Phenylpropanoid Esters of Rhamnose from *Buddleja asiatica*

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Four new phenylpropanoid esters of rhamnose, asiatisides A–D, along with the known compounds, buergeriside C_1 (**5**), *p*-methoxycinnamic acid, ferulic acid, and *O*-methylferulic acid were obtained from the aerial parts of *Buddleja asiatica* LOUR by chromatographic methods. The new compounds were elucidated as 3-*O*-acetyl-4-*O*-(*p*-methoxycinnamoyl)-α-L-rhamnopyranose (**1**), 3-*O*-acetyl-4-*O*-feruloyl-α-L-rhamnopyranose (**2**), 2-*O*-acetyl-4-*O*-(*O*-methylferuloyl)-α-L-rhamnopyranose (**3**), 2-*O*-acetyl-4-*O*-(*p*-methoxycinnamoyl)-α-L-rhamnopyranose (**4**) by spectral data (1D-, 2D-NMR, and MS), respectively.

Introduction. – The genus *Buddleja* belonging to the family Buddlejaceae consists of shrubs or half-shrubs, distributed in tropical and subtropical regions [1]. The flowers, leaves, and roots of various species of *Buddleja* are used in traditional medicine in several countries [2]. In particular, the leaves and flowers of *B. globosa* are used in Chile for washing wounds and treating ulcers [2]. '*Mi-meng-hua*', prepared from the flowers of *B. officinalis*, is a traditional Chinese medicine used for the treatment of conjunctival congestion and clustered nebulae [3], and *B. asiatica* is named '*Qi-li-xiang*' by local people in Guangxi province. Its roots, stems, and leaves are used as a popular traditional Chinese medicine for the treatment of fever, ache, diarrhea, and articular rheumatism [4]. Previous studies on *B. officinalis* and *B. globosa* led to the isolation of triterpenoid glycosides [5a][5b], flavonoid triglycosides [6], iridoid glycosides [7], sesquiterpenes [8], diterpenoids [9], and saponins [10]. Up to now, few chemical constituents [11a – c] have been reported from *B. asiatica*, including buddlin, flavonoids, and sterols. In the present study, we report the isolation and structure determination of four new phenylpropanoid esters of rhamnose named asiatisides A–D (*Fig. 1*), along with four known compounds from aerial parts of *B. asiatica* LOUR.

Results and Discussion. – Compound **1** was obtained as a white amorphous powder ($[\alpha]_D^{22} = +85.7$ ($c = 0.21$, acetone)). The molecular formula $C_{18}H_{22}O_8$ was determined by the HR-ESI-MS spectrum (*m/z* 389.1211 ($[M+Na]^+$; calc. 389.1212)) in combination with ^{1}H-, ^{13}C-NMR, and DEPT spectra, corresponding to eight degrees of unsaturation. The ^{1}H-, ^{13}C-NMR, and DEPT spectra displayed an α-L-rhamnosyl unit [12] on the basis of a H-atom signal at δ(H) 5.12 (*dd*, $J = 1.8$, 4.0, H−C(1)[1])), a secondary Me group signal at δ(H) 1.13 (*d*, $J = 6.3$, Me(6)) as well as C-atom signals for

[1]) Arbitrary numbering; for systematic names, see *Exper. Part.*

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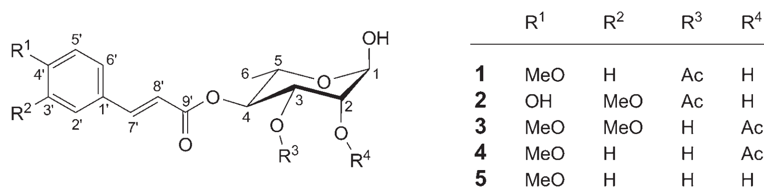

	R¹	R²	R³	R⁴
1	MeO	H	Ac	H
2	OH	MeO	Ac	H
3	MeO	MeO	H	Ac
4	MeO	H	H	Ac
5	MeO	H	H	H

Fig. 1. *Chemical structures of* **1**–**5**[1])

the anomeric C-atom (δ(C) 95.3 (*d*)), a Me group (δ(C) 18.1 (*q*)), and other four CH groups (δ(C) 72.7 (*d*), 72.0 (*d*), 70.6 (*d*), 66.9 (*d*)). The identification of the sugar unit was continued by hydrolysis with 10% HCl to afford L-rhamnose, which was confirmed by TLC comparison with an authentic sample and determination of its optical rotation value ($[\alpha]_D^{18} = +12.2$; MeOH) [13].

