disappearance of atrazine in the treated orchard soil resulted in the formation of various metabolites some of which persisted over a number of years.

Atrazine (I) or its hydroxy analogue (II) absorbed by plants from nutrient solution under controlled conditions have been shown to be metabolized and detoxified via 2-hydroxylation, N-dealkylation, and gluthione conjugation (Shimabukuro, 1967; Shimabukuro et al., 1970; Ashton and Crafts, 1973). However, very little consideration has been given to the uptake of metabolites actually present in the field-treated soil. The greenhouse experiment in the present study was primarily designed to determine the uptake of residues by oat plants from the orchard soil sampled in 1973 and 1974. Oats was chosen as it does not readily degrade *s*-triazines (Ashton and Crafts, 1973). The data indicate that residues of II were absorbed by oat plants grown in the fortified soils (Table IV). The compound was present in the shoot and root samples in the conjugated form as no free hydroxyatrazine was detected in eluate III obtained by eluting XAD-2 column with 100% methanol and was released only after the hydrolysis of the latter (eluate IV). Similarly, metabolites II, V, and VI were absorbed by oat plants grown in treated orchard soils sampled in 1973 and 1974. All of these metabolites were also present in plant tissues in the form of conjugates and were only released in the extracts after hydrolysis. In this study no attempt was made to determine the nature of the conjugates. There was no atrazine or deethylatrazine in shoots or roots of plants grown in soil sampled in 1973 and their absence indicates that either the compounds were not absorbed or that they were hydroxylated after their uptake.

The results of this study show that the mechanism of atrazine metabolism in soil involves hydrolysis and N-dealkylation reactions. The metabolites may persist in soil for a considerable length of time after the cessation of long-term application of high rates of the herbicide. The investigation indicates that residues of metabolites can be absorbed by oat plants grown in the treated soil and are subject to conjugation in plant tissues. It is logical to suggest that even where atrazine is applied on an annual basis in corn, atrazine degradation products may persist beyond the growing season and be absorbed by various crops planted the following year.

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LITERATURE CITED

Armstrong, D. E., Chesters, G., Harris, R. F., *Soil Sci. Soc. Am., Proc.* **31**, 61 (1967).
Armstrong, D. E., Chesters, G., *Environ. Sci. Technol.* **2**, 683 (1968).
Ashton, F. M., Crafts, A. S., "Mode of Action of Herbicides", Wiley, New York, N.Y., 1973, pp 310–346.
Best, J. A., Webber, J. B., *Weed Sci.*, **22**, 364 (1974).
Beynon, K. I., Stoydin, G., Wright, A. N., *Pestic. Biochem. Physiol.* **2**, 153 (1972).
Burnside, O. C., Fenster, C. R., Wicks, G. A., Drew, J. V., *Weed Sci.* **17**, 241–245 (1969).
Burnside, O. C., Fenster, C. R., Wicks, G. A., *Weed Sci.* **19**, 290–293 (1971).
Dupuis, G., Laanio, T., Marbach, P., Esser, H. O., *Int. Congr. Plant Protect., 7th, Abstr.*, 711 (1970).
Esser, H. O., Dupuis, G., Ebert, E., Marco, G. J., Vogel, C., in "Herbicides", Vol. 1, Kearney, P. C., Kaufman, D. D., Ed., Marcel Dekker, Inc., New York, N.Y., 1975, pp 129–208.
Fryer, J. D., Kirkland, K., *Weed Res.* **10**, 133 (1970).
Harris, C. I., *J. Agric. Food Chem.* **15**, 157 (1967).
Kaufman, D. D., Blake, J., *Soil Biol. Biochem.* **2**, 73 (1970).
Marriage, P. B., Saidak, W. J., Von Stryk, F. G., *Weed Res.*, **15**, 373 (1975).
Obien, S. R., Green, R. E., *Weed Sci.* **17**, 509 (1969).
Ramsteiner, K. A., Hörmann, W., Eberle, D., *Z. Pflanzenkr. (Pflanzenpathol.) Pflanzenschutz, Sonderheft*, **6**, 43 (1972).
Shimabukuro, R. H., *Plant Physyiol.* **42**, 1269 (1967).
Shimabukuro, R. H., Swanson, H. R., Walsh, W. C., *Plant Physiol.* **46**, 103 (1970).
Sirons, G. J., Frank, R., Sawyer, T., *J. Agric. Food Chem.* **21**, 1016 (1973).
Skipper, H. D., Gilmour, C. M., Furtick, W. R., *Soil Sci. Soc. Am. Proc.*, **31**, 653 (1967).
Skipper, H. D., Volk, V. V., *Weed Sci.* **20**, 344 (1972).
Wolf, D. C., Martin, J. P., *J. Environ. Qual.* 4, 134 (1975).
Zimdahl, R. L., Freed, V. H., Montgomery, M. L., Furtick, W. R., *Weed Res.* **10**, 18 (1970).

