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Changes in Place of Origin of Heroin Seized in Denmark from 1981 to 1986

"Chemical Fingerprint" of 138 Samples

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Summary. Hundred thirty-eight samples of heroin weighing more than 0.1 g seized between 1981 and 1986 were characterized according to their contents of opium alkaloids, adulterants, and diluents together with their form and color. The "chemical fingerprint" was used to establish a change in the heroin during the period. As compared to the first few years covered by the survey, a predominant number of the samples at the end of the period were in the base form and contained the opium alkaloids papaverine and noscapine. In particular, the concentration of noscapine as related to the heroin content of each sample had increased considerably, indicating Pakistan or Iran as being the places of origin of most of the heroin seized in Denmark at the end of the period.

Key words: Heroin – Opium alkaloids – Chemical fingerprint

Zusammenfassung. Einhundertachtunddreißig Heroin-Proben mit einem Gewicht von mehr als 0.1g, die in Dänemark in den Jahren 1981–1986 beschlagnahmt wurden, wurden nach ihrem Gehalt an Opiumalkaloiden, Verschnittsubstanzen, Form und Farbe charakterisiert. Über den betreffenden Zeitraum ließ sich ein Wandel in der Zusammensetzung der Heroinproben beobachten. Bei einer erhöhten Anzahl lagen vor allem in den letzten Jahren die Proben in Basenform vor, wobei die Opiumalkaloide Papaverin und Noscapin dominierten. Besonders die Konzentration des Noscapins stieg im Verhältnis zum Heroingehalt stark an, was auf Pakistan und Iran als Ursprungsland der meisten am Ende des Untersuchungszeitraums beschlagnahmten Proben hinweist.

Schlüsselwörter: Heroin – Opium-Alkaloide – Chemische Charakterisierung

Introduction

Heroin samples may be characterized by their contents of other opium alkaloids and of substances introduced for adulteration or dilution purposes ("chemical fingerprints").

The contents of adulterating and diluting substances may vary considerably due to inhomogenity of the samples and can only be used as an indication of the distribution routes of the samples.

In contrast, the contents of the opium alkaloids monoacetylmorphine, morphine, acetylcodeine, papaverine, and noscapine as related to the heroin content of each sample remain constant despite possible subsequent dilution of the sample. These proportions may therefore be used to characterize the place of origin of the heroin.

For the purpose of comparison, the contents of monoacetylmorphine and morphine are not as appropriate as the other opium alkaloids, as improper storage of the samples may alter the mutual relationship between diacetylmorphine (heroin), monoacetylmorphine, and morphine.

Impurities, adulterants, and diluents of heroin seized from 1981 to 1983 were compared in a previous survey [1]. In the survey no attention was paid to, e.g., the color and form of the samples.

In another survey in which "street" heroin was characterized, a change in the form and color of the heroin samples between 1980 and 1985 was one of the observations made [2].

Studies carried out in England into heroin samples seized at airports and seaports divide heroin into different categories according to its place of origin [3, 4].

In this survey all samples of heroin weighing more than 0.1 g seized between 1981 and 1986 are characterized by their contents of the opium alkaloids monoacetylmorphine, morphine, actylcodeine, papaverine, and noscapine along with their contents of caffeine, procaine, and sugars. The base/salt form and color of each sample are also described.

Based upon the results of the English investigations, an assumption regarding the place of origin of heroin seized in Denmark has been made using the "chemical fingerprint" of the samples.

Materials and methods

Hundred thirty-eight samples of illicit heroin seized in Jutland and Funen between 1981 and 1986 were examined. The weights of the samples upon receipt ranged from 0.1 g–373 g.

Cases in which several samples with the same heroin content were received are registered as one sample, whereas samples with the same heroin content received in different cases are registered as individual samples.

As color interpretation is rather individual, the color of the samples were described at the same time by one person. Only a description of the strength of the brown color (light, medium, or dark) and not the shades of red, yellow, or gray has been attempted.

