

# MICROGRAM

BUREAU OF NARCOTICS AND DANGEROUS DRUGS / U.S. DEPARTMENT OF JUSTICE

Washington, D.C. 20537

Office of Science and Drug Abuse Prevention  
Vol. II, No. 4 Laboratory Operations Division November, 1969

Forensic laboratories can furnish us with valuable drug intelligence. Instead of destroying all tablet and capsule evidence, send a portion to us after adjudication of a case. Forensic chemists in our Special Testing and Research Laboratory will attempt to identify the product and its manufacturer. This examination is of value in identifying counterfeit and other clandestinely made drugs; to detect newly abused products; and to obtain other information of value.

Send only tablets and capsules. Send up to fifty tablets, or up to twenty-five capsules, to:

Bureau of Narcotics and Dangerous Drugs  
Washington, D.C. 20537  
Attn: Dr. Albert Tillson  
Special Testing and Research Laboratory (SCILR)

Place the drugs in a rigid container packed with cotton or other material to prevent damage by movement. Write a note, or give us a copy of the laboratory report, to provide the date, the city in which the drugs were obtained and the name of the drug. Make a statement that BNDD may retain or destroy the drugs after laboratory examination. Place this information with the container of drugs into a mailing tube or other rigid container and send them by registered or certified mail.

LEAA funds can be used for a wide variety of projects to strengthen law enforcement. Specific proposals are now being developed throughout the country as states complete work on their comprehensive crime control plans. Depending upon priorities in each state--as determined by State Planning Agencies--grants could be made to establish or expand crime labs.

Analytical methods in Microgram do not have official status. Publication of Microgram was approved by the Bureau of the Budget, April 8, 1969.

**CAUTION:** Use of this publication should be restricted to forensic analysts or others having a legitimate need for this material.

Project proposals should be submitted to the State Planning Agency. For a directory of planning agencies, write the Office of Law Enforcement Programs, Law Enforcement Assistance Administration, U.S. Department of Justice, Washington, D.C. 20530.

Modern laboratory services are increasingly necessary for effective law enforcement. Federal funds may be available to help establish new crime laboratories--or to expand existing ones--through the Law Enforcement Assistance Administration. The LEAA, created last year by the Omnibus Crime Control and Safe Streets Act, has already begun to award some \$25 million in block grants to the 50 states to finance law enforcement improvement projects.

The role of technical evaluation of evidence is growing larger today for a number of reasons. A number of recent court rulings for example, require law enforcement agencies to rely more upon scientific analysis of evidence and less upon traditional investigation methods. The success of complicated investigations in many serious crimes may depend in large measure upon the finding and careful analysis of evidence from the crime scene. The growing use of a wide variety of dangerous drugs is another contributing factor. Law enforcement agencies need fast and reliable identification of the many new stimulant, depressant, and hallucinogenic drugs now moving in illicit traffic.

Chemical analysis, of course, is but one function of the crime lab. As the scientific arm of law enforcement, skilled personnel aided by sophisticated equipment provide a wide variety of analyses and tests. Tool marks, firearms, obliterated serial numbers, latent fingerprints, shoe impressions, tire marks, and trace materials are analyzed in the lab's microscopic and photographic sections. The questioned document section processes bad checks and other fraudulent papers. Blood and other body fluids are examined in the serology and biochemical sections. In addition to narcotics, the chemical analysis and instrumentation sections analyze alcohols, chemicals, pharmaceuticals, poisons, combustibles, and explosives. The instrumentation section also processes minute traces and contaminated samples of evidence, such as LSD in sugar cubes or chocolate kisses, or on the backs of postage stamps.

Standard laboratory equipment varies from portable instruments and kits transported to crime scenes to complex analytical instruments such as gas chromatographs and

infra-red and ultraviolet spectrophotometers, which are frequently used for drug identification.

Trained personnel are essential to a well-functioning laboratory. Except for personnel engaged in documents, firearms comparisons and explosives specialization, the minimum educational qualifications is generally a B.S. degree in analytical chemistry or criminalistics.

An adequately staffed and equipped laboratory is often beyond the means of many police departments. Minimum instrumentation costs for drug analysis alone could run close to \$30,000.

As drug abuses continue to mount, police departments may wish to improve existing laboratories, or to establish new local facilities. Regional facilities serving several counties within a state might well be considered for reasons of economy and to avoid duplication of services within a small geographical area.

Forensic chemist seminar was held September 22-26, 1969, at BNDD headquarters: Two participants were from laboratories in Canada, four were from federal laboratories in the United States, and the remainder were from various city, county and state laboratories in nine states.

Sessions were held on spectroscopy, thin layer chromatography, micro-techniques, narcotic analysis, ballistics and identification, x-ray diffraction, LSD analysis, optical crystallography and the pharmacology of drugs. One day was spent in the laboratory. Guest lecturer Leo R. Goldbaum, Ph.D., Chief Research Toxicologist, Armed Forces Institute of Pathology, Walter Reed Army Medical Center, Washington, D.C. led the final session. His topic was "Toxicology - Analysis for Narcotics and Dangerous Drugs."

Purple STP Tablets were recently analyzed in our Washington Regional Laboratory. The well made tablets were 6.8 millimeters diameter, 3.9 millimeters thick and were unscored. They contained 4.0 milligrams STP HCl per tablet.

Non-drug capsules giving a positive Marquis reaction were recently analyzed by our Special Testing and Research Laboratory. The No. 3 clear, hard gelatin capsules contained

dark reddish-brown material with a small amount of white particles. Average filled weight was about 400 milligrams.

Microscopic, microchemical, ultraviolet and x-ray analysis revealed only a small amount of calcium phosphate dibasic dihydrate and a large amount of calcium carbonate. No drug was detected. The material produced a purple color with Marquis reagent, probably due to the dye. The material was similar to yellow and dark orange-brown colored chalk, which also produced a purple colored reaction with Marquis reagent.

It has also been found that the creme rouge "Blondeen" by Max Factor, Hollywood, also gives the Marquis reaction.

Brown powder alleged to be mescaline was recently analyzed by our Chicago Regional Laboratory. It was found to be ground Hawaiian Baby Wood Rose.

Sniffing toilet bowl deodorants is reportedly a growing fad among youngsters in parts of the Northeast.

