原　著

New Insecticidal Cyclopropanecarboxylic Esters. Part IV. 4-Aryl-2-buten-1-yl Chrysanthemates and Related Esters(1)* Kaoru Sota, Takehiro Amano, Akifumi Hayashi, and Ichiro Tanaka (Research Laboratory, Taisho Pharmaceutical Co., Ltd., Toshima, Tokyo). Received April 17, 1973. *Botyu-Kagaku*, 38, 181, 1973.

25. 新殺虫性シクロプロパンカルボン酸エステル（第4報）4-アリル-2-ブテン-1-イル第一菊酸エステル類および関連エステル（1）

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48. 4. 17 受理

2,5-hexadien-1-yl 第一菊酸エステルと構造類似の，多数の 4-aryl-*trans*-2-buten-1-yl および 4-aryl-2-and/or 3-methyl-*trans*-2-buten-1-yl 第一菊酸エステルおよび関連エステル類を合成し，家バエに対する殺虫作用を検討した．これらのうち，未置換フェニルグループをもつエステルは，それぞれ，各系列でもっとも活性が高かった．そして，4-phenyl-*trans*-2-buten-1-yl 第一菊酸エステル (I) およびその 2-methyl (III), 3-methyl (II), 2,3-dimethyl (IV) 置換体は，それぞれ，アレスリンよりも高い活性を示した．この研究から，*trans* ＼C=C／ および，-C≡C- 構造は，cyclopentenone のような環状構造にかわる役割を果たすことを見出した．

In the previous paper,[1] we reported that *trans*-2,5-hexadien-1-yl chrysanthemate and its 2-methyl and 3-methyl substituted derivatives, which were prepared as simplified models of natural pyrethrins, retained sufficient insect toxicity against houseflies, but the *cis*-2,5-hexadien-1-yl isomer and two positional isomers, 2-methylene-4-penten-1-yl and 1,5-hexadien-3-yl chrysanthemates, were ineffective. From these results, we concluded that the *trans* configuration of the double bond between 2-and 3-carbon atoms in the alcohol moiety was important for insect toxicity. (Fig. 1)

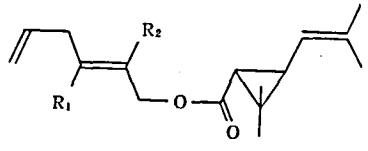


Fig. 1. R_1, R_2=H, H ; H, CH_3 ; CH_3, H

From this point of view, we prepared some chrysanthemic and 2,2,3,3-tetramethylcyclopropanecarboxylic acid esters (I～XX and XXVII～XXXII) of 4-aryl-*trans*-2-buten-1-ol and its homologous alcohols in which the terminal vinyl groups of *trans*-2,5-hexadien-1-yl alcohols were replaced by an aryl group.

4-Aryl-1-chloro-2-butenes and 4-aryl-1-chloro-2,3-dimethyl-2-butenes, alcoholic components of esters I and IV～XX, were prepared by the Meerwein arylation reaction[2] of 1,3-butadiene or 2,3-dimethyl-1,3-butadiene with aryldiazonium

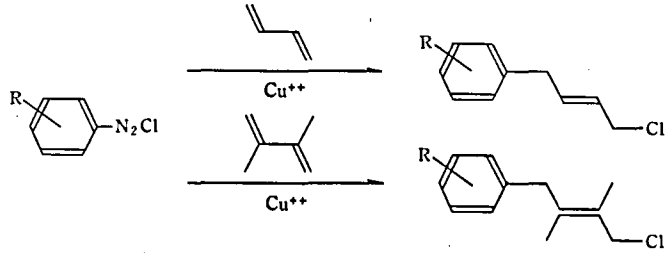


Chart 1

* A part of this paper was presented at Annual Meeting of Agricultural Chemical Society of Japan, Fukuoka, April 4, 1970.

chloride, as shown in Chart 1.

The NMR spectrum of the reaction products showed the presence of 1, 2-adduct as minor component. For example, the reaction of 1, 3-butadiene with benzenediazonium chloride gave 2-chloro-1-phenyl-3-butene in a ratio of about 3 : 7 to 1, 4-adduct ; NMR (CCl_4) δ : 2.96 (d, J=7.2 cps, $PhCH_2$ of 1, 2-adduct), 3.27 (d, J=5.6 cps, $PhCH_2$ of 1, 4-adduct), 3.87 (d, J=6 cps, CH_2Cl), 4.83 (dt, J=7.2, 7.2 cps, >CHCl). When the halide mixture of both 1, 4-and 1, 2-adduct was esterified with potassium chrysanthemate or 2, 2, 3, 3-tetramethylcyclopropanecarboxylate, the esters corresponding to the 1, 2-adducts could not be detected in the NMR spectrum. The esters obtained were listed in Tables 1, 2, and 3.

