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Synthesis of 1-Triazolyl-4-trimethylsilyl-2-butanol and 1-Triazolyl-5-trimethylsilyl-2-pentanol Derivatives and an Investigation of Their Fungicidal Activities

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A new series of azole derivatives of 1-triazolyl-4-trimethylsilyl-2-butanol and 1-triazolyl-5-trimethylsilyl-2-pentanol were synthesized and evaluated for fungicidal activities against rice blast, sheath blight, and powdery mildew on barley. The derivatives of 2,4-difluorobenzene exhibited high antifungal activities when applied by spray, but exhibited no fungicidal activity by submerged application.

Key words fungicidal activity; 1*H*-1,2,4-triazole; silicon; synthesis

In a previous paper,[1] we reported our research targeting a systemic fungicide and our discovery of silicon-containing azole compounds showing fungicidal activity against rice sheath blight by submerged application.

Azole fungicide acts on the fungus by inhibiting the biosynthesis of ergosterol,[2] an important component of the cell membrane of the fungus. The effectiveness of the azole fungicide against rice sheath blight might be due to the property of *Rhizoctonia solani* as a filamentous fungus possessing an ergosterol-containing cell membrane. However, an agent is likely to lack a systemic feature if it fails to consistently show excellent efficacy by submerged application. From this standpoint, it was very promising to find that a series of silicon-containing azole derivatives **1** exhibited excellent effects in comparison with the existing fungicides by submerged application.

In spite of these promising effects, the compounds **1** are structured with two carbons between a hydroxyl group and a trimethylsilyl group, hence they are liable to decompose to allyl compounds **2** by Peterson elimination[3—5] under acidic or alkaline conditions (Fig. 1). This may pose problems with the industrialized manufacture and use of these compounds.

In one limited case, however, we were able to prepare and evaluate a promising compound in which the number of carbons between the hydroxyl group and trimethylsilyl group increased. Given their small possibility of Peterson elimination, the compounds **3** were thought to be favorable from the viewpoint of synthesis.

Although the 4-fluorobenzene derivative **3a** exhibited a low efficacy compared to the 4-fluorobenzene derivative **1a** in testing, we tried to confirm the effect of variation on the substitution of the benzene ring to boost the activity (Fig. 2). We also examined the compounds **4** structured with an increased number of carbons. In addition to testing the antifungal activity of the agents against *Pyricularia oryzae* and *Rhizoctonia solani* and evaluating their efficacy by submerged application against rice blast and rice sheath blight, we examined their efficacy against the powdery mildew of barley, a fungus against which the azole fungicides are generally effective.

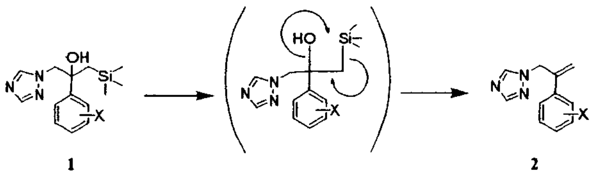

Fig. 1. Peterson Reaction

Before the development of the compounds **3**, Chollet *et al.* reported[6] that compounds in which the number of carbons increased were synthesized by the addition of trimethylsilylacetylene to triazolylacetophenone. The compounds **3** can be anticipated to follow by reduction of the triple bond (Fig. 3). In our experiment, the route required two reductions and afforded **3** in low yield.

In our program, the derivation was performed using the Grignard reaction with the epoxides **8** in the presence of cupper halide[7] (Fig. 4).

We speculated that the compounds **4** could be prepared by a similar method, using the oxetanes **9** of the intermediate to take the place of the epoxides **8** (Fig. 5). The oxetanes **9** could be generated by reaction with two equivalents of di-

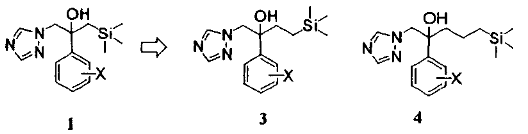

Fig. 2. Research Strategy

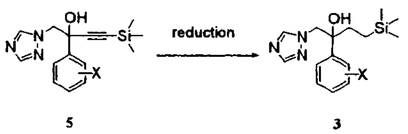

Fig. 3. 1-Triazolyl-4-trimethylsilyl-2-butanol Prepared from Chollet's Compound **5**

