Synthesis and Insecticidal Activities of Pyrethroids Derived from 3-Methyl-2-(3,4-dihydronaphthyl)butanoic Acids

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Sixteen pyrethroid esters derived from seven novel 3-methyl-(3,4-dihydronaphthyl)butanoic acids were synthesized. A major objective of the work was to investigate the impact on insecticidal activity of a lack of conformational rigidity in the acid moiety. Variations included within the examples are attachment of the butanoic acid to the C_1 or C_2 position of the 3,4-dihydronaphthyl ring, substitution of the 3,4-dihydronaphthyl group with chlorine, and esterification of the novel acids with a variety of known pyrethroid alcohols. Although several of these esters show good broad-spectrum insecticidal activity, none of the 3,4-dihydronaphthyl esters are as active as structurally similar materials that have already appeared in the literature.

The natural pyrethrins and the synthetic pyrethroids share several common structural features (A–E) shown in Figure 1 that are essential for high insecticidal activity. In general, the α-cyano-3-phenoxybenzyl moiety appears to afford the optimum definition of regions B–E in terms of maximizing insecticidal activity (Elliott, 1977). However, a variety of molecular structures have been shown suitable for the unsaturation requirement of region A. The commercial pyrethroids satisfy the region A requirements with the 2,2-dihalovinyl moiety attached to a 2,2-dimethylcyclopropane unit (L) or a simple aryl function attached to an isopropylmethinyl link (L). A variety of bicyclic and heterocyclic functionalities are reported in the patent and general literature as producing highly insecticidal esters when used to satisfy region A. These include benzofurans (Hadler and Woodward, 1980), indolines (Henrick et al., 1983), indenes (Anderson and Henrick, 1980), and naphthalene moieties (Schrider, 1977). In all of these examples the cyclic system in region A is conformationally rigid and planar. An objective of this work was to examine the impact on activity of using a nonplanar, conformationally mobile 3,4-dihydronaphthalene ring system in region A.

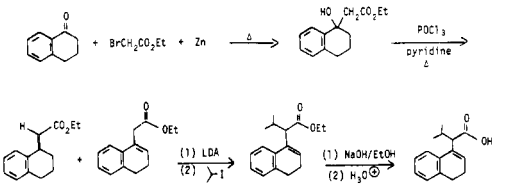
Sixteen esters derived from seven novel 2-[1- or 2-(3,4-dihydronaphthyl)]-3-methylbutanoic acids were synthesized to investigate the effect on activity of attaching the butanoic acid to C_1 or C_2 or the 3,4-dihydronaphthyl group, chlorine substitution on the ring, and use of a variety of known pyrethroid alcohols. The activity of these novel esters was directly compared with analogs having conformationally rigid rings in Region A.

EXPERIMENTAL SECTION

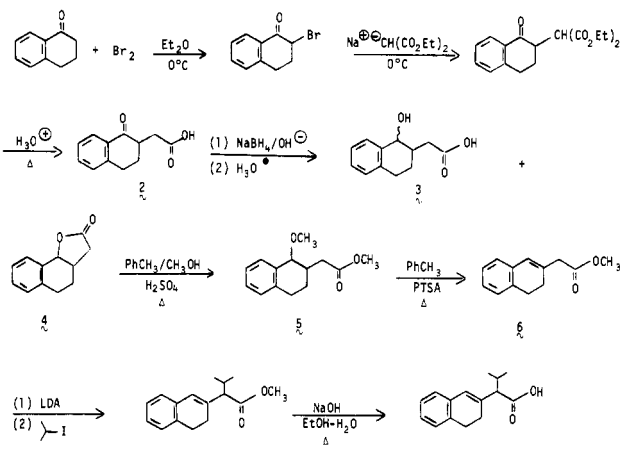
Synthetic Methods. The 3-methyl-2-(3,4-dihydro-1-naphthyl)butanoic acids were synthesized in four steps beginning with a Reformatsky reaction on a 1-tetralone (Scheme I). Fortunately, it is not necessary to separate the mixture of β,γ- and α,β-unsaturated esters obtained by dehydrating the Reformatsky product. Treatment of this mixture with lithium diisopropylamide followed by isopropyl iodide gives only the desired product resulting from alkylation at the position α to the ester function.