2-and 3-Methyl-4-phenyl-*trans*-2-buten-1-ols (XXIV, XXI) were synthesized by the phosphonate modification of the Wittig reaction followed by $LiAlH_3(OEt)$ reduction as shown in Chart 2. 3-Methyl-4-phenyl-*trans*-2-buten-1-ol (XXI) was obtained by $LiAlH_3(OEt)$ reduction of ethyl 3-methyl 4-phenyl-*trans*-2-butenoate (XXIII) (trans > 95%) which was prepared by the reaction of phenylacetone with triethyl-phosphonoacetate (XXII). Ethyl 2-methyl-4-phenyl-2-butenoate (XXVI) (*trans* 70%) was obtained similarly by the reaction of phenylacetaldehyde with triethyl-α-phosphonopropionate (XXV), and the mixture was chromatographed on silica gel column developing with hexane-benzene-ether and the refined *trans* ester was reduced similarly to give 2-methyl-4-phenyl-*trans*-2-buten-1-ol (XXIV). These alcohols were esterified by usual acid chloride method.

In order to clarify whether steric arrangement of benzyl group around the double bond of 4-phenyl-*trans*-2-buten-1-yl moiety of I is important for insect toxicity, 4-phenyl-*cis*-2-buten-1-yl (XXXIII), 2-benzylallyl (XXXIV), and 4-phenyl-2-butyn-1-yl (XXXV) chrysanthemates were prepared by procedure shown in Chart 3. 4-Phenyl-2-butyn-1-ol (XXXVI) was obtained by Grignard reaction according to the method of Dupont *et al.*[3] This alcohol was selectively hydrogenated to the *cis* alcohol (XXXVII) over Lindlar catalyst. 2-Benzylallyl alcohol (XXXVIII)[4] was prepared from 2-benzylacrylic acid[5] by $LiAlH_4$ reduction. All these alcohols were esterified using chrysanthemoyl chloride (Table 4).

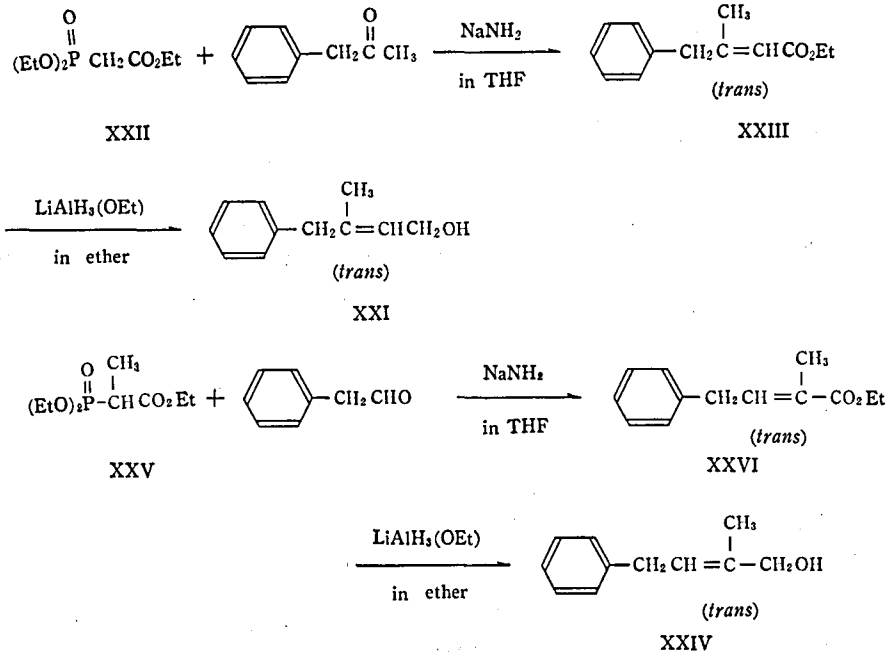


Chart 2

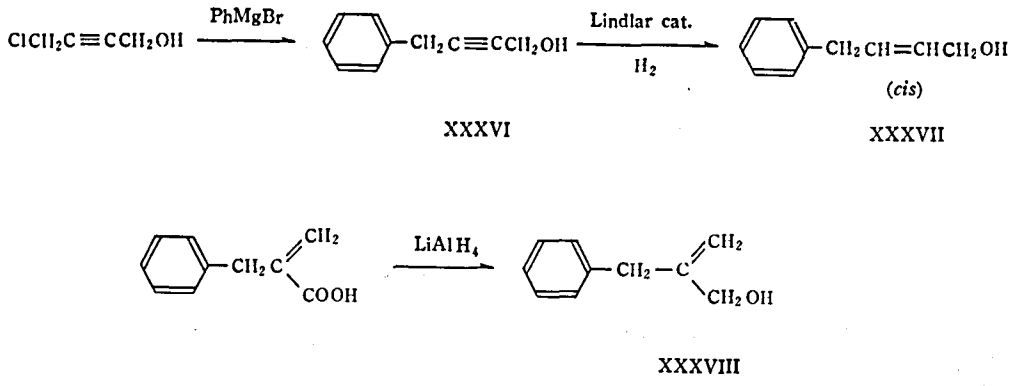
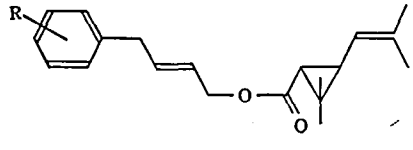


Chart 3

The insecticidal activities of these esters were determined by topical application method[6] and spray method[7] against houseflies, and given in Tables 5, 6, 7, 8, and 9.

