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IRIDOIDS FROM *GENTIANA VERNA*

E. Mpondo Mpondo* and J. Garcia

Laboratoire de Pharmacognosie, UFR de Pharmacie, Université J. Fourier-Grenoble I, Domaine de la Merci, 38700 La Tronche, France

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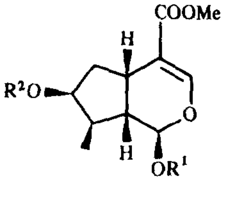
Key Word Index—*Gentiana verna*; Gentianaceae; iridoids.

Abstract—The isolation of three iridoids from *Gentiana verna* is reported. These include loganetin, loganin and 4'-*m*-hydroxybenzoyl loganin which are the first iridoids identified from the title species.

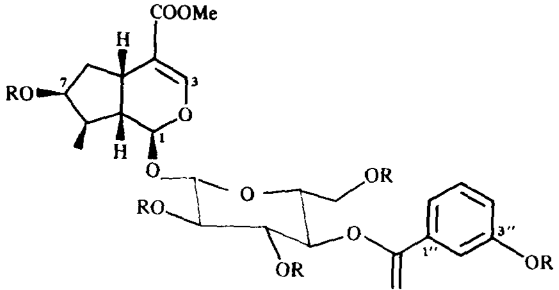
INTRODUCTION

Gentiana verna L. (Gentianaceae) has been investigated for flavones and xanthones [1–3]. Previous studies on this species also resulted in the identification of the known secoiridoid gentiopicroside [4] but no iridoid was reported. This paper deals with the occurrence in *G. verna* of the known iridoids loganetin (**1**), loganin (**2**) and a new iridoid 4'-*m*-hydroxybenzoyl loganin (**3**).



1 $R^1 = R^2 = H$

2 R^1 = β-D-glucopyranosyl, R^2 = H



3 R = H

3a R = Ac

RESULTS AND DISCUSSION

The acetone extract of dried and powdered aerial parts of *G. verna* was successively fractionated on a silica gel column and by centrifugal TLC. The final purification on an HPLC RP-18 column afforded three iridoids (**1**–**3**). Compound **1** was identified as loganetin by ^{1}H NMR with the aid of compared literature values [5] and by FABMS *m/z* 227 $[M-H]^-$, *m/z* 229 $[M+H]^+$. These facts were in accordance with spectral data of the aglycone of loganin (Table 1). Loganetin was first isolated [6] as a natural compound from *Desfontainia spinosa* (Loganiaceae). This is the second natural occurrence of this compound which we also detected in acetone extracts of fresh aerial parts. Compound **2** was identified as loganin by comparison (Co-TLC, HPLC and spectral data) with an authentic sample and literature values [7].

Compound **3** presented a sulphuric vanillin coloration identical to that of **2** suggesting that it was an iridoid. Its UV spectrum (λ_{max}^{MeOH} 232, 297 nm), as well as its ^{1}H NMR values (δ5.30 H-1, δ7.41 H-3, δ3.12 H-5, δ1.62–2.24 H-6 H-8 H-9, δ4.04 H-7), indicated that **3** consisted of a loganin-like structure and an aromatic moiety. The latter was identified as *m*-hydroxy benzoyl by comparison with the literature NMR values. [8]. Other evidence, such as FABMS *m/z* 137 [*m*-hydroxybenzoate]$^-$, *m/z* 227 [loganine aglucone]$^-$, FABMS *m/z* 229 [loganine aglucone]$^+$ and in the ^{1}H NMR spectrum protons above δ7.00, confirmed this fact. The ^{1}H NMR spectrum of the acetylated derivative of **3** displayed one aromatic acetyl group (δ2.34) and four alcoholic acetyls (δ2.10, 2.04, 2.03, 1.92) attributed to the glucose moiety. The downfield shift of H-4' (δ4.98) and C-4' (δ72.9) indicated the acylation by the benzoic acid on this position. These facts were confirmed by the upfield chemical shift of C-5' (δ76.4) and C-3' (δ75.8). Compound **3** was therefore identified as 4'-*m*-hydroxybenzoyl loganin, a new natural compound.

EXPERIMENTAL

General. NMR spectra were recorded with TMS as int. standard.

