showed good insecticidal activity, in some cases being superior to the parent material against certain insects. Derivatization of insecticidal methylcarbamates generally resulted in compounds of lower anticholinesterase activity and different physical properties. These two factors appear to provide an opportunity for alternate detoxification pathways to take place in mammals in which the derivatized material is degraded to nontoxic products (Fahmy et al., 1970; Krieger et al., 1976). In insects, however, the active methylcarbamate is generated in vivo, resulting in intoxication.

As in the case of the different derivatives mentioned above, the various N-sulfinylated products described in this paper also showed favorable properties of selectivity. The N-chlorosulfinyl intermediates which are easily synthesized by reaction of methylcarbamate esters with thionyl chloride may be converted into a wide variety of new derivatives with potential usefulness as insecticides and other pesticides. The reaction between different N-(chlorosulfinyl)methylcarbamates and other nucleophilic agents is currently being investigated.

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Synthesis and Insecticidal Activity of Some *gem*-Dicyanopyrethroid Analogues

Michael G. Wilkerson and Scott J. Norton*

The synthesis and insecticidal activity of a series of 2,2-dicyanocyclopropanecarboxylic acid (3-phenoxyphenyl)methyl esters were investigated. The 2,2-dicyanocyclopropanecarboxylic acid esters were also substituted at position 3 of the cyclopropane ring with phenyl or substituted phenyl groups, an alkenyl group, a combination of one of the foregoing groups with a methyl group (3,3' substitution), or a spiro cycloalkyl group. Synthesis of the compounds was accomplished by reaction of dimethylsulfonium 2-(3-phenoxyphenylmethoxy)-2-oxoethylide with alkylidenepropanedinitrile derivatives. Final products were purified by dry column chromatography employing silica gel. Insecticidal activity was determined at 500-ppm application with permethrin as the standard against houseflies, Mexican bean beetles, and southern army worms. Compared with the activity permethrin, the activity of these compounds was low; the spiro cycloalkyl compounds exhibited the greatest spectrum of insecticidal activity.

Synthetic pyrethroids have attracted considerable attention in recent years as potential replacements for current insecticides (Elliott and Janes, 1978). Several pyrethroids containing cyano groups in the acid moiety have appeared in the literature (Elliott et al., 1976a; Matsui and Yamada, 1964). To our knowledge, no substituted 2,2-dicyanocyclopropanecarboxylic acids esterified with pyrethroid alcohols have appeared in the literature. We decided to prepare a series of analogues of active pyrethroids in which the ring methyl groups have been replaced with cyano groups. Preparation of the compounds was effected in essentially one step by reaction of dimethylsulfonium 2-(3-phenoxyphenylmethoxy)-2-oxoethylide with an alkylidenedicyano compound. The dicyano alkylidene compounds were prepared by Knovenagel condensation of the appropriate ketone or aldehyde with malononitrile.

EXPERIMENTAL SECTION

General. ^{1}H NMR spectra were obtained on a 60-Hz Hitachi Perkin-Elmer R-24B spectrometer in CDCl$_3$ or CCl$_4$ with tetramethylsilane as an internal standard. In-

frared spectra were recorded on a Beckman IR-33 spectrometer. Melting points were taken in a Thomas-Hoover melting point apparatus and are uncorrected. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU 6E spectrometer at 70 eV. Elemental analyses were performed by Midwest Microlab Ltd., Indianapolis, IN. Hardwicke Chemical Co. kindly supplied the (3-phenoxyphenyl)methanol and 3-phenoxybenzaldehyde employed in the synthesis of the final compounds. Preparative dry column chromatography was performed on silica gel that had been heated at 120 °C for 2 days (Loev and Snader, 1965). Elemental analyses were conducted on selected compounds (below and Table I). The analytical data were within ±0.4% of the theoretical values in all cases.

Insecticidal Testing Procedures. Compounds were tested for insecticidal activity as 50:50 mixtures of their cis/trans isomers by an independent laboratory. In the case of 2,2-dicyano-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid (3-phenoxyphenyl)methyl ester, the compound was tested as its separate cis and trans isomers. All testing was performed at 500 ppm with permethrin as the standard; data are expressed as percent mortality at the end of 24 h. For houseflies (*Musca domestica*), 1 mL of

Department of Chemistry, North Texas State University, Denton, Texas 76203.

