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NINE PHENETHYL ALCOHOL GLYCOSIDES FROM *STACHYS SIEBOLDII*

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Key Word Index—*Stachys sieboldii*; Labiatae; phenethyl alcohol glycosides; stachysosides, *cis*-acteoside.

Abstract—Three new phenethyl alcohol glycosides together with six known compounds have been isolated from the leaves of *Stachys sieboldii*. On the basis of chemical and spectral analyses, the structures of three new compounds named stachysosides A, B and C have been established as 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-caffeoyl-β-D-glucopyranoside, 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-feruloyl-β-D-glucopyranoside and 2-(3-hydroxy-4-methoxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-feruloyl-β-D-glucopyranoside, respectively.

INTRODUCTION

Phenethyl alcohol glycosides are widely distributed in the plant kingdom and have been found to have various biological activities, such as antibacterial [1], antifeedant [2], cytotoxic [3], enzyme inhibitory activity against AMP phosphodiesterase and 5-lipoxygenase [4, 5] and protective effects on decreases of sex and learning behaviour in mice [6]. In the course of our chemical and biological studies on Rhemanniae radix, we have isolated 19 phenethyl alcohol glycosides and demonstrated their immunosuppressive activity [7–9]. We have been searching further for these compounds in other plants and have now isolated nine phenethyl alcohol glycosides, including three new compounds, from *S. sieboldii*. Previous studies on this plant resulted in the isolation of one phenethyl alcohol glycoside, acteoside, and two flavonoids [10]. We describe the isolation and structural elucidation of the new phenethyl alcohol glycosides.

RESULTS AND DISCUSSION

The methanolic extract was separated using a combination of Sephadex LH-20, MCI gel CHP20P and silica gel chromatographies to give nine compounds (**1–9**). Compounds **1**, **2**, and **4–6** were identified as decaffeoylacteoside, acteoside, isoacteoside, leucosceptoside A and martynoside, respectively, by direct comparison with authentic samples [7–9].

Stachysoside A (**7**)* was obtained as an off-white amorphous powder, whose molecular formula was confirmed by observation of a $[M+Na]^+$ ion peak at *m/z* 779 in its FD mass spectrum and elemental analysis ($C_{34}H_{44}O_{19} \cdot 5/2\ H_2O$). Its IR spectrum showed absorption bands due to hydroxyl groups (3392 cm^{-1}, br), an α,β-unsaturated ester ($\nu_{C=O}$ 1702 and $\nu_{C=C}$ 1632 cm^{-1}) and aromatic rings (1604 and 1524 cm^{-1}). The ^1H NMR spectrum of **7** (Table 1) exhibited signals arising from caffeic acid and 3,4-dihydroxyphenethyl alcohol moieties: two ABX signals due to aromatic protons at δ6.56–7.06, a pair of *trans*-olefinic proton signals at δ6.27 and 7.59 (each 1H, *d*, $J = 15.9$ Hz), and a benzylic methylene proton signal at δ2.80 (*t*, $J = 7.2$ Hz). Additionally three doublet methine signals attributable to sugar anomeric protons were observed at δ4.31 (*d*, $J = 6.8$ Hz), 4.38 (*d*, $J = 7.8$ Hz) and 5.48 (*d*, $J = 1.2$ Hz). On exhaustive acid hydrolysis with 5 M hydrochloride, **7** afforded 3,4-dihydroxyphenethyl alcohol, caffeic acid, glucose, rhamnose and arabinose, which were identified by HPLC, TLC and/or GC-MS. These data indicate that **7** is a triglycoside of 3,4-dihydroxyphenethyl alcohol with a caffeic acid

