Original Article

Synthesis and Bleaching Activity of 3-Propargylthio-4-(substituted phenyl)-4*H*-1,2,4-triazoles

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A number of 3-alkylthio-4-aryl-4*H*-1,2,4-triazoles were synthesized and evaluated for their bleaching activity by using a lettuce seedling test. In a series of 4-phenyl-4*H*-1,2,4-triazoles, 3-propylthio and 3-propargylthio analogs caused complete bleaching symptoms at 50 ppm, while the activity fell off with increasing or decreasing size of the alkylthio group at the 3-position of the triazole ring. The introduction of a chloro, trifluoromethyl, methyl or ethoxy substituent at the meta- or para-position on the benzene ring increased the activity in comparison with that of the phenyl analog. 4-(3-Chlorophenyl and 4-chlorophenyl)-3-propargylthio-4*H*-1,2,4-triazole (**16** and **17**) markedly reduced β -carotene content as well as chlorophyll in plants. Inhibition of β -carotene formation was accompanied by an accumulation of large amounts of phytoene, suggesting that these 1,2,4-triazoles inhibit the desaturation of phytoene.

INTRODUCTION

A mode of action of bleaching herbicides, which affect chloroplast pigments of plants by decreasing their carotenoid and chlorophyll content, have been discussed.¹⁾ A number of bleaching herbicides such as norflurazon, fluridone, fluorchloridone and diflufenican are known to interfere with phytoene desaturase in the carotenoid biosynthesis.¹⁾ The structures of these herbicides comprise various types of heterocycles, *e.g.*, pyridazinone, pyridone, pyrrolidone and pyridine. However, there have been few reports on the bleaching activity of 1,2,4-triazole derivatives except for amitrole, 3-amino-1,2,4-triazole.¹⁾ In the present paper, we report the bleaching activity of 3-propargylthio-4-(substituted phenyl)-4*H*-1,2,4-triazoles, and the effect of representative compounds on the carotenoid and chlorophyll content in plants.

MATERIALS AND METHODS

1. General Methods

Melting point (mp) was determined with Yanaco micro melting point apparatus, and the values are uncorrected. ¹H NMR spectra were taken with a JEOL FX-100 spectrometer, using tetramethylsilane as an internal reference. FD-Mass spectrometry was conducted on a JEOL DX-300.

2. Chemicals

2.1 3-Mercapto-4-phenyl-4*H*-1,2,4-triazole (**4**)

A solution of 10.0 g of phenylisothiocyanate and 5.33 g of formylhydrazine in 100 ml of tetrahydrofuran was heated to reflux for 7 hr. After cooling, the insoluble product was collected by filtration, washed with water, and recrystallized from ethyl acetate to afford 8.42 g (58%) of 1-formyl-4-phenyl-3-thiosemicarbazide (**1**, R=H). To a solution of 3.02 g of KOH in 100 ml water was added 8.42 g of the above thiosemicarbazide with stirring. The

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solution was stirred for 1.5 hr at 60–70°C. After cooling, the solution was poured into a dilute HCl solution. The precipitate was collected by filtration, washed with water, and recrystallized from hexane and ethyl acetate to yield 6.52 g (85%) of **4**, mp 174–175°C. ¹H NMR (CD₃OD) δ ppm: 4.76 (1H, s), 7.50–7.61 (5H, m), 8.27 (1H, s). Anal. Found: C, 54.17; H, 4.01; N, 23.66. Calcd. for C₈H₇N₃S: C, 54.22; H, 3.98; N, 23.71%.

2.2 3-Methylthio-4-phenyl-4H-1,2,4-triazole (**5**)

To a solution containing 0.50 g of compound **4** in 20 ml of acetone was added 0.58 g of K₂CO₃. After stirring for 1 hr at room temperature, to the mixture was added 0.48 g of methyl iodide, and stirred overnight. Insoluble solids were filtered off and the filtrate was concentrated under reduced pressure. The residue was chromatographed on silica gel by eluting with hexane–ethyl acetate (5:1), (3:1) and (1:1). Concentration of the hexane–ethyl acetate (1:1) eluate gave 0.39 g (72%) of **5**. ¹H NMR (CDCl₃) δ ppm: 2.72 (3H, s), 7.19–7.58 (5H, m), 8.25 (1H, s). Anal. Found: C, 55.64; H, 4.79; N, 21.55. Calcd. for C₉H₉N₃S: C, 56.52; H, 4.74; N, 21.97%.