Phencyclidine HCl (PCP) with d-lysergic acid diethylamide (LSD) has been found recently in exhibits analyzed in our New York and Washington Regional Laboratories. It was first analyzed in our New York laboratory after a pink powder was found during a seizure of a clandestine laboratory. Gross weight of the powder was 76.9 grams, of which 230.7 milligrams were PCP and 2,307 micrograms were LSD. Recently, the Washington laboratory analyzed No. "0", clear gelatin capsules containing a pink powder. PCP and LSD were found in the powder. If the powder came from the clandestine laboratory, each capsule would contain about 0.98 milligrams of PCP and 9.8 micrograms of LSD. The LSD is presumed to be a contaminant, because of the small amount present.

Phencyclidine HCl impregnated on plant material and promoted as "Hog" was recently analyzed by our Washington Regional laboratory. The evidence was seized in Virginia, and a local police department states that the term "Hog" has been used in the area for alleged "THC", reportedly mixed with strychnine.

Revised list of DACA controlled drugs is being printed. A copy will be sent to each recipient of Microgram.

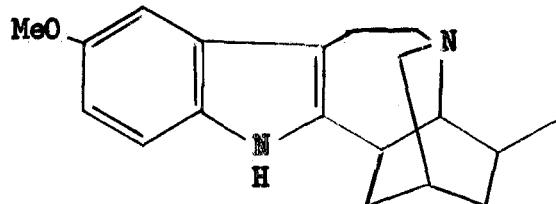
CORRECTIONS: The pages of Volume II, Number 3, were not numbered correctly. Page numbers should have followed consecutively from issue Number 2, the last page of which was page 57. The front page of issue Number 3 would then be page 58 and the pages following should be re-numbered accordingly. Note that blank pages are not numbered.

LETTERS TO THE EDITOR

"...Concerning Microgram, Vol. II, No. 3, p. 5, Dr. Shulgin was correct in pointing out an error in the previously published formula for Ibogaine, but the new formula which you present from Psychotropic Drugs and Related Compounds is also incorrect. The correct structure is to be found in Merck 7th and 8th edition and also in the Aldrich Chemical Catalog..."

/s/ James A. Heagy  
BNDD Forensic Chemist  
San Francisco Regional Laboratory

See also: Manske, R.H.F., Ed. THE ALKALOIDS, Vol. VIII, 1965. Academic Press, New York



Dihydroergotamine (DHE) or LSD? "...Question has been raised about the possibility of confusing DHE with LSD because they are alleged to have the same  $R_f$  in a TLC system. DHE has an ultraviolet spectrum similar to dimethyltryptamine (DMT) with absorption maxima at 290  $\mu\text{m}$  and 280  $\mu\text{m}$ , while LSD has a maximum at about 310  $\mu\text{m}$ . On silica gel G plates, DHE does not fluoresce while LSD does. A 9:1 chloroform-methanol system will separate the compounds. There is no reason why DHE should cause any problem in the identification of LSD..."

/s/ Albert R. Sperling, Ph.D.  
BNDD Forensic Chemist  
Special Testing and Research Laboratory

COLUMN CHROMATOGRAPHIC METHOD FOR THE SEPARATION OF  
MIXTURES OF METHADONE, HEROIN, AND COCAINE

C. R. Pyles and Buddy R. Goldston  
Forensic Chemists  
Dallas Regional Laboratory  
Bureau of Narcotics and Dangerous Drugs

The separation of Methadone and Heroin poses somewhat of a problem because of the like solubility of the hydrochlorides of the two compounds. Both are extractable from aqueous HCl solutions with  $\text{CHCl}_3$ . Methadone can be steam distilled or Heroin can be hydrolyzed to morphine and a separation can be effected by immiscible solvent extraction. Gas chromatography has been used to separate almost all active components of illicit narcotic samples that have been received in our laboratory and quantitation can be done by this method. However, identification by chromatography alone is not desirable. For this reason, a separation method using column chromatography and a mixed solvent system is described. Separations by this procedure permits the use of U.V. for quant. and I.R. for identification. We have also included the compound cocaine in our separation scheme because it has also been frequently encountered in conjunction with Heroin in our Region.

PROCEDURE: Place a small plug of glasswool in the bottom of a plain glass chromatographic column whose dimensions are about 20 mm by 250 mm. Prepare a trap layer in a 100 ml beaker from 1 gm of Celite 545 and 1 ml of .1N HCl, place this mixture over the plug of glasswool in the column and pack firmly. Mix a top layer consisting of 3 gms. of Celite 545 and 2 mls. of .1N HCl in a 150 ml beaker. Incorporate the Heroin, Methadone mixture into this layer, either as the solid or as a suitable aliquot made up in .1N HCl. Mix well and transfer quant. to the column. Wash the beaker with a small amount of Celite and transfer to the column. Wipe the beaker with a small piece of glass wool. Place this on top of the column and pack firmly. Wash the column with 75 mls. of water-washed ether and discard the ether wash. Place 100 ml volumetric flask containing 10 mls. of methyl alcohol and 10 drops of concentrated HCl under the column and elute the Methadone with about 90 mls. of a mixture of 60%  $\text{CHCl}_3$  in ether, both water-washed. Remove the flask and elute the Heroin with 90 mls. of water-washed  $\text{CHCl}_3$  into a 100 ml volumetric flask containing 10 mls methyl alcohol and 10 drops of concentrated HCl. Bring both eluates to volume with their respective solvents. Determine U.V. absorbance in stoppered cells using the proper solvent as a blank. The ether wash will remove some interfering drugs such as caffeine. 60%  $\text{CHCl}_3$  in ethyl ether will remove both Methadone and isomethadone. Heroin is removed with  $\text{CHCl}_3$ . Cocaine will not be eluted from the column with any of the above solvents, but can be removed quant. after the Heroin with  $\text{CHCl}_3$  saturated with concentrated  $\text{NH}_4\text{OH}$ .

