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PHLINOSIDES A, B and C, THREE PHENYLPROPANOID GLYCOSIDES FROM *PHLOMIS LINEARIS*

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Key Word Index—*Phlomis linearis*; Lamiaceae; phenylpropanoid glycosides; caffeic trisaccharide esters; phlinoside A; phlinoside B; phlinoside C; NMR; FABMS.

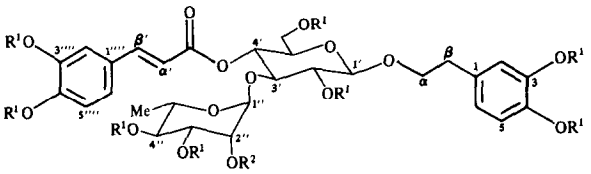
Abstract—Three new phenylpropanoid glycosides, phlinosides A, B and C were isolated from a methanolic extract of the aerial parts of *Phlomis linearis*. On the basis of chemical and spectral evidence their structures were determined as 3,4-dihydroxy-β-phenylethoxy-*O*-β-D-glucopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside, 3,4 dihydroxy-β-phenylethoxy-*O*-β-D-xylopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside and 3,4-dihydroxy-β-phenylethoxy-*O*-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside, respectively.

INTRODUCTION

Phenylpropanoid glycosides (glycoside esters of cinnamic acid derivatives) constitute a group of natural products which is increasing in number constantly. Hitherto, most interest was due to their importance from the point of view of chemotaxonomy and their distribution in dicotyledons has been reviewed [1]. Recently, significant physiological activities such as antiviral and cell growth inhibitory effects have also been reported [2, 3].

A rather small sub-group of compounds consisting of three carbohydrate moieties has also increased remarkably to over 30, several of them being listed in ref. [1]. The main structure of most of these trisaccharide esters is derived from acteoside (= verbascoside) (**4**) with β-D-glucopyranose as the central sugar. Additional to rhamnose, the third sugar is frequently glucose, galactose, rhamnose, xylose, arabinose or apiose [1]. Recently, teucrioside has been isolated from *Teucrium chamaedrys* (Lamiaceae), which has L-lyxose as the third sugar [4]. However, the type of sugars, different sequences or substitution patterns cause a great variation in the structures of the phenylpropanoid glycosides. This variability is exemplified by the caffeoyl conjugates from *Echinacea* species [3], by the mussatiosides (*Mussatia* species) containing a sugar sequence in which rhamnose is linked to the 6-position of the central glucose unit and the third sugar, xylose, is attached to the 3-position of the rhamnose moiety [5, 6] the acylation site being at C-4 of the rhamnose unity, or by the magnolosides (*Magnolia* species) which are unique among the phenylpropanoids in having β-D-allopyranoside as the core sugar [7].

During our research for phenylpropanoid glycosides and their distribution in Lamiaceae, *Galeopsis* [8], *Stachys* [9] and in the Scrophulariaceae, *Scrophularia* [10, 11], *Rhynchocorys* [12] and *Pedicularis* [paper in preparation], we have further studied an endemic



	R^1	R^2
1	H	D-glucose
2	H	D-xylose
3	H	L-rhamnose
4	H	H
5	Ac	D-glucose (Ac)$_4$
6	Ac	D-xylose (Ac)$_3$
7	Ac	L-rhamnose (Ac)$_3$

Phlomis species, *P. linearis* (Lamiaceae) which occurs in E. and S. E. Anatolia in Turkey.

We describe the isolation and structural elucidation of three new phenylpropanoid glycosides, phlinosides A (**1**), B (**2**) and C (**3**) from the aerial parts of *P. linearis*. Because **1**–**3** have all in common (*E*)-caffeic acid and 3,4-dihydroxyphenylethanol, the three new trisaccharide esters are closely related to teucrioside [4] and lavandulifolioside [9], the only differences being in the nature of the sugars attached to the rhamnose moiety of acteoside.

