Triterpenoids from the Aerial Parts of *Kalidium foliatum*

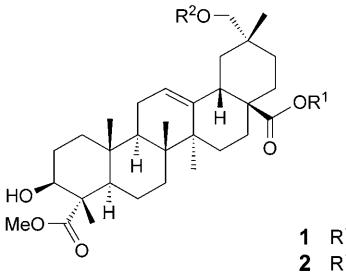
by **Bina Shaheen Siddiqui**[*a]), **Zhanat Zhymabekovna Karzhaubekova**[b]), **Gauhar Shahmanovna Burasheva**[b]), and **Nurgyl Adaibaevna Sultanova**[b])

[a]) International Centre for Chemical Sciences, H.E.J. Research Institute of Chemistry, and Dr. Panjwani Center for Molecular Medicine and Drug Research, University of Karachi, Karachi-75270, Pakistan (phone: +92-21-4824935; fax; 92-21-4819018-19; e-mail: bina@khi.comsats.net.pk)

[b]) Al-Farabi Kazakh National University, Chemistry Department, Almaty-050020, Kazakhstan

Studies on the chemical constituents of the aerial parts of *Kalidium foliatum* led to the isolation of three new olean-12-ene-23,28-dioic acids in their either partly or fully esterified forms (Me or glucosyl (Glc) esters), which were named kalidiumoside A (**1**), kalidiumin (**2**), and kalidiumoside B (**3**). Their structures were elucidated through spectral studies including 2D-NMR experiments (HMQC, HMBC, COSY, NOESY) and *J*-resolved spectra. Also isolated were the two known compounds dianic acid and dianoside F, which were identified through comparison of their spectroscopic data with those reported in the literature.

Introduction. – *Kalidium* is a genus within the family Chenopodiaceae, with five species thriving in soils of high mineral concentration, mainly growing in the plains of Southeast Europe, Central and Southwest Asia, southern Siberia, East China, Mongolia, and Kazakhstan [1]. In Kazakhstan, only three *Kalidium* species are known [2][3]: *K. caspicum* (L.), *K. foliatum* (PALL.), and *K. Schrenkianum* (BGE.) (endem.). In continuation of our work on chemical constituents of Kazakh medicinal plants [4–6], we herein report some secondary metabolites isolated from the aerial parts of *K. foliatum*, which has not been investigated phytochemically before. We isolated three new constituents, compounds **1**–**3**, together with two known ones, dianic acid and dianoside F [7][8].



Glc = β-D-Glucopyranosyl

1 R^1 = Glc R^2 = H
2 R^1 = H R^2 = H
3 R^1 = Glc R^2 = Ac

Results and Discussion. – The molecular formula of **1** was established as $C_{37}H_{58}O_{11}$ by negative-ion FAB-MS (*m*/*z* 677 ([*M* – H]$^-$)), corresponding to eight degrees of unsa-

turation. The compound was optically active, with $[\alpha]_D^{26} = +6.0$ ($c = 1.0$, MeOH). The IR spectrum showed characteristic absorption bands for OH (3241) and ester C=O (1744 cm^{-1}) groups. By means of in-depth ^{1}H- and ^{13}C-NMR experiments, including COSY, NOESY, HMQC, and HMBC spectra, the structure of **1** was derived as β-D-glucopyranosyl (3β)-3,29-dihydroxy-23-methoxy-23-oxoolean-12-en-28-oate, and named *kalidiumoside A*. This proposal was substantiated by various fragment ions observed in the EI mass spectrum (*Fig. 1*) [9], as well as by acetylation of **1** with Ac_2O/pyridine to obtain the peracetylated (six Ac groups) derivative (see *Exper. Part*).

