

Cycloartane Triterpene Glycosides from the Roots of *Astragalus brachypterus* and *Astragalus microcephalus*

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Three new cycloartane-type triterpene glycosides, brachyosides A (**1**), B (**3**), and C (**2**), from the roots of *Astragalus brachypterus* and one new glycoside, cyclocephalose II (**4**), from the roots of *Astragalus microcephalus* have been isolated together with five known saponins, astragalosides I, II, and IV, cyclocanthoside E, and cycloastragenol. The structures of the new compounds were established as 3-*O*-[β -D-xylopyranosyl(1 \rightarrow 3)- β -D-xylopyranosyl-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,24(S),25-pentahydroxycycloartane (**1**), 3-*O*- β -D-xylopyranosyl-6-*O*- β -D-glucopyranosyl-24-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,24(S),25-pentahydroxycycloartane (**2**), 20(*R*),24(*S*)-epoxy-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,25-tetrahydroxycycloartane (**3**), and 20(*R*),24(*S*)-epoxy-3-*O*-(4'-*O*-acetyl)- β -D-xylopyranosyl-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,25-tetrahydroxycycloartane (**4**). For the structure elucidations, 1D- and 2D-NMR experiments and FABMS were used.

In the course of a systematic investigation of *Astragalus* spp., we examined EtOH extracts of the roots of *A. brachypterus* Fischer and *A. microcephalus* Willd. (Fabaceae). The genus *Astragalus* is represented by 380 species in the flora of Turkey.¹ Roots of these plants are used in Turkish folkloric medicine as an antiperspirant, diuretic, and tonic drug and for treatment of diabetes mellitus, nephritis, leukemia, and uterine cancer. Earlier investigations performed on *Astragalus* species resulted in the isolation of a number of cycloartane-type triterpenic saponins.^{2–4} In this paper, we describe the isolation and structure elucidation of four new cycloartane triterpene glycosides named as brachyosides A (**1**), B (**3**), and C (**2**) from *A. brachypterus* and cyclocephalose II (**4**) from *A. microcephalus* (Chart 1). The related known glycosides, astragalosides I,⁶ II,⁶ and IV⁶ and cyclocanthoside E⁵ from *A. brachypterus* as well as cycloastragenol⁶ from both *A. brachypterus* and *A. microcephalus* were also isolated.

Results and Discussion

Nine saponins were isolated and purified by a combination of chromatographic methods from the EtOH extracts of *A. brachypterus* and *A. microcephalus*. The most polar compounds, brachyosides A (**1**) and C (**2**), showed [M – H][–] peaks at *m/z* 917 and 947 in their negative FABMS spectra corresponding to C₄₆H₇₈O₁₈ and C₄₇H₈₀O₁₉ molecular formulas, respectively. The NMR spectra of compounds **1** and **2** (Table 1) were characteristic of cycloartane glycosides. The ¹H NMR spectrum of brachyoside A (**1**) showed signals characteristic of cyclopropane-methylene protons at δ 0.27 and 0.61 (each d, *J* = 4.5 Hz, H₂-19), six tertiary methyl groups at δ 1.02, 1.04, 1.16, 1.17, 1.20, and 1.32, and a secondary methyl group at δ 1.00 (*J* = 6 Hz) in the aglycon moiety. Furthermore, the ¹H NMR spectrum of **1** clearly showed three anomeric proton doublets at δ 4.37 (*J* = 7.5 Hz), 4.50 (*J* = 7.8 Hz), and 4.51 (*J* = 7.8 Hz) in the downfield region, indicative of three β -linked sugar units. These correlated to carbons at δ 105.5, 106.1, and 106.8,

