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Novel Synthesis and Insecticidal Activity of MTI-800, Desfluoro MTI-800 and Their Intermediates*

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Abstract: A new route to the synthesis of 2-(4-ethoxyphenyl)-2-methyl-5-(3-phenoxyphenyl)pentane (desfluoro MTI-800) and 2-(4-ethoxyphenyl)-2-methyl-5-(4-fluoro-3-phenoxyphenyl)pentane (MTI-800) and the insecticidal activities of these compounds and some of the synthetic intermediates against the tobacco caterpillar *Spodoptera litura* (F.) is reported.

Key words: tandem Friedel–Crafts acylation, MTI-800, desfluoro MTI-800, insecticidal activity, *Spodoptera litura*.

1 INTRODUCTION

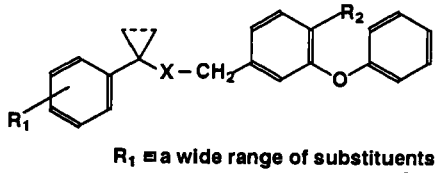
The insecticidal potency, combined with low oral toxicity to mammals and other non-target species, and low persistance in the ecosphere, has made the synthetic pyrethroids important candidates for pest control. Though the many modifications of the basic pyrethroid skeleton have often resulted in ineffective compounds, they provided valuable information on structure-related insecticidal activity.[1] The presence of a cyclopropane group next to the ester linkage has been shown not to be essential for insecticidal activity.[2,3] The effect of replacement of the central link in pyrethroids by isosteric and isoelectronic groups and the dependence of the insecticidal activity on groups present in other parts of the molecule has been reported by Elliott *et al.*[4–6] The most active compounds had structures represented by the general formula I (Fig. 1), in which the central ester group of a conventional pyrethroid is replaced by other carbon–carbon or carbon–oxygen links. In the cases shown, the non-ester groups are most effective when combined with a gem-dimethyl group or its cyclopropyl equivalent as part of, rather than attached to the main chain.

The present paper reports a simple route to the synthesis of 2-(4-ethoxyphenyl)-2-methyl-5-(3-phenoxyphenyl)pentane (desfluoro MTI-800; **7a**; **I**, $R_1 = p\text{-}OC_2H_5$, $X = -CH_2-CH_2-$, --- = no bond, R_2 = H) and 2-(4-ethoxyphenyl)-2-methyl-5-(4-fluoro-3-phenoxyphenyl)pentane (MTI-800; **7b**; **I**, $R_1 = p\text{-}OC_2H_5$, $X = -CH_2-CH_2-$, --- = no bond, R_2 = F) and the structure-related insecticidal activities of the aforesaid compounds and some of the synthetic intermediates on the tobacco caterpillar *Spodoptera litura* (F.). The synthetic route is outlined in Figs 2 and 3.

2 EXPERIMENTAL METHODS

2.1 General

Infra-red spectra of the synthesised compounds were recorded using IFS 85 Bruker FTIR. [^{1}H]NMR spectra



R_1 = a wide range of substituents
X = $-CH_2O$, $-CH_2CH_2-$, or $-CH=CH-$
— = bond or no-bond
R_2 = H or F

Fig. 1. General structure of pyrethroid insecticides.

* Dedicated to Prof. T. R. Govindachari on the occasion of his 80th birthday.
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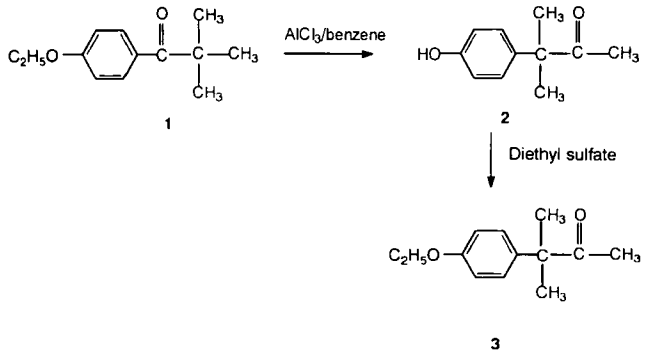