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# Herbicidal Activity of Novel Acrylamides

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A novel family of compounds, *cis*-β-alkylsulfenyl-, *cis*-β-alkylsulfinyl-, and *cis*-β-alkylsulfonylamide, were prepared and screened for their herbicidal activities. *N*-*n*-Propyl-*cis*-β-*n*-butylsulfinylacrylamide was highly active against both crabgrass *Digitaria adscendens* and pigweed *Amaranthus ascendens*, activity being a function of chain length attached to the sulfur atom.

The intensive studies on the antimicrobial activities of the β-keto acrylic acids have been conducted owing to the similarity of their chemical structures to penicillic acids, which are well known as an antibiotic (Cumper and Walker, 1956; Hellström, 1957; Kirchner et al., 1949; Omura et al., 1974; Papa et al., 1948; Price and Oae, 1962; Walton, 1957). In view of the isoelectronic nature of the sulfinyl and carbonyl groups (Birkinshaw et al., 1936), we synthesized a number of β-alkylsulfenyl-, β-alkylsulfinyl-, and β-alkylsulfonylacrylic acids and their derivatives, including the esters and the amides, with the hope of finding a novel class of antimicrobial compounds. In the

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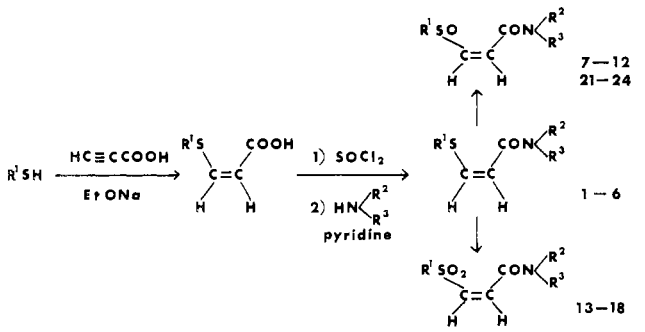
Scheme I




course of this research, it was incidentally found that some of the amide derivatives showed a remarkably high level of herbicidal activity against both crabgrass *Digitaria adscendens* and pigweed *Amaranthus ascendens*.

In this paper we report the structure–activity relationship of the herbicidally active, novel acrylamides.

## EXPERIMENTAL SECTION

**Synthesis.** As shown in Scheme I, *cis*-β-alkylsulfenylacrylic acids were obtained by the base-catalyzed addition of alkyl mercaptan to acetylenecarboxylic acid. Whereas the reaction of this type has been reported on aryl mercaptan, there seems to be no example of the addition reaction of alkyl mercaptan in the presence of the base. It has been reported that the base-catalyzed addition reaction of aryl mercaptan to acetylenecarboxylic acid gave rise to a mixture of *trans*-β-arylsulfenylacrylic acid and the cis isomer. In sharp contrast to this, we found on the basis of the NMR evidence that alkyl mercaptan afforded *cis*-β-alkylsulfenylacrylic acid as a single product. The β-sulfenylacrylic acid was readily converted to the corresponding amides **1–6** via the acid chloride. The successive oxidation was carried out with *m*-chloroperbenzoic acid and with hydrogen peroxide to afford the sulfinyl compounds **7–12** and **21–24** and the sulfonyl compounds **13–18**, respectively.