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the test compound was pipetted into a 9-cm Petri dish containing filter paper and 0.1 g of granular sugar. Ten adult houseflies were admitted and the dish was closed. For the southern army worm (*Cirphis unipuncta*) and Mexican bean beetle (*Epilachua corrupta*), lima beam leaves (*Phaseolus limensis*) of uniform size were momentarily dipped into a water–acetone solution of the test compound. The treated leaves were placed on moistened filter paper in 9-cm Petri dishes and allowed to air dry. The instar larvae of the southern army worm (or the Mexian bean beetle) were then introduced and encouraged to feed on the foilage by confinement.

Intermediates. The following methylenepropanedinitrile derivatives were prepared by methods appearing in the literature: 4-methoxyphenyl, 2-methoxyphenyl, 3,4-(methylenedioxy)phenyl, 2-chlorophenyl, and 2-furyl (Corson and Stoughton, 1928); 3-chlorophenyl, 4-chlorophenyl, 4-nitrophenyl, 2-methylphenyl, and 3-methylphenyl (Struz and Noller, 1949); 3,4-dimethoxyphenyl and 4-methylphenyl (Horner and Klupfel, 1955); 2,4,6-trimethylphenyl (Pritchard et al., 1967); 4-bromophenyl (Zabicky, 1961); (diphenylmethylene)propanedinitrile and (phenylmethylmethylene)propanedinitrile (Anderson et al., 1961); (2,3-dimethyl-2-butenylidene)propanedinitrile (Sepiol et al., 1978).

(3-Phenoxyphenyl)methyl Bromacetate (I). Freshly distilled bromoacetyl bromide, 24.24 g (0.12 mol), was added dropwise to 20.00 g (0.10 mol) of *N,N*-dimethylaniline in 100 mL of dry petroleum ether. The solution was refluxed for 3 h and then poured into 150 mL of cold 1 N H_2SO_4. The layers were separated and the acid layer was extracted with two 100-mL portions of benzene. The combined benzene extracts were washed with 150-mL portions of saturated NaCl solution, 5% $NaHCO_3$, and saturated NaCl successively. The solvent was removed in vacuo to yield 28.20 g (88%) of clear oil: ^{1}H NMR (CCl_4) δ 3.6 (s, 2 H), 4.9 (s, 2 H), 6.7–7.2 (m, 9 H); IR (neat) 3050, 1750 cm^{-1}.

Dimethyl[[2-oxo-2-(3-phenoxyphenyl)methoxy]-1-bromoethane]sulfur (II) (Lee, 1977). Bromoacetic acid (3-phenoxyphenyl)methyl ester, 23.00 g (0.072 mol), was dissolved in 150 mL of acetone, and 8.93 g (0.14 mol) of dimethyl sulfide was added in one portion. The flask was stoppered and allowed to stand at room temperature for 3 days. The resulting white precipitate was filtered and dried in a desiccator under reduced pressure to yield 23.52 g (85%), mp 105 °C with decomposition: ^{1}H NMR (CDCl$_3$) δ 3.2–3.45 (s, 6 H), 5.01 (s, 2 H)8 6.60–7.35 (M, 9 H); IR (KBr) 3020, 3010, 1740, 705 cm^{-1}.

Dimethylsulfonium 2-(3-Phenoxyphenylmethoxy)-2-oxoethylide (III). Dimethyl[[2-oxo-2-(3-phenoxyphenyl)methoxy]-2-bromoethane]sulfur, 1.15 g (0.003 mol), was dissolved in 20 mL of CHCl$_3$. Saturated aqueous K_2CO_3 (Payne, 1967), 15 mL, was added and the solution was allowed to stir for 20 min. The layers were separated, and the CHCl$_3$ layer was dried over anhydrous K_2CO_3 to yield a clear viscous oil, 0.85 g (92%): ^{1}H NMR (CDCl$_3$) δ 2.2–3.3 (s, 7 H), 4.95 (s, 2 H), 6.6–7.3 (m, 9 H); IR (neat) 3050, 3000, 1735, 1690–1650, 615 cm^{-1}.

