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).

REFERENCES

1. Kooiman, P. (1975) *Acta Bot. Neerl.* **24**, 459.
2. Jawad, F. H., Doorenbosx, N. J. and Chengt, P. C. (1977) *Egypt. J. Pharm. Sci.* **18**, 511.
3. Tantisewie, B. and Sticher, O. (1975) *Phytochemistry* **14**, 1462.
4. Garnier, J. (1977) *Plantes Medicinalis et Phytotherapie* **11**, 303.
5. De Luca, C. (1980) *Fitoterapia* **51**, 279.
6. Scarpati, M. L. and Guiso, M. (1969), *Gazz. Chim. Ital.* **99**, 1150.

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

0031–9422/84 $3.00 + 0.00

SECOIRIDOIDS FROM *EXACUM TETRAGONUM*

SANJIB DAS, RABINDRA N. BARUA, RAM P. SHARMA, JOGENDRA N. BARUAH, PALANIAPPAN KULANTHAIVEL* and WERNER HERZ*

Regional Research Laboratory, Jorhat 785 006, Assam, India; *Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

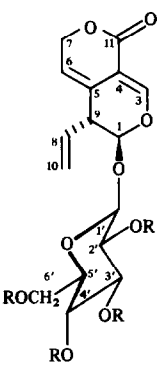
(*Received* 12 *August* 1983)

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

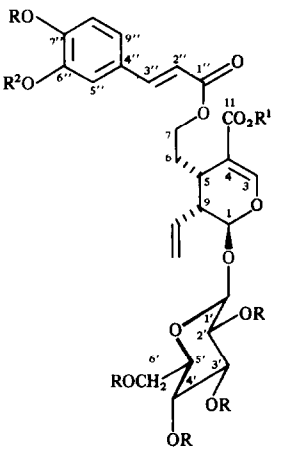
Abstract—Extraction of *Exacum tetragonum* furnished the secoiridoids gentiopicroside and methylgrandifloroside, the latter in the form of its methyl ester.

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

Table 1. ^{1}H NMR spectrum of **2c** (270 MHz, $CDCl_3$)

H	δ	H	δ
1	in 5.3 *m*	5′	3.70 (part. obsc).
3	7.38 *br*	6′a	4.30 *dd*
5	2.87 *dddd*	6′b	4.15 *dd*
6a	2.28 *m*	2″	6.30 *d*
6b	1.73 *m*	3″	7.61 *d*
7a	4.27 (obsc)	5″	7.26 *d*
7b	4.15 (obsc)	8″	6.98 *d*
8	5.63 *ddd*	9″	7.40 *dd*
9	2.70 *ddq*	OMe (ester)	3.87
10a	in 5.3 *m*	OMe (ether)	3.70
10b	in 5.2 *m*	Ac (arom)	2.33
1′	4.89 *d*	Ac (Glu)	2.09
2′	5.02 *dd*		2.03
3′	5.23 *t*		2.01
4	5.11 *t*		1.94

Coupling constants (Hz): 1, 9 = 9, 10a = 9, 10b = 1.5, 3, 5 = 1, 5, 9 = 5; 8, 9 = 9; 8, 10a = 17.5; 8, 10b = 9; 10a, 10b = 1.5; 1′, 2′ = 8; 2′, 3′ = 3′, 4′ = 4′, 5′ = 9; 5′, 6′a = 4.5; 5′, 6′b = 2.5; 6′a, 6′b = 12.5; 2″, 3″ = 16; 5″, 9″ = 1.5; 8″, 9″ = 8.5.

Table 2. ^{13}C NMR spectrum of **2c** (67.89 MHz, $CDCl_3$)

C	δ	C	δ
1	96.27 *d**	1″	166.89‡
3	150.73 *d*	2″	116.82 *d*
4	111.09	3″	143.54 *d*
	28.11 *d*	4″	127.74
6	27.81 *t*	5″	112.37 *d*
7	62.43 *t*†	6″	152.83
8	132.80 *d*	7″	140.08
9	43.14 *d*	8″	127.63 *d*
10	120.30 *t*	9″	122.05 *d*
1	166.97‡	OMe (ester)	51.29 *q*
1′	96.00 *d**	OMe (ether)	56.03 *q*
2′	70.64 *d*	Ac–C=O	170.56, 170.13, 169.31
3′	72.56 *d*		169.31, 168.93, 168.71
4′	68.27 *d*	Ac–Me	20.72 *q*, 20.59 *q* (3)
5′	72.27 *d*		20.24 *q*
6′	61.75 *t*†		

*, †, ‡Assignments may be interchanged.

β-D-glucosetetraacetate moiety on C-1 was obvious from the ^{1}H NMR spectrum. The sequence H-1, H-9, H-5, H-6a,b, H-7a,b with the vinyl group attached to C-9 was established by spin decoupling, the stereochemistry at C-1, C-9 and C-5 being apparent from the coupling constants. H-3 was allylically coupled to H-6 as in the ^{1}H NMR spectrum of **1b** and the presence of a methyl ester on C-11 was inferred from the presence of a three proton singlet at δ 3.87 and a carbon quartet at δ 51.29. NMR spectroscopy also indicated that the acid esterifying the C-7 hydroxyl was either acetylferulic or acetylisoferulic acid; a decision in favour of **2b** was reached by hydrolysis which resulted in isolation of ferulic acid.