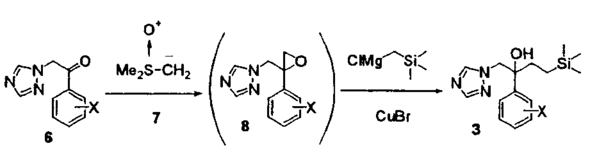

Fig. 4. 1-Triazolyl-4-trimethylsilyl-2-butanol Prepared by the Grignard Reaction

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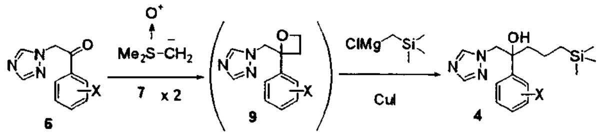

Fig. 5. 1-Triazolyl-5-trimethylsilyl-2-pentanol Prepared by the Grignard Reaction

methylsulfoxonium methylide[8,9)] **7** to triazolylacetophenones **6**. The target compounds **4** could be prepared from the oxetanes **9** under reaction conditions similar to those used for the preparation of the compounds **3**.

We performed tests on 1-triazolyl-4-trimethylsilyl-2-butanols and 1-triazolyl-5-trimethylsilyl-2-pentanols obtained by the above-described methods in order to assess their fungicidal activities against rice blast, rice sheath blight, and powdery mildew of barley, as well as to measure their IC_{50} values against the phytophathogenic fungi *Pyricularia oryzae* and *Rhizoctonia solani*. The results are shown in Table 3.

Among several derivatives on the substituted phenyl, 2,4-difluorobenzne derivatives **3g** and **4d** exhibited high antifungal activity against both fungi, and 2,4-disubstituted derivatives of 2-butanols **3g** and **3h** showed fungicidal activity for powdery mildew. However in spite of these high effects, none of these derivatives exhibited any effect whatever by submerged application. Based on the results obtained, we presume that these derivatives are missing a systemic feature.

In conclusion, a new series of azole derivatives of 1-triazolyl-4-trimethylsilyl-2-butanol and 1-triazolyl-5-trimethylsilyl-2-pentanol were synthesized and evaluated for fungicidal activities against rice blast, sheath blight, and powdery mildew on barley. Among them, the derivatives of 2,4-difluorobenzene exhibited high antifungal activities but did not show fungicidal activity by submerged application.

Experimental

All melting points (mp) were uncorrected. IR was recorded on a Perkin Elmer 1600 spectrometer and ^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer using tetramethylsilane as an internal standard. MS values were obtained on a JEOL JMS-D300 spectrometer and a VG Auto Spec M mass spectrometer. TLC was performed on a plate precoated with a 0.25 mm-thick layer of silica gel (E. Merck), and the spots were made visible by ultraviolet (UV) irradiation or by spraying with a solution made of 25 g ammonium molybdate and 1 g ceric sulfate in 500 ml of 10% sulfuric acid followed by heating. Silica gel (350—250 mesh, Yamamura Chemical Laboratories Co., Ltd.) was used for column chromatography. The following abbreviations are used hereafter: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; br, broad.

2-Phenyl-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3) The following compounds **3b**—**g** were prepared using the same procedure employing in our previous work.[1)] The yields are shown in Table 1.

2-(4-Chlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3b) mp 83—84 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1736, 1595, 1510, 1491, 1425, 1248, 1190, 1072, 1015. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.18 (1H, dt, J=4.5, 13.5 Hz), 0.50 (1H, dt, J=4.5, 13.5 Hz), 1.65 (1H, dt, J=4.5, 13.5 Hz), 1.85 (1H, dt, J=4.5, 13.5 Hz), 4.47 (2H, s), 7.23 (2H, d, J=9.0 Hz), 7.29 (2H, d, J=9.0 Hz), 7.91 (1H, s), 8.11 (1H, s). MS *m*/*z*: 323 (M$^+$), 308, 241, 222, 83, 73. High resolution (HR)-MS. Calcd for $C_{15}H_{22}ClN_3OSi$: 323.122069. Found: 323.122179.

