

The presence of the dimer products from basagran when irradiated on soil is interesting from both the environmental aspect and the theoretical viewpoint, particularly since they did not form in the thin film study. It may be that the dimers form on soil because the soil contains certain transition metals which could coordinate with two basagran molecules and hold them in the correct proximity for coupling. For example, Jennings and Hill (1970) and Salomon et al. (1974) have shown that chromium and copper, respectively, facilitate photodimerization and photocoupling of certain olefins. Further studies on the role of soil transition metal chemistry relative to environmental photolysis may provide such answers.

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Esters of Sulfonic Acids as Derivatives for the Gas Chromatographic Analysis of Carbamate Pesticides

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Esters of sulfonic acids (sulfonates) may be readily prepared on a micro scale by reacting benzene-sulfonyl chlorides with carbamate pesticides. The sulfonates are easily gas chromatographed and detected by a tritium electron capture detector at the 1-pg level. Flame photometric detec-

tion may also be employed at the 10-ng level. A simple analytical procedure for the analysis of carbamates on lettuce and cabbage is described; it can be adapted to other materials, such as soils. A sensitivity of 0.05 ppm is easily achieved.

The apparent thermal instability of carbamate pesticides has presented the pesticide chemist who chooses gas chromatography with a difficult problem. Degradation of the carbamate within the gas chromatograph usually occurs and results in small peaks or no peaks at all. Some success has been achieved using short columns and relatively low temperatures (Cook et al., 1969; Riva and Carisano, 1969) for the chromatography of the intact carbamate. Improving the thermal stability and chromatographic characteristics by derivatization has also produced some success.

Derivatives of the methylamine portion of the carbamate have been made (Crosby and Bowers, 1968; Holden et al., 1969; Moye, 1971); however, these suffer from non-specificity since they do not distinguish between carbamates. Making a derivative of the phenolic portion obviates this problem but frequently requires lengthy reaction times (Argauer, 1969; Butler and McDonough, 1968; Bowman and Beroza, 1967) or results in an incomplete reaction.

Recently, Seiber (1971) and Khalifa and Mumma (1972) formed a carbamate derivative by replacing the amine

portion hydrogen with a perfluoro acetate, propionate, or butyrate group.

The work described here concerns itself with the preparation of esters of sulfonyl chlorides (sulfonates) by the reaction of carbamate pesticides with halogenated benzenesulfonyl chlorides. These derivatives are easily prepared on a micro scale, are easily gas chromatographed, and respond well to electron capture detection. A somewhat reduced response is obtained with sulfur mode flame photometric detection. Analyses of spiked lettuce, cabbage, and weathered soil samples are illustrated.

EXPERIMENTAL SECTION

A Varian Model 1520B with a tritium electron capture detector was used except when otherwise noted. The column was glass, 6 ft × 0.25 in. o.d. × 2 mm i.d., packed with either 5% LSX-3-0295 or UCW98 on 100-120 Hi-Performance Chromosorb W. Column carrier, N₂, was 60 ml/min, at a temperature of 220°.

The *p*-bromo-, 2,5-dichloro-, and 3,4-dichlorobenzene-sulfonyl chlorides were obtained in 99%+ form from Eastman Organic Chemicals, Rochester, N.Y. The pentafluorobenzene-sulfonyl chloride was obtained in 99%+ form from Peninsula Chemical Research, Gainesville, Fla.

Preparation of Sulfonates. Four sulfonyl chlorides were allowed to react separately with 1-naphthol to produce 1-naphthyl-2,5-dichloro-, -3,4-dichloro-, -*p*-bromo-,

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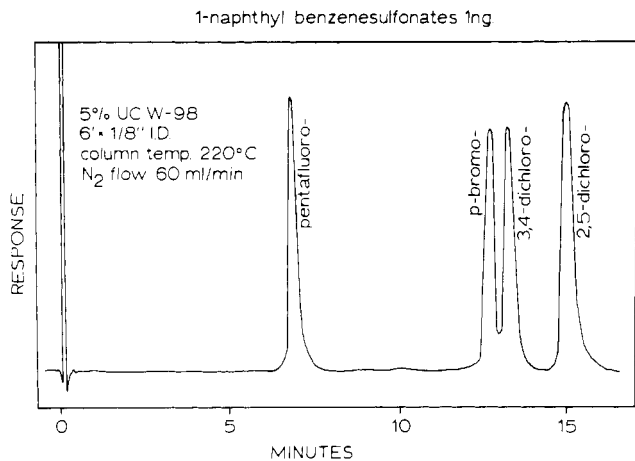


Figure 1. Composite chromatogram of 1-naphthylbenzenesulfonates.