Fig. 2. General synthetic route to compound **3**.

of the compounds were recorded using a Hitachi 60 MHz instrument and a JEOL 400 MHz instrument. Samples were dissolved in carbon tetrachloride, except the final compounds, which were dissolved in deuterochloroform, and tetramethylsilane was used as an internal standard. LRMS were recorded using a Shimadzu GCMS (QP1000A) mass spectrometer. HRMS were recorded using a Finnigan MAT 8230 mass spectrometer with perfluorokerosene as reference sample. Anhydrous sodium sulfate was used for drying the solvents. 'Petrol' refers to the fraction of petroleum distillate boiling between 60 and 80°C. For thin layer chromatography (TLC), pre-coated silica gel GF plates (5 × 20 cm, E-merck) were used and UV irradiation at 254 nm was used for detection. Silica gel (60–120 mesh, E-merck) was used for column chromatography. Catalytic hydrogenations were done using a Superfit low pressure hydrogenation apparatus made by Superfit India Ltd, India. Leaf area measurements were done in a ΔT leaf area measurement meter, ΔT devices, England.

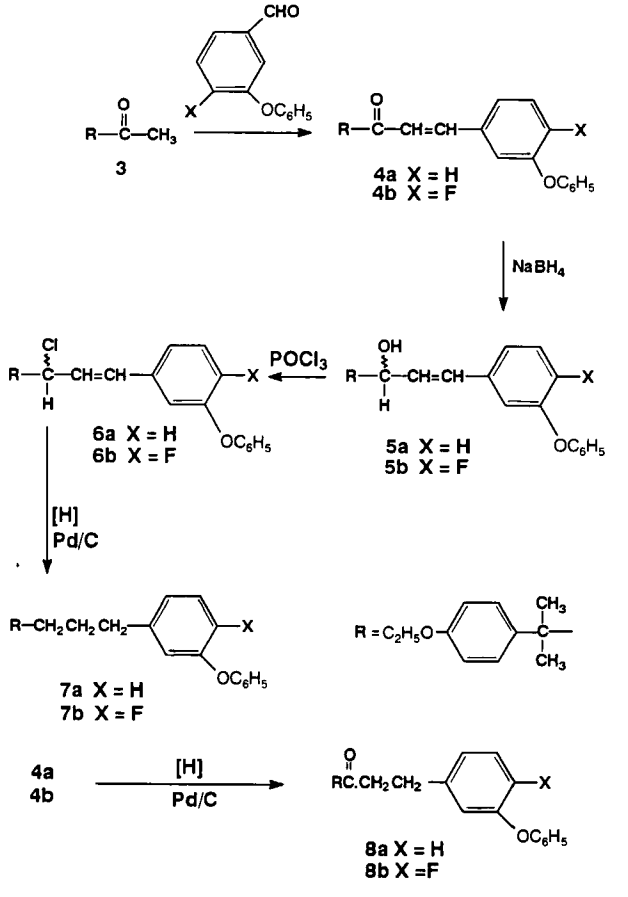

Fig. 3. General synthetic routes to test compounds.

2.2 Synthesis (procedures)

The spectral data for the synthetic intermediates and the final compounds are given in Table 1.

2.2.1 1-(p-Ethoxyphenyl)-2,2-dimethyl-1-propanone (**1**) Using phenetole (19·5 g, 160 mmol) in hexane (50 ml), aluminium chloride (26·7 g, 200 mmol) and pivaloyl chloride (12·1 g, 100 mmol) in hexane (100 ml), **1** was obtained, following the procedure of Rothstein *et al.*,[7] as a colourless liquid (15·9 g, 77·3%). b.p. 108–112°C at 0·5 mm; MS (*m/e*): 206 (M^+); IR: 1680 cm^{-1} (C = O); [^{1}H]NMR: δ 6·8 (d, J = 9 Hz, 2H) 7·8 (d, J = 9 Hz, d, 2H), 3·9 (q, J = 6·9 Hz, 2H), 1·3 (s, 9H), 1·2 (t, J = 6·9 Hz, 3H).

