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Chemotaxonomy of the pantropical genus *Merremia* (Convolvulaceae) based on the distribution of tropane alkaloids ☆

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Abstract

The occurrence and distribution of tropane and biogenetically related pyrrolidine alkaloids in 18 *Merremia* species of paleo-, neo-, and pantropical occurrence have been studied. The extensive GC–MS study included members of almost all sections of the genus and has been carried out with epigeal vegetative parts as well as with roots. It comprises altogether 74 tropanes and 13 pyrrolidines including nicotine. Along with datumetine known already from a solanaceous species, the study led to the isolation (from *M. dissecta* and *M. guerichii*, respectively) and structure elucidation (spectral data) of four novel 3α-acyloxytropanes, merresectines A–D: 3α-(4-methoxybenzoyloxy)nortropane (A), 3α-kurameroyloxytropane (B), 3α-nervogenoyloxytropane (C), 3α-[4-(β-D-glucopyranosyloxy)-3-methoxy-5-(3-methyl-2-butenyl)benzoyloxy]tropane (β-D-glucoside of D). Moreover, the novel 3α,6β-di-(4-methoxybenzoyloxy)tropane (merredissine) has been isolated from *M. dissecta* and structurally elucidated. In addition the structures of datumetine and merresectine A could be confirmed by synthesis. Spectral data for two known 3α-acyloxytropanes (merresectine E β-D-glucoside, 4′-dihydroconsabatine) and one known 3β-acyloxytropane (concneorine) are documented for the first time. The structures of three further merresectines (F-H) have been determined by mass spectrometry. Furthermore, the linkage (2′,3- and 2′,4-, respectively) of two position isomer *N*-methylpyrrolidinylhygrines was proven by synthesis. The results of the study contribute to the solution of infrageneric taxonomic problems. Whereas all species yield pyrrolidine alkaloids without suitably differentiating results the diverging occurrence of tropane alkaloids leads to three groups of sections: (1) taxa free of tropanes, (2) taxa with simple tropanes, and (3) taxa with merresectines in addition to simple tropanes.

Keywords: *Merremia*; Convolvulaceae; Merremieae; GC–MS; Structure elucidation; Nicotine; Pyrrolidine alkaloids; Tropane alkaloids; Concneorine; 4′-Dihydroconsabatine; Merredissine; Merresectines; Chemotaxonomy

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1. Introduction

The convolvulaceous genus *Merremia* Dennst. ex Endl. comprising about 70 species (Deroin, 2001) is

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nested together with, e.g. *Hewittia*, *Operculina* within the tribal clade Merremieae s.s. according to a phylogenetic classification based on a molecular cladistic analysis and aligned with the traditional point of view (Stefanović et al., 2003). Most of the *Merremia* species sampled (Stefanović et al., 2002) form a moderately supported subclade including *M. dissecta*, *M. aegyptia*, *M. vitifolia*, however with several segregates (e.g. *M. umbellata*, *M. peltata*). Unfortunately, the relationships between the *Merremia* subclade and the *Merremia* segregates are largely unresolved. This is also one reason why a tribal clade definition has not yet been provided. The number of species included in the cladistic analysis has been rather low.

On the other hand, the classical infrageneric division into five sections is based on morphological/anatomical characters as established by Hallier (1893, 1894) and afterwards modified by Van Ooststroom (1939, 1953). Furthermore, the classical section Streptandra has been divided – at least for the species occurring in the Americas – into three novel sections, Cissoides, Halliera, Schizips by O'Donell (1941). Later, members from section Schizips have been segregated into Vitifolia allies and Tuberosa allies (Austin, 1998a,b) as have from section Halliera into a novel genus, *Xenostegia* (Austin and Staples, 1980). However, this latter segregation is still disputed (Deroin, 2001).

Complex resin glycosides, unique constituents of the Convolvulaceae, have also been detected in some *Merremia* spp., e.g. *M. mammosa* Choisy (Kitagawa et al., 1988), *M. tuberosa* (L.) Rendle sub nom. *Ipomoea tuberosa* L. (Ono et al., 1993), *Merremia hungaiensis* Lingelish. and Borza (Noda et al., 1994). However, at present there is little knowledge about low-molecular secondary metabolites of the genus *Merremia* as well as of the other genera of the tribe Merremieae s.s. though phytochemical data should be able to contribute to the solution of taxonomic problems in both taxa. Single occurrences are reported in literature, e.g. long-chained caffeates have been detected in *M. dissecta* and *M. tuberosa*, respectively (Garcia-Argaez et al., 1999), cyanogenic glycosides have been isolated from *M. dissecta* (Nahrstedt et al., 1989, 1990) and from *M. vitifolia* (Jenett-Siems, 1996), pyrrolidine and simple tropane alkaloids have been found in *M. gemella* as well as in *M. tuberosa* (Jenett-Siems and Eich, 1994). The aim of our phytochemical study on *Merremia* spp. has been to examine if the occurrence and distribution of these both types of related alkaloids might contribute to the infrageneric classification. For this purpose 18 species from all parts of the tropics have been included (Table 2). The study led to the discovery and structure elucidation of five novel tropane alkaloids; two of them represent the first glycosidic tropanes at all.

2. Results and discussion

2.1. Tropane alkaloids

2.1.1. Isolation and structure elucidation of novel aromatic 3α-acyloxytropanes

Isolation of alkaloids from *M. dissecta* roots was achieved by column chromatography on silica gel and preparative HPLC or TLC if necessary. In addition to the known alkaloid datumetine (**1**) which was identified by comparison with data from the literature (Siddiqui et al., 1986) and authentic synthesized material, four previously unknown alkaloids **2**, **3**, **4**, and **5** could be isolated. The structures have been elucidated by spectroscopic means (EIMS, HRMS, FABMS, ^{1}H NMR,^{13}C NMR, DEPT, ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-COSY, NOE).

In the EIMS, compound **2** gave a molecular ion peak at *m/z* 261 and significant peaks at *m/z* 110 (base peak), 135, and 152. From the HRMS spectrum of **2**, its molecular formula could be established as $C_{15}H_{19}NO_3$, corresponding to a molecular weight of 261.1368, 14 mass units less than datumetine (**1**). Taking into account the base peak at *m/z* 110 in contrast to the usual base peak at *m/z* 124 of tropan-3-ol esters, **2** should be the *N*-desmethyl derivative of datumetine or its 3β-isomer. The ^{1}H NMR and ^{13}C NMR spectra indeed were very similar to those of **1**, with the exception of the *N*-methyl region. The stereochemistry of H-3 of the tropanol moiety was deduced as β based on the one-proton triplet at δ 5.31 (1 H, $J = 5.2$ Hz). Further confirmation of the structure was achieved by synthesis of **2** and comparison of the spectral properties. We propose the trivial name merresectine A for this novel nortropane alkaloid which has been isolated also from the roots of *M. quinquefolia*.

Compound **3**, named merresectine B, showed a molecular ion peak at *m/z* 559 in the EIMS and its molecular formula was determined to be $C_{31}H_{45}NO_8$ by HRMS. The base peak at *m/z* 124, and characteristic fragments at *m/z* 140, 94, 83, and 82 in the EIMS spectrum were indicative of a tropan-3-ol ester. The (−)-FABMS of **3** exhibited a quasi-molecular ion peak at *m/z* 558 $[M-H]^-$ whereas the ion at *m/z* 396 $[(M-H)-162]^-$ suggested the loss of one hexosyl residue. The occurrence of a tropan-3-ol moiety was further confirmed by the ^{1}H NMR spectrum. A one-proton triplet at δ 5.18 (1 H, $J = 5.2$ Hz) indicated a β-orientation of H-3. In addition, the acyl moiety displayed two singlets at δ 1.73 and 1.76 for six protons each, a broad doublet at δ 3.62 (4 H, $J = 7.4$ Hz) coupled to a broad triplet at δ 5.32 (2 H, $J = 7.4$ Hz). These characteristic signals indicated the presence of two prenyl groups. Moreover, a singlet for two aromatic protons at δ 7.71 was observed, indicative of a symmetric tetrasubstituted benzoyl moiety. A doublet at δ 4.82 ($J = 7.4$ Hz) was assigned to the anomeric proton of the hexose residue (H-1′′′′), thus revealing a β-linkage to the aglycone. In addition, irradiation of this anomeric proton signal caused a NOE enhancement of the signal at δ 3.62, indicating that the prenyl groups were attached to C-3′ and C-5′, respectively. Thus, the structure of the acyl moiety was identified as kurameric acid which had been discovered as acyl component of ester alkaloids of choline or a necine base, isolated from *Liparis kurameri* French and Sav. and *L. kumokiri* F. Maekawa (Orchidaceae), respectively (Nishikawa et al., 1967). Kurameric acid was then established to be the 4-β-D-glucoside of 3,5-bis-(3-methyl-but-2-enyl)-4-hydroxybenzoic acid (nervogenic acid). Merresectine B (**3**) has been isolated also from the roots of *M. cissoides* and *M. quinquefolia*, respectively.

The molecular formula of **4** was determined to be $C_{25}H_{35}NO_3$ by HRMS. In the EIMS spectrum, it was characterized by a molecular ion peak at *m*/*z* 397 and significant fragments hinted again to a derivative of tropan-3-ol. This was confirmed by the ^{1}H NMR and ^{13}C NMR spectra. The additional signals were similar to those of the kurameric acid moiety of merresectine B (**3**) but no signals of a glucosyl residue could be detected. Thus, compound **4** had to be the aglycone of merresectine B and was named merresectine C.

Compound **5** exhibited a molecular ion peak at *m*/*z* 425, corresponding to the molecular formula $C_{24}H_{27}NO_6$ determined by HRMS. Other diagnostic peaks could be observed at *m*/*z* 274, 138, 135, 122, 107, 95 and 94 (base peak). This pattern hinted to a derivative of 6-hydroxytropan-3-ol. The ^{1}H NMR (Table 5) exhibited signals for two *p*-substituted benzoyl moieties and a singlet for six protons at δ 3.87, hinting to two aromatic methoxy groups. The orientation of the hydroxyl groups of the tropane moiety was deduced from the coupling constants. H-3 exhibited a triplet ($J = 5.0$ Hz) at δ 5.33, characteristic for a β-orientation of this proton. H-6 was observed as a dd ($J = 3.0$ Hz, 7.5 Hz) at δ 5.87. This is in agreement with an angle of 90° between H-6 and H-5 corresponding to a coupling constant of more or less 0 Hz, thus proposing an α-orientation of H-6. According to MMX-calculations[1] for the epimer with a β-orientation of H-6 a dihedral angle of about 30° (coupling constant about 8.0 Hz) should be expected. These results were confirmed by NOE experiments. In conclusion compound **5** has to be 3α,6β-bis-(4-methoxybenzoyloxy)tropane which we named merredissine.