On account of the conformity between the high performance liquid chromatographic (HPLC) and the gas liquid chromatographic (GC) results in the previous survey, samples received from 1984 to 1986 have only been subjected to HPLC analysis, the method of which was described in a previous paper [1].

In cases where procaine was found, monoacetylmorphine was quantified by GC because of interference of the two substances when using the HPLC method. In contrast to the previous survey monoacetylmorphine was quantified as a BSA-derivative using a 3% SE-30 column.

All samples had been previously subjected to both UV-spectrophotometry and thin-layer chromatography as part of their routine forensic science examination.

Results

A detailed list (eight pages in manuscript) showing the composition of 138 illicit heroin samples seized from 1981 to 1986 and displaying the content of opium alkaloids and adulterants as percentage of sample weight and as percentage of the heroin content of each sample is due to lack of space omitted, but may be obtained from the author.

Contents of Opium Alkaloids

The content of heroin varied considerably from 1 year to the next as seen in Table 1, where both the mean and median concentration of heroin are shown. In 1983, the greatest number of samples (34) was seized, but both the mean and median concentration were low that year due to a preponderance of samples with a low heroin content. The mean and median concentration were also low in 1982, mostly on account of a lack of samples with a high heroin content. Only one sample (5%) in 1982 contained more than 50% heroin as compared to more than 20% of the samples the other years.

When comparing samples it is most reasonable, on account of the variation in the heroin content, to use the contents of opium alkaloids in relation to the heroin content of each sample and not the contents in relation to the sample weight.

Most of the samples contained monoacetylmorphine. The highest concentration found was 30%. Ten samples – all with a low heroin content – contained more monoacetylmorphine than heroin.

The number of samples positive of morphine varied from 10% of the samples in 1981 to 47% in 1983.

All but two of the 138 samples contained acetylcodeine, the highest concentration according to sample weight being 12%. Table 2 shows for each year the mean and median concentration of acetylcodeine in relation to the heroin content. A small decrease in the ratio at the end of the period can be noticed.

Table 1. Concentration of heroin according to the year of seizure

	1981	1982	1983	1984	1985	1986
Mean conc.	41%	26%	28%	44%	33%	38%
Median conc.	37%	26%	17%	42%	25%	39%
Number of samples	21	22	34	17	22	22

Table 2. Concentration of acetylcodeine in relation to the heroin content of each of 136 positive samples, 1981–1986

	1981	1982	1983	1984	1985	1986
Mean conc. (%)	8.6	14.4	9.8	8.0	7.9	6.7
Median conc. (%)	8.5	8.7	8.2	7.1	7.5	6.0
% positive	100%	100%	100%	100%	95%	95%

Table 3. Concentration of papaverine in relation to the heroin content of each of 79 positive samples, 1981–1986

	1981	1982	1983	1984	1985	1986
Mean conc. (%)	4.0	2.9	3.8	3.1	6.5	4.4
Median conc. (%)	2.4	3.1	3.0	3.3	6.3	4.7
% positive	48%	41%	41%	76%	73%	77%

Table 4. Concentration of noscapine in relation to the heroin content of each of 81 positive samples, 1981–1986

	1981	1982	1983	1984	1985	1986
Mean conc. (%)	5.8	3.5	7.7	10.9	23.3	27.3
Median conc. (%)	3.8	3.6	6.1	8.7	29.7	28.0
% positive	38%	23%	50%	88%	77%	86%

In the previous survey covering the period from 1981 to 1983 approximately half of the 77 samples contained the alkaloids papaverine and noscapine. Of the 30 samples containing noscapine only two had a concentration of more than 5% in relation to sample weight. Of the 51 samples containing noscapine seized between 1984 and 1986, 24 contained more than 5% noscapine.

Tables 3 and 4 show according to the year of seizure the mean and median concentrations of papaverine and noscapine in relation to the heroin content of each sample.

A marked increase in the number of samples containing the two alkaloids was seen during the period. From being found in approximately half of the samples, papaverine was found in three quarters from 1984. During the period a small increase in the concentration of papaverine relative to heroin can be noticed (Table 3).