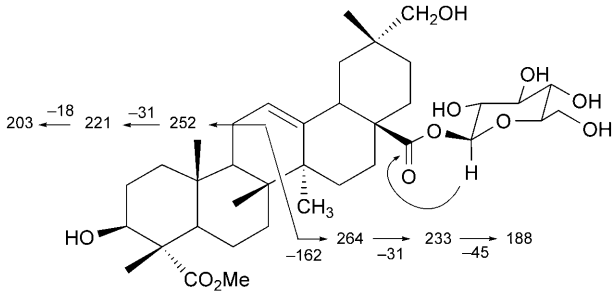


Fig. 1. *Diagnostic EI-MS fragment ions of* **1**

The ^{1}H- and ^{13}C-NMR spectra of **1** (*Table 1*) revealed the presence of one C=C bond, two oxygenated C-atoms, two C=O groups, seven quaternary C-atoms, and five Me groups located on quaternary C-atoms, in addition to a glucosyl (Glc) moiety. In the ^{1}H-NMR spectrum, the downfield shift for H–C(3) indicated that C(23) was part of a carboxy group [7], as suggested by δ(C) 177.9 (C(23)) and 52.1 (MeO). The resonance at δ(C) 52.1 showed a HMQC cross-peak with the MeO H-atoms at δ(H) 3.67. Further HMBC cross-peaks were found between δ(C) 178.2 and δ(H) 3.67. These data, along with an olefinic H-atom at δ(H) 5.26 (br. *t*, H–C(12)) and a methine at δ(H) 2.86 (*dd*, $J = 13.0$, 3.0 Hz, H–C(18)) suggested that **1** was a Δ^{12} oleanane-type triterpenoid [10].

The MS fragment ion at *m*/*z* 515 ($[M - H - 162]^-$) and the NMR data of **1** (*Table 1*) further indicated a β-glucoside. The anomeric sugar H-atom, H–C(1′), resonated at δ(H) 5.37 (*d*, $J = 8.0$ Hz) and δ(C) 95.7, and showed long a-range connectivity with C(28) at δ 179.9 in the HMBC spectrum. The NMR shifts of the Glc moiety matched well with those reported for a β-D-glucopyranosyl unit [11]. This was corroborated by acid hydrolysis (see *Exper. Part*), which yielded β-D-glucose according to thin-layer-chromatographic (TLC) and optical-rotation-dispersion (ORD) analyses.

An intense EI-MS fragment at *m*/*z* 264, resulting from a *retro-Diels–Alder* cleavage within ring *C* from the fragment at *m*/*z* 516 ($[M - 162]$), manifested that the second OH group was located on rings *D* or *E*. It was finally placed at C(29) based on the NMR resonance at δ(H) 3.18 (*s*, 2 H) [9], and according to key HMBC correlations (*Fig. 2*). All assignments were made with the help of 2D-NMR (COSY, NOESY, HMQC, and HMBC) spectroscopy, and compared well with the values of related partial structures reported in the literature [8][11–13]. It is worth mentioning that, in the ^{1}H-NMR spectrum of the hexaacetyl derivative of **1**, H_a–C(29) and H_b–C(29) resonated as two distinct *doublet*s at δ(H) 3.73 and 3.65 ($J = 10.9$ Hz), rather than as a *singlet* reported earlier in the case of 29-*O*-acetyl triterpenes [12].

The molecular formula of compound **2** was $C_{31}H_{48}O_6$ according to HR-EI-MS (M^+ at *m*/*z* 516.3450), in accord with eight degrees of unsaturation. The compound was also optically active ($[\alpha]_D^{26} = +97.7$ ($c = 1.0$, MeOH)). The IR spectrum indicated C=O (1734 and 1740), OH (3420), and C=C (1620 cm^{-1}) moieties. Based on the 2D-NMR

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1**. At 400 (^{1}H) and 100 MHz (^{13}C), resp., in CD_3OD; δ in ppm, J in Hz.

