

Original Article

Synthesis and Insecticidal Activity of Some Compounds Related to Tetramethylcyclopropanecarboxylate

Akimichi FURUHATA, Masachika HIRANO,* Izumi FUJIMOTO* and Masanao MATSUI**

*Kawasaki Research Center, T. Hasegawa Co., Ltd., Nakahara-ku, Kawasaki 211, Japan***Takarazuka Research Center, Pesticides Research Laboratory, Sumitomo Chemical Co., Ltd., Takatsukasa, Takarazuka 665, Japan****Tokyo University of Agriculture, Setagaya-ku, Tokyo 156, Japan*

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Four kinds of acids generated by conceptual cleavage of a bond between C-1 and C-2 bond in 2,2,3,3-tetramethylcyclopropanecarboxylic acid, the acid part of fenpropathrin, were prepared. Most of their esters with pyrethroidal alcohols did not show insecticidal activity. The insecticidally active esters of 2-isopropyl-3-methyl-3-butenic acid (**2**), a type which is cleaved at the cyclopropane ring between C-2 and C-3 bond, with 3-phenoxybenzyl (**a**) and 5-benzyl-3-furylmethyl (**b**) alcohols, were converted to ethers and a hydrocarbon. The former showed insecticidal activity to brown planthoppers and green rice leafhoppers, and the latter to carmine mites, while the mother esters did not show the activity to any of these insects. When alcohol part **a**, **b** or **c** of the esters **2** was changed to 2,4-, 2,5- or 2,6-dimethylbenzyl alcohol, the activity was relatively weaker than that of the mother esters.

INTRODUCTION

In the previous paper¹⁾ we reported the insecticidal activity of esters of acids whose structures were derived from conceptual cleavage of a bond between C-2 and C-3 of the cyclopropane ring in tetramethylcyclopropanecarboxylic acid (**1**). Esters with 3-phenoxybenzyl (**a**), 5-benzyl-3-furylmethyl (**b**) and α -cyano-3-phenoxybenzyl (**c**) alcohols were active. Iso-propyl-3-methyl-3-butenic acid (**2**) was the most active acid component.

Our interests are now in the activity of 1) esters of acids derived from the bond cleavage between C-1 and C-2 in acid **1** with **a**, **b** and **c** alcohols, 2) compounds which were produced by replacing the ester linkage of (**2a**) and (**2b**) with either an ether or a hydrocarbon linkage and 3) dimethylbenzyl esters of acid **2**. The compounds are illustrated in Fig. 1.

MATERIALS AND METHODS

1. Physical Measurements

All bps and mps are uncorrected. Analytical instruments were IR (Jasco IRA-2 or Hitachi R-EPI-G2), NMR (Jeol FX 200Q), MS (Shimadzu GC-MS 6020 or Hitachi M-80B), and GLC (Shimadzu GC-7A, PEG 20M, $5\phi \times 2$ m, N_2 : 40 ml/min).

2. Chemicals

2.1 Acids

2,2,3,3-Tetramethylbutanoic acid (3). Acid **3** was prepared by the Haaf-Koch reaction.²⁾ mp 194–196°C. (lit.²⁾ 194.5–196.5°C). IR ν_{\max}^{KBr} cm^{-1} : 3050, 1690, 1145. NMR($CDCl_3$) δ ppm: 0.99 (9 H, s), 1.16 (6 H, s). MS m/z : 129 (2%, $M^+ - Me$), 101 (10), 88 (88), 73 (16), 59 (21), 57 (100), 41 (48).

(E)-3,4,4-Trimethyl-2-pentenoic acid (4). A mixture of ethyl 3,4,4-trimethyl-2-pentenoate

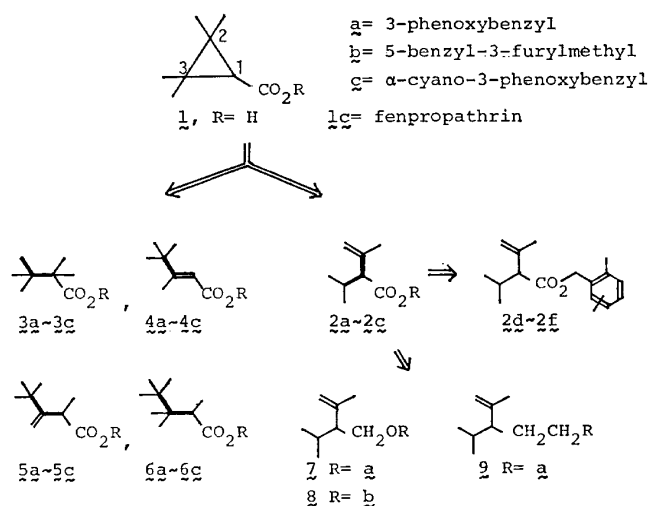


Fig. 1 Prepared compounds.

