# Chemical Compounds Isolated from Banisteriopsis and Related Species

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The Malpighiaceae, to which the genus *Banisteriopsis* belongs, is a family distributed in tropical and sub-tropical humid regions of Africa and America. The genus *Banisteriopsis* is represented by about 75 species, which grow in America from Mexico and Cuba to Argentina, most of them in South America (*1*).

Only a few species of *Banisteriopsis* have been investigated chemically, and the first stimulus for the chemical work was the finding in the middle of the last century by the British explorer Spruce that a woody vine, which he classified as *Banisteria caapi*, later known as *Banisteriopsis caapi*, was the main ingredient employed in the preparation of an intoxicating drink by certain tribes living in the Amazonian Brazil. It was later found that the preparation and use of a similar beverage extended to a larger region, to what is today known as the eastern parts of Colombia, Ecuador, Perú and Bolivia, where it was given different vernacular names: ayahuasca, caapi, yagé, yajé, natem, natema, etc., names which were also applied to the plants employed for their preparation. Other plants were added and mixed with the former.

The history of the botanical, chemical and pharmacological implications of the beverage has been told in several opportunities and from several angles (*2*, *3*). While at the beginning there were difficulties in the identification of the alkaloids isolated from the extracts of the plants, and which were made responsible for the activity of the intoxicating drink, it seems that today, with the improvement of the methods of identification and the use of new techniques, we know exactly which are the bases isolated. There seem to be more difficulties from the botanical side. The lack in many chemical studies of plant specimens, or of a rigorous identification of the botanical material worked by the chemists, makes it impossible to know exactly which were the species employed. It is with this qualification that some of the botanical names are quoted in this paper.

Early chemical investigation of the plant employed in Colombia by the natives indicated the presence of an alkaloid which was given the name of telepathine as early as 1905 by Zerda Barron (*4*). A base supposed to be responsible for the activity of the drink was isolated in 1923, no doubt in impure form, by Fischer Cardenas (*5*) who conserved the name of telepathine.

Another isolation was carried out two years later by Barriga Villalba (*6*), who seems to be the first who obtained a crystalline product, to which he gave the name of yajéine. From the assigned formula, $C_{14}H_8N_3O_3$ and from its m.p.206°, we have now to conclude that it was an impure substance, although the lack of rotation is in agreement with what can be expected for an aromatic β-carboline structure. Another base was present in the mother liquors and named yajénine, but no constants were mentioned in the paper. According to Barriga Villalba, he worked the stems of a vine which was known by the vernacular name of yajé, and which according to Reinburg was *Haemadictyon amazonicum* (*Prestonia amazonica Spruce*), which is an Apocynaceae. Rios, in his review on the ayahuasca, mentions that in a later paper, Barriga Villalba states (*7*) that the plant he worked was not *P. amazonica*, but *B. caapi*, which is in agreement with the investigations of Schultes and Raffauf (*8*) on the use of the former species as a narcotic.

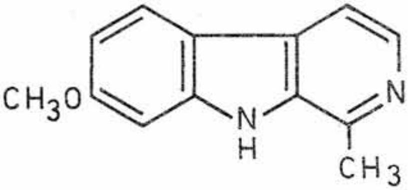
From what can be considered an authentic specimen of *B. caapi*, Perrot and Raymond-Hamet (*2*) isolated for the first time in pure condition one of the bases present in the plant (m.p.258°), for which they conserved the name of telepathine. A year later Lewin (*9*) described the isolation of an alkaloid from the same source, which he called banisterine. In his paper, Lewin says that the chemists from E. Merck (Darmstadt, Germany), considered banisterine identical to the base harmine (*I*), an alkaloid isolated more than a century ago from *Peganum harmala* L. (Zygophyllaceae). Two papers on the identification were published the same year almost simultaneously; one by Elger (*10*) and the other by Wolf and Rumpf (*11*), the latter workers being members of the Merck laboratories.

