Diterpenoids from the Flowers of *Rhododendron molle*

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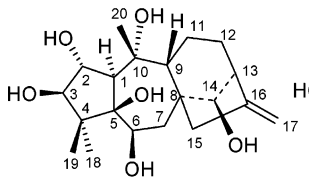
Five new grayanane-type diterpenoids, rhodomolleins IX (**1**), X (**2**), XI (**3**), XII (**4**), and XIII (**5**), a new kalmane-type diterpenoid, rhodomollein XIV (**6**), and seven known diterpenoids, grayanotoxin II, rhodomolleins I and XIX, rhodojaponins II, III, and VI (**7**), and kalmanol, were isolated from the flowers of *Rhododendron molle*. The structures of **1**−**6** were elucidated by spectroscopic methods, including 1D and 2D NMR experiments.

The diterpenoids from poisonous Ericaceae species are based on several specialized carbon skeletons with highly oxygenated functionalities. Some of them have shown significant physiological properties, including potent acute toxicity in mammals[1,2] and antifeedant, growth inhibitory, and insecticidal activities.[3,4] These diterpenoids occur mainly in the genera *Kalmia*, *Leucothoe*, *Lyonia*, *Pieris*, and *Rhododendron*. Their structures are in four types: (1) the grayanane-type with a 5/7/6/5 ring system; (2) the leucothane-type with a 6/6/6/5 ring system; (3) the 1,5-seco-grayanane-type with a 10/6/5 ring system; and (4) the kalmane-type with a 5/8/5/5 ring system.[5] It seems that all structural types are biosynthetically related to each other and derived from the *ent*-kaurane diterpenoids.[6] Up to the present, the number of this kind of diterpenoid found in the Ericaceae is around 100.

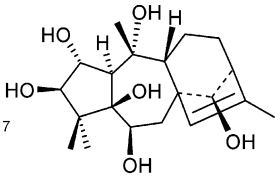
In the course of a search for diterpenoids with structural diversity and biological importance, we have studied the fruits and roots of *Rhododendron molle* G. Don, a well-known poisonous folk medicine in China.[7−9] The flowers of the plant had been previously studied, and several diterpenoids were reported.[3] Recently, we have reinvestigated the flowers of the plant. This paper describes the isolation and structure elucidation of five new grayanane-type diterpenoids, rhodomolleins IX (**1**), X (**2**), XI (**3**), XII (**4**), and XIII (**5**) and one new kalmane-type diterpenoid, rhodomollein XIV (**6**). Also obtained in this isolation were seven known diterpenoids.

The 70% EtOH extract of the flowers of *R. Molle* was partitioned between $CHCl_3$ and water. The water-soluble part was subjected to column chromatography on Resin 101, eluting with H_2O, 50% EtOH, and 95% EtOH. Guided by the brine shrimp lethality test,[10] the active 95% EtOH fraction was separated by repeated column chromatography on silica gel, Sephadex LH-20, and Lichroprep RP-18 to yield six new diterpenoids, **1**−**6**, and seven known diterpenoids, namely, grayanotoxin II,[11] rhodomolleins I and XIX,[12] rhodojaponins II,[13] III,[3] and VI (**7**),[14] and kalmanol.[5]

Rhodomollein IX (**1**), an amorphous powder, exhibited a molecular formula of $C_{20}H_{32}O_6$, as deduced from its HR-FABMS and NMR data. The IR spectrum indicated the presence of hydroxyl (3400 cm^{-1}) and double-bond (1660 cm^{-1}) functionalities. The ^1H spectrum of **1** (Table 1) contained signals for three singlet methyls (δ 1.57, 1.63, 1.93), four oxygenated methines (δ 4.09, 4.78, 4.98, 5.20), and two exocyclic olefinic protons (δ 4.98, 5.05). Altogether, 20 carbon signals were observed in the ^{13}C NMR (DEPT) spectrum (Table 2), including three methyls, five methylenes (one olefinic at δ 103.4), seven methines (four oxygenated at δ 72.3, 77.0, 81.2, 87.1), and five quaternary carbons (one olefinic at δ 156.8 and two oxygenated at δ 78.3, 83.5). The $^1H-^1H$ COSY spectrum revealed the presence of the following fragments: CH−CH(OH)−CH(OH), CH(OH)−CH_2, and CH−CH_2−CH_2−CH. These structural features suggested **1** is a grayanane-type diterpenoid with six sites of oxygenation. Further studies on the ^1H and ^{13}C NMR spectra of **1** revealed that these data closely resemble those of rhodojaponin VI (**7**). The obvious difference was that **1** has an exocyclic carbon−carbon double bond (H_2-17, δ 4.98, 5.05; C-16, 17, 156.8 s, 103.4 t) but lacked a quaternary carbon with a β-methyl and an α-hydroxyl like C-16 of **7**, suggesting **1** is a C-16/17 dehydrated derivative of **7**. This structure was confirmed by HMBC correlations between C-17/H-15, H-13; C-16/H-14, H-12; and C-15, C-13/H_2-17. Further HMBC, HSQC, and NOESY experiments enabled full assignments of the ^1H and ^{13}C NMR spectra of **1** to be



