

protein content of the sludge was near 40%.

The results of Damron et al. (1977) and the amino acid composition suggest that dried citrus sludges can be utilized as a protein source in broiler diets on a limited basis when supplemented with arginine, histidine, methionine, and cystine.

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Received for review December 3, 1976. Accepted February 25, 1977. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

Microsynthesis of [*ring*-¹⁴C]Diuron (3-(3,4-Dichlorophenyl)-1,1-dimethylurea) from 3,4-[¹⁴C]Dichloroaniline and Dimethylcarbamoyl Chloride

[*ring*-¹⁴C]Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) was synthesized from 3,4-[¹⁴C]dichloroaniline (DCA) and dimethylcarbamoyl chloride. After preparative thin-layer chromatography, radiochemical purity of [*ring*-¹⁴C]diuron was greater than 99%. Radiochemical yield was 71% from 89 μ Ci or 3.2 mg of [¹⁴C]DCA.

Ring-labeled substituted ureas are required for studying the environmental fate and bound residue formation of these herbicides (Hsu and Bartha, 1976). Multistep syntheses of [*ring*-¹⁴C]diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and other substituted ureas have been published, but the methods require relatively large amounts of starting materials (Tanaka, 1970; Attar et al., 1973).

A single-step conversion of 3,4-dichloroaniline (DCA) to diuron was desired because [¹⁴C]DCA was commercially available. [*ring*-¹⁴C]Monuron (3-(4-chlorophenyl)-1,1-dimethylurea) has been synthesized from 4-[¹⁴C]-chloroaniline and dimethylcarbamoyl chloride, but details of the synthesis were not published (Swanson and Swanson, 1968). This communication reports a one-step, microsynthesis of [*ring*-¹⁴C]diuron from [¹⁴C]DCA and dimethylcarbamoyl chloride.

MATERIALS AND METHODS

Unlabeled reference compounds were purchased or synthesized, and structures were confirmed by mass spectroscopy. Pyridine and acetonitrile were distilled. Acetonitrile was dried with phosphorus pentoxide before distillation.

Dimethylcarbamoyl chloride was purchased from Eastman. (Caution: Dimethylcarbamoyl chloride may be a carcinogen and causes skin, eye, and respiratory irritation (*Chem. Eng. News*, 1976; Van Duuren et al. 1972; Hey et al., 1974).

Labeled DCA (ring-U-¹⁴C, 4.5 mCi/mmol) was purchased from California Bionuclear Corporation. Radioactivity was measured with a Model 2002 Packard Tri-

Carb liquid scintillation spectrometer. Aquasol, from New England Nuclear, was added to solutions. Methanol and toluene scintillation solution were added to thin-layer chromatography segments. The toluene solution contained 5 g/L of 2,5-diphenyloxazole (PPO) and 0.3 g/L of 1,4-bis(2-(4-methyl-5-phenyloxazolyl))benzene (dimethyl-POPOP). Quenching was corrected by the channels ratio method.

In preliminary experiments to optimize reaction conditions, tracer [¹⁴C]DCA was added to an amount of unlabeled DCA equivalent to the total amount of [¹⁴C]-DCA. Reaction yields of the preliminary experiments and final reaction were measured by liquid scintillation and thin-layer chromatography.

[¹⁴C]DCA had been stored in benzene to reduce radiolysis. Forty-five milliliters of the benzene solution was evaporated to about 0.1 mL. One milliliter of acetonitrile, 0.2 mL of pyridine, and 0.3 mL of dimethylcarbamoyl chloride were added and kept in the dark at 20-22 °C for 3 days.

The reaction mixture was diluted with 50 mL of 2 N hydrochloric acid. The product was extracted with three 10-mL portions of dichloromethane. The product was purified by double development with benzene-acetone (80:20, v/v) on a silica gel 60, F-254, 0.5 mm thick thin-layer plate from EM Reagents.

