Vilasinin limonoids from *Malleastrum antsingyense* J.F.Leroy
(Meliodeae: Meliaceae)

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1. Subject and source

*Malleastrum antsingyense* J.F. Leroy was collected in April 1997 in the Bemaraha Tsingy area in southwestern Madagascar. A voucher specimen (009-Mj/Mdul) is deposited at the Department of Botany of the University of Antananarivo. Plant identification was confirmed by Dr Harison Rabarison of the Department of Botany at the Parc Zoologique et Botanique de Tsimbazaza.

2. Previous work

No phytochemical investigations have been reported for any species of the genus *Malleastrum*.

3. Present study

The air-dried, milled stembark (232 g) was extracted successively for 24 hours each in a Soxhlet apparatus with hexane, dichloromethane and methanol, yielding 7.8, 1.1 and 13.2 g of extract respectively. The methanol extract was shown by \(^1\)H NMR to contain only sugars and was not investigated further, while the hexane and dichloromethane extracts were sufficiently similar, by \(^1\)H NMR and TLC analysis, to be combined. Repeated combinations of gravity column chromatography on Merck 7729 and 9385 silica gels, and PTLC on aluminium backed analytical TLC (Merck 5554) plates, using hexane:EtOAc:MeOH mixtures, afforded a major component, 1,3-diacetylvilasinin (**1**, 1.8 g) (Mulholland et al., 1998), together with 1,3-diacetyl-12\(\alpha\)-hydroxy-7-tigloylvilasinin (**2**, 10 mg) (Kumar et al., 1996), and several other minor components which were visible on TLC but could not be isolated in sufficient quantities for identification. The structures of the isolated compounds were established by analysis of their spectroscopic data and comparison with values reported in the literature.

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4. Chemotaxonomic significance

The genus *Malleastrum* (Baill.) J.F.Leroy is a relatively new addition to the Meliaceae family, with the earliest members described by Baillon, within the genus *Cipadessa* Blume, only in 1874. Initially retained in *Cipadessa* by both de Candolle (1878) and Harms (1940), later species were subsequently placed by both authors in *Trichilia* P. Browne. In 1964 Leroy raised it to generic rank within the tribe Trichilieae, subfamily Meliodeae. Originally considered by both Leroy (1964) and Pennington and Styles (1975) to comprise twelve species, the genus has remained the subject of taxonomic interest; it currently has twenty-four, with the five most recent inclusions added by Leroy and Lescot in 1996.

Characterised by a 6α,28 ether linkage, over 140 vilasinin-type limonoids have been reported to date from various species of the Meliaceae (Dictionary of Natural Products, 2007). Although the vast majority of these have come from species of the genera *Azadirachta* A.Juss and *Melia* L., they have also been found in *Trichilia*, *Turraea* L., *Chisocheton* Blume, *Turreanthus* Baill. and *Walsura* Roxb., all of which are members of the subfamily Meliodeae of the Meliaceae. 1,3-diacetylvilasinin 1 itself has been reported from *Melia volkensii* Gürke (Rogers et al., 1998), *Chisocheton paniculatus* Hiern (Connolly et al., 1979), *Azadirachta indica* A.Juss (Kraus and Cramer, 1981), and two African *Turraea* species, *Turraea holstii* Gürke (Mulholland et al., 1998) and *T. parvifolia* Deflers (Cheplogoi and Mulholland, 2003), while 1,3-diacetyl-12α-hydroxy-7-tigloylvilasinin 2 has been reported only from *Azadirachta indica* (Kumar et al., 1996).

From a chemotaxonomic standpoint, the isolation of 1,3-diacetylvilasinin 1 and 1,3-diacetyl-12α-hydroxy-7-tigloylvilasinin 2 supports the placement of *Malleastrum* within the subfamily Meliodeae. Although no limonoids of the prieurianin or evodulone classes, which are characteristic of the Meliodeae (Mulholland et al., 2000), were isolated in this study, all other species that have yielded vilasinin limonoids are members of this subfamily of the Meliaceae, with *Trichilia* and *Walsura*, in particular, fellow members of the same tribe.

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