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The Forensic Identification of Heroin

As a result of the rapid increase in requests and the ever-rising backlog of cases, forensic science laboratories are developing an intense interest in analytical procedures that can provide rapid, inexpensive, and sensitive methods for identifying drugs. However, the forensic chemist must always be aware of the scientific accountability that is expected of him or her in our adversary system of justice. The necessity for performing a specific identification far outweighs any shortcuts that may be adopted to expedite a chemical analysis. As the importance of scientific testimony grows, the courts are becoming more conscious of criteria that must be met to support the admissibility of scientific evidence. The accuracy of heretofore accepted statements and descriptions relating to the identification and comparison of physical evidence is increasingly becoming subject to scrutiny and debate. Practitioners of the law are starting to take advantage of inconsistencies in the scientific literature and the lack of experimental data to discredit an entire scheme of analysis. One only has to examine recent court decisions pertaining to the forensic analysis of marihuana to confirm this trend. The contrasting opinions of experts regarding the number of *Cannabis* species have served to confuse and, in some instances, discredit a botanical and chemical scheme of analysis that until the present has found general acceptance in the forensic science community [*1,2*].

Today heroin (diacetylmorphine) is the most widely abused narcotic drug in the world. Its long history of abuse has produced an abundant number of suggested analytical techniques and procedures for its identification. These suggested methods incorporate classical color and microcrystalline tests, paper and thin-layer chromatography (TLC), gas chromatography (GC), ultraviolet (UV) and infrared spectrophotometry (IR), as well as mass spectrometry (MS). Some authors have gone so far as to make specific recommendations for combining some of these tests into an analytical scheme suitable for heroin's identification; others have simply chosen to list applicable tests, leaving it to the individual forensic examiner to determine the proper test or combination of tests that will prove the identity of heroin.

The *Analytical Manual* [*3*] prepared by the U.S. Drug Enforcement Administration lists the Marquis, Froehde, and nitric acid color tests, three microcrystalline tests (mercuric iodide in hydrochloric acid, platinum chloride, and mercuric choride), UV, IR, TLC, and GC as suggested tests suitable for heroin's identification. However, this manual makes no specific recommendation regarding the incorporation of any of these procedures into a specific analytical scheme. Curry and Patterson [*4*], on the other hand, recommend an

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initial examination of crude suspect heroin by IR. In the event this technique fails to confirm heroin's presence further examination by TLC and GC is suggested. Schaler and Jerpe [5] advocate combining GC with IR for heroin's identification; while Nakamura et al [6] demonstrated the utility of gas chromatography-mass spectrometry (GC-MS) for heroin's identification, Fulton [7] suggests that the Marquis, Froede, and Mecke color tests in combination with mercuric iodide and gold bromide microcrystalline tests will serve to provide a positive identification for heroin. Hider [8] proposed an analytical scheme consisting of the Marquis test and the mercuric chloride microcrystalline test to identify heroin. Splies and Shellow [9], however, have published data that question a reliance on color and microcrystalline tests for heroin's analysis. Their work showed that several common color tests, along with the platinum chloride and gold bromide microcrystalline tests, were incapable of distinguishing heroin from some structurally related morphine compounds. A detailed study comparing heroin with 17 structurally related compounds utilizing a variety of analytical techniques yielded the conclusion that GC-MS was the method of choice for identifying heroin mixtures [10].

Modern analytical technology has made available to the forensic chemist a variety of procedures useful for the analysis of drugs of abuse. A good overview of the methods presently being used by U.S. crime laboratories for heroin's analysis can be obtained from data published by the Law Enforcement Assistance Administration in conjunction with its laboratory proficiency testing program [11]. As part of this program, crime laboratories analyzed an unknown drug substance later reported to be a mixture of heroin and cocaine. One hundred twenty-five laboratories reported finding both heroin and cocaine, while 52 found only heroin. A listing of the methods used and the frequency of use is shown in Tables 1 and 2. In both tables the data reveal that for the most part the participating

TABLE 1—*Frequency of methods used in determining substance for laboratories that identified heroin and cocaine.*[a]

Method	Laboratories Reporting Use of This Method, *n*	Total Laboratories (*n* = 125), %
1. Color tests	104	83.2
2. Thin-layer chromatography	93	74.4
3. Gas chromatography	101	80.8
4. UV spectrometry	82	65.6
5. Microcrystalline tests	55	44.0
6. IR spectrometry	46	36.8
7. Gas chromatography/mass spectrometry	26	20.8
8. Extraction	22	17.6
9. Column chromatography	13	10.4

[a] Since most laboratories indicated more than one method, the total number is greater than the total number of laboratories reporting.

laboratories relied on a series of presumptive or nonspecific tests to effect the identification; that is, color tests, TLC, GC, UV, and microcrystalline tests. Surprisingly, IR and MS, both single tests specific for identification, are well down the list in Positions 6 and 7, respectively.