Elger employed plant material supplied by Raymond-Hamet and which was identified as *B. caapi*, according to A. W. Hill, then Director of the Kew Botanical Gardens. Sir Robert Robinson compared the alkaloid isolated by Elger (m.p.263–264°), with the harmine (*I*) from *P. harmala*, and with a synthetic sample, and concluded that they were identical. He comments on the difficulties of purifying harmine, which can explain the low melting point of the base obtained by Barriga Vallalba. Chen and Chen (*12*), who worked also with an authentic botanical specimen, confirmed the identification, and could isolate harmine from stems, leaves and roots.

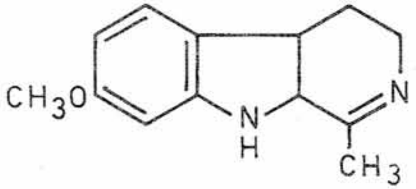
A plant identified as *B. caapi* Spruce was investigated many years later by Hochstein and Paradies (*13*). It was harvested near Iquitos, in Peru, where it was named ayahuasca. They confirmed the presence of harmine (I) and isolated also harmaline (II) and (+)-tetrahydroharmine (III). They state that the two latter alkaloids were found in a rather large amount. The same bases were also present in an aqueous extract of the plant "as used by the natives" but which appeared richer in harmaline and tetrahydroharmine than the extracts of the plant. They suggested that these two alkaloids may be the most active psychotomimetic components of the extracts.

All the bases isolated from *B. caapi* have a β-carboline skeleton, with different degrees of hydrogenation in the pyridine ring. Their structure was already known because of the interest of the chemists in similar alkaloids isolated from *P. harmala L.*, harmine (I) and harmaline (II), which culminated in the synthesis of harmaline (II) by Manske, Perkin and Robinson (*14*).

Although the racemic tetrahydroharmine had already been prepared in the laboratory, it was the first time that one of the enantiomers, (+)-tetra-



(I)



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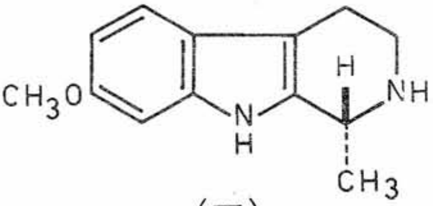

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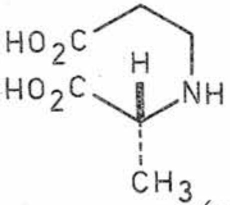


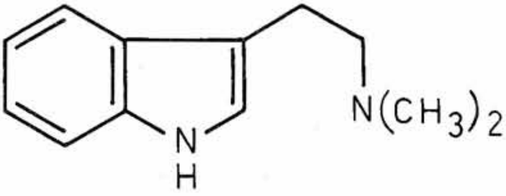
(IV)

hydroharmine (III), had been found in Nature. The dextro compound isolated by Hochstein and Paradies (*13*) was in fact a new natural base, and because of its pharmacological activity it was of interest to determine its absolute configuration. This was done recently by Koblicová and Trojánek (*15*), who found that its asymmetric carbon atom has the same chirality as the asymmetric carbon of D-alanine (IV), which is opposite to that of the protein aminoacid L-alanine.

Another species investigated has been *B. inebrians* Morton. O'Connell and Lynn (*16*) isolated harmine (I) from the stems of an authentic specimen collected by Schultes, and found that the leaves probably contains the same base. They could not detect harmaline nor harmalol. The same species was worked again by Poisson (*17*) in 1965, the plant being collected in a place named Nazareth, on the shores of the Marañon River, in Perú. He confirmed the presence of harmine in the stems and pointed out that another base, with the chromatographic properties of harmaline (II), was present in small amount.

Poisson investigated also the leaves of another species, *B. rusbyana* (Niedenzu) Morton, known to the natives as yajé, which were added to the stems of *B. inebrians* when ayahuasca was prepared. Surprisingly, this species did not contain alkaloids with a $\beta$-carboline structure, and the only base which he could identify was dimethyl-tryptamine (V). The amount was rather high (0.64%).

The species worked by Poisson were identified by Cuatrecasas. The finding of dimethyltryptamine (V) in *B. rusbyana*, a species used together with *B. inebrians* for the preparation of ayahuasca, is interesting for several reasons. One is that the same base was isolated by Hochstein and Paradies (*13*) from the extract of a plant which they considered to be *P. amazonica*, which received the local name of yagé, and which was used by the natives



(V)

to prepare ayahuasca as an additional component to *B. caapi*. Hochstein and Paradies received only an extract of the plant, whose identification is doubtful (*8*, *18*).

