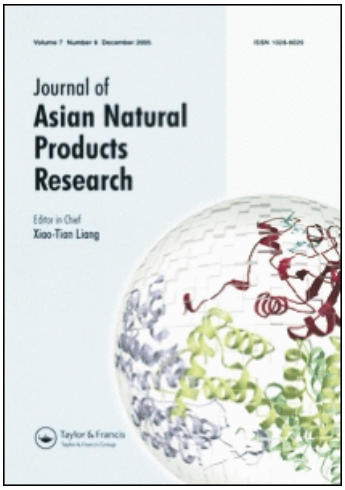

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Three new C_{21}-steroidal glycosides from the roots of *Cynanchum inamoenum*

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Three new C_{21}-steroidal glycosides presenting an unusual 13,14:14,15-disecopregnane-type skeleton, named inamosides A–C (**1**–**3**), together with two known C_{21}-steroidal glycosides, were isolated from the MeOH extract of the roots of *Cynanchum inamoeum* (Maxim.) Loes (Asclepiadaceae). The aglycone of compounds **1**, **2**, and **3** has a 2β-hydroxyl, which has not yet been reported in the literature. The structure and relative configuration of the aglycone of compounds **1**, **2**, and **3** were established by X-ray crystallographic analysis.

Keywords: *Cynanchum inamoenum* (Maxim.) Loes; Asclepiadaceae; Inamosides A, B, C; 2-*Epi*-glaucogenin A

1. Introduction

C_{21}-steroidal is rich in the plants of the genus *Cynanchum*. According to our groups' previous work, the existences of various C_{21}-steroidal in this genus show some chemotaxonomical significance [1,2]. *Cynanchum inamoenum* (Maxim.) Loes (Asclepiadaceae), widely distributed in China, is used as folk medicine to treat many diseases, such as scrofula, rupture, scabies, and internal fever [3]. A literature search revealed that no phytochemical study had been undertaken on this species. As part of our groups' ongoing investigation of the genus *Cynanchum*, we collected the roots of *C. inamoenum* from Mountain Tai in Shandong province, China. From the MeOH extract, three new C_{21}-steroidal glycosides presenting an unusual 13,14:14,15-disecopregnane-type skeleton, named inamosides A–C (**1**–**3**), together with two known compounds, were isolated. This report deals with the isolation and structural elucidation of these compounds.

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2. Results and discussion

Compound **1** (figure 1) was obtained as white amorphous solid. Its molecular formula was determined as $C_{47}H_{72}O_{20}$ by HRESI-MS at *m/z* 955.4521 $[M - H]^-$, which was identical to the ^{13}C NMR and DEPT experiments. In the ^1H NMR, ^{13}C NMR and HMQC spectra, four anomeric carbons at δ 98.6, 98.7, 99.9, and 105.0, and their corresponding anomeric protons at δ 4.94 (1H, d, 9.4 Hz), 5.43 (1H, d, 7.1 Hz), 5.26 (1H, brs), and 5.25 (1H, d, 7.8 Hz) were observed. From the coupling constants of the anomeric protons, three sugars of β-linkage and one sugar of α-linkage were revealed.