The crude alkaloid fraction of the roots of *M. guerichii* showed two main spots giving a positive reaction with Dragendorff's reagent on TLC. Preparative HPLC afforded merresectine B (**3**) and one further compound **6**. Its EI mass spectrum showed a molecular ion peak at *m*/*z* 521 corresponding to a molecular formula of $C_{27}H_{39}NO_9$ determined by HRMS. The fragment at *m*/*z* 359 (base peak) again indicated the loss of a hexosyl moiety. The ^{1}H NMR data of **6** were very similar to that of merresectine B, but showed only one prenyl residue. Instead, a signal for an aromatic methoxy group was observed. Thus, **6** which we named merresectine D β-D-glucoside, has to be an ester of tropan-3α-ol with 4-(β-D-glucopyranosyloxy)-3-methoxy-5-(3-methyl-but-2-enyl) benzoic acid.

The 4-β-D-glucoside (**72a**) of Merresectine E (**72**) has been identified in six *Merremia* spp. and was structurally elucidated based on the isolation from the roots of *Convolvulus sabatius* Viv. ssp. *sabatius*. The compound exhibited a quasi molecular ion peak at *m*/*z* 492 $[M+H]^+$ in the (+)-FABMS spectrum, corresponding to a molecular formula of $C_{26}H_{37}NO_8$. The base peak at *m*/*z* 124, and further characteristic fragments in the EIMS spectrum were again indicative of a tropan-3-ol ester. The structural features deduced from the ^{1}H NMR spectrum resembled those of merresectine D β-D-glucoside with the exception that three aromatic protons at δ 7.03, 7.82, and 7.84, but no methoxy group were observed. Thus the aglycone of merresectine E β-D-glucoside (**72a**) has to be 3α-[4-hydroxy-3-(3-methylbut-2-enyl)benzoyloxy]tropane which is glucosylated via the 4′-hydroxy group.

2.1.2. Occurrence of aromatic 3α-acyloxytropanes detected by GC–MS

Aromatic 3α-acyloxytropanes have been discovered in *Convolvulus* spp. from Middle Asia, e.g. convolamine (3α-veratroyloxytropane; Orechoff and Konowalowa, 1934) or phyllalbine (3α-vanilloyloxytropane, **65**; Sharova et al., 1980). **65** could be detected also in the genus *Merremia* (*M. guerichii*, *M. kentrocaulos*), but its veratroyl congener has not been found in any of its species. Instead, 3α-(4-hydroxybenzoyloxy)tropane (**62**) turned out to be a constituent of *M. dissecta*, *M. guerichii*, and *M. kentrocaulos*. Furthermore, its 4-*O*-methyl congener datumetine (**1**) and also the corresponding *N*-demethylated (nor) derivative merresectine A (**2**) have been present together in *M. dissecta* as well as in *M. quinquefolia*.

The merresectines C–E (**4**, **75**, **72**) have been detected in 3 species (**75**), 6 spp. (**72**), and 8 spp. (**4**), respectively. The β-D-glucoside B (**3**) is not detectable by GC–MS directly and therefore not included in the analysis; however, it is detectable as its aglycone C (**4**) after decomposition in the instrument. Thus, D (**75**) as well as E (**72**) may also be present as glycosides in the plants, as has been proven by isolation from *M. guerichii* and *C. sabatius*, respectively. All these compounds differ from the simple aromatic 3α-acyloxytropanes mentioned

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[1] PC Model 4.0, Serena Software.

above in that their aromatic acyl moieties are prenylated in one (**72**, **75**) or even both (**4**) ortho positions to the hydroxyl at C-4′. Finally, merresectine F (**79**) should be mentioned; it is unequivocally a dehydro derivative of merresectine C (**4**), i.e. **4** minus two hydrogen atoms. Since there is no other plausible possibility **79** should be 3α-[4-hydroxy-3-(3-methyl-buta-1,3-dienyl)-5-(3-methyl-but-2-enyl)benzoyloxy]tropane. **79** is present in all eight species containing **4** (Table 1). Again the 3β epimer of **79** (**80**) could be detected in four of the six species containing **4** as well as **83** and in addition even in one species, *M. aegyptia* in which **4** has been found but not **83**. Thus, merresectine G (**81**) lacking four hydrogen atoms, only present in *M. dissecta*, should be a congener of **4** with an additional double bond each in both prenyl residues. Furthermore, merresectine H (**69**) represents merresectine E (**72**) minus 2 H.

3α-(4-Hydroxybenzoyloxy)tropane (**62**) might be a precursor of a biogenetic sequence merresectine E (**72**) → C (**4**) → B (**3**) and on the other hand of a sequence phyllalbine (**65**) → merresectine D (**75**), respectively. The co-presence of 3α- as well as 3β-epimers of C (3α: **4**; 3β: **83**) in six species, of D (3α: **75**; 3β: **77**), and of 3-(4-hydroxybenzoyloxy)tropane (3α: **62**; 3β: **63**) in two species each may indicate that the corresponding acyl moieties have been synthesized first before they are transmitted to both 3-hydroxytropane epimers in a last step of the alkaloid biosynthesis. Anyhow, datumetine (**1**) and its *N*-demethylated congener merresectine A (**2**) both only formed in the same two species lead – apparently not lying on the principal pathway – to a dead end from the biogenetical point of view due to their 4-methoxy substituent.

*2.1.3. Occurrence of consabatine (**68**) and 4′-dihydroconsabatine (**70**) detected by GC–MS; isolation and structure elucidation of **70***

Consabatine (**68**), an ester of tropan-3α-ol with 1-hydroxy-3-(3-methyl-but-2-enyl)-cyclohex-2-en-4-one carboxylic acid (2-deoxyconsiculic acid) discovered in *Convolvulus sabatius* Viv. ssp. *mauritanicus* (Jenett-Siems et al., 1998) turned out to be also a metabolite of *M. quinata*. This is also true for its 4′-dihydro congener (**70**), 3α-[1,4-dihydroxy-3-(3-methyl-but-2-enyl)-cyclohex-2-enecarboxy]tropane which has been structurally elucidated based on the isolation from the roots of *Convolvulus sabatius* Viv. ssp. *sabatius*. 4′-Dihydroconsabatine (**70**) again showed characteristic fragments for a tropan-3-ol ester in the EIMS. Its molecular formula was deduced as $C_{20}H_{31}NO_4$ from the molecular ion peak at *m*/*z* 349 in the HRMS. The ^1H NMR spectrum also displayed typical tropan-3α-ol resonances. The acyl residue was characterized by a prenyl moiety as in the merresectines but in contrast to these, no aromatic proton resonances were observed. In the HMBC spectrum, the methylene protons of the prenyl moiety showed long-range correlations to a quaternary olefinic carbon at δ 145.4, another olefinic carbon at δ 123.5 corresponding to a singlet at δ 5.42 in the proton NMR spectrum, and an oxygen bearing carbon at δ 67.5. The ^{13}C NMR spectrum showed four further carbon atoms: two methylene carbons at δ 31.2 and 28.9 which had to be in neighbourhood due to the H-H-COSY, one quaternary oxygen bearing carbon at δ 72.1, and one carbonyl carbon at δ 175.3 which had to be esterified to the tropan-3-ol residue. These structural features very much resembled those of consabatine (**68**), the molecular mass of which is two units lower and which bears a carbonyl function in position 4′ instead of the secondary hydroxy group in 4′-dihydroconsabatine (**70**).

Since **68** and **70** are accompanied by the prenylated merresectines, especially E (**72**) in *C. sabatius* as well as in *M. quinata* it may be concluded that **72** has to be the precursor of **68** and **70** rather than vice versa. Otherwise it would not be plausible that merresectines are present in seven additional *Merremia* spp. which did not even show traces of **68** and/or **70**.

*2.1.4. Occurrence of 3α-benzoyloxytropane (**56**) and 3α-nicotinoyloxytropane (**57**) detected by GC–MS*

Two other, rare tropane alkaloids, 3α-benzoyloxytropane (**56**) and 3α-nicotinoyloxytropane (**57**), were discovered previously in the brassicaceous genus *Cochlearia* and structurally confirmed by synthesis (Bachmann, personal communication). Both have been detected unequivocally in *M. vitifolia* though in very low concentrations. Nicotinic acid is an unusual aromatic acyl component for tropanols because all known aromatic or arylaliphatic acids esterified with this skeleton are biogenetic derivatives of phenylalanine.

2.1.5. Occurrence of aliphatic 3α-acyloxytropanes detected by GC–MS

Esters of tropan-3α-ol (tropine, **16**) with aliphatic acids seem to be rather rare in the genus: 3α-acetoxytropane (**20**) could be detected in three *Merremia* spp. (*M. dissecta*, *M. kentrocaulos*, *M. vitifolia*); further aliphatic 3α-acyloxytropanes are confined to *M. guerichii* and *M. vitifolia*, respectively. Thus, such aliphatic esters have been detected only in altogether four out of 18 species. In addition a few corresponding *N*-demethylated (nor) derivatives (**25**, **34**, **39**) occur in *M. guerichii*.

2.1.6. Occurrence of 6-substituted tropanes detected by GC–MS

Remarkably only three species, *M. aegyptia*, *M. dissecta*, and *M. guerichii* have shown the additional occurrence of 6-substituted tropanes. 6β-Hydroxytropane-3-one (**23**) has been detected in every three species suggesting that a hydroxylation at C-6 might take place already at an early stage of the biosynthesis. Furthermore, in the samples of *M. dissecta* 6-acetoxytropan-3-ol (**32**) and 6-(methoxybenzoyloxy)tropan-3-ol (**67**) have been identified. However, *M. guerichii* turned out to possess an even more complex pattern concerning 6-substituted tropanes: 6-acyloxytropan-3-ols (**41**, **50**, **52**, **53**, **55**), 6-acyloxynortropan-3-ols (**40**, **48**), 6-hydroxy-3-acyloxytropanes (**49**, **54**), and one 3,6-diacyloxytropane (**59**). The stereochemistry at C-6 and also at C-3 could not be determined by GC–MS without corresponding references (Table 1). However, there are two facts supporting at least for some compounds 6β-configuration: (1) The co-occurrence of the unequivocal 6β-hydroxytropan-3-one (**23**); (2) the isolation and structure elucidation of 3α,6β-di-(4-methoxybenzoyloxy)tropane (merredissine, **5**) from *M. dissecta* leading to the assumption that the monoacylated congener (**67**) mentioned above might be its precursor, i.e. **67** should be 6β-(4-methoxybenzoyloxy)tropan-3α-ol. Moreover, this is additionally supported by the fact that the tropan-3α-ol derivative datumetine (**1**), the alternative potential precursor of **5** is also a component of the alkaloid pattern of this species. However, **5** and **67** are unique in the genus. Whether or not the 6-substituted tropanes of *M. guerichii* are also – in total or in part – 3α,6β-configurated remains to be elucidated though **23** is also present in this species, which could be in favour of 6β-configuration. Moreover, conspicuously neither any aromatic 6-acyloxy derivative nor any 6-hydroxy derivative of an aromatic 3-acyloxytropane and nortropane, respectively, was detected though *M. guerichii* is a rich source of, e.g. merresectines. Nevertheless, this might be at least in part due to methodological problems, since detection of authentic merredissine (**5**) was not possible with our GC–MS system. This is the first report on 6-substituted tropanes in the Convolvulaceae.

