Three New Diterpenoids from *Rabdosia lophanthoides* var. *gerardiana*

by **Chen-Yang Li**[a]), **Hao Gao**[b])[c]), **Wei-Hua Jiao**[a]), **Long Zhang**[a]), **Guang-Xiong Zhou**[b])[c]), and **Xin-Sheng Yao***[a])[b])[c])

[a]) School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, P. R. China (phone/fax: +86-24-23993994; e-mail: yaoxinsheng@vip.tom.com)

[b]) Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy, Jinan University, Guangzhou 510632, P. R. China

[c]) Guangdong Province Key Laboratory of Pharmacodynamic Constituents of TCM & New Drugs Research, Jinan University, Guangzhou 510632, P. R. China

Three new diterpenoids, together with three known ones, were isolated from the air-dried whole herbs of *Rabdosia lophanthoides* var. *gerardiana*. The structures of the new diterpenoids were established as 3,4-dihydro-11-hydroxy-10-(1-hydroxy-1-methylethyl)-2,2,6-trimethylnaphtho[1,8-*bc*]oxocin-5(2*H*)-one (**1**), 11,12,15-trihydroxyabieta-5,8,11,13-tetraen-7-one (**2**), (2*R*,3*S*,4*S*,4a*R*,8*S*,9a*S*,13a*S*,16a*S*)-3,4,4a,8,9,9a,10,11,12,13,14,16a-dodecahydro-2-(hydroxymethyl)-6,6,10,10-tetramethyl-2*H*-benzo[4,5]-cyclohepta[1,2-*h*]pyrano[2,3-*b*][1,4]benzodioxepine-3,4,8,13a,15(6*H*)-pentol (**3**) by spectroscopic methods, including extensive 1D- and 2D-NMR analyses. The structures of the known compounds were identified by comparison of their physical and spectroscopic data with those reported in the literature.

Introduction. – *Rabdosia lophanthoides* (BUCH.-HAM. EX. D. DON) HARA. var. *gerardiana* (BENTH.) HARA, belonging to the Labiatae family, is one source of Chinese medicine 'Xihuangcao'. Xihuangcao as a folk medicine is used for the treatment of acute hepatitis, cholecystitis, enteritis, dysentery, and trauma [1]. It was reported that *R. lophanthoides* var. *gerardiana* had protective effects on acute hepatic injury [2][3]. Therefore, it is widely used in Southern China as a folk medicine, and health-care food or drink. Previous phytochemical investigations of this plant led to the isolation of a series of diterpenoids [4–12].

In our current study, three new diterpenoids named as rabdosin D (**1**), (+)-15-hydroxysalvinolone (**2**), and rabdosiacoside A (**3**) were isolated from the air-dried whole plant of *R. lophanthoides* var. *gerardiana*, as well as three known ones, isodoforrestin (**4**) [13], 3α-hinokiol (**5**) [14], and 16-acetoxyhorminone (**6**) [15] (*Fig. 1*). The structures of new diterpenoids were elucidated by exhaustive spectroscopic analyses, especially by their 2D-NMR spectra. The known diterpenoids were indentified by comparison of their physical and spectroscopic data with those reported in the literature.

Results and Discussion. – The 95% aqueous EtOH extract of the air-dried whole plant of *R. lophanthoides* var. *gerardiana* was suspended in H_2O, and then partitioned with cyclohexane, AcOEt, and BuOH successively. The cyclohexane-soluble fraction

