Technical Note

Determination of Cocaine in Various South American Commercial Coca Products

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ABSTRACT: Cocaine content is provided for several coca products including coca tea, medicinal tonics and rubs, and alcohol. Although these products are legal in most of South America, they are considered controlled substances in the United States and in most other countries. The cocaine was separated from complex matrices utilizing trap column chromatography. Gas chromatography / mass spectrometry / selective ion monitoring was used for cocaine identification and quantitation. The amount of cocaine in for these products ranges from 0.00 - 0.65 μg/mg.

KEYWORDS: Cocaine, Coca Products, Quantitation, Mass Spectrometry, Selective Ion Monitoring, Forensic Chemistry

Introduction

Although cocaine is controlled virtually worldwide, coca is legitimately cultivated in the South American countries of Peru and Bolivia. While it is illegal to extract the cocaine from the coca leaf in all of these counties, the coca leaf and various coca leaf extracts have long been legally used to relieve fatigue, hunger, and provide nutritional value. Along these lines, Duke *et al.* determined that ingesting coca leaves met the recommended dietary allowance for calcium, iron, phosphorous, vitamin A, vitamin B, and vitamin E [1]. Traditional South American medicine also uses coca leaf to alleviate headaches, rheumatism, abrasions, malaria, ulcers, asthma, and parasites, and studies have shown that several of these traditional treatments are valid [2].

However, in the United States and in many other countries, it is illegal to obtain, possess, or use coca products. The U.S. Code of Federal Regulations (CFR) lists coca leaves and any derivative or preparation of coca leaves as Schedule II substances [3]. The CFR excludes substances that contain de-cocainized coca leaves and leaf extracts that do not contain cocaine and ecgonine [3]. Numerous studies have quantitated the amount of cocaine and alkaloids found in coca leaf [4-7]. Studies have also determined the percent cocaine in coca tea and how it is metabolized in the body [8-9].

Although the analyses of coca leaf, coca extracts, and illicit cocaine exhibits are routine, analyses of food, medicinal, and beauty products that contain small amounts of coca leaf or coca extracts can be challenging due to the variety and complexity of the matrices. This investigation determined the amounts of cocaine in various matrices, including coca tea, medicinal tonics, rubs, alcohol, beauty products, and food products. Cocaine was isolated from the matrices via trap column chromatography, and identified and quantitated via gas chromatography / mass spectrometry / selective ion monitoring (GC/MS/SIM).

Experimental

Materials: Chloroform was a product of Burdick and Jackson Laboratories (Muskegon, MI). Diethylamine (DEA) and acid-washed Celite 545 were products of Sigma-Aldrich Chemical (Milwaukee, WI). Isopropylcocaine (used as an internal standard, ISTD) was synthesized in-house [10]. All standard solutions were prepared in 50 mL acid-washed glass volumetric vials. Trap column chromatography was performed using Lab Glass columns (260 mm x 22 mm). All the commercial coca products that were analyzed in this study were obtained from open markets in La Paz, Bolivia.

Gas Chromatography / Mass Spectrometry / Selective Ion Monitoring (GC/MS/SIM): Analyses were performed using an Agilent (Palo Alto, CA) Model 5973 quadrupole mass selective detector (MSD) interfaced with an Agilent Model 6890 gas chromatograph. The GC was fitted with a 30 m x 0.25 mm ID fused silica capillary column coated with 0.25 μm DB-1 (J&W Scientific, Rancho Cordova, CA). The oven temperature was programmed as follows: Initial temperature 100^{O}C; initial hold 0.0 min; program rate 6.0^{O}C/min; final temperature 300^{O}C; final hold 5.67 min. The injector was operated in the split mode (21.5 : 1) at 280^{O}C. The MSD was operated in selective ion monitoring (SIM) mode. The fragment ions 82.1, 182.1, and 303.2 Daltons were monitored with a 500 millisecond dwell time for cocaine. The fragment ions 82.1, 210.2, and 331.2 Daltons were monitored with a 500 millisecond dwell time for isopropylcocaine. The auxiliary transfer line to the MSD and the source were maintained at 280^{O}C and 230^{O}C, respectively.