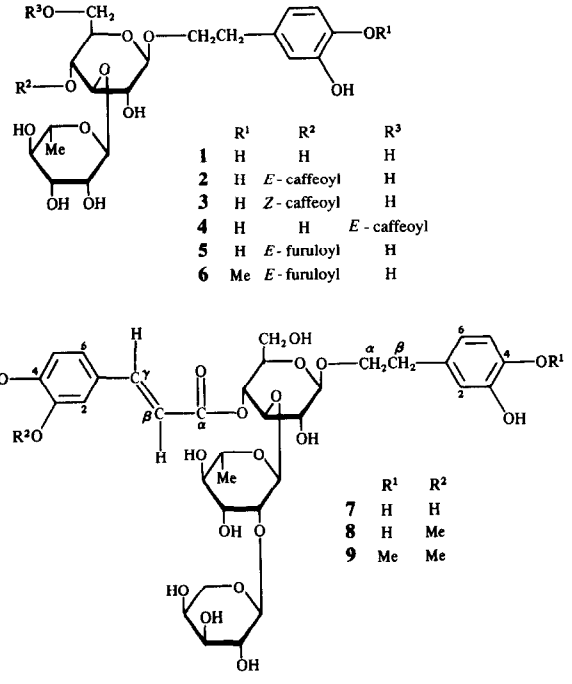

Table 1. ^{1}H NMR spectral data for compounds **2**, **3**, **7**–**9** (200 MHz, CD_3OD)

H	2	3	7	8	9
Aglycone					
2	6.70 *d*	6.70 *d*	6.70 *d*	6.71 *d*	6.74 *d*
	(2.0)	(2.2)	(2.0)	(2.0)	(2.0)
5	6.69 *d*	6.68 *d*	6.69 *d*	6.68 *d*	6.82 *d*
	(8.1)	(8.1)	(8.1)	(8.1)	(8.1)
6	6.56 *d*	6.56 *d*	6.56 *d*	6.56 *d*	6.68 *d*
	(8.1, 2.0)	(8.1, 2.2)	(8.1, 2.0)	(8.1, 2.0)	(8.1, 2.0)
α	3.3–4.2 *m*	3.3–4.2 *m*	3.2–4.2 *m*	3.3–4.2 *m*	3.3–4.2 *m*
β	2.79 *t*	2.79 *t*	2.80 *t*	2.79 *t*	2.82 *t*
	(7.3)	(7.3)	(7.2)	(7.2)	(7.2)
Acid moiety					
2	7.07 *d*	7.53 *d*	7.06 *d*	7.19 *d*	7.19 *d*
	(2.0)	(2.2)	(2.0)	(1.7)	(2.0)
5	6.78 *d*	6.74	6.81 *d*	6.78 *d*	6.81 *d*
	(8.1)	(8.3) *d*	(8.1)	(8.1)	(8.1)
6	6.96 *dd*	7.10 *dd*	6.96 *dd*	7.08 *dd*	7.08 *dd*
	(8.1, 2.0)	(8.3, 2.2)	(8.1, 2.0)	(8.1, 1.7)	(8.1, 1.7)
β	6.28 *d*	5.76 *d*	6.27 *d*	6.37 *d*	6.37 *d*
	(15.9)	(13.0)	(15.9)	(15.9)	(15.9)
γ	7.60 *d*	6.87 *d*	7.59 *d*	7.66 *d*	7.66 *d*
	(15.9)	(13.0)	(15.9)	(15.9)	(15.9)
Glucose					
1	4.38 *d*	4.35 *d*	4.38 *d*	4.37 *d*	4.38 *d*
	(7.8)	(7.8)	(7.8)	(7.8)	(8.1)
2, 3	3.3–4.2 *m*	3.3–4.2 *m*	3.2–4.2 *m*	3.3–4.2 *m*	3.3–4.2 *m*
4	4.94 *t*	4.94 *t*	4.93 *t*	4.93 *t*	4.93 *t*
	(9.3)	(9.3)	(9.0)	(9.5)	(9.0)
5, 6	3.3–4.2 *m*	3.3–4.2 *m*	3.2–4.2 *m*	3.3–4.2 *m*	3.3–4.2 *m*
Rhamnose					
1	5.19 *d*	5.17 *d*	5.48 *d*	5.49 *d*	5.49 *d*
	(1.7)	(1.7)	(1.2)	(1.2)	(1.2)
2–5	3.3–4.2 *m*	3.3–4.2 *m*	3.2–4.2 *m*	3.3–4.2 *m*	3.3–4.2 *m*
6	1.10 *d*	1.17 *d*	1.06 *d*	1.07 *d*	1.07 *d*
	(6.4)	(6.1)	(6.1)	(6.1)	(6.4)
Arabinose					
1	—	—	4.31 *d*	4.31 *d*	4.32 *d*
			(6.8)	(7.1)	(7.1)
2–5	—	—	3.2–4.2 *m*	3.3–4.2 *m*	3.3–4.2 *m*
OMe				3.88 *s*	3.81, 3.88 *s*