As shown in Table 5, all of the chrysanthemate esters (I~IV) with unsubstituted phenyl group were superior to allethrin in toxicity by topical application method, and particularly 4-phenyl-*trans*-2-buten-1-yl chrysanthemate (I) was approximately 3 times as toxic as allethrin. Thus, replacement of the vinyl group in the *trans*-2, 5-hexadien-1-yl chrysanthemate series by a phenyl group resulted in a great increase in potency. Namely, esters I, II, and III were shown to be, respectively, 80, 20, and 8 times more active than the corresponding 2, 5-hexadien-1-yl chrysanthemates[1] to houseflies. From a structure-activity point of view, it is especially noteworthy that I and benathrin,[8,9] whose alcoholic moieties are consisted of a benzyl group and an allyl

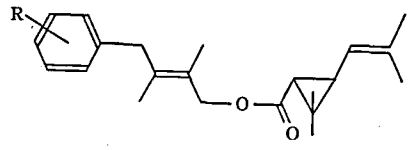
Table 1. 4-Aryl-*trans*-2-buten-1-yl Chrysanthemates



No.	R	bp°C(mmHg)	n_D^{20}	Formula	*Anal.* (%) Calcd. C	Calcd. H	Found C	Found H
I	H[a]	127~9 (0.15)	1.5207	$C_{20}H_{26}O_2$	80.49	8.78	80.71	8.77
V	2-CH_3[a]	141~4 (0.10)	1.5232	$C_{21}H_{28}O_2$	80.73	9.03	80.84	9.26
VI	3-CH_3	134~5 (0.08)	1.5178		80.73	9.03	80.51	8.93
VII	4-CH_3	136~7 (0.10)	1.5207		80.73	9.03	80.49	9.11
VIII	2-Cl	141~3 (0.10)	1.5317	$C_{20}H_{25}ClO_2$	72.16	7.57	71.88	7.52
IX	3-Cl	143~5 (0.08)	1.5305		72.16	7.57	72.04	7.67
X	4-Cl	142~4 (0.10)	1.5317		72.16	7.57	71.93	7.40
XI	2-CH_3O	145~8 (0.10)	1.5263	$C_{21}H_{28}O_3$	76.79	8.59	76.51	8.53
XII	3-CH_3O	151~3 (0.12)	1.5245		76.79	8.59	76.58	8.62
XIII	4-CH_3O	156~8 (0.10)	1.5253		76.79	8.59	76.70	8.46
XIV	4-C_2H_5	146~8 (0.14)	1.5208	$C_{22}H_{30}O_2$	80.93	9.26	80.66	9.18
XV	2,3-di-CH_3	145~7 (0.14)	1.5258	$C_{22}H_{30}O_2$	80.93	9.26	80.71	9.05
XVI	2,5-di-CH_3	142~5 (0.08)	1.5233		80.93	9.26	80.82	9.14
XVII	2,6-di-CH_3	144~5 (0.11)	1.5249		80.93	9.26	80.73	9.27

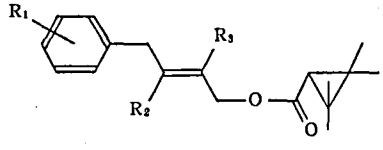
a) see Ref. 17)

Table 2. 4-Aryl-2,3-dimethyl-*trans*-2-buten-1-yl Chrysanthemates



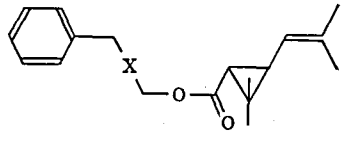
No.	R	bp°C(mmHg)	n_D^{20}	Formula	*Anal.* (%) Calcd. C	H	Found C	H
IV	H	144~6 (0.12)	1.5219	$C_{22}H_{30}O_2$	80.93	9.26	80.63	9.34
XVIII	4-CH_3	148~51 (0.15)	1.5245	$C_{23}H_{32}O_2$	81.13	9.47	80.98	9.47
XIX	4-Cl	150~2 (0.10)	1.5313	$C_{22}H_{29}ClO_2$	73.21	8.10	73.48	8.02
XX	4-CH_3O	159~62 (0.15)	1.5277	$C_{23}H_{32}O_3$	77.49	9.05	77.31	8.95

Table 3. 4-Aryl-*trans*-2-buten-1-yl 2,2,3,3-Tetramethylcyclopropane Carboxylates