2-(4-Bromophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3c) mp 112—113 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1725, 1585, 1510, 1490, 1425, 1248, 1190, 1072, 1015. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.17 (1H, dt, J=4.5, 13.5 Hz), 0.50 (1H, dt, J=4.5, 13.5 Hz), 1.65 (1H, dt, J=4.5, 13.5 Hz), 1.85 (1H, dt, J=4.5, 13.5 Hz), 4.47 (2H, s), 7.18 (2H, d, J=8.5 Hz), 7.49 (2H, d, J=8.5 Hz), 7.91 (1H, s), 8.10 (1H, s). MS *m*/*z*: 369 (M$^+$+2), 367 (M$^+$), 354, 352, 287, 285, 268, 266, 83, 73. HR-MS. Calcd for $C_{15}H_{22}BrN_3OSi$: 367.071552. Found: 367.071487.

Table 1. Synthesis of 1-Triazolyl-4-trimethylsilyl-2-butanols **3**

Compd.	X	Yield (%)
3a	4-F	63[a)]
3b	4-Cl	61
3c	4-Br	73
3d	H	27
3e	4-Me	76
3f	4-MeO	67
3g	2,4-F$_2$	49
3h	2,4-Cl$_2$	[b)]

a) Data from our previous work.[1)] *b*) Prepared from Chollet's compound **5**.

2-Phenyl-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3d) mp 76—77 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1510, 1494, 1248, 1202, 1136, 1062, 1011. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.22 (1H, dt, J=4.5, 13.5 Hz), 0.51 (1H, dt, J=4.5, 13.5 Hz), 1.70 (1H, dt, J=4.5, 13.5 Hz), 1.90 (1H, dt, J=4.5, 13.5 Hz), 4.48 (2H, s), 7.21—7.37 (5H, m), 7.90 (1H, s), 8.00 (1H, s). MS *m*/*z*: 289 (M$^+$), 274, 207, 188, 83, 73. HR-MS. Calcd for $C_{15}H_{23}N_3OSi$: 289.161041. Found: 289.161107.

2-(4-Methylphenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3e) mp 93—94 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1736, 1512, 1425, 1277, 1250, 1188, 1136, 1075, 1032. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.23 (1H, dt, J=4.5, 13.5 Hz), 0.50 (1H, dt, J=4.5, 13.5 Hz), 1.69 (1H, dt, J=4.5, 13.5 Hz), 1.89 (1H, dt, J=4.5, 13.5 Hz), 2.32 (3H, s), 4.50 (2H, s), 7.12 (2H, d, J=8.5 Hz), 7.18 (2H, d, J=8.5 Hz), 7.92 (1H, s), 8.26 (1H, s). MS *m*/*z*: 303 (M$^+$), 288, 221, 202, 83, 73. HR-MS. Calcd for $C_{16}H_{25}N_3OSi$: 303.176691. Found: 303.176674.

2-(4-Methoxyphenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3f) mp 87—88 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1734, 1611, 1512, 1423, 1250, 1178, 1134, 1072, 1031. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.23 (1H, dt, J=4.5, 13.5 Hz), 0.50 (1H, dt, J=4.5, 13.5 Hz), 1.68 (1H, dt, J=4.5, 13.5 Hz), 1.88 (1H, dt, J=4.5, 13.5 Hz), 3.79 (3H, s), 4.49 (2H, s), 6.84 (2H, d, J=8.5 Hz), 7.19 (2H, d, J=8.5 Hz), 7.94 (1H, s), 8.31 (1H, s). MS *m*/*z*: 319 (M$^+$), 304, 237, 218, 121, 83, 73. HR-MS. Calcd for $C_{16}H_{25}N_3O_2Si$: 319.171606. Found: 319.171722.

2-(2,4-Difluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3g) mp 76—77 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1610, 1512, 1423, 1250, 1138, 1094, 1032. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.05 (9H, s), 0.13 (1H, dt, J=4.5, 13.5 Hz), 0.58 (1H, dt, J=4.5, 13.5 Hz), 1.74 (1H, dt, J=4.5, 13.5 Hz), 1.90 (1H, dt, J=4.5, 13.5 Hz), 4.49 (1H, d, J=14.0 Hz), 4.81 (1H, d, J=14.0 Hz), 6.69—6.83 (2H, m), 7.37—7.49 (1H, m), 7.85 (1H, s), 8.12 (1H, s). MS *m*/*z*: 325 (M$^+$), 310, 243, 224, 83, 73. HR-MS. Calcd for $C_{15}H_{21}F_2N_3OSi$: 325.142197. Found: 325.142052.

