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Synthesis and Fungicidal Activity of 1-[(1H-1,2,4-triazol-1-yl)alkyl]-1-silacyclohexanes

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A series of six-membered ring organosilicon compounds, 1-aryl-1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclohexanes **3a-c**, have been synthesized by four-step reactions starting from 1-(chloroalkyl)trichlorosilanes. Their fungicidal activities were tested in *in vitro* for ten fungi and *in vivo* assay for four fungi occurring in rice, barley, tomato, and etc. and compared with the flusilazole. Especially, 1-*p*-fluorophenyl-1-[1-(1H-1,2,4-triazol-1-yl) alkyl]-1-silacyclohexanes (**3a**, alkyl=methyl; **3b**, alkyl=ethyl) showed good fungicidal activity with broad spectrum close to the flusilazole in *in vivo* assay.

Introduction

Much attention has been paid to a synthetic approach, which can modify organic compounds with good biological activity to new silicon-introduced compounds in agrochemicals.[1,2] Several modified organosilicon compounds[1a-c] have shown superior biological activities to the original organic compounds. Since it was found that especially bis(4-fluorophenyl)methyl(1H-1,2,4-triazol-1-yl)methylsilane known as flusilazole was effective in control of a broad spectrum of plant diseases in 1985,[1a,2] this is now one of the leading agricultural fungicides in silicon-based biological compounds.[3,4] Many organosilicon compounds with the triazole group as an active site were then patented as good fungicides.[5-7] The biological activity of these compounds is dependent on substituents on silicon at organosilicon compounds with triazolyl group and on the space length between silicon and the triazolyl group.[1a,2-7] Generally the organosilicon compounds containing both a *p*-substituted phenyl group and a triazolylmethyl group on the silicon atom, have shown good biological activities. The potency of biological activity was found to be increased in the broad spectrum for fungi, as the space length between the silicon and triazole is decreased to methylene from propylene.[3] In a series of compounds, the structures of which *p*-fluorophenyl and (triazolyl)methyl group on the silicon atom are best for the fungicidal activity.[2] Based on literatures on these subjects, we synthesized the modified 1-aryl-1-(1H-1,2,4-triazol-1-yl) alkyl-1-silacyclopentanes which were cyclized with butylene instead of both groups, methyl and *p*-fluorophenyl group, on the silicon of flusilazole.[8] These compounds show good biological activities comparable to the flusilazole. In the expansion of this series, we wish to report the synthesis and the biological activity of six-membered ring compounds, 1-aryl-1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclohexanes **3a-c**, and compared with five-membered ring compounds

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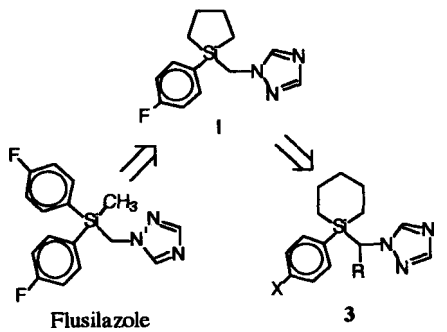


Scheme 1. Relation of Test Compounds (3) to Flusilazole.

(Scheme 1).

Experimental

Solvents, *n*-hexane, ethyl ether and tetrahydrofuran (THF), were dried by distillation from sodium benzophenone ketyl, respectively, prior to use, and dimethylformaldehyde (DMF) over molecular sieve. (Chloromethyl)trichlorosilane (**1a**) and (1-chloroethyl)trichlorosilane (**1b**) were obtained from Hls Co. 1,2,4-Triazole, sodium hydride, 1,5-dichloropentane, 4-biphenyl bromide, and 4-fluorophenyl magnesium bromide (2 M) in THF from Aldrich Co. All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All air-sensitive liquids, and the dried solvents were transferred by a standard syringe or double tipped-needle techniques. Products obtained were analyzed by GLC over a 30 m capillary column coated with SE-30 or SE-54 using a Varian 3300 gas chromatograph with flame ionization detector, and a Varian 4290 integrator. The samples for elemental analyses were purified by a preparative GLC using a Varian Aerograph series 1400 gas chromatograph with thermal conductivity detector and a 4 m by 1/8 inch stainless steel column packed with 15% SE-30 or SE-54 on 80-100 mesh Chromosorb P/AW. Proton NMR spectra were obtained on a Bruker AM 200-SY or a Varian Gem 300-spectrometer in chloroform-*d* solvent and chemical shifts are reported in parts per million down-field from the internal standard tetramethylsilane. Elemental analyses for the new compounds, **2a-c** and **3a-c**, were performed by the Chemical Analysis Laboratory in Korea Institute of Science and Technology.

