quences we have used to establish the absolute configuration of **1b**. L(+)-Lactic acid (**2**) was purchased from Sigma Chemical Co. The esterification of **2** and the tosylation of **3** did not affect the bonds linked to the asymmetric center; therefore, **3** and **4** should have the L configurations. The reaction of **4** with sodium 1-naphthoxide involves inversion of configuration, or SN2 displacement and thus **5** would have the D configuration. Resolution of racemic 2-(1-naphthyloxy)propionic acids (Tseng et al., 1973) was carried out according to the method of Fourneau and Balaceano (1925). The esterification of **6b** gave **7b**. The rotational property of **7b** suggests that **7b** has the same configuration as **5**. Therefore, **7b** should have the D configuration.

The subsequent reactions of **6b** with phosgene and then with diethylamine involved retention of configurations, and thus the product **1b** had the D configuration. The product made from **6a** would be the L configuration.

Comparative herbicidal activities of the racemic, D, and L forms of **1** are listed in Table I. The average L C_{90} for racemic, D, and L forms are 0.62, 0.33, and 2.86 ppm, respectively. This indicated that the D form is approximately eightfold more active than the L form, whereas the racemic mixture gave an intermediate response.

Matell (1953) suggested that the biologically most active forms of 2-aryloxypropionic acids could be attributed to the same steric configuration, the D configurations. Our results seem to confirm his postulation, and the postulation may even be extended to the derivatives of 2-aryloxypropionic acids.

LITERATURE CITED

Aberg, B., *Lantbrukshoegsk. Ann.* **20,** 241 (1953).
Aberg, B., *Lantbrukshoegsk. Ann.* **31,** 333 (1965).
Fourneau, M. E., Balaceano, *Bull. Soc. Chim. Fr.* **4,** 1602 (1925).
Fredga, A., Matell, M., *Ark. Kemi* **3,** 429 (1951).
Listowsky, I., Avigad, G. T., England, S., *J. Org. Chem.* **35,** 1080 (1970).
Matell, M., *Lantbrukshoegsk. Ann.* **20,** 205 (1953).
Sjoberg, B., *Ark. Kemi* **15,** 481 (1960).
Tseng, C. K., Chan, J. H., Baker, D. R., Walker, F. H., *Tetrahedron Lett.*, 3053 (1971).
Tseng, C. K., Simone, R. A., Walker, F. H., *J. Org. Chem.* **38,** 1746 (1973).

James H. H. Chan
Francis Walker
Chien K. Tseng*
Don R. Baker
Duane R. Arneklev

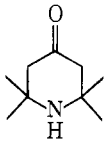
Stauffer Chemical Company
Richmond Research Center
Richmond, California 94804

Received for review January 20, 1975. Accepted May 15, 1975.

Triacetonamine Formation in Fungal Extracts

Triacetonamine is found to be an artifact formed during the acetone extraction of fungal material.

The selection of an appropriate extraction solvent is a problem which is often encountered when general screening programs are initiated for biological activity of complex mixtures. In most cases the best solvents for extraction of biological material are relatively volatile with both hydrophilic and lipophilic characteristics. Use of such solvents will result in the extraction of a broad spectrum of mainly nonpolymeric compounds. Our survey of fungi for production of certain types of mycotoxins requires such a solvent for extraction of fungal material. Acetone was selected for extraction because of its excellent solvent characteristics and relatively high volatility. Extraction of *Aspergillus oryzae* with acetone has led to the production of 2,2,6,6-tetramethyl-4-piperidone (triacetonamine) (**1**) as the major component of the extract. This compound is an artifact and its production may be avoided by use of other solvents for extraction purposes.



