# Chemical Constituents of the Aerial Parts of *Kalidium foliatum*

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**Studies on the chemical constituents of the aerial parts of *Kalidium foliatum* have led to the isolation of three new and one known compounds. The structures of new constituents have been elucidated through spectral studies including 2D-NMR experiments (HMQC, HMBC, COSY, NOESY and *J*-resolved) and MS/MS fragmentation using Q-TOF mass spectrometer equipped with an ESI source as kalidiumoside C (=3$\beta$-hydroxy-29-methylmalonoxy-olean-12-en-23,28-dioic acid-23-methyl-28-$\beta$-D-glucopyranosyl ester; 1), kalidiunin (=3$\beta$,23,29-trihydroxy-olean-12-en-28-methyl-oate; 2) and kalidiumoside D (=3$\beta$,23,29-trihydroxyolean-12-en-28-oic acid-$\beta$-D-glucopyranosyl ester; 3). The known compound was identified as 3$\beta$,23,29-trihydroxy-olean-12-en-28-oic acid 4) through comparison of its spectral data with those reported in literature. Acid hydrolysis of both 2 and 3 yielded the known compound 4 providing a conclusive evidence of the proposed structures.**

**Key words** *Kalidium foliatum*; Chenopodiaceae; triterpene

The Kalidium genus (Family Chenopodiaceae) has five species which thrive in soils with a high mineral concentration and are distributed in the South-East European, Central and South-West Asia, Russia (south Siberia), East China, Mongolia and Kazakhstan.[1)] In Kazakhstan only three species *K. caspicum* (L.), *K. foliatum* (Pall.) and *K. schrenkianum* (Bge) (endemic) are known.[2,3)] In continuation of our work on the chemical constituents of Kazakh medicinal plants,[4—6)] we examined the secondary metabolites present in the aerial parts of *Kalidium foliatum* and isolated three new triterpenes including two glycosides (kalidiumoside C and kalidiumoside D) and one methyl ester (kalidiunin) and elucidated their structures as 3$\beta$-hydroxy-29-methylmalonoxy-olean-12-en-23,28-dioic acid-23-methyl-28-$\beta$-D-glucopyranosyl ester (**1**), 3$\beta$,23,29-trihydroxy-olean-12-en-28-methyl-oate (**2**) and 3$\beta$,23,29-trihydroxyolean-12-en-28-oic acid-$\beta$-D-glucopyranosyl ester (**3**), respectively, on the basis of spectral analysis including extensive 2D NMR experiments (COSY-45, NOESY, *J*-resolved, HMQC and HMBC). The isolation and structure elucidation of the new compounds forms the basis of this paper.

The molecular weight of compound **1** was deduced from the ESI-QTOF-MS (+ve), which displayed protonated molecular ion $[M+H]^+$ and adduct ion $[M+Na]^+$ at *m/z* 779.4262 and 801.4121 corresponding to their molecular formula $C_{41}H_{63}O_{14}$ and $C_{41}H_{62}O_{14}Na$, respectively. The MS-MS experiment of $[M+H]^+$ion at *m/z* 779 afforded aglycon part $[M+H-\text{hexose}]^+$ at *m/z* 617 and retro-Diels-Alder (rDA) product at *m/z* 264 as a base peak at 20 eV collision energy. In the positive mode FAB-MS of **1**, pseudomolecular and fragment ions were detected at *m/z* 779 $[M+H]^+$ and *m/z* 617 $[(M+H)-162]^+$ for $C_{41}H_{63}O_{14}$ and $C_{35}H_{53}O_9$, respectively, and the corresponding ions in the negative FAB-MS were present at *m/z* 777 $[M-H]^-$ and *m/z* 615 $[(M-H)-162]^-$, respectively. The IR spectrum showed characteristic absorption bands caused by hydroxyl group at 3241.0 and ester carbonyl groups at 1743.9 $cm^{-1}$. Its specific rotation was $[\alpha]_D^{26}$ +26.6° (*c*=1.5, MeOH). The UV spectrum displayed a maximum at 204.2 nm ($\log\varepsilon$ 3.32). From the normal $^1$H- and $^{13}$C-NMR data as well as the proton–proton and proton–carbon connectivities observed in the COSY, NOESY, HMQC and HMBC spectra (Fig. 1), the structure of **1** was derived as 3$\beta$-hydroxy-29-methylmalonoxy-olean-12-en-23,28-dioic acid-23-methyl-28-$\beta$-D-glucopyranosyl ester. The structure was substantiated by various fragment ions observed in the EI-MS spectrum including the characteristic fragment resulting from the retro Diels-Alder cleavage around ring C[7)] (Fig. 2) (*vide* structure and Experimental).