2.2.2.1 3-(4-Hydroxyphenyl)-3-methyl-2-butanone (**2**)[8] A suspension of aluminium chloride (133·4 g, 1000 mmol) in benzene (300 ml) was stirred at room temperature for 15 min. To this slurry, 1-(*p*-ethoxyphenyl)-2,2-dimethyl-1-propanone (103 g, 500 mmol) in benzene (300 ml) was added at room temperature dropwise over a period of 1 h. Stirring was continued for another 3 h. The reaction mixture was poured onto crushed ice (500 ml) and extracted with ethyl acetate (2 × 400 ml). The ethyl acetate layer was washed with sodium hydroxide solution (300 g $litre^{-1}$; 2 × 250 ml). The basic solution was neutralised with cold dilute hydrochloric acid and the separated phenolic compound extracted with ethyl acetate (2 × 300 ml) and dried. Removal of the solvent and distillation under vacuum yielded **2** as a colourless liquid. (68·4 g, 80%); b.p. 202–204°C at 0.5 mm; HRMS (M^+): 178·097 49 (observed), 178·099 38 (calculated). IR: 1718 cm^{-1} (C = O); [^{1}H]NMR: δ 6·6–7·1 (m, 4H), 1·8 (s, 3H), 1·3 (s, 6H).

2.2.2.2 One-pot synthesis of 3-(p-Hydroxyphenyl)-3-methyl-2-butanone (**2**). After the Friedel-Crafts reaction using phenetole (19·5 g, 160 mmol) in hexane (50 ml), pivaloyl chloride (12·1 g, 100 mmol) in hexane (100 ml) and aluminium chloride (26·5 g, 200 mmol) in hexane (100 ml), the corresponding acyl complex was obtained after removal of the solvent. The acyl complex was suspended in benzene (200 ml) and aluminium chloride (26·5 g, 200 mmol) was added and stirred at room temperature for 45 min. Usual work-up gave **2**: yield 22·2 g (92%).