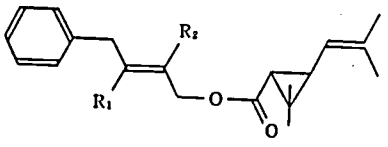
No.	R_1	R_2	R_3	bp°C(mmHg)	n_D^{20}	Formula	*Anal.* (%) Calcd. C	H	Found C	H
XXVII	H	H	H	117~8 (0.13)	1.5150	$C_{18}H_{24}O_2$	79.37	8.88	79.28	8.74
XXVIII	4-CH_3	H	H	121 (0.15)	1.5145	$C_{19}H_{26}O_2$	79.68	9.15	79.43	9.00
XXIX	2-Cl	H	H	138~9 (0.32)	1.5261	$C_{18}H_{23}ClO_2$	70.46	7.55	70.32	7.58
XXX	H	CH_3	H	122~4 (0.10)	1.5160	$C_{19}H_{26}O_2$	79.68	9.15	79.61	9.07
XXXI	H	CH_3	CH_3	126~7 (0.08)	1.5171	$C_{20}H_{28}O_2$	79.95	9.39	79.66	9.34
XXXII	4-CH_3	CH_3	CH_3	132~4 (0.10)	1.5168	$C_{21}H_{30}O_2$	80.21	9.62	80.18	9.72

Table 4. Some Chrysanthemates Related to I.



No.	X	bp°C(mmHg)	Formula	*Anal.* (%) Calcd. C	H	Found C	H
XXXIII	⟩CH=CH⟨(*cis*)	130~2 (0.18)	$C_{20}H_{26}O_2$	80.49	8.78	80.35	8.89
XXXIV	CH_2=C⟨	123~5 (0.12)	$C_{20}H_{26}O_2$	80.49	8.78	80.51	8.98
XXXV	-C≡C-	141~2 (0.15)	$C_{20}H_{24}O_2$	81.04	8.16	80.77	8.12

Table 5. Insecticidal Activities



No.	R_1	R_2	Topical application method LD_{50} (μg/fly)	Relative potency	Spray method KT_{50}	Mortality (%)
I	H	H	0.36	310	15′31″	97.6
II	CH_3	H	0.47	230	25′00″	97.6
III	H	CH_3	0.97	110	19′13″	100
IV	CH_3	CH_3	0.86	130	25′42″	96.9
	allethrin*		1.10	100		

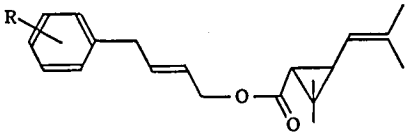
* *dl-cis, trans*-chrysanthemate

group respectively, are equipotent. Introduction of methyl substituent on the double bond of the 2-buten-1-yl moiety resulted in a slight decrease in potency without regard to the position and number of substituent, and the 2-methyl and 2,3-dimethyl substitution showed a greater decrease than the 3-methyl substitution. Therefore, a substitution at the position 2 seems to be more responsible for the diminution in potency. However, since the order of activity in these chrysanthemates (H>3-CH_3>2-CH_3≒2, 3-diCH_3) is not consistent with those in the 2, 2, 3, 3-tetramethylcyclopropanecarboxylates (2, 3-diCH_3>3-CH_3>H) and *trans*-2, 5-hexadien-1-yl chrysanthemates[1] (2-CH_3≧3-CH_3>H), the meaning of methyl substitution for activity is not obvious. Methyl substitution on the double bond may not be indispensable but supplementary for insect toxicity. Recently, Elliott *et al.*,[10] have reported that 3-benzyl-4-oxo-2-cyclopentenyl *d-trans*-chrysanthemate was approximately 3 times more potent than pyrethrin I against houseflies, and the methyl group on the cyclopentenone ring of the natural esters is probably not essential for insect toxicity. Benzythrin was found to be only 1/6 as potent as allethrin to houseflies by Gersdorff *et al.*[11] The methyl group on the cyclopentenone ring of benzythrin is undoubtedly unwanted for insect toxicity.

Subsequently, the effect of substitution on the benzene ring of 4-aryl-2-buten-1-yl moiety was investigated for the chrysanthemate series (Tables 6 and 7) and 2, 2, 3, 3-tetramethylcyclopropanecarboxylate series (Table 8), respectively. As can be seen in Table 6, all of the monosubstitution on the phenyl ring in the 4-aryl-*trans*-2-buten-1-yl chrysanthemate series decreased the activity of the unsubstituted phenyl compound (I), without regard to the position of substitution and the nature of substituent. Introduction of monomethyl, monochloro, or monomethoxy substituent on the benzene ring of the esters resulted in a decrease in potency which was in the order of unsubstituted > *para*-substituted > *meta*-substituted ≒ *ortho*-substituted for each substituent, and in the order of H > CH_3 > Cl ≧ CH_3O for *ortho*, *meta*, and *para* positions, respectively. For example, the methylsubstituted compounds (VII, V, and VI) at the *para*, *ortho*, and *meta* positions of the benzene ring were about 1/2, 1/8, and 1/8 as active as the unsubstituted parent compound (I), respectively, and the monochlorosubstituted compounds (X, VIII, and IX) were similarly 1/5, 1/10, and 1/25 or less, respectively. With regard to the *para*-substitution, the methyl-, chloro- and methoxy- substituted compounds (VII, X, and XIII) showed about 1/2, 1/5, and 1/16 of the potency of I, respectively. On the other hand, *para*-ethyl (XIV) and three dimethylsubstituted esters (XV, XVI, and XVII) showed litttle or no activity at 5μg/fly. The activities of five monomethyl substituted isomers (II, III, V, VI, and VII) decreased in the following order; H>3-CH_3>*para*-CH_3>2-CH_3>*ortho*-CH_3≧*meta*-CH_3.

