Glycosidic Constituents of *Celastrus orbiculatus*

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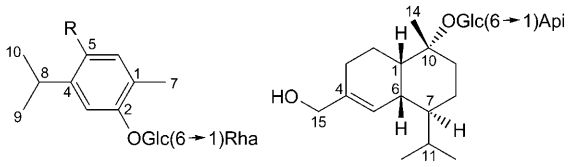
Three new, **1**–**3**, and seven known phenolic and terpenic glycosides were isolated from the BuOH-soluble fraction of 95% EtOH extract of the roots and rhizomes of *Celastrus orbiculatus*. The structures of the new compounds were elucidated as carvacrol 2-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside (**1**), 5-methoxycarvacrol 2-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside (**2**), and 15-hydroxytorreyol 10-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**3**) on the basis of spectroscopic analysis and chemical methods.

Introduction. – *Celastrus orbiculatus* THUNB. (Celastraceae) is a traditional medicinal plant which has been widely used for the treatment of rheumatic arthritis, systemic lupus erythematosus, and tumors in China [1]. Previous studies of this plant led to the isolation of sesquiterpenoids, mostly of *β*-dihydroagarofuran type [1–4], diterpenoids [4], triterpenoids [4], flavonoids [5], and alkaloids [6]. Our investigation on the H_2O-soluble components of the title plant resulted in the isolation of ten glycosides, including two new monoterpenoid diglycosides, *i.e.*, carvacrol 2-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside (**1**) and 5-methoxycarvacrol 2-*O*-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside (**2**), and one new sesquiterpenoid diglycoside, *i.e.*, 15-hydroxytorreyol 10-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**3**), along with seven known phenolic and terpenic glycosides, *i.e.*, 2,4,6-trimethoxyphenol 1-*O*-*β*-D-glucopyranoside [7], glucosyringic acid [8], 1-(*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyloxy)-3,4,5-trimethoxybenzene [9], 3,4-dimethoxyphenyl-6-*O*-(*α*-L-rhamnopyranosyl)-*β*-D-glucopyranoside [10], (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole-*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside [11], (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside [12], and pumilaside A [13]. The latter six known compounds were obtained from the genus *Celastrus* for the first time. Here, we report the isolation and structure elucidation of the three new compounds, **1**–**3**.

Results and Discussion. – The dried and powdered roots and rhizomes of *C. orbiculatus* were extracted with 95% EtOH. The concentrated extract was suspended in H_2O and partitioned successively with petroleum ether, AcOEt, and BuOH. After



purification by repeated chromatography, the BuOH-soluble fraction afforded three new diglycosides, **1**–**3**, and seven known glycosides.

Compounds **1** and **2** were obtained as white amorphous powders. The molecular formula $C_{22}H_{34}O_{10}$ for **1** and $C_{23}H_{36}O_{11}$ for **2** were established from the *quasi*-molecular-ion peaks $[M+Na]^+$ at *m*/*z* 481.2048 and 511.2157, respectively, in the HR-ESI-MS. Acid hydrolysis and GC analysis of both **1** and **2** gave L-rhamnose and D-glucose as sugar moiety. The analysis of 1D- and 2D-NMR allowed us to elucidate the structures of **1** and **2** to be carvacrol 2-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside and 5-methoxycarvacrol 2-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside, respectively.

The ^{1}H- and ^{13}C-NMR spectra of **1** showed signals for a β-glucopyranosyl (δ(H) 4.80 (*d*, *J* = 7.3, 1 H); δ(C) 103.5 (*d*), 78.4 (*d*), 77.0 (*d*), 75.3 (*d*), 71.7 (*d*), and 68.1 (*t*)), an α-rhamnopyranosyl (δ(H) 4.69 (*d*, *J* = 1.5, 1 H); 102.3 (*d*), 74.4 (*d*), 72.6 (*d*), 72.3 (*d*), 70.0 (*d*), and 18.2 (*q*)), and a C_{10} aromatic aglycone which contained a 1,2,4-trisubstituted aromatic ring (δ(H) 7.03 (*d*, *J* = 7.7, 1 H), 6.97 (*d*, *J* = 1.2, 1 H), and 6.80 (*dd*, *J* = 7.7, 1.2, 1 H)), an ^{i}Pr group (δ(H) 2.84 (*sept.*, *J* = 6.9, 1 H) and 1.23 (*d*, *J* = 6.9, 6 H)), and a Me group attached to the aromatic ring (δ(H) 2.23 (*s*, 3 H)). The above evidences suggested a phenolic monoterpenoid diglycoside.

