Robert O. Bost,[1] *Ph.D.*

3,4-Methylenedioxymethamphetamine (MDMA) and Other Amphetamine Derivatives

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ABSTRACT: As various substances of abuse come under Drug Enforcement Administration (DEA) Schedule restrictions, slightly modified derivatives (designer drugs) replace them. A series of amphetamine derivatives are discussed in this presentation. Applicable analytical methods are presented. Details of cases handled by the office (hospital patients, driving while under the influence/driving under the influence of drugs [DWI/DUID], and medical examiner cases) are discussed.

KEYWORDS: workshop, toxicology, designer drugs, 3,4-methylenedioxymethamphetamine

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These are names that we recognize as "designer labels." They are lines of apparel that represent only a slight modification of existing items, but with an intense marketing effort they have come to command a significant market share.

The same concept has been applied in the pharmaceutical industry for a long time. Slight changes of molecular structure lead from chlordiazepoxide to diazepam to flurazepam to the host of benzodiazepines that are available today. Librium® was introduced in 1960, Valium® in 1963, Serax® in 1965, Dalmane® in 1970, Tranxene® in 1972, Klonopin® in 1975, and Ativan® and Verstran® in 1977. And these are only the ones marketed in the United States. In one listing published in 1985, there are some 36 different benzodiazepines marketed in the United States and in other countries. Similar changes in chemistry have been applied in such pharmacological groups as barbiturates, tricyclic antidepressants, phenothiazines, and so forth. And we expect that pharmaceutical research should continue in this pattern.

People who provide materials for marketing and distribution in the drug abuse segment of society are also technically and economically sophisticated. Concepts that represent good science in the legitimate sphere also represent good science to them. Thus, they are quick to pick up on the concept of molecular designing and modification. They also work under the impetus of finding ways to circumvent legal restrictions on their activities. As any one drug they are involved with is placed under scheduled restrictions, they must decide whether to

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[1]Chief toxicologist, Southwestern Institute of Forensic Sciences, and assistant professor, Department of Pathology, University of Texas Health Science Center, Dallas, TX.

continue distributing it or to seek something else. In recent years, the choice often has been to shift to a similar substance that is still not scheduled.

The public is becoming well acquainted with these concepts. Some of you may have seen the series of Doonesbury cartoons by Gary Trudeau dealing with a designer drug symposium. In one panel, two organic chemists described how by simply snapping off one portion of the molecule, they produced a substance that was "legal as sea salt."

And there is at least one novel in the bookstores today that deals with this problem. *The Alchemist* by Kenneth Goddard [*1*] revolves around a Mafia-like group that hires a professor of organic chemistry to prepare a batch of an analog to phencyclidine. He persuades them to distribute a series of other drug analogs in which he is interested but cannot ethically test. The effects on the users are reported back to the chemist, who uses this "research data" to plan his next synthetic steps. It is interesting that the cover artist for this book reflects the concept that the treasure at the end of the rainbow is a white powder rather than that mundane pot of gold.

As members of the health care profession, we are all aware of the value of medications to our society. In fact, I expect that each of us at one time or another has opened a bottle of medication, removed some of the contents, and administered it to a patient or to a member of our family or to ourselves. We have faith that it is for the benefit of the person receiving the drug. We have faith that the pharmacology had been studied and found acceptable. We have faith in the pharmaceutical manufacturer that the medicine is what it purports to be and nothing else.

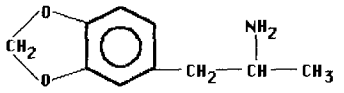
Illicit labs are often set up in kitchens, in mobile trailers, in garages, and so forth. They may use cookie jars or other large containers for their reaction vessels. Solid products may be removed with coffee filters; and the coffee filter may be thrown back into the reaction vessel for a second synthesis step. Reaction conditions will be only poorly controlled if at all. And none of us would administer a product from such a lab to ourselves or our family. Yet, labs such as this are the source of much of the illicit drugs being used in our society today.

According to Frank Sapienza [*2*] of the Drug Enforcement Administration headquarters in Washington, DC, the practice of shifting from a controlled substance to an analogous but uncontrolled substance is not a new occurrence. When lysergic acid diethylamide (LSD), mescaline, and some of the substituted amphetamines were controlled in the early 1960s, underground chemists produced analogs that could be legally distributed. When phencyclidine (PCP) was later controlled, new analogs were formulated. Included in this symposium series are a paper on fentanyl analogs [*3*] (Dr. Gary Henderson) and a paper on a meperidine analog [*4*] (Ms. Halle Weingarten).

