

An In-Depth Study of the Peruvian *Base Llavada* (“Washed Base”) Technique for Purification of Crude Cocaine Base

Danielle K. Boudreau,* B.S., and John F. Casale, B.S.

U.S. Department of Justice
Drug Enforcement Administration
Special Testing and Research Laboratory
22624 Dulles Summit Court
Dulles, VA 20166
[email address withheld at author’s request]

ABSTRACT: An in-depth study of the Peruvian *base llavada* (“washed base”) technique for cleanup of crude cocaine base with ethanol is presented. Used as a substitute method for the traditional potassium permanganate purification process, the technique selectively decreases or removes many alkaloid and colored impurities. Authentic crude Peruvian cocaine base was subjected to the method, and the resulting washed base samples and their respective ethanolic washings were examined immediately thereafter and again 14 months later. The results confirm that the technique gives a whiter appearing but only slightly more pure base versus standard (unwashed) base. The fate of several alkaloid impurities is tracked. The presence of cocaethylene in illicit cocaine (resulting from transesterification of cocaine with ethanol) *may* be indicative of use of the *base llavada* technique; however, ethanol is known to be utilized in several other variants of illicit cocaine processing, so the presence of cocaethylene alone does not confirm the use of the *base llavada* technique.

KEYWORDS: Cocaine, Cocaine Impurities, Cocaethylene, Ethanol, Chromatographic Signature Analysis, Forensic Chemistry

Introduction

In traditional illicit cocaine production, coca leaf is processed to give crude cocaine base, which is purified with potassium permanganate to give a whiter, more refined base, which is then converted to cocaine hydrochloride [1]. Although the potassium permanganate purification is reasonably effective, the method is somewhat time intensive and technique sensitive, and potassium permanganate is both costly and difficult to acquire in cocaine processing regions. Recent interviews of South American cocaine processors indicated that a new technique is being used by some Peruvian chemists to purify their crude cocaine base. In this new variant, referred to locally as the *base llavada* or “washed base” technique, the crude base is first mixed with ethanol until a dough-like consistency is achieved, then wrapped in cloth and hydraulically compressed in a hydraulic press to force out as much of the ethanol solution (containing dissolved impurities) as possible. The process results in a whiter and slightly more pure product, similar in appearance to that produced by the potassium permanganate purification technique.

Prior work at this laboratory demonstrated how the use of the *base llavada* technique affects the signature profile of the resulting cocaine [2]. In the current study, the technique was performed on numerous samples of authentic Peruvian crude cocaine base in order to better understand what is occurring to give the whiter appearing product. The selected samples were analyzed at the time of the process (both before and after the washing), and again 14 months later. The residual ethanol/impurities solutions pressed from the samples were also analyzed both at the time of the process, and again 14 months later. This study also investigated the slow production of cocaethylene in washed samples during storage, resulting from transesterification of cocaine by the residual ethanol still remaining after the wash and pressing.

Experimental

Materials and Solvents: Ethanol and chloroform were distilled-in-glass products of Burdick and Jackson Laboratories (Muskegon, MI). N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) was obtained from Pierce Chemical (Rockford, IL). All other reagents and chemicals were reagent-grade quality products of Sigma-Aldrich Chemical Company (Milwaukee, WI). The authentic crude Peruvian cocaine base used in this study was from the reference collection of the DEA Special Testing and Research Laboratory.

Gas Chromatography / Mass Spectrometry (GC/MS): An Agilent (Palo Alto, CA) Model 5973 quadrupole mass-selective detector (MSD) interfaced with an Agilent Model 6890 gas chromatograph was used to conduct all GC/MS analyses. The MSD was operated in the electron ionization mode with an ionization potential of 70 eV, scan range of 34 - 700 mass units at 1.34 scans/s. The GC system was fitted with a 30 m x 0.25 mm ID fused-silica capillary column coated with 0.25 μ m DB-1 (J&W Scientific). Helium (99.999% UHP) was used as a carrier gas at an average linear velocity of 40 cm/s. The oven temperature was programmed as follows: Initial temperature, 100°C; initial hold, 0.0 min; program rate, 6°C/min; final temperature, 300°C; final hold, 5.67 min. Samples (1 μ L) were injected in the split mode (21.5 : 1) by an Agilent 7683 Series Auto Injector. The injection temperature and the auxiliary transfer line to the MSD were both maintained at 280°C.