2-(2,4-Dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilyl-2-butanol (3h) A solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (0.59 ml, 2.0 mmol) was diluted with teterahydrofuran (50 ml), and a solution of 2-(2,4-dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilylbut-3-yn-2-ol was added to the mixture at 0 °C. The mixture was stirred at room temperature for 3 h, and neutralized with 20% sulfuric acid, poured into ice for quenching and extracted with ethyl acetate. The organic layer was washed with water and dried over magnesium sulfate, and the solvent was evaporated to give 2-(2,4-dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-4-trimethylsilylbut-3-en-2-ol (98 mg, 55%) as colorless crystals (recrystallized from diisopropyl ether), mp 118—120 °C. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: 4.65 (1H, d, J=14.1 Hz), 5.12 (1H, d, J=14.1 Hz), 6.05 (1H, d, J=18.8 Hz), 6.55 (1H, d, J=18.8 Hz), 7.19 (1H, dd, J=2.2, 8.4 Hz), 7.36 (1H, d, J=2.2 Hz), 7.67 (1H, d, J=8.4 Hz), 7.84 (1H, s), 7.99 (1H, s). MS *m*/*z*: 357 (M$^+$+2), 355 (M$^+$), 342, 340, 275, 273, 258, 256, 216, 214, 83, 73. This product (126 mg, 0.35 mmol) was dissolved in ethanol (5 ml) and subjected to hydrogenation with a hydrogen balloon in the presence of 10% palladium on carbon for 5 h at room temperature. The catalyst was then filtered off and the solvent was removed *in vacuo* to afford **3h** (115 mg, 90%) as colorless crystals (recrystallized from diisopropyl ether), mp 91—93 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1586, 1518, 1370, 1248, 1188, 1136, 1092, 1026. ^{1}H-NMR (200 MHz, CDCl$_3$) δ: -0.06 (9H, s), 0.04 (1H, dt, J=4.5, 13.5 Hz), 0.57 (1H, dt, J=4.5, 13.5 Hz), 1.77 (1H, dt, J=4.5, 13.5 Hz), 2.36 (1H, dt, J=4.5, 13.5 Hz), 4.48 (1H, d, J=14.0 Hz), 5.25 (1H, d, J=14.0 Hz), 7.14 (1H, dd, J=2.0, 8.5 Hz), 7.32 (1H, d, J=2.0 Hz), 7.58 (1H, d, J=8.5 Hz), 7.82 (1H, s), 7.92 (1H, s). MS *m*/*z*: 359 (M$^+$+2), 357 (M$^+$), 344, 342, 258, 256, 83, 73. HR-MS. Calcd for $C_{15}H_{21}Cl_2N_3OSi$:

Table 2. Synthesis of 1-Triazolyl-4-trimethylsilyl-2-pentanols **4**

Compd.	X	Yield (%)
4a	4-F	49
4b	4-Cl	26
4c	H	21
4d	2,4-F_2	37
4e	3,4-Cl_2	36

357.083096. Found: 357.083022.

2-(4-Fluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-5-trimethylsilyl-2-pentanol (4a) A solution of sodium hydride (60% mineral oil dispersion, 880 mg, 22.0 mmol) in dimethyl sulfoxide (20 ml) was heated at 70 °C for 1 h. When the hydrogen gas ceased to evolve, the mixture was cooled to room temperature and trimethylsulfoxonium iodide (4.8 g, 21.8 mmol) was added. After stirring at room temperature for 0.5 h, 1-(4-fluorophenyl)-2-(1*H*-1,2,4-triazol-1-yl)ethanone **5a** (2.05 g, 10.0 mmol) was added and the mixture was stirred for 4 h at the same temperature. The reaction mixture was partitioned between ethyl acetate and brine, the organic layer was dried over magnesium sulfate and concentrated to give a solid, and the solid obtained was chromatographed on silica gel (ethyl acetate–hexane, 1 : 1, v/v) to afford 1-{[2-(4-fluorophenyl)oxetane-2-yl]methyl}-1*H*-1,2,4-triazole **9a** (1.29 g, 55%) as an oil. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.66 (1H, m), 3.00 (1H, m), 4.28 (1H, m), 4.31 (1H, d, J=14.7 Hz), 4.44 (1H, m), 4.54 (1H, d, J=14.7 Hz), 7.09 (2H, t, J=8.8 Hz), 7.30 (2H, dd, J=5.3, 8.8 Hz), 8.00 (1H, s), 8.30 (1H, s). This product was used for the next reaction without further purification. Cuprous iodide (95 mg, 0.5 mmol) was added to a solution of **9a** (117 mg, 0.5 mmol) in teterahydrofuran (2 ml) at room temperature. A solution of trimethylsilylmethylmagnesium chloride in diethyl ether (1.9 ml, 1.5 mmol) was added dropwise to the mixture at room temperature for 1 h. The reaction mixture was poured into ice, and quenched with a saturated aqueous solution of ammonium chloride, and extracted with ethyl acetate. The organic layer was washed with water and dried over magnesium sulfate. The solvent was evaporated to give a solid, which was purified by column chromatography (ethyl acetate–hexane, 1 : 1, v/v) to afford **4a** (143 mg, 89%) as colorless crystals (recrystallized from diisopropyl ether), mp 133—135 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1913, 1775, 1736, 1605, 1510, 1425, 1370, 1248, 1188, 1136, 1092, 1026. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: −0.10 (9H, s), 0.36—0.46 (2H, m), 1.01—1.23 (1H, m), 1.26—1.42 (1H, m), 1.71 (1H, dt, J=5.0, 12.0 Hz), 1.88 (1H, dt, J=5.0, 12.0 Hz), 4.39 (2H, s), 6.99 (2H, t, J=8.5 Hz), 7.28 (2H, dd, J=5.0, 8.5 Hz), 7.83 (1H, s), 7.88 (1H, s). MS *m/z*: 321 (M^+), 306, 239, 206, 83, 73. HR-MS Calcd for $C_{16}H_{24}FN_3OSi$: 321.167269. Found: 321.167289.

The following compounds were prepared by a similar method. The yields are shown in Table 2.

2-(4-Chlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-5-trimethylsilyl-2-pentanol (4b) mp 121—122 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1913, 1775, 1720, 1595, 1505, 1425, 1270, 1249, 1090, 1025, 1010. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: −0.09 (9H, s), 0.35—0.46 (2H, m), 1.01—1.15 (1H, m), 1.25—1.42 (1H, m), 1.71 (1H, dt, J=4.5, 13.5 Hz), 1.88 (1H, dt, J=4.5, 13.5 Hz), 4.40 (2H, s), 7.26 (4H, m), 7.85 (1H, s), 7.89 (1H, s). MS *m/z*: 339 (M^++2), 353 (M^+), 324, 322, 255, 222, 83, 73. HR-MS. Calcd for $C_{16}H_{24}ClN_3OSi$: 337.137719. Found: 337.137675.

2-Phenyl-1-(1*H*-1,2,4-triazol-1-yl)-5-trimethylsilyl-2-pentanol (4c) mp 120—121 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1960, 1775, 1740, 1595, 1505, 1450, 1249, 1190, 1025, 1010. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: −0.10 (9H, s), 0.37—0.47 (2H, m), 1.05—1.16 (1H, m), 1.25—1.42 (1H, m), 1.73 (1H, dt, J=5.0, 12.0 Hz), 1.93 (1H, dt, J=5.0, 12.0 Hz), 4.42 (2H, s), 7.04—7.32 (5H, m), 7.82 (1H, s), 7.88 (1H, s). MS *m/z*: 303 (M^+), 288, 221, 188, 146, 83, 73. HR-MS. Calcd for $C_{16}H_{25}N_3OSi$: 303.176691. Found: 303.176738.

2-(2,4-Difluorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-5-trimethylsilyl-2-pentanol (4d) mp 97—98 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1775, 1620, 1510, 1425, 1240, 1190, 1094, 1025. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: −0.09 (9H, s), 0.40—0.48 (2H, m), 0.99—1.15 (1H, m), 1.34—1.48 (1H, m), 1.77 (1H, dt, J=5.0, 12.0 Hz), 1.98 (1H, dt, J=5.0, 12.0 Hz), 4.44 (1H, d, J=14.0 Hz), 4.77 (1H, d, J=14.0 Hz), 6.68—6.82 (2H, m), 7.39—7.51 (1H, m), 7.83 (1H, s), 7.89 (1H, s). MS *m/z*: 339 (M^+), 324, 257, 224, 83, 73. HR-MS. Calcd for $C_{16}H_{23}F_2N_3OSi$: 339.157847. Found: 339.157849.