In addition to the above described signals, the ^{1}H-NMR spectrum of **1** exhibited signals of a *p*-substituted cinnamoyl moiety and a MeO group [14a][14b]: four H-atoms of an aromatic ring (*AABB* system, δ(H) 7.65 (*d*, $J = 8.7$, H–C(2′), H–C(6′)), and 6.98 (*d*, $J = 8.7$, H–C(3′), H–C(5′))), as well as two (*E*)-olefinic H-atoms (*AB* system, δ(H) 6.38, 7.64 (*d*, $J = 16.1$, 2×1 H)). The ^{13}C-NMR spectrum also exhibited signals of a cinnamoyl moiety, *i.e.*, six aromatic C-atoms (δ(C) 162.6, 130.9, 130.9, 127.9, 115.2, 115.2) and two olefinic C-atoms (δ(C) 115.8, 145.7). In the HMBC spectrum (*Fig. 2*), the MeO signal at δ(H) 3.84 (*s*) showed a cross-peak with the signal at δ(C) 162.6 (*s*, C(4′)), indicating a MeO substituent at C(4′). In the ^{1}H,^{1}H-COSY spectrum (*Fig. 2*), a signal at δ(H) 4.10–4.12 (*m*, 1 H) showed correlations with Me(6) (δ(H) 1.13), assigning the signal to H–C(5). Likewise, the signal at δ(H) 4.05–4.06 (*m*, 1 H) correlated with H–C(1) (δ(H) 5.12), was attributed to H–C(2). Two remaining overlapping signals at δ(H) 5.27–5.29 (*m*, 2 H) were assigned to H–C(3) and H–C(4). Further, these two H-atoms corresponded to δ(C) 72.7 (*d*) and 72.0 (*d*) in the HSQC spectrum. Considering that δ(C) 72.7 (*d*) showed a correlation with H–C(1) in the HMBC spectrum, this signal was attributed to C(3). The other signal (δ(C) 72.0, *d*) was assigned to C(4), which could be supported by a correlation of the signal of H–C(6) with δ(C) 72.0 (*d*). In the HMBC experiment (*Fig. 2*), two overlapping H-atom signals at δ(H) 5.27–5.29 (*m*, 2 H) were correlated with the CO group at δ(C) 166.7 (C(9′), *s*) and an Ac CO group at δ(C) 170.5 (*s*), suggesting that the cinnamoyl moiety and the AcO group might be connected to C(4) and C(3), respectively. The respective position of the acyl residues was deduced from the correlation of the Ac

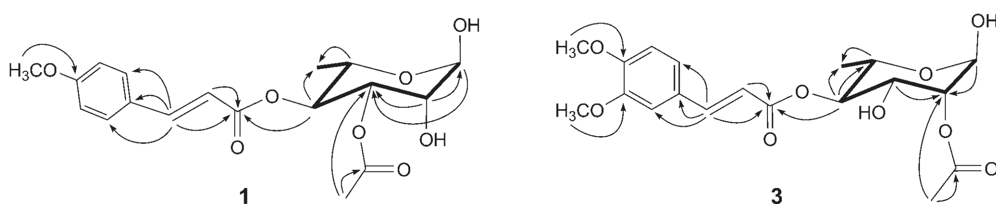

Fig. 2. *Key COSY* (—) *and HMBC* (→) *correlations for* **1** *and* **3**

H-atoms (δ(H) 1.93 (s, 3 H)) and C(3). Thus, compound **1** was identified as 3-*O*-acetyl-4-*O*-(*p*-methoxycinnamoyl)-α-L-rhamnopyranose[1]), and named asiatiside A. Full assignments of the signals of ^{1}H- and ^{13}C-NMR of **1** were determined by detailed analysis of ^{1}H,^{1}H-COSY, HSQC, and HMBC spectra (*Tables 1* and *2*).

