
Bioscience, Biotechnology, and Biochemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tbbb20

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Published online: 22 May 2014.

To cite this article: Babak Heidary ALIZADEH, Takeyoshi SUGIYAMA, Takayuki ORITANI & Shigefumi KUWAHARA (2002) Preparation of N-Substituted Aryl and Alkyl Carbamates and Their Inhibitory Effect on Oat Seed Germination, Bioscience, Biotechnology, and Biochemistry, 66:2, 422-425, DOI: 10.1271/bbb.66.422

To link to this article: http://dx.doi.org/10.1271/bbb.66.422

*Biosci. Biotechnol. Biochem.*, **66** (2), 422–425, 2002

*Note*

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Received July 3, 2001; Accepted October 25, 2001



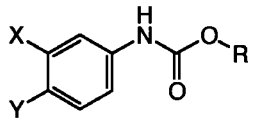
**A series of *N*-substituted aryl and alkyl carbamates (RNHCOOR′; R: aryl, alkyl; R′: aryl, alkyl) was prepared and screened for inhibitory activity toward the germination of oat seeds. The activity of each compound was compared with that of chlorpropham (isopropyl 3-chlorocarbanilate). Some of the synthetic carbamates possessing the *N*-(phenylthio)methyl group, $PhSCH_2NHCOOR'$, showed inhibitory activity close or comparable to that of chlorpropham.**

**Key words:** carbamate; germination inhibitor; isocyanate; *N*-(phenylthio)methylcarbamate

*N*-Substituted carbamic acid esters (RNHCOOR′) are widely used as insecticides and herbicides in agriculture.[1] Carbanilic acid aliphatic esters such as chlorpropham (**1**) and propham (**2**) (isopropyl carbanilate) are selective pre- and post-emergence herbicides that are used for the control of annual grasses and broad-leaf species among a variety of tolerant crops (Fig. 1).[2] Swep (**3**; methyl 3,4-dichlorocarbanilate) is also used in rice production in Japan.[2] We attempt in this study to find new herbicidal carbamates by changing the *O*-alkyl and *N*-aryl substituents of the above-mentioned herbicides.

The carbamate derivatives prepared in this study are shown in Table 1. First, a variety of aromatic carboxylic acids were converted into carbamates **I-1**–**I-5** by reacting the corresponding isocyanate with phenol (Table 1, Method A),[3–5] and their inhibitory activity toward the germination of oat seeds was evaluated. As shown in Table 2, these *O*-phenyl carbamates possessing various *N*-aryl groups had poor inhibitory activity against the growth of both the coleoptile and roots. The introduction of an electron-donating (**I-2** and **I-3**) or electron-withdrawing group (**I-4** and **I-5**) to the *N*-phenyl substituent of **I-1** did not lead to any improvement in the activity of **I-1** possessing the simplest structure. We next investigated the effect of the distance between the carbamoyl functionality and aromatic moiety attached to the oxygen atom by adding methylene unit(s) to the O-phenyl bond of **I-1**. The phenyl isocyanate derived from benzoic acid was allowed to react with some $\omega$-phenylalkyl alcohols to give carbamates **II-1**–**II-5**. Another carbamate possessing a double bond on the linking chain (**II-6**) was also prepared. Among this type of carbamates, compound **II-2** exhibited considerable inhibitory activity against the growth of both the coleoptile and roots, and compound **II-6** showed a similar level of activity against root growth, although their effectiveness was not promising enough for use as practical herbicides.

We next turned our attention to the somewhat drastic modification of the *N*-substituent (R in Table 1), and displaced the *N*-phenyl substituent in carbamates **II** by *N*-(phenylthio)methyl which contains a sulfur atom. Based on the observation that carbamate **II-2** with an *O*-2-phenylethyl group showed considerable activity, carbamate **III-3** possessing the same *O*-substituent was first prepared and evaluated for its effect on oat germination. As shown in Table 2, **III-3** showed potent inhibitory activity comparable to that of chlorpropham at a concentration of 1 $\mu$M. Encouraged by this desirable result, we prepared a series of *N*-(phenylthio)methyl carbamates (**III-1**, **III-2**, and **III-4**–**III-7**) by treating the corresponding carboxylic acids with DPPA and then reacting the resulting acyl azides with various alcohols or phenols (Table 2, Method B).[6,7] As shown in

