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TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXXVI. CHEMICAL TRANSFORMATION OF CYCLOARTANES. VIII. SYNTHESES BASED ON CYCLOORBICOSIDE A

I. M. Isaev, M. A. Agzamova, and M. I. Isaev*

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*Nine new compounds **3**–**11** were synthesized from the principal glycoside of* Astragalus orbiculatus *Ledeb. (Leguminosae), cycloorbicoside A, and may be interesting on their own as potential biologically active compounds and synthons for other compounds.*

Keywords: *Astragalus*, Leguminosae, cycloartanes, cycloorbicoside A, PMR, ^{13}C NMR, DEPT, ^{1}H–^{1}H COSY, HSQC spectra.

Cycloorbicoside A (**1**) is the principal glycoside of *Astragalus orbiculatus* Ledeb. (Leguminosae) [1, 2] and exhibits interferon-inducing activity [3]. Therefore, chemical transformation of **1** is interesting for creating biologically active compounds and finding biological structure–activity relationships. Herein we continue studies on the chemical modification of the genin of **1** with retention of carbohydrats. For this, we synthesized the appropriately protected synthons. Secondary hydroxyls were protected using acetylation.

Acetylation of **1** by acetic anhydride in Py gave a mixture of acetates **2**–**5**. These were separated by column chromatography. According to PMR and ^{13}C NMR spectra, **2** was the tetraacetate of **1** that was previously reported [2]. We optimized the method for preparing **2** because it is the key compound in the chemical transformations performed by us. The method enabled quantitative conversion of starting **1** into **2** (see Experimental and Table 1).

PMR and ^{13}C NMR spectra of **3** showed resonances for three acetyls. Resonances of H-3 and H-4 of D-xylose and H-7 of the genin in the same PMR spectrum experienced low-field shifts and were observed at δ 5.58, 5.17, and 4.85, respectively. This defined **3** as the 3′,4′,7-triacetate of **1**.

The PMR spectrum of **4** also exhibited resonances for three acetyls at δ 1.84, 1.91, and 1.99 ppm. The H-15 protons in this same spectrum resonated at δ 2.49 and 2.68 as ^{1}H doublets of an AX system with ^{2}J = 14 Hz. It should be noted that the two H-15 protons in the spectrum at 100 MHz resonated at δ 2.58 as an AB quartet with ^{2}J = 14 Hz. This indicated that the 7β-hydroxyl was free [4], which was consistent with the resonance of H-7 observed at δ 3.67 as a triplet of doublets (td, $^{3}J_1 = {}^{3}J_2 = 10.8$, $^{3}J_3 = 3.6$ Hz). Therefore, all acetyls of **4** were located in the carbohydrate part of the glycoside. As expected, resonances of H-2′, H-3′, and H-4′ were shifted to low field at δ 5.31, 5.57, and 5.19, respectively. This means that **4** was the 2′,3′,4′-triacetate of **1**.

The PMR spectrum of **5** contained sharp resonances for two acetyls at δ 1.87 and 1.91. The chemical shifts of H-2′ (δ 3.91) and H-7 (δ 3.67) indicated that the hydroxyls geminal to these H atoms were free. In fact, H-3′ and H-4′ resonated in the PMR spectrum at δ 5.58 and 5.16, respectively. Therefore, **5** was the 3′,4′-diacetate of **1**.

Jones oxidation [5] was used to introduce the ketone at C-7 of **1** in acetate **4** and produced keto-derivative **6**. The PMR spectrum of **6** exhibited resonances for seven methyls and three acetyls. As expected, the resonance of H-8 became a singlet and appeared at δ 2.76 whereas the resonance of H-7 disappeared. In agreement with this, the ^{13}C NMR spectrum of **6** showed a resonance for a ketone C atom at δ 212.76. These spectral data defined **6** as 3-*O*-β-D-(2′,3′,4′-tri-*O*-acetyl)-xylopyranoside-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloartan-3β,25-diol-7-one.

Alkaline hydrolysis of **6** produced ketoglycoside **8**, the PMR and ^{13}C NMR spectra of which lacked resonances for acetyls. Therefore, **8** was 7-dehydrocycloorbicoside A.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75, e-mail: m_isaev@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 339–344, May–June, 2010. Original article submitted September 18, 2009.

