Rapid determination of the isomeric truxillines in illicit cocaine via capillary gas chromatography/flame ionization detection and their use and implication in the determination of cocaine origin and trafficking routes

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1. Introduction

Minor alkaloids present in illicit cocaine have been utilized in the determination of geographic origin and signature profiling for many years [1–19]. These minor alkaloids are carried through the processing of coca leaf to cocaine base and refined cocaine hydrochloride (HCl). Variables that are important for cocaine source determination include minor alkaloids such as trimethoxy-cocaine and isomeric truxillines, as well as carbon and nitrogen isotopic data of the cocaine [19].

Truxillines are a group of tropane alkaloids that have been of interest for over 100 years; the two most abundant isomers, alpha- and beta-truxilline (Fig. 1), were structurally elucidated at the end of the nineteenth century [20,21]. The remaining truxillines were detected and characterized in illicit cocaine and coca leaf by Moore et al. [22]. The presence of truxillines in coca leaf is due to 2+2 photodimerization of cis- and/or trans-cinnamoylcocaine [23]. Although many studies with various separation techniques for the detection and determination of truxillines have been previously reported, the procedures typically are tedious and do not give sufficient resolution of all isomers [24–26]. Only one method has been shown to separate and successfully quantitate 10 of the 11 isomers (mu-truxilline is rarely detected in illicit cocaine) [27].

Gas chromatography/electron capture detection (GC/ECD) has been utilized at this laboratory for the determination and quantitation of total truxillines in illicit cocaine for over 20 years [22,27]. The GC/ECD methodology, however, required a lengthy sample preparation process consisting of multiple extractions, esterification with boron trifluoride-methanol (BF3-methanol), reduction with lithium aluminum hydride (LiAlH4), acylation with hexafluorobutyric anhydride (HFBA) prior to analysis [27]. In addition, the GC/ECD method is rather costly. In order to purchase and utilize a GC/ECD, a laboratory must first obtain a U.S. Nuclear Regulatory Commission (NRC) license. Once licensed, bi-annual radiation checks of the 63Ni detector must be completed. Furthermore, prior to each analysis, the 63Ni detector must be stabilized with multiple
by-pass injections. In an effort to streamline the sample preparation and conserve resources, the GC/ECD methodology was modified significantly and transferred to a gas chromatograph with flame ionization detection (GC/FID).

The present study significantly modifies the GC/ECD sample preparation by excluding the initial extractions and esterification steps. Instead, the samples are reduced directly with LiAlH₄, and the 10 individual truxilline isomers are then separated via liquid-liquid extraction, derivatized with HFBA, and analyzed by GC/FID. The results compare favorably with the previously utilized GC/ECD method. Additionally, data obtained from the GC/ECD analyses of over 23,000 samples seized from ten different countries are presented. Authentic cocaine samples from Bolivia, Colombia, and Peru were analyzed via GC/FID and compared to the extensive data collected over ten years.

2. Materials and methods

2.1. Cocaine samples

Cocaine HCl samples (N = 104, average 75.9% purity) seized within the United States were sent to this laboratory soon after seizure. The samples were stored under ambient conditions prior to analyses. Authentic cocaine base and HCl samples (N = 9) were taken from this laboratory’s reference materials collection. A standard cocaine HCl sample with known truxilline values (RTI-KG) was utilized as a normalized reference material, and was also taken from this laboratory’s reference materials collection.

2.2. Materials

All solvents were reagent grade or better and were obtained from Sigma Aldrich (St. Louis, MO). HFBA was purchased from Thermo Scientific (Waltham, MA) in 1 ml sealed glass ampules. Lithium aluminum hydride (1.0 M) was obtained from Aldrich (St. Louis, MO). The reference standard dimethyl-α-truxillate was taken from this laboratory’s reference materials collection. The internal standard (IS) used for the quantitation of truxillines was 4’,4”-dimethyl-α-truxilllic acid dimethyl ester (Fig. 1).

2.2.1. 4’,4”-Dimethyl-α-truxilllic acid

4-Methyl-trans-cinnamic acid (10.0 g, 0.062 mol) was irradiated for one month with an ultraviolet tanning lamp (Wolff System, Sun-100). The crude material was extracted with CHCl₃ in a soxlet apparatus for 45 min to remove unreacted starting material. The insoluble material was dried to provide a chromatographically pure material (6.2 g, 62%).