TECHNICAL NOTE

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Illicitly Imported Heroin* Products: Some Physical and Chemical Features Indicative of Their Origin

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ABSTRACT: Samples taken from over 200 seizures of imported illicit heroin preparations of known geographical origin have been examined by gas liquid chromatography (GLC) and high performance liquid chromatography (HPLC). The chromatographic characteristics were considered in conjunction with the physical appearance of the materials and it was found possible in many instances to discriminate between samples of different origin. Thus by carrying out GLC and HPLC and a visual inspection on a sample of unknown provenance, it may be possible to give an opinion as to its geographical origin.

KEYWORDS: toxicology, heroin, chromatographic analysis

Diacetylmorphine is by no means the only constituent of illicit heroin [*1-3*] that at importation may contain several related narcotics including codeine, acetylcodeine, the acetylmorphines and morphine, together with noscapine and papaverine. It is relatively rare to find diluents in illicit heroin at importation into the United Kingdom, but, where present they are highly indicative of the exporting country. A means both of identifying the geographical origin of illicit heroin by its physical appearance and chemical composition, and of comparing samples to establish the frequency that a particular chemical profile occurs, would be extremely useful in the ensuing criminal investigation, for forensic science purposes and in aiding international control.

Discussion

It is recognized that the chemical and physical appearance of illicit heroin varies between different countries or regions of origin and that some areas produce more than one type of

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*In this paper "heroin" means pure diacetylmorphine. "Illicit heroin" means impure diacetylmorphine that contains related narcotics and other materials and is of clandestine origin.

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material [4,5]. Frequently, the major component of the illicit preparation at importation into the United Kingdom is heroin itself (that is, diacetylmorphine), with a purity typically between 30 and 80%. The unequivocal identification of the diacetylmorphine present in such seizures can be most easily performed by infrared spectroscopy, but this technique reveals little or no information about most of the minor components in the sample. Thin-layer chromatographic systems have been developed that will resolve the major and minor opiates present in illicit heroin [6–8], but many of these systems involve the use of dilute alkali which affects the chemical composition of the heroin by hydrolysis. The constituents separated by thin-layer chromatography can only be quantified approximately.

Many gas and liquid chromatographic methods for the quantitation of the opiates present in illicit heroin have been described in the literature, which has recently been reviewed [9,10]. Some of these methods were developed with the specific intention of comparing illicit heroin samples for forensic science purposes [11]. For example, Vandeloo et al [12] used a stationary phase of OV-1 in a gas chromatographic separation of the opiates and common cutting agents found in illicit heroin. Neumann and Gloger [13] used a capillary column coated with a stationary phase of SE54 to produce chemical fingerprints from derivatized heroin samples. The gas liquid chromatographic (GLC) system used in the present study, direct injection onto a packed column containing silanized OV-210, results in minimal and reproducible losses of the opiates, and gives sufficient resolution for quantitation. Meconin and noscapine are not, however, satisfactorily chromatographed under these conditions. Details of the reliability of this method in the analysis of samples of illicit heroin have been published [14].

High performance liquid chromatography (HPLC) overcomes the problems associated with gas chromatography and a number of workers have successfully separated the opiates in illicit heroin [15,16]. Huizer et al [17] resolved the major constituents in illicit samples of heroin traditionally referred to as "Chinese No. 3 and No. 4."

The method used in the present study quickly and simply resolves the major heroin opiates and cutting agents and gives satisfactory quantitative results. However, meconin, noscapine, and papaverine, which may be present at minor or trace level in illicit heroin, are only partially resolved. A detailed account of this HPLC system, including detector linearity, response factors, and reproducibility, has been published [18]. Because no single chromatographic procedure can overcome the coelution of compounds, each sample in the present study has been subjected to both gas liquid and high performance liquid chromatographic analysis. A collaborative study undertaken with the Department of Scientific Services, Republic of Singapore, recently published [19], has shown that these two methods give satisfactory quantitative results for the heroin content of a wide range of illicit heroin samples of varying purity originating from all the major sources of supply to the United Kingdom.

Although forensic scientists in many countries recognize that illicit heroin may vary in physical appearance and chemical composition from origin to origin, very few have access to samples of known provenance. Moreover it is not indicated in the literature whether such samples have been intercepted at importation or were seized within the recipient country. Knowledge of country of origin is invariably more certain in the former case. The claim that most heroin seized in the Netherlands during 1975 was of the type known as "Chinese No. 3" must be placed against the reported discovery [20] of two heroin laboratories in Rotterdam and Amsterdam, each of which were converting high purity heroin base into a product resembling the type of material traditionally imported from southeast Asia.

The Laboratory of The Government Chemist in the United Kingdom is particularly fortunate in that virtually all of its extensive collection of illicit heroin is derived from illegal importations, seized at points of entry, where the country of origin is deduced with high probability. This has provided an opportunity to examine the physical appearance and chemical composition of many such samples and correlate the results with the country of origin.

