3,3',4,4'-TETRACHLOROAZOBENZENE AS A CONTAMINANT IN COMMERCIAL PROPANIL
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The toxic azo compound 3,3',4,4'-tetrachloroazobenzene (TCAB) is found as a contaminant
in commercial samples of 3,4-dichloroaniline (3,4-DCA), and presumably in herbicides prepared
from 3,4-DCA.1 TCAB bears a striking resemblance in molecular shape to the highly toxic
2,3,7,8-tetrachlorodibenzo-p-dioxin, and like the latter compound induces aryl hydrocarbon
hydrolase activity in mice and in chick embryos. TCAB is thought to be the agent responsible
for outbreaks of chloracne in workers involved in the manufacture of 3,4-DCA, and is in addition
a potential carcinogen.

Residues of TCAB have been detected2 in soils treated with the herbicide Propanil, which
is manufactured from 3,4-DCA.3 It has been supposed that the TCAB residues arise by the
following documented route (eq. 1).

Propanil 3,4-DCA TCAB

Propanil is known to be hydrolysed to 3,4-DCA4, which is further transformed microbially to TCAB.
A peroxidase mechanism has been proposed for this latter transformation5, but our recent work6
indicates that the reaction may involve a sequence of diazotisation, reduction, and coupling.

We therefore considered that a plausible source of at least some of the TCAB detected in
soils was as a contaminant in the original Propanil formulation. We now report our analysis of
samples of Propanil and of 3,4-DCA for their TCAB content. Since this project was begun,
Sundström et al have reported7 a similar study on the TCAB content of commercial samples of
Diuron and Linuron, both of which contain the 3,4-dichloroanilino moiety. The major difference
between our results and theirs is the vastly greater amount of the TCAB contaminant that we have
detected in our samples.

Experimental

An authentic sample of TCAB was prepared by AgO oxidation8 of 3,4-DCA, m.p. 156-157°;
λ max (ligroin) 443 nm, ε 680; mass spectrum m/e 318 (M+), 173 (C6H3Cl2N2+), 145 (C6H3C12+).

The extraction of TCAB from 3,4-DCA or from Propanil was based on our purification
procedure for 3,4-DCA, which involves chromatography over alumina, discarding the first eluting
orange eluant followed by recrystallisation. In the standard procedure, duplicate 2.0 g samples
of the test material were dissolved in benzene-ligroin and chromatographed over 25 g of alumina
until all the yellow material had eluted. The eluant was checked for TCAB content by tlc on
silica gel and by mass spectrometry. Quantitation was by visible spectrophotometry at 443 nm,
and confirmed by quantitative glc using a 10' x 1/8" column of 2.5% SE30 on acid-washed
Chromosorb W at 205°. The results are in Table 1.

Conclusions

Commercial samples of 3,4-DCA and of Propanil contain variable, but sometimes substantial
quantities of TCAB as a contaminant. The amounts of TCAB present in Propanil formulations are
typically hundreds of times greater than those found in the dichlorophenylurea herbicides by Sandström et al. This raises the distinct possibility that some of the TCAB detected in Propanil treated soils may have been deposited there along with the herbicides rather than having been formed exclusively by a biological route. TCAB applied to soil in this way might be especially resistant to biodegradation because of its very low water solubility. We are currently studying the persistence of TCAB in soils, both as applied chemically and also when it is formed biologically from 3,4-DCA. However, our studies on the biological transformation of 3,4-DCA indicate that only a very small percentage of the original aniline is converted to the azocompound. Consequently it would seem that the problem of TCAB build up in Propanil treated soils could largely be eliminated by controlling the amount of the contaminant originally present in the herbicide. By contrast, TCAB build-up in soils treated by the dichlorophenylurea herbicides should be much less of a problem in that these herbicides contain so much less of the contaminant.

Acknowledgement

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TABLE 1. TCAB Content of 3,4-Dichloroaniline and of Propanil

<table>
<thead>
<tr>
<th>Sample</th>
<th>TCAB mg per gram by spectrophotometry</th>
<th>by glc</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4-DCA, Manufacturer 1</td>
<td>8.6</td>
<td>8.5</td>
</tr>
<tr>
<td>3,4-DCA, Manufacturer 2</td>
<td>&lt;0.1</td>
<td>0.09</td>
</tr>
<tr>
<td>3,4-DCA, Manufacturer 3</td>
<td>&lt;0.1</td>
<td>0.06</td>
</tr>
<tr>
<td>Propanil, unknown Technical (granular)</td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Propanil, Manufacturer 4, emulsifiable liquid</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Propanil, Manufacturer 4, emulsifiable liquid</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Propanil, Manufacturer 4, emulsifiable liquid, research sample</td>
<td>2.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

References and Notes

3. Herbicide Handbook, Third Edition, Weed Science Society of America, 1974, p. 333. In this paper, the name Propanil does not imply a single manufacturer, but is used generically for 3,4-dichloropropionanilide.

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