New Phenolic Glycosides from *Clematis mandshurica*

by **She-Po Shi**[a]), **Dan Jiang**[b]), **Cai-Xia Dong**[c]), and **Peng-Fei Tu***[a])

[a]) School of Pharmaceutical Sciences, Peking University Health Science Center, No. 38 Xueyuan Road, Beijing 100083, P. R. China (phone/fax: +86-10-82802750; e-mail: pengfeitu@bjmu.edu.cn)

[b]) School of Life Sciences, Northeast Normal University, No. 5268 Renmin Street, Changchun 130024, P. R. China

[c]) School of Pharmaceutical Sciences, Shanxi College of Traditional Chinese Medicine, Shiji Road, Xianyang 712046, P. R. China

Three new phenolic glycosides, clemomandshuricosides A–C (**1**–**3**, resp.) and two new D-ribono-γ-lactone derivatives, **4** and **5**, were isolated from the roots and rhizomes of *Clematis mandshurica* RUPR., together with six known compounds. Their structures were elucidated on the basis of chemical, physicochemical, and spectroscopic evidence.

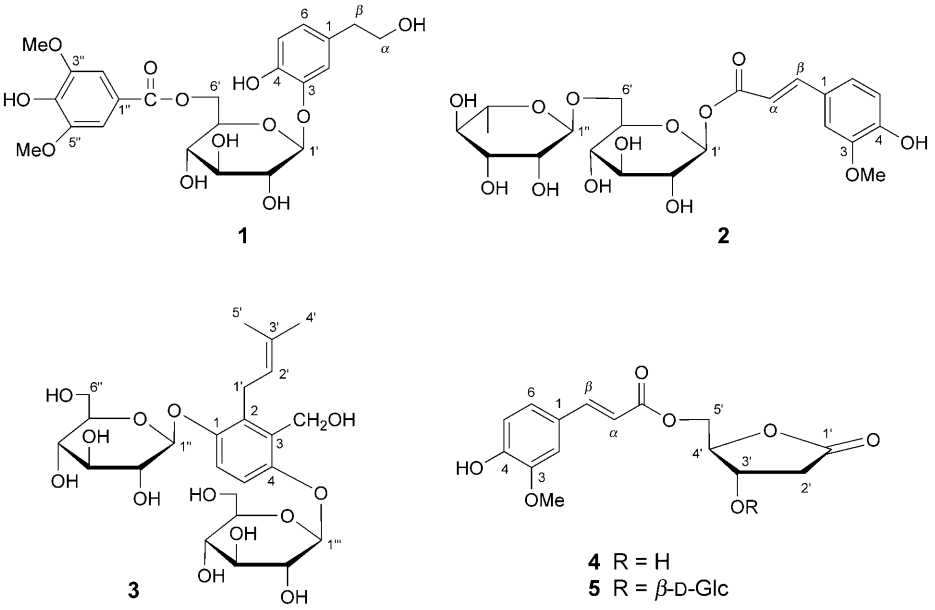
Introduction. – The genus *Clematis* (Ranunculaceae) is a large genus in Dicotyledoneae, with *ca*. 300 species being known worldwide. In Chinese Pharmacopoeia, the roots and rhizomes of *C. chinensis* OSBECK, *C. mandshurica* RUPR., and *C. hexapetala* PALL. are all named '*weilingxian*', which is commonly used as an anti-inflammatory, antitumor, and analgesic agent. Previous investigations were mainly directed towards *C. chinensis*, from the roots and rhizomes of which more than 40 triterpene saponins and lignans have been isolated [1–9]. In contrast, there are only few phytochemical investigations concerning *C. mandshurica*. From this latter species, only four triterpene saponins, clematosides A–C and clematoside A′, have been reported by *Chirva et al.* in 1967 [10].

Herein, we report the isolation and characterization of three new phenolic glycosides (**1**–**3**) and two new 2-deoxy-D-ribono-γ-lactone derivatives (**4** and **5**) from *C. mandshurica.* Also isolated were six known compounds: calophymembranside B [11], 4-(2-hydroxyethyl)benzene-1,2-diol, ferulic acid, vanillic acid, clemochinenoside B [12], and 2-deoxy-D-ribono-γ-lactone [13], which were identified by comparison of spectroscopic data and/or by co-eluting TLC using authentic samples.