Atom	δ(H)	δ(C)	HMBC
CH_2(1)	1.01–1.06 (*m*)	39.7	
	1.62–1.66 (*m*)		
CH_2(2)	1.01–1.06 (*m*)	28.9	
	1.75–1.80 (*m*)		
H–C(3)	3.91 (*t*, *J* = 7.1)	73.9	C(23), C(24)
C(4)		37.5	
H–C(5)	1.46–1.50 (*m*)	52.8	
CH_2(6)	1.54–1.59 (*m*)	22.2	
	1.65–1.71 (*m*)		
CH_2(7)	1.15–1.19 (*m*)	29.2	
	1.43–1.49 (*m*)		
C(8)		41.0	
H–C(9)	1.65–1.71 (*m*)	47.5	
C(10)		37.5	
CH_2(11)	1.55–1.62 (*m*)	27.3	
H–C(12)	5.26 (br. *t*, *J* = 3.4)	123.6	C(9), C(14)
C(13)		144.8	
C(14)		42.9	
CH_2(15)	1.01–1.07 (*m*)	24.5	
	2.15–2.25 (*m*)		
CH_2(16)	1.89–1.93 (*m*)	23.9	
	2.15–2.25 (*m*)		
C(17)		55.3	
H–C(18)	2.88 (*dd*, *J* = 13.0, 3.0)	41.8	C(12), C(14), C(28)
CH_2(19)	1.07–1.10 (*m*)	41.4	
	1.78–1.82 (*m*)		
C(20)		36.7	
CH_2(21)	1.65–1.71 (*m*)	32.4	
CH_2(22)	1.25–1.45 (*m*)	33.5	
C(23)		177.9	
Me(24)	1.09 (*s*)	11.5	C(3), C (5), C(23)
Me(25)	0.95 (*s*)	16.3	C(1), C(5)
Me(26)	0.77 (*s*)	17.5	C(9), C(14)
Me(27)	1.16 (*s*)	26.3	C(8), C(13), C(15)
C(28)		179.9	
CH_2(29)	3.18 (*s*)	74.3	C(21), C(30)
Me(30)	0.91 (*s*)	19.5	C(19), C(21), C(29)
MeO	3.67 (*s*)	52.4	C(23)
H–C(1′)	5.37 (*d*, *J* = 8.0)	95.7	C(28)
H–C(2′)	3.33–3.36 (*m*)	76.4	
H–C(3′)	3.37–3.39 (*m*)	78.3	
H–C(4′)	3.30–3.32 (*m*)	78.7	
H–C(5′)	3.32–3.33 (*m*)	71.1	
CH_2(6′)	3.81 (*dd*, *J* = 11.5, 4.5)	62.0	
	3.65 (*dd*, *J* = 11.6, 3.1)		

spectra, the structure of **2** was established as (3β)-3,29-dihydroxy-23-methoxy-23-oxo-olean-12-en-28-oic acid, and named *kalidiumin*.

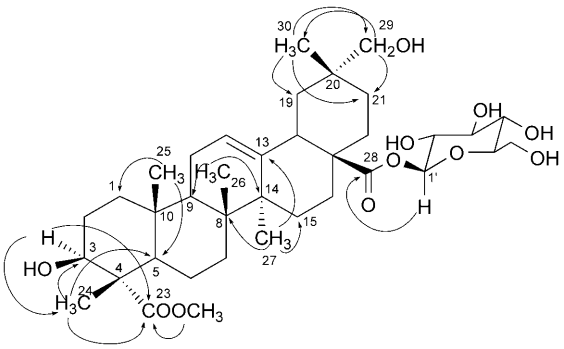


Fig. 2. *Key HMBC correlations of* **1**

The ^{1}H- and ^{13}C-NMR data of compound **2** (*Table 2*) showed that it differed from **1** only in lacking the Glc moiety. This was further supported by acetylation, which yielded the corresponding diacetyl derivative (see *Exper. Part*). All 2D-NMR assignments were made with the help of *J*-resolved, HMBC, HMQC, COSY, and NOESY spectra, and by comparison with the values of related partial structures reported in the literature [7].

The configuration of **2** and the assignments of the Me groups were based on NOE difference spectra. Thus, irradiation of H–C(26) at δ(H) 0.80 enhanced the Me(30), Me(25), and H–C(18) resonances at δ(H) 0.95, 0.91, and 2.88, respectively; and irradiation of Me(25) enhanced the signals of Me(24) and Me(26) at δ(H) 1.09 and 0.80, respectively. Similarly, irradiation of Me(27) at δ(H) 1.17 caused enhancement of the MeO resonance at δ(H) 3.67 and of CH_2(29) at 3.18. A further notable observation was the separation of the resonances for CH_2(29) as two *AB*-type doublets (δ(H) 3.79, 3.70 ($^2J = 11.1$ Hz)) in the ^{1}H-NMR spectrum of the diacetyl derivative of **2**.