RESULTS AND DISCUSSION

Compounds **1**–**3** were obtained as amorphous compounds, $C_{35}H_{46}O_{20}$, $C_{34}H_{44}O_{19}$ and $C_{35}H_{46}O_{19}$ (FAB mass spectrometry), respectively. They exhibited similar UV absorptions (see Experimental), confirming their polyphenolic nature. Their IR spectra also showed similar absorption bands, hydroxyl groups (3400 cm^{-1}), α,β-unsaturated esters (νC = O 1690, νC = C 1630 cm^{-1}, for

each), and aromatic rings (1600 and 1510 cm^{-1}, for each).

The ^1H NMR spectra of **1–3** (see Experimental) exhibited the characteristic signals belonging to (*E*)-caffeic acid and 3,4-dihydroxyphenylethanol moieties. Additionally the signals of anomeric protons appeared at δ5.57 (*d*, J = 1.5 Hz, H-1″), 4.39 (*d*, J = 7.6 Hz, H-1′) and 4.37 (*d*, J = 7.9 Hz, H-1‴) for **1**, at δ5.44 (*br s*, H-1″), 4.47 (*d*, J = 7.7 Hz, H-1′) and 4.55 (*d*, J = 7.8 Hz, H-1‴) for **2** and δ5.29 (*d*, J = 1.7 Hz, H-1″), 4.52 (*d*, J = 7.9 Hz, H-1′) and 4.95 (*d*, J = 1.5 Hz, H-1‴) for **3**, indicating their trisaccharide structure with the same acyl [(*E*)-caffeoyl] and aglycone (3,4-dihydroxy-phenylethyl) moieties. Moreover, the methyl signals at 1.07 (*d*, J = 6.2 Hz) and 1.05 (*d*, J = 6.1 Hz) suggested the presence of a rhamnose moiety in **1** and **2**, whereas **3** revealed corresponding signals at δ1.07 and 1.27 (each *d*, J = 6.2 Hz), hence consisting of two rhamnose units. On the other hand, negative ion FAB mass spectrometry of **1–3** exhibited $[M-H]^-$ ions at *m/z* 784.5, 754.3 and 768.5, respectively, confirming two hexoses and one methylpentose for **1**, one hexose, one methylpentose and one pentose for **2**, and one hexose and two methylpentoses for **3**. Acid hydrolysis followed by PC revealed glucose and rhamnose for **1**, glucose, rhamnose and xylose for **2** and glucose and rhamnose for **3**. GC analysis of the sugars of **2** also supported this proposal.

The ^1H NMR spectra of **1–3** suggested that the caffeoyl moieties occupy the 4′ position in the central D-glucopyranoside, because the H-4′ signals are shifted paramagnetically (δ4.93, *t*, J = 9.3 Hz; 5.0, *t*, J = 10 Hz; 4.99, *t*, J = 9.6 Hz, respectively) indicating the same acylation site.

In order to establish the complete structures, **1–3** were methylated by Hakomori's method [13]. Subsequent acid hydrolysis of the methylated derivatives yielded 2,3,4,6-tetramethyl-D-glucose for **1**, 2,3,4-trimethyl-D-xylose for **2** and 2,3,4-trimethyl-L-rhamnose for **3**, thus establishing the terminal position of glucose, xylose and rhamnose linked to rhamnoses for **1–3**, respectively.

On the other hand ^{13}C NMR spectral data of **1–3** (Table 1) were very similar to each other except for the signals arising from their different terminal sugar moieties. All the chemical shift values attributed to the terminal sugar moieties of **1–3** are equally comparable to those of terminal glucose as in echinacoside [14], xylose as in mussatiosides [5, 6] and rhamnose as in angorosides [10, 11], respectively. The rest of the signals were very close to those of teucrioside [4] and lavandulifolioside [9], indicating their similar substitution pattern. These conclusions were fully supported by the analysis of their acetylated derivatives **5–7**.