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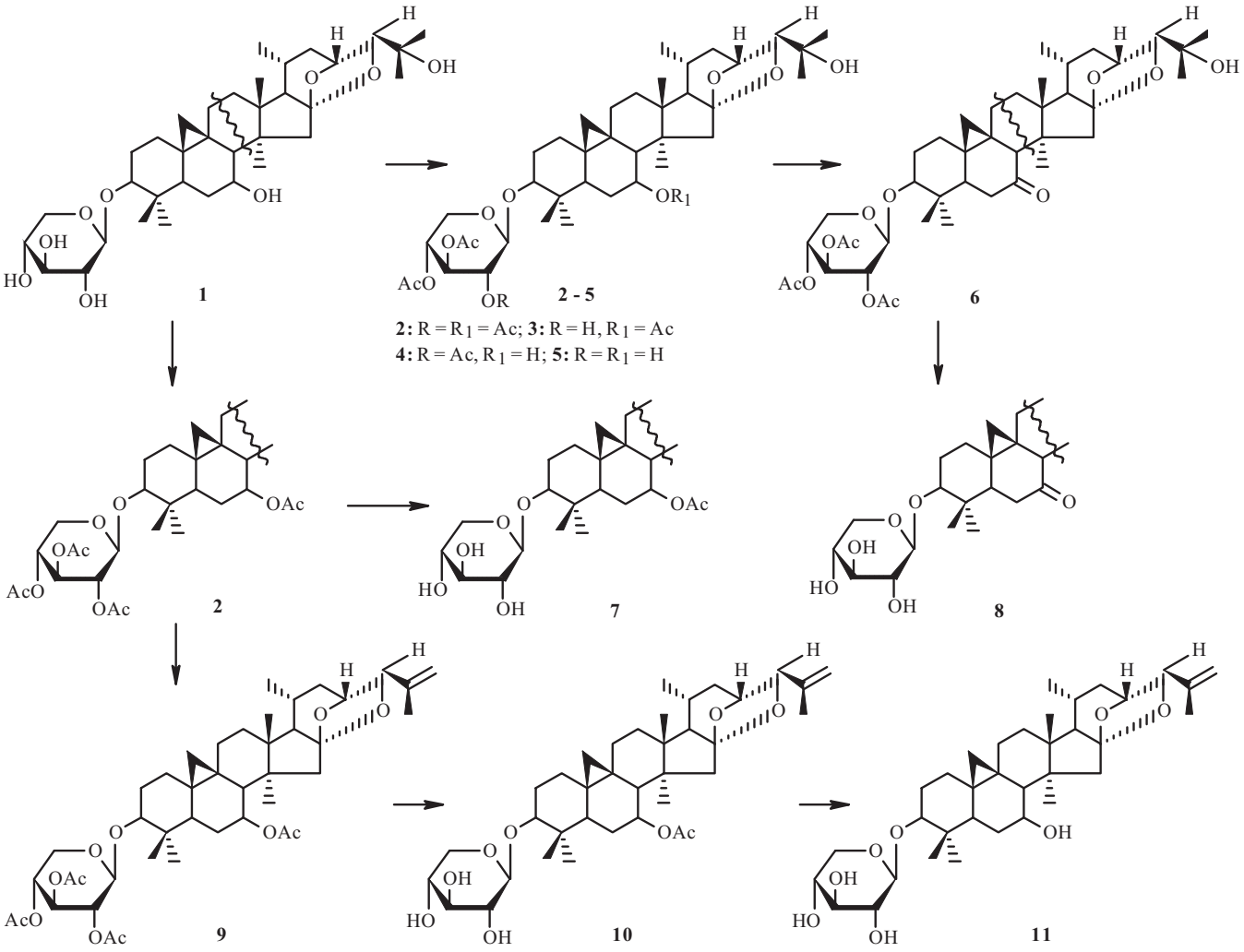

Partial alkaline hydrolysis of tetraacetate **2** produced monoacetate **7** in quantitative yield. PMR and ^{13}C NMR spectra of **7** had resonances for one acetyl. The resonance for H-7 in the same PMR spectrum shifted to weak field and was observed at δ 4.87 (td, $^3J_1 = {}^3J_2 = 10.7$, $^3J_3 = 4$ Hz). The resonance for C-7 was also shifted to weak field in the ^{13}C NMR spectrum and was observed at δ 73.36. Therefore, the acetyl was located on C-7 and **7** was the 7-monoacetate of **1**.

Tetraacetate **2** in Py was treated with benzenesulfonylchloride and left at room temperature for 12 h in order to eliminate a molecule of water from the hydroxyl on C-25. Pure compound **9** was obtained from the reaction mixture. The PMR spectrum (100 MHz) of **9** exhibited at high field resonances for four acetyls and six methyls instead of the seven in starting **2**. The same spectrum showed broad singlets belonging to the newly created exomethylene group (CH_2-26) at δ 4.80 and 5.02. As expected, the resonance of the methyl on the double bond (CH_3-27) was found at δ 1.64. In agreement with this, the ^{13}C NMR spectrum of **9** contained resonances for olefinic C atoms C-25 and C-26 at δ 146.15 and 111.76, respectively. These data defined **9** as the peracetate 3-*O*-*β*-D-xylopyranoside-(23*R*,24*S*)-16*β*,23;16*α*,24-diepoxycycloart-25(26)-en-3*β*,7*β*-diol.

Partial saponification of **9** gave the monoacetate **10** in quantitative yield. The chemical shifts of H-7 and C-7 in the PMR and ^{13}C NMR spectra of **10** were δ 4.86 (td, $^3J_1 = {}^3J_2 = 10.8$, $^3J_3 = 3.9$ Hz) and 73.35. Thus, the acetyl was located on C-7. Therefore, **10** was the 7-monoacetate of 3-*O*-*β*-D-xylopyranoside-(23*R*,24*S*)-16*β*,23;16*α*,24-diepoxycycloart-25(26)-en-3*β*,7*β*-diol.

Further alkaline hydrolysis of **10** formed **11**, the PMR and ^{13}C NMR spectra of which lacked resonances for acetyls and defined it as 3-*O*-*β*-D-xylopyranoside-(23*R*,24*S*)-16*β*,23;16*α*,24-diepoxycycloart-25(26)-en-3*β*,7*β*-diol.

