Identification of Endosulfan Based on the Products of Laboratory Photolysis[1,2]

by TERYL B. PUTNAM, DONALD D. BILLS, and LEONARD M. LIBBEY
Department of Food Science and Technology
Oregon State University
Corvallis, Oreg. 97331

Endosulfan (Thiodan®), an insecticide used in crop protection, is a mixture of two isomers, α and β (Figure 1), present in a ratio of 7:3, respectively.

In this study, the endosulfan isomers were individually exposed to a laboratory ultraviolet (UV) lamp, and the photolytic products were separated by gas chromatography (GC). The purpose of this work was to investigate the possibility of obtaining "fingerprint" GC patterns of photolytic products which might aid in the routine identification of a few ng of endosulfan. As a matter of interest, mass spectrometry (MS) was used to characterize some of the photolytic products.

METHODS

Separations of α- and β-endosulfan and their photolytic products were carried out with a F & M Model 810 GC equipped with a tritium electron capture detector and a 122 cm x 4 mm I.D. glass column packed with 2% SE-30/2% QF-1 on Anakrom ABS 70/80 mesh. The injector, column, and detector temperatures were 210° C, 180° C and 200° C, respectively. Argon-methane (95:5) was used as the carrier gas with a column flow of 60 ml/min.

A Hanovia medium-pressure mercury lamp, No. 616A (Englehard-Hanovia, Inc., Newark, NJ) was used for irradiating separately the α- and β-isomers of endosulfan. As described by KAUFMAN et al. (1972), the individual isomers were trapped at the end of the GC column in a Teflon tube cooled with dry ice, then, following the addition of 50 µl of hexane (Mallinkrodt, Nanograde), irradiated for the shortest time required to yield approximately equal GC peak areas for the most abundant photolytic product and the remainder of the parent compound when aliquots of the hexane solution were re-chromatographed. Quantities of endosulfan isomers trapped and irradiated varied from 25 ng to 75 ng.

Mass spectral analyses were performed on a Finnigan 1015C GC-MS system. The operating conditions were: column temperature 180°; injector 238° C; helium carrier gas flow rate 60 ml per minute; filament current, 300 µA; electron voltage, 70 eV; interface 210° C, manifold, 150° C; and analyzer pressure, 5 x 10^{-5} torr. Scans were made from

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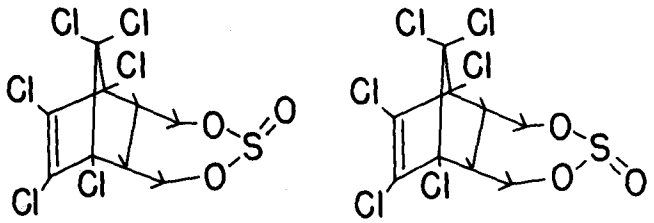
m/e 28 to m/e 465 in one second. A 200 cm x 6.3 mm I.D. glass column packed with 2% SE-30/2% QF-1 on Chromosorb G 70/80 AW was used.



α-endosulfan β-endosulfan

Figure 1. Structures of α-endosulfan and β-endosulfan.

RESULTS AND DISCUSSION

Figure 2 represents the typical gas chromatograms of endosulfan (2a), irradiated α-endosulfan (2b) and irradiated β-endosulfan (2c). The GC retention times and irradiation exposures for the two isomers are shown in Table 1.

α-Endosulfan was photolyzed to yield three new GC peaks labeled A_1, A_2, and A_3. β-Endosulfan yielded four new peaks labeled B_1, B_2, B_3, and B_4. MS analysis suggests that Peak A_3 could result from the loss of Cl and H_2S from endosulfan, giving a m/e of 335. Peaks A_1 and A_2 as well as B_1 and B_4 were not present in quantities large enough to obtain strong mass spectra. Peak B_3 has an m/e of 287 and could possibly result from the loss of $[Cl + SO_2 + H_2O]^+$ from the parent at m/e 404.

Peak B_2 was identified as α-endosulfan by comparison of retention times and MS. Based on retention times, Peaks A_3 and B_1 may be the same compound.