The 3-methyl-2-(3,4-dihydro-2-naphthyl)butanoic acids cannot readily be prepared by a similar Reformatsky reaction on β-tetralones for two reasons: (1) when subjected to the conditions of the Reformatsky reaction, β-tetralones undergo enolization with destruction of the organozinc reagent; (2) the necessary chlorinated β-tetralones for the synthesis of halogenated analogues of the parent acid are not readily available.

Scheme I



Scheme II



The eight-step synthetic route used to prepare 3-methyl-2-(3,4-dihydro-2-naphthyl)butanoic acids is shown in Scheme II. The sodium borohydride reduction of the γ-keto acid (**2**) gives a mixture of γ-hydroxy acid (**3**) and γ-lactone (**4**). These can be readily separated, but all attempts to alkylate the γ-lactone (**4**) with lithium diisopropylamide and isopropyl iodide gave only a low yield of the desired α-alkylated lactone and at least four unidentified byproducts. The α-alkylation of γ-butyrolactone is known to occur in good yield under these conditions (Hermann and Schlessinger, 1973), and the reason for the failure of **4** to undergo alkylation is not clear.

It is not necessary to separate γ-hydroxy acid (**3**) and γ-lactone (**4**). This mixture can be converted to the desired methyl 2-(3,4-dihydro-2-naphthyl)acetate (**6**) by prolonged refluxing with 30% (v/v) of concentrated sulfuric acid in methanol. Shorter reaction times or lower acid concentrations result in the formation of appreciable amounts of methyl 1-methoxy-2-(1,2,3,4-tetrahydro-2-naphthyl)acetate (**5**). This material may be converted to the desired methyl 2-3,4-dihydro-2-naphthyl)acetate (**6**) by refluxing in tolu-

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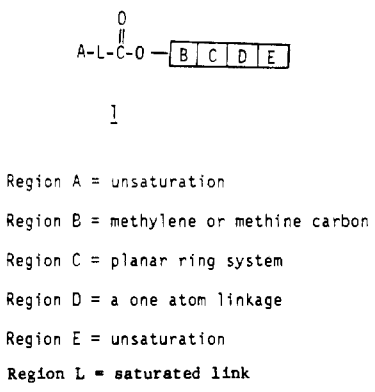


Figure 1.

ene with a small quantity of *p*-toluenesulfonic acid. Pyrethroid esters of these acids were prepared by conventional methods via the acid chloride reacting with an alcohol in the presence of a proton acceptor. All of the esters were purified by low-pressure liquid chromatography.

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 197 or Beckman Accu-Lab 2 spectrometer. NMR spectra were obtained with a Varian A-60 or EM 360L spectrometer with Me_4Si as an internal standard. Elemental analyses were obtained by the Union Carbide South Charleston Technical Center Analytical Group. Supplementary material containing spectral, biological, and analytical data is available (see paragraph at end of paper regarding supplementary material).

2-(5-Chloro-3,4-dihydro-1-naphthyl)-3-methylbutanoic Acid (8). [This procedure is representative of the syntheses of the 2-(3,4-dihydro-1-naphthyl)-3-methylbutanoic acids.] A mixture of 25.2 g (0.151 mol) of ethyl bromoacetate and 26.0 g (0.144 mol) of 5-chloro-1-tetralone (Strehlke et al., 1975) was converted to 33.4 g (86%) of the expected β-hydroxy ester by using standard Reformatsky procedures (Gruber et al., 1976): NMR ($CDCl_3$) δ 1.21 (t, 3 H), 1.50–2.40 (m, 4 H), 2.50–3.20 (m, 4 H), 4.15 (q, 2 H), 4.70 (br s, 1 H), 6.83–7.73 (m, 3 H).

The β-hydroxy ester (30.5 g, 0.113 mol) was dehydrated with phosphorus oxychloride–pyridine (Butenandt and Schmidt-Thome, 1938) to give 22.2 g (78%) of a mixture of β,γ- and α,β-unsaturated esters: NMR ($CDCl_3$) δ 1.23 (t pair, 3 H), 1.58–2.57 (m, 2 H); 2.57–3.35 (m, 2 H), 3.42 (br s, 2 H), 4.18 (q pair, 2 H), 6.02–6.33 (t pair, 1 H), 6.89–7.68 (m, 3 H).