Compounds **6–9** and **11–13** were prepared in the same manner as **5** by using the corresponding alkyl halide instead of methyl iodide.

2.3 3-Ethylthio-4-phenyl-4H-1,2,4-triazole (**6**)

Yield 76%, mp 56–57°C. ¹H NMR (CDCl₃) δ ppm: 1.42 (3H, t, *J* = 7 Hz), 3.28 (2H, q, *J* = 7 Hz), 7.07–7.63 (5H, m), 8.25 (1H, s). Anal. Found: C, 58.34; H, 5.43; N, 20.35. Calcd. for C₁₀H₁₁N₃S: C, 58.51; H, 5.40; N, 20.47%.

2.4 4-Phenyl-3-propylthio-4H-1,2,4-triazole (**7**)

Yield 79%. ¹H NMR (CDCl₃) δ ppm: 1.01 (3H, t, *J* = 7 Hz), 1.79 (2H, q, *J* = 7 Hz), 3.24 (2H, t, *J* = 7 Hz), 7.18–7.63 (5H, m), 8.25 (1H, s). Anal. Found: C, 59.83; H, 6.05; N, 18.88. Calcd. for C₁₁H₁₃N₃S: C, 60.25; H, 5.98; N, 19.16%.

2.5 3-Butylthio-4-phenyl-4H-1,2,4-triazole (**8**)

Yield 85%, mp 62–64°C. ¹H NMR (CDCl₃) δ ppm: 0.91 (3H, t, *J* = 7 Hz), 1.13–1.89 (4H, m), 3.26 (2H, t, *J* = 7 Hz), 7.21–7.62 (5H, m), 8.25 (1H, s). Anal. Found: C, 61.72; H, 6.50; N, 17.91. Calcd. for C₁₂H₁₅N₃S: C, 61.77; H, 6.48; N, 18.01%.

2.6 3-Benzylthio-4-phenyl-4H-1,2,4-triazole (**9**)

Yield 82%, mp 95–96°C. ¹H NMR (CDCl₃) δ ppm: 4.46 (2H, s), 7.00–7.53 (10H, m), 8.24 (1H, s). Anal. Found: C, 67.56; H, 4.97; N, 15.70. Calcd. for C₁₅H₁₃N₃S: C, 67.39; H, 4.90; N, 15.72%.

2.7 4-Phenyl-3-propylsulfonyl-4H-1,2,4-triazole (**10**)

A mixture of 0.70 g of 4-phenyl-3-propylthio-4H-1,2,4-triazole (**7**) and 1.38 g of 80% *m*-chloroperbenzoic acid in 30 ml of dichloromethane was stirred for 30 min. After filtration, the filtrate was washed with 10% Na₂SO₃ solution, 5% NaHCO₃ solution, water and brine, and dried over Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was recrystallized from hexane and ethyl acetate to yield 0.71 g (89%) of **10**. mp 117–119°C. ¹H NMR (CDCl₃) δ ppm: 1.10 (3H, t, *J* = 7 Hz), 1.70–2.08 (2H, m), 3.61 (2H, t, *J* = 7 Hz), 7.49 (5H, s), 8.29 (1H, s). Anal. Found: C, 53.24; H, 5.29; N, 16.81. Calcd. for C₁₁H₁₃N₃O₂S: C, 52.57; H, 5.21; N, 16.72%.

2.8 3-Allylthio-4-phenyl-4H-1,2,4-triazole (**11**)

Yield 95%. ¹H NMR (CDCl₃) δ ppm: 3.99 (2H, d, *J* = 7 Hz), 5.13 (1H, d, *J* = 9 Hz), 5.28 (1H, d, *J* = 17 Hz), 5.92–5.99 (1H, m), 7.34–7.37 (2H, m), 7.51–7.55 (3H, m), 8.29 (1H, s). Anal. Found: C, 60.07; H, 5.14; N, 19.07. Calcd. for C₁₁H₁₁N₃S: C, 60.80; H, 5.10; N, 19.34%.

2.9 4-Phenyl-3-propargylthio-4H-1,2,4-triazole (**12**)

Yield 80%, mp 112–114°C. ¹H NMR (CDCl₃) δ ppm: 2.24 (1H, t, *J* = 3 Hz), 3.98 (2H, d, *J* = 3 Hz), 7.20–7.60 (5H, m), 8.29 (1H, s). Anal. Found: C, 61.31; H, 4.32; N, 19.25. Calcd. for C₁₁H₉N₃S: C, 61.37; H, 4.21; N, 19.52%.