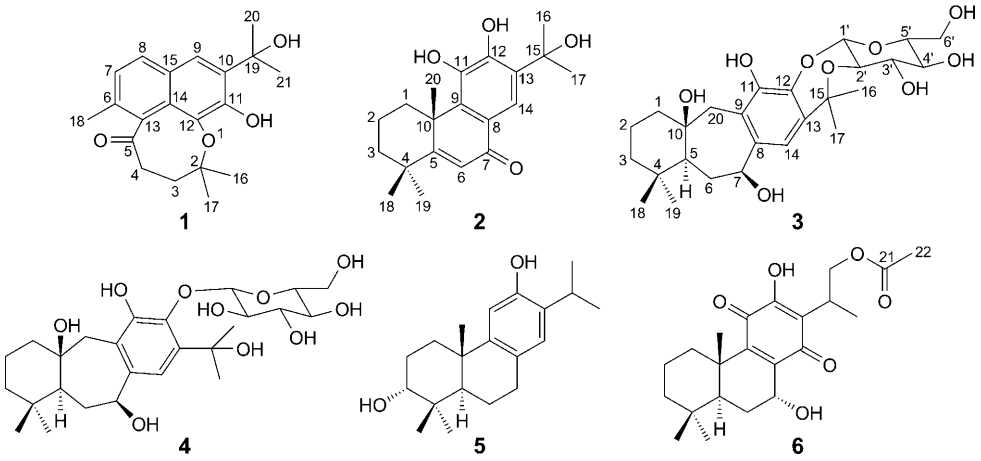

Fig. 1. *Structures of compounds* **1**–**6**

was further chromatographed separately over silica gel, *Sephadex LH-20*, and *ODS*, and by preparative HPLC to afford diterpenoids **1**–**6**.

Compound **1** was obtained as yellowish crystals. Its molecular formula of $C_{20}H_{24}O_4$ was determined by HR-ESI-MS (*m*/*z* 351.1586 ($[M+Na]^+$); calc. 351.1572). The structure of **1** was established as 3,4-dihydro-11-hydroxy-10-(1-hydroxy-1-methylethyl)-2,2,6-trimethylnaphtho[1,8-*bc*]oxocin-5(2*H*)-one by analyses of ^{1}H- and ^{13}C-NMR, DEPT-135, ^{1}H,^{1}H-COSY, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*). This new diterpenoid was named rabdosin D.

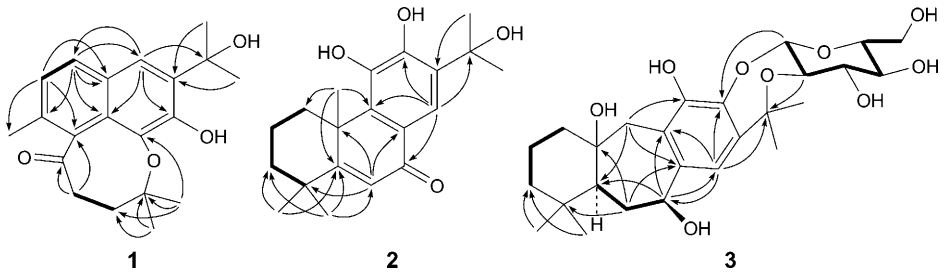

Fig. 2. *Key correlations in the HMBC* (H → C) *and* ^{1}*H,*^{1}*H-COSY* (—) *spectra of compounds* **1**–**3**

The ^{1}H-NMR spectrum of compound **1** displayed three aromatic H-atom signals at δ(H) 7.50 (*d*, *J* = 8.4, 1 H), 7.43 (*s*, 1 H), and 7.03 (*d*, *J* = 8.4, 1 H), and five Me signals at δ(H) 2.32, 1.73, 1.68, 1.61, and 1.24 (each *s*). A total of 20 C-atom signals were observed in the ^{13}C-NMR and DEPT-135 spectra of **1** (*Table 2*), which showed a CO signal at δ(C) 210.2, ten aromatic C-atom signals at δ(C) 147.4, 134.5, 133.4, 132.3, 131.2, 128.6, 128.2, 126.6, 126.1, and 120.8, two oxygenated quaternary C-atom signals at δ(C) 84.3 and 73.6, two signals for CH_2 at δ(C) 41.2 and 35.4, and five Me signals at δ(C) 29.5, 29.3, 26.1, 25.8, and 19.0. These data revealed that compound **1** was a diterpenoid.

Table 1. *^{1}H-NMR* (400 MHz) *Data of Compounds* **1**–**3**. δ in ppm, J in Hz.

