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Variations in the Infrared Spectra of Heroin Base

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ABSTRACT: The infrared spectrum of the heroin base standard supplied with the Georgia State Crime Laboratory (GSCL) library index has a carbonyl doublet with absorbance maxima at 1756.6 and 1728.3 cm^{-1} . Most heroin base samples from actual cases have carbonyl absorbance maxima at 1761.3 and 1741.1 cm^{-1} with additional differences in the spectra at 2800 to 3200 cm^{-1} and in the fingerprint region. These differences could not be accounted for as a result of impurities, decomposition products, additives, or diluents. At least two polymorphic forms of heroin base exist with various crystal habits. The main parameters determining which polymorph and crystal habit are obtained are the temperature conditions and solvent used for crystallization.

KEYWORDS: toxicology, heroin, spectroscopic analysis, polymorphism, crystal habit, Fourier transform infrared spectrophotometry, X-ray diffraction

A common analytical technique used to identify heroin in drug samples is infrared spectrophotometry. This method is particularly useful when the samples are at the dealer level where the heroin content is high or even at street level concentrations of heroin base used for smoking where the heroin concentration is also quite high. A library database system widely used in Fourier transform infrared spectrophotometry (FTIR) is the Georgia State Crime Laboratory (GSCL) library index. The spectrum of the heroin base supplied with the GSCL library index has a carbonyl doublet with absorbance maxima at 1756.6 and 1728.3 cm^{-1} . Similar values have also been published elsewhere in the literature [1,2].

It was observed that most heroin base samples from actual cases have carbonyl absorbance maxima at 1761.7 and 1741.1 cm^{-1} with additional differences in the spectra at 2800 to 3200 cm^{-1} and in the fingerprint region (see Figs. 1 and 2). The laboratory heroin base standard that was prepared by neutralizing standard heroin · hydrochloride (HCl) and crystallizing from acetone by rapidly heating to dryness produced an infrared spectrum with carbonyl absorbance maxima at 1756.6 and 1728.3 cm^{-1} very similar to the spectrum from the GSCL library index. As a result of these spectral differences, the Hardware Augmented Vector Correlation (HAVEC) spectral search program would frequently produce the "best fit" as heroin · HCl even though the sample was known to be heroin base. Spectral subtraction of heroin base from actual case samples would produce numerous artifacts. The main object of this investigation was to determine the causes of these variations in the infrared spectrum of heroin base.

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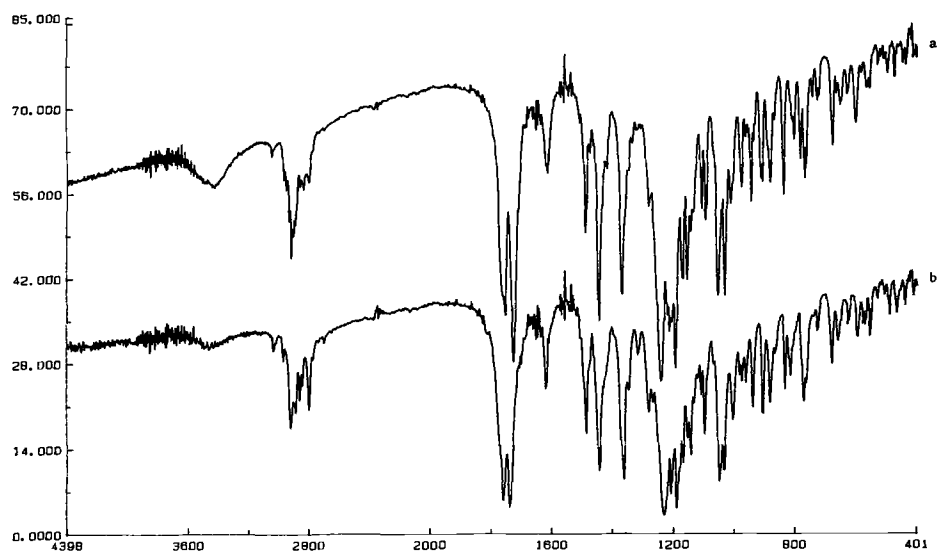


FIG. 1—Infrared spectra of heroin base: (a) needle crystals with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} and (b) plate crystals with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} .

