PERGAMON

Phytochemistry 53 (2000) 931–935

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

Phlorigidosides A–C, iridoid glucosides from *Phlomis rigida*

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Received 9 March 1999; received in revised form 28 June 1999

Abstract

From the aerial parts of *Phlomis rigida*, three iridoid glucosides, phlorigidoside A (2-*O*-acetyllamiridoside), B (8-*O*-acetyl-6-β-hydroxyipolamide) and C (5-deoxysesamoside), were isolated together with the known iridoid glucosides, shanzhiside methyl ester, 8-*O*-acetylshanzhiside methyl ester, deoxypulcheloside I, lamiridoside, and 6-β-hydroxyipolamide. The structures of the new compounds were elucidated based on spectral and chemical evidence.

Keywords: *Phlomis rigida*; Labiatae; Phlorigidosides A, B and C; Iridoid glucosides

1. Introduction

Plants belonging to the genus *Phlomis* have been shown to contain iridoid glucosides (Al-Hazinn & Alkhathlan, 1996), flavonoid glycosides (Harborne, 1988), phenylethanoid glycosides (Jimenez & Riguera, 1994), diterpene glycosyl esters (Katagiri, Ohtani, Kasai, Yamasaki, Yang & Tanaka, 1994) and nortriterpenes (Kumar, Bhan, Kalla & Dhar, 1992). To the best of our knowledge, no reports have appeared on the constituents of *Phlomis rigida* Labil. During the course of chemical studies on the constituents of Turkish medicinal plants and related ones, we have investigated the glycosidic constituents of *P. rigida* and isolated three new iridoid glucosides, phlorigidosides A (**1**), B (**2**) and C (**3**) together with five known iridoid glucosides, shanzhiside methyl ester (**4**) (Takeda, Nishimura & Inouye, 1977), 8-*O*-acetylshanzhiside methyl ester (**5**) (Damtoft, Jensen & Nielsen, 1982), deoxypulcheloside I (**6**) (Ganapaty, Heni, Rao & Rimpler, 1988), lamiridoside (**7**) (Eigtved, Nielsen & Nielsen, 1974), and 6-β-hydroxyipolamide (**8**) (de Luca, Guiso & Martino, 1983). This paper describes the isolation and structure elucidation of the new compounds.

2. Results and discussion

Compounds **1–8** were isolated from the 1-butanol-fraction of a methanolic extract of the aerial parts of *P. rigida* as described in Section 3.

Phlorigidoside A (**1**), $[\alpha]_D$ −81° (MeOH), was obtained as an amorphous powder and the molecular formula was determined as $C_{19}H_{28}O_{13}$ based on negative ion HR-FABMS. The ^{1}H- and ^{13}C-NMR spectra were very similar to those of lamiridoside (**7**) (Ganapaty et al., 1988) except for the presence signals from an additional acetyl group. Thus, phlorigidoside A (**1**) was presumed to be as a monoacetate of lamiridoside (**7**). In fact, compounds **1** and **7** gave the same acetate (**1a**). An additional acetyl group was inferred to be located at *O*-2′ of **1** based on the observation that the ^{13}C-signal due to C-1′ resonated 2.5 ppm higher in the

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0031-9422/00/$ - see front matter
PII: S0031-9422(99)00431-8

^{13}C-NMR spectrum as compared to lamiridoside (**7**). This was further verified by the observation of cross peaks between a doublet at δ 4.76 assigned to the anomeric proton of the glucose moiety and the triplet at δ 4.65, corresponding to H-2′. In **7**, the latter signal was observed at δ 3.16. Thus, phlorigidoside A is represented by **1**.