respectively, in the HSQC spectrum. The ¹³C NMR spectrum contained 46 resonances; 30 of them, attributed to the sapogenol moiety, were in good agreement with cyclocanthogenin.⁵ Full assignment of the ¹H and ¹³C signals of the aglycon part of **1**, secured by ¹H–¹H DQF–COSY and HSQC spectra, showed marked glycosylation shifts for C-3 (δ 90.1) and C-6 (δ 80.4). All connectivities within **1** were also confirmed by a HMBC experiment. These results suggested that **1** was a bisdesmosidic saponin in which the sugar residues were linked to C-3 and C-6 of cyclocanthogenin. A combination of DQF–COSY and 1D TOCSY and 2D HOHAHA experiments allowed unambiguous assignment of all proton sugar signals and identified the sugar moiety as consisting of one β -D-glucopyranosyl and two β -D-xylopyranosyl units, respectively. The HSQC experiments correlated each proton sugar signal to the corresponding carbon resonances and showed the absence of glycosylation shifts for the carbon resonances of the glucopyranosyl and one xylopyranosyl unit; a glycosylation shift (ca. 6.6 ppm) was observed for C-3 (δ 83.6) of the second xylopyranosyl unit. All connectivities, including the sites of attachment of sugar moieties on the aglycon of **1** as well as the position of the interglycosidic linkage, were determined by an HMBC experiment. In the HMBC spectrum, the anomeric proton signal at relatively high field (δ 4.37, H-1'), assigned to the β -D-glucopyranosyl, showed long-range correlation with the carbon at δ 80.4 (C-6). The second anomeric proton signal at δ 4.50 (H-1'), assigned to the 3-substituted β -D-xylopyranosyl, showed long-range correlation with the carbon resonance at δ 90.1 (C-3). Thus, glucose must be linked to C-6 and the bridging xylose residue should be attached to C-3. The third anomeric proton signal at δ 4.51 (H-1''), assigned to the terminal β -D-xylopyranosyl unit, showed long-range correlation with the carbon resonance at δ 83.6 (C-3') of the bridging xylose unit attached to the aglycon, revealing the presence of a disaccharide unit at C-3. Thus, the structure of **1** was elucidated as 3-*O*-[β -D-xylopyranosyl(1 \rightarrow 3)- β -D-xylopyranosyl]-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,24(S),25-pentahydroxycycloartane.

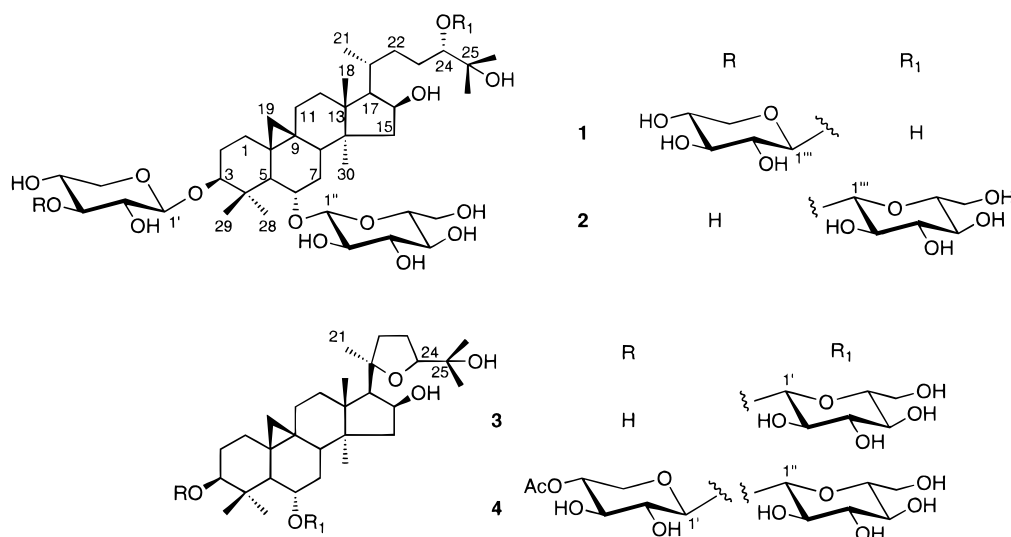
The ¹H NMR spectrum of **2** showed three anomeric proton resonances at δ 4.32 (*J* = 7.6 Hz), 4.37 (*J* = 7.8 Hz), and 4.45 (*J* = 7.8 Hz) correlated by HSQC to the resonances