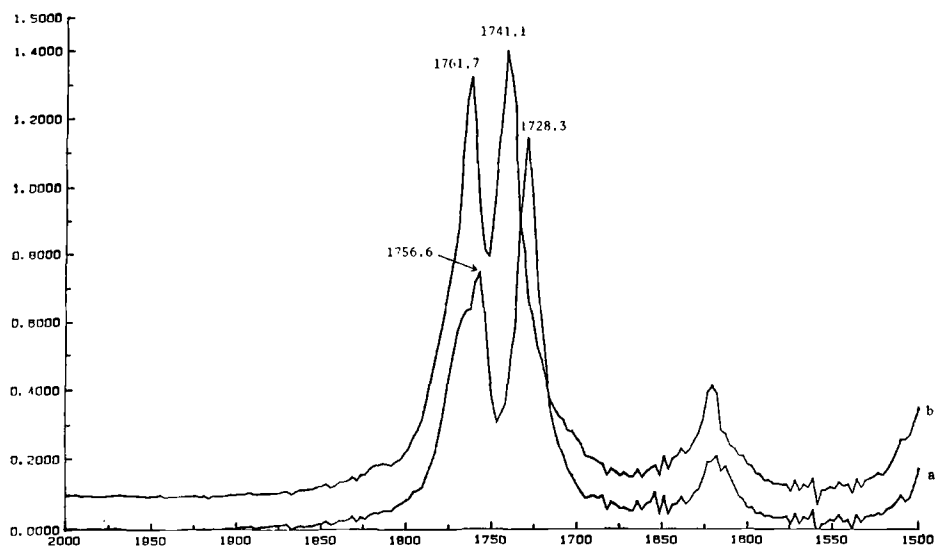


FIG. 2—Absorbance spectra of carbonyl region of heroin base: (a) needle crystals and (b) plate crystals.

Experimental Procedure

The infrared spectra were obtained using an Analect model Fx6160 Fourier transform infrared spectrophotometer with a triglycine sulfate (TGS) detector. Spectra of samples from cases were recorded using 32 scans whereas standards were recorded using 64 scans. Sample size was approximately 1 to 2 mg in 100 mg of KBr. A Wilks 0.5-in. (12.7-cm) diam-

eter pellet holder was used and 7-ton (6350-kg) ram pressure was applied. Crystal axes measurements and microscopy were performed with a Zeiss Universal® Polarizing microscope. Powder X-ray diffraction (XRD) measurements were made with a Phillips diffractometer Model 1710.

Results and Discussion

Initial experiments to explain the carbonyl shifts observed between the heroin base standard and the heroin base from actual cases concentrated on common impurities and decomposition products such as narcotine, monoacetylmorphine, and acetylcodeine. Experiments involving a synthetic mixture of the above three compounds with the heroin base standard and a spectral addition of mixtures of these compounds with the heroin base standard did not produce carbonyl absorbance maxima at 1761.7 and 1741.1 cm^{-1} . Common additives and diluents such as caffeine, procaine, and various carbohydrates were also rapidly eliminated as potential causes since this carbonyl shift was observed numerous times in actual case samples when these additives or diluents were not present.