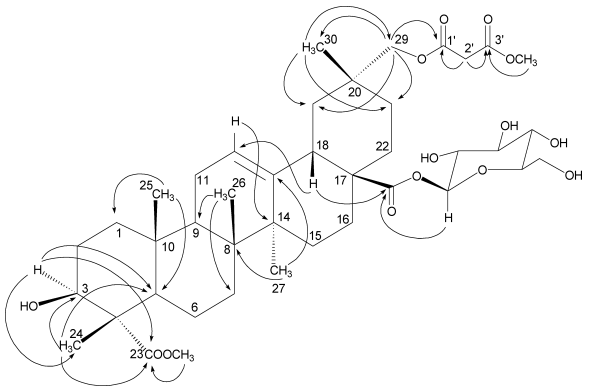

Fig. 1. HMBC Correlation of Compound **1**

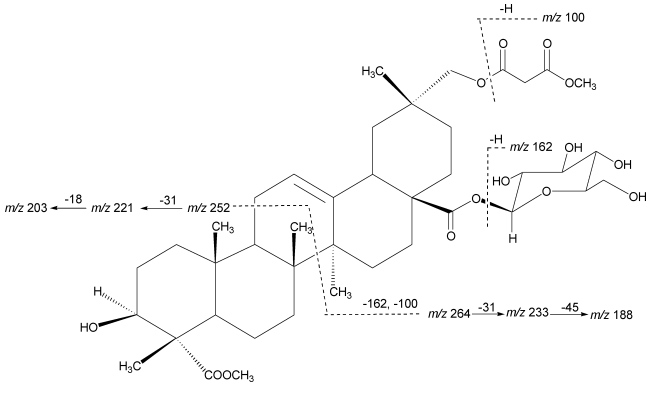


Fig. 2. Mass Fragmentation of **1**

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Table 1. $^{1}$H- (300 MHz) and $^{13}$C- (150 MHz) NMR Data of Compound **1** (Pyridine-$d_5$, $\delta$ in ppm, $J$ in Hz)

| No. C | $^{1}$H | Multiplicity ($J$ in Hz) | $^{13}$C | Type C | HMBC |
|---|---|---|---|---|---|
| 1 | | | 38.8 | $CH_2$ | |
| 2 | | | 28.4 | $CH_2$ | |
| 3 | 4.01 | dd (10.3, 4.6) | 79.3 | CH | C-5, C-23, C-24 |
| 4 | — | — | 54.8 | C | |
| 5 | | | 52.1 | CH | |
| 6 | | | 21.6 | $CH_2$ | |
| 7 | | | 32.7 | $CH_2$ | |
| 8 | — | — | 40.3 | C | |
| 9 | | | 40.7 | CH | |
| 10 | — | — | 47.0 | C | |
| 11 | | | 23.2 | $CH_2$ | |
| 12 | 5.41 | br.t (3.2) | 123.0 | CH | C-14 |
| 13 | — | — | 143.6 | C | |
| 14 | — | — | 42.0 | C | |
| 15 | | | 27.5 | $CH_2$ | |
| 16 | | | 23.7 | $CH_2$ | |
| 17 | — | — | 47.3 | C | |
| 18 | 3.20 | dd (13.0, 4.5) | 40.6 | CH | C-12, C-28 |
| 19 | | | 41.6 | $CH_2$ | |
| 20 | — | — | 36.7 | C | |
| 21 | | | 28.8 | $CH_2$ | |
| 22 | | | 31.9 | $CH_2$ | |
| 23 | — | — | 178.7 | C | |
| 24 | 1.48 | s | 11.8 | $CH_3$ | C-3, C-5, C-23 |
| 25 | 0.91 | s | 16.0 | $CH_3$ | C-1, C-5 |
| 26 | 1.09 | s | 17.3 | $CH_3$ | C-7, C-9 |
| 27 | 1.19 | s | 26.0 | $CH_3$ | C-8, C-13 |
| 28 | — | — | 176.1 | C | |
| 29a | 3.90 | d (10.6) | 75.3 | $CH_2$ | C-1′, C-19, C-21, C-30 |
| b | 3.93 | d (10.6) | | | |
| 30 | 0.95 | s | 19.0 | $CH_3$ | C-19, C-21, C-29 |
| $COO\underline{CH_3}$ | 3.67 | s | 51.8 | $CH_3$ | C-23 |
| $COO\underline{CH_3}$ | 3.61 | s | 52.2 | $CH_3$ | C-3′ |
| $OC\underline{CH_2}CO$ | 3.70 | s | 41.8 | $CH_2$ | C-1′, C-3′ |
| $\underline{C}OCH_3$ | — | — | 167.0 | C | |
| $\underline{C}OCH_3$ | — | — | 167.5 | C | |
| Glu 1″ | 6.34 | d (8.1) | 95.7 | CH | C-28 |
| 2″ | 4.20 | t (8.3) | 74.0 | CH | |
| 3″ | 4.05 | t (8.0) | 78.8 | CH | |
| 4″ | 4.36 | t (8.8) | 71.1 | CH | |
| 5″ | 4.28 | t (8.3) | 78.9 | CH | |
| 6″a | 4.50 | dd (10.3, 3.0) | 62.1 | $CH_2$ | |
| b | 4.48 | dd (10.3, 3.5) | | | |