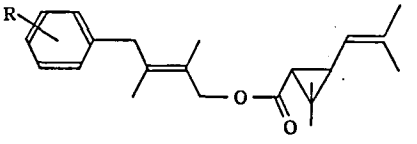
As seen in Table 7, all of the substitutions at the *para*-position of 4-phenyl-*trans*-2, 3-dimethyl

Table 6. Insecticidal Activities



No.	R	Topical application method LD_{50}(μg/fly)	Relative potency	Spray method KT_{50}	Mortality(%)
V	2-CH_3	1.55	13	19′27″	100
VI	3-CH_3	1.85	11	>30′	77.4
VII	4-CH_3	0.36	56	>30′	50.0
VIII	2-Cl	2.35	9	>30′	91.3
IX	3-Cl	>5	<4	>30′	45.8
X	4-Cl	0.95	21	>30′	91.3
XI	2-CH_3O	>5	<4	20′53″	86.4
XII	3-CH_3O	>5	<4	15′40″	81.8
XIII	4-CH_3O	3.21	6	15′25″	40.7
XIV	4-C_2H_5	>5	<4	>30′	—
XV	2,3-diCH_3	>5	<4	>30′	—
XVI	2,5-diCH_3	>5	<4	>30′	—
XVII	2,6-diCH_3	>5	<4	>30′	—
I	H	0.2	100		

Table 7. Insecticidal Activities



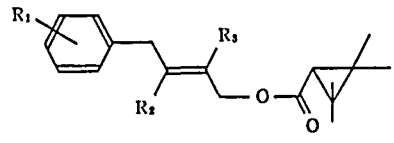
No.	R	Topical application method LD_{50}(μg/fly)	Relative potency	Spray method KT_{50}	Mortality(%)
XVIII	4-CH_3	>10	<9	>30′	—
XIX	4-Cl	>10	<9	>30′	—
XX	4-CH_3O	>10	<9	>30′	—
IV	H	0.86	100		

-2-buten-1-yl ester (IV) resulted in greater decrease in potency than that in the case of 4-phenyl-*trans*-2-buten-1-yl ester series; *para*-methyl-(XVIII), *para*-chloro-(XIX), and *para*-methoxy-(XX) substituted compounds of IV were 1/10 or less active than the parent ester IV, respectively. This was analogous to the result reported by Gersdorff *et al.*,[11] that *para*-methoxybenzythrin was only 1/9 as active as benzythrin to houseflies.

For the activities of the 2,2,3,3-tetramethylcyclopropanecarboxylate esters, as seen in Table 8, 4-phenyl-*trans*-2-buten-1-yl ester (XXVII) was about 1/4 and 1/10 as active as allethrin and the corresponding chrysanthemate (I). However, 4-phenyl-3-methyl-*trans*-2-buten-1-yl ester (XXX) was about 1/2 as active as allethrin, and 4-phenyl-2,3-dimethyl-*trans*-2-buten-1-yl ester (XXXI) was found to be 2 times more than XXX.

The substitution on the benzene ring of 2,2,3,3-tetramethyl-cyclopropanecarboxylate esters (XXVII and XXXI) resulted in a great loss in potency, as in the case of the crysanthemate series. In general, 2,2,3,3-tetramethylcyclopro-

Table 8. Insecticidal Actitities



No.	R_1	R_2	R_3	Topical application method LD_{50}(μg/fly)	Spray method KT_{50}	Mortality (%)
XXVII	H	H	H	4	11′10″	60.0
XXVIII	4-CH_3	H	H	>5	>30′	—
XXIX	2-Cl	H	H	>5	>30′	—
XXX	H	CH_3	H	2.33	16′40″	36.8
XXXI	H	CH_3	CH_3	1.00	13′10″	97.4
XXXII	4-CH_3	CH_3	CH_3	>5	>30′	—
	allethrin*			1.12		

* *dl-cis, trans*-chrysanthemate

panecarboxylate esters were less effective in toxicity than the corresponding chrysanthemate esters. This is analogous to the structure-activity relationship of allethrolone series.[12]

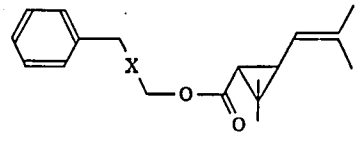
For the knockdown effect, both the chrysanthemates and 2,2,3,3-tetramethylcyclopropanecarboxylates of 4-aryl-2-buten-1-yl series were considerably less active than allethrin, but of the two series, 2,2,3,3-tetramethylcyclopropanecarboxylates were, in general, more active. Although both the *cis* isomer (XXXIII) of I and 2-benzylallyl chrysanthemate (XXXIV) showed no activity at 10 μg/fly, 4-phenyl-2-butyn-1-yl chrysanthemate (XXXV) was found to be as active as I in toxicity and markedly more potent than I in knockdown effect.