Gas Chromatography / Flame Ionization Detection (GC/FID) and Gas Chromatography / Electron Capture Detection (GC/ECD): GC/FID and GC/ECD analyses were performed using an Agilent 6890N gas chromatograph. Prepared solutions were placed into an autosampler vial and analyzed using previously published methods and conditions [3,4]. MSTFA was utilized as the derivatization reagent for GC/FID analyses.

Headspace - Gas Chromatography / Mass Spectrometry (HS-GC/MS): Determination of occluded ethanol was accomplished using the method described by Morello *et al.* [5].

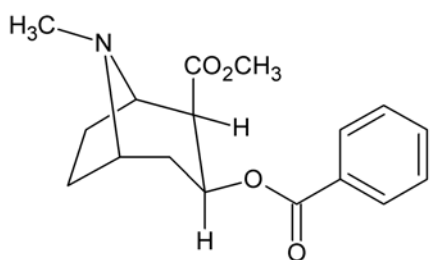
Preparation of Base Llavada Samples: Seven samples from an authentic Peruvian crude cocaine base exhibit were subjected to the *base llavada* technique, using 90% ethanol. The amount of sample and amount of ethanol used were varied slightly from sample to sample (Table 1). The residual ethanol/impurities solution from each pressing was collected for analysis. The ethanol was evaporated *in vacuo* to a dark brown oil prior to analysis. All samples were then subjected to chromatographic impurity analysis to quantitatively determine the alkaloids present. All samples were stored at room temperature for 14 months and then re-examined to determine any changes that had occurred.

* * * * *

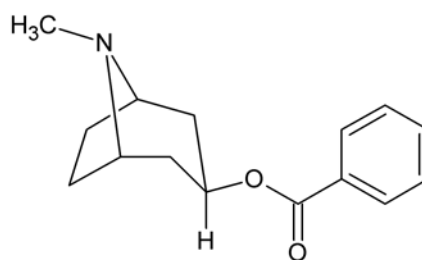
Table 1. Preparation of *Base Llavada* Samples.

Sample	Amount of Cocaine Base Used* (g)	Amount of Ethanol Used (mL)
1	300	45
2	600	90
3	500	75
4	400	60
5	500	75
6	500	75
7	456	65

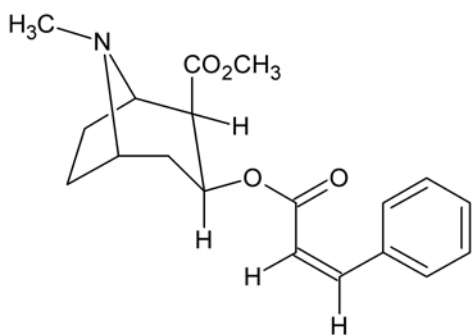
* Authentic Crude Peruvian Cocaine Base.



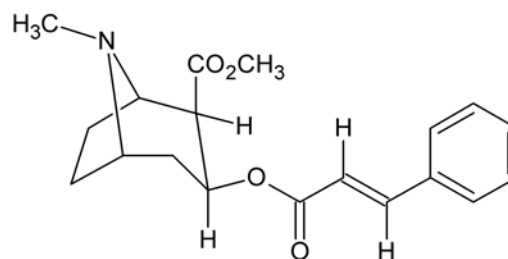
Cocaine



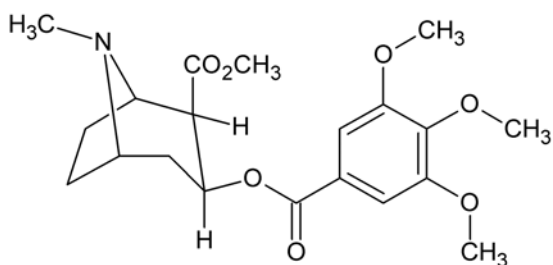
Tropacocaine



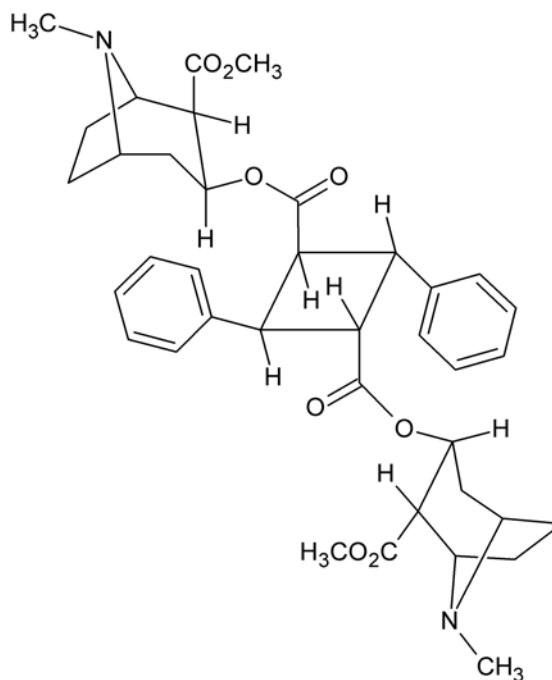
cis-Cinnamoylcocaine



trans-Cinnamoylcocaine



Trimethoxycocaine



α -Truxilline

Figure 1. Structures of Major Alkaloids Found in Illicit Cocaine.