Even within each presumptive test category there exist differences with respect to the type of test used. For example, Table 3 lists various microcrystalline tests and the number of crime laboratories reporting their use. It can be assumed that of the tests listed mercuric iodide, mercuric chloride, gold bromide, sodium acetate, potassium acetate, and possibly platinum chloride were all employed for heroin's identification.

The only absolute criterion that can be applied for confirming the specificity of an ana-

TABLE 2—*Frequency of methods used in determining substance for laboratories that identified heroin only.*[a]

Method	Laboratories Reporting Use of This Method, *n*	Total Laboratories (*n* = 52), %
1. Color tests	48	92.3
2. Thin-layer chromatography	27	51.9
3. Gas chromatography	18	34.6
4. UV spectrometry	35	67.3
5. Microcrystalline tests	33	63.5
6. IR spectrometry	18	34.6
7. Gas chromatography/mass spectrometry	1	1.9
8. Extraction	3	5.8
9. Column chromatography	4	7.7

[a]Since most laboratories indicated more than one method, the total number is greater than the total number of laboratories reporting.

TABLE 3—*Frequency of microcrystalline tests used in determining substance.*[a]

Microcrystalline Tests	Laboratories Reporting Use of This Test, *n*
a. Mercuric iodide	43
b. Mercuric chloride	13
c. Gold chloride	13
d. Platinum chloride	12
e. Wagner's test	10
f. Gold bromide	6
g. Sodium acetate	4
h. Acetic acid	3
i. Lead iodide	1
j. Potassium acetate	1
k. Platinum bromide	1
l. Sodium chloride	1

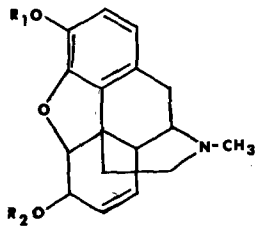
[a]Ninety-six laboratories reported using microcrystalline test(s); 32 (33.3%) did not specify which test, and 64 (66.6%) did specify which test was used. Since many laboratories reported using more than one microcrystalline test, the total number of tests is greater than the total number of laboratories reporting.

lytical scheme comprised of presumptive tests is to subject all known chemical substances to the same series of examinations, ultimately proving that one and only one compound, the substance in question, responds to the tests in a unique manner. Considering the vast number of chemical substances known to man, this approach is certainly unreasonable if not impossible to carry out. However, no alternate guidelines exist to help either the forensic analyst or trier of fact evaluate the validity of such a proposed analytical scheme.

For most drugs, such as heroin, the value of presumptive tests has always been predicated on their ability to distinguish the drug from other commonly abused drugs as well as from a drug's common diluents and adulterants. In the light of the widespread reliance on presumptive tests by the forensic community, and the reported inability of some of these tests to distinguish heroin from some closely related morphine derivatives [*9,10*], there exists a significant gap in the knowledge necessary to evaluate the evidential value and specificity of heroin-testing procedures. As a result of questions that have arisen in some New Jersey courts with respect to this very issue, a study was undertaken to assess the

specificity and utility of analytical techniques commonly employed for heroin's identification.

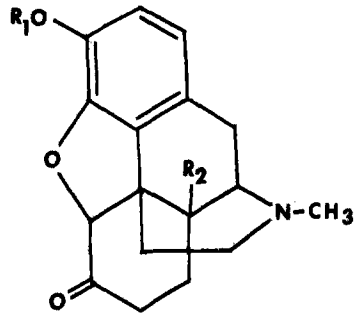
Forty-five morphine and dihydromorphine derivatives were synthesized. These compounds, along with twelve commercially available morphine derivatives, were subjected to color, microcrystalline, chromatographic, and spectrophotometric analysis to determine whether these techniques can differentiate heroin from 56 of its most closely structurally related morphine derivatives. Figures 1 to 3 show the structure of each of the compounds



