spectrum of the azonaphthol shows a prominent molecular ion at m/e 316. When the experiment was run by using ^{15}N labeled sodium nitrate, the molecular ion was then observed at m/e 317. A substantial peak at M - 1 indicated that hydrogen loss is a major route for the molecular ion of the azonaphthol, but after correction for this, the azonaphthol was found to incorporate one ^{15}N essentially quantitatively. This shows that one nitrogen atom in the azonaphthol originates with the $NaNO_3$. Since the bacteria were shown to reduce nitrate to nitrite, this result provides additional confirmation for the diazonium ion pathway proposed in our previous paper (Corke et al., 1979) for the microbial transformations of anilines under anaerobic conditions.

Further studies are in progress to determine (1) the genesis of the other compounds (triazenes, azobenzenes and biphenyls) and (2) whether these model systems are operative in soils.

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Residues of Dibromochloropropane in Fresh and Preserved Peaches

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1,2-Dibromo-3-chloropropane (DBCP) was found at a level of 24.7 ppb in ripened peaches from orchards which had been fumigated 144 days prior to harvest. Peaches from trees in soil that was fumigated 270 days prior to harvest contained DBCP at 0.32 ppb. Peaches from nonfumigated orchards were found to contain either DBCP or a compound which could not be distinguished from DBCP at levels of 0.13–0.26 ppb. Peaches preserved in 1948, prior to the release of DBCP, were found to contain 0.25 ppb of DBCP. The compund present in the preserved peaches could not be differentiated from authentic DBCP by either gas chromatography or mass spectrometry. Background levels of this compound complicate determination of DBCP residues in fresh peach fruit.

1,2-Dibromo-3-chloropropane (DBCP) was used as a soil fumigant for nematode control in South Carolina peach orchards until its use was suspended pending cancellation hearings in Oct 1979. DBCP use was voluntarily canceled in March 1981 for all uses except pineapples in Hawaii. Voluntary cancellation was based on the toxic and carcinogenic nature of DBCP and preliminary findings that DBCP use could result in potential exposure from drinking water, potential exposure from food residues, and potential occupational exposure. Due to voluntary cancellation, reregistration of DBCP is a possibility based on further research presently being conducted by the EPA and other interested parties. After peach trees are planted, a nematicide such as DBCP is required in sandy soils of South Carolina to prevent decimation of peach orchards by peach tree short life (Chandler et al., 1962). Peach tree short life is less severe when soil fumigation is used before and after planting (Zehr et al., 1976), and DBCP was the only chemical which was labeled for fumigation after planting. The relative lack of reported information on DBCP residues in peach fruits as well as other crops where DBCP has been used (Newsome et al., 1977) led to the present study conducted to determine presence and persistence of DBCP in peach fruit.

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MATERIALS AND METHODS

Sample Collection. Samples of fresh peaches were colected from orchards where DBCP (a) had been used 14, 77, 144, and 270 days prior to harvest, (b) had been used but not within 365 days, and (c) had never been used. Peaches were collected in wide-mouth canning jars rinsed with ethyl acetate. Ethyl acetate rinsed aluminum foil was placed between the jar and lid. Samples were placed on dry ice immediately and kept frozen until extracted. Preserved peaches including those which predated the release of DBCP were obtained by asking South Carolina county extension agents to assist. County agents requested, through personal contact and organized meetings attended, that peach fruit documented as to the date of preservation be forwarded to this laboratory for study.

Extraction Procedure. The procedure obtained from the California Department of Food and Agriculture for extraction of DBCP was used with only minor modifications (Jackson and Fredrickson, 1978). The peaches (pits removed) were mixed with dry ice in a Waring blender and ground until a homogeneous friable mixture was obtained.

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The blender was washed and rinsed with distilled water and ethyl acetate prior to grinding each sample. The mixture was placed back into the canning jar, and ethyl acetate rinsed aluminum foil was used to cover the jar. Samples were placed in a freezer overnight to allow carbon dioxide sublimation.

Fifty grams of sample was combined with five ethyl acetate rinsed glass beads, 160 mL of distilled water, and 10 mL of ethyl acetate in a round-bottom boiling flask. The boiling flask was placed in a heating mantle and a modified Stark and Dean trap (Fisher Scientific Co.) and condenser were attached. Full voltage was applied until the mixture began to boil, and then the voltage was reduced to one-third of the maximum. The mixture was allowed to reflux for 15 min or until the ethyl acetate was distilled into the trap. The condenser was washed with distilled water and the mixture was cooled for 5 min at room temperature. The ethyl acetate layer was centrifuged for 10 min at 17500*g*. The ethyl acetate was then pipetted into an ethyl acetate washed screw-cap tube to which a small amount of anhydrous sodium sulfate was added. An aluminum foil liner rinsed with ethyl acetate was placed between the test tube and screw cap. Samples were kept in a freezer after extraction and prior to gas chromatographic analysis.