TABLE 1. Chemical Shifts of C Atoms of Glycosides **1**–**11** (100 MHz, C_5D_5N, δ, ppm, 0 = TMS)

C atom	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
1	31.97	31.26	31.41	31.74[a]	31.89	29.18	31.49	29.28	31.30	31.57	31.98
2	29.68	29.34	29.61	29.67	29.70	28.75	29.80	29.08	29.33	29.15	29.66
3	88.27	88.39	87.95	88.80	88.56	87.77	87.68	87.14	88.33	87.63	88.24
4	41.05	40.59	40.94	40.67	40.99	40.25	41.02	40.52	40.57	41.03	41.07
5	46.55	45.25	45.35	46.36	46.81	42.46	45.43	42.50	45.31	45.54	46.55
6	31.78	27.18	27.20	31.74[a]	31.75	37.28	27.24	37.23	27.23	27.33	31.83
7	70.12	73.33	73.32	70.08	70.09	212.76	73.36	213.02	73.29	73.35	70.08
8	55.27	50.93	50.90	55.36	55.63	54.17	50.90	54.08	51.08	51.09	55.17
9	19.65	19.39	19.33	19.74	19.67	20.65[a]	19.29	20.45	19.27	19.20	19.65
10	27.16	26.91	26.97	27.02	27.10	25.87	27.03	25.85	26.84	26.99	27.17
11	26.74	26.54	26.55	26.73	26.75	26.44	26.52	26.28	26.36	26.37	26.71
12	33.06	32.73	32.72	33.07	33.07	32.88	32.71	32.74	32.59	32.59	33.01
13	44.20	43.78	43.78	44.20	44.20	45.73	43.75	45.59	43.71	43.71	44.25
14	46.80	46.76	46.73	46.84	47.16	46.35	46.71	46.19	46.55	46.53	46.63
15	48.82	48.19	48.11	48.90	49.50	45.80	48.10	45.66	48.30	48.25	48.88
16	115.17	114.66	114.63	115.19	115.18	114.05	114.63	113.91	114.81	114.80	115.39
17	60.85	60.28	60.24	60.59	60.92	59.43	60.21	59.27	60.80	60.76	61.08
18	19.00	19.04	18.81	19.08	19.04	19.56[b]	18.80	19.44	18.96	18.96	18.96
19	29.96	28.87	28.89	29.54	29.78	18.96	28.89	18.92	29.08	29.83	29.98
20	23.78	23.75	23.73	23.82	23.81	23.65	23.72	23.52	23.62	23.61	23.69
21	20.01	20.01	19.98	20.06	20.03	19.56[b]	19.95	20.22	19.61	19.58	19.72
22	38.37	38.20	38.17	38.41	38.40	38.15	38.15	37.98	37.72	37.69	37.99
23	71.72	71.95	71.92	71.77	71.74	71.92	71.89	71.76	75.17	74.81	75.06
24	90.50	90.65	90.62	90.56	90.55	90.47	90.59	90.31	86.41	86.39	86.53
25	71.04	70.96	70.95	71.03	71.04	70.95	70.95	70.84	146.15	146.13	146.30
26	24.63	24.88	24.83	24.70	24.66	24.72	24.81	24.54	111.76	111.76	111.71
27	27.88	27.60	27.58	27.91	27.90	27.87	27.56	27.74	18.31	18.32	18.29
28	18.88	18.86	19.02	18.89	18.89	13.63	19.01	13.80	18.86	18.83	18.92
29	25.74	25.11	25.30	25.37	25.60	24.77	25.41	25.02	25.05	25.37	25.73
30	15.32	14.89	15.03	15.05	15.20	16.47	15.16	16.34	14.88	15.17	15.33
7-OAc	–	170.01	170.03	–	–	–	170.04	–	170.01	170.01	–
		21.56	21.54				21.55		21.53	21.55	
						β-D-Xyl*p*					
1	107.52	103.30	106.71	103.33	106.80	103.22	107.48	107.35	103.26	107.49	107.55
2	75.50	72.32	72.79	72.28	72.72	72.29	75.54	75.45	72.28	75.53	75.53
3	78.56	72.66	75.55	72.63	75.55	72.60	78.57	78.53	72.62	78.57	78.60
4	71.19	69.81	70.52	69.79	70.52	69.77	71.21	71.09	69.76	71.21	71.21
5	67.08	62.53	62.76	62.50	62.77	62.53	67.12	67.02	62.49	67.12	67.10
2-OAc	–	169.58	–	169.54	–	169.56	–	–	169.58	–	–
		20.53[a]		20.52[b]		20.52			20.51[a]		
3-OAc	–	170.22	170.41	170.23	170.44	170.22	–	–	170.21	–	–
		20.68	20.85	20.70	20.85	20.65[a]			20.66		
4-OAc	–	170.09	170.25	169.99	170.25	170.01	–	–	170.07	–	–
		20.53[a]	20.63	20.52[b]	20.62	20.40			20.51[a]		

Resonances denoted by the same letters overlap within the columns.

Thus, nine new compounds **3**–**11** that are of interest on their own as potential biologically active compounds and as synthons for other compounds were synthesized from the principal glycoside of *A. orbiculatus*, cycloorbicoside A. The PMR and ^{13}C NMR spectra of 7-ketones **6** and **8** showed that one of the H-19 protons and C-19 experienced significant strong-field shifts and were located at δ –0.05 and 18.92–18.96.

EXPERIMENTAL

General comments have been published [6]. We used solvent systems $CHCl_3$:MeOH (50:1, 1; 25:1, 2) and $CHCl_3$:MeOH:H_2O (70:12:1).

PMR spectra were recorded on UNITYplus 400 (Varian) and Tesla BS-567A spectrometers using solutions in deuteropyridine (δ, ppm, 0 = HMDS); ^{13}C NMR spectra, on the UNITYplus spectrometer with full C–H decoupling and under DEPT conditions. Two-dimensional NMR spectra (^1H–^1H COSY, HSQC) were obtained using standard Varian programs. Chemical shifts of C atoms were measured relative to the β-C resonances of deuteropyridine (δ 123.493 vs. TMS).