Results and Discussion

The *base llavada* technique experiments resulted in a minor (4.5% average) increase in cocaine base purity, primarily due to the partial removal of the cinnamoylcocaines, truxillines, tropacocaine, and trimethoxycocaine (Figure 1). In addition (and in accordance with the information provided by the Peruvian cocaine processors), the resulting product was also noticeably whiter in appearance after the wash, due to the partial removal of the cinnamoylcocaines and other colored impurities (as noted above, the residual ethanol/impurities solution is dark brown in color). Partial reconstructed chromatographic profiles of the crude cocaine base, washed cocaine base, and residual ethanol/impurities solution are illustrated in Figure 2. The retention times of the target compounds are given in Table 2. As seen in Figures 2a and 2b, the cinnamoylcocaine content was reduced in the washed sample. Table 3 illustrates the effects of the wash on the relative concentrations of tropacocaine, *cis*-cinnamoylcocaine, *trans*-cinnamoylcocaine, trimethoxycocaine, and total truxillines. These naturally occurring alkaloids are more soluble than cocaine in ethanol, and as a result, are selectively extracted from the illicit cocaine (with minimal loss due to co-extraction of cocaine). Quantitative determinations confirmed decreases ranging from 21 - 78% relative to cocaine. The truxilline concentration was the least affected, while the trimethoxycocaine concentration was the most affected. Re-analysis of the samples 14 months later showed further decreases in alkaloid concentrations, ranging from 32 - 100%, versus the original crude cocaine base values, indicating further hydrolysis of those alkaloids over time (Table 3).

The residual ethanol/impurities solutions were also examined immediately after completion of the *base llavada* technique and not surprisingly were found to contain significant amounts of tropacocaine, *cis*-cinnamoylcocaine, *trans*-cinnamoylcocaine, trimethoxycocaine, and total truxillines relative to cocaine (Figure 2c). While the residual oil also contained some cocaine, the bulk of the material was primarily comprised of the alkaloidal impurities, approaching an order of magnitude concentration increase over their respective starting values relative to cocaine in the original crude base.

The hydrolysis of the cocaine was also examined. Hydrolysis of cocaine occurs at both ester bonds, giving ecgonine, ecgonine methyl ester, and benzoylecgonine (Figure 3). Hydrolysis of *cis*-cinnamoylcocaine and *trans*-cinnamoylcocaine will also occur, giving *cis*-cinnamoylecgonine, *trans*-cinnamoylecgonine, and ecgonine (Figure 3). The respective concentrations of the hydrolysis products was determined immediately after completion of the *base llavada* technique and again 14 months later. As shown in Table 4, the cleanup immediately increased these hydrolysis products from 18% to nearly 400% relative to cocaine in the resulting washed base. The residual oil also contained an increased concentration of the hydrolysis products. In addition, the ethanol remaining in the washed base samples continued to hydrolyze the cocaine, *cis*-cinnamoylcocaine, and *trans*-cinnamoylcocaine during the 14 month storage period, resulting in even more significant increases in the concentrations of *cis*-cinnamoylecgonine, *trans*-cinnamoylecgonine, and benzoylecgonine. When compared to the original samples, after 14 months, the hydrolysis products had increased from 57% to nearly 1,400% relative to cocaine.

Finally, although not quantitatively determined, the transesterification of cocaine to cocaethylene due to the presence of residual ethanol was also observed during storage [6]. Both the original sample and the washed base (immediately following the wash) showed no traces of cocaethylene. However, storage of the sample for 14 months allowed transesterification to occur, resulting in a measurable quantity of cocaethylene; the ethyl esters of *cis*- and *trans*-cinnamoylcocaine were also detected (Figure 5). Thus, the presence of cocaethylene in illicit cocaine *may* be indicative of use of the *base llavada* technique - however, ethanol is known to be utilized in several other variants of illicit cocaine processing, so the presence of cocaethylene alone does not confirm the use of the *base llavada* technique.

