

The spider *Paracoelotes birulai*: detection and structure elucidation of new acylpolyamines by on-line coupled HPLC-APCI-MS and HPLC-APCI-MS/MS.

Chesnov, Sergiy; Bigler, Laurent; Hesse, Manfred
Helv. Chim. Acta (2000), 83(12), 3295-3305

Abstract

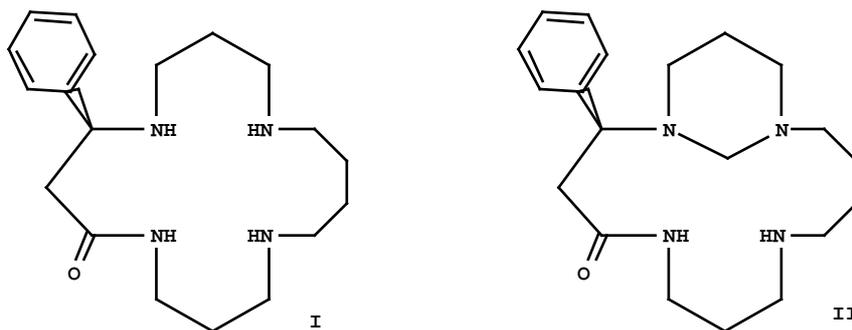
The lyophilized venom of the spider *Paracoelotes birulai* (Araneidae: Amaurobiidae) has been analyzed. A no. of acylpolyamines were found and sepd. By online coupled high-performance liq. chromatog. and atm.-pressure chem.-ionization mass spectrometry, the structures of the three most abundant compds. PB 490 (N-(16-guanidino-4-hydroxy-4,8,12-triazahexadecyl)-2-(4-hydroxyindol-3-yl)acetamide), PB 421 (N-(16-guanidino-4,8,12-triazahexadecyl)-4-hydroxybenzamide), and PB 448 (N-(16-amino-4-hydroxy-4,8,12-triazahexadecyl)-2-(4-hydroxyindol-3-yl)acetamide) were elucidated. Two different types of polyamines were found in the ?-palutoxins and compared with acylpolyamines from the Agelenidae spider family. The results of this investigation will initiate further chemotaxonomical studies on spiders.

Protoverbine, the parent member of a class of macrocyclic spermine alkaloids.

Guggisberg, Armin; Drandarov, Konstantin; Hesse, Manfred
Helv. Chim. Acta (2000), 83(11), 3035-3042

Abstract

The 17-membered macrocyclic spermine alkaloids protoverbine (8*S*)-8-phenyl-1,5,9,13-tetraazacycloheptadecan-6-one (I) and its N(9),N(13)-methylene-bridged deriv. protomethine (2*S*)-2-phenyl-1,5,9,14-tetraazabicyclo[12.3.1]octadecan-4-one (II) were isolated from *Verbascum pseudonobile* Stoj. et Stef. (Scrophulariaceae) and characterized. The synthesis of their racemates is described. The possible role of I and II as precursors in the biogenesis of the whole class of N(1),N(9)- and/or N(13)-substituted alkaloids, the groups of verbamethine, verbacine, incasine B/verdoline, verbamedine, and verbascenine is discussed.



Synthetic analogues to the spermidine-spermine alkaloid tenuilobine.

Popaj, Kasim; Guggisberg, Armin; Hesse, Manfred
Helv. Chim. Acta (2000), 83(11), 3021-3034

Abstract

Naturally occurring spider and wasp toxins are potent inhibitors of glutamate receptors in the central nervous system. They consist of a polyamine backbone and carboxylic acids or amino acids linked by peptide bonds. In some respects, the plant alkaloid tenuilobine, a deriv. of spermine and spermidine, shows structural similarities to these toxins. In the present paper, the synthesis of the five tenuilobine analogs is described. These derivs. differ in their arom. carboxylic acid subunits and in the polyamine moiety.