HMBC Experiments of **1** (*Fig. 1*) exhibited clear cross-peaks H–C(7)/C(1), C(2), and C(6), as well as H–C(8)/C(3), C(4), and C(5), demonstrating that the ^{i}Pr and the Me groups were in *para*-position of the aromatic ring, and an O-atom connected with the disaccharides was in the *ortho*-position to the Me group, *i.e*, carvacrol as the aglycone of **1** [14]. Furthermore, HMBCs H–C(1′)/C(2) and H–C(1″)/C(6′) revealed α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl as the sugar sequence connected with the O-atom at C(2). Therefore, the structure of **1** was elucidated to be carvacrol 2-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside.

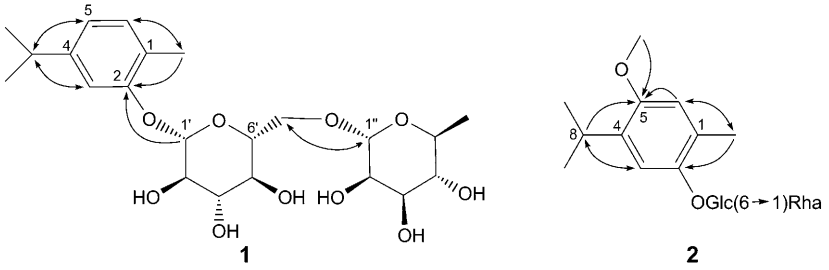


Fig. 1. *Significant HMBCs of* **1** *and* **2**

The ^{1}H- and ^{13}C-NMR spectra of **2** were very similar to those of **1**, except for a 1,2,4,5-tetrasubstituted benzene ring (δ(H) 6.99 and 6.69 (2*s*)) instead of the 1,2,4-trisubstituted one of **1**, and one additional MeO group (δ(H) 3.77 (*s*, 3 H); δ(C) 56.6 (*q*)), which suggested **2** to be a methoxylated derivative of **1**. The MeO group was located at C(5) by the HMBCs (*Fig. 1*) between C(5) and MeO, H–C(8), and H–C(6). Thus, **2** was proved to be 5-methoxycarvacrol 2-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside.

Compound **3** had the molecular formula $C_{26}H_{44}O_{11}$ based on the HR-ESI-MS data (*m*/*z* 555.2790 ([*M* + Na]$^+$; calc. 555.2781)). The 1D- and 2D-NMR studies and chemical methods revealed **3** to be 15-hydroxytorreyol 10-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside.

Two anomeric H-atom signals (δ(H) 4.98 (*d*, *J* = 2.2), 4.49 (*d*, *J* = 7.8)) in the ^{1}H-NMR spectrum (*Table*) together with acidic hydrolysis and GC analysis indicated a β-D-apiofuranosyl and a β-D-glucopyranosyl unit as the sugar residues. The ^{13}C-NMR spectrum showed signals for 15 C-atoms (3 Me, 5 CH_2, and 5 CH groups, one quaternary sp^2-C- and one O-bearing quaternary C-atom) for the aglycone, indicative of a dicyclic sesquiterpenoid. The ^{1}H-NMR spectrum of **3** revealed the presence of a tertiary Me group (δ(H) 1.35), two secondary Me groups (δ(H) 0.85 (*d*, *J* = 7.0), 0.90 (*d*, *J* = 7.0)), one olefinic H-atom (δ(H) 5.82 (*d*, *J* = 5.3)), and one HO–CH_2 group (δ(H) 3.91 (*s*, 2 H)). The above NMR data were similar to those of 15-hydroxy-T-muurolol, a sesquiterpenoid isolated from the marine *Streptomyces* sp. M491 [15]. On comparing the ^{13}C-NMR data of **3** with those of 15-hydroxy-T-muurolol, the most important differences were the downfield shift of C(10), C(8), and C(6), and upfield shift of C(14) ($\Delta\delta$ = +8.5, +3.2, +3.7, and −4.5, resp., going from 15-hydroxy-T-muurolol to **3**, data obtained in $CDCl_3$ (for 15-hydroxy-T-muurolol) or CD_3OD (for **3**)), which suggested the aglycone unit of **3** to be a stereoisomer of 15-hydroxy-T-muurolol at C(10), *i.e.*, a torreyol-type sesquiterpenoid [16]. The ^{1}H,^{1}H-COSY and HMBC correlations (*Fig. 2*) established that the aglycone of **3** had the same planar structure as 15-hydroxy-T-muurolol. Furthermore, the glycone moiety was elucidated to be α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyl linked with the O-atom at C(10) by HMBC correlations (*Fig. 2*) H–C(1′)/C(10) and H–C(1″)/C(6′).