Standard Solutions for Quantitative Determination of Cocaine: Individual $CHCl_3$ solutions each containing 22.50 μg/mL of isopropylcocaine and 9.90, 20.62, 25.57, 30.51, 35.47, and 41.24 μg/mL of cocaine base, respectively, were prepared. Linearity was confirmed over the concentration ranges; linear regression analysis determined the correlation coefficient (R^2) as exceeding 0.996.

Sample Preparation and Extractions: Cocaine was isolated from wax-like, aqueous, and candy-like coca products utilizing a slight modification of the trap column chromatography utilized by Moore *et al.* [5].

Wax-Like Samples: Between 500 - 1000 mg of wax-like samples were dissolved in 1 mL of $CHCl_3$ containing 22.50 μg/mL of isopropylcocaine and 1 mL of water-saturated $CHCl_3$ (hereafter WSC). This solution was vortexed and then placed onto a glass chromatographic column containing 4 g of Celite 545 mixed with 2 mL of 0.36 N sulfuric acid. The column was eluted with 50 mL of WSC (discarded) followed by 50 mL WSC containing 500 μL DEA (collected and evaporated *in vacuo* to a residue). The residue was reconstituted in approximately 1 mL of $CHCl_3$, dried over anhydrous sodium sulfate, filtered, and examined via GC/MS/SIM.

Aqueous Samples: Between 2 - 10 mL of liquid samples were evaporated *in vacuo* to a residue. The residue was reconstituted in a mixture of 1 mL of $CHCl_3$, 1 mL of the $CHCl_3$ containing 22.50 μg isopropylcocaine, and 3 drops of water. This solution was placed onto a glass chromatographic column containing 4 g of Celite 545 mixed with 2 mL of 0.36 N sulfuric acid. The cocaine from these samples was isolated and analyzed in the same manner as detailed above under "Wax-Like Samples."

Candy Samples: Two pieces (approximately 8 g) of candy were ground and dissolved in water (approximately 2 mL). The solution was basified with saturated NaOH until pH 8 - 9, and the cocaine was extracted with 1 mL of $CHCl_3$ containing 22.50 μg isopropylcocaine and placed onto a glass chromatographic column containing 4 g of Celite 545 mixed with 2 mL of 0.36 N sulfuric acid. The cocaine from these samples was isolated and analyzed in the same manner as detailed above under "Wax-Like Samples."

Leaf, Vitamin, and Alcohol Samples: Cocaine was isolated from coca tea and the coca vitamin by weighing approximately 2 mg directly into a GC vial containing 1 mL of $CHCl_3$ containing 22.50 μg of isopropylcocaine and 250 μL of DEA. The samples were examined via GC/MS/SIM. A 250 μL aliquot of the alcohol sample was added to 1 mL of $CHCl_3$ containing 22.50 μg of isopropylcocaine spiked with 50 μL of DEA.

Results and Discussion

Two typical GC/MS/SIM chromatograms are shown in Figure 1. Figure 1a (Vitamins) illustrates a relatively low concentration of cocaine, while Figure 1b (Medicinal Tonic) illustrates a significant quantity of cocaine. Collectively, the analyses indicated that the products contained from 0.00 - 0.65 μg/mg cocaine (Table 1). The cocaine (if any) in the shampoo could not be determined due to the difficulty of isolating cocaine from this matrix. In addition, one of the alcohol products did not contain cocaine (see below). The appearance and manufacturer of all of the aqueous medicinal tonics was the same; their cocaine content ranged from 0.01 - 0.38 μg/mg, indicating that there were significant differences in the amount of coca leaf added to each product. All of the medicinal rubs had the same waxy appearance and a strong odor of coca leaf; their cocaine content ranged from 0.01 - 0.10 μg/mg (relatively low). Visual inspection of these latter products confirmed that only small amounts of particles were distributed (unevenly) throughout the waxy matrix. The cocaine content in the teas and the ground leaf samples ranged from 0.46 - 0.65 μg/mg. The cocaine content of the ground leaf and tea samples were consistent with coca leaf [4-7]. Both candy samples were brown, sticky substances that smelled similar to coca leaf; one had the consistency of chewing gum, while the other was more like a hard candy. They were determined to contain 0.003 - 0.01 μg/mg cocaine. The Ajayu de Coca Pachamama (liquor) was a clear liquid with a distinct alcohol smell. Despite its suggestive name, this product did not contain cocaine. The Ron Fernando Ron De Coca (liquor) was a green liquid that smelled similar to coca leaf and alcohol; it contained 0.22 μg/mg of cocaine.