RECOVERY:

	Mgs. Added	Mgs. Recovered	% Recovery
Heroin HCl	11.4	10.9	95.6
	9.8	9.1	92.9
	13.3	12.6	94.7
Methadone HCl	47.2	47.0	99.6
	17.3	17.1	98.8
	82.4	83.6	101.5

TLC AND GC PROCEDURES FOR METHADONE  
AND SOME RELATED COMPOUNDS

C. R. Pyles and Buddy R. Goldston  
Forensic Chemists  
Dallas Regional Laboratory  
Bureau of Narcotics and Dangerous Drugs

An interesting aspect that developed from investigation of a clandestine Methadone laboratory was the discovery that  $\text{CHCl}_3$  and  $\text{MeOH}$  9:1 is an excellent TLC solvent for Methadone and related compounds. In preparing the field test kit for the assignment, an investigation of different TLC solvent systems suitable for the separation of Methadone, isomethadone, and other closely related position isomers was made. Steel (Internal Revenue Publication 341, Rev. 6-67) lists five different solvent systems for Methadone but does not list any data for isomethadone. Of these five systems, only S-4 (ethylacetate 60 ml, benzene 35 ml, and  $\text{NH}_4\text{OH}$  5 ml) gives a separation of Methadone and isomethadone.

The outstanding feature that makes the  $\text{CHCl}_3$   $\text{MeOH}$  solvent worth mentioning is its ability to separate not only Methadone and isomethadone, but also the two isomeric intermediate aminonitriles. 2,2-diphenyl-4-dimethylaminovaleronitrile and 2,2-diphenyl-3-methyl-4-dimethylamino-butynonitrile. The two precursors, diphenylacetonitrile and 1-dimethylamino-2-chloropropane HCl, are also separated. All compounds can be detected by iodoplatinate, except diphenylacetonitrile which fluoresces, and can be detected under U.V. light. The precursor 1-dimethylamino-2-chloropropane HCl does not move an appreciable distance and remains practically at the starting line.

Acetone and  $\text{CHCl}_3$  4 plus 1 also was found to be a usable TLC solvent system for Methadone and the above mentioned compounds. While it is not as good in all respects as the  $\text{CHCl}_3$  and  $\text{MeOH}$  system, it is far better than the S-4 system previously mentioned. Some undesirable features of this system are Methadone and isomethadone tail badly unless the concentrations are maintained at a minimum. Also, isomethadone and the intermediate 2,2-diphenyl-4-dimethylaminovaleronitrile do not show much separation. It is doubtful that a mixture of the two compounds could be differentiated. However, isomethadone does have a slightly lower  $R_f$  than the intermediate. The Methadone precursor, 1-dimethylamino-2-chloropropane HCl as in the  $\text{CHCl}_3$   $\text{MeOH}$  system, is not moved an appreciable distance and remains practically at the starting line. Silica gel, 0.25 mm thickness, on glass plates manufactured by Brinkmann were used on all samples done in the Dallas Regional Laboratory. Eastman TLC sheets were used in the field test kit.

Rf values for  $\text{CHCl}_3$  and MeOH 9 plus 1 and acetone and  $\text{CHCl}_3$  4 plus 1 on Brinkmann Silica gel 0.25 mm thickness on glass plates, 10 cm solvent front travel.

Compound	$\text{CHCl}_3$ and MeOH 1 $\mu\text{l}$ of 1% Solution Spotted	Acetone & $\text{CHCl}_3$ 1 $\mu\text{l}$ of 1% Solution Spotted
	.5 $\mu\text{l}$ of 1% Solution Spotted	
Methadone	.15	.23
Isomethadone	.37	.47
2,2-diphenyl-4-dimethylaminovaleronitrile	.50	.50
2,2-diphenyl-3-methyl-4-dimethylamino- butyronitrile	.63	.66
Diphenylacetonitrile	.71	.79

With respect to gas chromatography, Methadone and the above mentioned compounds were subjected to investigation on both a 3% SE 30 column and a 2% OV 17 column. Both liquid phases were supported on 60/80 mesh gas chrom Q. The SE 30 column was installed in a Micro Tek 2000 R with helium as the carrier while the OV 17 was in a B.C. 5000 using nitrogen as the carrier. Both instruments were equipped with flame ionization detectors. Methadone and isomethadone were not separated on either column. The precursor 1-dimethylamino-2-chloropropane was not seen on either column. However, the possibility that this material came out with the solvent peak cannot be overlooked. This aspect was not investigated in any detail. The three remaining compounds were separated better by 3% SE 30 than they were by OV 17. Both columns gave good separation of diphenylacetonitrile from both the isomeric aminonitrile intermediates. OV 17, however, would not separate Methadone and 2,2-phenyl-4-dimethylaminovaleronitrile sufficiently to distinguish between the two compounds. SE 30 gave sufficient separation. Both columns separated the intermediate isomeric aminonitriles. The following conditions were used.

SE 30

Micro Tek 2000 R  
Column - 6 ft. glass  
Packing - SE 30 3% on gas  
chrom Q 60/80  
Carrier - He at approximately  
30 ml/min.  
Detector - flame  
Injector Temp. -  $250^{\circ}$   
Column Temp. -  $220^{\circ}$   
Detector Temp. -  $250^{\circ}$

OV 17

Barber-Colman 5000  
Column - 6 ft. glass  
Packing OV 17 2% on gas  
chrom Q 60/80  
Carrier - N<sub>2</sub> at approximately  
85 ml/min.  
Detector - flame  
Injector Temp. -  $255^{\circ}$   
Column Temp. -  $220^{\circ}$   
Detector Temp. -  $255^{\circ}$

METHOD FOR THE PREPARATION OF METHADONE

C. R. Pyles and Buddy R. Goldston  
Forensic Chemists  
Dallas Regional Laboratory  
Bureau of Narcotics and Dangerous Drugs

<sup>1</sup>  
Condensation: In a 1 l flask heat for 6 or 7 hours on a steam bath or in a heating mantle at steam bath temperature 30 gms. NaOH (.75 moles), 39 gms. diphenylacetonitrile (.2 moles), 40 gms. 1-dimethyl-amino-2-chloropropane HCl (.25 moles) with occasional stirring. Continuous stirring is not necessary but will probably increase the yield. Cool and add 250 mls. of ethyl ether to the flask and mix. Transfer the ethyl ether to a 1 liter separatory funnel. Add second 250 mls. of ethyl ether to the flask and mix well. Combine with first 250 mls. in the same 1 liter separatory funnel, rinse the flask with 150 mls. of water and transfer to the separatory funnel. Rinse with a second 150 mls. of water and combine in the 1 liter separatory funnel. Shake funnel for about 1 minute and let layers separate. Draw the aqueous layer off into second separatory and extract with another 250 mls. of ethyl ether and discard aqueous. Combine the ethyl ether and wash with 2 x 150 mls. of water. Extract the combined ethyl ether with 1 N HCl until no precipitate is produced when a portion of the last extract is made strongly basic with NaOH. Make combined aqueous strongly basic with NaOH and extract with ethyl ether 3 x 200 mls. Dry ethyl ether with anhydrous sodium sulfate, filter, and evaporate ethyl ether on steam bath under current of air.