Experimental Procedure

At the completion of the forensic science examination of all large seizures of illicit heroin a minimum of 10 g of representative sample of the material was removed. All samples were homogenized immediately before analysis and solutions containing the illicit heroin were examined within a few hours of preparation. The samples in this study were collected over the period October 1978 to October 1982 and represent virtually all illicit heroin intercepted by Officers of Her Majesty's Customs and Excise at importation into the United Kingdom during that period. The most probable country of origin was assigned by taking into account information from the carrier, from Officers of Her Majesty's Customs and Excise and from the route of importation. There were very few examples of illicit heroin on importation into the United Kingdom being wrapped in paper or packaging bearing indications of a purported country of origin.

For each country, the results are listed in chronological order of seizure of the illicit heroin. Every sample was examined by GLC and HPLC, although only the latter results are tabulated because there was excellent agreement between the two sets of data in the vast majority of cases. In a small number of samples there were discrepencies between the quantitative results for some of the minor constituents. All of these samples were subjected to combined GLC and mass spectrometry (MS) to check that there was no coelution with nonnarcotic compounds by either of the chromatographic methods. No interfering compounds were found and the discrepencies were attributed to transacetylation between the narcotics, which occasionally occurs in the injection port of the gas chromatograph. A detailed study of transacetylation is in hand. In some of the samples, chromatography revealed the presence of compounds in addition to the narcotics under study. All of these samples were subjected to combined GLC and MS and the compounds identified on the basis of their low resolution electron impact spectra. Pure authentic compounds were then examined by the standard GLC and HPLC systems, to confirm retention data.

Gas Liquid Chromatography

Solutions for Analysis

The solutions contained 50 mg of the sample of illicit heroin per 100 mL of a 1:1 mixture (by volume) of ethanol and chloroform.

Apparatus

The gas chromatograph was a Philips model PU 4500 operated as follows: column packing: 3% silanized OV-210 on 80–100 mesh Diatomite CLQ in 2.8-m by 4-mm inside diameter glass at 225° C; injection: on-column at 225° C; and sample size: 5 μL.

A flame ionization detector was used at 300° C. The gases were: nitrogen at 48 mL per min, hydrogen at 50 mL per min, and air at 302 mL per min.

For retention times see Table 1.

High Performance Liquid Chromatography

Solutions for Analysis

The solutions contained 100 mg per 100 mL of a 1:4 mixture (by volume) of 0.02*N* sulphuric acid and acetonitrile.

TABLE 1—*Retention data on compounds detected in illicit heroin.*

Compound	GLC	HPLC
Acetylcodeine	0.50	1.13
3-acetylmorphine	0.60	1.44
6-acetylmorphine	0.56	1.42
Amphetamine	0.01	ND[a]
Antipyrine	0.34	0.89
Barbital	0.01	0.90
Caffeine	0.14	0.90
Codeine	0.34	2.14
Heroin	1.00(25 min)	1.00(3.1 min)
Meconin	0.17	0.76
Morphine	0.43	4.55
Noscapine	...[b]	0.74
Papaverine	1.34	0.77
Paracetamol	0.20	0.90
Phenacetin	0.12	0.75
Phenobarbital	0.24	0.75
Procaine	0.18	1.69
Vitamin C	...[b]	4.4

[a] ND = not detected.
[b] ... = not examined.

Apparatus

The pump was an ACS model 750/03 operating at 8274 kPa (1200 psi). The detector was a Philips model LC/UV instrument. The operating conditions were: column: $S5NH_2$ (aminopropyl bonded silica) in 250- by 4-mm stainless steel; injection: 2 μL on-column with stopped flow; detection: ultraviolet at 284 nm; and eluant: 85% acetonitrile + 15% 0.005*M* PIC A reagent (Waters Associates, Northwich, UK) at 1 mL per min.

For retention times see Table 1.

Mass Spectrometry

The gas chromatographic column described above was also used in combination with an MS-30 mass spectrometer (Kratos Ltd, Manchester, UK). A glass jet interface was used at 200°C. The output was via a DS-55 data system, which generated a total ion current chromatogram and low resolution electron impact spectrum of each compound. These spectra were matched against reference spectra in the data system library.

Physical Appearance

Chinese No. 3

Chinese No. 3 (see Table 2) is a hard granular material (usually 1 to 5 mm in diameter), often only containing a very small amount of powder. The granules are hard and unyielding to pressure. Samples encountered in this study have been gray, but the Hong Kong authorities have also encountered dirty brown material.

Chinese No. 4

Chinese No. 4 (see Table 2) is a white microfine dry powder, often crystalline.