	1 ($CDCl_3$)	**2** ((D_6)DMSO)	**3** (CD_3OD)
CH_2(1)		1.25–1.29 (*m*), 3.35–3.37 (*m*)	1.52–1.56 (*m*), 1.76–1.79 (*m*)
CH_2(2)		1.53–1.56 (*m*), 1.88–1.98 (*m*)	1.40–1.42 (*m*), 1.85–1.88 (*m*)
CH_2(3)	1.56–1.60 (*m*), 2.07 (*td*, *J* = 14.6, 3.5)	1.37–1.44 (*m*), 1.65–1.76 (*m*)	1.28–1.33 (*m*), 1.37–1.40 (*m*)
CH_2(4)	2.56 (*dt*, *J* = 15.0, 4.2), 3.01 (*td*, *J* = 14.7, 3.6)		
H–C(5)			1.48 (*dd*, *J* = 11.9, 2.0)
H–C(6) or CH_2(6)		6.23 (*s*)	1.63–1.71 (*m*), 1.98 (*d*, *J* = 13.2)
H–C(7)	7.03 (*d*, *J* = 8.4)		4.71 (*d*, *J* = 9.9)
H–C(8)	7.50 (*d*, *J* = 8.4)		
H–C(9)	7.43 (*s*)		
H–C(14)		7.39 (*s*)	7.00 (*s*)
Me(16)	1.61 (*s*)	1.53 (*s*)	1.61 (*s*)
Me(17)	1.24 (*s*)	1.56 (*s*)	1.63 (*s*)
Me(18)	2.32 (*s*)	1.23 (*s*)	0.95 (*s*)
Me(19)		1.32 (*s*)	0.87 (*s*)
Me(20) or CH_2(20)	1.73 (*s*)	1.60 (*s*)	2.35 (*d*, *J* = 14.4), 3.33 (*d*, *J* = 14.3)
Me(21)	1.68 (*s*)		
Sugar moiety 12-*O*-Glc			
H–C(1′)			4.65 (*d*, *J* = 7.7)
H–C(2′)			3.49–3.51 (*m*)
H–C(3′)			3.45–3.48 (*m*)
H–C(4′)			3.19 (*t*, *J* = 9.5)
H–C(5′)			3.39–3.42 (*m*)
CH_2(6′)			3.57–3.63 (*m*), 3.91 (*dd*, *J* = 11.6, 2.1)

Based on the analyses of the ^{1}H,^{1}H-COSY and HSQC data, the following fragments of C(2)–C(3)–C(4)–C(5) and C(7)–C(8) should exist. In the HMBC spectrum, the ^{1}H,^{13}C long-range correlations between H–C(7)/C(18), C(13), and C(15), H–C(8)/C(6), C(9), C(14), and C(15), H–C(9)/C(8), C(11), C(14), and C(19), Me(18)/C(7) and C(13), Me(20)/C(10), C(19), and C(21), Me(21)/C(10), C(19), and C(20) (*Fig. 2*) suggested the naphthalene moiety was present in the molecule, while an ^{i}Pr group and a Me group were located at C(10) and C(6), respectively. Furthermore, the ^{1}H,^{13}C long-range correlations between Me(16)/C(2), C(3), and C(17), Me(17)/C(2), C(3), and C(16) suggested that C(16) and C(17) were connected to C(2). In addition, the HMBCs between H–C(4) (δ(H) 3.01 (*td*, *J* = 14.7, 3.6)) and C(13) (δ(C) 132.3), and between H–C(16) (δ(H) 1.61 (*s*)) and C(12) (δ (C) 133.4) (*Fig. 2*) indicated that C(5) was connected to C(13), while C(12) was connected to C(2) through an O-bridge.

Compound **2** was obtained as colorless crystals with $[\alpha]_D^{27} = +35.6$ ($c = 0.26$, $CHCl_3$). The molecular formula of $C_{20}H_{26}O_4$ was determined by HR-ESI-MS (m/z 353.1707 ($[M + Na]^+$); calc. 353.1729). The structure of **2** was established as 11,12,15-trihydroxyabieta-5,8,11,13-tetraen-7-one by analyses of ^{1}H- and ^{13}C-NMR, DEPT-135,

Table 2. *^{13}C-NMR* (100 MHz) *Data of Compounds* **1**–**3** *and Salvinolone*[a]). δ in ppm.