Compound **3** was assigned the molecular formula $C_{39}H_{60}O_{12}$, based on HR-EI-MS (M^+ at *m*/*z* 516.3450) and ^{13}C-NMR (DEPT) spectroscopy. The compound was optically active, with $[\alpha]_D^{26} = +67.90$ ($c = 1.3$, MeOH). The IR spectrum showed absorption bands for C=O (1734, 1740), OH (3420), and C=C (1620 cm^{-1}) moieties. The ^{13}C-NMR spectrum (*Table 3*) led to the identification of five Me, eleven CH_2, and five CH groups, as well as nine quaternary C-atoms, together with a Glc, a MeO, and an AcO group. These data, in combination with 2D-NMR experiments (*Table 3*), helped to identify compound **3** as β-D-glucopyranosyl (3β)-29-acetoxy-3-hydroxy-23-methoxy-23-oxo-olean-12-en-28-oate, which was named *kalidiumoside B*.

The triterpenoid nature of **3** was indicated by the presence of five Me *singlet*s at δ(H) 0.95, 1.02, 1.20, 1.25, and 1.63 in the ^{1}H-NMR spectrum (*Table 3*), which were assigned to C(25), C(26), C(30), C(27), and C(24), respectively, on the basis of 1D- and 2D-NMR analyses. The resonance at δ(H) 3.22 (*dd*, $J = 13.0$, 3.0, H–C(18)) indicated a β-amyrin skeleton [10]. The olefinic resonance at δ(H) 5.45 (br. *t*) was characteristic for H–C(12) in a pentacyclic triterpene. The resonance at δ(H) 2.47 (*s*, 3 H) was ascribed to an AcO group, and that at 3.72 (*s*, 3 H) was due to a MeO function. In the HMBC spectrum (*Fig. 3*), the resonance at δ(H) 2.47 showed a long-range connectivity with at δ(C) 170.8 (acetyl C=O). Further, two H-atoms were present at δ(H) 3.83 (*d*, $J = 10.6$) and 3.94 (*d*, $J = 10.6$ Hz) showing a cross-peak with δ(C) 74.8, and HMBC long-range connectivities with C(19), C(21), C(30), and the C=O group of Ac at δ(C) 41.6, 27.6, 19.1, and 170.8, respectively.

Table 2. *^{1}H- and ^{13}C-NMR Data of* **2**. At 400 (^{1}H) and 100 MHz (^{13}C), resp., in CD_3OD; δ in ppm, J in Hz.

Atom	δ(H)	δ(C)	HMBC
CH_2(1)	1.01–1.05 (*m*)	38.0	
	1.63–1.66 (*m*)		
CH_2(2)	1.60–1.63 (*m*)	26.3	
H–C(3)	3.93 (*t*, *J* = 7.1)	75.5	C(23), C(24)
C(4)		53.7	
H–C(5)	1.45–1.52 (*m*)	51.1	
CH_2(6)	0.99–1.02 (*m*)	21.2	
	1.43–1.48 (*m*)		
CH_2(7)	1.20–1.27 (*m*)	32.1	
	1.46–1.49 (*m*)		
C(8)		41.5	
H–C(9)	1.66–1.70 (*m*)	47.6	
C(10)		36.5	
CH_2(11)	1.58–1.62 (*m*)	22.8	
H–C(12)	5.21 (br. *t*, *J* = 3.4)	122.6	C(18)
C(13)		143.3	
C(14)		39.5	
CH_2(15)	1.01–1.14 (*m*)	28.1	
	1.38–1.42 (*m*)		
CH_2(16)	1.82–1.91 (*m*)	23.3	
C(17)		46.7	
H–C(18)	2.88 (*dd*, *J* = 13.7, 4.0)	40.0	C(12), C(14), C(28)
CH_2(19)	1.10–1.12 (*m*)	41.5	
	1.78–1.82 (*m*)		
C(20)		35.7	
CH_2(21)	1.12–1.16 (*m*)	27.6	
	1.43–1.48 (*m*)		
CH_2(22)	1.53–1.60 (*m*)	31.5	
	1.72–1.78 (*m*)		
C(23)		178.2	
Me(24)	1.09 (*s*)	10.8	C(3), C(23)
Me(25)	0.91 (*s*)	15.7	C(5), C(9)
Me(26)	0.80 (*s*)	17.5	C(7), C(9), C(14)
Me(27)	1.17 (*s*)	26.0	C(13)
C(28)		183.2	
CH_2(29)	3.18 (*s*)	74.2	C(19), C(30)
Me(30)	0.95 (*s*)	18.9	C(29)
MeO	3.67 (*s*)	52.1	C(23)