Cycloorbicoside A (1) was the starting compound and was isolated from the aerial part of *A. orbiculatus* using the literature method [1]. $C_{35}H_{56}O_9$, mp 267–269°C (EtOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.17 and 0.60 (d, ^2J = 4.3, 2H-19), 0.75 (d, ^3J = 6.3, CH_3-21), 0.95, 1.10, 1.22, 1.26, 1.32, 1.35 (s, 6×CH_3), 1.46 (d, ^3J = 10.8, H-17), 1.73 (d, ^3J = 9.3, H-8), 2.49 and 2.67 (d, ^2J = 14, 2H-15), 3.40 (dd, $^3J_1$ = 11.8, $^3J_2$ = 4.3, H-3), 3.58 (d, ^3J = 1, H-24), 3.61 (dd, ^2J = 11.3, ^3J = 9.8, D-xylose H-5*a*), 3.69 (td, $^3J_1$ = $^3J_2$ = 10.8, $^3J_3$ = 3.7, H-7), 3.90 (dd, $^3J_1$ = 8.6, $^3J_2$ = 7.7, D-xylose H-2), 4.05 (t, $^3J_1$ = $^3J_2$ = 8.6, D-xylose H-3), 4.10 (ts, $^3J_1$ = $^3J_2$ = 8.7, $^3J_2$ = 5.3, D-xylose H-4), 4.24 (dd, ^2J = 11.1, ^3J = 5.2, D-xylose H-5e), 4.63 (br.d, ^3J = 8.7, H-23), 4.72 (d, ^3J = 7.6, D-xylose H-1).

Table 1 lists the ^{13}C NMR spectrum.

2′,3′,4′,7-Tetraacetate (2); 3′,4′,7-Triacetate (3); 2′,3′,4′-Triacetate (4); and 3′,4′-Diacetate (5) of Cycloorbicoside A from 1. Cycloorbicoside A (**1**, 1.034 g) in Py (10 mL) was treated with acetic anhydride (5 mL), left at 14°C for 1 h, and poured onto ice. The products were filtered, washed with water, dried (1.162 g), and chromatographed over a column of silica gel using system 1 to isolate **2** (96 mg), $C_{43}H_{64}O_{13}$, mp 201–203°C (MeOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.15 and 0.54 (d, ^2J = 4.5, 2H-19), 0.74 (d, ^3J = 6.8, CH_3-21), 0.78, 0.85, 1.04, 1.11, 1.29, 1.35 (s, 6×CH_3), 1.40 (d, ^3J = 10.8, H-17), 1.82 (d, ^3J = 10.2, H-8), 1.84, 1.98, 1.90, 1.99 (s, 4×Ac), 1.98 and 2.28 (d, ^2J = 14, 2H-15), 3.18 (dd, $^3J_1$ = 11.7, $^3J_2$ = 4.5, H-3), 3.52 (dd, ^2J = 11.6, ^3J = 9.8, D-xylose H-5*a*), 3.57 (d, ^3J = 0.9, H-24), 4.17 (dd, ^2J = 11.5, ^3J = 5.4, D-xylose H-5e), 4.61 (br.d, ^3J = 8.9, H-23), 4.73 (d, ^3J = 7.4, D-xylose H-1), 4.84 (td, $^3J_1$ = $^3J_2$ = 10.8, $^3J_3$ = 3.9, H-7), 5.19 (td, $^3J_1$ = $^3J_2$ = 9.7, $^3J_3$ = 5.4, D-xylose H-4), 5.30 (dd, $^3J_1$ = 9.5, $^3J_2$ = 7.4, D-xylose H-2), 5.57 (t, $^3J_1$ = $^3J_2$ = 9.2, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.16 and 0.54 (d, ^2J = 4, 2H-19), 0.74 (d, ^3J = 6, CH_3-21), 0.76, 0.84, 1.02, 1.10, 1.28, 1.33 (s, 6×CH_3), 1.86, 1.90, 1.92, 2.00 (s, 4×Ac), 3.16 (m, H-3), 3.52 (t, ^3J = ^2J = 10, D-xylose H-5*a*), 3.54 (s, H-24), 4.18 (dd, ^2J = 10, ^3J = 4, D-xylose H-5e), 4.58 (br.d, ^3J = 8, H-23), 4.73 (d, ^3J = 6, D-xylose H-1), 4.80 (m, H-7), 5.00–5.64 (m, D-xylose H-2, H-3, and H-4).

