Various Alkaloid Profiles in Decoctions of *Banisteriopsis Caapi*†

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Abstract—Twenty nine decoctions of *Banisteriopsis caapi* from four different sources and one specimen of *B. caapi* paste were analyzed for *N,N*-dimethyltryptamine (DMT), tetrahydroharmine (THH), harmaline and harmine. Other plants were also used in the preparation of these products, typically *Psychotria viridis*, which provides DMT. There were considerable variations in alkaloid profiles, both within and between sample sources. DMT was not detected in all samples. Additional THH may be formed from both harmine and harmaline during the preparation of these products. The alkaloid composition of one decoction sample did not change significantly after standing at room temperature for 80 days, but the initial acidic pH was neutralized by natural fermentation after 50 days.

Keywords—*ayahuasca, caapi, Daime, hoasca, natemä, vegetal, yagé*

Ayahuasca, caapi, yajé and *natemä* are just some of the many indigenous names for a decoction from the woody liana *Banisteriopsis caapi*; it is a rich source of harmine, tetrahydroharmine (THH) and, to a lesser extent, harmaline. Other plants are often added to this brew, particularly the leaves of *Psychotria viridis*, which provides *N,N*-dimethyltryptamine (DMT). Modern groups call this ancient sacrament *hoasca, daime, cha, tea* or *vegetal.* In any event, this complex beverage forms the spiritual core of numerous indigenous and contemporary religions in South America. The phytochemical compositions and pharmacologic activities of these beverages have been described in several publications (McKenna 2004; Riba et al. 2003; Callaway et al. 1999; Ott 1994), but only rarely has more than one beverage been analyzed within a single study (McKenna, Towers & Abbot 1984). Moreover, the alkaloids in *B. caapi* have demonstrated medicinal properties, such as antimicrobial (Aqeel et al. 1992), anthelmintic (Hassan 1967) and vasorelaxant (Shi, Liao & Chen 2001) effects, in addition to sociopsychotherapeutic (Andritzky 1989), ethnopsychiatric (Shepard 1998) and rehabilitative functions (Mabit, Giove & Vega 1995).

The earliest known European accounts of this beverage were made by Jesuits, who described it as a "diabolical brew." The actual utility of these decoctions was only later described to Europeans by Richard Spruce (1873), after the publication of his summary observations on the tonic effects of such beverages: "From all that has been said, it may be gathered that the domestic medicine of the South American Indians is chiefly hygienic, as such medicine ought to be, it being of a greater daily importance to preserve health than to cure disease."

Unfortunately, the tone of a recent report on ayahuasca (where this is misspelled as "ayahoasca") seems to have fallen back into the regressive perspective of the early Jesuits in both depth and scope (Pomilio et al. 1999). It is, indeed, unfortunate that the religious effects of pharmacologic sacraments are still considered as models of endogenous psychosis by some (Ciprian-Ollivier &

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TABLE 1
Variations in Alkaloid Profiles of *Vegetal* Decoctions from Various Sources

	Source	DMT	THH	Harmaline	Harmine
1	UDV	0.80 mg/ml	1.83 mg/ml	0.09 mg/ml	1.72 mg/ml
2	UDV	0.66	2.10	0.08	0.97
3	UDV	0.70	1.74	0.70	0.87
4	UDV	0.87	1.99	0.10	2.61
5	UDV	0.61	1.79	0.08	0.98
6	UDV	0.83	1.94	0.08	2.38
7	UDV	0.00	1.27	0.05	1.58
8	UDV	0.77	1.20	0.04	0.45
9	UDV	0.95	1.23	0.04	1.58
10	UDV	1.05	1.80	0.08	3.82
11	UDV	2.00	1.49	0.90	6.25
12	UDV	0.36	5.26	0.28	3.78
13	UDV	3.13	3.11	0.16	3.36
14	UDV	0.38	1.81	0.23	1.96
15	UDV	0.16	0.49	0.15	1.39
16	UDV	0.20	0.92	0.21	1.76
17	UDV	0.30	0.48	0.15	0.96
18	UDV	0.25	1.63	0.30	1.80
19	UDV	2.57	2.78	0.13	4.89
20	UDV	5.84	1.47	<0.01	1.83
21	Barquinha	12.67	5.42	0.09	5.58
22	Santo Daime	14.15	1.68	<0.01	1.98
23	Santo Daime	2.49	8.65	0.02	9.80
24	Santo Daime	3.17	12.79	0.02	8.74
25	Shuar	0.76	23.80	0.66	21.62
26	Shuar	0.56	18.40	0.58	22.85
27	Shuar	0.00	15.28	0.64	11.66
28	Shuar	4.12	12.51	0.02	14.46
29	Shuar	0.25	1.63	<0.01	1.80
Shuar paste		0.40	68.83	12.40	93.75