Although increasingly utilized in Peru, the *base llavada* method is currently not known to be in use in either Bolivia or Colombia.

Conclusions

The *base llavada* technique is a partially effective purification technique. Ethanol selectively removes significant amounts of major alkaloid impurities from crude cocaine base, due to their higher solubility versus cocaine. In contrast to the more time intensive and costly potassium permanganate purification method, the *base llavada* technique is relatively easy and inexpensive to perform. Although this new methodology results in only a moderate increase in cocaine base purity, it does give a noticeably whiter product.

References

1. Casale JF, Klein RFX. Illicit production of cocaine. *Forensic Science Review* 1993;5(2):95-107.
2. Casale JF, Boudreau DK, Jones LM. Tropane ethyl esters in illicit cocaine: Isolation, detection, and determination of new manufacturing by-products from the clandestine purification of crude cocaine base with ethanol. *Journal of Forensic Sciences* 2008;53(3):661-667.
3. Casale JF, Waggoner RW. A chromatographic impurity signature profile analysis for cocaine using capillary gas chromatography. *Journal of Forensic Sciences* 1991;36(5):1312-1330.
4. Moore JM, Casale JF, Cooper DA. Comparative determination of total isomeric truxillines in illicit, refined, South American cocaine hydrochloride using capillary gas chromatography - electron capture detection. *Journal of Chromatography A* 1996;756:193-201.
5. Morello DR, Meyers RP. Qualitative and quantitative determination of residual solvents in illicit cocaine HCl and heroin HCl. *Journal of Forensic Sciences* 1995;40(6):957-63.
6. Casale JF, Moore JM. An in-depth analysis of pharmaceutical cocaine: Cocaethylene and other impurities. *Journal of Pharmaceutical Sciences* 1994;83(8):1186.

Table 2. Relative Retention Times (RRT) of Coca Alkaloids.

Compound	Peak #	GC/FID RT	GC/MS RT
Ecgonine-di-TMS	1	5.24	----
Tropacocaine	2	10.96	17.51
<i>para</i> -Fluorococaine	3	14.92	----
Cocaine	4	15.81	21.38
Benzoylecgonine-TMS	5	16.18	----
<i>cis</i> -Cinnamoylcocaine	6	18.56	23.80
<i>cis</i> -Cinnamoylecgonine-TMS	7	18.90	----
<i>trans</i> -Cinnamoylcocaine	8	20.32	25.61
<i>trans</i> -Cinnamoylecgonine-TMS	9	20.52	----
Trimethoxycocaine	10	24.59	----
Cocaethylene	11	16.41	22.09
<i>cis</i> -Cinnamoylecgonine ethyl ester	12	----	24.55
Benzoylecgonine	13	----	25.95
<i>trans</i> -Cinnamoylecgonine ethyl ester	14	----	26.31

Table 3. Average Change in Alkaloid Values and (Percent Change) Relative to Percent Cocaine.

	Original Values	Day 1	14 Months Later	Enriched Ethanolic Oil
% Cocaine	79.5	83.0 (4.4)	84.3 (6.0)	32.5 (-59.1)
% Tropacocaine	0.12	0.07 (-41.7)	0.06 (-50.0)	1.02 (750.0)
% <i>cis</i> -Cinnamoyl-cocaine	6.36	4.31 (-32.2)	3.08 (-51.6)	47.13 (641.0)
% <i>trans</i> -Cinnamoyl-cocaine	4.08	2.68 (-34.3)	1.88 (-53.9)	32.94 (707.4)
% Trimethoxycocaine	0.18	0.04 (-77.8)	0.00 (-100)	1.02 (466.7)
% Truxillines	4.41	3.49 (-20.9)	3.01 (-31.7)	40.04 (87.9)
% EtOH relative to Cocaine	n/a	<0.1%	<0.1%	n/a

* * * * *

Table 4. Average Change in Hydrolysis Product Values and (Percent Change) Relative to Percent Cocaine.

	Original Values	Day 1	14 Months Later	Enriched Ethanolic Oil
% <i>cis</i> -Cinnamoyl-ecgonine	0.08	0.38 (375.0)	1.19 (1387.5)	4.49 (5512.5)
% <i>trans</i> -Cinnamoyl-ecgonine	0.00	0.18 (18.0)	0.57 (57.0)	1.45 (145)
% Ecgonine	0.81	1.20 (48.1)	1.51 (86.4)	19.02 (2248.1)
% Methylecgonine	0	0	0	0
% Benzoylecgonine	0.12	0.48 (300.0)	1.57 (1208.3)	5.23 (4258.3)

* * * * *

[Figures 2 - 5 Follow.]