On the other hand, the number of samples containing noscapine grew to about 90% of all samples, and the content of noscapine increased considerably during the period. Both the mean and median concentration increased from approximately 5% to approximately 30% of the heroin content (Table 4).

Table 5 shows for each year the content of noscapine in relation to heroin grouped according to the concentration ratio. It appears from the table that it is in particular the number of samples with a very high noscapine content (ratio > 30) which has increased during the last years, while no significant change is seen in the relative number of samples containing low concentrations of noscapine.

In the HPLC chromatogram an unknown peak with a relative retention time of 1.2 appeared sometimes. The peak only appeared in samples containing the alkaloids papaverine and/or noscapine and mainly in samples with high alkaloid concentrations. Therefore, it is assumed that the unknown substance is another alkaloid for which the laboratory has no reference. In 48 of the 138 samples the unknown was found. The number of samples containing the unknown increased during the period. In 1981, 5% of the samples contained the unknown, while in 1986 the substance appeared in 68% of the samples.

Contents of Adulterants and Diluents

Fifty-three of the 138 samples had been adulterated by adding caffeine or procaine. In six cases both drugs had been added. As expected, adulteration was most common in samples with a low heroin content. No samples with a heroin concentration of more than 50% contained caffeine or procaine. Most of the samples had an adulterant content of under 10%, but six samples seized in 1982 and 1983 had a caffeine content of more than 40%. All six samples were chloride in form. Only one sample seized in 1986 had a procaine content of more than 40%.

Table 5. Concentration of noscapine in relation to the heroin content of each sample, 1981–1986. Results of each concentration group as percentage of total number of samples each year. Ratio = conc. noscapine/conc. heroin × 100

Ratio	1981	1982	1983	1984	1985	1986
0	62%	77%	50%	12%	23%	14%
0.1– 4.9	29%	14%	21%	24%	5%	18%
5.0– 9.9	5%	9%	18%	29%	9%	0%
10.0–19.9	5%	0%	9%	18%	14%	9%
20.0–29.9	0%	0%	3%	12%	14%	18%
≥30	0%	0%	0%	6%	36%	41%

Table 6. Samples containing adulterants (caffeine, procaine) and diluents (glucose, lactose, sucrose, mannitol) grouped according to the year of seizure. Results as percentage of total number of samples each year

	1981	1982	1983	1984	1985	1986
Caffeine/procaine	29%	27%	35%	41%	50%	50%
Sugars	86%	95%	74%	65%	77%	36%

Table 6 shows for each year the number of samples containing the adulterants caffeine or procaine and diluents (sugars). From period 1981 to 1983 approximately one third of the samples were adulterated by caffeine or procain, while the proportion increased to half of the samples in 1985 and 1986. The increase in the number of adulterated samples was mostly due to an increase in samples containing caffeine, while the number containing procaine did not change significantly.

Although caffeine and procaine were the most commonly found additives, other drugs, such as phenacetin, phenazone, salicylic acid, and ascorbic acid, were detected in two, two, two, and seven cases, respectively.

The use of sugars for diluting purposes is well known [1]. From 1981 to 1985 one or two of the sugars glucose, lactose, sucrose, or mannitol had been added to most of the samples. The presence of sugars was, as expected, most common in samples with a low heroin content. The reason for the sudden decrease in 1986 in the number of samples containing sugars is not clear, but the presence of an unknown peak in the TMS-GC-chromatogram [1] for three samples that year may indicate the use of a new, unidentified additive.

Form and Color of the Heroin Samples

Of the 138 samples, half appeared as heroin base and half as chloride, but the proportions between the two forms varied considerably during the period. In 1981 and 1982 by far the most samples were in the chloride form, while from 1983 the base form dominated (Table 7).

Table 8 shows the color of the 138 samples according to their base/salt character. Of the 138 samples, only 15 were white, while the rest were in shades of beige, light brown, brown, of dark brown. The majority (54 samples) of the colored samples were brown, while approximately equal numbers were beige, light brown, or dark brown (25, 23, and 21 samples, respectively).