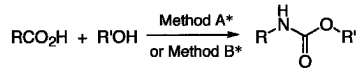



**1** (propham): X=Y=H, R=$CH(CH_3)_2$
**2** (chlorpropham): X=Cl, Y=H, R=$CH(CH_3)_2$
**3** (swep): X=Y=Cl, R=$CH_3$

**Fig. 1.** Structures of Typical Herbicidal Carbamates.

† To whom correspondence should be addressed. Tel: +81-22-717-8785; Fax: +81-22-717-8783; E-mail: babak@biochem.tohoku.ac.jp
*Abbreviation*: DPPA, diphenylphosphoryl azide

**Table 1.** Preparation of the Carbamate Derivatives




| Carbamate | R | R′ | Carbamate | R | R′ |
|---|---|---|---|---|---|
| **I-1** | Ph | Ph | **III-1**[#] | $PhSCH_2$ | Ph |
| **I-2** | *m*-MePh | Ph | **III-2** | $PhSCH_2$ | $PhCH_2$ |
| **I-3** | *p*-MeOPh | Ph | **III-3** | $PhSCH_2$ | $Ph(CH_2)_2$ |
| **I-4** | *p*-ClPh | Ph | **III-4** | $PhSCH_2$ | $Ph(CH_2)_3$ |
| **I-5** | *p*-FPh | Ph | **III-5** | $PhSCH_2$ | 2,4-$Cl_2$Ph |
| **II-1** | Ph | $PhCH_2$ | **III-6** | $PhSCH_2$ | *p*-$MeOPhCH_2$ |
| **II-2** | Ph | $Ph(CH_2)_2$ | **III-7** | $PhSCH_2$ | $PhCH=CHCH_2$ |
| **II-3** | Ph | $Ph(CH_2)_3$ | **III-8** | $PhSCH_2$ | $CH_3$ |
| **II-4** | Ph | $Ph(CH_2)_4$ | **III-9** | $PhSCH_2$ | $CH_3CH_2$ |
| **II-5** | Ph | $Ph(CH_2)_5$ | **III-10** | $PhSCH_2$ | $CH_3(CH_2)_2$ |
| **II-6** | Ph | $PhCH=CHCH_2$ | **III-11** | $PhSCH_2$ | $(CH_3)_2CH$ |
| **IV** | $Ph(CH_2)_2$ | $PhCH_2$ | **III-12** | $PhSCH_2$ | $CH_3(CH_2)_3$ |

* Method A: 1) $RCO_2H$, $SOCl_2$, toluene, reflux; 2) $NaN_3$, toluene, rt; 3) toluene, reflux; 4) R′OH, $Et_3N$, THF, rt. This method was applied for the preparation of compounds **I-1**–**I-5** and **II-1**–**II-6**.
Method B: 1) DPPA, $Et_3N$, toluene, rt; 2) R′OH, $Et_3N$, THF, rt. This method was applied for the preparation of compounds **III-1**–**III-12** and **IV**.
[#] New compounds are underlined.

**Table 2.** Effects of the Synthetic Carbamates on the Germination of Oat Seeds at a Concentration of 1 $\mu$M

| Carbamate* | C[#] | R[#] | Carbamate | C | R |
|---|---|---|---|---|---|
| untreated | 9.5 | 7.0 | **III-1** | 0.0 | 0.0 |
| chlorpropham | 0.0 | 0.0 | **III-2** | 0.0 | 0.0 |
| **I-1** | 4.7 | 1.9 | **III-3** | 0.0 | 0.0 |
| **I-2** | 5.6 | 4.4 | **III-4** | 4.6 | 3.9 |
| **I-3** | 8.3 | 7.7 | **III-5** | 0.0 | 0.0 |
| **I-4** | 8.1 | 4.1 | **III-6** | 1.4 | 0.9 |
| **I-5** | 6.4 | 4.8 | **III-7** | 2.2 | 2.6 |
| **II-1** | 2.8 | 1.2 | **III-8** | 0.0 | 0.0 |
| **II-2** | 0.3 | 0.2 | **III-9** | 0.8 | 1.0 |
| **II-3** | 3.5 | 1.9 | **III-10** | 1.7 | 1.4 |
| **II-4** | 4.9 | 1.2 | **III-11** | 0 | 0.0 |
| **II-5** | 6.6 | 2.1 | **III-12** | 2.6 | 3.4 |
| **II-6** | 3.4 | 0.4 | **IV** | 5.2 | 2.8 |