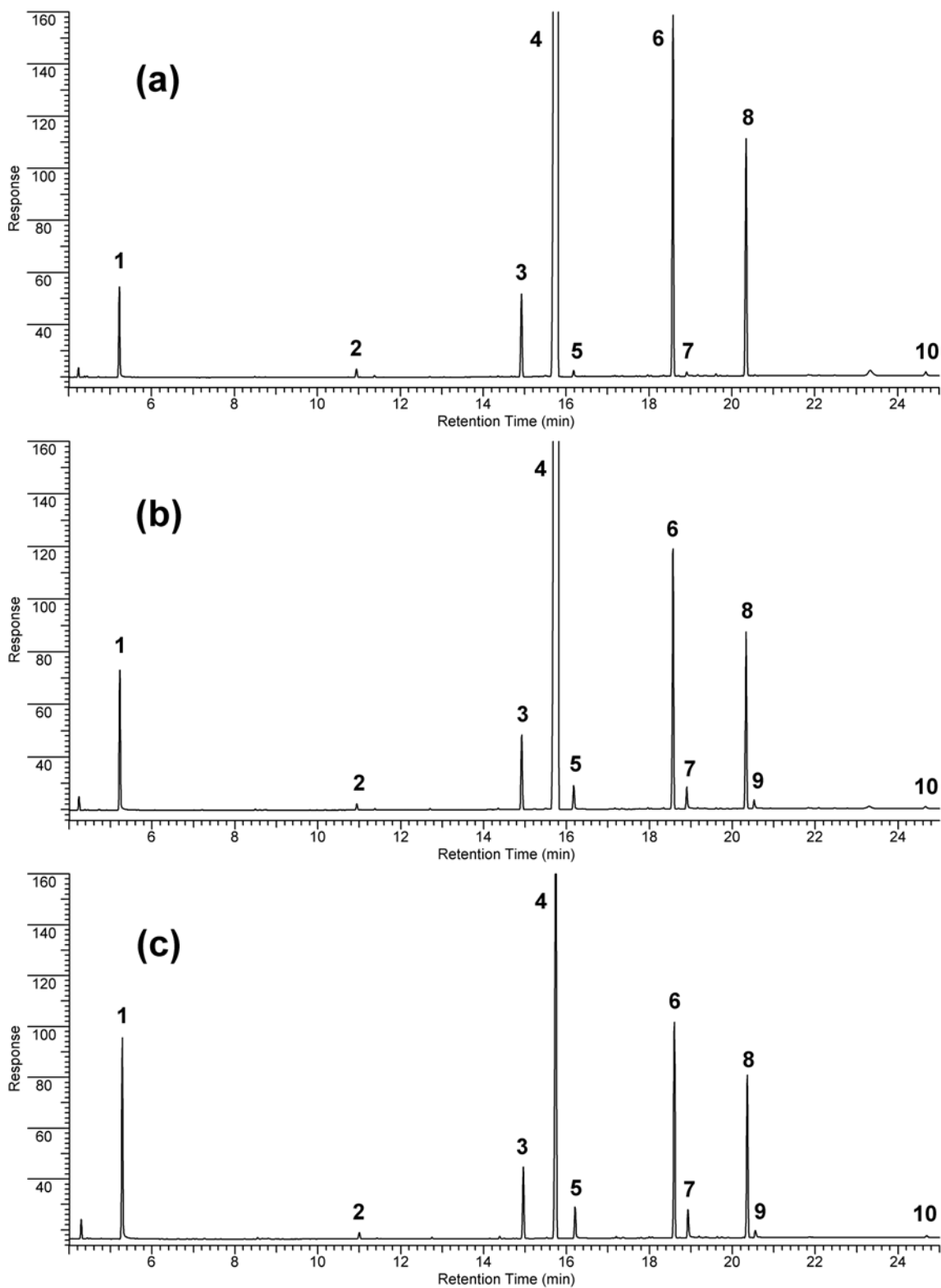
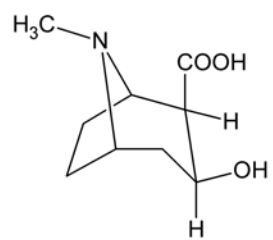
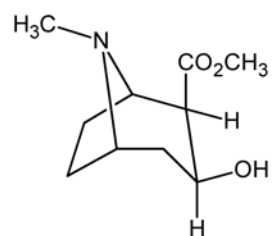


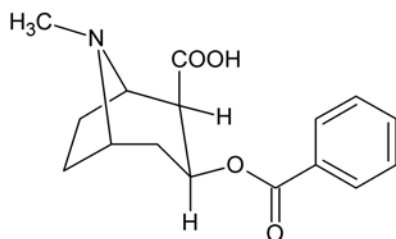
Figure 2. Partial Reconstructed GC/FID Chromatograms of: (A) Crude Cocaine Base; (B) Washed Cocaine Base; and (C) Enriched Oil. See Table 2 for Peak Identification.