*2.1.7. Occurrence of 3β-acyloxytropanes detected by GC–MS; isolation and structure elucidation of concneorine (**66**)*

The broad occurrence and distribution of calystegines (polyhydroxynortropan-3β-ols) as well as their lipophilic precursors tropan-3β-ol (pseudotropine, **17**) and nortropan-3β-ol (**15**), respectively, in the family Convolvulaceae in general and also within the genus *Merremia* has been documented recently (Schimming et al., 2005). In the present study **17** could be detected in 10 species. However, the occurrence of acylated derivatives is confined to altogether seven species suggesting that not all *Merremia* spp. which are synthesizers of 3α-acyloxytropanes seem to possess pseudotropine acyl transferase activities (Robins et al., 1991, 1994, Rabot et al., 1995). Only four aliphatic 3β-esters have been detected: the acetyl derivative **22** in *M. dissecta* and the *n*-butyryl derivative **26** as well as its congeners **36** and **47** in *M. guerichii*. In both species these metabolites are accompanied by their corresponding 3α-isomers. Five 3β-acyloxytropanes bearing aromatic acyl residues (**63**, **66**, **77**, **80**, **83**) turned out to be constituents of *M. guerichii* and *M. kentrocaulos*, respectively. The 3β-epimer **83** of merresectine C (**4**) has also been present in *M. cissoides*, *M. dissecta*, *M. quinquefolia*, and *M. vitifolia*, whereas the 3β-epimer **80** of merresectine F (**79**) is also a constituent of *M. aegyptia*, *M. cissoides*, and *M. dissecta*. All these aromatic 3β-acyloxytropanes again are accompanied by their 3α-congeners (see also Section 2.1.2). 3β-Vanilloyloxytropane, named concneorine (**66**) has been originally isolated from the epigeal vegetative parts of the Mediterranean silver bush, *Convolvulus cneorum* L. (Mann, 1997). The structure elucidation by spectral data is documented now for the first time. The compound displayed a molecular ion peak at *m*/*z* 291 in the EIMS spectrum corresponding to a molecular formula of $C_{16}H_{21}NO_4$ (HRMS) and thus should be an isomer of phyllalbine (=3α-vanilloyloxytropane, **65**). Indeed, the proton NMR spectrum showed characteristic signals for a vanilloyl residue and resonances of a tropanol moiety with the typical multiplet of H-3α at δ 5.24. Thus, concneorine is the 3β-isomer of phyllalbine. This is the first report on 3β-acyloxytropanes in the Convolvulaceae.

*2.1.8. Occurrence of methylpseudoecgonine (**30**) detected by GC–MS*

Methylpseudoecgonine (2α-methoxycarbonyltropan-3β-ol, **30**) has been discovered in *Datura stramonium* (Solanaceae) by comparison of all four synthesized isomers (Bachmann and Witte, personal communication). Interestingly, it has been detected also in the genus *Merremia*, but only in *M. aegyptia* and *M. gemella*, respectively. This is the first report on **30** in the Convolvulaceae.

2.2. Pyrrolidine alkaloids including nicotine

*2.2.1. Structure elucidation of two N-methylpyrrolidinylhygrines (**7**, **8**) by synthesis*

GC–MS analysis revealed the occurrence of a large number of pyrrolidine and tropane alkaloids. The detected *N*-methylpyrrolidinylhygrines, isomers of cuscohygrine (**43**), were, like most other aliphatic tropane esters, previously known from the Solanaceae (Witte et al., 1987), where their structures were established on the basis of MS-data alone. They were proposed to be isomeric 2′,4-*N*-methylpyrrolidinylhygrines. We now synthesized both compounds according to a method proposed by Galinovsky et al. (1951) for the preparation of cuscohygrine and elucidated their structures by NMR spectrometry. The ^{13}C NMR was interpreted in analogy to that of **43**. For compound **7** C-2/C-2′

Table 1
Pyrrolidine and tropane alkaloids in *Merremia* species detected by GC–MS (relative abundance in %); for mass fragmentation patterns see Table 3

Alkaloid	RI	M^+	medium	tridentata	aurea	tuberosa	emarginata[a]	gemella	hederacea	pterygocaulos[a]	umbellata	peltata[a]	aegyptia	dissecta	vitifolia	guerichii	quinata[a]	cissoides	quinquefolia	kentrocaulos
Pyrrolidine alkaloids																				
Hygrine (**9**)	1060	141	t/-	t/-	t/-	60/-	t	7/50	13/1	t	8/-	t	9/5	t/-	2/-	6/25	2	10/1	5/-	10/-
Hygroline A (**10**)	1075	143	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/-	-	-/-	5/t	-/-
Hygroline B (**11**)	1088	143	-/-	-/-	-/-	-/-	-	-/-	-/-	t	-/-	-	-/-	-/-	-/-	-/-	-	-/-	8/t	-/-
Nicotine (**21**)	1310	162	t/t	t/t	t/t	-/-	-	t/t	t/t	-	t/t	t	t/t	-/t	-/t	-/-	8	-/-	t/t	t/-
5-(2-Oxopropyl)-hygrine (**27**)	1442	197	-/-	-/-	t/-	-/-	-	5/5	1/1	-	-/-	-	-/-	t/-	t/-	1/t	-	-/-	-/-	t/-
5-(2-Hydroxypropyl)-hygrine (**28**)	1452	199	-/-	-/-	t/-	-/-	t	t/5	t/-	-	5/-	-	3/t	-/-	2/-	t/-	-	-/-	-/-	1/-
5-(2-Hydroxypropyl)-hygroline (**31**)	1478	201	-/-	-/-	t/-	-/-	t	t/-	1/-	-	20/-	-	35/80	3/-	10/t	t/-	-	-/-	-/-	4/-
2',4-*N*-Methyl-pyrrolidinylhygrine (**8**)	1567	224	-/-	-/-	-/-	5/-	-	5/1	55/20	-	t/-	-	40/-	-/-	t/-	1/t	-	2/-	1/-	3/-
2',3-*N*-Methyl-pyrrolidinyhygrine (**7**)	1577	224	-/-	-/-	-/-	4/-	-	10/3	23/60	-	t/-	-	5/t	-/-	t/?	1/t	-	3/-	1/-	2/-
Cuscohygrine (**43**)	1650	224	-/-	-/-	-/-[b]	25/-	-	65/15	2/10	-	48/-	t	3/t	-/?	75/?	50/60	t	70/95	5/-	70/-
Phygrine (**58**)	2043	280	-/-	-/-	-/-	-/-	-	-/-	-/3	-	-/-	-	-/-	-/-	2/-	3/1	-	-/-	-/-	1/-
N-Methylpyrrolidinyl-cuscohygrine A (**60**)	2165	307	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	1/-	-	-/-	-/-	1/-
N-Methylpyrrolidinyl-cuscohygrine B (**61**)	2173	307	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	1/-	-	-/-	-/-	1/-
Simple tropanes and aliphatic 3-acyloxytropanes																				
Nortropan-3-one (**12**)	1133	125	-/-	-/-	-/-	-/-	-	-/-	-/-	t	-/-	-	t/8	2/-	t/-	-/-	-	-/-	1/t	t/-
Cyclotropine[c] (**13**)	1137	139	-/-	-/-	-/-	-/-	-	t/-	t/t	-	1/-	t	-/-	1/-	t/-	-/-	-	-/-	1/-	-/-
Tropan-3-one (**14**)	1150	139	-/-	-/-	t/-	1/t	t	3/15	t/t	t	-/-	-	t/1	40/-	1/t	t/1	-	t/-	1/-	1/-
Nortropan-3β-ol (**15**)	1160	127	-/-	-/-	-/-	-/-	-	-/-	-/-	-	2/-	-	-/-	5/-	-/-	-/-	-	-/-	-/-	-/-
Tropan-3α-ol (**16**)	1167	141	-/-	-/-	-/-	-/-	-	-/-	-/-	-	2/-	t	-/-	30/-	t/-	t/-	-	-/-	t/-	t/-
Tropan-3β-ol (**17**)	1187	141	-/-	-/-	-/-	-/-	t	-/-	-/-	-	12/-	t	1/-	5/-	3/t	t/-	-	1/-	t/-	t/-
3α-Acetoxynortropane (**18**)	1292	169	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	t/-	-/-	-	-/-	-/-	-/-
3β-Acetoxynortropane (**19**)	1296	169	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
3α-Acetoxytropane (**20**)	1308	183	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	1/-	-/-	-	-/-	-/-	t/-
3β-Acetoxytropane (**22**)	1315	183	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
3α-Propionyloxy-tropane (**24**)	1405	197	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	-/-	-	-/-	-/-	-/-
3α-*n*-Butyroxy-nortropane (**25**)	1435	197	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3β-*n*-Butyroxy-nortropane (**26**)	1440	197	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3α-Isobutyroxytropane (**29**)	1455	211	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/t	3/t	-	-/-	-/-	-/-
Methylpseudoecgonine (**30**)	1473	199	-/-	-/-	-/-	-/-	-	1/1	-/-	-	-/-	-	-/-	-/-	-/-	-/-	-	-/-	-/-	-/-
3-(Hydroxybutyroxy)-tropane (**33**)	1524	227	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3-(2-Methylbutyroxy)-nortropane (**34**)	1532	211	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3α-(2-Methylbutyr-oxy)tropane (**35**)	1547	225	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	2/t	-	-/-	-/-	-/-

(*continued on next page*)

Table 1 (*continued*)

