Photodegradable Formulations of DDT[1]

B. S. Parmar, S. Y. Pandey and S. K. Mukerjee

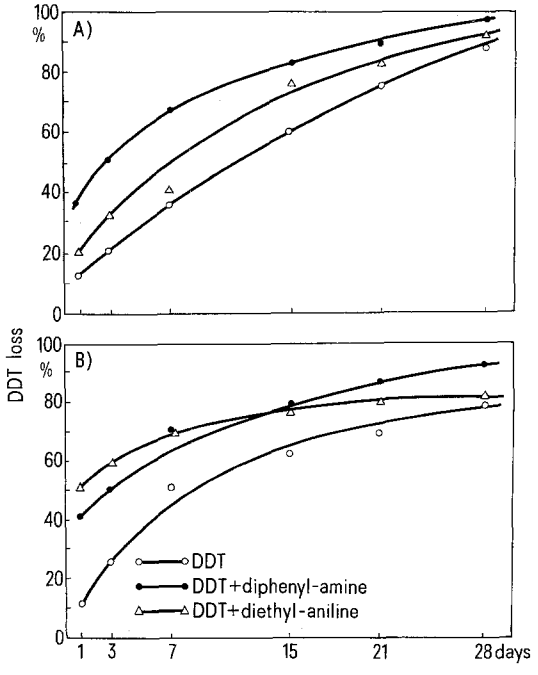
Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110012 (India), 18 June 1975.

Summary. The incorporation of diphenylamine and diethylaniline in commercial DDT-WDP formulations sprayed on *Phaseolus aureus* and *Tabernaemontana coronaria* revealed that both these chemicals enhanced the initial rate of loss of DDT. Both these sensitizers exhibited no immediate adverse effect on the storage stability, pH, sieve requirement and colour of the formulations and introduced no phytotoxicity. Diphenylamine addition, however, had some adverse effects on the suspensibility.

The contribution of DDT to the welfare of mankind is undoubtedly far more than that of any other pesticide developed till date. The major defect for its being branded as an environment pollutant is its persistent character. Mitigation of this effect may be problematic once DDT finds its way into soil or body fat. However, there is a possibility of enhancing its degradation on surfaces exposed to light by combining it suitably with photosensitizers.

Effect of diphenylamine and diethylaniline on some of the characteristics of DDT water dispersible powders (DDT: sensitizer, 1:1)

Characteristic	DDT	DDT + diphenylamine	DDT + diethylaniline
Storage stability (under all tried containers)	Stable	Stable	Stable
Suspensibility (%)	78.0	60.8	75.7
pH	9.00	8.95	9.00
Sieve requirement (200 mesh)	100% passes	100% passes	100% passes
Colour	Cream	Cream	Cream
Phytotoxicity	Nil	Nil	Nil



Effect of diphenyl-amine and diethyl-aniline in enhancing the photodegradation of DDT on plants. A. *Phaseolus aureus*. B. *Tabernaemontana coronaria*.

Useful leads in this direction have been obtained by various workers[2–7] in extensive laboratory and/or field studies, and a number of sensitizer chemicals have been reported. Practical utilization of these results necessitates an investigation of the performance of these photosensitizers when incorporated into the commercial DDT compounds, and their effect on the physico-chemical characteristics of such compounds. This aspect has been investigated in the present communication.

Materials and methods. Literature revealed that 2 sensitizers, namely diphenylamine and diethylaniline, were quite efficient in bringing about photodegradation of DDT. These were, therefore, used as the test sensitizers. For spraying on plants, a suitable amount of commercial 50% DDT water dispersible powder formulation (DDT-WDP) was taken so as to get a 0.1% DDT suspension in water. In sensitizer treatments, the sensitizers were added in finely powdered or neat liquid form maintaining a DDT: sensitizer ratio of 1:1. The well shaken suspensions were sprayed with a hand sprayer (Ganesh pneumatic) on the leaves of *Phaseolus aureus* and *Tabernaemontana coronaria* in 2 replications in the field. Concomitant controls were run simultaneously. Sampling was done by random picking of 5 leaves at 0,1, 3, 7, 15, 21 and 28 days interval. 20 circular discs (diam. 10 mm) were cut out of these leaves and crushed together with anhydrous sodium sulphate in a glass pestle mortar. The resultant substance was extracted in *n*-hexane, and the extract cleaned through a column containing layers of anhydrous sodium sulphate, activated charcoal and anhydrous sodium sulphate. The extracts were finally made upto 50 ml and analyzed by GLC (Tracor MT 220 gas chromatograph) using Ni^{63} electron capture detector. A U-shaped $6' \times 1/4''$ O.D. glass column packed with 3% OV-1 coated on 80/100 mesh chromosorb-W was used. Column temperature 200 °C; detector temperature 250 °C; carrier gas, N_2, 80 ml/min, were found satisfactory for the analysis.

The effect of these photosensitizers on some of the physico-chemical characteristics of laboratory prepared DDT-WDP compounds was investigated, maintaining a DDT: sensitizer ratio of 1:1. The storage stability was investigated up to 1 month under room storage (diffused light) conditions in transparent and coloured glass bottles, as well as white and black polyethylene bags. The samples, drawn periodically, were analyzed by GLC as given in detail above. The samples were considered stable when

[1] Contribution No. 103.
[2] G. W. Ivie and J. E. Casida, Science *167*, 1620 (1970).
[3] G. W. Ivie and J. E. Casida, J. agric. Fd. Chem. *19*, 405 (1971).
[4] L. L. Miller and R. S. Narang, Science *169*, 368 (1970).
[5] L. L. Miller, R. S. Narang and G. D. Nordblom, J. org. Chem. *38*, 340 (1973).
[6] A. R. Mosier, W. D. Guenzi and L. L. Miller, Science *164*, 1083 (1969).
[7] G. W. Ivie and J. E. Casida, J. agric. Fd. Chem. *19*, 411 (1971).