	R_1	R_2	
I	H	H	MORPHINE
II	CH_3CO	H	O^3-MONOACETYLMORPHINE
III	H	CH_3CO	O^6-MONOACETYLMORPHINE
IV	CH_3CO	CH_3CO	DIACETYLMORPHINE
V	CH_3CH_2CO	H	O^3-MONOPROPIONYLMORPHINE
VI	H	CH_3CH_2CO	O^6-MONOPROPIONYLMORPHINE
VII	CH_3CH_2CO	CH_3CH_2CO	DIPROPIONYLMORPHINE
VIII	CH_3CO	CH_3CH_2CO	O^3ACETYL-O^6-PROPIONYLMORPHINE
IX	CH_3CH_2CO	CH_3CO	O^3-PROPIONYL-O^6-ACETYLMORPHINE
X	$CH_3CH_2CH_2CO$	H	O^3-MONOBUTIONYLMORPHINE
XI	H	$CH_3CH_2CH_2CO$	O^6-MONOBUTIONYLMORPHINE
XII	$CH_3CH_2CH_2CO$	$CH_3CH_2CH_2CO$	DIBUTIONYLMORPHINE
XIII	$CH_3CH_2CH_2CO$	CH_3CO	O^3-BUTIONYL-O^6-ACETYLMORPHINE
XIV	CH_3CO	$CH_3CH_2CH_2CO$	O^3-ACETYL-O^6-BUTIONYLMORPHINE
XV	$CH_3CH_2CH_2CO$	CH_3CH_2CO	O^3-BUTIONYL-O^6-PROPIONYLMORPHINE
XVI	CH_3CH_2CO	$CH_3CH_2CH_2CO$	O^3-PROPIONYL-O^6-BUTIONYLMORPHINE
XVII	CH_3	H	CODEINE
XVIII	CH_3	CH_3CO	ACETYLCODEINE
XIX	CH_3	CH_3CH_2CO	PROPIONYLCODEINE
XX	CH_3	$CH_3CH_2CH_2CO$	BUTIONYLCODEINE
XXI	CH_3CH_2	H	ETHYLMORPHINE
XXII	CH_3CH_2	CH_3CO	ACETYLETHYLMORPHINE
XXIII	CH_3CH_2	CH_3CH_2CO	PROPIONYLETHYLMORPHINE
XXIV	CH_3CH_2	$CH_3CH_2CH_2CO$	BUTIONYLETHYLMORPHINE

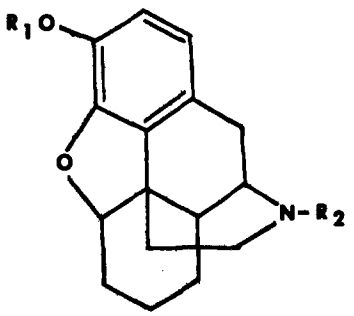
[1]The corresponding DIHYDRO derivatives are designated by the letter A

FIG. 1—*Morphine derivatives.*



	R_1	R_2	
XXV	H	OH	OXYMORPHONE
XXVI	H	H	DIHYDROMORPHINONE
XXVII	CH_3	OH	OXYCODONE
XXVIII	CH_3	H	DIHYDROCODEINONE

FIG. 2—*Dihydromorphine derivatives.*



	R_1	R_2	
XXIX	H	CH_3	RACEMORPHAN
XXX	CH_3	CH_3	RACEMETHORPHAN
XXXI	H	$CH_2CH=CH_2$	LEVALLORPHAN

FIG. 3—*Racemorphan derivatives.*

studied. In addition, commercially purchased apomorphine (XXXII) and thebaine (XXXIII) were included in the study.

Experimental Procedure

Morphine (I), codeine (XVII), and ethylmorphine (XXI) were reduced to their respective dihydro derivatives. The reduction was accomplished under hydrogen with a platinum-black catalyst and a Parr hydrogenator set at a pressure of 379 kPa (55 psi).

The diacylmorphine compounds (IV, IVA, VII, VIIA, XII, XIIA), the acylcodeine compounds (XVIII, XVIIIA, XIX, XIXA, XX, XXA), and the acylethylmorphine derivatives (XXII, XXIIA, XXIII, XXIIIA, XXIV, XXIVA) were synthesized according to the method described by Splies and Shellow [*9*] with acetic, propionic, or *n*-butyric anhydride, depending on the ester desired. The O^3-monoacylmorphine compounds (II, IIA, V, VA, X, XA) were prepared according to the method described by Welsh [*12*]. The O^6-monoacylmorphine compounds (III, IIIA, VI, VIA, XI, XIA) were prepared according to the procedures described by Wright [*13*] from the appropriate diacylmorphine compound. Preparation of the mixed diacylmorphine derivatives (VIII, VIIIA, IX, IXA, XIII, XIIIA, XIV, XIVA, XV, XVA, XVI, XVIA) was accomplished by the acylation of O^3-monoacylmorphine with the appropriate anhydride [*9*].

Morphine (I), codeine (XVII), ethylmorphine (XXI), oxymorphone (XXV), dihydromorphinone (XXVI), oxycodone (XXVII), dihydrocodeinone (XXVIII), racemorphan (XXIX), racemethorphan (XXX), levallorphan (XXXI), apomorphine (XXXII), and thebaine (XXXIII) were purchased commercially. Additionally, all compounds studied were purified by several recrystallizations from suitable solvents. Purity was confirmed by GC and isobutane chemical ionization mass spectrometry (CIMS). The following microcrystalline test reagents were prepared:

(1) saturated solution of mercuric iodide in 10% hydrochloric acid,
(2) 10% aqueous sodium acetate,
(3) 5% aqueous mercuric chloride,
(4) 5% platinum chloride in hydrochloric acid, and
(5) 5% gold bromide and 5% sodium bromide in hydrochloric acid.