Acetylation of **1** yielded the dodecaacetate **5**, $C_{59}H_{70}O_{32}$ (FAB mass spectrum: *m/z* 1291 $[M+H]^+$). The main fragment peaks recorded were at *m/z* 981.4 $[(M+Na)-331]^+$ for the loss of the tetraacetyl-glucose moiety and at *m/z* 561.2 [hexaacetyl − glucosyl − rhamnose]$^+$ for the diglycosidic side chain [Glc − rham $(Ac)_6$] and at *m/z* 331.2 [tetraacetyl − glucose]$^+$ (terminal sugar). The ^1H NMR spectrum of **5** revealed four aromatic and eight aliphatic acetyl groups (Table 2). No downfield shifts occurred upon acetylation for H-3′ (δ4.0, *t*, J = 9.4 Hz) and H-2″ (δ3.99, *dd*, J = 1.6/3.2 Hz) confirming the sequences and the linkages of the sugars in the oligoglycosidic chain to be glucose-(1 → 2)-rhamnose-(1 → 3)-glucose → aglycone. Consequently, the structure of phlinoside A (**1**) has been established as 3,4-dihyd-

Table 1. ^{13}C NMR spectral data of compounds **1–3** (100 MHz, CD_3OD, δ in ppm, TMS = 0)

C	1	2	3
Aglycone			
1	131.8 *s*	131.5 *s*	131.7 *s*
2	116.8 *d*	116.6 *d*	116.8 *d*
3	146.4 *s*	146.1 *s*	146.4 *s*
4	145.0 *s*	144.7 *s*	144.9 *s*
5	117.4 *d*	117.1 *d*	117.4 *d*
6	121.6 *d*	121.3 *d*	121.6 *d*
α	72.5 *t*	72.2 *t*	72.5 *t*
β	36.8 *t*	36.6 *t*	36.8 *t*
Glucose			
1′	104.6 *d*	104.2 *d*	104.5 *d*
2′	76.4 *d*	76.0 *d*	76.4 *d*
3′	83.3 *d*	82.4 *d*	80.3 *d*
4′	70.7 *d*	70.4 *d*	70.5 *d*
5′	76.3 *d*	76.0 *d*	76.2 *d*
6′	62.6 *t*	62.4 *t*	62.6 *t*
Rhamnose			
1″	102.5 *d*	102.1 *d*	101.9 *d*
2″	83.3 *d*	82.9 *d*	82.0 *d*
3″	72.0 *d*	71.9 *d*	72.3 *d*
4″	74.4 *d*	74.2 *d*	74.3 *d*
5″	70.7 *d*	70.5 *d*	70.7 *d*
6″	18.7 *q*	18.4 *q*	18.2 *q*
Glucose			
1‴	107.2 *d*		
2‴	75.6 *d*		
3‴	78.2 *d*		
4‴	71.6 *d*		
5‴	78.4 *d*		
6‴	63.1 *t*		
Xylose			
1‴		107.5 *d*	
2‴		75.3 *d*	
3‴		77.9 *d*	
4‴		71.1 *d*	
5‴		67.0 *t*	
Rhamnose			
1‴			104.0 *d*
2‴			72.0 *d*
3‴			70.8 *d*
4‴			74.3 *d*
5‴			70.5 *d*
6‴			18.9 *q*
Caffeic acid			
1⁗	127.9 *s*	127.7 *s*	127.9 *s*
2⁗	114.9 *d*	114.7 *d*	114.9 *d*
3⁗	147.2 *s*	146.8 *s*	147.1 *s*
4⁗	150.2 *s*	149.8 *s*	150.0 *s*
5⁗	116.6 *d*	116.3 *d*	116.6 *d*
6⁗	123.5 *d*	123.2 *d*	123.5 *d*
α′	115.5 *d*	115.3 *d*	115.5 *d*
β′	148.5 *d*	148.0 *d*	148.3 *d*
C=O	168.5 *s*	168.3 *s*	168.6 *s*

roxy-β-phenylethoxy-*O*-β-D-glucopyranosyl-(1 → 2)-α-L-rhamnopyranosyl -(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside.