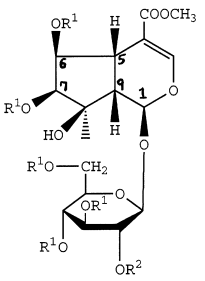
Phlorigidoside B (**2**), $[\alpha]_D$ −88° (MeOH), was obtained as an amorphous powder and the molecular formula was determined as $C_{19}H_{28}O_{13}$ based on negative ion HR-FABMS. The ^{1}H- and ^{13}C-NMR spectra were very similar to those of 6-β-hydroxyipolamide (**8**) (de Luca et al., 1983) except for the signals from an additional acetyl group. Acetylation of **2** with Ac_2O and pyridine gave the pentaacetate (**2a**) which was identical to the hexaacetate of **8**. The location of the acetyl group of **2** was determined to be attached to the oxygen functionality at C-8 based on the fact that the C-8 signal was downfield shifted (86.0 ppm) compared to that in **8**. Thus, phlorigidoside **B** has the structure **2**, which corresponds to 8-*O*-acetyl-6-β-hydroxyipolamide.

Phlorigidoside C (**3**), $[\alpha]_D$ −66° (MeOH), was obtained as an amorphous powder and the molecular formula was determined as $C_{17}H_{24}O_{11}$ based on its negative ion HR-FABMS. It showed a UV absorption at 239 nm and a ^{1}H-NMR signal at δ 7.54 (1H, *s*) characteristic of iridoid glucosides having either a carboxy or carbomethoxy group at C-4. In addition, the ^{1}H-NMR spectrum showed signals due to a carbomethoxy group as well as a tertiary methyl group on an oxygenated carbon. The ^{13}C-NMR spectral data (Table 1) showed, in addition to signals due to the β-glucopyranosyl moiety and above-mentioned functional groups, resonances due to four methine groups, two of which have an oxygen atom, a quaternary carbon bound to an oxygen atom, and an acetal carbon. Based on the chemical shifts (64.8 and 63.1 ppm) of the oxygenated carbon atoms, phlorigidoside C (**3**) was proposed to have an oxirane ring in the structure. The planar structure was elucidated by ^{1}H–^{1}H spin–spin decoupling experiments on the pentaacetate (**3a**). The results clearly showed correlations from H-1 to H-5, H-6 and H-7, and hence confirmed the location of the oxirane ring between C-7 and C-8. The stereochemistry was then examined by differential NOE experiments. The results showed NOE between H-5 and H-9, H-6 and H-7, and between H-7 and H-10 resulting in the proposed structure of phlorigidoside C as **3**.

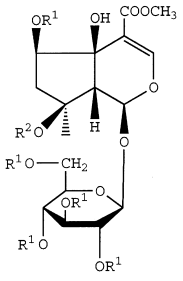
Table 1
^{13}C-NMR data for Phlorigidoside A (**1**), B (**2**) and C (**3**) (CD_3OD, 100 MHz)

C	1	2	3
1	94.9	95.3	96.5
3	152.5	155.5	154.2
4	112.2	112.3	108.6
5	37.3	72.7	38.5
6	77.7	74.9	77.9
7	74.7	45.8	64.8
8	79.0	86.0	63.1
9	51.9	57.6	45.2
10	22.0	22.0	18.0
11	169.0	167.8	170.9
1′	97.3	100.2	99.9
2′	75.8	74.3	74.9
3′	78.5	77.5	77.9
4′	71.5	71.6	71.8
5′	77.9	78.3	78.7
6′	62.6	62.8	63.1
OMe	[a]	51.8	52.3

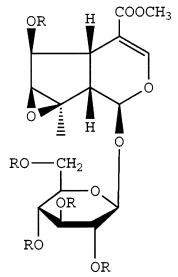
[a] Overlapped with solvent signals.



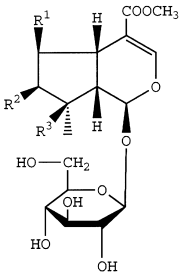
(**1**) R^1=H; R^2=$COCH_3$
(**1a**) R^1=R^2=$COCH_3$
(**7**) R^1=R^2=H