Synthesis of 1-Chloromethyl-1-(4-fluorophenyl)-1-silacyclohexane (2a). To an 100 mL THF solution of **1a** (7.8 g, 42.4 mmol) at ice-water bath temperature was added slowly dropwise di-Grignard reagent, prepared by the reaction of 1,5-dichloropentane (6.0 g, 42.5 mmol) with magnesium turnings (2.5 g, 102.9 mmol) in THF (150 mL). The reaction mixture was allowed to warm up to room temperature, and stirred for another 1 h. 2 M 4-Fluorophenyl magnesium bromide (21.5 mL, 43.0 mmol) in THF was added for 30 min, stirred for another 1 h, and treated with a saturated NaCl-aqueous solution (20 mL). After three extractions of reaction mixture with 80 mL portions of ethyl ether. The combined ethereal extracts were dried over anhydrous sodium sulfate. The solvent was removed from the organic solution under reduced pressure and the residue was distilled in vacuo to give **2a** (5.8 g, bp 74 °C/0.1 mmHg) in 56% yield.

Data for **2a**; ^{1}H NMR δ 1.07 (m, 4H, SiCH_2), 1.52 (m, 2H, CH_2), 1.77 (m. 4H, CH_2), 3.02 (s, 2H, CH_2Cl), 7.12, (*m*, 2H), 7.59 (*m*, 2H) (phenyl-*H*). ^{13}C NMR δ 9.74 (SiCH_2), 24.05 (CH_2), 28.23 (CH_2), 29.53 (CH_2Cl), 115.18 ($J_{C\text{-}F}$=20 Hz), 129.99 ($J_{C\text{-}F}$=4 Hz), 136.07 ($J_{C\text{-}F}$=8 Hz), 164.06 ($J_{C\text{-}F}$= 249 Hz) (phenyl-carbons). Anal. calcd. for $SiC_{12}H_{16}ClF$: C, 59.36; H, 6.64. Found; C, 59.19; H, 6.57.

As an alternative procedure, the reaction was carried out by changing in the order of additions of both Grignard reagents under the same reaction condition above. Consecutive additions of 4-fluorophenyl magnesium bromide, and di-Grignard reagent derived from 1,5-dichloropentane to **1a** gave **2a** in 48% yield.

Synthesis of 1-(1-Chloroethyl)-1-(4-fluorophenyl)-1-silacyclohexane (2b). Reaction of **1b** (12.0 g, 60.6 mmol) with di-Grignard reagent, derived by the reaction of 1,5-dichloropentane (8.6 g, 61.0 mmol) with magnesium turning (4.3 g, 180 mmol) in THF, and 2 M 4-fluorophenyl magnesium bromide (32.0 mL, 64.0 mmol) in THF was carried out as described in the synthesis of **2a** above. Vacuum distillation gave **2b** (5.5 g, bp 91 °C/0.4 mmHg) in 33% yield. Data for **2b**: ^{1}H NMR δ 0.96-1.17 (m, 4H, SiCH_2), 1.47 (d, *J*=8 Hz, 3H, CH_3), 1.38-1.62 (m, 3H, CH_2), 1.73-1.92 (m, 3H, CH_2), 3.57 (q, *J*=8 Hz, 1H, *CH*Cl), 7.11 (m, 2H), 7.59 (m, 2H) (phenyl-*H*). ^{13}C NMR δ 9.09 (SiCH_2), 20.17 (CH_3), 24.06 (CH_2), 29.61 (CH_2), 43.49 (CH_2Cl), 115.12 ($J_{C\text{-}F}$=20 Hz), 128.93 ($J_{C\text{-}F}$=4 Hz), 136.55 ($J_{C\text{-}F}$=8 Hz), 164.07 ($J_{C\text{-}F}$=249 Hz) (phenyl-carbons). Anal. calcd. for $SiC_{13}H_{18}ClF$: C, 60.80; H, 7.06. Found; C, 60.50; H, 7.10.

