of 2mgkg^{-1} when calculated[10].

Recovery of bioresmethrin ranging from 93.9 to 95.2% was found, which indicates the high accuracy and reproducibility of the proposed differential pulse polarographic method.

Analysis of bioresmethrin in wheat and rice under FCIs storage system

Rice and wheat stacks of usual dimension and capacity were selected in the food corporation of India godowns at palamaner. Small jute bags of 4kg capacity were chosen for these studies. The jute bags were filled with wheat and rice and properly stitched. The dosages used were 1.0 and 1.5gm^{-2} of e.i. of

TABLE 3: Recovery of bioresmethrin from fortified samples using DPP

Bioresmethrin formulation	Labelled amount (mg)	Amount found (mg)[a]		Average recover	
		Cabbage	Tomato	Cabbage	Tomato
Chrysron	2.0	1.91	1.88	95.8	94.2
	6.0	5.73	5.73	95.6	95.5
	10.0	9.49	9.62	94.9	96.2
Pynosect	15.0	14.15	14.09	94.3	93.9
	20.0	18.98	18.92	94.9	94.6

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TABLE 4: Persistence of residues of Bioresmethrin on wheat and rice penetrated during spraying on jute bags

Sample	Period after treatment	Bioresmethrin dose							
		1.0 g				1.5g			
		R_1	R_2	R_3	Mean	R_1	R_2	R_3	Mean
Wheat	1 h	1.68	0.86	0.34	0.96	1.91	0.97	1.45	1.44
	15 days	0.44	0.60	0.55	0.53	0.96	0.78	0.50	0.75
Rice	1 h	1.62	0.84	0.52	0.99	1.75	0.82	1.34	1.30
	15 days	0.52	0.46	0.32	0.43	0.96	0.75	0.51	0.77

bioresmethrin(Chrysron). The quantity required of bioresmethrin was dissolved in 50ml of acetone and spraying was done on the jute bags with the help of a small hand sprayer. Every cared was taken to prevent loss of bioresmethrin during spraying and to see that there was uniform deposit over the bag surface.

The observations of residual toxicity were recorded on the first day and after 15 days. The samples for analysis of residues of bioresmethrin were drawn 1h after mixing and after 15 days. At each sampling the stitching of the bags was undone, the grains poured over a tray and thoroughly mixed. Each sample comprised a bag of 50g of wheat and rice. The samples of wheat and rice were ground to a powder in an electrically operated grinder. The samples were extracted with acetone and the extract was filtered through a buckner funnel. Then the extract was allowed to dry. The residue of bioresmethrin was dissolved in DMF and transferred to a 50ml volumetric flask. The residues of bioresmethrin in wheat and rice in jute bags were estimated by DPP and the results are presented in TABLE 4.

It is clear from the data that the residues of bioresmethrin on the wheat were 1.02, and 1.34ppm, and on the rice were be 0.99 and 1.30ppm just after spraying of bioresmethrin 1.0 and 1.5g m^{-2} a.i., respectively. The residues of bioresmethrin on wheat in samples collected 15 days after of spraying were 0.5 and 0.75ppm. Similarly, on rice they were 0.43 and 0.77ppm. Thus the residues of bioresmethrin penetrated during the spraying on jute bags were below the tolerance limit of FAO[11]. These results suggest that, even after 15 days of application, of the bioresmethrin fell within the detection limit. Hence in the light of above data, the use of Bioresmethrin at dosages of 1.0 and 1.5g m^{-2} a.i treatments for the control of storage pests is without any health hazard whatsoever to the consumers.

The proposed method is free from interferences due to ingredients present in bioresmethrin and also other constituents present in vegetables and storage bags of rice and wheat. Therefore the proposed method is simple, inexpensive, rapid reliable, and sensitive. The proposed method does not involve the elaborate cleanup procedures required with the other methods. The method can also be extended for the study of the efficacy of bioresmethrin against insect infestation in various stored samples.

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