Table 1. *^{1}H-NMR Data of* **1**–**4**[1]). At 500 MHz in (D$_6$)acetone; δ in ppm, J in Hz.

Position	**1**	**2**	**3**	**4**
1	5.12 (dd, J = 1.8, 4.0)	5.10 (dd, J = 1.7, 4.1)	5.07–5.09 (m)[a])	5.06–5.08 (m)[a])
2	4.05–4.06 (m)	4.04–4.05 (m)	5.07–5.09 (m)[a])	5.06–5.08 (m)[a])
3	5.27–5.29 (m)[a])	5.26–5.29 (m)[a])	4.14–4.16 (m)	4.13–4.17 (m)
4	5.27–5.29 (m)[a])	5.26–5.29 (m)[a])	4.99 (br. t, J = 9.8)	4.99 (br. t, J = 9.8)
5	4.10–4.12 (m)	4.09–4.11 (m)	4.03–4.06 (m)	4.03–4.07 (m)
6	1.13 (d, J = 6.3)	1.11 (d, J = 6.3)	1.11 (d, J = 6.5)	1.13 (d, J = 6.5)
2′	7.65 (d, J = 8.7)	7.18 (d, J = 2.0)	7.34 (d, J = 1.8)	7.63 (d, J = 8.7)
3′	6.98 (d, J = 8.7)	–	–	6.99 (d, J = 8.7)
5′	6.98 (d, J = 8.7)	6.98 (d, J = 8.3)	6.98 (d, J = 8.5)	6.99 (d, J = 8.7)
6′	7.65 (d, J = 8.7)	7.13 (dd, J = 2.0, 8.3)	7.21 (dd, J = 1.8, 8.5)	7.63 (d, J = 8.7)
7′	7.64 (d, J = 16.1)	7.58 (d, J = 15.9)	7.64 (d, J = 16.0)	7.67 (d, J = 16.0)
8′	6.38 (d, J = 16.1)	6.32 (d, J = 15.9)	6.45 (d, J = 16.0)	6.42 (d, J = 16.0)
MeO–C(3′)		3.88 (s)	3.84 (s)	
MeO–C(4′)	3.84 (s)		3.88 (s)	3.85 (s)
Ac	1.93 (s)	1.92 (s)	2.09 (s)	2.09 (s)

[a]) Overlapping signals.

Table 2. *^{13}C-NMR Data of* **1**–**4**[1]). At 125 MHz in (D$_6$)acetone, δ in ppm. Assignments are based on DEPT, HSQC, and HMBC spectra.

Position	**1**	**2**	**3**	**4**
1	95.3 (d)	95.4 (d)	92.6 (d)	92.6 (d)
2	70.6 (d)	70.6 (d)	74.4 (d)	74.4 (d)
3	72.7 (d)	72.7 (d)	67.9 (d)	67.9 (d)
4	72.0 (d)	72.0 (d)	75.3 (d)	75.3 (d)
5	66.9 (d)	66.9 (d)	66.7 (d)	66.7 (d)
6	18.1 (q)	18.1 (q)	18.0 (q)	18.0 (q)
1′	127.9 (s)	128.5 (s)	128.1 (s)	127.9 (s)
2′	130.9 (d)	112.3 (d)	110.9 (d)	130.8 (d)
3′	115.2 (d)	147.8 (s)	152.6 (s)	115.2 (d)
4′	162.6 (s)	150.8 (s)	150.6 (s)	163.5 (s)
5′	115.2 (d)	114.6 (d)	112.3 (d)	115.2 (d)
6′	130.9 (d)	122.5 (d)	123.7 (d)	130.8 (d)
7′	145.7 (d)	146.1 (d)	145.9 (d)	145.4 (d)
8′	115.8 (d)	115.9 (d)	116.3 (d)	116.2 (d)
9′	166.7 (s)	166.7 (s)	167.1 (s)	167.1 (s)
*Me*O–C(3′)		56.3 (q)	56.0 (q)	
*Me*O–C(4′)	55.8 (q)		56.0 (q)	55.7 (q)
Me*C*O	170.5 (s)	170.5 (s)	170.8 (s)	170.8 (s)
*Me*CO	20.9 (q)	20.9 (q)	20.9 (q)	20.9 (q)