TABLE 1
Spectral Data of Compounds **4–8**

Compound No.	*IR C=O* (cm^{-1})	[^1H] *NMR* (CCl_4) *Chemical shift δ in ppm*	*Molecular formula*	M^+ *Observed mass (calculated mass)*
4a	1672	6·3–7·3 (m, 15H), 3·9 (q, J = 6·9 Hz, 2H), 1·4 (s, 6H), 0·9 (t, J = 6·9 Hz, 3H)	$C_{26}H_{26}O_3$	386 (386)
4b	1670	6·2–7·6 (m, 14H), 3·7 (q, J = 6·9 Hz, 2H), 1·4 (s, 6H), 0·9 (t, J = 6·9 Hz, 3H)	$C_{26}H_{25}FO_3$	404 (404)
5a	—	6·8–7·4 (m, 15H), 4·4 (s, 1H), 4·0 (q, J = 6·9 Hz, 2H), 1·9, broad, —OH), 1·3 (s, 6H), 1·0 (t, J = 6·9 Hz, 3H)	$C_{26}H_{28}O_3$	388 (388)
5b	—	6·7–7·2 (m, 14H), 4·3 (s, 1H) 3·9 (q, J = 6·9 Hz, 2H), 2·1 (broad, —OH), 1·3 (s, 6H), 0·9 (t, J = 6·9 Hz, 3H)	$C_{26}H_{27}FO_3$	406 (406)
6a	—	6·7–7·4 (m, 15H), 4·4 (s, 1H), 3·9 (q, J = 6·9 Hz, 2H), 1·4 (s, 6H), 1·2 (t, J = 6·9 Hz, 3H)	$C_{26}H_{27}ClO_2$	
6b	—	6·6–7·2 (m, 14H), 4·2 (s, 1H), 3·9 (q, J = 6·9 Hz, 2H), 1·3 (s, 6H), 1·2 (t, J = 6·9 Hz, 3H)	$C_{26}H_{26}FClO_2$	
7a	—	6·6–7·4 (m, 13H), 4·1 (q, J = 6·9 Hz, 2H), 2·4 (t, J = 7·7 Hz, 2H), 1·2 (t, J = 6·9 Hz, 3H), 0·88–1·7 (m, 4H), 1·2 (s, 6H)	$C_{26}H_{30}O_2$	374 (374)
7b	—	6·5–7·4 (m, 12H), 3·9 (q, J = 6·9 Hz, 2H), 2·4 (t, J = 7·7 Hz, 2H), 1·3 (t, J = 6·9 Hz, 3H), 1·0–1·7 (m, 4H), 1·2 (s, 6H)	$C_{26}H_{29}FO_2$	392 (392)
8a	1705	6·5–7·2 (m, 13H), 3·9 (q, J = 6·9 Hz, 2H), 2·6 (t, J = 7·5 Hz, 2H), 2·4 (t, J = 7·5 Hz, 2H), 1·4 (s, 6H), 1·3 (t, J = 6·9 Hz, 3H)	$C_{26}H_{28}O_3$	388 (388)
8b	1706	6·6–7·3 (m, 12H), 4·0 (q, J = 6·9 Hz, 2H), 2·5–2·7 (m, 4H), 1·4 (s, 6H), 1·3 (t, J = 6·9 Hz, 3H).	$C_{26}H_{27}FO_3$	406 (406)

2.2.3 3-(4-Ethoxyphenyl)-3-methyl-2-butanone (**3**)
Reaction of 3-(4-hydroxyphenyl)-3-methyl-2-butanone (**2**; 8·9 g, 50 mmol) with diethyl sulfate (7·7 g, 50 mmol; 6·5 ml, d = 1·177) and sodium hydroxide (2·1 g, 50 mmol as a 105 g litre^{-1} solution), after usual work-up, yielded **3** as a colourless liquid. (8·2 g, 80%); b.p. 108°C at 0·5 mm; HRMS (M^+): 206·1336 (observed), 206·13068 (calculated); IR: 1712 cm^{-1} (C = O); [^{1}H]NMR: δ 6·6–7·2 (m, 4H), 3·9 (q, J = 6·9 Hz, 2H), 1·8 (s, 3H), 1·4 (s, 6H), 0·9 (t, J = 6·9 Hz, 3H).

2.2.4 1-(3-Phenoxyphenyl)-4-(4-ethoxyphenyl)-4-methyl-pent-1-ene-3-one (**4a**)
3-Phenoxybenzaldehyde (9·9 g, 50 mmol; 7·1 ml, d = 1·153) in ethanol (20 ml) was added dropwise to a stirred solution of **3** (10·3 g, 50 mmol), potassium hydroxide (4·2 g, 75 mmol) and ethanol (30 ml) at room temperature. After the addition was over, the reaction mixture was stirred for a further period of 6 h at room temperature. Ethanol was removed from the reaction mixture in a rotovac and the resulting residue poured

onto ice (100 ml) and extracted with ethyl acetate (2 × 50 ml). The organic layer was dried. Removal of the solvent and purification of the crude product by vacuum distillation yielded **4a** as a colourless liquid. (11·9 g, 62%); b.p. 202°C at 0·5 mm.

2.2.5 1-(4-Fluoro-3-phenoxyphenyl)-4-(4-ethoxyphenyl)-4-methyl-pent-1-ene-3-one (**4b**)
Reaction of 4-fluoro-3-phenoxybenzaldehyde (10·8 g, 50 mmol), **3** (10·3 g, 50 mmol), potassium hydroxide (4·2 g, 75 mmol) in ethanol yielded **4b** as a colourless liquid after purification by vacuum distillation (11·8 g, 60%); b.p. 192°C at 0·5 mm.

