Pergamon

0031-9422(94)00687-3

Phytochemistry, Vol. 38, No. 3, pp. 793–794, 1995

0031-9422/95 $9.50 + 0.00

MINOR IRIDOIDS FROM *THEVETIA PERUVIANA**

FUMIKO ABE, TATSUO YAMAUCHI,† SHOJI YAHARA‡ and TOSHIHIRO NOHARA‡

Faculty of Pharmaceutical Sciences, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-80, Japan; ‡Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oehonmachi, Kumamoto 862, Japan

(*Received in revised form* 1 *August* 1994)

Key Word Index—*Thevetia peruviana*; Apocynaceae; 10-*O*-β-D-fructofuranosyltheviridoside; 6′-*O*-β-D-glucopyranosyltheviridoside.

Abstract—Two minor iridoids isolated from the leaves of *Thevetia peruviana* were shown to be 10-*O*-β-D-fructofuranosyltheviridoside and 6′-*O*-β-D-glucopyranosyltheviridoside.

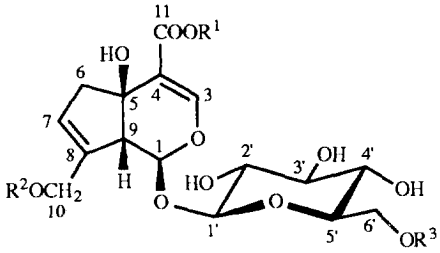
INTRODUCTION

Thevetia peruviana (Pers.) K. Schum. is indigenous to tropical America and grown widely throughout the world. In the preceding paper, we reported on the cardenolide and pregnane glycosides isolated from the frozen leaves [1]. Two iridoids, theviridoside [2] and theveside [3] have been isolated from *Thevetia*. This paper reports on the isolation from frozen leaves of two minor iridoids composed of theviridoside combined with either one D-fructose or one D-glucose moiety.

RESULTS AND DISCUSSION

When the crude extract obtained from frozen leaves was subjected to reversed-phase column chromatography, two glycosides (**1**, **2**) were isolated. These glycosides preceded theviridoside (**3**) and showed a similar blue staining on TLC after heating with H_2SO_4. FAB-mass spectometry of **1** afforded a $[M + Na]^+$ peak at *m/z* 589.1743, suggesting a molecular formula, $C_{23}H_{34}O_{16}$, one hexose unit greater than that of **3**. In the ^{1}H NMR spectrum, signals from theviridoside, including -CO_2Me, H-1, H-3, H-6, H-7, H-10a, b and H-1′ were observed. In addition, the presence of two sets of hydroxylated methylene group were indicated: δ4.20 (2H), and δ4.26 and 4.33, in addition to the signals of H-6′a, b (δ4.34, 4.54). In the ^{13}C and ^{1}H–^{13}C COSY spectra, the signals from the fructofuranosyl moiety were easily assignable. The β-linkage of the furanose moiety to C-10 was confirmed by the NOEs between H-10a, b (δ4.64, 5.02)/H-1″ (δ4.20), and H-1″/H-3″ (δ5.14). Although no downfield shift of C-10 was observed, the β-carbon (C-8) showed an uplift shift (− 3.9 ppm) owing to glycosylation at C-10.

Glycoside **2** gave the same molecular formula as **1**. In the ^{1}H and ^{13}C NMR spectra, all signals owing to theviridoside were assignable, and the hexose unit was identified as glucose. The linkage to theviridoside was assigned to be at C-6′ based on the cross-peak between H-1″/C-6′ and H-6′ a, b/C-1″ in the 2D HMBC spectrum and by comparison of the ^{13}C NMR signals with those of other gentiobiosides.



	R^1	R^2	R^3
1	Me	β - D - fructofuranosyl	H
2	Me	H	β - D - glucopyranosyl
3	Me	H	H
4	H	H	H

As in the case of 10-benzoyltheviridoside [4], which was previously obtained from the fresh leaves of *Cerbera manghas*, **1** was not observed, possibly owing to hydrolysis to **3**, while **2** was unaltered in the air-dried leaves.

EXPERIMENTAL

General. NMR: 400 or 500 MHz (^{1}H), and 100 MHz or 125 MHz (^{13}C) in pyridine-d_5 with TMS as int. standard; CC and TLC: silica gel, solvent (1) $CHCl_3$–MeOH–H_2O (7:3:1, bottom layer), solvent (2) EtOAc–MeOH–H_2O (8:2:1, top layer). Spray reagent for TLC: 10% H_2SO_4.

Plant material. Thevetia peruviana (Pers.) K. Schum. was cultivated in the greenhouse of Kumamoto University and harvested in October 1993. The leaves were frozen immediately at − 25°.

*Part 4 in the series '*Thevetia*'. For Part 3, see ref. [1].

†Author to whom correspondence should be addressed.

Extraction and isolation of iridoids. Frozen leaves (1.5 kg) were percolated with cold MeOH. The percolate was concd *in vacuo* and extracted with C_6H_6. The H_2O layer was passed through polystyrene column (MCI-gel) eluted with H_2O, and 25, 50 and 75% MeOH. The 25% H_2O eluted was then chromatographed on a YMC-gel column eluted with 10% MeCN. The fraction showing blue staining on TLC with H_2SO_4 reagent at a more polar R_f value than **3** was purified by silica gel CC with solvent 1, and finally by HPLC (eluting with 10% MeCN) to afford **1** (7 mg) and **2** (7 mg). The fractions containing **3** (10 g) and theveside (**4**) (1.4 g) were not purified further.

