Iridoid and Phenylethanoid Glycosides from *Phlomis nissolii* and *P. capitata*

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Z. Naturforsch. **59b,** 609 – 613 (2004); received February 16, 2004

A new iridoid glucoside, lamiidic acid was isolated from *Phlomis nissolii*, along with one known iridoid glucoside, lamiide and 13 phenylethanoid glycosides, verbascoside, isoverbascoside, leucosceptosides A and B, martynoside, arenarioside, forsythoside B, alyssonoside, lamiophlomiside A, samioside, integrifoliosides A and B, and hattushoside. A new iridoid glucoside, ipolamiidic acid was isolated from *Phlomis capitata* together with two known iridoid glucosides, lamiide and ipolamiide. The known phenylethanoid glycosides, isoverbascoside, forsythoside B, alyssonoside and hattushoside, a known lignan glycoside, liriodendrin, three flavonoid glycosides, luteolin 7-*O*-(6”-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside, luteolin 7-*O*-(6”-*O*-β-D-apiofuranosyl)-β-D-glucopyranoside and chrysoeriol 7-*O*-β-D-glucopyranoside, an acyclic monoterpene, betulalbuside A, and a quinic ester derivative, chlorogenic acid were also obtained and characterized. The structures of the isolated compounds were elucidated by means of spectroscopic (HRESI-MS, 1D and 2D NMR) evidence.

Key words: Phlomis nissolii, Phlomis capitata, Lamiaceae, Iridoid Glucosides, Lamiidic Acid

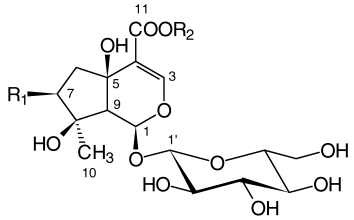
Introduction

The genus *Phlomis* L. (Lamiaceae) is represented by 34 species in the Flora of Turkey [1]. In Anatolian folk medicine some *Phlomis* species are used as tonic and stimulant [2]. As a part of our ongoing phytochemical studies on *Phlomis* species growing in Turkey, we have investigated two endemic species, *P. nissolii* and *P. capitata*. *P. nissolii* has previously only been investigated from the point of view of flavonoids [3], while *P. capitata* has not been studied. In this paper we describe the isolation and the structure elucidation of a new iridoid glucoside, lamiidic acid (**1**) from *P. nissolii* as well as a new iridoid glucoside, ipolamiidic acid (**2**) from *P. capitata*.

Experimental Section

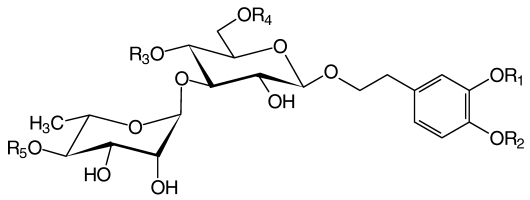
General experimental procedures

UV spectra were recorded on a Shimadzu UV-160A spectrophotometer. IR spectra (KBr) were measured on a Perkin Elmer 2000 FT-IR spectrometer. Bruker AMX 600 instruments (600 MHz for ^{1}H and 150 MHz for ^{13}C) with



	R_1	R_2
1	OH	H
2	H	H
3	OH	CH_3
4	H	CH_3

XWIN NMR software package were used to acquire NMR data. Positive-and negative-mode ESIMS were recorded on a Finnigan TSQ 7000 instrument. Exact masses were measured on a Q-TOF Ultima (Micromass) triple-quadrupole orthogonal time-of-flight (TOF) instrument. Nanospray ionization was used in TOF mode at 8.500 resolving power. Samples were dissolved in pure methanol, mixed with the internal calibrant, and introduced directly into the ion source by direct infusion. Calibration was performed on the peaks of a synthetic peptide (TOF positive ion calibration solution, Bachem,) at m/z 785.8426. Sodium-containing molec-