(**10**) and ethyl 3-*t*-butyl-3-butenate (**11**) (1:1, 12.2 g) obtained by the Reformatsky reaction^{3,4)} was refluxed with sodium hydroxide (6.6 g) in 95% ethanol (60 g) for 3 hr. The reaction mixture was treated in the conventional manner to give crystalline acid **4** (9.4 g, 92%). Recrystallization from pentane gave pure acid **4** (5.6 g). mp 81–82°C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3600–2400, 1685, 1625, 1265, 1230, 940. NMR (CDCl_3) δ ppm: 1.12 (9 H, s), 2.18 (2 H, d, $J = 1.2$ Hz), 5.78 (1 H, d, $J = 1.2$ Hz). MS m/z : 127 (43%, $M^+ - \text{Me}$), 126 (30), 109 (14), 97 (45), 86 (20), 45 (100).

3-*t*-Butyl-2-methyl-3-butenic acid (5). Ethyl 3-hydroxy-2,3,4,4-tetramethylpentanoate (**12**, 24 g) obtained by the Reformatsky reaction of pinacolone (28 g) with ethyl 2-bromopropionate (51 g) was dehydrated by thionyl chloride (16 g) in the presence of pyridine (23 g) to give a mixture of **13** and **14** (5:95, 18.1 g, 82%). The mixture (9.2 g) was hydrolyzed as in the same manner as **4** to give acid **5** (7.2 g, 92%). The mixture of **13** and **14**: bp 116–120°C/65 mmHg. **13**: GLC t_R : 4.4 min (110°C). MS m/z : 184 (2%, M^+), 169 (7), 102 (33), 97 (21), 83 (100), 74 (17), 55 (54). **14**: GLC t_R : 2.1 min (110°C). NMR (CDCl_3) δ ppm: 1.03 (9 H, s), 1.18 (3 H, t, $J = 7.0$ Hz), 1.24 (3 H, d, $J = 7.0$ Hz), 3.26 (1 H, q, $J = 7.0$ Hz), 4.03 (2 H, q, $J = 7.0$ Hz), 4.92 (2 H, bs). MS m/z : 184 (6%, M^+), 169 (60), 141 (28), 111 (30), 102 (20), 95 (34), 83 (100), 69 (64), 57 (60), 55 (66). Acid **5**: mp 64–65.5°C (from hexane). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3600–2400, 1705, 1635, 910. NMR (CDCl_3) δ ppm: 1.10 (9 H, s), 1.32

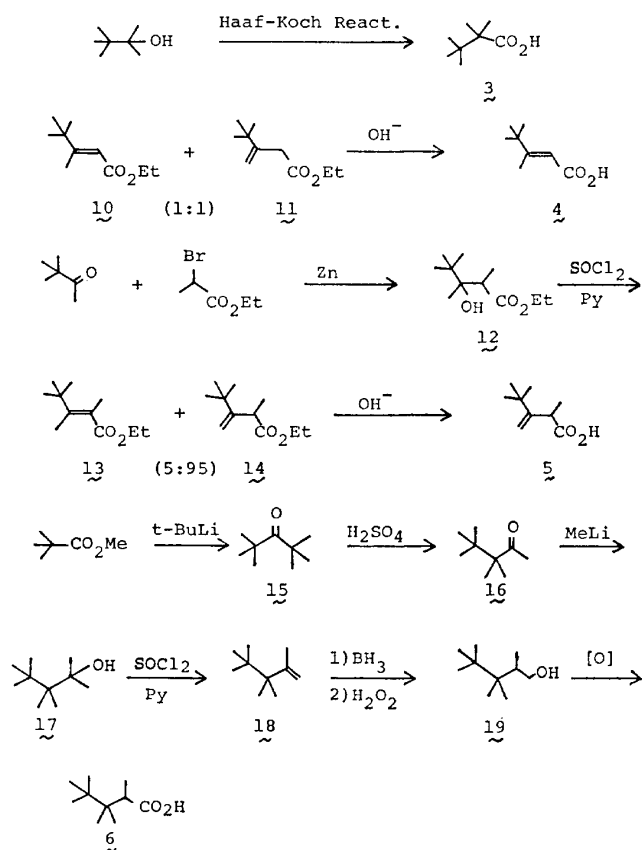
(3 H, d, $J = 7.3$ Hz), 3.26 (1 H, q-d, $J = 1.5, 7.3$ Hz), 5.03 (1 H, s), 5.06 (1 H, d, $J = 1.5$ Hz). MS m/z : 156 (1%, M^+), 141 (8), 95 (24), 83 (100), 57 (32), 55 (48).

