Four New 13,28-Epoxyoleanane Saponins from *Lysimachia lobelioides*

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Four new oleanane saponins, lobelioidosides A – D (**1** – **4**, resp.), all endowed with 16-oxo and a 23-OH group, as well as with a 13,28-epoxy bridge as a common moiety, have been isolated from the 75% EtOH extract of the whole plant of *Lysimachia lobelioides*. Their structures were elucidated on the bases of MS, ^{1}H- and ^{13}C-NMR, HMQC, HMBC, and ^{1}H,^{1}H-COSY data analysis.

Introduction. – *Lysimachia lobelioides*, an annual herb, is a member of the genus of *Lysimachia* (Primulaceae), distributed widely in southwestern China [1]. This plant has mainly been used as Chinese *Miao Minzu* medicine [2] for treatment of mastosis, menoxenia, rheumatalgia, edema, dysentery, and traumatic injury [3][4]. Previous phytochemical investigation showed that 13,28-epoxyoleanane saponins were the characteristic constituents of the family Primulaceae and they possessed various biological properties, such as cytotoxic and antimicrobial activities [5], especially the genus of *Lysimachia* [6 – 11]. Our ongoing study on the chemical constituents of this plant led to the isolation of four new 13,28-epoxyoleanane saponins, named lobelioidosides A – D (**1** – **4**, resp., *Fig. 1*). Herein, we report the isolation and structure elucidation of those new compounds.

Results and Discussion. – Lobelioidoside A (**1**) was obtained as white powder. The molecular formula, $C_{35}H_{56}O_8$, was established on the basis of the positive-ion-mode HR-ESI-MS (*m*/*z* 627.3870 ([M + Na]$^+$, $C_{35}H_{56}NaO_8^+$; calc. 627.3872)) and NMR data (see *Tables 1* and *2*). The ^{1}H-NMR spectrum data showed the signals of six angular Me