Thin-layer chromatography was performed on Analtech plates coated with silica gel G at a thickness of 100 μm.

Gas chromatographic determinations were performed on a Hewlett-Packard 7620A instrument equipped with flame ionization detectors. The injection port and detector temperatures were set at 250 and 300 °C, respectively. The following columns were utilized.

Column 1: 3% OV-1 on 80-100 Chromosorb W packed into a 1.2-m by 6.35-mm outside diameter (4-ft by 0.25-in.) glass column. Column temperature was 250 °C; nitrogen flow, 60 ml/min.

Column 2: 3% OV-17 on 80-100 Chromosorb W, packed into a 1.2-m by 6.35-mm outside diameter (4-ft by 0.25-in.) glass column. Column temperature was 280 °C; nitrogen flow, 60 ml/min.

Column 3: 3% OV-25 on 80-100 Gas Chrom Q packed into a 1.8-m by 3.18-mm outside diameter (6-ft by 1/8-in.) stainless steel column. Column temperature was 240 °C; nitrogen flow, 30 ml/min.

Column 4: 6% Dexsil 400 on 80-100 Gas Chrom Q packed into a 1.8-m by 3.18-mm outside diameter (6-ft by 1/8-in.) stainless steel column. Column temperature was 240 °C; nitrogen flow, 30 ml/min.

Ultraviolet spectra were recorded on a Perkin-Elmer Model 356 spectrophotometer.

Spectra were recorded both in 0.1*N* sulfuric acid and 0.1*N* sodium hydroxide for each compound examined.

Infrared spectra were taken on a Pye Unicam Model 1000 spectrophotometer. All compounds were run both as the hydrochloride salt and in their free-base form. A KBr pellet was prepared for each analysis.

Results and Discussion

Color Tests

Color tests are widely recognized as the logical first step in a drug analysis scheme. Often these tests will provide the necessary information to allow the analyst to intelligently select testing procedures that will complete the identification process. The most widely used general screening reagent for detecting heroin's presence is undoubtedly the Marquis reagent (two drops of formaldehyde solution with 1 ml of sulfuric acid). As seen in Table 4, most morphine derivatives analyzed, including heroin, produced indistinguishable colors that ranged from red-purple to purple. The only exceptions observed were compounds XXV to XXXI and XXXIII.

Like other commonly used color test reagents the Marquis reagent is not specific; in fact, many other types of materials other than morphine and its derivatives will produce a purple color with Marquis. A fairly comprehensive list of such materials has been compiled by Clarke [*14*] and Gonzales et al [*15*]. No reaction mechanism, as yet, has been suggested to explain the Marquis color development in the presence of morphine derivatives.

Lerner [*16*] has reported the nitric acid color test to be specific for heroin. Our experience offers sufficient data to refute this observation. In fact, 24 compounds tested with concentrated nitric acid produced colors indistinguishable from that of heroin. This data is summarized in Table 4. Interestingly, of the morphine derivatives studied, only those having a free hydroxyl group in the C-3 position produced an orange color with nitric acid. This color relationship may be due to oxidative attack by nitric acid on the hydroxy group with the subsequent occurrence of dimerization.

Normally, street doses of heroin are found to contain a mixture of one or more types of diluents or adulterants. As shown in Table 5, the type and percentage of the cutting agent will have a significant effect on the sensitivity of the Marquis and nitric acid color tests. Apparently the presence of quinine, the most common heroin diluent, will significantly reduce the sensitivity of these color tests by as much as 50-fold. Also, depending on the diluent or adulterant present, the Marquis test is shown to be as much as 200 times more sensitive for heroin's detection when compared to nitric acid.

Microcrystalline Tests

Microcrystalline tests are frequently used by forensic analysts to either confirm or refute information obtained from color tests and other presumptive analytical procedures. The Drug Enforcement Administration's *Analytical Manual* [*3*] recommends three crystal tests for analyzing heroin: mercuric iodide, platinum chloride, and mercuric chloride. All the morphine derivatives studied in this paper were subjected to these tests as well as to the sodium acetate and gold bromide microcrystalline tests. A drop of each reagent was added to approximately 100 μg of powder. Crystalline formations were observed under a compound microscope at $\times 100$. Table 4 contains a description of crystal morphology for each compound yielding a crystalline precipitate.