2,3,3,4,4-Pentamethylpentanoic acid (6). Acid **6** was prepared as follows. 2,2,4,4-Tetramethyl-3-pentanone (**15**)⁵⁾ was prepared by a modified method in step one. To a solution of methyl pivalate (28 g, 0.24 mol) in ether (30 ml) was added dropwise *t*-butyllithium in pentane (2.2 M sol. 110 ml, 0.24 mol) at -30 – -35°C under Ar and the mixture was stirred for 30 min. The reaction mixture was poured into 2 N aq. HCl (150 ml) and the upper layer was separated. The aqueous layer was extracted with ether (50 ml) and the extracts were combined. The routine workup gave **15** (24.6 g, 81%). bp 150–152°C/760 mmHg (lit.⁵⁾ 152–153°C). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1685 (lit.⁵⁾ = 5.93 μ = 1685 cm^{-1}). NMR (CDCl_3) δ ppm: 1.24 (18 H, s). MS m/z : 142 (3%, M^+), 85 (16), 57 (100).

After the ketone **15** was converted to ketone **16** by the Bartlett method,⁵⁾ methyllithium in ether (1.6 M sol., 67 ml) was added to **16** (8.8 g, 70 mmol) in ether (40 ml) at -40 – -30°C under Ar and then the mixture was allowed to warm up to 0°C . The reaction mixture was poured into aq. sat. NH_4Cl (100 ml), and the routine workup gave alcohol **17** (7.6 g, 77%). bp 78–80°C/15 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3630, 3490. NMR (CDCl_3) δ ppm: 0.91 (6 H, s), 1.03 (9 H, s), 1.31 (6 H, s), 1.65 (1 H, bs). MS m/z : 100 (1%), 99 (1), 58 (11), 56 (6), 31 (100).

Alcohol **17** (4.8 g) was dehydrated in the same manner as **12** to give **18** (2.7 g, 64%). bp 95–96°C/120 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3080, 1625, 890. NMR (CDCl_3) δ ppm: 0.90 (9 H, s), 1.05 (6 H, s), 1.81 (3 H, d, $J = 1.2$ Hz), 4.75 (1 H, bs), 4.93 (1 H, bs). MS m/z : 125 (2%), 84 (48), 83 (28), 69 (31), 57 (100).

To a solution of **18** (2.2 g, 16 mmol) and THF (15 ml) was added BH_3 -THF (1 M sol., 8 ml) at 0 – 10°C over 30 min under Ar and the mixture was stirred for 1 hr. Following the addition of water (0.8 ml) and 3 N aq. sodium hydroxide (2.5 ml), 30% aq. hydrogen peroxide (1.8 ml) was added over 30 min and the mixture was stirred for 1 hr. Saturated aq. NaCl (10 ml) was added and the organic layer was separated. The aqueous layer was extracted with ether (20 ml), and the combined

Fig. 2 Synthetic routes of **3-6**.

organic layer was worked up in the conventional manner to give **19** (2.2 g, 90%). bp: 103–104°C/12 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3340, 1010. NMR (CDCl_3) δ ppm: 0.81 (3 H, s), 0.90 (9 H, s), 1.03 (3 H, d, $J=6.8$ Hz), 1.22 (1 H, bs), 1.76 (1 H, m), 2.34 (1 H, d-d, $J=7.4, 10.8$ Hz), 2.88 (1 H, d-d, $J=3.4, 10.8$ Hz). MS m/z : 101 (8%, $\text{M}^+ - t\text{-Bu}$), 99 (16), 83 (22), 69 (23), 57 (100).