	1 ($CDCl_3$)	**2** ((D$_6$)DMSO)	**3** (CD_3OD)	Salvinolone ((D$_6$)DMSO)[a])
C(1)		33.6	42.7	33.8
C(2)	84.3	18.1	19.6	18.2
C(3)	35.4	39.0	43.4	39.0
C(4)	41.2	37.5	35.1	37.5
C(5)	210.2	173.9	56.5	173.9
C(6)	131.2	122.5	35.1	122.6
C(7)	126.6	183.7	73.9	183.8
C(8)	128.6	121.6	144.0	122.6
C(9)	120.8	137.8	122.1	137.6
C(10)	134.5	41.5	72.0	41.5
C(11)	147.4	142.1	149.0	142.5
C(12)	133.4	148.2	138.5	147.5
C(13)	132.3	130.9	136.7	134.2
C(14)	128.2	113.4	111.6	114.1
C(15)	126.1	74.0	80.6	24.6
C(16)	26.1	30.0	30.6	22.8
C(17)	25.8	29.8	27.5	22.6
C(18)	19.0	32.8	32.8	26.1
C(19)	73.6	29.1	22.2	29.1
C(20)	29.5	24.2	40.9	32.8
C(21)	29.3			
Sugar moiety 12-*O*-Glc				
C(1′)			103.4	
C(2′)			76.8	
C(3′)			76.0	
C(4′)			71.5	
C(5′)			79.4	
C(6′)			62.9	

[a]) ^{13}C-NMR Data for salvinolone from [16].

^{1}H,^{1}H-COSY, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*). The compound, a new diterpenoid, was named (+)-15-hydroxysalvinolone.

The ^{1}H-NMR spectrum of compound **2** displayed two signals at δ(H) 6.23 (*s*, 1 H) and 7.39 (*s*, 1 H), which were assigned to two aromatic H-atoms, and five Me signals at δ(H) 1.60, 1.56, 1.53, 1.32, and 1.22 (each *s*). A total of 20 C-atom signals were observed in the ^{13}C-NMR, DEPT-135, and HSQC spectra of **2** (*Table 2*): a signal at δ(C) 183.7, corresponding to a CO group, eight unsaturated-C-atom signals at δ(C) 173.9, 148.2, 142.0, 137.8, 130.9, 122.5, 121.6, and 113.4, three quaternary C-atom signals at δ(C) 74.0, 41.5, and 37.5, three signals for CH_2 at δ(C) 39.0, 33.6, and 18.1, and five Me signals at δ(C) 32.8, 30.0, 29.8, 29.1, and 24.2. On the basis of the above data, compound **2** was also deduced as a diterpenoid. Analyses of the ^{1}H,^{1}H-COSY and HSQC data allowed the deduction of fragment C(1)–C(2)–C(3) (*Fig. 2*). The ^{1}H,^{13}C long-range correlations of H–C(6)/C(4), C(8), and C(10), H–C(14)/C(7), C(9), C(12), and C(15), Me(16)/C(13), C(15), and C(17), Me(17)/C(13), C(15), and C(16), Me(18)/C(3), C(4), C(5), and C(19), Me(19)/C(3), C(4), C(5), and C(18), Me(20)/C(1), C(5), C(9),

and C(10) in the HMBC plots suggested an abietane skeleton, while a CO group was placed at C(7), and a conjugated C=C bond was located between C(5) and C(6). The ^{13}C-NMR spectrum showed very similar chemical shifts for C(1) to C(10) to those of salvinolone [16] (*Table 2*). However, the molecular formula $C_{20}H_{26}O_4$ together with the ^{1}H- and ^{13}C-NMR spectra indicated the presence of an additional OH group. The comparison of the ^{13}C-NMR data of **2** with those of salvinolone showed a downfield shift $\Delta\delta = +49.4$ for C(15), a downfield shift $\Delta\delta = +7.2$ for C(16), a downfield shift $\Delta\delta = +7.2$ for C(17), and an upfield shift $\Delta\delta = -3.3$ for C(13), suggesting that the OH group was placed at C(15). The assignments of ^{1}H- and ^{13}C-NMR signals of C(18) and C(19) were on the basis of the correlation of the Me(20)/Me(18) in a selective NOESY experiment.

Compound **3** was obtained as brown amorphous powder with $[\alpha]_D^{27} = -18.5$ ($c = 0.40$, MeOH). Its molecular formula of $C_{26}H_{38}O_9$ was determined by HR-ESI-MS (m/z 517.2409 ($[M+Na]^+$); calc. 517.2414). The structure of **3** was established as (2*R*,3*S*,4*S*,4a*R*,8*S*,9a*S*,13a*S*,16a*S*)-3,4,4a,8,9,9a,10,11,12,13,14,16a-dodecahydro-2-(hydroxymethyl)-6,6,10,10-tetramethyl-2*H*-benzo[4,5]cyclohepta[1,2-*h*]pyrano[2,3-*b*][1,4]-benzodioxepine-3,4,8,13a,15(6*H*)-pentol by analyses of ^{1}H- and ^{13}C-NMR, DEPT-135, ^{1}H,^{1}H-COSY, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*). This new diterpenoid was named rabdosiacoside A.