Conclusions

Trap column chromatography can be utilized to isolate cocaine from complex bulk matrices. The utilization of GC/MS/SIM, coupled with a structurally related internal standard, gave excellent sensitivity and linearity, and could determine cocaine content down to the microgram per gram level. Utilizing the described methodology, cocaine was readily detected and determined in all the commercial products except for a shampoo and one alcoholic liquor. In the case of coca leaf, the described method was able to determine cocaine content from as little as 2 milligrams of sample.

References

1. Duke JA, Aulik D, Plowman T. Nutritional value of coca. Botanical Museum Leaflets Harvard University 1975;24(6):113-8.

2. Weil AT. The therapeutic value of coca in contemporary medicine. Journal of Ethnopharmacology 1981;3(2-3):367-76.

3. Code of Federal Regulations 2002;21(1308.12):85.

4. Holmstedt B, Jaatmaa E, Leander K, Plowman T. Determination of cocaine in some South American species of Erythroxylum using mass fragmentation. Phytochemistry 1977;16:1753-5.

5. Moore JM, Casale JF, Klein RFX, Cooper DA, Lydon J. Determination and in-depth chromatographic analyses of alkaloids in South America and greenhouse cultivated coca leaves. Journal of Chromatography A 1994;659:163-75.

6. Plowman T, Rivier L. Cocaine and cinnamoylcocaine content of Erythroxylum species. Annals of Botany 1983;51:641-59.

7. Rivier L. Analysis of alkaloids in leaves of cultivated Erythroxylum and characterization of alkaline substances used during coca chewing. Journal of Ethnopharmacology 1981;3:313-35.

8. Jenkins AJ, Llosa T, Montoya I, Cone, E. Identification and quantitation of alkaloids in coca tea. Forensic Science International 1996;77:179-89.

9. Engelke BF, Gentner WA. Determination of cocaine in "Mate de Coca" herbal tea. Journal of Pharmaceutical Sciences 1991;80(1):96.

10. Piñero EL, Casale JF. Quantitation of cocaine by gas chromatography - flame ionization detection utilizing isopropylcocaine as a structurally related internal standard. Microgram Journal 2006;4(1-4):47-53.

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Table 1. Cocaine Content of Selected Coca Products.

Product	Treatment	Matrix	µg/mg Cocaine
Ron Fernando Ron De Coca	liquor	Alcohol	0.22
Ajayu de Coca Pachamama	liquor	Alcohol	Not detected
Adelgazante	Diet	Aqueous	0.39
Anti Diabetico	Diabetes	Aqueous	0.15
Tos Asma	Asthma	Aqueous	0.29
Prostata	Prostate Problems	Aqueous	0.38
Parasitos	Parasites	Aqueous	0.33
Ulceras	Ulcers	Aqueous	0.01
Tonico	Tonic	Aqueous	0.26
Pomada Natural de Coca Contra Dolores: Reumaticos, Musculares, Varices Y Huesos	rheumatic, muscular, veins, and bones	Wax	0.07
Pomada Natural de Coca Para: Artritis Y Gota	Cream for arthritis and foot pain	Wax	0.10
Pomada Natural de Coca Para: Hemorroides	Cream for hemorrhoids	Wax	0.04
Pomada de Molle	Cream for moles	Wax	0.01
Chicle Cocaplus	Chewing gum	Candy	0.01
Caramelos Y ElixirEnergizante de Altura	Caramel candy for energy booster	Candy	0.003
Mate Windsor	Tea	Tea	0.59
Kokasana	Tea	Tea	0.46
Harina De Coca	Nutritional Supplement	Ground Leaf	0.65
Coca Premium	Nutritional Supplement	Ground Leaf	0.59
Shampoo	Beauty Product	Liquid	N/A