TABLE 2—*Results of analysis of illicit heroin of southeast Asian origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
196	91.1	6.0	1.4	ND	ND	ND	ND	HCl	white	
197	20.4	4.4	4.1	ND	ND	ND	ND	HCl	4B2	caffeine = 61.5
198	18.0	3.5	3.8	ND	ND	1	1	HCl	4B4	caffeine = 62.6
199	91.6	6.3	1.6	ND	ND	ND	ND	HCl	white	
200	81.4	6.6	1.1	ND	ND	ND	ND	HCl	white	
201	81.8	3.6	0.7	ND	ND	ND	ND	HCl	white	caffeine = 14.5
202	82.8	2.4	0.8	ND	ND	ND	ND	HCl	white	barbital
203	55.8	3.1	1.5	ND	ND	ND	ND	HCl	white	
204	6.6	0.7	3.0	ND	ND	ND	ND	HCl	5B1	caffeine = 90.5
205	6.5	0.7	2.9	ND	ND	ND	ND	HCl	5B1	caffeine = 88.8
206	6.9	0.7	3.1	ND	ND	ND	ND	HCl	5B1	caffeine = 83.2
207	8.0	1.3	3.8	ND	ND	ND	ND	HCl	5B1	caffeine = 83.3
208	77.7	10.6	2.3	ND	ND	ND	ND	HCl	white	
209	93.1	7.7	3.8	ND	ND	ND	ND	HCl	white	meconin
210	82.1	12.5	2.9	ND	ND	ND	ND	HCl	white	
211	71.3	6.5	6.8	ND	ND	ND	ND	HCl	4A2	
212	74.5	5.4	6.8	ND	ND	ND	ND	HCl	white	
213	84.9	4.3	3.0	ND	ND	ND	ND	HCl	white	
214	37.0	5.9	3.7	ND	ND	ND	ND	base	5A3	meconin
215	90.3	5.0	2.4	ND	ND	ND	ND	HCl	white	

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*], and
Others = presence of other compounds.

Indian

Indian (see Table 3) is creamy or a dirty white color, often powders but may be aggregated.

Pakistan

Pakistan (see Table 4) is two types.

1. It is very variable in color and consistency and has been encountered in virtually every shade from beige to dark brown. It is virtually always a powder, often fine, but occasionally small aggregates that are soft and which yield to slight pressure. This category constitutes virtually all the Pakistan heroin encountered in this survey; the physical variation is paralleled by a wide range of chemical composition but the later samples indicate that a more consistent product is being made. Typically it is a fine light-brown powder with characteristic opium derived odor, the purity is in the range 70 to 80% and the heroin is present as the free base.

2. It is white or off-white fine dry powder, less odor than Type 1, the purity is in the range 80 to 90%, and the heroin is present as the hydrochloride salt.

TABLE 3—*Results of analysis of illicit heroin of Indian origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL
096	88.5	6.1	0.3	ND	ND	ND	ND	HCl	white
097	74.6	ND	5.2	ND	ND	ND	ND	HCl	white
099	82.1	ND	1.6	ND	ND	ND	ND	HCl	white
100	75.5	8.9	2.2	ND	ND	ND	ND	HCl	white
101	46.5	2.1	9.8	ND	ND	ND	ND	HCl	4A2
102	52.3	2.9	9.2	ND	ND	ND	ND	HCl	4A2
103	56.9	0.9	9.6	ND	ND	ND	ND	HCl	4A3
104	8.6	1.4	55.6	ND	ND	ND	ND	base	5D4
105	78.0	2.2	2.8	ND	ND	ND	ND	HCl	4B1
106	85.7	1.9	1.3	ND	ND	ND	ND	HCl	4B1
107	54.8	1.1	8.1	ND	ND	ND	ND	HCl	5A2
108	78.3	1.9	5.0	ND	ND	ND	ND	HCl	4A2
109	84.5	6.4	0.8	ND	ND	ND	ND	HCl	white
110	91.8	4.6	0.7	ND	ND	ND	ND	HCl	white

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
Form = chemical status of opiates: free base or hydrochloride salt, and
COL = color [*21*], and
Others = no other chemicals detected.

Iranian

Similar to Pakistan Type 1 but less variable in both physical appearance and chemistry; nearly always a fine brown powder containing about 70% heroin as free base (see Table 5).

Turkey

This type is beige colored or very light-brown powders, most often without aggregation (see Table 6).

Syrian

This is a pale orange-brown powder (one sample) (see Table 7).

Lebanon

One sample was beige color, four samples white or off-white. All were fine powders (see Table 7).

Nigerian

This is a fine off-white powder (one sample) (see Table 8).