Alkaloid	RI	M^+	medium	tridentata	aurea	tuberosa	emarginata[a]	gemella	hederacea	pterygocaulos[a]	umbellata	peltata[a]	aegyptia	dissecta	vitifolia	guerichii	quinata[a]	cissoides	quinquefolia	kentrocaulos
3β-(2-Methylbutyr-oxy)tropane (**36**)	1552	225	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	1/t	-	-/-	-/-	-/-
3-(Hydroxypentanoyl-oxy)nortropane (**37**)	1603	227	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3-(Hydroxypentanoyl-oxy)tropane (**38**)	1616	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3α-Tigloyloxy-nortropane (**39**)	1630	209	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3α-Tigloyloxytropane (**42**)	1646	224	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/t	-	-/-	-/-	-/-
3-(Hydroxyisovaler-oxy)tropane (**44**)	1669	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-/-	-/-	-/-	-/-
3-(Hydroxybutyroxy)-tropane (**45**)	1672	227	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
3α-(Hydroxy-2-methyl-butyroxy)tropane (**46**)	1698	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	t/-	-	-/-	-/-	-/-
3β-(Hydroxy-2-methyl-butyroxy)tropane (**47**)	1705	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	t/-	-	-/-	-/-	-/-
3-Hexanoyloxytropane (**51**)	1755	255	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Substituted tropanes																				
6β-Hydroxytropan-3-one (**23**)	1325	155	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	1/t	5/-	-/-	t/1	-	-/-	-/-	-/-
6-Acetoxytropan-3-ol (**32**)	1500	199	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	2/-	-	-/-	-/-	-/-
6-Butyroxynortropan-3-ol (**40**)	1632	213	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Butyroxytropan-3-ol (**41**)	1634	227	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Pentanoyloxy-nortropan-3-ol (**48**)	1719	227	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Hydroxy-3-(2-methylbutyroxy)-tropane (**49**)	1728	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-(2-Methylbutyroxy)-tropan-3-ol (**50**)	1730	241	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	8/-	-	-/-	-/-	-/-
6-(2-Hydroxy-2-methylbutyroxy)-tropan-3-ol (**52**)	1809	257	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-(2-Hydroxy-2-methylbutyroxy)-tropan-3-ol (**53**)	1811	257	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Hydroxy-3-tigloyloxytropane (**54**)	1823	239	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-Tigloyloxytropan-3-ol (**55**)	1835	239	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-(Hydroxybutyroxy)-3-pentanoyloxytropane (**59**)	2150	327	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	-/-
6-(Methoxybenzoyl-oxy)tropan-3-ol (**67**)	2412	291	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
Aromatic 3-acyl-oxytropanes and derivatives																				
3α-Benzoyloxytropane (**56**)	1907	245	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	-/-	-	-/-	-/-	-/-
3α-Nicotinoyloxy-tropane (**57**)	1953	246	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	t/-	-/-	-	-/-	-/-	-/-

Table 1 (*continued*)

Alkaloid	RI	M$^+$	medium	tridentata	aurea	tuberosa	emarginata[a]	gemella	hederacea	pterygocaulos[a]	umbellata	peltata[a]	aegyptia	dissecta	vitifolia	guerichii	quinata[a]	cissoides	quinquefolia	kentrocaulos
Merresectine A (**2**)	2195	261	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	1/-	-/-	-/-	-	-/-	t/-	-/-
Datumetine (**1**)	2207	275	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	1/-	-/-	-/-	-	-/-	t/-	-/-
3α-(4-Hydroxybenzoyl-oxy)tropane (**62**)	2275	261	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	1/-	-/-	t/-	-	-/-	-/-	t/-
3β-(4-Hydroxybenzoyl-oxy)tropane (**63**)	2282	261	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/t	-	-/-	-/-	t/-
3-(Hydroxybenzoyl-oxy)nortropane (**64**)	2290	247	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
Phyllalbine (**65**)	2340	291	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	1/-	-	-/-	-/-	t/-
Concneorine (**66**)	2365	291	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	t/-
Consabatine (**68**)	2482	347	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/-	10	-/-	-/-	-/-
Merresectine H (**69**)	2522	327	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-/-	t/-	-/-	-/-
4'-Dihydroconsabatine (**70**)	2540	349	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/-	10	-/-	-/-	-/-
3-Acyloxytropane (**71**)	2598	?	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	-/-	-/-	-/-	-	-/-	-/-	-/-
Merresectine E (**72**)	2685	329	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	1/-	5/1	5	1/-	t/-	t/-
3-Acyloxytropane (**73**)	2737	353	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
3β-Feruloyloxytropane (**74**)	2738	317	-/-	-/-	-/-	-/-	-	t/-	-/-	-	-/-	-	-/-	-/-	-/-	-/-	-	-/-	-/-	-/-
Merresectine D (**75**)	2785	359	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	8/1	t	-/-	-/-	t/-
3-Acyloxytropane (**76**)	2790	?	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	-/-	-	-/-	t/-	-/-
3β-Merresectine D (**77**)	2813	359	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	-/-	-/-	t/-	-	-/-	-/-	t/-
3-Acyloxytropane (**78**)	2890	?	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	-/-	-/-	-/-	-	-/-	-/-	-/-
Merresectine F (**79**)	2895	395	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	t/-	t/-	t/t	t	t/-	t/-	t/-
3β-Merresectine F (**80**)	2955	395	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	t/-	-/-	t/-	-	t/-	-/-	t/-
Merresectine G (**81**)	2983	393	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
3-Acyloxytropane (**82**)	3022	379	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	-/-	-/-	-/-	-	-/-	-/-	-/-
Merresectine C (**4**)	3042	397	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	1/-	2/-	1/-	5/5	60	8/-	55/-	5/-
3β-Merresectine C (**83**)	3070	397	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	1/-	t/-	1/-	-	t/-	15/-	t/-
3-Acyloxytropane (**84**)	3080	469	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	t/-	t/-	-/-
3-Acyloxytropane (**85**)	3090	397	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	t/-	-/-	-/-	-/-	-	-/-	-/-	-/-
3-Acyloxytropane (**86**)	3095	411	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-
3-Acyloxytropane (**87**)	3215	487	-/-	-/-	-/-	-/-	-	-/-	-/-	-	-/-	-	-/-	t/-	-/-	-/-	-	-/-	-/-	-/-

RI = retention index; t = traces; – = not detected; symbol before the oblique: roots; symbol behind the oblique: epigeal vegetative parts. [a]Epigeal vegetative parts. [b]Detected by TLC. [c]Cyclotropine might be an artefact due to GC–MS analysis.

were located at δ_C 65.0 and 66.0, whereas C-5/C-5′ exhibited two signals at 56.6 and 57.4. C-6 appeared as a triplet at 47.3, the *N*-methyl groups and C-8 as quartets at 40.5, 40.6 and 31.2, respectively. In contrast to cuscohygrine there are only three signals above 30.0 ppm. Those at 22.6 and 23.6 were assigned to C-4/C-4′ and the one at 26.3 to C-3′. Compared to **43** there was an additional doublet at 45.7 corresponding to C-3, thus proposing a linkage between C-2′ and C-3. The other isomer (**8**) exhibited a very similar ^{13}C NMR. The main difference was that there were two tripletts at 26.6 and 27.0 corresponding to C-3/C-3′ but only one triplets at 23.0 which was assigned to C-4′. In this case the linkage has to be between C-4 (45.0) and C-2′. The absolute configurations remain to be determined. In GC–MS 2′,3-*N*-methylpyrrolidinylhygrine eluted before its 2′,4-isomer.

2.2.2. Occurence of pyrrolidine alkaloids including nicotine (21) detected by GC–MS

Tropane alkaloids in solanaceous and convolvulaceous species are always accompanied by simple pyrrolidine alkaloids like hygrine (**9**) or cuscohygrine (**43**). This is not surprising since both groups of alkaloids share basal parts of the biogenetic pathway (Huang et al., 1996 and literature therein). **9** has been detected in all 18 *Merremia* species of the present study (Table 1), followed by nicotine (**21**; 13 spp.), **43** (12 spp.), and two *N*-methylpyrrolidinylhygrines (**7**, **8**) as well as 5-(2-hydroxypropyl)hygroline (**31**) (9 spp. each). Moreover, seven further structurally known pyrrolidines (**10**, **11**, **27**, **28**, **58**, **60**, **61**) have been found as metabolites of 1–8 species, respectively. Phygrine (**58**), an alkaloid discovered in *Physalis* spp. (Solanaceae) and apparently not occurring in other solanaceous genera (Basey et al., 1992) turned out to be also a constituent of *M. guerichii*, *M. hederacea*, and *M. kentrocaulos*. Two species (*M. medium*, *M. tridentata*) have shown only hygrine (**9**) and nicotine (**21**) out of altogether 13 pyrrolidines, *M. pterygocaulos* only **9** and hygroline B (**11**), respectively. *M. kentrocaulos* (11 pyrrolidines) and *M. guerichii* (10) apparently comprise the most complex pattern. However, it should be taken into account in general that especially **43** could lead at least in part to an artificial formation of **9** due to degradation by the GC–MS procedure (Moore et al., 1995). Thus, we could detect **43** by TLC control but not in the corresponding GC–MS profile in the samples of *M. aurea.* This may explain why only 12 out of 18 species have been found **43**-positive. Similarly, **58** turned out to be rather unstable (degradation already by air) yielding at least in part **27** and **43**, respectively, as degradation products (Basey et al., 1992).

Anyhow, cuscohygrine (**43**) has been the principal alkaloid of the common pathway with tropanes in six species, especially in the samples from the roots. Nicotine (**21**) was dominating in *M. peltata*, the propylhygrines **27** and **28** in *M. aurea*, the *N*-methylpyrrolidinylhygrines **7** and **8** in *M. hederacea*, hygrine (**9**) in *M. tuberosa*, and 5-(2-hydroxypropyl)hygroline (**31**) in *M. aegyptia*. Tropanes as major metabolites have only been characterized for three species: the simple alkaloids tropan-3-one (**14**) and tropan-3α-ol (**16**) in *M. dissecta* as well as merresectine C (**4**) in the epigeal vegetative parts of *M. quinata* and the roots of *M. quinquefolia.*

2.3. Chemotaxonomic conclusions

The results of this study of altogether 18 *Merremia* spp. led to three distinguishable groups of species from the phytochemical point of view: (1) species synthesizing only two simple pyrrolidines, i.e. hygrine (**9**) and nicotine (**21**) but neither any other pyrrolidine nor any tropane

Table 2
Merremia species of this study listed according to the occurrence of tropane alkaloids and assignment to sections; for details see Table 1

Occurrence of metabolites in species of the genus *Merremia*	Austin (1998a,b)	O'Donell (1941)	Van Ooststroom (1939,1953) [a]	Origin
No tropanes				
M. medium (L.) Hallier f.	Transfered to *Xenostegia*[b]	n.i.[c]	Streptandra[d]	South Madagascar
M. tridentata (L.) Hallier f.	Transfered to *Xenostegia*[b]	Halliera	Streptandra	Phuket/Thailand
Simple tropanes like **12–17**				
M. aurea (Kell.) O' Donell	Tuberosa allies	Schizips	Streptandra	Baja California/Mex.
M. tuberosa (L.) Rendle	Tuberosa allies	Schizips	Streptandra	Gran Canaria
M. emarginata (Burm. f.) Hall. f.	Merremia	n.i.	Eu-Merremia	Java/Indonesia
M. gemella (Burm. f.) Hallier f.[e]	Merremia	n.i.	Eu-Merremia	Java/Indonesia
M. hederacea (Burm. f.) Hallier f.	Merremia	Eu-Merremia	Eu-Merremia	Queensld/Australia
M. pterygocaulos (Steud. ex Choisy) Hallier f.	n.i.	n.i.	Xanthips[d]	East Madagascar
M. umbellata (L.) Hallier f.	n.i.	n.i.	Xanthips	Guayaquil/Ecuador
M. peltata (L.) Merr.	n.i.	n.i.	Hailale	Java/Indonesia
Simple tropanes like **12–17** plus merresectines				
M. aegyptia (L.) Urban	Vitifolia allies	Schizips	Streptandra	West Madagascar
M. dissecta (Jacq.) Hallier f.[f,g]	Vitifolia allies	Schizips	Streptandra	Zanzibar/Tanzania
M. vitifolia (Burm. f.) Hallier f.[g]	Vitifolia allies	n.i.	Streptandra	Java/Indonesia
M. guerichii A. Meeuse[f,g]	n.i.	n.i.	Streptandra[d]	Brandberg/Namibia
M. quinata (R.Br.) Ooststr.	n.i.	n.i.	Streptandra	North.Terr./Australia
M. cissoides (Lam.) Hallier f.[g]	Cissoides	Cissoides	Streptandra	West Madagascar
M. quinquefolia (L.) Hallier f.[g]	Cissoides	Cissoides	Streptandra	Guayaquil/Ecuador
M. kentrocaulos (C.B.Clarke) Rendle[g]	n.i.	n.i.	n.i.; nested in *Operculina*[h]	Southeast Zimbabwe