	R_1	R_2	R_3	R_4	R_5
5	H	H	*trans*-caffeoyl	H	H
6	H	H	H	*trans*-caffeoyl	H
7	H	H	*trans*-feruloyl	H	H
8	H	CH_3	*trans*-feruloyl	H	H
9	H	H	*trans*-caffeoyl	β-xylose	H
10	H	H	*trans*-caffeoyl	β-apiose	H
11	H	H	*trans*-feruloyl	β-apiose	H
12	H	CH_3	*trans*-feruloyl	β-apiose	H
13	CH_3	H	*trans*-feruloyl	β-apiose	H
14	H	H	*trans*-caffeoyl	H	β-apiose
15	H	H	*trans*-feruloyl	H	β-apiose
16	H	CH_3	*trans*-feruloyl	H	β-apiose

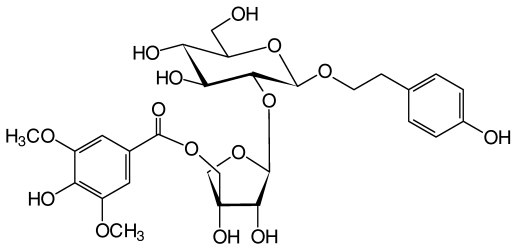


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Fig. 1. Phenylethanoid (**5 – 17**) glycosides from *P. nissolii* and *P. capitata*.

ular ions of analytes were revealed and the elemental composition calculated by the exact mass obtained with four significance numbers. TLC analyses were carried on silica gel 60 F_{254} precoated plates (Merck, Darmstadt), detection by 1% vanillin/H_2SO_4. For medium-pressure liquid chromatographic (MPLC) separations, a Lewa M5 pump, a LKB 17000 Minirac fraction collector, a Rheodyne injector, and Büchi columns (column dimensions 2.6×46 cm, and 1.8×35 cm) were used. Semi-preperative HPLC (Agilent 1100 series, from Agilent Technologies, Palo Alto, CA, USA) separations were performed on C_{18} μ-Bondapack column (7.8×300 mm, particle size 10 μm, Waters Corporation, Milford, MA, USA), equipped with a Binary Pump (G-1312), a Rheodyne Injector (20 μl loop) (G-1328A), a degasser (G-1322A) and a DAD analyser (G-1315A). Silica gel 60 (0.063 – 0.200 mm; Merck, Darmstadt) and polyamide (Fluca) were utilized for open column chromatography (CC). LiChroprep C-18 (Merck) material was used for MPLC and VLC.

Plant materials

Phlomis nissolii L. (Lamiaceae) was collected from Mersin, Gülnar, South Anatolia, Turkey, in July 2001 and *Phlomis capitata* Boiss. was collected from Sivas, Gürün, Inner Anatolia, Turkey in June 2001. The plant materials were identified by Dr. A. Ali Donmez (Department of Biology, Faculty of Science, Hacettepe University) and the voucher specimens (AAD 9499 and AAD 9440 respectively) have been deposited at the Herbarium of the Department of Biology, Faculty of Science, Hacettepe University, Ankara, Turkey.

Extraction and isolation (P. nissolii)