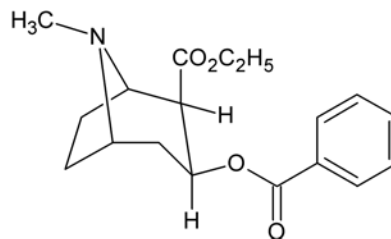
Ecgonine



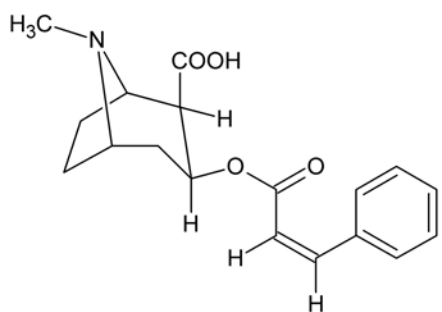
Ecgonine methyl ester



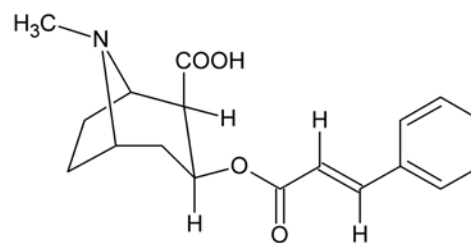
Benzoylecgonine



Cocaethylene



cis-Cinnamoylecgonine



trans-Cinnamoylecgonine

Figure 3. Structures of Hydrolysis Products.