Table 2. $^{1}$H- (300 MHz) and $^{13}$C- (100 MHz) NMR Data of Compound **2** ($CD_3OD$ in ppm, $J$ in Hz)

| No. C | $^{1}$H | Multiplicity ($J$ in Hz) | $^{13}$C | Type C | HMBC correlation |
|---|---|---|---|---|---|
| 1 | | | 39.5 | $CH_2$ | |
| 2 | | | 27.4 | $CH_2$ | |
| 3 | 3.56 | dd (10.0, 4.0) | 74.1 | CH | C-23, C-24 |
| 4 | — | — | 42.9 | C | |
| 5 | | | 49.6 | CH | |
| 6 | | | 19.1 | $CH_2$ | |
| 7 | | | 33.5 | $CH_2$ | |
| 8 | — | — | 40.6 | C | |
| 9 | | | 45.9 | CH | |
| 10 | — | — | 36.7 | C | |
| 11 | | | 24.5 | $CH_2$ | |
| 12 | 5.23 | br.t (3.1) | 123.6 | CH | C-9, C-18 |
| 13 | — | — | 144.0 | C | |
| 14 | — | — | 41.5 | C | |
| 15 | | | 27.4 | $CH_2$ | |
| 16 | | | 24.1 | $CH_2$ | |
| 17 | — | — | 47.5 | C | |
| 18 | 2.88 | dd (13.0, 3.0) | 40.5 | CH | C-12, C-28 |
| 19 | | | 41.5 | $CH_2$ | |
| 20 | — | — | 36.6 | C | |
| 21 | | | 29.3 | $CH_2$ | |
| 22 | | | 33.1 | $CH_2$ | |
| 23a | 3.51 | d (10.5) | 67.6 | $CH_2$ | C-5, C-24 |
| b | 3.33 | d (10.5) | | | |
| 24 | 0.69 | s | 12.6 | $CH_3$ | C-3, C-5 |
| 25 | 0.96 | s | 16.2 | $CH_3$ | C-1, C-5 |
| 26 | 0.84 | s | 17.8 | $CH_3$ | C-7, C-14 |
| 27 | 1.16 | s | 26.4 | $CH_3$ | C-13 |
| 28 | — | — | 178.0 | C | |
| 29 | 3.17 | s | 74.5 | $CH_2$ | C-19, C-21, C-30 |
| 30 | 0.92 | s | 19.5 | $CH_3$ | C-21, C-29 |
| $OCH_3$ | 3.63 | s | 52.0 | $CH_3$ | C-28 |

The NMR spectra ($^{1}$H- , $^{13}$C-NMR) (Table 1) revealed the presence of one double bond, one hydroxy containing CH, one $CH_2$ of ester, four ester carbonyl carbons, six quaternary carbons and five methyl groups located on quaternary carbons, eleven methylenes, three methines and two *O*-methyls in addition to a glucose moiety.

Its triterpenoidal nature was indicated by the presence of five quaternary methyl singlets at $\delta$ 0.91, 1.09, 1.19, 0.95 and 1.48 in the $^{1}$H-NMR spectrum (in pyridine-$d_5$) which were assigned to the protons at C-25, C-26, C-27, C-30 and C-24 (Table 1), respectively, on the basis of 1D and 2D NMR analysis. A double doublet at $\delta$ 3.20 (1H, $J$=13.0, 4.5 Hz, H-18), a broad triplet for an olefinic proton at $\delta$ 5.41 were characteristic of the $\Delta^{12}$ $\beta$-amyrin skeleton[8] while a one-proton double doublet at $\delta$ 4.01 (1H, $J$=10.3, 4.6 Hz, H-3) favored a hydroxyl group at C-3 also supported biogenetically.[9,10] Two three-proton singlets at $\delta$ 3.61 and $\delta$ 3.67 were due to *O*-methyl moieties which had long range connectivity (HMBC) with acyl carbons at $\delta$ 178.7 (C-23) and 167.5 (C-3′), respectively. Cross peaks in the HMBC plot were also present for connectivity between H-3 and H-24 with C-23 ($\delta$ 178.7) revealing that C-23 is functionalized to a carboxymethyl group. Further, two protons were present at $\delta$ 3.90 (d, $J$=10.6 Hz) and $\delta$ 3.93 (d, $J$=10.6 Hz) showing a cross peak at $\delta$ 75.3 in the HMQC plot and long range connectivity (HMBC) with C-19 ($\delta$ 41.6), C-21 ($\delta$ 28.8), C-30 ($\delta$ 19.0) and the acyl carbonyl carbon at $\delta$ 167.0 (C-1′). These observations and NOE correlations of H-18 with H-12 and H-30 revealed that C-29 is acylated. Moreover a singlet was present at $\delta$ 3.70 (H-2′) connected which a carbon at $\delta$ 41.8 ($CH_2$) in the HMQC spectrum which manifested a –$CH_2$– moiety between two carbonyl groups. These findings and connectivety of H-2′ with both C-1′ ($\delta$ 167.0) and C-3′ ($\delta$ 167.5) were suggestive of a methoxymalonoxy group at C-29.[11] It may be noted that both H-29a and H-29b usually appear as a two-proton singlet in 29-hydroxy compounds being their unhindered equatorial disposition[12] as also observed in case of compounds **2** and **3** (*vide infra*). The appearance of two AB doublets for H-29a and H-29b in the $^{1}$H-NMR spectrum of **1** may be related to larger methylmalonyl group at C-29-*O* position. The mass fragments in FAB-positive and -negative modes and NMR data also indicated a glucose moiety (Table 1) and the anomeric proton resonance as a doublet at $\delta$ 6.34 (d, $J$= 8.1 Hz) attached to a carbon at $\delta$ 95.7 in the HMQC plot and its HMBC correlation with C-28 ($\delta$ 176.1) implied its $\beta$-link-