2.10 3-Methoxymethylthio-4-phenyl-4H-1,2,4-triazole (**13**)

Yield 51%, mp 83–85°C. ¹H NMR (CDCl₃) δ ppm: 3.54 (3H, s), 5.56 (2H, s), 7.51 (5H, s), 7.91 (1H, s). Anal. Found: C, 54.54; H, 5.07; N, 18.79. Calcd. for C₁₀H₁₁N₃OS: C, 54.28; H, 5.01; N, 18.99%.

2.11 5-Methyl-4-phenyl-3-propylthio-4H-1,2,4-triazole (**14**)

This compound was prepared in the same manner as compound **7** via compound **4** with

use of phenylisothiocyanate and acetylhydrazine, instead of formylhydrazine. Yield 72%. ^1H NMR (CDCl_3) δ ppm: 0.97 (3H, t, $J=7$ Hz), 1.30–1.92 (2H, m), 2.28 (3H, s), 3.14 (2H, t, $J=7$ Hz), 7.08–7.61 (5H, m). Anal. Found: C, 60.83; H, 6.51; N, 17.65. Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{S}$: C, 61.77; H, 6.48; N, 18.01%.

Compounds **15–22** were prepared in the same manner as that for compound **12** from a corresponding substituted phenylisothiocyanate, instead of phenylisothiocyanate. The yields were calculated as based on substituted phenylisothiocyanate.

2.12 4-(2-Chlorophenyl)-3-propargylthio-4H-1,2,4-triazole (15)

Yield 71%, mp 122–124°C. ^1H NMR (CDCl_3) δ ppm: 2.24 (1H, t, $J=3$ Hz), 3.97 (2H, d, $J=3$ Hz), 7.19–7.66 (4H, m), 8.24 (1H, s). Anal. Found: C, 53.61; H, 3.33; N, 17.01. Calcd. for $\text{C}_{11}\text{H}_8\text{N}_3\text{SCl}$: C, 52.91; H, 3.23; N, 16.83%.

2.13 4-(3-Chlorophenyl)-3-propargylthio-4H-1,2,4-triazole (16)

Yield 47%, mp 106–107°C. ^1H NMR (CDCl_3) δ ppm: 2.25 (1H, t, $J=3$ Hz), 4.02 (2H, d, $J=3$ Hz), 7.12–7.56 (4H, m), 8.27 (1H, s). Anal. Found: C, 52.94; H, 3.30; N, 16.77. Calcd. for $\text{C}_{11}\text{H}_8\text{N}_3\text{SCl}$: C, 52.91; H, 3.23; N, 16.83%.

2.14 4-(4-Chlorophenyl)-3-propargylthio-4H-1,2,4-triazole (17)

Yield 58%, mp 108–110°C. ^1H NMR (CDCl_3) δ ppm: 2.25 (1H, t, $J=3$ Hz), 4.01 (2H, d, $J=3$ Hz), 7.18–7.57 (4H, m), 8.27 (1H, s). Anal. Found: C, 53.63; H, 3.63; N, 16.29. Calcd. for $\text{C}_{11}\text{H}_8\text{N}_3\text{SCl}$: C, 52.91; H, 3.23; N, 16.83%.

2.15 4-(3,4-Dichlorophenyl)-3-propargylthio-4H-1,2,4-triazole (18)

Yield 53%, mp 131–132°C. ^1H NMR (CDCl_3) δ ppm: 2.25 (1H, t, $J=3$ Hz), 3.98 (2H, d, $J=3$ Hz), 7.20–7.72 (3H, m), 8.26 (1H, s). Anal. Found: C, 46.77; H, 2.65; N, 14.49. Calcd. for $\text{C}_{11}\text{H}_7\text{N}_3\text{SCl}_2$: C, 46.50; H, 2.48; N, 14.79%.

2.16 4-(3-Trifluoromethylphenyl)-3-propargylthio-4H-1,2,4-triazole (19)

Yield 56%, mp 72–73°C. ^1H NMR (CDCl_3) δ ppm: 2.26 (1H, t, $J=7$ Hz), 4.04 (2H, d, $J=3$ Hz), 7.61–7.82 (4H, m), 8.38 (1H, s). Anal. Found: C, 51.02; H, 2.91; N, 14.79.

