Pergamon

Phytochemistry Vol. 49, No. 8, pp. 2409–2411, 1998
© 1998 Published by Elsevier Science Ltd. All rights reserved
Printed in Great Britain
0031-9422/98/$ - see front matter

PII: S0031-9422(98)00355-0

IRIDOID GLUCOSIDES FROM *BOUCHEA FLUMINENSIS*

IVÂNIA T. ALBRECHT SCHUQUEL, ANGELA MALHEIROS, MARIA HELENA SARRAGIOTTO and GENTIL JOSÉ VIDOTTI*

Departamento de Quimica, Universidade Estadual de Maringá, Avenida Colombo 5790, Maringá, PR 87020–900, Brazil

(*Received* 14 *April* 1998)

Key Word Index—*Bouchea fluminensis*; Verbenaceae; iridoid glucoside; boucheoside.

Abstract—From the aerial parts of *Bouchea fluminensis*, a new iridoid glucoside, named boucheoside, along with four known iridoid glucosides, lamiide, lamiidoside, durantoside II, and duranterectoside C, were isolated. The structure of the new compound was elucidated based on the spectroscopic evidence. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Bouchea fluminensis (Vell.) Mold. [1] is an herbaceous plant, growing in Brazil and Bolivia. Infusions of the plant are used in traditional medicine for stimulating and regulating the digestive apparatus [2]. From the genus *Bouchea*, iridoid glucosides of the lamiide-type have been isolated [3, 4]. A phytochemical study on *B. fluminensis* describes only the isolation of lamiide (**1**) [5]. Our phytochemical investigations on the aerial parts of *B. fluminensis* resulted in the isolation of 3-*O*-*β*-D-glucopyranosylsitosterol [6]. In a continuation of our studies, we isolated a new iridoid glucoside, which we have named boucheoside (**2**), together with the following known iridoid glucosides, lamiide (**1**) [7–9], durantoside II (**3**) [9], lamiidoside (**4**) [10], and duranterectoside C (**5**) [11]. This paper deals with the isolation and structure elucidation of the new compound.

RESULTS AND DISCUSSION

Boucheoside (**2**) was obtained as an amorphous powder and showed ion peaks at *m/z* 605 $[M + Na]^+$ and at 582 $[M]^+$ in its FAB mass spectrum, consistent with $C_{27}H_{34}O_{14}$. The ^1H and ^{13}C NMR spectra of **2** (see experimental) showed a close similarity with those of durantoside II (**3**) [9], except for the signals arising from the ester moiety. The ^1H NMR spectra of **2** showed upfield shifts (0.82 and 0.53 ppm) for H-7″ and H-8″, respectively, compared with those of **3** [9]. The ^{13}C NMR spectrum of **2** showed olefinic carbons signals at δ 117.8 and 145.0 (C-8″ and C-7″, respectively) instead of at δ 116.5 and 146.3 as in **3** [9]. These data, together with the coupling constant ($J_{7'',8''} = 13.0$ Hz) for the olefinic protons, clearly demonstrated that the *trans*-*p*-methoxycinnamoyl group in **3** was replaced by *cis*-*p*-methoxycinnamoyl group in the structure of boucheoside (**2**). This was confirmed by a comparison of the NMR data of **2** with those reported [11] for the duranterectoside C (**5**), which posses a *cis*-*p*-coumaroyl group at C-7. Thus, boucheoside (**2**) was determined to be the 7-*O*-*cis*-*p*-methoxycinnamoyl ester of lamiide (**1**). The extensive use of 2D NMR methods (^1H-^1H COSY, HMQC and HMBC), further confirmed the proposed structure for **2** and allowed unequivocal assignments of all ^1H and ^{13}C chemical shifts.

Iridoid glucosides **1** and **3–5** were identified by comparison of their spectral data with those reported for lamiide (**1**) [7, 8], durantoside II (**3**) [9], lamiidoside (**4**) [10], and duranterectoside C (**5**) [11]. As no details were found for the ^{13}C NMR data for lamiidoside (**4**), the ^{13}C NMR data for **4** are presented (Experimental) in this paper. The assignments of the signals were supported by 2D NMR experiments, such as ^1H-^1H COSY and HMQC.