DBCP was extracted from preserved peaches in the same manner as described for fresh fruit.

Recovery precentages were determined by adding DBCP standards to samples and extracting as previously described. (DBCP was added to yield a final concentration of 5 pg of DBCP/μL in the extracted sample when 100% recovery was assumed.) A control sample (same source) with no added DBCP was extracted simultaneously, and the difference between the samples was used as the amount of DBCP recovered.

Gas Chromatography. The concentration of DBCP in peach samples was determined by using a Varian 3700 gas chromatograph connected to a CDS 111 chromatography data system and recorder. The gas chromatograph was equipped with a ^{63}Ni electron capture detector and a 2 m × 2 mm (inner diameter) glass column packed with 10% OV-101 on 80–100-mesh Chromosorb W-HP. The column temperature was held at 100 °C for 3 min, then increased at 4 °C/min for 7 min, then increased at 18 °C/min for 5.66 min, and finally held at 230 °C for 4.33 min for a total run time of 20 min. Temperature programming was used to decrease retention times of later eluting coextractants. Injector and detector temperatures were 220 and 280 °C, respectively. The nitrogen carrier gas flow rate was maintained at 30 mL/min. The retention time for DBCP was 5.75 min by using the preceding conditions, and the detection limit was 0.025 ppb at a S/N ratio of 2/1. The average recovery percentage was determined to be 88% and was entered into the calculation of DBCP present in the samples. Levels of DBCP were calculated by using the external standard method.

DBCP standards were made up in ethyl acetate by using a 99.6% analytical standard (AMVAC Chemical Corp.) and kept in a different freezer from the sample extracts. Caution should be exercised since DBCP is a potential carcinogen and mutagen (Babich et al., 1981). The gas chromatograph was calibrated by using a 5 pg of DBCP/μL standard as the first sample every day. Ethyl acetate blanks were run after every sample containing DBCP.

The presence of DBCP was confirmed by GLC using either a 2 m × 2 mm (inner diameter) glass column packed with 3% OV-210 on 80–100-mesh Chromosorb W-HP with column, injector, and detector temperatures of 75, 270, and 250 °C, respectively (DBCP retention time 2.1 min), or a 2 m × 2 mm (inner diameter) glass column packed with 2% DEGS on 80–100-mesh Chromosorb W/AW, with column, injector, and detector temperatures of 100, 250, and 250 °C, respectively (DBCP retention time 1.2 min). The nitrogen carrier gas flow rate was 30 mL/min for both columns, and the detection limit was 0.025 ppb at a S/N ratio of 2/1.

Selected samples were split between this laboratory and the Agricultural Chemical Services Laboratory, Clemson University. Agricultural Chemical Services samples were handled as described previously except that (1) the tissue was ground in a Hobart food chopper, (2) the distillate was not centrifuged, and (3) a Tracor gas chromatograph was used. The Tracor gas chromatograph was equipped with a ^{63}Ni electron capture detector and a 1.85 m × 4 mm (inner diameter) glass column packed with 3% OV-1 on 80–100-mesh Gas-Chrom Q. The column, injector, and detector temperatures were 90, 220, and 345 °C, respectively. The nitrogen carrier gas flow rate was maintained at 45 mL/min, and the DBCP retention time was 4.8 min. Confirmation samples were run on a 1.85 m × 4 mm (inner diameter) glass column packed with 5% OV-225 on 80–100-mesh Chromosorb W/AW-DMCS. The column, injector, and detector temperatures were 70, 220, and 345 °C, respectively. The nitrogen carrier gas flow rate was maintained at 60 mL/min, and the DBCP retention time was 5.5 min. The detection limit was 0.050 ppb, and the average recovery percentage was determined to be 96% at a S/N ratio of 2/1.

Mass Spectrometry Analysis. Selected samples were taken to Research Triangle Institute, Research Triangle Park, NC, for mass spectrometer analysis. Methane-enhanced negative ion chemical ionization mass spectrometer analysis was conducted on a LKB 2091 gas chromatograph–mass spectrometer equipped with a 25-m WCOT SE-30 capillary column which was used under the following conditions: column temperature, 100 °C for 4 min and then 8 °C/min to 240 °C; injector temperature, 210 °C; ion source temperature, 210 °C; electron energy, 50 eV; box current, 250 μA; accelerating voltage, 3.5 kV; helium flow, 1.8 mL/min; makeup gas, 13.2 mL/min; and reagent gas, methane, 10^{-4} torr. The appearance of the characteristic ions (m/z 79, 81, 158, 160, and 162) in the correct retention time window was used to confirm the presence of DBCP in the samples. Tentative confirmation was based on the observation of the m/z 79 and 81 ions in the correct retention window. Selected samples were concentrated before analysis by placing in ice with a stream of nitrogen flowing over them.