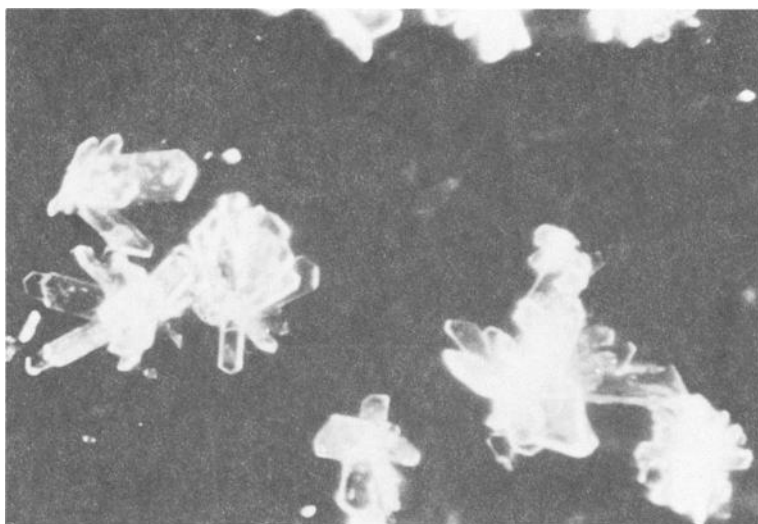
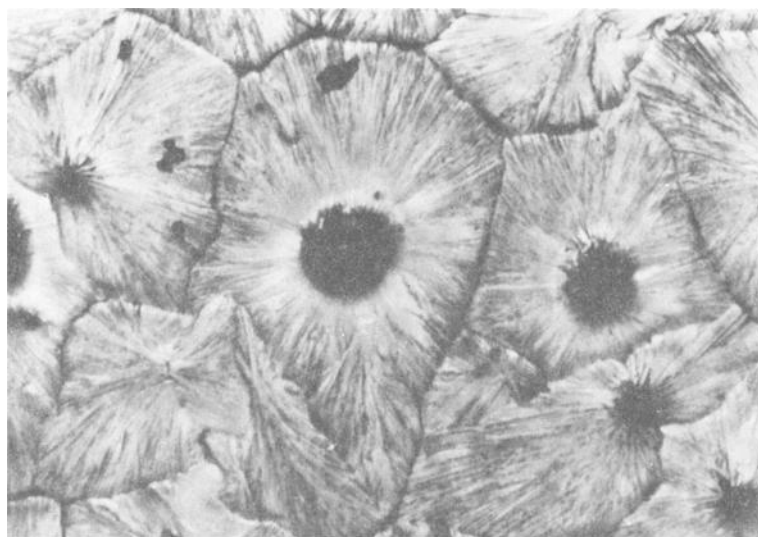
Inorganic reaction products and excess starting materials such as acetic acid, sodium bicarbonate, calcium carbonate, and sodium acetate were also considered as potential sources of this carbonyl shift. An examination of the infrared spectra of these compounds quickly eliminated them as possible sources. The magnitude of the carbonyl shifts both in terms of absorbance and wavelength shift could not be accounted for by trace or minor components. Analysis of several case samples by gas chromatography/mass spectrometry (GC-MS) did not reveal any unexpected compounds.

The well-known phenomenon of KBr matrix interaction as a result of the degree of grinding did not seem a feasible explanation [3] since heroin base samples from cases so consistently produced carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} , whereas the heroin base standard consistently produced carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . Since most heroin base samples frequently have a strong odor of acetic acid, the possibility of a heroin acetate salt was not ruled out, although no data were found in the literature on this salt, if it indeed exists. The possibilities of a hydrate or solvate were not excluded.

In a partial simulation of the final stages of heroin base synthesis, an excess of acetic acid was added to an aqueous solution containing heroin hydrochloride standard, neutralized with sodium bicarbonate to pH 8, and set aside to crystallize out slowly. The crystals obtained were washed with deionized water to remove any soluble inorganic salts and heroin hydrochloride. The heroin base obtained had an orthorhombic plate habit (see Fig. 3) and an infrared spectrum with carbonyl absorbance maxima at 1761.7 and 1741.1 cm^{-1} and matching that of heroin base from actual cases.

Different solvents, neutralization conditions, and temperature conditions were used for recrystallizing heroin base. Heroin hydrochloride standard was neutralized with sodium hydroxide and sodium bicarbonate to pH 8, the heroin base was extracted into chloroform and heated to near dryness, and the remaining chloroform air-evaporated. The crystals obtained were spherulite habit (see Fig. 4) with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . Heroin hydrochloride standard was neutralized with sodium hydroxide and sodium bicarbonate to pH 9 and the heroin base extracted into chloroform and heated to dryness. The crystals obtained were needle habit with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . A repeat experiment using the same conditions as those to obtain the spherulite habit resulted in a crystalline agglomerate with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} . As a solvent, chloroform was very unreliable when trying to obtain a given crystal habit with reproducible carbonyl absorbance maxima.

Heroin hydrochloride standard was slowly neutralized with the stoichiometric equivalent of sodium hydroxide and the crystals obtained were filtered and washed with deionized water and recrystallized from acetone by rapidly heating to dryness. The crystals had carbonyl

FIG. 3—Plate crystals, $\times 40$.FIG. 4—Spherulite crystals, $\times 20$.

absorbance maxima at 1728.3 and 1756.6 cm^{-1} . In similar experiments using acetone as the solvent but varying the rate of evaporation of the solvent needle, rod and dendritic habits were obtained and sometimes an absorbance maxima occurred at 1730.9 cm^{-1} . Never was a carbonyl absorbance maximum obtained at 1741.1 cm^{-1} using acetone as the solvent.