TABLE 4—*Results of analysis of illicit heroin of Pakistani origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
001	40.4	1.0	14.2	ND	ND	ND	ND	HCl	5A3	
002	13.8	2.8	15.3	6.3	ND	ND	ND	HCl	5D4	
003	18.9	0.6	16.2	11.2	ND	ND	ND	HCl	5C5	
004	14.7	1.6	21.6	ND	ND	ND	ND	HCl	4A2	
005	97.0	2.5	0.5	ND	ND	ND	ND	HCl	white	
006	36.1	1.4	23.6	36.6	ND	ND	ND	HCl	white	
007	3.5	1.1	22.3	79.3	0.5	ND	ND	HCl	4B1	
008	91.6	1.4	1.8	ND	ND	ND	ND	HCl	off-white	
009	3.6	2.5	34.7	14.5	ND	ND	ND	HCl	4B2	codeine
010	65.1	6.1	9.4	ND	ND	8	5	base	5E6	
012	49.1	5.6	20.1	ND	ND	*	*	base	5D4	
013	17.9	3.7	49.5	ND	ND	*	*	HCl	5D4	
014	47.1	1.6	20.9	ND	ND	*	*	HCl	5D3	
015	86.4	10.9	4.1	ND	ND	ND	ND	HCl	4A2	
016	12.8	1.3	17.6	ND	ND	*	*	HCl	5B3	
017	15.1	2.2	29.6	ND	ND	*	*	HCl	5B3	
018	71.1	5.3	3.3	ND	ND	*	*	base	5D4	
019	70.2	6.5	0.8	ND	ND	*	*	base	5D6	
020	83.8	7.0	3.7	ND	ND	*	*	base	5D4	
021	81.8	6.5	2.1	ND	ND	*	*	base	5D5	
022	79.0	6.7	2.2	ND	ND	*	*	base	5D5	
023	34.0	2.4	31.7	ND	ND	*	*	HCl	5B3	meconin
024	82.5	1.2	4.1	ND	ND	*	*	HCl	5B3	
025	80.2	1.8	7.6	ND	ND	ND	ND	HCl	5B2	meconin
026	14.6	t	12.0	70.0	ND	ND	ND	HCl	5C3	
027	35.7	3.7	26.0	ND	ND	*	*	base	5C4	meconin
028	77.5	6.1	3.5	ND	ND	ND	ND	base	5B4	meconin
029	86.5	7.3	3.8	ND	ND	ND	ND	base	5C4	meconin
030	78.4	6.1	1.9	ND	ND	ND	ND	base	5C4	meconin
031	73.2	5.8	2.2	ND	ND	*	*	base	5D5	
032	85.5	6.5	0.6	ND	ND	ND	ND	base	5B3	meconin
033	72.5	5.9	3.9	ND	ND	*	*	base	5C4	
034	13.1	5.8	47.3	ND	ND	*	*	base	5C4	
035	15.0	4.5	45.1	ND	ND	*	*	base	5B4	
036	85.9	1.6	5.5	ND	ND	ND	ND	HCl	5A2	
037	78.9	5.7	1.4	ND	ND	*	*	base	5C4	
038	42.2	3.2	1.6	ND	ND	*	*	base	5B3	
039	82.3	1.8	6.8	ND	ND	ND	ND	HCl	5A2	
040	19.7	2.9	34.0	ND	ND	*	*	HCl	5B3	
041	84.3	1.5	5.3	ND	ND	ND	ND	HCl	5A2	
042	75.5	6.1	2.1	ND	ND	*	*	HCl	5C4	
043	66.3	5.8	3.3	ND	ND	*	*	base	5C4	
044	86.2	5.9	3.3	ND	ND	*	*	base	5B4	
045	78.9	5.9	2.2	ND	ND	ND	ND	base	5C4	meconin
046	74.4	5.8	1.8	ND	ND	*	*	base	5C4	
047	84.3	1.8	6.1	ND	ND	ND	ND	HCl	5A2	
048	62.1	5.7	2.8	ND	ND	*	*	base	5D4	
049	72.2	1.6	11.4	ND	ND	ND	ND	HCl	white	
050	73.0	5.0	2.4	ND	ND	*	*	base	5C4	
051	53.5	4.0	1.2	ND	ND	*	*	base	5D4	
052	74.8	5.4	2.0	ND	ND	*	*	base	5C4	
053	74.1	4.8	3.4	ND	ND	6	6	base	5C4	
054	73.7	4.3	1.9	ND	ND	12	3	base	5D4	
055	76.0	5.0	2.1	ND	ND	12	3	base	5D5	
056	77.0	5.7	1.9	ND	ND	15	3	base	5C4	
057	8.6	1.8	55.6	ND	ND	ND	ND	HCl	5C3	
058	80.6	7.0	1.8	ND	ND	12	3	base	5D4	
059	70.3	6.2	2.1	ND	ND	10	5	base	5D4	
060	84.2	7.7	2.2	ND	ND	1	0.5	base	4A3	