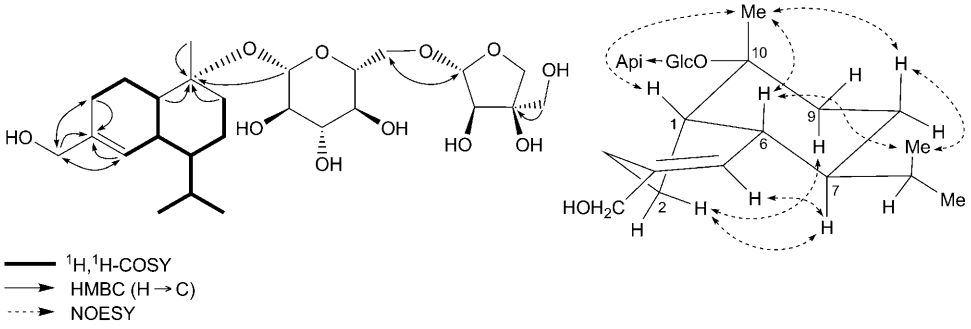


Fig. 2. *Selected 2D-NMR correlations of* **3**

Table. *^{1}H- and ^{13}C-NMR Data of* **3** (in CD_3OD)

	δ(H)	δ(C)
H–C(1)	1.70–1.79 (*m*)	46.2 (*d*)
CH_2(2)	1.50–1.55 (*m*, H_α), 2.29 (*dd*, *J* = 11.6, 5.2, H_β)	19.2 (*t*)
CH_2(3)	2.08 (*d*, *J* = 5.2, H_α), 1.97–2.01 (*m*, H_β)	28.1 (*t*)
C(4)	–	139.5 (*s*)
H–C(5)	5.82 (*d*, *J* = 5.3)	126.9 (*d*)
H–C(6)	2.13 (*dd*, *J* = 12.1, 5.3)	37.9 (*d*)
H–C(7)	1.34–1.44 (*m*)	45.7 (*d*)
CH_2(8)	1.48–1.56 (*m*, H_α), 1.15 (*qd*, *J* = 13.5, 3.8, H_β)	22.5 (*t*)
CH_2(9)	1.78 (*td*, *J* = 13.5, 3.8, H_α), 1.58–1.64 (*m*, H_β)	34.1 (*t*)
C(10)	–	80.8 (*s*)
H–C(11)	1.97–2.01 (*m*)	28.0 (*d*)
Me(12)	0.85 (*d*, *J* = 7.0)	15.9 (*q*)
Me(13)	0.90 (*d*, *J* = 7.0)	22.3 (*q*)
Me(14)	1.35 (*s*)	24.8 (*q*)
CH_2(15)	3.91 (*s*)	67.7 (*t*)
H–C(1′)	4.49 (*d*, *J* = 7.8)	98.4 (*d*)
H–C(2′)	3.16 (*dd*, *J* = 9.2, 7.8)	75.7 (*d*)
H–C(3′)	3.28–3.37 (*m*)	78.6 (*d*)
H–C(4′)	3.21–3.26 (*m*)	72.3 (*d*)
H–C(5′)	3.32–3.35 (*m*)	76.7 (*d*)
CH_2(6′)	3.91–3.96 (*m*), 3.53–3.55 (*m*)	69.0 (*d*)
H–C(1″)	4.98 (*d*, *J* = 2.2)	111.2 (*d*)
H–C(2″)	3.86 (*d*, *J* = 2.2)	78.3 (*d*)
C(3″)	–	80.8 (*s*)
CH_2(4″)	3.95 (*d*, *J* = 9.6), 3.75 (*d*, *J* = 9.6)	75.3 (*t*)
CH_2(5″)	3.57 (*s*)	66.0 (*t*)