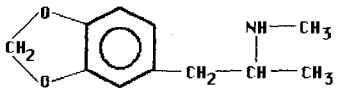
A third group of compounds included in this designer drug phenomenon is amphetamine and its derivatives. And this group of compounds is the main subject of this paper. The structures of several members of this family are shown in Fig. 1 and illustrate the slight molecular changes involved.

Amphetamine is the parent of this series. Insertion of a methyl group at the nitrogen on the side chain results in methamphetamine. Methylenedioxyamphetamine (MDA) (Structure I) is the third compound of the series of amphetamine compounds that have been around and abused for quite a few years. Approximately three years ago, a street drug called Ecstasy started appearing. I first heard of it in a phone call from the North Central Texas Regional Poison Control Center. I asked chemists in our own controlled substance lab for information, but they did not recognize the name either. I then called an officer with the Dallas Police Narcotics squad. He did know it and added that they had submitted some to our office and it was identified. According to his records, it was a substance named 3,4-methylenedioxymethamphetamine. When I passed this information to our controlled substance lab, they remembered the chemical but had not known the street name.

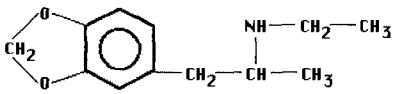
Analogous to the amphetamine/methamphetamine relationship, insertion of a methyl group into MDA produces 3,4-methylenedioxymethamphetamine (II, MDMA, Ecstasy).



3,4 - Methylenedioxyamphetamine
MDA



3,4 - Methylenedioxymethamphetamine
MDMA
"Ecstasy" "Adam"



3,4 - Methylenedioxyethamphetamine
MDEA
"Eve"

FIG. 1—*Chemical structures of methylenedioxyamphetamine and analogs.*

Synthesis to produce a compound with an ethyl group on the nitrogen results in 3,4-methylenedioxyethamphetamine (III, MDEA, Eve). Ecstasy was the more popular substance, and a considerable amount was distributed in Dallas. At the height of activity in the summer of 1985, the news media were reporting on the problem quite frequently. One report described the arrest of four individuals, with the headline "Drug Agents Seize 31,200 Tablets of Ecstasy."

We had numerous calls for information about these drugs, both locally and from other locations. One physician in Salt Lake City called, asking what we could tell him about Ecstasy. After sharing what we knew at the time, we then asked why he had called us. The physician replied that he was a general practitioner and some of his patients were businessmen who traveled quite a lot. Recently some of them had been to Dallas and had brought back some of this stuff. They were having some problems and he needed to know what he was facing.

Some of the evidence delivered to our controlled substance lab suggests[2] that illicit synthesis is not all being done in garages or mobile homes or other small time operations. When several of these items of evidence were examined together, it was noticed that the final products have nice pharmaceutical grade appearance. We further noted that several drugs were submitted in multiple formulations; Ecstasy and Eve each were identified in both elongated and several different round tablets. But we also noticed some similarities between drugs; these similarities included tablet size and shape and slight variations in color. It appears that one laboratory might be responsible for each of these products and may have instituted color

[2]K. Hine and E. L. Todd, forensic chemist and chief of controlled substances section, respectively, Southwestern Institute of Forensic Sciences, Dallas, TX, personal communication, 1986.

coding as a means of product identification. The controlled substance laboratory also reported that some exhibits contained more than one of these substances. Some submissions contained both MDMA (Ecstasy) and MDEA (Eve); again, there are slight variations in appearance suggesting a common source.

Laboratory Analysis Methods

These compounds are detectable by the standard analytical procedures routinely in use today, which will be reviewed briefly. Hearn [5] has reported on some of the analytical work his group has been doing. The enzyme multiplied immunoassay technique (EMIT®) amphetamine assay responds to MDA, MDMA, and MDEA. However, a concentration of 10 to 13 mg/L of MDA is required to give a response equivalent to 0.3 mg/L of amphetamine. For MDMA, the cutoff concentration is around 5 to 8 mg/L, and for MDEA the concentration is around 4 to 7 mg/L.