Cetkovich-Bakmas 1997), as if there were no other point of reference for this unique experience (Callaway 1988). While it may be difficult to render an entirely impartial analysis of either the theological or psychological nature of this phenomenon, objective methods can be applied to obtain reliable information on the phytochemical content of these beverages and their pharmacologic effect in healthy humans (Callaway et al. 1999, 1996, 1994).

The purpose of this article is to present the results from a phytochemical survey of several samples of *B. caapi* decoctions from a variety of sources to provide more accurate information on the nature of this inspiring beverage.

MATERIAL AND METHODS

All samples were collected from 1993 to 1998, and frozen at –20 C until the day of analysis. These samples were prepared by traditional methods, according to the religious doctrine of each source. In general, sections of *B. caapi* were respectfully collected and washed in water, pounded with a wooden mallet and carefully placed in a caldron, alternating layers with the carefully washed leaves of *P. viridis*. Water covered the vegetation and the mixture was thoroughly boiled, extracted and concentrated over several hours. The resulting extracts were a turbid to dark red-brown liquid, typically having the viscosity of fresh orange juice and a peculiar acrid taste. The preparation of these *vegetal* samples was always under the direction of experienced *vegetalistas* from the União do Vegetal (UDV), Santo Daime (SD), or Barquinha (Barq), all of which are religious groups in Brazil, or the indigenous Shuar peoples in Equador. All samples were analyzed using methods previously described (Callaway et al. 1996). Briefly, high pressure liquid chromatography (HPLC) with fluorescence detection was used to analyze all samples in a method previously described (Callaway et al. 1996). The

TABLE 2
Average Values (mean ± S.D., in mg/ml), Number of Samples (N) and Ranges of Alkaloid Profiles (mg/ml) for *Vegetal* Decoctions from Various Sources

Source	(N)	DMT	THH	Harmaline*	Harmine	THH:Harmine
Barquinha	(1)	12.67	5.42	0.09	5.58	0.97
Santo Daime	(3)	6.60 ± 6.65	7.71 ± 5.61	0.00	6.84 ± 4.24	1.13
		2.49 - 14.15	1.68 - 12.79	0.00	1.98 - 9.80	
Shuar	(5)	1.14 ± 1.69	14.32 ± 8.24	0.38 ± 0.34	14.48 ± 8.51	0.99
		0.00 - 4.12	1.63 - 23.80	0.00 - 0.66	1.80 - 22.85	
UDV	(20)	1.12 ± 1.37	1.82 ± 1.03	0.23 ± 0.26	2.25 ± 1.48	0.81
		0.00 - 5.84	0.45 - 5.26	0.00 - 0.90	0.45 - 6.25	
Total	(29)	2.09 ± 3.43	4.71 ± 6.01	0.23 ± 0.27	4.95 ± 5.91	0.95
		0.00 - 14.15	0.48 -23.80	0.00 - 0.90	0.45 - 22.85	

*Harmaline values less than 0.01 mg/ml are reported as 0.00 mg/ml

chromtographic column was packed with C-8 material and the mobile phase was 20% methanol, 20% acetonitrile and 60% 0.1 M ammonium acetate buffer, adjusted to pH 6.9 with acetic acid. Individual signals in the chromatogram were verified according to retention time and molecular weight by liquid chromatographic mass spectrometry (LC-MS), using a VG thermospray-plasma probe coupled to a VG Trio-2 quadropole mass spectrometer.

