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Identification and Quantitation of Disulfoton in Urine and Blood of a Cadaver by Gas Chromatography/Mass Spectrometry

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Abstract. We have experienced an autopsy case suspected to have died of disulfoton intoxication. The identification and quantitation of disulfoton in his urine and blood were successfully performed by gas chromatography/mass spectrometry. It could be concluded, together with the findings obtained from autopsy and histology, that disulfoton caused his death.

Key words : Toxicology, Disulfoton, Organophosphate insecticides, Gas chromatography/mass spectrometry

Introduction

Gas chromatography/mass spectrometry (GC/MS) is one of the most powerful methods for identification and quantitation of toxic substances.

Recently, we have experienced an autopsy case, which was suspected to die of intoxication by disulfoton, an organophosphate pesticide. In this paper, we report that this compound was successfully identified and quantitated in urine and blood of this cadaver by GC/MS. To our knowledge, this is the first report to identify disulfoton by GC/MS for a medicolegal purpose, although some reports dealing with mass spectrometric comparison of authentic organophosphate pesticides have appeared.¹⁾⁻⁴⁾

Materials and Methods

Authentic disulfoton was purchased from Wako Pure Chemical Industries, Ltd., Osaka.

A 0.2 ml aliquot of urine or blood was homogenized with a glass homogenizer fitted with a Teflon pestle in 10 ml of acetonitrile, and centrifuged at 3000 r.p.m. for 5 min. To

the clear supernatant, were added 20 ml of water, 5.0 ml of saturated NaCl solution and 10 ml of *n*-hexane. After shaking the mixture vigorously for 5 min, it was left for 5 min for precipitation. The clear organic phase was removed and the same extraction procedure with *n*-hexane was repeated twice. The combined organic extracts were evaporated to dryness and the residue was dissolved in 1.0 ml of acetonitrile. This was used as a test sample for the GC/MC analyses. After this extraction procedure, 70-90% of disulfoton could be recovered, when 0.2 μ g of disulfoton was added to 0.2 ml of urine or blood.

The analyses were carried out on a JEOL D-300 GC/MS instrument equipped with a computer-controlled data analysis system. The GC separation was made on a 2.0 m \times 2 mm glass column packed with 10% Silicon DC-200P on 60/80 mesh Uniport HPS (Gasukuro Kogyo Co., Ltd., Tokyo). The GC conditions were: injection temperature 240°C, column temperature 200°C and helium flow rate 30 ml/min. The MS conditions were: electron energy 70 eV, ionization current 300 μ A, separator temperature 200°C and ion source temperature 170°C.

Results and Discussion

A male of about 30 years was found dead with bubbling saliva from his open mouth at a hotel in Osaka on Dec. 10, 1980. Strong rigor mortis was observed at every muscle of the body, despite the time-lapse of more than 24 h estimated by lividity and rectum temperature. A paper bag, the label of which showed that the content was disulfoton, an organophosphate pesticide, and a glass cup with residues apparently identical to the bag content, were found in his vicinity. His pupils were miotic (0.25 cm diameter). Therefore, this pesticide was strongly suspected to cause his death. No criminality was suspected from his situations though there was no testamentary letter left.

Autopsy showed lung edema (left lung, 400 g; right lung, 470 g) and remarkable bloody secrete in the bronchus.

Histological examinations of the organs showed intra-alveolar bleeding and remarkable edema of the lung tissues, swelling of glomerulus of the kidney and congestion of the most organs.

To identify the suspected compound, mass spectra were recorded for the authentic disulfoton and the extracts of urine and blood of this cadaver as shown in Fig. 1. The authentic disulfoton showed characteristic peaks at m/z 88, 89, 97, 125, 142, 153, 186 and 274; the peaks at m/z 88 and 274 were the base and the molecular peak, respectively. The suspected fragmentation mechanism is also illustrated in Fig. 1. The spectra of the urine and blood extracts were almost the same as the spectrum of the authentic compound, showing the presence of disulfoton in urine and blood of this cadaver.