age. The NMR shifts of the glucose moiety matched well with those reported for a $\beta$-D-glucopyranosyl unit.[13] This was corroborated by acid hydrolysis of **1** (*vide* Experimental), which yielded $\beta$-D-glucose according to thin-layer-chromatographic (TLC) and optical-rotation-dispersion (ORD) analyses. All the NMR assignments were made with the help of 2D *J*-resolved, HMBC, HMQC, COSY, NOESY and compare well with the values of related partial structures reported in literature.[12—15] Finally, the stereochemistry at C-4 as depicted in Figs. 1 and 2 could be deduced from the interactions of Me-25 with both Me-24 and Me-26 in the NOESY spectrum.

ESI-QTOF-MS (+ve) of compound **2** showed protonated molecular $[M+H]^+$ ion peak at *m/z* 503.3730 corresponding to the molecular formula $C_{31}H_{51}O_5$. The CID experiment of $[M+H]^+$ ion at *m/z* 503 gave rDA product at *m/z* 207. The $^{13}$C-NMR (Broad band and DEPT contained eight quaternary carbons including one olefinic (C-13) and one carbonyl (C-28); five CH including one olefinic (C-12); twelve $CH_2$ including two carbinylic (C-23 and C-29) and six methyls including one $OCH_3$. The HR-EI-MS of **2** showed fragment ion peaks arising from the characteristic retro-Diels-Alder cleavage arround ring C at *m/z* 278.1879 and 247.1693 (278-31).[7] The IR spectrum showed characteristic absorption bands caused by hydroxyl group at 3241.0 and ester carbonyl group at 1743.9 $cm^{-1}$. Its specific rotation was $[\alpha]_D^{26}$ +35.0° (*c*= 1.2, MeOH). The UV spectrum displayed a maximum at 202.4 nm (log $\varepsilon$ 3.62).

The $^1$H-NMR spectrum exhibited five quaternary methyl singlets at $\delta$ 0.69 (Me-24), 0.96 (Me-25), 0.84 (Me-26), 1.16 (Me-27) and 0.92 (Me-30), a broad triplet for an olefinic proton at $\delta$ 5.23 characteristic of the $\Delta^{12}$ proton in the pentacyclic triterpenes and a double doublet at $\delta$ 2.88 (1H, *J*= 13.0, 3.0 Hz) attributable to H-18 of $\Delta^{12}$ oleanane skeleton.[8] The $^1$H-NMR spectrum further showed a one-proton double doublet at $\delta$ 3.56 (*J*=10.0, 4.0 Hz) due to H-3, a two-proton singlet at $\delta$ 3.17 assignable to H-29 and two one-proton doublets at 3.51 and $\delta$ 3.33 (*J*=10.5 Hz) attributable to H-23a and H-23b. The carbons for these carbinylic protons were identified at $\delta$ 74.1, $\delta$ 74.5 and $\delta$ 67.6, respectively, in the HMQC plot. In the HMBC spectrum (Fig. 3) H-3 had cross peaks for C-23 ($\delta$ 67.6) and C-24 ($\delta$ 12.6) which led to place a hydroxyl group at C-23. The remaining hydroxyl group could be located at C-29 in light of the singlet at $\delta$ 3.17 which is comparable with the value of the H-29 in similar partial structures.[12—14] Further, $OCH_3$ ($\delta$ 3.63) showed its connectivities with a carbon at $\delta$ 178.0 (C-28) while H-18 showed its connectivities with carbons at $\delta$ 123.6 (C-12) and 178.0 (C-28) in the HMBC spectrum. These data led to elucidate the structure of **2** as 3$\beta$,23,29-trihydroxy-olean-12-en-28-methyl-oate. The stereochemistry of various centres was manifested by the contours present in the NOESY spectrum showing connectivities between Me-24 and Me-25; H-3 and H-23a and H-23b; and H-18 and Me-30. The structure was further supported by significant MS ions (Fig. 4) and hydrolysis of **2** (*vide* Experimental) to obtain the known compound **4**.