Calcd. for $\text{C}_{12}\text{H}_8\text{N}_3\text{SF}_3$: C, 50.88; H, 2.85; N, 14.83%.

2.17 4-(4-Trifluoromethylphenyl)-3-propargylthio-4H-1,2,4-triazole (20)

Yield 42%, mp 103–105°C. ^1H NMR (CDCl_3) δ ppm: 2.26 (1H, t, $J=3$ Hz), 4.06 (2H, d, $J=3$ Hz), 7.55 (2H, d, $J=9$ Hz), 7.84 (2H, d, $J=9$ Hz), 8.36 (1H, s). Anal. Found: C, 51.54; H, 3.12; N, 14.55. Calcd. for $\text{C}_{12}\text{H}_8\text{N}_3\text{SF}_3$: C, 50.88; H, 2.85; N, 14.83%.

2.18 4-(4-Methylphenyl)-3-propargylthio-4H-1,2,4-triazole (21)

Yield 44%, mp 105–106°C. ^1H NMR (CDCl_3) δ ppm: 2.24 (1H, t, $J=3$ Hz), 2.43 (3H, s), 3.98 (2H, d, $J=3$ Hz), 7.08–7.38 (4H, m), 8.26 (1H, s). Anal. Found: C, 62.88; H, 4.89; N, 18.26. Calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{S}$: C, 62.86; H, 4.84; N, 18.33%.

2.19 4-(4-Ethoxyphenyl)-3-propargylthio-4H-1,2,4-triazole (22)

Yield 63%, mp 104–106°C. ^1H NMR (CDCl_3) δ ppm: 1.45 (3H, t, $J=7$ Hz), 2.24 (1H, t, $J=3$ Hz), 3.98 (2H, d, $J=3$ Hz), 4.06 (2H, q, $J=7$ Hz), 6.79–7.29 (4H, m), 8.22 (1H, s). Anal. Found: C, 60.22; H, 5.11; N, 16.08. Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{OS}$: C, 60.21; H, 5.05; N, 16.20%.

3. Bioassay

The bioassay using lettuce seedlings (*Lactuca sativa* L. cv. Sacramento) was performed according to the method previously described by Yamada *et al.*^{2,3)} A filter paper in a Petri dish (9 cm in diameter) was soaked with 1 ml of acetone solution containing a test compound. After evaporation of the solvent, 20 lettuce seeds were placed on the filter paper and 5 ml of distilled water was added. The plants were incubated for 4 days at 25°C under 12 hr photoperiod. The bleaching activity was evaluated on a scale of 0–4 according to the following categories: 0, no visual change compared with the control; 1, faintly bleaching of the cotyledon; 2, intermediate between 1 and 3; 3, slightly remaining color; 4, complete bleaching. All treatment was performed three times.

4. Determination of Chlorophyll and Total Carotenoid Content

Radish (*Raphanus sativus* L. cv. Osaka)

seedlings with greener and bigger cotyledons than lettuce were used in order to determine chlorophyll and total carotenoid content. A filter paper in a tall Petri dish (10 cm in diameter) was soaked with 2 ml of acetone solution containing a test compound. After evaporation of the solvent, 30 radish seeds were placed on the filter paper and 20 ml of distilled water was added. After incubation for 4 days at 25°C under 12 hr photoperiod, the radish cotyledons were cut and 1.0 g of the fresh cotyledons were lyophilized and stored at -60°C until the time of extraction and analysis. Pigments were extracted by immersing the frozen cotyledons in 15 ml of hot methanol (60°C) for 20 min. One milliliter of the solution was taken out and the chlorophyll content was determined using a spectrophotometer (at 665 and 650 nm) according to the method described by Mackinney.^{4,5)} For the determination of total carotenoid content, to the remaining methanol solution 14 ml of methanol containing 12% (w/v) KOH was added, and the mixture was kept at 60°C for 20 min. After cooling, the cotyledons were filtered off and the filtrate was extracted twice with an equal volume of 10% (v/v) diethyl ether in petroleum ether. The combined ether solution was washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was dissolved in 3 ml of diethyl ether and the absorbance value at 445 nm was measured.⁶⁾ These experiments were carried out in the dark or in very dim light and performed three times. Chlorophyll and total

carotenoid content in the treated cotyledons was calculated as percentage of that in the control.