ester group. Acetylation of **7** yielded the undecaacetate (**7a**) whose FAB mass spectrum exhibited a $[M+H]^+$ ion peak at *m/z* 1219 and characteristic fragment peaks resulting from cleavage of interglycosidic linkages: *m/z* 981 for the loss of tri-*O*-acetylarabinosyl $[M+Na-Ara(OAc)_3]^+$, *m/z* 489 for penta-*O*-diglycosyl $[Ara\text{-}Rha(OAc)_5]^+$ and *m/z* 259 for terminal tri-*O*-acetylarabinose $[Ara(OAc)_3]^+$. These data suggested that sequence of sugars in **7** to be arabinosyl-rhamnosyl-glucose [11]. Indeed, hydrolysis of **7** with 1 M hydrochloride gave desarabinosyl (**2**) and desarabinorhamnosyl (**7b**), derivatives of **7** which were identified as acteoside and derhamnosylacteoside, respectively. With regard to the location of arabinose, the ^{1}H NMR spectrum of **7a** showed that the eight sugar proton signals appeared downfield at δ4.16–5.22 by acetylation on comparison with those of **7**, while the two methine proton signals at δ3.99 (*t*, $J=9.4$ Hz) and 3.91 (*dd*, $J=3.2$ and 1.9 Hz) remained upfield. The former of the last two was necessarily assigned to the H-3 proton of glucose from its coupling constant and a ^{1}H–^{1}H COSY experiment; the latter could be attributable to the methine proton of rhamnose where the terminal arabinose is linked. This methine was found to couple with the anomeric proton of rhamnose at δ5.00 (*d*, $J=1.9$ Hz) and hence the terminal arabinose linked to the C-2 position of rhamnose. This was further supported by comparing the ^{13}C chemical shift values for the rhamnose moiety of **7** with those of **2** (Table 2): the signal due to the C-2 carbon of rhamnose shifted downfield by 10.6 ppm, while the neighbouring C-1 and C-3 carbons shifted upfield by 1.0 and 0.4 ppm, respectively. The mode of arabinosyl linkage must be in the α-form from the coupling constant of its anomeric proton signal at δ4.34 (*d*, $J=6.6$ Hz) [12]. On the basis of these results, the

Table 2. ^{13}C NMR spectral data for compounds **2**, **3**, **5**–**9** (50 MHz, CD_3OD)

