Tetramethylenedisulfotetramine: Old Agent and New Terror

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Tetramethylenedisulfotetramine has accounted for numerous intentional and unintentional poisonings in China. In May 2002, the first known case of human illness in the United States caused by tetramethylenedisulfotetramine, a banned neurotoxic rodenticide from China, occurred in New York City. The clinical presentation after tetramethylenedisulfotetramine exposure is dose dependent, and the most recognized complication is status epilepticus. Poisonings may be fatal within hours. No known antidote exists, and treatment is mainly supportive. Anecdotal reports, case reports, and 2 animal studies suggest possible success with certain pharmacologic interventions, including pyridoxine and chelation therapy. Pesticide and rodenticide poisonings, whether intentional or unintentional, pose a serious threat to populations, and the availability of a banned rodenticide such as tetramethylenedisulfotetramine, with its associated morbidity and lethality, is a serious public health concern. Given the recent case report that confirms the presence of tetramethylenedisulfotetramine in the United States, the toxicity of the compound, its unique physical properties, the absence of an antidote, and the history of its use as an agent of intentional mass poisoning, public health entities have undertaken educational efforts to inform the public, health care providers, and emergency personnel of this potentially lethal rodenticide. [Ann Emerg Med. 2005;■■:■■■.]

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INTRODUCTION

Banned pesticides and rodenticides illicitly imported into the United States have been responsible for numerous intentional and unintentional human poisonings.[1-3] The labels on chemical substances illicitly imported from other countries are often difficult to interpret, or they list ingredients in foreign languages. In some cases, the chemical substance may be unlabeled. The inability to identify the chemicals can delay accurate diagnosis and timely management of illnesses resulting from acute exposure. For example, "Tres Pasitos," or "3 little steps," is a rodenticide that contains aldicarb, a potent carbamate not permitted in the United States, is often sold unlabeled, and has caused more than 50 human poisonings in New York City.[1,2]

Recently, a governmentally banned rodenticide from China, tetramethylenedisulfotetramine, was reported responsible for human poisoning in the United States.[3] Tetramethylenedisulfotetramine is a lethal, neurotoxic rodenticide that has been the source of numerous intentional and unintentional poisonings in China.[4-6] This review describes the mechanism of action, clinical manifestations, laboratory detection, and management of tetramethylenedisulfotetramine poisoning and heightens public health awareness of the potential use of this toxic substance as a terrorist weapon. Tetramethylenedisulfotetramine is particularly dangerous if used to deliberately contaminate food or water, given its unique physical properties.

HISTORY

Tetramethylenedisulfotetramine is a little-known, often unrecognized, highly lethal neurotoxic rodenticide that was once used throughout the world. Tetramine is the popular name for this chemical; however, tetramine is also a general name for a group of unrelated chemical compounds derived from hexamethylenetetramine and is commonly associated with the red whelk toxin tetramethylenedinitrosotetramine but manifests different clinical toxicities.[7,8] In China, tetramethylenedisulfotetramine is still sold illegally under the names "Dushuqiang," "Meishuming," or "Shanbudao," which translate to "strong rat poison," "eliminate rat," and "4-2-4," respectively.[9]

The human toxicity of tetramethylenedisulfotetramine has been most recognized in China, where the World Health Organization lists poisoning in general as 1 of the top 10 causes of death for Chinese people 5 to 29 years of age. This is compounded by the multiple large intentional and unintentional exposures illustrated by potent rat poisons becoming a tool for criminals with malicious intent. This behavior has represented a "massive threat to public health and safety" in China.[10] In July 1991, a mass poisoning occurred in Heibei Province, China, where 78 people were purposely poisoned with tetramethylenedisulfotetramine-contaminated rice.[11] In September 2002, in a rural district of Nanjing City, China, approximately 400 people were intentionally poisoned with tetramethylenedisulfotetramine-contaminated food, and 38 people died.[4] Also during 2002 in Huangpo, Guangdong Province, China, 70 kindergarten children and 2 teachers became ill after eating porridge intentionally adulterated with tetramethylenedisulfotetramine.[5] In September 2003, 214 students in Yueyang, China, were poisoned with tetramethylenedisulfotetramine-contaminated food from their school cafeteria; 61 were hospitalized.[6] In October 2003, 16 people in Shaanxi Province were hospitalized for tetramethylenedisulfotetramine poisoning.[10] In November 2003, 31 people were poisoned, with 24 reported ill, and 1 death at a wedding ceremony in Jiangsu Province.[12] In December 2003, 76 college students in Yizhou City were poisoned through intentional contamination of their breakfast.[13] Most recently, during April 2004 in Tongchuan City, 74 people were intentionally poisoned through scallion-flavored pancakes.[14]

The first and only reported case of tetramethylenedisulfotetramine exposure and toxicity to date in the United States occurred in May 2002 in New York City. A 15-month-old female was exposed by accidental ingestion to tetramethylenedisulfotetramine used as an indoor rodenticide. She was severely poisoned and manifested recalcitrant seizures. Six months after exposure, the child remained severely developmentally delayed and required pharmacologic therapy for seizure control[3] (Figure 1).