5. Determination of β -Carotene and Phytoene

The ether solution as described above was used to determine β -carotene and phytoene content. Carotenoids were separated by the reversed phase HPLC on a Shimadzu ODS-II 5 μ m column 250 mm in length with acetonitrile/methanol/2-propanol [70/10/20 (v/v/v)] as an eluent and a flow rate of 1.5 ml/min. All solvents used were HPLC grade. The wavelengths monitored were 445 and 287 nm, characteristic of the absorption spectrum of β -carotene and phytoene respectively. All experiments were performed three times. Authentic β -carotene was purchased from Sigma Chemical Co. Phytoene was extracted from radish seedlings treated with the herbicide fluridone, which is an inhibitor of phytoene desaturation resulting in large amounts of accumulation of phytoene. Phytoene purification was based on the method of Lay & Niland.⁷⁾ The structure of isolated phytoene was confirmed by its FD-mass spectrum (M^+ ion at m/z 544) and its UV spectrum (λ_{max} at 277, 286 and 298 nm). β -Carotene and phytoene content in the treated cotyledon was calculated as percentage of those in the control.

RESULTS AND DISCUSSION

1. Synthesis

4-Aryl-3-mercapto-4*H*-1,2,4-triazoles (**2**)

Fig. 1 Synthesis of 3-alkylthio-4-substituted phenyl-4*H*-1,2,4-triazoles.

were synthesized according to procedures described by Wikel & Paget⁹⁾ and Sung & Lee⁹⁾ (Fig. 1). 4-Aryl-1-formyl-3-thiosemicarbazides (**1**) were prepared by treatment of formylhydrazine with substituted phenyl isothiocyanates. Cyclization of the thiosemicarbazide **1** by refluxing with potassium hydroxide aqueous solution afforded 4-aryl-3-mercapto-4*H*-1,2,4-triazoles (**2**), which were alkylated by an appropriate alkyl halide to give 3-alkylthio-4-aryl-4*H*-1,2,4-triazoles (**3**).

2. Bleaching Activity

Table 1 shows the bleaching activity of 3-alkylthio-4-phenyl-4*H*-1,2,4-triazoles and related compounds on lettuce seedlings. 4-Phenyl-3-propylthio-4*H*-1,2,4-triazole (**7**) caused complete bleaching at 50 ppm, while 3-mercapto analog **4** had no activity. The activity was found to fall off with increasing or decreasing size of the alkyl group at the 3-position of the triazole ring. Oxidation of the sulfide group of the compound **7** to sulfone **10** completely eliminated the activity. Interestingly, propargylthio analog **12** showed slightly higher activity than that of the propylthio analog **7**, while allylthio analog **11** did not cause bleaching even at a high concentration of 50 ppm. Methoxymethylthio analog **13** caused no visible bleaching injury at 50 ppm. It is noteworthy

that in the compound **7** the introduction of a methyl group into the 5-position of the triazole ring gave rise to an inactive compound **14**.

Since propargylthio analog **12** showed considerably higher bleaching activity than other alkylthio analogs, further modification was made by introducing several substituents into the benzene ring of compound **12** (Table 2). The introduction of a chlorine atom at the 3- or 4-position of the benzene (**16** and **17**) extremely increased the activity in comparison with that of compound **12**, while 2-chlorophenyl analog **15** showed much lower activity than that of compound **12**. 3,4-Dichlorophenyl analog **18** caused complete bleaching injury at 10 ppm, however, it had no significant effect at 1 ppm. The introduction of a trifluoromethyl (**19** and **20**), methyl (**21**) or an ethoxy (**22**) group at the 3- or 4-position of the benzene ring also resulted in much higher activity than compound **12**. However, in contrast to compounds **16** and **17**, these compounds did not cause complete bleaching symptoms at a high concentration of 25 ppm.

Table 1 Bleaching activity of 3-alkylthio-4-phenyl-4*H*-1,2,4-triazoles and related compounds against lettuce seedlings.

No.	R ²	Concentration (ppm)		
		50	25	10
4	SH	0	0	0
5	SCH ₃	0	0	0
6	SC ₂ H ₅	3	2	1
7	SC ₃ H ₇	4	2	1
8	SC ₄ H ₉	2	1	0
9	SCH ₂ C ₆ H ₅	2	1	1
10	SO ₂ C ₃ H ₇	0	0	0
11	SCH ₂ CH=CH ₂	0	0	0
12	SCH ₂ C≡CH	4	3	1
13	SCH ₂ OCH ₃	0	0	0

For rating: see MATERIALS AND METHODS.