While crystal tests have proven to be a useful and highly popular technique for identifying drugs, their interpretation can be quite subjective. Hence their usefulness often de-

pends on the ability of the analyst to recognize the characteristic shape and arrangement of the crystals. However, these shapes and formations often depend on the amount and type of adulterant present in the drug mixture, making it very difficult to develop precise terminology to describe a positive test. In compiling the data included in Table 4 wide latitude has been taken in classifying the crystal shapes obtained with the pure drugs studied. Though many of the crystalline formations observed were distinguishable, we chose to obscure these differences by reporting crystalline forms, not spatial arrangements or habit. This was done to take into account possible changes in crystalline arrangements that may arise from variations in drug concentration as well as the presence of adulterants and diluents normally found in illicit heroin preparations.

Of the crystalline tests examined sodium acetate proved to be the most specific for heroin's identification. The crystals formed with this reagent resembled clear hexagons. No other compound tested displayed this particular configuration. Apparently the hexagonal crystals are merely the free-base form of heroin since identical formations are observed by combining heroin with other weak bases such as 0.01*N* sodium hydroxide, 0.01*N* ammonium hydroxide, 5% sodium carbonate, and 10% sodium bicarbonate.

Mercuric iodide and platinum chloride were equal in their ability to discriminate heroin from other morphine derivatives. Eight compounds were shown to form crystals comparable with heroin with each of these reagents. Similarly, of the morphine derivatives examined, 10 yielded crystals with gold bromide and 16 with mercuric chloride that were comparable with heroin (Table 4).

As with the color test reagents, the sensitivity of microcrystalline tests for heroin's detection is closely dependent on the type of diluent present in the heroin specimen. The effect of diluents on the sodium acetate and mercuric iodide microcrystalline tests for heroin is shown in Table 5.

Thin-Layer and Gas Chromatography

Thin-layer chromatography has been extensively applied for the detection and identification of drugs. Like other forms of chromatography the technique is particularly attractive since it offers the drug analyst a rapid means for separating drugs from diluents and adulterants while providing a tentative identification. In this study all of the morphine derivatives were chromatographed with the following solvent systems:

System A: ammonium hydroxide:benezene:dioxane:ethanol (5:50:40:5),
System B: ethyl acetate:methanol:ammonium hydroxide (85:10:5),
System C: methanol:ammonium hydroxide (100:1.5), and
System D: ethanol:glacial acetic acid:water (60:30:10).

Systems A and D are both cited in the *Analytical Manual* [*3*] as being recommended for heroin's identification, while Systems A, C, and D are recommended by Clarke [*14*] for heroin's analysis. System B was introduced by Davidow et al [*17*] and is widely used as a TLC developing solvent in drug screening programs.

For the purpose of this study we have assumed an error factor of ± 10 for the R_f values contained within Table 4. From these R_f values it can be established that the four development systems selected for this study cannot individually or collectively effect the separation of heroin from all the morphine derivatives. Thus, while TLC may be a useful technique for isolating heroin from its diluents and adulterants, as well from other commonly abused drugs, it has limited forensic value in establishing heroin's identification.

Gas chromatographic analysis of the morphine derivatives was carried out on four different stationary phases of varying polarities. All of the retention times are listed relative to heroin in Table 4. Assuming that all compounds differing by 0.05 retention time units are distinguishable, then GC proves itself to be a very potent technique for differentiating