<sup>2</sup>  
Vacuum Distillation: Transfer the residue from the ethyl ether extraction to a 250 ml. round-bottomed flask and connect to a vacuum distillation apparatus capable of reducing the pressure to about 1 mm. Start the vacuum and remove final traces of ethyl ether. Finally, distill both isomeric amino nitriles at about 199 degrees and 1 mm. No cooling water is necessary in the condenser; an air condenser can be used. For maximum yield wash material from condenser and receivers with hot pet ether and add to distilled product. Take up the oily residue in an equal volume of pet ether. (Make final volume of pet ether and distilled product ca 1½ to 2 times the original volume of distilled aminonitriles). Let 2,2-diphenyl-4-dimethylaminovaleronitrile crystallize from the solution. At least two crops of crystals can be obtained. Yield at this point should be ca 18 gms. 2,2-diphenyl-3-methyl-4-dimethylaminobutyronitrile remains in solution, as does some of the valeronitrile. Dry 2,2-diphenyl-4-dimethylaminovaleronitrile in vacuum dessicator overnight.

<sup>3</sup>  
Grignard Solution: Use a 250 ml 3 neck flask with efficient stirring device. For this quantity a magnetic stirrer is probably sufficient. Fit the flask with a thermometer, dropping funnel, and condenser, all previously dried and free from water and alcohol.

Add 3.5 gms. clean magnesium turnings to the flask and a small crystal of iodine. Mix 17 gms. ethyl bromide with 30 mls. dry ethyl ether in the dropping funnel and run about 10 to 15 mls. of the solution into the flask containing the magnesium turnings. When the reaction starts add 15-20 mls. of dry ether through top of condenser to moderate the reaction. Add the remainder of the ethyl bromide and ethyl ether solution dropwise at rate sufficient to maintain ebullition of the ethyl ether without external heat. After most of the magnesium has dissolved and the reaction has subsided somewhat, reflux the Grignard solution on a water bath for 30 minutes.

<sup>4</sup>  
Grignard Reaction: Cool the Grignard solution to room temperature and add 9-10 gms. 2,2-diphenyl-4-dimethylaminovaleronitrile dissolved in 15-20 mls. of dry toluene through the dropping funnel. Turn condenser water off and distill off the ethyl ether. Reflux the toluene solution for 3 hours. Cool and pour into a well stirred solution of 40 mls. of concentrate HCl in 90 mls. of water. Apply enough heat to evaporate remaining toluene. Cool the mixture in an ice bath and collect the crystals of Methadone hydrobromide or make the aqueous basic with NaOH and extract completely with ethyl ether. Remove the ethyl ether on steam bath. Take the residue up in minimum volume of dilute HCl and extract completely with CHCl<sub>3</sub>. Remove CHCl<sub>3</sub> on steam bath and, if necessary, recrystallize residue from minimum amount of hot isopropyl alcohol. The resulting methadone hydrochloride crystals should have a melting point of 235°C.

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- 1/ Cusic, J. W., J. Am. Chem. Soc., 71, 3546 (1949).
  - 2/ Ibid.
  - 3/ Adams, Roger and Johnson, J. R., Laboratory Experiments in Organic Chemistry, 4th edition, p. 397.
  - 4/ Larsen, A. A., Tullar, F. F., Elpern, B., and Buck, J. S., J. Am. Chem. Soc., 70, 4194 (1948).

## THE INFRARED IDENTIFICATION OF SUGAR EXCIPIENTS IN SMALL AMOUNTS OF ILLICIT HEROIN SAMPLES

By James M. Moore  
Bureau of Narcotics and Dangerous Drugs  
Washington, D. C.

Infrared spectroscopy provides a reliable identification in the analysis of narcotics and other control drugs. Additionally, it is quite useful for identification of excipients associated with these drugs. The sugar excipients most commonly associated with illicit heroin samples are mannitol and lactose. When the analyst has sufficient sample, physical separation of the sugar from the heroin, quinine, etc. and subsequent identification presents no serious problem. The sample is triturated with ammoniacal CHCl<sub>3</sub> and passed through filter paper, trapping the sugar. However, when only several mgs of sample are available the small amount of sugar present would be very difficult to isolate on filter paper. Furthermore, using centrifugal techniques to isolate the residue is difficult owing to the flocculent nature of some sugars. The procedure described herein is ideally suited for very small amounts of sample. The method was used successfully on heroin-mannitol and heroin-quinine sulfate-mannitol samples.

PROCEDURE

A. Heroin-mannitol samples

Triturate sample with several milliters of chloroform in a small beaker. Pass the chloroform and insoluble residue through a glass eyedropper containing about 200 mgs. of moderately packed KBr (the weight of KBr used depends on amount of sugar in sample - 200 mgs. KBr for 1-2 mgs. sugar). See Fig. 1. After passage of  $\text{CHCl}_3$  through dropper, wash KBr with 2 or 3 2-ml portions of  $\text{CHCl}_3$ . After the washing is complete, invert dropper and using a small bulb gently squeeze out the KBr into a small mortar. Evaporate residual  $\text{CHCl}_3$  in the KBr by heating moderately under a gentle air current. Prepare a KBr disk from the dry sample in the usual manner and scan in the infrared region from 2-15  $\mu$ .

B. Heroin-mannitol-quinine sulfate samples

Proceed as in A. except in the initial trituration of sample use  $\text{CHCl}_3$  that has been saturated with ammonia (prepared by shaking vigorously 100 mls.  $\text{CHCl}_3$  with 2 mls. of ammonia, allowing layers to separate and passing  $\text{CHCl}_3$  layer through filter paper).