A 500-mL flask fitted with mechanical stirrer, reflux condenser with nitrogen inlet, low-temperature thermometer, and addition funnel was dried and charged with 11.7 g (0.115 mol) of diisopropylamine and 100 mL of dry THF. This was cooled to −5 °C and 83 mL (0.133 mol) of 1.6 M *n*-butyl lithium added dropwise. The mixture was stirred at −5 °C for 15 min and then cooled to −76 °C and 22.2g (0.0885 mol) of the mixture of β,γ- and α,β-unsaturated esters prepared above was added dropwise. The mixture was stirred 0.5 h at −76 °C, and then 22.6 g (0.133 mol) of 2-iodopropane in 25 mL of dry THF was added dropwise. When this addition was complete, the mixture was allowed to warm to room temperature and stirred 12 h. The mixture was concentrated under reduced pressure, the residue was poured into ice–water acidified with concentrated HCl, extracted into ether, washed with water, and dried ($MgSO_4$), and the solvent was removed to leave 23.3 g (90%) of ethyl 2-(3,4-dihydro-5-chloro-1-naphthyl)-3-methylbutanoate as a viscous, yellow oil: NMR ($CDCl_3$) δ 0.50–1.40 (d pair, 6 H; t, 3 H), 1.80–2.50 (m, 3 H), 2.50–3.04 (m, 2 H), 3.20 (d, 1 H), 4.07 (q, 2 H), 6.25 (t, 1 H), 6.81–7.53 (m, 3 H).

A mixture of 23.3 g (0.0796 mol) of the above ester, 9.6 g (0.239 mol) of NaOH, 35 mL of water, and 35 mL of ethanol was heated at reflux overnight under nitrogen. The mixture was diluted with a 3-fold volume of water, extracted 2× with ether, acidified with concentrated HCl, and extracted into ether. The ether was washed with water and dried ($MgSO_4$), and the solvent was removed to leave 18.1 g of crude product. This was recrystallized from hexane–ethyl acetate to give 13.0 g (62%) of the desired acid as a white, crystalline solid, mp 104–105 °C: NMR ($CDCl_3$) δ 0.95 (d pair, 6 H), 1.80–3.10 (m, 5 H), 3.25 (d, 1 H), 6.30 (t, 1 H), 6.92–7.53 (m, 3 H), 10.80 (br s, 1 H).

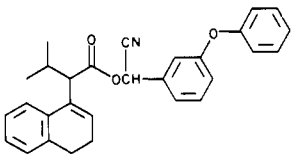
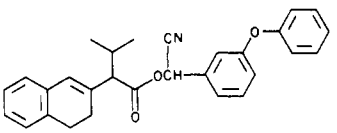
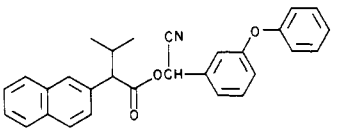
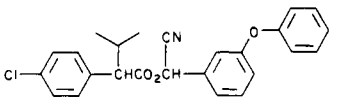
2-(7-Chloro-3,4-dihydro-2-naphthyl)-3-methylbutanoic Acid (11). [This procedure is representative of the syntheses of the 2-(3,4-dihydro-2-naphthyl)-3-methylbutanoic acids.] A 1-L flask equipped with a mechanical stirrer, reflux condenser with N_2 inlet, and addition funnel was dried and charged with 350 mL of dry ether and 59.0 g (0.33 mol) of 7-chloro-1-tetralone (Strehlke et al., 1975). This solution was cooled to −5 °C and bromine (52.7 g, 0.33 mol) added dropwise while maintaining the temperature at 0–5 °C. When all the bromine had been added, the mixture was stirred for 10 min and then poured onto ice. The ether layer was separated, the water was extracted 2× with ether, and the combined ether extracts were washed 2× with water, 2× with 10% Na_2CO_3, and 2× with water. The solution was dried ($MgSO_4$) and the solvent removed to leave 79.6 g (93%) of 2-bromo-7-chloro-1-tetralone as a pale yellow oil.