* Each carbamate was applied at a concentration of 1 $\mu$M.
[#] C: average length (cm) of coleoptiles. R: average length (cm) of the longest roots.

Table 2, carbamate **III-1** containing an *O*-phenyl functionality instead of the *O*-2-pheylethyl in **III-3** also had potent inhibitory activity. The introduction of electron-withdrawing chlorine atoms to the phenyl substituent (**III-5**) had no effect on the activity of **III-1**. On the other hand, the distance between the carbamoyl moiety and the phenyl group seemed to be important, since carbamate **III-4** having three methylene units between the two functionalities had lower inhibitory activity, while the activity was maintained in the case of **III-2** having one methylene unit. The introduction of an electron-donating methoxy functionality to the phenyl group of **III-2** resulted in lower activity (**III-6**). The activity of **III-4** was somewhat improved by introducing a double bond (**III-7**) to the three-methylene chain, which would have resulted in some shortening of the chain. This result, as well as some improvement in the activity of **II-6** by introducing a double bond to **II-3**, might also imply the importance of the distance between the two functional groups.

We next examined the inhibitory activity of *N*-(phenylthio)methyl carbamates containing a simple *O*-alkyl substituent (**III-8**–**III-12**). The inhibitory activities of these carbamates, as shown in Table 2, reveal that the presence of an aromatic ring in the *O*-substituent was not necessarily required for the activity, as demonstrated by the potent activities of the *N*-methyl and *N*-isopropyl carbamates, **III-8** and **III-11**. In addition, the data for **III-9**, **III-10** and **III-12** seem to show decreasing activity as the carbon number of the *O*-alkyl substituent was increased, although carbamate **III-1** did not follow this trend.

Finally, to verify the importance of the presence of the sulfur atom in the *N*-substituent, carbamate **IV** possessing an *N*-2-phenylethyl group instead of *N*-(phenylthio)methyl was prepared and compared with **III-2** for its inhibitory activity. As shown in Table 2, carbamate **IV** had a much lower inhibitory effect on oat germination, which means that the presence of a sulfur atom in the *N*-substituent was an important factor for the activity.

Sulfur-containing herbicides of the carbamate type such as benthiocarb (*S*-4-chlorobenzyl diethylthiocarbamate) and molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate) are now widely used in agricultural production. However, to the best of our knowledge, the newly prepared carbamates containing an *N*-(phenylthio)methyl substituent are unprecedented in respect of the basic skeleton for a pesticide, although the synthesis of **III-9** and **III-12** has already been reported in the literature without any comment on their biological activity.[8)]

## Experimental

IR spectra were measured with a Jasco IR Report-100 spectrometer. $^1$H-NMR spectra were recorded with a Varian Gemini 2000 (300 MHz) spectrometer in $CDCl_3$, with tetramethylsilane used as an internal standard. Mass spectra were recorded with a Jeol JMS-700 spectrometer, and Merck silica gel 60 (70–230 mesh) was used for column chromatography.

*Biological test.* The biological test was carried out according to the procedure described by Motando *et al.*[2] A solution of a carbamate sample in acetone (1 $\mu$M, 1 ml) was put on filter paper in a sterilized Petri dish (4 cm in diameter). After evaporating the solvent, water (1 ml) was added. Four oat seeds (*Avena sativa* L. var. Zenshin) were rinsed with sodium hypochlorite, placed on the filter paper, and kept in the dark at 25°C. After 6 days, the lengths of the coleoptiles and the longest roots were measured. Each experiment was conducted twice. As a control, four oat seeds were put on filter paper that had been moistened only with 1 ml of water in the Petri dish, and kept under the same conditions as those for the test.