C	2	3	5	6	7	8	9
Aglycone							
1	131.5	131.4	131.5	132.9	131.5	131.5	132.9
2	116.6	116.3	116.3	113.0	116.5	116.3	112.9
3	144.7	144.6	144.6	147.5	144.6	144.7	147.5
4	146.1	146.1	146.0	147.4	146.1	146.1	147.4
5	117.2	117.1	117.1	117.1	117.1	117.1	117.1
6	121.3	121.2	121.2	121.1	121.3	121.3	121.1
α	72.4	72.2	72.2	72.1	72.2	72.3	72.1
β	36.6	36.5	36.5	36.5	36.6	36.6	36.6
Acid moiety							
1	127.6	128.0	127.6	127.7	127.6	127.6	127.7
2	114.6	118.9	111.8	111.9	114.7	111.8	111.8
3	149.8	148.6	150.7	150.8	149.7	150.8	150.8
4	146.8	145.5	149.3	149.4	146.8	149.4	149.4
5	116.4	115.7	116.5	116.5	116.3	116.5	116.5
6	123.4	125.8	124.3	124.3	123.2	124.4	124.4
α	168.3	168.8	168.2	168.2	168.3	168.4	168.2
β	115.3	115.7	115.1	115.1	115.2	115.1	115.1
γ	148.0	147.4	147.8	147.8	148.0	147.9	147.8
Glucose							
1	104.2	104.1	104.1	104.2	104.2	104.2	104.2
2	76.0	75.9	75.9	76.0	76.0	76.0	76.0
3	81.7	81.8	81.4	81.5	82.3	82.3	82.3
4	70.4[a]	70.3[a]	70.3[a]	70.4[a]	70.3[a]	70.3[a]	70.3[a]
5	76.2	76.0	76.1	76.2	76.0	76.0	76.0
6	62.4	62.3	62.3	62.4	62.3	62.4	62.4
Rhamnose							
1	103.0	103.0	102.9	102.9	102.0	102.0	102.0
2	72.1[b]	72.1[b]	72.0[b]	72.1[b]	82.7	82.8	82.8
3	72.3[b]	72.3[b]	72.3[b]	72.4[b]	71.9	72.0	72.0
4	73.8	73.8	73.8	73.8	74.2	74.2	74.2
5	70.6[a]	70.3[a]	70.6[a]	70.7[a]	70.5[a]	70.6[a]	70.6[a]
6	18.5	18.2	18.4	18.4	18.4	18.5	18.5
Arabinose							
1	—	—	—	—	107.4	107.4	107.4
2	—	—	—	—	72.8	72.9	72.9
3	—	—	—	—	74.3	74.4	74.4
4	—	—	—	—	69.8	69.8	69.8
5	—	—	—	—	67.3	67.3	67.3
OMe	—	—	56.5	56.5 56.6	—	56.5	56.5 56.6

[a,b] May be interchanged in each column.

structure of **7** was elucidated as 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-caffeoyl-β-D-glucopyranoside.

Stachysoside B (**8**)*, $C_{35}H_{46}O_{19}\cdot 3\ H_2O$, $[\alpha]_D$ −49.3° (MeOH), FAB mass spectrum *m/z*: 793 $[M+Na]^+$, an off-white amorphous powder, was also presumed to be an arabinosyl-(1→2)-rhamnosyl-(1→3)-glucoside of 3,4-dihydroxy phenethyl alcohol with acid ester at C-4 of glucose, from the similarity of its IR and NMR spectral data to those of **7**. The ^1H and ^{13}C NMR spectra showed the existence of a methoxyl group in **8** [δ_H 3.88 (3H, *s*): δ_C 56.5 (*q*)]. Its ^{13}C NMR spectrum showed that the signals due to the aglycone and sugar moieties were in good agreement with those of **7** except for the signals arising from the acid moiety. This indicates that the methoxyl group must be present in the acid moiety. It is easy to presume this acid to be ferulic acid by comparing the ^{13}C chemical shift values with those of the acid moiety of leucosceptoside A (**5**). Indeed, exhaustive acid hydrolysis of **8** gave ferulic acid, 3,4-dihydroxyphenethyl alcohol, glucose, rhamnose and arabinose. The structure of **8** was thus shown to be 2-(3,4-dihydroxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-feruloyl-β-D-glucopyranoside.