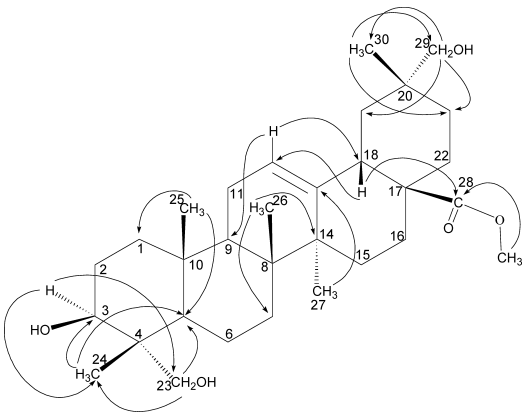


Fig. 3. HMBC Correlation of Compound **2**

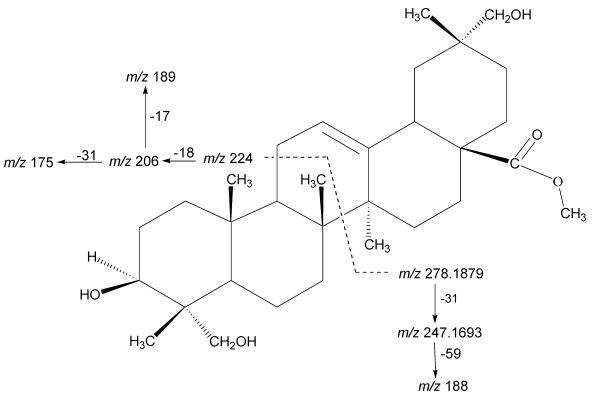


Fig. 4. Mass Fragmentation of **2**

The molecular weight of compound **3** was deduced from the ESI-QTOF-MS (+ve), which displayed $[M+H]^+$ and $[M+Na]^+$ ions at *m/z* 651.4170 and 673.4012 corresponding to elemental compositions $C_{36}H_{59}O_{10}$ and $C_{36}H_{58}O_{10}Na$ respectively. The MS-MS experiment of $[M+H]^+$ ion at *m/z* 651 gave aglycon part $[M+H-hexose]^+$ at *m/z* 489.37 and rDA product at *m/z* 207. The HR-EI mass spectrum showed ions at *m/z* 442.3279 $[M^+-16-31-15]$ and *m/z* 264.1719 arising from characteristic retro Diels-Alder cleavage of ring C[7] along with other characteristic ions (*vide* Experimental and Fig. 6). The $^{13}$C-NMR (Broad band and DEPT) displayed 36 carbons including a glucose moiety, a carboxyl ester (C-28), two carbinylic methylenes (C-23 and C-29) and one carbinilyc methine (C-3) besides other carbons of $\Delta^{12}$-$\beta$-amyrin skeleton[8] (see Table 3). A hydroxyl group at C-3 was evident from a double doublet at $\delta$ 3.58 (1H, *J*=10.0, 4.0 Hz, H-3) having its connectivity with a carbon at $\delta$ 73.9 (C-3; HMQC) and long range connectivity with carbons at $\delta$ 67.4 (C-23) and 12.6 (C-24). A double doublet at $\delta$ 2.85 (1H, *J*= 13.0, 3.0 Hz, H-18), and a broad triplet at $\delta$ 5.25 (H-12) indicated its $\beta$-amyrin skeleton with a double bond at C-12. H-18 showed its connectivity with a carbon at $\delta$ 42.9 (C-18; HMQC) and with carbons at $\delta$ 123.8 (C-12) and 178.0 (C-28) in the HMBC spectrum. H-12 showed its connectivity with a carbon at $\delta$ 123.8 (C-12) in the HMQC plot. Five methyl singlets at $\delta$ 0.68, 0.79, 0.91, 0.95 and 1.17 connected to Me-24, Me-26, Me-30, Me-25 and Me-27, respectively, in the HMQC plot further showed that two methyl groups of the parent skeleton are functionalized. Both of these could be decided as $-CH_2OH$ from the appearance of a two-proton singlet at $\delta$ 3.17 correlated to a methylene carbon at $\delta_C$ 74.8 in the HMQC spectrum and two doublets at $\delta$ 3.51, 3.27 (H-23a and H-23b, each *J*=10.5 Hz) connected with a carbon at $\delta$ 67.4 in the HMQC spectrum. The cross