The ^{1}H-NMR spectrum of compound **3** displayed a signal at δ(H) 7.01 (*s*, 1 H), which was assigned to an aromatic H-atom, and four Me signals at δ(H) 1.63, 1.63, 0.94, and 0.87 (each *s*). In the ESI-MS^n experiments, the MS^2 spectrum of the ion at m/z 493 ($[M-H]^-$) gave a negative fragment-ion peak at m/z 331 ($[M-H-162]^-$); moreover, the analyses of the ^{1}H,^{1}H-COSY and HSQC data allowed the deduction of fragment C(1′)–C(2′)–C(3′)–C(4′)–C(5′)–C(6′) (*Fig. 2*), confirming that a hexose moiety was present. In the ROESY spectrum, the correlations of H–C(1′)/H–C(3′)/H–C(5′) suggested they were all axially oriented; moreover, the configurations of H–C(2′) and H–C(4′) were determined as α from the coupling constants of H–C(1′) (δ(H) 4.65 (*d*, $J = 7.7$)) and H–C(4′) (δ(H) 3.19 (*t*, $J = 9.5$)). Therefore, the hexose moiety was determined as β-glucopyranoside. The absolute configuration of the sugar residue was assumed to be D-glucose. This assumption was based on the usual configuration of naturally occurring monosaccharides. Comparison of the ^{13}C-NMR data of **3** with those of isodoforrestin (**4**) [13] revealed that the signals of their aglycons were similar. In the ROESY spectrum, the correlations of H–C(7) (δ(H) 4.71 (*d*, $J = 9.9$))/H–C(5) (δ(H) 1.48 (*dd*, $J = 11.9, 2.0$)), H–C(3) (δ(H) 1.31 (*m*))/H–C(5) (δ(H) 1.48 (*dd*, $J = 11.9, 2.0$)) indicated that the *A*/*B* rings were in *trans*-oriented, and confirmed that HO–C(7) and HO–C(10) were in β-orientation. The binding site of the sugar to the aglycon was determined by 2D-NMR experiments. As observed in the HMBC spectrum (*Fig. 2*), correlations of H–C(1′) of the sugar unit with C(12), and H–C(2′) of the sugar unit with C(15) were used to establish that the sugar had two binding sites to the aglycon, with C(1′) attached to C(12), and C(2′) attached to C(15). Thus, C(12), C(13), C(15), C(1′), and C(2′) formed a heptacyclic ring, including two O-atoms.

The three known diterpenoids isodoforrestin (**4**) [13], 3α-hinokiol (**5**) [14], and 16-acetoxyhorminone (**6**) [15] were also isolated from this plant and identified on the basis of their physical and spectroscopic data.

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Haiyang Chemical Group Corp.*, Qingdao, P. R. China), *Sephadex LH20* (*Amersham Biosciences AB*), and *ODS* (60–80 μm; *Merck*). Anal. HPLC: *Welch XB-C18* column (5 μm, 5 × 250 mm); *PDA* detector (*Dionex PDA-100 Photodiode Array Detector*). Prep. HPLC: *Welch XB-C18* column (5 μm, 21 × 250 mm); UV detector (*Varian Prostar 210*). TLC: precoated SiO_2 GF_{254} plates (*Qingdao Marine Chemical Factory*, Qingdao, P. R. China). Optical rotations: *JASCO P-1020* polarimeter. UV Spectra: *JASCO V-550* UV/VIS spectrometer; λ_{max} in nm. IR Spectra (KBr): *JASCO FT-IR-400* spectrometer; in cm^{-1}. ^1H- and ^{13}C-, and 2D-NMR spectra: *Bruker AV-400* spectrometer; δ in ppm with reference to the solvent signals, *J* in Hz. MS: *Finnigan LCQ Advantage MAX Mass* (ESI-MS) and *Micromass Q-TOF Mass* (HR-ESI-MS) spectrometer; in *m*/*z*.

Plant Material. The air-dried whole herbs of *Rabdosia lophanthoides* var. *gerardiana* were collected from the planting base of *Hutchison Whampoa Guangzhou Baiyunshan Chinese Medicine Company Limited*, Guangdong Province of China, in June, 2005, and authenticated by Prof. *Xiao-Ping Lai*, Guangzhou University of Traditional Chinese Medicine. A voucher specimen has been deposited with the herbarium of Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou, P. R. China.