Stachysoside C (**9**)*, $C_{36}H_{48}O_{19}\cdot 7/2\ H_2O$, $[\alpha]_D$ −42.0° (MeOH), FAB mass spectrum *m/z*: 807 $[M+Na]^+$,

seemed to be a similar triglycoside [Ara-(1→2)-Rha-(1→3)-Glc] of a phenethyl alcohol to **7** and **8**. Its NMR spectrum showed signals due to two methoxyl groups [δ_H 3.81 and 3.88 (each 3H, *s*)]. Excellent agreement of the ^{13}C chemical shift values for the aglycone and acid moieties with those of martynoside (**6**) pointed to the existence of 3-hydroxy-4-methoxyphenethyl alcohol and a feruloyl group in **9**. In fact, exhaustive hydrolysis of **9** yielded 3-hydroxy-4-methoxyphenethyl alcohol, ferulic acid, glucose, rhamnose and arabinose. The structure of **9** was thus determined to be 2-(3-hydroxy-4-methoxyphenyl)ethyl *O*-α-L-arabinopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-4-*O*-*E*-feruloyl-β-D-glucopyranoside.

Compound **3**, $C_{29}H_{36}O_{15}\cdot 5/2\ H_2O$, FAB mass spectrum *m/z*: 625 $[M+H]^+$, $[\alpha]_D$ −39.3° (MeOH), was obtained an off-white amorphous powder. Its IR, FAB mass, ^1H and ^{13}C NMR spectral data and chromatographic behaviour were very similar to those of acteoside (**2**). Compound **3** appeared to be converted to **2** in the daylight (the volume ratio of **3** to **2** is *ca* 1:9 in solution). These properties of **3** suggested that it might be an isomer of **2**, such as jionosides A_1 and A_2. These compounds are characterized as phenethyl alcohol triglycosides having a feruloyl group and geometrical isomers on the configuration of the olefin in the feruloyl moiety [8]. In the ^1H NMR spectrum of **3**, a pair of olefinic proton signals appeared at δ5.76 and 6.87 (each 1H, *d*) and their coupling constant ($J=13.0$ Hz) was smaller than that of **2** (δ6.28 and 7.60; each 1H, *d*, $J=15.9$ Hz). This showed that **3** is the *cis*-isomer of **2**, that is *cis*-acteoside. Kikuchi *et al.* have reported the isolation of *cis*-acteoside from *Osmanthus* sp., but they purified it after acetylation of the fractions of the methanolic extract [13, 14]. It is for the first time that the glycoside itself has been isolated. Results of biological tests on these compounds will be reported elsewhere.

EXPERIMENTAL

Mps: uncorr. ^1H NMR spectra were measured at 500 or 200 MHz and ^{13}C NMR spectra were measured at 50 MHz with TMS as int standard. TLC was conducted on precoated silica gel plates and spots were visualized by spraying with $FeCl_3$ and dil. H_2SO_4. Prep. HPLC was done using a TSK gel ODS-120T (2.1 cm i.d. × 30 cm) column.

Plant material. Stachys sieboldii was cultivated at Ibaraki Experimental Farm, Tsumura & Co., and collected in September 1989. Plant material was identified by Dr M. Okada of this laboratory.

Extraction and isolation. Dried leaves (1.1 kg) were crushed and then extracted with MeOH (30 l) at room temp. After removal of chlorophyll with Et_2O (1.5 l), the MeOH extract (226 g) was applied to a Diaion HP-20 column which was eluted with H_2O (10 l, fr. I), 50% aq. MeOH (15 l, fr. II) and then MeOH (15 l). Fr. II was rechromatographed on Sephadex LH-20 by developing with increasing amounts of MeOH in H_2O (1:0→9:11) and divided into 6 further frs: fr. II–1 (2.6 g), fr. II–2 (720 mg), fr. II–3 (3.2 g), fr. II–4 (7.1 g), fr. II–5 (31.4 g) and fr. II–6 (2.0 g). Subsequent sepn of fr. II-2 by silica gel CC, eluting with $CHCl_3$–MeOH–H_2O (150:50:7) and then with EtOAc–MeOH–H_2O (20:3:2), afforded **1** (417 mg). Fr. II–4 was subjected to a combination of CC on MCI gel CHP20P, developing with increasing amounts of MeOH (1:0→1:4) and silica gel, eluting with EtOAc–MeOH–H_2O (30:2:1→20:3:2) or $CHCl_3$–MeOH–H_2O (465:35:1→150:50:7), to give **5** (1.20 g), **6** (21 mg), **7** (960 mg), **8** (1.20 g) and **9** (21 mg). Fr. II–5 was repeatedly chromatographed on MCI gel CHP20P, developing with H_2O–MeOH (1:0→1:1), Sephadex LH-20, eluting with 60% aq. MeOH and prep. HPLC eluting with 22% aq. MeCN containing 1% HOAc to yield **2** (28 g) and **3** (36 mg). Fr. II–6 was passed through a charcoal column eluting with 90% aq. Me_2CO and was subjected to silica gel CC, developing with EtOAc–MeOH–H_2O (30:2:1) to furnish **4** (680 mg). Known compounds except for *cis*-acteoside (**3**) were identified by direct comparison with authentic samples [7–9].