The molecular formula of **2** was determined as $C_{18}H_{22}O_9$ by the HR-ESI mass spectrum (*m/z* 405.1161 ([*M* + Na]$^+$; calc. 405.1161)). The ^{1}H-, ^{13}C-NMR, and DEPT spectra of **2** displayed similarities to those of **1**, except for one more OH group in the cinnamoyl moiety of **2**. In the ^{1}H-NMR spectrum of **2**, *ABX* system signals of three H-atoms of an aromatic ring (δ(H) 7.18 (*d*, *J* = 2.0), 7.13 (*dd*, *J* = 2.0, 8.3), and 6.98 (*d*, *J* = 8.3)) gave a feruloyl moiety [14b][15], which was also confirmed by the HMBC spectrum. Thus, compound **2** was identified as 3-*O*-acetyl-4-*O*-feruloyl-α-L-rhamnopyranose[1]) and named asiatiside B.

Compound **3** was obtained as a white amorphous powder. The molecular formula of **3** was determined as $C_{19}H_{24}O_9$ by the HR-ESI mass spectrum (*m/z* 419.1319 ([*M* + Na]$^+$; calc. 419.1318)). Comparison of the ^{1}H-, ^{13}C-NMR, and DEPT spectra of **3** with those of **2** displayed similarities of **2** and **3**, except for the chemical shifts of the sugar unit and one more MeO group. As for compound **1**, the signals for Me(6) (δ(H) 1.11, *d*) and for three H-atoms (4.03 – 4.06 (*m*, H–C(5)), 4.99 (br. *t*, H–C(4)), 4.14 – 4.16 (*m*, H–C(3))) were assigned to the sugar moiety by careful analysis of the ^{1}H,^{1}H-COSY spectrum. Two remaining overlapping signals at δ(H) 5.07 – 5.09 (*m*, 2 H) were assigned to H–C(2) and H–C(1). In the HSQC spectrum, these two H-atoms were correlated to δ(C) 74.4 (*d*) and 92.6 (*d*), respectively. In the HMBC spectrum (*Fig. 2*), the Ac Me group at δ(H) 2.09 (*s*, 3 H) showed a cross-peak with C(2) (δ(C) 74.4, *d*), indicating that the Ac group was connected to C(2). Furthermore, H–C(4) (δ(H) 4.99) was correlated with the CO group at δ(C) 167.1 (*s*, C(9′)), suggesting that the feruloyl moiety was located at C(4). In addition, the MeO signals at δ(H) 3.88 (*s*) and 3.84 (*s*) were correlated with the C-atoms δ(C) 150.6 and 152.6, placing the two MeO groups at C(4′) and C(3′), respectively. Therefore, compound **3** was identified as 2-*O*-acetyl-4-*O*-(*O*-methylferuloyl)-α-L-rhamnopyranose[1]) and named asiatiside C.

Compound **4** has the molecular formula $C_{18}H_{22}O_8$ as evidenced by the HR-ESI mass spectrum (*m/z* 389.1203 ([*M* + Na]$^+$; calc. 389.1212). Compounds **4** and **1** have the same molecular formula. The ^{1}H-, ^{13}C-NMR, and DEPT spectra of **4** displayed similarities to those of **1**, except for the chemical shifts of the sugar unit. Comparison of the ^{1}H-, ^{13}C-NMR, and DEPT spectra of **4** with those of **3** showed that there are the similar chemical shifts for the sugar unit, indicating the same substituents in the sugar unit. Therefore, compound **4** was identified as 2-*O*-acetyl-4-*O*-(*p*-methoxycinnamoyl)-α-L-rhamnopyranose[1]) and named asiatiside D.

In the ^{1}H-NMR spectra of **1** – **4**, a second set of signals of weaker intensity was assigned to the corresponding β-L-rhamnose derivatives.

