

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. guericchii*, respectively) and structure elucidation (spectral data) of four novel 3 α -acyloxytropanes, merresectines A–D: 3 α -(4-methoxybenzoyloxy)nortropine (A), 3 α -kurameroyloxytropine (B), 3 α -nervogenoyloxytropine (C), 3 α -[4-(β -D-glucopyranosyloxy)-3-methoxy-5-(3-methyl-2-butenyl)benzoyloxy]tropine (β -D-glucoside of D). Moreover, the novel 3 α ,6 β -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 3 α -acyloxytropanes (merresectine E β -D-glucoside, 4'-dihydroconsabatine) and one known 3 β -acyloxytropine (conceorine) 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.

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1. Introduction

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

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, Cissoïdes, Halliera, Schizips by O'Donnell (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* Lingelsh. 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 3 α -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, ¹H NMR, ¹³C NMR, DEPT, ¹H-¹H-COSY, ¹H-¹³C-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 C₁₅H₁₉NO₃, 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 3 β -isomer. The ¹H NMR and ¹³C 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 C₃₁H₄₅NO₈ 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 ¹H 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 dou-

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