TABLE 4—*Results of tests used to iden*

Compound	Color Tests		Microcrystalline Tests				
	Marquis	Nitric Acid	Mercuric Iodide	Sodium Acetate	Platinum Chloride	Gold Bromide	Mercuric Chloride
I	P	O-Br-Y	needles	plates	NR	plates	needles
IA	P	O-Y	NR	NR	NR	NR	NR
II	P	Y-G	NR	plates	needles	NR	blades
IIA	P	Y-G	NR	NR	NR	NR	NR
III	P	Y-O	NR	NR	needles	NR	NR
IIIA	P	O	NR	NR	NR	needles	needles
IV	P	Y-G	needles	hexagon	needles	needles	blades and needles
IVA	P	Y-G	NR	NR	needles	needles	NR
V	P	Y-G	NR	plates	needles	NR	blades
VA	P	Y-G	NR	plates	NR	NR	NR
VI	P	O	NR	plates	blades	NR	blades
VIA	P	Y-O	NR	plates	NR	needles	needles
VII	P	Y-G	needles	NR	needles	needles	needles
VIIA	P	Y-G	NR	NR	NR	NR	NR
VIII	P	Y-G	needles	plates	blades	needles	needles
VIIIA	P	Y-G	NR	NR	NR	needles	NR
IX	P	Y-G	needles	plates	needles	needles	needles
IXA	P	Y-G	NR	NR	NR	NR	NR
X	P	Y-G	NR	NR	NR	NR	blades
XA	P	Y-G	NR	NR	NR	NR	NR
XI	P	Y-O	NR	NR	NR	NR	blades
XIA	P	Y-O	plates	NR	NR	NR	NR
XII	P	Y-G	blades	NR	NR	NR	needles
XIIA	P	Y-G	NR	NR	NR	NR	NR
XIII	P	Y-G	needles	rods	NR	needles	needles
XIIIA	P	Y-G	NR	NR	NR	NR	NR
XIV	P	Y-G	NR	NR	NR	NR	needles
XIVA	P	Y-G	NR	NR	NR	needles	NR
XV	P	Y-G	NR	NR	NR	NR	burrs
XVA	P	Y-G	NR	NR	NR	needles	NR
XVI	P	Y-G	NR	NR	NR	NR	needles
XVIA	P	Y-G	NR	NR	NR	NR	NR
XVII	P	Y	needles	NR	NR	NR	NR
XVIIA	P	Y	NR	plates	NR	NR	NR
XVIII	P	Y	needles	NR	NR	NR	needles
XVIIIA	P	Y	NR	NR	...	...	...
XIX	P	Y	NR	NR	...	...	...
XIXA	P	Y	plates	plates	...	...	...
XX	P	Y	NR	NR	...	...	...
XXA	P	Y	NR	NR	...	...	...
XXI	P	Y	NR	NR	...	...	...
XXIA	P	Y	NR	NR	...	...	...
XXII	P	Y	NR	NR	...	...	...
XXIIA	P	Y	NR	NR	...	...	...
XXIII	P	Y	NR	NR	...	...	...
XXIIIA	P	Y	NR	NR	...	...	...
XXIV	P	Y	NR	NR	...	...	...
XXIVA	P	Y	NR	NR	...	...	...
XXV	O-R-P	Y-O	NR	NR	...	...	...
XXVI	O-P	Y-O	NR	NR	...	...	...
XXVII	Y-Br-P	Y	NR	plates	...	...	...
XXVIII	O-P	Y	NR	NR	...	...	...
XXIX	O-Br-G	Y	NR	NR	...	...	...
XXX	R-G-Bl	O	NR	NR	...	...	...
XXXI	O-G	Y	NR	NR	...	...	...
XXXII	P	P-Br-O	NR	NR	...	...	...
XXXIII	O	Y	NR	plates	...	...	...

[a] Bl = black O = orange Y = yellow
Br = brown P = purple NR = no reaction
G = green R = red

eroin and structurally related compounds.[a]

Thin-Layer Chromatography				Gas Chromatography				Ultraviolet Spectrophotometry	
A	B	C	D	1	2	3	4	0.1*N* Sulfuric Acid	0.1*N* Sodium Hydroxide
10	10	40	52	0.56	0.60	NR	NR	285	297
10	8	25	50	0.60	0.59	0.40	0.36	282	295
20	20	45	53	0.73	0.74	0.67	0.80	281,227	296
15	25	25	45	0.71	0.69	0.63	0.82	277,226	295
50	50	47	58	0.79	0.74	0.67	0.85	283	295
45	40	25	45	0.73	0.68	0.64	0.86	278	295
60	57	50	50	1.00	1.00	1.00	1.00	278	295
50	40	45	55	0.90	0.91	0.86	0.86	278	295
20	20	45	50	0.88	0.86	0.83	1.05	273,227	295
10	20	30	45	0.94	0.83	0.79	0.96	273	295
55	55	45	70	0.96	0.88	0.82	1.00	282	295
35	40	30	48	0.98	0.80	0.74	0.97	280	295
65	60	55	55	1.63	1.48	1.54	1.66	278	295
50	50	35	50	1.48	1.35	1.26	1.40	278	295
65	60	50	50	1.31	1.23	1.23	1.29	278	295
35	40	30	38	1.08	1.07	1.04	1.09	278	295
65	60	50	50	1.38	1.30	1.23	1.29	278	295
75	40	30	44	1.13	1.09	1.05	1.12	278	296
55	55	47	50	1.17	1.09	1.03	1.38	280	296
48	50	35	50	1.19	1.07	0.98	1.23	280	296
67	60	30	55	1.17	1.09	1.02	1.27	273,225	295
40	45	35	60	1.14	0.95	0.88	1.10	275	295
63	65	50	60	2.58	2.21	2.36	2.78	278	296
63	55	45	50	2.25	1.85	2.28	2.64	278	296
65	65	55	52	1.75	1.56	1.59	1.70	278	295
50	50	35	42	1.50	1.33	1.30	1.45	278	295
65	65	55	58	1.58	1.48	1.51	1.66	278	295
40	45	45	52	1.33	1.31	1.24	1.36	278	295
50	65	55	55	2.17	1.89	1.88	2.12	278	295
35	55	40	54	1.74	1.60	1.54	1.77	278	295
50	65	50	55	2.13	1.85	1.86	2.12	278	296
50	40	35	52	1.70	1.58	1.51	1.71	278	295
38	40	45	52	0.57	0.51	0.44	0.63	284	282
40	30	40	52	0.55	0.49	0.42	0.61	282	282
55	65	50	55	0.77	0.69	0.63	0.67	282	282
55	50	35	54	0.70	0.60	0.53	0.59	282	282
62	65	45	50	1.02	0.83	0.77	0.85	283	280
60	55	35	55	0.93	0.75	0.63	0.74	282	282
72	69	47	55	1.30	1.04	0.96	1.10	282	280
65	60	32	57	1.05	0.86	0.74	0.90	280	280
47	47	40	55	0.64	0.55	0.46	0.69	285	283
45	42	30	55	0.61	0.54	0.43	0.65	280	280
70	65	50	55	0.84	0.73	0.64	0.72	280	280
62	55	35	55	0.75	0.65	0.54	0.62	280	282
72	65	50	55	1.07	0.86	0.78	0.92	280	282
65	55	35	55	0.95	0.75	0.64	0.76	280	280
75	65	50	55	1.32	1.10	0.98	1.17	282	282
65	55	37	55	1.14	0.89	0.75	0.94	280	280
25	42	60	47	0.86	NR	NR	NR	280	290
15	20	25	42	1.11	NR	NR	NR	280	291,237
20	70	60	45	0.80	0.83	NR	NR	278	295
25	32	25	35	0.66	0.65	0.61	0.69	280,233	279
40	35	28	58	0.39	0.28	0.22	0.30	279	297
55	55	30	60	0.30	0.21	0.14	0.19	277	278
72	75	65	70	0.52	0.40	0.31	0.44	278	298
45	55	70	58	0.55	NR	NR	NR	272,305	265
60	60	47	50	0.77	0.82	0.84	0.73	283	282