Synthesis of 1-Chloromethyl-1-biphenyl-1-silacyclohexane (2c). Reaction of **1a** (14.3 g, 77.8 mmol) with di-Grignard reagent, derived by the reaction of 1,5-dichloropentane (11.0 g, 78.0 mmol) with magnesium turnings (4.4 g, 181.0 mmol) in THF and a biphenyl Grignard reagent derived by the reaction of 4-bromobiphenyl (18.8 g, 80.7 mmol) with magnesium turning (3.4 g, 139.9 mmol) in THF was carried out as described in the synthesis of **2a** above. Vacuum distillation gave **2c** (9.5 g, 170 °C/0.4 mmHg) in 41% yield. Data for **2c**; ^{1}H NMR δ 1.20 (m, 4H, SiCH_2), 1.62 (m, 2H, CH_2), 1.89 (m, 4H, CH_2), 3.15 (s, 2H, CH_2Cl), 7.42-7.86 (m, 9H, phenyl-*H*). ^{13}C NMR δ 9.68 (SiCH_2), 24.12 (CH_2), 28.36 (CH_2), 29.57 (CH_2), 126.65, 127.11, 127.46, 128.75, 133.24, 133.56, 140.81, 142.39 (phenyl-carbons). Anal. calcd. for $SiC_{18}H_{21}Cl$: C, 71.85; H, 7.03. Found; C, 71.54; H, 6.99.

Iodination of 1-Aryl-1-chloroalkyl-1-silacyclohexanes. The 1:2 mixture of **2** and sodium iodide in acetone solvent was refluxed for 6 h. The white precipitate (NaCl) occurred during refluxing solvent. After completing the reaction, the reaction mixture was diluted with a saturated $Na_2S_2O_3$-aqueous solution. Then, the three extractions of the reaction mixture with 50 mL portions of ethyl ether were combined and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The products, 1-aryl-1-iodoalkyl-1-silacyclohexanes, were obtained in 93-97% yield. These were used in next triazolylation step.

Synthesis of 1-(4-Fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)methyl-1-silacyclohexane (3a). An 1,2,

4-triazole sodium salt, prepared from the reaction of 80 wt% NaH (0.43 g, 14.3 mmol) in mineral oil with 1,2,4-triazole (1.1 g, 15.9 mmol) in DMF (20 mL), was added slowly dropwise to 30 mL DMF solution of 1-(4-fluorophenyl)-1-iodomethyl-1-silacyclohexane (4.4 g, 13.2 mmol), obtained from the iodination of **2b**, at room temperature and then stirred at 40 °C for 30 min. Resulting slurry treated with a saturated NH_4Cl-aqueous solution. After three extractions of reaction mixture with 20 mL portions of ethyl ether, the combined ethereal extracts were dried over anhydrous magnesium sulfate. **3a** (2.9 g, 74%) was purified by silica gel chromatography (ethyl ether: hexane=1 : 1).