*cis*-β-*Alkylsulfenylacrylic Acid.* A solution prepared from sodium (2.3 g, 0.10 mol), alkyl mercaptan (0.10 mol), and ethanol (100 mL) was added dropwise, with stirring, to a solution prepared from sodium (2.5 g, 0.11 mol), ethanol (100 mL), and acetylenecarboxylic acid (7.7 g, 0.11 mol). Water (30 mL) was added to redissolve the solid formed upon mixing the two solutions. After stirring the aqueous alcoholic solution for 5 h, it was made acidic with dilute hydrochloric acid and extracted with ether. Drying ($Na_2SO_4$) and evaporation afforded *cis*-β-alkylsulfenylacrylic acid. The cis configuration of the acid was determined on the basis of the coupling constants (10.0–10.5 Hz) of the olefinic protons.

*cis*-β-*Alkylsulfenylacrylamide* **(1–6).** To a chloroform (50 mL) solution of acrylic acid (0.10 mol), thionyl chloride (18 g, 0.15 mol) was added with stirring at 0 °C. The reaction mixture was heated under reflux for 3 h and then evaporated in vacuo to remove the excessive thionyl chloride together with chloroform. The crude acid chloride thus obtained was subjected to the successive amidation without the purification. To an ethereal (50 mL) solution of pyridine (12 g, 0.15 mol) and the amine (0.15 mol) was added an ethereal (30 mL) solution of the crude acid chloride with stirring at 0 °C. After 1 h, the reaction mixture was poured into water (100 mL). The ethereal layer was washed with aqueous hydrochloric acid, then with aqueous sodium carbonate, and finally with bromine. Evaporation of the solvent afforded the desired amides **1–6**, which were purified either by recrystallization or through silica gel column chromatography.

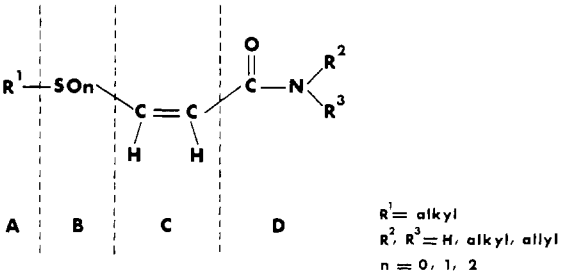



**Figure 1.** Structural units of acrylamide.

*cis*-β-*Alkylsulfinylacrylamide* **(7–12, 21–24).** To a chloroform (40 mL) solution of the sulfenylacrylamide (**1–6**, 0.10 mol) was added a chloroform (30 mL) solution of *m*-chloroperbenzoic acid (19.0 g, 0.11 mol) with stirring at −10 °C. The reaction mixture was stirred at room temperature for 1 h. The chloroform solution was then washed twice with aqueous sodium carbonate and dried ($Na_2SO_4$). The solvent was removed in vacuo to afford the β-sulfinylamides **7–12** and **21–24**.

*cis*-β-*Alkylsulfonylacrylamide* **(13–18).** To an acetic acid (40 mL) solution of the sulfenylamide (**1–6**, 0.10 mol) was added 30% hydrogen peroxide (0.30 mol) at room temperature. The reaction mixture was stirred at room temperature for 72 h and then poured into water (100 mL). Ether extraction and successive washing with aqueous sodium carbonate yielded the β-sulfonylamides **13–18**.

**Biological Tests.** Tests for herbicidal activity were carried out using routine greenhouse procedures. Plastic pots were packed with silt loam soil and were sown with seeds of *Digitaria adscendens* and *Amaranthus ascendens*. After 6 days, the postemergence herbicidal activity was evaluated by spraying chemicals on the first leaf stage plants. The preemergence herbicidal activity was assayed by spraying the pots seeded a day before with the test materials. The compounds dissolved in about 0.2 mL of acetone were diluted with water to 20 mL and applied to the top of the plants at the rate of 3 kg/ha or 5 kg/ha. The sprayed pots were then placed in the greenhouse for 14 days, and the effects of the test compounds on the plants were evaluated by determining the fresh weight of the plant, the result being rated at a 0 (no effect) to 5 (plants dead) scale relative to the control.