Acetylation of **2** gave the undecaacetate **6**, $C_{56}H_{66}O_{30}$ (FAB mass spectrum: *m/z* 1219 $[M+H]^+$). The ^1H NMR spectrum of **6** revealed the presence of eleven acetyl signals belonging to four aromatic and seven aliphatic acetyl groups (Table 2). The assignment of the proton signals in the sugars is based on the 2D-(homonuclear COSY) of **6**. The 2D-^1H, ^1H NMR-COSY spectrum of **6** revealed all the connectivities and exhibited no downfield shifts upon acetylation for H-3′ (δ3.98, *t*, *J* = 9.4 Hz) and H-2″ (δ3.91, *dd*, *J* = 1.8/3.2 Hz). These observations made clear that the linkages and the sugar sequences must be xylose-(1 → 2)-rhamnose-(1 → 3)-glucose → aglycone. These results were also supported by FAB mass spectrometry. The characteristic fragments resulting from the cleavage of the interglycosidic linkages at *m/z* 981.3 $[(M+Na)-259]^+$ for the loss of the triacetyl-xylose and *m/z* 489.1 [pentaacetyl − xylosyl − rhamnose]$^+$ for the diglycosidic chain [xyl − rham $(Ac)_5$] and *m/z* 259.3 [triacetyl − xylose]$^+$ (terminal sugar). Based on these results, the structure of phlinoside B (**2**) has been established as 3,4-dihydroxy-β-phenylethoxy-*O*-β-D-xylopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside.

The substitution pattern of phlinoside C (**3**) on the sugar moiety was also determined by high resolution ^1H NMR spectral analysis of its peracetyl derivative **7** (Table 2). Acetylation of **3** afforded the undecaacetate **7**, $C_{57}H_{68}O_{30}$ (FAB mass spectrum: *m/z* 1233 $[M+H]^+$). The chemical shift values of H-3′ of glucose and H-2″ of rhamnose were in good agreement with earlier observations for compounds **1** and **2** (δ3.95, *t*, *J* = 9.3 Hz and 3.89, *dd*, *J* = 1.8/3.0 Hz, respectively). These results indicate that **3** has a similar substitution pattern on the glucose and rhamnose moieties. These conclusions were also corraborated by the FAB mass spectrum of **7**. It showed the $[M+Na]^+$ ion at *m/z* 1255, an $[M+H]^+$ ion at *m/z* 1233, the [pentaacetyl − rhamnosyl − rhamnose]$^+$ ion at *m/z* 503.1 and a [triacetyl − rhamnose]$^+$ ion at *m/z* 273.3, indicating the sugar sequence to be rhamnose → rhamnose → glucose → aglycone. Therefore, phlinoside C (**3**) is 3,4-dihydroxy-β-phenylethoxy-*O*-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside.

EXPERIMENTAL

General. Experimental procedures were the same as reported in ref. [10]. ^1H and ^{13}C NMR spectra (δ ppm, *J* Hz) were obtained at 400 (^1H NMR) and 100 MHz (^{13}C NMR) in the FT mode. GC: column BP-5 fused silica, 25 m × 0.3 mm; H_2, 0.4 atm, split 15, temp. 195°.

Plant material. Phlomis linearis Boiss. et Bal was collected from Malatya, Darende in June 1987. A voucher specimen has been deposited in the Herbarium of the Pharmacognosy Department, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey.

Extraction and prepurification. Air-dried aerial parts of the plant (300 g) were extracted in MeOH at 50° (× 2, 2 l). The combined extracts were evapd under vacuum nearly to dryness, H_2O (0.5 l) was added and the H_2O-insol. material removed by filtration. The filtrate was extracted with $CHCl_3$ (× 5, 250 ml) and the $CHCl_3$ phase rejected. The aq. phase was concd to *ca* 100 ml and chromatographed over polyamide (200 g) eluting with H_2O, followed by increasing concns of MeOH to yield five frs: A (H_2O, 46.2 g), B (25% MeOH, 2.9 g), C (50% MeOH, 2.5 g), D (75% MeOH, 1.56 g), and E (MeOH, 1.62 g).