Results and Discussion. – Compound **1** was obtained as a colorless, amorphous powder, with the molecular formula $C_{23}H_{28}O_{12}$, as deduced from the $[M+Na]^+$ peak at *m/z* 519.1468 by HR-FAB-MS. Acid hydrolysis afforded syringic acid (=4-hydroxy-3,5-dimethoxybenzoic acid), 4-(2-hydroxyethyl)benzene-1,2-diol, and D-glucose (D-Glc).

The ^{1}H- and ^{13}C-NMR spectra of **1** (*Table 1*) showed the signals of a syringoyl moiety (δ(H) 7.28 (*s*, 2 H), 3.82 (*s*, 6 H); δ(C) 119.8 (C(1″)), 108.5 (C(2″,6″)), 149.3 (C(3″,5″)), 132.1 (C(4″))), 168.3 (C=O), 56.8

© 2006 Verlag Helvetica Chimica Acta AG, Zürich



(2 MeO))[1]) and a Glc unit, the anomeric H-atom resonating at δ(H) 4.80 (*d*, J = 8.0 Hz, 1 H), and the anomeric C-atom at δ(C) 104.4. The large coupling constant of the anomeric H-atom (J = 8.0 Hz) suggested a β-configured Glc unit. In addition, the ^{1}H-NMR spectrum revealed a substituted (hydroxyethyl)-phenol, with resonances at δ(H) 6.85 (br. *s*, 1 H), 6.67 (br. *s*, 2 H), and 3.47–3.49 (overlapped, 2 H), and 2.35 (*t*, J = 7.5 Hz, 2 H) [14]. All the H- and C-atoms of **1** were unambiguously assigned by ^{1}H,^{1}H-COSY, HMQC, DEPT, HMBC, and NOESY experiments. The skeletal structure was established by the HMBC correlations between H–C(1′) (δ(H) 4.80 (*d*, J = 8.0 Hz)) and C(3) ((δ(C) 146.4), and between CH_2(6′) (δ(H) 4.73 (*dd*, J = 2.4, 12.0 Hz), 4.46 (*dd*, J = 6.9, 12.0 Hz)) and C=O (δ(C) 168.3). In the NOESY spectrum of **1**, cross-peaks between H–C(1′) and H–C(2), H–C(β) and H–C(2), and H–C(β) and H–C(6) were observed.

From the above data, the structure of **1** was elucidated as 2-hydroxy-5-(2-hydroxyethyl)phenyl 6-*O*-syringoyl-β-D-glucopyranoside, and the compound was named *clemomandshuricoside A*.

Compound **2** was obtained as a pale-yellow, amorphous powder. HR-FAB-MS showed the $[M+Na]^+$ peak at *m/z* 525.1591, in accord with the molecular formula $C_{22}H_{30}O_{13}$, as supported by the ^{1}H- and ^{13}C-NMR data (*Table 1*). Acid hydrolysis of **2** afforded ferulic acid, L-rhamnose (L-Rha), and D-Glc.

The ^{1}H-NMR spectrum of **2** exhibited the characteristic pattern of a feruloyl (=4-hydroxy-3-methoxycinnamoyl) moiety (δ(H) 6.96 (*d*, J = 8.1 Hz, 1 H), 7.05 (*dd*, J = 2.1, 8.1 Hz, 1 H), 7.09 (*d*, J = 2.1 Hz, 1 H)), 3.89 (*s*, 3 H), 6.38 (*d*, J = 15.9 Hz, 1 H), 7.71 (*d*, J = 15.9 Hz, 1 H)) and two sugar moieties, the anomeric H-atoms of which resonated at δ(H) 5.55 (*d*, J = 7.8 Hz, 1 H) and 4.71 (br. *s*, 1 H). In the ^{13}C-NMR spectrum, the anomeric C-atoms appeared at δ(C) 95.8 and 102.3, respectively. The coupling constant (J = 7.8 Hz) of the anomeric H-atom suggested a β-configured Glc unit. The α-configura-

[1]) Arbitrary atom numbering. For systematic names, see *Exper. Part.*

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2**. At 300 and 75 MH, resp., in CD_3OD; δ in ppm, J in Hz. Arbitrary atom numbering.