In the HMBC spectrum of **3**, the MeO H-atoms at δ(H) 3.72 had a connectivity with δ(C) 178.6 (C(23)). The anomeric H-atom at δ(H) 6.34 (*d*, *J* = 8.4 Hz) was connected to C(1′) at δ(C) 95.8, indicating a β-D-glucopyranosyl (Glc) moiety, as further confirmed by acidic hydrolysis, followed by TLC and ORD analyses. Further, H–C(1′) showed a long-range connectivity with C(28) at δ(C) 178.6.

All 2D-NMR assignments were made with the help of *J*-resolved, HMBC, HMQC, COSY, and NOESY experiments, and by comparison with related partial structures reported in the literature [7] [8]. The relative configurations of the stereogenic centers were inferred from NOE difference spectra. Thus, irradiation of H–C(18) at δ(H) 3.22 enhanced the signals of Me(30) (δ(H) 1.20) and Me(26) (δ(H) 1.02); irradiation of Me(25) (δ(H) 0.95) enhanced the signals of Me(24) (δ(H) 1.63) and Me(26) (δ(H)

Table 3. *^{1}H- and ^{13}C-NMR Data of* **3**. At 400 (^{1}H) and 75 MHz (^{13}C), resp., in (D_5)pyridine; δ in ppm, J in Hz.

Atom	δ(H)	δ(C)	HMBC
CH_2(1)	1.01–1.08 (*m*)	38.8	
	1.60–1.62 (*m*)		
CH_2(2)	1.90–1.95 (*m*)	28.9	
H–C(3)	4.67 (*t*, *J* = 7.0)	75.2	C(23), C(24)
C(4)		54.8	
H–C(5)	1.96–2.02 (*m*)	52.1	
CH_2(6)	1.55–1.59 (*m*)	21.6	
	1.68–1.72 (*m*)		
CH_2(7)	1.60–1.62 (*m*)	31.4	
	1.28–1.30 (*m*)		
C(8)		41.2	
H–C(9)	1.83–1.86 (*m*)	40.7	
C(10)		36.8	
CH_2(11)	1.95–2.15 (*m*)	23.3	
H–C(12)	5.45 (br. *t*, *J* = 3.2)	123.1	C(14)
C(13)		143.7	
C(14)		42.0	
CH_2(15)	1.11–1.14 (*m*)	28.7	
	2.28–2.32 (*m*)		
CH_2(16)	2.10–2.18 (*m*)	28.1	
C(17)		54.8	
H–C(18)	3.22 (*dd*, *J* = 13.0, 3.0)	40.7	C(12), C(28)
CH_2(19)	1.49–1.51 (*m*)	41.6	
	2.05–2.09 (*m*)		
C(20)		34.6	
CH_2(21)	1.73–1.78 (*m*)	27.6	
	1.36–1.39 (*m*)		
CH_2(22)	1.85–1.89 (*m*)	32.8	
C(23)		176.1	
Me(24)	1.63 (*s*)	11.8	C(3), C(23)
Me(25)	0.95 (*s*)	16.0	C(1), C(5)
Me(26)	1.02 (*s*)	17.3	C(9), C(14)
Me(27)	1.25 (*s*)	25.9	C(8), C(13), C(15)
C(28)		178.6	
CH_2(29)	3.83 (*d*, *J* = 10.6)	74.8	C(19)
	3.94 (*d*, *J* = 10.6)		C(21), C(30)
Me(30)	1.20 (*s*)	19.1	C(19), C(21), C(29)
MeO	3.72 (*s*)	51.7	C(23)
AcO	2.47 (*s*)	23.4	
		170.8	
H–C(1′)	6.34 (*d*, *J* = 8.1)	95.8	C(28)
H–C(2′)	4.20 (*t*, *J* = 8.3)	74.7	
H–C(3′)	4.05 (*t*, *J* = 8.0)	79.3	
H–C(4′)	4.36 (*t*, *J* = 8.8)	71.1	
H–C(5′)	4.28 (*t*, *J* = 8.3)	78.9	
CH_2(6′)	3.81 (*dd*, *J* = 10.8, 4.6)	62.2	
	3.65 (*dd*, *J* = 10.9, 3.0)		

