

2-(3-Phenoxybenzoyl)-2-Propyl Ester of Tralomethrin: A New Derivative of Synthetic Pyrethroids

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ABSTRACT

The α -cyano-3-phenoxybenzyl ester of tralomethrin reacts readily with acetone at the benzylic position of the alcohol moiety in the presence of Na_2CO_3 to produce 2-(3-Phenoxybenzoyl)-2-propyl ester (Tralomethrin acetone derivative) in crystalline form. The yield product of the new derivative was 97.4%. The spectrometry, using N.M.R, I.R and GC/M.S technique was carried out to confirm the chemical structure of the acetone derivative. The N.M.R. spectra for the derivative showed the loss of CHCN group at 6.32 ppm of the benzylic carbon (alcohol moiety) and an addition of two methyl groups from acetone molecule at 0.74 and 1.13 ppm. The I.R spectra established the presence of both ester and Ketone carbonyl bands at 1715 and 1680 cm^{-1} respectively. The GC/MS Fragmentation patterns confirmed the spectral data of N.M.R and I.R, However tralomethrin acetone derivative gave a single peak at $t_R=10.65$ min., while the parent compound gave a single peak at $t_R=7.13$ min. In addition, the fragmentation products confirmed the derivatization at the benzylic position of the alcohol moiety. The synthesis technique exhibited that tralomethrin reacts with the acetone molecule to give tralomethrin acetone adduct in the mechanism of kinetic acidic proton exchange.

Key Words: Synthetic Pyrethroids; Tralomethrin; Tralomethrin acetone derivative Synthesis; Spectroscopy

INTRODUCTION

Synthetic pesticides used during 1950's and since this time, extensive studies on structural modification have revealed a number of new synthetic pyrethroids (Corral & Elliott 1965; Roger 1976, Bosone *et al.*, 1986, Ahmet *et al.*, 1988; Kazunori *et al.*, 1989). The major commercial and experimental pyrethroid insecticides are esters of α -cyano-3-phenoxybenzyl alcohol with either chrysanthemic acid, e.g., deltamethrin, cypermethrin (Farooq, 1980) and tralomethrin, tralocythrin (Roussel Uclaf, 1978) or with valeric acid, e.g., fenvalerate and flucythrinate (Elliott *et al.*, 1983). The synthesis of 3-phenoxybenzyl chrysanthemates and their dihalovinyl analog substituted with cyano group has been described by. Elliott *et al.* (1978), Omura *et al.* (1980), Michael *et al.* (1986; 1988) and Ackermann *et al.* (1980) who found that bromination of the dichlorovinyl group of cypermethrin yielded a new compound (tralocythrin) which was highly potent insecticide. Similar results were obtained by Ruzo *et al.* (1981) for tralomethrin and tralocythrin. α -cyanophenoxybenzyl ester of pyrethroids reacts with pentafluorobenzyl bromide molecule at the benzylic position of the alcohol moiety to give pentafluorobenzyl derivative to enhance analytical ECD-GC (Saleh *et al.*, 1980 and Osman *et al.*, 1994) and reacts with acetone at the benzylic position (Marei *et al.*, 1988; Marzouk, 1990), or vinyl and α -isopropyl position of the acid moiety to give acetone derivatives to enhance the insecticidal activity (Marzouk *et al.*, 1995; Marzouk, 1996; 2005).

The present research was aimed to synthesize a new generation of synthetic pyrethroids, i.e, 2-(3- phenoxy benzoyl) ester of pyrethroids to be used as insecticides.

MATERIALS AND METHODS

Tested pesticides. Tralomethrin (98%) technical grade, α -cyano-3-phenoxy benzyl-3- (1-bromo-2, 2, 2-tribromoethane)-2,2,-dimethylcyclopropane carboxylate was obtained from Roussel Uclaf Chemical Co., France. Tralomethrin acetone derivative was synthesized according to the method described by Marzouk 1985. However, acetone solution of (0.2 mM) of tested pyrethroids was refluxed for 48 hrs in the presence of suspension of Na_2CO_3 . The product was filtrated, evaporated to dryness, dissolved in ether, washed with water saturated with NaCl, dried over anhydrous MgSO_4 and solvent evaporated.

Synthesis of tralomethrin acetone derivative. The chemical reaction of α -cyanophenoxy benzyl of tralomethrin with acetone was applied in the present study. However, acetone solution of tralomethrin (0.2mM) was refluxed for 48 hrs in the presence of suspension of Na_2CO_3 . The product was filtrated, evaporated to dryness, dissolved in ether, washed with water saturated with NaCl, dried over anhydrous MgSO_4 and finally solvent evaporated.

Confirmation of synthesized compound. The confirmatory tests of the synthesized compound was done using spectroscopic and chromatographic analysis.

