

CHEMICAL ADDITIVES OF STREET HEROIN IN CAIRO

BY

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ABSTRACT

Street heroin powder from seized samples had been sent to Forensic Toxicology Laboratory. Fifty-one samples were collected through year 2005 from Cairo City. Samples had different colours: white, brown and grey. Samples were analyzed using thin layer chromatography (TLC). Twenty-four samples were positive for opiates and 27 samples were negative for any opioids. These results were confirmed by HPLC and GC/MS. Heroin concentrations in heroin positive samples ranged from 0.27 % to 34.56 %. Adulterants included paracetamol, caffeine, tramadol, theophylline, methomyl, ephedrine, carbamazepin and others. Adulteration of heroin carries the risk of toxicity from these chemicals which could be missed in diagnosis and hence treatment. Physicians should put in mind the idea of mixed toxicity during treatment of acute overdose of heroin. This should encourage physicians working in Emergency Units to analyze for all available drugs and chemicals to avoid miss- diagnosis because heroin additives will lead to change in the classical clinical picture of heroin abuse over dose or withdrawal.

INTRODUCTION

Heroin (diacetyl morphine) is a semi-synthetic narcotic derived from morphine that was first synthesized in 1874. It was originally marketed as a safer, non-addictive substitute to morphine. Soon after introduction, it became clear that heroin was as addictive as morphine. In the United States, heroin was the most frequently abused narcotic, followed by codeine and methadone (Darke et al., 1999).

In its pure form, heroin is a white powder with a bitter taste. Street heroin sam-

ples are frequently mixed with other substances so dealers may maximize their profits. Because of these impurities and additives, street heroin may appear in a variety of hues and colours, ranging from white to dark brown (Ellenhorn, 1997).

A heroin sample, apparently only 65 % pure, may in fact has no adulterants/ diluents present. Depending on country of origin, and thus on method of manufacture, the production of the heroin itself produces a more or less pure product. In some cases, various other opiate alkaloids, such as noscapine, papaverine and acetylco-

deine (which is a by-product of heroin manufacture), may account for the bulk of the other 35 %. In this sense those substances might be more properly referred to as impurities (Gough, 1991).

The term adulterant is used to refer to substances added to illicit drugs in the process of selling and distribution. Adulterants proper are in fact other psychoactive drugs (like caffeine or paracetamol), which are much cheaper than the main substance, have a similar or complimentary effect when mixed with it and therefore help to hide the fact that the substance has been diluted. Substances, which are not psychoactive, such as glucose and lactose, are more formally known as diluents. These are added to a drug to increase the amount of drug available to be sold. Most adulteration/ dilution is carried out by the street dealers themselves (Coomber, 1997a).

Variations in clinical presentation commonly occur. Patients often co-ingest other psychoactive substances, as alcohol, benzodiazepines, amphetamines, cocaine and other opiates. Furthermore, street heroin is commonly contaminated or diluted with substances having clinical effects of their own. These include cocaine, amphetamines, quinine, quinidine, chloroquine, phenobarbital, lidocaine, benzocaine, tetracaine, caffeine, methaqualone, fentanyl and other opiates (Ellenhorn, 1997).

This study aimed at analysis of seized heroin samples to verify their heroin concentrations, presence of adulterants and the nature of these adulterants.

MATERIAL AND METHODS

Samples:

Suspected heroin samples seized by police were sent to Forensic Chemist Laboratory in Cairo, for analysis. Samples were of different colours; white, grey and brown. Fifty-one samples were collected through year 2005 from Cairo city.

Methods:

All samples were first analyzed by thin layer chromatography (TLC). Then results were confirmed by high performance liquid chromatography (HPLC). HPLC also was performed to detect chemicals not detected by TLC. Lastly all samples were analyzed by gas chromatography/ mass spectrometry (GC/ MS) for quantification of different chemicals found.

1-Extraction; Four methods were used:

a- Opiates and alkaline drugs (Meadway et al., 1998): Briefly, 1 ml of hydrochloric acid was added to 1 mg of each sample. After heat hydrolysis, sodium bicarbonate was added. Then 1 ml Narcs buffer and 5 ml of chloroform: isopropanol (8:1) were added. After filtration and evaporation, extract was reconstituted with 100 μ l chloroform.

b- Acidic drugs (Ghanem and Gad El - Hak, 1997): 1 ml of 1 N hydrochloric acid and 5 ml of chloroform were added to 1 mg of each sample. After centrifugation, filtration and evaporation, extract was reconstituted with 100 µl chloroform.

c- Benzodiazepines (George and Braithwaite, 1995): 1 ml of hydrochloric acid was added to 1 mg of each sample. After heat hydrolysis, 10 ml petroleum spirit was added. After centrifugation, solvent layer was aspirated, evaporated and reconstituted with 100 µl chloroform.

d- Pesticides (Fysh and Whitehouse, 1986): Samples were extracted using diethylether. The ether fraction was separated, evaporated and the residue was dissolved in a small portion of ethanol.