A mixture of **19** (0.8 g, 5.1 mmol), KMnO_4 (3.2 g, 25 mmol), sodium hydroxide (0.2 g) and water (60 ml) was stirred at room temperature for 1 day and NaHSO_3 (7.8 g) was added. The reaction mixture was filtered. The filtrate was acidified with dil. aq. HCl and extracted with ether (30 ml \times 2). The organic layer was washed with sat. aq. NaCl and dried over MgSO_4 . The ether was removed and acid **6** (0.80 g, 91%) was obtained as a colorless oil. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3080, 2725, 2640, 2540, 1705, 940. NMR (CDCl_3) δ ppm: 0.92 (3 H, s), 0.93 (9 H, s), 0.99 (3 H, s), 1.20 (3 H, d, $J=7.1$ Hz), 2.67 (1 H, q, $J=7.1$ Hz). MS m/z : 159 (2%, $\text{M}^+ - \text{Me}$), 117 (12), 115 (8), 101 (25), 57 (100).

2.2 Esterification

1) Acids **3-6** were converted to their acyl

chlorides with thionyl chloride and esterified with 3-phenoxybenzyl (**a**), 5-benzyl-3-furylmethyl (**b**) and α -cyano-3-phenoxybenzyl (**c**) alcohols in the presence of pyridine. The products were purified by silica-gel chromatography. In the same manner acid **2** was esterified with 2,4-dimethylbenzyl (**d**) and 2,5-dimethylbenzyl (**e**) alcohols to give esters **2d** and **2e**. ^1H NMR spectra of the esters supported their structures.

2) *2,6-Dimethylbenzyl 2-isopropyl-3-methyl-3-butenolate (2f)*. 2,6-Dimethylbenzyl alcohol (**f**, 1.0 g, 7.4 mmol) prepared by the reduction of 2,6-dimethylbenzoic acid with LiAlH_4 (96% yield) was stirred with aq. 47% HBr (5 ml) at room temperature for 4 hr and the mixture was shaken with ether (20 ml). The extract was washed with sat. aq. NaCl, dried over MgSO_4 and concentrated to give 2,6-dimethylbenzyl bromide (**20**, 1.42 g, 97%). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3070, 3020, 1585, 765, 605, 505. NMR (CDCl_3) δ ppm: 2.42 (6 H, s), 4.57 (2 H, s), 6.98–7.15 (3 H, m). To the sodium salt of acid **2** in THF (prepared from **2** (1.14 g, 8 mmol), 55% sodium hydride (0.35 g, 8 mmol) and THF 7 ml) was added bromide **20** (1.32 g) in DMF (5 ml), and the mixture was refluxed for 5 hr. The reaction mixture was washed with water (15 ml \times 2) and distilled to give ester **2f** (1.2 g, 69%). bp 126–127°C/1 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3080, 3025, 1730, 1640, 1590, 1465, 1160, 1120, 900, 770, 740. NMR (CDCl_3) δ ppm: 0.82 (3 H, d, $J=6.8$ Hz), 0.90 (3 H, d, $J=6.8$ Hz), 1.72 (3 H, bs), 2.13 (1 H, m), 2.36 (6 H, s), 2.69 (1 H, d, $J=10.8$ Hz), 4.89 (2 H, bs), 5.16 (2 H, d, $J=5.1$ Hz), 7.0–7.2 (3 H, m). MS m/z : 158 (1%), 119 (100).