I. Nuclear Magnetic Resonance (^1H -N.M.R). Spectroscopic data for the compound was prepared throughout the course of this study as well as its parent compound (tralomethrin) was obtained using proton nuclear magnetic resonance, Varian EM-390 spectrometer with tetramethyl silane (TMS) as internal standard and deuteriochloroform as solvent. The N.M.R chemical shifts of the tetrahalo esters are generally similar to the chemical shifts of

the dihalo esters (Marzouk, 1990) as shown in Table I.

II. Infra red (I.R) spectroscopy. Infra red (I.R) spectra were recorded for the derivative prepared in this study, as well as the parent compound, (tralomethrin) using Nicolet FT Raman spectrometer and KBr disks were used to collect these data. The I.R spectra of α -cyano phenoxybenzyl ester of pyrethroids and their pentafluoro benzyl or acetone derivatives were mentioned according to the methods described by Saleh *et al.*, (1980) and Marzouk (1990).

III. GC / MS spectroscopy. Spectroscopic analysis using GC/MS Finnigan mat SSQ7000 spectrometer with fused silica glass capillary column (0.25 mm i.d. x 30m) helium as the carrier gas (40 cm/s) and an electron capture detector (ECD) was run to confirm the chemical structure of the acetone derivative prepared. The temperature conditions were 300oC, 280oC and 350oC for the injector, column and detector respectively (Saleh *et al.*, 1980). For mass spectral fragments, all data were for the electron impact mode. Relative intensities were based on the most intense ion as 100% "molecular ion" (Katritzky *et al.*, 1995).

RESULTS AND DISCUSSION

Synthesis of 2-(3-phenoxybenzoyl)-2-propyl ester of tralomethrin. 2-(3-phenoxybenzoyl)-2-propyl ester of deltamethrin was synthesized according to the reaction of acetone at the benzylic position of α -cyano-3-phenoxy benzyl ester of deltamethrin in the presence of Na_2CO_3 as base medium (Marzouk, 1990). Since the present work is a continuation of synthesized a new derivative of synthetic pyrethroids, the acetone derivative of tralomethrin was prepared in a similar manner as described before (Marzouk, 1985). Fig. 1. illustrates the chemical reaction of acetone with α -cyano position of tralomethrin. The yield of isolated derivative was 97.4%.

Confirmatory tests. The spectrometry methods were carried out to confirm the chemical structure of the new acetone derivative using spectroscopic analysis of:

I. Nuclear magnetic Resonance (^1H .N.M.R). Spectroscopic data obtained for ^1H .N.M.R spectra are in agreement with results of Marzouk (1990) for deltamethrin (dihalo ester). However N.M.R spectra for tralomethrin (tetrahalo ester) established that the "**CHCN**" proton was lost at 6.32 ppm and two additional methyl groups were introduced at 0.74, 1.13 ppm (Table I & Fig. 1) thus the product of the acetone derivative was an ester derived by loss of the elements of "**HCN**" and an addition of two (CH_3) groups of acetone at the benzylic position of the alcohol moiety.

II. Infra red (I.R) Spectroscopy. I.R spectra were carried out for tralomethrin and its acetone adduct. The results obtained were similar to those mentioned by Marzouk (1990). The data presented in Table II and illustrated in Fig. 1, established the presence of both ester and ketone carbonyl bands at 1715 and 1680 cm^{-1} respectively.

III. GC/MS spectroscopy. Gas chromatography (GC) coupled with mass spectrometry (MS), was used to confirm

Fig. 1. Chemical synthesis of 2-(3-phenoxybenzoyl) 2-propyl ester derivative of tralomethrin.