Continued elution of the column by the same solvent system isolated **3** (40 mg), $C_{41}H_{62}O_{12}$, mp 205–210°C (MeOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.17 and 0.58 (d, ^2J = 4.5, 2H-19), 0.74 (d, ^3J = 6.4, CH_3-21), 0.84, 1.03, 1.08, 1.12, 1.29, 1.34 (s, 6×CH_3), 1.40 (d, ^3J = 10.7, H-17), 1.45 (dd, $^3J_1$ = 13.3, $^3J_2$ = 4.1, H-5), 1.82 (d, ^3J = 10.2, H-8), 1.862, 1.877, 1.883 (s, 3×Ac), 1.97 and 2.26 (d, ^2J = 14, 2H-15), 3.29 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.3, H-3), 3.52 (dd, ^2J = 11.5, ^3J = 9.7, D-xylose H-5*a*), 3.56 (d, ^3J = 0.9, H-24), 3.91 (dd, $^3J_1$ = 9.4, $^3J_2$ = 7.4, D-xylose H-2), 4.18 (dd, ^2J = 11.5, ^3J = 5.5, D-xylose H-5e), 4.60 (br.d, ^3J = 8.8, H-23), 4.72 (d, ^3J = 7.4, D-xylose H-1), 4.85 (td, $^3J_1$ = $^3J_2$ = 10.8, $^3J_3$ = 4, H-7), 5.17 (td, $^3J_1$ = $^3J_2$ = 9.7, $^3J_3$ = 5.3, D-xylose H-4), 5.58 (t, $^3J_1$ = $^3J_2$ = 9.3, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.16 and 0.56 (d, ^2J = 4, 2H-19), 0.72 (d, ^3J = 4, CH_3-21), 0.82, 1.02, 1.06, 1.10, 1.28, 1.34 (s, 6×CH_3), 1.84, 1.86, 1.86 (s, 3×Ac), 3.28 (dd, $^3J_1$ = 10, $^3J_2$ = 4, H-3), 3.50 (t, ^3J = ^2J = 10, D-xylose H-5*a*), 3.54 (s, H-24), 3.90 (dd, $^3J_1$ = 8, $^3J_2$ = 7, D-xylose H-2), 4.18 (dd, ^2J = 12, ^3J = 5, D-xylose H-5e), 4.59 (br.d, ^3J = 10, H-23), 4.70 (d, ^3J = 7, D-xylose H-1), 4.83 (m, H-7), 5.16 (td, $^3J_1$ = $^3J_2$ = 9, $^3J_3$ = 4, D-xylose H-4), 5.58 (t, $^3J_1$ = $^3J_2$ = 10, D-xylose H-3).

Elution of the column with the same system isolated **4** (209 mg), $C_{41}H_{62}O_{12}$. Acetate **4** that was recrystallized from MeOH melted at 137°C, solidified at 140°C, and melted again at 246–247°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.15 and 0.56 (d, ^2J = 4, 2H-19), 0.76 (d, ^3J = 6.4, CH_3-21), 0.82 (s, CH_3-30), 0.92 (s, CH_3-29), 1.11 (s, CH_3-18), 1.26 (s, CH_3-26), 1.31 (s, CH_3-28), 1.35 (s, CH_3-27), 1.47 (d, ^3J = 10.8, H-17), 1.71 (d, ^3J = 9.8, H-8), 1.84, 1.91, 1.99 (s, 3×Ac), 2.49 and 2.68 (d, ^2J = 14, 2H-15), 3.22 (dd, $^3J_1$ = 11.8, $^3J_2$ = 5.5, H-3), 3.51 (dd, ^2J = 11.6, ^3J = 9.8, D-xylose H-5a), 3.58 (d, ^3J = 1, H-24), 3.67 (td, $^3J_1$ = $^3J_2$ = 10.8, $^3J_3$ = 3.6, H-7),

4.17 (dd, ^2J = 11.5, ^3J = 5.5, D-xylose H-5e), 4.63 (br.d, ^3J = 8.8, H-23), 4.75 (d, ^3J = 7.4, D-xylose H-1), 5.19 (td, $^3J_1 = {}^3J_2$ = 9.7, $^3J_3$ = 5.3, D-xylose H-4), 5.31 (dd, $^3J_1$ = 9.3, $^3J_2$ = 7.4, D-xylose H-2), 5.57 (t, $^3J_1 = {}^3J_2$ = 9.2, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.15 and 0.56 (d, ^2J = 4, 2H-19), 0.76 (d, ^3J = 5, CH_3-21), 0.81, 0.92, 1.10, 1.26, 1.31, 1.34 (s, 6×CH_3), 1.84, 1.90, 1.98 (s, 3×Ac), 2.58 (AB q, ^2J = 14, 2H-15), 3.22 (m, H-3), 3.50 (m, D-xylose H-5*a*), 3.56 (s, H-24), 3.60 (m, H-7), 4.18 (dd, ^2J = 11, ^3J = 5, D-xylose H-5e), 4.58 (br.d, ^3J = 9, H-23), 4.75 (d, ^3J = 7, D-xylose H-1), 5.00–5.64 (m, D-xylose H-2, H-3, and H-4).

Continued elution of the column by system 2 isolated **5** (220 mg), $C_{39}H_{60}O_{11}$, mp 140°C (MeOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.18 and 0.59 (d, ^2J = 4.3, 2H-19), 0.76 (d, ^3J = 6.4, CH_3-21), 0.88 (s, CH_3-30), 1.09 (s, CH_3-18), 1.14 (s, CH_3-29), 1.24 (s, CH_3-26), 1.29 (s, CH_3-28), 1.33 (s, CH_3-27), 1.87, 1.91 (s, 2×Ac), 2.45 and 2.63 (d, ^2J = 14.3, 2H-15), 3.34 (dd, $^3J_1$ = 11.7, $^3J_2$ = 4.4, H-3), 3.53 (dd, ^2J = 11.5, ^3J = 9.8, D-xylose H-5*a*), 3.57 (d, ^3J = 0.9, H-24), 3.67 (td, $^3J_1 = {}^3J_2$ = 10.2, $^3J_3$ = 3.4, H-7), 3.91 (dd, $^3J_1$ = 9.5, $^3J_2$ = 7.4, D-xylose H-2), 4.18 (dd, ^2J = 11.5, ^3J = 5.4, D-xylose H-5e), 4.60 (br.d, ^3J = 8.8, H-23), 4.75 (d, ^3J = 7.3, D-xylose H-1), 5.16 (td, $^3J_1 = {}^3J_2$ = 9.6, $^3J_3$ = 5.4, D-xylose H-4), 5.58 (t, $^3J_1 = {}^3J_2$ = 9.3, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.18 and 0.60 (d, ^2J = 4, 2H-19), 0.75 (d, ^3J = 4, CH_3-21), 0.88, 1.10, 1.14, 1.26, 1.31, 1.34 (s, 6×CH_3), 1.85, 1.90 (s, 2×Ac), 2.58 (AB q, ^2J = 14, 2H-15), 3.24 (m, H-3), 3.50 (m, D-xylose H-5*a*), 3.58 (s, H-24), 3.58 (m, H-7), 3.90 (t, $^3J_1 = {}^3J_2$ = 8, D-xylose H-2), 4.19 (dd, ^2J = 10, ^3J = 4, D-xylose H-5e), 4.62 (br.d, ^3J = 9, H-23), 4.73 (d, ^3J = 6, D-xylose H-1), 5.20 (m, D-xylose H-4), 5.60 (t, $^3J_1 = {}^3J_2$ = 9, D-xylose H-3).