*General procedure for preparation of the carbamate derivatives.*

*Method A (exemplified by the preparation of phenyl N-(p-methoxyphenyl)carbamate* ***I-3****).* To a stirred solution of *p*-methoxybenzoic acid (2.00 g, 13.1 mmol) in toluene (30 ml) was added dropwise thionyl chloride (2.46 g, 20.6 mmol). The mixture was heated at refluxing temperature for 30 min and then concentrated *in vacuo*. The resulting acyl chloride was dissolved in toluene (20 ml), and active sodium azide[4] (1.53 g, 23.6 mmol) was added to the solution. The mixture was stirred for 24 h at room temperature under a nitrogen atmosphere and then filtered. The filtrate was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue containing the corresponding acyl azide (IR, $\nu_{max}$ 2140 $cm^{-1}$) was dissolved in toluene (20 ml). After being stirred for 2 h at refluxing temperature, the mixture was concentrated *in vacuo* to give 1.57 g (80%) of *p*-methoxyphenyl isocyanate (IR, $\nu_{max}$ 2260 $cm^{-1}$). The isocyanate obtained (0.30 g, 2.01 mmol) was dissolved in THF (10 ml), and phenol (0.13 g, 1.34 mmol) and triethylamine (5 drops) were added to the solution. The mixture was stirred for 2 h at 0–5°C and then overnight at room temperature. The mixture was concentrated *in vacuo*, and the resulting residue was diluted with ether. The ethereal solution was successively washed with 10% hydrochloric acid, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was crystallized from ether-hexane to give 0.39 g (80%) of **I-3** as crystals (mp 152–154°C); IR $\nu_{max}$ (film) $cm^{-1}$: 3350 (N–H), 1720 (C=O); $^1$H-NMR $\delta$: 3.80 (3H, s, $CH_3$), 6.81 (1H, br s, NH), 6.87–6.09 (2H, m), 7.21–7.26 (3H, m), 7.35–7.42 (4H, m). Basically the same procedure was used for the preparation of carbamates **I** and **II**, except that commercially available isocyanates were employed directly for **I-1**, **I-4**, **I-5**, and **II-1**–**II-6**.

*Method B (exemplified by the preparation of benzyl N-(phenylthio)methylcarbamate* ***III-2****).* DPPA (3.59 g, 13.1 mmol) and triethylamine (1.32 g, 13.1 mmol) were added to a solution of (phenylthio) acetic acid (2.00 g, 11.9 mmol) in toluene (20 ml). The mixture was stirred overnight at room temperature, washed with water, dried over $MgSO_4$ and concentrated *in vacuo* to give 2.20 g (quantitative) of (phenylthio)acetyl azide. To a stirred solution of (phenylthio)acetyl azide (0.200 g, 1.04 mmol) in toluene (5 ml) was added benzyl alcohol (0.110 g, 1.04 mmol) and triethylamine (5 drops), and the mixture was stirred overnight at refluxing temperature under a nitrogen atmosphere. The mixture was then concentrated *in vacuo*, and the residue was dissolved in ether. The ethereal solution was successively washed with 10% hydrochloric acid, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over silica gel (40 g; hexane-ethyl acetate, 6:1) to give 0.11 g (37%) of **III-2** as an oil, IR $\nu_{max}$ (film) $cm^{-1}$: 3320 (N–H), 1700 (C=O); $^1$H-NMR $\delta$: 4.65 (2H, d, $J$=6.3 Hz, $SCH_2$), 5.09 (2H, s, $CH_2$), 5.18 (1H, br s, NH), 7.23–7.40 (8H, m), 7.41–7.48 (2H, m); EIMS $m/z$: 274, 273 ($M^+$), 219, 164, 154 (base peak), 149, 137, 136, 107, 91, 69, 57; HREIMS $m/z$ ($M^+$): found, 273.0823; calcd. for $C_{15}H^{15}NO_2S$, 273.0823. Basically the same method was used for the preparation of carbamates **III** and **IV**. The physical properties of the new carbamates were as follows: Phenyl *N*-(phenylthio)methylcarbamate (**III-1**): IR $\nu_{max}$ (film) 3310 (N–H), 1730 (C=O); $^1$H-NMR $\delta$: 4.71 (2H, d, $J$=5.8 Hz, $SCH_2$), 5.39 (1H, br s, NH), 7.04–7.07 (2H, m), 7.15–7.23 (1H, m), 7.27–7.40 (5H, m), 7.48–7.56 (2H, m); EIMS $m/z$: 259, 205, 185, 165 (base peak), 150, 137, 123, 110, 109, 107, 94, 77, 65, 56; HREIMS $m/z$ ($M^+$): found, 259.0660; calcd. for $C_{14}H_{13}NO_2S$, 259.0667. 2-Phenylethyl *N*-(phenylthio)methylcarbamate (**III-3**): IR $\nu_{max}$ (film) $cm^{-1}$: 3310 (N–H), 1710 (C=O); $^1$H-NMR $\delta$: 2.88 (2H, t, $J$=6.7 Hz, $PhCH_2$), 4.27 (2H, t, $J$=6.7 Hz, $OCH_2$), 4.62 (2H, d, $J$=6.6 Hz, $SCH_2$), 5.03 (1H, br s, NH), 7.16–7.23 (2H, m), 7.25–7.28 (3H, m), 7.29–7.34 (3H, m), 7.41–7.46 (2H, m); EIMS $m/z$: 287, 178, 123, 110, 105 (base peak), 104, 91, 77, 69, 65, 57; HREIMS $m/z$ ($M^+$): found, 287.0985; calcd. for $C_{16}H_{17}NO_2S$, 287.0980. 3-Phenylpropyl *N*-(phenylthio)methylcarbamate (**III-4**): IR $\nu_{max}$ (film) $cm^{-1}$: 3310 (N–H), 1720 (C=O); $^1$H-NMR $\delta$: 1.91

