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Composition and characterization of illicit cocaine seized at The Netherlands Antilles

Ensing, Jacob Geert

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SUMMARY

The coca shrub, *Erythroxylum coca*, is growing mainly in the warm and moist valleys of the Andes mountains. From ancient times, the leaves of the coca shrub have been used for medicine as well as for pleasure. In the mid 1800's the main active substance was isolated from the coca leaves and this substance was called "cocaine". Because of its anesthetic properties, cocaine was successfully applied during surgery, but its use was later overtaken by synthetic anesthetics. Through the years, however, cocaine developed an enormous popularity as an illicit drug. During the clandestine cocaine processing, more or less crude cocaine base is first obtained, while a cocaine salt (mostly cocaine.HCl) can be formed in a subsequent refinery step. "Crack" refers to a more refined form of cocaine-base (more than 90% cocaine), which is usually prepared from cocaine.HCl. Cocaine-base is normally smoked and its effects appear to be much higher and more addictive than those obtained after the snorting of cocaine.HCl.

In the 1980's both the illegal trade and the use of cocaine base increased drastically in The Netherlands Antilles. As a result, more crude cocaine samples were submitted to our laboratory. This allowed us to take a closer look at the accompanying minor alkaloids in the samples, some of which having an unknown identity at that time. Because of their persisting presence in the illicit cocaine, the identification of the natural congeners is of great importance in order to get more insight about the origin of the illicit cocaine. The botanical background, the growing area, the nature of the illicit production process etc. may be reflected to some extent in the characteristics of illicit cocaine. This prompted us to establish the identity of these minor alkaloids encountered.

In Chapter 2 the unknown minor alkaloids, visible during TLC analysis, are described and investigated. The substances gave isomerization during work-up, producing confusing analytical results, which partly appeared to be due to decomposition. After investigating existing similarities with known cocaine congeners, the substances were identified as truxillines: For the first time

they were observed, isolated and identified using TLC. The spot with the highest abundance showed the same retention behaviour as a very recently obtained reference sample of α -truxilline.

Truxillines are built up from two 1-methylecgonine moieties, which are connected through an acid. This acid may be either truxillic or truxinic acid. The truxillines can also be considered as the dimerization product of two molecules of cinnamoylcocaine, in which the 2X2 carbon atoms at the double bonds in the cinnamic acid moiety form a 4-membered ring. Although the possible existence of the truxillines was postulated more than 100 years ago, these substances had not yet been identified until very recently. It has been suggested that truxinic acid may exist in 6 and truxillic acid in 5 isomeric forms. However, we believe that since there are 4 additional enantiomeric structures for truxinic acid, the total number of possible truxillines is 15. Because the truxillines are formed in the coca leaf, their presence as well as their quantitative profile in the illicitly produced cocaine may furnish important information about its background.

Chapter 3 describes the detection and isolation of 3 unknown congeners, observed during gas chromatographic analysis of illicit cocaine. Once isolated, their identities were established to be norcocaine, N-formylnorcocaine and N-benzoylnorecgonine methyl ester, respectively.

The first two substances mentioned can be considered as oxidation products of cocaine, whereas the latter may be a transformation product of norcocaine. The relative amount of N-benzoyl norecgonine methyl ester is dependent on the pH during the production. We were the first to detect these N-substituted substances in illicit cocaine, while noticing that N-formylnorcocaine even never has been described. Because oxidation (bleaching) is one of the routinely performed steps during the processing of illicit cocaine, it is very conceivable that this step is responsible for the presence of the 3 congeners. We could prove that they can be formed by oxidation of pure cocaine under laboratory conditions. Their presence in illicit cocaine is variable and so these substances are very valuable for the characterization of cocaine samples.

In the fourth Chapter an approach is being presented for the fingerprinting of cocaine samples, i.e. the characterization by means of the minor constituents. First, the various cocaine congeners are evaluated for their use as parameter for cocaine characterization. Subsequently, a GC analysis is developed, which enabled us to detect, besides cocaine, 6 congeners in a quantitative manner, and their abundance was expressed relative to the most prominent congener present in the sample under investigation. The resulting parameters could then be expressed graphically in so-called pictograms, or numerically. In total, 71 samples were examined by this fingerprinting approach. These samples were collected over a few years and assumed to be unrelated. The results of the GC analysis was surprising: A few samples showed similarities in their fingerprints, whereas the large majority showed no similarity at all. This is exemplified by a subdivision of the analyzed samples in different categories, based on the number and types of congeners found. According to these observations it is clear that the method will be very useful for the characterization of illicit cocaine.

Additionally illustrative is the example of 2 cocaine samples possessing the same fingerprint and also having the same cocaine base content. One sample originated from a cocaine dealer and the other one from a user. The thus determined similarity gave valuable support to the forensic investigation.

The fifth chapter starts with a discussion on the formation of the natural congeners in the coca-leaf: Tropacocaine, *cis*- and *trans*- cinnamoylcocaine, and the truxillines. Especially the formation of the truxillines is not fully understood at the moment. However, the presence of the natural congeners can serve to prove the natural origin of the cocaine.

Cocaine may also be prepared synthetically but such products may distinguish itself from natural cocaine by the presence of the diastereoisomers pseudo-, allo-, and allo-pseudococaine, respectively.

Based on the techniques which are described in the foregoing Chapters, a procedure for the characterization of illicit cocaine is suggested. This procedure is based on the origin and content of the cocaine, the presence of natural congeners (truxillines and GC parameters), the presence of synthetic isomers, as well as

the presence of adulteration.

Since every batch of cocaine possesses its own unique character, the characterization of illicit cocaine may provide important information concerning its background, and may offer valuable clues regarding the illegal production method and transportation routes.

The value of the proposed methodology for the latter two areas should be further established, although it is clear that with the identification of the cocaine congeners, together with the GC fingerprinting approach, a new research area is created for the characterization of illicit cocaine.