Acid hydrolysis of **1** furnished the aglycone **1a**. Moreover, oleandrose, cymarose, and glucose were detected in the hydrolysate by TLC comparison with authentic samples. The molecular formula of **1a** was determined as $C_{21}H_{28}O_6$ by HRESI-MS ion peak at *m/z* 399.1792 $[M + Na]^+$. The ^1H NMR spectrum of **1a** showed signals for methyl groups at δ 1.36 (3H, s, H-19) and 1.56 (3H, s, H-21), one trisubstituted olefinic proton at δ 5.46 (1H, m, H-6), one trisubstituted olefinic deshielded proton at δ 6.49 (1H, s, H-18), three oxygen-substituted methine protons at δ 5.46 (1H, m, H-16), 4.47 (brs, H-2), 3.94 (brd, 11.8 Hz, H-3), and two oxygen-substituted methylene protons at δ 3.97 (d, 7.4 Hz, H_α-15) and 4.31 (t, 7.4 Hz, H_β-15). The ^{13}C NMR spectrum revealed the presences of two pairs of characteristic olefinic carbon atoms at δ 142.4 and 119.4, 114.5 and 143.8, one carbonyl carbon at δ 175.7 (table 1). All of the above data were very similar to those of glaucogenin A [4]. A careful comparison showed that the orientation of 2-OH of **1a** was not the same as that of glaucogenin A. For a chairlike confirmation of the A-ring, the orientation of the H-2 was deduced to be α-oriented from its broad singlet signal. Thus the orientation of the 2-OH was β-oriented. However, this elucidation was questionable, since there were several signals overlapped in the ^1H NMR spectrum and the NOESY correlation cannot be assigned. Finally, we obtained its singlet crystal for X-ray analysis. The structure and the configuration of **1a** were confirmed unambiguously by X-ray crystallographic analysis (figure 2). From the above, the structure of **1a** was determined to be a new compound named 2-*epi*-glaucogenin A. This was the first report of 2-*epi*-glaucogenin A.

The NMR data of the sugar moieties of compound **1** and the inter-sugar linkages were very identical to those of komaroside D [2], which was confirmed by the acid hydrolysis results and HMBC correlations between H-1$''''$ of glucose (δ 5.25) and C-4$'''$ of oleandrose (δ 82.3); H-1$'''$ of oleandrose (δ 5.26) and C-4$''$ of digitoxose (δ 82.2); H-1$''$ of digitoxose (δ 5.43) and C-4$'$ of oleandrose (δ 83.1); and H-1$'$ of oleandrose (δ 4.94) and C-3 of the aglycone (δ 80.4). In addition, comparison the ^{13}C NMR spectral data of **1** with those of **1a** revealed glycosidation shifts in the resonances of C-2 (−1.1 ppm), C-3 (+7.4 ppm) and C-4 (−3.5 ppm) of the aglycone moiety, which further supported that the sugar moiety was located at the C-3 position of the aglycone. On the basis of the above evidence, the structure of **1** was deduced to be 2-*epi*-glaucogenin A 3-*O*-β-D-glucopyranosyl-(1 → 4)-α-D-oleandropyranosyl-(1 → 4)-β-D-digitoxopyranosyl-(1 → 4)-β-D-oleandropyranoside, and was named inamoside A.

Compound **2** (figure 1) was assigned a molecular formula $C_{47}H_{72}O_{20}$ by its HRESI-MS ion peak at *m/z* 955.4518 $[M - H]^-$, which was supported by the ^{13}C NMR and DEPT experiments. The aglycone was identified as 2-*epi*-glaucogenin A by comparison its spectroscopic data with those of **1a**. The glycosidation shift of the aglycone was observed at C-2 (−1.1 ppm), C-3 (+7.4 ppm) and C-4 (−3.5 ppm), comparing with the corresponding