Cycloorbicoside A 2′,3′,4′,7-Tetraacetate (2) from 1. Cycloorbicoside A (1.613 g) was acetylated by acetic anhydride (4 mL) in Py (16 mL) for 8 h at 18°C. Then the mixture was poured onto ice. The resulting precipitate was filtered, washed with water, and dried. Yield 1.987 g. The product was chromatographically pure **2**.

3-*O*-β-D-(2′,3′,4′-Tri-*O*-acetyl)-xylopyranoside-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloartan-3β,25-diol-7-one (6) from 4. A solution of **4** (202 mg) in acetone (20 mL) was cooled to –5°C, treated with Jones reagent (0.25 mL) [3], and stirred for 30 min at the same temperature. The excess of oxidant was decomposed by adding MeOH (1 mL). The mixture was diluted with water and extracted with $CHCl_3$. The solid left after the usual work up and evaporation of $CHCl_3$ was recrystallized from MeOH to afford **6** (130 mg), $C_{41}H_{60}O_{12}$, mp 313–315°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): –0.05 and 0.51 (d, ^2J = 5.5, 2H-19), 0.71 (d, ^3J = 6.3, CH_3-21), 0.79, 0.86, 0.90, 1.08, 1.27, 1.36 (s, 6×CH_3), 1.44 (d, ^3J = 10.5, H-17), 1.84, 1.92, 2.01 (s, 3×Ac), 1.96 and 2.57 (d, ^2J = 14, 2H-15), 2.32 (dd, ^2J = 18.8, ^3J = 5, H-6e), 2.76 (s, H-8), 3.20 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.3, H-3), 3.53 (d, ^3J = 0.7, H-24), 3.57 (dd, ^2J = 11.6, ^3J = 9.9, D-xylose H-5*a*), 4.21 (dd, ^2J = 11.6, ^3J = 5.4, D-xylose H-5e), 4.63 (br.d, ^3J = 8.6, H-23), 4.75 (d, ^3J = 7.5, D-xylose H-1), 5.21 (td, $^3J_1 = {}^3J_2$ = 9.6, $^3J_3$ = 5.4, D-xylose H-4), 5.33 (dd, $^3J_1$ = 9.4, $^3J_2$ = 7.5, D-xylose H-2), 5.59 (t, $^3J_1 = {}^3J_2$ = 9.3, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.54 (d, ^2J = 4, H-19), 0.70 (d, ^3J = 6, CH_3-21), 0.79, 0.86, 0.90, 1.08, 1.28, 1.36 (s, 6×CH_3), 1.84, 1.92, 2.02 (s, 3×Ac), 2.76 (s, H-8), 3.20 (m, H-3), 3.52 (s, H-24), 3.56 (t, $^2J = {}^3J$ = 10, D-xylose H-5*a*), 3.60 (m, H-7), 4.22 (dd, ^2J = 10, ^3J = 4, D-xylose H-5e), 4.58 (br.d, ^3J = 9, H-23), 4.78 (d, ^3J = 6, D-xylose H-1), 5.00–5.64 (m, D-xylose H-2, H-3, H-4).

3-*O*-β-D-Xylopyranoside-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloartan-3β,25-diol-7-one (8) from 6. Triacetate **6** (50 mg) was treated with NaOH (40 mg) solution in MeOH (5 mL), shaken vigorously until fully dissolved, left at 18°C for 1 h, poured into water, and extracted with EtOAc. The EtOAc extract was washed with water and evaporated. The solid was crystallized from MeOH to afford **8**, $C_{35}H_{54}O_9$, 35 mg, mp 240–242°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): –0.05 and 0.51 (d, ^2J = 5.5, 2H-19), 0.70 (d, ^3J = 6.4, CH_3-21), 0.88 (s, CH_3-28), 0.89 (s, CH_3-30), 1.10 (s, CH_3-18), 1.17 (s, CH_3-29), 1.27 (s, CH_3-26), 1.36 (s, CH_3-27), 1.43 (d, ^3J = 10.5, H-17), 1.96 and 2.57 (d, ^2J = 14, 2H-15), 2.76 (s, H-8), 3.38 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.3, H-3), 3.54 (d, ^3J = 0.9, H-24), 3.65 (dd, ^2J = 11.2, ^3J = 10, D-xylose H-5*a*), 3.93 (dd, $^3J_1$ = 8.7, $^3J_2$ = 7.6, D-xylose H-2), 4.06 (t, $^3J_1 = {}^3J_2$ = 8.7, D-xylose H-3), 4.14 (td, $^3J_1 = {}^3J_2$ = 8.7, $^3J_3$ = 5, D-xylose H-4), 4.28 (dd, ^2J = 11.2, ^3J = 5, D-xylose H-5e), 4.63 (ddd, $^3J_1$ = 10.5, $^3J_2$ = 1.3, $^3J_3$ = 0.7, H-23), 4.71 (d, ^3J = 7.6, D-xylose H-1).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.50 (d, ^2J = 4, H-19), 0.70 (d, ^3J = 6, CH_3-21), 0.88, 0.88, 1.10, 1.16, 1.26, 1.34 (s, 6×CH_3), 2.74 (s, H-8), 3.52 (s, H-24), 4.58 (br.d, ^3J = 8, H-23), 4.68 (d, ^3J = 7, D-xylose H-1).