Data for **3a**; ^{1}H NMR δ 0.98 (m, 4H, SiCH_2), 1.42 (quin., J=5.5 Hz, 2H, CH_2), 1.66 (m, 4H, CH_2), 3.91 (s, 2H, NCH_2), 7.00 (m, 2H), 7.39 (m, 2H) (phenyl-*H*), 7.72 (s, 1H), 7.81 (s, 1H) (triazole-*H*). ^{13}C NMR δ 9.77 (SiCH_2), 23.56 (CH_2), 29.00 (CH_2), 38.42 (CH_2N), 115.00 ($J_{C\text{-}F}$=20 Hz), 128.86 ($J_{C\text{-}F}$ =4 Hz), 135.63 ($J_{C\text{-}F}$=8 Hz), 163.71 ($J_{C\text{-}F}$=250 Hz) (phenyl-carbons), 142.61, 150.91 (triazolyl-carbons). Anal. calcd. for $SiC_{14}H_{18}FN_3$: C, 61.06; H, 6.59; N, 15.26. Found; C, 59.70; H, 6.38; N, 15.50.

Synthesis of 1-(4-Fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)ethyl-1-silacyclohexane (3b). Reaction of 1-(4-fluorophenyl)-1-(1-iodoethyl)-1-silacyclohexane (4.5 g, 12.9 mmol), obtained from the iodination of **2b**, with 1,2,4-triazole sodium salt which was prepared from reaction of 80 wt% NaH (0.43 g, 14 mmol) in mineral oil with 1,2,4-triazole (1.1 g, 18 mmol) in DMF (20 mL) was carried out as described in the synthesis of **3a** above. 2.4 g of **3b** was isolated in 64% yield by silica gel chromatography (ethyl ether : hexane=1 : 1). Data for **3b**; ^{1}H NMR δ 0.79-0.98 (m, 2H), 0.98-1.14 (m, 2H) (SiCH_2), 1.24-1.37 (m, 1H), 1.37-1.54 (m, 3H), 1.68-1.88 (m, 2H) (CH_2), 1.47 (d, J=7.6 Hz, 3H, CH_3), 4.09 (q, 1H, C*H*N), 7.00 (m, 2H), 7.35 (m, 2H) (aryl-*H*), 7.72 (s, 1H), 7.83 (s, 1H) (triazole-*H*). ^{13}C NMR δ 9.00 (SiCH_2), 16.14, 23.64, 29.24 (CH_2), 46.18 (*C*HN), 115.14 ($J_{C\text{-}F}$=20 Hz), 128.02 ($J_{C\text{-}F}$=4 Hz), 136.14 ($J_{C\text{-}F}$=9 Hz), 163.71 ($J_{C\text{-}F}$=250 Hz) (phenyl-carbons), 142.40, 151.04 (triazolyl-carbons). Anal. calcd. for $SiC_{15}H_{20}FN_3$: C, 62.25; H, 6.96; N, 14.52. Found; C, 62.35; H, 6.81; N, 14.42.

Synthesis of 1-biphenyl-1-(1H-1,2,4-triazol-1-yl)-1-silacyclopentane (3c). Reaction of 1-iodomethyl-1-(4-phenylphenyl)-1-silacyclopentane (11.2 g, 28.6 mmol), obtained from the iodination of **2c**, with 1,2,4-triazole sodium salt which was prepared from the reaction of 80 wt% NaH (1.0 g, 33 mmol) in mineral oil with 1,2,4-triazole (2.3 g, 33.3 mmol) in DMF (20 mL) was carried out as described in the synthesis of **3a** above. 6.0 g of **3c** was isolated in 63% yield by silica gel chromatography (ethyl ether : hexane=1 : 1). Data for **3c**; ^{1}H NMR δ 1.08 (m, 4H, SiCH_2), 1.49 (quin., J=5.5 Hz, 2H, CH_2), 1.77 (m, 4H, CH_2), 4.01 (s, 2H, CH_2N), 7.36-7.62 (m, 9H, phenyl-*H*), 7.80 (s, 1H), 7.90 (s, 1H) (triazole-*H*). ^{13}C NMR δ 10.00 (SiCH_2), 23.95, 29.35 (CH_2), 38.87 (*C*HN), 126.79, 126.93, 127.47, 128.75, 132.27, 134.38, 140.58, 142.59 (phenyl-carbons), 142.89, 151.28 (triazolyl-carbons). Anal. calcd. for $SiC_{20}H_{23}N_3$: C, 72.03; H, 6.95; N, 12.60. Found; C, 71.80; H, 6.98; N, 12.87.

