Two carbamate pesticides namely S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate (a) and N-phenyl-(ethylcarbamoyl)propyl carbamate (b) [C₆H₅NH-COO-CH(CH₃)-CO-NH(C₃H₇)] were synthesized in the laboratory. With the help of elemental analysis, IR and NMR spectra their structures were elucidated. The biological studies showed that S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate (a) acts as insecticide against insects causing damages to potato, tomato, cabbage plants, while N-phenyl-(ethylcarbamoyl)propyl carbamate (b) has herbicidal character and can be used for cabbage and legume family crops. For estimation of the toxicity of these pesticides LC₅₀ and LD₅₀ were determined. The results revealed that for fish and rats compound (a) was more toxic than compound (b).

As organochlorine compounds were highly persistent and so strongly dissolved into animal fat, that they get concentrated as they moved up to the food chain causing damaging effects, were banned; therefore, broad spectrum biodegradable short lived chemical compounds such as organophosphates, carbamates and pyrethroids were developed. Carbamate pesticides are mainly used in agriculture as insecticides, fungicides, herbicides, nematicides. They are also used as biocides for industrial purposes. Carbamate-pesticides are also effective against those pests which are resistant to organochlorine and organophosphates.

Oxamyl, a product of E.L. DuPont de Nemours & Co Inc., Wilmington, Delaware, is a broad spectrum insecticide-nematicide with excellent biological efficacy on a variety of crops. To compare efficacy of oxamyl it was considered worthwhile to synthesize following two new carbamate pesticides (1) compound (a) S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate, (2) compound (b) N-phenyl-(ethylcarbamoyl)propyl carbamate and study their physical, chemical and biological properties.

Table 1. Physical properties of S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate (a) and N-phenyl-(ethylcarbamoyl)-propyl carbamate (b)

| Physical property          | Pesticide a | Pesticide b |
|----------------------------|-------------|-------------|
| Physical state             | Crystalline | Solid       |
| Colour                     | White       | Colourless  |
| Odour                      | Sulphurous  | Odourless   |
| M.p.(°C)                   | 80°         | 126°        |
| Vapour pressure            | 0.73 mpa (25°) | Negligible |
| Molecular formula          | C₆H₁₂N₂O₂S  | C₁₃H₁₆O₂N₂  |
| Density                    | 1.296 kg dm⁻³ | 1.362 kg dm⁻³ |
| Solubility :               |             |             |
| Water                      | 58 g dm⁻³   | 3.7 g dm⁻³  |
| Methanol                   | 1000 g dm⁻³ | 4000 g dm⁻³ |
| Acetone                    | 700 g dm⁻³  | 830 g dm⁻³  |
| Toluene                    | 28 g dm⁻³   |             |
| Ethanol                    | 400 g dm⁻³  | 720 g dm⁻³  |
| Diethyl formamide          | –           | 1360 g dm⁻³ |

Results and discussion

The physical properties of synthesized compounds a and b, determined by usual methods, are given in Table 1. Their structure were confirmed by element analysis, IR and NMR spectra. For compound a, C₆H₁₂N₂O₂S experimental analysis gave: C, 41.02 (41.91); H, 6.80 (6.82); N, 15.76 (15.91); O, 18.04 (18.18); S, 18.38 (18.18) (calculated values are given in parentheses) νmax (KBr) 3340 (NH), 3020 (C-H), 1675 (>C=O), 1600 (C-O) and 1380 cm⁻¹ (C-N); δ (CDCl₃) 7.2 (SH, s, aromatic), 12.55 (1H, s, NH-CO), 11.60 (1H, s, NH-C=O), 1.60 (2H, NH-CH₂-CH₂), 2.30 (3H, t, CH₂-CH₂-CH₂), 0.95 (3H, t, CH₃), 5.35 (2H, q, CH₂CH₃), 2.30 (3H, t, CH₂CH₃). For compound b, C₁₃H₁₈O₃N₂ experimental value were: C, 62.12 (62.4); H, 7.36 (7.2); N, 11.42 (12.2); O, 10.10 (19.28) (calculated values are in parentheses) νmax (KBr) 3340 (NH), 3020 (C-H), 1675 (>C=O), 1600 (C–O) and 1380 cm⁻¹ (C–N); δ (CDCl₃) 7.2 (SH, s, aromatic), 12.55 (1H, s, NH-CO), 11.60 (1H, s, NH-C=O), 1.60 (2H, NH-CH₂-CH₂), 2.30 (3H, t, CH₂-CH₂-CH₂), 0.95 (3H, t, CH₃), 5.35 (2H, q, CH₂CH₃), 2.30 (3H, t, CH₂CH₃).
Table 2. Effect of different concentration of S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate (a) on larval population of Plutella xylostella and herbicidal activity of N-phenylethylcarbamoyl propyl carbamate (b)