Hearn [5] also reported on the use of the Toxi-Lab thin-layer chromatography (TLC) system for the analysis of these drugs. He noted that amphetamine and MDA had approximately the same R_f, methamphetamine and MDMA had approximately equivalent R_f, and MDEA had an R_f about that of phentermine. The appearance of each of the drug spots was similar except for the fluorescence stage; MDMA appeared as a blue halo around an absorbent center, and MDEA was completely absorbent.

Gas chromatography (GC) is also applicable to these compounds. At the Southwesten Institute of Forensic Sciences, we follow a normal three-step extraction scheme [6] and inject the extract into a Hewlett-Packard capillary GC, with two columns installed into one injection port. This provides two simultaneous chromatograms. The columns are DB-1 and DB-5; both are 25 m long and 0.31 mm in inside diameter (ID). A temperature program is used, because we look for these amphetamine analogs as part of our routine procedure for alkaline drugs. The two chromatograms are shown in Fig. 2. The elution order on both is amphetamine, methamphetamine, MDA, MDMA, and MDEA.

Mass spectral identification of these compounds is also accomplished by routine methods. Although the higher mass ranges are fairly weak, the molecular ion can be detected, and there are sufficient other fragments to allow identification. Representative spectra for these compounds, as obtained on a Hewlett-Packard 5890 capillary GC and 5970 mass selective detector, are shown in Figs. 3 through 7.

Case Reports

In February 1985, we detected our first instance of MDMA use in a hospital patient. Since then we have detected this drug or its ethyl analog in three more clinical cases, in seven cases of driving while intoxicated/driving under the influence of drugs (DWI/DUID) arrests, and in five fatal cases.

DWI/DUID Cases

Our laboratory serves as a backup to the Dallas Police Department for DWI/DUID cases. In those individuals that appear to be more intoxicated than would be expected based on a breath-alcohol result, a blood sample may be submitted with a request for drug analysis. In some instances, the officer may obtain evidence (admission of defendant, or finding of physical evidence in car or on person) that suggests the defendant has used drugs other than ethanol. A blood sample may be submitted in these cases also. For the period of June 1985 to November 1986, we detected MDEA in five cases and MDMA in two cases. Table 1 shows the information obtained by reviewing the arrest records combined with our laboratory results.