Of three isomers, only *trans* isomer was specifically toxic against insect, as previously observed in 2,5-hexadien-1-yl chrysanthemate series.[11] From these results, it was confirmed that a *trans* ＼C=C＼ and -C≡C- group play a similar role to planar cyclic nucleus such as cyclopentenone in pyrethrins, which has been considered to be indispensable for insect toxicity of pyrethroids.[8,13,14]

Experimental

IR spectra were recorded on a Hitachi IR spectrometer in film. NMR spectra were measured on a Hitachi Perkin-Elmer R-20 type (60 Mc) spectrometer in CCl_4 (unless otherwise stated) with TMS as internal standard. All the chrysanthemic acid used in our experiment were *dl-cis, trans*-mixtures.

Table 9. Insecticidal Activities



No.	X	Topical application LD_{50}(μg/fly)	Relative potency	Spray method KT_{50}	Mortality (%)
XXXIII	／CH=CH＼ (*cis*)	>10	<5	>30′	—
XXXIV	CH_2=C＜	>10	<5	>30′	—
XXXV	-C≡C-	0.49	98	3′48″	100
I	＼CH=CH＼ (*trans*)	0.48	100		

4-Aryl-1-chloro-2-butenes.

General method. A solution of ArN_2Cl, prepared from 0.1 mole of $ArNH_2$, 0.1 mole of $NaNO_2$, and 0.35 mole of conc. HCl, was neutralized to pH 6~7 with $NaHCO_3$ at −5~−10°C. To this ice-cold solution was added 0.12 mole of 1,3-butadiene in 50ml of Me_2CO and 0.01 mole of $CuCl_2 \cdot 2H_2O$, and the mixture was vigorously stirred until N_2 evolution was completed. The resultant oily layer was then extracted with Et_2O, washed with water, and dried (Na_2SO_4). After evaporation of the solvent, the residual oil was distilled *in vacuo* to give the following 4-aryl-1-chloro-2-butenes.

Phenyl, bp 124~5°C (14mmHg) (lit.[15] 92~3°C (3 mmHg)); 4-tolyl, bp 74~85°C (0.5 mmHg) (lit.[15] 112~4°C (6mmHg)); 3-tolyl, bp 63~7°C (0.25mmHg) (lit.[15] 107~9°C (3mmHg)); 2-tolyl, bp 76~82°C (0.4 mmHg) (lit.[15] 94~5°C (2mmHg)); 4-Cl-phenyl, bp 72~6°C (0.4mmHg) (lit.[15] 125~6°C (2 mmHg)); 3-Cl-phenyl, bp 82~8°C (0.45 mmHg); 2-Cl-phenyl, bp 80~6°C (0.2 mmHg); 4-anisyl bp 88~99°C (0.25 mmHg) (lit.[15] 124~6°C (2 mmHg)); 3-anisyl, bp 88~94°C (0.4 mmHg); 2-anisyl, bp 82~92°C (0.16 mmHg); 4-Etphenyl, bp 80~4°C (0.23 mmHg); 2.3-diMephenyl, bp 82~6°C (0.2 mmHg); 2,5-diMephenyl, bp 82~7°C (0.2 mmHg); 2,6-diMephenyl, bp 83~8°C (0.2 mmHg).

Similarly, 2,3-dimethyl-1,3-butadiene gave the following 4-aryl-1-chloro-2,3-dimethyl-2-butenes: phenyl, bp 75~8°C (0.2 mmHg) (lit.[16] 116~7°C (5 mmHg)); 4-tolyl, bp 79~81°C (0.15 mmHg) (lit.[16] 121~2°C (3mmHg); 4-Clphenyl, bp 90~4 (0.2mmHg) (lit.[16] 145~7°C (6mmHg)); 4-anisyl, bp 97~100°C (0.3 mmHg) (lit.[16] 144~6°C (5 mmHg)).

4-Phenyl-*trans*-2-buten-1-yl chrysanthemate (I).[17] A mixture of 5.0 g of 1-chloro-4-phenyl-2-butene, 4.1 g of potassium chrysanthemate, and 30 m*l* of isoPrOH was refluxed for 16 hr. The solvent was removed and the residue was poured onto 50 m*l* of water. The mixture was extracted with Et_2O and the etheral solution was washed with water, dried (Na_2SO_4), and distilled *in vacuo* to afford 5.0 g (75%) of the ester I. NMR δ: 3.33 (2H, d, J=5.9 cps, $PhCH_2$), 4.47 (2H, d, J=5.0 cps, CH_2O), 5.23~6.14 (2H, m, CH=CH). Similarly, the other 4-aryl-*trans*-2-buten-1-yl esters were prepared (Tables 1 and 3).

4-Phenyl-2,3-dimethyl-*trans*-2-buten-1-yl chrysanthemate (IV). This ester was prepared from 1-chloro-4-phenyl-2,3-dimethyl-2-butene by a similar procedure to that described above for I, in 70% yield. NMR δ: 3.38 (2H, s, $PhCH_2$), 4.59 (2H, s, CH_2O). The other 2,3-dimethyl-*trans*-2-buten-1-yl esters were similarly prepared as shown in Tables 2 and 3.