TABLE 4—*Continued.*

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
061	83.4	7.5	2.2	ND	ND	ND	ND	base	4A3	
062	87.9	7.7	2.4	ND	ND	ND	ND	base	4A3	
063	84.5	2.0	4.2	ND	ND	ND	ND	HCl	4A2	
064	74.5	6.5	4.7	ND	ND	5	5	base	5C4	
065	79.2	6.8	1.3	ND	ND	6	6	base	5C4	
066	85.5	6.6	1.9	ND	ND	ND	ND	base	4A2	
067	75.1	6.6	1.3	ND	ND	9	9	base	5C4	
068	83.8	6.7	1.7	ND	ND	ND	ND	base	5A2	
069	82.8	3.1	2.2	ND	ND	4	4	base	5C4	
070	78.0	4.7	2.1	ND	ND	4	4	base	5C4	
071	78.4	5.0	2.1	ND	ND	4	3	base	5C3	
072	87.2	5.6	2.2	ND	ND	ND	ND	base	5A2	meconin trace
073	69.2	5.3	2.2	ND	ND	15	5	base	5D4	
074	48.3	0.3	7.1	ND	ND	ND	ND	base	4A2	meconin trace
075	67.9	6.0	2.5	ND	ND	12	5	base	5D5	
076	86.4	6.3	1.9	ND	ND	ND	ND	base	4A2	meconin trace
077	82.6	5.8	2.3	ND	ND	6	5	base	5C3	
078	80.6	6.6	2.0	ND	ND	ND	ND	base	5B3	meconin trace
079	38.9	1.3	16.2	ND	ND	ND	ND	base	4C6	meconin trace
080	t	ND	22.1	ND	ND	ND	ND	base	5B3	
081	71.5	7.2	1.7	ND	ND	6	5	base	5C4	
082	56.9	1.7	11.0	ND	ND	ND	ND	HCl	white	
083	75.8	6.1	2.3	ND	ND	16	6	base	5C4	
084	77.3	6.4	2.0	ND	ND	17	6	base	5C4	
085	83.5	7.6	1.8	ND	ND	ND	ND	base	4A2	meconin trace
086	78.1	7.0	1.3	ND	ND	9	5	base	5C4	
087	72.3	6.6	2.1	ND	ND	9	6	base	5D4	
088	70.9	6.4	1.7	ND	ND	9	5	base	5C4	
089	75.2	6.9	1.9	ND	ND	5	5	base	5D5	
090	75.8	6.8	1.8	ND	ND	9	6	base	5C4	
091	74.3	7.0	3.2	ND	ND	3	5	base	5D4	
092	68.8	6.6	1.8	ND	ND	9	6	base	5D4	
093	71.4	4.5	4.3	ND	ND	ND	ND	base	5C4	
094	86.0	7.4	1.8	ND	ND	ND	ND	base	4A2	meconin trace
095	86.0	7.4	1.8	ND	ND	ND	ND	base	4A2	meconin trace

[a]No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
* = present but not quantified,
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*],
Others = presence of other compounds, and
t = trace.