Position	**1**		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
1	–	132.1	–	128.7
2	6.85 (br. *s*)	119.8	7.09 (*d*, *J* = 2.1)	112.5
3	–	146.4	–	148.1
4	–	146.9	–	151.8
5	6.67 (br. *s*)	117.0	6.96 (*d*, *J* = 8.1)	114.8
6	6.67 (br. *s*)	125.5	7.05 (*dd*, *J* = 2.1, 8.1)	123.1
α	3.47–3.49 (*m*)	62.5	6.38 (*d*, *J* = 15.9)	148.1
β	2.35 (*t*, *J* = 7.5)	39.5	7.71 (*d*, *J* = 15.9)	115.4
1′	4.80 (*d*, *J* = 8.0)	104.4	5.55 (*d*, *J* = 7.8)	95.8
2′	3.45 (*dd*, *J* = 8.0, 9.0)	74.9	3.44–3.47 (*m*)	74.0
3′	3.64 (*dd*, *J* = 9.0, 9.0)	75.8	3.61–3.67 (*m*)	78.0
4′	3.41–3.44 (*m*)	71.9	3.38–3.43 (*m*)	71.2
5′	3.41–3.44 (*m*)	77.4	3.38–3.43 (*m*)	77.7
6′	4.73 (*dd*, *J* = 2.4, 12.0), 4.46 (*dd*, *J* = 6.9, 12.0)	64.2	3.97 (*dd*, *J* = 2.8, 12.0), 3.61–3.67 (*m*)	67.7
1″	–	119.8	4.71 (br. *s*)	102.3
2″	7.28 (*s*)	108.5	3.61–3.67 (*m*)	72.1
3″	–	149.3	3.61–3.67 (*m*)	72.3
4″	–	132.1	3.38–3.43 (*m*)	74.0
5″	–	149.3	3.82–3.84 (*m*)	69.8
6″	7.28 (*s*)	108.5	1.21 (*d*, *J* = 6.0)	18.0
MeO	3.82 (*s*)	56.8	3.89 (*s*)	56.4
C=O	–	168.3	–	167.4

tion of Rha was deduced from the NOE between H–C(1″) and H–C(4″). Analysis of the HMBC spectrum of **2** showed correlations between H–C(1′) (δ(H) 5.55 (*d*, *J* = 7.8 Hz)) and C=O (δ(C) 167.4), and between H–C(1″) (4.71 (br. *s*)) and C(6′) (δ(C) 67.7).

From the above data, the structure of compound **2** was determined as feruloyl 6-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside, and this new compound was named *clemomandshuricoside B.*

Compound **3** was obtained as a colorless, amorphous powder, with the molecular formula $C_{24}H_{36}O_{13}$, based on the $[M+Na]^+$ peak at *m/z* 555.2028 in the HR-FAB mass spectrum, and confirmed by ^{1}H- and ^{13}C-NMR (DEPT) experiments (*Table 2*). Acid hydrolysis of **3** afforded D-Glc.

The ^{1}H-NMR spectrum of **3** showed the presence of two aromatic H-atoms at δ(H) 7.04 (*d*, *J* = 9.0 Hz, 1 H) and 7.07 (*d*, *J* = 9.0 Hz, 1 H), an oxygenated CH_2 at δ(H) 4.67 (*s*, 2 H), a prenyl moiety (δ(H) 5.10 (br. *t*, *J* = 7.0 Hz, 1 H), 3.57 (*d*, *J* = 7.0 Hz, 2 H), 1.65 (*s*, 3 H), 1.80 (*s*, 3 H)), and *two* Glc units, with their anomeric H- and C-atoms resonating at δ(H) 4.75 (*d*, *J* = 7.2 Hz, 1 H) and 4.79 (*d*, *J* = 7.5 Hz, 1 H), and at δ(C) 104.6 and 103.7, respectively. The corresponding coupling constants (*J* = 7–8 Hz) suggested that both Glc units were β-configured. The skeletal structure of **3** was established by analysis of the HMBC spectrum (*Figure*). NOEs were observed between H–C(1″) (δ(H) 4.75 (*d*, *J* = 7.2 Hz))

Table 2. *^{1}H- and ^{13}C-NMR Data of* **3**. At 300 and 75 MHz, resp., in CD_3OD; δ in ppm, J in Hz. Arbitrary atom numbering.

