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Phytochemistry, Vol. 23, No. 4, pp. 907–908, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

THE IDENTITY OF THE IRIDOID GLUCOSIDE TARPHETALIN WITH IPOLAMIIDE

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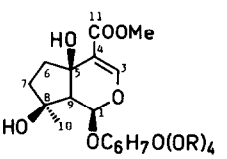
(*Received* 10 *May* 1982)

Key Word Index—*Stachytarpheta jamaicensis*; Verbenaceae; iridoid glucoside; tarphetalin; ipolamiide.

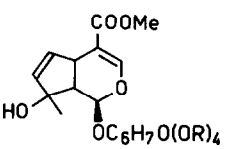
Abstract—^{1}H, ^{13}C NMR and MS data as well as chemical evidence show that the structure of tarphetalin should be corrected to that of ipolamiide.

As a part of our biosynthetic investigations on iridoid glucosides, we have studied the later stages in the biosynthesis of the main iridoid in *Stachytarpheta jamaicensis* (L.) Vohl (Verbenaceae). It has been reported [1] that *S. jamaicensis* contains ipolamiide (**1**), whereas later work [2] reports the occurrence of tarphetalin (**2**) as the main constituent of this plant. Other species of *Stachytarpheta* contain ipolamiide (**1**) [1, 3–5].

In the present work we isolated the glucosides from 123 g of *S. jamaicensis*. One iridoid glucoside **A** (635 mg, 0.5%) was obtained by reversed phase chromatography. The ^{1}H NMR spectrum (90 MHz, D_2O, DSS) of **A** was identical with that of authentic **1**. Some of its features are: δ 7.52 (*s*, H-3), 5.81 (*d*, $J_{1,9}$ = 0.8 Hz, H-1), 3.74 (*s*, CO_2Me), 2.49 (*d*, $J_{1,9}$ = 0.8 Hz, H-9), and 1.15 (*s*, 10-Me). The ^{13}C NMR spectrum of **A**: 169.0 (C-11), 153.0 (C-3), 113.8 (C-4), 99.2 (C-1′), 94.4 (C-1), 79.0 (C-8), 77.1 (C-5′), 76.1 (C-3′), 73.2 (C-2′), 71.3 (C-5), 70.4 (C-4′), 61.5 (C-6′), 60.6 (C-9), 52.6 (OMe), 39.4 (C-7), 37.9 (C-6), and 22.7 (C-10). The ^{13}C NMR spectrum of **1** has been published [4] but contains some misassignments. The physical data of **A** (given in Table 1) are virtually identical to those of **1** [6], and we thus conclude that *A* is ipolamiide (**1**).



R
1 H
1a Ac



R
2 H
2a Ac

As the physical data of **1** and **1a** are very similar to those of **2** and **2a** (Table 1) it was indicated that tarphetalin is identical with ipolamiide. The ^{1}H NMR (60 MHz,

Table 1. Physical data for **A**, **1**, **2**, **1a**, and **2a**

	A	**1** [6]	**2** [2]	**1a** [6]	**2a** [2]
mp	142–3°	144–5°	140–150.5°	173–174.5°	166.7°
$[\alpha]_D$	−139°	−136°	120.4°*	−107°	
	(*c* 1.2, MeOH)	(*c* 0.5, dioxane)	(*c* 1.16, EtOH)	(*c* 0.8, dioxane)	

*No sign is given for $[\alpha]_D$.

CD_3OD, TMS) data reported for tarphetalin [2] δ 7.48 (*s*, 1H), 5.78 (*d*, 0.8 Hz, 2H), 5.65–6.00 (2 × *dd*, 2H), 3.77 (*s*, 3H), and 1.25 (*s*, 3H) are in reasonable agreement with those of **2**. The only major difference is the two double doublets centered between δ5.65–6.00. Tarphetalin is reported [2] to give fragment ions in MS at *m/z* 226, 208, 139, 109, 73 and 61. With the exception of *m/z* 139, these peaks are also encountered in the mass spectrum of **1** in which 226 [aglucone $-2H_2O$] is the highest mass peak.

Based on the ^1H NMR, MS and physical data we thus conclude that tarphetalin is identical with ipolamiide (**1**).

Acknowledgements—Financial assistance from the Danish Natural Research Council and access to MS facilities from Danish Council for Scientific and Industrial Research are acknowledged. We thank Dr. J. Øgaard Madsen for recording the mass spectrum of ipolamiide, and Dr. K. Rahn for confirming the identity of the plant material (voucher No. 51–81, IOK).

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Phytochemistry, Vol. 23, No. 4, pp. 908–909, 1984.
Printed in Great Britain.

0031-9422/84 $3.00 + 0.00

SECOIRIDOIDS FROM *EXACUM TETRAGONUM*

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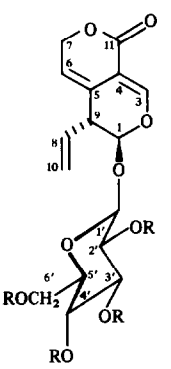
(*Received* 12 *August* 1983)

Key Word Index—*Exacum tetragonum*; Gentianaceae; secoiridoids; methyl ester of methylgrandifloroside; gentiopicroside.

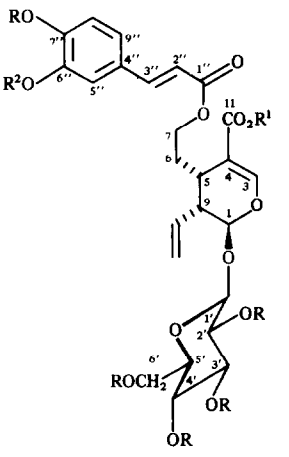
Abstract—Extraction of *Exacum tetragonum* furnished the secoiridoids gentiopicroside and methylgrandifloroside, the latter in the form of its methyl ester.

INTRODUCTION

Exacum is a genus of about 20 species, mostly Indian, whose chemical examination has been limited to brief reports on *E. affine* (traces of *p*-coumaric acid) [1], *E. bicolor* (ursolic acid, apigenin, luteolin, hydroxybenzoic and hydrocinnamic acids) [1, 2], *E. pedunculatum* (luteolin, diosmetin, hydroxybenoic and hydroxycinnamic acids) [2] and *E. macranthum* (linarin) [3]. In the following we describe isolation of gentiopicroside (**1a**) and the methyl ester **2b** of methylgrandifloroside (**2a**) from *E. tetragonum* Roxb., (Loganiaceae) a species found in the Himalayas from Komaon to Bhutan, in Khasia and in China.



1a R = H
1b R = Ac



2a R, R^1 = H, R^2 = Me
2b R = H, R^1, R^2 = Me
2c R = Ac, R^1, R^2 = Me
2d R, R^1, R^2 = H

RESULTS AND DISCUSSION

Gentiopicroside (**1a**) was identified by its properties and by ^1H NMR analysis, including spin-decoupling, of its tetraacetate **1b**. The structure of **2b** was established by conversion to the pentaacetate **2c** and analysis of its ^1H and ^{13}C NMR spectra (Tables 1 and 2). The presence of a