3-*O*-β-D-Xylopyranoside of 7-*O*-Acetyl-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloartan-3β,7β,25-triol (7) from 2. Tetraacetate **2** (910 mg) in MeOH (25 mL) was treated with NaOH (321 mg) solution in MeOH (15 mL). A single product formed immediately. The mixture was diluted with water and extracted with EtOAc. The EtOAc extract was washed with water and evaporated. The solid was chromatographed over a column with elution by system 3 to afford **7** (650 mg), $C_{37}H_{58}O_{10}$, mp 246–249°C (MeOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.16 and 0.58 (d, ^2J = 4.5, 2H-19), 0.72 (d, ^3J = 6.4, CH_3-21), 0.91, 1.03, 1.12, 1.16, 1.30, 1.35 (s, 6×CH_3), 1.39 (d, ^3J = 10.9, H-17), 1.82 (d, ^3J = 9.6, H-8), 1.88 (s, Ac), 1.99 and 2.27 (d, ^2J = 14.7, 2H-15), 3.36 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.3, H-3), 3.57 (d, ^3J = 0.8, H-24), 3.64 (dd, ^2J = 11.2, ^3J = 10, D-xylose H-5*a*), 3.85 (dd, $^3J_1$ = 8.6, $^3J_2$ = 7.6, D-xylose H-2), 4.04 (t, $^3J_1$ = $^3J_2$ = 8.8, D-xylose H-3), 4.11 (td, $^3J_1$ = $^3J_2$ = 9.5, $^3J_3$ = 5, D-xylose H-4), 4.25 (dd, ^2J = 11.2, ^3J = 5, D-xylose H-5e), 4.62 (br.d, ^3J = 8.8, H-23), 4.72 (d, ^3J = 7.5, D-xylose H-1), 4.87 (td, $^3J_1$ = $^3J_2$ = 10.7, $^3J_3$= 4, H-7).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.20 and 0.60 (d, ^2J = 4, 2H-19), 0.74 (d, ^3J = 5, CH_3-21), 0.88, 1.02, 1.08, 1.10, 1.25, 1.30 (s, 6×CH_3), 1.90 (s, Ac), 3.30 (m, H-3), 3.52 (s, H-24), 4.52 (br.d, ^3J = 9, H-23), 4.68 (d, ^3J = 7, D-xylose H-1), 4.80 (m, H-7).

Peracetate of 3*O*-β-D-Xylopyranoside-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloart-25(26)-en-3β,7β-diol (9) from 2. Tetraacetate **2** (300 mg) in Py (2 mL) was treated with benzenesulfonylchloride (2 mL), left at room temperature for 12 h, and poured onto ice. The resulting precipitate was filtered off, washed with water and dried. Recrystallization from MeOH afforded **9** (237 mg), $C_{43}H_{62}O_{12}$, mp 184–187°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.16 and 0.53 (d, ^2J = 4.6, 2H-19), 0.73 (d, ^3J = 6.4, CH_3-21), 0.78, 0.84, 1.02, 1.10, 1.64 (s, 5×CH_3), 1.37 (d, ^3J = 10.8, H-17), 1.78 (d, ^3J = 10, H-8), 1.85, 1.91, 1.92, 2.00 (s, 4×Ac), 2.05 and 2.28 (d, ^2J = 14, 2H-15), 3.19 (dd, $^3J_1$ = 11.9, $^3J_2$ = 4.6, H-3), 3.54 (dd, ^2J = 11.6, ^3J = 9.9, D-xylose H-5*a*), 3.96 (s, H-24), 4.16 (dd, $^3J_1$ = 9, $^3J_2$ = 1.6, H-23), 4.18 (dd, ^2J = 11.5, ^3J = 5.5, D-xylose H-5e), 4.75 (d, ^3J = 7.5, D-xylose H-1), 4.80 (narrow m, H-26A), 4.84 (td, $^3J_1$ = $^3J_2$ = 10.7, $^3J_3$ = 4, H-7), 5.04 (narrow m, H-26B), 5.18 (td, $^3J_1$ = $^3J_2$ = 9.7, $^3J_3$ = 5.4, D-xylose H-4), 5.30 (dd, $^3J_1$= 9.5, $^3J_2$ = 7.4, D-xylose H-2), 5.58 (t, $^3J_1$ = $^3J_2$ = 9.2, D-xylose H-3).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.16 and 0.54 (d, ^2J = 4, 2H-19), 0.74 (d, ^3J = 4, CH_3-21), 0.78, 0.84, 1.02, 1.10, 1.64 (s, 5×CH_3), 1.84, 1.90, 1.92, 1.99 (s, 4×Ac), 3.20 (m, H-3), 3.54 (m, D-xylose H-5a), 3.96 (s, H-24), 4.72 (d, ^3J = 6, D-xylose H-1), 4.80 and 5.02 (br.s, 2H-26), 5.00–5.64 (m, D-xylose H-2, H-3, H-4).