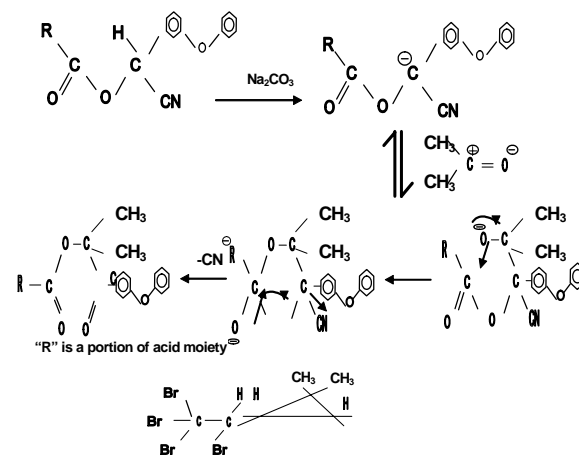
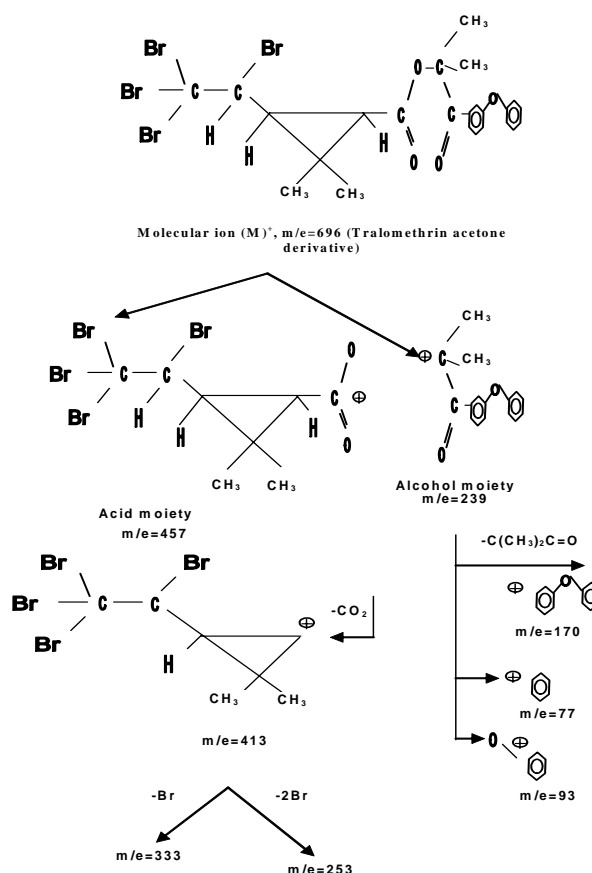


Fig. 2. Electron impact mass spectrum scheme of 2-(3-phenoxybenzoyl)-2-propyl ester of tralomethrin.



the chemical structure of the product i.e., tralomethrin acetone derivative the data established the difference of retention time between tralomethrin (single peak at $t_R = 7.13$

min) and tralomethrin acetone derivative (single peak at t_R = 10.65 min). While, the mass spectrum showed that tralomethrin acetone derivative is formed, i.e., m/e (molecular ion) was 696. The mass spectral data in Fig. 2 confirms the N.M.R. and I.R evidence that the acetone molecule is at the benzilic carbon of the alcohol moiety, i.e., the CHCN is absent and the $2CH_3$ is introduced.

Table I. Nuclear magnetic resonance (1H -N.M.R) shifts (ppm) of tralomethrin and its acetone derivative comparing with deltamethrin and its acetone derivative.

Synthetic Pyrethroids	deltamethrin	deltamethrin-acetone derivative (dihalo esters)	Tralomethrin	tralomethrin acetone derivative (tetrahalo esters)
	Marzouk (1990)	Marzouk (1990)	Present Work	Present work
Substituents	Chemical shifts (ppm)			
CHCN	6.32	-----	6.32	-----
CH ₃	1.21, 1.31	1.25, 1.36, 0.79, 1.16	1.18, 1.29	1.20, 1.32, 0.74, 1.13

Table II. Infrared (I.R) bands (cm^{-1}) of tralomethrin and its acetone derivative comparing with deltamethrin and its acetone derivative.

Synthetic Pyrethroids	deltamethrin	deltamethrin acetone derivative (dihalo pyrethroids)	tralomethrin	tralomethrin acetone derivative (tetrahalo pyrethroids)
	Marzouk (1990)	Marzouk (1990)	Present work	Present work
Function group (bands)	Wave number (cm^{-1})			
R-COO-R	-----	1720	-----	1715
R-CO-R	-----	1685	-----	1680

CONCLUSIONS

Generally, the combined results of these study lead to the conclusion that the new product of the present reaction is 2-(3-phenoxybenzoyl)-2-propyl ester derivative of tralomethrin. It was obtained to develop a highly active, low cost and environment friendly method for new generation of pesticides.