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Chart 1



at δ 107.1 and 104.6 ($\times 2$) (Table 1). The three sugar units were identified using a combination of 1D TOCSY and 2D HOHAHA, DQF-COSY, and HSQC as a terminal β -D-xylopyranose and two β -D-glucopyranoses, respectively. The ^{13}C NMR resonances arising from the sapogenol moiety were very close to those of **1**, except for the signals assigned to C-24 (δ 89.7) exhibiting a significant glycosidation shift and small upfield shifts (Table 1) for carbons neighboring C-24. These results suggested a tridesmosidic structure for **2** in which the three sugar units were attached to the hydroxyl groups at C-3, C-6, and C-24. An HMBC experiment performed on **2** established the glycosidation sites showing significant cross-peaks, due to $^2J_{\text{C-H}}$ correlations, between C-1' (δ 107.1) of the β -D-xylopyranosyl unit and H-3 (δ 3.23), between C-1'' (δ 104.6) of the first β -D-glucopyranosyl and H-6 (δ 3.58), and between C-24 (δ 89.7) and H-1''' (δ 4.45) of the second β -D-glucopyranosyl. Consequently, the structure of **2** was established as 3-*O*- β -D-xylopyranosyl-6-*O*- β -D-glucopyranosyl-24-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,24(*S*),25-pentahydroxycycloartane.

The FABMS of brachyoside B (**3**) ($\text{C}_{36}\text{H}_{60}\text{O}_{10}$) displayed a quasimolecular ion peak at m/z 651. The ^1H NMR spectrum of **3** showed signals due to a cyclopropane methylene at δ 0.31 and 0.63 (each d, $J = 4.5$ Hz) and seven tertiary methyls at δ 0.98, 1.05, 1.16, 1.24, 1.29 ($\times 2$), and 1.32. Furthermore, the ^1H NMR spectrum of **3** showed only one anomeric doublet signal at δ 4.36 ($J = 7.8$ Hz), indicative of one β -linked sugar unit. The ^{13}C NMR spectrum of **3** displayed 36 carbon signals. On the basis of DQF-COSY, DEPT, HSQC, and HMBC spectra and by comparison with data of related compounds,⁶ all signals were assigned (see the Experimental Section). Thus, the aglycon of compound **3** was identified as a cycloastragenol.⁶ From 1D- and 2D-NMR experiments, the presence of a β -D-glucopyranosyl moiety was recognized. The attachment of the glucose moiety at C-6 (δ 80.0) of the aglycon was determined by means of the diagnostic glycosidation shift of this carbon atom and confirmed by the results of the HMBC spectrum. The resonances of C-3 (δ_{C} 79.0) and H₃-29 (δ_{H} 0.98) were indicative of an unsubstituted -OH group at C-3. Brachyoside B (**3**) is, therefore, 20(*R*),24(*S*)-epoxy-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,25-tetrahydroxycycloartane and has been isolated here for the first time as a genuine saponin.

The FABMS spectrum of **4** ($\text{C}_{43}\text{H}_{70}\text{O}_{15}$) exhibited the $[\text{M} - \text{H}]^-$ at m/z 825. Detailed examination of the 1D- and 2D-NMR spectra of **4** and comparison with those of **3**

indicated the presence of cycloastragenol, glycosylated at C-3 (δ 89.8) and C-6 (δ 79.8) as well as a terminal glucopyranosyl unit. Moreover, the presence of an extra sugar moiety (C-1': δ 107.1, H-1': δ 4.31, $J = 7.8$ Hz) and an acetyl function (COCH_3 ; δ 20.6, COCH_3 ; δ 171.9, COCH_3 ; δ 2.09) was verified. Location of the acetoxy group in the xylopyranosyl moiety was ascertained using a combination of HSQC and 1D- and 2D-HOHAHA measurements which showed that the second sugar moiety was 4'-*O*-acetyl- β -D-xylopyranose. A downfield acetylation shift was observed for the signal due H-4' (δ 4.70, ddd, $J = 4.5, 8.5, 10.5$ Hz) of the xylose moiety. The HMBC spectrum established that 4'-*O*-acetyl- β -D-xylopyranose was linked to C-3 and β -D-glucopyranose to C-6. On the basis of above results, the structure of cyclocephaloside II (**4**) was elucidated as 20(*R*),24(*S*)-epoxy-3-*O*-(4'-*O*-acetyl)- β -D-xylopyranosyl-6-*O*- β -D-glucopyranosyl-3 β ,6 α ,16 β ,25-tetrahydroxycycloartane.