2.3 Ethers

2-Isopropyl-3-methyl-3-butenyl 3-phenoxybenzyl ether (7). Acid **2** (12.8 g, 90 mmol) in ether (20 ml) was added to a mixture of LiAlH_4 (3.1 g, 60 mmol) and ether (150 ml) over 30 min and refluxed for 1 hr. The reaction mixture was poured into sat. aq. NH_4Cl (100 ml) and the ether layer was worked up in the conventional manner to give alcohol **21** (10.9 g, 95%). To alkoxide obtained from **21** (1.02 g, 8 mmol), sodium hydride (0.19 g, 8 mmol) and DME (5 ml) was added 3-phenoxybenzyl chloride (1.53 g, 7 mmol), and the mixture was stirred for 6 hr at room temperature. The reaction mixture was treated in the conventional manner to

give crude **7** (2.3 g) and this crude mixture on column chromatography (hexane: CH_2Cl_2 = 2: 1) gave pure **7** (0.9 g, 42%). **21**: bp 99–101°C/70 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3370, 3060, 1640, 1060, 1035, 1005, 880. NMR(CDCl_3) δ ppm: 0.86 (3 H, d, J = 6.6 Hz), 0.93 (3 H, d, J = 6.2 Hz), 1.43 (1 H, bs), 1.61 (1 H, m), 1.77 (3 H, bs), 1.94 (1 H, d–d–d, J = 4.5, 9.7, 10.3 Hz), 3.45 (1 H, d–d, J = 10.3, 10.3 Hz), 3.73 (1 H, d–d, J = 4.5, 10.3 Hz), 4.83 (1 H, bs), 4.98 (1 H, bs). MS m/z : 128 (1%, M^+), 110 (8), 98 (14), 97 (19), 95 (22), 86 (33), 83 (34), 71 (40), 68 (100), 55 (68). **7**: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3075, 3050, 1640, 1585, 1485, 1445, 1255, 1215, 1105, 890, 775, 690. NMR(CDCl_3) δ ppm: 0.83 (3 H, d, J = 6.3 Hz), 0.88 (3 H, d, J = 6.3 Hz), 1.64 (3 H, bs), 1.5–1.75 (1 H, m), 2.03 (1 H, d–t, J = 5.1, 9.7 Hz), 3.38–3.57 (2 H, m), 4.42 (1 H, d, J = 13.1 Hz), 4.50 (1 H, d, J = 13.1 Hz), 4.70 (1 H, m), 4.80 (1 H, m), 6.8–7.6 (9 H, m). MS m/z : 310 (2%, M^+), 198 (48), 184 (50), 183 (100), 112 (76), 97 (16), 83 (10), 57 (29), 55 (18).

2-Isopropyl-3-methyl-3-butenyl 5-benzyl-3-furylmethyl ether (8). In the same manner as above ether **8** was prepared from alcohol **21** (1.02 g, 8 mmol) and 5-benzyl-3-chloromethylfuran (1.53 g, 7 mmol) in 47% yield (1.11 g). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3030, 3015, 1640, 1600, 1550, 1450, 1090, 950, 885, 730, 700. NMR(CDCl_3) δ ppm: 0.82 (3 H, d, J = 6.3 Hz), 0.89 (3 H, d, J = 6.3 Hz), 1.65 (3 H, bs), 1.75 (1 H, m), 2.02 (1 H, d–t, J = 5.1, 7.1 Hz), 3.45 (2 H, m), 3.92 (2 H, s), 4.25 (1 H, d, J = 11.4 Hz), 4.33 (1 H, d, J = 11.4 Hz), 4.70 (1 H, m), 4.81 (1 H, m), 7.20 (1 H, s), 7.1–7.4 (6 H, m). MS m/z : 298 (34%, M^+), 269 (81), 187 (11), 172 (72), 171 (75), 143 (70), 128 (100), 115 (44), 91 (69), 69 (40), 55 (58), 43 (42), 41 (76).

2.4 Hydrocarbon

3-Isopropyl-2-methyl-6-(3-phenoxyphenyl)-1-hexane (9). Hydrocarbon **9** was prepared as follows. To a solution of 3-phenoxybenzylmagnesium chloride obtained from Mg (1.0 g, 42 mmol) and 3-phenoxybenzyl chloride (7.65 g, 35 mmol) in ether (100 ml) was added small pieces of dry ice (30 g), and the mixture was stirred for 10 min. The reaction mixture was poured into 2 N aq. HCl (40 ml) and the ether layer was worked up in the conventional manner to give crude acid **22** (6.7 g). Recrystallization from hexane (150 ml) gave pure **22** (6.4

g, 85%). mp 86–87.5°C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3020, 1700. NMR(CDCl_3) δ ppm: 3.62 (2 H, s), 6.9–7.4 (9 H, m). MS m/z : 228 (100%, M^+), 183 (54), 168 (15), 153 (11), 91 (17), 87 (22), 77 (38), 51 (38), 45 (14).