(2H, qui, $J = ca.$ 7.1 Hz, $CH_2$), 2.66 (2H, t, $J =$ 7.6 Hz, $CH_2$), 4.09 (2H, t, $J = 6.5$ Hz, $CH_2$), 4.65 (2H, d, $J = 6.6$ Hz, $SCH_2$), 5.11 (1H, br s, NH), 7.16–7.24 (3H, m), 7.24–7.38 (5H, m), 7.44–7.50 (2H, m); EIMS *m/z*: 302, 301 ($M^+$), 300, 192 (base peak), 154, 119, 91, 69, 55; HREIMS *m/z* ($M^+$): found, 301.1134; calcd. for $C_{17}H_{19}NO_2S$, 301.1131. 2,4-Dichlorophenyl *N*-(phenylthio)methylcarbamate (**III-5**): mp 76–77°C; IR $\nu_{max}$ (KBr) $cm^{-1}$: 3320 (N–H), 1730 (C=O); $^1$H-NMR $\delta$: 4.71 (2H, d, $J =$ 6.3 Hz, $SCH_2$), 5.53 (1H, br s, NH), 7.08 (1H, d, $J =$ 8.5 Hz), 7.21–7.26 (1H, dd, $J = 8.5$, 2.5 Hz), 7.32–7.40 (3H, m), 7.42 (1H, d, $J = 2.5$ Hz), 7.50–7.56 (2H, m); EIMS *m/z*: 332, 331 ($M^+$ for $C_{14}H_{11}{}^{37}Cl_2NO_2S$), 330, 329 ($M^+$ for $C_{14}H_{11}{}^{37}Cl_{35}$-$ClNO_2S$), 328, 327 ($M^+$ for $C_{14}H_{11}{}^{35}Cl_2NO_2S$), 289, 218, 165, 155, 154 (base peak), 138, 137, 136, 123, 120, 107, 89, 77, 57; HREIMS *m/z* ($M^+$): found, 326.9890; calcd. for $C_{14}H_{11}{}^{35}Cl_2NO_2S$, 326.9892. *p*-Methoxybenzyl *N*-(phenylthio)methylcarbamate (**III-6**): IR $\nu_{max}$ (film) $cm^{-1}$: 3320 (N–H), 1700 (C=O); $^1$H-NMR $\delta$: 3.80 (3H, s, $OCH_3$), 4.62 (2H, d, $J =$ 6.0 Hz, $SCH_2$), 5.01 (2H, s, $CH_2$), 5.09 (1H, br s, NH), 6.85–6.88 (2H, d, $J = 8.2$ Hz), 7.23–7.36 (5H, m), 7.39–7.43 (2H, d, $J = 8.2$ Hz); EIMS *m/z*: 303 ($M^+$), 279, 256, 230, 167, 149, 137, 121 (base peak), 109, 91, 77, 57, 55; HREIMS *m/z* ($M^+$): found, 303.0930; calcd. for $C_{16}H_{17}NO_3S$, 303.0930. 