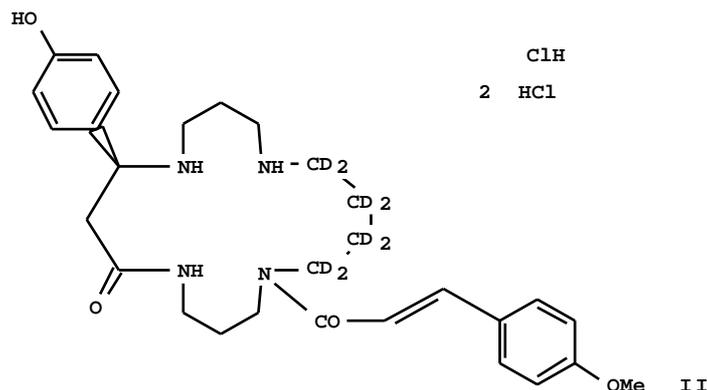
The asymmetric synthesis of the [D8]-labeled (-)-(S)-dihydroxyverbacine, the terminal precursor in the biogenesis of the macrobicyclic spermine alkaloids aphelandrine and orantine.

Nezbedova, Lenka; Drandarov, Konstantin; Werner, Christa; Hesse, Manfred
Helv. Chim. Acta (2000), 83(11), 2953-2960

Abstract

The asym. synthesis of the unlabeled and [D8]-labeled terminal precursors, (I) ((-)-(S)-dihydroxyverbacine) and (II), resp., in the biogenesis of the spermine alkaloids aphelandrine and

orantine, resp., is described. A partial synthesis of the alkaloid (-)-(S)-[(E)-4-methoxycinnamoyl]buchnerine (III) is also presented.



Dihydroxyverbacine is the terminal precursor in the biosynthesis of aphelandrine and orantine.

Nezbedova, Lenka; Hesse, Manfred; Drandarov, Konstantin; Werner, Christa
Tetrahedron Lett. (2000), 41(41), 7859-7862

Abstract

A microsomal-bound cytochrome P 450 enzyme system has been discovered in the roots of *Aphelandra squarrosa* that is responsible for the stereospecific intramol. phenol coupling of (S)-dihydroxyverbacine to aphelandrine. The biogenesis of the closely related alkaloids orantine (ephedradine A) and ephedradines B, C and D should follow a similar biogenetic pattern.

The main products of the low molecular mass fraction in the venom of the spider *Latrodectus menavodi*.

Horni, Albert; Weickmann, Dirk; Hesse, Manfred
Toxicon (2000), Volume Date 2001, 39(2-3), 425-428

Abstract

The low mol. mass fraction of the venom of the spider *Latrodectus menavodi*, a black widow spider domiciled in Madagascar, was analyzed with HPLC combined with electrospray mass spectrometry as lyophilized powder and as freshly milked liq. venom. The main components were found to be the purine derivs. adenosine, guanosine, inosine, and 2,4,6-trihydroxypurine. Compds. 1-3 are known as components of spider or snake venoms, but they have never been found previously in the venom of the species *Latrodectus*, whereas compd. 4 has not previously been found in any spider venoms. The lyophilized and unlyophilized venoms were found to have identical compn.

Antimicrobial activities of secondary metabolites produced by endophytic fungi from *Spondias mombin*.

Rodrigues, Katia F.; Hesse, Manfred; Werner, Christa
J. Basic Microbiol. (2000), 40(4), 261-267

Abstract

We performed a search for bioactive compds. produced by fungal endophytes from *Spondias mombin* (Anacardiaceae). Culture broth exts. of *Guignardia* sp., *Phomopsis* sp. and *Pestalotiopsis guepinii* were sep'd. by chromatog. methods and tested for biol. activities. The crude exts. of these endophytes were tested against fourteen organisms, including actinomycetes, Gram-neg. and Gram-pos. bacteria, yeast, and filamentous fungi. All fungal exts. inhibited actinomycete growth. *Guignardia* sp. was also active against *Escherichia coli*, *Staphylococcus aureus*, *Saccharomyces cerevisiae*, *Geotrichum* sp., and *Penicillium canadensis*. Culture exts. of *P. guepinii* were active against *S. cerevisiae*, while strains of *Phomopsis* sp. showed a pronounced antifungal effect against *Cladosporium elatum*, *Mycotypha* sp. and *S. cerevisiae*.