In previous studies, phenylpropanoid esters of rhamnose display quite interesting pharmacological properties including antioxidant, and antiviral activities, as well as inhibition of blood platelet aggregation and LTB_4 synthesis [16]. Many phenylpropanoid esters of rhamnose have been isolated from plants of the genus *Scrophularia* (Scrophulariaceae), such as ningposides A – D [14b][17] and buergerisides A_1, B_1, B_2, and C_1 [18]. In these known compounds, the phenylpropanoid moiety is usually located at C(2) or C(3) of the sugar unit. However, in our study, this substituent was attached to C(4).

Experimental Part

General. RP-18 Silica gel (SiO_2, 40–65 μm): *Merck* Company, Germany. *Sephadex LH-20* (40–70 μm): *Amersham Pharmacia Biotech AB*, Uppsala, Sweden. Silica gel (SiO_2, 200–300 mesh) for column chromatography (CC) and GF_{254} for TLC: *Qindao Marine Chemical Factory*, Qingdao, P. R. China. Compounds were detected under UV (254 nm and 365 nm), and after spraying with an anisaldehyde sulfuric acid soln., followed by heating. Optical rotation: *Horiba SEAP-300* spectropolarimeter. UV Spectra: *Shimadzu* double-beam *210A* spectrophotometer. IR Spectra: *Bruker Tensor 27* spectrometer with KBr pellets. 1D- and 2D-NMR Spectra: *Bruker DRX-500* MHz NMR spectrometer with TMS as internal standard. Pos. ESI-MS and HR-ESI-MS Spectra: *VG Autospec-3000* spectrometer.

Plant Material. The aerial parts of *B. asiatica* LOUR were collected in Guangxi Province, P. R. China, in July, 2006, and identified by Mrs. *Chun-Xia Zeng*, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (Zeng 0718) has been deposited with the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried aerial parts (12.5 kg) were crushed and extracted with 90% aq. MeOH (40 l × 4) at r.t. (48 h × 4). After evaporation of the solvent under reduced pressure, the viscous residue was redissolved in H_2O, and then partitioned with AcOEt (15 l × 4) to afford AcOEt and H_2O layers. The AcOEt fraction (218 g) was chromatographed on a SiO_2 column (2.0 kg, 200–300 mesh), using a $CHCl_3$/acetone gradient (from $CHCl_3$ to $CHCl_3$/acetone 1:1), to give 9 fractions (*I*–*IX*). *Fr. VII* (21.0 g) was submitted to SiO_2 CC (600 g) and eluted with petroleum ether (PE)/acetone 8:1, 6:1, 4:1, 2:1, 1:1, to yield five subfractions (*A*–*E*). *Subfrs. B* and *E* were purified by recrystallization from cold MeOH to give *O*-methylferulic acid (9.2 mg) and *p*-methoxycinnamic acid (30 mg), respectively. *Subfr. C* was purified by *RP-18* CC with MeOH/H_2O 80:20, 85:15, 90:10 to afford compounds **4** (208.5 mg) and **3** (86.6 mg). *Fr. VIII* (15.0 g) was submitted to SiO_2 CC (450 g) and eluted with PE/AcOEt 6:1, 4:1, 2:1, to yield three subfractions (*F*–*H*). *Subfr. G* was first applied to *RP-18* CC with MeOH/H_2O 60:40, 70:30, 75:25, 80:20, and then to *Sephadex LH-20* (MeOH) to give compounds **5** (834.2 mg), **2** (57.8 mg), and **1** (88.5 mg). *Subfr. H* was purified by recrystallization in cold MeOH to give ferulic acid (9.8 mg).

Asiatiside A (=*6-Deoxy-4-*O*-[(2*E*)-3-(4-methoxyphenyl)-1-oxoprop-2-en-1-yl]-α-*L*-mannopyranose 3-Acetate*; **1**). White amorphous powder. $[\alpha]_D^{22} = +85.7$ ($c = 0.21$, acetone). UV (MeOH): 311 (3.82), 298 (3.28), 222 (2.21), 208 (2.66). IR (KBr): 3463, 3385, 2972, 1738, 1692, 1629, 1610, 1512, 1040. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (pos.): 755 ($[2M + Na]^+$), 389 ($[M + Na]^+$). HR-ESI-MS: 389.1211 ($[M + Na]^+$, $C_{18}H_{22}NaO_8^+$; calc. 389.1212).