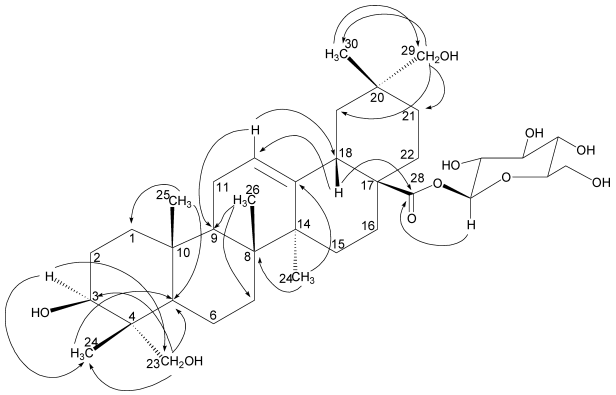

Fig. 5. HMBC Correlation of Compound **3**

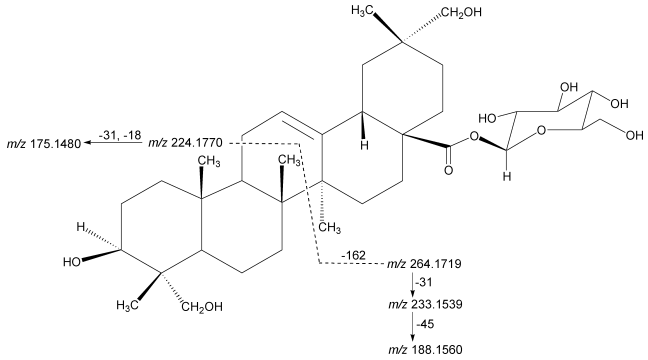

Fig. 6. Mass Fragmentation of **3**

Table 3. $^{1}$H- (300 MHz) and $^{13}$C- (75 Hz) NMR Data of Compound **3** ($CD_3OD$ in ppm, $J$ in Hz)

| No. C | $^{1}$H | Multiplicity ($J$ in Hz) | $^{13}$C | Type C | HMBC correlation |
|---|---|---|---|---|---|
| 1 | | | 39.5 | $CH_2$ | |
| 2 | | | 24.5 | $CH_2$ | |
| 3 | 3.58 | dd (10.0, 4.0) | 73.9 | CH | C-23, C-24 |
| 4 | — | | 41.5 | C | |
| 5 | | | 49.3 | CH | |
| 6 | | | 19.3 | $CH_2$ | |
| 7 | | | 32.3 | $CH_2$ | |
| 8 | — | — | 40.6 | C | |
| 9 | | | 47.5 | CH | |
| 10 | — | — | 36.7 | C | |
| 11 | | | 23.9 | $CH_2$ | |
| 12 | 5.25 | br.t (3.2) | 123.8 | CH | C-9, C-18 |
| 13 | — | — | 144.0 | C | |
| 14 | — | — | 36.7 | C | |
| 15 | | | 27.3 | $CH_2$ | |
| 16 | | | 23.2 | $CH_2$ | |
| 17 | — | — | 48.6 | C | |
| 18 | 2.85 | dd (13.0, 3.0) | 42.9 | CH | C-12, C-28 |
| 19 | | | 41.3 | $CH_2$ | |
| 20 | — | — | 35.6 | C | |
| 21 | | | 28.8 | $CH_2$ | |
| 22 | | | 29.2 | $CH_2$ | |
| 23a | 3.51 | d (10.5) | 67.4 | $CH_2$ | C-3, C-5, C-24 |
| b | 3.27 | d (10.5) | | | |
| 24 | 0.68 | s | 12.6 | $CH_3$ | C-5 |
| 25 | 0.95 | s | 16.5 | $CH_3$ | C-1, C-5 |
| 26 | 0.79 | s | 17.7 | $CH_3$ | C-7, C-9 |
| 27 | 1.17 | s | 26.5 | $CH_3$ | C-8, C-13 |
| 28 | — | — | 178.0 | C | |
| 29 | 3.17 | s | 74.8 | $CH_2$ | C-19, C-21, C-30 |
| 30 | 0.91 | s | 19.5 | $CH_3$ | C-29 |
| Glu 1′ | 5.36 | d (7.9) | 95.1 | CH | C-28 |
| 2′ | 3.33 | m | 73.8 | CH | |
| 3′ | 3.49 | m | 78.6 | CH | |
| 4′ | 3.36 | m | 78.2 | CH | |
| 5′ | 3.35 | m | 71.0 | CH | |
| 6′a | 3.81 | dd (10.2, 3.4) | 62.3 | $CH_2$ | |
| b | 3.66 | dd (10.1, 3.6) | | | |

peaks in the HMBC plot (Fig. 5) were present between protons at $\delta$ 3.17 and the carbons at $\delta$ 19.5 (C-30), 41.3 (C-19) and 28.8 (C-21) and between protons at $\delta$ 3.51 and 3.27 and carbons at $\delta$ 12.6 (C-24), 73.9 (C-3) and 49.3 (C-5) which helped to locate these hydroxyl groups at C-29 and C-23 respectively. The sugar was identified as D-glucose from the NMR shifts[13] (Table 3) and further confirmed by acidic hydrolysis of **3** (*vide* Experimental) followed by TLC and ORD analyses of the glycone. The aglycone obtained on hydrolysis was identified as **4** through comparison of their spectral data. The $\beta$-linkage of the sugar was manifested by the anomeric proton resonance as a doublet at $\delta$ 5.36 (d, $J$=7.9 Hz) connected to a carbon at $\delta$ 95.1 (C-1′) in the HMQC plot, and the attachment with C-28 was revealed by the $^{13}$C-NMR shift of C-1′ and the long range connectivity of H-1′ with C-28 ($\delta$ 178.0). These data led to elucidate the structure of **3** as 3$\beta$,23,29-trihydroxy-olean-12-en-28-oic acid-$\beta$-D-glucopyranosyl ester. The contours present in the NOESY spectrum for interaction between Me-24 and Me-25; H-3 and H-23a and H-23b; H-18 and Me-30 manifested the stereochemistry as shown in Fig. 6. The structure was confirmed by acetylation ($Ac_2O$/Pyr) of **3** to yield heptaacetyl derivative **3a** as manifested by seven acetyl methyls in the $^{1}$H-NMR spectrum (*vide* Experimental). Further, H-29a and H-29b now appeared as two AB doublets ($J$=11.8 Hz) due to acetylation at C-29-*O*-position, instead of a two-proton singlet observed in case of **3**.

