Trebst A, Harth E & Draber W. On a new inhibitor of photosynthetic electron transport in isolated chloroplasts. *Z. Naturforsch.* 25b:1157-9, 1970.
[Abt. Biologie, Ruhr-Universität Bochum und Farbenfabriken Bayer, Forschungszentrum, Wuppertal-Elberfeld, Germany]

The plastoquinone analogue dibromothymoquinone, better known as DBMIB, turned out to be the first effective inhibitor of plastoquinol oxidation in photosynthesis—at a new inhibition site at the then not yet defined cytochrome b_6/f-complex. [The *SCI*® indicates that this paper has been cited in more than 240 publications.]

Herbicide and Photosynthesis Research

A. Trebst
Department of Biology
Ruhr-University
D-4630 Bochum 1
Germany

The prediction and synthesis of new chemical structures for potential herbicides and the chemistry of quinones has been Wilfried Draber's successful metier in the Bayer Chemical Company since his thesis time. He had synthesized halogenated benzoquinones as possible crosslinkers for the SH groups in the chemical synthesis of insulin. These quinone derivatives also seemed promising candidates for photosystem II herbicides because these inhibitors might be predicted to interfere specifically with plastoquinone reduction.

We routinely tested his compounds for possible inhibition of photosynthetic electron flow in isolated chloroplast membranes: a quick screening for photosynthesis herbicides. Already one of his first halogenated benzoquinones, dibromothymoquinone, abbreviated DBMIB for dibromo-methyl-isopropyl-benzoquinone, was a hit. We checked it in provisional laboratories in the newly founded University of Bochum, still under construction, where I had just moved to from Göttingen to take the chair of plant biochemistry.

First, though, to our disappointment, DBMIB was not a good photosystem II inhibitor, as a promising herbicide should and how the many commercial photosystem II herbicides indeed do. But it caught the attention of the able technician, Erich Harth, that although the compound was poorly inhibiting in the routine screening (with ferricyanide as acceptor) and—rather perplexing—with less potency at higher concentrations, it did inhibit in another test system (methylviologen as acceptor).

We began to realize that we got an inhibitor somewhere beyond photosystem II at a new inhibition site not well definable at that time. PS II checked with ferricyanide is not very sensitive to DBMIB, and at higher concentrations it becomes even a reasonable artificial electron acceptor of photosystem II. This way bypasses its own (second) inhibition site. But, it does effectively inhibit the reoxidation of plastoquinol—by the cytochrome b_6/f-complex not known at the time.

When, several years later, the existence of this integral complex was established,[1] the inhibition site was specified at its Rieske iron sulfur center.[2] DBMIB proved, and still is,[3] very useful for photosynthesis research. It specifically knocks out the cytochrome b_6/f-complex and makes it possible to test photosystem II activity separate from the rest of the electron flow system.

DBMIB led in 1973 to the discovery of a second coupling site in photosynthesis.[4,5] This second ATP formation site at the water splitting reaction of photosystem II is still not fully appreciated in all textbooks. DBMIB is now commercially available, but for many years our lab was the only source that freely distributed about a hundred grams of DBMIB for many that requested it. As they used it successfully and quoted us in return, our short paper became a *Citation Classic*.

The original challenge to design a new herbicide did eventually lead to a new effective group of photosystem II inhibitors (some herbicides) represented by bromonitrothymol—indeed, a close relative of a bromothymoquinone.[6] The paper demonstrates a long and still continuing close interaction of herbicide and photosynthesis research in industry and university.

1. **Hauska G, Hurt E, Gabellini N & Lockau W.** Comparative aspects of quinol-cytochrome c/plastocyanin oxidoreductases. *Biochim. Biophys. Acta* 726:97-133, 1983. (Cited 230 times.)
2. **Chain R K & Malkin R.** On the interaction of 2,5-dibromo-3-methyl-6-isopro-pyl-benzoquinone (DBMIB) with bound electron carriers in spinach chloroplasts. *Arch. Biochem. Biophys.* 197:52-6, 1979.
3. **Barber J.** *The light reactions, topics in photosynthesis. Volume 8.* Amsterdam, The Netherlands: Elsevier, 1987.
4. **Izawa S, Gould J M, Ort D R, Felker P & Good N E.** Electron transport and photo-phosphorylation in chloroplasts as a function of the electron acceptor. *Biochim. Biophys. Acta* 305:119-28, 1973. (Cited 125 times.)
5. **Trebst A & Reimer S.** Properties of photoreductions by photosystem II in isolated chloroplasts. *Biochim. Biophys. Acta* 305:129-39, 1973. (Cited 110 times.)
6. **Trebst A & Draber W.** Structure activity correlations of recent herbicides in photosynthetic reactions. (Geissbuhler H. ed.) *Advances in pesticide science, part 2.* Oxford, England: Pergamon Press, 1979. p. 223-34.

Received August 15, 1991