The relative configuration of **3** was established by NOESY experiments. As shown in *Fig. 2*, NOE cross-peaks Me–C(10)/H–C(1), H–C(6), and H–C(8), H_α–C(2)/H_α–C(9) and H–C(7) were observed, indicating a chair-form *B*-ring with β-oriented and axial Me–C(10), H–C(6), and H–C(8), and an envelope-form *A*-ring with the CH_2(2) as the down-folded terminal.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Haiyang, Co., Ltd.*, P. R. China), *Sephadex LH-20* (*Pharmacia Biotech AB*, S-Uppsala), *MCI gel CHP-20P* and *ODS-A gel* (*Mitsubishi Chemical Industries Co., Ltd.*, Japan). TLC: silica gel *HSGF$_{254}$* (*Yantai Jiangyou Guijiao Kaifa Co., Ltd.*, P. R. China). Semiprep. HPLC: *Waters* HPLC system, *Waters-515-HPLC* pump, *Waters-2487* detector, column: *Kromasil 100-5-C18*, 5 μ, i.d. 10 × 250 mm. Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Shimadzu UV-2550* spectrophotometer. IR Spectra: *Nicolet-Magna-750-FTIR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AV-400* instrument at 400 (^{1}H) and 100 MHz (^{13}C); in CD_3OD soln.; δ in ppm rel. to Me_4Si; *J* in Hz. ESI-MS and HR-ESI-MS: *Bruker Esquire 3000 plus* and *Finnigan LC QDECA* mass spectrometers, resp.; in *m*/*z* (rel. int.).

Plant Material. The roots and rhizomes of *C. orbiculatus* were collected in Hengyang County, Hunan Province, P. R. China, in July 2008. The plant was identified by Prof. *Tong Wu* of Shanghai Institute of Pharmaceutical Industry. A voucher specimen (No 08-55) was deposited with the Herbarium of Shanghai Institute of Materia Medica.

Extraction and Isolation. The dried roots and rhizomes of *C. orbiculatus* (6 kg) were extracted three times with 20 l of 95% EtOH at 60°. The concentrated extract was suspended in H_2O (total 2.5 l) and partitioned with petroleum ether (PE), $CHCl_3$, AcOEt, and BuOH, resp., each 3×2.5 l. The BuOH fraction (47 g) was subjected to CC (SiO_2, 2 kg, i.d. 10×80 cm; $CHCl_3$, $CHCl_3$/MeOH 20:1, 10:1, 6:1, 3:1 (*v*/*v*), finally MeOH): *Frs. 1–6*. *Fr. 3* (5.5 g) gave glucosyringic acid (8 mg) and 2,4,6-trimethoxyphenol 1-*O*-*β*-D-glucopyranoside (8 mg) after purification by two CC (1. SiO_2; $CHCl_3$/MeOH 10:1; 2. *ODS-A gel*; MeOH/H_2O 15%). *Fr. 4* (16 g) was successively separated by two CC (1. *MCI gel CHP-20P*; H_2O, then 30, 50, 70, 95% (*v*/*v*) MeOH; 2. *ODS-A gel*; MeOH/H_2O 20%): *Frs. 4.2.1–4.2.6*. *Fr. 4.2.2* (1.28 g) was purified by three CC (1. *Sephadex LH-20*; MeOH; 2. SiO_2; $CHCl_3$/MeOH/H_2O: 8:1:0.1; 3. *ODS-A gel*; MeOH/H_2O 12–30%) to yield 1-(*α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranosyloxy)-3,4,5-trimethoxybenzene (40 mg), and 3,4-dimethoxyphenyl-6-*O*-(*α*-L-rhamnopyranosyl)-*β*-D-glucopyranoside (6 mg). *Fr. 4.2.3* (189 mg) afforded (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole *α*-L-rhamnopyranosyl-(1→6)-*β*-D-glucopyranoside (9 mg) and (1*S*,2*S*,4*R*)-2-hydroxy-1,8-cineole *β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (54 mg) by repeated CC (1. SiO_2; 30 g, $CHCl_3$/MeOH/H_2O, 6:1:0.1; 2. *ODS-A gel*; MeOH/H_2O 23%). *Fr. 4.2.4* (684 mg) furnished pumilaside A (25 mg) on purification by CC (1. *Sephadex LH-20*; MeOH; 2. *ODS-A gel*; MeOH/H_2O 35%). *Fr. 4.2.6* (192 mg) was subjected to CC (1. SiO_2, 30 g; $CHCl_3$/MeOH/H_2O 4:1:0.1; 2. *Sephadex LH-20*; MeOH): *Frs. 4.2.6.1–4.2.6.3*. Compounds **1** (6 mg) and **2** (11 mg) were obtained from *Fr. 4.2.6.2* (92 mg) by CC (*ODS-A gel*; MeOH/H_2O 50%) and then HPLC (*Waters-515-HPLC* pump, *Waters-2487* detector, 201 nm, column: *Kromasil100-5-C18*, 5 μ, i.d. 10×250 mm, MeOH/H_2O 55%). *Fr. 4.2.6.3* (56 mg) afforded **3** (13 mg) after repeated CC (*ODS-A gel*; MeOH/H_2O 50%; 2. *Sephadex LH-20*; MeOH).