The second point of interest is that bases of the tryptamine type are typical components of other plants which have been used by the natives in many places of South America and in the Caribbean, for the preparation of intoxicating snuffs. They belong to the *Piptadenia* (Leguminosae) (*19*) and *Virola* (Myristicaceae) genus (*20*).

Other *Banisteriopsis* species have been mentioned as the main or additional ingredients employed in the preparation of ayahuasca. They are *B. quitensis* (Ndz) Morton (*21*), which according to Cuatrecasas (*1e*) is identical to *B. caapi* Spruce, *B. longialata* (*21*), and *B. metallicolor* Juss. (*B. lutea* Ruiz) (*3*).

I have not found in the literature any indication that authentic specimens of those plants have been submitted to chemical research, but because they are used in the preparation of intoxicating drinks, their investigation will be of much interest.

On the other hand, *B. crysophylla* Lam. a species which grows in Australia, is reported to contain alkaloids (*22*) and *B. nitrosiodora* Griseb, which is one of the species found in Argentina, is practically devoid of alkaloids (*23*). There remain a large number of species which have not even been submitted to a preliminary chemical investigation.

Harmine (I) has been isolated by Mors and Zaltzman (*24*) from the stems and leaves of another South American Malpighiaceae, *Cabi paraensis* Ducke, which is closely related to the *Banisteriopsis* genus. It grows in Brazil, in the upper Amazonian region and also in Perú (*3*). According to Duke (*25*), it is employed in popular medicine, although not for the preparation of intoxicating drinks.

It is worthwhile to note that only a few other species of Malpighiaceae have been investigated for alkaloids. One of them is *Lophantaera lactecens* (*L. longifolia*) which grows in the Amazonian, and is employed for the preparation of a kind of tea. Ribeiro and Machado (*26*) isolated from extracts of that plant a new base, lophanterine, which structure is unknown.

In his review on the Botanical Sources of the New World narcotics, Schultes (*21*) mentions in relation with the preparation of ayahuasca, two Malpighiaceae which, if botanical material became available, will deserve chemical attention. They are *Tetrapterys methystica*, from which an hallucinogenic drink is prepared in Colombia, on the limits of Brazil, and *Mascagnia psilophylla* var. *antifebrilis*, which was pointed out by Niedenzu as a source for the preparation of ayahuasca which in the opinion of Schultes is doubtful.

To my knowledge harmine (I), harmaline (II) and tetrahydroharmine (III), have never been isolated from other original American plants. They have been found to be present in intoxicating snuffs prepared by the natives from unknown botanical sources. We have two almost simultaneous reports. One is by Biocca, Galeffi, Montalvo and Marini-Bettolo (*27*), who from a snuff prepared by Tukano and Tariana Indians living in the valley of the Uaupes River, isolated harmine (I), harmaline (II) and tetrahydroharmine (III), exactly the same bases found in *B. caapi* by Hochstein and Paradies (*13*). According to the Italian authors, the snuff is named paricá and is prepared from a vine, which is also employed for the preparation of a drink. The species remained undetermined.

On the other hand, Bernhauer (*28*), has investigated a snuff employed by the Surara and Pakidai Indians, living near the River Demeni, a subsidiary of the Negro River, which he says is known as paricá, yopo, ebená or epená. He could isolate harmine (I) and (+)-tetrahydroharmine (III), while harmaline (II) was absent. The series of names given by Bernhauer to the drug that he investigated, shows how confused is its identification because samples of snuffs named epená, which were investigated not long ago by Holmstedt (*20*) and Marini Bettolo, Delle Monache and Biocca (*29*), contained only tryptamine bases. In my opinion this is a nice proof of the importance of the future interdisciplinary work, which is needed to clarify the botanical sources and the chemically active substances in the plants and in the drugs prepared by the natives.

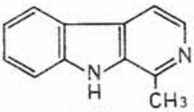
Both types of bases isolated from *Banisteriopsis* species are related to tryptamine. Tryptamine or a precursor, is one of the intermediates in the biogenesis of a large number of indole alkaloids, most of them with a more elaborate structure than the simpler β-carboline bases.