[a] Based on Hallier (1893).
[b] Novel genus: *X. medium* D.F.Austin & G.W.Staples; *X. tridentata* D.F.Austin & G.W.Staples.
[c] n.i. = not included in the corresponding classification of the genus.
[d] Not included by van Ooststroom but classified by Hallier (1893).
[e] ssp. *gemella*.
[f] In addition 6-acyloxytropanes.
[g] In addition 3β -acyloxytropanes.
[h] By Hallier (1894) as *Operculina kentrocaulos* (Steud.) Hallier.

alkaloid; (2) species synthesizing up to 11 pyrrolidines and unacylated tropanes like **12**–**17**; (3) species synthesizing different pyrrolidines, unacylated tropanes, and in addition aromatic 3-acyloxytropanes, particularly merresectines (Table 1). Especially the lack or presence of certain tropane alkaloids in general turned out to be of chemotaxonomic value. The two species segregated from the genus and transferred to a novel one, *Xenostegia* (Austin and Staples, 1980) are unique in this study in lacking tropanes, thus supporting this transfer chemotaxonomically. Furthermore, there are four taxa with species synthesizing simple, unacylated tropanes like **12**–**17**: the sections Eu-Merremia van Oostroom for which Austin claims the name Merremia, Xanthips (Griseb.) Hallier f., and Hailale Hallier f. as well as the Tuberosa allies (Table 2). From the chemotaxonomic point of view it is obvious that each species included in this study and assigned to one of these four taxa is capable in producing simple tropanes. Therefore it may be assumed that such metabolites are a common trait in the genus since this is also true for the remaining taxa to be discussed just below. However, it has to be taken into account that the very small section Wavula van Ooststroom (2 spp.) is not represented in this study.

The simple tropanes **12**–**17** can be considered as plesiomorphic characters since they are also frequent metabolites in the sister family Solanaceae (e.g. Hartmann et al., 1986; Witte et al., 1987). In contrast, the merresectines B–H (**3**, **4**, **75**, **72**, **79**, **69**), their derivatives **68/70**, and the 3β-epimers **83**, **77**, **80** represent apomorphic characters of certain Convolvulaceae. Such apomorphic characters, especially the merresectines are metabolites in members (a) of the section Cissoides (House) O'Donell, (b) of the Vitifolia allies (Austin, 1998a), (c) of two species originally assigned to section Streptandra by Hallier (*M. guerichii*) and van Ooststroom (*M. quinata*) like many other species but in contrast to the latter have never been classified elsewhere and finally (d) *M. kentrocaulos* which has been nested within the genus *Operculina* again by Hallier but has never been assigned to a certain section of *Merremia*. Thus, the segregation of the section Cissoides O'Donell from the section Streptandra Hallier is supported by the phytochemical results. Furthermore, this is true for the segregation of another group from the section Schizips O'Donell, Vitifolia allies by Austin. In this connection it should be remembered that the three Vitifolia allies of this study form also a moderately supported subclade in the molecular cladistic analysis.

The 3β-merresectines are also present in the section Cissoides, the Vitifolia allies, and two African species (*M. guerichii*, *M. kentrocaulos*) which are not classified since 1893. Thus, they make no further contribution from the chemotaxonomic point of view. This is also true for 6-acyloxytropanes which are limited to only two species (*M. dissecta*, *M. guerichii*). In addition previous results on the occurrence and structure elucidation of cyanogenic glycosides in two of the three species of Vitifolia allies, *M. dissecta* (Nahrstedt et al., 1989, 1990) and *M. vitifolia* (Jenett-Siems, 1996) are also in favour of the segregation of Vitifolia allies and Tuberosa allies from Schizips. Cyanogenic glycosides are extremely rare in the Convolvulaceae; there are no other reports on structurally elucidated compounds of this type in the family.

Both species of the section Cissoides integrated in the present study (*M. cissoides*, *M. quinquefolia*) have already been characterized previously by the discovery of lycopsamine type pyrrolizidine alkaloids (Mann, 1997). These metabolites well-known, e.g. from the Boraginaceae turned out to be unique in the Convolvulaceae (>120 species checked). The additional detection of merresectines and their 3β-epimers in these species represents an extraordinary support also from the chemotaxonomic point of view for the segregation of the section Cissoides O'Donell from the original section Streptandra Hallier f.

3. Experimental

3.1. General

^{1}H NMR (300 MHz, 400 MHz) and ^{13}C NMR (75 MHz, 100 MHz) spectra were recorded on a Bruker AC 300 or Bruker AC 400. EIMS, HRMS, and FABMS spectra were obtained using Varian MAT CH_7A, Finnigan MAT 711, and Finnigan MAT CH_5DF, respectively. Optical rotations were measured on a Perkin Elmer 241 MC polarimeter. Preparative HPLC was carried out on an Eurospher 100 C-18 column (10 μm, 24 × 250 mm) or a Nucleosil 300 C-18 column (10 μm, 16 × 250 mm).

3.2. Plant material

Seeds were collected in the wild (Table 2). The plants were grown in the greenhouse and provided roots and shoots for alkaloid extraction. Voucher specimens are deposited at the Institut für Pharmazie (Pharmazeutische Biologie), Freie Universität Berlin.

3.3. Extraction and isolation

3.3.1. Isolation of compounds *1* and *2*

Ground roots of *M. dissecta* (270 g) were extracted with aq. MeOH (80%) for 72 h. The alcoholic extract was concentrated under reduced pressure and dissolved in aq. tartaric acid (2%). The acidic soln was extracted successively with $CHCl_3$ and EtOAc, its pH adjusted to 8 (10% aq. $NaHCO_3$) and extracted with CH_2Cl_2-*iso*-PrOH (3:1). For isolation the alkaloids were subjected to column chromatography on silica gel with $CHCl_3$-MeOH-diethylamine mixtures to yield **1** (23 mg) and **2** (11 mg).

*3.3.2. Isolation of compounds **3**, **4**, and **5***

Ground roots of *M. dissecta* (490 g) were extracted with 70% aq. MeOH. The concentrated extract was partitioned between acid and base in the usual manner to yield 531 mg of basic material. The crude alkaloids were chromatographed on silica gel with $CHCl_3$–MeOH–NH_3 (20%) mixtures to yield **3** (154 mg) and **5** (27 mg). Fractions 33–43 were purified by preparative HPLC (Eurospher 100 C-18 column, MeOH–0.5% aq. H_3PO_4 mixtures) to give **4** (6 mg).

*3.3.3. Isolation of compound **6***

Ground roots of *M. guerichii* (92 g) were extracted three times with MeOH at room temperature. The alcoholic extract was concentrated under reduced pressure and dissolved in aq. tartaric acid (2%). The acidic soln was extracted successively with $CHCl_3$ and EtOAc, its pH adjusted to 8 (3% aq. NH_3) and extracted with $CHCl_3$. For isolation the crude alkaloids were subjected to preparative HPLC (Eurospher 100 C-18 column, 0.5 % aq. H_3PO_4–MeOH 60:40 to 30:70 after 30 min) to yield **6** (1 mg) and again **3** (5 mg).

*3.3.4. Isolation of compound **66***

Ground epigeal vegetative parts of *C. cneorum* (500 g) were moistened with aq. NH_3 (17%) and extracted with CH_2Cl_2 at room temperature. The lipophilic extract was concentrated under reduced pressure and then extracted five times with aq. tartaric acid (2%). The acidic soln was alkalinized with aq. Na_2CO_3 to pH 8 and extracted with CH_2Cl_2. For isolation the crude alkaloids were subjected to preparative TLC on silica gel ($CHCl_3$–MeOH–NH_3 (25%) 80:20:1, R_f 0.45) to yield **66** (8 mg).

*3.3.5. Isolation of compounds **70** and **72a***

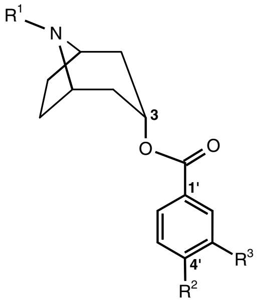
Ground roots and rhizomes of *C. sabatius* ssp. *sabatius* (400 g) were extracted three times with MeOH at room temperature. The alcoholic extract was concentrated under reduced pressure and dissolved in aq. tartaric acid (2%). The acidic soln was extracted successively with petrol ether, CH_2Cl_2 and EtOAc, its pH adjusted to 8 (3% NH_3) and extracted with $CHCl_3$/isopropanol 3:1. For isolation the crude alkaloids were subjected to preparative HPLC (Nucleosil 300 C-18 column, 0.5% aq. H_3PO_4–MeOH 60:40 to 30:70 after 30 min) to yield **70** (3 mg) and **72a** (3 mg).

*3.4. Datumetine (**1**)*

Yellow solid. ^1H NMR ($CDCl_3$): δ 1.84 (2 H, d, $J = 14.7$ Hz, H-2b, H-4b), 2.08 (4 H, br s, H_2-6, H_2-7), 2.24 (2 H, dt, $J = 14.7$, 5.0 Hz, H-2a, H-4a), 2.32 (3 H, s, *N*-CH_3), 3.17 (2 H, br s, H-1, H-5), 3.87 (3 H, s, OCH_3), 5.24 (1 H, t, $J = 5.0$ Hz, H-3), 6.95 (2 H, d, $J = 8.0$ Hz, H-3′, H-5′), 7.99 (2 H, d, $J = 8.0$ Hz, H-2′, H-6′); ^{13}C NMR data, see Table 4; EIMS 70 eV, *m/z* (rel. int.): 275 $[M]^+$ (19), 152 (1), 140 (17), 135 (13), 125 (9), 124 (100), 94 (16), 83 (30), 82 (27); HRMS 80 eV, *m/z*: 275.1516 ($C_{16}H_{21}NO_3^{+\bullet}$, calc. 275.1521), 152.0481 ($C_8H_8O_3^{+\bullet}$, calc. 152.0474), 140.1067 ($C_8H_{14}NO^+$, calc. 140.1075), 135.0451 ($C_8H_7O_2^+$, calc. 135.0446), 124.1123 ($C_8H_{14}N^+$, calc. 124.1126), 83.0735 ($C_5H_9N^{+\cdot}$, calc. 83.0735), 82.0661 ($C_5H_8N^+$, calc. 82.0655).