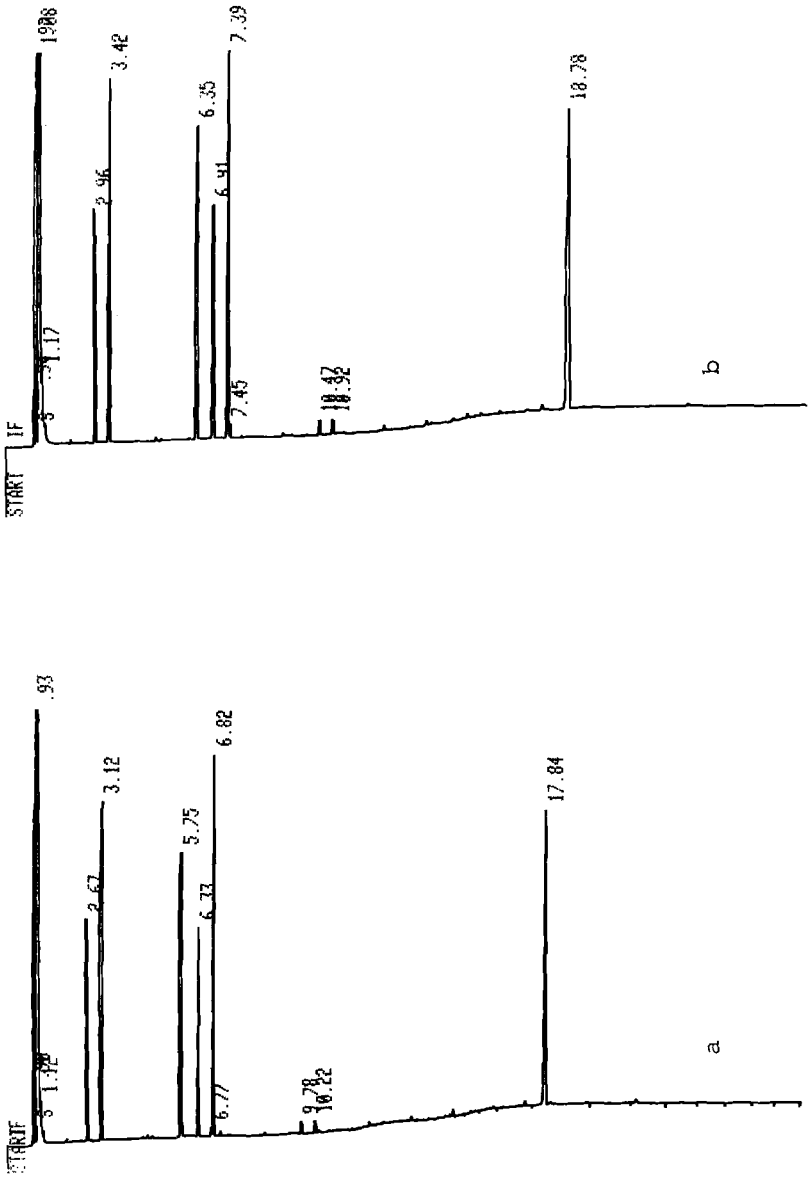


FIG. 2—*Simultaneous gas chromatograms:* (a) *DB-1,* (b) *DB-5; both columns are 25 m long, 0.31-mm ID, and 53-μm film thickness. Temperature program as follows: initial temperature 110° C, initial hold 0 min, program rate 12°/min, final temperature 290° C, final hold 15 min. Elution order: amphetamine, methamphetamine, MDA, MDMA, and MDEA.*

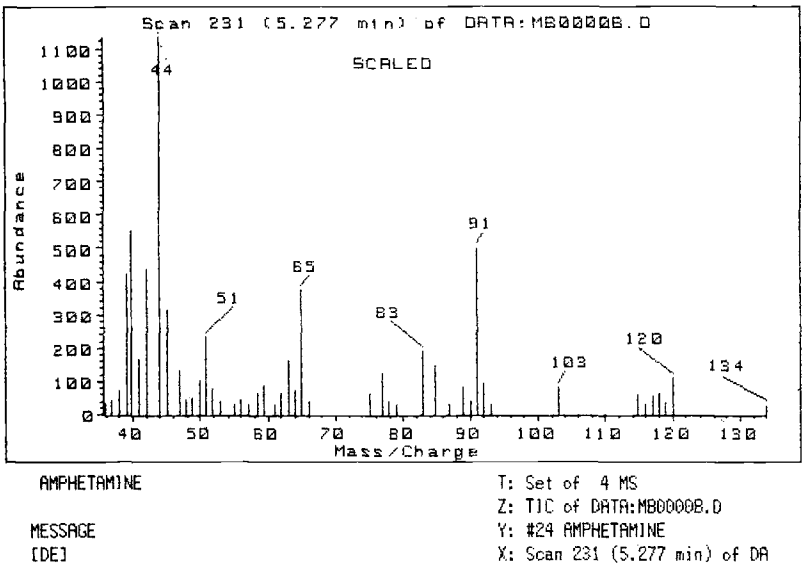


FIG. 3—*Mass spectrum of amphetamine.*

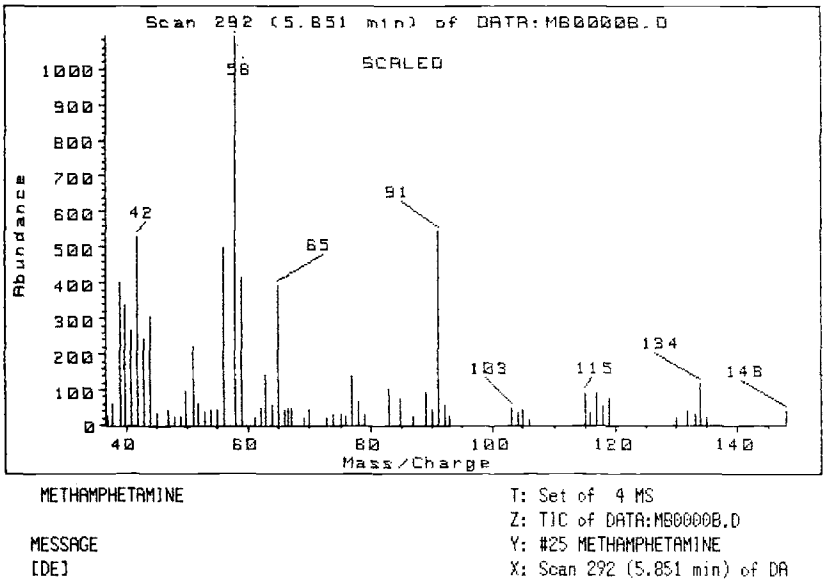


FIG. 4—*Mass spectrum of methamphetamine.*

In the first case, two officers transporting a prisoner observed another car pull up beside them. The driver looked at the officers and then sped off at an estimated 140 miles per hour. The officers alerted other officers by radio to be watching for this car. Approximately 1 to 2 min later, they came upon an accident in which this driver was involved. According to their report, "officer(s) further determined from personal observation that the suspect was intoxicated, from introduction of alcohol and controlled substance into the body, having blood