TABLE 5—*Results of analysis of illicit heroin of Iranian origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
152	78.6	4.8	1.2	ND	ND	*	*	base	5C5	
153	44.1	8.0	17.3	ND	ND	*	*	base	5E6	
154	44.6	10.8	13.4	ND	ND	*	*	base	4B3	caffeine, 17.2%
155	39.4	6.8	23.8	7.2	ND	ND	ND	base	5D5	caffeine, 8.5%
156	43.3	7.8	24.3	ND	ND	ND	ND	base	4B4	caffeine, 13.8%
157	19.9	1.2	7.0	ND	ND	ND	ND	base	4A3	caffeine, 61.2%
158	14.2	1.8	8.0	ND	ND	4	0.5	base	4B3	caffeine, 56.6%
159	55.8	7.2	16.3	ND	ND	4	6	base	5E7	caffeine trace
161	71.4	6.6	2.8	ND	ND	*	*	base	5C5	
162	72.5	5.7	3.0	ND	ND	5	6	base	5C5	
163	73.6	6.5	2.7	ND	ND	5	3	base	5C5	
164	75.5	6.9	2.8	ND	ND	5	6	base	5C5	
165	74.7	6.7	4.1	ND	ND	5	6	base	5C5	
166	65.4	1.8	ND	ND	ND	ND	ND	base	white	
	32.7		ND	ND	ND	ND	ND	HCl		
167	76.0	5.7	2.2	ND	ND	5	6	base	4B3	
168	73.5	4.8	0.7	ND	ND	15	4	base	4B3	
169	73.7	4.8	0.8	ND	ND	15	4	base	4B3	
170	71.6	4.7	2.6	ND	ND	12	4	base	4C3	
171	64.5	5.5	0.8	ND	ND	12	6	base	5D5	
172	46.0	3.8	1.3	ND	ND	*	*	base	4C2	antipyrine, meconin
173	57.0	3.6	3.0	ND	ND	*	*	base	4C3	phenacetin, meconin phenobarbital
174	70.2	4.4	2.3	ND	ND	4	6	base	5D5	
175	71.2	6.3	3.1	ND	ND	9	6	base	5D4	
176	71.0	5.5	0.4	ND	ND	7	6	base	5D4	
177	76.0	6.2	0.4	ND	ND	*	*	base	5D6	
178	77.0	6.3	5.3	ND	ND	4	6	base	4D3	
179	65.6	5.0	5.9	ND	ND	15	6	base	5C4	meconin
180	74.3	6.0	0.5	ND	ND	9	6	base	4B3	
181	66.9	5.0	0.4	ND	ND	16	6	base	4C4	
182	72.8	6.0	2.6	ND	ND	7	7	base	4C5	
183	82.8	6.3	1.7	ND	ND	3	5	base	5C5	
184	70.2	5.7	3.7	ND	ND	12	6	base	5D5	
185	78.5	5.3	0.8	ND	ND	5	5	base	4C3	
186	70.5	4.2	0.5	ND	ND	12	3	base	4C4	amphetamine, meconin
187	71.4	4.9	0.1	ND	ND	12	3	base	4B3	
188	69.6	5.0	0.1	ND	ND	12	3	base	4B3	amphetamine, meconin
189	82.6	5.5	0.8	ND	ND	*	*	base	4C3	
190	70.3	4.7	0.2	ND	ND	12	3	base	4B3	meconin
191	80.4	5.4	0.8	ND	ND	5	5	base	4C3	
192	75.1	4.9	0.4	ND	ND	9	5	base	4C3	
194	69.4	5.4	0.8	ND	ND	6	4	base	4C5	phenacetin, phenobarbital
195	75.1	5.3	0.8	ND	ND	12	3	base	4D5	phenobarbital, meconin

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
* = present but not quantified,
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*], and
Others = presence of other compounds.

TABLE 6—*Results of analysis of illicit heroin of Turkish origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
110	53.5	4.2	2.1	ND	ND	1	0.5	HCl	4B2	procaine
111	72.3	5.8	3.4	ND	ND	2	1.5	HCl	4B2	procaine
112	60.5	4.2	3.5	ND	ND	5	3	HCl	4A2	meconin
113	37.8	3.3	2.4	ND	ND	3	2	HCl	3A2	procaine
114	42.2	2.7	2.8	ND	ND	4	0.5	HCl	3A2	procaine
115	42.1	3.1	4.3	ND	ND	4	0.5	HCl	3A2	procaine
116	61.8	3.3	0.3	ND	ND	3	2.5	HCl	4A2	
117	60.3	4.0	0.2	ND	ND	1	2	HCl	4A2	procaine
118	62.7	3.5	0.6	ND	ND	*	*	HCl	4A2	
119	62.1	3.2	0.6	ND	ND	4	2	HCl	4A2	procaine
120	63.1	6.5	9.2	ND	ND	8	7	base	5C5	
121	75.6	4.5	ND	ND	ND	11	3	HCl	3A2	meconin
122	55.1	2.9	0.3	ND	ND	7	2.5	HCl	4A2	sugar
123	79.6	4.4	0.6	ND	ND	9	2	HCl	4B2	meconin
124	58.8	3.1	0.3	ND	ND	*	*	HCl	4B4	amphetamine, meconin paracetamol, vitamin C
125	62.8	3.9	2.0	ND	ND	8	2.5	HCl	4B3	meconin
126	43.5	4.7	4.0	ND	ND	*	*	HCl	4A3	procaine
127	73.0	7.3	1.7	ND	ND	*	*	HCl	5B3	
128	72.1	7.0	5.4	ND	ND	*	*	HCl	5B4	
129	69.7	5.9	1.7	ND	ND	*	*	HCl	5A3	procaine
130	22.7	2.2	1.8	ND	ND	*	*	HCl	5D3	
131	30.3	2.5	2.0	ND	ND	*	*	HCl	5B3	procaine
132	75.5	6.2	4.1	ND	ND	*	*	HCl	5B3	
133	50.0	3.7	1.8	ND	ND	*	*	HCl	5B3	procaine
134	56.9	5.3	5.4	ND	ND	*	*	HCl	5C3	
135	52.6	4.3	2.6	ND	ND	*	*	HCl	5C3	
136	34.5	2.7	5.5	ND	ND	*	*	HCl	5B4	procaine
137	51.6	4.2	2.3	ND	ND	*	*	HCl	5C3	
138	58.2	4.3	2.7	ND	ND	*	*	HCl	5C3	
139	60.1	3.9	1.4	ND	ND	*	*	HCl	5C3	
140	59.6	3.8	1.0	ND	ND	*	*	HCl	5C3	
141	53.6	3.4	2.3	ND	ND	ND	ND	HCl	5C3	
142	21.7	3.0	1.3	ND	ND	*	*	HCl	5C3	procaine
143	24.9	1.6	1.2	ND	ND	*	*	HCl	5C3	procaine
144	46.8	2.9	1.3	ND	ND	*	*	HCl	5C4	procaine
145	50.0	2.8	1.1	ND	ND	*	*	HCl	5C3	procaine
146	36.7	2.8	3.6	ND	ND	*	*	HCl	5B4	procaine, meconin
147	9.7	0.6	0.1	ND	ND	1	0.5	HCl	4A2	
148	40.0	2.8	ND	ND	ND	ND	ND	HCl	5C4	
149	40.2	2.8	ND	ND	ND	ND	ND	HCl	5D6	meconin trace
150	11.5	1.1	0.6	ND	ND	ND	ND	HCl	5A3	
151	24.7	1.9	3.0	ND	ND	ND	ND	HCl	5D4	