A solution of the sodium salt of diethyl malonate in 250 mL of benzene containing 15 mL of DMF was prepared from 17.3 g (0.36 mol) of 50% NaH and 57.7 g (0.36 mol) of diethyl malonate and cooled to 0–5 °C, and 79.0 g (0.31 mol) of the 2-bromo-7-chloro-1-tetralone prepared above in 50 mL of benzene added dropwise. After the addition, the mixture was allowed to come to room temperature and heated 12 h on the steam bath. The mixture was allowed to cool and poured into water, and the benzene was separated. The benzene layer was washed 2× with water and dried ($MgSO_4$), and the benzene was removed to leave a red oil. The excess diethyl malonate was removed by vacuum distillation to leave 93.4 g (89%) of diethyl (7-chloro-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)malonate: NMR ($CDCl_3$) δ 1.25 (t pair, 6 H), 1.80–2.41 (m, 2 H), 2.63–3.52 (m, 3 H), 4.13 (q pair, 5 H), 6.91–7.55 (m, 2 H), 7.90 (d, 1 H).

A mixture of the above malonate (93.4 g, 0.276 mol), 500 mL of concentrated HCl, and 500 mL of water was heated at reflux for 24 h. The mixture was then cooled, and extracted thoroughly with 1:1 CH_2Cl_2–acetone, the combined organic extracts were washed with H_2O and dried ($MgSO_4$), and the solvent was removed to leave 57.8 g of tan solid. This was recrystallized from acetone–ethyl acetate to give 48.0 g (73%) of the desired (7-chloro-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)acetic acid, mp 166–167 °C: NMR (Me_2SO-d_6) δ 1.45–3.89 (m, 7 H), 7.17–7.85 (m, 3 H), 12.15 (br s, 1 H).

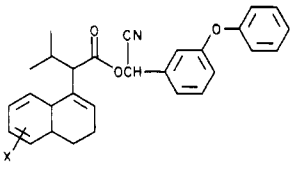
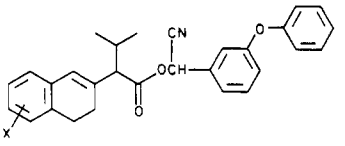
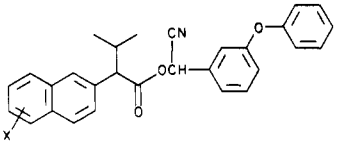
A solution of the above naphthylacetic acid (47.0 g, 0.197 mol) in 258 mL of water containing 15.8 g (0.39 mol) of NaOH was added dropwise to a solution of 4.6 g (0.122 mol) of sodium borohydride in 42 mL of 0.2 N NaOH. The reaction exothermed mildly and a white precipitate formed. The mixture was stirred overnight, then poured onto ice, and acidified with 6 N HCl, and the white solid was collected by filtration. The solid was taken up in acetone, and dried ($MgSO_4$), and the solvent was removed

Table I. Importance of Planarity in Region A to Insecticidal Activity

compd no.	structure	LC_{50}, ppm aphid	mite	SAW[a]	MBB	HF
14		5	i[b]	~250	23	i
15		~2	i	~65	9	400
16		0.3	i	10	3	90
17		~2	~82	3	~1	9

[a] SAW = southern armyworm; MBB = Mexican bean beetle; HF = house fly. [b] i = no activity at 500 ppm.

Table II. Effect of Halogen Substitution in the Naphthalene Ring on Insecticidal Activity

compd no.	X	structure	LC_{50}, ppm aphid	mite	SAW[a]	MBB	HF
14	H		5	i[b]	~250	23	i
18	5-Cl		3	i	~125	3	i
19	7-Cl		~12	i	i	~500	i
15	H		~2	i	~65	9	400
20	5-Cl		3	~350	>500	18	i
21	6-Cl		~4	i	>500	~50	i
22	7-Cl		4	i	~500	~7.5	i
23	H		0.3	i	10	3	~90
24	5-Cl		1.5	i	165	5	i
25	6-Cl		0.4	i	~62	13	i
26	7-Cl		0.2	i	42	13	i

[a] SAW = southern armyworm; MBB = Mexican bean beetle; HF = house fly. [b] i = inactive at 500 ppm.

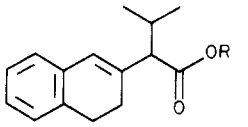
to leave 45.2 g of white solid. Spectral analysis showed this to be a mixture of (7-chloro-1-hydroxy-1,2,3,4-tetrahydro-2-naphthyl)acetic acid and the lactone resulting from its cyclization. This mixture was used in the next step without purification: NMR (acetone-d_6) δ 1.00–3.30 (m, 7 H), 4.38 (d, 1 H), 5.40 (d, 1 H), 6.73–7.68 (m, 3 H); IR (CH_2Cl_2) 2500–3500, 1780, 1710, 1170 cm^{-1}.