Determination of Sugar Components. The acid hydrolysis and detection of sugars were conducted according to the method described in [17]. Briefly, compounds **1**–**3** (1 mg each) were refluxed in 10% HCl/dioxane 1:1 (2 ml) for 2 h, and the soln. was evaporated under N_2. The residue was dissolved in anh. pyridine (100 μl), 0.1M L-cysteine methyl ester hydrochloride (200 μl) was added, and the mixture was warmed at 60° for 1 h. The trimethylsilylation reagent HMDS–TMCS (hexamethyldisilazane/Me_3SiCl/pyridine 2:1:10; *Acros Organics*, B-Geel) was added, and warming at 60° was continued for another 30 min. The thiazolidine derivatives were subjected to GC analysis to identify the sugars. Conditions for GC were: cap. column, *DB5-MS* (30 m × 0.25 mm × 0.25 μm); oven temp. program, 180–300° at 6°/min; injection temp. 350°; carrier gas, He at 1 ml/min. D-Glucose (t_R 12.24 min) was detected from **1**–**3**, L-rhamnose (t_R 10.21 min) was detected from **1** and **2**, D-apiose (t_R 9.30 min) was detected from **3**. (Identical to authentic materials.)

*Carvacrol 2-*O*-α-*L*-Rhamnopyranosyl-(1→6)-β-*D*-glucopyranoside* (=*2-Methyl-5-(1-methylethyl)-phenyl 6-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranoside*; **1**). White amorphous powder. $[\alpha]_D^{25} = -64$ ($c = 0.100$, MeOH). UV (MeOH): 215 (3.99), 276 (2.98). IR: 3419, 2960, 2927, 1637, 1508, 1384, 1249, 1096. ^{1}H-NMR (CD_3OD, 400 MHz): 7.03 (*d*, *J* = 7.7, H–C(6)); 6.97 (*d*, *J* = 1.2, H–C(3)); 6.80 (*dd*, *J* = 7.7, 1.2, H–C(5)); 4.80 (*d*, *J* = 7.3, H–C(1′)); 4.69 (*d*, *J* = 1.5, H–C(1″)); 4.03 (*dd*, *J* = 10.5, 0.8, H_a–C(6′)); 3.84 (*dd*, *J* = 3.4, 1.5, H–C(2″)); 3.68 (*dd*, *J* = 9.5, 3.4, H–C(3″)); 3.64–3.43 (*m*, H–C(5″), H_b–C(6′), H–C(5′), H–C(2′), H–C(3′)); 3.41 (*dd*, *J* = 10.2, 6.3, H–C(4′)); 3.36 (*d*, *J* = 9.5, H–C(4″)); 2.84 (*sept.*, *J* = 6.9, H–C(8)); 2.23 (*s*, Me–C(1)); 1.23 (*d*, *J* = 6.9, 2 Me–C(8)); 1.19 (*d*, *J* = 6.2, Me–C(5″)). ^{13}C-NMR (CD_3OD, 100 MHz): 157.5 (*s*, C(2)); 149.4 (*s*, C(4)); 131.7 (*d*, C(6)); 126.6 (*s*, C(1)); 121.5 (*d*, C(5)); 115.2 (*d*, C(3)); 103.5 (*d*, C(1′)); 102.3 (*d*, C(1″)); 78.4 (*d*, C(3′)); 77.0 (*d*, C(5′)); 75.3 (*d*, C(2′)); 74.4 (*d*, C(4″)); 72.6 (*d*, C(3″)); 72.3 (*d*, C(2″)); 71.7 (*d*, C(4′)); 70.0 (*d*, C(5″)); 68.1 (*t*, C(6′)); 35.5 (*d*, C(8)); 24.9 (*q*, Me(9), Me(10)); 18.2 (*q*, C(6″)); 16.4 (*q*, Me(7)). ESI-MS (pos.): 481.3 ($[M + Na]^+$). ESI-MS (neg.): 503.7 ($[M + COOH]^-$). HR-ESI-MS: 481.2048 ($[M + Na]^+$, $C_{22}H_{34}NaO_{10}^+$; calc. 481.2050).