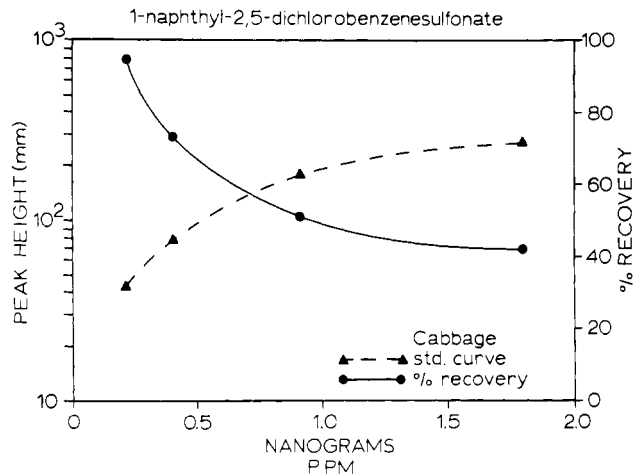


Figure 4. Standard curve and percent recoveries for cabbage spiked with Sevin.

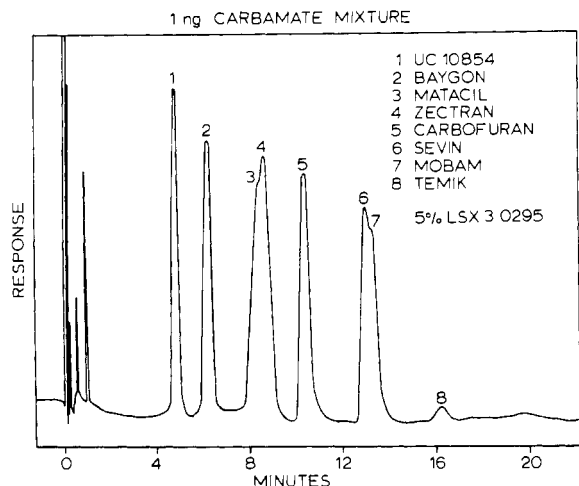


Figure 2. Chromatogram of 1 ng each of seven carbamates and two carbamoyl oximes after derivatization with 2,5-dichlorobenzenesulfonyl chloride. Lannate (not shown) gave no response.

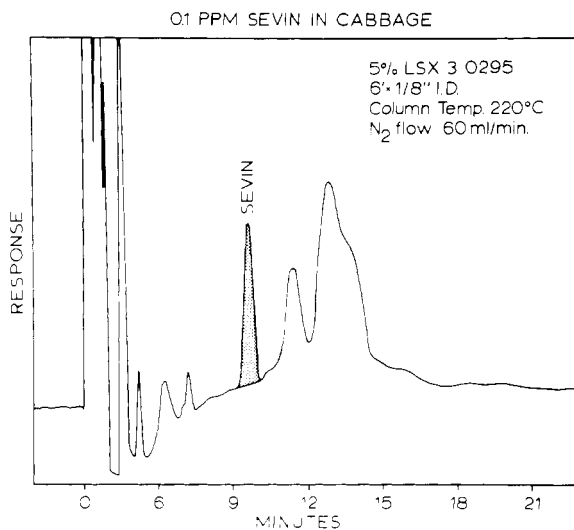


Figure 5. Chromatogram of cabbage spiked with 0.1 ppm of Sevin.

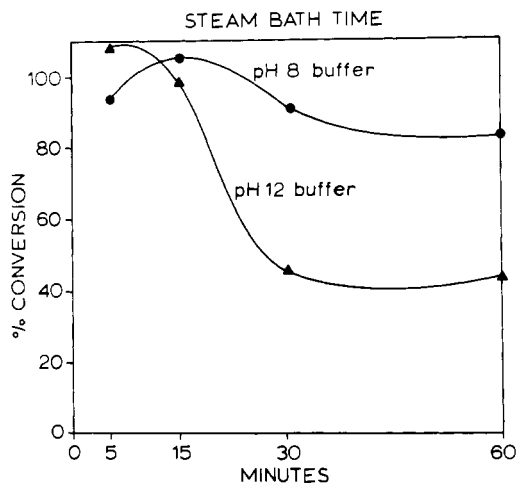


Figure 3. Effect of pH on conversion of Sevin to 1-naphthyl-2,5-dichlorobenzenesulfonate.