3-*O*-β-D-Xylopyranoside of 7-*O*-Acetyl-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloart-25(26)-en-3β,7β-diol (10) from 9. Peracetate **9** (1.122 g) in MeOH (75 mL) was treated with NaOH (324 mg) solution in MeOH (30 mL), stirred at room temperature for 10 min, poured into water, and extracted with EtOAc. After the usual work up and evaporation of EtOAc, the solid was recrystallized from $CHCl_3$:MeOH (1:1) to afford **10** (606 mg), $C_{37}H_{56}O_9$, mp 243–245°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.19 and 0.57 (d, ^2J = 4.5, 2H-19), 0.73 (d, ^3J = 6.4, CH_3-21), 0.91, 1.02, 1.11, 1.14 (s, 4×CH_3), 1.36 (d, ^3J = 10.8, H-17), 1.50 (dd, $^3J_1$ = 12.8, $^3J_2$ = 4, H-5), 1.64 (dd, $^4J_1$ = 1.2, $^4J_2$ = 0.9, CH_3-27), 1.80 (d, ^3J = 10, H-8), 1.91 (s, Ac), 2.02 and 2.26 (d, ^2J = 14.6, 2H-15), 3.34 (dd, $^3J_1$ = 11.7, $^3J_2$ = 4.4, H-3), 3.62 (dd, ^2J = 11.1, ^3J = 9.7, D-xylose H-5*a*), 3.88 (dd, $^3J_1$ = 8.7, $^3J_2$ = 7.5, D-xylose H-2), 3.96 (s, H-24), 4.03 (t, $^3J_1$ = $^3J_2$ = 8.6, D-xylose H-3), 4.09 (td, $^3J_1$ = $^3J_2$ = 9.8, $^3J_3$ = 5.2, D-xylose H-4), 4.15 (dd, $^3J_1$ = 9.3, $^3J_2$ = 1.5, H-23), 4.23 (dd, ^2J = 11.1, ^3J = 4.8, D-xylose H-5e), 4.70 (d, ^3J = 7.5, D-xylose H-1), 4.80 (dq, ^2J = ^4J = 1.2, H-26A), 4.86 (td, $^3J_1$ = $^3J_2$ = 10.8, $^3J_3$ = 3.9, H-7), 50.3 (dq, ^2J = 1.2, ^4J = 0.9, H-26B).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.20 and 0.60 (d, ^2J = 4, 2H-19), 0.74 (d, ^3J = 4, CH_3-21), 0.88, 1.00, 1.10, 1.12, 1.62 (s, 5×CH_3), 1.90 (s, Ac), 3.32 (m, H-3), 3.94 (s, H-24), 4.68 (d, ^3J = 7, D-xylose H-1), 4.76 and 4.99 (br.s, 2H-26), 4.84 (m, H-7).

3-*O*-β-D-Xylopyranoside-(23*R*,24*S*)-16β,23;16α,24-diepoxycycloart-25(26)-en-3β,7β-diol (11) from 10. Monoacetate **10** (52 mg) in MeOH (10 mL) was treated with NaOH (52 mg) solution in MeOH (5 mL), stirred at 28–30°C for 7 d, poured into water, and extracted with EtOAc. The EtOAc extract was washed with water and evaporated. The solid was recrystallized from EtOAc to afford **11** (42 mg), $C_{35}H_{54}O_8$, mp 246–247°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.17 and 0.60 (d, ^2J = 4.3, 2H-19), 0.74 (d, ^3J = 6.4, CH_3-21), 0.95 (s, CH_3-30), 1.09 (s, CH_3-18), 1.22 (s, CH_3-29), 1.31 (d, ^4J = 1, CH_3-28), 1.44 (d, ^3J = 11.2, H-17), 1.59 (dd, $^4J_1$ = 1.3, $^4J_2$ = 1, CH_3-27), 1.74 (d, ^3J = 9.5, H-8), 2.51 (dq, ^2J = 14.3, ^4J = 1.1, H-15β), 2.74 (d, ^2J = 14.3, H-15α), 3.40 (dd,

$^3J_1$ = 11.6, $^3J_2$ = 4.3, H-3), 3.62 (dd, ^2J = 11.3, ^3J = 10, D-xylose H-5*a*), 3.69 (td, $^3J_1 = {}^3J_2$ = 9.6, $^3J_3$ = 3.8, H-7), 3.92 (dd, $^3J_1$ = 8.8, $^3J_2$ = 8.6, D-xylose H-3), 4.119 (td, $^3J_1 = {}^3J_2$ = 8.6, $^3J_3$ = 5.4, D-xylose H-4), 4.121 (ddd, $^3J_1$ = 7.3, $^3J_2$ = 1.8, $^3J_3$ = 1.1, H-23), 4.25 (dd, ^2J = 11.2, ^3J = 5.2, D-xylose H-5e), 4.72 (narrow m, H-26A), 4.74 (d, ^3J = 7.6, D-xylose H-1), 5.02 (narrow m, H-26B).

Table 1 lists the ^{13}C NMR spectrum.

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.18 and 0.62 (d, ^2J = 4, 2H-19), 0.76 (d, ^3J = 4, CH_3-21), 0.94, 1.10, 1.20, 1.30, 1.60 (s, 5×CH_3), 2.60 (AB q, ^2J = 16, 2H-15), 3.96 (s, H-24), 4.72 (d, ^3J = 6, D-xylose H-1), 4.72 and 4.98 (br.s, 2H-26).

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