Heroin base plate habit recrystallized from ethyl acetate yielded crystals in the shape of a needle tree (see Fig. 5) with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} . A minor shift occurred in the relative absorbance of the two carbonyl maxima, but there was no



FIG. 5—Needle tree, transmitted light, $\times 40$.

wavelength shift. Heroin base recrystallized from chloroform : heptane (1 : 3) produced a needle habit with carbonyl absorbance maxima at 1741.1 and 1761.7 to 1764.3 cm^{-1} . No significant melting point differences were observed between the various crystal habits. The results of the crystallization experiments are summarized in Table 1.

Polarized light microscope examination was performed on the various heroin crystal habits. Samples of the heroin base plate habit were redissolved on a slide in water, chloroform, and xylene and allowed to recrystallize at room temperature on the microscope stage. All three solvents yielded a mixture of crystal habits. Conoscopy of the plate, needle, and the rod habits demonstrated that the three crystal axis angles in each habit were 90°. Also note that the angle of extinction in all crystal habits was equal to 90°. The plate habit appeared to have the most clearly defined and reproducible crystals, and based on the external symmetry supported by the crystal angle axis measurements above, it was determined that it belongs to the orthorhombic crystal system.

Powder XRD was performed on four heroin base samples (see Fig. 6). Two of the samples were plate habit with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} . The results of these two samples agreed with those reported by Barnes and Sheppard [4]. Two of the samples had carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} , one with a spherulite habit and the other with a needle habit. The powder XRD patterns of these two samples were very similar to each other but quite different from those of the plate habit samples. The results were also different from those reported by Canfield [5]. This suggests polymorphism with temperature conditions and crystallization solvent being major parameters determining which polymorphic form and crystal habit(s) are obtained. This view is supported by Borka [6].

A survey was performed over a period of several months of one hundred heroin cases. Eighty-two cases contained heroin base with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} . None of the cases contained heroin base with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . Four cases contained heroin with carbonyl absorbance maxima at 1738.6 and 1759.1 or 1761.7 cm^{-1} . It was suspected that the absorbance maximum at 1738.6 cm^{-1} was due to a mixture of heroin hydrochloride and heroin base. This was con-

TABLE 1—Summary of the conditions used for the crystallization of heroin base.

Experiment	Method of Crystallization	λ max, cm^{-1}	Crystal Habit
1	Standard heroin · HCl neutralized with NaOH, recrystallized from acetone by rapidly heating to dryness.	1756.6 and 1728.1	dendritic
2	Standard heroin · HCl and excess acetic acid, neutralized with NaHCO_3 , crystals washed with water.	1761.7 and 1741.1	plate
3	Standard heroin · HCl neutralized with NaOH and NaHCO_3 , extracted into CHCl_3 , heated to near dryness, crystallized overnight.	1761.7 and 1741.1	crystalline agglomerate
4	Standard heroin · HCl neutralized with NaOH and NaHCO_3 , extracted into CHCl_3 , heated to dryness and formation of crystals on steam bath.	1756.6 and 1728.3	needle
5	Same as Experiment 4 but crystallized overnight at room temperature.	1761.7 and 1741.1	
6	Repeat of Experiment 3.	1756.6 and 1728.3	spherulite and needle plate
7	Heroin · HCl and excess acetic acid, neutralized with Na_2CO_3 and NaHCO_3 , crystals washed with water.	1761.7 and 1741.1	plate
8	Same as Experiment 7 but second crystals from supernatant.	1764.3 and 1741.1	
9	Heroin base recrystallized from ethyl acetate.	1761.7 and 1741.1	rod, needle, dendritic
10	Heroin base recrystallized from chloroform : heptane (1 : 3).	1764.3 and 1741.1	needle
11	Heroin base recrystallized from acetone, heated to dryness on steam bath.	1761.7, 1736.0, and 1730.9	mainly needle
12	Heroin base recrystallized from acetone, heated to near dryness.	1764.3 and 1730.9	rod and dendritic
13	Heroin base recrystallized from acetone, rapidly heated to dryness on steam bath.	1759.1 and 1728.1	needle and dendritic
14	Heroin · HCl and excess acetic acid, neutralized with Na_2CO_3 and NaHCO_3 , crystallized overnight from water.	1761.7 and 1741.1	plate
15	Standard heroin · HCl and excess acetic acid, neutralized with Na_2CO_3 , crystallized overnight from water.	1761.7 and 1741.1	plate
16	Standard heroin · HCl neutralized with NaOH and NaHCO_3 , extracted into CHCl_3 , heated slowly to dryness on steam bath.	1764.3 and 1736.0	glassy residue

firmed from the infrared spectra of synthetic mixtures of heroin base plate habit and heroin hydrochloride (see Fig. 7).