## RESULTS AND DISCUSSION

The herbicidal activity was examined for the compounds **1–18** and **21–24** possessing the general structure shown in Figure 1. The change in the herbicidal activity was observed according to the change in the structure of each moiety (A, B, C, and D) of the molecule: the alkyl group attached to the sulfur atom (moiety A), $SO_n$ group conjugated with the olefinic bond (moiety B), the olefinic bond (moiety C), and the amide group adjacent to the olefinic bond (moiety D).

Generally the preemergence and postemergence treatments did not afford the different herbicidal activity except for compound **9** which showed a higher herbicidal effect in the preemergence treatment than in the postemergence treatment. Both weeds of *Digitaria adscendens* and *Amarathus ascendens* showed almost the same level of sensitivity to those chemicals.

**Effect of the Chain Length of the Alkyl Moiety (Moiety A and D).** As shown in Table I, the highest activity in the series of the compounds including *cis*-β-alkylsulfenyl- **1–6**, *cis*-β-alkylsulfinyl- **7–12**, and *cis*-β-alkylsulfonylacrylamide **13–18** was found in the *N*-*n*-propyl-*cis*-β-*n*-butylsulfinylacrylamide (**8**, A = *n*-butyl, B

Table I. Physical and Biological Properties of Novel Acrylamides

| | Compound[b] | | | Relative herbicidal activity[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Digitaria adscendens* (crabgrass) | | | | *Amaranthus ascendens* (pigweed) | | | |
| | | | | Pre-emergence | | Post-emergence | | Pre-emergence | | Post-emergence | |
| No. | $R_1$ = alkyl | $SO_n$ | Mp, ° | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha |
| 1 | *n*-Propyl | | 84 | 4 | 3 | 4 | 3 | 3 | 2 | 3 | 2 |
| 2 | *n*-Butyl | | 86 | 5 | 5 | 5 | 4 | 5 | 5 | 5 | 4 |
| 3 | *n*-Hexyl | S | 89 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 |
| 4 | *n*-Octyl | | 92 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 5 | *n*-Dodecyl | | 98 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 6 | *n*-Tetradecyl | | 110 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | *n*-Propyl | | 126 | 4 | 4 | 4 | 4 | 3 | 3 | 3 | 3 |
| 8 | *n*-Butyl | | 130 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 9 | *n*-Hexyl | SO | 133 | 3 | 2 | 1 | 1 | 3 | 2 | 1 | 1 |
| 10 | *n*-Octyl | | 135 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 11 | *n*-Dodecyl | | 142 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 12 | *n*-Tetradecyl | | 148 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 13 | *n*-Propyl | | 132 | 4 | 3 | 4 | 3 | 3 | 3 | 3 | 3 |
| 14 | *n*-Butyl | | 138 | 5 | 5 | 4 | 4 | 4 | 4 | 4 | 4 |
| 15 | *n*-Hexyl | $SO_2$ | 142 | 2 | 1 | 1 | 1 | 2 | 1 | 1 | 1 |
| 16 | *n*-Octyl | | 143 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 17 | *n*-Dodecyl | | 150 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 18 | *n*-Tetradecyl | | 162 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

[a] 0 = no effect, 5 = 100% kill. [b] *cis*-$R_1SO_nCH{=}CHCONH$-*n*-$C_3H_7$.