| Dose g ai ha | Population % decrease from control after (days) | Dose g ai ha | Mean % of herbicidal control |
|--------------|--------------------------------------------------|--------------|-----------------------------|
|              | 1                                                | 7            | 14                          |
| 100          | 41.6                                             | 52.8         | 27.5                        |
| 200          | 49.1                                             | 59.9         | 33.0                        |
| 300          | 56.5                                             | 65.2         | 30.4                        |
| 400          | 61.1                                             | 72.2         | 34.3                        |

Note

Table 3. Effect of different concentration of S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate (a) and N-phenyl-(ethylcarbamoyl)propyl carbamate (b) on the survival percentage of twenty five Heteropneustes fossilis after 96 h; and oral toxicity in twelve male albino rats according to probit analysis

| Fishes | Pesticide a | Pesticide b |
|--------|-------------|-------------|
|        | Concentration (ppm) |Survival %| LC50 ppm | Concentration (ppm) |Survival %| LC50 ppm |
| 2      | 80          | 10         | 92       |
| 3      | 64          | 15         | 80       |
| 4      | 48          | 20         | 64       |
| 5      | 32          | 25         | 52       |
| 6      | 20          | 30         | 32       |
| 8      | 12          | 40         | 20       |
| 10     | 0           | 50         | 4        |
|       |             | 60         | 0        |

| Rats | Pesticide a | Pesticide b |
|------|-------------|-------------|
|      | Dose mg/kg body wt. | Log dose | % mortality | Probit LD50 mg/kg body wt. | Dose mg/kg body wt. | Log dose | % mortality | Probit LD50 mg/kg body wt. |
| 750  | 2.875       | 8.33       | 3.631     | 3018 mg/kg body wt. | 750  | 2.875       | 8.33       | 3.631     |
| 1000 | 3.000       | 16.67      | 4.034     | 3018 mg/kg body wt. | 1000 | 3.000       | 16.67      | 4.034     |
| 2000 | 3.301       | 25.00      | 4.294     | 3018 mg/kg body wt. | 2000 | 3.301       | 25.00      | 4.294     |
| 5000 | 3.477       | 41.67      | 4.790     | 3018 mg/kg body wt. | 5000 | 3.477       | 41.67      | 4.790     |
| 7500 | 3.875       | 66.67      | 5.431     | 3018 mg/kg body wt. | 7500 | 3.875       | 66.67      | 5.431     |
| 10000| 4.096       | 91.66      | 6.383     | 3018 mg/kg body wt. | 10000| 4.096       | 91.66      | 6.383     |

crop, the larval population of insect P. xylostella decreased 50 to 72% after seven days of application (Table 2). But after 14 days of application, the larval population increased (27–69%) from 1st day of application, indicating the degradation of compound a. Table 2 also denotes that with the increase in concentration from 400 to 1000 g ai ha⁻¹ of compound b, the herbicidal activity was increased and more effective in garden legume.

The LC₅₀ (Table 3) for fish of compound a was 3.9 ppm while that of compound b was 25.2 ppm denoting that compound a had more aquatic toxicity than compound b.

The oral LC₅₀ (Table 3) value for male rats of compound a was 31.7 mg kg⁻¹ body weight and compound b was 3018 mg kg⁻¹ body weight.

From these studies it may be inferred that compound a has more pesticidal activity than compound b but later has more stability.