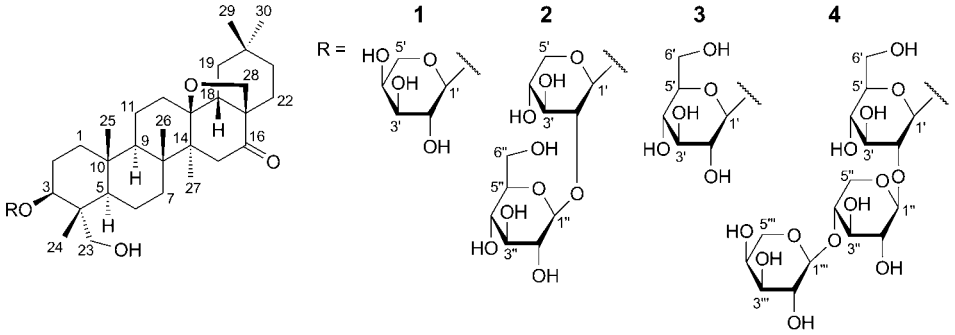

Fig. 1. S*tructures of compounds* **1** – **4**

Table 1. *^{1}H- and ^{13}C-NMR Data of the Aglycon Parts of* **1**–**4**

Position	**1**[a])		**2**[b])		**3**[a])		**4**[a])	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	1.73–1.77 (*m*), 0.95 (overlap)	39.0	1.70–1.76 (*m*)	39.8	1.77–1.81 (*m*)	38.4	0.92 (overlap), 1.73–1.79 (*m*)	39.0
2	1.98 (overlap), 1.74 (overlap)	25.4	1.85–1.87 (*m*)	26.4	1.86 (overlap)	29.2	1.85 (overlap)	25.3
3	3.60 (*dd*, *J* = 12.4, 4.4)	83.5	3.61 (overlap)	83.2	3.60 (overlap)	82.6	3.64 (overlap)	83.9
4	–	43.1	–	44.0	–	42.3	–	43.2
5	1.13–1.16 (*m*)	47.5	1.11–1.18 (*m*)	47.9	1.12–1.17 (*m*)	46.6	1.06–1.21 (*m*)	47.6
6	1.52 (overlap), 1.28 (overlap)	18.9	1.28–1.33 (*m*)	19.7	1.25 (overlap)	18.0	1.15–1.23 (*m*)	18.9
7	1.10 (overlap)	33.4	0.93 (overlap)	34.1	1.08 (overlap)	32.6	0.93 (overlap)	33.5
8	–	43.0	–	43.9	–	42.3	–	43.0
9	1.22 (overlap)	50.2	1.22–1.28 (*m*)	51.2	1.23 (overlap)	49.3	1.22 (overlap)	50.2
10	–	36.8	–	37.5	–	36.0	–	36.9
11	1.45–1.49 (*m*)	17.5	1.43–1.47 (*m*)	18.1	1.46–1.51 (*m*)	16.6	1.42–1.58 (*m*)	17.5
12	1.55–1.58 (*m*)	31.8	1.53 (overlap)	32.4	1.51–1.54 (*m*)	31.1	1.52 (overlap)	31.8
13	–	86.9	–	87.6	–	86.1	–	86.9
14	–	50.2	–	51.1	–	49.6	–	56.5
15	1.86 (*d*, *J* = 16.0), 2.74 (*d*, *J* = 16.0)	45.8	1.78 (*d*, *J* = 16.0), 2.76 (*d*, *J* = 16.0)	46.4	1.86 (*d*, *J* = 16.4), 2.79 (*d*, *J* = 15.6)	45.9	1.85 (*d*, *J* = 16.0), 2.73 (*d*, *J* = 16.4)	45.8
16	–	215.3	–	215.7	–	215.5	–	215.3
17	–	56.4	–	57.2	–	60.0	–	69.7
18	1.98–2.02 (*m*)	55.0	1.99 (*dd*, *J* = 14.8, 2.0)	55.9	1.82–1.92 (*m*)	54.3	1.98–2.01 (*m*)	55.0
19	1.29–1.33(*m*), 1.43–1.46 (*m*)	40.3	1.31–1.37 (*m*), 1.45 (*d*, *J* = 10.4)	41.0	1.55–1.62 (*m*), 1.77–1.80 (*m*)	44.1	1.21–1.51 (*m*), 1.41–1.49 (*m*)	40.3
20	–	32.0	–	32.6	–	33.1	–	32.0
21	1.20–1.24 (*m*), 1.52 (overlap)	35.5	1.19–1.22 (*m*)	36.4	0.95 (overlap), 1.73–1.77 (*m*)	38.1	1.22 (overlap), 1.58 (overlap)	35.5
22	2.12–2.15 (*m*)	25.0	1. 87–1.89 (*m*)	25.6	1.91–1.97 (*m*)	24.5	2.10–2.14 (*m*)	25.0
23	3.32 (*d*, *J* = 12.8), 3.53 (overlap)	64.7	3.25–3.30 (*m*), 3.62 (overlap)	64.5	3.32 (*d*, *J* = 11.6), 3.55 (overlap)	63.7	3.32 (overlap), 3.64 (*d*, *J* = 10.8)	64.7

Table 1 (cont.)

Position	**1**[a])		**2**[b])		**3**[a])		**4**[a])	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
24	0.72 (*s*)	12.7	0.69 (*s*)	13.2	0.72 (*s*)	11.8	0.73 (*s*)	12.7
25	0.94 (*s*)	16.7	0.92 (*s*)	17.0	0.94 (*s*)	15.8	0.94 (*s*)	16.8
26	1.24 (*s*)	18.9	1.25 (*s*)	19.3	1.24 (*s*)	18.0	1.24 (*s*)	19.0
27	1.07 (*s*)	22.0	1.06 (*s*)	22.2	1.08 (*s*)	21.2	1.06 (*s*)	22.0
28	3.48 (*d*, *J* = 8.4), 3.91 (*d*, *J* = 8.0)	75.5	3.45 (*d*, *J* = 8.4), 3.83 (*d*, *J* = 10.4)	76.1	3.71 (*d*, *J* = 8.8), 4.19 (*d*, *J* = 8.8)	73.9	3.52 (*d*, *J* = 8.4), 3.90 (*d*, *J* = 8.0)	75.5
29	0.89 (*s*)	23.7	0.88 (*s*)	23.8	0.92 (*s*)	23.7	0.88 (*s*)	23.7
30	0.95 (*s*)	33.5	0.93 (*s*)	33.8	1.02 (*s*)	32.4	0.95 (*s*)	33.5

[a]) Recorded at 400 (^{1}H) and 100 MHz (^{13}C) in CD_3OD and $CDCl_3$, respectively. [b]) Recorded at 400 (^{1}H) and 100 MHz (^{13}C) in CD_3OD.

