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Chlorobenzylidene malononitrile tear gas exposure: Rinsing with amphoteric, hypertonic, and chelating solution

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Abstract

Objective: Chlorobenzylidene malononitrile (CS) is the tear gas used by the police. The aim was to evaluate an amphoteric, hypertonic, and chelating rinsing solution in CS exposure.

Methods: The first (CS) group of six police officers was exposed to CS only. The second (preexposure) group of eight sprayed their faces with an aqueous, hypertonic, amphoteric, and chelating solution before CS exposure. The third (postexposure) group of eight sprayed their faces with an aqueous, hypertonic, amphoteric, and chelating solution after CS exposure. The time between exiting the CS cloud and arriving at the "ready for action" checkpoint was measured. Their facial pain both inside the CS cloud and at the checkpoint was assessed (0–10 points).

Results: The pain level inside the CS cloud was significantly lower in the preexposed group (5.6 $\pm$ 1.1; $p = 0.01$) than in the CS group (9.7 $\pm$ 0.5) and in the postexposure group (9.1 $\pm$ 0.4) where it was similar. The time interval between CS exposure and arrival at the checkpoint in the preexposure group (1:26 $\pm$ 0:44 min) was significantly shorter than both in the CS group (2:28 $\pm$ 0:25 min; $p = 0.04$) and postexposure group (2:30 $\pm$ 0:48 min; $p = 0.02$) where it was not different. The residual pain at the checkpoint in the preexposure (1.1 $\pm$ 0.4) and postexposure (1.4 $\pm$ 0.7) groups was similar with a significant lower pain level than in the CS group (2.3 $\pm$ 0.5; $p = 0.02$).

Conclusion: CS decontamination with an aqueous, hypertonic, amphoteric, and chelating solution reduces facial pain, whereas prevention with it reduces pain and recovery time.

Keywords

Chlorobenzylidene malononitrile, tear gas, decontamination, hypertonic, amphoteric, chelating solution

Introduction

Chlorobenzylidene malononitrile (CS) is the tear gas most commonly used by the police and also by demonstrators against police forces.

CS reacts with the moisture on the mucous membranes and irritates the eyes, nose, mouth, skin, and respiratory tract.[1,2] In the presence of moisture, CS rapidly hydrolyzes to malononitrile and 2-chlorobenzaldehyde, which has acidic characteristics (pK_a 2.9), and each of these then undergo further reaction to some additional acidic metabolites (Figure 1).[3] In addition, chlorine released from CS at high temperatures, while dispersing with pyrotechnic methods reacts with moisture on the mucous membranes producing hydrochloric acid.[4,5] Accordingly, CS and its acidotic products have direct irritating effects on the mucous membranes. On the other hand, CS interacts with TRPA1 mucocutaneous sensory nerve receptors and causes severe facial pain with reflex blepharospasm and lacrimation.[6,7] After absorption, CS also causes alkylation of intracellular sulfhydryl groups inhibiting SH-containing enzymes.[8,9]

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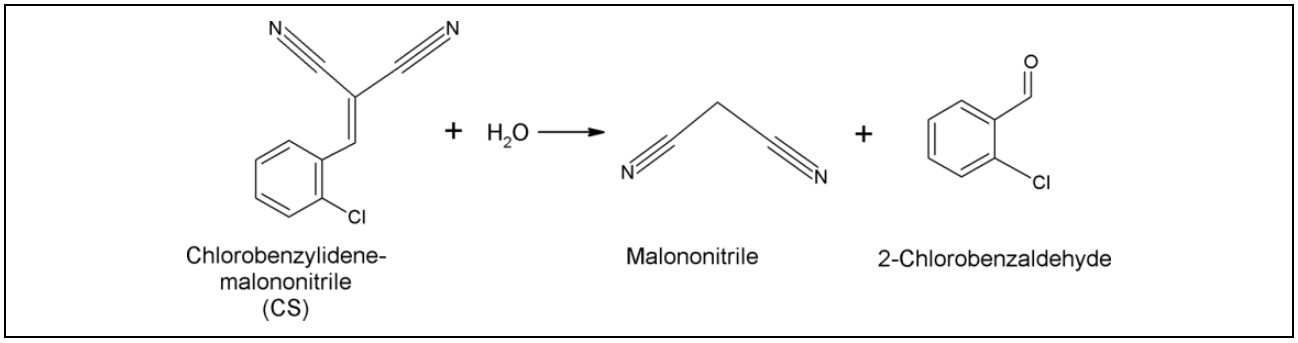