The air-dried and powdered aerial parts of *P. nissolii* (400 g) were extracted with MeOH at 45 °C (2×3 L, 5 h). The concentrated extract (40 g, yield 10%) was suspended in H_2O and successively extracted with CH_2Cl_2 (22 g). The lyophilised H_2O extract (27 g) was fractionated over polyamide column using H_2O with increasing amount of MeOH (0 – 100%) to give nine main fractions, A-I. An aliquot of the fraction B (1.5 g) was subjected to C_{18}-Medium Pressure Liquid Chromatography (C_{18}-MPLC) using 0 to 50% MeOH in H_2O as eluent to yield fr. B_1 and lamiide (**3**, 100 mg). Fr. B_1 (40 mg) was rechromatographed over Si gel column eluting with $CHCl_3$-MeOH mixtures (7:3 to 1:1) to afford lamiidic acid (**1**, 11 mg). Fr. E was applied to a semi-preparative HPLC-ODS utilising a gradient system (15 – 45% MeCN in H_2O) to obtain forsythoside B (**10**, 3 mg), verbascoside (**5**, 4 mg), arenarioside (**9**, 7 mg), samioside (**14**, 3 mg), alyssonoside + hattushoside (**11**+**17**, 8 mg), integrifolioside A (**15**, 4 mg), lamiophlomiside A (**13**, 6 mg), leucosceptoside B (**12**, 6 mg) and integrifolioside B (**16**, 7 mg) respectively. Fraction F was similarly subjected to semi-preperative HPLC-ODS using the same method to yield samioside (**14**, 7 mg), isoverbascoside (**6**, 5 mg), leucosceptoside A (**7**, 4 mg) and martynoside (**8**, 5 mg).

Extraction and isolation (P. capitata)

The powdered aerial parts of *P. capitata* (500 g) were extracted with MeOH (2*x*4 L, 5 h) at 45 °C and then filtered. The filtrates were combined and evaporated to dryness *in vacuo* to yield 50.0 g crude extract (yield 10%). The MeOH extract was suspended in water, and then extracted five times with CH_2Cl_2 (yield 9.0 g). The water phase yielded 33.79 g crude extract upon concentration. An aliquot of water extract (31.0 g) was dissolved in 40 ml water and then subjected on a column packed with Polyamide (100 g). Elu-

tion with increasing amount of MeOH in H_2O (0 – 100%) yielded 30 fractions, which were combined into ten major fractions A – J. Fraction A (15.5 g) was subjected to Vacuum Liquid Chromatography (VLC) using reversed phase material (LiChroprep C_{18}; 100 g), eluted with firstly with H_2O, 5% MeOH in H_2O, and MeOH to get rid of sugars. Fractions eluted with MeOH (1.5 g) was further subjected to C_{18}-MPLC (column dimensions: 26 × 460 mm), eluted with MeOH in H_2O (0 – 75% MeOH) to yield ipolamiide (**4**, 807 mg) and betulalbuside A (46 mg) in addition to eight main fractions, A_1-A_8. Fraction A_4 (37 mg) was subjected to a si gel column chromatography (CC) using CH_2Cl_2-MeOH-H_2O mixtures (80:20:2 and 75:25:2.5) to afford lamiide (**3**, 6 mg). Fraction B (6.5 g) was similarly subjected to C_{18}-MPLC (column dimensions: 26 × 225 mm) eluting with MeOH-H_2O mixtures (0 – 40%) to obtain four main fractions, B_1, B_3-B_5 along with ipolamiide (**4**, 577 mg). Fraction B_1 (174 mg) was subjected to a si gel column chromatography (25 g) using CH_2Cl_2-MeOH-H_2O mixtures (80:20:2 to 61:32:7) to afford ipolamiidic acid (**2**, 36 mg). Fraction B_5 (133 mg) was applied to a si gel CC using CH_2Cl_2-MeOH-H_2O mixtures (80:20:1 and 80:20:2) to yield betulalbuside A (24 mg) and liriodendrin (11 mg). Fraction G (1490 mg) was subjected to C_{18}-MPLC (column dimensions: 26 × 460 mm), eluted with MeOH-H_2O mixtures (20 – 80% MeOH) to yield thirteen subfractions, G_1-G_{13}. Fraction G_5 yielded pure forsythoside B (**10**, 569 mg). Fraction G_2 was applied to a to si gel CC using CH_2Cl_2-MeOH-H_2O mixture (61:32:7) to afford chlorogenic acid (30 mg). Purification of fraction G_7 (47 mg) by si gel CC using CH_2Cl_2-MeOH-H_2O (80:20:2) furnished hattushoside (**17**, 6 mg) and alyssonoside (**11**, 7 mg). Fraction G_9 (77 mg) was rechromatographed over si gel column (CH_2Cl_2-MeOH-H_2O, 80:20:2) to give isoverbascoside (**6**, 31 mg) and luteolin 7-*O*-(6”-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside (14 mg). Fraction J (777 mg) was chromatographed over silica gel column employing EtOAc-MeOH-H_2O (100:10:2.5 to 100:15:10 and MeOH) gradient to yield six major fractions, fr. J_1 – J_6. Fraction J_6 (210 mg) eluted with MeOH was further applied to C_{18}-MPLC (column dimensions: 30 × 240 mm) to yield the mixture of luteolin 7-*O*-(6”-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside and luteolin 7-*O*-(6”-*O*-β-D-apiofuranosyl)-β-D-glucopyranoside (23 mg) and chrysoeriol 7-*O*-β-D-glucopyranoside (17 mg). Fraction H (1113 mg) was rich in verbascoside. HPLC (C_{18} μ-Bondapack column 3.9 × 300 mm, particle size 10 μm, MeCN in H_2O 15 – 30% gradient) studies performed on this fraction indicated the presence of leucosceptoside A (t_R 21.85) and martynoside (t_R: 26.72) in addition to verbascoside (t_R: 16.83).