Position	δ(H)	δ(C)	Position	δ(H)	δ(C)
1	–	152.8	1″	4.75 (*d*, *J* = 7.2)	104.6
2	–	131.7	2″	3.43–3.49 (*m*)	75.2[a])
3	–	133.2	3″	3.30–3.41 (*m*)	78.1[b])
3-CH_2O	4.67 (*s*)	153.6	4″	3.30–3.41 (*m*)	71.4[c])
4	–	116.7	5″	3.30–3.41 (*m*)	78.3[d])
5	7.04 (*d*, *J* = 9.0)	117.7	6″	3.86–3.90 (*m*), 3.67–3.72 (*m*)	62.6[e])
6	7.07 (*d*, *J* = 9.0)	26.2	1‴	4.79 (*d*, *J* = 7.5)	103.7
1′	3.57 (*d*, *J* = 7.0)	125.0	2‴	3.43–3.49 (*m*)	75.1[a])
2′	5.10 (br. *t*, *J* = 7.0)	131.5	3‴	3.30–3.41 (*m*)	78.0[b])
3′	–	25.9	4‴	3.30–3.41 (*m*)	71.4[c])
4′	1.65 (*s*)	18.2	5‴	3.30–3.41 (*m*)	78.2[d])
5′	1.80 (*s*)	56.7	6‴	3.86–3.90 (*m*), 3.67–3.72 (*m*)	62.6[e])

[a])–[e]) Assignments may be interchanged.

and H–C(6) (δ(H) 7.07 (*d*, *J* = 9.0 Hz)), and between H–C(1‴) (δ(H) 4.79 (*d*, *J* = 7.5 Hz)) and H–C(5) (δ(H) 7.04 (*d*, *J* = 9.0 Hz)), which suggested that the Glc units were attached at C(1) and C(4), respectively.

From the above data, the structure of compound **3** was elucidated as 4-[(β-D-glucopyranosyl)oxy]-2-(hydroxymethyl)-3-(3-methylbut-2-en-1-yl)phenyl β-D-glucopyranoside, and this new constituent was named *clemomandshuricoside C*.

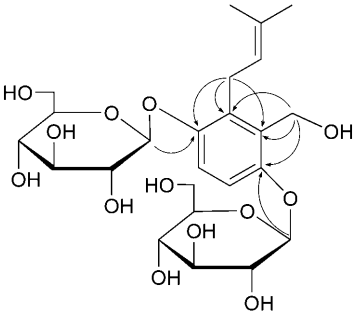


Figure. *Selected HMBC correlations for* **3**

Compound **4** was obtained as a colorless, amorphous powder. HR-FAB-MS showed the $[M+Na]^+$ peak at *m/z* 331.0795, in accord with the molecular formula $C_{15}H_{16}O_7$, as supported by the ^{1}H- and ^{13}C-NMR (DEPT) data (*Table 3*).

The ^{1}H- and ^{13}C-NMR spectra of **4** indicated the presence of a feruloyl moiety, similar as in **2**. In addition, signals due to a hydroxylated γ-lactone were observed [8]: δ(H) 2.49 (*dd*, *J* = 3.3, 18.0 Hz, H_a–C(2′)), 3.01 (*dd*, *J* = 6.9, 18.0 Hz, H_b–C(2′)), 4.45–4.47 (*m*, H–C(3′)), 4.57–4.60 (*m*, H–C(4′)), 4.21 (*dd*, *J* = 4.8, 12.3 Hz, H_a–C(5′)), 4.41 (*dd*, *J* = 3.6, 12.3 Hz, H_b–C(5′)); δ(C) 177.7 (C(1′)), 38.6 (C(2′)),

Table 3. *^{1}H- and ^{13}C-NMR Data of* **4** *and* **5**. At 300 and 75 MH, resp., in CD_3OD; δ in ppm, J in Hz. Arbitrary atom numbering.