Isolation of phenylpropanoid glycosides. A portion of fr. B (0.75 g) was chromatographed over Sephadex LH-20 (800 × 36 mm, i.d.) with MeOH to give phenylpropanoid-containing frs (0.5 g). Purification was carried out by LPLC (735 × 26 mm, packed with Sepralyte C_{18}) using a H_2O–MeOH gradient (0–40% MeOH, linear in 40 hr) at a flow rate of 1.5 ml/min and five main frs (B1–B5) were collected. Frs B1 and B3 yielded pure **1** (9 mg) and **3** (138 mg), respectively. Fr. B2 (141 mg) containing **1** and **2** was subjected again to LPLC using the same conditions except column dimensions (380 × 13 mm, i.d.) and sepn time (48 hr) to give **1** (32 mg) and **2** (61 mg). Fractions B4 and B5 were also rich in phenylpropanoid glycosides which are currently under investigation.

Phlinoside A (**1**). $[\alpha]_D^{20}$ −59.7 (MeOH; *c* 0.46). UV λ_{max}^{MeOH} nm (log ε): 203 (4.17), 220 (3.95), 242 (sh), 292 (3.72) and 332 (3.88). IR ν_{max}^{KBr} cm^{-1}: 3400 (*br*, OH), 1690 (C=O), 1630 (C=C), 1600, 1510 (arom. rings). ^1H NMR (400 MHz, CD_3OD): aglycone moiety: δ6.70 (1H, *d*, *J* = 2 Hz, H-2), 6.67 (1H, *d*, *J* = 8 Hz, H-5), 6.56 (1H, *dd*, *J* = 2, 8 Hz, H-6), 4.05 and 3.76–3.69 (each 1H, *m*, H_2-α) and 2.79 (2H, *t like*, *J* = 7 Hz, H_2-β); glucose moiety (central): δ4.39 (1H, *d*, *J* = 7.6 Hz, H-1′) and 4.93 (1H, *t*, *J* = 9.3 Hz, H-4′); rhamnose moiety: δ5.57 (1H, *d*, *J* = 1.5 Hz, H-1″), 3.97 (1H, *dd*, *J* = 1.5, 3.3 Hz, H-2″) and 1.07 (3H, *d*, *J* = 6.2 Hz, Me-5″); glucose moiety (terminal): δ4.37 (1H, *d*, *J* = 7.9 Hz, H-1‴); caffeoyl moiety: δ7.59 and 6.27 (each 1H, *d*, *J* = 15.9 Hz, H-β′ and H-α′, resp.) 7.05 (1H, *d*, *J* = 2 Hz, H-2⁗), 6.95 (1H, *dd*, *J* = 8.2, 2 Hz, H-6⁗), and 6.77 (1H, *d*, *J* = 8.2 Hz, H-5⁗). ^{13}C NMR (100 MHz, CD_3OD): see Table 1. FABMS *m/z* (rel. int. %) 784.5 (92.3) ($[M-H]^-$, calc. for $C_{35}H_{46}O_{20}$; 786.74), 622.7 (15) $[M-glucose-H]^-$ and 476.8 (5.9) $[M-glucose-rhamnose-H]^-$.