Compound **4** was identified as 3$\beta$,23,29-trihydroxyolean-12-en-28-oic acid through comparison of its physical data with those reported for the known compound[16] as well as through 1D and 2D NMR data. Further, ESI-QTOF-MS (+ve) of compound **4** provided a pseudomolecular ion $[M+H]^+$ at $m/z$ 489.3600 which established its molecular formula as $C_{30}H_{49}O_5$ (Calcd 489.3567). Fragmentation of $[M+H]^+$ at $m/z$ 409 produced rDA product at $m/z$ 207.

**Experimental**

Column chromatography: silica gel 60, mesh size 70—230 (Merck, 0.063—0.200 mm). Flash column chromatography: silica gel 9385 (Merck, 0.040—0.063 mm). Prep. TLC: silica gel 60 $PF_{254}$ (Merck); visualized under UV and detection with $I_2$ and $CeSO_4$ spray. UV spectra (MeOH): Hitachi-U-3200 spectrophotometer; $\lambda_{max}$ (log $\varepsilon$) in nm. IR spectra (KBr): Jasco-A-302 spectrophotometer; $\nu$ in $cm^{-1}$. $^{1}$H-NMR, COSY, NOESY, and $J$-resolved: Bruker spectrometers, Avance Av 300 operating at 300 MHz; chemical shifts $\delta$ in ppm coupling consants $J$ in Hz. $^{13}$C-NMR: Bruker spectrometer, Avance AV 600, operating at 150 MHz.

ESI-MS: Q-STAR XL of Applied Biosystem. Each compound (2 $\mu$g/ml, solution in acetonitrile : 0.1% HCOOH (aq.), 1 : 1) was directly infused into the mass spectrometer at a flow rate of 3 $\mu$l/min to acquire full scan and product ion mass spectra. The electrospray voltage at the spraying needle was optimized at 5200 V. Low-energy collision-induced dissociation (CID) experiments were performed using nitrogen (CID gas valve set to 4) as collision gas, and collision energy of 20 eV was used. FAB-MS and HR-EI-MS: Jeol-JMS-HX-110 mass spectrometer; EI, source at 250° and 70 eV.

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

sity.

**Extraction and Isolation** The air dried parts (5 kg) of *Kalidium foliatum* were repeatedly (×3) extracted with MeOH at room temperature. The combined extract was concentrated under vacuum and partitioned between EtOAc and water. The EtOAc phase was dried (anhyd. $Na_2SO_4$), charcoaled and concentrated under vacuum. The syrupy residue obtained was further divided into *n*-hexane soluble (HS) and insoluble (HI) fractions. Fraction HI (35 g) was subjected to VLC silica gel 9385 (Merck, 0.040—0.063 mm) ($CHCl_3$, $CHCl_3$–MeOH, MeOH in increasing order of polarity). As a result, 60 fractions were obtained and combined on the basis of TLC to ultimately afford 10 fractions (A—J). Fraction C (2.5 g) was subjected to CC silica gel 60, mesh size 70—230 (Merck, 0.063—0.200 mm), $CHCl_3$, $CHCl_3$–EtOAc, $CHCl_3$-EtOAc, EtOAc. As a result, 45 fractions were obtained and combined on the basis of TLC to ultimately afford 15 fractions (C-1 to C-15). Compounds **1** (7 mg), **3** (18 mg) and **4** (11 mg) were obtained from fraction C-6 by TLC in solvent system $CHCl_3$–MeOH (9.2 : 1.8), (9.5 : 0.5) and (9.0 : 1.0), respectively. Fraction C-3 furnished compound **2** as an amorphous powder (15 mg) by prep. TLC ($CHCl_3$–MeOH 9.5 : 0.5).

Kalidiumoside C (**1**): A white amorphous powder; $[\alpha]_D^{26}$ +26.6° (*c*=1.5, MeOH); IR (KBr): 1743.9, 3241.0; UV $\lambda_{max}$ (MeOH) 204.2 nm (log $\varepsilon$ 3.32); $^1$H-NMR (pyridine-$d_5$, 300 MHz) and $^{13}$C-NMR (150 MHz), see Table 1; ESI-QTOF-MS, *m/z*: 779.4262 $[M+H]^+$ ($C_{41}H_{63}O_{14}$, Calcd for 779.4215), 801.4121 $[M+Na]^+$ ($C_{41}H_{62}O_{14}Na$, Calcd for 801.4031). ESI-QTOF-MS-MS on *m/z* 779 $[M+H]^+$ (ce 20 eV) *m/z* (%): 779 (4), 617 (21), 559 (80), 499 (12), 481 (20), 235 (100), 175 (6); positive FAB-MS *m/z* 779 $[M+H]^+$, 617 $[(M+H)-162]^+$; negative FAB-MS *m/z* 777 $[M-H]^-$, 615 $[(M+H)-162]^-$. HR-EI-MS *m/z*: 516.3450 (M−162−100) (Calcd for $C_{31}H_{48}O_6$: 516.3452). EI-MS *m/z* 306 (3.2), 264 (67), 251 (10.2), 247 (24) and 233 (100).