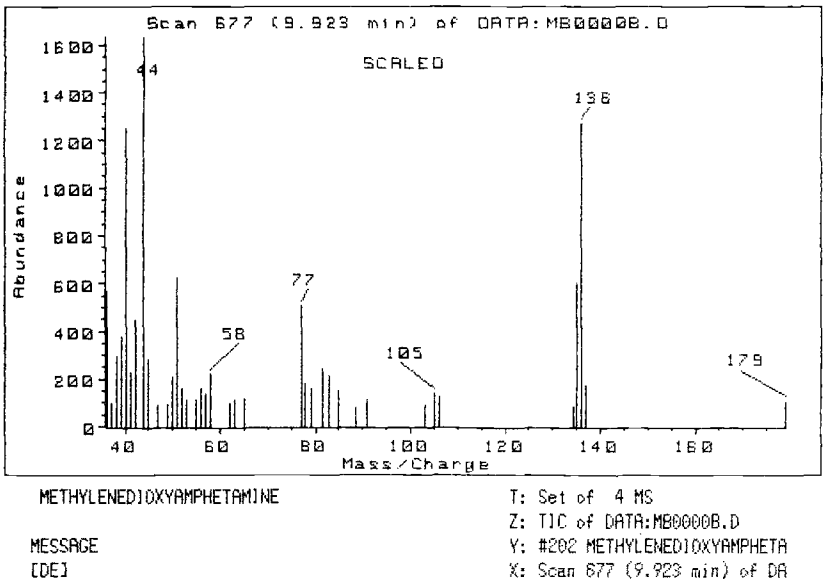


FIG. 5—*Mass spectrum of methylenedioxyamphetamine (MDA).*

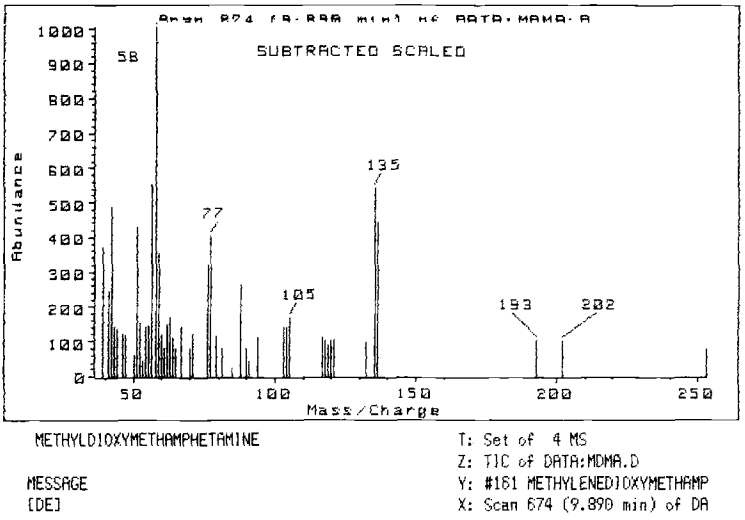


FIG. 6—*Mass spectrum of methylenedioxymethamphetamine (MDMA).*

shot eyes, slurred speech, and breath smelling of an alcoholic beverage." The suspect told an officer "I took off because I didn't want to go to jail because I have a warrant out for my arrest and its homecoming." Later at the hospital, he told a nurse he was taking Ecstasy and Eve drugs. Analysis of his blood showed ethanol at 0.09% and the presence of MDEA.