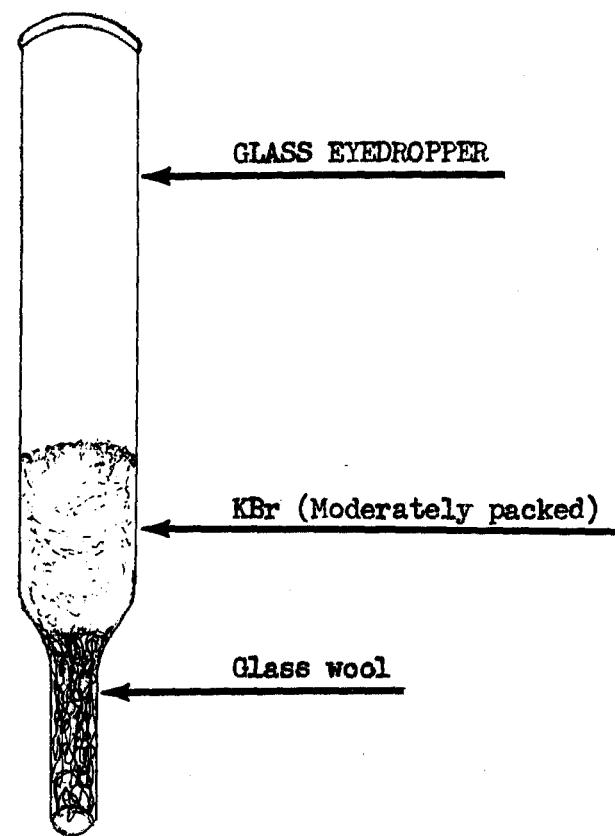


Fig. 1 - Glass eyedropper used in infrared identification of sugar excipients.

## ASSAY FOR HEROIN IN QUININE AND SUGAR MIXTURES

by James Moore  
Washington Regional Laboratory  
Bureau of Narcotics and Dangerous Drugs

The following procedure is suitable for heroin samples in which the heroin and quinine concentrations are roughly the same or the quinine content is considerably higher. A mixture of 5% heroin in quinine was carried through the method with a result of 96% heroin recovered. Additionally, a routine sample consisting of 6% heroin and 7% quinine was analyzed by this procedure and by the method given in the "Internal Revenue Service Methods of Analysis." Attached are u.v. curves of the "cleaned-up" sample and the sample determined directly by the Internal Revenue method. It is apparent that as the ratio of the quinine to heroin concentrations go up the accuracy of calculating a mixture without prior cleanup is questionable.

### PROCEDURE

The following procedure worked well for a sample containing 6% heroin. Place 2 Gms. Celite 545 in 100-ml. beaker and add 1 ml. of 1 N HCl. Mix until fluffy. Transfer to a chromatographic column and pack moderately. Weigh accurately about 100 mgs. of sample into a 100-ml. beaker.

Add 2 mls. 1N HCl and swirl to completely wet powder. Add 3 Gms. Celite 545 and mix until fluffy. Quantitatively transfer to same column and pack moderately. Dry-wash beaker with a 0.5 Gm. portion of Celite and a few drops of water and place on column. Overlay with a plug of glass wool. Elute heroin with 100 mls. of water-washed chloroform into a 150-ml. beaker. Evaporate to about 30 mls. and quantitatively transfer to a 50-ml. volumetric flask. Dilute with 2 mls. of methanol containing a few drops of HCl and then to volume with chloroform. (1) If the solution is slightly turbid add a few drops of methanol (the absorbance of this solution was 0.8; to avoid the evaporation step one may elute directly into a 100-ml. volumetric flask which would yield an absorbance of about 0.4 in 1 cm cells). Prepare a standard heroin in the same solvent as the sample and having a concentration of about 10 mgs./100 mls. Prepare a blank from the same solvent used for the sample and standard. Scan the sample and standard against the blank in the u.v. from 360 to 250 mu using absorption maximum at about 281 mu for quantitation.

$$\frac{\text{Total Absorbance Sample} \times \text{Standard Conc. (mg/ml)} \times \text{Dilution}}{\text{Total Absorbance Standard}} \times 100 = \% \text{ Heroin}$$