10-O-β-D-*Fructofuranosyltheviridoside* (**1**). Solid, $[\alpha]_D^{25}$ − 17.1° (MeOH; *c* 0.48). FAB-MS *m/z*: 589.1743, $C_{23}H_{34}O_{16}Na$ requires 589.1745. ^{1}H NMR: δ2.95, 3.10 (1H each, *br d*, *J* = 17 Hz, H-6), 3.50 (1H, *d*, *J* = 6 Hz, H-9), 3.57 (3H, *s*, -CO_2Me), 3.95 (1H, *m*, H-5′), 4.08 (1H, *t*, *J* = 8 Hz, H-2′), 4.20 (2H, *br s*, H-1″), 4.26 (1H, *dd*, *J* = 12, 6 Hz, H-6″a), 4.33 (1H, *dd*, *J* = 12, 3 Hz, H-6″b), 4.34 (1H, *dd*, *J* = 12, 6 Hz, H-6′a), 4.50 (1H, *m*, H-5″), 4.54 (1H, *dd*, *J* = 12, 2 Hz, H-6′b), 4.64, 5.02 (1H each, *br d*, *J* = 12 Hz, H-10), 4.94 (1H, *t*, *J* = 8 Hz, H-4″), 5.14 (1H, *d*, *J* = 8 Hz, H-3″), 5.33 (1H, *d*, *J* = 8 Hz, H-1′), 5.86 (1H, *br s*, H-7), 6.12 (1H, *d*, *J* = 6 Hz, H-1), 7.66 (1H, *s*, H-3); ^{13}C NMR: δ47.3 (*t*, C-6), 50.8 (*q*, OMe), 57.3 (*d*, C-9), 60.7 (*t*, C-10), 62.5 (*t*, C-6′), 63.1 (*t*, C-1″), 64.0 (*t*, C-6″), 71.3 (*d*, C-4′), 74.6 (*d*, C-2′), 75.7 (*s*, C-5), 77.1 (*d*, C-4″), 78.3 (*d*, C-3′), 78.8 (*d*, C-5′), 79.4 (*d*, C-3″), 83.8 (*d*, C-5″), 97.8 (*d*, C-1), 100.9 (*d*, C-1′), 105.5 (*s*, C-2″), 114.8 (*s*, C-4), 126.0 (*d*, C-7), 139.4 (*s*, C-8), 152.5 (*d*, C-3), 167.0 (*s*, C-11).

6′-O-β-D-*Glucopyranosyltheviridoside* (**2**). Solid, $[\alpha]_D^{32}$ − 28.3° (MeOH; *c* 0.30), FAB-MS *m/z*: 589.1746, $C_{23}H_{34}O_{16}Na$ requires 589.1745. ^{1}H NMR: δ3.20, 3.22 (1H each, *br d*, *J* = 17 Hz, H-6), 3.46 (1H, *d*, *J* = 7 Hz, H-9), 3.58 (3H, *s*, -CO_2Me), 3.92 (1H, *t*, *J* = 9 Hz, H-4′), 4.21 (1H, *dd*, *J* = 11, 4 Hz, H-6′a), 4.34 (1H, *dd*, *J* = 12, 5 Hz, H-6″a), 4.49 (1H, *dd*, *J* = 12, 2 Hz, H-6″b), 4.61, 4.87 (1H each, *d*, *J* = 15 Hz, H-10), 4.77 (1H, *dd*, *J* = 11, 1 Hz, H-6′b), 5.09 (1H, *d*, *J* = 7 Hz, H-1″), 5.27 (1H, *d*, *J* = 8 Hz, H-1′), 5.90 (1H, *d*, *J* = 7 Hz, H-1), 6.18 (1H, *br s*, H-7), 7.61 (1H, *s*, H-4); ^{13}C NMR: δ47.7 (*t*, C-6), 50.8 (*q*, OMe), 57.1 (*d*, C-9), 60.9 (*t*, C-10), 62.7 (*t*, C-6″), 69.8 (*t*, C-6′), 71.6 (*d*, C-4′), 71.7 (*d*, C-4″), 74.5 (*d*, C-2′), 75.3 (*d*, C-2″), 76.5 (*s*, C-5), 77.9 (*d*, C-5′), 78.2 (*d*, C-3′, C-3″, C-5″), 99.7 (*d*, C-1), 101.0 (*d*, C-1′), 105.2 (*d*, C-1″), 115.1 (*s*, C-4), 125.9 (*d*, C-7), 143.2 (*s*, C-8), 152.3 (*d*, C-3), 167.1 (*s*, C-11). HMBC cross peaks: H-1/C-1′, 8, H-9/C-1, 5, 8, 9, OMe/CO_2Me, H-1′/C-1, H-2′/C-1′, H-6′ a,b/C-1″, H-1″/C-6′.

Acknowledgements—We thank Ms Y. Iwase, J. Honda, and Mr H. Hanazono of Fukuoka University for NMR and MS measurements.

REFERENCES

1. Abe, F., Yamauchi, T., Yahara, S. and Nohara, T. (1994) *Phytochemistry* (in press).
2. Sticher, O. and Schmid, H. (1969) *Helv. Chim. Acta* **52**, 478.
3. Sticher, O. (1970) *Tetrahedron Letters* 3195.
4. Yamauchi, T., Abe, F. and Wan, S. C. (1990) *Phytochemistry* **29**, 2327.