Phlinoside B (**2**). $[\alpha]_D^{20}$ −66.4 (MeOH; *c* 0.40). UV λ_{max}^{MeOH} nm (log ε): 203 (4.67), 218 (4.41), 242 (sh), 292 (4.23) and 332 (4.37). IR ν_{max}^{KBr} cm^{-1}: 3400 (*br*, OH), 1695 (C=O), 1630 (C=C), 1600 and 1510 (arom. rings). ^1H NMR (400 MHz, D_2O): aglycone moiety: δ6.91 (1H, *d*, *J* = 1.5 Hz, H-2), 6.90 (1H, *d*, *J* = 8 Hz, H-5), 6.80 (1H, *dd*, *J* = 1.5, 8 Hz, H-6), 4.13 and 3.9–3.7 (each 1H, *m*, H_2-α) and 2.88 (2H, *t like*, *J* = 6.5 Hz, H_2-β); glucose moiety: δ4.47 (1H, *d*, *J* = 7.7 Hz, H-1′) and 5.0 (1H, *t*, *J* = 10 Hz, H-4′); rhamnose moiety: δ5.44 (1H, *br s*, H-1″), 4.07 (1H, *dd*, *J* = 1.5, 3.2 Hz, H-2″) and 1.05 (3H, *d*, *J* = 6.1 Hz, Me-5″); xylose moiety: δ4.55 (1H, *d*, *J* = 7.8 Hz, H-1‴); caffeoyl moiety: δ7.74 and 6.44 (each 1H, *d*, *J* = 16 Hz, H-β′ and H-α′, resp.), 7.25 (1H, *d*, *J* = 1.1 Hz, H-2⁗), 7.19 (1H, *dd*, *J* = 1.1, 8.2 Hz, H-6⁗) and 6.98 (1H, *d*, *J* = 8.2 Hz, H-5⁗). ^{13}C NMR (100 MHz, CD_3OD): see Table 1. FABMS *m/z* (rel. int.%): 754.3 (100) ($[M-H]^-$, calc. for $C_{34}H_{44}O_{19}$; 756.7), 622.5 (9.9) $[M-xylose-H]^-$ and 460.7 (1.4) $[M-xylose-caffeoyl]^-$.

Phlinoside C (**3**). $[\alpha]_D^{20}$ −75.7 (MeOH; *c* 0.46). UV λ_{max}^{MeOH} nm (log ε): 203 (4.56), 218 (4.32), 246 (sh), 292 (4.14) and 332 (4.29). IR ν_{max}^{KBr} cm^{-1}: 3400 (*br*, OH), 1690 (C=O), 1630 (C=C), 1595 and 1510 (arom. rings). ^1H NMR (400 MHz, D_2O): aglycone moiety: δ6.89 (1H, *br s*, H-2), 6.89 (1H, *d*, *J* = 8 Hz, H-5), 6.79 (1H, *br d*, *J* = 8 Hz, H-6), 4.13 and 3.93–3.84 (each 1H, *m*, H_2-α) and 2.86 (2H, *t like*, *J* = 6.6 Hz, H_2-β); glucose moiety: δ4.52 (1H, *d*, *J* = 7.9 Hz, H-1′) and 4.99 (1H, *t*, *J* = 9.6 Hz, H-4′); rhamnose moiety (next to glucose): δ5.29 (1H, *d*, *J* = 1.7 Hz, H-1″), 4.04 (1H, *dd*, *J* = 1.7, 3.3 Hz, H-2″) and 1.07 (3H, *d*, *J* = 6.2 Hz, Me-5″); rhamnose moiety (terminal): δ4.95 (1H, *d*, *J* = 1.5 Hz, H-1‴); 4.02 (1H, *dd*, *J* = 1.5, 3.3 Hz, H-2‴) and 1.27 (3H, *d*, *J* = 6.2 Hz, Me-5‴); caffeoyl moiety: δ7.73 and 6.43 (each 1H, *d*, *J* = 16 Hz, H-β′ and H-α′, resp.), 7.23 (1H, *br s*, H-2⁗), 7.17 (1H, *br d*, *J* = 8 Hz, H-6⁗) and 6.97 (1H, *d*, *J* = 8 Hz, H-5⁗). ^{13}C NMR (100 MHz,