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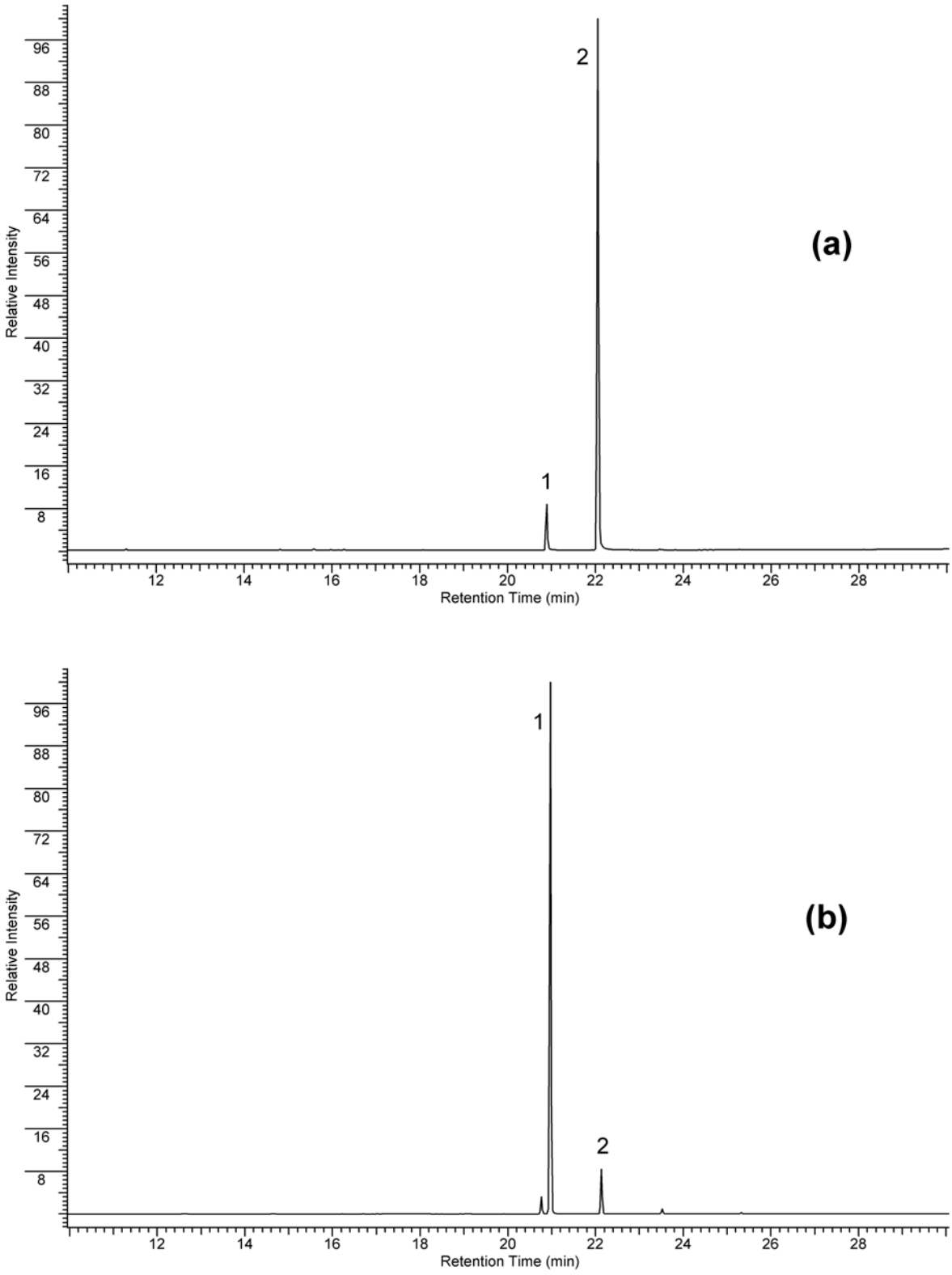

Figure 1. Partial Reconstructed Selected Ion Chromatograms of: (A) 2.73 mg of Coca Premium Vitamins Containing 0.593 µg/mg Cocaine; and (B) 5.00 g of Adelgazante Medicinal Tonic Containing 0.385 µg/mg Cocaine. Peak Identification: 1 = Cocaine; and 2 = Isopropylcocaine (ISTD).