SAFE and HUTZINGER'S (2) MS analysis of both endosulfan isomers gave virtually identical spectra with a molecular ion peak at m/e 404, relatively weak ions at m/e 369 and m/e 356, and more intense m/e 337, m/e 327, m/e 311, and m/e 299 ions. In our MS analysis of α- and β-endosulfan, identical spectra were obtained, with a molecular ion peak at m/e 404, relatively weak ions at m/e 311 and m/e 327 and more intense m/e 321 and m/e 305 ions.

SCHUMACHER, et al., (3) irradiated α-endosulfan in hexane and β-endosulfan in dioxane/water and found that each gave one main irradiation product with a molecular weight of 370. α-Endosulfan also gave weak ion fragments at m/e 335, m/e 322, m/e 303 and m/e 287. Their inability to degrade β-endosulfan in hexane could have been due to the use of UV

irradiation of wavelengths greater than 300 nm, whereas our work was carried out with a wider spectrum of wavelengths including shorter wavelengths to 222 nm.

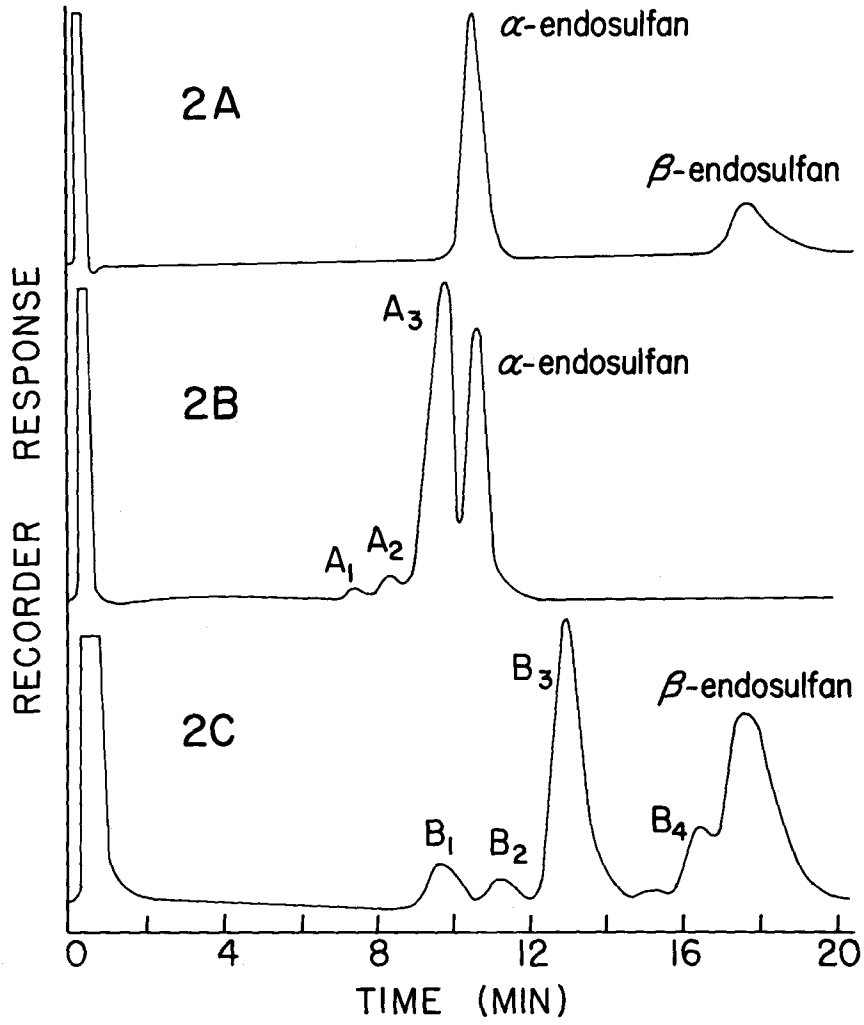


Figure 2. Chromatograms of endosulfan (2a), irradiated α-endosulfan (2b) and irradiated β-endosulfan (2c).

The photolytic products resulting from irradiation of α- and β-endosulfan by our procedure form characteristic GC "fingerprint" patterns which would be useful for routine confirmation of the identity of endosulfan without resorting to MS. Smaller laboratories without MS capability could easily be equipped to carry out such an analysis.

TABLE 1

Retention time and irradiation exposure of α- and β-endosulfan.

Peak	Retention time relative to aldrin	Retention time (min)	Irradiation time (sec)
α-endosulfan	1.87	11	135
β-endosulfan	3.07	18	190

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