Position	**4**		**5**	
	δ(H)	δ(C)	δ(H)	δ(C)
1	–	128.7	–	128.4
2	7.08 (*d*, *J*=2.1)	112.5	7.09 (*d*, *J*=2.1)	112.4
3	–	148.1	–	147.7
4	–	151.7	–	151.5
5	6.95 (*d*, *J*=8.1)	115.2	6.95 (*d*, *J*=8.1)	115.0
6	7.05 (*dd*, *J*=2.1, 8.1)	123.0	7.05 (*dd*, *J*=2.1, 8.1)	123.1
α	6.35 (*d*, *J*=15.9)	147.4	6.31 (*d*, *J*=16.0)	147.3
β	7.61 (*d*, *J*=15.9)	114.8	7.56 (*d*, *J*=16.0)	114.8
1′	–	177.7	–	177.7
2′	2.49 (*dd*, *J*=3.3, 18.0), 3.01 (*dd*, *J*=6.9, 18.0)	38.6	2.77 (*dd*, *J*=3.0, 18.5), 3.16 (*dd*, *J*=8.0, 18.5)	37.4
3′	4.45–4.47 (*m*)	69.6	4.56–4.58 (*m*)	77.2
4′	4.57–4.60 (*m*)	86.9	3.79–4.81 (*m*)	84.5
5′	4.21 (*dd*, *J*=4.8, 12.3), 4.41 (*dd*, *J*=3.6, 12.3)	64.4	4.32–4.38 (*m*)	64.6
1″	–	–	4.40 (*d*, *J*=8.0)	103.8
2″	–	–	3.43 (*dd*, *J*=8.0, 9.0)	74.7
3″	–	–	3.33–3.37 (*m*)	77.9
4″	–	–	3.33–3.37 (*m*)	71.2
5″	–	–	3.27–3.30 (*m*)	77.7
6″	–	–	3.82 (*dd*, *J*=3.0, 11.5) 3.59 (br. *d*, *J*=11.5)	62.5
MeO	3.88 (*s*)	56.4	3.81 (*s*)	56.3
C=O	–	168.2	–	168.1

69.6 (C(3′)), 86.9 (C(4′)), 64.4 (C(5′)). In the HMBC spectrum, the long-range correlations between CH_2(5′) (δ(H) 4.21 (*dd*, *J*=4.8, 12.3 Hz), 4.41 (*dd*, *J*=3.6, 12.3 Hz)) and C=O (δ(C) 168.2) suggested that the feruloyl moiety was at C(5′). In the NOESY spectrum, no NOE was observed between H–C(3′) and H–C(4′), which suggested a *trans* arrangement for H–C(3′) and H–C(4′).

The optical rotation of **4**, $[\alpha]_D^{20} = +9.8$ (c=0.5, MeOH) was comparable to that of 5-*O*-tetradecanoyl-2-deoxy-D-ribonolactone ($[\alpha]_D^{21} = +13.57$ ($CHCl_3$))[2]), supporting that **4** was also a D-ribono-γ-lactone [15]. Thus, from the above data, the structure of **4** was established as 5-*O*-feruloyl-2-deoxy-D-ribono-γ-lactone.

Compound **5**, obtained as a colorless, amorphous powder, had the molecular formula $C_{21}H_{26}O_{12}$, based on the $[M+Na]^+$ peak at *m/z* 493.1312, and confirmed by ^{1}H- and ^{13}C-NMR (DEPT) spectra (*Table 3*). When **5** was hydrolyzed with β-glucosidase, compound **4** was obtained, which, upon acid hydrolysis, gave ferulic acid and D-Glc.