Table 2. ^{1}H NMR spectral data of compounds **5**–**7** (400 MHz, $CDCl_3$)*

H	5	6	7
Aglycone			
2	7.02 *br s*	7.03 *br s*	7.03 *br s*
5	7.08 *br s*	7.09 *br s*	7.09 *br s*
6	7.08 *br s*	7.09 *br s*	7.09 *br s*
α	4.18–4.09 *m*†	4.11 *m*	4.12 *m*
	3.70–3.60 *m*†	3.69–3.61 *m*†	3.70–3.61 *m*
β	2.87 *m*	2.87 *m*	2.87 *m*
β-glucose			
1′	4.47 *d* (8.0)	4.40 *d* (7.9)	4.42 *d* (8.0)
2′	5.05 *dd* (8.0/9.4)	5.06 *dd* (8.0/9.4)	5.06 *dd* (8.1/9.2)
3′	4.0 *t* (9.4)‡	3.98 *t* (9.4)‡	3.95 *t* (9.3)‡
4′	5.22 *t* (9.6)	5.20 *t* (9.6)	5.23 *t* (9.6)
5′	3.70–3.60 *m*†	3.69–3.61 *m*†	3.70–3.61 *m*†
$6'_A$	4.18–4.09 *m*†	4.15 *dd* (2.9/12.3)	4.16 *dd* (2.9/12.3)
$6'_B$	4.22 *dd* (4.9/12.2)	4.20 *dd* (4.8/12.3)	4.21 *dd* (4.6/12.3)
α-rhamnose			
1″	4.93 *d* (1.6)	4.95 *d* (1.8)	4.91 *d* (1.8)
2″	3.99 *dd* (1.6/3.2)‡	3.91 *dd* (1.8/3.2)‡	3.89 *dd* (1.8/3.0)‡
3″	4.92 *dd* (9.8/3.2)	4.93 *dd* (3.2/10.1)	5.00 *dd* (3.0/9.9)
4″	5.01 *t* (9.8)	4.80 *t* (9.9)	4.95 *t* (9.9)
5″	3.74 *m*	3.72 *m*	3.74 *m*
6″	1.07 *d* (6.2)	1.04 *d* (6.2)	1.08 *d* (6.2)
β-glucose			
1‴	4.41 *d* (8.0)		
2‴	5.00 *dd* (8.0/9.6)		
3‴	4.78 *t* (9.9)		
4‴	5.18 *t* (9.5)		
5‴	3.70–3.60 *m*†		
$6'''_A$	4.18–4.09 *m*†		
$6'''_B$	4.31 *dd* (4.8/12.2)		
β-xylose			
1‴		4.42 *d* (6.6)	
2‴		4.93 *dd* (8.7/6.8)	
3‴		5.15 *t* (8.7)	
4‴		4.88 *ddd* (8.7/5.1/9.1)	
$5'''_A$		3.29 *dd* (11.8/9.1)	
$5'''_B$		4.05 *dd* (5.1/11.2)	
α-rhamnose			
1‴			4.73 *d* (1.6)
2‴			5.22 *dd* (1.8/3.4)
3‴			5.27 *dd* (3.4/9.9)
4‴			5.03 *t* (9.9)
5‴			3.70–3.61 *m*†
6‴			1.18 *d* (6.2)
Caffeic acid			
2⁗	7.37 *d* (2)	7.36 *d* (2)	7.36 *d* (2)
5⁗	7.22 *d* (8.4)	7.23 *d* (8.4)	7.23 *d* (8.4)
6⁗	7.40 *dd* (2/8.4)	7.39 *dd* (2/8.4)	7.40 *dd* (2/8.4)
α′	6.35 *d* (16)	6.34 *d* (16)	6.36 *d* (16)
β′	7.69 *d* (16)	7.69 *d* (16)	7.69 *d* (16)
COMe	2.30, 2.296, 2.289, 2.27 (arom.), 2.10 (× 2), 2.08, 2.01 (× 2), 2.00, 1.92, 1.62 (aliph.)	2.30, 2.296, 2.29, 2.28 (arom.), 2.10, 2.08, 2.04 (× 2), 2.01, 1.99, 1.98, 1.76 (aliph.)	2.301, 2.299, 2.286, 2.273 (arom.), 2.13, 2.09, 2.03, 2.01, 1.99, 1.98, 1.76 (aliph.)

*Chemical shifts in ppm relative to internal TMS.

Values in parentheses are coupling constants in Hz.

†Signal patterns unclear due to overlapping.

‡The chemical shift values H-3′ and H-2″ for all compounds correlate well with the corresponding signals of teucrioside [4] and lavandulifolioside [9] which have a similar substitution pattern on the glucose and rhamnose moieties.

CD_3OD): see Table 1. FABMS *m/z* (rel. int. %): 768.5 (7.1) ($[M-H]^-$, calc. for $C_{35}H_{46}O_{19}$; 770.7).