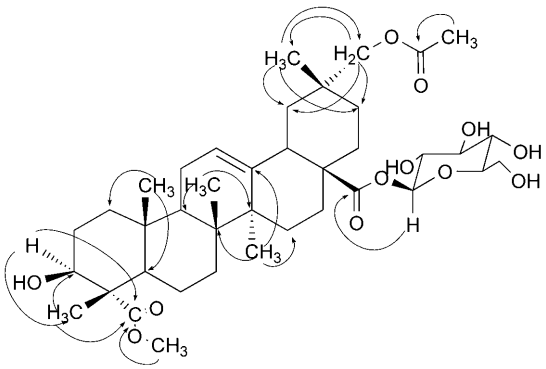


Fig. 3. *Key HMBC correlations of* **3**

1.02); and irradiation of H–C(3) (δ(H) 4.67) enhanced the MeO resonance (δ(H) 3.72). The NOE between Me(30) and H–C(18) was particularly important for locating the OH group at C(29). Interestingly, the CH_2(29) ^{1}H-NMR resonances appeared as two *AB*-type *doublet*s, as observed in the case of the peracetylated derivatives of **1** and **2** (see above). In one report, however, these resonances had been described as a *singlet* (2 H) in the 29-*O*-acetyl derivative [12].

This is the first report of the isolation of compounds **1**–**3** as *natural* constituents. Actually, **1** and **2** had been reported earlier as *synthetic* derivatives of dianoside F [7]. The two known compounds were identified as dianic acid and dianoside F (data not shown) through comparison of their spectroscopic data with those reported in the literature [7][8].

Z. Z. K. thanks COMSTECH for covering travel support, fellowship, and living expenses for six months during her visit at H.E.J., where these studies were undertaken.

Experimental Part

General. Hexanes had a b.p. of 60–80°. Column chromatography (CC): *Merck* silica gel *60* (70–230 mesh, 0.063–0.200 mm). Flash chromatography (FC): *Merck* silica gel *9385* (0.040–0.063 mm). Prep. TLC: *Merck* silica gel *60* PF_{254}; visualization under UV light and by exposure to I_2 or cerium sulfate soln. UV Spectra: *Hitachi U-3200 spectrophotometer*; λ_{max} (log ε) in nm. Optical rotation: *Jasco DIP-360* polarimeter. IR spectra: *Jasco A-302* spectrophotometer, KBr samples; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AMX-500* or *AM-400* apparatus; chemical shifts δ in ppm, coupling constants *J* in Hz. EI-MS: *Finnigan Mat-311A* mass spectrometer; source at 250°, 70 eV; in *m*/*z* (rel. %). FAB- and HR-EI-MS: *Jeol JMS-HX-110* mass spectrometer.

Plant Material. The aerial parts of *Kalidium foliatum* were collected from the Almaty region during August 2004, and were identified by Mr. *A. Aleshkovskii*, Department of Botany, Al-Farabi Kazakh National University, Kazakhstan.

Extraction and Isolation. The air-dried parts of *K. foliatum* (5 kg) were extracted with MeOH (3×) at r.t. The combined extract was concentrated under vacuum, and partitioned between AcOEt and H_2O. The org. phase was dried (Na_2SO_4), decolored over charcoal, filtered, and concentrated under vacuum. The syrupy residue obtained was further divided into hexane-soluble and -insoluble fractions.

The latter part (35 g) was subjected to FC (SiO_2; $CHCl_3$/MeOH gradient of increasing polarity): fractions *Fr. A–J. Fr. C* (2.5 g) was subjected to CC (SiO_2 *60*; $CHCl_3$/AcOEt gradient): *Fr. C1–C15. Fr. C2* was purified by prep. TLC (SiO_2; $CHCl_3$/MeOH 9:1) to furnish **1** (70 mg). *Fr. C3* was also purified by

prep. TLC (SiO_2; $CHCl_3$/MeOH 95:5) to afford **2** (15 mg). Compound **3** (10 mg) was isolated from *Fr. C6* by prep. TLC (SiO_2; $CHCl_3$/MeOH 95:5). Dianic acid (8 mg) and dianoside F (16 mg) were isolated from *Fr. C4* by prep. TLC (SiO_2; $CHCl_3$/MeOH 85:15).