Table 2. *^{1}H- and ^{13}C-NMR Data for the Sugar Moieties of* **1**–**4**

Position	**1**[a])		**2**[b])		**3**[a])		**4**[a])	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
Sugar 1′	Ara		Xyl		Glc		Glc	
1′	4.31 (*d*, *J* = 6.8)	105	4.30 (*d*, *J* = 6.4)	106.4	4.31 (*d*, *J* = 6.4)	104.1	4.24 (*d*, *J* = 7.2)	105.3
2′	3.54 (overlap)	72.1	3.89–3.91 (*m*)	80.0	3.59 (overlap)	71.3	3.46 (overlap)	85.1
3′	3.53 (overlap)	73.7	3.30–3.37 (*m*)	77.8	3.56 (overlap)	72.5	3.36 (overlap)	76.5
4′	3.81–3.88 (*m*)	68.6	3.54 (overlap)	74.5	3.80–3.88 (*m*)	67.7	3.56 (overlap)	69.6
5′	3.57 (overlap), 3.89 (*dd*, *J* = 9.6, 2.8)	66	3.54 (overlap), 4.17 (*dd*, *J* = 13.6, 3.2)	66.6	3.53 (overlap)	72.8	3.36 (overlap)	76.7
6′	–	–	–	–	3.54 (overlap), 3.89 (*dd*, *J* = 12.4, 2.8)	65.1	3.72 (*dd*, *J* = 12.0, 4.4), 3.84 (*d*, *J* = 4.4)	61.6
Sugar 2″			Glc				Xyl	
1″			4.46 (*d*, *J* = 7.2)	106.3			4.45 (*d*, *J* = 7.6)	106.9
2″			3.30 (overlap)	71.3			3.36 (overlap)	74.9
3″			3.32 (overlap)	78.0			3.24–3.34 (*m*)	76.3
4″			3.30 (overlap)	73.4			3.82–3.84 (*m*)	80.4
5″			3.56 (overlap)	75.4			3.98 (*dd*, *J* = 10.8, 5.2), 4.23–4.26 (*m*)	66.2
6″			3.53 (overlap), 3.83 (*d*, *J* = 3.2)	62.6				
Sugar 3‴							Ara	
1‴							4.48 (*d*, *J* = 7.6)	104.1
2‴							3.41–3.55 (*m*)	69.7
3‴							3.48–3.59 (*m*)	73.2
4‴							3.48 (overlap)	73.9
5‴							3.22 (*d*, *J* = 10.8), 3.55 (overlap)	66.4

[a]) Recorded at 400 (^{1}H) and 100 MHz (^{13}C) in CD_3OD and $CDCl_3$, respectively. [b]) Recorded at 400 (^{1}H) and 100 MHz (^{13}C) in CD_3OD.

groups (δ(H) 0.72 (Me(24)), 0.89 (Me(29)), 0.94 (Me(25)), 0.95 (Me(30)), 1.07 (Me(27)), and 1.24 (Me(26))). Signals of a pair of O-bearing CH_2 H-atoms as an *AB* system at δ(H) 3.48 and 3.91 (2*d*, $^2J = 8.4$, 8.0, CH_2(28)), along with a quaternary C-atom signal at δ(C) 86.9 (C(13)) indicated that the aglycone of **1** contained a 13,28-epoxyoleanane as structural unit, which was confirmed by 2D-NMR data. HMBCs (see *Fig. 2*) from CH_2(28) to C(13), C(15), C(16), and C(18) were observed, and the C=O signal at δ(C) 215.3 correlated to CH_2(15) (δ(H) 1.86 (*d*, $J = 12.0$) and 2.74 (*d*, $J = 16.0$)), CH_2(28), and H–C(18) (δ(H) 1.98–2.02 (*m*)) was assigned as C(16)=O. One CH_2 C-atom at δ(C) 64.7 correlated with H–C(24) and assigned to C(23). The axial α-orientation and position of H–C(3) was determined by its spin-spin coupling constants (δ(H) 3.60 (*dd*, $J = 12.4$, 4.4)) and correlation with C(4), C(23), and C(24), respectively. Based on the comparison with spectroscopic data reported [12][13], the aglycone of **1** was in accordance with anagalligenone, except that δ(C) of C(3) at 76.2 was moved to 83.5, the other chemical shifts showing no difference. Acid hydrolysis of **1** afforded L-arabinose, which was identified by comparing its HPLC retention time and optical rotation with those of an authentic sample. The HMBC spectrum showed that the anomeric H-atom (δ(H) 4.31 (*d*, $J = 6.8$)) correlated with C(3), and the α-linkage of L-arabinose was determined on the basis of the ^3J(1,2) value (for the remaining data of the sugar unit see *Table 2*). Therefore, the structure of **1** was elucidated as anagalligenone 3-*O*-α-L-arabinopyranoside.