*5-Methoxycarvacrol 2-*O*-α-*L*-Rhamnopyranosyl-(1→6)-β-*D*-glucopyranoside* (=*4-Methoxy-2-methyl-5-(1-methylethyl)phenyl 6-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranoside*; **2**). White amorphous powder. $[\alpha]_D^{25} = -69$ ($c = 0.140$, MeOH). UV (MeOH): 219 (3.97), 284 (3.48). IR: 3388, 2929, 2871, 1637, 1504, 1384, 1201, 1058. ^{1}H-NMR (CD_3OD, 400 MHz): 6.99 (*s*, H–C(3)); 6.69 (*s*, H–C(6)); 4.69 (br. *s*, H–C(1″)); 4.65 (*d*, *J* = 6.8, H–C(1′)); 4.0 (br. *d*, *J* = 10.7, H_a–C(6′)); 3.84 (br. *s*, H–C(2″)); 3.77 (*s*, MeO–C(5)); 3.66 (*dd*, *J* = 9.4, 3.3, H–C(3″)); 3.63–3.35 (*m*, H–C(5″), H_b–C(6″), H–C(5′), H–C(2′), H–C(3′), H–C(4′)); 3.36 (*d*, *J* = 9.5, H–C(4″)); 3.23 (*sept.*, *J* = 7.0, H–C(8)); 2.26 (*s*, Me(7));

1.20 (*d*, *J* = 6.6, Me(6″)); 1.18 (*d*, *J* = 7.0, Me(9)); 1.17 (*d*, *J* = 7.0, Me(10)). ^{13}C-NMR (CD_3OD, 400 MHz): 153.9 (*s*, C(5)); 151.6 (*s*, C(2)); 136.5 (*s*, C(4)); 127.8 (*s*, C(1)); 116.7 (*d*, C(3)); 114.5 (*d*, C(6)); 105.0 (*d*, C(1′)); 102.4 (*d*, C(1″)); 78.4 (*d*, C(3′)); 77.0 (*d*, C(5′)); 75.3 (*d*, C(2′)); 74.4 (*d*, C(4″)); 72.6 (*d*, C(3″)); 72.3 (*d*, C(2″)); 71.7 (*d*, C(4′)); 70.0 (*d*, C(5″)); 68.2 (*t*, C(6′)); 56.6 (*q*, MeO), 28.2 (*d*, C(8)); 23.6 (*q*, Me(10)); 23.5 (*q*, Me(9)); 18.2 (*q*, C(6″)); 16.7 (*q*, Me(7)). ESI-MS (pos.): 511.3 ($[M + Na]^+$). ESI-MS (neg.): 533.6 ($[M + COOH]^-$). HR-ESI-MS: 511.2157 ($[M + Na]^+$, $C_{23}H_{36}NaO_{11}^+$; calc. 511.2155).