Table II. Relationship between Amide Groups and Herbicidal Activity

| | Compound[b] | | | Relative herbicidal activity[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *Digitaria ascendens* (crabgrass) | | | | *Amaranthus ascendens* (pigweed) | | | |
| | | | | Pre-emergence | | Post-emergence | | Pre-emergence | | Post-emergence | |
| No. | $R^2$ | $R^3$ | Mp, °C | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha |
| 21 | Methyl | H | 99 | 4 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| 22 | Methyl | Methyl | 110 | 5 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| 8 | *n*-Propyl | H | 130 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 23 | 2-Propenyl | H | 118 | 5 | 5 | 5 | 5 | 5 | 4 | 5 | 5 |
| 24 | *n*-Butyl | H | 134 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |

[a] 0 = no effect, 5 = 100% kill. [b] *n*-$C_4H_9SOCH{=}CHCONR^2(R^3)$.

Table III. Relationship between Olefinic Bond and Herbicidal Activity

| | | | Relative herbicidal activity[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *Digitaria adscendens* (crabgrass) | | | | *Amaranthus ascendens* (pigweed) | | | |
| | | | Pre-emergence | | Post-emergence | | Pre-emergence | | Post-emergence | |
| No. | X[b] | Mp, °C | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha | 5 kg/ha | 3 kg/ha |
| 19 | $CH_2$ | 110 | 3 | 2 | 3 | 2 | 3 | 2 | 3 | 2 |
| 20 | $CH_2CH_2$ | 119 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 |
| 8 | CH=CH | 130 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |

[a] 0 = no effect 5 = 100% kill. [b] *n*-$C_4H_9$-$SOXCONH$-*n*-$C_3H_7$.

= SO, C = -CH=CH-, D = -CONH-*n*-propyl). The amide 8 showed the highest growth inhibitory effect against both *Digitaria adscendens* and *Amarathus ascendens*. It should be noted that the activities of all the acrylamides examined are influenced by the alkyl chain length attached to the sulfur atom (moiety A). With the maximum activity for the *n*-butyl compound 8, either higher or lower alkyl homologues showed rather decreased activity. The tendency was observed in any group of moiety B. Contrary to this, the alkyl group in the moiety D was less influential upon the herbicidal activities. The influence of various alkyl groups in the moiety D was examined as in Table II. The secondary amide **21** exhibited the same degree of the herbicidal activity as that of the tertiary amide **22**.

**Effect of the Oxidation State of Sulfur Atom (Moiety B).** As seen in Table I, the sulfinyl compounds **7** and **8** were more active compared to the corresponding sulfenyl of sulfonyl analogues **1**, **2**, **13**, or **14**.

**Necessity of the Olefinic Bond (Moiety C) for the Expression of the Herbicidal Activity.** The presence of the olefinic bond (moiety C) between the sulfinyl group

(moiety B) and the amide (moiety D) is essential to obtain a high level of the herbicidal activity. As shown in Table III, the saturation of the ethylenic bond in the amide **8** to give compound **20** considerably decreased the herbicidal activity.

Soybean, corn, carrot, peanut, rice, and tobacco, etc. were examined for the phytotoxicity of these compounds but none of them showed injurious effect at 3 or 5 kg/ha.

In conclusion, the remarkably high level of the herbicidal activity of *N*-*n*-propyl-*cis*-$\beta$-butylsulfinylacrylamide **8** suggests its potential use as a novel herbicide. The mechanism of the action is now being investigated and will be given in the following paper.

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LITERATURE CITED

Birkinshaw, T. H., Oxford, A. E., Raistrick, H., *Biochem. J.* **30**, 394 (1936).
Cumper, G. W. N., Walker, S., *Trans. Faraday Soc.* **52**, 193 (1956).
Hellström, N., *Nature (London)* **179**, 589 (1957).
Kirchner, F. K., Baily, J. H., Gavallito, C. J., *J. Am. Chem. Soc.* **71**, 1210 (1949).
Omura, S., Katagiri, K., Awaya, J., Furukawa, T., Umezawa, I., Oi, N., Mizoguchi, M., Aoki, B., Shindo, M., *Antimicrob. Agents Chemother.* **6**, 207 (1974).
Papa, D., Schwenk, E., Villani, F., Klingsberg, E., *Antimicrob. Agents Chemother.* **70**, 3356 (1948).
Price, C. C., Oae, S., "Sulfur Bonding", Ronald Press, New York, N.Y., 1962.
Walton, H. M., *J. Org. Chem.* **22**, 308 (1957).