Acetylation. Treatment of **1–3** (each *ca* 10 mg) separately with Ac_2O (0.5 ml) and pyridine (0.5 ml) at room temp. overnight, followed by CC over silica gel using C_6H_6–Me_2CO (4:1) gave dodecaacetate **5**, undecaacetate **6** and undecaacetate **7** derivatives, respectively.

Phlinoside A dodecaacetate (**5**). IR ν_{max}^{KBr} cm^{-1}: 1730 (C=O), 1620 (C=C) and 1490 (arom. ring). ^1H NMR (400 MHz, $CDCl_3$): see Table 2. FABMS *m/z*: 1291 ($[M+H]^+$, calc. for $C_{59}H_{70}O_{32}$), 1312.7 $[M+Na]^+$, 981.4 $[(M+Na)-331]^+$, 561.2 and 331.2.

Phlinoside B undecaacetate (**6**). IR ν_{max}^{KBr} cm^{-1}: 1735 (C=O), 1620 (C=C) and 1490 (arom. ring). ^1H NMR (400 MHz, $CDCl_3$): see Table 2. FABMS *m/z*: 1219 ($[M+H]^+$, calc. for $C_{56}H_{66}O_{30}$), 1241 $[M+Na]^+$, 981.3 $[(M+Na)-259]^+$, 489.1 and 259.3.

Phlinoside C undecaacetate (**7**). IR ν_{max}^{KBr} cm^{-1}: 1740 (C=O), 1630 (C=C) and 1500 (arom. ring). ^1H NMR (400 MHz, $CDCl_3$): see Table 2. FABMS *m/z*: 1233 ($[M+H]^+$, calc. for $C_{57}H_{68}O_{30}$), 1255 $[M+Na]^+$, 503.1 and 273.3.

Acid hydrolysis. Compounds **1–3** (each 5 mg) were separately dissolved in 5 ml 5% HCl and heated at 100° for 2 hr, cooled and filtered. The filtrates were neutralized by passing through Dowex (Cl^- form) and evapd to dryness. The residues were examined for sugars by PC (descending method) using *n*-BuOH–pyridine–H_2O (9:5:4).

Hydrolysis of **2** *and silylation of sugar component for GC.* A soln of **2** (5 mg) in 3% H_2SO_4 (5 ml) was hydrolysed at 90° for 3 hr. After neutralization with $BaCO_3$ and filtration through Celite, the filtrate was evapd and dried *in vacuo* (2 hr, 25°/10^{-3} Torr). The residue was dissolved in pyridine (1 ml) and hexamethyldisilazane (0.2 ml) and trimethylsilyl chloride (0.1 ml) were added and the mixt. shaken vigorously for 30 sec. After standing for 5 min at room temp. the reaction mixt. was dissolved with Et_2O and pyridine removed by washing with a satd $CuSO_4$ soln. The Et_2O layer was dried ($MgSO_4$) and subjected to GC analysis [15, 16]. R_t: 2.90 and 3.55 min (TMSi derivatives of L-rhamnose); 3.67 and 4.24 min (TMSi derivatives of D-xylose) and 6.37 and 8.54 min (TMSi derivatives of D-glucose).

Methylation. Compounds **1–3** (each 5 mg) were separately methylated by Hakomori's method [13]. The methylated products were dissolved in 5 ml 5% HCl in MeOH and heated at 100°. After 2 hr 5 ml H_2O was added and the mixt. reheated for an additional 1 hr. After removing MeOH, the H_2O phase was extracted with $CHCl_3$ (2 × 5 ml). The combined $CHCl_3$ extracts were dried (Na_2SO_4), concd and subjected to TLC using C_6H_6–Me_2CO (2:1) and C_6H_6–EtOH (4:1). Identification of methylated sugars was made by comparison with authentic samples. 2,3,4,6-tetramethylglucopyranoside, 2,3,4-trimethylxylopyranoside and 2,3,4-trimethylrhamnopyranoside were identified for **1**, **2** and **3** respectively.

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