1

EXPERIMENTAL SECTION

Aspergillus oryzae was grown by shaking it for 10 days at 26° in 1 l. of potato dextrose broth (pH 6.4) (Lodder and Kreger-Van Rij, 1952). The mycelium and growth medium were lyophilized to dryness and the residue was extracted with acetone for 18 hr under a nitrogen atmosphere with the Soxhlet cup draining with a frequency of once every 15 min. The extract was evaporated to dryness in vacuo and the dark oily residue (2.3 g) was fractionated on a 2.5 × 30 cm column of silica gel G (<0.063 mm, EM reagent). The column was eluted with chloroform–methanol (3:1) and 20-ml fractions were collected. Fractions were monitored by thin-layer chromatography (TLC) on silica gel pre-coated 60 F-254 chromatoplates (5 × 10 cm, 0.25 mm thick, EM Laboratories Inc.). The TLC plates were developed with chloroform and substances were visualized by their reaction with iodine. Fractions 16–26 were combined and evaporated in vacuo leaving a yellow oil which was crystallized from chloroform–hexane yielding a salt of triacetonamine (225 mg, mp 134–136°) as indicated by its spectral and solubility properties. The free amine was obtained by dissolution of the crystalline material in cold 10% $NaHCO_3$ and extraction of the basic solution with chloroform. Evaporation of the solvent produced a colorless oil which was purified by sublimation at 35° (20 mmHg). The resulting colorless, crystalline material has melting point (34–36°) (Heintz, 1875), ir, NMR, and mass spectra identical with those of an authentic sample prepared from commercially available triacetonamine hydrochloride. Triacetonamine was not present in acetone extracts of sterile potato dextrose broth.

The production of triacetonamine can be avoided by not using acetone for the extraction of fungal material. Methanol was the solvent of choice in most cases in our study. Extraction of fungal material with methanol, which readily extracts triacetonamine salt from spiked samples, did not result in the isolation of this artifact from unspiked samples.

RESULTS AND DISCUSSION

Triacetonamine has been identified as an artifact of plant extractions which utilized ammonium hydroxide or ammonium iodide solutions and acetone in various steps of

the isolation procedures (Stewart and Wheaton, 1967; Orazkuliev et al., 1962; Housholder and Camp, 1965). It has also been claimed to be a plant natural product (Rimington and Rocts, 1937). However, triacetonamine could not be isolated when different methods of extraction were used in this latter case.

The present communication shows that this artifact is produced by reaction of acetone with endogenous components of biological materials.

Due to the natural occurrence of ammonium salts and other reactive amines in fungal material we suggest the use of solvents which do not contain carbonyl functionality in order to minimize artifact production during extraction.

LITERATURE CITED

Heintz, W., *Annalen* **178**, 320 (1875).
Housholder, D. E., Camp, B. J., *J. Pharm. Sci.* **54**, 1676 (1965).
Lodder, J., Kreger-Van Rij, N. J. W., "The Yeasts—A Taxonomic Study", North-Holland Publishing Co., Amsterdam, 1952, pp 12–13.
Orazkuliev, I. K., Otroshchenko, O. S., Sadykov, A. S., *Zh. Obshch. Khim.* **32**, 3827 (1962).
Rimington, C., Rocts, G. C. S., *Onderstepoort J. Vet. Sci. Anim. Ind.* **9**, 193 (1937).
Stewart, I., Wheaton, T. A., *Phytochemistry* **6**, 1587 (1967).

Leonard F. Bjeldanes*
George W. Chang

Department of Nutritional Sciences
University of California
Berkeley, California 94720

Received for review March 10, 1975. Accepted July 7, 1975.

Identification of the Major Thermal Degradation Products of the Insecticide Mirex

The thermal decomposition of mirex has been studied at temperatures up to 700°. Infrared, mass spectral, gas chromatographic, and ultraviolet data were used to establish that hexachlorobenzene was the major thermal degradation product. Hexachlorocyclopentadiene was also found in small amounts in the thermal residue. The products identified from the vapor phase were carbon monoxide, carbon dioxide, hydrogen chloride, chlorine, carbon tetrachloride, and phosgene.