The second case involves a 19-year-old white male who was observed by an officer to drive out of a parking lot and subsequently turn left without stopping for a stop sign. The officer

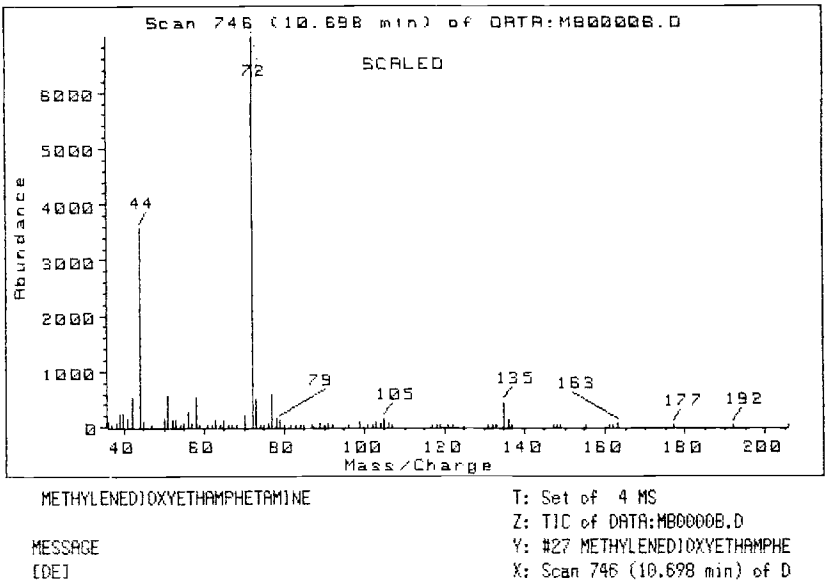


FIG. 7—*Mass spectrum of methylenedioxyethamphetamine (MDEA).*

TABLE 1—*DWI-DUID cases.*

Age/Race/Sex	Ethanol, %	Drugs, mg/L	Stopped For?
18/W/M	0.09	MDEA pos.	speed, accident
19/W/M	0.03	MDEA 0.16	ran stop sign
24/W/M	0.07	MDEA 0.37	speed
26/W/M	0.06	MDEA 0.11	accident
20/W/M	neg	MDEA 0.59	speed
22/W/M	neg	MDMA pos.	right of way
22/W/M	0.06	MDMA pos.	accident

reported that he "found the suspect to be intoxicated, from introduction of drugs into the body, having slurred speech, breath smelling of an alcoholic beverage, and pupils remaining undilated." Analysis of his blood showed ethanol at 0.03% and MDEA at 0.16 mg/L.

The third individual was stopped for exceeding the speed limit. As with the previous cases, the suspect was observed to "be intoxicated, from introduction of alcohol into the body, having blood shot eyes, slurred speech, breath smelling of an alcoholic beverage, and staggered walk." The laboratory results included 0.07% ethanol and 0.37 mg/L of MDEA.

In the fourth case, a 26-year-old white male was involved in a vehicular accident. He, too, was "intoxicated, from introduction of controlled substance into the body, having blood shot eyes, slurred speech, and breath smelling of an alcoholic beverage." The suspect later admitted to being under the influence of a prescription drug (pain killer) and marijuana. Note however, that the lab reported ethanol and MDEA; no analgesic prescription drug was found. We do not look for marijuana.

In the fifth case, the suspect was stopped for exceeding the speed limit. He could not produce a driver's license or evidence of insurance; he also lied about his employment and place of residence. He, too, was intoxicated "having blood shot eyes and breath smelling of

an alcoholic beverage." In this instance, no ethanol was detected by the laboratory, but we did find MDEA.

The sixth driver changed lanes abruptly in front of another vehicle. The second driver had to brake sharply to avoid a collision. Officers stopped the offending driver for failure to yield right of way. He was similarly described as intoxicated. Before the car was impounded, officers conducted an inventory and found a baggie with 6.7 g of marijuana and a partial tablet in a second baggie. The suspect stated it was an EVE tablet and he had taken portions of it about 2½ h earlier. The lab results however showed that he had MDMA or Ecstasy in his blood, not the MDEA or Eve that he thought.

And, in the last case listed, officers responded to the scene of a major accident. The driver was similarly found to be intoxicated. The laboratory reported both alcohol and MDMA.

Observe that all of these arrests occurred at night, from 11:00 p.m. to 3:20 a.m. Two arrests occurred mid-week and the others were on Friday night, Saturday night, or early Sunday morning. This is consistent with arrest patterns for other DWI/DUID cases. In fact, the Dallas Police Department's special DWI squad of officers are on duty from 4:00 p.m. till 4:00 a.m. on Thursday, Friday, Saturday, and Sunday.