2,2-Dicyanospiro[2.5]octanecarboxylic Acid (3-Phenoxyphenyl)methyl Ester (IV). Dimethyl[[2-oxo-2-(3-phenoxyphenyl)methoxy]-1-bromoethane]sulfur, 1.30 g (0.0035 mol), was dissolved in 25 mL of CHCl$_3$, and 2.0 g of anhydrous K_2CO_3 added. The solution was cooled in ice and 0.38 g (0.0068 mol) of powdered KOH added. The solution was filtered and 0.50 g (0.0035 mol) of cyclohexylidenepropanedinitrile (Cope and Hoyle, 1941), in 5 mL of CHCl$_3$, was added. The solution was allowed to sit

for 2 h and the solvent removed in vacuo. The resulting light yellow oil, 1.35 g, was chromatographed on 200 g of silica gel with a solution of 85% cyclohexane–15% ethyl acetate (v/v), giving a clear viscous oil weighing 0.85 g (62%): ^{1}H NMR (CCl$_4$) δ 1.45–1.90 (s, 10 H), 2.35 (s, 1 H), 5.00 (s, 2 H), 6.65–7.30 (m, 9 H); IR (neat) 3080, 3000, 2260 cm^{-1}. Anal. C, H, N.

2,2-Dicyanospiro[2.4]heptanecarboxylic acid (3-phenoxyphenyl)methyl ester (V) was prepared as above by using cyclopentylidenepropanedinitrile (Baty et al., 1969) to yield 69% of a clear viscous oil: ^{1}H NMR (CCl$_4$) δ 1.65–2.05 (s, 8 H), 2.50 (s, 1 H), 4.98 (s, 2 H), 6.60–7.30 (m, 9 H); IR (neat) 3060, 2260 cm^{-1}. Anal. C, H, N.

(2-Butenylidene)propanedinitrile (VI) (Ooms et al., 1976). Crotonaldehyde (15% H$_2$O), 9.93 g (0.14 mol), was added to a solution of 70 mL of CH$_2$Cl$_2$, 30 mL of saturated aqueous NaCl, and 0.5 g of of β-alanine. Propanedinitrile, 9.25 g (0.14 mol), was added in five equal portions every ten 10 h. The aqueous layer was separated and the organic layer evaporated. The tarry residue was dissolved in hot ligroin and decanted from the insoluble material. When the mixture cooled, white crystals formed: mp 52–53 °C, 5.74 g (35%); ^{1}H NMR (CDCl$_3$) δ 2.00, 2.10 (d, 3 H), 6.5–6.65 (m, 1 H), 6.7–7.0 (m, 1 H)8 7.30–7.50 (m, 1 H); IR (KBr) 2260, 1570 cm^{-1}.

(3-Phenoxyphenyl)methylenepropanedinitrile (VII) was prepared in 43% yield by the above procedure and had a mp of 67–68 °C: ^{1}H NMR (CDCl$_3$) δ 6.65–7.6 (m); IR (KBr) 3080, 2240, 1590–1580 cm^{-1}; mass spectrum *m/e* 247 (M + 1), 246, (M).

(3-Methyl-2-butenylidene)propanedinitrile (VIII) was prepared as above from a mixture of 3-methyl-2-buten-1-ol and 3-methyl-2-butenal which was obtained by oxidation of 3-methyl-2-buten-1-ol with activated MnO$_2$. The product had a mp of 102–103 °C: ^{1}H NMR (CDCl$_3$) δ 2.0 (s, 6 H), 6.22, 6.42 (d, 1 H), 7.58, 7.75 (d, 1 H); IR (KBr) 2260, 1630, 1570 cm^{-1}; mass spectrum *m/e* 132 (M).

General Procedure for Reaction of Propanedinitriles with III. II, 1.15 g (0.006 mol), was dissolved in 20 mL of CHCl$_3$, and 15 mL of saturated aqueous K_2CO_3 was added. The solution was allowed to stir for 20 min, and the CHCl$_2$ layer separated and dried for 30 min over anhydrous K_2CO_3. The appropriate propanedinitrile derivative (0.003 mol) and the ylide were combined in a flask with 3 g of 3-Å molecular sieves. The flask was stoppered and allowed to stand at room temperature for 24 h. The solvent was removed in vacuo, and the residual oil taken up in CH$_2$Cl$_2$ and evaporated on silica gel for separation by dry column chromatography as described earlier. Generally, several bands were visible, including those of decomposition products of the ylide (Payne, 1967). Of the two product bands, the forerunning band was consistently found to be of trans configuration. Infrared spectra were recorded for each compound and showed absorption at 3090–2900 (aliphatic and aromatic), 2260 (C≡N), and 1740 cm^{-1} (carbonyl).

