FUNGICIDE LABELING

Preparation of Labeled 2,6-Dichloro-4-nitroaniline (Botran)

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A procedure is described for the preparation of chlorine-36–labeled 2,6-dichloro-4-nitroaniline, Botran, by the chlorination of *p*-nitroaniline with the labeled chlorine gas.

THE compound 2,6-dichloro-4-nitroaniline (Botran, The Upjohn Co.) has been used on several fruits and vegetables for the control of certain fungi on a no-residue basis, and the use of tracer methods should facilitate the investigations of its residues in soils and plants. A carbon-14 label would be satisfactory, but the synthesis requires several steps from expensive labeled intermediates. The chlorine-36–labeled compound was found to be easily prepared, although the maximum specific activity obtainable is low.

p-Nitroaniline can be readily chlorinated with elemental chlorine-36 to form Botran:

$$NO_2C_6H_4NH_2 + 2\ Cl_2^* \rightarrow NO_2C_6H_2NH_2Cl_2^* + 2\ HCl^*$$

Experimental

The chlorine-36 gas in break-seal tubes, obtained from The Radiochemical Centre, England, had a specific activity of 44.2 microcuries per millimole. The apparatus for the synthesis is shown in Figure 1.

A mixture of 86 mg. (0.62 mmole) of *p*-nitroaniline and 2.5 ml. of glacial acetic acid was placed in the reaction tube, *B*, and the mixture warmed until the *p*-nitroaniline was dissolved. The break-seal tube containing 54 microcuries (1.22 mmoles) of chlorine-36 was joined to the connecting tube, *C*, and tube *B* was attached by means of the 24/40 joint.

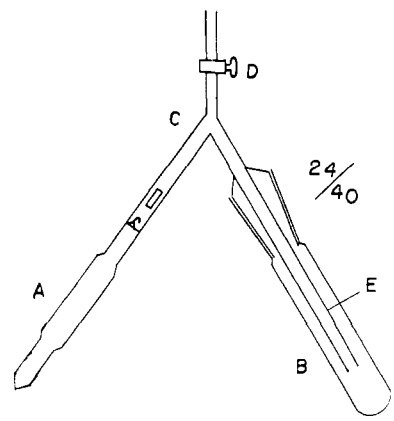

Figure 1. Chlorination apparatus

The lower parts of the break-seal tube and the reaction tube were immersed in liquid nitrogen. After the chlorine had condensed, the seal was broken, and the system was evacuated through *D*. The stopcock was closed and liquid nitrogen bath was removed from the break-seal tube and, as it warmed, the chlorine passed into tube *B* and was condensed. After the transfer was completed, air was admitted through stopcock *D*, tube *C* was disconnected from the reaction tube, *B*, and the latter was closed with a glass stopper. Tube *B* was then removed from the liquid nitrogen bath and allowed to warm to room temperature. The contents were shaken occasionally, and after the tube had stood an hour ice water was added until the tube was three fourths full, and the mixture was shaken. A milliliter of water dissolves about 0.8 mg. of *p*-nitroaniline, but only about 8 μg. of Botran. The mixture was filtered, and the product was washed with cold water. Half the chlorine used for the synthesis was in the form of HCl in the filtrate, and was saved for future use. The yield was about 80%, based on the weight of the Botran and the theoretical yield from *p*-nitroaniline. The product was recrystallized from a mixture of glacial acetic acid and alcohol (*1*, *2*). It melted at 193–195° C. alone, and mixed with Eastman Kodak No. 1033 2,6-dichloro-4-nitroaniline.

The labeled Botran had an activity of 440 counts per minute per microgram when counted in toluene containing 4 grams of PPO and 0.1 gram of POPOP per liter in a Model 3314 TriCarb scintillation spectrometer. No chlorine standard was available for efficiency determinations, but the counting efficiency was probably above 80%. Gas chromatography yielded only one peak, identical in elution time with the Eastman Kodak sample.

Literature Cited

(1) Witt, O. N., *Ber.* **8**, 143 (1875).
(2) Witt, O. N., Toeche-Mittler, S., *Ibid.*, **36**, 4390 (1903).

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FUNGICIDE RESIDUES

Determination of Lanstan Residues on Crops

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LANSTAN (1-chloro-2-nitropropane) is a broad-spectrum soil fungicide. It is particularly effective for the control of "damping off" diseases attacking emerging and emergent seedling cotton, *Fusarium* root rot of large-seeded legumes, and *Pythium ultimum* attacking sugar beets and red beets. The mode and rate of dissipation of Lanstan in soil are directed by the type of soil, temperature, amount of moisture, concentration, and other factors.

A sensitive method of analysis is required for registration of the compound for use on various crops.

The development of the method was complicated by the high volatility of Lanstan. The solution could not be concentrated by evaporation without substantial loss of the Lanstan.

Because of its extreme sensitivity and high selectivity, electron capture gas chromatography was found to be the best method for determining Lanstan in