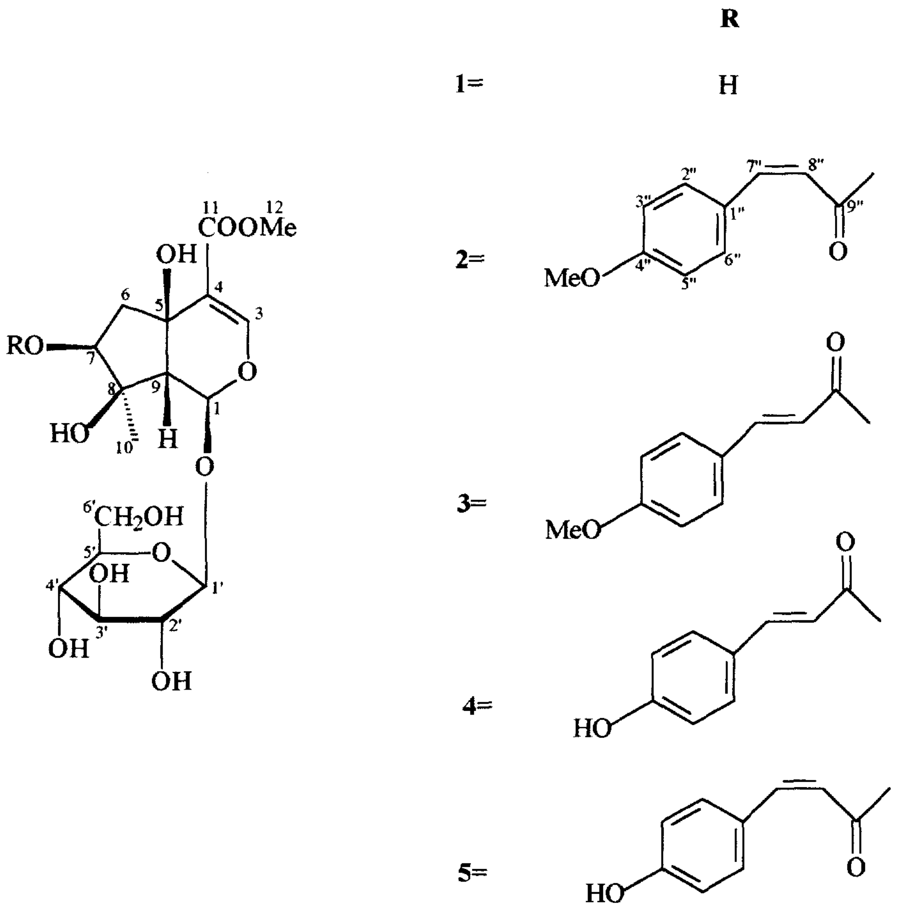
EXPERIMENTAL

General

IR: film NaCl plates; ^1H (300 or 400 MHz) and ^{13}C (75.5 or 100 MHz) NMR: CD_3OD with TMS

---

*Author to whom correspondence should be addressed.



as int. standard; FABMS: glycerol as a matrix, positive ion mode; CC: silica gel 60 (230–400 mesh); TLC: silica gel plates F_{254} (0.25 mm in thickness); prep. HPLC: (reverse phase C_{18}, 10 x 250 mm; solvent: MeOH-H_2O; flow rate, 2.0 or 1.5 ml min^{-1}, detection, 230 nm).

Plant material

The plant material used was collected in Horto Didático de Plantas Medicinais Professora Irenice Silva of the Universidade Estadual de Maringá, Paraná State, Brazil in November, 1994 and identified by Dra. Carmem Cristovam, Instituto de Botânica de Corrientes, Argentina. A voucher specimen (HUM 3321) is deposited in the Herbarium of the Biological Department, Universidade Estadual de Maringá.

Isolation

Air-dried and powdered aerial parts (0.6 kg) of *B. fluminensis* were extracted with 95% aq. EtOH (6 l) at room temperature. The combined EtOH extracts were concd *in vacuo* to give a residue (69.6 g). Part of this residue (10 g) was fractionated by CC on silica gel, eluated with *n*-hexane, $CHCl_3$, $CHCl_3$-EtOAc (1:1), EtOAc, EtOAc-MeOH (1:1), and MeOH. The EtOAc-MeOH (1:1) fraction (5.4 g) was subjected to repeated CC on silica gel, eluted with EtOAc-MeOH mixts of increasing polarity to give lamiide (**1**) (230 mg) as an amorphous powder, and two fractions, fr. A (75.9 mg) and fr. B (154.4 mg).

An aliquot (40.0 mg) of fr. A was purified by repeated prep. HPLC (solvent: MeOH-H_2O 9:11; flow rate, 1.5 ml min^{-1}) to yield boucheoside (**2**) (4.1 mg) and durantoside II (**3**) (18.5 mg) as amorphous powders.

An aliquot (42.0 mg) of fr. B was sepd by repeated prep. HPLC (solvent: MeOH-H_2O, 9:11; flow rate, 2.0 ml min^{-1}) to give lamiidoside (**4**) (16.3 mg) and duranterectoside C (**5**) (5.6 mg) as amorphous powders.

