

CASE REPORT

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Identification of Dog Repellent in the Clothes of an Assault Suspect Using Gas Chromatography/Mass Spectrometry

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ABSTRACT: Clothes from an assault case were recently submitted to our laboratory in order to determine if the suspect had been sprayed with Halt! Dog Repellent. The three major capsaicinoids of the *Capsicum* species, capsaicin, dihydrocapsaicin and nordihydrocapsaicin were extracted and identified using GC/MS. The spectra compared favorably with the remaining repellent in the can and cited literature values.

KEYWORDS: forensic science, criminalistics, dog repellent, chromatographic analysis

The transfer of trace evidence from an individual to a crime scene or between two individuals has long been used to establish the existence of a relationship or the probability of contact. This transfer could be fingerprints, hair, body fluids, or many other types of physical evidence. Our laboratory recently received a case in which trace evidence was deposited on an attacker's clothing by means of an aerosol spray. The spray used was a dog repellent that contained capsaicinoids, a class of compounds derived from the *Capsicum* fruit, commonly known as red or hot peppers. The capsaicinoids are the major components responsible for the pungent flavor in many hot foods. In the mouth they produce an irritation to the nerve endings responsible for heat and pain sensation. It is this chemical response that makes pepper-based sprays an effective deterrent [1]. This report details the method by which we extracted and analyzed, by means of gas chromatography/mass spectrometry, capsaicinoids found on the evidentiary material.

Case Report

A 37-year-old female was assaulted in her driveway after being pursued for several miles. During the assault she sprayed her assailant with "Halt!" dog repellent. The suspect fled the scene covered with the repellent and his stained clothes were later submitted to the laboratory as evidence. Also submitted was the remainder of the "Halt!" dog repellent.

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Materials and Methods

Sample Extraction

When sprayed, the "Halt!" dog repellent produces an oily orange stain on clothing. A portion (2 cm × 3 cm) of a stain found on the suspect's t-shirt was removed for analysis along with an equal sized unstained sample for use as a control. The cloth samples were extracted with 0.5 mL of methanol. A sample of "Halt!" dog repellent was prepared as a 1:1 dilution with methanol. To all samples, 0.5 mL of 0.2 M NaOH was added and mixed. The samples were washed twice with 1.5 mL of chloroform. The washed aqueous phase was then acidified with 0.3 mL of 3 N HCl and extracted with 1.5 mL chloroform. The chloroform extract was then analyzed by GC/MS. A chemical standard containing 60% capsaicin and 30% dihydrocapsaicin (Sigma Chemical Co.) was diluted in chloroform for GC/MS analysis.

GC/MS Conditions

Samples were analyzed on a Hewlett Packard 5890 Gas Chromatograph equipped with a Model 5970 Mass Selective Detector. The GC/MS was aided by a Pascal based ChemStation software and an Automated Liquid Sampler. The gas chromatographic conditions were as follows:

Column: 20 m by 0.18 mm, DB-5
Injector Temperature: 250°C
Transfer Line Temperature: 280°C
Oven Temperature: 60°C initial for 1 min then 15°C/min to 300°C, MS solvent delay 2 minutes, total run time 20 minutes.
Carrier Gas: Helium at 25 psi
Ion Range: 30 to 400 amu

The even hydrocarbons from C₁₀-C₃₄ were used to establish retention indexes using the retention index program included in the ChemStation Software.

Results and Discussion

The five naturally occurring capsaicinoids that have been documented are: capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin and homodihydrocapsaicin [2]. These capsaicinoids all have phenolic hydrogens which allow for an acid/base extraction and purification. Once extracted, capsaicin and its major

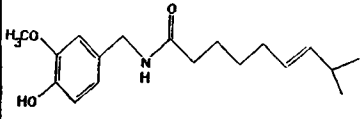
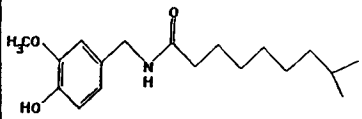
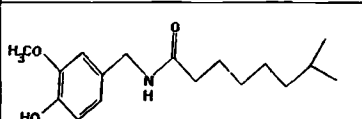
Compound	Structure	Retention Time/Index
Capsaicin M.W. = 305		14.54 min/ 2564 RI
Dihydro-capsaicin M.W. = 307		14.65 min/ 2587 RI
Nordihydro-capsaicin M.W. = 293		14.10 min/ 2479 RI

FIG. 1—Structures and chromatographic data.

analogues can be easily identified by GC/MS. Three major components were identified in the Halt! dog repellent, as described below, corresponding to the compounds capsaicin, dihydrocapsaicin and nordihydrocapsaicin. The structures and chromatographic data for these capsaicinoids are shown in Fig. 1.