The known saponins were identified as cycloastragenol,⁶ astragaloside I,⁶ astragaloside II,⁶ astragaloside IV,⁶ and cyclocanthoside E⁵ by spectral data and comparison of their physical properties with those reported previously for these compounds.^{5,6} Compounds **3**, **4**, and cycloastragenol were isolated from *A. microcephalus*, whereas compounds **1–3** and the other saponins, except **4**, were isolated from *A. brachypteris*.

Experimental Section

General Experimental Procedures. A Bruker DRX-600 spectrometer operating at 599.19 MHz for ^1H and 150.858 MHz for ^{13}C using the UXNMR software package was used for NMR measurements in CD_3OD solutions. 2D experiments: ^1H - ^1H DQF-COSY,⁷ inverse-detected ^1H - ^{13}C HSQC⁸ and HMBC,⁹ and ROESY¹⁰ were obtained by employing the conventional pulse sequences as described previously. The selective excitation spectra, 1D TOCSY,¹¹ were acquired using waveform generator-based GAUSS-shaped pulses, mixing time ranging from 100 to 120 ms, and a MLEV-17 spin-lock field of 10 kHz preceded by a 2.5 ms trim pulse. Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a sodium lamp operating at 589 nm in 1% w/v solutions in MeOH. FABMS were recorded in a glycerol matrix in the negative-ion mode on a VG ZAB instrument (XE atoms of energy of 2–6 KV).

Plant Material. The roots of *A. microcephalus* Willd. and *A. brachypteris* Fischer were collected from Central Anatolia, Nevsehir, Mucur-Avanos, Turkey, in June 1995. Voucher specimens (95-016 and 95-017, respectively) have been depos-

Table 1. ^1H and ^{13}C NMR Data of Brachyosides A (**1**) and C (**2**)^a

position	1		2	
	δ_{H} (J, Hz)	δ_{C}	δ_{H} (J, Hz)	δ_{C}
1	1.30, m	33.4	1.29, m	32.7
	1.57, m		1.58, m	
2	1.72, m	30.9	1.71, m	30.1
	1.96, m		1.97, m	
3	3.23, dd (4.5, 11.2)	90.1	3.23, dd (4.5, 11.1)	89.8
4		43.0		42.7
5	1.64, d (9.5)	53.7	1.65, d (9.5)	52.9
6	3.57, ddd (4.5, 9.5, 9.5)	80.4	3.58 ddd (4.5, 10.0, 10.0)	79.9
7	1.63, m	35.3	1.63, m	34.8
	1.92, m		1.93, m	
8	1.89, m	46.1	1.90, m	46.6
9		22.0		21.9
10		30.0		29.8
11	1.38, m	27.4	1.37, m	26.8
	1.89, m		1.93, m	
12	1.60, m	34.2	1.62, m	33.7
	1.67, m		1.67, m	
13		46.6		46.3
14		47.6		47.1
15	1.43, dd (5.2, 12.0)	48.0	1.44, (5.2, 12.0)	48.1
	2.13, dd (8.2, 12.0)		2.13, dd (8.0, 12.0)	
16	4.47, ddd (5.2, 8.0, 8.2)	73.8	4.44, ddd (5.2, 8.0, 8.0)	72.5
17	1.74, m	58.3	1.75, m	57.6
18	1.16, s	18.8	1.18, s	18.0
19	0.27, d (4.5)	29.3	0.27, d (4.5)	28.9
	0.61, d (4.5)		0.61, d (4.5)	
20	1.85, m	32.6	1.88, m	30.9
21	1.00, d (6.0)	19.2	0.97, d (6.0)	17.5
22	1.03, m	35.8	1.91, m	33.0
23	1.21, m	30.0	1.62, m	29.4
	1.82, m		1.65, m	
24	3.27, dd (4.5, 12.0)	81.2	3.54, dd (4.5, 12.0)	89.7
25		74.0		73.5
26	1.17, s	25.7	1.19, s	26.5
27	1.20, s	26.4	1.21, s	24.0
28	1.32, s	28.7	1.32, s	28.1
29	1.04, s	16.8	1.05, s	16.2
30	1.02, s	20.8	1.01, s	19.8
1'	4.50, d (7.8)	106.1	4.32, d (7.6)	107.1
2'	3.60, dd (7.8, 8.5)	74.5	3.23, dd (7.6, 8.5)	75.2
3'	3.47, t (8.5)	83.6	3.33, t (8.5)	77.7
4'	3.83, ddd (4.0, 8.5, 11.0)	69.9	3.50, ddd (4.0, 8.5, 11.0)	71.0
5	3.56, t (11.0)	67.8	3.21, t (11.0)	66.4
	3.93, dd (4.0, 11.0)		3.86, dd (4.5, 11.0)	
1''	4.37, d (7.5)	105.5	4.37, d (7.8)	104.6
2''	3.23, dd (7.5, 9.0)	75.8	3.21, dd (7.8, 9.0)	75.2
3''	3.37, t (9.0)	78.7	3.38, t (9.0)	78.2
4''	3.31, t (9.0)	72.2	3.32, t (9.0)	71.3
5''	3.29, ddd (3.5, 4.5, 9.0)	77.8	3.28, ddd (3.0, 4.5, 9.0)	77.6
6''	3.70, dd (4.5, 12.0)	63.5	3.69, dd (4.5, 12.0)	62.7
	3.84, dd (3.5, 12.0)		3.89, dd (3.0, 12.0)	
1'''	4.51, d (7.8)	106.8	4.45, d (7.8)	104.6
2'''	3.69, dd (7.8, 8.5)	74.1	3.28, dd (7.8, 9.0)	75.2
3'''	3.56, t (8.6)	77.0	3.41, t (9.0)	77.8
4'''	3.55, ddd (4.5, 8.6, 11.0)	71.3	3.35, t (9.0)	71.3
5'''	3.23, t (11.0)	66.5	3.36, t (3.0, 4.5, 9.0)	78.2
6'''	3.90, (4.5, 11.0)		3.69 (4.5, 12.0)	62.2
			3.89, dd (3.0, 12.0)	