*3.5. Merresectine A (**2**)*

Yellow solid. ^1H NMR ($CDCl_3$): δ 1.96 (4 H, m, $2 \times$ H-2, $2 \times$ H-4), 2.21 (4 H, m, H_2-6, H_2-7), 2.85 (1 H, br s, –NH), 3.68 (2 H, br s, H-1, H-5), 3.87 (3 H, s, OCH_3), 5.31 (1 H, t, $J = 5.2$ Hz, H-3), 6.95 (2 H, d, $J = 8.0$ Hz, H-3′, H-5′), 7.98 (2 H, d, $J = 8.0$ Hz, H-2′, H-6′); ^{13}C NMR data, see Table 4; EIMS 70 eV, *m/z* (rel. int.): 261 $[M]^+$ (11), 220 (9), 152 (40), 135 (21), 126 (5), 110 (100); HRMS 80 eV, *m/z*: 261.1368 ($C_{15}H_{19}NO_3^{+\bullet}$, calc. 261.1365), 220.0966 ($C_{12}H_{14}NO_3^+$, calc. 220.0974), 152.0469 ($C_8H_8O_3^{+\bullet}$, calc. 152.0474), 135.0446 ($C_8H_7O_2^+$, calc. 135.0446), 126.0909 ($C_7H_{12}NO^+$, calc. 126.0919), 110.0974 ($C_7H_{12}N^+$, calc. 110.0970).



Datumetine (**1**): $R^1 = CH_3$, $R^2 = OCH_3$, $R^3 = H$

Merresectine A (**2**): $R^1 = H$, $R^2 = OCH_3$, $R^3 = H$

Phyllalbine (**65**): $R^1 = CH_3$, $R^2 = OH$, $R^3 = OCH_3$

*3.6. Merresectine B (**3**)*

Oil. $[\alpha]_D^{20}$ −10.2 (MeOH; *c* 0.1); ^1H NMR (acetone-d_6): δ 1.72 (2 H, d, $J = 15.0$ Hz, H-2a, H-4a), 1.74 (6 H, s, $2 \times$ –CH_3), 1.76 (6 H, s, $2 \times$ –CH_3), 2.08 (4 H, m, H_2-6, H_2-7), 2.17 (2 H, br dt, $J = 15.0$, 5.0 Hz, H-2b, H-4b), 2.26 (3 H, s, *N*-CH_3), 3.12 (2 H, br s, H-1, H-5), 3.25–3.50 (4 H, m, glycosidic protons), 3.62 (4 H, br d, $J = 7.4$ Hz, $2 \times$ H-1″, $2 \times$ H-1‴), 3.67 (1 H, dd, $J = 12.0$, 6.0 Hz, H-6⁗′a), 3.78 (1 H, dd, $J = 12.0$, 3.0 Hz, H-6⁗′b), 4.82 (1 H, d, $J = 7.4$ Hz, H-1⁗′),

Table 3
Mass fragmentation patterns of pyrrolidine and tropane alkaloids identified by GC–MS taken from Table 1[a]

Compound	RI	M$^+$ (%)	*m*/*z* (%)
Cyclotropine (**13**)	1137	139 (98)	110 (58), 108 (40), 96 (60), 82 (20), 68 (100)
3α-Acetoxynortropane (**18**)	1292	169 (5)	110 (100), 97 (5), 83 (5), 68 (17)
3β-Acetoxynortropane (**19**)	1296	169 (5)	110 (100), 97 (5), 83 (5), 68 (17)
3α-*n*-Butyroxynortropane (**25**)	1435	197 (5)	110 (100), 80 (30), 68 (29)
3β-*n*-Butyroxynortropane (**26**)	1440	197 (2)	110 (100), 80 (32), 68 (28)
5-(2-Oxopropyl)hygrine (**27**)	1442	197 (1)	140 (82), 124 (3), 96 (17), 82 (100)
5-(2-Hydroxypropyl)hygrine (**28**)	1452	199 (2)	142 (40), 140 (100), 82 (88)
Methylpseudoecgonine (**30**)	1473	199 (19)	182 (12), 168 (10), 155 (9), 96 (70), 82 (100)
5-(2-Hydroxypropyl)hygroline (**31**)	1478	201 (1)	142 (100), 84 (30)
6-Acetoxytropan-3-ol (**32**)	1500	199 (25)	140 (9), 113 (100), 96 (53), 94 (28), 82 (18)
3-(Hydroxybutyroxy)tropane (**33**)	1524	227 (11)	140 (5), 124 (100), 96 (15), 94 (20), 82 (23), 59 (30)
3-(2-Methylbutyroxy)nortropane (**34**)	1532	211 (2)	110 (100), 80 (24), 68 (23), 57 (10)
3-(Hydroxypentanoyloxy)nortropane (**37**)	1603	227 (2)	110 (100), 80 (18), 73 (28), 68 (19)
3-(Hydroxypentanoyloxy)tropane (**38**)	1616	241 (10)	140 (8), 124 (100), 96 (18), 94 (23), 82 (25), 73 (31)
6-Butyroxynortropan-3-ol (**40**)	1632	213 (7)	142 (10), 110 (40), 99 (100), 80 (42), 68 (25)
6-Butyroxytropan-3-ol (**41**)	1634	227 (17)	140 (18), 113 (100), 96 (41), 94 (60), 82 (17)
3-(Hydroxyisovaleroxy)tropane (**44**)	1669	241 (12)	140 (5), 124 (100), 94 (25), 82 (28), 59 (8)
3-(Hydroxybutyroxy)tropane (**45**)	1672	227 (10)	140 (8), 124 (100), 96 (12), 94 (27), 82 (30), 59 (5)
3α-(Hydroxy-2-methylbutyroxy)-tropane (**46**)	1698	241 (7)	140 (6), 124 (100), 96 (12), 94 (20), 82 (25), 45 (7)
3β-(Hydroxy-2-methylbutyroxy)-tropane (**47**)	1705	241 (8)	140 (5), 124 (100), 96 (8), 95 (9), 94 (22), 82 (30), 45 (7)
6-Pentanoyloxynortropan-3-ol (**48**)	1719	227 (5)	142 (10), 99 (100), 80 (19)
6-Hydroxy-3-(2-methyl-butyroxy)tropane (**49**)	1728	241 (6)	197 (2), 140 (23), 94 (100), 57 (15)
3-Hexanoyloxytropane (**51**)	1755	255 (5)	140 (5), 124 (100), 96 (12), 94 (18), 82 (22)
6-(2-Hydroxy-2-methyl-butyroxy)tropan-3-ol (**52**)	1809	257 (15)	140 (28), 113 (100), 96 (33), 82 (25), 73 (12)
6-(2-Hydroxy-2-methyl-butyroxy)tropan-3-ol (**53**)	1811	257 (10)	140 (25), 113 (100), 96 (38), 82 (25), 73 (15)
3α-Benzoyloxytropane (**56**)	1907	245 (10)	140 (18), 124 (100), 96 (18), 94 (18), 83 (40), 82 (25)
3α-Nicotinoyloxytropane (**57**)	1953	246 (15)	140 (15), 124 (100), 96 (22), 94 (23), 82 (38)
6-(Hydroxybutyroxy)-3-pentanoyloxytropane (**59**)	2150	327 (6)	242 (2), 226 (20), 138 (12), 122 (62), 95 (100), 94 (99), 57 (23)
3α-(4-Hydroxybenzoyloxy)tropane (**62**)	2275	261 (18)	140 (17), 124 (100), 94 (30), 83 (48), 82 (47)
3β-(4-Hydroxybenzoyloxy)tropane (**63**)	2282	261 (13)	140 (7), 124 (100), 94 (25), 83 (30), 82 (49)
3-(Hydroxybenzoyloxy)nortropane (**64**)	2290	247 (1)	163 (8), 138 (15), 110 (100), 91 (30), 80 (20)
6-(Methoxybenzoyloxy)tropan-3-ol (**67**)	2412	291 (8)	135 (22), 113 (100), 96 (29)
Consabatine (**68**)	2482	347 (3)	330 (1), 179 (2), 140 (5), 124 (100), 96 (10), 94 (8)
Merresectine H (**69**)	2522	327 (6)	144 (5), 140 (18), 124 (100), 94 (28), 83 (28), 82 (32)
3-Acyloxytropane (**71**)	2598	?	233 (3), 140 (20), 124 (100), 95 (29), 82 (32)
Merresectine E (**72**)	2685	329 (8)	312 (1), 244 (1), 189 (5), 140 (25), 124 (100), 94 (22), 83 (25), 82 (24)
3-Acyloxytropane (**73**)	2737	353 (9)	140 (22), 124 (100), 94 (25), 83 (38), 82 (37)
Merresectine D (**75**)	2785	359 (18)	274 (2), 236 (4), 219 (10), 140 (35), 124 (100), 94 (42), 83 (52), 82 (48)
3-Acyloxytropane (**76**)	2790	?	265 (5), 140 (22), 124 (100), 94 (21), 83 (17), 82 (16)
3β-Merresectine D (**77**)	2813	359 (18)	274 (1), 236 (2), 219 (8), 140 (10), 124 (100), 94 (30), 83 (25), 82 (40)
3-Acyloxytropane (**78**)	2890	?	208 (12), 140 (8), 124 (100), 94 (24), 83 (44), 82 (58)
Merresectine F (**79**)	2895	395 (10)	257 (10), 212 (4), 140 (25), 124 (100), 94 (27), 83 (30), 82 (32)
3β-Merresectine F (**80**)	2955	395 (12)	257 (28), 140 (8), 124 (100), 94 (20), 83 (28), 82 (50)
Merresectine G (**81**)	2983	393 (7)	255 (11), 140 (28), 124 (100), 94 (30), 83 (35), 82 (38)
3-Acyloxytropane (**82**)	3022	379 (12)	140 (8), 124 (100), 94 (36), 83 (38), 82 (65)
3β-Merresectine C (**83**)	3070	397 (18)	312 (1), 257 (8), 140 (10), 124 (100), 94 (30), 83 (30), 82 (42)
3-Acyloxytropane (**84**)	3080	469 (3)	329 (3), 319 (22), 140 (40), 124 (100), 94 (19), 83 (34), 82 (24)
3-Acyloxytropane (**85**)	3090	397 (18)	257 (4), 140 (8), 124 (100), 94 (22), 83 (22), 82 (24)
3-Acyloxytropane (**86**)	3095	411 (7)	140 (28), 124 (100), 94 (26), 83 (30), 82 (26)
3-Acyloxytropane (**87**)	3215	487 (12)	429 (10), 140 (35), 124 (100), 94 (30), 83 (34), 82 (25)

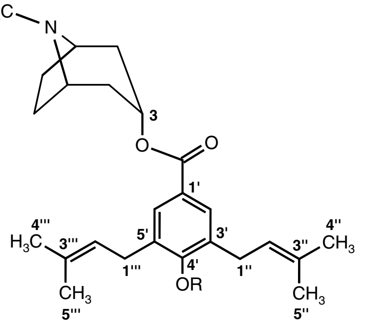
[a] For mass spectral data of newly isolated compounds see Section 3, for known compounds please refer to Witte et al. (1987), Doerk et al. (1991), Basey et al. (1992), Christen et al. (1993), and Ionkova et al. (1994).