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
* = present but not quantified,
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*], and
Others = presence of other compounds.

TABLE 7—*Results of analysis of illicit heroin of Near Eastern origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL	Others
216	23.7	2.2	10.0	ND	ND	*	*	HCl	5B4	meconin, caffeine (S)
217	51.0	2.7	2.3	ND	ND	ND	ND	HCl	5A2	meconin (L)
218	74.2	4.2	1.5	ND	ND	ND	ND	HCl	5A2	(L)
219	33.4	2.6	0.5	ND	ND	*	*	HCl	5A3	caffeine (L)
220	22.1	1.3	4.2	ND	ND	*	*	HCl	5A3	caffeine (L)
221	80.2	2.5	3.0	ND	ND	ND	ND	HCl	white	(L)

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
* = present but not quantified,
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*]
Others = presence of other compounds,
L = Lebanese, and
S = Syrian.

TABLE 8—*Results of analysis of illicit heroin of Nigerian origin.*[a]

No	H	AC	6AM	MOR	COD	N	P	Form	COL
222	87.4	2.2	4.9	ND	ND	ND	ND	HCl	4A3

[a] No = heroin sample serial number,
H = heroin,
AC = acetylcodeine,
6AM = 6-acetylmorphine,
MOR = morphine,
COD = codeine,
N = noscapine,
P = papaverine,
ND = not detected (limit of detection 0.5%),
Form = chemical status of opiates: free base or hydrochloride salt,
COL = color [*21*].

Discussion of Results

Taken overall, the chromatographic data show that specific countries or regions are characterized by identifiable, but not necessarily unique, illicit heroin presentations, each of which has a particular physical appearance and recognizable chemical profile. This is illustrated by consideration of illicit heroin from Iran. With a few exceptions (Table 5, Nos. 153-8, 166, and 172), samples from this source contain between 55 and 85% heroin (mean 79%). The acetylcodeine content is approximately 5% and the 6-acetylmorphine level 1 to 2%; high levels of noscapine and papaverine are present, and the opiates are in the form of the base. This particular pattern is also applicable to the majority of illicit heroin seizures from Pakistan, especially if the early, less representative examples are excluded. All of the Iranian illicit heroin was imported between 1978 and the spring of 1980. This source ceased

thereafter, its place rapidly being taken by the Pakistani product. Many of the early samples from Pakistan were of low heroin content, but contained appreciable levels of 6-acetylmorphine or morphine or both. A few samples of this type had previously been encountered from Iran (as listed above). After a short period, the Pakistani product achieved a consistently high heroin content with a mean level of 77%. Chemically and physically, however, the Iranian and Pakistani highly pure products are indistinguishable, at least using the methods described in this paper. The strong similarities between the products of these two countries and their geographical contiguity suggest that a single group may control heroin production.

The other category of highly pure illicit heroin is represented by preparations from India and the type from southeast Asia known as "Chinese No. 4." This often contains as much as 80 to 90% heroin and in the present study the mean was 81%. This type rarely contains more than 5% 6-acetylmorphine, and an absence (less than 0.1%) of noscapine and papaverine. The acetylcodeine content of Indian illicit heroin is significantly lower (2.9%) than the southeast Asian (5.9%), Pakistani (4.7%), or Iranian (5.4%) illicit heroin of comparable purity. This suggests that either Indian opium contains less codeine relative to morphine than other types, or, less likely, that morphine is purified more rigorously in India before acetylation. Low levels of acetylcodeine (AC) in a highly pure sample of illicit heroin indicates India as the most likely country of origin.

Two alternative methods may be postulated for the production of illicit heroin:

Method 1

Opium → Morphine Separated and Purified → Acetylation → southeast Asian "No. 4" or Indian

Method 2

Opium → Powdered or Crude Separation of the Morphine → Acetylation → Iranian or Pakistani

This results in the following chemical profiles listed in Table 9.