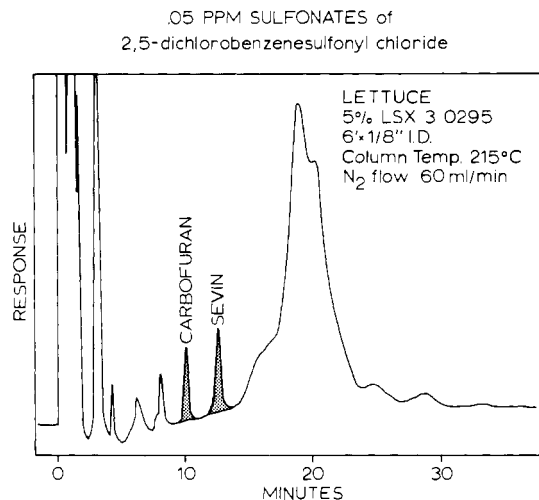


Figure 6. Chromatogram of lettuce spiked with 0.05 ppm of carbofuran and Sevin.

and -pentafluorobenzenesulfonate, respectively. A composite chromatogram is shown in Figure 1. All gave about the same electron capture response; however, the retention times differed, with 1-naphthyl-2,5-dichlorobenzenesulfonate being the last eluter. The sulfonates were prepared on a macro scale by the method of Bost and Nicholson (1935) for making ethers from 1-chloro-2,4-dinitroben-

zene and a phenol. To 0.01 mol of phenol was added 0.01 mol of sodium hydroxide in 5 ml of H₂O. This solution was added to 30 ml of ethanol (95%) containing 0.01 mol of sulfonyl chloride. It was refluxed on a steam bath for about 1 hr. A white precipitate formed for 3,4-dichloro- and *p*-bromobenzenesulfonyl chloride. A dark oil formed

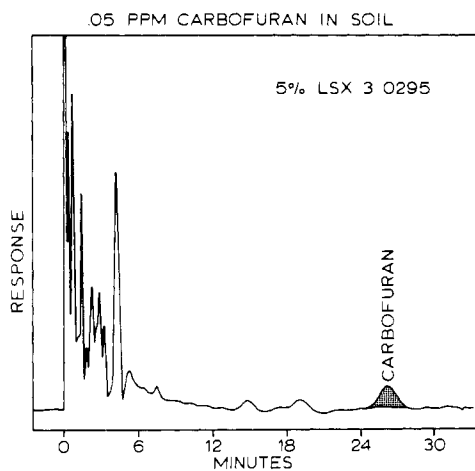


Figure 7. Chromatogram of soil found to contain 0.05 ppm of carbofuran.

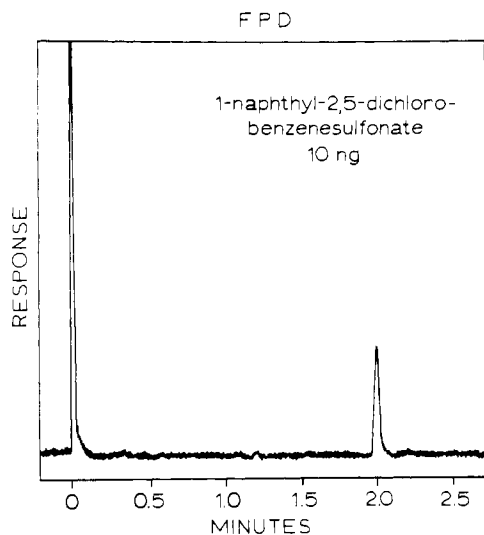


Figure 8. FPD response to 10 ng of 1-naphthyl-2,5-dichlorobenzenesulfonate.

for pentafluoro- and 2,5-dichlorobenzene. Recrystallization was from isoctane.