Acid **22** (6.4 g, 30 mmol) in THF (20 ml) was reduced with LiAlH_4 (1.14 g, 30 mmol) in THF (10 ml) at 50–60°C for 1 hr to give alcohol **23** (5.8 g, 89%). bp: 150–152°C/1.5 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3360, 1580. NMR(CDCl_3) δ ppm: 1.72 (1 H, bs), 2.82 (2 H, t, J = 6.6 Hz), 3.82 (2 H, t, J = 6.6 Hz), 6.8–7.4 (9 H, m). MS m/z : 214 (100%, M^+), 183 (85), 168 (14), 91 (52), 77 (47), 51 (50), 49 (45), 31 (63).

Alcohol **23** (5.5 g) was chlorinated by the method of Calzada and Hood⁶⁾. The crude product was purified by silica-gel column chromatography (CH_2Cl_2) to give chloride **24** (4.6 g, 79%). IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3075, 3050, 1580, 1480, 1440, 1255, 1210, 1160, 1140, 750, 690. NMR(CDCl_3) δ ppm: 3.03 (2 H, d, J = 7.4 Hz), 3.68 (2 H, d, J = 7.4 Hz), 6.85–7.4 (9 H, m). MS m/z : 234 (30%, M^+), 232 (100, M^+), 197 (12), 183 (84).

The Grignard reagent obtained from Mg powder (0.27 g, 11 mmol) and chloride **24** (2.3 g, 10 mmol) in ether (20 ml) was added to a mixture of tosylate (2.0 g, 7.1 mmol) of alcohol **21**, Li_2CuCl_4 ⁷⁾ (110 mg) and THF (10 ml) at –65°C, and the mixture was allowed to stand overnight. The routine workup gave crude **9** (3.5 g). Column chromatography (hexane: CH_2Cl_2 = 1: 1) gave pure **9** (0.13 g, 6.2%) and a mixture of 3-phenoxyphenylethane and 3-phenoxystyrene (2.0 g, 3: 2), and recovered the tosylate

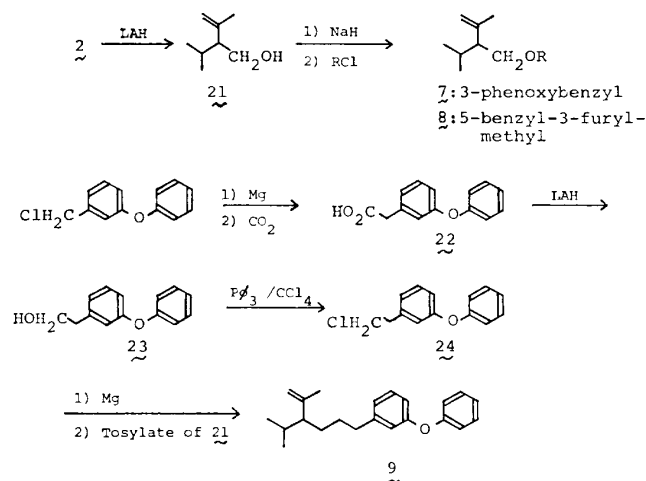


Fig. 3 Synthetic routes of **7**–**9**.

(1.3 g). By-products were identified by MS. **9**: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 3075, 3040, 1640, 1585, 1440, 1255, 1220, 890, 690. NMR(CDCl_3) δ ppm: 0.79 (3 H, d, $J=5.7$ Hz), 0.88 (3 H, bs), 1.1–1.7 (6 H, m), 1.53 (3 H, bs), 2.55 (2 H, m), 4.62 (1 H, bs), 4.74 (1 H, bs), 6.75–7.35 (9 H, m). MS m/z : 308 (13%, M^+), 210 (14), 196 (100), 183 (29), 115 (10), 91 (11), 77 (17), 69 (18), 57 (18), 55 (29), 43 (30), 41 (32).