Kalidiunin (**2**): A white amorphous powder; $[\alpha]_D^{26}$ +35.0° (*c*=1.2, in MeOH); IR (KBr): 1743.9, 3241.0; UV $\lambda_{max}$ (MeOH) 202.4 nm (log $\varepsilon$ 3.62); $^1$H-NMR ($CD_3OD$, 300 MHz) and $^{13}$C-NMR (100 MHz), see Table 2; ESI-QTOF-MS, *m/z*: 503.3730 $[M+H]^+$ ($C_{31}H_{51}O_5$, Calcd for 503.3733). ESI-QTOF-MS-MS on *m/z* 503 $[M+H]^+$ (ce 20 eV); HR-EI-MS *m/z*: 278.1879 (Calcd for $C_{17}H_{26}O_3$: 278.1883), 247.1693 ($C_{16}H_{16}O_2$). EI-MS *m/z*: 278 (2.3), 247 (100), 224 (2.8), 206 (4.0), 189 (4.7), 188 (2.5), 175 (7.4).

Kalidiumoside D (**3**): A white amorphous powder; $[\alpha]_D^{26}$ −31.1° (*c*=2.6, MeOH); IR (KBr): 1743.9, 3241.0; UV $\lambda_{max}$ (MeOH) 204.0 nm (log $\varepsilon$ 3.52); $^1$H- (300 MHz) and $^{13}$C-NMR (75 MHz), see Table 3; ESI-QTOF-MS, *m/z*: 651.4170 $[M+H]^+$ ($C_{36}H_{59}O_{10}$, Calcd for 651.4102), 673.4012 $[M+Na]^+$ ($C_{36}H_{58}O_{10}Na$, Calcd for 673.3922). ESI-QTOF-MS-MS on *m/z* 651 $[M+H]^+$(ce 20 eV) *m/z* (%): 651 (2), 489 (35), 471 (92), 453 (67), 441 (26), 425 (17), 207 (100), 189 (23). HR-EI-MS *m/z*: 442.3279 (Calcd for $C_{28}H_{42}O_4$: 442.3282), 264.1719 (Calcd for $C_{16}H_{24}O_3$: 264.1726), 233.1539 (Calcd for $C_{15}H_{21}O_2$: 233.1542), 224.1770 (Calcd for $C_{24}H_{24}O_2$: 224.1777), 175.1480 (Calcd for $C_{13}H_{19}$: 175.1488) and 188.1560 (Calcd for $C_{14}H_{20}$: 188.1566).

**Acetylation of 3** To a solution of **3** (5.0 mg) in pyridine (0.5 ml), $Ac_2O$ (1 ml) was added and the mixture left at r.t. overnight. The mixture was poured over crushed ice and extracted with AcOEt. After usual workup of the AcOEt phase and purification by TLC (silica gel, $CHCl_3$), the acetyl derivative **3a** was obtained as an amorphous powder (3.5 mg).

Heptaacetyl Derivative (**3a**) of **3**: IR (KBr) $\nu_{max}$: 1743.9 br. cm$^{-1}$. $^1$H-NMR ($CD_3OD$) 1.01, 0.85, 0.78, 1.16 and 0.97 (s, each 3H), 3.74 (d, *J*= 11.8 Hz, H-29b), 3.83 (d, *J*=11.8 Hz, H-29a), 4.15 (d, *J*=10.9 Hz, H-23b), 4.36 (d, *J*=10.9 Hz, H-23a), 4.24 (dd, *J*=12.3, 4.1 Hz, H-C-3), 5.32 (br.t, H-12), 2.89 (dd, *J*=13.0, 3.6 Hz, H-18), 5.70 (d, *J*=8.2 Hz, H-1′), 5.06 (m, 4H, H-2′—H-5′), 4.06 (d, *J*=11.6 Hz, H-6′a), 4.00 (d, *J*=11.8 Hz, H-6′b), 2.03 (6H, s, 2×OAc), 1.99, 1.97, 2.00, 2.01, 2.02 (each 3H, s, 5×OAc).

**Acid Hydrolysis of 1 and 3** A solution of the triterpenoid (8.0 mg) in MeOH (4 ml) containing 2 N aq. HCl (4 ml) was heated at reflux 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; 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. The AcOEt phases (of both **1** and **3**) on usual workup yielded a common product which was identified as **4** through Co-TLC and comparison of spectral data.

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