The sulfonates may be made on a micro scale by refluxing 1 μ g to 1 mg amounts of phenol with 20 ml of sulfonyl chloride in 15 ml of acetone (pH 12)-0.01 M phosphate (7.5 ml of each) buffer for 15 min to 1 hr. Crystalline sulfonyl chloride must be added just prior to reflux for good yields. Addition to unbuffered acetone gives poor results. The solution is cooled and 6 ml of benzene is added, shaken well, and separated from the aqueous phase. Following three water washes the benzene is dried with Na_2SO_4 and stored for GC analysis.

2,5-Dichlorobenzenesulfonates from Carbamates. As previously mentioned, unhydrolyzed carbamates may be substituted for phenols with similar results. A chromatogram of a solution containing seven carbamates and two carbamoyl oximes is shown in Figure 2. Of the two carbamoyl oximes, Temik produced a very poor response, and Lannate (not shown) gave no peak at all.

Reaction Conditions. By using an aqueous buffer-acetone mix the reaction can be speeded up considerably when compared to other reported reaction conditions for the Schotten-Bauman reaction (Borsche and Scholten, 1917; Sekera, 1933). Fifty percent acetone provides adequate solubility for the excess sulfonyl chloride reagent whereas the aqueous buffer allows a choice of optimum pH.

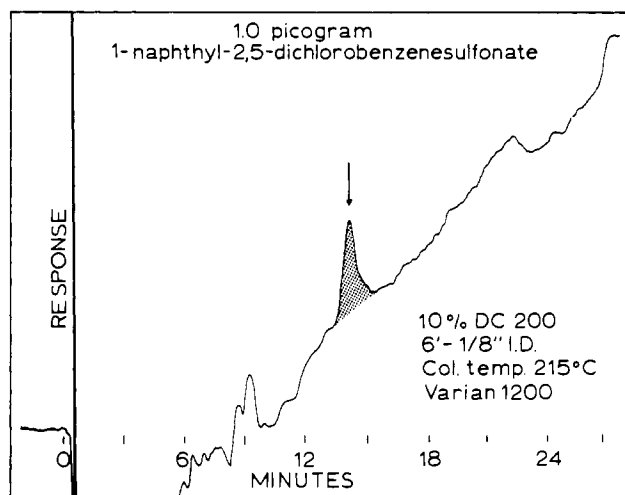


Figure 9. Chromatogram of 1 pg of 1-naphthyl-2,5-dichlorobenzenesulfonate as obtained with a Varian 1200 gas chromatograph equipped with tritium electron capture detector.

Buffer pH strongly affects the rate of sulfonate formation. Figure 3 shows the percent conversion of carbaryl to 1-naphthyl-2,5-dichlorobenzenesulfonate as a function of reaction time for two pH values. The pH 12 buffer gave complete conversion within 5 min; however, subsequent degradation of the sulfonate made the time at which the reaction mixture was to be removed from the steam bath highly critical. By using a pH 8 buffer the reaction was just as complete, but required longer time. However, the degradation was not as pronounced, making the timing requirement less critical.

Carbamate Residues on Leafy Vegetables. A relatively simple procedure was worked out to analyze for conjugated and unconjugated carbamates in leafy vegetables. To 6 g of crop in a 500-ml round-bottomed flask add 100 ml of 0.25 N HCl. Attach a condenser and reflux for 1 hr. Filter through glass wool; cool and transfer to a separatory funnel. Extract three times with 150-ml portions of methylene chloride. Dry extract with Na_2SO_4 and evaporate to 1 ml with Danish-Kuderna. Evaporate to dryness with dry N_2 and pick up residue in 10 ml of benzene. Wash benzene three times with 3-ml portions of 0.25 N NaOH, chilled to 5° in ice water. Dry benzene with Na_2SO_4 and transfer to a 20-ml culture tube having a Teflon-lined screw cap. Evaporate to dryness with N_2 ; add 3 ml of pH 8 phosphate buffer and 20 mg of 2,5-dichlorobenzenesulfonyl chloride. Add 3 ml of redistilled acetone, cap, and incubate at 80° for 15 min. Cool and add 6 ml of benzene. Pipet off lower aqueous phase and wash benzene three times with an equal volume of H_2O . Dry over Na_2SO_4 and analyze by GC.

The recoveries obtained from cabbage spiked with Sevin are shown in Figure 4, along with the accompanying analytical curve. A chromatogram of a 0.1-ppm level sample is shown in Figure 5. This sample was prepared and analyzed five times in succession and gave a relative standard deviation of 5.2%. The type of background interference is very similar to that of lettuce spiked with 0.05 ppm of carbofuran and Sevin as seen in Figure 6.