Asiatiside B (=*6-Deoxy-4-*O*-[(2*E*)-3-(4-hydroxy-3-methoxyphenyl)-1-oxoprop-2-en-1-yl]-α-*L*-mannopyranose 3-Acetate*; **2**). White amorphous powder. $[\alpha]_D^{22} = +56.1$ (c = 0.19, acetone). UV (MeOH): 327 (1.34), 298 (1.16), 244 (0.95), 205 (2.43). IR (KBr): 3422, 3376, 2941, 1737, 1692, 1629, 1610, 1512, 1041. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (pos.): 787 ($[2M + Na]^+$), 764 ($[2M]^+$), 405 ($[M + Na]^+$). HR-ESI-MS: 405.1161 ($[M + Na]^+$, $C_{18}H_{22}NaO_9^+$; calc. 405.1161).

Asiatiside C (=*6-Deoxy-4-*O*-[(2*E*)-3-(3,4-dimethoxyphenyl)-1-oxoprop-2-en-1-yl]-α-*L*-mannopyranose 2-Acetate*; **3**). White amorphous powder. $[\alpha]_D^{22} = +115.2$ ($c = 0.22$, acetone). UV (MeOH): 323 (1.39), 297 (1.09), 235 (0.95), 205 (2.28). IR (KBr): 3445, 3316, 2940, 1741, 1704, 1633, 1597, 1517, 1067. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (pos.): 815 ($[2M + Na]^+$), 419 ($[M + Na]^+$), 397 ($[M + H]^+$). HR-ESI-MS: 419.1319 ($[M + Na]^+$, $C_{19}H_{24}NaO_9^+$; calc. 419.1318).

Asiatiside D (=*6-Deoxy-4-*O*-[(2*E*)-3-(4-methoxyphenyl)-1-oxoprop-2-en-1-yl]-α-*L*-mannopyranose 2-Acetate*; **4**). White amorphous powder. $[\alpha]_D^{18} = +58.7$ ($c = 0.24$, DMSO). UV (MeOH): 309 (3.84), 298 (3.40), 222 (2.36), 208 (2.71). IR (KBr): 3463, 3385, 2962, 1741, 1704, 1629, 1597, 1517, 1067. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (pos.): 755 ($[2M + Na]^+$), 389 ($[M + Na]^+$), 367 ($[M + H]^+$). HR-ESI-MS: 389.1203 ($[M + Na]^+$, $C_{18}H_{22}NaO_8^+$; calc. 389.1212).

Known Compounds. The structures of the known compounds were identified as buergeriside C_1 (4-O-(*p*-methoxycinnamoyl)-α-L-rhamnopyranose; **5**) [18], *p*-methoxycinnamic acid [14a], ferulic acid [15][19], *O*-methylferulic acid [15] by ESI-MS, and ^{1}H- and ^{13}C-NMR spectral data.

Acid Hydrolysis of **1**–**4**. Compounds **1**–**4** (20 mg each) were refluxed with 10% HCl/MeOH (20 ml) on a H_2O bath at 60° for 5 h. After cooling, the mixture was evaporated to dryness and redissolved in

H_2O, then partitioned with AcOEt, to afford AcOEt and H_2O layers. The sugar was identified as rhamnose by TLC comparison with an authentic sample using $CHCl_3$/MeOH 6:4, $R_f = 0.62$. Purification of the aq. layer was performed by prep. TLC eluted four times with $CHCl_3$/MeOH/H_2O 70:30:1 to afford L-rhamnose ($R_f = 0.68$) with positive values of $[\alpha]_D$ (11.1, 11.8, 12.2, and 13.6 from **1**–**4**, resp.). The AcOEt soln. was monitored by HP-TLC SiO_2 GF_{254} plate using $CHCl_3$/acetone 5:1 and PE/acetone 2:1, and showed several decomposition products.

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