Table 2 Bleaching activity of 3-propargylthio-4-(substituted phenyl)-4*H*-1,2,4-triazoles against lettuce seedlings.

No.	R	Concentration (ppm)				
		25	10	5	3	1
12	H	3	1	0	0	0
15	2-Cl	0	0	0	0	0
16	3-Cl	4	3	3	2	0
17	4-Cl	4	3	2	1	0
18	3,4-Cl ₂	4	4	3	2	0
19	3-CF ₃	3	3	2	1	0
20	4-CF ₃	3	3	2	1	0
21	4-CH ₃	3	3	3	1	0
22	4-OC ₂ H ₅	3	3	2	1	0

For rating: see MATERIALS AND METHODS.

Fig. 2 Effect of 3-propargylthio-4-substituted phenyl-4H-1,2,4-triazoles on chlorophyll and total carotenoid content of radish cotyledons.

N.T.*: not tested. Vertical bars represent standard deviation.

Fig. 3 Effect of 3-propargylthio-4-substituted phenyl-4H-1,2,4-triazoles on β -carotene and phytoene content of radish cotyledons.

N.T.*: not tested. N.D.**: not detected. Vertical bars represent standard deviation.

The effect of representative compounds (**15**, **16** and **17**) on chlorophyll and carotenoid content was examined by using radish seedlings with greener and bigger cotyledons than lettuce. Compounds **16** and **17** with a distinct bleaching activity markedly reduced total carotenoid content as well as chlorophyll in the radish seedlings four days after treatment, while 2-chlorophenyl analog **15** did not show any significant effect on such pigment content even at a high concentration of 100 μ M (Fig. 2). Radish seedlings treated with 10 μ M of compounds **16** and **17** showed an approximately 60% decrease in chlorophyll and total carotenoid content, and the reduction of both pigments correlated well with the treated dosage. Compounds **16** and **17** at 10 μ M re-

markably reduced total carotenoid content in darkness as well as in light (data not shown). These results suggest that the loss of chlorophyll was due to the inhibition of carotenoid formation. β -Carotene decreased proportionally with the total carotenoid content by treatment of these compounds (Fig. 3). On the other hand, the reduction of the total carotenoid content by compounds **16** and **17** was accompanied by an accumulation of large amounts of phytoene, a precursor of β -carotene, indicating that these 1,2,4-triazoles as well as norflurazon and fluridone inhibit the desaturation of phytoene. 3-Chlorophenyl analog **16** inhibited more strongly β -carotene formation than 4-chlorophenyl analog **17**, however, the accumulation of phytoene caused

by compound **16** was less than that of compound **17**. These data suggested that compound **16** inhibited some biosynthetic stage prior to phytoene desaturation in addition to phytoene desaturase. In the seedlings treated with 50 μM of compound **17**, phytoene accumulated up to over 150-fold compared with that in control. However, a higher concentration (100 μM) of compound **17** resulted in a decrease in accumulation of phytoene, probably due to the inhibition of early stages in the terpenoid biosynthesis.

The desaturation of phytoene is known to be inhibited by various chemical types of compounds.¹⁰⁾ Preliminary biological data described in this article indicate that 1,2,4-triazole derivatives might constitute a new class of bleaching herbicides.

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要 約

3-プロパルギルチオ-4-置換フェニル-4H-1,2,4-トリアゾール類の合成とその白化活性

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種々の 3-アルキルチオ-4-アリル-4H-1,2,4-トリアゾールを合成し, その白化活性をレタス実生試験を用いて調べた. 一連の 4-フェニル-4H-1,2,4-トリアゾールにおいて, 3-プロピルチオと 3-プロパルギルチオ体は 50 ppm で完全な白化作用を示した. しかし, トリアゾール環 3 位のアルキルチオ基を炭素数 4 以上あるいは 2 以下のアルキルチオ基に置き換えると活性は減少した. 塩素原子, トリフルオロメチル, メチルあるいはエトキシ基をベンゼン環のメタあるいはパラ位に導入すると活性は増大した. 4-(3-クロロフェニル)-あるいは 4-(4-クロロフェニル)-3-プロパルギルチオ-4H-1,2,4-トリアゾールは植物体中のクロロフィルと β -カロチン含量を著しく減少させ, 多量のフィトエンを蓄積させた.