J Forensic Sci, Oct. 1974, Vol. 19, No. 4

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Discoloration Effect of Diluents in Contraband Cocaine

In the course of police investigations of confiscated drug samples, cocaine mixtures of various shades from white to brown have been encountered and analyzed at the Crime Laboratory of the New York City Police Department. Slight discoloration of cocaine mixtures is within reason, in view of the reported discoloration of lactose [*1,2*] and of lactose-amphetamine [*3-5*] upon storage.

Recently a very interesting case involving cocaine was resubmitted to the laboratory, wherein a drastic change in the physical appearance of the confiscated evidence was observed. The evidence, originally a tan powder, was analyzed in July 1972. It contained aspirin tablets along with the contraband cocaine powder. The other diluents present were not analyzed at that time. This case was reanalyzed in February 1973 and at that time the powder was brown in color, as compared to the original tan powder. Finally, during a court trial in June 1973, the evidence was opened and found to be a dark tarry substance and the aspirin tablets were no longer present. Due to the discrepancy in the physical appearance of the evidence from the time of the original analysis to its appearance in court, the court had reservations in accepting the evidence unless a reasonable scientific explanation was furnished for this change. Since the trial was in progress, the court permitted a maximum of two days to conduct the related experiments with the evidence in question so that an explanation for this drastic change could be ascertained.

This paper presents the experimental work done with evidence in conjunction with the studies on the discoloration effects of known cocaine and the common diluents associated with it. The interaction of the diluents, which causes discoloration and tarry transformation, is also discussed.

Experimental

Studies were conducted in two parts: The first part deals with the analysis of the evidence and the second part deals with a study on the discoloration of various combinations of diluents commonly associated with contraband cocaine.

Analysis of Evidence

1. Positive cocaine identification was determined from the alkaline chloroform extraction of the water-soluble part of the tarry substance. Identification was made by

Received for publication 17 Sept. 1973; revised manuscript received 7 Jan. 1974; accepted for publication 22 Jan. 1974.

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color and microcrystalline tests [6,7]. Additional confirmation was obtained on a gas chromatograph/mass spectrometer (GC/MS).

2. The tarry substance was acidic and had the odor of acetic acid. The presence of acetate ions was determined by $FeCl_3$ test and ethyl acetate tests [8,9].

3. 5-hydroxymethyl furfural and related compounds are the degradation products of lactose, especially when the spray-dried process lactose is used [1,2]. Identification of these furfural compounds was made from the benzene extraction of the tarry substance in acid media. The McCance method [10] and Sanchez reaction [7] were used for this identification.

4. The tarry substance dissolved in methanol giving a brown solution and leaving a white crystalline solid. The solid was filtered, purified by further washings with methanol, and identified as lactose. Lactose identification was made by primary screening test for reducing sugars with benedict's solution, followed by X-ray diffraction and GC/MS identification.

5. All organic nitrogeneous compounds were isolated from the tarry substance by repeated extractions with water and chloroform in acid and alkaline media. The residual tarry substance was submitted to the classical sodium fusion test, and presence of nitrogen in that tarry substance was detected.

6. Furfural derivatives were isolated by benzene extraction of the tarry substance in an acidic medium. The cocaine was then extracted with benzene in sodium bicarbonate media. The extracted cocaine was passed through an acid-washed celite column and quantitation was done using a Perkin-Elmer 350 spectrophotometer [11,12].

Discoloration Due to Diluents

Procaine, benzocaine, tetracaine, lidocaine, quinine, and sugars such as lactose are the most common diluents mixed with cocaine. On occasion other chemicals, such as aspirin, have been found with the other diluents. A 5-hydroxymethyl furfural and other furfural derivatives are also present as contaminants when spray-dried lactose is used as a cutting agent [1,2].

Studies on discoloration were conducted using USP-grade lactose and hydrochlorides of cocaine, procaine, benzocaine, tetracaine, lidocaine, and quinine. The thermal stability of each of the compounds was studied by heating them up to four hours in sealed plastic bags on a steam bath. Each was found thermally stable and no color change nor browning was observed.

Experiments on the discoloration effects of various combinations of these compounds, which under normal storage conditions at ambient temperatures would take long periods of time, were conducted. To increase the rate of reaction and to study the discoloration effect in a short period of time the samples were heated on a steam bath.

Table 1 shows the discoloration effect due to the interaction of lactose with those amines which are commonly used as cutting agents with cocaine. Tables 2 to 4 show the effect of other contaminants, such as aspirin, furfural, and moisture, on the lactose-amine reaction resulting in the brown tar formation.

Discussion and Results

The results of this study indicate that lactose, if mixed with cocaine and stored for a long period of time, will not react and give discoloration. However, some discoloration may occur due to the condensation reactions of the degradation products of lactose, such as 5-hydroxymethyl furfural and other furfural derivatives which are associated with lactose due to its spray-drying process [1,2]. If other amines, commonly used for cutting cocaine, are present in addition to lactose, browning on storage is likely to occur due to

TABLE 1—*Browning due to lactose-amine interaction. Heating on steam bath was done for 3 h in heat-sealed plastic bags.*

Reactants	Ratio[a]	Discoloration
Lactose + procaine	7:1	gradual discoloration finally resulting in dark brown color in 3 h
Lactose + benzocaine	7:1	very slow and slight discoloration observed in 3 h
Lactose + tetracaine	7:1	no discoloration observed
Lactose + lidocaine	7:1	very slow and slight discoloration observed in 3 h
Lactose + quinine	7:1	no discoloration observed
Lactose + cocaine	7:1	no discoloration observed

[a] Ratio of 7:1 was chosen since it was the most realistic ratio pertaining to the evidence in question.