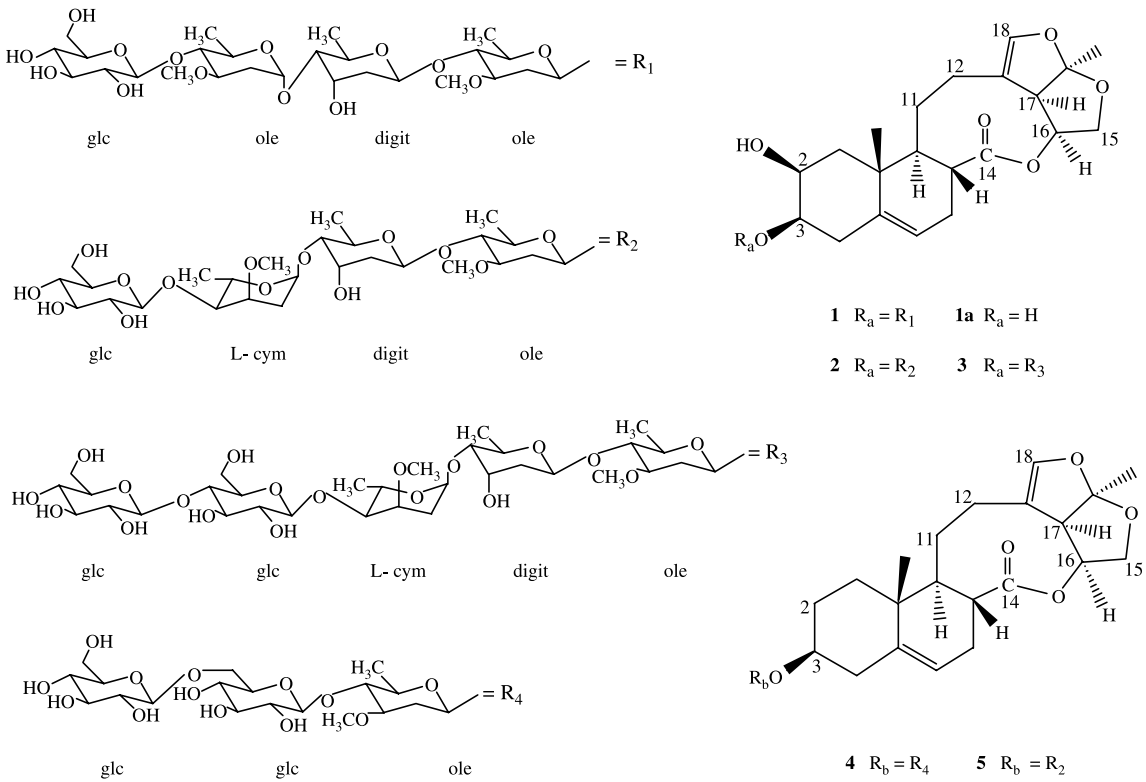

Figure 1. The structures of compounds **1**, **2**, **3**, **4**, and **5**.

Table 1. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectral data of **1a** (ppm, in C_5D_5N).

	δc	δ_H		δc	δ_H
1α	43.4 t	1.26–1.19 overlap	12α	30.2 t	2.22 overlap
1β		2.44 overlap	12β		1.31 m
2α	70.3 d	4.47 brs	13	114.5 s	–
3α	73.0 d	3.94 brd 11.8 Hz	14	175.7 s	–
4α	36.9 t	2.44 overlap	15α	67.8	3.97 d 7.4 Hz
4β		3.11 t 11.8, 11.8 Hz	15β		4.31 t 7.4, 7.4 Hz
5	142.4 s	–	16	75.6 d	5.46 m
6	119.4 d	5.46 m	17	56.3 d	3.60 d 7.8 Hz
7α	28.4 t	2.57 m	18	143.8 d	6.49 s
7β		2.22 m			
8	40.4 d	2.55 m	19	21.4 q	1.36 s
9	53.9 d	1.26–1.19 overlap	20	118.6 s	–
10	38.6 s	–	21	24.9 q	1.56 s
11α	24.1 t	2.66 overlap			
11β		1.41 m			

chemical shifts of **1a**, which indicated the attachment of the sugar chain at the C-3 position of 2-*epi*-glaucogenin A. Four anomeric protons at δ 4.87 (1H, d, 9.0 Hz), 5.43 (1H, d, 9.9 Hz), 5.06 (1H, brs), and 5.00 (1H, d, 7.8 Hz) were observed in its sugar moiety, indicating that there were four sugar units with one α-linkage and three β-linkages in **2**. Acid hydrolysis of compound **2** yielded an aglycone (**1a**) and four sugar components digitoxose, oleandrose, cymarose, and glucose, identified by comparison with authentic samples. The data of the sugar moiety and the interlinkage between the sugars were the same as those of komaroside E [2], which was confirmed by the ^{1}H–^{1}H COSY, HMQC, and HMBC spectra of **2**. Hence, the structure of **2** was deduced to be 2-*epi*-glaucogenin A 3-*O*-β-D-glucopyranosyl-(1 → 4)-α-L-cymaropyranosyl-(1 → 4)-β-D-digitoxopyranosyl-(1 → 4)-β-D-oleandropyranoside, and was named inamoside B.

