Phytochemistry, Vol 28, No 6, pp 1759–1760, 1989
Printed in Great Britain

0031–9422/89 $3.00 + 0.00
Pergamon Press plc

SHORT REPORTS

TWO PHTHALIDE GLUCOSIDES FROM *GENTIANA PYRENAICA*

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(*Received* 19 *September* 1988)

Key Word Index—*Gentiana pyrenaica*, Gentianaceae, phthalide glucoside.

Abstract—From the aerial parts of *Gentiana pyrenaica* two new phthalide glucosides have been isolated. Their structures have been established by spectroscopic means as 3-(3-*O*-β-D-glucosylpropyl)phthalide and 3-[3-(6-vanilloyloxy-*O*-β-D-glucosyl)propyl]phthalide

INTRODUCTION

Gentiana pyrenaica L. (Gentianaceae) was collected when in flower from the Pyrenees. Five *C*-glycosylflavones and one flavonol glucoside have been reported in leaves and stems of this species [1]. Our investigation on the aerial parts led to the isolation of two new phthalide glucosides, pediglucoside (**1**) and 6′-vanilloylpediglucoside (**2**). This paper deals with the structural elucidation of these compounds based on spectral evidence.

RESULTS AND DISCUSSION

Dried and powdered aerial parts of *G. pyrenaica* were extracted by solvents of increasing polarity as described in the Experimental. The chloroform extract was separated by centrifugal TLC and HPLC to afford compounds **1** and **2**.

Compound **1** presented a UV spectrum characteristic of the phthalide ring (λ_{max}nm. 225, 275, 278), identical to that of pedirutinoside (**3**), previously isolated from leaves of *Gentiana pedicellata* [2]. The comparison of the ^{1}H NMR spectrum of **1** and **3** showed a close relationship between these compounds and revealed for **1** the lack of the rhamnose moiety present in **3**. This result was confirmed by the R_f value of **1** being higher than that of **3** and by FABMS data (*m/z* 355 $[M+H]^+$).

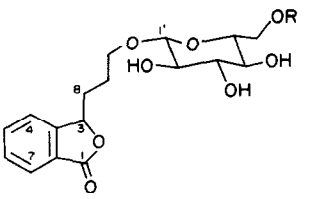
The proposed structure was also supported by the ^{13}C NMR spectrum of **1** which displayed a signal at δ62.8, indicating a free hydroxyl group at C-6′. Thus, **1** is 3-(3-*O*-β-D-glucosylpropyl)phthalide for which we propose the name pediglucoside.

Compound **2** showed UV maxima at 226, 263, 278, 292 nm. ^{1}H NMR data of **2** were closely similar to those of **1**, except for the presence of additional signals above 6.7 ppm characteristic of a 1,3,4-trisubstituted aromatic ring and at δ3.84 attributable to a methoxy group. NOE experiments showed enhancements between this methoxy and H-2″, indicating **2** to be a vanilloyl ester of **1**. The deshielding of H-6′A and H-6′B at δ4.58 and 4.39 when compared to **1** showed that the vanilloyl unit was located at position 6′ of the glucose. This result was also confirmed, in the ^{13}C NMR spectrum, by the corresponding downfield shift of the C-6′ signal ($\Delta\delta = +2.2$ ppm) while C-5′ was shifted upfield by a similar amount. This structure was in accordance with FABMS which showed a fragment at *m/z* 313 arising from the glucose part esterified with vanillic acid. Thus **2** is 3-[3-(6-vanilloyloxy-*O*-β-D-glucosyl)propyl]phthalide or 6′-vanilloylpediglucoside.

In the Gentianaceae, phthalides were first reported from *Gentiana pedicellata* [2–5] which belong, like *G. pyrenaica*, to the *Chondrophylla* section. The isolation from the latter species of further phthalides closely related to those of *G. pedicellata* may be of chemotaxonomic interest.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded with TMS as int. standard.