Material and methods:

Synthesis route of S-ethyl-N-[(methylcarbamoyl)oxy]thioacetimidate a:

Scheme 1:

\[
CH_3-C≡N + \text{anhy. HCl} + C_2H_5SH
\]

(i) 5± 3° (ii) kept for 3 days at 8° (iii) Temp. raised to 13° for one day (iv) Supernatant withdrawn

Replaced by equal amount of anhy. ether

\[
\text{CH}_3\text{C≡NH.HCl} \quad \text{SC}_2\text{H}_5
\]

S-Ethyl thioacetamide hydrochloride (75% yield)
Scheme 1:

\[
\begin{align*}
\text{CH}_3\text{-C}=\text{NOH} & + \text{CH}_3\text{-NH}_2 \\
\text{SC}_2\text{H}_5 & + \text{C}_2\text{H}_5\text{-OH} \\
\text{(in C}_6\text{H}_6, \text{C}_6\text{H}_{12}, \text{1 : 1}) & \text{DCT} \\
\text{(90% yield)} & \\
\text{S-Ethyl-N-(methylcarbamoyl)oxythioacetimidate (Pure compound a)} & \\
\end{align*}
\]

Scheme 2:

\[
\begin{align*}
\text{CH}_3\text{-CH-C-NHC}_3\text{H}_7 & + \text{C}_2\text{H}_5\text{-N=C=O} \\
\text{HO} & \text{O} \\
(\text{in C}_6\text{H}_6 + \text{C}_6\text{H}_{12}; 1 : 1) & \text{DCT} \\
\text{(i) DCT} & \text{70 ± 2° for 6 h} \\
\text{N-Propyl(ethylcarbamoyl)propyl carbamate (80% yield)} & (Pure compound b) \\
\end{align*}
\]

**Biological studies:** Preliminary studies showed that compound \text{S-ethyl-N-\{methylcarbamoyl\}oxythioacetimidate (a)} possessed insecticidal property while \text{N-phenyl(ethylcarbamoyl)propyl carbamate (b)} showed herbicidal activity.

**Studies on insecticidal activity of S-ethyl-N-(methylcarbamoyl)oxythioacetimidate (a):**

The field trial was laid to study insecticidal activity of \text{compound a} in five 5 m² plots. The cabbage was selected for the field trial. Four aqueous solutions of \text{compound a} with concentration 100, 200, 300, 400 g ai ha⁻¹ were sprayed separately in four plots (fifth was for blank). Before day one and after 1, 7 and 14 days of spraying population counts of insect, \text{Plutella xylostella} were recorded. From these data mean larval population on cabbage was estimated. The data are recorded in Table 2.

**Evaluation of herbicidal activity of N-phenyl(ethylcarbamoyl)propyl carbamate (b):**

For the foliar application test the aqueous solution of \text{compound b} was sprayed over the foliage of cabbage, lettuce, garden legume and wheat plants at the spray doses of 400, 800, 1000 g ai ha⁻¹ separately. Spraying was performed with the plants employed at either the two or three leaf stage. The growth inhibition of compounds was evaluated at 400, 800 and 1000 g ai ha⁻¹. Approximately three weeks after the spraying the herbicidal activity of each dose was assessed by visual observation of the treated plants in comparison with the untreated controls. According to the extent of the injury of plants herbicidal potency was assessed. Mean values are recorded in Table 2.

**Determination of LC₅₀:**

To determine the LC₅₀ of synthesized compounds \text{a} and \text{b} for fish a solution of 2 to 10 ppm of \text{compound a} and 10 to 60 ppm of \text{compound b} was prepared separately in 20 L of water and stored in aquaria. Twenty five fish were transferred to each aquarium containing test solution, which was
Note

changed after 24 h to maintain the test concentration. No food was provided during the experimental period. The survival number in each concentration was recorded after 96 h. A control aquaria with equal number of fish was also maintained under similar condition. The data are recorded in Table 3.

Determination of $LD_{50}$:

For determination of $LD_{50}$ of synthesized compounds a and b, nine sets of experiments of each compound with 12 male rats were performed separately with suitable blank. The concentration of compound a was from 15 mg kg$^{-1}$ to 100 mg kg$^{-1}$ body weight while of compound b was 750 to 12500 mg kg$^{-1}$ body weight (average body weight of rat was 180 ± 20 g). After 96 h of treatment the mortality number and percentage for each dose was noted. The data are given in Table 3.

Log-dose and probit mortality method$^8$ was used for calculation of $LD_{50}$. The data are recorded in Table 3.

IR (KBr) and NMR of both the compounds a and b were also recorded.

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