RESULTS AND DISCUSSION

Considerable variation was observed in alkaloid profiles between these samples, both within each source set and between sets (see Tables 1 and 2). All samples contained considerable amounts of harmine and THH and, to a lesser extent, harmaline. Harmaline was always detected, but sometimes this amount was below the limit of precise quantification in this study (<0.01 mg/ml). DMT was not detected in two samples; number 7 from the UDV and number 27 from the Shuar. Apparently the visual phenomenon from DMT may not be the main attraction in these products, as both were considered with the same reverence as DMT-containing samples for their utility as a sacrament. The suggestion that DMT may not be the main attraction in the human use of ayahuasca has already been put forward in an earlier publication (Freedland & Mansbach 1999).

Shuar Paste

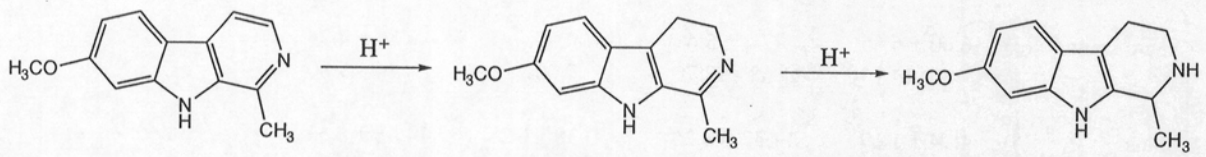
The highly concentrated paste from the Shuar (also know as the Jivaro) listed at the bottom of Table 1 was a unique sample, as both its preparation and use vary from the *vegetals*. As a semi-solid, this substance is sucked or licked to achieve the desired effect, and the peculiar bitter taste is a strong incentive to moderate the inevitable process of dose titration. It was surprising, however, to see such low amounts of DMT in this sample. The trace amount of DMT suggests that it was added to the decoction, probably through the leaves of *P. viridis* or *Diplopterys* spp., but the compound itself may have been lost through oxidation during the lengthy preparation and concentration of this *vegetal* paste. Alternatively, perhaps not much of the DMT-containing plant was added to this preparation, or maybe the plant material simply did not contain much DMT to begin with (see Callaway, Brito & Neves 2005 in this issue; also Verotta et al. 1999).

Phytochemical Variations Between Sources

The means and ranges for each source set of *vegetal* are presented in Table 2, again illustrating the phytochemical variations both within and between source sets. Overall, the alkaloid concentrations were lowest in *hoasca* from the UDV, where typical doses ranged between 100 to 200 ml. Only one sample was available from the Barquinha, which also had the highest level of DMT. It is not possible to say if this outstanding result is actually representative of this syncretic group, nor is there any information on the typical dosage for this *vegetal*. Except for one sample, the Shuar *vegetal* had considerably higher amounts of harmala alkaloids and surprisingly low amounts of DMT (Table 2). The typical dose of these concentrated *vegetals* from the Shuar was on the order of 20 to 30 ml. *Vegetals* from the Santo Daime were surprisingly low in harmaline, which could reflect some special aspect of the decoction process for those samples. Typical doses for these *vegetals* from the Santo Daime were about 50 to 100 ml.

