

Note

Derivatization of Oryzalin for characterization by gas chromatography-mass spectrometry*

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Surflan® or Oryzalin (the formulation of 3,5-dinitro-N⁴,N⁴-dipropylsulfani-
lamide) is a broad spectrum and selective preemergent herbicide with international
utility. It disrupts mitosis¹ in the meristematic cells of seedling plants by inhibiting
the formation of microtubules.

Its solubility² is *ca.* 2.5 µg g⁻¹ at 25°C and LD₅₀ is greater than 10,000 mg
kg⁻¹. Many dinitroanilines are also indicated to be strongly adsorbed³ on soil. Be-
cause of its water solubility and adsorption on soil particles sediment-water run-off
can cause field losses of the herbicide. Such behavior may pose potential hazard to
aquatic fauna if abnormal amounts of the chemical are released into the environment.
The herbicide was also implicated at one time to cause human birth defects in children
of parents claimed to be exposed to this chemical⁴. In order to gather information
regarding its occurrence, distribution and fate in soil, water, plants and animals, a
general derivatization method is required for the herbicide, since the intact chemical
does not possess good gas chromatographic properties. The resulting derivative has
to be stable, efficiently formed at the microgram level and amenable to character-
ization by combined gas chromatography-mass spectrometry (GC-MS). The di-N-
methyl derivative has been well-recognized and conversion of Oryzalin to this de-
rivative has been long used for gas chromatographic determination of the herbicide
residues in various matrices⁵⁻⁷. The conventional method⁷ for preparing this deriva-
tive involves alkylation of the herbicide in presence of sodium carbonate and incu-
bating overnight, and is long and time-consuming. An alternative and rapid proce-
dure to prepare the same derivative has recently been reported¹¹. Impetus for the
present work stems from the obvious need to study its MS properties to aid char-
acterization and determination of the herbicide. It is believed to be the first report
on this aspect, since no report published in the literature or existing otherwise is
known to the authors.

In the present work we report the use of strongly basic dimethylsulfinyl anion
and methyl iodide to prepare the N-methylated derivative of Oryzalin and examine
its GC and MS pattern based on electron impact (EI) and chemical ionization (CI).

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mond, VA 23220, U.S.A.

EXPERIMENTAL

Oryzalin was obtained from Pesticides and Industrial Chemicals Repository of U.S. Environmental Protection Agency. Dimethyl sulfoxide (DMSO) (analytical reagent grade) was purchased from Mallinckrodt (St. Louis, MO, U.S.A.) and sodium hydride (dry or 50% dispersion in mineral oil) from Alfa Div., Ventron (Danvers, MA, U.S.A.). Pesticide-grade solvents were used throughout.

*Preparation of dimethylsulfinyl anion*⁸⁻¹⁰

Dimethylsulfinyl anion was prepared by the reaction of sodium hydride (0.5 g if it is dry and 1.0 g with 50% dispersion in mineral oil) and 5 ml dry DMSO. The technique was essentially the same reported elsewhere¹¹, and the only modifications applied in the present study were in scaling down the quantities of materials. Substitution of potassium hydride for sodium hydride has been reported¹² to be better with the advantages that the anion can be prepared rapidly and without heating.

Derivatization with dimethylsulfinyl anion

The solution or extract of sample containing Oryzalin was taken up with *ca.* 0.5-ml DMSO and concentrated all the way to *ca.* 0.5 ml in a serum bottle and allowed to react with 0.5 ml of dimethylsulfinyl anion solution in a nitrogen atmosphere for *ca.* 10-15 min, followed by alkylation with 2-3 ml of methyl iodide. The procedure adopted was the same as described previously¹¹. A suitable microliter aliquot of the derivatized herbicide in hexane was taken up for analysis by GC-MS.