cis-Acteoside (**3**). Off-white amorphous powder, $[\alpha]_D^{25}$ −39.3° (MeOH; *c* 0.65). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1706 (C=O), 1604 (C=C), 1604 and 1520 (arom ring). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z*: 647 $[M+Na]^+$, 625 $[M+H]^+$, 479 $[M-Rha+2H]^+$, 471 $[M-aglycone]^+$, 325 $[471-Rha+H]^+$. (Found: C, 52.24; H, 6.18. Calc. for $C_{29}H_{36}O_{15}\cdot 5/2\ H_2O$: C, 51.97; H, 6.12%).

Stachysoside A (**7**). Off-white amorphous powder, $[\alpha]_D^{26}$ −49.7° (MeOH; *c* 1.10). IR ν_{max}^{KBr} cm^{-1}: 3392 (OH), 1702 (C=O), 1632 (C=C), 1604 and 1524 (arom ring). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FDMS *m/z*: 779 $[M+Na]^+$, 647 $[M+Na-Ara+H]^+$, 617 $[M+Na-Caf+H]^+$, 501 $[M+Na-(Ara-(1\rightarrow2)-Rha)+H]^+$. (Found: C, 51.22; H, 6.35. $C_{34}H_{44}O_{19}\cdot 5/2\ H_2O$ requires: C, 51.22, H, 6.16%).

Stachysoside A undecaacetate (**7a**). White amorphous powder, $[\alpha]_D^{25}$ −60.6° ($CHCl_3$; *c* 0.50). ^1H NMR ($CDCl_3$; 500 MHz): δ1.06 (3H, *d*, $J=6.2$ Hz, Rha H-6), 1.69, 1.92, 2.01, 2.04, 2.08, 2.09, 2.13 (each 3H, *s*, aliph OAc), 2.27, 2.29, 2.30, 2.31 (each 3H, *s*, arom OAc), 2.87 (2H, *m*, H-β), 3.54 (1H, *dd*, $J=13.0$ and 1.9 Hz, Ara H-5), 3.63 (1H, *m*, H-α), 3.67 (1H, *ddd*, $J=9.6$, 4.8 and 2.9 Hz, Glc H-5), 3.72 (1H, *dq*, $J=10.0$ and 6.2 Hz, Rha H-5), 3.91 (1H, *dd*, $J=3.2$ and 1.9 Hz, Rha H-2), 3.94 (1H, *dd*, $J=13.0$ and 3.7 Hz, Ara H-5), 3.99 (1H, *t*, $J=9.4$ Hz, Glc H-3), 4.12 (1H, *dt*, $J=12.3$ and 2.9 Hz, H-α), 4.16 (1H, *dd*, $J=12.3$ and 2.9 Hz, Glc H-6), 4.20 (1H, *dd*, $J=12.3$ and 4.8 Hz, Glc H-6), 4.34 (1H, *d*, $J=6.6$ Hz, Ara H-1), 4.39 (1H, *d*, $J=8.0$ Hz, Glc H-1), 4.82 (1H, *t*, $J=10.0$ Hz, Rha H-4), 4.92 (1H, *dd*, $J=10.0$ and 3.2 Hz, Rha H-3), 5.00 (1H, *d*, $J=1.9$ Hz, Rha H-1), 5.01 (1H, *dd*, $J=9.2$ and 3.5 Hz, Ara H-3), 5.05 (1H, *dd*, $J=9.4$ and 8.0 Hz, Glc H-2), 5.17 (1H, *dd*, $J=9.2$ and 6.7 Hz, Ara H-2), 5.20 (1H, *t*, $J=9.6$ Hz, Glc H-4), 5.22 (1H, *td*, $J=3.7$ and 1.9 Hz, Ara H-4), 6.35 (1H, *d*, $J=16.0$ Hz, Caf H-β), 7.02 (1H, *d*, $J=2.0$ Hz, H-2), 7.08 (2H, *m*, H-5 and 6), 7.22 (1H, *d*, $J=8.4$ Hz, Caf H-5), 7.36 (1H, *d*, $J=2.0$ Hz, Caf H-2), 7.39 (1H, *dd*, $J=8.4$ and 2.0 Hz, Caf H-6), 7.69 (1H, *d*, $J=16.0$ Hz, Caf H-γ). This assignment was confirmed by ^1H–^1H COSY. FABMS *m/z*: 1219 $[M+H]^+$, 1241 $[M+Na]^+$, 981 $[M+Na-Ara(OAc)_3]^+$, 489 $[Ara-(1\rightarrow2)-Rha(OAc)_5]^+$, 259 $[Ara(OAc)_3]^+$.