Lamiidic acid (**1**): Amorphous powder; $[\alpha]_D$ −83.9 (*c* 0.1, MeOH); ESI-MS *m/z*: 431 $[M+Na]^+$; 407 $[M-H]^-$; HRESI-MS: $C_{16}H_{24}O_{12}Na$ found 431.1176; calcd. 431.1165. UV λ_{max} (MeOH, nm): 224; IR ν_{max} (KBr, cm^{-1}) 3421, 1650; ^1H NMR (600 MHz, CD_3OD): Table 1; ^{13}C NMR (CD_3OD, 150 MHz): Table 1.

Table 1. The ^{13}C and ^1H NMR spectroscopic data and HMBC correlations for lamiidic acid (**1**) (CD_3OD, ^{13}C: 150 MHz; ^1H: 600 MHz)*.

C/H		δ_C ppm	δ_H ppm, *J* (Hz)	HMBC (H→C)
1	CH	93.9	5.76 br s	C-1’, C-3, C-5
3	CH	146.8	7.13 s	C-1, C-4, C-5, C-11
4	C	119.8		
5	C	70.7		
6	CH_2	48.0	2.29 d (3.9)	C-4, C-5, C-8
7	CH	78.1	3.57 t (3.9)	
8	C	79.7		
9	CH	56.7	2.71 br s	C-4, C-5, C-8, C-10
10	CH_3	21.6	1.16 s	C-8, C-9
11	C	174.3		
1’	CH	99.4	4.61 d (7.8)	C-1
2’	CH	74.4	3.24 dd (7.8, 9.0)	C-1’
3’	CH	77.4	3.41 t (9.0)	C-4’
4’	CH	71.7	3.34 t (9.0)	C-3’, C-5’
5’	CH	78.3	3.36 m	
6’	CH_2	62.8	3.92 dd (11.5, 1.8)	C-5’
			3.68 dd (11.5, 5.9)	

Table 2. The ^{13}C and ^1H NMR spectroscopic data and HMBC correlations for ipolamiidic acid (**2**) (CD_3OD, ^{13}C: 150 MHz; ^1H: 600 MHz)*