2- Detection by TLC:

a- Opiates and alkaline drugs (Meadway et al., 1998): Samples extract (20 µl) were spotted along side of opiate standard onto an activated plate, then it was dried and placed in TLC tank containing ethyl acetate: methanol: concentrated ammonia (85: 10: 5). It was allowed to run and then removed when the front had reached the predetermined end (10 cm from the starting point), dried and finally visualized by spraying with acidified iodoplatinate reagent. Brown spots indicated the presence of an opiate.

b- Paracetamol (Ghanem and Gad El - Hak, 1997): As in opiates but dried plates were sprayed with 5 % ferric chloride reagent. Blue spots indicated the presence of paracetamol.

c- Benzodiazepines (George and Braithwaite, 1995): As in opiates but the eluent was toluene: glacial acetic acid (97: 3) and plates were sprayed with 18 N sulphuric acid followed by freshly prepared 1 % sodium nitrite. After dryness, plates were sprayed with ammonium sulphamate then 1 % naphthyl - ethylene - diamine in 80 % acetone.

d- Pesticides (Clarke, 1986): As in opiates but the eluent was hexan: acetone: chloroform (70: 25: 5) then dried plates were sprayed with 2 % furfuraldehyde in acetone followed by spraying with diluted sulphuric acid.

3- Detection by high performance liquid chromatography:

Extract was reconstituted with 100 µl methanol and examined according to Love and Pannell (1980), under the following conditions: Mobile phase: methylene chloride: methanol (1: 1), flow rate: 0.5 ml / min, UV 254 nm detector, and column: sorbet, C 8. Conditions were reset for pesticides (methomyl) analysis as: mobile phase: 40 % acetonitrile in water, flow rate: 1 ml/ min, pressure: 144 psi and column: C 18, ODS, 30 - 35 µ.

4- Detection by GC/MS:

It was performed to determine the different concentrations of heroin and other adulterants/diluents. Conditions for opiates were set according to Besacier et al., (1997): instrument: Agilent 6890, column: DB-1, 30 m X 0.25 mm i.d., 0.25 µm, carrier: Helium at 1 ml/ min, oven: 200 °C for 1.0 min, 280°C at 4°C / min and held at 280°C for 12 min, injector: split mode, 250°C and detector: flame ionizations (HP 5890 series II). For impurities, conditions were reset according to Allen et al., (1984).

RESULTS

Analysis of seized samples by TLC revealed that 24 samples (47.06 %) were containing opiates while 27 samples (52.94 %) were negative for any opioids. These results were confirmed by HPLC and GC/MS.

1- Heroin positive samples showed:

a- Heroin (diacetylmorphine) : concentrations ranged from 0.27 mg % to 34.56 mg % with an average concentration of 9.59 mg %.

b- Alkaloid impurities: 6- mono acetyl morphine in 87.5 % of samples with average concentration 7.89 mg %, acetyl codeine in 50 % of samples with average concentration 2.88 mg %, morphine in 25 % of samples with average concentration 3.62 mg %, papaverine in 25 % of

samples with average concentration 0.58 mg % and meconin in 12.5 % of samples with average concentration 1.3 mg %.

c- Predominant adulterants: paracetamol in all samples with average concentration 37.58 mg %, caffeine in 62.5 % of samples with average concentration 32.76 mg % and ephedrine in 37.5 % of samples with average concentration 10.36 mg %.

d- Other adulterants : chlorpheniramine in 12.5 % of samples with average concentration 7.89 mg %, phenobarbitone in 25 % of samples with average concentration 2.64 mg%, methylene-dioxy-meth-amphetamine (MDMA) in 25 % of samples with average concentration 3.4 mg %, carbamazepine in 12.5 % of samples with average concentration 8.92 mg % and theophylline in 12.5 % of samples with average concentration 34.78 mg %.