Figure 1. The Chinese rodenticide package involved in the New York City poisoning.

Chemical Properties and Mechanism of Action

Tetramethylenedisulfotetramine is an odorless, tasteless, white, crystalline powder that easily dissolves in water. The most common route of exposure is ingestion. Occupational exposures through inhalation have occurred, and it is not absorbed through intact skin (C. Sun, personal communication, November 5, 2002). The compound binds noncompetitively and irreversibly to the chloride channel on the γ-aminobutyric acid receptor complex (an inhibitory neurotransmitter in the central nervous system) of the neuronal cell membrane, where it blocks the influx of chloride and alters the intraneuronal potential. Tetramethylenedisulfotetramine, like picrotoxin from the plant *Anamirta cocculus*, or "fish berry," is a "cage convulsant" with a similar mechanism of action (noncompetitive γ-aminobutyric $acid_A$ receptor antagonism) and a cyclical or ring-like molecular structure[4,15,16] (Figure 2).

Toxicity of Tetramethylenedisulfotetramine

The LD_{50} (lethal dose 50%, or the single dose of an agent that kills 50% of exposed laboratory animals) of tetramethylenedisulfotetramine in mammals is 0.1 to 0.3 mg/kg, and 7 to 10 mg (total dose) is considered to be a lethal dose for human beings.[17,18] Tetramethylenedisulfotetramine is more potent than sodium fluoroacetate, the most toxic rodenticide registered by the Environmental Protection Agency, and it meets the criteria for inclusion in the World Health Organization's list of "extremely hazardous" pesticides.[19]

Tetramethylenedisulfotetramine has been banned in China since 1984 because of its human toxicity, but it remains easily purchased in many areas and is popular as an effective rodenticide. Tetramethylenedisulfotetramine has never been registered for use in the United States, and current law prohibits its importation, production, manufacture, or use. A further illustration of the relative toxicity of tetramethylenedisulfotetramine is that the government of India, under the Environment Protection Act of 1996, classifies a spill of 1 kg or more of tetramethylenedisulfotetramine as a "major" accident. The same government does not consider an aldicarb spill to be a major accident unless it is 100 kg or more, which further suggests tetramethylenedisulfotetramine's relative danger and toxicity.[20]

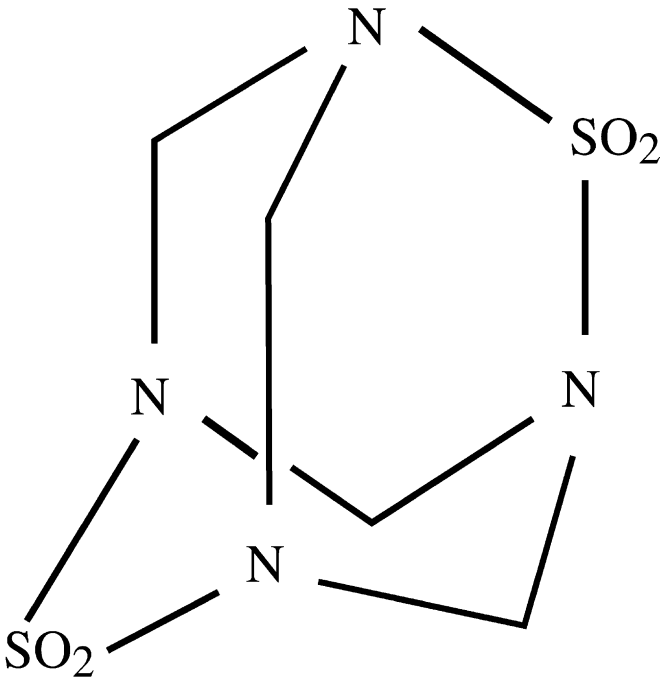

Figure 2. The chemical structure of tetramethylenedisulfotetramine ($C_4H_8N_4O_4S_2$).