Synthetic mixtures of the two polymorphs were prepared in various ratios using heroin base plate habit with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} and heroin base needle habit with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} (see Fig. 8). The infrared spectrum of the 2:1 needle habit:plate habit mixture produced a carbonyl triplet with absorbance maxima at 1730.9, 1741.1, and 1761.7 cm^{-1} . This carbonyl triplet was never observed in case samples indicating that the polymorph with absorbance maxima at 1728.3 and 1756.6 cm^{-1} is rarely if ever the predominant form in actual cases. The carbonyl absorbance maximum at 1730.9 cm^{-1} was observed in some crystallization experiments using acetone as the solvent, as previously noted. What was obtained was almost cer-

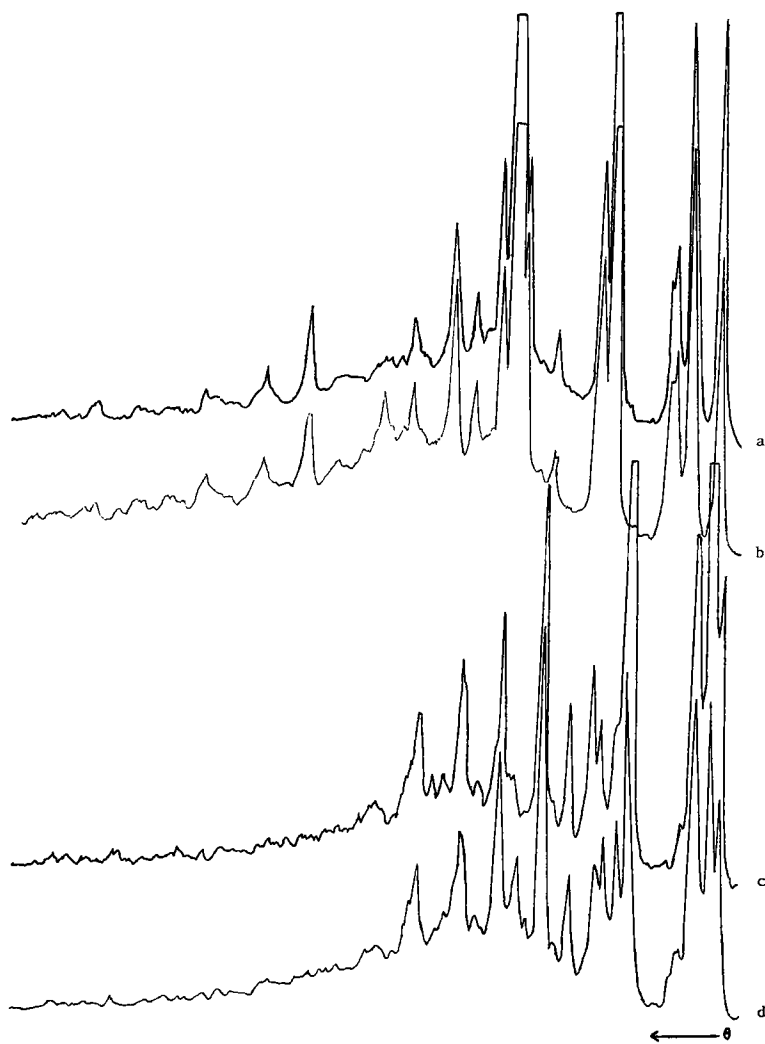


FIG. 6—XRD spectra of heroin base: (a) and (b) plate crystals with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} , (c) spherulite crystals with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} , and (d) needle crystals with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} .

tainly a mixed polymorph with the predominant form being the heroin base with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} .

Minor variations were observed in the intensity of the absorbance ratio at 1761.7 versus 1741.1 cm^{-1} depending on the specific crystallization procedure used. This is of minimal importance for qualitative identification but does have significance for quantitative determination based on carbonyl absorbance. Calibration graphs of absorbance versus weight were plotted at 1741.1 and 1761.7 cm^{-1} for heroin base plate habit (see Fig. 9). Area integration over the range 1675 to 1825 cm^{-1} versus weight for heroin base plate habit is illustrated in Fig. 10.