The ^{1}H- and ^{13}C-NMR spectra of **5** showed the presence of a feruloyl group, a γ-lactone, and a Glc unit, the anomeric H- and C-atoms of which appeared at δ(H) 4.40 (*d*, *J*=8.0 Hz, 1 H) and δ(C) 103.8,

[2]) The value for 5-*O*-tetradecanoyl-2-deoxy-L-ribonolactone was reported as $[\alpha]_D^{21} = -15.0$ ($CHCl_3$) [15].

respectively. Based on the corresponding coupling constant ($J=8.0$ Hz), a β-Glc moiety was inferred. Comparison of the ^{13}C-NMR data of **5** with those of **4** showed a downfield shift of C(3′) (δ(C) 77.2) in **5**, which suggested that the Glc unit was linked at C(3′). This was corroborated by a HMBC cross-peak between H–C(1″) (δ(H) 4.40 (*d*, $J=8.0$ Hz)) and C(3′) (δ(C) 77.2).

From the above considerations, the structure of **5** was established as 5-*O*-feruloyl-3-*O*-(β-D-glucopyranosyl)-2-deoxy-D-ribono-γ-lactone.

We would like to thank the Ministry of Science and Technology of the People's Republic of China for financial support (2004AA2Z3730).

Experimental Part

General. Column chromatography (CC): silica gel *H* (200–300 mesh; *Qingdao Marine Chemical Industry*), *Sephadex LH-20* gel (*Pharmacia*), and *D101* porous polymer resin (*Tianjin Chemical Industry*). Prep. HPLC: *ODS* column (250×10 mm, 5 μm; *Alltech*), with *Waters 2996* photodiode-array detector (280 nm); flow rate, 2.5 ml/min. GC: *Agilent 6890N* gas chromatograph, with a *HP-5* capillary column (28 m×0.32 mm) and a FID detector operated at 260° (column temp. 180°), 1.0 ml/min N_2 as carrier gas. Melting points (m.p.): *X-4* micro-melting-point apparatus; uncorrected. UV Spectra: *TU-1901* spectrometer; λ_{max} (log ε) in nm. Optical rotations: *Perkin-Elmer 243B* digital polarimeter. NMR Spectra: *Inova 300* apparatus; at 300 (^{1}H) or 75 MHz (^{13}C), resp., in CD_3OD at r.t.; δ in ppm rel. to Me_4Si, *J* in Hz. HR-FAB-MS (pos.): *Autospec Ultima ETOF* spectrometer; in *m*/*z*.

Plant Material. The roots and rhizomes of *C. mandshurica* RUPR. were collected in August 2002 from Heilongjiang province, Northeast China. The plant was identified by *Peng-Fei Tu*. A voucher specimen (CM200208) was deposited at the Herbarium of Peking University, Modern Research Center for Traditional Chinese Medicine.

Extraction and Isolation. The dried roots and rhizomes (15 kg) of *C. mandshurica* were extracted with 95% EtOH (3×). After removal of the solvent under reduced pressure at 60°, the residue (1.7 kg) was suspended in H_2O, and defatted with petroleum ether. The aq. layer was further extracted with AcOEt and then BuOH. The BuOH extract (250 g) was subjected to CC (*D101*) eluting first with H_2O, then with 10, 30, and 50% aq. MeOH. The fraction eluted with 10% MeOH (25 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 6:1, then $CHCl_3$/MeOH/H_2O 7:3:0.1): fractions *Fr. 1–3*. *Fr. 1* was purified by CC (*Sephadex LH-20*; H_2O) and prep. HPLC (MeOH/H_2O 30:70) to furnish 4-(2-hydroxyethyl)benzene-1,2-diol (4 mg) and **4** (9 mg). *Fr. 2* was subjected to CC (*Sephadex LH-20*; H_2O): subfractions *Fr. 2.1* and *2.2*. *Fr. 2.1* crystallized from MeOH to afford ferulic acid (30 mg). *Fr. 2.2* was repeatedly purified by CC (*Sephadex LH-20*) to afford vanillic acid (6 mg). *Fr. 3* was subjected to CC (*Sephadex LH-20*; H_2O) and prep. HPLC (MeOH/H_2O 45:55) to yield compounds **1** (8.4 mg) and **2** (60 mg). The fraction eluted with 30% MeOH was further chromatographed (*Sephadex LH-20*; H_2O, MeOH): *Fr. 4–6*. *Fr. 4* was purified by prep. HPLC (MeOH/H_2O 45:55) to yield **3** (5.6 mg) and **5** (21.3 mg). *Fr. 5* was repeatedly subjected to CC (SiO_2; AcOEt/EtOH/H_2O 6:2:1) to furnish calophymembranside B (8 mg), together with subfraction *Fr. 5.1*. The latter was subjected to CC (*Sephadex LH-20*; H_2O) to afford clemochinenoside B (12 mg). *Fr. 6* was subjected to CC (SiO_2; $CHCl_3$/MeOH 5:1) to provide 2-deoxy-D-ribono-γ-lactone (62 mg).