Ethyl 4-phenyl-3-methyl-*trans*-2-butenoate (XXIII). To a suspension of 2 g of $NaNH_2$ in 30 m*l* of THF, a solution of 11.2 g of triethylphosphonoacetate (XXII) was added dropwise with stirring over 20 min at 20~25°C. After stirring was continued for 2 hr at room temperature and then $NaNH_2$ disappeared, a solution of 6.7 g of phenylacetone in 10 m*l* of THF was added dropwise over 20 min at 20~25°C. When the addition was complete, stirring was continued for 2 hr and the mixture was allowed to stand overnight at room temperature, and poured onto ice water. The mixture was extracted with Et_2O, and the extract was washed, and dried ($MgSO_4$). After removal of the solvent, the residue was distilled to give the ester XXIII, bp 97°C (0.8 mmHg). NMR δ: 2.10 (3H, s, $C=\overset{1}{C}-CH_3$), 3.34 (2H, s, $PhCH_2$), 5.57~5.76 (1H, m, $>C=\overset{2}{C}H-CO$).

Anal. Found: C, 76.18; H, 7.81. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

4-Phenyl-3-methyl-*trans*-2-buten-1-ol (XXI). To a suspension of 1 g of $LiAlH_4$ in 100 m*l* of Et_2O, 1.2 g of abs. EtOH in 10 m*l* of Et_2O was added dropwise over 1 hr under reflux, and reflux was continued for 2 hr. To the stirred solution at −40°C, 5.1 g of the ester XXIII in 10 m*l* of Et_2O was added dropwise over 20 min and the mixture was stirred for a further 2 hr at the same temperature. After the stirring was continued for 2 hr at 3°C, and then for 2 hr at 20°C, 3 m*l* of EtOAc was added, and the mixture was poured onto ice water, extracted with Et_2O, and dried ($MgSO_4$). Evaporation of the solvent followed by distillation *in vacuo* gave 3.4 g (84%) of the alcohol XXI, bp 88°C (0.5 mmHg). NMR δ: 1.55 (3H, s, $C=\overset{1}{C}-CH_3$), 3.24 (2H, s, $PhCH_2$), 3.40 (1H, br, OH), 4.03 (2H,

d, J=7.2 cps, CH_2O), 5.22～6.65 (1H, m, >C=CH).

Anal. Found: C, 81.22; H, 8.79. Calcd. for $C_{11}H_{14}O$: C, 81.44. H, 8.70%.

4-Phenyl-3-methyl-*trans*-2-buten-1-yl chrysanthemate (II). To a solution of 3.2 g of XXI and 2 m*l* of pyridine in 30 m*l* of petroleum ether, 3.7 g of chrysanthemoyl chloride in 10 m*l* of petroleum ether was added dropwise at 0°C. After standing overnight at room temperature, the mixture was shaken with 2N-HCl, water, aq. Na_2CO_3, and water, and dried ($MgSO_4$). The solvent was evaporated and the resultant residue was distilled *in vacuo* to give 5.6 g (90%) of the ester II, bp 142～3°C (0.2 mmHg), n_D^{20} 1.5218. NMR δ: 3.29 (2H, s, $PhCH_2$), 4.54 (2H, d, J=7.5 cps, CH_2O), 5.23～5.65 (1H, m, >C=CH). *Anal.* Found: C, 80.54; H, 9.05. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

Ethyl 4-phenyl-2-methyl-*trans*-2-butenoate (XXVI). In the same manner as described above for XXI, the reaction of phenylacetaldehyde with XXV was carried out to give the ester, bp 82～94°C (0.6 mmHg). NMR spectrum of this fraction showed a presence of the *cis* isomer of XXVI. The ratio of the *cis* isomer to the *trans* isomer was about 30 : 70 by peak area. NMR δ: 3.44 (d, $PhCH_2$ of *trans* isomer), 3.66～3.89 (m, $PhCH_2$ of *cis* isomer), 5.81～6.18 (m, >CH=C-CO of *cis* isomer), 6.67～7.04 (m, >CH=C-CO of *trans* isomer). This *cis* and *trans* mixture was purified by chromatography on Silica gel. Elution with n-hexane-Et_2O-benzene (100 : 1 : 2) gave the pure *trans* isomer XXVI. NMR δ: 1.91 (3H, m, >C=C-CH_3), 3.44 (2H, d, J=7.2 cps, $PhCH_2$), 6.66～7.05 (1H, m, >CH=C-CO).

4-Phenyl-2-methyl-*trans*-2-buten-1-ol (XXIV). In the same manner as described above for XXI, XXIV was synthesized from XXVI by $LiAlH_3$(OEt) reduction in 85% yield, bp 81～2°C) 0.08 mmHg). NMR δ: 1.71 (3H, s, >C=C-CH_3), 2.87 (1H, br s, OH), 3.33 (2H, d, J=7.2 cps, $PhCH_2$), 3.90 (2H, s, CH_2O), 5.34～5.73 (1H, m, CH=C<). *Anal.* Found: C, 81.36; H, 8.57. Calcd. for $C_{11}H_{14}O$: C, 81.44, H, 8.70%.