RESULTS AND DISCUSSION

Peaches from soil that was never fumigated with DBCP were shown to have between 0.1 and 0.3 ppb of DBCP (Table I). When samples were split with a second laboratory to rule out the possibility of contamination in the laboratory, similar results were obtained in both laboratories.

An explanation for the higher level of DBCP residue found in peaches from trees treated 144 days prior to harvest were compared with peaches from trees treated 14 or 77 days prior to harvest is impossible at this time. It could be a result of several factors such as soil type, amount of DBCP applied, method of application, temperature at time of application, or translocation in the tree.

Preserved peaches were collected for analysis for DBCP, including two samples preserved prior to the release of DBCP. As shown in Table II the samples preserved prior

Table I. DBCP Residues in South Carolina Fresh Peach Samples

DBCP treatment	no. of samples	mean DBCP concn, ppb	MS
treated 270 days prior to harvest	2	0.32	tentatively confirmed
treated 144 days prior to harvest	3	24.7	confirmed
treated 77 days prior to harvest	1	9.0	confirmed
treated 14 days prior to harvest	3	9.5	confirmed
treated 5 years prior to harvest	3	0.22	one not confirmed, two tentatively confirmed
never fumigated	2	0.13	tentatively confirmed
never fumigated	2	0.26	tentatively confirmed

Table II. DBCP Residues in Preserved Peaches in South Carolina

year preserved	replicates	mean DBCP concn, ppb	MS
1974	2	0.199	NR[a]
1963	2	0.057	NR
1959	2	ND[b]	NR
1953	2	0.083	tentatively confirmed
1948	4	0.252	confirmed

[a] NR = sample not run. Reagent blanks were shown to contain no DBCP. [b] ND = none detected.

to the release of DBCP (1953 and 1948) appeared to contain DBCP residues up to 0.3 ppb. Mass spectrometer analysis of selected samples extracted from fresh fruit and preserved fruit confirmed or tentatively confirmed DBCP in all the samples except one (Tables I and II). However, in the sample which was not confirmed, DBCP was tentatively confirmed in one replicate. No differentiation was obtained when the extract from the peaches preserved in 1948 was combined with a DBCP standard and injected into the mass spectrometer.

There appears to be either naturally occurring DBCP in peaches or a low level of a compound which cannot be distinguished from DBCP by the methods presently available. There may be a low-level residue of DBCP in peaches when it is applied while the peach fruit is on the tree. DBCP residues in peach fruit after the fall application were not different from the residues in peaches preserved in 1948. More research is required to determine the effect of fall fumigation on the presence of DBCP residues in peach fruit the following spring.

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Preprocessing Oxidative Washes with Alkaline Hypochlorite To Remove Ethylenebis(dithiocarbamate) Fungicide Residues from Tomatoes and Green Beans

William D. Marshall

A four-minute preprocessing wash with dilute alkaline hydrochlorite followed by a 30-s dip into dilute sodium sulfite was demonstrated to reduce field residues of ethylenebis(dithiocarbamate) (EBDC) and ethylenethiourea (ETU) on green beans and tomatoes, to the limits of analytical significance. Subsequent processing of the washed tomatoes into juice did not raise levels of ETU whereas boiling unwashed green beans resulted in significant ETU residues on the beans and in the cooking water. This decontamination technique is thus demonstrated effective on a second crop and for a second EBDC fungicide.

Previous work (Marshall and Jarvis, 1979) has demonstrated the effectiveness of an oxidative wash with dilute hypochlorite as a technique for removing ethylenebis(dithiocarbamate) (I) (mancozeb) residues from field tomatoes. Concern regarding the continued use of EBDCs in vegetable production centers on the possibility that residues present on the surface of field-treated crops may be converted to 2-imidazolidinethione (II) (ethylenethiourea, ETU) during normal industrial processing of the crop. The nonbiological conversion of EBDCs to ETU is accelerated thermally (Newsome and Laver, 1973; Watts et al., 1974; Marshall, 1977). The conversion of surface residues of EBDC by cooking, blanching, or other processing (involving heat treatment) has been demonstrated on a variety of crops: on snap beans (Newsome et al., 1975;

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