Biological Activity. The biological activity of new compounds, 1-aryl-1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclohexanes **3a-c** and 1-(4-fluorophenyl)-1-(1H-1,2,4-triazol-1-yl)methyl-1-silacyclopentane (I) was tested in *in vitro* and *in vivo* assay reported previously.[8]

***In Vitro* Assay.** The fungicidal activities of compounds against ten plant pathogens, *Alternaria mali, Glomerella cingulata, Glomerella cingulata* (apple), *Phytophthora capsici* (red pepper), *Magnaporthe grisea, Rhizoctonia solani, Fusarium moniliforme, Rhizopus* sp. (rice), *Botrytis cinerea* (cucumber) listed in Table 1 were determined in an agar plate diffusion test.[8]

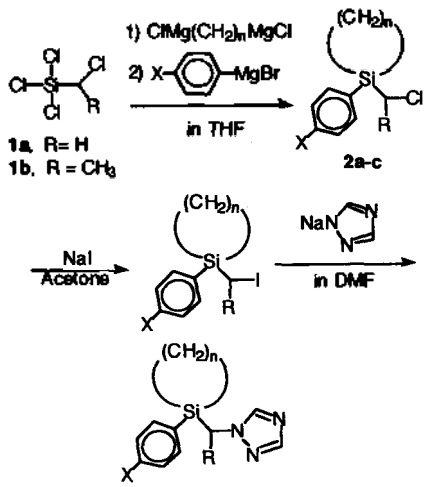
***In Vivo* Assay.** New compounds **3a-c**, I, and the flusilazole given in Table 1 were tested under greenhouse conditions[8] for fungicidal activity against four fungi of three crop species, *Magnaporthe grisea* (rice blast disease), *Rhizoctonia solani* (rice sheath blight disease) at rice plants, *Sphaerotheca fulliginea* (powdery mildow disease) at cucumber plants and *Hytophthora infestans* (late blight disease) at tomato plants as listed in Table 2.

Results and Discussion

Based on the structures of five-membered ring organosilicon compounds, 1-aryl-1-[1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclopentanes, showing the good biological activities with broad spectrum, new ring-expanded organosilicon compounds, 1-aryl-1-[1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclohexanes **3a** (aryl=4-FPh, alkyl=Me), **3b** (aryl=4-FPh, alkyl=Et), **3c** (aryl=4-biphenyl, alkyl=Me) were synthesized and tested by both *in vitro* for ten fungi and *in vivo* assay for four fungi. Their biological activities were compared with 1-(4-fluorophenyl)-1-[(1H-1,2,4-triazol-1-yl)methyl]-1-silacyclopentanes (I) and with the flusilazole.

Syntheses. 1-Aryl-1-[1-(1H-1,2,4-triazol-1-yl)alkyl-1-silacyclohexanes **3a-c** were synthesized by the four step reactions starting from commercially available (chloromethyl) trichlorosilane (**1a**) and (1-chloroethyl)trichlorosilane (**1b**) (Scheme 2). First, 1-aryl-1-(1-chloroalkyl)-1-silacyclohexanes **2a-c** were synthesized in 33-56% yields with two step reactions by Grignard synthetic method: (1) cyclization reaction by adding di-Grignard reagent, derived from the reaction of 1,5-dichloropentane with magnesium turnings, to **1** in THF; (2) phenyl group addition reaction with *p*-substituted phenyl Grignard reagents, which were obtained from the chemical company or derived by the reactions of biphenyl bromide with magnesium in THF, to the intermediates in (1) above. Compounds **3a-c** were synthesized in 63-74% yields by the iodination of **2** and the triazolylation: (1) the iodination (95-98% yields) of **2a-c** by sodium iodide was carried out through the exchange reaction of chloride and iodide; (2) finally, the triazolylation of 1-aryl-1-(1-iodoalkyl)-1-silacyclohexanes with triazole sodium salt, obtained from the reaction of triazole with sodium hydride in DMF, gave **3a-c** in 63-74% yields. **3a-c** were purified by column chromatography with the 1 : 1 mixture of hexane and diethyl ether as an eluent. Five-membered ring organosilicon compound (I) was synthesized by the procedure reported previously.[8]