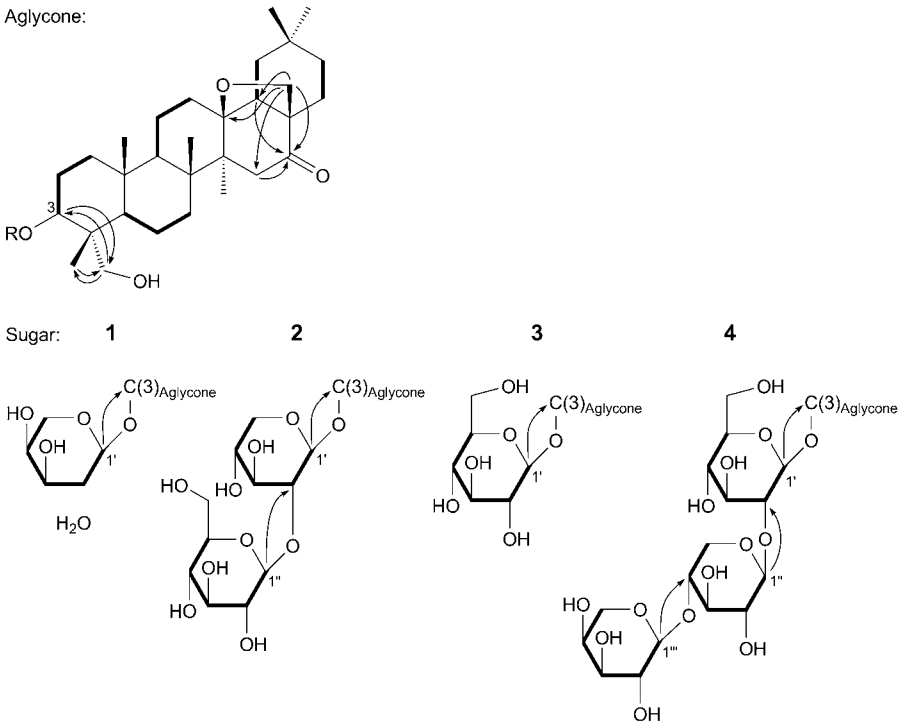

Fig. 2. *Key HMBC* (→) *and COSY* (—) *correlations of compounds* **1**–**4**

Lobelioidoside B (**2**), was obtained as white amorphous powder. The positive-ion-mode HR-ESI-MS (*m/z* 789.4412 ($[M+Na]^+$; calc. 789.4401)) provided the molecular formula $C_{41}H_{66}O_{13}$. A comparison of 1D- (*Tables 1* and *2*) and 2D-NMR (see *Fig. 2*) spectroscopic data with those of compound **1** showed that the two compounds had similar structures, except that acid hydrolysis of **2** afforded one D-xylopyranose and one D-glucopyranose, which was confirmed by comparing their HPLC retention times and optical rotations with those of authentic sugar samples. Two *doublet*s at δ(H) 4.30 (*d*, $J=6.4$) and 4.46 (*d*, $J=7.2$) were assigned to two anomeric H-atoms, and the coupling constants of two anomeric H-atoms indicated the α- and β-configuration, respectively. HMBC from δ(H) 4.30 (H–C(1′)) to the signal of C(3), and from δ(H) 4.46 (H–C(1″)) to that of C(2′) implied that the D-glucose was linked to C(2′) of the D-xylose unit, and the latter to O–C(3) of aglycone, respectively. On the basis of this analysis, the structure of **2** was elucidated as anagalligenone 3-*O*-β-D-glucopyranosyl-(1 → 2)-α-D-xylopyranoside.

Lobelioidoside C (**3**) was obtained as white amorphous powder. The molecular formula, $C_{36}H_{58}O_9$, was deduced from by HR-ESI-MS (*m/z* 657.3980 ($[M+Na]^+$; calc. 657.3979)). Comparison of the 1D-NMR data (*Tables 1* and *2*) and 2D-NMR correlations (see *Fig. 2*) of **3** with those of **1** indicated similar structures, except that the L-arabinose was replaced by D-glucose. The above conclusion was supported by acid hydrolysis of **3**, and comparison of the HPLC retention time and optical rotation of the resulting sugar with those of authentic sample. The anomeric H-atom sinal at δ(H) 4.30 (*d*, $J=6.4$) correlated with that of C(3), suggesting the D-glucose was linked to C(3), and the coupling constant indicated β-orientation for the anomeric H-atom. Thus, the structure of **3** was elucidated as anagalligenone 3-*O*-β-D-glucopyranoside.