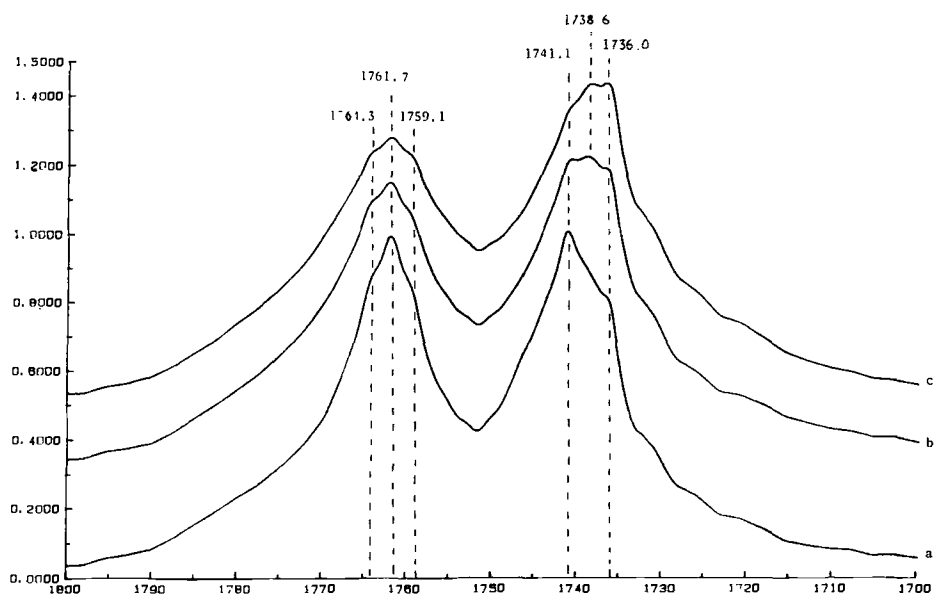


FIG. 7—Absorbance spectra of expanded carbonyl region of mixtures of heroin base plate crystals and heroin · HCl: (a) 2: 1 heroin base plate crystals: heroin · HCl, (b) 1: 1 heroin base plate crystals: heroin · HCl, and (c) 2: 1 heroin · HCl: heroin base plate crystals.

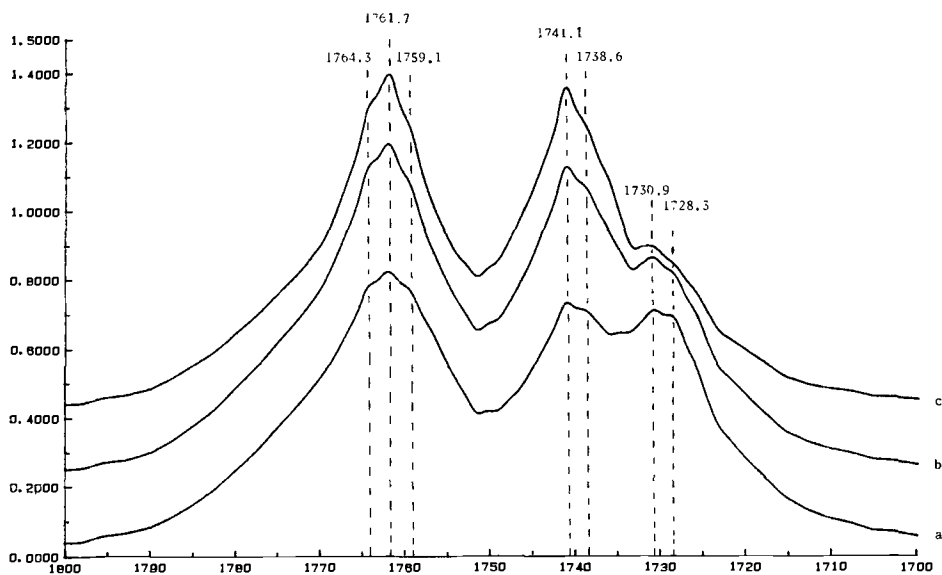


FIG. 8—Absorbance spectra of expanded carbonyl region of heroin base plate crystals and heroin base needle crystals: (a) 2: 1 heroin base needle crystals: heroin base plate crystals, (b) 1: 1 heroin base needle crystals: heroin base plate crystals, and (c) 2: heroin base plate crystals: heroin base needle crystals.