Mirex (dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[*cd*]pentalene) has commonly been used in the southern United States to control the imported fire ant. Alley (1973) has reviewed the uses of mirex and the problems caused by its use. This persistent chlorocarbon has been shown to be inert to many common acids, bases, and oxidizing and reducing agents (McBee et al., 1956). Mirex does, however, react with lithium and *tert*-butyl alcohol to give the corresponding hydrocarbon and *endo*-dicyclopentadiene (Dilling et al., 1967). The chlorocarbon also undergoes photolysis in hydrocarbon solvents to yield the monohydro and dihydro derivatives (Alley et al., 1973, 1974).

McBee et al. (1956) and Eaton et al. (1960) have indicated mirex to be thermally stable, pyrolysis occurring only at temperatures above 500°. The thermal degradation products reported in each case are somewhat conflicting. McBee indicated the products to be largely carbonaceous material and chlorine with a trace of hexachlorocyclopentadiene. Eaton, however, reported no carbonaceous material and only trace amounts of hexachlorocyclopentadiene at 500°. The purpose of the present investigation was to investigate the thermal degradation products of mirex in relationship to disposal of this insecticide by incineration.

EXPERIMENTAL SECTION

Analytical standard grade, 99.9% mirex, donated by Allied Chemical Corporation, was used without further purification. Hexachlorocyclopentadiene was obtained from Aldrich Chemical Co. Reagent grade hexachlorobenzene (Eastman Chemical Co.) was further purified by recrystallization. The thermal lability of mirex was circumvented by sealing 50–100-mg samples in 10-ml Neutraglas ampules. The samples were heated in a muffle furnace for 30 min at the selected temperatures, removed and allowed to cool, and broken, and the contents dissolved in pesticide grade hexane.

Identification of Hexachlorobenzene. The major component of pyrolysis of mirex was identified by the retention times on four columns of differing polarities with McReynolds constants for benzene ranging from 15 to 321. Specifically, gas–liquid chromatographic identification was accomplished by use of a Barber-Colman 5000 series gas chromatograph equipped with a tritium foil electron capture detector and a Varian Aerograph Model 1400 gas chromatograph equipped with a flame ionization detector. Both columns used in the Barber-Colman chromatograph were 1.8 m × 4 mm i.d. glass and were packed with 3% OV-1 on Chromosorb W 80–100 mesh and 1.5% OV-17, 1.95% QF-1 on Chromosorb W 100–120 mesh. Chromatographic conditions for both columns were as follows: injector, column, and detector temperatures of 225, 110, and 215°, respectively. Carrier gas was nitrogen at a flow rate of 100 ml/min. Two columns were also used in the Varian Aerograph chromatograph. The 5% SE-30 on Anakrom ABS 80–90 mesh (1.2 m × 2 mm i.d.) was operated with injector, column, and detector temperatures of 175, 150, and 180°, respectively. The 5% Carbowax 20M on Anakrom ABS 60–80 mesh (2.4 m × 2 mm i.d.) was operated with injector, column, and detector temperatures of 200, 120, and 210°, respectively. Nitrogen was used as a carrier gas in both instances. Flow rates were 15 ml/min for both the SE-30 column and the Carbowax 20M column.

Mass spectral analysis was accomplished by use of a Perkin-Elmer Model 270 GC–MS equipped with a 5% SE-30 on Anakrom ABS 60–80 column (2.4 m × 3 mm i.d.) operated at 100° with a nitrogen flow rate of 10 ml/min. The mass spectrum was identical with that of hexachlorobenzene.

Prior to infrared analysis, isolation was accomplished by the passing of the thermal residue through a 19 in. × 1 in. alumina column and elution with cyclohexane. The major component was recrystallized by solvent evaporation and redissolved in carbon disulfide. Analysis was performed on a Perkin-Elmer Model 457 spectrophotometer. The in-