Carbofuran in Soil. The above procedure, with appropriate modifications to the extraction portion, was used to analyze carbofuran in soil after direct application. Acetone was used to extract the soil by tumbling for 1 hr; the acetone extract was filtered, evaporated to dryness, and, as before, allowed to react with the 2,5-dichlorobenzenesulfonyl chloride. Figure 7 shows a chromatogram of a sample found to contain 0.05 ppm.

Response to FPD. Although no work has yet been done on residues, the Tracor flame photometric detector (FPD)

in the sulfur mode gave good response to 1-naphthyl-2,5-dichlorobenzenesulfonate, as seen in Figure 8. A Research Specialties gas chromatographic oven, Model 660, was equipped with an FPD which had the metal base lined with Teflon tubing throughout the carrier gas portion. A 6 ft × 0.25 in. × 5 mm i.d. glass column was packed with 5% LSX 3-0295 packing and operated at 60 ml/min and 220°.

DISCUSSION

Somewhat low, but consistent (relative standard deviation <12%), recoveries were obtained for those levels of carbamate approaching 1 ppm (Figure 4). Most of this loss was found to be due to hydrolysis of the carbamate when the benzene phase containing the pesticide was washed with the cold 0.25 N NaOH. However, this washing procedure removed almost all of the interferences and was considered to contribute greatly to the simplicity of the procedure.

The thermal stability of the sulfonates was demonstrated by sealing microgram quantities in glass ampoules for various lengths of time. After heating at 250° for 1 hr and then analyzing by GC it was determined that no measurable amount of loss had occurred.

If competing side reactions occurred in the derivatization they were not indicated, as evidenced by the complete absence of multiple peaks and by the 100%+ conversion efficiency of the derivatization reaction.

The Varian Model 1520B gas chromatograph used in this study was modified by removing the stainless steel connecting lines running from the column over to the detector base and replacing them with short sections of glass tubing. This produced an essentially all glass system which was found to be necessary to minimize the catalytic degradation of the sulfonates. Even then the 1520B was found not to be as sensitive as other instruments of some-

what newer design. Figure 9 is a typical chromatogram obtained with a glass column equipped Varian 1200 showing a limit of detection of about 1 pg compared to 50 pg which is the limit of detection for a Varian 1520B.

The sulfonates have not only found great use in this laboratory as derivatives of carbamates but also of certain ring hydroxylated compounds, such as 2,4-dichlorophenol, a metabolite of 2,4-dichlorophenoxyacetic acid. This usage will be reported at a later date.

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Preservation of Grain with Aliphatic 1,3-Diols and Their Esters

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A series of linear, aliphatic 1,3-diols and certain of their monoesters have been found to be safe, effective preservatives for raw grain and animal feeds. The safety of these materials was established by rat feeding experiments which showed them to be nontoxic and readily metabolized. In antifungal tests, using tube dilution methods, several of the diols and esters were significantly more active than either calcium propionate or calcium sorbate. The most effective diols are those with carbon numbers ranging from 7 to 9.

The best esters have carbon contents, diol plus acid fragments, in the range of C₁₀ to C₁₅. The most promising new compounds were evaluated as preservatives for chick feeds and for raw grains at various humidity levels. They appeared to be at least as effective as current, acidic grain preservatives and to possess certain unique advantages. These include greater safety, lack of corrosivity, and improved odor and flavor characteristics.

Deterioration of grain due to microbial attack during storage continues to be a serious problem. Moldy grain is unpalatable, difficult to handle, and malodorous. Damaged flour, for example, has a deleterious effect on bread making (Daftary et al., 1970). In addition, the mycotoxins

produced by many molds present a serious health threat to both humans and animals (Ciegler et al., 1971). Traditionally, grain is preserved from microbial attack by drying to 14% moisture content or less (Huitson, 1968; Christensen and Kaufmann, 1969) although refrigeration and aeration processes are also employed (Christensen and Kaufmann, 1969). Recently, various types of chemical preservatives have been added to stored grain. For the most part these have been aliphatic acids, especially acetic and propionic acid, and their calcium and sodium salts. These materials, while effective, have drawbacks in

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