2.2.6 1-(3-Phenoxyphenyl)-4-(4-ethoxyphenyl)-4-methyl-pent-1-ene-3-ol (**5a**)
To a stirred solution of **4a** (19·3 g, 50 mmol) in tetrahydrofuran + methanol (9 + 1 by volume; 50 ml) sodium borohydride (0·7 g, 25 mmol) was added at room temperature and stirring continued for 5 h. Solvent was removed in a rotovac and the residue poured onto ice pieces (25 g) and extracted with ethyl acetate (3 × 50 ml). The organic layers were combined and washed with brine (2 × 25 ml) and dried. Removal of the solvent and purification by distillation in vacuum yielded **5a** as a colourless thick liquid (11·2 g, 58%); b.p. 225°C at 0·5 mm.

2.2.7 1-(4-Fluoro-3-phenoxyphenyl)-4-(4-ethoxyphenyl)-4-methylpent-1-ene-3-ol (**5b**)
Following the above procedure, reaction of **4b** (20·2 g, 50 mmol) in tetrahydrofuran + methanol, (9 + 1 by volume; 50 ml) with sodium borohydride (0·7 g, 25 mmol) at room temperature yielded **5b** as a colourless liquid (14·2 g, 70%); b.p. 221°C at 0·5 mm.

2.2.8 1-(3-Phenoxyphenyl)-3-chloro-4-(ethoxyphenyl)-4-methyl-2-pent-1-ene (**6a**)
To a stirred solution of **5a** (19·4 g, 50 mmol) in dry dichloromethane (150 ml) was added phosphorus oxychloride (2·3 g, 15 mmol; 1 ml, d = 1·675) and pyridine (9 drops) and the resulting mixture stirred at room temperature for 4 h. The reaction mixture was then washed thoroughly with water (3 × 100 ml) and dried. Removal of the solvent yielded a pale yellow residue which on purification on a silical gel column (eluant: 2% ethyl acetate in hexane) yielded **6a** as a colourless liquid (15·4 g, 76%).

2.2.9 1-(4-Fluoro-3-phenoxyphenyl)-3-chloro-4-(ethoxyphenyl)-4-methylpent-1-ene (**6b**)
Following the above procedure, reaction of **5b** (20·3 g, 50 mmol) with phosphorus oxychloride (2·3 g, 15 mmol) and pyridine (9 drops) in dichloromethane (150 ml), after purification by column chromatography (silica gel, ethyl acetate + hexane, 2 + 98 by volume, as eluant) yielded **6b** (13·8 g, 65%) as a colourless liquid.

2.2.10 2-(4-Ethoxyphenyl)-2-methyl-5-(3-phenoxyphenyl) pentane, (desfluoro MTI-800; **7a**)
To a solution of the chloro compound **6a** (20·3 g, 50 mmol) in dry ethyl acetate (30 ml) and triethylamine (6 drops), 10% Pd/C (Fluka, 450 mg) was added and the mixture hydrogenated in a Parr hydrogenation apparatus at 40 psi for 6 h. The reaction mixture was filtered and the ethyl acetate layer was washed with water (2 × 25 ml) and dried. Removal of the solvent and purification of the residue by chromatography (silica gel, eluant as in Section 2.2.9) yielded **7a** as a colourless liquid (11 g, 59%).

2.2.11 2-(4-Ethoxyphenyl)-2-methyl-5-(4-fluoro-3-phenoxyphenyl)pentane, (MTI 800; **7b**)
Following the above procedure, catalytic hydrogenation of **6b** (20·7 , 50 mmol) in the presence of 10% Pd/C yielded **7b** as a colourless liquid after purification by column chromatography (silica gel, eluant: hexane) (12·9 g, 68%).

