Disposition of Cyromazine in Plants under Environmental Conditions[†]

Lori O. Lim,*[,‡] Susan J. Scherer,[‡] Kenneth D. Shuler,[§] and John P. Toth[‡]

Pesticide Research Laboratory, Department of Food Science and Human Nutrition, University of Florida, Gainesville, Florida 32611, and Florida Cooperative Extension Service, 345 South Congress Avenue, Delray Beach, Florida 33445

The disposition of cyromazine (Trigard) in plants under environmental conditions and the role of photodegradation in the formation of melamine were studied. Cyromazine was applied to three *Brassica sp.* vegetables, and residues were analyzed by high-pressure liquid chromatography. After multiple applications, both cyromazine and melamine were detected. Melamine residues constituted 14–36% of the total residues. After one application, the average half-life for cyromazine was 7 days. Melamine levels increased (3–5-fold) with time. Both compounds were readily removed by water. Percent residues removed decreased with increased elapsed time between application and washing. The role of photodegradation in the formation of melamine was studied by in vitro experiments. In glass dishes, cyromazine was dealkylated with the formation of melamine. Since the amount of melamine formed did not account for all of the lost cyromazine, volatilization of cyromazine and degradation to other metabolites is likely.

Cyromazine (*N*-cyclopropyl-1,3,5-triazine-2,4,6-triamine, Trigard; Figure 1) is a systematic insecticide and an insect growth regulator effective against fly larvae and leaf miners. Its primary target for activity is the insect cuticle (Binnington et al., 1987, Friedel et al., 1988). Unlike other compounds in this triazine class, it lacks herbicidal activity.

The environmental fate of certain triazines, such as atrazine and simazine, has been reviewed. In general, they are metabolized by biological systems including bacteria, plants, and mammals (Fishbein, 1975) as well as degraded by photochemical reactions (Jordan et al., 1970; Marcheterre et al., 1988). The major degradative reactions are dealkylation and hydroxylation, and they are involved in the development of resistance to atrazines (Shimbabukuro, 1967; Shimbabukuro and Swanson, 1969). In contrast, there are limited data published on the environmental fate of cyromazine. Bacteria *Pseudomonas spp.* have been shown to utilize cyromazine as a nitrogen source (Cook et al., 1984; Cook and Hutter, 1981). Dealkylation of cyromazine may lead to the formation of melamine (1,3,5-triazine-2,4,6-triamine; Figure 1). Most of the published studies concerning melamine were initiated because of its use in melamine–formaldehyde amino resins and in fire-retardant finishes. Early studies in rats showed that melamine may be carcinogenic (Melnick et al., 1984); however, the toxicity may be due to a secondary effect from the development of renal bladder stones induced by melamine (Heck and Tyl, 1985). Melamine was not mutagenic in the Ames assay (Zeiger, 1987). Current Environmental Protection Agency guidelines require the analysis of both cyromazine and melamine for the establishment of tolerances in food commodities (*Fed. Regist.*, 1984).

[†] Florida Agricultural Experimental Station Journal Series R-00043. Preliminary report of the data was presented at the 197th National Meeting of the American Chemical Society, Dallas, TX, 1989.

[‡] University of Florida.

[§] Florida Cooperative Extension Service.

The purpose of the present study was to investigate the disposition of cyromazine in crops under environmental conditions. In particular, we will study (1) the dealkylation of cyromazine after multiple and single applications, (2) the binding of residues to foliage, and (3) the role of photochemical reactions in the degradation of cyromazine. Three *Brassica spp.* vegetables, bok choy, napa cabbage, and Chinese mustard, were studied due to current interest in expanding the use of cyromazine on these minor crops.

EXPERIMENTAL SECTION

Materials. Analytical standards of cyromazine (purity 97.98%) and melamine (purity 99%) were obtained from the EPA Pesticides and Industrial Chemicals Repository (Research Triangle Park, NC). Stock solutions were made in methanol. Trigard 75W containing 75% cyromazine was obtained from Ciba-Geigy (Greensboro, NC). All other reagents were HPLC grade or analytical grade (Fisher Scientific Co., Springfield, NJ; Baxter Healthcard Corp., Muskegon, MI).

Multiple-Application Field Trials. Cyromazine (Trigard 75W) was applied to mature plants of bok choy, napa cabbage, and Chinese mustard in separate plots at a rate of 0.25 lb of active ingredient (AI)/acre with use of a CO_2 backpack sprayer. The trials were conducted at different times between 1987 and 1988 in Florida. Applications were made at weekly intervals for 7 weeks, and plants were harvested 7 and 14 days after the last application (preharvest interval, PHI). Each treatment condition was replicated in four plots. Four plants were harvested from each plot and frozen at −30 °C until analysis.

Single-Application Field Trials. Cyromazine (Trigard 75W) at a rate of 0.50 lb of active ingredient/acre were applied to the three vegetables planted in separate plots. The trials were conducted at the same time from April to May, 1989, at farms in the same vicinity as for the trials with multiple-application trials. Four plants were harvested at 2 h, 1 day, and 7 days after the application. Of the four plants collected per time period, two were subjected to washing by dipping ten times into a bucket containing 3–4 gal of fresh tap water. The napa and Chinese mustard were collected and washed as whole plants. After washing, the bok choy plants were separated into the top leafy portion (blade) and the bottom portion (petiole). The samples were frozen at −30 °C until analysis.

Residue Analysis. Each replicate was chopped in a food chopper, and 25.0-g subsamples were analyzed. The method

0021-8561/90/1438-0860$02.50/0