Figure 1. CS hydrolyzes in malononitrile and 2-chlorobenzaldehyde. CS: chlorobenzylidene malononitrile.

The management of CS-exposed victims is still a matter of debate. It is evident that rinsing should be commenced as soon as possible, but the optimum type of rinsing solution is not clear. Ocular rinsing is mostly recommended with water or isotonic 0.9% sodium chloride and cutaneous rinsing with soap or even shampoo and copious flowing water since CS is sparingly soluble in water.[10–12] CS dissolved in water is rapidly split by hydrolyzation that can be further increased by adding alkali solutions such as 7% sodium bicarbonate, 3% sodium carbonate, and 1% benzalkonium chloride.[8,9] All the above-mentioned alkali rinsing solutions are hypertonic and therefore decrease CS penetration into injured tissue with the reversion of its osmotic movement. Accordingly, it seems that the pH and osmolarity of the rinsing solution might play an important role in the effectiveness of CS decontamination. Unfortunately, the alkali solutions are not recommended for ocular rinsing, which is almost always required in CS exposure. Interestingly, it was recently shown that a commercially available hypertonic, amphoteric, and chelating agent with six binding sites prevented or rapidly ameliorated the ocular and cutaneous effects in five police officers exposed to CS, but no further studies were published.[13]

The aim of this clinical study was to evaluate a hypertonic, amphoteric, and chelating rinsing solution in CS exposure.

Materials and methods

Study group

Twenty-two police officers voluntarily participated in the study. Police officers are exposed to CS during their regular training exercises, their objective being to show police officers the symptoms of CS. The exercises with CS are usually performed by the police force with no immediate decontamination measures. The police officers who participated in this study gave their verbal informed consent and Slovenian National Medical Ethics Committee approved the use of Diphoterine® as a rinsing solution.

Rinsing solution

A commercially available hypertonic, amphoteric, and chelating agent was used (Diphoterine® solution, Prevor Laboratory, Valmondois, France). It is a washing solution recommended in case of skin or eye chemical exposures.[14–18] It is a nontoxic, nonirritating, and nonsensitizing first aid solution.[19] Police officers sprayed their faces continuously with 200 ml of Diphoterine solution from low-pressure spray containers before or after CS exposure by themselves until they emptied the whole containers. They had to spray their faces from a 20 cm distance and perpendicularly to the face. In addition, 200 ml low-pressure spray containers filled with water were prepared for the control group, but the police officers refused to use water sprays due to their previous bad experiences with water decontamination after CS exposure. Indeed, CS tear gas dissolved in water intensifies the irritation.[6,20] As a consequence, the blinded decontamination of the rinsing solution (water/Diphoterine solution) was not possible due to this refusal of the police.

CS exposure

CS exposure was achieved by the police officers running in a group for 20 s through the center of a CS cloud prepared with eight hand grenades, each containing 24 g CS during regular police training in an open-air field to simulate street conditions (Figure 2).

Figure 2. CS exposure by running for 20 s through a CS cloud prepared with eight CS hand grenades during regular police training. CS: chlorobenzylidene malononitrile.

Study design

In the field, 22 police officers were randomly lined up in the open-air field and successively assigned into three groups. The first (CS) group of six was exposed to CS only. The second (preexposure) group of eight sprayed their faces and eyes with 200 ml of the hypertonic, amphoteric, and chelating Diphoterine solution just before CS exposure. The third (postexposure) group of eight sprayed their faces and open eyes with 200 ml of the hypertonic, amphoteric, and chelating solution immediately after CS exposure.