Lobelioidoside D (**4**) was obtained as white amorphous powder. On the basis of the HR-ESI-MS (*m/z* 921.4458 ($[M+Na]^+$; calc. 921.4450)), the molecular formula was determined as $C_{46}H_{74}O_{17}$. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), and 2D-NMR correlation (see *Fig. 2*) evidenced that the aglycone of **4** was similar to that of **1**. Acid hydrolysis of **4** afforded one L-arabinose, one D-xylose, and one D-glucose unit, which were identified by comparing their HPLC retention times and optical rotations with those of authentic samples. The coupling-constant analysis of the anomeric H-atoms with signals at δ(H) 4.24 (*d*, $J=7.2$), 4.45 (*d*, $J=7.6$), and 4.48 (*d*, $J=7.6$) revealed that the D-glucose, D-xylose, and L-arabinose were β-, α-, and β-configured, respectively. The HMBCs from H–C(1′) to C(3), from H–C(1″) to C(2′), and from H–C(1‴) to C(4″) indicated that the sugar sequence within the trisaccharide chain as depicted in *Fig. 1*. Thus, the structure of **4** was elucidated as anagalligenone 3-*O*-α-L-arabinopyranosyl-(1 → 4)-β-D-xylosopyransyl-(1 → 2)-β-D-glucopyranoside.

This work was funded by the *National Basic Research 973 Program of China* (No. 2012CB722601), the *Major Special Project of Guizhou Province* (No. 2013-6006), the *Modernization Project of Guizhou Province Chinese Traditional Medicine* (No. 2011-5085), and the *Construction of Guizhou Province Scientific and Technological Innovation Talent Team* (2013-4006).

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2, 200–300 mesh; *Qingdao Marine Chemical Factory*, Qingdao, P. R. China), *Sephadex LH-20* (*Amersham Pharmacia Biotech*, Sweden), and *D-101* macroporous adsorption resin (*Tianjin Pesticide Chemical Company*, Tianjin, P. R. China). TLC: silica gel GF_{254} (*Qingdao Marine Chemical Factory*, Qingdao, P. R. China). HPLC: *Agilent 1100* system, equipped with a quaternary pump, a DAD detector, an autosamples, and *Hypersil NH2* column (5 μm, 250 × 4.6 mm); t_R in min. Optical rotations: *Auto Pol I* automatic polarimeter. M.p.: *XT-4* microscopic melting point apparatus; uncorrected. IR Spectra: *Bruker Vector 22* spectrometer, KBr pellets; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Inova 400* spectrometer at 400 (^1H) and 100 MHz (^{13}C); in $CDCl_3$ or CD_3OD soln.; δ in ppm rel. to Me_4Si, *J* in Hz. HR-ESI-MS: *API QSTAR Pulsar* mass spectrometer; in *m/z*.

Plant Material. The whole plants of *Lysimachia lobelioides* were collected in Xingyi, Guizhou Province, P. R. China, in July 2009, and identified by Prof. *De-Yuan Chen*, Guiyang College of Traditional Chinese Medicine. A voucher specimen (No. GZCN 09002) was deposited with the Key Laboratory of Chemistry for Natural Products of Guizhou Province and Chinese Academy of Sciences, P. R. China.

Extraction and Isolation. Air-dried and powdered whole plants of *L. lobelioides* (4.5 kg) were extracted with 75% aq. EtOH (3 × 10 l) at reflux. After evaporation of the solvent, the crude extract was suspended in H_2O, and extracted with petroleum ether (PE), AcOEt, and BuOH, successively. The BuOH extract (300 g) was absorded with diatomite and extracted with Me_2CO, MeOH, and H_2O, successively. The MeOH extract was submitted to CC (SiO_2; 70% aq. EtOH) to afford *Fractions A–C*. *Fr. C* (39 g) was subjected to CC (SiO_2; AcOEt/MeOH/H_2O 20:1:0.5; 10:1:0.5; 8:1:0.5; 5:1:0.5; 3:1:0.5; 2:1:0.5; 1:1:0.5) to yield seven *Subfractions*, C_1–C_7. The *Subfr.* C_4 (2.8 g) was separated and purified by CC (*Sephadex LH-20*; MeOH) to yield **1** (35 mg) and **3** (22.3 mg). *Fr.* C_5 (4.6 g) was separated and purified by repeated CC (*MCI*; 70% MeOH) to afford **3** (19.7 mg). *Fr.* C_6 (6.0 g) was subjectedto CC (SiO_2; $CHCl_3$/MeOH from 8:1 to 1:2), and then purified by CC (*Sephadex LH-20*; MeOH), to afford compound **4** (18.1 g).