4-Phenyl-2-methyl-*trans*-2-buten-1-yl chrysanthemate (III). III was obtained from XXIV in 94% yield, bp 126～7°C (0.06 mmHg), n_D^{20} 1.5221. NMR δ: 3.32 (2H, d, J=7.3 cps, $PhCH_2$, 4.42 (2H, s, CH_2O) 5.33～5.77 (1H, m, >CH=C(Me)−). *Anal.* Found: C, 80.80; H, 9.09. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

4-Pheuyl-2-butyn-1-ol (XXXVI). According to the method of Dupont *et al.*,[3] this alcohol was prepared by Grignard reaction of PhMgBr with 4-chloro-2-butyn-1-ol, bp 150～2°C (18 mmHg) (lit.[3] 147～8°C (15 mmHg)).

4-Phenyl-*cis*-2-buten-1-ol (XXXVII). A solution of 4.2 g of XXXVI and 0.5 m*l* of quinoline in 30 m*l* of benzene was hydrogenated over 0.2 g of Lindlar catalyst. After absorption of 630 m*l* of H_2, the catalyst was filtered off, and the filtrate was washed with dil. HCl, aq $NaHCO_3$, and water. After the solution was dried (Na_2SO_4) and concentrated, the residual oil was distilled *in vacuo* to give 3.7 g (90%) of the alcohol XXXVII, bp 73～4°C (0.13 mmHg), n_D^{20} 1.5425. NMR δ: 2.65～2.87 (1H, br, OH), 3.32 (2H, d, J=5.5 cps, $PhCH_2$), 4.15 (2H, d, J=5.5 cps, CH_2O), 5.34～5.93 (2H, m, CH=CH). *Anal.* Found: C, 80.89; H, 7.98. Calcd. for $C_{10}H_{12}O$: C, 81.04, H, 8.16%.

4-Phenyl-*cis*-2-buten-1-yl chrysanthemate (XXXIII). XXXIII was prepared from XXXVII in the same manner as described above for II, n_D^{20} 1.5308 (Table IV). NMR δ: 3.42 (2H, d, J=5.5 cps, $PhCH_2$), 4.64 (2H, d, J=5.5 cps, CH_2O) 5.34～5.93 (2H, m, CH=CH) (Table 4).

2-Benzylallyl chrysanthemate (XXXIV). To a solution of 0.7 g of $LiAlH_4$ in 20 m*l* of Et_2O was added 1.4 g of 2-benzylacrylic acid[5] in 10 m*l* of Et_2O. The reaction mixture was refluxed during the addition and for a further 4 hr. The resultant mixture was then colded and treated with MeOH in the usual fashion. After acidification with dil. HCl, the mixture was extracted with Et_2O and dried ($MgSO_4$). Evaporation of the solvent gave crude 2-benzylallyl alcohol (XXXVIII)[4], IR (cm^{-1}) : 3340 (OH), 900, 1650 (>C=CH_2). This oil was esterified without further purification. NMR ($CDCl_3$) δ: 3.38 (2H, s, $PhCH_2$), 4.47 (2H, s, CH_2O), 4.73～5.16 (3H, m, >C=CH_2 and $(Me)_2C$=CH). (Table 4).

4-Phenyl-2-butyn-1-yl chrysanthemate (XXXV).[17] XXXV was prepared from XXXVI in the same manner as described above for II, n_D^{20}

1.5308. NMR δ : 3.58 (2H, t, J=3 cps, $PhCh_2$) 4.65 (2H, t, J=3 cps, CH_2O) (Table 4).

Evaluation of insecticidal activities

Topical application method.[6] Susceptible houseflies ("Takatsuki"), *Musca domestica vicina* Macq., were tested on the dorsum of the thorax with 0.5 μl of an acetone solution of the the test compound by means of a micrometer syringe, and kept at 24~27°C. Mortality accounts were made after twenty-four hours.

Spray chamber method. The knockdown test was carried out according to the method of Nagasawa[7] against houseflies by spraying 0.5 ml of 1% Deo-base solution of the test compound, and knockdown (%) after 30 min and mortality (%) after twenty-four hours were assessed.

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Summary

A number of chrysanthemates and related esters of 4-aryl-*trans*-2-buten-1-ol and its 2-methyl, 3-methyl, and 2,3-dimethyl derivatives were synthesized and their insecticidal activity was tested against houseflies. Of these compounds, the esters bearing the unsubstituted phenyl-butenyl moiety were the most active in each series. 4-Phenyl-*trans*-2-buten-1-yl chrysanthemate (I) and the 2-methyl (III), 3-methyl (II) and 2,3-dimethyl (IV) derivatives were more active than allethrin in insect toxicity.

From this study, *trans* $\backslash C=C\backslash$ and $-C\equiv C-$ groups were found to play a similar role to planar cyclic nucleus, such as cyclopentenone in pyrethrins.