2- Heroin negative samples showed:

paracetamol in 44.4 % of samples with average concentration 67.9 mg %, caffeine in 44.4 % of samples with average concentration 16.26 mg % and ephedrine in 22.2 % of samples with average concentration 4.4 mg %, chlorpheniramine in 22.2 % of samples with average concentration 3.67 mg %, methomyl in 11.1 % of samples with average concentration 42.5 mg %, tramadol in one sample with concentration 36 mg % and amitriptylline in 11.1 mg % of samples with average concentration 34 % .

DISCUSSION

The World Drug Report (2005), stated that global illicit opium cultivation increased by 16 % in 2004. Heroin is the most frequently abused narcotic (Darke et al., 1999).

The results of the present study showed that the purity of seized heroin samples is relatively low compared to reports from other countries. In UK, during years 1991, 1992 and 1993 the average difference between customs seizers and street seizers was only between 8- 14 % with the average purity of street heroin being 45 %, 46 % and 39.25 % respectively (Coomber, 1997b). Turkish heroin seized in UK almost had no adulteration. In UK, illicit heroin from Africa showed adulteration in 84 % of seized samples (from 1990- 1993), while illicit heroin from Europe showed 100 % adulteration (Coomber, 1997a).

In the present study, seized heroin samples were mainly adulterated by paracetamol, caffeine, ephedrine and phenobarbitone. Other adulterants were theophylline, chlorpheniramine, amphetamine and carbamazepin. Coomber (1997a), found that in 44 % (of 228 samples), no adulterants were found. The predominating adulterants of heroin were paracetamol and caffeine. Average concentrations were 41 % for paracetamol and 33 % for caffeine.

Small quantity of griseofulvin was found in one sample. Also, aflatoxin and phencyclidine intoxication were reported. Street samples produced strychnine and arsenic poisoning (Ellenhorn, 1997). Low concentrations of other drugs as benzocaine, diazepam, procaine and phenobarbitone were found (Kaa, 1994).

In USA, during January- April 2005, 26 cases of atypical reactions after heroin use were reported in five states. Analysis of drug specimens or testing of urine was performed in certain cases; in eight patients, the veterinary pharmaceutical clenbuterol (β_2 adrenergic receptor agonist) was detected (Hoffman et al., 2005).

Impure street drugs can be dangerous and these dangers are sometimes exaggerated. Drugs additives carry the risk of drug interactions. Such interactions can either increase or decrease a drug's expected effects. Both caffeine and paracetamol for example, increase the amount of heroin retained in the volatilisation (the heating, melting and then vaporization of the drug for inhalation or chasing) process. Concomitant use of anti-epileptic drugs as carbamazepin and barbiturates can speed up the metabolism of opioids in the liver. Tricyclic antidepressants as amitriptyline significantly increase the plasma availability of morphine. Antihistamines can cause breathing difficulties, confusion and muscle twitches (Coomber, 1997 b).

Surprisingly, the present study showed that 27 out of 51 samples were negative for any opioids. Some samples contained the main adulterants for heroin (paracetamol, caffeine and ephedrine). Lower concentrations of chlorpheniramine and tramadol were encountered in some samples. However, methomyl (a carbamate insecticide) was

detected in 11.1 % of samples. This dangerous adulteration can produce toxic effects that may mimic acute toxicity of opiates or its withdrawal that may be missed in diagnosis and/ or treatment. This should encourage physicians working in Emergency Hospitals to analyze for all available drugs and chemicals to avoid miss-diagnosis.