Sample Weight

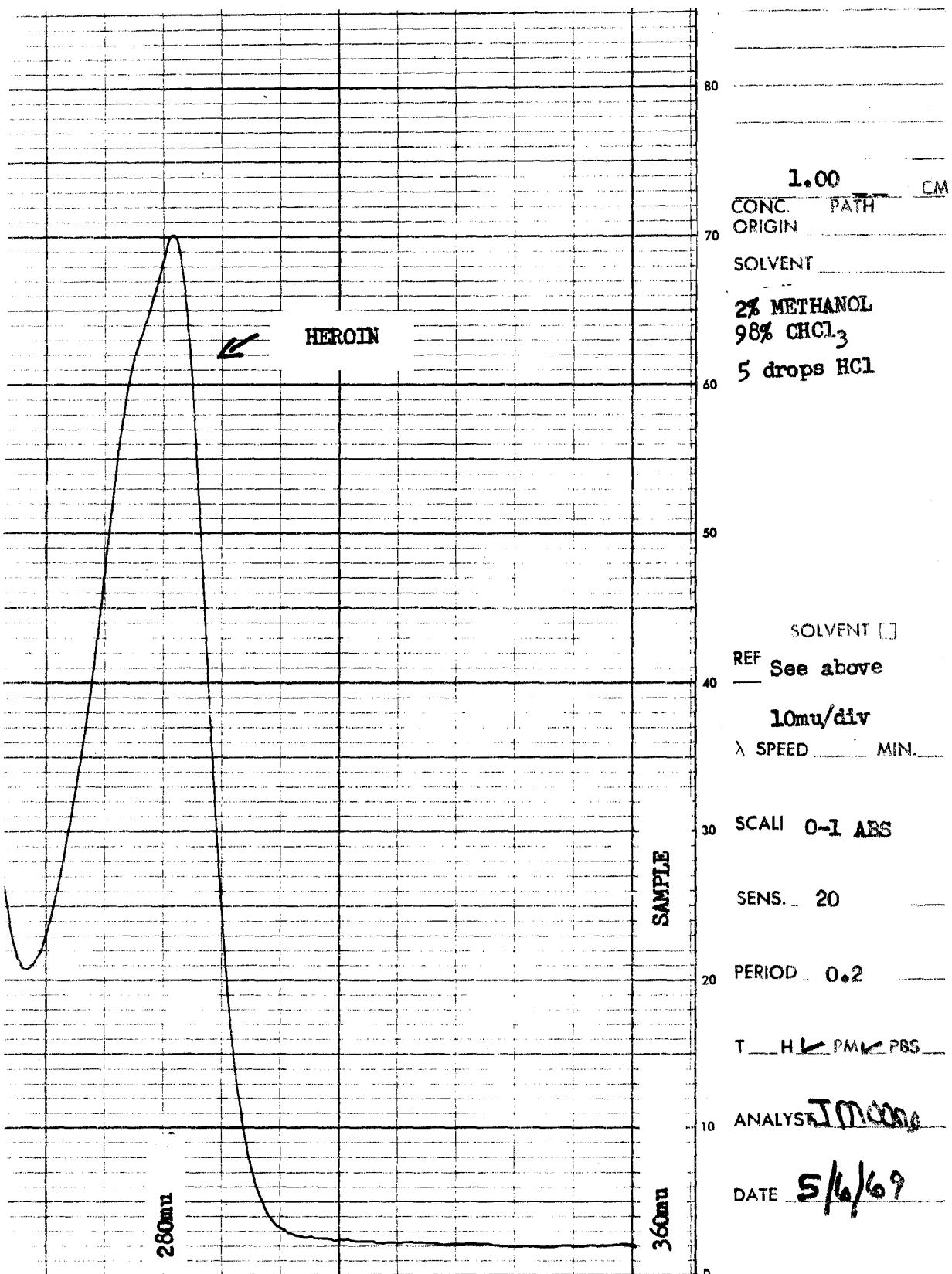
#### IDENTIFICATION

This procedure is ideally suited for infrared identification. Take aliquots of sample and standard equivalent to between 1 and 2 mgs. of heroin and evaporate to about 3 mls. Transfer to small mortar containing 200 mgs. KBr and carefully continue the evaporation to dryness (take care not to overheat). After the evaporation is complete prepare a KBr disk in the usual manner and scan between 2 and 40 u. If desired a few microliters of the evaporated u.v. solution may be used for TLC identification.

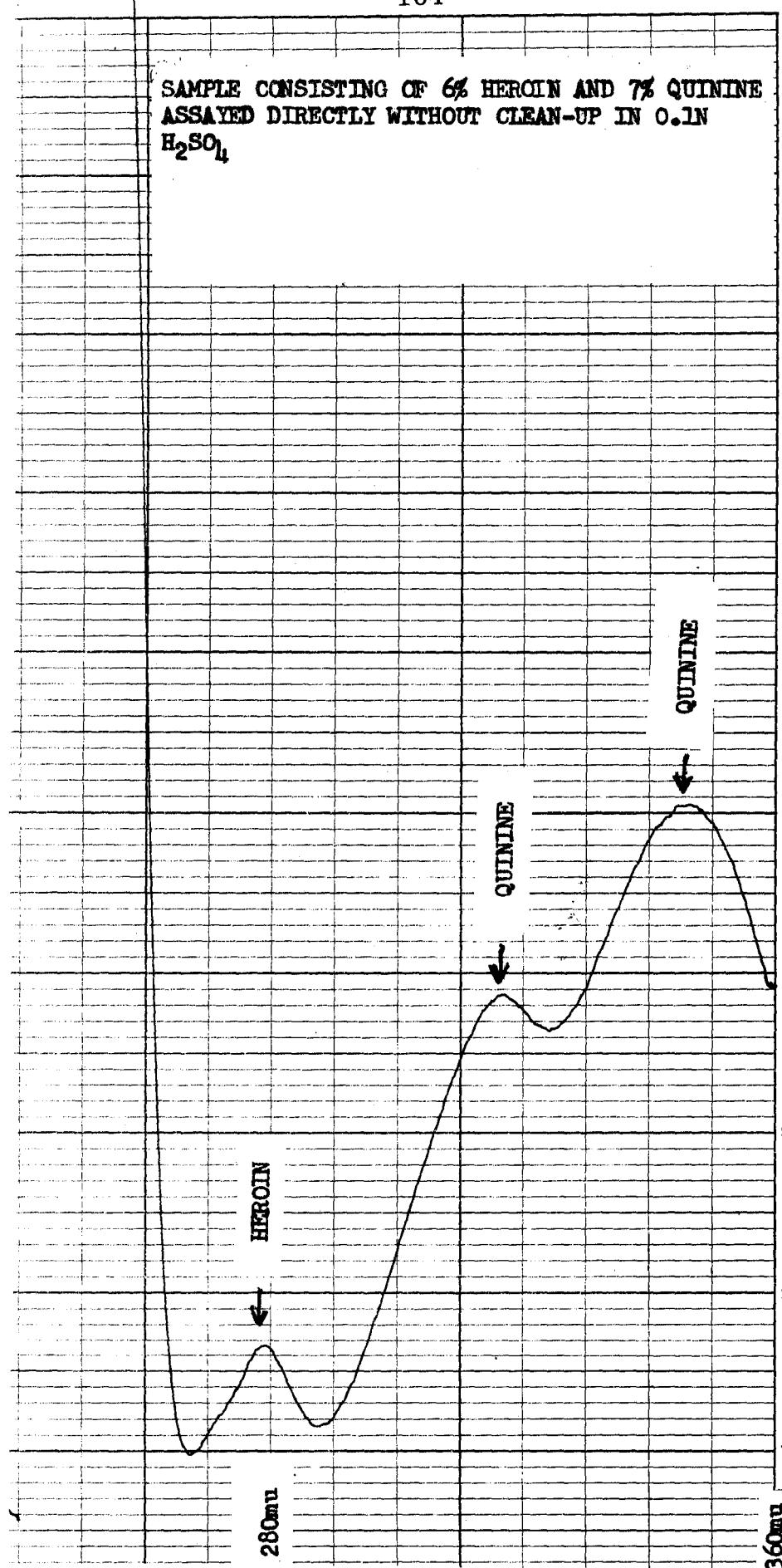
#### REFERENCE

- (1) Private communication, Dr. Albert Sperling, SCILR  
Bureau of Narcotics and Dangerous Drugs  
Washington, D. C.