3. Test Insects and Methods

Insecticidal activity was examined on adults of brown planthoppers (*Nilaparvata lugens*) and green rice leafhoppers (*Nephotettix cincticeps*) by the foliar dipping test¹⁾ and female adults of houseflies (*Musca domestica*) by the filter paper contact test.⁸⁾

Carmine mites (*Tetranychus cinnabarinus*) were tested by pot spray and soil treatments: Twenty milliliters of aqueous solution of a test chemical diluted to predetermined concentrations was sprayed to potted kidney bean plants infected by carmine mites in various

growth stages, and 2 ml of the same solution was also treated on the pot soil. The plants were observed for damage after 8 days by using the following criteria; ++: as damaged as the untreated pot, +: 50% of the plants in a pot were damaged, -: no damage.

RESULTS AND DISCUSSION

The results of bioassay are shown in Table 1.

Esters, a type which is cleaved between C-1 and C-2 bonds of the cyclopropane ring (3a–6c). Ester **3c** showed relatively strong insecticidal activity to *Nephotettix cincticeps* and *Musca domestica*, but its activity was weaker by one-tenth than that of the corresponding mother ester **1c** (fenpropathrin). The other esters were inactive (**4a**, **5a**, **5b** and **6a**) or very weakly active (**3a**, **3b**, **4b**, **4c**, **5c**, **6b** and **6c**), which led to the conclusion that the acids of this type were ineffective to produce esters with strong insecticidal activity.

Ethers and hydrocarbon analogues (7–9). Ethers **7** and **8** showed insecticidal activity to

Table 1 Toxicity of active compounds to insects.^{a)}

	% mortality at 500 ppm			Damage on host at 500 ppm
	N.l. ^{b)}	N.c. ^{b)}	M.d. ^{b)}	T.c. ^{b)}
1c	100	100	100	—
2a	0	0	100	++
2b	40	0	90	++
2c	80	20	100	—
3a	20	0	0	++
3b	40	20	0	++
3c	50	100	100	++
4b	20	0	10	++
4c	0	20	0	++
5c	0	20	10	++
6b	10	20	10	++
6c	10	50	0	++
7	80	70	0	++
8	70	80	0	++
9	—	0	0	— +
2d	10	20	0	++
2e	10	10	0	++
2f	0	10	0	++

^{a)} Compounds (**4a**, **5a**, **5b** and **6a**) which showed no toxicity are neglected from this table.

^{b)} N.l.: *Nilaparvata lugens*, N.c.: *Nephotettix cincticeps*, M.d.: *Musca domestica*, T.c.: *Tetranychus cinnabarinus*.

Nilaparvata lugens and *Nephotettix cincticeps* and hydrocarbon **9** only to *Tetranychus cinnabarinus*. Both of them were not active to *Musca domestica*, while the corresponding mother esters **2a** and **2b** were active. It has been known that pyrethroids decrease the activity when an ester linkage is replaced with an ether linkage. Our results, however, indicate that insecticidal spectra for insects change when an ester linkage is replaced to an ether or hydrocarbon linkage.

Dimethylbenzyl esters (2d-2f). Esters **2d**, **2e** and **2f** were inactive to *M. domestica* and weakly active to *Nilaparvata lugens* and *Nephotettix cincticeps*, while esters **2a**, **2b** and **2c** were active to *M. domestica*. This result is similar to the finding that the insecticidal activity decreases by one-fifth when the alcohol part of allethrin (allethronyl chrysanthemate) is changed to a 2,4-dimethylbenzyl group (dimethrin).^{9,10)}

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要 約

テトラメチルシクロプロパンカルボン酸エステルと関連した化合物の合成と殺虫活性

古幡明道, 平野雅親, 藤本いずみ, 松井正直
フェンプロパスリンの酸部分である, テトラメチルシクロプロパンカルボン酸の三員環を C-1 位と C-2 位の間で開裂した型の酸, 四種類を合成した. これらとピレスロイドアルコールとのエステルには, ほとんど殺虫活性が認められなかった. 殺虫活性を有する 3-フェノキシベンジル (**2a**), または 5-ベンジル-3-フリルメチル 2-イソプロピル-3-メチル-3-ブテノエート (**2b**) のエステル結合を, エーテルあるいは炭化水素結合に変えた化合物を合成した. これらは, 元のエステルとは違う種類の昆虫に対して殺虫活性を示した. また, エステル **2a**, **2b** のアルコール部分をジメチルベンジルに変換したエステルには, 殺虫活性はほとんど認められなかった.