Stachysoside B (**8**). Off-white amorphous powder, $[\alpha]_D^{26}$ −49.3° (MeOH; *c* 1.05). IR ν_{max}^{KBr} cm^{-1}: 3396 (OH), 1702 (C=O), 1632 (C=C), 1602 and 1516 (arom. ring). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z*: 793 $[M+Na]^+$, 771 $[M+H]^+$, 493 $[M-(Ara-(1\rightarrow2)-Rha)+2H]^+$, 339 $[439-aglycone]^+$. (Found: C, 50.73; H, 6.27. $C_{35}H_{46}O_{19}\cdot 3\ H_2O$ requires: C, 50.97; H, 6.31%).

Stachysoside C (**9**). Off-white amorphous powder, $[\alpha]_D^{26}$ −42.0° (MeOH; *c* 0.52). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1704 (C=O), 1632 (C=C), 1594 and 1514 (arom. ring). ^1H and ^{13}C NMR (CD_3OD): see Tables 1 and 2. FABMS *m/z*: 807 $[M+Na]^+$, 506 $[M-(Ara-(1\rightarrow2)-Rha)+H]^+$, 339 $[506-aglycone]^+$. (Found: C, 50.87; H, 6.59. $C_{36}H_{48}O_{19}\cdot 7/2\ H_2O$ requires; C, 51.00; H, 6.54%).

Exhaustive acid hydrolysis of compounds **7–9**. A soln of the compound (3 mg) in 5 M HCl (1 ml) was heated at 90° for 2.5 hr. After cooling, the reaction mixt. was extracted with EtOAc, which was concd to dryness. The following compounds were detected in the EtOAc layer by HPLC and TLC: 3,4-dihydroxy-