Clinical Manifestations

The clinical presentation, prognosis, and spectrum of clinical effects after tetramethylenedisulfotetramine exposure are dose dependent. Mild to moderate poisoning produces headache, dizziness, fatigue, nausea, vomiting, perioral paresthesias, weakness, anorexia, and lethargy (C. Sun, personal communication, November 5, 2002).[9,18] The signs and symptoms of severe intoxication include tachycardia, palpitations, arrhythmias (with possible ECG evidence of ischemia), and agitation. Refractory status epilepticus and coma appear to be the hallmarks of severe tetramethylenedisulfotetramine poisoning. Liver and renal dysfunction (ie, hematuria and proteinuria) may also occur, although it is unclear whether these are primary or secondary effects of tetramethylenedisulfotetramine poisoning (C. Sun, personal communication, November 5, 2002).[9,18] The onset of symptoms ranges from 30 minutes to 13 hours postexposure. Severe poisonings may be fatal within hours (C. Sun, personal communication, November 5, 2002).[9] Given the nonspecific signs or symptoms of poisoning, the patient's medical history and the provider's clinical suspicion are the primary means of rapidly recognizing tetramethylenedisulfotetramine intoxication.

Postmortem studies of tetramethylenedisulfotetramine-poisoned patients demonstrate anoxic brain-injury patterns, cerebral edema, focal brainstem hemorrhages, myolysis of cardiac papillary muscles, and contraction band necrosis of the myocardium.[21]

Laboratory Analysis

Laboratory identification of the compound is not practical in patients with acute poisoning because of difficulty in identification by routine laboratory analysis, but if tetramethylenedisulfotetramine poisoning is suspected, every attempt should be made to subsequently confirm the presence of tetramethylenedisulfotetramine. Local public health authorities, such as the New York City Department of Health Laboratories, may be able to provide assistance. The compound has been identified in blood by several methods, including gas chromatography with nitrogen-phosphorous detection, gas chromatography with flame photometric detection, and gas chromatography mass spectrophotometer.[11,22,23] Because of the difficulty of obtaining an analytic standard in the New York City poisoning, as previously described, the laboratory synthesized a tetramethylenedisulfotetramine standard with a purity of at least 95% with the method described in Barrueto et al[3] and Mo and His-Yuan.[24]

Management

Because of the banned status of tetramethylenedisulfotetramine in most of the world, few reports exist in the medical literature on treating patients with tetramethylenedisulfotetramine poisoning. The information in this section is based on a literature review, case reports, and anecdotal evidence presented from the few international clinicians who have experience with tetramethylenedisulfotetramine-poisoned patients (C. Sun, personal communication, November 5, 2002).[9] No known antidote exists, and treatment is mainly supportive.

Treatment of tetramethylenedisulfotetramine-poisoned patients should follow accepted modalities for the poisoned patient presenting with altered mental status or seizures.[25] Seizure control might be achieved with large doses of benzodiazepines, barbiturates, or pyridoxine as for any continuously seizing patient with exposure to an unknown toxin (C. Sun, personal communication, November 5, 2002).[9,18,26] Endotracheal intubation, chemical paralysis, and pharmacologically-induced coma should be used for recalcitrant seizures. People who have been exposed externally should be removed from that exposure and decontaminated (eg, clothing removal, wash with soap and water) immediately.[27] For ingestions, internal decontamination with gastric lavage and activated charcoal are recommended, and emesis should be avoided.[18] Standard universal precautions should be used to prevent secondary exposure of health care workers. Because patients with seizure activity may be prone to rhabdomyolysis, adequate intravenous hydration should be provided, and symptomatic patients should be admitted to an intensive care setting. The sedated or paralyzed patient should be observed for seizure activity by using continuous electroencephalographic monitoring. Cardiac function using ECG monitoring should also be used to observe for development of arythmias (C. Sun, personal communication, November 5, 2002).[9,18] Physicians should contact their regional poison control center for information and guidance from a medical toxicologist.

Anecdotal reports and 1 animal study using 30 Kunming mice (10 mice per study group: control group, immediate-treatment group, and delayed-treatment group) suggest possible