* * * * *

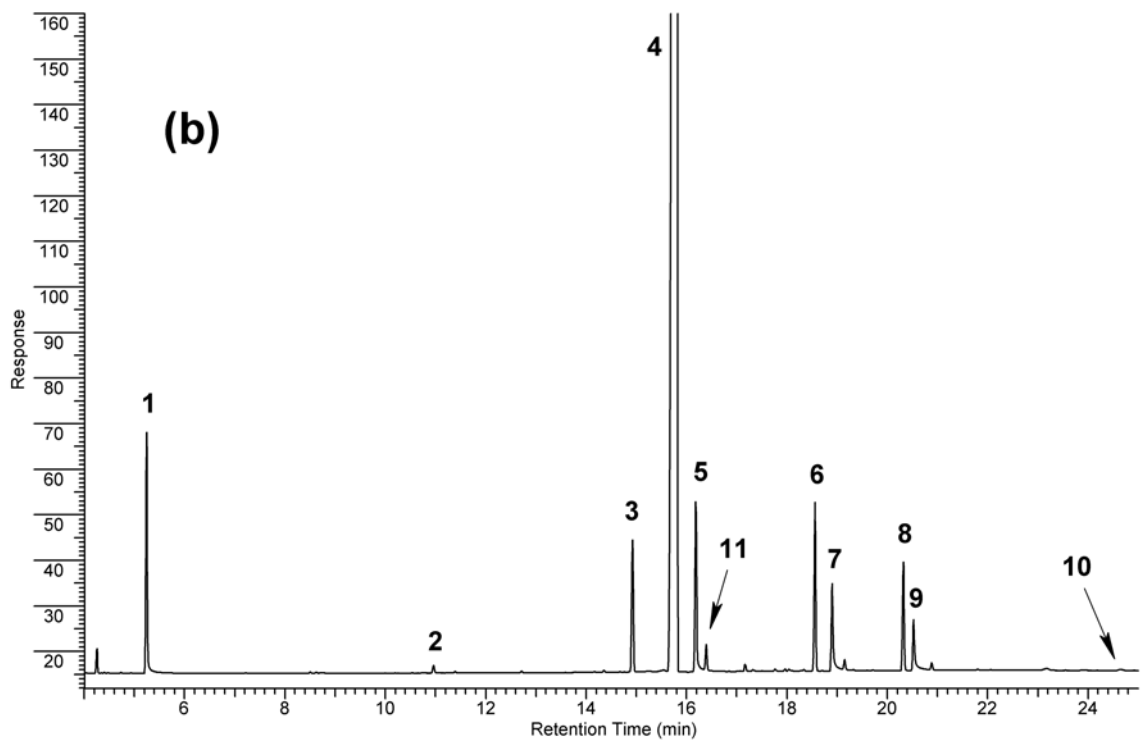
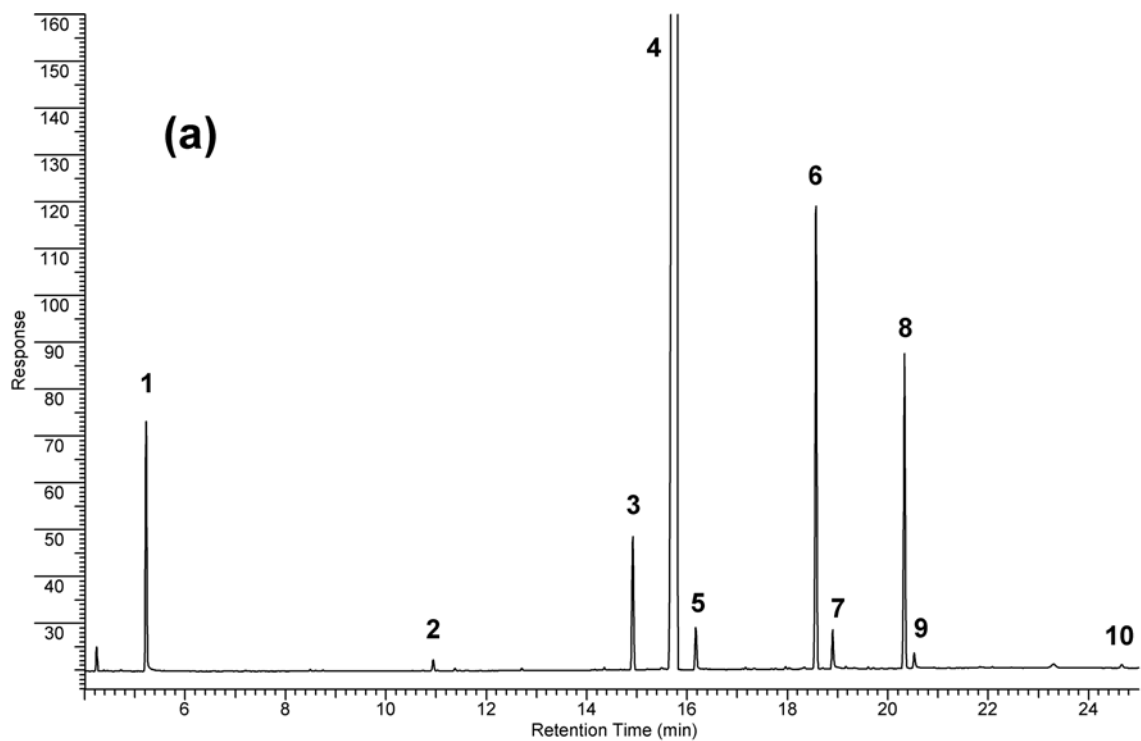


Figure 4. Partial Reconstructed GC/FID Chromatograms of: (A) Washed Cocaine Base after 1 Day; and (B) Washed Cocaine Base after 14 Months. See Table 2 for Peak Identification.