There is some evidence from samples not covered in this survey that Pakistan is now producing both Type 1 and Type 2. Turkish illicit heroin cannot be accommodated into the above scheme. With one exception (No. 120) it occurs as the hydrochloride, but only 6 of the 42 samples had a heroin content greater than 70% (none above 80%). Thirty-six samples had a heroin content between 40 and 70%. The average acetylcodeine content is approximately 3%, which, given the lower average heroin content of 52% for all Turkish samples, is comparable to the acetylcodeine levels in the higher purity heroin samples. In Turkish samples 6-acetylmorphine levels are rarely above 5% which indicates skill in production and a short importation time into western Europe. Turkish heroin is also distinguished by the higher frequency of the presence of diluents at importation. Overwhelmingly, the diluents in

TABLE 9—*Chemical profiles of Types 1 and 2 of heroin.*

	Optimum Purity, %	AC, %	Noscapine	Papaverine	Form
Type 1	80 to 90	5 (SE Asian) 3 (Indian)	−	−	HCl
Type 2	65 to 75	5	+	+	base

illicit heroin from Iran and Turkey are pharmaceutical compounds rather than carbohydrates. Procaine was found in 17 of the 42 Turkish samples. No examples from Turkey contained caffeine, although caffeine is the most widespread diluent, occurring in some illicit heroin samples from Syria, Lebanon, Iran, and southeast Asia.

Only one sample in the entire survey (Number 122 from Turkey) contained a sugar and only one (No. 9 from Pakistan) contained codeine. This sample also contained large amounts of morphine and 6-acetylmorphine, but very little heroin. The presence of codeine can therefore be attributed to incomplete acetylation during manufacture, rather than addition as a diluent. The infrequent occurrence of other diluents in samples at importation confirms that cutting normally takes place after the illicit heroin reaches its country of destination. The retention times of all diluents encountered over the period of this study have been measured using GLC and HPLC. These are listed in Table 1, together with the retention times of the opiates. Reference to Table 1 shows that using GLC, all of the narcotics are separated from each other and, apart from meconin and procaine, none are coeluted with the diluents encountered. Several of the diluents are eluted rapidly and as a result are only partially resolved.

Reexamination by combined GLC and MS is used to check whether more than one of the unresolved diluents is present in a given sample. In such cases, which are unusual, separation for quantitative purposes may be achieved by operating the column at a lower temperature. Using HPLC, meconin and procaine are well resolved. Meconin is only partially resolved from two of the pharmaceuticals and papaverine, but by combining gas and liquid chromatographic data, these compounds can be quantified. All of the major narcotics are resolved from each other and none suffer from interference from any of the diluents. Chromatograms have been previously published [*18*].

Many illicit heroin samples, especially those of high purity, are stable on storage. For these samples, the heroin content determined for this survey was within experimental error of the values obtained when they were first analysed for forensic science purposes as much as two years previously. However, some samples do undergo significant chemical transformation within a relatively short period. High levels of 6-acetylmorphine in samples containing small amounts of morphine (for example, Pakistan, Nos. 1, 4, and 13) may be the result of poor acetylation. Prolonged storage in the Laboratory of some samples of illicit heroin containing small amounts of morphine resulted in decomposition of the heroin entirely to 6-acetylmorphine. One particular sample, which contained 20% heroin on receipt, was found on reexamination two years later to have completely hydrolyzed to 6-acetylmorphine. It is therefore more likely that illicit samples, which on receipt have high levels of 6-acetylmorphine, have undergone spontaneous hydrolysis and are therefore old. In contrast, samples containing high levels of morphine (for example, Pakistan, Nos. 6, 7 and 9) are most probably the result of incomplete acetylation.

The strongest indication of recent manufacture of illicit heroin is the presence of 3-acetylmorphine. Under the GLC and HPLC conditions used in the present study, 3-acetylmorphine is partially resolved from 6-acetylmorphine and its fate can therefore be monitored, at least qualitatively. This compound was detected only in samples of illicit heroin analyzed soon after seizure and none was found in those samples which had been stored before the commencement of this survey. On storage of the solutions containing illicit heroin, the 3-acetylmorphine concentration decreased rapidly and after a few days was below the detection limit. Standard solutions of synthetic 3-acetylmorphine, prepared for either of the chromatographic systems, were also unstable.

The only salt form found in this survey has been hydrochloride, which constituted 50% of all samples examined. The chemical form of heroin is highly indicative of certain countries of origin: only one Turkish sample (Number 120) was not the hydrochloride and only one Iranian sample (Number 166) was not the base. This Iranian sample was also unusual in that it consisted of very pure heroin present as a mixture of the base and hydrochloride.

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