Table 7. Base/salt character of 138 heroin samples grouped according to the year of seizure. Results as percentage of total number of samples each year

	1981	1982	1983	1984	1985	1986	Total
Heroin chloride	86%	73%	32%	47%	32%	41%	50%
Heroin base	14%	27%	68%	53%	68%	59%	50%

Table 8. Color of 138 heroin samples in relation to base/salt character. Results as percentage of total number of each color

	White	Beige	Light brown	Brown	Dark brown	Total
Heroin chloride	100%	96%	30%	33%	24%	50%
Heroin base	0%	4%	70%	67%	76%	50%
Number of samples	15	25	23	54	21	138

Table 9. Base/salt character of 138 heroin samples grouped according to the concentration of noscapine in relation to the heroin content of each sample. Results as percentage of total number of each concentration group

	0	0.1–4.9	5.9–9.0	10.0–19.9	20.0–29.9	≥30
Heroin chloride	75%	64%	40%	23%	10%	0%
Heroin base	25%	36%	60%	77%	90%	100%
Number of samples	57	25	15	13	10	18

Ratio = conc. noscapine/conc. heroin × 100

All the white samples and all but one of the beige were in the chloride form, while the brown color dominated the heroin base samples.

The content of acetylcodeine relative to heroin varied according to the color of the sample. The mean concentration of acetylcodeine as related to heroin was 6.5 for the white samples and increased in proportion to the darkness of the samples, the ratio being twice as high for the dark brown samples.

The white and beige samples seldom contained the opium alkaloids papaverine and noscapine, and no significant relationship between the shades of brown and the concentrations of papaverine or noscapine was observed.

Table 9 shows the base/salt character of the samples according to their content of noscapine. As in Table 5, the samples are grouped according to the noscapine/heroin ratio. It can be seen that the chloride form dominated samples without or with a low noscapine content and declined with increasing ratio, while the opposite was found for the samples containing the base form of heroin. All samples with a ratio of 30 or more were in the base form.

Of the 81 samples containing noscapine, all but five were brownish in color. Four were beige, all with a noscapine/heroin ratio of less than 5.0. One sample with a ratio of 5.0 was white, but the sample only contained 2.0% heroin, the whiteness undoubtedly being due to diluting agents and not to the heroin.

Discussion

One of the categories of heroin characterized by the English surveys [3, 4] has features which distinguishes the heroin as originating from Iran or Pakistan. Heroin from these countries often comes in the form of free base and is brownish in color. It often contains fairly large amounts of the opium alkaloids papaverine and noscapine which indicates that the basic material (morphine) had not been effectively purified.

Another category consists of heroin originating from India or South East Asia. Heroin from these parts of the world comes in chloride form and is most frequently white. It seldom contains papaverine and noscapine, which indicates that the basic material had been effectively purified. In addition, heroin from India contains less acetylcodeine than heroin from other countries. This suggests that the proportion of codeine to morphine in Indian opium is lower than in other countries. Lately, Pakistan has started production of heroin chloride, the chemical profile and physical appearance of which are indistinguishable from Indian heroin [4].

A third type of heroin comes from Turkey. This heroin is beige or light brown in color and often comes in the chloride form. Turkish heroin is also distinguished by a higher frequency of diluents/adulterants upon importation. Procaine was often found, while Turkish heroin seldom contained caffeine although it is the most widespread additive in heroin samples from, e.g., South East Asia and Iran.

On the basis of the change in the "chemical fingerprint" of the heroin which comes onto the Danish market, it is obvious to assume that the place of origin has altered during the survey period. The increase in the number of samples containing the opium alkaloids papaverine and noscapine, together with an increase in the base form of heroin and especially an increase in the noscapine content may indicate that, as compared to the first years covered by the survey, a predominant proportion of the heroin now comes from countries such as Pakistan and Iran.

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