^a Assignments confirmed by 1D-TOCSY and 2D-DQF-COSY, HSQC, and HMBC experiments.

ited at the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey.

Extraction and Isolation. The air-dried powdered roots of *A. microcephalus* (260 g) were extracted with 80% EtOH under reflux. The water-soluble part of the ethanolic extract (19 g) was subjected to VLC using reversed-phase material (Sepralyte 40 μm), employing H_2O , H_2O -MeOH (95:5, 90:10, 85:15), and MeOH as the eluents. Fractions rich in saponins eluted with MeOH (2.48 g) were further subjected to column chromatography (silica gel, 100 g) to give six main fractions (fractions A-F). Fraction A (23 mg) was subjected to a silica

gel column (10 g) using CHCl_3 and CHCl_3 -MeOH (95:5) to yield **5** (10 mg). Fraction C (73 mg) was applied to the silica gel column (20 g) using a mixture of CHCl_3 -MeOH (9:1) and CHCl_3 -MeOH- H_2O (85:15:1) to give **4** (35 mg). Fraction E (225 mg) was chromatographed on a silica gel column (35 g) eluted with CHCl_3 -MeOH- H_2O (80:20:2) to yield **3** (52 mg).

The air-dried powdered roots of *A. brachypterus* (250 g) were extracted with 80% EtOH under reflux. The water-soluble part of the ethanolic extract (20 g) was extracted with *n*-BuOH. The *n*-BuOH extract (12.5 g) was subjected to VLC using silica gel (250 g) as the stationary phase eluting with CHCl_3 -MeOH (9:1) and CHCl_3 -MeOH- H_2O (80:20:1, 80:20:2, 70:30:3, and 61:32:7) to give 14 fractions (fractions A-N). Further chromatography on silica gel yielded cycloastragenol (24 mg) from fraction A, astragaloside I (57 mg) from fraction B, **3** (20 mg) from fraction D, astragaloside II (40 mg) from fraction E, astragaloside IV (455 mg) from fraction G, cyclocanthoside E (124 mg) from fraction I, and finally **1** (20 mg) and **2** (7.5 mg) from fraction J.

Brachyoside A (1): $[\alpha]_{\text{D}}^{25} +15.5^\circ$ (*c* 0.1, MeOH); NMR data are reported in Table 1; FABMS m/z 917 $[\text{M} - \text{H}]^-$, 755 $[(\text{M} - \text{H}) - 162]^-$, 775 $[(\text{M} - \text{H}) - 132]^-$, 491 $[(\text{M} - \text{H}) - (162 + 132 \times 2)]^-$.