The time between exiting the CS cloud prepared with eight CS hand grenades and arriving at the "ready for action" checkpoint established by themselves according to their previous experience of operating in riots was measured. The ready for action checkpoint was located 20 m from CS cloud.

Their facial pain both inside the CS cloud and at the checkpoint was assessed by the Numeric Intensity Rating Scale (NRS-11; 0–10 points).[21]

Statistical methods

All data are presented as mean $\pm$ SD. The statistical significance of differences between the values was evaluated by the one-way between groups analysis of variance followed by the Bonferroni post hoc test for multiple-group comparisons. A p value of less than 0.05 was considered to be significant. Data analysis was performed using Statistical Package for Social Sciences (version 11.5; SPSS Inc., Chicago, Illinois, ZDA).

Results

The results are shown in Table 1. CS exposure results in severe facial pain (9.7 $\pm$ 0.5 points) putting police officers out of action for almost 3 min (2:28 $\pm$ 0:25 min).

An analysis of the differences in pain and time between the different groups revealed a significant difference in global. The post hoc test results showed that the pain level inside the CS cloud was significantly lower in the preexposed group (5.6 $\pm$ 1.1; $p = 0.01$) than in the CS group (9.7 $\pm$ 0.5) and in the postexposure group (9.1 $\pm$ 0.4) where it was similar ($p = 0.55$; Table 1). The time interval between CS exposure and arrival at the checkpoint in the preexposure group (1:26 $\pm$ 0:44 min) was significantly shorter than both in the CS group (2:28 $\pm$ 0:25 min; $p = 0.04$) and postexposure group (2:30 $\pm$ 0:48 min; $p = 0.02$) where it was not different ($p = 1.00$; Table 1). The residual pain at the checkpoint in the preexposure (1.1 $\pm$ 0.4) and postexposure (1.4 $\pm$ 0.7)

Table 1. Pain level and time interval between exposure and arrival at the "ready for action" checkpoint in 22 police officers treated with amphoteric, hypertonic, and chelating solution before and after tear gas (CS) exposure.

Group (number of police officers)	Pain level inside the CS cloud (0–10 points)	Time interval between CS exposure and arrival at the ready for action checkpoint (min)	Residual pain at the ready for action checkpoint (0–10 points)
CS group (6)	9.7 ± 0.5	2:28 ± 0:25	2.3 ± 0.5
Preexposure group (8)	5.6 ± 1.1[a]	1:26 ± 0:44[a]	1.1 ± 0.4[a]
Postexposure group (8)	9.1 ± 0.4	2:30 ± 0:48	1.4 ± 0.7[a]

CS: chlorobenzylidene malononitrile.
[a]$p < 0.05$.

groups was similar ($p = 1.00$) with a significantly lower pain level than in the CS group (2.3 ± 0.5; $p = 0.01$ and $p = 0.02$, respectively; Table 1).

Discussion

In this study, the police officers preventively exposed to Diphoterine solution just before entering the CS cloud had lower facial pain during CS exposure and became ready for action more rapidly after CS exposure. These findings might be very important in real-life situations, such as riots, where every second counts and can save police officers' lives. In addition, decontamination with Diphoterine solution after CS exposure effectively reduced facial pain, but the police officers did not feel ready for action any earlier compared with the police officers exposed to CS only.

These results confirm those observed in the preliminary study with five police officers performed by Viala et al.[13] In this former study, Diphoterine solution was used as pre-CS exposure prophylaxis both in the eyes and on the face skin with fast recovery within a few minutes and no facial or ocular irritation was observed.[13] However, this observation was done only in one volunteer and it was just qualitative. On the other hand, this study confirms faster recovery with the preexposure use of Diphoterine solution with quantitative and comparative data, both in terms of pain level and recovery time in case of CS cloud exposure. In the same way, the present study confirms that decontamination with Diphoterine solution after CS exposure reduces facial pain and that Diphoterine solution does not intensify CS gas symptoms. Interestingly, recovery time using Diphoterine solution after CS exposure is shorter in the present study (around 2 min 30 s) than in the preliminary study by Viala et al. (around 4 min), since CS exposure was probably stronger in the former study.[13] Indeed, Viala's exposure area was a closed chamber and the time of exposure was based on symptom observations from each police officer's point of view, which can lead us to think that it was more than 20 s. Nevertheless, in the present study, all police officers observed classical symptoms of CS tear gas exposure, despite it happening in an open space with a short duration (20 s).