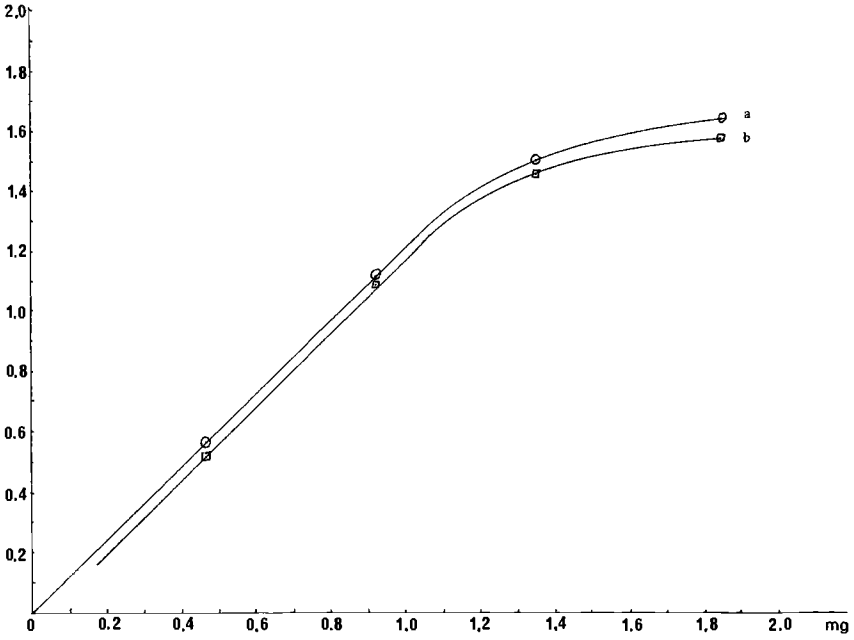


FIG. 9—Absorbance versus weight of heroin base plate crystals at (a) $\lambda = 1741.1 \text{ cm}^{-1}$ and (b) $\lambda = 1761.7 \text{ cm}^{-1}$.

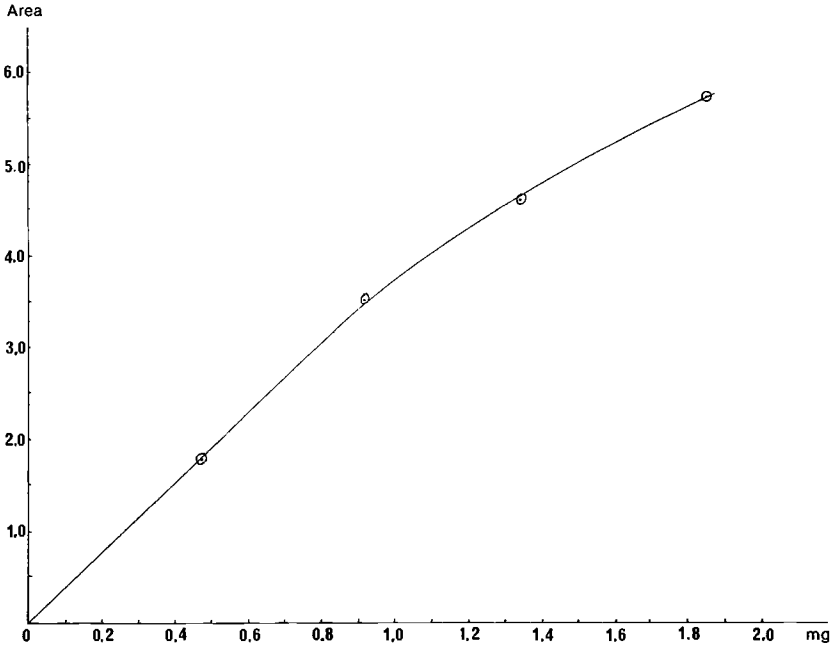


FIG. 10—Area from 1675 to 1825 cm^{-1} versus weight of heroin base plate habit.

Conclusions

There is strong evidence to support the view that at least two polymorphic forms of heroin base with various crystal habits exist. Crystallization from chloroform and acetone, depending on temperature conditions, yields the polymorph with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . Spherulite habit is characteristic of the polymorph with carbonyl absorbance maxima at 1728.3 and 1756.6 cm^{-1} . This form was never observed as the predominant polymorph in actual case samples. Plate habit is characteristic of the polymorph with carbonyl absorbance maxima at 1741.1 and 1761.7 cm^{-1} . The polymorph and crystal habit(s) obtained appear to be a function of the crystallization procedure used.

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