The type and distribution of the simple tryptamine bases found in plants have been recently reviewed (*30*). Work done in several laboratories in recent years have shown that bases with a typical β-carboline structure are also, like the tryptamines, not restricted in botanical or geographical distribution (see Table I).

The earlier representatives were isolated from *Peganum harmala* L. (Zygophyllaceae) more than a hundred years ago: harmaline (II) (1841), and harmalol (XVIII) (1841). The simplest base, harman (XI), was isolated from a Rubiaceae growing in Brazil in 1861 (*Arariba rubra* Mart., *Sickinga rubra* K. Schumm), and a few years later (1878) from *Symplocos racemosa* (Symplocaceae), indigenous to India.

Research in the last few years has lead to the isolation of other β-carbolines from plants growing in America. Bächli *et al.* (*31*), were isolated from *Strychnos melinoniana* Baill. (Loganiaceae), the quaternary base which is known as melinonine-F (XIV), and Antonaccio and Budzikiewicz (*32*)

Table I. Other β-Carboline Bases Found in Plants[a]



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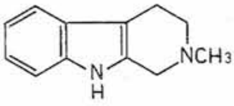

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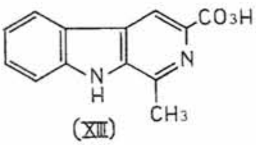

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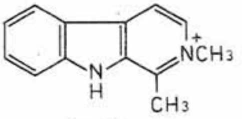

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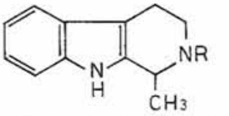
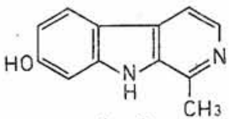


(XV) R = H ; (XVI) R = CH3



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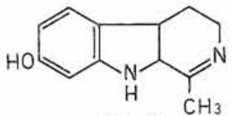

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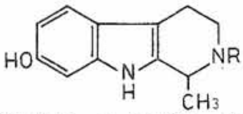


(XIX) R = H ; (XX) R = CH3

(XI) Harman. *Peganum harmala* L. (Zygophyllaceae) ; *Passiflora* spp. (Passifloraceae) (*39*) ; *P. incarnata L.* (*40, 41*) ; *Calligonum minimum* Lipski (Polygonaceae) (*42*).

(XII) *N*-Methyl-tetrahydro-β-carboline. *Hammada leptoclada* M. Iljin (*Arthrophytum leptocladum* Popov) (Chenopodiaceae) (*43*).

(XIII) Harman-3-carboxylic acid. *Aspidosperma polyneuron* Müll. Arg. (Apocynaceae) (*32*).

(XIV) Melinonine F. *Strychnos melinoniana* Baillon (Loganiaceae) (*31*).

(XV) Tetrahydroharman, elaeagnine (R=H). *Petalostyles labicheoides* R. Br. (Leguminosae) (*44*) ; *Elaeagnus angustifolia* L. (Elaeagnaceae) (*45*) ; *Leptactina densiflora* Hook. f. (Rubiaceae) (*38*) ; *Hammada leptoclada* M. Iljin (*46*) ; *Calligonum minimum* Lipski (*42*).

(XVI) *N*-Methyl-tetrahydroharman, leptocladine ($R=CH_3$). *H. leptoclada* M. Iljin (*43*) ; *Acacia complanata* A. Cunn. (Leguminosae) (*47*).

(XVII) Harmol. *P. incarnata* L. (*40*) ; *Zygophyllum fabago* L. (Zygophyllaceae) (*48*).

(XVIII) Harmalol. *P. harmala L.*

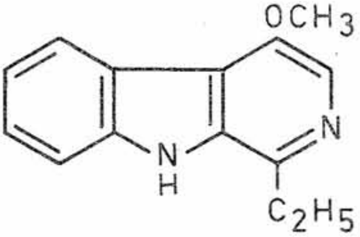
(XIX) Tetrahydroharmol (R=H). *Elaeagnus angustifolia* L. (*49*).

(XX) *N*-Methyl-tetrahydroharmol ($R=CH_3$). *E, angustifolia* L. (*49*).