(**2**) R^1=H; R^2=$COCH_3$
(**2a**) R^1=R^2=$COCH_3$
(**8**) R^1=R^2=H



(**3**) R=H
(**3a**) R=$COCH_3$



(**4**) R^1=R^3=OH; R^2=H
(**5**) R^1=OH; R^2=H; R^3=$OCOCH_3$
(**6**) R^1=R^2=OH; R^3=H

3. Experimental

3.1. General

NMR: ^{1}H (400 MHz) and ^{13}C (100 MHz), TMS as int. standard; FABMS: matrix, PEG-400 or *m*-nitrobenzyl alcohol; CC: silica gel 60 (230–400 mesh, Merck); TLC: precoated silica gel plates 60 F_{254} (0.25 and 0.5 mm in thickness); HPLC: column, Cosmosil

10 C_{18} (20 × 250 mm L), detection 230 nm, solvent; MeOH–H_2O, 6 ml min^{-1}.

3.2. Plant material

Plant material was collected in the suburbs of Akseki, Turkey on the 16th of July, 1995 and identified as *P. rigida* Labil. by the authors (G. H. and E. S.). Voucher specimens (95 E 039) are deposited in the herbaria of Graduate School of Pharmaceutical Sciences, Kyoto University and Faculty of Pharmacy, Gazi University.

3.3. Isolation

The dried aerial parts (6.5 kg) of *P. rigida* were extracted (×2) with MeOH (90 l) at room temperature for 2 weeks. The combined methanolic extracts were condensed. in vacuo. The residue was dissolved in 90% MeOH (2.5 l) and the solution was washed with *n*-hexane (1 l × 3). The 90% MeOH layer was condensed in vacuo, the resultant residue suspended in H_2O (2 l) and the suspension extracted successively with EtOAc (1 l × 3) and *n*-BuOH (1 l × 3). The *n*-BuOH extract was evaporated in vacuo to give a residue (105 g) which was chromatographed over Diaion HP-20 (highly porous synthetic resin, Mitsubishikagaku, Tokyo) ($\Phi = 11$ cm, $L = 35$ cm) with a stepwise increase of MeOH in H_2O [0(5 l), 10(7 l), 30(7 l), 40(7 l), 50(7 l)and 70(7 l)% aq. MeOH, and MeOH (7 l)]. Frs. of 1 l were collected.

Frs. 12–14 were combined and the solvent was removed in vacuo to give a residue (2.85 g) which was subjected to silica gel CC (200 g) with increasing amounts of MeOH in $CHCl_3$ [$CHCl_3$(400 ml), $CHCl_3$–MeOH 97:3 (600 ml), 19:1 (700 ml), 93:7 (700 ml), 9:1 (700 ml), 22:3 (700 ml), 17:3 (700 ml), 4:1 (700 ml) and 7:3 (700 ml)], (100 ml Frs.). Frs. 52–59 were combined and the solvent was removed in vacuo to give **7** (594 mg).

Frs. 15–17 gave a residue (6.85 g) on evaporation in vacuo. The residue was subjected to silica gel CC (400 g) with increasing amounts of MeOH in $CHCl_3$ [$CHCl_3$ (1 l), 2 l each of $CHCl_3$–MeOH 97:3, 19:1, 93:7, 9:1, 22:3, 17:3, 4:1, 7:3 and MeOH (700 ml)], (200 ml Frs.). Frs. 44–53 gave a residue (838 mg) which was separated by prep. HPLC (solvent: MeOH–H_2O, 1:3) to give **3** (249 mg). Frs. 54–57 gave a residue (691 mg), a portion (200 mg) of which was purified by prep. HPLC (solvent: MeOH–H_2O, 1:3) to give **4** (62.2 mg). Frs. 58–61 gave a residue (1.21 g), a portion (200 mg) of which was separated by prep. HPLC (solvent: MeOH–H_2O, 1:3) to give **6** (14.9 mg) and **4** (25.1 mg). Frs. 62–66 gave a residue (663 mg) which was separated by prep. HPLC (solvent: MeOH–H_2O, 1:4) to give **2** (27.2 mg), **8** (24.4 mg), **3** (49.2 mg) and **1** (26.8 mg). Frs. 67–73 gave a residue (600 mg) which was separated by prep. HPLC (solvent: MeOH–H_2O, 1:3) to give **1** (32.9 mg), **6** (93.3 mg) and **7** (69.6 mg).