Compound **3** (figure 1) was assigned a molecular formula $C_{53}H_{82}O_{25}$ by its HRESI-MS at *m*/*z* 1117.5061 $[M - H]^-$, which was supported by the ^{13}C NMR and DEPT experiments. A careful comparison of the ^{1}H NMR and ^{13}C NMR spectral data of **3** with those of compound **2** indicated that the two structures were very similar except that there was an additional glucose unit in compound **3**. In the HMBC spectrum, long-range correlations were observed between H-1$''''$ of terminal β-D-glucose (δ 5.20) and C-4$''''$ of β-D-glucose (δ 81.3); H-1$''''$ of β-D-glucose (δ 4.96)

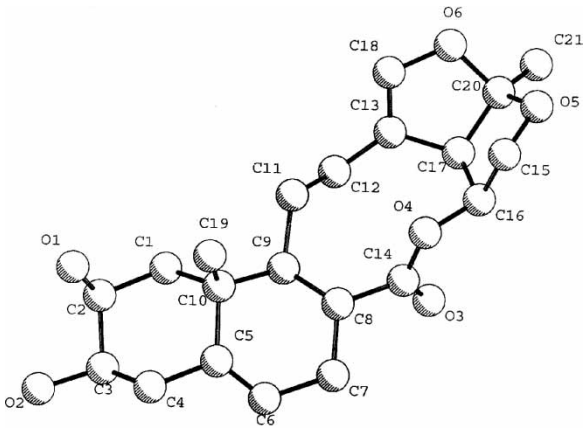

Figure 2. X-ray crystal structure of **1a**.

and C-4‴ of cymarose (δ 78.5); H-1‴ of cymarose (δ 5.04) and C-4″ of digitoxose (δ 81.2); H-1″ of digitoxose (δ 5.42) and C-4′ of oleandrose (δ 82.9); and H-1′ of oleandrose (δ 4.84) and C-3 (δ 80.4), so the linkage between the sugars was established as shown in figure 1. On the above evidence, the structure of **3** was deduced to be 2-*epi*-glaucogenin A 3-*O*-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 4)-α-L-cymaropyranosyl-(1 → 4)-β-D-digitoxopyranosyl-(1 → 4)-β-D-oleandropyranoside, which was confirmed by its ^{1}H–^{1}H COSY, HMQC, HMBC, and HMQC-TOCSY spectra. Compound **3** was named inamoside C.

Along with three new compounds, two known compounds were also obtained. By comparison their spectral data with those reported in the literature [5,6], these compounds were identified as komaroside C (**4**) and cynatratoside D (**5**), which were isolated from this plant for the first time.

3. Experimental

3.1 General experimental procedures

All melting points were measured on an X-4 micromelting apparatus and uncorrected. Optical rotations were measured on a SEPA-300 polarimeter. The IR spectrum was recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. The NMR spectra were recorded on Bruker AV-400 and DRX-500 spectrometers in pyridine-d_5 solution with TMS as an internal standard. MS data were obtained on a VG Autospec-3000 spectrometer. HRESI-MS data were recorded with an API QSTAR Pulsar 1 spectrometer.

3.2 Plant material

The materials were collected from Mountain Tai in Shandong province of China in 2002 and identified by Wang Yong in Shandong Senior Technicians School of Chinese Traditional Medicines, where a voucher specimen (No. yc02100811wch) is deposited.