RESULTS AND DISCUSSION

In addition to the spiro compounds (IV and V), all of the compounds listed in Table I were tested for insecticidal activity in three insect species. Only those compounds which exhibited toxicity (at the levels tested) in at least one of the insect species are listed in Table II; all other compounds were inactive. The insect toxicity shown for compounds in Table II is generally low when compared to the toxicity given by the standard pyrethroid, permethrin. The spiro compounds, unlike the other compounds tested, were found to be active (albeit quite low) against more than one of the insect test species. The

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Table I. *gem*-Dicyanocyclopropanecarboxylic Acid (3-Phenoxyphenyl)methyl Esters

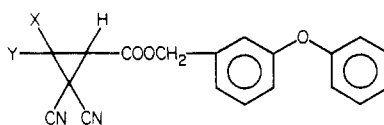| compd no.[a]	X	Y	physical state	yield,[b] %	¹H NMR[c]	elemental analysis
IXa	C_6H_5	H	oil		2.93 (d, 1 H), 3.34 (d, 1 H), 4.90 (s, 2 H), 6.65–7.35 (m, 14 H)	ND
IXb	C_6H_5	H	oil	88	3.04 (d, 1 H), 3.53 (d, 1 H), 5.05 (s, 2 H), 6.65–7.35 (m, 14 H)	ND
Xa	2-$CH_3C_6H_4$	H	oil		2.19 (s, 3 H), 2.93 (d, 1 H), 3.34 (d, 1 H), 4.94 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
Xb	2-$CH_3C_6H_4$	H	oil	59	2.20 (s, 3 H), 3.04 (d, 1 H), 3.52 (d, 1 H), 5.03 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XIa	3-$CH_3C_6H_4$	H	oil		2.19 (s, 3 H), 2.92 (d, 1 H), 3.32 (d, 1 H), 4.94 (s, 2 H), 6.5–7.3 (m, 13 H)	ND
XIb	3-$CH_3C_6H_4$	H	oil	89	2.20 (s, 3 H), 3.51 (d, 1 H), 3.03 (d, 1 H), 5.03 (s, 2 H), 6.6–7.1 (m, 13 H)	ND
XIIa	4-$CH_3C_6H_4$	H	oil		2.18 (s, 3 H), 2.90 (d, 1 H), 3.32 (d, 1 H), 4.91 (s, 2 H), 6.65–7.35 (m, 13 H)	C, H, N
XIIb	4-$CH_3C_6H_4$	H	oil	70	2.22 (s, 3 H), 2.99 (d, 1 H), 3.46 (d, 1 H), 5.02 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XIIIa	2-$CH_3OC_6H_4$	H	oil		2.92 (d, 1 H), 3.16 (d, 1 H), 3.61 (s, 3 H), 4.93 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XIIIb	2-$CH_3OC_6H_4$	H	oil	69	2.98 (d, 1 H), 3.52 (d, 1 H), 3.77 (s, 3 H), 5.08 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XIVa	4-$CH_3OC_6H_4$	H	oil		2.93 (d, 1 H), 3.34 (d, 1 H), 3.60 (s, 3 H), 4.91 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XIVb	4-$CH_3OC_6H_4$	H	oil	63	3.02 (d, 1 H), 3.49 (d, 1 H), 3.63 (s, 3 H), 5.05 (s, 2 H), 6.65–7.35 (m, 13 H)	C, H, N
XVa	3-ClC_6H_4	H	oil		2.99 (d, 1 H), 3.37 (d, 1 H), 4.98 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XVb	3-ClC_6H_4	H	oil	59	3.08 (d, 1 H), 3.58 (d, 1 H), 5.10 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XVIa	4-ClC_6H_4	H	mp 94 °C		2.99 (d, 1 H), 3.37 (d, 1 H), 4.98 (s, 2 H), 6.65–7.35 (m, 13 H)	C, H, N
XVIb	4-ClC_6H_4	H	oil	65	3.08 (d, 1 H), 3.58 (d, 1 H), 5.10 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XVIIa	4-BrC_6H_4	H	mp 108 °C		2.97 (d, 1 H), 3.32 (d, 1 H), 4.99 (s, 2 H), 6.65–7.35 (m, 13 H)	C, H, N
XVIIb	4-BrC_6H_4	H	oil	70	3.04 (d, 1 H), 3.52 (d, 1 H), 5.09 (s, 2 H), 6.65–7.35 (m, 13 H)	C, H, N
XVIIIa	3-$C_6H_5OC_6H_4$	H	oil		2.93 (d, 1 H), 3.37 (d, 1 H), 4.90 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XVIIIb	3-$C_6H_5OC_6H_4$	H	oil	27	3.01 (d, 1 H), 3.52 (d, 1 H), 5.05 (s, 2 H), 6.65–7.35 (m, 18 H)	ND
XIXab	4-NO_2Ph	H	mp 116–118 °C	49	3.00–3.72 (m, 2 H), 4.99, 5.11 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XXab	2-ClPh	H	oils	48	2.98–3.65 (m, 2 H), 4.96, 5.09 (s, 2 H), 6.65–7.35 (m, 13 H)	ND
XXIab	3,4-(CH_2O_2)Ph	H	oils	48	2.83–3.55 (m, 2 H), 4.94, 5.05 (s, 2 H), 5.65, 5.70 (s, 2 H), 6.65–7.35 (m, 13 H)	N
XXIIab	3,4-CH_3OPh	H	oils	59	2.90–3.5 (m, 2 H), 3.63–3.73 (m, 6 H), 4.97, 5.08 (s, 2 H), 6.50–7.30 (m, 12 H)	ND
XXIIIab	2,4,6-CH_3Ph	H	oils	76	2.12, 2.20 (d, 9 H), 2.81–3.24 (m, 2 H), 4.90, 5.05, (s, 2 H), 6.65–7.35 (m, 11 H)	ND
XXIVa	*E*-$(CH_3,H)C=CH$	H	oil	93	1.75, 1.67 (d, 3 H), 2.70–2.87 (m, 2 H), 5.05 (s, 2 H), 5.25–5.60 (m, 1 H), 5.65–6.08 (m, 1 H), 6.60–7.40 (m, 9 H)	ND
XXIVb	*E*-$(CH_3,H)C=CH$	H	oil	93	1.72, 1.62 (d, 3 H), 2.52, 2.65 (d, 1 H), 2.79, 2.92, 3.06 (t, 1 H), 4.99 (s, 2 H), 5.52–5.98 (m, 1 H), 5.21–5.86 (t, 1 H), 6.65–7.35 (m, 9 H)	C, H, N