[a] This list of species is not exhaustive. They have been selected to show the distribution of bases in different families.

harman-3-carboxilic acid (XIII) from *Aspidosperma polyneuron* Müll. Arg. (Apocynaceae).

Recently, in our laboratory Sanchez and Comin (*33*), found β-carbolines in *Aeschrion crenata* Vell., a Simaroubaceae which grows is Southern Brazil, Paraguay and Argentina. Although it is used in popular medicine, there is no indication that its extracts have intoxicating properties. The bases crenatine (VI) and crenatidine (VII) were isolated, together with 1-carbomethoxy-β-carboline (VIII), which has been formerly found in *Pleiocarpa mutica* Benth. (Apocynaceae) (*34*).



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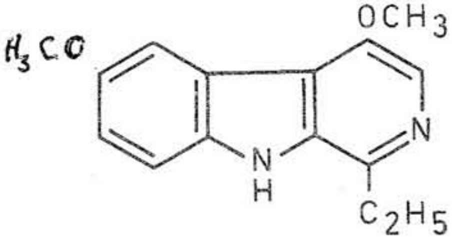

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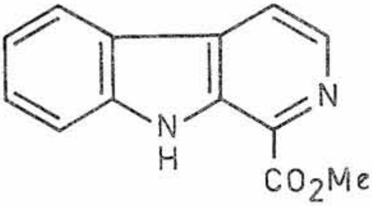


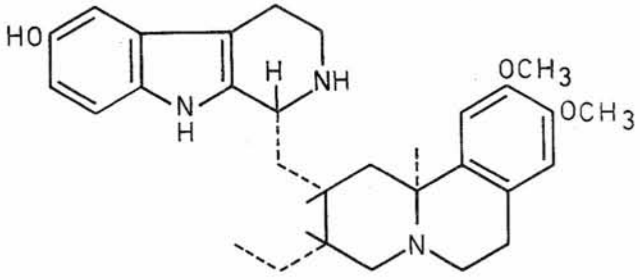
(VIII)

A $\beta$-carboline alkaloid with a more elaborated, novel type of structure, was isolated also in our laboratory by Brauchli *et al* (*35*), from *Pogonopus tubulosus* (DC) Schum. a Rubiaceae which grows in the Central and Northern part of Argentina, where in some places it is employed against fever. The base was named tubulosine (IX), and is structurally related to emetine (X) the tetrahydroisoquinoline moiety of the latter alkaloid being replaced by a $\beta$-carboline. Bases with this typical skeleton have been latter identified in *Alangium lamarckii* Thw. (Alangiaceae) (*36*) and in *Cassinopsis ilicifolia* Kuntze (Icacinaceae) (*37*).

It is of interest to note that besides *P. harmala*, the typical $\beta$-carbolines present in the *Banisteriopsis* species, have been isolated from a few species indigenous to other continents. In an African Rubiaceae, *Leptactine densiflora* Hook (±)-tetrahydroharmine (leptaflorine) (III) have been found (*38*). *Passiflora incarnata* L. and possible other *Passiflora* species (Passifloraceae) (*39*), contain harmine (I), which has also been found in *Zygophyllum fabago*, (*48*).

Other simple $\beta$-carbolines closely related in structure to the *Banisteriopsis* alkaloids have been isolated from other plants. They are listed in Table I with an indication of the source of isolation.

Many of the species containing $\beta$-carboline alkaloids have been used in popular medicine and several of the bases isolated have been submitted to pharmacological studies, and a few of them even employed in therapeutics. But outside America, so far as I know, plants containing those alkaloids have not been employed for their hallucinogenic properties.



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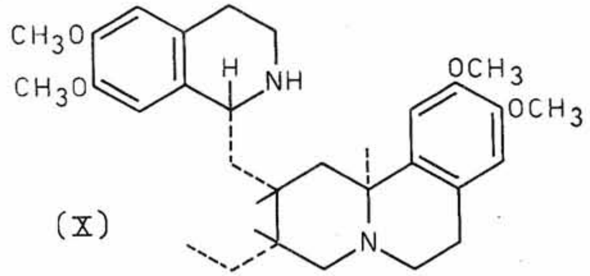

(X)

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