C/H		δ_C ppm	δ_H ppm, *J* (Hz)	HMBC (H→C)
1	CH	92.5	5.78 br s	C-1’, C-3, C-5
3	CH	148.4	7.25 s	C-1, C-4, C-5, C-11
4	C	117.2		
5	C	71.5		
6	CH_2	39.0	2.28 m	
			2.04 m	
7	CH_2	40.1	1.97 m	C-6, C-8, C-9
			1.61 m	
8	C	78.2		
9	CH	60.4	2.44 br s	C-1, C-5, C-8
10	CH_3	23.0	1.21 s	C-7, C-8, C-9
11	C	171.6		
1’	CH	98.4	4.59 d (7.9)	C-1
2’	CH	74.3	3.23 dd (7.9, 9.0)	C-1’, C-3’
3’	CH	77.3	3.40 t (9.0)	C-2’, C-4’
4’	CH	71.5	3.30 t (9.0)	C-3’
5’	CH	78.1	3.35 m	
6’	CH_2	62.4	3.93 dd (11.9, 1.9)	
			3.68 dd (11.9, 6.2)	C-5’

* All proton and carbon assignments are based on 2D NMR (DQF-COSY, HSQC, and HMBC).

Ipolamiidic acid (**2**): Amorphous powder; $[\alpha]_D$ −69.9 (*c* 0.1, MeOH); ESI-MS *m/z*: 415 $[M+Na]^+$, HRESI-MS: $C_{16}H_{24}O_{11}Na$ found 415.1232; calcd. 415.1216; UV λ_{max} (MeOH, nm): 226; IR ν_{max} (KBr, cm^{-1}) 3421, 1652; ^1H NMR (600 MHz, CD_3OD): Table 2; ^{13}C NMR (CD_3OD, 150 MHz): Table 2.

Results and Discussion

Compound **1** was obtained as an amorphous powder. The ESI-MS afforded positive- and negative-ions at *m/z* 431 $[M+Na]^+$, 407 $[M-H]^-$, implying a molecular formula of $C_{16}H_{24}O_{12}$, which was confirmed by the HRESI-MS. The UV spectrum showed maxima at 224 nm typical for C-4 substituted iridoids. The ^{1}H NMR spectrum (see Table 1) displayed signals due to a tertiary methyl ($\delta_H = 1.16$), one methylene ($\delta_H = 2.29$), one methine ($\delta_H = 2.71$), one oxymethine ($\delta_H = 3.57$) one acetal ($\delta_H = 5.76$) and one olefinic ($\delta_H = 7.13$) functions. Additionally, the anomeric proton resonance at $\delta_H = 4.61$ (d, $J = 7.8$ Hz) and the signals in the region 3.24 – 3.92 ppm indicated the presence of a β-glucopyranosyl unit in **1**. The ^{13}C NMR spectrum (see Table 1) exhibited 16 signals, six of which were ascribed to a β-glucopyranosyl moiety, all the remaining 10 resonances were characteristic for an iridoid aglycon bearing a carboxyl group at C-4 position. The chemical shift value of the olefinic H-3 signal ($\delta_H = 7.13$) revealed that the carboxyl group is attached at C-4. All of the ^{1}H and ^{1}3C chemical shifts of **1** were determined on the basis of 2D NMR experiments [DQF-COSY, HSQC and HMBC (see Table 1)]. In the DQF-COSY spectrum of **1** the oxymethine proton ($\delta_H = 3.57$) coupled with methylene protons at $\delta_H = 2.29$, which were attributed to H-7 and H_2-6 of the cyclopentane ring of the aglycon, respectively. No other coupling was observed for H_2-6 and H-7 suggesting that both C-5 and C-8 were totally substituted. The complete assignments were confirmed by the HMBC spectrum. The long-range correlations between H-3 and C-11 ($\delta_C = 174.3$) confirmed that the carboxyl group is located to C-4. Furthermore, the cross-peaks between H-1 and C-1' and *vice versa*, revealed that the β-glucopyranose is attached to C-1(OH). These NMR data were very similar to those of lamiide [4], except for lacking the methoxy signal due to the carbomethoxy group, which established the presence of a free carboxyl group. On the basis of these spectroscopic data, the structure of compound **1** was determined as demethyl derivative of lamiide and named as lamiidic acid.