Identity and purity of ¹⁴C compounds were confirmed by cochromatography on thin-layer sheets of silica gel F254, layer thickness 0.25 mm on aluminum support from EM Reagents. Developed strips were cut into 2-mm segments for zonal-profile analysis (Snyder, 1970). The developing solvents were benzene-acetone (2:1, v/v),

chloroform-ethanol (95:5, v/v), and benzene-dioxane-ethanol (75:20:5, v/v).

Mass spectra were determined by solid probe introduction into a Finnigan Series 3000, quadrupole mass spectrometer.

RESULTS AND DISCUSSIONS

The yield of [*ring*-¹⁴C]diuron was 63 μ Ci from 89 μ Ci of [¹⁴C]DCA, a radiochemical yield of 71%. The corresponding masses were calculated from the specific activity stated by the supplier of [¹⁴C]DCA and were 3.2 mg of DCA and 3.26 mg of diuron. Radiochemical purity of diuron was greater than 99% in three different solvents. Structure was confirmed by mass spectroscopy (Benson and Damico, 1968).

Radiochemical yield of 3-(3,4-dichlorophenyl)-1-methylurea was 9.5%. The compound was identified by cochromatography and mass spectroscopy (Safe and Hutzinger, 1973). The commercial dimethylcarbamoyl chloride was not purified and may have contained methylcarbamoyl chloride, which caused the formation of 3-(3,4-dichlorophenyl)-1-methylurea.

Total recovery of ¹⁴C in solutions was 86%. Some DCA may have been lost during solvent evaporation (Bartha, 1968). Recovery of ¹⁴C was 95% in a preliminary trial in which evaporation of benzene had not been necessary. Residual activity of eluted silica gel from the preparative TLC plate was not checked, but diuron was almost completely eluted in a preliminary trial.

The reaction was faster at temperatures above 20 °C, but a minor product formed. At 80 °C, the yield of a compound which cochromatographed with 1,3-bis(3,4-dichlorophenyl)urea was 10–15%. This minor product did not form at 20 °C.

Dimethylcarbamoyl chloride should be a useful reagent

for radiochemical synthesis of ring-¹⁴C-substituted phenyl dimethylureas from labeled anilines.

ACKNOWLEDGMENT

Mass spectral analysis was performed by Karl Yanagihara, Department of Agricultural Biochemistry, University of Hawaii.

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Received for review December 13, 1976. Accepted March 4, 1977.
 Hawaii Agricultural Experiment Station Journal Series No. 2081.
 This work was supported by Western Regional Research Funding for Project W-82.

CORRECTION

FATE OF POLYBROMINATED BIPHENYLS (PBB'S) IN SOILS. RETENTION OF HEXABROMOBIPHENYL IN FOUR MICHIGAN SOILS

In this article by Alexander B. Filonow, Lee W. Jacobs, and Max M. Mortland [*J. Agric. Food Chem.* 24, 1201 (1976)], on p 1203, the wrong values were used for the adsorption equilibrium concentrations of HBB. This error changes the regression equations given to express Freundlich-type adsorption and the values in Table III derived from those equations. The correct equations are: Spinks, $\log x/m = 0.57 + 1.25 \log C$; Miami (eroded), $\log x/m = 1.08 + 0.94 \log C$; Miami, $\log x/m = 2.04 + 0.50 \log C$; and Brookston, $\log x/m = 1.33 + 1.31 \log C$. These corrections do not change the conclusions made from our research data.

TOXAPHENE AND 1,1,1-TRICHLORO-2,2-BIS(P-CHLOROPHENYL)ETHANE (DDT) LOSSES FROM COTTON IN AN AGROECOSYSTEM CHAMBER

In this article by Ralph G. Nash, M. Leroy Beall, Jr., and William G. Harris [*J. Agric. Food Chem.* 25(2), 336 (1977)] the following corrections should be made. On p 338, column 1 (1) lines 4 and 5 should read "5 equal areas by taking ten measurements at the intersections of the pipe"; (2) line 15, substitute "0.29" for "0.35"; (3) line 17, substitute "2.5 m³/min (3.3 chamber air changes/min)" for "2.9 m³/min (3.9 chamber air changes/min)". On p 340, column 1, (4) the μ g/m³ concentrations in Figure 3 and 4 are ca. 18% too low.