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Table I *(Continued)*

compd no.[a]	X	Y	physical state	yield,[b] %	¹H NMR[c]	elemental analysis
XXVa	furyl	H	oil	93	3.39 (d, 1 H), 2.96 (d, 1 H), 5.00 (s, 2 H), 6.0–6.35 (m, 2 H), 6.65–7.30 (m, 10 H)	ND
XXVb	furyl	H	oil	93	3.14 (d, 1 H), 3.56 (d, 1 H), 5.05 (s, 2 H), 6.0–6.35 (m, 2 H), 6.60–7.30 (m, 10 H)	C, H, N
XXVIa	(CH₃)₂C=CH	H	oil	93	1.70 (s, 6 H), 2.65, 2.82 (d, 1 H, J = 10 Hz), 2.96, 3.13, 2.82 (t, 1 H, J = 10 Hz), 4.99 (s, 2 H), 4.96–5.10 (m, 1 H), 6.50–7.25 (m, 9 H)	C, H, N
XXVIb	(CH₃)₂C=CH	H	oil	93	1.70 (s, 6 H), 2.42, 2.55 (d, 1 H, J = 8 Hz), 2.87, 3.00, 3.12 (t, 1 H, J = 8 Hz), 5.02 (s, 2 H), 4.80, 4.67, 4.52 (t, 1 H), 6.60–7.35 (m, 9 H)	ND
XXVIIab	(CH₃)₂C=CH	CH₃	oil	53	1.30, 1.50 (s, 9 H), 2.45 (s, 1 H), 5.05 (s, 1 H), 6.70–7.30 (m, 10 H)	ND
XXVIIIab	C₆H₅	CH₃	oil	93	1.60, 1.65 (s, 3 H), 1.50, 2.50, 2.75, 3.05 (m, 1 H), 4.93, 5.10 (s, 2 H), 6.55–7.25 (m, 14 H)	ND