FIGURE 1

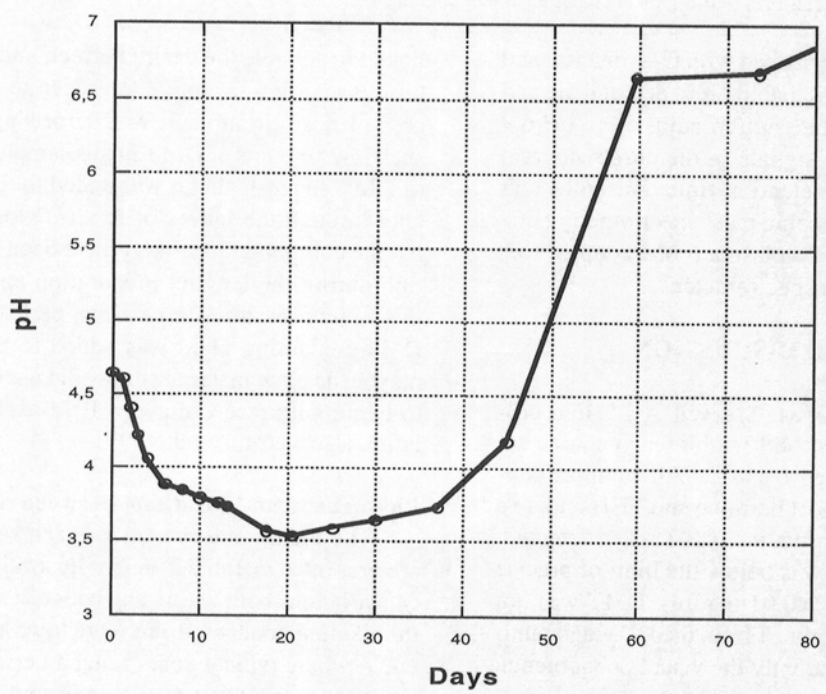
Chemical Reduction of Harmine and Harmaline to Tetrahydroharmine (THH) from *B. Caapi* Over Time During the Decoction Process, Under Naturally Acid Conditions



Harmine Harmaline Tetrahydroharmine

FIGURE 2

Variation in pH from a Single Sample of *Hoasca* from the UDV Over Time



In Situ Production of THH

The average ratio of THH to harmine in the *vegetals* was consistently near 1:1, from all sources (Table 2), while this ratio was closer to 1:5 in a large survey of source plant material (i.e., *B. caapi*; see Callaway, Brito & Neves 2005 in this issue). It is presently unclear whether harmine and harmaline are being chemically reduced to THH during the acidic process of decoction, or if THH is simply more stable than the other two harmala alkaloids, which maybe lost through decomposition, or a combination of both processes. Figure 1 illustrates a likely chemical pathway for the conversion of both harmine and harmaline to THH through reduction under acidic conditions.

Vegetal pH

One sample from the UDV was put on a shelf in the dark for 80 days at a room temperature of 23 C. There was no significant change in either alkaloid profile or composition during this time. However, the acidic pH of this beverage gradually changed to neutral as it began to ferment over time (Figure 2). Thus, it is not unusual to detect the sweet smell of ethanol in batches of *vegetal* that are

more than a few weeks old. The fiberous material in all *vegetals* will eventually settle out to form a thick sludge on the bottom of the container. Both the supernatant and the sludge are rich in alkaloids, and the fermented sediment can be diluted with acidic fruit juice before consumption, if at all.

CONCLUSION

A broad distribution of alkaloid profiles may be expected from such a extensive survey of plant-based decoctions from several sources, and particularly in combined plant derivatives that are produced under a wide variety of conditions. Dedicated groups and individuals use these preparations as their central sacrament on a regular basis, typically twice a month, although weekly usage is not uncommon. Those who are experienced with such decoctions universally report that every plant, every *vegetal* and especially every experience is unique, while at the same time similar. Of course, the same can be said of any psychedelic expedition, as the mental set of an individual is never quite the same from one moment to the next. Typically, the environmental setting can be fairly well controlled in such circumstances, and the actual dose is another important variable to consider. This underscores the responsibility of the presiding *mestre*, *shaman* or *padrinho* who has a working knowledge of both the *vegetal* and the individual. The use of such beverages has been demonstrated to be safe in a ceremonial setting, and provides an important catalyst for spiritual renewal.

Currently, the ceremonial use of *B. caapi* decoctions is protected by law in Brazil, and the religious use of these beverages can now be found in most urban areas of South America. These beverages form the spiritual core of several modern religions, which originate from a widespread indigenous practice throughout the Amazon River basin. Considering the apparent utility of this practice over such long periods of time, and across vast geographic regions, it should not be surprising that this unique plant technology has also found favor in contemporary urban cultures as well.

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