SAMPLE CONSISTING OF 6% HEROIN AND 7%  
QUININE (AS SULFATE) BY COLUMN  
PROCEDURE



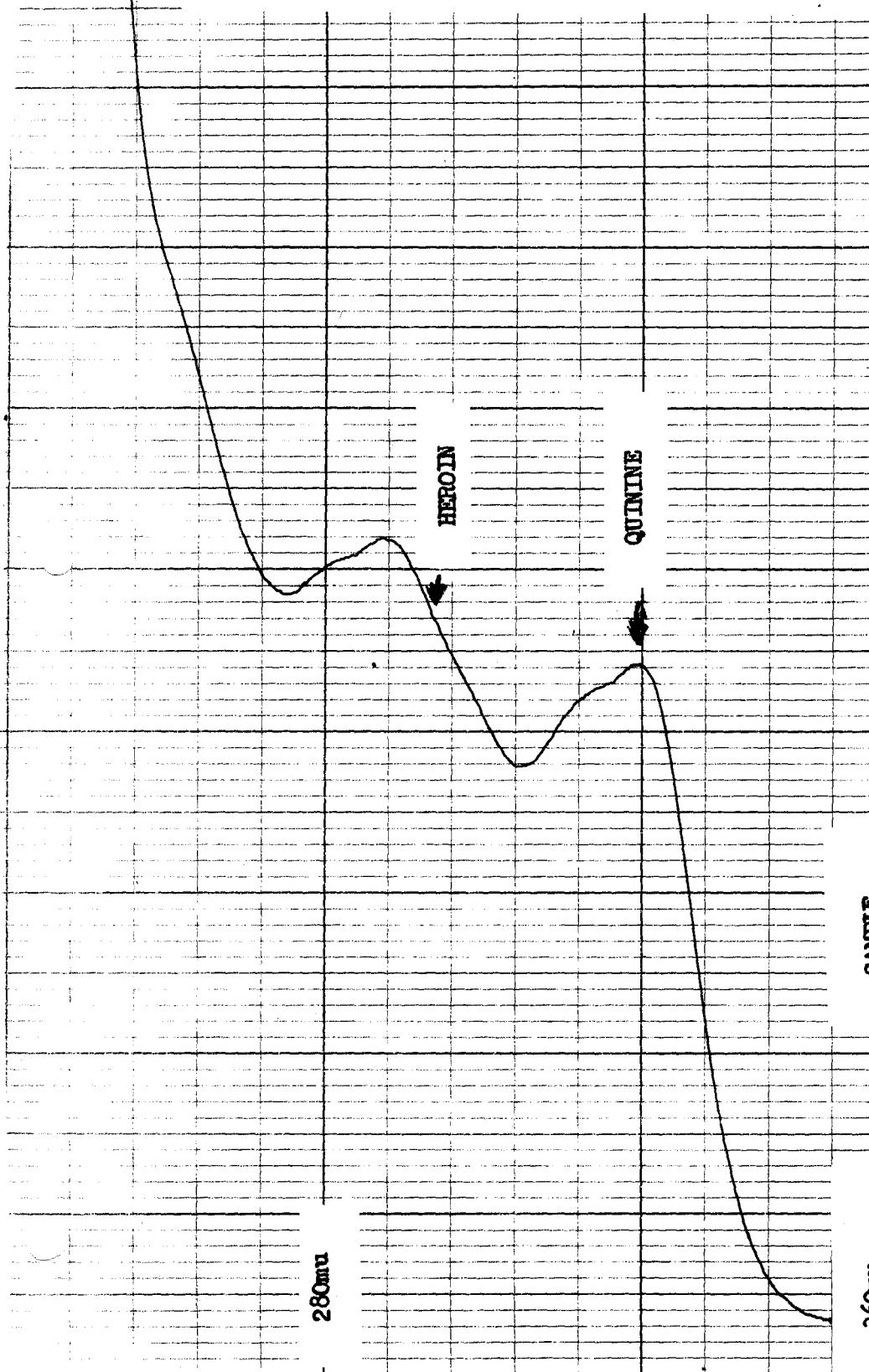
SAMPLE CONSISTING OF 6% HEROIN AND 7% QUININE  
ASSAYED DIRECTLY WITHOUT CLEAN-UP IN 0.1N  
 $H_2SO_4$



SAMPLE \_\_\_\_\_  
1.00 CM  
CONC. PATH  
ORIGIN \_\_\_\_\_  
SOLVENT 0.1N  $H_2SO_4$   
SOLVENT  0.1N  $H_2SO_4$   
REF. C 10mu/Div.  
λ SPEED MIN.  
SCALE 0-1 ABS  
SENS. 20  
PERIOD. 0.2  
T H PM PBS  
ANALYST J. D. G.  
DATE 5/6/69

SAMPLE CONSISTING OF 6% HEROIN AND 7% QUININE ASSAYED DIRECTLY WITHOUT CLEAN-UP IN 0.1N NaOH - 20% METHANOL (IRS METHOD OF ANALYSIS)

-105-



SAMPLE

↙

90

80

1.00

CM

CONC. PATH  
ORIGIN

SOLVENT ↘

SEE ABOVE

60

50

REF. SEE ABOVE

40 10mμ/Div.

λ SPEED MIN.

SCALE 0-1 ABS

SENS. 20

PERIOD 0.2

T H PM PBS

ANALYST J.M.

DATE 5/6/69

IDENTIFICATION OF SEEDS CONTAINING ERGOLINE ALKALOIDS  
BY THIN LAYER CHROMATOGRAPHY

by Victor A. Folen, Forensic Chemist  
Special Testing and Research Laboratory  
Bureau of Narcotics and Dangerous Drugs

A method for the identification of ground seeds of *Argyreia nervosa* (small wood rose) and *Ipomoea purpurea* cultivars ("Pearly Gates" and "Heavenly Blue") employing thin layer chromatography is suggested as a chemical approach to the problem and as a supplement to microscopic observations.

The advantages of the use of thin layer chromatography as a means of identifying ground seeds containing ergoline alkaloids are (1) added criteria to support microscopic observations; (2) to assist those chemists with limited botanical experience.

