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PHLINOSIDES D AND E, PHENYLPROPANOID GLYCOSIDES, AND IRIDOIDS FROM *PHLOMIS LINEARIS**

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Key Word Index—*Phlomis linearis*; Lamiaceae; phenylpropanoid glycosides; phlinoside D; phlinoside E; iridoids; lamiide; ipolamiide; auroside.

Abstract—Two new phenylpropanoid glycosides, phlinosides D and E were isolated from the methanolic extract of the aerial parts of *Phlomis linearis*, along with the known iridoid glucosides, lamiide, ipolamiide and auroside (=5-hydroxy-8-epiloganin). On the basis of chemical and spectral evidence the structures of phlinosides D and E were determined as 3,4-dihydroxy-β-phenylethoxy-*O*-β-D-xylopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-feruloyl-β-D-glucopyranoside and 3,4-dihydroxy-β-phenylethoxy-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-feruloyl-β-D-glucopyranoside, respectively.

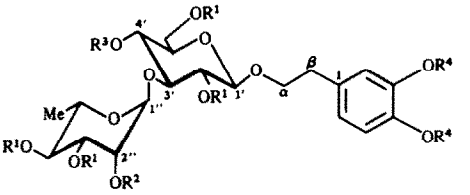
INTRODUCTION

Our systematic phytochemical investigations on the aerial parts of *Phlomis linearis* Boiss. & Bal. have resulted in the isolation of phenylpropanoid glycosides, such as phlinosides A, B, C [1], verbascoside (=acteoside), leucosceptoside A and martynoside [2]. In a continuation of our work on the glycosidic constituents of *P. linearis*, we further isolated two new trisaccharide esters named phlinosides D (**1**) and E (**2**) which are closely related to phlinosides B and C only differing from the nature of their acyl moieties. We have also isolated two minor iridoid glucosides, ipolamiide (**4**) and auroside (**5**) together with lamiide (**3**) reported as a major iridoid glucoside [2].

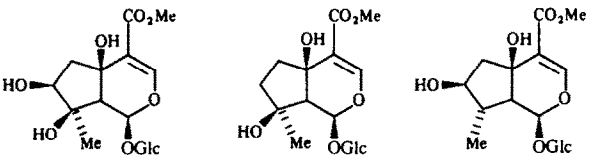
RESULTS AND DISCUSSION

Compounds **1** and **2** were obtained as amorphous compounds $C_{35}H_{46}O_{19}$ and $C_{36}H_{48}O_{19}$ (FAB mass spectrometry), respectively. The UV spectra of **1** and **2** confirmed their polyphenolic nature. Their IR spectra also showed similar absorption bands, hydroxyl groups, α,β-unsaturated esters and aromatic rings (see Experimental). The ^{1}H NMR spectra of **1** and **2** exhibited characteristic signals belonging to (*E*)-ferulic acid and 3,4-dihydroxyphenylethanol moieties (six aromatic protons, two ABX systems, and olefinic protons, AB system, for each). Additionally a methoxyl group, a benzylic methylene and two non-equivalent protons were observed for each. Moreover, three doublets of the anomeric protons for **1** and **2** indicated their trisaccharide structures. Three signals of anomeric protons appeared at δ4.33 (J = 7.2 Hz), 4.37 (J = 7.8 Hz) and 5.45 (J = 1.5 Hz) for **1**, are consistent with the following C-1 configurations: β for D-glucose, β for D-xylose and α for L-rhamnose, respectively. On the other hand, the signals at δ4.38 (J = 7.9 Hz), 4.89 (J = 1.5 Hz) and 5.36 (J = 1.7 Hz) for **2**, are assigned to the anomeric protons of D-glucose and two L-rhamnose units.

The FAB-mass spectra of **1** and **2** exhibited $[M+H]^+$ ions at m/z 771 and 785 confirming the proposed structures. In both spectra, a fragment observed at m/z 177



	R¹	R²	R³	R⁴
1	H	Xyl	Fer	H
2	H	Rha	Fer	H
6	Ac	Xyl(Ac)₃	4‴-*O*-Ac-Fer	Ac
7	Ac	Rha(Ac)₃	4‴-*O*-Ac-Fer	Ac
8	H	Xyl	H	Me
9	H	Rha	H	Me



3 **4** **5**

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(176) gives evidence for ferulic acid as their acyl moieties. The signals of H-4′ of the glucose units of **1** (δ4.92, *t*, J = 9.2 Hz) and **2** (δ4.92, *t*, J = 9.3 Hz) indicate that acylations at these locations are by *trans*-feruloyl units.

