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Sourcing Brazilian marijuana by applying IRMS analysis to seized samples

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Abstract

The stable carbon and nitrogen isotopic ratios were measured in marijuana samples (*Cannabis sativa* L.) seized by the law enforcement officers in the three Brazilian production sites: Pernambuco and Bahia (the country's Northeast known as Marijuana Polygon), Pará (North or Amazon region) and Mato Grosso do Sul (Midwest). These regions are regarded as different with respect to climate and water availability, factors which impact upon the isotope fractionations of these elements within plants. It was possible to differentiate samples from the dry regions (Marijuana Polygon) from those from Mato Grosso do Sul and Pará, that present heavier rainfall. The results were in agreement with the climatic conditions of the suspected regions of origin and this demonstrates that seized samples can be used to identify the isotopic signatures of marijuana from the main producing regions in Brazil.

Keywords: Forensic science; Drug sourcing; Marijuana; Stable isotopes mass spectrometry; Isotope signature

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1. Introduction

1.1. Chemical fingerprint and the origin of illicit drugs

According to the United Nations Office on Drugs and Crime (UNODC), last year's global use of illicit drugs rose from 4.3 to 4.7% in the 15-year-old population bracket, which represents an increase of 200 million-odd users, and a total value of about US$ 500 billions around the world. Although cocaine and heroin represent the most consequential problems in terms of state welfare, marijuana stands by far as the most produced and consumed drug, involving about 150 million users around the world [1]. It is estimated that the worldwide cultivation ranges from 670,000 to 1,800,000 ha with productivity from 20,000 to 30,000 tonnes a year [2].

Due to its nature of illicit trade, statistics on production, trafficking and drug dealing are mostly based on seized quantities. The UNODC mentions numerous difficulties concerning the reported figures, such as differences in the

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criteria of reporting information supplied by national governments, and lack of consistent data and information regarding plantation sites, production and trafficking routes [3]. Among these difficulties, the latter is critical for an effective strategic plan against drug traffic [3], and even today most of the information concerning traffic routes is based mainly on unreliable information given by users and drug dealers. For this reason, the development of a methodology to trace these samples to their geographical origin would be extremely helpful as a key element in anti-drug law enforcement.

One of the strategies adopted in order to identify and track down the origin of those materials is based on the concept of chemical fingerprint. This fingerprint is established by determining the organic, inorganic or isotopic profile of the samples, which are associated with plant growth conditions such as climate and availability of elements on the site [4–15].

The relative amounts of the main organic constituents in cannabis plants (THC, tetrahydrocannabinol; CBD, cannabidiol; CBN, cannabinol) vary widely depending on many factors, mainly the genetic variety and the environment in which the plant was grown [16,17]. These parameters are also affected by time and conditions of sample storage once THC was transformed to CBN in these plant tissues. Thus, the use of the organic profile as a chemical tracer is hindered by its complexity, requiring further information related to plant maturity and storage conditions [8,14,17,18].

In comparison to the stable isotopic ratio, the elemental profile of the plants provides further knowledge of the soil. Despite this they cannot establish explicitly their geographic origin and appear rather inconclusive [13–15,19,20]. The carbon and nitrogen isotope ratio on the other hand, reflects the climatic conditions, and consequently, it delimits the potential geographic source when the producing areas present different climates [9,11,12,21–26].

The stable isotopes most commonly used as indicative of global changes are hydrogen, oxygen, carbon and nitrogen, and among them, the variation of stable isotope ratio (δ) of C and N are the most useful for sourcing the geographical origin of plant materials [21,26].

Unlike drugs such as heroin and cocaine, *Cannabis sativa* or marijuana is not processed for consumption and maintains its original elemental and isotopic profiles. Thus, these parameters have been used as an important indicative of its geographical origin [21,26].

Handley et al. evaluated the δ^{15}N variation in plants and soil influenced by the following parameters: rainfall, temperature, latitude, altitude and soil pH. Their model excluded samples from regions where atmospheric N_2 was a potentially major source of plant N, sites with anomalous pH values or with very high rainfall (>2500 mm annually), and regions with very low temperatures (high altitude or latitude). It was concluded that rainfall affects foliar δ^{15}N values more strongly than whole soil δ^{15}N, 35 and 8%, respectively [26].

Denton et al. [24] measured the δ^{13}C and δ^{15}N levels in marijuana samples seized in Australia, New Guinea and Thailand, with the aim of identifying their provenance. It was not possible to classify the samples according to their origin, but some important conclusions were presented: (1) δ^{13}C and δ^{15}N exhibit low dependence on temperature but present a direct relationship with water availability, particularly in the case of δ^{13}C; (2) marijuana δ^{15}N values strongly reflect the δ^{15}N of growth substrate and fertilizer. This methodology also proved to be efficient to identify of indoor-grown sample, producing fairly characteristic δ^{13}C values of around −31.8‰.

More recently, Galimov et al. [27] proved the potentiality of IRMS technique as a tool to source drugs using samples from different regions of Russia and Ukraine. The δ^{13}C and δ^{15}N results for hemp leaves showed a large variation range for δ^{15}N (from −3.17 to 9.65‰), while for δ^{13}C this range was narrow (from −28.38 to −26.43‰).

Although these results show the potentiality of the carbon and nitrogen isotopes ratios in assigning the geographic origin of marijuana samples, these studies are scarce in the scientific literature and still do not appear conclusive. The major difficulty reported by the authors in the development of such methodologies lies in obtaining a sufficient number of samples, particularly of recognized origin. Thus, most of these works have been achieved using samples obtained from seizures for which the original geographical origin is unclear [9,15].

The aim of this work was to verify the differences in the stable carbon and nitrogen isotopic compositions for samples seized in the main Brazilian regions of marijuana production and to evaluate the possibility of using these parameters to track the provenance of marijuana samples traded in the country. The first data for δ^{13}C and δ^{15}N in marijuana samples seized in South America, especially in Brazil will be presented.

1.2. Stable carbon and nitrogen isotopes in plants

The main mechanism of C fixation and fractionation in plants is photosynthesis, whereby absorption of CO_2 from the atmosphere occurs. Plant tissues are deficient in ^{13}C in relation to the atmospheric CO_2, indicating that there is a discrimination against ^{13}C absorption. This C fractionation is regulated by the plant photosynthetic pathway and is related to both stomatal limitation and enzymatic processes [23].

The three basic C pathways are Hatch–Slack–Kortschak (C4), Benson–Calvin (C3) and Crassulacean Acid Metabolism (CAM). The C3 plants reduce atmospheric CO_2 to phosphoglycerate with low ^{13}C/^{12}C ratio, presenting δ^{13}C average values of around −27‰. About 85% of terrestrial plants are comprehended here, including marijuana. For this plant in particular δ^{13}C values varying from less than −30‰ to more than −24‰ have been reported according to growth conditions [24]. In general, the δ^{13}C values decrease with