Clinical Cases

Our lab serves Parkland Memorial Hospital as its backup toxicology reference lab. During the past two and a half years, their chemistry lab has been doing a Toxi-Lab TLC screen on all samples submitted for the "general toxicology screen." The presumptive positives are sent to us for confirmation and quantitation when appropriate.

During this period, we reported finding MDMA in two patients and MDEA in two patients. Table 2 summarizes some of the information about these patients. The first young man was brought to hospital unconscious, with a history of having taken an overdose of Elavil®. Analysis of blood for alkaline drugs confirmed the diagnosis, with a finding of amitriptyline at 2.1 mg/L and nortriptyline at 0.4 mg/L, as well as alcohol at 0.16%. The urine was found to also contain some MDEA. His treatment was directed to the tricyclic overdose; no particular mention was made in the record of the MDEA finding. Following his recovery, he was discharged to follow-up at the Student Health Center at the university he was attending.

The second man was found lying on a sidewalk, exhibiting "bizarre behavior"; he complained of weakness and dizziness, and his pupils were dilated and reactive. He reported that he had taken "Eves" because he was having trouble with his family. He said he had moved

TABLE 2—*Clinical cases.*

Age/Race/Sex	Condition	Laboratory Results
30/W/M	unconscious; Elavil overdose	blood: ethanol 0.16%; amitriptyline 2.1 mg/L; nortriptyline 0.4 mg/L urine: amitriptyline, nortriptyline, lidocaine, nicotine, and MDEA present
38/W/M	bizarre behavior; psychiatric evaluation	blood: ethanol 0.23%; MDEA present
26/W/M	hallucinations, combative; psychiatric evaluation	blood: cocaine 1.6 mg/L urine: amphetamine, cocaine, nicotine, and MDMA present
32/W/F	unresponsive; cyanotic; aspiration syndrome	blood: diazepam and demethyldiazepam present urine: lidocaine, cocaine and MDMA present

from Memphis because his family was associated with the fiance of Elvis Presley and he was not able to do any modeling or acting because of this association. Following a psychiatric evaluation, he was released. Analysis of his blood showed an ethanol concentration of 0.24% and also that MDEA was present.

The third man was brought to the hospital by police, who had found him in the middle of the street. He was described as having hallucinations and delusions and being combative. During an altercation with police, he received injuries to his head that required skull X-rays (which were negative). He reported that he had taken cocaine. He was from a wealthy Virginia family, had attended private schools, was supported by his family and by gay lovers, and had been using cocaine for the past nine years. Analysis of his blood showed 1.6 mg/L of cocaine; his urine contained amphetamine, cocaine, and MDMA.

The fourth patient was a female. Upon arrival at hospital, she was unresponsive with peripheral cyanosis. Several hours before arrival she had been involved in what was described as an alcohol debauch with cocaine, MDMA, valium, and her first episode of intravenous (IV) drug abuse. Laboratory analysis showed traces of diazepam and demethyldiazepam in the blood; ethanol was negative. A urine specimen submitted about 7 h later showed lidocaine, cocaine, and MDMA. She was admitted to intensive care for an aspiration syndrome and treated predominantly for that problem. She remained hospitalized for 40 days.

Because of the mixed drug findings in each case, no set of presenting symptoms can be identified as a result of the amphetamine analogs alone. Nor is it possible to differentiate between behavior caused by the drugs in these patients and any mental disturbance they may have been suffering.

Fatal Cases

During the normal course of death investigation and toxicological analysis, we found five cases of death associated with the use of MDMA and MDEA. In four cases, the drugs are thought to have caused or contributed to death by induction of cardiac arrhythmias. In the fifth case, MDMA caused bizarre behavior in an individual resulting in his death. These cases have been described in detail in a previous publication [*7*] and the details will not be repeated here. Table 3 summarizes the pertinent facts, including laboratory results.