As an alternative reaction procedure, when **1a** reacted first with 4-fluorophenyl Grignard reagent and then with di-Grignard reagent derived from 1,5-dichloropentane. **2a** were obtained in little lower yield. The results show that the formation of cyclic compounds is easier as the number of chlorine substituents on the silicon increase,[9] in spite of the fact



Scheme 2.

that the opportunity of polymer formation is greater when the functionality of the silicon is higher, reflecting that the inductive and steric effects[10] of substituents on silicon play important roles in the cyclization reaction.

In the synthesis of silacycloalkanes, the productions of six-membered ring compounds (**2a**, 56%; **2c**, 41%) were slightly lower yields than those of five-membered ring compounds, 1-(chloromethyl)-1-aryl-1-silacyclopentanes (aryl=4-FPh, 73%; aryl=4-biphenyl, 49%),[8] using Grignard method in our experimental conditions. These seems likely that the formation of five membered ring in the cyclization of silicon-introduced organosilicon compound is more favorable than that of six membered ring as shown in the intramolecular cyclization of alkenylsilanes through the hydrosilylation reaction.[11]

The new compounds **2a-c** and **3a-c** were characterized by the analysis of ^1H and ^{13}C NMR data. The ^1H NMR data of **2a** and **2c** show the two $SiCH_2$ resonances (m, 4H) at δ 1.07 and 1.20, the two CH_2 resonances (m, 4H) at δ 1.77 and 1.89, the central-CH_2 resonances (m, 2H) at δ 1.52 and 1.62, the CH_2Cl (s) resonances at δ 3.02 and 3.15, and the typical phenyl-resonances at the down-field of δ 7.12-7.86 in the expected regions[12] of protons resonances, respectively. In the case of **2b**, the proton spectrum disclosed more complicated splitting patterns than that of **2a** for the ring-pentylene protons due to the different chemical environment for the protons of both sides at six-membered ring, and the resonances of 1-chloroethyl group at δ 1.47 (d, 3H, CH_3) and δ 3.57 (q, 1H, CH). The conversions of **2a-c** to 1-aryl-1-(1-iodoalkyl)-1-silacyclohexanes were monitored by GLC and the iodination products were used in next step without characterization. In ^1H NMR data of **3a** and **3c** the typical resonances[1d] for the two CHs on triazole ring appear with singlets at δ 7.72, 7.83 and at δ 7.80, 7.90, and the CH_2N resonances at the down-field shifts of δ 3.91 and δ 4.01, respectively. Other cyclic pentylene-protons are shifted to up-field about 0.1 ppm in the chemical shifts with similar splitting patterns to that of **2a** and **2c**. **3c** are generally shifted to down-field about 0.1 ppm in the chemical shifts with similar splitting patterns to those of **3a** except for phenyl group.