Kalidiumoside A (=*β*-D-*Glucopyranosyl (3β)-3,29-Dihydroxy-23-methoxy-23-oxoolean-12-en-28-oate*; **1**). Colorless, amorphous powder. UV (MeOH): 203.8 (3.69). $[\alpha]_D^{26} = +6.0$ ($c = 1.0$, MeOH). IR (KBr): 3241, 1744. ^{1}H- and ^{13}C-NMR Spectra (CD_3OD): see *Table 1*. ^{1}H-NMR ($CDCl_3$): 0.67, 0.84, 0.86, 1.04, 1.06 (5*s*, 5 Me); 2.88 (*dd*, $J = 13.0$, 3.6, H–C(18)); 3.17 (*s*, CH_2(29)); 3.31–3.38 (*m*, H–C(2′) to H–C(4′)); 3.63 (*s*, MeO); 3.71 (*d*, $J = 11.6$, H_a–C(6′)); 3.75 (*d*, $J = 10.3$, H_b–C(6′)); 3.89 (*dd*, $J = 11.0$, 4.8, H–C(3)); 5.23 (br. *t*, H–C(12)); 5.33 (*d*, $J = 7.6$, H–C(1′)). FAB-MS (neg.): 677 ($[M-H]^-$), 515. EI-MS (pos.): 516 (3.3, $[M-162]^+$), 264 (93.8), 233 (100), 219 (11.2), 201 (80.3), 187 (28.5). HR-EI-MS (pos.): 516.3450 ($C_{31}H_{48}O_6^+$; calc. 516.3452).

Acetylation of **1**. To a soln. of **1** (8.0 mg) in anh. pyridine (0.5 ml), Ac_2O (1 ml) was added, and the mixture was left standing at r.t. overnight. The mixture was poured on crushed ice, and extracted with AcOEt. After usual workup and purification by prep. TLC (SiO_2; $CHCl_3$), the hexaacetyl derivative (6 mg) of **1** was obtained as an amorphous powder. IR (KBr): 1744 (br.). ^{1}H-NMR ($CDCl_3$) 0.68, 0.91, 0.94, 1.08, 1.15 (5*s*, 5 Me); 1.94, 1.96, 1.97, 1.99 (4*s*, 4 AcO); 2.03 (*s*, 2 AcO); 2.88 (*dd*, $J = 13.0$, 3.6, H–C(18)); 3.62 (*s*, MeO); 3.65 (*d*, $J = 10.9$, H_b–C(29)); 3.73 (*d*, $J = 10.9$, H_a–C(29)); 3.99 (br. *d*, $J = 10.3$, H_b–C(6′)); 4.03 (*d*, $J = 11.6$, H_a–C(6′)); 4.22 (*dd*, $J = 12.3$, 4.2, H–C(3)); 4.97–5.12 (*m*, H–C(2′) to H–C(4′)); 5.30 (br. *t*, H–C(12)); 5.52 (*d*, $J = 7.8$, H–C(1′)).

Kalidiumin (=*(3β)-3,29-Dihydroxy-23-methoxy-23-oxoolean-12-en-28-oic Acid*; **2**). Colorless, amorphous powder. UV (MeOH): 205.0 (3.91). $[\alpha]_D^{26} = +97.7$ ($c = 1.0$, MeOH). IR (KBr): 3420, 1740, 1734, 1620. ^{1}H- and ^{13}C-NMR: see *Table 2*. EI-MS (pos.): 516 (3.3, M^+), 264 (93.8), 233 (100), 219 (11.2), 201 (80.3), 187 (28.5). HR-EI-MS (pos.): 516.3450 (M^+, $C_{31}H_{48}O_6^+$; calc. 516.3451).