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# *N*-Nitroso Compound Impurities in Herbicide Formulations

Ronald D. Ross,* John Morrison, David P. Rounbehler, Steven Fan, and David H. Fine

Determination of gas chromatograph amenable nitrosamines in several herbicide formulations revealed levels of *N*-nitrosodimethylamine and *N*-nitrosodipropylamine from 0 to 640 ppm and 0 to 195 ppm, respectively. A Thermal Energy Analyzer was employed for detection after separation by gas chromatography or high-performance liquid chromatography. With additional chromatographic cleanup the identity of the compounds was confirmed by high-resolution mass spectrometry. These results indicate that formulations of amine salts can form nitrosamines on storage, and nitrosamines can be formed in preparations of nitroaniline based herbicides.

*N*-Nitroso compounds have been identified as a major class of carcinogens that are likely to be causally related to human cancer (Lijinsky and Epstein, 1970). Dialkyl nitrosamines have been shown to be carcinogenic in a wide range of animal species (Magee and Barnes, 1967). *N*-Nitrosodimethylamine (NDMA), for example, has been shown to be carcinogenic in mink at 0.05 mg/kg of body weight (given in the diet two times/week) with most of the animals succumbing to tumors after a total uptake of 25–70 mg of NDMA/kg of body weight (Koppang and Rimeslatten, 1975).

Previous studies (Mirvish, 1975; Elespura and Lijinsky, 1973) were concerned with the capability of pesticides (including herbicides) to form *N*-nitroso compounds. However, evaluation of potential human exposure also requires a knowledge of the amount of *N*-nitroso compound which is already present in formulations for home or agricultural use. We report here on the *N*-nitroso compound content of some samples of formulated herbicides.

## MATERIALS AND METHODS

Formulated materials were obtained from garden supply stores and commercial agricultural applicators. Authenticated standards of NDMA and *N*-nitrosodipropylamine (NDPA) were obtained from the U.S. National Cancer Institute. Solvents were obtained from Burdick and Jackson (Muskegon, Mich.) of a grade which had been distilled in glass.

Thermo Electron Research Center, Waltham, Massachusetts 02154.

The Thermal Energy Analyzer–gas chromatograph (TEA–GC) was constructed from a Thermo Electron Model 661 single-column gas chromatograph interfaced to a Thermo Electron TEA Model 502 detector. A 14-ft stainless steel tube, $^1/_8$ in. o.d. was used as the chromatographic column, packed with Porapak P 80–100 mesh (Waters, Milford, Mass.). Argon was used as the carrier gas at a flow rate of 15 mL/min.

The high-pressure liquid chromatograph–Thermal Energy Analyzer (TEA–HPLC) was constructed from a high-pressure pump (Waters Associates, Model 6000A), an injector (Waters Model U6K), a $\mu NH_2$ column (Waters Associates), and a Thermo Electron TEA Model 502 detector fitted with the TEA–HPLC interface or, alternatively, a UV detector (Waters Associates Model 440). Typical HPLC operating conditions were 2 mL/min of 1:1 dichloromethane and *n*-hexane.

## RESULTS

Figures 1b and 1d are the TEA–GC and TEA–HPLC chromatograms for 10 $\mu$L of a 100:1 dilution of 2,3,6-trichlorobenzoic acid formulated as the dimethylamine salt (sample 4). The TEA–GC and TEA–HPLC chromatograms of a NDMA standard solution are shown in Figures 1a and 1c, respectively. The chromatographic peak corresponding in retention time to NDMA was isolated on the TEA–HPLC, concentrated, and then injected onto the TEA–GC; only a single peak eluting at the retention time of NDMA was observed. For gas chromatography–mass spectrometry (GC–MS) confirmation, the NDMA was isolated from the formulated material following elution on the UV–HPLC. Using high-resolution mass spectrometry, the molecular ion was shown to have a mass of 74.0484,