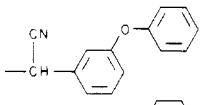
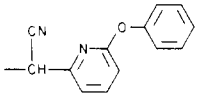
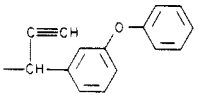
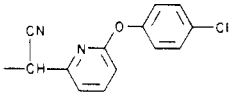
The mixture (15.0 g, 0.0623 mol) of hydroxy acid and lactone described above was heated at reflux overnight in 150 mL of 1:1 toluene–methanol containing 3 mL of concentrated sulfuric acid. The condensate from the reflux was passed through Type 3A molecular sieves. The mixture was then cooled to room temperature, poured into water, and extracted into ether. The ether was washed 2× with saturated $NaHCO_3$ and then water, and dried ($MgSO_4$), and the ether was removed to give 13.9 g (88%) of methyl (7-chloro-1-methoxy-1,2,3,4-tetrahydronaphthyl)-acetate as a tan semisolid: NMR ($CDCl_3$) δ 1.33–3.10 (m, 7 H), 3.40 (s pair, 3 H), 3.75 (s, 3 H), 4.18 (d, 1 H), 5.83–7.60 (m, 3 H).

The above methyl acetate (13.9 g, 0.0517 mol) was refluxed for 4 h in 100 mL of toluene containing 2 g of *p*-toluenesulfonic acid. The solution turned a dark blue-violet color during this period. The mixture was then cooled to room temperature, poured into water, and extracted into ether. The ether was washed 2× with saturated $NaHCO_3$ and 2× with water, dried ($MgSO_4$), and treated with decolorizing charcoal. The solvent was removed to leave 10.3 g (84%) of methyl (7-chloro-3,4-dihydro-2-naphthyl)acetate as a yellow oil: NMR ($CDCl_3$) δ 1.97–2.93 (m, 4 H), 3.12 (s, 2 H), 3.50 (s, 3 H), 6.13 (m, 1 H), 6.70–7.39 (m, 3 H).

A solution of lithium diisopropylamide was prepared from 35 mL (0.056 mol) of 1.6 M *n*-butyl lithium and 5.7 g (0.056 mol) of diisopropylamine in 56 mL of dry THF. This solution was cooled to −76 °C, and 11.0 g (0.0465 mol) of the above methyl acetate in 15 mL of THF was added dropwise followed by the dropwise addition of 10.0 g (0.056 mol) of hexamethylphosphoramide in 10 mL of THF. After the mixture was stirred for 30 min at −76 °C, a

Table III. Effect of the Alcohol Moiety on Insecticidal Activity



compd	R	LC_{50}, ppm a-phid	mite	SAW	MBB	HF
15		~2	i	~65	9	400
27		3	i	~45	38	~160
28		~4	~500	270	19	i
29		0.8	i	150	~500	250

solution of 15.8 g (0.093 mol) of 2-iodopropane in 15 mL of the THF was added dropwise. The mixture was stirred for 1 h at −76 °C and then allowed to warm overnight to room temperature. The mixture was concentrated under reduced pressure, poured into ice water, acidified with concentrated HCl, and extracted into ether. The ether extracts were washed 2× with 5% HCl and 2× with water and dried ($MgSO_4$), and the ether was removed to leave a red oil. This material was purified by LPLC on silica gel using 95:5 hexane–ethyl acetate to give 8.1 g (62%) of methyl 2-(7-chloro-3,4-dihydro-2-naphthyl)-3-methylbutanoate as a pale yellow oil: NMR ($CDCl_3$) δ 0.97 (d pair, 6 H), 1.80–2.95 (7, 6 H), 3.64 (s, 3 H), 6.21 (s, 1 H), 6.95 (br s, 3 H).

The above methyl ester (8.1 g, 0.029 mol), 3.5 g (0.0870 mol) of NaOH, and 100 mL of 1:1 ethanol-water were refluxed overnight under N_2. The mixture was concentrated under reduced pressure, taken up in water, and extracted 2× with ether, and the aqueous layer was acidified with concentrated HCl. The resulting precipitate was extracted into ether, washed with water, and dried ($MgSO_4$), and the ether removed to give 6.6 g of a yellow solid. This was recrystallized from hexane–ethyl acetate to give 5.5 g (72%) of 2-(7-chloro-3,4-dihydro-2-naphthyl)-3-methylbutanoic acid as a white solid, mp 135–137 °C: NMR ($CDCl_3$) δ 0.90 (d pair, 6 H), 1.80–3.00 (m, 6 H), 6.35 (s, 1 H), 7.00 (br s, 3 H), 10.9 (br s, 1 H).