Acidic Hydrolysis Lobelioidosides A–D (**1**–**4**, resp.). Each of the compounds **1**–**4** (10 mg) dissolved in 2N HCl was refluxed for 2 h. The mixture was extracted with AcOEt (3 × 5 ml). The H_2O layer was neutralized with $NaHCO_3$, and then concentrated to dryness under reduced pressure and purified by *Sephadex LH-20* chromatography to give a sugar fraction. The sugar fraction was analyzed by HPLC under the following conditions: column, *Hypersil NH2* (250 × 4.6 mm, 5 μm); column temp., 30°; mobile phase, MeCN/H_2O 84:16 (*v/v*); and flow rate, 1.0 ml/min. Identifications of D-glucose, L-arabinose, and D-xylose were carried out by comparison of their retention times and optical rotations with those of authentic samples. D-Glucose: t_R 4.3 min, positive optical rotation; L-arabinose: t_R 4.1 min, negative optical rotation; D-xylose: t_R 3.9 min, positive optical rotation.

Lobelioidoside A (=*Anagalligenone 3-*O*-α-*L*-Arabinopyranoside*=*(3β)-23-Hydroxy-16-oxo-13,28-epoxyoleanan-3-yl α-*L*-Arabinopyranoside*; **1**). White amorphous powder. M.p. 263–265°. $[\alpha]_D^{20} = -9.94$ ($c = 1.13$, $CHCl_3$/MeOH 1:1). IR (KBr): 3451, 2948, 2858, 1705, 1640, 1449, 1387, 1048. ^1H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 627.3870 ($[M+Na]^+$, $C_{35}H_{56}NaO_8^+$; calc. 627.3873).

Lobelioidoside B (=*Anagalligenone 3-*O*-β-*D*-Glucopyranosyl-(1→2)-α-*D*-xylopyranoside*=*(3β)-23-Hydroxy-16-oxo-13,28-epoxyoleanan-3-yl 2-*O*-β-*D*-Glucopyranosyl-(1→2)-α-*D*-xylopyranoside*; **2**). White amorphous powder. M.p. 273–275°. $[\alpha]_D^{20} = +40.26$ ($c = 0.44$, $CHCl_3$/MeOH 1:1). IR (KBr): 3451, 2926, 2856, 1704, 1640, 1385, 1079. ^1H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 789.4412 ($[M+Na]^+$, $C_{41}H_{66}NaO_{13}^+$; calc. 789.4401).

Lobelioidoside C (=*Anagalligenone 3-*O*-β-*D*-Glucopyranoside*=*(3β)-23-Hydroxy-16-oxo-13,28-epoxyoleanan-3-yl β-*D*-Glucopyranoside*; **3**). White amorphous powder. M.p. 256–257°. $[\alpha]_D^{20} = -16.96$ ($c = 0.85$, $CHCl_3$/MeOH 1:1). IR (KBr): 3446, 2951, 2925, 1694, 1640, 1387, 1085. ^1H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 657.3980 ($[M+Na]^+$, $C_{36}H_{58}NaO_9^+$; calc. 657.3979).

Lobelioidosides D (=*Anagalligenone 3-*O*-α-*L*-Arabinopyranosyl-(1→4)-β-*D*-xylopyranosyl-(1→2)-β-*D*-glucopyranoside*=*(3β)-23-Hydroxy-16-oxo-13,28-epoxyoleanan-3-yl α-*L*-Arabinopyranosyl-(1→4)-β-*D*-xylopyranosyl-(1→2)-β-*D*-glucopyranoside*; **4**). White amorphous powder. M.p. 271–273.5°. $[\alpha]_D^{20} = -5.47$ ($c = 0.73$, $CHCl_3$/MeOH 1:1). IR (KBr): 3441, 2929, 2860, 1703, 1640, 1448, 1173,

1076. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 921.4458 ($[M+Na]^+$, $C_{46}H_{74}NaO_{17}^+$; calc. 921.4450).

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Received July 25, 2013