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A rare secoiridoid monoterpene and a xanthone from *Tachia grandiflora* Maguire & Weaver

Adrian Martin Pohlit [a,*], Elba Vieira Mustafa dos Santos [a,b], Tatiane Cristina Mesquita da Silva [a], Sabrina Kelly Reis de Morais [a,b], Sergio Massayoshi Nunomura [a], Lena Struwe [c,d]

[a] Department of Technology and Innovation, National Institute of Amazon Research, 69060-001 Aleixo, Manaus, Brazil
[b] Graduate School in Chemistry, Federal University of Amazonas, Coroado, Manaus, Brazil
[c] Department of Ecology, Evolution, and Natural Resources, Rutgers University, New Brunswick, USA
[d] Department of Plant Biology and Pathology, Rutgers University, New Brunswick, USA

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1. Subject and source

The plant genus *Tachia* Aublet (Gentianaceae) was first described by the botanist Aublet based on plants collected in French Guiana. It is comprised of 13 species of mainly understory shrubs or small trees (Peters et al., 2005). *Tachia* sp. occur also in the wet forests of the Amazon Basin and the lower elevations of mountainous areas of Peru, Ecuador, Colombia, Venezuela, and Brazil, as well as Panama (one species). Seven species of *Tachia* are found in Brazil and in the greater Amazon watershed (Jensen and Shripsema, 2002). Whole *Tachia grandiflora* Maguire & Weaver plants were collected in the Campina and Adolpho Ducke Forest Reserves, both protected reserves located in the greater Manaus area, Brazil, and owned by the National Institute for Amazonian Research (INPA), Manaus, Brazil. Voucher specimens were deposited at the INPA Herbarium under the accession numbers 208104 (collector A. M. Pohlit, Sept. 26, 2000) and 205948 (collector A. M. Pohlit, Oct. 10, 2000), and species identity was corroborated by L. Struwe.

2. Previous work

There have been no phytochemical studies reported on any plant of the genus *Tachia*.

* Corresponding author. Tel./fax: +55 92 3643 3177.
E-mail addresses: ampohlit@inpa.gov.br, ampohlit@gmail.com (A.M. Pohlit).

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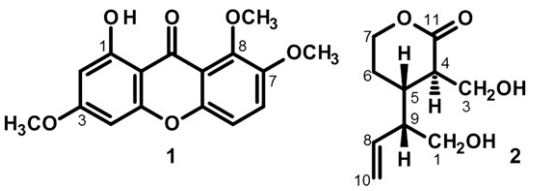

Fig. 1. Structures of decussatin (**1**) and amplexine (**2**) isolated from *Tachia grandiflora* in the present work.

3. Present study

Roots and mature leaves were separately dried in the shade and ground. Powdered roots were continuously extracted with MeOH (3 × 6 h). The combined extracts were rotary evaporated in a heat bath (≤40 °C) and then freeze-dried. The resulting dry MeOH extract (5 g) was dissolved in MeOH/H_2O (9:1) and partitioned with hexanes, then $CHCl_3$. The $CHCl_3$ fraction (950 mg) was subjected to silica gel CC. 10 fractions were obtained. Fraction 8 contained small crystalline plates or needles of 1-hydroxy-3,7,8-trimethoxyxanthone (decussatin, **1**, 24 mg) (Tchamo et al., 2000; Dua et al., 2004).

Powdered leaves (211 g) of *T. grandiflora* Maguire & Weaver were macerated in EtOH (2 × 1 wk). After total evaporation, dry EtOH extract (49.0 g) was dissolved in MeOH–H_2O (9:1) and this mixture was partitioned with hexanes, then $CHCl_3$. These fractions were rotary evaporated and freeze-dried to yield hexane (4.4 g) and $CHCl_3$ (13.6 g) fractions, respectively. Dry $CHCl_3$ fraction (10.0 g) was subjected to silica gel CC (elution with hexanes, then acetone/$CHCl_3$ gradient). Five pooled fractions resulted. Fraction 2 (2.00 g) was subjected to silica gel CC (acetone/$CHCl_3$ gradient). Nine pooled fractions were obtained. Fraction 7 (323 mg) was subjected to silica gel MPLC (elution with hexanes, hexanes-$CHCl_3$-*i*-PrOH, $CHCl_3$-*i*-PrOH). Six pooled fractions were obtained and fraction 5 (101 mg) was further separated on a column of Sepak silica (elution with hexanes, hexanes-Et_2O-*i*-PrOH gradient, then *i*-PrOH). Three pooled fractions were obtained and fraction 3 (46 mg) was subjected to pTLC to yield amplexine (djalonenol) (**2**, 25 mg) as a clear liquid ($R_F = 0.60$, 2:1 EtOAc–MeOH) (Rasoanaivo et al., 1994; Onocha et al., 1995; Santos, 2003).

4. Chemosystematic significance

Gentianaceae is a worldwide family of about 97 genera and 1700 species (Struwe and Albert, 2002). Its characteristic compounds include many unique xanthones and secoiridoids (Jensen and Shripsema, 2002). In fact, the Gentianaceae family is the source of the majority of xanthone compounds described so far. Most gentian species whose chemical composition has been investigated are temperate or subtropical herbs (*e.g.*, *Centaurium*, *Chironia*, *Eustoma*, *Orphium*, *Swertia* sp.). However, the greatest taxonomic diversity of gentians is found in the tropics, especially in South America. Only a few tropical species have been chemically investigated (*e.g. Anthocleista*, *Canscora*, *Macrocarpaea*, and *Schultesia* spp.) despite their diverse evolutionary history and ecological niches (Jensen and Shripsema, 2002). Of these four genera, African *Anthocleista* spp. and Andean *Macrocarpaea* are the only strictly woody species (Struwe et al., 2002), and only the latter is a member of the same evolutionary lineage (tribe Helieae) as *Tachia*. This is the first report on the chemical structure of components of a *Tachia* sp. (Fig. 1).

Tetra-oxygenated xanthones are characteristic chemical constituents in species of the Gentianaceae family (Peres et al., 2000; Jensen and Shripsema, 2002). The tetra-oxygenated xanthone decussatin (**1**) isolated herein from *T. grandiflora* Maguire & Weaver has been previously found in four gentian tribes (taxonomic subgroups of the family): Chironieae (*Canscora*, *Centaurium*, *Chironia*, *Eustoma*, *Orphium* and *Schultesia*; Peres et al., 2000), Gentianeae (*Comastoma*; Fan et al., 1988), *Gentiana*, *Gentianopsis* (Peres et al., 2000), *Halenia* (Zhang et al., 2003), *Lomatogonium* (You et al., 2007), *Swertia* (Peres et al., 2000), and *Tripterospermum* (Zhu et al., 2007)), Helieae (*Macrocarpaea*; Stout et al., 1969) and Potalieae (*Anthocleista*; Peres et al., 2000). The present work is thus the second report on the isolation of decussatin from a species of the strictly neotropical Helieae tribe.

Secoiridoids are found in all the tribes of Gentianaceae (Jensen and Shripsema, 2002). Amplexine (**2**), isolated from the leaves of *T. grandiflora* Maguire & Weaver in this work, is a rare dihydroxy monoterpene lactone aglycone of the secoiridoid 1-O-β-D-glucopyranosylamplexine. Previously, amplexine has been isolated from the leaves of *Anthocleista amplexicaulis* Baker (Gentianaceae, formerly classified in Loganiaceae; Rasoanaivo et al., 1994) and from the stems of *Anthocleista djalonensis* A. Chev. (Onocha et al., 1995).

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