* * * * *

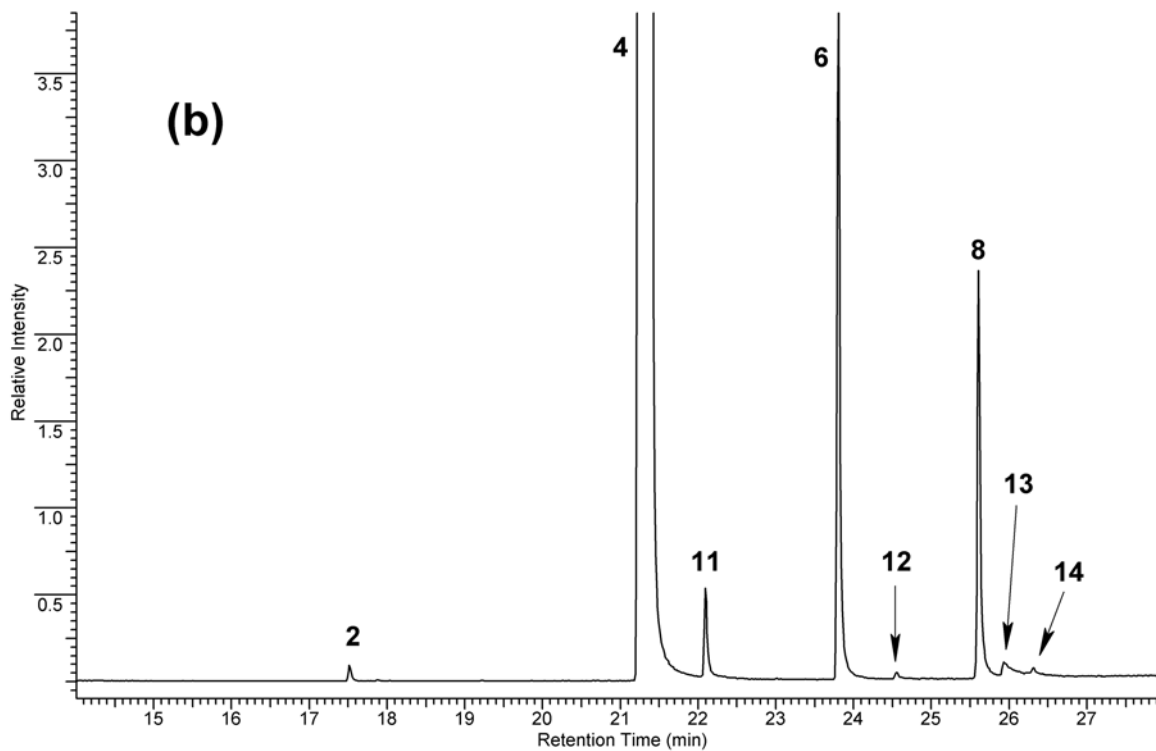
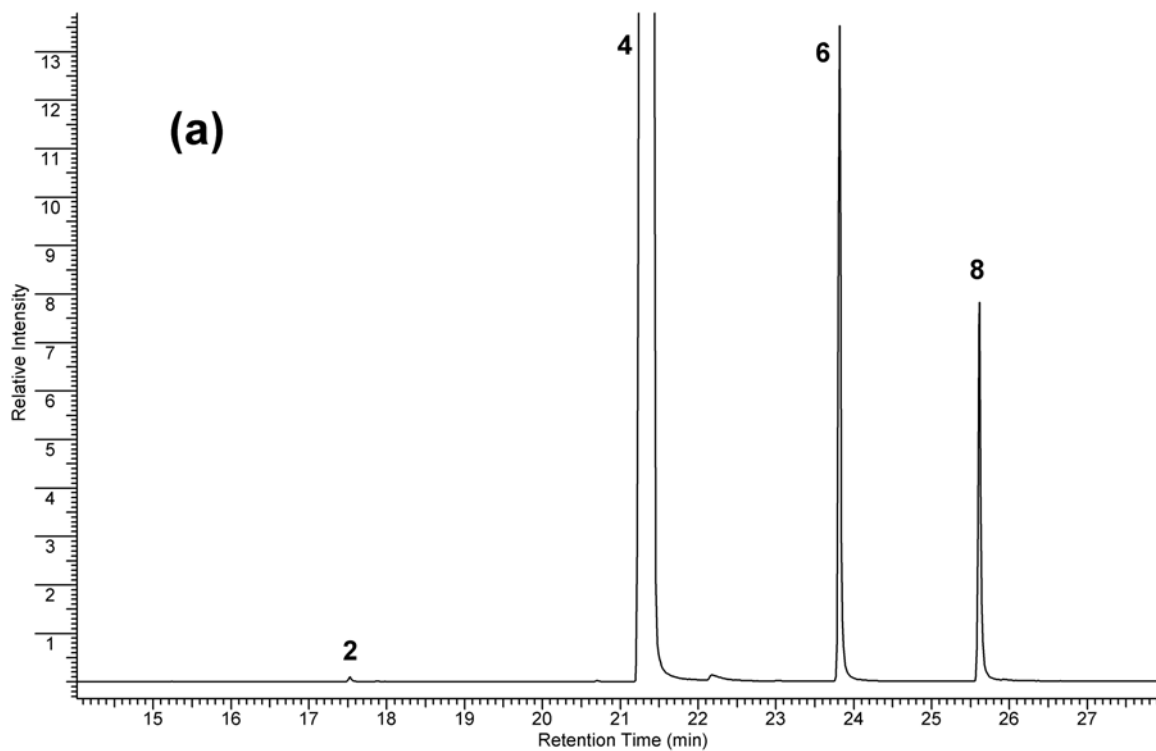


Figure 5. Partial Reconstructed Total Ion Chromatograms Showing Cocaethylene's Development Over Time: (A) Day One; and (B) 14 Months Later. See Table 2 for Peak Identification.

* * * * *