2.2.12 2-(4-Ethoxyphenyl)-2-methyl-5-(3-phenoxyphenyl) pentan-3-one **8a**
To a solution of the enone **4a** (19·3 g, 50 mmol) in dry ethyl acetate (30 ml) was added 10% Pd/C (Fluka, 300 mg) and the mixture hydrogenated in a Parr hydrogenation apparatus at 40 psi for 4 h. The reaction mixture was filtered and the ethyl acetate layer washed with water (2 × 25 ml) and dried. Removal of the solvent and purification of the residue by column chromatography (silica gel, eluant: hexane) yielded **8a** as a colourless liquid (16·5 g, 85%).

2.2.13 2-(4-Ethoxyphenyl)-2-methyl-5-(4-fluoro-3-phenoxyphenyl)pentan-3-one (**8b**)
Hydrogenation of **4b** (19·7 g, 50 mmol) in the presence of catalytic amount of 10% Pd/C (300 mg) yielded **8b** as a colourless liquid after purification by column chromatography (silica gel, eluant: hexane) (17·8 g, 90%).

2.3 Bioassay

The insecticidal and insect antifeedant activities against the third-instar larvae of *Spodoptera litura* (F.) (Tobacco caterpillar) were assessed as follows: *Ricinus communis* L. leaves were chosen for the bioassay since it is the primary host of *S. litura*. Fresh, field-collected *R. communis* leaves (two leaves per replicate), with their petioles dipped in conical flasks containing water to retain freshness, were sprayed with the test compounds at dif-

ferent concentrations (10 μg, 50 μg and 100 μg cm^{-2}) in acetone and were offered to 20 third-instar larvae. Triplicates for each concentration and compound were maintained. After 24 h, larval mortality and leaf area fed (using a ΔT area measurement meter) were noted. Percentage mortality and percentage relative feeding in relation to untreated control were calculated and computed, using analysis of variance. The results are presented in Table 2. Fenvalerate and cypermethrin were used as comparative standards.

3 RESULTS AND DISCUSSION

3.1 Synthesis

The synthetic route followed to give desfluoro MTI-800 **7a** and MTI-800 **7b** is outlined in Fig. 3. Reported synthetic method for these compounds involves costly reagents and special precautions (i.e. inert atmosphere, special apparatus etc.).[6] The synthetic schemes presented here were simple and involved less costly reagents. The key step involves a tandem Friedel-Crafts acylation followed by a novel aluminium chloride rearrangement of *p*-ethoxypivalophenone (**1**) to give 1-(4-hydroxyphenyl)-1,1-dimethylpropan-2-one (**2**) in 90% yield, which on alkylation, using diethyl sulfate, gave **3** in 82% yield (Fig. 2). The phenolic compound **2** was obtained from phenetole either by two steps (Sections 2.2.1 and 2.2.2.1) or by a one-pot reaction (2.2.2.2). This tandem Friedel-Crafts acylation may be considered as similar to the well-known acid-catalysed rearrangement observed in the case of aldehydes and ketones.[9] The propiophenone **3** underwent smooth aldol condensation in the presence of alcoholic potassium hydroxide with both 3-phenoxybenzaldehyde and 4-fluoro-3-phenoxybenzaldehyde to yield the enones **4a** and **4b** respectively. The sodium borohydride reduction of the enones in tetrahydrofuran + methanol at room temperature yielded the isomeric alcohols **5a** and **5b**. These alcohols were then converted to the respective chlorides **6a** and **6b** with phosphorus oxychloride. Finally, catalytic hydrogenation of the alkyl chlorides gave MTI-800 and its desfluoro analogue **7b** and **7a** respectively. The enones **4a** and **4b**, on catalytic hydrogenation yielded the ketones **8a** and **8b** respectively. Similar compounds of the type **4** and **8** have been reported in the literature.[10]

3.2 Insecticidal activity

The results of the insecticidal and insect antifeedant activities are summarised in Table 2.