TABLE 2—*Effect of furfural on browning. Heating on steam bath was done for 3 h in heat-sealed plastic bags.*

Reactants	Ratio	Discoloration
Lactose + furfural	7:1	gradual and slight browning only
Lactose + procaine + furfural	7:1:1	immediate red coloration which turns to a brown tarry substance
Lactose + benzocaine + furfural	7:1:1	immediate red coloration which turns to a brown tarry substance
Lactose + tetracaine + furfural	7:1:1	gradually turns brown
Lactose + lidocaine + furfural	7:1:1	gradually turns brown
Lactose + cocaine + furfural	7:1:1	gradual and slight browning only

TABLE 3—*Effect of acetate ions on browning. Heating on steam bath was done for 3 h in heat-sealed plastic bags.*

Reactants	Ratio	Discoloration
Lactose + aspirin + CH_3COOH	7:1:1	no color change
Lactose + procaine + CH_3COOH + aspirin	7:1:1:1	starts browning almost immediately, 35 min to a dark tarry substance, no procaine detected
Lactose + procaine + aspirin + 1 drop of water	7:1:1	starts browning almost immediately, 35 min to a dark tarry substance, no procaine detected after the physical change[a]
Lactose + procaine + CH_3COOH	7:1:1	starts browning almost immediately, 35 min to a dark tarry substance, no procaine detected after the physical change
Lactose + cocaine + aspirin	7:1:1	no change
Lactose + benzocaine + aspirin	7:1:1	browning starts slow, benzocaine still present
Lactose + tetracaine + aspirin	7:1:1	slight browning

[a] An acetic-acid-like odor was detected.

TABLE 4—*Effect of moisture on lactose-amine reaction. Heating on steam bath was done for 3 h in heat-sealed plastic bags.*

Reactants	Ratio	Discoloration
Cocaine + lactose + aspirin (ovendried)	7:1:1	no discoloration
Cocaine + lactose + aspirin + moisture	7:1;1	no discoloration
Procaine + lactose + aspirin (ovendried)	7:1:1	slow discoloration towards browning
Procaine + lactose + aspirin + moisture	7:1:1	starts turning brown within 5 min and completes tar formation in 30 min, no procaine found present after tar formation[a]

[a] An acetic-acid-like odor was detected.

lactose-amine reaction, commonly known as the Milliard reaction [*1*].[2] The extent of browning would depend on the reactivity of amines with lactose (Table 1). Procaine, (and other primary amines), is very reactive because it requires a low order of initiation energy and exhibits autocatalytic qualities once the reaction has begun [*1*]. The furfurals associated with lactose will also react with the amines, as can be seen from Table 2. It has been further reported that certain ions such as acetates, stearates, etc catalyze the Milliard reaction [*2*]. Table 3 indicates the effect of acetate ions on the Milliard reaction. Aspirin brings about the same catalytic effect as that of acetates, since on hydrolysis it releases acetic acid. Moisture has been found to be an equally important factor in bringing about the Milliard reaction, as can be seen from Table 4.

The evidence in question, after transformation, was found to contain lactose, acetate ions, cocaine, furfural derivatives, and moisture. Quantitation of the evidence indicated that the amount of cocaine found in the tarry substance is in agreement with the amount of cocaine reported in the original analysis and, as previously stated, known mixtures of cocaine and lactose do not result in discoloration (Table 1). Therefore, it can be concluded that cocaine was not involved in the formation of the tarry substance. A sodium fusion test on the isolated tarry substance indicated the presence of nitrogen. In view of the presence of nitrogen in the isolated tarry substance, the experimentation with the common diluents (Table 3), and the similarity in the physical appearance between the evidence and the known lactose-procaine mixture, it was deduced that the most probable reaction which resulted in the tar formation was that of procaine with lactose.

The original evidence, which was analyzed in July 1972, was a tan powder which turned brown by February 1973 during storage. This indicates the initiation of the lactose-procaine browning reaction. The tar formation, which occured in a relatively short period of time between February and June 1973, could be explained by the catalytic effect of acetates resulting from the decomposition of aspirin during storage.

The hydrolysis of procaine in dilute acetic acid did not occur. However, the effects of moisture and acetate ions on the mechanism of browning due to the lactose-procaine reaction, and the isolation and identification of the end products formed, are presently under study and will be presented in a subsequent communication.

Summary

Discoloration in contraband drugs may occur on storage. The extent of this discoloration depends on the time of storage and the type of cutting agent present with

[2]The Milliard reaction is a Schiff base reaction.

the drug. In the investigation of the evidence in question the main cause of the brown tarlike transformation of the tan powder was attributed to the procaine-lactose reaction, which was catalyzed by the acetic acid due to the hydrolysis of the aspirin present in the contraband seizure. The self-condensation of the degradation products of lactose, such as 5-hydroxymethyl furfural, can also contribute to the discoloration.

Comments

The explanation for the brown tarry transformation of the confiscated cocaine powder, as a result of the experimental work detailed herein, was accepted by the court. The confiscated cocaine was then admitted as evidence and subsequent convictions were obtained.

Acknowledgments

Our thanks go to Captain Charles V. Rorke and Lieutenant Patrick McCarthy for their encouragement during this investigation. Our special thanks go to Chemist James Fava and members of the Chemistry Section for their cooperation and help in this investigation.

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