Extraction and Isolation. The air-dried whole herbs of *Rabdosia lophanthoides* var. *gerardiana* (5 kg) were extracted two times with 95% EtOH reflux for 3 h. The EtOH extract was concentrated under reduced pressure to give a residue (467 g) which was partitioned with cyclohexane, AcOEt, BuOH, and H_2O. The cyclohexane layer (193 g) was first subjected to CC (SiO_2; cyclohexane/AcOEt 100 : 0 → 0 : 100): *Frs. 1–26*.

Fr. 18 was subjected to CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1 : 1): *Frs. 18.1–18.3*. *Fr. 18.2* was subjected to CC (*ODS*; MeOH/H_2O 30 : 70 → 0 : 100), and the fraction obtained with 60 and 70% MeOH was purified by prep. HPLC (65 and 75% MeOH): **2**, **1**, and **5** (14, 15, and 10 mg, resp.). *Fr. 25* was subjected to CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1 : 1): *Frs. 25.1–25.3*. *Fr. 25.2* was subjected to CC (*ODS*; MeOH/H_2O 30 : 70 → 0 : 100), and the fraction obtained with 60% MeOH was purified by prep. HPLC (70% MeOH): **3** (15 mg). *Fr. 26* was subjected to CC (SiO_2, $CHCl_3$/MeOH 100 : 0 → 0 : 100): *Frs. 26.1–26.21*. *Fr. 26.11* was subjected to CC (*ODS*, MeOH/H_2O 30 : 70 → 0 : 100), and the fraction obtained with 60% MeOH was purified by prep. HPLC (70% MeOH): **4** (8 mg) and **6** (3 mg).

Rabdosin D (= *3,4-Dihydro-11-hydroxy-10-(1-hydroxy-1-methylethyl)-2,2,6-trimethylnaphtho[1,8-*bc*]oxocin-5(2*H*)-one*; **1**). Yellowish crystals. UV ($CHCl_3$): 216 (4.10), 238 (4.45), 297 (3.34), 337 (3.34). IR (KBr): 3445, 3178, 2959, 2924, 2361, 1688, 1447, 1386, 1334, 1244, 1202, 1118. ^1H- and ^{13}C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 351.1586 ($[M+Na]^+$, $C_{20}H_{24}NaO_4^+$; calc. 351.1572).

(+)-15-Hydroxysalvinolone (= *11,12,15-Trihydroxyabieta-5,8,11,13-tetraen-7-one*; **2**). Colorless crystals. $[\alpha]_D^{27} = +35.6$ ($c = 0.26$, $CHCl_3$). UV ($CHCl_3$): 249 (4.12), 301 (3.60), 321 (3.51). IR (KBr): 3447, 2964, 2932, 2360, 2335, 1636, 1585, 1557, 1376, 1265, 1144. ^1H- and ^{13}C-NMR: *Tables 1* and *2*, resp. HR-ESI-MS: 353.1707 ($[M+Na]^+$, $C_{20}H_{26}NaO_4^+$; calc. 353.1729).

Rabdosiacoside A (= *(2*R*,3*S*,4*S*,4a*R*,8*S*,9a*S*,13a*S*,16a*S*)-3,4,4a,8,9,9a,10,11,12,13,14,16a-Dodecahydro-2-(hydroxymethyl)-6,6,10,10-tetramethyl-2*H*-benzo[4,5]cyclohepta[1,2-*h*]pyrano[2,3-*b*][1,4]benzodioxepine-3,4,8,13a,15(6*H*)-pentol*; **3**). Brown amorphous powder. $[\alpha]_D^{27} = -18.5$ ($c = 0.40$, MeOH). UV (MeOH): 213 (4.10), 226 (3.95), 284 (3.49). IR (KBr): 3395, 1646, 1587, 1300, 1216, 1147, 1054. ^1H- and ^{13}C-NMR: *Tables 1* and *2*, resp. ESI-MS (neg.): 493 ($[M-H]^-$). ESI-MS^2 (neg.; 493): 331 ($[M-H-162]^-$). HR-ESI-MS: 517.2409 ($[M+Na]^+$, $C_{26}H_{38}NaO_9^+$; calc. 517.2414).

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