GLC failed to reveal any additional peak compared to reference samples of DDT and sensitizers. The suspensibility was determined by WHO/SIF/1.R_3 (1967) method[8]. Glass cylinders wrapped in black carbon paper were used for the purpose. To avoid sensitizer interference during the colour change at end point of titration, the solution, after precipitating AgCl, was extracted with petroleum ether. This removed the sensitizers. pH of 1:5 (compound:water) suspensions was measured using a line operated, glass electrode pH meter. Sieving requirement after accelerated storage was determined as per WHO/M/4 method[8]. Colour after storage (since sensitizers attain colour on exposure to light) and phytotoxicity symptoms of compounds were visually observed. Phytotoxicity observations were made against rice, cowpea, wheat, moong and a few ornamentals.

Results and discussion. The results in the Figure reveal that both diphenylamine and diethylaniline enhance the photodegradation of DDT. The enhancement is initially more; almost 30–40% more DDT being lost in sensitized compounds compared to DDT in the control. The subsequent slowing down of the rate could be attributed to the volatile nature of these amine sensitizers. The relative efficiency of these sensitizers seems to be influenced by plant surfaces. An overall better performance is also apparent with diphenylamine.

It is seen from observations reported in the Table that incorporation of diphenylamine or diethylaniline in the compounds neither affects their storage stability, pH, sieve requirement and colour, nor introduces any phytotoxicity. However, the addition of diphenylamine lowers the suspensibility, which, though still marginally above the WHO prescribed limit of 60%, could be a slight cause of concern.

[8] W. H. O., *Specifications for Pesticides used in Public Health*, 3rd edn. (W.H.O., Geneva 1967), p. 80 and 253.

A Possible Chemical Basis for the Higher Mutagenicity of Marijuana Smoke as Compared to Tobacco Smoke

M. NOVOTNY[1], M. L. LEE and K. D. BARTLE[2]

Department of Chemistry, Indiana University, Bloomington (Indiana 47401, USA), and Department of Physical Chemistry, University of Leeds (England), 22 September 1975.

Summary. The results of comparative analyses of polynuclear aromatic hydrocarbons in marijuana and tobacco smoke indicate a considerably higher content of potential carcinogens in the former. A model experiment involving Δ^9-tetrahydrocannabinol suggests that the pyrolysis products of cannabinoids are major contributors to the polynuclear aromatic hydrocarbons.

Certain adverse effects of marijuana smoking observed both clinically and in laboratory experiments are bronchial irritation and the action of smoke in lung tissue that produces biochemical and cellular abnormalities characteristic of the early stages of cancer[3]. Leuchtenberger et al.[4–6], studied the effects of marijuana and tobacco smoke, passed under standard conditions over mouse[4] and human[4,6] lung explants, on DNA synthesis and chromosomal complement. More pronounced abnormalities from marijuana smoke were observed.

Obviously, a chemical basis must exist for the above observed phenomena. Although many details concerning the complex chemistry of marijuana smoke have been so far unavailable because of purely methodological reasons (e.g., the problems of chromatographic resolution and identification methods), we have chosen to investigate the occurrence of the potent carcinogens, polynuclear aromatic hydrocarbons, in marijuana smoke condensate as the primary objective. Detailed structural studies performed in our laboratory (using liquid-chromatographic methods, NMR-spectroscopy, and the combination of high-resolution gas chromatography-mass spectrometry) resulted in identification of over 150 polynuclear aromatic hydrocarbons in marijuana smoke condensate. The results were further compared with those obtained with smoke condensate from an equal amount of standard high-tar tobacco cigarettes.

Cigarettes prepared from equal weights of Mexican marijuana (standard material obtained from the National Institute of Mental Health, Rockville, Maryland; the content of Δ^9-tetrahydrocannabinol: 2.8%) and standard tobacco cigarettes (from Tobacco-Health Research Institute, University of Kentucky, Lexington, Kentucky) were smoked by means of a standard smoking machine[7] and smoke collected. Approximately 2,000 cigarettes from each were used in the pilot study. Smoke condensates were further processed by a modified previously reported fractionation procedure[8].

Total weights of the polynuclear aromatic fractions containing 3 rings and greater were 73.7 mg and 56.9 mg for marijuana and tobacco, respectively. High-resolution gas chromatography using a glass capillary column and precolumn concentration technique (Figure 1) shows the profiles of polynuclear aromatic hydrocarbons for both materials within the volatility range of tricyclic to hexacyclic molecules. The profile comparison indicates a larger proportion of heavier polynuclears encountered in mari-

[1] We thank Dr. JOHN BENNER and Ms. CAROLYN KEENE of the University of Kentucky for help with the smoking experiments. This work was supported by Grant No. R01-DA-00507-01 from the National Institute of Mental Health.

[2] Department of Physical Chemistry, University of Leeds, Leeds, England.

[3] T. H. MAUGH II, Science *185*, 683 (1974).

[4] C. LEUCHTENBERGER and R. LEUCHTENBERGER, Nature, Lond. *234*, 227 (1971).

[5] C. LEUCHTENBERGER, R. LEUCHTENBERGER and A. SCHNEIDER, Nature, Lond. *241*, 137 (1973).

[6] C. LEUCHTENBERGER, R. LEUCHTENBERGER, U. RITTER and N. INUI, Nature, Lond. *242*, 403 (1973).

[7] F. SEEHOFER and J. E. MILLER, Beitr. Tabakforsch. *3*, 75 (1965).

[8] M. NOVOTNY, M. L. LEE and K. D. BARTLE, J. Chromatogr. Sci. *12*, 606 (1974).