Isolation. G. verna was collected when in flower (August 1987) at the Col du Galibier (Isère-France). A voucher specimen has been deposited at the Pharmacognosy laboratory herbarium. Dried and powdered aerial parts (180 g) were successively extracted with *n*-hexane, C_6H_6, Me_2CO and MeOH. The Me_2CO extract (6 g) was fractionated on silica gel CC ($CHCl_3$ with increasing MeOH content) and over centrifugal TLC ($CHCl_3$ with increasing MeOH content). The final purification using

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*Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR data of the iridoids **1**–**3** and **3a**

H	**1**	**2**	**3**	**3a**
1	4.85 *d* (4.5)	5.37 *d* (4.5)	5.30 *d* (4.5)	5.22 *d* (4.5)
3	7.40 *d* (1.5)	7.37 *d* (1.5)	7.41 *d* (1.5)	7.35 *d* (1.5)
4	—	—	—	—
5	3.10 *m*	3.10 *dddd* (9.5–8–7.5–1.5)	3.12 *m*	3.00 *m*
6A	2.26 *m*	2.25 *ddd* (14–8–1.5)	2.24 *ddd* (14–8–1.5)	*1.67–2.24
6B	1.56 *m*	1.60 *ddd* (14–7.5–4.5)	1.62 *ddd* (14–8–5)	*1.67–2.24
7	4.02 *m*	4.04 *ddd* (5–4.5–1.5)	4.04 *td* (5–1.5)	5.25 *m*
8	1.86 *m*	1.86 *dqd* (9–7.5–5)	1.88 *dqd* (9–6.5–5)	*1.67–2.24
9	2.07 *m*	2.03 *ddd* (9.5–9–4.5)	2.06 *td* (9–4.5)	*1.67–2.24
10	1.06 *d* (6.5)	1.08 *d* (7.5)	1.11 *d* (6.5)	1.03 *d* (6.5)
COOMe	3.68 *s*	3.68 *s*	3.68 *s*	3.71 *s*
Ac	—	—	—	1.92–2.34
1′		4.65 *d* (8)	4.76 *d* (8)	4.86 *d* (8)
4′		3.25–3.40	4.98 *t* (9)	5.13 *t* (9)
2″			7.44 *dd* (1.5–1)	7.76 *dd* (1.5–1)
4″			7.02 *ddd* (7.5–1.5–1)	7.46 *ddd* (7.5–1.5–1)
5″			7.29 *t* (7.5)	7.26 *t* (7.5)
6″			7.52 *dt* (7.5–1)	7.93 *dt* (7.5–1)

Values in parenthesis are coupling constants in Hz.
*Not clear due to overlapping.

Table 2. ^{13}C NMR data of compounds **2** and **3**

C	**2***	**3**
1	97.6	97.6
3	152.0	152.0
4	114.0	114.2
5	32.1	32.1
6	42.7	42.7
7	74.9	74.9†
8	42.1	42.1
9	46.4	46.5
10	13.4	13.4
COOMe	169.4 and 51.6	167.4 and 51.6
1′	100.0	100.1
2′	74.7	75.0†
3′	77.9	75.8
4′	71.5	72.9
5′	78.3	76.4
6′	62.7	62.4
1″		132.4
2″		117.2
3″		158.6
4″		121.5
5″		130.6
6″		121.8
Ar-CO		169.5

†Values may be interchanged.
*Values contained in ref. [7].

HPLC on an RP-18 column afforded **1** (1.5 mg) and **3** (5 mg) with H_2O–MeOH (2:3) as eluent and **2** (1.5 mg) with H_2O–MeOH (7:3) as eluent.

Loganetin (**1**). UV λ_{max}^{MeOH} nm: 230. FABMS *m/z*: 229 [M + H]$^+$, 211, 179, 151, 107. FABMS *m/z*: 227 [M − H]$^-$, 137, 127, 101. ^{1}H NMR: CD_3OD, 200 MHz (see Table 1).

Loganin (**2**). UV λ_{max}^{MeOH} nm: 230. FABMS *m/z*: 413 [M + Na]$^+$, 391 [M + H]$^+$, 369, 299, 277, 229 [M + H − glc]$^+$, 207. ^{1}H NMR: CD_3OD, 300 MHz (see Table 1). ^{13}C NMR: CD_3OD, 75 MHz (see Table 2).

4′-m-Hydroxybenzoyl loganin (**3**). UV λ_{max}^{MeOH} nm: 232, 297. FABMS *m/z*: 533 [M + Na]$^+$, 511 [M + H]$^+$, 455, 283, 253, 229 [M + H − glucobenzoyl]$^+$, 211, 179, 151, 107. FABMS *m/z*: 509 [M − H]$^-$, 319, 305, 277, 227 [M − glucobenzoyl]$^-$, 153, 137, 127, 101. ^{1}H NMR: CD_3OD, 300 MHz (see Table 1). ^{13}C NMR: CD_3OD, 75 MHz (see Table 2).

Acetylation of **3**. This was conducted by the usual method with Ac_2O–pyridine. The acetylated derivative (**3a**) was purified by HPLC on silica gel using *n*-hexane–*iso*-*Pr*OH–MeOH (14:3:3) as eluent.

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