Selected ion monitoring was performed with ions at m/z 153, 186 and 274, for the authentic disulfoton, and for the urine and blood extracts as shown in Fig. 2. The peaks of disulfoton appeared at 3.38 min of retention time. There were no interfering peaks of impurities around the disulfoton peaks, show-

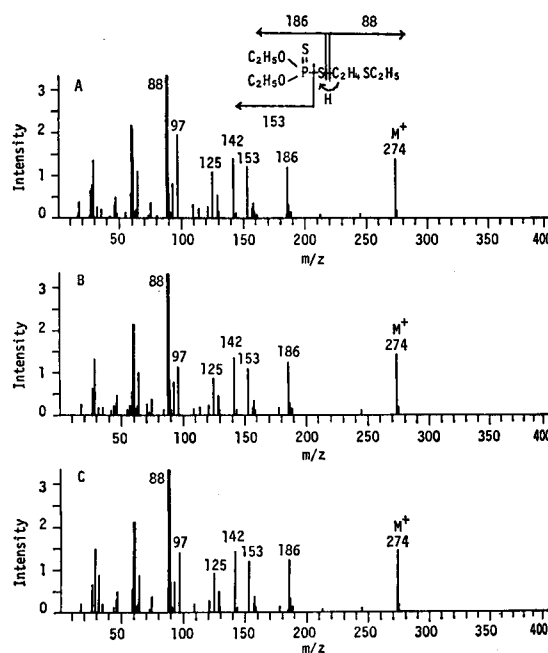


Fig. 1. Mass spectra of the authentic disulfoton (A), the urine extract (B) and the blood extract (C).

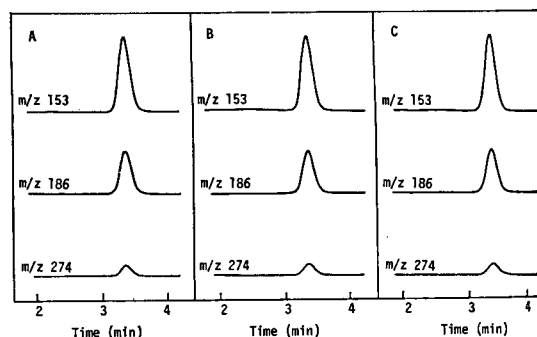


Fig. 2. Selected ion monitoring with the authentic disulfoton (A), the urine extract (B) and the blood extract (C).

ing that all these peaks can be used for quantitation.

For quantitation, single ion monitoring, using the molecular ion at m/z 274, was performed. The calibration curves were made by injecting known amounts of the authentic disulfoton, and the linearity was obtained from 10.0 to 100 ng of this compound per vial. In addition, the calibration curves after the addition of 300 and 600 ng of disulfoton to

0.2 ml of urine or blood also confirmed the linearity. The concentrations of disulfoton thus measured in urine and blood were 391 and 399 ng/ml, respectively.

Disulfoton is classified as one of the most toxic organophosphate pesticides; its LD₅₀ in rats was reported to be as low as 6.8 mg/kg⁵⁾ (oral administration). It is well known that the =S moiety of an organophosphate pesticide can be substituted by =O moiety in the body⁵⁾; this is probably one of the reasons for the low levels of disulfoton detected in urine and blood of this cadaver. Therefore, it can be concluded, together with the characteristic findings for organophosphate poisoning⁶⁾ such as miosis, strong rigor mortis and lung edema, that disulfoton caused his death.

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剖検死体の尿ならびに血液中 Disulfoton の GC/MS による同定と定量

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摘要 われわれは, 有機燐農薬である disulfoton を服用して自殺したと疑われる一剖検例を経験した。尿ならびに心臓血を採取し, アセトニトリル等で抽出し, GC/MS を用いて検討したところ, 首尾よく, disulfo-

ton を同定, 定量することができた。縮腫, 強度の死体硬直や肺浮腫等の死体所見と合わせ, 本例は disulfoton によつて死亡したものと考えられる。