REFERENCES

- Ackermann, P., F. Bourgeois and J. Drabek, 1980. The optical isomers of α -cyano-3-phenoxybenzyl-3-(1,2-dibromo-2,2-dichloroethyl)-2,2-dimethylcyclopropane carboxylate and their insecticidal activities. *Pestic. Sci.*, 11: 169-79.
- Ahmet, E.B., M. Elliott, A.W. Farnham, N.F. Janes and B.P.S. Khambay, 1988. The pyrethrins and related compounds Part XXXIII. Effective combinations, in the gemdimethyl-central group region of non-ester pyrethroids. *Pestic. Sci.*, 23: 231-46.
- Bosone, E., F. Crod, F. Gozzo, A. Meconi, P. Piccardi and V. Caprioli, 1986. Synthesis and insecticidal activity of 3-(Haloalkyl-1,3-dienyl)-2,2-dimethylcyclopropanecarboxylates. *Pestic. Sci.*, 17: 621-30.
- Corral, C. and M. Elliott, 1965. The pyrethrins and related compounds VII. New pyrethrin like compound with ester and ketonic group in the alcoholic side chain. *J. Sci. Fd. Agric.*, 16: 514-18.
- Elliott, M., A.W. Farnham, N.F. Janes, B.P.S. Khambay and D.A. Pulman, 1983. The pyrethrins and related compounds. Part XXVI. Analogues of fenvalerate from a cyclic-substituted 3-methylbutyric and related acids. *Pest. Sci.* 14: 1-8.
- Elliott, M., J. Norman, P. David and S. David, 1978. The pyrethroids related compounds. Part XXII. Preparation of isomeric cyanosubstituted-3-phenoxybenzyl esters. *Pestic. Sci.* 9: 105-11.
- Farooq, S., 1980. The vinyllogous relationship in some pyrethroids. *Pestic. Sci.* 11: 242-48.
- Katritzky, A.R., S. El-Zemati and L. Hengyuan, 1995. Conversion of 2-aminopyridines into 5-substituted derivatives mediated by 1-hydroxymethylbenzotriazole. *J. Chem. Soc. Perkin Trans.* 1: 3129-33.
- Kazunori, T., T. Yano, K. Umeda, N. Matsuo, M. Hirano and N. Ohno, 1989. Synthesis, insecticidal activity and pyrethroidal mode of action of new derivatives. *Pestic. Sci.*, 25: 17-23.
- Marei, A.S.M., M.A. Marzouk and A.E. Khamis, 1988. Studies on synthetic pyrethroids. 6-synthesis of 2-(3-phenoxybenzoyl)-2-propyl esters for deltamethrin and fenprothrin. *J. Pest Control & Environ. Sci.* 1: 77-83.
- Marzouk, M.A., 1985. Chemical and toxicological studies on certain pyrethroid type compounds. *M. Sc. Thesis*. Univ. of Alex., Egypt.
- Marzouk, M.A., 1996. Toxicological studies on cybolt acetone adduct, α -cyano-3-phenoxybenzyl-1-(2,2-dimethyl-2-hydroxy ethyl)-1-isopropyl-P-difluoromethoxyphenyl acetate as a new derivative of synthetic pyrethroid. *Alex. J. Agric. Res.* 41: 289-93.
- Marzouk, M.A., 2005. Chemical synthesis and toxicity of α -cyano-3-phenoxybenzyl-1-(2,2-dimethyl-2-hydroxy ethyl)-1-isopropyl-P-chlorophenyl acetate as a new compound of synthetic pyrethroid. *In Publication*.
- Marzouk, M.A., H.R. Soltan, and A.R.H. Mansy, 1995. Studies on synthetic pyrethroids: Synthesis, Confirmation and insecticidal activity of cypermethrin acetone dervative. *J. Agric. Res. Tanta Univ.*, 21: 523-34.
- Marzouk, M.A., 1990. Toxicological studies on certain pyrethroids and their mixture with novel chlorinated compound. *Ph.D. Thesis*. Fac Agric. Alex. Univ, Egypt.
- Michael, E., A.W. Farnham, N.F. Janes and B.P.S. Kharmby, 1988. The pyrethrins and related compounds Part XXXI: Alkoxyiminosubstituted esters. *Pestic. Sci.* 22: 231-49.
- Michael, E., R.L. Elliott, N.F. Janes, B.P.S. Kharmby and D.A. Pulman, 1986. The pyrethrins and related compounds. Part XXVIII: Alkenyl- and alkynyl substituted benzyl esters. *Pestic. Sci.* 37: 691-700.
- Omura, H., M.F. Yoshiji, N. Taskasbi, H. Takco, W. Fumio, A. Fukuji, T. Hiroyuki and I. Kazuo, 1980. Insecticidal cyclopropanecarboxylic acid esters. Japan, Kokai, Tokkyo, Koho 80, 23, 917, (*Chemical Abst.*, 1980, 93, 114027q).
- Osman, K.A. H.R. Soltan, M.A. Marzouk and A.S.M. Marei, 1994. Toxicity and biochemical effects of cypermethrin, fenvalerate and their pentafuorobenzyl derivatives on the Egyptian cotton leafworm *Spodoptera littoralis*. *Com. in Sci and Dev. Res.*, 47: 19-32.
- Roger, G.B., 1976. 1-Alkylcyclopropane carboxylates: An extension of pyrethroid structure activity relationships. *Pestic. Sci.*, 7: 251-57.
- Roussel, Uclaf France., 1978. *Patent* 2375161.
- Ruzo, I.O., I.C. Gaughan and J.E. Casida, 1981. Metabolism and degradation of the pyrethroids tralomethrin and tralocytin in insects. *Pestic. Biochem. Phys.*, 15: 137-42.
- Saleh M.A., A.S.M. Marei and J.E. Casida, 1980. α -cyano-3-phenoxybenzyl pyrethroid: Derivatization at the benzylic position. *J. Agric. Food Chem.*, 28: 592-94.

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