The mechanism of preventive and decontamination effectiveness of Diphoterine solution on CS exposure could be explained with its main physical and secondary chemical properties, namely, mechanical washing, dilution, hypertonicity, and amphoteric character. Spraying with Diphoterine solution mechanically washes CS from the skin and its hypertonicity osmotically prevents the penetration of CS into injured skin and eyes in contrast to hypotonic tap water. This wash-in effect has been demonstrated as it favors the diffusion of a part of the chemical agent, while water washes out and dilutes the chemical agent at the surface of the tissues.[22] In addition, amphoteric Diphoterine solution could stop the aggressiveness of acidotic 2-chlorobenzaldehyde released by CS hydrolysis and promote CS hydrolysis by increasing moisture pH.[18,23,24] Amphoteric Diphoterine solution could also limit the danger of hydrochloric acid probably synthesized from chlorine atoms released from CS at high temperatures during pyrotechnic methods.[4,5] Furthermore, amphoteric Diphoterine solution can encapsulate and chelate electrophiles, such as CS, malononitrile, and 2-chlorobenzaldehyde, with its multiple binding sites and further prevent their contact with skin and mucous membranes, which reduces its alkylating effects and interactions with mucocutaneous sensory nerve receptors TRPA1.[6,7]

The advantages of Diphoterine solution with regard to other rinsing solutions are also nonirritating properties, no side effects, and general use since it can be used for cutaneous and ocular decontamination. In the present study, no police officer reported any ocular or cutaneous problem after using Diphoterine

solution. Its use as an ocular decontaminant was studied by Merle et al. on 66 patients with alkali injuries presented to the Emergency Department.[14] The use of Diphoterine solution as a washing solution within the first step of the hospital protocol helps to significantly reduce reepithelialization time in grade 1 and 2 injury (Ropper-Hall's classification of eye injuries) when compared with water washing followed by the same treatment.[14] The use of Diphoterine solution also significantly decreased complications such as corneal opacity.[14] A reported case of delayed use of Diphoterine solution on grade IV ocular burns resulted in no need for cornea graft and healing with classical topical and systemic treatment.[15] Interestingly, a recent in vivo study of rinsing with Diphoterine solution found it to be significantly more effective than saline solution in the treatment of mustard ocular injuries.[25]

The main limitation of the presented study is the lack of a control group using water for cutaneous and ocular decontamination after CS exposure. As has already been presented, the police officers refused to use prepared 200 ml low-pressure container sprays filled with water for decontamination after CS exposure due to their previous bad experience with water rinsing. However, the police officers participating in this study, who experienced CS rinsing with water in the past, favored Diphoterine solution over water rinsing in their reports. This agrees with the fact that CS dissolved in water intensifies irritation and worsens the symptoms, whereas washing with Diphoterine solution did not increase the CS effects.[6,20,23] Other limitations of this study are the relatively low number of included volunteers and measurement of qualitative symptoms. Nevertheless, this study might stimulate further similar studies including a larger number of volunteers or victims of real riots. In addition, in future experimental studies should be performed to demonstrate the key parameters of the decontamination mechanism in CS exposure, since these could be useful also for the prehospital emergency care and decontamination at the Emergency Departments in case of CS exposures.

Conclusion

An aqueous, hypertonic, amphoteric, and chelating solution used prior to entering a riot reduces pain and recovery time after CS exposure. Moreover, in cases of CS exposures, decontamination with the aqueous, hypertonic, amphoteric, and chelating solution reduces facial pain.

Conflict of interest

The authors declared no conflicts of interest.

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