The seeds of *I. purpurea* have an almost black hull, and when finely milled, are grey in color, somewhat lighter than that of ground black pepper. Fragments of the black hulls are seen throughout. The seeds of *A. nervosa* have a light brown parchment - like covering under which there is a fibrous layer. After grinding they are of a light brown color. Since the seeds are larger than those of *I. purpurea* there is less hull in relation to the endosperm, as seen microscopically. Also, a large number of the dissociated fibres are present in the ground material.

Method:

Standards and Sample:

For standards, finely ground seeds of *A. nervosa* and *I. purpurea* cultivars ("Pearly Gates" or "Heavenly Blue") are used.

Triturate about 200 mg of each with 5 ml. of 1% citric acid. Make basic with small additives of sodium carbonate. Add 8 grams of celite 545 (acid washed), mix thoroughly, and pack in a 25 x 300 mm chromatographic tube. Add 50 ml. of chloroform to the column and collect in a beaker. Evaporate on a steam bath to < 1 ml. and bring to volume in a 1 ml. volumetric flask. Spot 10 microliters of the standards and sample on silica gel G plates (250 microns in thickness) and develop with a chloroform - ethanol solvent system (8:2). Use a 10 cm. developing distance. After developing, compare under long-wave ultraviolet light. Spray plate with p-dimethylamino-benzaldehyde reagent (2grams p-dimethylaminobenzaldehyde, 50 ml. ethanol and 50 ml. conc. hydrochloric acid).

#### Results and Discussion

When the seed mixtures in citric acid were made alkaline with sodium carbonate, that of the "Heavenly Blue" turned deep reddish-brown, whereas "Pearly Gates" was a less intense greenish brown. The basic triturate of *A. nervosa* had the same color as that of "Pearly Gates".

Considerable differences were found in the chromatographic patterns of *A. nervosa* and *I. purpurea*. With "Pearly Gates" and "Heavenly Blue", similar patterns were produced. More spots develop with *A. nervosa*; they are of much greater intensity and there are pronounced differences in the intensities of the various spots. The spots from *I. purpurea*, on the other hand, are all of roughly equal intensity. These findings are in accord with those of Hylin and Watson (1) who compared quantitatively certain alkaloids from *A. nervosa*, "Pearly Gates" and "Heavenly Blue" and found much more alkaloidal material in *A. nervosa*, present in differing proportions as compared to the varieties of *I. purpurea*.

Because of the marked differences in the patterns, it is probable that variations caused by differing geographical and environmental conditions could not alter the content of ergoline alkaloids to the extent where the chromatographic patterns of the seed extracts would be indistinguishable. Chromatographic columns were resorted to since extraction with chloroform in separators resulted in the formation of emulsions which were difficult to resolve.

McJunkins, et. al. (2) have used thin layer chromatography to assist in the identification of *A. nervosa*, using different extraction procedures and T.L.C. solvent systems. Several systems have been used for the study of the alkaloidal content of *A. nervosa* and *I. purpurea* (3,4,5), of which chloroform-ethanol (8:2) (5) provided the best separation with the method of extraction described above.

REFERENCES

1. J. W. Hylin, D. P. Watson, Science 148, 499 (1965).
2. S. P. McJunkins, J. I. Thornton, D. J. Dillon, J. Forensic Sci. Soc. 8, 121 (1968).
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4. K. Genest, J. Chromatog 19, 531 (1965).
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FEDERAL REGISTER

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**Title 26—INTERNAL REVENUE**

**Chapter I—Internal Revenue Service,  
Department of the Treasury**

[Treasury Decision 7017]

**PART 151—REGULATORY TAXES ON  
NARCOTIC DRUGS**

**Excepted Narcotic Pharmaceutical  
Preparations**

On September 10, 1969, a notice was published in the FEDERAL REGISTER (34 F.R. 14224) stating that the Director, Bureau of Narcotics and Dangerous Drugs, pursuant to the provisions of section 4702(a)(3) of the Internal Revenue Code of 1954, as amended by section 4(c) of the Narcotics Manufacturing Act of 1960 (74 Stat. 58); § 151.426 of Title 26 of the Code of Federal Regulations; and under the authority vested in the Attorney General by Reorganization Plan No. 1 of 1968 (33 F.R. 5611) and redelegated to the Director, Bureau of Narcotics and Dangerous Drugs by § 0.200 of Title 28 of the Code of Federal Regulations, proposed certain additional restrictions on the retail sales of Class "X" exempt pharmaceutical preparations.

After due notice and opportunity for public hearing, and after consideration of all comments received on the proposed new restrictions, it is hereby found that the proposed regulations are necessary to restrict the existing abusive use of Class "X" exempt pharmaceutical preparations and to insure that such preparations are used for medicinal purposes only.

Therefore, § 151.424 of Title 26 of the Code of Federal Regulations is hereby amended by adding to the existing section the following new paragraphs:

**§ 151.424 Conditions of exemption for  
Class "X" products.**

(d) *Retail sale restrictions.* A Class "X" product may only be sold at retail without a prescription by a registered pharmacist and not by a nonpharmacist employee even if under the direct supervision of a pharmacist. However, after the pharmacist has fulfilled his professional and legal responsibilities set forth in this section, the actual cash, credit transaction, or delivery, may be completed by a nonpharmacist. A pharmacist must exercise professional discretion in the sale of a Class "X" product to insure that the product is being sold for medical purposes only. An abuse of such discretion shall subject the pharmacist to the penalties provided for violations of the law relating to narcotic drugs.

(e) *Age of purchaser and identification.* A Class "X" product may only be sold at retail without a prescription to a person at least 18 years of age. The pharmacist must require every retail purchaser of a Class "X" product to furnish suitable identification, including proof of age when appropriate, in order to purchase a Class "X" product. The name and address obtained from such identification shall be entered in the record of disposition to consumers required by paragraph (b)(2) of this section.

(f) *Quantity restrictions.* Not more than 2 ounces of camphorated opium tincture (paregoric), nor more than 8 ounces of any other Class "X" product containing opium, nor more than 4 ounces of any other Class "X" product, may be sold at retail to the same consumer in any given 48-hour period without a prescription.

*Effective date.* These amendments shall become effective on November 1, 1969.