Table 1. *In Vitro* Biological Activity of 1-(1-(1*H*-1,2,4-Triazol-1-yl)alkyl)-1-silacycloalkanes

Pathogen (Plant)	Conc. (mg/L)	Compounds				Flusila-zole[8]
		3a	**3b**	**3c**	**I**[8]	
Alternaria mali	50	100	100	95	100	100
(apple)	12.5	100	55		90	100
	1	67	35		63	100
Phytophthora capsici	50	30	50	15	70	70
(red pepper)	12.5	22	20		30	35
	1	13	0		0	9
Pysalospora baccae	50	84	100	80	100	100
(grape)	12.5	79	50		79	100
	1	21	25		21	63
Botryosphaeria dothidea	50	90	78	75	100	100
	12.5	83	60		86	100
(apple)	1	62	35		62	76
Glomerella cingulata	50	100	100	95	100	100
(apple)	12.5	100	90		100	100
	1	68	40		58	100
Magnaporthe grisea	50	100	100	95	100	100
(rice)	12.5	100	80		100	100
	1	33	45		26	100
Rhizoctonia solani	50	90	100	70	85	100
(rice)	12.5	68	85		60	80
	1	53	50		38	60
Fusarium moniliforme	50	100	100	75	100	100
(rice)	12.5	81	100		81	100
	1	67	95		62	76
Rhizopus sp.	50	65	59	65	90	87
(rice)	12.5	65	40		65	78
	1	22	25		22	39
Botrytis cinerea	50	100	64	78	100	100
(cucumber)	12.5	82	45		82	100
	1	30	30		48	82

Table 2. *In Vivo* Biological Activity of 1-(1-1H-1,2,4-Triazol-1-yl)alkyl)-1-silacycloalkanes

Pathogen (plant disease)	Conc. (mg/L)	Compounds				Flusila-zole[8]
		3a	**3b**	**3c**	**I**[8]	
Magnaporthe grisea	50	100	100	35	88	100
(rice blast)	25	64	75	25	83	89
	12.5	47	47		55	67
Rhizoctonic solani	50	86	55	0	88	69
(rice sheath blight)	25	51	55		82	58
	12.5	47	35		74	33
Sphaerotheca fulliginea	50	100	90	98	100	100
(cucumber powdery	25	100	75	75	100	100
mildow)	12.5	96	65		95	100
Phytophthora infestans	50	43	75	70	42	83
(tomato late blight)	25	32	35	50	37	57
	12.5	0	0		0	29

Biological Activities. The biological activities for new six-membered ring organosilicon compounds **3a-c** were evaluated by both *in vitro* for ten fungi and *in vivo* assay

for four fungi occurring in rice, cucumber, etc. and compared with 1-(4-fluorophenyl)-1-[(1H-1,2,4-triazol-1-yl) methyl]-1-silacyclopentanes (I) found as a representative among five-membered ring organosilicon compounds, and the flusilazole commercialized. The results are listed in Table 1 and Table 2.

As shown in the tables, new compounds **3a-c** disclose good biological activities in *in vitro* and *in vivo* assay. Especially, **3a** and **3b** containing *p*-fluorophenyl group showed better biological activity in broad spectrum. Compared with the five-membered ring compound (I) and flusilazole in *in vivo* assay, no remarkable difference is noticed with the biological activity indicating that the structure introducing 1-(triazolyl)alkyl group to and *p*-fluorophenyl group to the silicon of silacycloalkanes is one of good fungicidal compounds. On the study for the relationship between the biological activity and the structures, it has been found that the structures of which both groups, a 4-fluorophenyl and an 1-(triazolyl)alkyl group on the silicon atom keep good biological activities, even though other two groups of a methyl and a 4-fluorophenyl group on the silicon atom of the flusilazole are modified to the cyclic silacyclopentanes and the silacyclohexanes.

In summary, the modified six-membered ring compounds, 1-(*p*-fluorophenyl)-1-(1-(1H-1,2,4-triazol-1-yl)alkyl)-1-silacyclohexanes, **3a** (alkyl=Me) and **3b** (alkyl=Et), which are cyclized with pentylene instead of both groups, methyl and *p*-fluorophenyl group, at the silicon of the flusilazole showed good fungicidal activity with broad spectrum close to the five-membered ring compound (I) and the flusilazole in *in vivo* assay. Such a modified synthetic method may give a chance to develop new good biological active compounds.

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