Brachyoside B (3): $[\alpha]_{\text{D}}^{25} +40.1^\circ$ (*c* 0.1, MeOH); ^1H NMR (600 MHz, CD_3OD) aglycon moiety δ 4.68 (1H, ddd, $J = 8.5, 8.5, 5.2$ Hz, H-16), 3.78 (1H, dd, $J = 8.0, 5.0$ Hz, H-24), 3.58 (1H, ddd, $J = 9.5, 9.5, 4.5$ Hz, H-6), 3.24 (1H, dd, $J = 11.2, 4.5$ Hz, H-3), 2.64 (1H, m, H-22a), 2.40 (1H, d, $J = 8.0$ Hz, H-17), 2.07 (1H, m, H-15a), 2.06 (2H, m, H-23), 1.95 (1H, m, H-11a), 1.94 (1H, m, H-7a), 1.88 (1H, m, H-8), 1.74 (1H, m, H-2a), 1.71 (1H, m, H-12a), 1.67 (1H, m, H-22b), 1.65 (1H, m, H-2b), 1.62 (1H, m, H-5), 1.60 (1H, m, H-7b), 1.59 (1H, m, H-12b), 1.57 (1H, m, H-1a), 1.42 (1H, m, H-15b), 1.36 (1H, m, H-11b), 1.32 (3H, s, H-28), 1.30 (1H, m, H-1b), 1.29 (6H, s, H-18, H-27), 1.24 (3H, s, H-21), 1.16 (3H, s, H-26), 1.05 (3H, s, H-30), 0.98 (3H, s, H-29), 0.31 and 0.63 (each 1H, d, $J_{\text{AB}} = 4.5$ Hz, H-19a and H-19b, respectively); sugar moiety δ 4.36 (1H, d, $J = 7.8$ Hz, H-1'), 3.86 (1H, dd, H-6'a), 3.68 (1H, dd, H-6'b), 3.36 (1H, t, H-3'), 3.30 (1H, m, H-4'), 3.27 (1H, ddd, H-5'), 3.21 (1H, dd, H-2'); ^{13}C NMR (150 MHz, CD_3OD) aglycon moiety δ 88.1 (s, C-20), 82.4 (d, C-24), 80.0 (d, C-6), 79.0 (d, C-3), 74.2 (d, C-16), 72.1 (s, C-25), 58.6 (d, C-17), 52.8 (d, C-5), 46.7 (s, C-14), 46.3 (s, C-13), 46.0 (d, C-8), 46.0 (t, C-15), 42.3 (s, C-4), 35.1 (t, C-22), 34.8 (t, C-7), 32.8 (t, C-1), 32.6 (t, C-12), 30.6 (t, C-2), 30.0 (s, C-10), 29.5 (t, C-19), 28.1 (q, C-21), 27.7 (q, C-28), 27.1 (q, C-27), 26.5 (t, C-23), 26.4 (q, C-26), 26.0 (t, C-11), 22.0 (s, C-9), 21.1 (q, C-18), 20.0 (q, C-30), 15.6 (q, C-29); sugar moiety δ 104.5 (d, C-1'), 78.3 (d, C-3'), 77.4 (d, C-5'), 75.3 (d, C-2'), 71.4 (d, C-4'), 62.6 (t, C-6'); FABMS m/z 651 $[\text{M} - \text{H}]^-$, 489 $[(\text{M} - \text{H}) - 162]^-$.

Compound **3** has been derived from astragaloside IV by enzymatic hydrolysis.⁶

Brachyoside C (2): $[\alpha]_{\text{D}}^{25} +12.5^\circ$ (*c* 0.1, MeOH); NMR data are reported in Table 1; FABMS m/z 947 $[\text{M} - \text{H}]^-$, 785 $[(\text{M} - \text{H}) - 162]^-$, 623 $[(\text{M} - \text{H}) - (2 \times 162)]^-$, 491 $[(\text{M} - \text{H}) - (162 \times 2 + 132)]^-$.