but not proven success with pharmacologic interventions. All 3 groups of mice were orally poisoned with 0.1 mL/10 mg of tetramethylenedisulfotetramine. The control group was then abdominally injected with saline solution, whereas the immediate-treatment group was treated with 0.1 mL/10 g of sodium-(RS)-2,3-dimercaptopropane-1-sulfonate and 0.2 mL/10 g of pyridoxine (vitamin B_6) intra-abdominally at poisoning. The delayed-treatment group was given equivalent doses of tetramethylenedisulfotetramine, sodium-(RS)-2,3-dimercaptopropane-1-sulfonate, and pyridoxine; however, the ''antidotes'' were administered 10 minutes after poisoning. This pyridoxine and chelation therapy resulted in 100% 3-day survival in the immediate-treatment group and 40% 3-day survival in the delayed-treatment group. The treatment also delayed onset of symptoms in both groups.[26] The mechanism by which this delay occurred is unclear. A second Chinese study in mice showed that sodium-(RS)-2,3-dimercaptopropane-1-sulfonate (a sulfhydryl compound) inhibited the γ-aminobutyric acid antagonist effects of tetramethylenedisulfotetramine directly at the γ-aminobutyric acid receptor.[28] One Chinese publication with 39 tetramethylenedisulfotetramine-poisoned patients suggests that sodium-(RS)-2,3-dimercaptopropane-1-sulfonate (0.125 to 0.25 g intramuscularly every 30 minutes to 1 hour during seizure activity) will control tetramethylenedisulfotetramine-induced seizures.[29] Fu et al[30] and Wei et al[31] reported that sodium-(RS)-2,3-dimercaptopropane-1-sulfonate and pyridoxine provided 100% survival in 2 case series of tetramethylenedisulfotetramine-poisoned patients. Sodium-(RS)-2,3-dimercaptopropane-1-sulfonate is not US Food and Drug Administration approved for use and is available in the United States only as a compounded medication from Heyltex Corporation, a division of Heyl Chem.-Pharm.-Fabrik (Berlin, Germany), and pyridoxine is readily available in most hospital pharmacies. Charcoal hemoperfusion and hemodialysis have been used in tetramethylenedisulfotetramine poisoning, but the role of extracorporeal removal in management is not well studied and not recommended (C. Sun, personal communication, November 5, 2002).[9,11,18]

PUBLIC HEALTH APPLICATIONS

Since September 11, 2001, concern has increased about potential terrorist attacks involving the use of chemical agents. The properties of water solubility, lack of taste and odor, rapid onset, high lethality, and lack of antidotal therapy make tetramethylenedisulfotetramine a potential chemical agent of terror, particularly by contamination of food or water. Deliberate food and water contamination remains the easiest way to distribute biological or chemical agents for the purpose of terrorism, and it has already occurred in the United States.[32,33] Therefore, the entrance of this banned rodenticide into the United States should be viewed as a potentially serious threat to public health. US public health entities (ie, the Environmental Protection Agency, the US Department of Agriculture, and the United States Customs) have undertaken increased educational efforts to inform health care providers of tetramethylenedisulfotetramine's properties and potential toxicity through scientific publications.

The appearance of tetramethylenedisulfotetramine in the United States, as demonstrated by the recent case report in New York City, may represent challenges to clinicians; emergency departments; and regulatory, enforcement, and public health agencies. Imported pesticides represent a special public health risk in large urban areas with significant immigrant populations whose members may have used these substances successfully as rodenticides in their countries of origin. Their lack of knowledge of the human toxicity of tetramethylenedisulfotetramine or its banned status may encourage its importation for use in the United States. Its appearance in the United States should instill prudent caution in light of the unintentional exposures and intentional poisonings seen in China.[4-6,10,12-14]

The Toxic Exposure Surveillance System of the American Association of Poison Control Centers reported 1,365,471 human exposures to nonpharmaceuticals in 2000. Rodenticides were involved in 90,010 of those exposures, and 19,495 victims were treated in a health care facility. Of the rodenticide exposures, 1,694 were classified as ''unknown'' or ''other.''[34] Although these cases likely represent a lack of information, the intriguing possibility remains that these ''unknown'' or ''other'' pesticides may represent exposures to other dangerous substances used in other countries and go unrecognized in the United States.

DISCUSSION

The extreme toxicity of the compound, the lack of properties that enable detection, the absence of a specific antidote, and the history of tetramethylenedisulfotetramine's use in intentional mass poisonings suggests that tetramethylenedisulfotetramine may be considered a potential agent of terror. Tetramethylenedisulfotetramine should be included in the differential diagnosis of any patient presenting with unexplained seizures or the nonspecific clinical signs and symptoms consistent with tetramethylenedisulfotetramine poisoning and the lack of other reasonable explanations for the illness. Patients should be externally and internally decontaminated as appropriate, with close attention being paid to preventing secondary contamination of health care workers through broken skin.

Tetramethylenedisulfotetramine-induced seizures should be aggressively treated. Detection of the compound in biological specimens will not be clinically useful but is necessary to confirm exposure and alert appropriate agencies to its appearance. Public health entities and regulatory, enforcement, and investigative agencies should be alerted on suspicion or confirmation of an exposure to tetramethylenedisulfotetramine. Increased regulatory, enforcement, and educational activity about the appearance, recognition, and subsequent handling of suspected tetramethylenedisulfotetramine exposures may prevent more widespread exposures, in addition to preventing an intentional mass poisoning or terrorist event.

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Short abstract for Whitlow et al, YMEM
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