5.18 (1 H, t, *J* = 5.0 Hz, H-3), 5.34 (2 H, t, *J* = 7.5 Hz, H-2″, H-2‴), 7.71 (2 H, s, H-2′, H-6′); ^{13}C NMR data, see Table 4; EIMS 70 eV, *m*/*z* (rel. int.): 559 [M]$^+$ (3), 397 (30), 257 (5), 140 (23), 124 (100), 94 (12), 83 (24), 82 (15); (−)-FABMS *m*/*z*: 558 [M−H]$^-$, 396 [(M−H)-162]$^-$; HRMS 80 eV, *m*/*z*: 559.3147 ($C_{31}H_{45}NO_8^{+\bullet}$, calc. 559.3145), 397.2619 ($C_{25}H_{35}NO_3^{+\bullet}$, calc. 397.2617), 257.1543 ($C_{17}H_{21}O_2^+$, calc. 257.1542), 140.1075 ($C_8H_{14}NO^+$, calc. 140.1075), 124.1125 ($C_8H_{14}N^+$, calc. 124.1126).

Table 4
^{13}C NMR (75 MHz, δ = ppm) data of compounds **1**–**4**

Carbon	**1** ($CDCl_3$)	**2** ($CDCl_3$)	**3** (DMSO-d_6)	**4** (acetone-d_6)
1	59.8	53.4	59.1	61.7
2	36.7	36.6	35.4	37.0
3	67.7	67.5	67.0	67.4
4	36.7	36.3	35.4	37.0
5	59.8	53.4	59.1	61.7
6	25.8	28.4	25.1	26.3
7	25.8	28.4	25.1	26.3
N-CH_3	40.4		39.8	40.1
1′	123.3	122.9	126.0	122.4
2′/6′	131.4	131.4	128.0	129.4
3′/5′	113.7	113.8	132.8	129.6
4′	163.3	163.4	156.4	158.7
7′	165.7	165.5	164.8	167.2
4′-OCH_3	55.4	55.5		
1″/1‴			27.7	29.1
2″/2‴			122.2	122.8
3″/3‴			135.9	134.6
4″/4‴			25.4	26.0
5″/5‴			17.6	17.9
1⁗			104.4	
2⁗			73.8	
3⁗			76.0[a]	
4⁗			70.0	
5⁗			76.8[a]	
6⁗			61.0	

[a] Assignments interchangeable.



Merresectine B (**3**): R = β-D-glucose

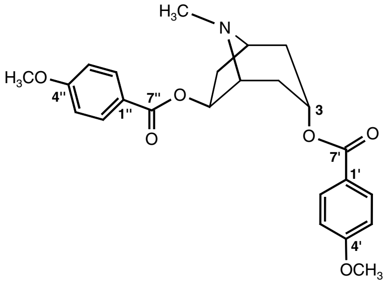
Merresectine C (**4**): R = H

3.7. Merresectine C (4)

Oil. ^1H NMR (acetone-d_6): δ 1.72 (6 H, s, 2 × –CH_3), 1.75 (2 H, d, *J* = 15.0 Hz, H-2a, H-4a), 1.77 (6 H, s, 2 × –CH_3), 2.13 (4 H, br s, H_2-6, H_2-7), 2.26 (2 H, br dt, *J* = 15.0, 5.0 Hz, H-2b, H-4b), 2.33 (3 H, s, *N*-CH_3), 3.21 (2 H, br s, H-1, H-5), 3.40 (4 H, d, *J* = 7.4 Hz, 2 × H-1″, 2 × H-1‴), 5.16 (1 H, t, *J* = 5.0 Hz, H-3), 5.37 (2 H, br t, *J* = 7.4 Hz, H-2″, H-2‴), 7.68 (2 H, s, H-2′, H-6′); ^{13}C NMR data, see Table 4; EIMS 70 eV, *m/z* (rel. int.): 397 $[M]^+$ (19), 257 (4), 140 (24), 124 (100), 94 (18), 83 (41), 82 (27); HRMS 80 eV, *m/z*: 397.2619 ($C_{25}H_{35}NO_3^{+\bullet}$, calc. 397.2617), 257.1540 ($C_{17}H_{21}O_2^+$, calc. 257.1542), 140.1076 ($C_8H_{14}NO^+$, calc. 140.1075), 124.1123 ($C_8H_{14}N^+$, calc. 124.1126).

3.8. Merredissine (5)

Oil. $[\alpha]_D^{20}$ −8.6 (MeOH; *c* 0.2); ^1H NMR data, see Table 5; ^{13}C NMR data, see Table 5; EIMS 70 eV, *m/z* (rel. int.): 425 $[M]^+$ (3), 290 (2), 274 (5), 138 (12), 135 (37), 122 (31), 107 (8), 95 (91), 94 (100); HRMS 80 eV, *m/z*: 425.1832 ($C_{24}H_{27}NO_6^{+\bullet}$, calc. 425.1838), 290.1390 ($C_{16}H_{20}NO_4^{+\bullet}$, calc. 290.1392), 274.1442 ($C_{16}H_{20}NO_3^+$, calc. 274.1443), 152.0473 ($C_8H_8O_3^+$, calc. 152.0474), 94.0656 ($C_6H_8N^+$, calc. 94.0657).



Merredissine (**5**)

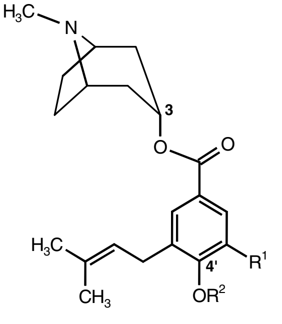
3.9. Merresectine D β-D-glucoside (6)

Oil. ^1H NMR (acetone-d_6): δ 1.71 (3 H, s, H-5″), 1.74 (3 H, s, H-4″), 1.80 (2 H, br d, *J* = 15.0 Hz, H-2a, H-4a), 2.15 (4 H, m, H_2-6, H_2-7), 2.29 (2 H, m, H-2b, H-4b), 2.34 (3 H, s, *N*-CH_3), 3.22 (2 H, m, H-1, H-5), 3.25-3.50 (4 H, m, H-2‴-H5‴), 3.51 (1 H, br d, *J* = 7.5 Hz,

Table 5
^{1} H (400 MHz, δ = ppm, $CDCl_3$) and ^{13}C (100.6 MHz, δ = ppm, $CDCl_3$) NMR data of **5**

Carbon	δ_H	δ_C
1	3.64 br s	60.4
2	1.86 br d (14.7), 2.54 m	34.5
3	5.33 t (5.0)	66.2
4	2.10 br d (14.7), 2.54 m	33.1
5	3.58 br s	66.7
6	5.87 dd (3.0, 7.5)	79.0
7	2.32 m, 2.84 dd (7.5, 14.2)	36.1
N-CH_3	2.72 s	40.1
1′		122.6
2′/6′	8.06 d (8.0)	131.6
3′/5′	6.98 d (8.0)	114.0
4′		163.6
7′		166.1
4′-OCH_3	3.87 s	55.5
1″		122.4
2″/6″	7.98 d (8.2)	131.6
3″/5″	6.93 d (8.2)	113.7
4″		163.6
7″		165.4
4″-OCH_3	3.87 s	55.5

H-1″), 3.64 (1H, dd, *J* = 3.0, 12.0 Hz, H-6‴a), 3.77 (1 H, dd, *J* = 6.0, 12.0 Hz, H-6‴b), 3.91 (3 H, s, OCH$_3$), 5.03 (1 H, d, *J* = 6.0 Hz, H-1‴), 5.18 (1 H, t, *J* = 5.0 Hz, H-3), 5.33 (1 H, t, *J* = 7.5 Hz, H-2″), 7.48 (1 H, d, *J* = 2.0 Hz, H-2′), 7.49 (1 H, d, *J* = 2.0 Hz, H-6′); EIMS 70 eV, *m/z* (rel. int.): 521 [M]$^+$ (4), 359 (100), 219 (7), 140 (20), 124 (80), 83 (17), 82 (10); (−)-FABMS *m/z*: 520 [M−H]$^-$, 358 [(M−H)-162]$^-$; HRMS 80 eV, *m/z*: 521.2621 ($C_{27}H_{39}NO_9^{+\bullet}$, calc. 521.2625), 359.2096 ($C_{21}H_{29}NO_4^{+\bullet}$, calc. 359.2097).



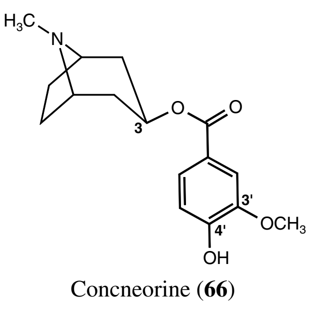
Merresectine D (**75**): R^1 = OCH$_3$, R^2 = H

Merresectine D β-D-glucoside (**6**): R^1 = OCH$_3$,
R^2 =β -D-glucose

Merresectine E (**72**): R^1 = H, R^2 = H
Merresectine E β-D-glucoside (**72a**): R^1 = H,
R^2 =β -D-glucose

3.10. Concneorine (**66**)

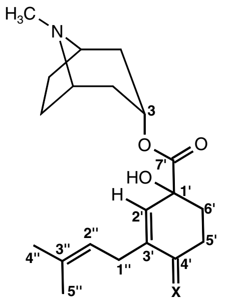
Oil. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.82 (2 H, m, H-6a, H-7a), 2.02 (4 H, m, H$_2$-2, H$_2$-4), 2.14 (2 H, m, H-6b, H-7b), 2.45 (3 H, s, *N*-CH$_3$), 3.39 (2 H, br s, H-1, H-5), 3.94 (3 H, s, OCH$_3$), 5.24 (1 H, m, H-3), 6.92 (1 H, d, *J* = 8.5 Hz, H-5′), 7.50 (1 H, d, *J* = 2.0 Hz, H-2′), 7.61 (1 H, dd, *J* = 8.5, 2.0 Hz, H-6′); ^{13}C NMR (CDCl$_3$): δ (ppm) 26.48 (t, C-6/C-7), 35.90 (t, C-2/C-4), 38.83 (q, *N*-CH$_3$), 55.99 (q, OCH$_3$), 60.47 (d, C-1/C-5), 67.27 (d, C-3), 111.83 (d, C-2′), 114.41 (d, C-5′), 122.30 (s, C-1′), 124.16 (d, C-6′), 146.57 (s, C-3′), 150.63 (s, C-4′), 165.95 (s, C-7′); EIMS 70 eV, *m/z* (rel. int.): 291 [M]$^+$ (32), 168 (3), 151 (10), 140 (9), 124 (100), 94 (19), 82 (44); HRMS 80 eV, *m/z*: 291.1471 ($C_{16}H_{21}NO_4^{+\bullet}$, calc. 291.1471).