GC

GC was performed on a Hewlett-Packard (Avondale, PA, U.S.A.), Model 5840A instrument equipped with a ⁶³Ni electron-capture detector and using a 1.83 m × 4 mm I.D. glass column packed with 1.95% QF-1 + 1.5% OV-17 on 80-100 mesh Gas-Chrom Q (Applied Science, PA, U.S.A.) at 225°C or 3% OV-17 on the same kind of support at 175°C with a carrier argon-methane (95:5) gas flow-rate of 60 ml min⁻¹. Alternatively, GC was also performed on a Hewlett-Packard 5880A gas chromatograph equipped with a nitrogen-phosphorus detector operating with a hydrogen flow-rate of 5 ml min⁻¹ and an air flow-rate of 50 ml min⁻¹. Voltage to detector was adjusted for *ca.* 10% at attenuation 2². A 1.83 m × 2 mm I.D. glass column packed with 1.95% QF-1 + 1.5% OV-17 on 80-100 mesh Gas-Chrom Q was used at temperature 225°C and a nitrogen carrier gas flow-rate of 30 ml min⁻¹.

MS

A Finnigan 4021 GC-MS instrument in the positive ion mode was used. Samples were introduced through the gas chromatograph equipped with a 1.83 m × 2 mm I.D. glass column of 3% OV-17 packings under the following conditions: helium carrier gas flow-rate of 20 ml min⁻¹, an injection volume of 1 μl, an injection port temperature of 250°C and a column oven temperature of 225°C. EI mass spectra were obtained at 70 eV. CI studies were conducted with methane reagent gas at ionizing gas pressure of 0.2 Torr.

RESULTS AND DISCUSSION

The principles of the derivatization reaction and the relative advantages of the operation were discussed¹¹. The detection limit of the herbicide derivatized to its di-N-methylated compound is 0.05 ng on electron-capture detection (ECD) and 1 ng on the nitrogen-phosphorus detection (NPD). ECD in the present case is more sensitive than NPD, but the latter is far more convenient and practical in view of the fact that removal of the last traces of DMSO is far from facile, and trace amounts of DMSO may cause enormous interference when ECD is used. The retention time of the derivatized herbicide was 4.6 min on 3% OV-17 column, and 6 min on 1.95% QF-1 + 1.5% OV-17 under the conditions employed.

The structure of Oryzalin is shown in Fig. 1. When complete N-methylation is achieved the resulting derivative N¹,N¹-dimethyl-3,5-dinitro-N⁴,N⁴-dipropylsulfanilamide (molecular weight 374) should have the structure shown in Fig. 2. The EI

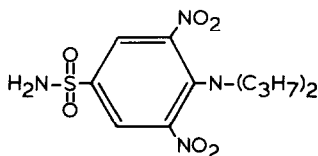


Fig. 1. The structure of Oryzalin.

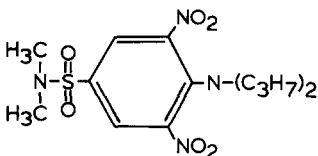


Fig. 2. The structure of the di-N-methyl derivative of Oryzalin.

mass spectrum of the compound is shown in Fig. 3. The EI mass spectrum gives the molecular ion M^+ at m/e 374, and the base peak at m/e 345 which is $(M - C_2H_5)^+$ ion. The line at m/e 357 occurs due to $(M - OH)^+$ ion. The line at m/e 329 can be rationalized by $(M - CH_3NO)^+$ ion or $(M - C_2H_5O)^+$ ion and the line at m/e 303 can be explained by the loss of CH_3CH_2 radical followed by subsequent rearrangement and elimination of $CH_3 - CH = CH_2$.

Additional confirmation of the structure is derived from methane CI mass spectrum shown in Fig. 4. The base peak is at $(M + 1)^+$ having m/e 375. The sequence for $(M + 29)^+$ at m/e 403 and $(M + 41)^+$ at m/e 415 are also present to confirm the assignment of m/e 375 as the $(M + 1)^+$ ion.

It should be mentioned that the assignment of various fragmentation ions are only tentative, since the precise confirmation needs spectra acquisition with exact mass measurements and/or linked scans.