1 R=H
2 R=vanilloyl
3 R=rhamnosyl

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Table 1 ^{1}H NMR data (300 MHz, CD_3OD) of the phthalides

H	1	2
3	5 66 *dd* (7–3 5)	5 56 *dd* (7–3.5)
4	7 63 *br d* (7 5)	7 54 *br d* (7 5)
5	7 76 *td* (7 5–1)	7 67 *td* (7 5–1)
6	7 58 *br t* (7 5)	7 48 *br t* (7 5)
7	7 85 *br d* (7 5)	7 77 *br d* (7 5)
8A	2 28 *m*	2 23 *m*
8B	1 69–1 94 *m*	1 65–1 82 *m*
9		
10A	3.98 *ddd* (9.5–7–5.5)	3 91 *ddd* (9 5–7–5.5)
10B	3.63 *dt* (9 5–6)	3 69 *dt* (9 5–5)
1′	4 25 *d* (8)	4 32 *d* (7 5)
2′–5′	3 17–3 34 *m*	3 20–3 60 *m*
6′A	3 85 *dd* (12–2)	4.58 *dd* (12–2)
6′B	3 65 *dd* (12–5)	4 39 *dd* (12–6)
2″		7.46 *d* (2)
5″		6 79 *d* (8 5)
6″		7 49 *dd* (8 5–2)
OMe		3 84 s

Values in parentheses are coupling constants in Hz

Table 2. ^{13}C NMR data (75 46 MHz, CD_3OD) of the phthalides

C	1	2
1	172.7	172 6
3	83 1	82 8
3a	151.9	151 7
4	123 5	123 4
5	135 5	135 5
6	130 3	130.2
7	126 2	126.2
7a	127 0	126.8
8	26 2	26 4
9	32 4	32 3
10	70 0	69 9
1′	104 3	104 5
2′	75 1	75 1
3′	77 9	78 0
4′	71 7	72 0
5′	78 2	75 5
6′	62 8	65 1
Ar-CO		168 0
1″		122 5
2″		116 0
3″		148 8
4″		153 0
5″		113 7
6″		125 1
OMe		56 5

Isolation. The plant material was collected at Puymorens pass in the French Pyrenees (Pyrénées Orientales, France) in July 1986. A voucher specimen is deposited at the Pharmacognosy Laboratory Herbarium Dried and powdered aerial parts (240 g) were successively extracted with *n*-hexane, C_6H_6, $CHCl_3$, Me_2CO and MeOH at room temp The $CHCl_3$ extract was submitted to centrifugal TLC eluting by $CHCl_3$–MeOH with increasing MeOH content Fraction eluted with $CHCl_3$–MeOH (9 1) afforded compound **2** (3 5 mg) purified by HPLC on a silica gel column (C_6H_{14}–*iso*-PrOH–MeOH 14.3 3) and on RP-18 (MeOH–H_2O 9 11) The fraction eluted with $CHCl_3$–MeOH (3 2) yielded **1** (9 mg) after final purification by HPLC on RP-18 (MeOH–H_2O 7 13).

Pediglucoside (**1**) UV λ_{max}^{MeOH} nm 225, 275, 278 FABMS *m/z* 355 $[M+H]^+$, 193 $[M+H-Glc]^+$, 175, 133 ^{1}H NMR Table 1 ^{13}C NMR Table 2

6′-Vanilloylpediglucoside (**2**) UV λ_{max}^{MeOH} nm 226, 263, 278, 292. FAB$^+$MS *m/z* 527 $[M+Na]^+$, 505 $[M+H]^+$, 313, 193, 175, 151, 133 FAB-MS *m/z*: 503 $[M-H]^-$, 167 ^{1}H NMR. Table 1 ^{13}C NMR Table 2

Acknowledgements—We thank Mr C Bosso (CERMAV) for FABMS measurements and Miss N. Durand for secretarial help

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