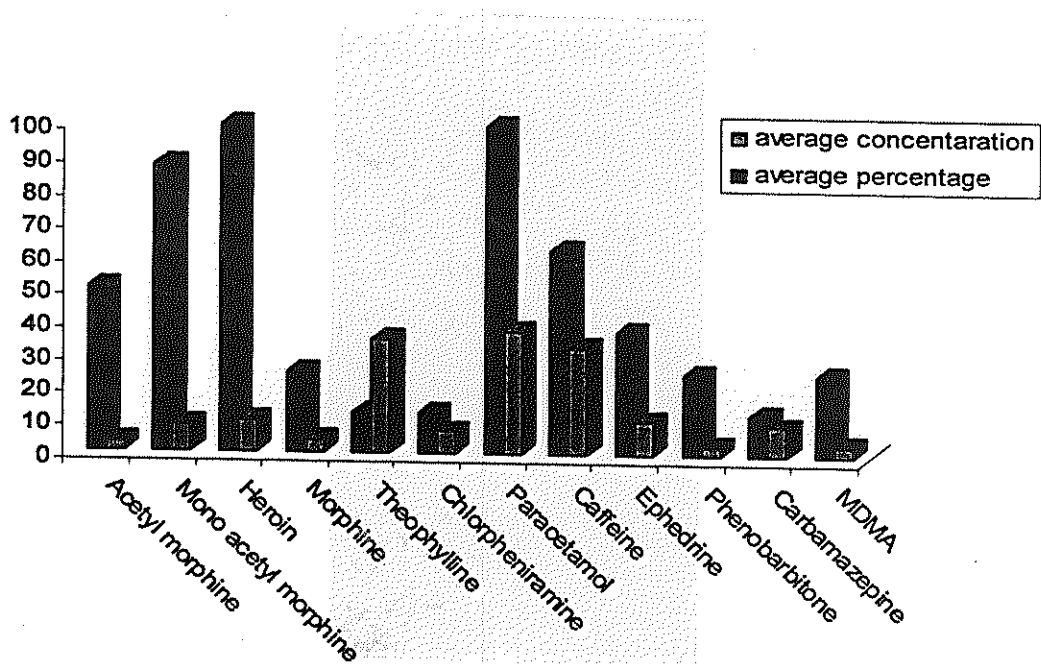


Diagram (1): Results of analysis of heroin positive samples.

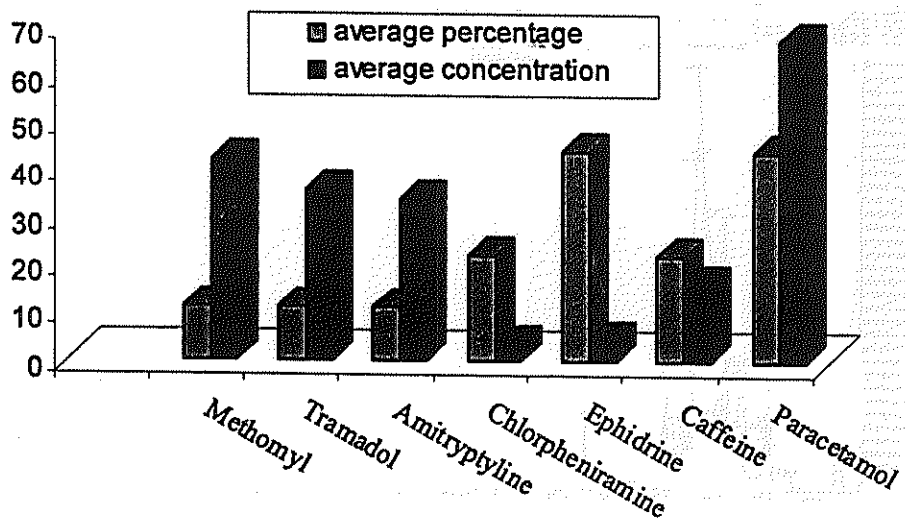


Diagram (2): Results of analysis of heroin negative samples.

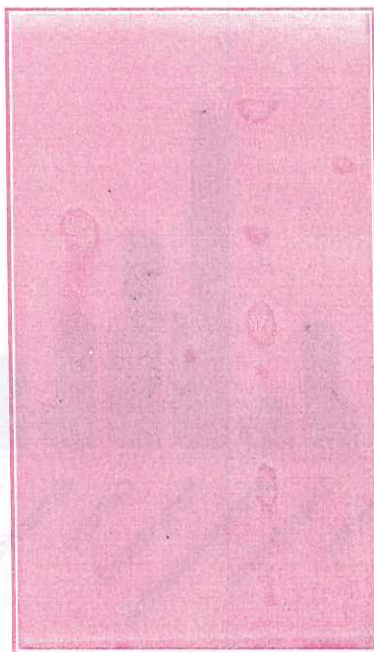


Fig. (1): Thin layer chromatogram showing spots of heroin and some opioid impurities detected in some street heroin samples.