Concneorine (**66**)

3.11. 4′-Dihydroconsabatine (**70**)

Oil. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.58 (2 H, m, H-2a, H-4a), 1.61 (3 H, s, H-5″), 1.70 (3 H, br s, H-4″), 1.82 (1 H, m, H-5′a) 1.85–1.95 (6 H, m, H$_2$-6′, H$_2$-6, H$_2$-7), 1.97 (1 H, m, H-5′b), 2.04 (2 H, m, H-2b, H-4b), 2.20 (3 H, s, *N*-CH$_3$), 2.85 (1 H, dd, *J* = 16.0, 8.0 Hz, H-1″a), 2.91 (1 H, dd, *J* = 16.0, 8.0 Hz, H-1″b), 3.01 (2 H, br s, H-1, H-5), 4.03 (1 H, br t, *J* = 6.0 Hz, H-4′), 4.90 (1 H, t, *J* = 5.0 Hz, H-3), 5.20 (1 H, tdq, *J* = 8.0, 1.0, 1.0 Hz, H-2″), 5.42 (1 H, br s, H-2′); ^{13}C NMR (CDCl$_3$): δ (ppm) 17.8 (q, C-5″), 25.6 (t, C-6/C-7), 25.8 (q, C-4″), 28.9 (t, C-5′), 31.2 (t, C-6′), 32.2 (t, C-1″), 36.4 (t, C-2), 36.5 (t, C-4), 40.3 (q, *N*-CH$_3$), 59.6 (d, C-1/C-5), 67.5 (d, C-4′), 69.8 (d, C-3), 72.1 (s, C-1′), 120.8 (d, C-2″), 123.5 (d, C-2′), 134.2 (s, C-3″), 145.4 (s, C-3′), 175.3 (s, C-7′); EIMS 70 eV, *m/z* (rel. int.): 349 [M]$^+$ (14), 332 (5), 280 (1), 181 (5), 163 (6), 140 (5), 124 (100), 96 (13), 94 (13), 83 (10), 82 (15); HRMS 80 eV *m/z*: 349.2252 [M]$^+$($C_{20}H_{31}NO_4^{+\bullet}$, calc. 349.2253), 332.2224 ($C_{20}H_{30}NO_3^+$, calc. 332.2226), 124.1126 ($C_8H_{14}N^+$, calc. 124.1126).



Consabatine (**68**): X = O

4'-Dihydroconsabatine (**70**):
X = H, OH

3.12. Merresectine E β-D-glucoside (**72a**)

Oil. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.72 (3 H, s, H-5″), 1.76 (3 H, s, H-4″), 1.82 (2 H, br d, *J* = 15.0 Hz, H-2a, H-4a), 2.07 (4 H, m, H$_2$-6, H$_2$-7), 2.20 (2 H, m, H-2b, H-4b), 2.30 (3 H, s, *N*-CH$_3$), 3.16 (2 H, m, H-1, H-5), 3.29 (1 H, dd, *J* = 7.0, 16.0 Hz, H-1″a), 3.42–3.76 (4 H, m, H-2‴-H5‴), 3.44 (1 H, m, H-1″b), 3.87 (1H, dd, *J* = 5.0, 12.0 Hz, H-6‴a), 3.93 (1 H, dd, *J* = 3.0, 12.0 Hz, H-6‴b), 4.98 (1 H, d, *J* = 7.0 Hz, H-1‴), 5.08 (1 H, t, *J* = 5.0 Hz, H-3), 5.16 (1 H, tdq, *J* = 8.0, 1.0, 1.0 Hz, H-2″), 7.03 (1 H, d, *J* = 8.0 Hz, H-5′), 7.82 (1 H, d, *J* = 1.0 Hz, H-2′), 7.84 (1 H, dd, *J* = 8.0, 1.0 Hz, H-6′); EIMS 70 eV, *m/z* (rel. int.): 347 (11), 140 (5), 124 (100), 96 (17), 95 (18); (+)-FABMS, *m/z*: 492 [M+H]$^+$.

3.13. Synthesis of **1**

500 mg of tropan-3α-ol were dissolved in 3 ml pyridine and 2 ml 4-methoxybenzoylchloride in 50 ml $CHCl_3$ added at 0 °C. After further addition of catalytic amounts of 4-dimethylaminopyridine the mixture was stirred for 24 h at room temp. The reaction was stopped by the addition of 20 ml ice-water. After evaporation the residue was taken up in saturated aq. $NaHCO_3$ and extracted with $CHCl_3$. The organic layers were purified by flash CC on silica gel ($CHCl_3$–MeOH–diethylamine 92:4:4) to yield 580 mg of **1**.

3.14. Synthesis of **2**

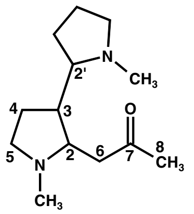
200 mg of tropan-3α-yl-4′-methoxybenzoate and 23 mg of K_2CO_3 were dissolved in 50 ml toluene. After addition of 464 mg of 2,2,2-trichlorethylchlorformiate the mixture was refluxed for 36 h under nitrogen. The reaction was stopped by addition of icewater and the aq. layer extracted with CH_2Cl_2. The organic layers were purified by flash CC on silica gel (CH_2Cl_2–MeOH 95:5) to yield 268 mg of *N*-(2,2,2-trichlorethoxycarbonyl)-tropan-3α-yl-4′-methoxybenzoate. This was dissolved in 10 ml HOAc and stirred with 550 mg Zn for 36 h at room temp. under nitrogen. The reaction was stopped by the addition of icewater. The aq. layer was adjusted to pH 9 (NH_3) and extracted with EtOAc. The final purification was achieved by CC on silica gel ($CHCl_3$–MeOH–diethylamine 96:2:2) to yield 65 mg of **2**.

3.15. Synthesis of 7 and **8**

1.28 g of *N*-methyl-α-pyrrolidone dissolved in Et_2O were reduced with $LiAlH_4$ for 1 h. Then a mixture of 0.9 g of 3-oxoglutaric acid, phosphat buffer (pH 7) and 1 N NaOH was added. The Et_2O was evaporated and the reaction mixture left for 40 h at room temp. For working up it was acidified with HCl and extracted with CH_2Cl_2, then alkalinised with NH_3 and again extracted with CH_2Cl_2. 550 mg of crude alkaloids were purified by column chromatography on silica gel ($CHCl_3$–MeOH 95:5 to $CHCl_3$–MeOH–$NH_{3\,\mathrm{conc.}}$ 90:10:1) to give 120 mg cuscohygrine and 6 mg of a three to one mixture of **7** and **8**.

3.16. 2′,3-N-Methylpyrrolidinylhygrine (7)

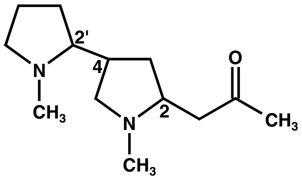
Oil. ^{1}H NMR ($CDCl_3$): δ 2.21 (3 H, s), 2.27 (6 H, s), 1.52–3.12 (m); ^{13}C NMR ($CDCl_3$): δ (ppm) 22.5 (t, C-4), 23.6 (t, C-4′), 26.3 (t, C-3′), 31.2 (q, C-8), 40.5 (q, *N*-CH_3), 40.6 (q, *N*-CH_3), 45.7 (d, C-3), 47.3 (t, C-6), 56.5 (t, C-5), 57.4 (t, C-5′), 65.0 (d, C-2), 67.0 (d, C-2′), 209.5 (s, C-7); EIMS 70 eV, *m*/*z* (rel. int.): 224 $[M]^+$ (8), 209 (1), 167 (8), 152 (12), 140 (5), 124 (5), 110 (5), 96 (2), 84 (100); HRMS 80 eV, *m*/*z*: 224.1887 ($C_{13}H_{24}N_2O$, calc. 224.1889).



2’,3-*N*-Methylpyrrolidinylhygrine (**7**)

3.17. 2′,4-N-Methylpyrrolidinylhygrine (**8**)

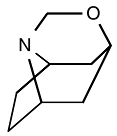
Oil. ^{1}H NMR ($CDCl_3$): δ 2.21 (3 H, s), 2.27 (6 H, s), 1.52–3.12 (m); ^{13}C NMR ($CDCl_3$): δ (ppm) 23.0 (t, C-4′), 26.6 (t, C-3), 27.0 (t, C-3′), 31.1 (q, C-8), 40.2 (q, *N*-CH_3), 41.4 (q, *N*-CH_3), 45.0 (d, C-4), 47.3 (t, C-6), 55.5 (t, C-5), 57.6 (t, C-5′), 63.2 (d, C-2), 67.6 (d, C-2′), 209.7 (s, C-7); EIMS 70 eV, *m*/*z* (rel. int.): 224 $[M]^+$ (8), 209 (1), 167 (8), 152 (12), 140 (5), 124 (5), 110 (5), 96 (2), 84 (100); HRMS 80 eV, *m*/*z*: 224.1887 ($C_{13}H_{24}N_2O$, calc. 224.1889).



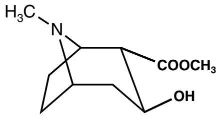
2’,4-*N*-Methylpyrrolidinylhygrine (**8**)

3.18. GC–MS analysis

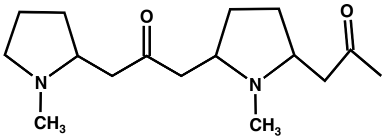
Ground plant parts (50 g) were extracted three times with 500 ml MeOH (80%). After evaporation the extract was acidified and partitioned between water and organic solvents. The aqueous layer was alkalinized and extracted with $CHCl_3$. The crude alkaloids were subjected to GC–MS analysis. The GC–MS system consisted of a Carlo Erba 5160/Fisons 8060 GC equipped with a 30 m × 0.32 mm fused silica capillary column coated with the methyl silicone stationary phase DB 1 (J&W Scientific, California). Helium was used as carrier gas. Conditions during split injection: injector 250 °C, split 1:20, temperature program 70–300 °C, 6 °C/min. The capillary column was directly coupled to the quadrupole mass spectrometer Finnigan MAT 4515/MD800. Retention indices (RI): Kovats indices (Kovats, 1958) were calculated in respect to a set of co-injected hydrocarbons.



Cyclotropine (**13**)



Methylpseudoecgonine (**30**)



Phygrine (**58**)

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