Reynolds[3] has provided the following details of a fatality investigated by his office. The deceased was a 35-year-old white male who came to the residence of a physician at 3:50 p.m.,

TABLE 3—*Fatal cases.*

Age/Race/Sex	Cause of Death	Laboratory Results, mg/L
22/W/M	electrocution, multiple injuries	MDMA present in blood
25/W/M	atherosclerotic cardiovascular disease	blood: MDEA 0.95 butalbital 0.8
32/W/M	acute asthma	blood: MDMA 1.1
18/W/F	acute MDMA intoxication	blood: MDMA 1.0 ethanol 0.04%
21/W/M	idiopathic cardiomyopathy	blood: MDEA 2.0 propoxyphene 0.26 norpropoxyphene 1.0 liver: MDEA 4.51 mg/kg kidney: MDEA 2.55 mg/kg heart: MDEA 1.68 mg/kg lung: MDEA 4.54 mg/kg spleen: MDEA 3.33 mg/kg

[3]P. C. Reynolds, chief toxicologist, Institute of Forensic Sciences, Oakland, CA, personal communication, 1987.

who had treated him for stress several months before this accident. The subject did not look well and began to doze off. On questioning, he reportedly responded that he had taken LSD, valium, and MDMA. He slumped over and became unresponsive. Cardiopulmonary resuscitation (CPR) was started, 911 was called, and he was transported to the hospital where he was pronounced dead at 5:30 p.m. A complete autopsy was performed with findings of acute hemorrhagic gastritis (from shock) and pulmonary edema, but otherwise unremarkable. Positive findings in this case included a concentration of MDMA of 1.46 mg/L and of MDA of 0.03 mg/L in the blood, and MDMA in other fluids.

Table 4 summarizes the age/race/sex data for all these categories of cases. Note that the DWI cases are all at or below the mean age, the clinical cases are all at or above that mean age, and that the fatalities are spread over the age range. All individuals were white. Fifteen were males and two were females. The concentrations of drugs ranged from 0.16 to 0.59 mg/L in those individuals who survived their incident and from 0.95 to 2.0 mg/L in the fatal cases.

Summary

When I began to prepare this presentation and realized that I had access to information about three population groups (arrestees, emergency room patients, and fatalities), I hoped that I could extract some common feature(s) that might connect back to the drugs involved. But you will recall that the officers' descriptions of the people arrested were all quite similar. Note also that some alcohol was present in five of the seven cases. None of the clinical cases provided a clear indication of the effect of these drugs. Each case involved multiple drugs, and some were further complicated by mental problems. In fact, in some of these cases, the amphetamine analog was only an incidental finding. The symptoms of the young woman who died provided some indication that the toxic effect is related to the heart. The man who had a vehicle accident after leaving his doctor also suggests cardiac involvement. The other three are less clear-cut about the specific contribution of the amphetamine analog to the death.

So our own cases do not give us any clear picture. Another factor complicates this picture. Illicitly produced substances do not benefit from any type of confirmed identification or quality control procedures. Thus, the actual substances used may or may not be as represented. And recall that at least two of the cases discussed in this report were not taking the drug they thought they were. Thus, the toxic effects we observe may be due to some by-product or to some other substance entirely. And certainly patient history is unreliable. The patient may try to hide the nature of his drug use. Even if he wants to be truthful, he can only

TABLE 4—*Summary of case information.*

Class	Age	Race	Sex
DWI/DUID	18, 19, 24, 26, 20, 22, 22	7 W	7 M
Clinical	30, 38, 26, 32	4 W	3 M/1 F
Fatal	21, 32, 18, 25, 22, 35		
		6 W	5 M/1 F
All	mean 25.3 range 18-38	17 W	15 M/2 F
Drug concentration ranges—nonfatal cases 0.16-0.59 mg/L fatal cases 0.95-2.0 mg/L			

be as correct as his supplier is right. Poklis [*8*] has reported on the death of a young man who was himself a dealer in the illicit drug market. During a party, this man and others took what they believed to be a mixture of *M*orphine, LS*D*, and *A*mphetamine; they knew it by the initials MDA. And he was right up to a point. The laboratory confirmed that he had taken MDA, but the MDA involved was 3,4-methylenedioxyamphetamine rather than the three-drug mixture expected.

Where does this leave us? Some counselors and psychiatrists have claimed that MDMA is a useful adjunct to their therapy programs. I have shown cases where these drugs are involved in fatality. These drugs are not tremendously powerful toxins, as some of the fentanyls are. But neither are they benign, safe materials that should be readily available at your neighborhood bar or campus watering hole. After reviewing our cases and reading some of the literature available, I believe that one newspaper article expressed it well with the headline "Ecstasy Remains a Mystery to Researchers."

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Address requests for reprints or additional information to
Robert O. Bost, Ph.D.
5230 Medical Center Dr.
P.O. Box 35728
Dallas, TX 75235-0728