Compound **2** was obtained as an amorphous powder. The molecular formula, $C_{16}H_{24}O_{11}$, was deduced by ESI-MS (*m/z* 415 $[M+Na]^+$) and verified by HRESI-MS. Its UV spectrum (226 nm) revealed the presence of C-4 substituted iridoid skeleton as in **1**. The ^{1}H NMR spectrum (see Table 2) exhibited signals due to conjugated iridoid glucoside. The anomeric proton resonance at $\delta_H = 4.59$ (d, $J = 7.9$ Hz) indicated the presence of a β-glucopyranosyl unit in **2**. Moreover, one tertiary methyl ($\delta_H = 1.21$), two methylenes ($\delta_H =$ 1.61, 1.97 and 2.04, 2.28), one methine ($\delta_H = 2.44$), one acetal ($\delta_H = 5.78$) and one olefinic ($\delta_H = 7.25$) resonances were observed in the ^{1}H NMR spectrum. The proton and carbon signals of compound **2**, secured by 2D NMR [DQF-COSY, HSQC and HMBC (see Table 2)] were similar to those of **1** except for the signals belonging to the cyclopentane ring. The resonances attributed to the C-7 ($\delta_C = 40.1$) and H_2-7 ($\delta_H = 1.97$ m and 1.61) revealed the presence of a methylene functionality at C-7 instead of hydroxymethine. The signal at $\delta_C = 171.6$ suggested the presence of carboxyl group at C-4. The HMBC experiment allowed assignments of the entire molecule. The complete NMR data of **2** were closely related to that of ipolamiide [5], except for lacking the methoxy signal due to the carbomethoxy group, which established the presence of a free carboxyl group. By the above observations, compound **2** was found to be demethyl analogue of ipolamiide and named as ipolamiidic acid.

In addition to these new compounds, from *P. nissolii* a known iridoid glucoside, lamiide (**3**) [4] and 13 known phenylethanoid glycosides, verbascoside (**5**) [6], isoverbascoside (**6**) [7], leucosceptoside A (**7**) [7] and B (**12**) [7], martynoside (**8**) [8], arenarioside (**9**) [9], forsythoside B (**10**) [10], alyssonoside (**11**) [11], lamiophlomiside A (**13**) [12], samioside (**14**) [13], integrifolioside A (**15**) [14] and B (**16**) [14], and hattushoside (**17**) [15] were also isolated. From *P. capitata*, two known iridoid glucosides, lamiide (**3**) [4], ipolamiide (**4**) [5], and four phenylethanoid glycosides, isoverbascoside [7], forsythoside B [10], alyssonoside [11] and hattushoside [15], and a lignan glucoside, liriodendrin [16], three flavonoid glycosides, luteolin 7-*O*-(6"-*O*-α-L-rhamnopyranosyl)-β-D-glucopyranoside [17], luteolin 7-*O*-(6"-*O*-β-D-apiofuranosyl)-β-D-glucopyranoside [3] and chrysoeriol 7-*O*-β-D-glucopyranoside [17, 18], an acyclic monoterpene, betulalbuside A [19], and a quinic ester derivative, chlorogenic acid [20] were isolated and identified by comparison of their spectroscopic (NMR and MS) data with those published in the literature.

Concerning the iridoid glucosides isolated from the genus *Phlomis*, lamiidic acid (**1**) and ipolamiidic acid

(**2**) are the second examples, bearing a free carboxyl group at C-4. The phenylethanoid glycosides, arenarioside and lamiophlomiside A, are also being first reported from the genus *Phlomis*. Integrifoliosides A and B are the monomethyl and dimethyl derivatives of samioside [13] and has just been reported as new compounds from *P. integrifolia* [14] and this is the second report for these compounds from nature. Our previous studies carried on *Phlomis* species indicated that forsythoside B is the prevalent phenylethanoid triglycoside, while samioside and its methylated derivatives so far seem to be rare compounds.

Acknowledgements

This work was supported by the Research Institute of Pharmaceutical Sciences and the Scientific and Technical Research Council of Turkey (TUBITAK, Project No: SBAG-2304).

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