phenethyl alcohol from **7** and **8**; 3-hydroxy-4-methoxyphenethyl alcohol from **9**; caffeic acid from **7**; ferulic acid from **8** and **9**. HPLC conditions: column, TSK gel ODS-80TM (4.6 mm i.d. × 25 cm); mobile phase, 28% MeCN–H_2O containing 1% HOAc; flow rate, 0.7 ml min^{-1}; R_t 5.72 min (3,4-dihydroxyphenethyl alcohol), R_t 8.77 min (caffeic acid), 9.37 min (3-hydroxy-4-methoxyphenethyl alcohol), R_t 15.87 min (ferulic acid). TLC, Kieselgel 60 F_{254}; $CHCl_3$–EtOH (9:1); R_f 0.22 (3,4-dihydroxyphenethyl alcohol), R_f 0.11 (caffeic acid), R_f 0.45 (3-hydroxy-4-methoxyphenethyl alcohol), R_f 0.30 (ferulic acid). Glucose, rhamnose and arabinose in the aq. layers of **7–9** were detected as their TMSi-ethers by GC-MS. GC-MS conditions: column, DB-1 (0.53 mm i.d. × 30 m); flow rate, He 22 ml min^{-1}; temp., 160°; R_t 9.31, 10.51 and 12.21 (TMSi-ethers of Ara); R_t 10.09 and 13.52 (TMSi-ethers of Rha); temp., 190°; R_t 9.45 and 14.01 (TMSi-ethers of Glc).

Partial hydrolysis of compound **7**. A soln of **7** (120 mg) in 1 M HCl (10 ml) was heated at 70° for 2 hr. After cooling, the reaction mixt. was directly subjected to MCI gel CHP20P chromatography by developing with increasing amounts of MeOH in H_2O (4:1→11:9) to give a fr. containing 3 compounds. Rechromatography on silica gel with $CHCl_3$–MeOH–H_2O (4:1:0.1) gave **2** (9 mg), **7b** (10 mg) and recovery of **7** (11 mg).

Desrhamnosylacteoside (**7b**). Off-white amorphous powder, $[\alpha]_D^{25}$ −23.4° (MeOH; *c* 0.32). ^{1}H NMR (CD_3OD; 200 MHz): δ2.80 (2H, *t*, *J* = 7.6 Hz, H-β), 3.3–4.2 (7H, *m*, H-α, Glc H-2, 3, 5 and 6), 4.36 (1H, *d*, *J* = 7.8 Hz, Glc H-1), 4.80–5.00 (1H, Glc H-4), 6.29 (1H, *d*, *J* = 15.9 Hz, Caf H-β), 6.57 (1H, *br d*, *J* = 8.1 Hz, H-6), 6.68 (1H, *d*, *J* = 8.1 Hz, H-5), 6.70 (1H, *br s*, H-2), 6.78 (1H, *d*, *J* = 8.3 Hz, Caf H-5), 6.96 (1H, *br d*, *J* = 8.3 Hz, Caf H-6), 7.05 (1H, *br s*, Caf H-2), 7.59 (1H, *d*, *J* = 15.9 Hz, Caf H-γ). ^{13}C NMR (CD_3OD; 50 MHz): δ36.6 (*t*, C-β), 62.5 (*t*, glc C-6), 72.2 (*t*, C-α), 72.6 (*d*, Glc C-4), 75.3 (*d*, Glc C-2), 75.9 (*d*, Glc C-3), 76.2 (*d*, Glc C-5), 104.4 (*d*, Glc C-1), 114.8 (*d*, Caf C-2), 115.3 (*d*, Caf C-β), 116.4 (*d*, Caf C-5), 116.6 (*d*, C-2), 117.2 (*d*, C-5), 121.3 (*d*, C-6), 123.1 (*d*, Caf C-6), 127.7 (*s*, Caf C-1), 131.6 (*s*, C-1), 144.7 (*s*, C-3), 146.1 (*s*, C-4), 146.8 (*s*, Caf C-4), 147.6 (*d*, Caf C-γ), 149.7 (*s*, Caf C-3), 168.7 (*s*, Caf C-α). FDMS *m/z*: 478 $[M]^+$. Compound **7b** was identified as desrhamnosylacteoside by comparing the physicochemical and spectral data with those described in the lit. [1, 15–17].

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* While this manuscription was in submission, we noticed papers reporting the isolation of compounds **7** and **8**, designated lavandulifolioside [18] and stachysoside C [19], respectively. To avoid possible confusion, we should change the names of compounds **7–9** to lavandulifolioside, stachysosides C and D, respectively.