Although **2b** is new, the free acids methylgrandifloroside (**2a**) and grandifloroside (**2d**) have been reported previously [4] as constituents of *Anthocleista grandiflora**. It is possible that **2b** is an artifact arising from **2a** as methanol was used in one step of the purification procedure.

EXPERIMENTAL

Above ground parts of *E. tetragonum* (1 kg), collected in the Itanagar area of Arunachal Pradesh, India (voucher on deposit in herbarium of RRL, Jorhat) were extracted with $CHCl_3$ in a Soxhlet apparatus until the extract was colourless. After removal of solvent at red pres. the residue (66 g) was dissolved in 300 ml MeOH–H_2O (9:1), allowed to stand overnight and filtered. The filtrate was washed with petrol (bp 60–80°, 6 × 200 ml), the MeOH portion was concd at red pres. and the residue was extracted with $CHCl_3$ (8 × 200 ml). Evaporation of the washed and dried extract furnished 24 g of a gum which was chromatographed over 425 g of silica gel (60–120 mesh, BDH, India), 200 ml fractions being collected as follows. Fr. 1–5 (C_6H_6), 6–15 (C_6H_6–EtOAc, 9:1), 16–31 (C_6H_6–EtOAc, 4:1), 32–51 (C_6H_6–EtOAc, 2:1), 52–70 (C_6H_6–EtOAc, 1:1), 71–83 (C_6H_6–EtOAc, 1:2), 84–99 (EtOAc), 100–111 (EtOAc–MeOH, 19:1), 112–139 (EtOAc–MeOH, 9:1), 140–150 (EtOAc–MeOH, 4:1), 151–163 (EtOAc–MeOH, 1:1).

Fr. 103–110 (2 g), each of which gave the same major spot on TLC, were combined and purified to give 1.2 g **2b** as a gum, $[\alpha]_D$ −59.5° (MeOH, *c* 0.4 g/100 ml); IR ν_{max}^{film} cm^{-1}: 3400, 1700, 1625, 1150 and 1060. Due to its insolubility in $CDCl_3$ 60 mg **2b** in 1.5 ml pyridine and 3 ml Ac_2O was kept overnight at room temp. The usual work-up and purification by prep. TLC (C_6H_6–EtOAc, 4:1) furnished 55 mg of the pentaacetate **2c** as a gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1700, 1635, 1625, 1605, 1200, 1150, 1050, 915, 865 and 765; ^{1}H and ^{13}C NMR: Tables 1 and 2.

Fr. 114–124 (1.5 g), each of which gave the same major spot on TLC, were combined and purified by prep. TLC ($CHCl_3$–MeOH, 4:1) to give 600 mg gentiopicroside as a gum, IR ν_{max}^{film} cm^{-1}: 3400, 1700, 1605, 1200, 1100 and 1050. Acetylation of 30 mg of this substance (1 ml pyridine, 2 ml Ac_2O) in the way described for **2b** and purification by prep. TLC (C_6H_6–EtOAc, 3:1) gave 30 mg **1b**; IR ν_{max} cm^{-1}: 1740, 1700, 1600, 1200, 1065, 975 and 910; ^{1}H NMR ($CDCl_3$, 270 MHz): δ 5.42 (*d*, *J* = 2 Hz, H-1), 7.42 (*br*, H-3), 5.58 (*m*, $W_{1/2}$ = 6 Hz, H-6), 5.08 (*d* (*br*), *J* = 17 Hz, H-7a), 4.96 (*d* (*br*), *J* = 17 Hz, H-7b), 5.67 (*ddd*, *J* = 17, 10.5, 7 Hz, H-8), 3.29 (*d* (*br*), *J* = 7 Hz, H-9), 5.24 (*d* (*br*), *J* = 17 Hz, H-10a), 5.23 (*d* (*br*), *J* = 10.5 Hz, H-10b), 4.87 (*d*, *J* = 8 Hz, H-1′), 4.91 (*t*, *J* = 8.5 Hz, H-2′), 5.23 (*t*, *J* = 9 Hz, H-3′), 5.09 (*t*, *J* = 9 Hz, H-4′), 3.75 (*ddd*, *J* = 9, 5, 2.5 Hz, H-5′), 4.22 (2p, centre of AB system, H-6′), 2.10, 2.03, 2.00 and 1.95 (Ac).

Acknowledgement—Work at the Florida State University was supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.

REFERENCES

1. Hegnauer, R. (1966) *Chemotaxonomie der Pflanzen*, Vol. 4. Birkhäuser, Basel.
2. Daniel, M. and Sabnis, S. D. (1978) *Curr. Sci.* **47**, 109.
3. Gunatilaka, A. A. L., Sultanbawa, M. U., Wimalasena, K. and Balasubramaniam, S. (1983) *Planta Med.* **48**, 61.
4. Chapelle, J.-P. (1976) *Phytochemistry* **15**, 1305.

*In ref. [4], the formulas of **2a** and **2d** misrepresent the 2″,3″-double bond as *Z* instead of *E*.