Boucheoside (**2**)

Amorphous powder. IR ν_{max}^{NaCl} cm^{-1}: 3360, 1717, 1649, 1619, 1527, 1299, 1174, 1080 and 872; FABMS *m/z* (rel. int.): 605 $[M + Na]^+$ (1), 582 $[M]^+$ (1), 547 (5), 385 (6), 277 (8), 225 (8), 207 (50), 185 (100), 161 (73), 147 (2), 133 (14) and 115 (18); ^1H NMR (400 MHz, CD_3OD): δ 1.15 (3H, *s*, H-10), 2.36 (1H, *dd*, J = 16.1 and 1.6 Hz, H-6), 2.47 (1H, *dd*, J = 16.1 and 4.9 Hz, H-6), 2.88 (1H, *s*, H-9), 3.19 (1H, *dd*, J = 9.1 and 7.8 Hz, H-2′), 3.26 (1H, *m*, H-4′), 3.30 (1H, *m*, H-5′), 3.37 (1H, *dd*, J = 9.1 and 8.2 Hz, H-3′), 3.65 (1H, *dd*, J = 11.9 and 6.0 Hz, H-6′), 3.72 (3H, *s*, H-12), 3.81 (3H, *s*, OCH_3), 3.88 (1H, *dd*, J = 11.9 and 2.0 Hz, H_I-6′), 4.61 (1H, *d*, J = 7.8 Hz, H-1′), 4.79 (1H, *dd*, J = 4.9 and 1.6 Hz, H-7), 5.82 (1H, *d*, J = 0.6 Hz, H-1), 5.94 (1H, *d*, J = 13.0 Hz, H-8″), 6.89 (2H, *d*, J = 8.9 Hz, H-3″, H-5″), 6.92 (1H, *d*, J = 13.0 Hz, H-7′), 7.44 (1H, *s*, H-3), and 7.77 (2H, *d*, J = 8.9 Hz, H-2″, H-6″); ^{13}C NMR (100 MHz, CD_3OD): δ 21.3 (C-10), 45.5 (C-6), 51.7 (C-12), 55.8 (OCH_3), 58.2 (C-9), 62.8 (C-6′), 69.0 (C-5), 71.7 (C-4′), 74.5 (C-2′), 77.5 (C-3′), 78.4 (C-5′), 78.7 (C-8), 80.3 (C-7), 94.0 (C-1), 99.6 (C-1′), 114.4 (C-3″, 5″), 115.7 (C-4), 117.8 (C-8″), 128.7 (C-1′), 133.6 (C-2″, 6″), 145.0 (C-7″), 152.2 (C-3), 162.1 (C-4″), 167.4 (C-9′), and 167.9 (C-11).

Lamiidoside (**4**)

^{13}C NMR (100 MHz, CD_3OD): δ 21.3 (C-10), 45.5 (C-6), 51.7 (C-12), 58.4 (C-9), 62.8 (C-6′), 69.0 (C-5), 71.7 (C-4′), 74.5 (C-2′), 77.5 (C-3′), 78.4 (C-5′), 80.5 (C-7), 94.1 (C-1), 99.6 (C-1′), 115.5 (C-8′), 115.6 (C-4), 116.8 (C-3″,5″), 127.3 (C-1″), 131.2 (C-2′,6″), 146.7 (C-7″), 152.2 (C-3), 161.3 (C-4″), 167.9 (C-11), and 168.7 (C-9″).

Acknowledgements—The authors are grateful to the Brazilian National Research Concil, CNPq, for financial support, to Dr. Carmem Cristovam and to MSc Irenice Silva for collect and identification of the plant material.

REFERENCES

1. Troncoso, N. S., *Darwiniana*, 1974, **18**(3-4), 348.
2. Pio Correa, M., *Dicionário de Plantas úteis do Brasil e das Exóticas Cultivadas*. Imprensa Nacional, Rio de Janeiro, RJ, 1984, p. 395.
3. Kooiman, P., *Acta Bot. Neerl.*, 1975, **24**(5-6), 459.
4. Rimpler, H. and Sauerbier, H., *Bioch. Syst. Ecol.*, 1986, **14**(3), 307.
5. von Poser, G. L., Toffoli, M. E., Sobral, M. and Henriques, A. T., *Pl. Syst. Evol.*, 1997, **205**, 265.
6. Matida, A. K., Rossi, M. H., Blumenthal, E. E. A., Schuquel, I. T. A., Malheiros, A. and Vidotti, G. J., *Anais Assoc. Bras. Quim.*, 1996, **45**(3), 147.
7. Scarpati, M. L. and Guiso, M., *Gazz. Chim. Ital.*, 1969, **99**, 1150.
8. Junior, P., *Planta Med.*, 1985, **51**, 229.
9. Krebs, H. C. and Habermehl, G. G., *Mag. Res Chem.*, 1992, **30**, S56.
10. Bianco, A., Bonini, C., Guiso, M., Iavarone, C. and Trogolo, C., *Gazz. Chim. Ital.*, 1977, **107**, 67.
11. Takeda, Y., Morimoto, Y., Matsumoto, T., Ogimi, C., Hirata, E., Takushi, A. and Otsuka, H., *Phytochemistry*, 1995, **39**(4), 829.