Frs. 24–28 gave a residue (12.3 g) which was subjected to silica gel CC (550 g) with increasing amounts of MeOH in $CHCl_3$ [$CHCl_3$ (3 l), 3 l each of $CHCl_3$–MeOH 97:3, 19:1, 93:7, 9:1, 17:5, 4:1, $CHCl_3$–MeOH 7:3 (10 l) and MeOH (600 ml)] (500 ml Frs). Frs. 28–32 gave a residue (2.24 g), 200 mg of which was purified by prep. HPLC (solvent: MeOH–H_2O 3:7) to give **5** (32.0 mg). Frs. 33–39 gave a residue (1.34 g), 200 mg of which was purified by prep. HPLC (solvent: MeOH–H_2O, 7:13) to give **9** (14.3 mg).

3.3.1. Known compounds isolated

Shanzhiside methyl ester (**4**), amorphous powder, $[\alpha]_D^{24}$ −115° (MeOH; *c* 5.52) (Takeda et al., 1977). 8-*O*-Acetylshanzhiside methyl ester (**5**), amorphous powder, $[\alpha]_D^{24}$ −61° (MeOH; *c* 3.34) (Damtoft et al., 1982). Deoxypulcheloside I (**6**), amorphous powder, $[\alpha]_D^{24}$ −111° (MeOH; *c* 0.75) (Ganapaty et al., 1988). Lamiridoside (**7**), amorphous powder, $[\alpha]_D^{29}$ −85° (MeOH; *c* 0.71) (Eigtved et al., 1974). 6-β-Hydroxyipolamide (**8**), amorphous powder, $[\alpha]_D^{16}$ −137° (MeOH; *c* 0.85) (de Luca et al., 1983). All compounds were identified based on comparisons of their ^{1}H- and ^{13}C-NMR spectral data with those reported.

3.4. Phlorigidoside A (*1*)

Amorphous powder, $[\alpha]_D^{28}$ −81° (MeOH: *c* 0.57). IR ν_{max} (dry film) cm^{-1}: 3419, 1733, 1698, 1645, 1078; UV λ^{max}(MeOH) nm (log ϵ): 235 (3.90); ^{1}H-NMR spectral data (CD_3OD): δ 1.19 (3H, *s*, H_3-10), 1.93 (3H, *s*, OAc), 2.80 (2H, *s*, H-5 and H-9), 3.49 (1H, *d*, J = 4.4 Hz, H-7), 3.52 (1H, *t*, J = 9.7 Hz, H-2), 3.68 (1H, *dd*, J = 12.2 and 5.6 Hz, Ha-6′), 3.74 (3H, s, OMe), 3.90 (1H, *br d*, J = 12.2 Hz, Hb-6′), 3.97 (1H, *br d*, J = 4.4 Hz, H-6), 4.65 (1H, *dd*, J = 7.8 and 9.7 Hz, H-2′), 4.76 (1H, *d*, J = 7.8 Hz, H-1′), 5.61 (1H, *s*, H-1) and 7.39 (1H, *s*, H-3); ^{13}C-NMR spectral data: Table 1; HR–FABMS (negative) *m/z*: 463.1440 $[M-H]^-$ ($C_{19}H_{27}O_{13}$ requires 463.1452).

3.5. Phlorigidoside B (*2*)

Amorphous powder, $[\alpha]_D$ −88° (MeOH; *c* 0.63). IR ν_{max} (dry film) cm^{-1}: 3386, 1708, 1628, 1294, 1078; UV λ_{max}(MeOH) nm (log ϵ): 231 (3.86); ^{1}H-NMR spectral data (CD_3OD); δ1.40 (3H, *s*, H_3-10), 2.02 (3H, *s*, OAc), 2.12(2H, *d*, J = 4.9 Hz, H_2-7), 2.90 (1H, *s*, H-9), 3.19 (1H, *dd*, J = 7.8 and 8.8 Hz, H-2′), 3.72 (3H, *s*, OMe), 3.69 (1H, *dd*, J = 12.1 and 5.9 Hz, Ha-6′), 3.90 (1H, *dd*, J = 12.2 and 2.0 Hz, Hb-6′), 4.34 (1H, *t*, J = 4.9 Hz, H-6), 4.59 (1H, *d*, J = 8.0 Hz, H-1′), 6.15 (1H, *s*, H-1) and 7.58 (1H, *s*, H-3); ^{13}C-NMR