Synthesis of Aza-1,2-thiophenophanes by Double Ring Enlargement.

Heerklotz, J.; Linden, A.; Hesse, M
Tetrahedron (2000), 56(37), 7205-7210

Abstract

Two ring enlargement reactions are used to transform the alicyclic 8-membered allyl 2-oxocyclooctane-1-carboxylate to the 13-membered 10-aza-[11]-(2,3)-thiophenophane-1,9-dione. The first step yielded the macrocyclic imide allyl N-(3-thienylmethyl)-2,10-dioxo-1-azacyclodecane-3-carboxylate and, after deprotection, N-(3-thienylmethyl)-1-azacyclodecane-2,10-dione. In the second step, the N-thienyl substituent is incorporated in the large ring by the use of LDA. The overall yield was 45%. This method was also used to convert the 12-membered allyl 2-oxocyclododecane-1-carboxylate to the 17-membered 14-aza-[15]-(2,3)-thiophenophane-1,13-dione.

Photochemical ring enlargement of macrocyclic N-phenyl imides into cyclophanes.

Heerklotz, Jorg A.; Fu, Changchun; Linden, Anthony; Hesse, Manfred
Helv. Chim. Acta (2000), 83(8), 1809-1824

Abstract

Allylic N-Ph imides contg. 12- and 14-membered rings, such as 1-phenylazacyclododecane-1,2-dione (I) and 1-phenylazacyclotetradecane-2,14-dione (II), are easily synthesized by ring enlargement from cycloalkanones and Ph isocyanates. Irradn. of I and II in EtOH and MeCN, with high- and low-pressure Hg lamps, led, via the photo-Fries rearrangement, to the same primary products: an orthocyclophane and a paracyclophane. Besides the primary photorearrangement products, secondary products, aminocyclophanes were also formed. The total yields of the four products were very high when the N-Ph imides were irradiated in MeCN with a low-pressure Hg lamp (97 and 93%, resp.). If the para-position in I or II is blocked by a Me group, the para-photo-Fries rearrangement is prevented. In this case, only one primary photoproduct is formed (the corresponding orthocyclophane). The most remarkable result was obsd. on irrads. of the 12-membered 1-(4-methylphenyl)azacyclododecane-1,2-dione in MeCN (low-pressure lamp). It reacted nearly quant. to give only two products: 15-methyl-1-aza[12]orthocyclophane-2,12-dione (16-methyl-2-azabicyclo[12.4.0]octadeca-1(14),15,17-triene-3,13-dione) in 80% yield and 17-amino-14-methyl[11]metacyclophane-1,11-dione (17-amino-15-methylbicyclo[11.3.1]heptadeca-1(17),13,15-triene-2,12-dione) in 16% yield.

Benzoxazinoids-cyclic hydroxamic acids, lactams and their corresponding glucosides in the genus *Aphelandra* (acanthaceae).

Baumeler, Andreas; Hesse, Manfred; Werner, Christa
Phytochemistry (2000), 53(2), 213-222

Abstract

An improved method of sample prepn. and simultaneous HPLC sepn. was developed that allowed the sepn. of 2,4-dihydroxy-1,4-benzoxazin-3(4H)-one (DIBOA), 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3(4H)-one (DIMBOA), 2-hydroxy-1,4-benzoxazine-3(2H)-one (HBOA), 2-hydroxy-7-methoxy-1,4-benzoxazine-3(2H)-one (HMBOA) and their corresponding glucosides. The amt. and distribution of these compds. was detd. in the roots of *Aphelandra squarrosa* and *A. fuscopunctata* plants. There is a significant difference in the amt. and distribution of this substance class in the two species analyzed. The results are discussed in relation to their function as defense compds. and allelochems.