3.3 Extraction and isolation

The air-dried and powdered roots of *Cynanchum inamoenum* (Maxim.) Loes (3.7 kg) were extracted with MeOH under reflux to give a crude extract. After concentration of the combined extracts, the resulting gummy material was suspended in water and then partitioned with $CHCl_3$ to afford $CHCl_3$ and aqueous residues (110 g and 60 g, respectively). The $CHCl_3$ residue was subjected to column chromatography over silicon gel and eluted with $CHCl_3$/CH_3OH (9:1) to give three fractions. The second fraction was repeatedly subjected to column chromatography over silicon gel, Sephadex LH-20, and RP-18 to afford compound **5** (61 mg). The third fraction was repeatedly subjected to column chromatography over silicon gel, Sephadex LH-20, and RP-18 to afford compounds **1** (34 mg), **2** (15 mg), **3** (16 mg), and **4** (36 mg).

3.3.1 Inamoside A (1). $C_{47}H_{72}O_{20}$, white amorphous solid, mp 140–143°C, $IR^{KBr}_{\nu max}$ (cm^{-1}): 3441, 2932, 1731, 1651, 1452, 1383, 1310, 1163, 1057, $[\alpha]_D^{16.2}$ −2.40 (*c* 0.417, CH_3OH), negative FAB-MS *m/z* (%): 956 $[M]^-$ (100), 793 $[M - H\text{-}162]^-$ (2), 649 $[M - H\text{-glucose-}144]^-$ (3); HRESI-MS *m/z* 955.4521 $[M - H]^-$ (calcd for $C_{47}H_{72}O_{20}$, 955.4538). ^{1}H NMR and ^{13}C NMR spectral data: see table 2.

Table 2. ^{13}C NMR (125 MHz) and partial ^{1}H NMR (500 MHz) spectral data of compounds **1**, **2**, and **3** (ppm, in C_5D_5N).

	1 δc	***2*** δc	***3*** δc		***1*** δc	***1*** δ_H	***2*** δc	***2*** δ_H	***3*** δc	***3*** δ_H
1	43.1	43.1	43.1		β-D-ole	β-D-ole	β-D-ole	β-D-ole	β-D-ole	β-D-ole
2	69.2	69.2	69.1	1′	98.6	4.94 d (9.4)	98.8	4.87 d (9.0)	98.8	4.84 d (10.2)
3	80.4	80.4	80.4	2′	37.8	1.75m	37.8	1.73 m	37.7	1.73 m
						2.49†		2.47†		2.41†
4	33.4	33.4	33.3	3′	79.1	3.58†	79.1	3.56†	79.1	3.57†
5	141.7	141.7	141.6	4′	83.1	3.52 t (9.4)	83.0	3.51†	82.9	3.50†
6	120.2	120.2	120.2	5′	71.9	3.60†	71.8	3.56†	71.5	3.57†
7	28.5	28.5	28.4	6′	18.3	1.43 d (6.0)	18.3	1.43 d (6.0)	18.8	1.42 d (5.8)
8	40.4	40.4	40.4	OMe	57.5	3.50 s	57.5	3.54 s	57.4	3.51 s
9	53.9	53.9	53.9		β-D-digit	β-D-digit	β-D-digit	β-D-digit	β-D-digit	β-D-digit
10	38.7	38.7	38.7	1″	98.7	5.43 d (7.1)	98.6	5.43 d (9.9)	98.5	5.42 d (9.0)
11	24.1	24.1	24.1	2″	40.0	1.99 brt (9.6)	38.7	1.93 brt (9.9)	38.7	1.93 brt (9.0)
						2.66†		2.47†		2.40†
12	30.0	30.0	30.0	3″	69.0	4.49†	69.2	4.49†	69.1	4.48†
13	114.5	114.5	114.5	4″	82.2	3.44 dd (2.0,8.0)	81.3	3.46 dd (3.0,9.2)	81.2	3.44 dd (3.2,9.6)
14	175.8	175.8	175.7	5″	67.7	4.33†	68.0	4.26†	67.8	4.26 m
15	67.9	67.9	67.8	6″	18.6	1.39 d (6.4)	18.6	1.39 d (6.4)	18.6	1.35 d (6.3)
16	75.7	75.7	75.6		α-D-ole	α-D-ole	α-L-cym	α-L-cym	α-L-cym	α-L-cym
17	56.3	56.3	56.3	1‴	99.9	5.26 s	98.5	5.06 s	98.4	5.04 brs
18	143.9	143.9	143.9	2‴	35.6	1.72 brd (10.0)	32.6	1.87 brd (11.6)	32.6	1.84 brd (11.0)
						2.49†		2.47†		2.41†
19	21.3	21.4	21.4	3‴	78.8	3.98†	73.7	3.96†	73.7	3.89†
20	118.6	118.6	118.6	4‴	82.3	3.85 t (8.6)	78.5	3.96†	78.5	3.89†
21	24.9	24.9	24.8q	5‴	68.1	4.36†	66.1	4.64 dq (7.3, 6.4)	65.8	4.58 dq (7.3, 6.3)
				6‴	18.8	1.39 d (6.4)	18.8	1.39 d (6.4)	18.2	1.32 d (6.3)
				OMe	56.8	3.32 s	57.2	3.49 s	57.3	3.48 s
					β-D-glc	β-D-glc	β-D-glc	β-D-glc	β-D-glc	β-D-glc
				1⁗	105.0	5.25 d (7.8)	102.4	5.00 d (7.8)	104.3	4.96 d (7.5)
				2⁗	75.9	3.96†	75.4	4.00†	74.9	4.10 t (8.3)
				3⁗	78.4	4.02†	78.2	4.02†	76.6	4.02†
				4⁗	71.9	4.19 t (9.0)	71.8	4.19 t (9.0)	81.3	4.31†
				5⁗	78.4	4.26†	78.7	4.26†	76.7	4.31†
				6⁗	62.9	4.54 dd (11.5, 2.5)	62.9	4.55 dd (11.5, 2.5)	62.2	4.54 dd (11.8, 3.0)