spectral data: Table 1; HR-FABMS (negative) *m/z*: 463.1459 $[M-H]^-$ ($C_{19}H_{27}O_{13}$ requires 463.1452).

3.6. Phlorigidoside C (*3*)

Amorphous powder, $[\alpha]_D^{28}$ −66° (MeOH; *c* 0.87). IR ν_{max} (dry film) cm^{-1}: 3387, 1682, 1636, 1075; UV λ_{max} (MeOH) nm (log ϵ): 239 (3.99); ^{1}H-NMR spectral data (CD_3OD): δ 1.53 (3H, *s*, H_3-10), 2.40 (1H, *dd*, *J* = 9.8 dd 7.6 Hz, H-9), 2.66 (1H, *br t*, *J* = 7.6 Hz, H-5), 3.34 (1H, *br s*, H-7), 3.61 (1H, *dd*, *J* = 12.0 and 7.1 Hz, Ha-6′), 3.74 (3H, *s*, OMe), 3.92 (1H, *br d*, *J* = 12.0 Hz, Hb-6′), 3.99 (1H, *br d*, *J* = 7.6 Hz, H-6), 4.79 (1H, *d*, *J* = 7.8 Hz, H-1′), 5.26 (1H, *d*, *J* = 9.8 Hz, H-1) and 7.54 (1H, *s*, H-3); ^{13}C-NMR spectral data: Table 1; HR–FABMS (negative) *m/z*: 403.1232 $[M-H]^-$ ($C_{17}H_{23}O_{11}$ requires 403.1240).

3.7. Phlorigidoside A pentaacetate (*1a*)

1 (9.2 mg) was acetylated using a mixture of pyridine (0.1 ml) and Ac_2O (0.1 ml) at room temp. for 3 h. Excess MeOH was added and the solvent was removed in vacuo to give a residue which was purified by silica gel CC (3 g) with $CHCl_3$ as eluent to give the pentaacetate (**1a**) (10.2 mg) as an amorphous powder, $[\alpha]_D^{26}$ −86° (MeOH; *c* 0.51). IR ν_{max} ($CHCl_3$) cm^{-1}: 3600, 1745 and 1645; ^{1}H-NMR spectral data ($CDCl_3$): δ 1.29 (3H, *s*, H_3-10), 1.90, 2.01, 2.04, 2.07, 2.11, 2.14 (each 3H, *s*, 6 × OAc), 2.88 (1H, *br d*, *J* = 11.2 Hz, H-9), 3.05 (1H, *dd*, *J* = 11.2 and 4.4 Hz, H-5), 3.67 (3H, *s*, OMe), 3.74 (1H, *m*, H-5′), 4.14 (1H, *dd*, *J* = 12.5 and 2.2 Hz, Ha-6′), 4.31 (1H, *dd*, *J* = 12.5 and 4.6 Hz, Hb-6′), 4.85 (1H, *d*, *J* = 8.3 Hz, H-1′), 4.93 (1H, *d*, *J* = 4.4 Hz, H-7), 4.97 (1H, *dd*, *J* = 8.3 and 9.8 Hz, H-2′), 5.09 (1H, *t*, *J* = 9.8 Hz, H-4′), 5.22 (^{1}H, *t*, *J* = 9.8 Hz, H-3′), 5.26 (1H, *t*, *J* = 4.4 Hz, H-6), 5.49 (1H, *d*, *J* = 1.0 Hz, H-1), 7.37 (1H, *s*, H-3); HR FABMS (positive, +NaI) *m/z*: 697.1960 $[M+Na]^+$ ($C_{29}H_{38}O_{18}Na$ requires 697.1956).