TABLE 5—*Percentage of heroin detectable for color and microcrystalline tests.* [a]

Diluent	Marquis	Nitric Acid	Sodium Acetate	Mercuric Iodide
Lactose	0.1	2.0	0.5	0.5
Brown sugar	0.1	20.0	10.0	0.5
Lactose-quinine (9:1)	0.1	2.0	1.0	0.5
Lactose-procaine (1:1)	0.1	10.0	5.0	5.0
Lactose-quinine (1:1)	1.0	5.0	1.0	2.0
Quinine	5.0	10.0	50.0	50.0

[a] All values shown are for a 1-mg mixture.

heroin from most, if not all, other morphine derivatives. While no single column is capable of separating heroin from all the morphine derivatives, this can readily be accomplished by the proper selection of two columns. Hence, a combination of either columns one and two, three and four, two and four, or one and three will accomplish this intended objective.

Ultraviolet and Infrared Spectrophotmetry

An examination of Table 4 demonstrates that UV is far from a specific technique for characterizing heroin. Assuming an error of ±2 nm, 25 compounds have indistinguishable UV spectra in both acid and base solutions from that of heroin. As expected, the reverse is true of IR analysis. All the compounds examined yielded distinguishable spectra, both as their hydrochloride salts and in their free-base forms. Figures 4 to 6 depict the IR spectra of heroin and two closely related structural derivations, O^3-propionyl-O^6-acetyl morphine (IX), and O^3-acetyl-O^6-propionyl morphine (VIII). No difficulty is encountered in distinguishing each of these compounds by IR spectrophotometry.

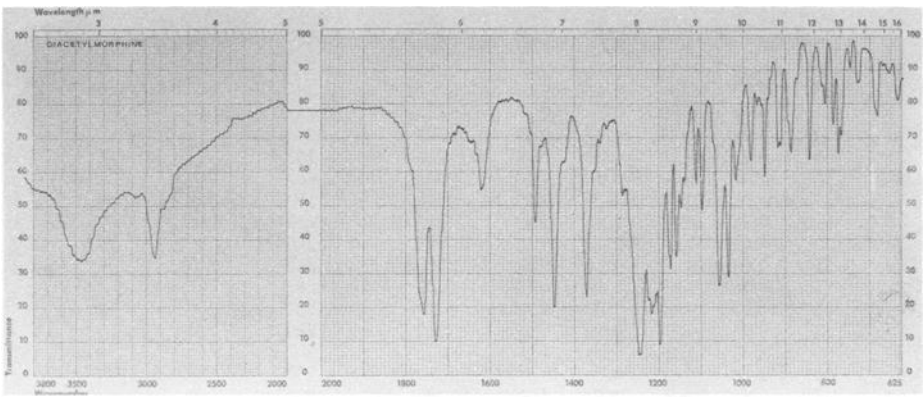


FIG. 4—*Infrared spectrum of heroin (diacetylmorphine), free base, KBr disk.*

Conclusion

It is not the purpose of this study to recommend any particular analytical scheme suitable for heroin's identification. The ultimate selection of such procedures will be determined by numerous factors such as the quantity and purity of the sample, the nature of the adulterants and diluents present, the experience of the analyst, the availability of