Two of the compounds detected in the dog repellent were com-

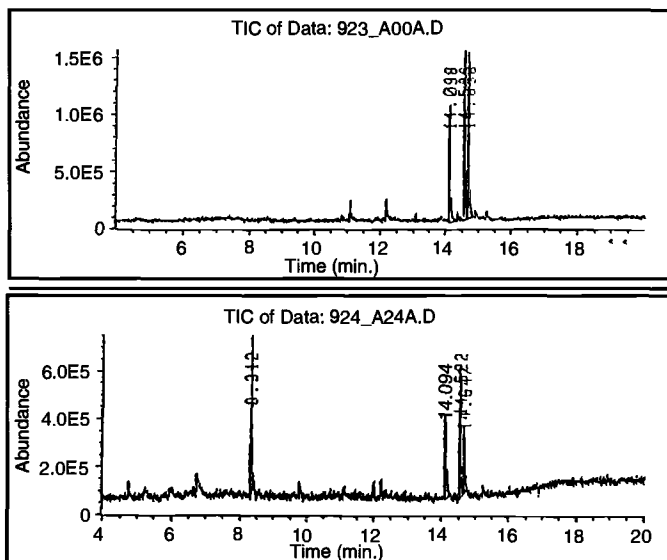


FIG. 2—Chromatograms.

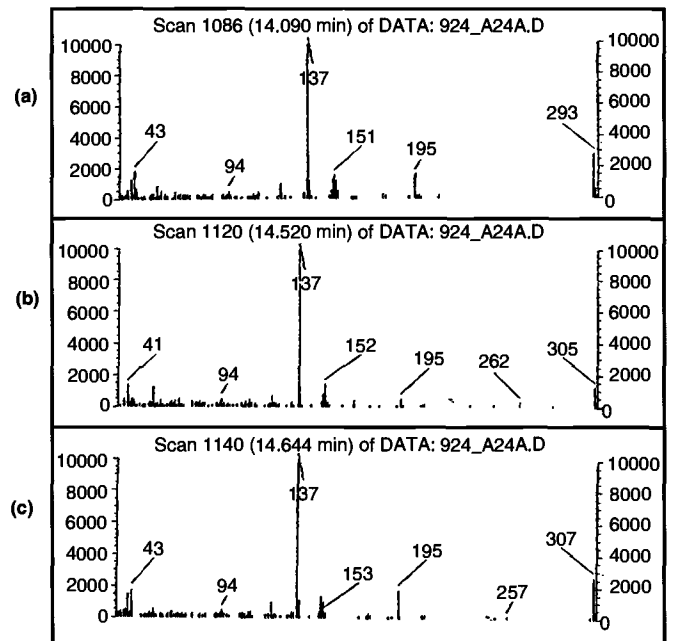


FIG. 3—Mass spectra.

pared to the Sigma standard and gave comparable retention times and mass spectra to capsaicin and dihydrocapsaicin. The other compound in Halt! dog repellent, nordihydrocapsaicin, gave a mass spectra consistent with what is expected for its structure [1]. The extract of the orange stain from the suspect's t-shirt gave a chromatogram and resulting mass spectra that matched that obtain from the "Halt!" dog repellent. The chromatograms are shown in Fig. 2 and mass spectra are shown in Fig. 3. No capsaicinoids were identified in the unstained portion of the suspect's t-shirt.

The samples were also analyzed using ultraviolet and visible spectroscopy and thin layer chromatography, but no valuable data for comparison was obtained.

The use of personal protection devices has been on the increase over the last few years. The device detailed in this report is just one of many devices that may be encountered. The stains produced by this aerosol required no special handling of the evidence to maintain the viability of the material since the capsaicinoids appear to persist on clothing for relatively long periods of time. Other devices with more volatile components may require special handling to avoid loss due to their volatility.

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