[a] Compounds having numbers with an "a" suffix have been assigned the cis configuration. A "b" suffix designates the trans configuration. [b] Yield for the cis-trans isomeric products. [c] cis, J = 10 Hz; trans, J = 8 Hz.

Table II. Insecticidal Activity of Selected *gem*-Dicyanopyrethroids[a]

compd no.	% mortality		
	housefly	Mexican bean beetle	southern army worm
IV	10	10	10
V	20	10	0
Xab	20	0	0
XIIIab	10	0	0
XIVab	20	0	0
XVab	0	20	0
XVIab	0	20	0
XXab	0	40	0
XXIIab	10	0	0
XXVIIIab	0	10	0
permethrin	100	100	100

[a] Percent mortality with 500 ppm at the end of 24 h.

presence of saturated rings undoubtedly adds to the lipophilic nature of the compounds but does not fully explain their activity. A comparison of the activity of the spiro cyclopentyl and cyclohexyl compounds indicates that these compounds follow the same trends observed in other spiro series (Davis and Searle, 1977). The chlorophenyl series (XV, XVI, and XX) showed activity against the Mexican bean beetle. The difference in activvity of the 2-chlorophenyl compound as compared with the 3-chlorophenyl and the 4-chlorophenyl compounds is interesting in light of the finding of Ohno et al. (1976) with noncyclopropane systems in which the 4-methylphenyl, 4-chlorophenyl, and 3,4-(methylenedioxy)phenyl compounds showed the greatest activity. The fact that the 4-bromophenyl compound does not show activity is possibly due to the increased radius of the bromine atom. The order of activity of the 2-methoxyphenyl and the 4-methoxyphenyl compounds is in agreement with that observed by Elliott et al., (1976b) for the *gem*-dimethylcyclopropanecarboxylic acid 5-benzylfuryl or methyl ester analogues of these compounds. Elliott et al. (1976b) observed a relative toxicity of 20 for the 4-methoxyphenyl compound against houseflies on a scale of 1000 while the 2-methoxyphenyl compound had a relative toxicity of 1.

A lack of activity of the phenyl and furyl compounds in the *gem*-dicyano series is surprising since Elliott et al. (1976a) found enhanced activity of these compounds relative to the methoxyphenyl compound in the *gem*-dimethyl series.

The 2-methylphenyl compound shows greater activity compared to that of the 3-methylphenyl and 4-methylphenyl compounds. Lack of activity in the dimethylvinyl, *gem*-dicyano compound is surprising since it is apparently quite analogues in structure to that of an active pyrethroid. Activity in the *E*-methylvinyl, *gem*-dicyano compound is surprising in light of the fact that the analogue of this compound in the *gem*-dimethyl series is not active (Elliott, 1977). In the case of the 3-methyl-3-phenyl compound, one would not have expected any activity since pyrethroids of this type have failed to show activity (Elliott, 1977).

It appears from the data presented in this study that the insecticidal activities of the *gem*-dicyano compounds are possibly of a different nature than those of other pyrethroids. Those compounds expected to show activity based on structural similarities to active pyrethoids were found in general to be less active (or inactive) than anticipated. While the steric bulk of the cyano group is certainly less than that of the methyl group, it was predicted that the dimethylvinyl compound (XXVI) would have shown activity. On the other hand, compounds with lesser structural resemblance to known potent pyrethroids generally had greater activity than anticipated. Thus, factors other than increased polarity (due to the cyano groups) may be affecting the potency of the *gem*-dicyano compounds. It appears that the cyano group does not mimic the methyl group but rather has its own activity parameters. It can also be concluded that the toxicity of these compounds is not related to the release of cyanide compounds since one would expect to see a base line of activity if such a mechanism of action occurred.