Cyclocephaloside II (4): $[\alpha]_{\text{D}}^{25} +19.6^\circ$ (*c* 0.1, MeOH); ^1H NMR (600 MHz, CD_3OD) aglycon moiety δ 4.69 (1H, ddd, $J = 8.0, 8.2, 5.2$ Hz, H-16), 3.79 (1H, dd, $J = 8.0, 5.0$ Hz, H-24), 3.57 (1H, ddd, $J = 10.0, 10.0, 4.5$ Hz, H-6), 3.23 (1H, dd, $J = 11.2, 4.5$ Hz, H-3), 2.65 (1H, m, H-22a), 2.40 (1H, d, $J = 8.0$ Hz, H-17), 2.07 (1H, m, H-15a), 2.06 (2H, m, H-23), 1.96 (1H, m, H-2a), 1.95 (1H, m, H-11a), 1.93 (1H, m, H-7a), 1.89 (1H, m, H-8), 1.71 (1H, m, H-12a), 1.70 (1H, m, H-2b), 1.67 (1H, m, H-22b), 1.64 (1H, m, H-5), 1.62 ($\times 2$) (each 1H, m, H-7b and H-12b), 1.57 (1H, m, H-1a), 1.42 (1H, m, H-15b), 1.36 (1H, m, H-11b), 1.32 (3H, s, H-28), 1.29 ($\times 2$) (each 3H, s, H-18, H-27), 1.28 (1H, m, H-1b), 1.24 (3H, s, H-21), 1.15 (3H, s, H-26), 1.05 (3H, s, H-30), 1.04 (3H, s, H-29), 0.30 and 0.62 (each 1H, d, $J_{\text{AB}} = 4.5$ Hz, H-19a and H-19b, respectively); sugar moiety δ 4.70 (1H, ddd, $J = 4.5, 8.5, 10.5$ Hz, H-4'), 4.36 (1H, d, $J = 7.5$ Hz, H-1'), 4.31 (1H, d, $J = 7.8$ Hz, H-1'), 3.95 (1H, dd, $J = 10.5, 4.5$ Hz, H-5'a), 3.87 (1H, dd, $J = 12.0, 3.5$ Hz, H-6'a), 3.69 (1H, dd, $J = 12.0, 4.5$ Hz, H-6'b), 3.56 (1H, t, $J = 8.5$ Hz, H-3'), 3.35 (1H, t, $J = 9.0$ Hz, H-3'), 3.30 (1H, dd, $J = 7.8, 8.5$

Hz, H-2'), 3.30 (1H, t, $J = 9.0$ Hz, H-4'), 3.26 (1H, t, $J = 10.5$, H-5'b), 3.26 (1H, ddd, $J = 9.0, 4.5, 3.5$ Hz, H-5'), 3.20 (1H, dd, $J = 9.0, 7.5$ Hz, H-2''); ^{13}C NMR (150 MHz, CD_3OD) aglycon moiety δ 89.8 (d, C-3), 88.1 (s, C-20), 82.5 (d, C-24), 79.8 (d, C-6), 74.4 (d, C-16), 72.9 (s, C-25), 58.6 (d, C-17), 53.7 (d, C-5), 47.0 (s, C-14), 46.7 (t, C-8), 46.3 (s, C-13), 46.0 (t, C-15), 42.8 (s, C-4), 35.4 (t, C-22), 35.0 (t, C-7), 33.8 (t, C-12), 32.7 (t, C-1), 30.3 (t, C-2), 30.0 (s, C-10), 29.3 (t, C-19), 29.0 ($\times 2$) (each q, C-21 and C-28), 27.4 (q, C-27), 26.8 (t, C-11), 26.4 (t, C-23), 26.4 (q, C-26), 22.0 (s, C-9), 21.1 (q, C-18), 20.0 (q, C-30), 16.2 (q, C-29); sugar moiety δ 107.0 (d, C-1'), 104.9 (d, C-1''), 78.4 (d, C-3'), 77.8 (d, C-5'), 75.3 (d, C-2''), 75.1 (d, C-2'), 74.7 (d, C-3'), 73.0 (d, C-4'), 71.5 (d, C-4''), 63.1 (t, C-6'), 62.7 (t, C-6''); FABMS m/z 825 $[\text{M} - \text{H}]^-$, 663 $[(\text{M} - \text{H}) - 162]^-$, 783 $[(\text{M} - \text{H}) - 42]^-$, 489 $[(\text{M} - \text{H}) - (162 + 42 + 132)]^-$.

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