Table 3. Fungicidal Activities of Azole Derivatives

Compd.	P.O. IC$_{50}$ (ppm)	R.B. MIC (g/10a)	R.S. IC$_{50}$ (ppm)	S.B. MIC (g/10a)	P.M. MIC (ppm)
3a	10	>100	>1.0	>100[a]	3
3b	>10	>100	>1.0	>100	3
3c	>10	>100	>1.0	>100	3
3d	>10	>100	>1.0	>100	3
3e	>10	>100	>1.0	>100	>3
3f	>10	>100	>1.0	>100	>3
3g	3.10	>100	0.12	>100	0.3
3h	2.57	>100	0.05	>100	0.3
4a	>3	>100	0.42	>100	3
4b	>3	>100	0.61	>100	1
4c	>10	>100	>1.0	>100	3
4d	0.89	>100	0.01	>100	1
4e	>10	>100	1.94	>100	>3
1a	1.09[b]	3[b]	0.04[b]	12.5[a]	0.3[b]

P.O., *Pyricularia oryzae*; R.B., Rice blast; R.S., *Rhizoctonia solani*; S.B., Sheath blight; P.M., Powdery mildew; *a*) data from our previous work[1]; *b*) data from our previous work.[10]

2-(2,4-Dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)-5-trimethylsilyl-2-pentanol (4e) mp 96—97 °C. IR (KBr) cm^{-1}: 3250, 2950, 2880, 1755, 1610, 1550, 1510, 1375, 1248, 1135, 1030. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: −0.10 (9H, s), 0.36—0.46 (2H, m), 0.90—1.16 (1H, m), 1.25—1.50 (1H, m), 1.69 (1H, dt, J=5.0, 12.0 Hz), 1.85 (1H, dt, J=5.0, 12.0 Hz), 4.38 (2H, s), 7.14 (1H, dd, J=2.0, 8.5 Hz), 7.38 (1H, d, J=8.5 Hz), 7.47 (1H, d, J=2.0 Hz), 7.89 (1H, s), 7.91 (1H, s). MS *m/z*: 373 (M^++2), 371 (M^+), 358, 356, 330, 328, 289, 256, 83, 73. HR-MS. Calcd for $C_{16}H_{23}Cl_2N_3OSi$: 371.098746. Found: 371.098628.

Antifungal Activity Four-millimeter mycelial agar discs were placed on potato dextrose agar plates containing test compounds. The plates were incubated at 25 °C for 7 d as for the test of efficacy against *Pyricularia oryzae*, and at 25 °C for 3 d for the test of efficacy against *Rhizoctonia solani*. The diameters of the mycelium colonies were then measured to examine the effects of the chemicals on fungal growth. The results are shown in Table 3.

Curative Activity against Rice Blast Rice seedlings (variety Sachikaze) at the 4—5 leaf stage were sprayed with a spore suspension of the fungus *Pyricularia oryzae* and kept in a moist chamber (relative humidity: 100%) at 20—22 °C. After 24 h, the rice seedlings were sprayed with aqueous suspensions of the test compound at different concentrations, and placed back in the moist chamber. The concentration with the highest efficacy against rice blast was identified after 6 d. The results are shown in Table 3.

Preventive Activity against Rice Sheath Blight by Submerged Application Rice seedlings (variety Nipponbare) at the 3—4 leaf stage were flooded to a depth of 1 cm with water in pots, then the test compound was dispensed into the water. After keeping the seedlings in a greenhouse for 7 d, 4—5 oat grains cultured with *Rhizoctonia solani* were placed around the base of each seedling. The seedlings were then kept in a moist chamber (relative humidity: 100%) for 5 d at 25—27 °C. The number of grams per 10 acres required to eradicate rice sheath blight was determined after 5 d. The results are shown in Table 3.

Curative Activity against Powdery Mildew of Barley Barley seedlings (variety Sekishinriki) at the first leaf stage were inoculated with conidia of *Erysiphe graminis* f. sp. *hordei* by sprinkling spores of the fungus on the seedlings. After being kept in a greenhouse at 15—50 °C for 1 d, the seedlings were sprayed with an aqueous suspension of the test compound and kept in the greenhouse at the same temperature for 10 more days. On the 10th day, the most effective concentration against powdery mildew of barley was determined. The results are shown in Table 3.

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