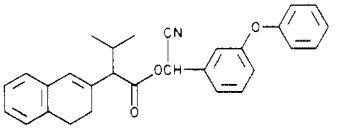
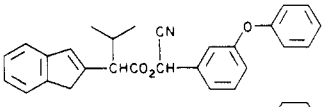
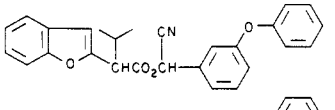
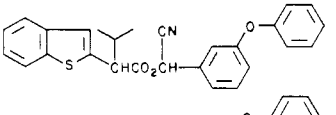
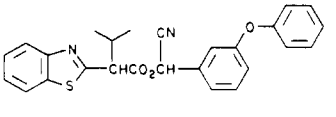
α-Cyano-3-phenoxybenzyl 2-(3,4-Dihydro-2-naphthyl)-3-methylbutanonate (**15**). Using a previously described esterification procedure (Ayad and Wheeler, 1984), 2.5 g (0.0109 mol) of 2-(3,4-dihydro-2-naphthyl)-3-methylbutanoic acid was converted to 4.56 g of the crude ester **15**. This was purified by LPLC to give 3.9 g (82%) of the desired ester as a clear colorless, viscous oil that shows one spot (R_f 0.41) on TLC (80:20 hexane–ethyl acetate): NMR ($CDCl_3$) δ 0.70–1.15 (m, 6 H), 1.80–2.80 (m, 5 H), 2.90 (d, 1 H), 6.30 (br s, 2 H), 6.75–8.05 (m, 13 H).

Biological Methods. The biological activity of all compounds was evaluated on insects and mites by using procedures described by Payne et al. (1966) and Weiden et al. (1967). Suspensions of the test compounds were prepared by dissolving 1 g of compound in 50 mL of acetone containing 0.1 g of an alkylphenoxypolyethoxyethanol surfactant. This suspension was diluted with 150 mL of water and stirred well to give a 0.005 g/mL suspension of test compound. The test concentrations were obtained by appropriate dilutions of this stock suspension with water.

Bioassays with the buckthorn aphid (*Aphis nasturtii* Kaltenbach) were conducted by spraying nasturtium plants previously infested with approximately 125 adults and nymphas with aqueous formulations of the test compound. After spraying, plants were held at 18–21 °C and 50–70% relative humidity, and mortality counts were taken after 24 h.

Tests on the southern armyworm, *Spodoptera eridania* (Cramer), and Mexican bean beetle, *Epilachna varivestis* (Mulsant), were conducted by placing five third instar larvae in Petri dishes that contained two leaves of tendergreen bean plant previously treated with aqueous formulations of the toxicants. The closed dishes were held at 27 ± 3 °C and 50 ± 5% relative humidity, and mortality was assessed after 3 days.

Table IV. Comparison of Insecticidal Activity of (3,4-Dihydronaphthyl)butanoic Acid Esters to That of Other Bicyclic and Heterocyclic Esters

compd no.	structure	LC_{50}, ppm aphid	mite	SAW	MBB	HF
15		~2	i	~65	9	400
30		0.8	500	17	3	~40
31		~0.7	210	~45	11	23
32		0.20	400	7	1	33
33		5	500	>500	~500	~290

The pyrethroids were screened against 25 4–6-day-old adult house flies (*Musca domestica*, L.) by allowing the flies to feed for up to 24 h on a 10% sugar solution of the test compounds at which time mortality was recorded.

Bioassays on the two-spotted spider mite, *Tetranychus urticae* Koch, were conducted by spraying tendergreen bean plants infested with 150–200 mites with aqueous formulations of the test compounds. The treated plants were held at 27 ± 3 °C and 50 ± 5% relative humidity for a period of 7 days, and mortality counts of motile forms (adults and nymphs) were made.

Insecticidal and acaricidal activities are reported as LC_{50} values (ppm).