Acetylation of **2**. Following the procedure described above for **1**, the diacetyl derivative of **2** was obtained. Amorphous powder. IR (KBr): 1744 (br.). ^{1}H-NMR ($CDCl_3$): 0.70, 0.90, 0.97, 1.10, 1.16 (5*s*, 5 Me); 1.95, 2.05 (2*s*, 2 AcO); 2.81 (*dd*, $J = 13.3$, 3.7, H–C(18)); 3.64 (*s*, MeO); 3.70 (*d*, $J = 11.1$, H_b–C(29)); 3.79 (*d*, $J = 11.1$, H_a–C(29)); 5.12 (*dd*, $J = 11.1$, 4.6, H–C(3)); 5.27 (br. *t*, H–C(12)).

Kalidiumoside B (=*β*-D-*Glucopyranosyl (3β)-29-Acetoxy-3-hydroxy-23-methoxy-23-oxoolean-12-en-28-oate*; **3**). Colorless, amorphous powder. $[\alpha]_D^{26} = +67.90$ ($c = 1.3$, MeOH). UV (MeOH): 204.6 (5.90). IR (KBr): 3420 (OH); 1740, 1734 (C=O); 1620 (C=C). ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 438 (3.4, $[M-162-60-60]^+$), 396 (2.2), 306 (6.3), 247 (6.2), 201 (27.5), 179 (20.4), 175 (37.0), 161 (100). HR-EI-MS: 306.1830 ($C_{18}H_{26}O_4^+$; calc. 306.1831).

Acid Hydrolysis of **1** *and* **3**. A soln. of the triterpenoid (7.0 mg) in MeOH (4 ml) containing 2N aq. HCl (4 ml) was heated at reflux for 6 h. After concentration at reduced pressure, the mixture was diluted with H_2O, and extracted with AcOEt. The aq. phase was neutralized (Ag_2CO_3), filtered, and evaporated *in vacuo* to give an off-white residue, which was identified as glucose by co-TLC with an authentic sample (SiO_2; BuOH/AcOH/H_2O 4:1:5), followed by visualizing with aniline phthalate. The observed optical rotation of the sugar, $[\alpha]_D^{25} = +52$ ($c = 0.05$, MeOH), indicated D-glucose.

REFERENCES

[1] V. Krever, O. Pereladova, M. Williams, H. Jungius, 'Biodiversity Conservation in Central Asia: An Analysis of Biodiversity and Current Threats and Initial Investment Portfolios', WWF, Washington DC, 1998.

[2] M. S. Baitenov, 'Flora of Kazakhstan' (in Russian), Gilim, Almaty, 1999, Vol. 1, p. 70–73.

[3] V. L. Komarov, B. K. Shishkin, 'Flora of USSR' (in Russian), Academy of Science USSR, Moscow-Leningrad, 1936, Vol. 6, p. 167–168.

[4] Z. Z. Karzhaubekova, G. S. Burasheva, *Chem. Nat. Compounds* **2002**, *38*, 100.

[5] Z. Z. Karzhaubekova, G. S. Burasheva, K. D. Rakhimov, *Pharm. Kazakhstan* **2003**, *6*, 36.

[6] B. K. Yeskaliyeva, G. O. Turtaeva, G. S. Burasheva, V. U. Ahmad, Z. A. Abilov, 9th International Symposium on Natural Product Chemistry, 2004, Karachi, p. 335.

[7] Y. Oshima, T. Ohsawa, H. Hikino, *Planta Med.* **1984**, *50*, 43.

[8] M. Hani, A. Elgamal, H. S. M. Soliman, G. Toth, J. Halasz, H. Duddeck, *Magn. Reson. Chem.* **1996**, *34*, 697.
[9] H. Budzikiewicz, J. M. Wilsone, C. Djerassi, *J. Am. Chem. Soc.* **1963**, *85*, 3688.
[10] M. Shamma, R. E. Glick, R. O. Mumma, *J. Org. Chem.* **1962**, *27*, 4512
[11] S. Park, C. Yook, T. Noharara, *Chem. Pharm. Bull.* **2005**, *53*, 1147.
[12] W.-H. Hui, M.-M. Li, *Phytochemistry* **1977**, *16*, 1309.
[13] L. Fu, S. Zhang, N. Li, J. Wang, M. Zhao, J. Sakai, T. Hasegawa, T. Mitsui, T. Kataoka, S. Oka, M. Kiuchi, K. Hirose, M. Ando, *J. Nat. Prod.* **2005**, *68*, 198.

Received February 6, 2006