3.8. Acetylation of 7

7 (14.1 mg) was acetylated and purified as above to give the hexaacetate (**1a**) (15.6 mg), $[\alpha]_D^{26}$ −98° (MeOH; *c* 0.78). HR-FABMS (positive, +NaI) *m/z*: 697.1987 $[M+Na]^+$ ($C_{29}H_{38}O_{18}$ Na requires 697.1956).

3.9. Phlorigidosie B pentaacetate (*2*)

2 (24.1 mg) and **8** (14.1 mg) were acetylated as before, except for 7 h and 3 days reaction time respectively. Pentaacetate (**2a**) (22.2 and 12.3 mg, respectively) colorless needles, mp 190–191°C (from EtOH), $[\alpha]_D^{20}$ −-116° ($CHCl_3$; *c* 1.05); IR ν_{max} ($CHCl_3$) cm^{-1}: 3525, 1730, 1620, 1220, 1070, 1030; ^{1}H-NMR spectral data ($CDCl_3$):δ 1.42 (3H, *s*, H_3-10), 1.84 (1H, *dd*, *J* = 15.4 and 3.7 Hz, Ha-7), 1.93, 1.996, 2.003, 2.03, 2.11, 2.12 (each 3H, *s*, 6 × OAc), 2.27 (1H, d, *J* = 15.4 Hz, H_b-7), 3.13 (1H, *s*, H-9), 3.26 (1H, *s*, OH-5), 3.78 (3H, *s*, OMe), 3.80 (1H, *m*, H-5′), 4.15 (1H, *dd*, *J* = 12.2 and 2.4 Hz, H_a-6′), 4.39 (1H, *dd*, *J* = 12.2 and 4.7 Hz, H_b-6′), 4.82 (1H, *d*, *J* = 8.1 Hz, H-1′), 4.99 (1H, *dd*, *J* = 8.1 and 9.8 Hz, H-2′), 5.08 (1H, *dd*, *J* = 9.8 and 9.8 Hz, H-4′), 5.26 (1H, *dd*, *J* = 9.8 and 9.8 Hz, H-3′), 5.65 (1H, *br d*, *J* = 3.7 Hz, H-6), 6.18 (1H, *s*, H-1) and 7.51 (1H, *s*, H- 3); HR FABMS (negative) *m/z*: 673.2003 $[M-H]^-$. $C_{29}H_{37}O_{18}$ requires 673.1980.

3.10. Phlorigidoside C pentaacetate (*3*)

3 (14.7 mg) was acetylated overnight, with isolation as before, to give pentaacetate (**3a**) (17.2 mg) as an amorphous powder. IR ν_{max} ($CHCl_3$) cm^{-1}: 1740 and 1640; ^{1}H-NMR spectral data ($CDCl_3$): 1.53 (3H, *s*, H_3-10), 2.02, 2.045, 2.051, 2.08, 2.11 (each 3H, *s*, 5 × OAc), 2.33 1H, *dd*, *J* = 9.3 and 7.3 Hz, H-9), 3.00 (1H, *t*, *J* = 8.1 Hz, H-5), 3.37 (1H, *br s*, H-7), 3.74 (1H, *m*, H-5′), 4.24 (2H, H_2- 6′), 5.00 (1H, *d*, *J* = 9.3 Hz, H-1), 5.03–5.09 (2H, H-1′ and H-2′), 5.06 (1H, *dd*, *J* = 8.1 Hz, H-6), 5.13 (1H, *t*, *J* = 9.8 Hz, H-4′), 5.26 (1H, *t*, *J* = 9.8 Hz, H-3′), 7.40 (1H, *s*, H-3); HR-FABMS (negative) *m/z*: 613.1766 $[M-H]^-$ ($C_{27}H_{33}O_{16}$ requires 613.1769).

Acknowledgements

The authors thank the Cooperative Center of the University of Tokushima for opportunities to record NMR spectra. This work was supported in part by a grant-in-aid from the Ministry of Education, Science, Sports and Culture of Japan (No. 06041069).

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