Clemomandshuricoside A (=*2-Hydroxy-5-(2-hydroxyethyl)phenyl 6-O-(4-Hydroxy-3,5-dimethoxybenzoyl)-β-D-glucopyranoside*; **1**). Colorless, amorphous powder. M.p. 116–118°. UV (MeOH): 277 (3.22), 218 (4.33). $[\alpha]_D^{20}=-27.9$ ($c=2.1$, MeOH). ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-FAB-MS: 519.1468 ($[M+Na]^+$, $C_{23}H_{28}NaO_{12}^+$; calc. 519.1478).

Clemomandshuricoside B (=*(*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoyl 6-O-(α-L-Rhamnopyranosyl)-β-D-glucopyranoside*; **2**). Pale-yellow, amorphous powder. M.p. 122°. UV (MeOH): 329 (3.22), 299 (3.16), 244 (2.96). $[\alpha]_D^{20}=-23.9$ ($c=0.6$, MeOH). ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-FAB-MS: 525.1591 ($[M+Na]^+$, $C_{22}H_{30}NaO_{13}^+$; calc. 525.1584).

Clemomandshuricoside C (=*4-[(β-*D*-Glucopyranosyl)oxy]-2-(hydroxymethyl)-3-(3-methylbut-2-en-1-yl)phenyl β-*D*-Glucopyranoside*; **3**). Colorless, amorphous powder. M.p. 138–140°. UV (MeOH): 279 (2.96), 224 (3.88). $[\alpha]_D^{20} = -32.1$ ($c = 0.6$, MeOH). ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-FAB-MS: 555.2028 ($[M+Na]^+$, $C_{24}H_{36}NaO_{13}^+$; calc. 555.2054).

*5-*O*-Feruloyl-2-deoxy-*D*-ribono-γ-lactone* (=*[(2*R*,3*S*)-1,2,3,4-Tetrahydro-3-hydroxy-5-oxofuran-2-yl]methyl (*Z*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate*; **4**). Colorless, amorphous powder. UV (MeOH): 323 (3.20), 296 (3.18), 241 (3.02). M.p. 102°. $[\alpha]_D^{20} = +9.8$ ($c = 0.5$, MeOH). ^{1}H- and ^{13}C-NMR: see *Table 3*. HR-FAB-MS: 331.0795 ($[M+Na]^+$, $C_{15}H_{16}NaO_7^+$; calc. 331.0794).

*5-*O*-Feruloyl-3-*O*-(β-*D*-glucopyranosyl)-2-deoxy-*D*-ribono-γ-lactone* (=*[(2*R*,3*S*)-3-[(β-*D*-Glucopyranosyl)oxy]-1,2,3,4-tetrahydro-5-oxofuran-2-yl]methyl (*Z*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate*; **5**). Colorless, amorphous powder. M.p. 108°. UV (MeOH): 325 (3.24), 290 (3.18), 242 (3.06). $[\alpha]_D^{20} = +11.6$ ($c = 3.2$, MeOH). ^{1}H- and ^{13}C-NMR: see *Table 3*. HR-FAB-MS: 493.1312 ($[M+Na]^+$, $C_{21}H_{26}NaO_{12}^+$; calc. 493.1322).