RESULTS AND DISCUSSION

None of the esters synthesized in this study exhibit insecticidal activity equivalent to esters derived from isovaleric acids substituted at the 2-position by fully unsaturated, planar rings. Thus, in Table I it can be seen that **15** is not as active as its naphthyl analogue **16** or fenvalerate. It is also evident from Table I that the ester derived from 2-(3,4-dihydro-2-naphthyl)-3-methylbutanoic acid (**15**) is considerably more active on lepidopterous insects than the ester derived from 2-(3,4-dihydro-1-naphthyl)-3-methylbutanoic acid (**14**). If the fused benzene ring is viewed as an "ortho substituent" on the cyclohexene ring, the diminished activity of **14** relative to **15** is similar to the substantial reduction in activity when an ortho substituent is placed on a phenylacetate ester (Elliott, 1977).

In the pyrethroid esters derived from 2-isopropyl-2-phenylacetic acids, substitution of the benzene ring by chlorine in the para position affords substantial improvement in insecticidal activity. However, as Table II indicates, when any of the esters derived from naphthalene is substituted with chlorine at any benzo ring position, the overall insecticidal activity is reduced. The single exception is the ester derived from 2-(3-,4-dihydro-1-naphthyl)-3-methylbutanoic acid (**14**). Substitution of chlorine at the 5-position appears to increase insecticidal activity on the Mexican bean beetle (compare **18** and **14**).

Table III demonstrates that no significant improvements in insecticidal activity could be obtained by using a variety of other known pyrethroid alcohols in place of α-cyano-3-phenoxybenzyl alcohol.

Finally, in Table IV the insecticidal activity of the pyrethroid ester derived from 2-(3,4-dihydro-2-naphthyl)-3-methylbutanoic acid is compared to pyrethroids derived from structurally similar bicyclic and heterocyclic acids. The dihydro naphthalene ester is less active than any of these analogues except **33**.

In summary, seven novel acids derived from 3,4-dihydronaphthalenes have been synthesized and converted to insecticidal pyrethroid esters. None of these esters affords an activity advantage to structurally similar, known materials.

Registry No. **8**, 91111-21-6; **11**, 91111-22-7; **14**, 91111-23-8; **15**, 91111-24-9; **16**, 64497-81-0; **17**, 51630-58-1; **18**, 91111-25-0; **19**, 91159-18-1; **20**, 91111-26-1; **21**, 91111-27-2; **22**, 91111-28-3; **23**, 64497-81-0; **24**, 91111-29-4; **25**, 65225-39-0; **26**, 91111-30-7; **27**, 91111-31-8; **28**, 91111-32-9; **29**, 91111-33-0; **30**, 73818-25-4; **31**, 75566-30-2; **32**, 75894-10-9; **33**, 91111-34-1; **34**, 91111-35-2; **35**, 91111-36-3; **36**, 91111-37-4; **37**, 91111-38-5; **38**, 91111-39-6; **39**, 91111-40-9; ethyl bromoacetate, 105-36-2; 5-chloro-1-tetralone, 26673-30-3; ethyl(1-hydroxy-1,2,3,4-tetrahydro-1-naphthyl)acetate, 91111-41-0; ethyl 2-(3,4-dihydro-5-chloro-1-naphthyl)3-methylbutanoate, 91111-42-1; (7-chloro-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)acetic acid, 70603-11-1; (7-chloro-1-hydroxy-1,2,3,4-tetrahydro-2-naphthyl)acetic acid, 91111-43-2; 7-chloro-1-tetralone, 26673-32-5; 2-bromo-7-chloro-1-tetralone, 56820-57-6; diethyl malonate, 105-53-3; diethyl(7-chloro-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)malonate, 91111-44-3; methyl(7-chloro-1-methoxy-1,2,3,4-tetrahydronaphthyl)acetate, 91111-45-4; methyl(7-chloro-3,4-dihydro-2-naphthyl)acetate, 91111-46-5; methyl 2-(7-chloro-3,4-dihydro-2-naphthyl)-3-methylbutanoate, 91111-47-6; 2-(3,4-dihydro-2-naphthyl)-3-methylbutanoic acid, 91111-48-7.

Supplementary Material Available: Table I, pyrethroid acids from 3,4-dihydronaphthylbutanoic acids, Table II, insecticidal activity of 3-methyl-2-(3,4-dihydronaphthyl)butanoic acid esters, Table III, elemental analyses, Table IV, NMR parameters, and Table V, principal infrared bands of the pyrethroid esters (12 pages). Ordering information is given on any current masthead page.

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