The ease of formation of the di-N-methyl derivative of Oryzalin, quantitative-ly, and the presence of the $(M - 29)^+$ ion as the base peak in EI mass spectrum and

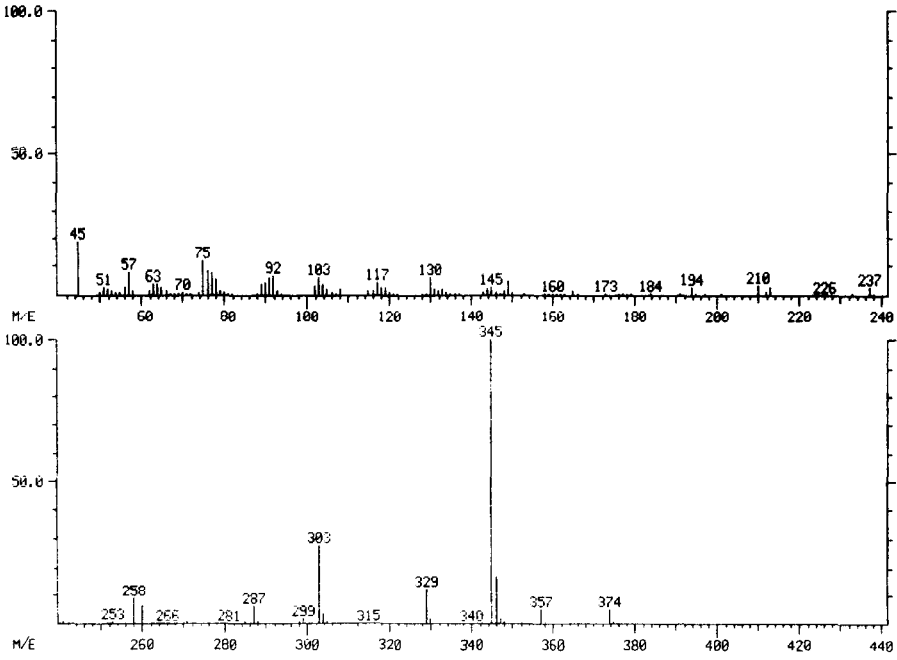


Fig. 3. EI mass spectrum for derivatized Oryzalin.

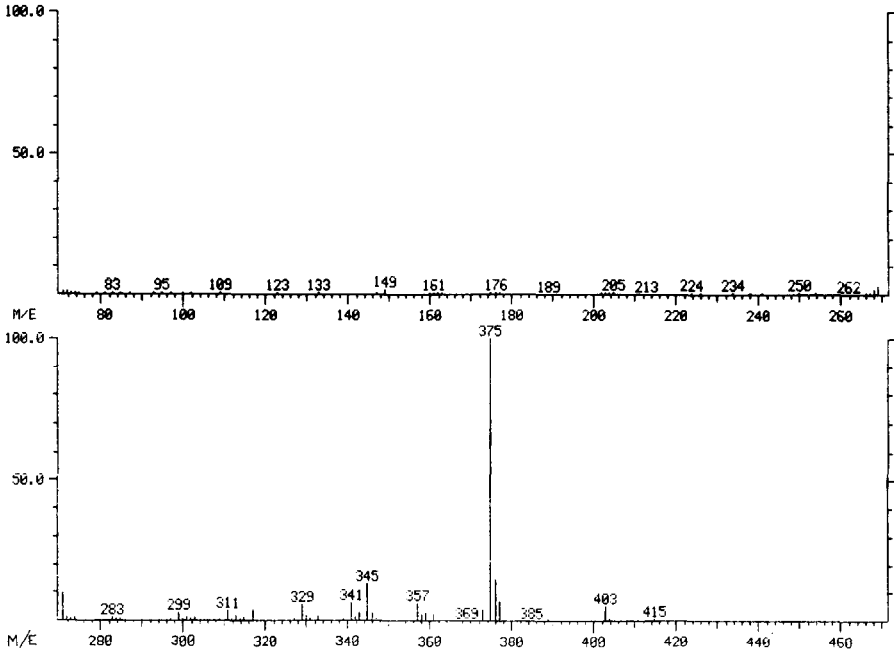


Fig. 4. Methane CI mass spectrum for derivatized Oryzalin.

the $(M + 1)^+$ ion as the base peak in the CI mass spectrum have potential and advantageous use for detection of Oryzalin by ion monitoring in low concentration and in complex mixtures.

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