Acid Hydrolyses of **1**–**3** *and* **5**. The appropriate compound (2 mg) was hydrolyzed with 2N aq. CF_3COOH (10 ml) at 110° for 8 h in a sealed tube. The mixture was diluted with H_2O (20 ml), and extracted with AcOEt (3×10 ml). The combined org. extract was evaporated under reduced pressure, and analyzed by TLC. The aq. layer was repeatedly evaporated with MeOH under vacuum. The resulting dry residue was dissolved in anh. pyridine (0.10 ml), and mixed with L-cysteine methyl ester hydrochloride in pyridine (0.10 ml). After warming at 60° for 1 h, hexamethyldisilazane (0.10 ml) and Me_3SiCl (0.04 ml) were added, and the temp. was maintained at 60° for another 30 min. Then, the mixture was filtered (0.45 μm), and analyzed by GC. The retention times t_R were 5.410 and 11.628 min for L-Rha and D-Glc, resp.

Enzymatic Hydrolysis of **5**. Acid hydrolysis of **5** (see above) afforded only ferulic acid and D-Glc, but not the aglycone **4**. Thus, compound **5** (10 mg) was incubated with β-glucosidase (25 mg) in phosphate buffer (4 ml; pH 5–6) for 48 h at 37°. The mixture was extracted with AcOEt (3×10 ml), the combined org. extract was evaporated under reduced pressure, and the resulting residue was subjected to CC (SiO_2; $CHCl_3$/MeOH 6:1) to afford **4** (3.6 mg).

REFERENCES

[1] H. Kizu, T. Tomimori, *Chem. Pharm. Bull.* **1979**, *27*, 2388.
[2] H. Kizu, T. Tomimori, *Chem. Pharm. Bull.* **1980**, *28*, 2827.
[3] H. Kizu, T. Tomimori, *Chem. Pharm. Bull.* **1980**, *28*, 3555.
[4] H. Kizu, T. Tomimori, *Chem. Pharm. Bull.* **1982**, *30*, 859.
[5] H. Kizu, T. Tomimori, *Chem. Pharm. Bull.* **1982**, *30*, 3340.
[6] B.-P. Shao, G.-W. Qin, R.-S. Xu, H.-M. Wu, K. Ma, *Phytochemistry* **1995**, *38*, 1473.
[7] B.-P. Shao, G.-W. Qin, R.-S. Xu, H.-M. Wu, K. Ma, *Phytochemistry* **1996**, *42*, 821.
[8] M. He, J. H. Zhang, C. Q. Hu, *Acta Pharm. Sin.* **2001**, *36*, 278.
[9] Y. Mimaki, A. Yokosuka, M. Hamanaka, C. Sakuma, T. Yamori, Y. Sashida, *J. Nat. Prod.* **2004**, *67*, 1511.
[10] Y. Y. Chirva, V. P. Konyikhov, P. L. Cheban, G. V. Lazurevskii, in 'Khim Biokhim Uglevodov Mater Vses Konf'; Eds. N. K. Kochetkov, Nauka, Moscow, 1967, Vol. 4, p. 98.
[11] J. Zou, D. Z. Jin, W.-L. Chen, J. Wang, Q.-F. Liu, X.-Z. Zhu, W.-M. Zhao, *J. Nat. Prod.* **2005**, *68*, 1514.
[12] C. Q. Song, R. S. Xu, *Chin. Chem. Lett.* **1993**, *4*, 505.
[13] J. Kitajima, T. Ishikawa, Y. Tanaka, Y. Ida, *Chem. Pharm. Bull.* **1999**, *47*, 988; M. C. Francisco, A. L. M. Nasser, L. M. X. Lopes, *Phytochemistry* **2003**, *62*, 1265.
[14] C. J. Li, D. H. Chen, P. G. Xiao, *Acta Pharm. Sin.* **1994**, *29*, 195.
[15] K. Teng, V. E. Marquez, G. W. A. Milne, J. J. Barchi, M. G. Kazanietz, N. E. Lewin, P. M. Blumberg, E. Abushanab, *J. Am. Chem. Soc.* **1992**, *114*, 1059.

Received February 15, 2006