Acetylation of **1** and **2** gave undecaacetates, **6** and **7**, respectively. The ^{1}H NMR spectra of **6** and **7** revealed the presence of three aromatic and seven aliphatic acetyl groups for each (Table 1). In the FAB-mass spectra of **6** and **7** the $[M]^+$ peaks were not observed. The peaks recorded were at *m/z* 259 [triacetyl − xylose]$^+$ and 489 [pentaacetyl − xylosyl − rhamnose]$^+$ for **6**, and at *m/z* 273 [triacetylrhamnose]$^+$ and 503 [pentaacetyl − rhamnosyl-rhamnose]$^+$ for **7**. In the ^{1}H NMR spectra of **6** and **7** no downfield shifts occurred upon acetylation for H-3′ (δ3.99 and 3.96, respectively, each *t*, J = 9.4 Hz) and H-2″ (δ3.91 and 3.89, respectively, each *dd*, J = 1.7/3.3 Hz) confirming the interglycosidic linkages. The above data shows that **1** and **2** have similar structures to those of phlinosides B and C, respectively, except for their acyl moieties [1].

In order to verify this assumption, phlinosides B, C and **1**, **2** were methylated with diazomethane and treated with aqueous KOH. Phlinoside B and **1** yielded **8** assigned as deacyl phlinoside B dimethyl ether, while phlinoside C and **2** yielded **9** assigned as deacyl phlinoside C dimethyl ether supporting the same glycosidation pattern in **1** as that of phlinoside B and **2** with that of phlinoside C.

On the basis of chemical and spectral evidence the structures of **1** and **2** were determined as 3,4-dihydroxy-β-phenylethoxy-*O*-β-D-xylopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-feruloyl-β-D-glucopyranoside and 3,4-dihydroxy-β-phenylethoxy-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-feruloyl-β-D-glucopyranoside, respectively.

All spectral data (UV, IR, ^{1}H, ^{13}C NMR and FAB-MS) obtained for **3**–**5** are in good agreement with the reported

Table 1. ^{1}H NMR spectral data of compounds **6** and **7** (400 MHz, $CDCl_3$, δ ppm)

	H	6		7		J (Hz)
Aglycone	2	7.03	*br s*	7.03	*br s*	—
	5	7.10	*br s*	7.09	*br s*	
	6	7.10	*br s*	7.09	*br s*	—
	α	4.12	*m*	4.12	*m*	—
		3.7–3.6	*m*	3.72–3.62	*m*	—
	β	2.88	*m*	2.88	*m*	—
Glucose	1′	4.39	*d*	4.42	*d*	(8.0)
	2′	5.06	*dd*	5.07	*dd*	(8.0/9.4)
	3′	3.99	*t*	3.96	*t*	(9.4)
	4′	5.21	*t*	5.23	*t*	(9.5)
	5′	3.7–3.6	*m*	3.72–3.62	*m*	—
	6′A	4.13	*dd*	4.17	*dd*	(12/3)
	6′B	4.18	*dd*	4.22	*dd*	(12/4.6)
Rhamnose	1″	4.96	*d*	4.92	*d*	(1.7)
	2″	3.91	*dd*	3.89	*dd*	(1.7/3.3)
	3″	4.93	*dd*	5.04	*dd*	(3.3/10)
	4″	4.79	*t*	4.95	*t*	(9.6)
	5″	3.73	*m*	3.76	*m*	—
	6″	1.04	*d*	1.08	*d*	(6.3)
Xylose (terminal)	1‴	4.41	*d*		—	(7.0)
	2‴	4.93	*dd*		—	(7.0/8.7)
	3‴	5.15	*t*	—	—	(8.7)
	4‴	4.88	*ddd*		—	(8.7/4.9/9.0)
	5‴A	3.29	*dd*		—	(11.9/9.0)
	5‴B	4.05	*dd*	—	—	(11.9/5.1)
Rhamnose (terminal)	1⁗			4.74	*d*	(1.6)
	2⁗			5.24	*dd*	(1.6/3.4)
	3⁗			5.28	*dd*	(3.4/9.7)
	4⁗	—		5.03	*t*	(9.8)
	5⁗			3.72–3.62	*m*	—
	6⁗	—	—	1.19	*d*	(6.3)
Feruloyl moiety	2⁗′	7.08	*d*	7.08	*d*	(1.8)
	5⁗′	7.05	*d*	7.05	*d*	(8.1)
	6⁗′	7.11	*dd*	7.12	*dd*	(8.1/1.8)
	α′	6.34	*d*	6.36	*d*	(16.0)
	β′	7.70	*d*	7.71	*d*	(16.0)
	OMe	3.85	*s*	3.85	*s*	—

Ac (for **6**): 2.32, 2.30, 2.29 (arom.), 2.1, 2.09, 2.05 (× 2), 2.02, 1.96, 1.70 (aliph.); (for **7**): 2.32, 2.29, 2.27 (arom.), 2.13, 2.09, 2.03, 2.02, 1.99, 1.98, 1.77 (aliph.).