It would appear that the structural parameters that have been found to affect insecticidal activity in *gem*-dimethylpyrethroids are not the same as those of the *gem*-dicyano series of compounds. With the parameters found in this series, it may be possible to design new *gem*-dicyano compounds which show greater activity than the compounds in this study have exhibited.

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Tricyclic Amides: A New Class of Systemic Fungicides Active against Rice Blast Disease

Robert J. Bass, Richard C. Koch, H. Colin Richards,* and John E. Thorpe

The preparation of several pyrrolo[3,2,1-*ij*]- and pyrido[3,2,1-*ij*]quinoline derivatives and their activity against rice blast disease are described. Although a wide range of substitution is permitted within these classes, highest activity is displayed by the simplest amide members, particularly 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (20, 4-lilolidone), which shows excellent protectant activity in greenhouse evaluation at concentrations of 5–10 ppm.

Rice blast disease (RBD), caused by *Piricularia oryzae*, is one of the major fungal diseases of crop plants in the world and the most important diseases of rice (Ou and Jennings, 1969). A number of fungicides for its control have been developed, including copper salts, the antibiotics blasticidin S and kasugamycin, organophosphates (Hinosan and Kitazin), and pentachlorobenzyl alcohol (Blastin). Despite extensive control measures, however, it remains widely prevalent and troublesome. In recent years, there has been a particularly strong interest in discovering systemic fungicides for its control, since these would require less frequent application than the traditional locally acting foliar protectants.

In the course of screening selected compounds representing a variety of structures, we discovered that the tricyclic amide 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-one (compound 3 in Table I) protects rice plants against experimental RBD in the greenhouse. While this compound ("2-lilolidone") had been described in the literature by Kato et al. (1971), we have found no previous reference to fungicidal activity associated with it or closely related structures; it might conceivably be distantly related to the systemic carboxanilide fungicides, even though the latter controls a different spectrum of fungal diseases (Snel et al., 1970). Its activity was particularly surpising because in vitro, this compound showed little or no activity against *P. oryzae*. Greenhouse studies revealed that 3 applied to the floodwater of rice plants is *systemically* active against RBD and well tolerated by the plants, and these findings led to the preparation and testing of the pyrrolo[3,2,1-*ij*]-

and pyrido[3,2,1-*ij*]quinolones described herein, with the aim of optimizing activity in this promising new class of fungicides.

CHEMICAL SYNTHESIS

The primary tricyclic ring structures listed in Tables I and II were generally synthesized either from tetrahydroquinoline (THQ) or from indoline (I) by N-acylation with the appropriate reagent (ω-chloroacyl chloride, diester, etc.), followed by ring closure [in the presence of aluminum chloride, polyphosphoric acid, etc. (Scheme I)]. Substituted derivatives of these systems were synthesized either from the appropriately substituted THQ or I or by chemical derivatization as indicated in Tables I and II. References relating to the exact synthetic procedure are given in Tables I and II, apart from the following, hithero undescribed in the literature.

Decahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-one (19). Compound 3 (5.4g) was hydrogenated (room temperature; 50 psi) over platinum oxide (0.2 g) in glacial acetic acid (170 mL) in a Parr apparatus for 6 h. More platinum oxide was then added and hydrogenation continued for another 2 h. The catalyst was separated and the solution evaporated. Water was added to the residue and the whole extracted with ether (2 × 100 mL). The ether layer was washed with sodium hydrogen carbonate solution and water and dried (MgSO₄). Evaporation afforded an oil which solidified after drying in vacuo. Recrystallization from hexane afforded a solid (1.8 g) of mp 49–50 °C, *m/e* 179, assumed to be a mixture of isomers. Anal. Calcd for $C_{11}H_{17}NO$: C, 73.7; H, 9.6; N, 7.8. Found: C, 73.6; H, 9.6; N, 7.8.

Decahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (25) was prepared in a similar manner from 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-4-one (20) as an oil, *m/e*

Pfizer Central Research, Sandwich, Kent, United Kingdom, and Pfizer Central Research, Pfizer Inc., Groton, Connecticut.