Table 2 – *continued*

1 δc	***2*** δc	***3*** δc		***1*** δc	***1*** δ_H	***2*** δc	***2*** δ_H	***3*** δc	***3*** δ_H
					4.33[†]		4.35 dd (11.5, 5.5)		4.31[†]
								β-D-glc	β-D-glc
			$1''''$					104.9	5.20 d (7.8)
			$2''''$					74.9	3.97[†]
			$3''''$					78.3	4.22 t (9.1)
			$4''''$					71.8	4.22 t (9.1)
			$5''''$					78.5	3.89[†]
			$6''''$					62.4	4.54 dd (11.8, 3.0)
									4.31[†]

[†] Overlapping with other signals: ole, oleandropyranosyl; digit, digitoxoyranosyl; cym, cymaropyranosyl; glc, glucopyranosyl.

3.3.2 2-*epi*-glaucogenin A (1a). $C_{21}H_{28}O_6$, colourless sheet ($CH_3OH/CHCl_3$), mp 220–224°C, $IR_{\nu max}^{KBr}$ (cm^{-1}): 3548, 3404, 1700, 1625, 1347, 1279, 1113; EIMS *m/z* (%): 376 [M]$^+$(34), 330 (100), 312 (27), 137 (59), HRESI-MS *m/z*: 399.1792 $[M + Na]^+$ (calcd for $C_{21}H_{28}O_6$, 399.1783). ^1H NMR and ^{13}C NMR spectral data: see table 1.

3.3.3 Inamoside B (2). $C_{47}H_{72}O_{20}$, white amorphous solid, mp 110–114°C, $IR_{\nu max}^{KBr}$ (cm^{-1}): 3432, 2930, 1733, 1678, 1452, 1382, 1308, 1161, 1127, 1065, $[\alpha]_D^{16.1} + 0.69$ (*c* 0.242, CH_3OH), negative FAB-MS *m/z* (%): 955 $[M - H]^-$ (100), 649 $[M - 162\text{-}144\text{-}H]^-$ (3), HRESI-MS *m/z* 955.4518 $[M - H]^-$ (calcd for $C_{47}H_{72}O_{20}$, 955.4538). ^1H NMR and ^{13}C NMR spectral data: see table 2.