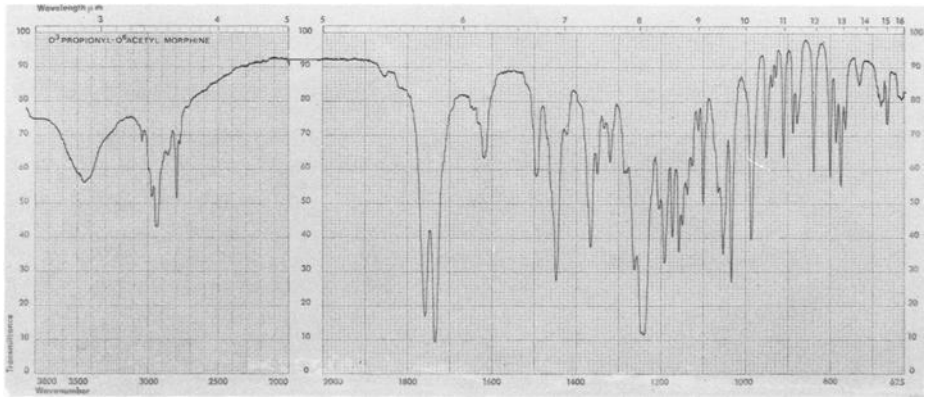


FIG. 5—*Infrared spectrum of O^3-acetyl-O^6-propionyl morphine, free base, KBr disk.*

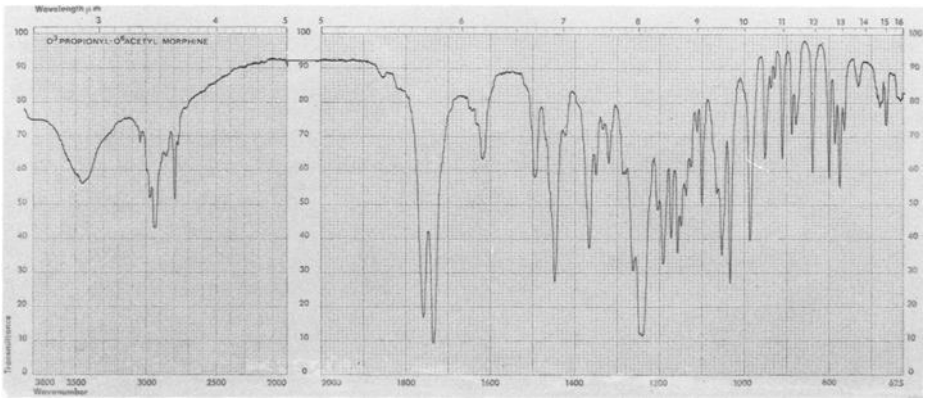


FIG. 6—*Infrared spectrum of O^3-propionyl-O^6-acetyl morphine, free base, KBr disk.*

analytical techniques and instrumentation, and the amount of time available to perform the analysis. If specificity were the sole criterion for choosing a particular test, undoubtedly IR analysis would be preferred. However, Tables 1 and 2 show this technique to be far from the most popular among crime laboratories.

Undoubtedly, practical considerations enter into the selection of forensic analytical schemes. Heroin is rarely received by crime laboratories in pure form. Its concentration usually ranges between 2 and 5%, with lactose, mannitol, quinine, starch, phenylpropanolamine, and methapyrilene serving as common diluents or adulterants. Such circumstances will often combine to make extraction a necessary prerequisite for heroin's IR identification. This situation apparently discourages many crime laboratories from utilizing the IR technique and accounts for the popularity of methods better suited for the direct analysis of drug mixtures: microcrystalline tests and chromatography.

The data contained within this study will be useful for evaluating the specificity of presumptive analytical tests frequently used by crime laboratories for heroin's identification. The compounds most likely to be mistaken for heroin are the morphine derivatives having a molecular structure closely related to heroin. The results of this study amply demonstrate that such morphine compounds can be distinguished from heroin and that a valid

and legally defensible analytical scheme can be devised for heroin's identification with the prudent selection of a combination of presumptive testing procedures.

Summary

Heroin and 56 morphine derivatives were studied to assess the specificity of a number of analytical techniques commonly used by forensic science laboratories. The analytical procedures evaluated include two color tests, five microcrystalline tests, four TLC systems, four GC columns, and UV and IR spectrophotometry. The only single test found totally specific for heroin's identification is IR spectrophotometry. However, the distinction of heroin from other morphine derivatives is possible through the combination of nonspecific or presumptive tests.

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