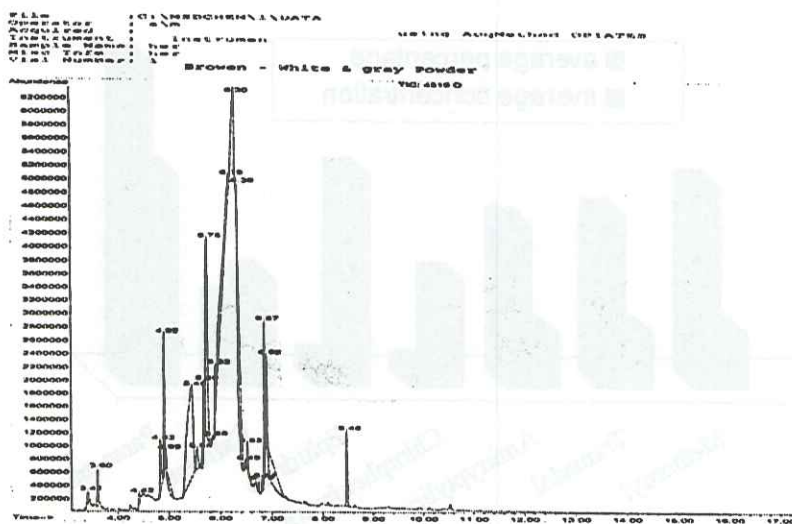


Fig. (2): HPLC of seized heroin sample showing the presence of multiple adulterants.

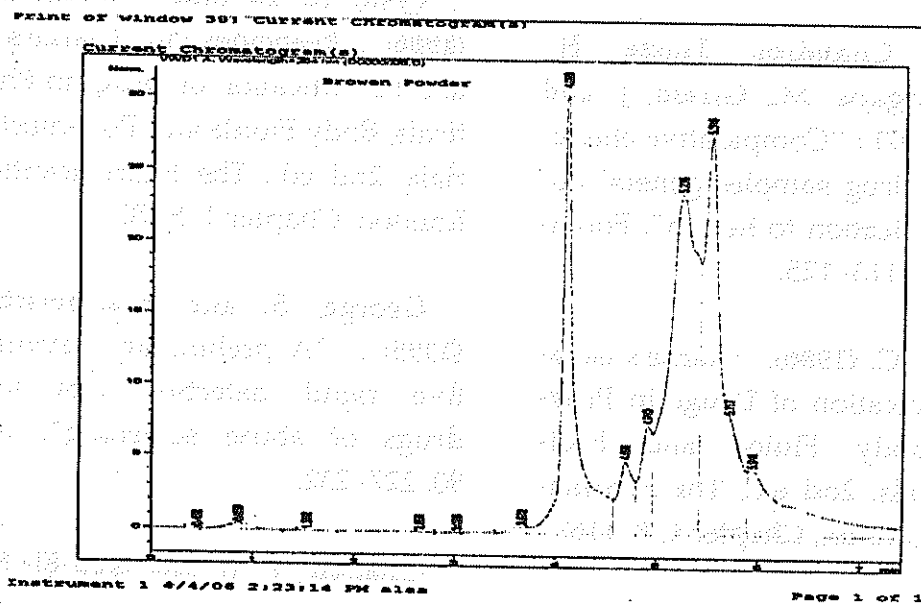


Fig. (3): HPLC of a seized heroin sample showing the presence of multiple adulterants.

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الإضافات الكيميائية لهرويين الشوارع في القاهرة

المشركون في البحث

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لقد تم تحليل عينات من البودرة المضبوطة بواسطة الشرطة في مدينة القاهرة خلال عام ٢٠٠٥م والتي قد تم إرسالها إلى معامل الطب الشرعى لتحليلها، كان عدد هذه العينات ٥١ عينة وكانت ألوانها مختلفة منها البيضاء والبني والرمادي، ثم تم تحليلها بعدة طرق مختلفة : TLC, HPLC and GC/MS :

كانت نتائج التحاليل كالتالى : هناك ٢٧ عينة خالية تماماً من الأفيون أو أحد مشتقاته، أما نسبة الهرويين في العينات الإيجابية فقد تراوحت بين ٢٧٪ - ٣٤,٥٦٪ كما وجدت نسب مختلفة من المورفين والكوداين في بعض هذه العينات وهذه المواد تنشأ أثناء تخليق الهرويين.

أما بالنسبة للمواد الأخرى والتي تم العثور عليها في العينات فقد اشتملت على الباراسيتامول والكافيين في كل العينات وهناك بعض المواد الأخرى والتي وجدت بنسب متفاوتة مثل : الترامادول والثيوفيلين والميثوفيل.

هذه الإضافات غالباً لا يمتبه إليها أثناء علاج حالات التسمم بالهرويين كما أنها تسبب أعراض مختلفة للتسمم الحاد أو الأعراض الإنسحابية لذلك يجب على كل طبيب يعالج حالات التسمم أو الانسحاب من تعاطى الهرويين أن يقوم بعمل كل التحاليل المتوفرة للكشف عن كل المواد التي قد تضاف إلى الهرويين والتي قد تحتاج إلى علاج مختلف. وذلك من أجل تمام علاج المرضى والمحافظة على سلامتهم.