Insecticidal activities of the eight compounds (Fig. 2 and Table 1) against third-instar larvae of *S. litura* were assessed. Fenvalerate and cypermethrin, two well-known synthetic pyrethroids, were used for comparison. Perusal of the earlier literature revealed that higher insecticidal activities of synthetic pyrethroids are related to:

(a) a 1,1-disubstituted cyclopropyl moiety[11] or gem-dimethyl[5] in the acid fragment in the central part of the molecule;

TABLE 2
Insecticidal and Antifeedant Activities of Test Compounds against *Spodoptera litura*

	Mortality (%)					*Relative feeding* (%)				
	Dose (μg cm^{-2})			*LSD*	(±*SE*)	*Dose* (μg cm^{-2})			*LSD*	(±*SE*)
Compound	*100*	*50*	*10*	*5%*	*5%*	*100*	*50*	*10*	*5%*	*5%*
4a	3·33	1·67	0	6·54	1·67	94·88	119·4	11·8	24·5	6·26
4b	15·00	6·67	3·33	14·63	3·73	57·16	66·22	90·11	95·93	24·43
5a	51·67	30	26·67	21·54	5·49	35·57	37·9	36·37	61·37	15·63
5b	38·33	21·67	28·33	52·08	13·26	63·69	70·35	63·51	93·91	23·92
7a	100	100	100	—	—	4·88	0·81	1·62	8·44	2·15
7b	96·67	95	83·33	15·35	3·91	0·27	0	2·14	4·64	1·18
8a	38·33	23·33	5·00	26·04	6·63	39·40	82·85	89·13	146·6	37·32
8b	91·67	76·67	61·67	26·18	6·67	3·29	5·66	9·16	10·65	2·71
FEN[a]	100	100	100	—	—	0	0	0	—	—
CYP[b]	100	100	100	—	—	0	0	0	—	—
LSD (0·05)	28·93	17·24	19·57	—	—	41·44	69·88	35·43	—	—
(±)SE (0·05)	9·74	5·80	6·59	—	—	13·95	23·52	11·93	—	—

[a] **FEN**: Fenvalerate.
[b] **CYP**: Cypermethrin.

(b) a central group containing two oxygen and carbon atoms, possibly all having some element of unsaturation (either as C=O or −C=C−);[5,6]
(c) a three-dimensional arrangement of key groups,[6] and
(d) mono-fluoro substitution at the C-4 position compared to C-3 or C-2 positions in non-ester pyrethroids.[11]

The compounds tested here are non-ester pyrethroids, with variations in the central link and with either F or H at C-4. A cursory glance at the table shows that compounds **7a**, **7b** (with alkane central link) and **8b** (having an unsaturation in the central link in the form of C=O) have excellent insecticidal activity comparable to fenvalerate and cypermethrin.

In the case of compounds with a carbonyl function (**4a**, **4b**, **8a** and **8b**), an α,β-unsaturated ketone group in the central link resulted in drastic reduction in activity (**4a**, **4b**). Higher activities of compounds **7a** and **7b** exemplified the fact that the degree of unsaturation may not necessarily be linked to higher insecticidal activities.

In our experiments we also found that fluoro substitution at C-4 appreciably increased insecticidal activity only in compounds having unsaturation as a carbonyl function in the central link, while in the alkanes (as central link), this effect could not be seen. An alcoholic group instead of a carbonyl function also drastically reduced the activity (**5a**, **5b**). These results confirm the earlier observations on the extreme sensitivities of the central part of the molecule, when the latter is modified in imparting insecticidal activities.[5,6] As suggested by Elliott *et al.*[4–6] the three-dimensional arrangement of key groups may play a pivotal role in modifying the insecticidal activities of these compounds.

None of the tested compounds showed any appreciable antifeedancy and the feeding was clearly related to the mortality/survival of the larvae.

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