*15-Hydroxytorreyol 10-*O*-(6-*O*-β-*D*-apiofuranosyl)-β-*D*-glucopyranoside* (=(*1*R,*4*S,*4a*R,*8a*S)-*1,2,3,4,4a,7,8,8a-Octahydro-6-(hydroxymethyl)-1-methyl-4-(1-methylethyl)naphthalen-1-yl 6-*O*-[(2*R*,3*R*,4*R*)-Tetrahydro-3,4-dihydroxy-4-(hydroxymethyl)furan-2-yl]-β-*D*-glucopyranoside*; **3**). White amorphous powder. $[\alpha]_D^{25} = -5$ ($c = 0.160$, MeOH). IR: 3421, 2929, 1637, 1459, 1384, 1058. ^{1}H- and ^{13}C-NMR: *Table*. ESI-MS (pos.): 555.3 ($[M + Na]^+$). ESI-MS (neg.): 578.0 ($[M + COOH]^-$). HR-ESI-MS: 555.2790 ($[M + Na]^+$, $C_{26}H_{44}NaO_{11}^+$; calc. 555.2781).

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REFERENCES

[1] J. Xu, Y.-Q. Guo, X. Li, K. Wei, X.-J. Zhao, *J. Ethnopharmacol.* **2008**, *117*, 175.
[2] S. E. Kim, H. S. Kim, Y. S. Hong, Y. C. Kim, J. J. Lee, *J. Nat. Prod.* **1999**, *62*, 697.
[3] Y. Zhu, Z. Miao, J. Ding, W. Zhao, *J. Nat. Prod.* **2008**, *71*, 1005.
[4] H. Z. Jin, B. Y. Hwang, H. S. Kim, J. H. Lee, Y. H. Kim, J. J. Lee, *J. Nat. Prod.* **2002**, *65*, 89.
[5] B. Y. Hwang, H. S. Kim, J. H. Lee, Y. S. Hong, J. S. Ro, K. S. Lee, J. J. Lee, *J. Nat. Prod* **2001**, *64*, 82.
[6] Y. Guo, X. Li, J. Wang, J. Xu, N. Li, *Fitoterapia* **2005**, *76*, 273.
[7] G. Nonaka, H. Nishimura, I. Nishioka, *Chem. Pharm. Bull.* **1982**, *30*, 2061.
[8] K. Sano, S. Sanada, Y. Ida, J. Shoji, *Chem. Pharm. Bull.* **1991**, *39*, 865.
[9] J. O. Andrianaivoravelona, C. Terreaux, S. Sahpaz, J. Rasolondramanitra, K. Hostettmann, *Phytochemistry* **1999**, *52*, 1145.
[10] K. Graikou, N. Aligiannis, I. Chinou, A.-L. Skaltsounis, F. Tillequin, M. Litaudon, *Helv. Chim. Acta* **2005**, *88*, 2654.
[11] T. Isikawa, J. Kitajima, Y. Tanaka, M. Ono, Y. Ito, T. Nohara, *Chem. Pharm. Bull.* **1998**, *46*, 1738.
[12] J. Kitajima, N. Suzuki, T. Isikawa, Y. Tanaka, *Chem. Pharm. Bull.* **1998**, *46*, 1583.
[13] J. Kitajima, K. Kimizuka, Y. Tanaka, *Chem. Pharm. Bull.* **2000**, *48*, 77.
[14] K. Shimoda, Y. Kondo, T. Nishida, H. Hamada, N. Nakajima, H. Hamada, *Phytochemistry* **2006**, *67*, 2256.
[15] L. Ding, R. Pfoh, S. Rühl, S. Qin, H. Laatsch, *J. Nat. Prod.* **2009**, *72*, 99.
[16] A.-K. Borg-Karlson, T. Norin, A. Talvitie, *Tetrahedron* **1981**, *37*, 425.
[17] A. Ito, H.-B. Chai, L. B. S. Kardono, F. M. Setowati, J. J. Afriastini, S. Riswan, N. R. Farnsworth, G. A. Cordell, J. M. Pezzuto, S. M. Swanson, A. D. Kinghorn, *J. Nat. Prod.* **2004**, *67*, 201.

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