3-Phenyl-2-propenyl *N*-(phenylthio)methylcarbamate (**III-7**): IR $\nu_{max}$ (film) $cm^{-1}$: 3310 (N–H), 1700 (C=O); $^1$H-NMR $\delta$: 4.66 (2H, d, $J = 6.6$ Hz, $OCH_2$), 4.72 (2H, d, $J = 6.0$ Hz, $SCH_2$), 5.18 (1H, br s, NH), 6.24 (1H, dt, $J = 15.9$, 6.6 Hz, C*H*=CHPh), 6.62 (1H, d, $J = 15.9$ Hz, =CHPh), 7.25–7.41 (8H, m), 7.44–7.50 (2H, m); EIMS *m/z*: 300, 299 ($M^+$), 154, 136, 117 (base peak), 91, 81, 69, 55; HREIMS *m/z* ($M^+$): found, 199.0982; calcd. for $C_{17}H_{17}NO_2S$, 199.0984. Methyl *N*-(phenylthio)methylcarbamate (**III-8**): IR $\nu_{max}$ (film) 3320 (N–H), 1720 (C=O); $^1$H-NMR $\delta$: 3.66 (3H, s, $CH_3$), 4.62 (2H, d, $J = 6.3$ Hz, $SCH_2$), 5.10 (1H, br s, NH), 7.21–7.39 (3H, m), 7.43–7.46 (2H, m); EIMS *m/z*: 197, 123, 110, 109, 88 (base peak), 77, 65, 59; HREIMS *m/z* ($M^+$): found, 197.0514; calcd. for $C_9H_{11}NO_2S$, 197.0510. Propyl *N*-(phenylthio)methylcarbamate (**III-10**): IR $\nu_{max}$ (film) $cm^{-1}$: 3340 (N–H), 1720 (C=O); $^1$H-NMR $\delta$: 0.90 (3H, t, $J = 7.4$ Hz, $CH_3$), 1.58 (2H, d t, $J = 7.4$, 6.7 Hz, $CH_2CH_3$), 4.00 (2H, t, $J = 6.7$ Hz, $OCH_2$), 4.62 (2H, d, $J = 6.3$ Hz, $SCH_2$), 5.04 (1H, br s, NH), 7.23–7.35 (3H, m), 7.43–7.47 (2H, m); EIMS *m/z*: 225 (base peak), 205, 168, 123, 116, 110, 109, 84, 77; HREIMS *m/z* ($M^+$): found, 225.0825; calcd. for $C_{11}H^{15}NO_2S$, 225.0824. Isopropyl *N*-(phenylthio) methylcarbamate (**III-11**): IR $\nu_{max}$ (film) $cm^{-1}$: 3310 (N–H), 1700 (C=O); $^1$H-NMR $\delta$: 1.19 (6H, d, $J =$ 6.3 Hz, $CH(CH_3)_2$), 4.62 (2H, d, $J = 6.0$ Hz, $SCH_2$), 4.89, (1H, sep, $J = 6.3$ Hz, CH), 4.96 (1H, br s, NH), 7.28–7.36 (3H, m), 7.42–7.49 (2H, m); EIMS *m/z*: 226, 225 ($M^+$), 145, 138, 123, 116 (base peak), 111, 95, 81, 69, 55; HREIMS *m/z* ($M^+$): found, 225.0822; calcd. for $C_{11}H^{15}NO_2S$, 225.0821.

## Acknowledgment

We are grateful to Ms. T. Yamada (Tohoku University) for measuring the mass spectra.

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