3.3.4 Inamoside C (3). $C_{53}H_{82}O_{25}$, white amorphous solid, mp 142–146°C, $IR_{\nu max}^{KBr}$ (cm^{-1}): 3426, 2931, 1730, 1678, 1452, 1381, 1310, 1162, 1101, 1071, $[\alpha]_D^{20.2} -118.18$ (*c* 0.55, $CHCl_3$), negative FAB-MS *m/z* (%): 1117 $[M - H]^-$ (50), 955 $[M - 162\text{-}H]^-$ (8), HRESI-MS *m/z* 1117.5061 $[M - H]^-$ (calcd for $C_{53}H_{82}O_{25}$, 1117.5066). ^1H NMR and ^{13}C NMR spectral data: see table 2.

3.4 X-ray structure of compound 1a

Crystal data: $C_{21}H_{28}O_6$, M = 376.45, monoclinic system, space group: $P2_1$, $a = 7.548$ (1), $b = 9.721$ (1), $c = 13.190$ (2) Å, $\beta = 74.89$ (1) °, $V = 934.3$ (2) Å^3, $Z = 2$, $d = 1.324$ g/cm^3. A crystal of dimensions 0.05 × 0.10 × 0.20 mm was used for X-ray measurements on a MAC DIP-2030K diffractometer with a graphite monochromator, with maximum 2θ value of 50.0°, MoKα radiation. The total number of independent reflections measured was 1775, of which 1386 were considered to be observed ($|F|^2 \geq 3\sigma|F|^2$). The crystal structure was solved by the direct method SHELX-86 and expanded using difference Fourier techniques, refined by the program and method NOMCSDP and full-matrix least-squares calculation. The final indices were $R_f = 0.074$, $R_w = 0.072$ ($w = 1/\sigma|F|^2$). Crystallographic data for the structure has been deposited in the Cambridge Crystallographic Data centre (deposition number: CCDC271588).

3.5 Acid hydrolysis of compound 1

Compound **1** (20 mg) was hydrolysed with 1:2 (v/v) 0.2 N H_2SO_4-dioxane (15 ml) for 2 h under reflux in a water bath at 70°C, then diluted with 10 ml water and concentrated to the initial volume, and neutralised with sat. $Ba(OH)_2$ aq., and the precipitate was filtered off. The filtrate was extracted with $CHCl_3$ (10 ml × 4) to afford $CHCl_3$ and aqueous residues. The $CHCl_3$ residue was subjected to column chromatography over silica gel and eluted with petroleum ether/CH_3COCH_3 to give **1a** (6 mg). From the aqueous residue, oleandrose and digitoxose were detected by TLC comparison with authentic samples using solvent system A: petroleum ether/CH_3COCH_3 (3:2), B: CH_2Cl_2/C_2H_5OH (9:1), and C: $CHCl_3/CH_3OH$ (9:1). Glucose was identified by TLC comparison with authentic sample with solvent system $CHCl_3/CH_3OH/H_2O$ (4:3:1).

3.6 Acid hydrolysis of compounds 2 and 3

Each solution of 2 mg of **2** and **3** in 3 ml dioxane was treated with 1.5 ml 0.2 N H_2SO_4 and the mixture was under reflux in a water bath at 70°C for 2 h, then diluted with 3 ml water and concentrated to the initial volume, then neutralised with sat. $Ba(OH)_2$ aq., and the precipitate was filtered off. The filtrate was extracted with $CHCl_3$ (3 ml × 3) to afford $CHCl_3$ and aqueous residues. In the aqueous residues, oleandrose, cymarose, digitoxose and glucose for **2**; oleandrose, cymarose, digitoxose and glucose for **3** were individually detected by TLC comparison with authentic samples with the same solvent systems as those of **1**. The R_f values of oleandrose, cymarose, digitoxose were 0.45, 0.50, 0.23 with solvent A, 0.44, 0.53, 0.27 with solvent B, 0.42, 0.49, 0.17 with solvent C, respectively. The R_f values of glucose was 0.58 with solvent $CHCl_3/CH_3OH/H_2O$ (4:3:1).

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