1



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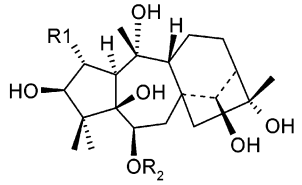
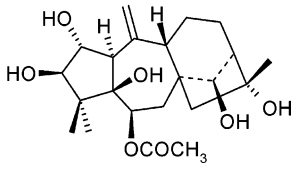


3 R_1=OH R_2=$COCH_3$
5 R_1=H R_2=$COCH_3$
7 R_1=OH R_2=OH



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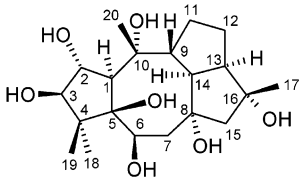

6 R=OH

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Table 1. ^{1}H NMR Data of Compounds **1**−**7** (in C_5D_5N)[a]

position	1	2	3	4	5	6	7
1	3.02 d (7.9)	3.12, d (8.0)	3.00 d (7.3)	3.27 d (8.2)	3.26 dd (4.3, 11.9)	3.05 d (4.7)	2.97 d (8.0)
2α					2.50 (ddd, 4.3, 11.9, 15.0)		
2β	5.20 dd (3.5, 7.9)	5.25 dd (3.7, 8.0)	5.17 dd (4.2, 7.3)	5.06 dd (3.2, 8.2)	2.66 td (4.3, 15.0)	5.27 dd (3.4, 4.7)	5.17 d (3.9, 8.0)
3	4.09 d (3.5)	4.16 d (3.7)	4.24 d (4.2)	4.00 d (3.2)	3.95 t (4.3)	4.19 d (3.4)	4.08 d (3.9)
6	4.78 dd (3.0, 10.0)	4.80 dd (3.1, 9.6)	5.86 dd (4.4, 10.9)	4.86 d (9.4)	5.78 dd (4.4, 9.2)	5.00 d (10.6)	4.71 d (3.6, 10.3)
7α	2.86 dd (3.0, 15.0)	2.86 dd (3.6, 13.6)	2.95 dd (4.4, 13.4)	2.81 d (13.5)	2.84 dd (4.4, 13.0)	2.56 d (14.7)	2.87 dd (3.6, 13.3)
7β	2.57 dd (10.0, 15.0)	2.58 (dd, 9.6, 13.6)	2.25 dd (10.9, 13.4)	2.08 dd (9.4, 13.5)	2.56 dd (9.2, 13.0)	3.00 dd (10.6, 14.7)	2.53 dd (10.3, 13.3)
9	2.31 d (6.3)	2.35 d (7.3)	2.25 d (6.4)	2.43 d (6.6)	2.30 d (4.7)	2.80 ddd (7.8, 8.7, 11.1)	2.13 m
11α	2.19 m	2.25 m	2.16 m	1.93 m	2.13 m	2.14 m	2.06 m
11β	1.84 m	1.84 m	1.68 m	1.84 m	1.75 m	1.95 m	1.60, m
12α	2.84 m	2.15 m	2.71 m	2.00 m	2.74 m	1.88 m	2.53 m
12β	1.66 m	1.65 m	1.79 m	1.58 m	1.79 m	1.08 m	1.69 m
13	3.05 brs	2.85 brs	2.59 brs	2.98 dd (6.5, 9.4)	2.69 brs	2.93 t (10.3)	2.58 brs
14	4.98 s	5.21 s	5.20 s	4.78 s	5.16 s	3.43 t (8.9)	5.05 s
15α	2.81 d (17.5)	5.40 s	2.34 d (14.5)	2.38 d (13.9)	2.32 d (14.6)	3.43 s	2.31 d (14.5)
15β	2.67, d (17.5)		2.22 d (14.5)	2.14 d (13.9)	2.21 d (14.6)	3.43 s	2.15 d (14.5)
17	4.98, 5.05, each s	1.74 s	1.60 s	1.57 s	1.60 s	1.47 s	1.54 s
18	1.57 s	1.64 s	1.39 s	1.44 s	0.97 s	1.80 s	1.57 s
19	1.63 s	1.67 s	1.63 s	1.67 s	1.61 s	1.92 s	1.62 s
20	1.93 s	2.01 s	1.98 s	5.37, 5.56, each s	1.94 s	2.06 s	1.89 s
OAc			2.10 s	2.12 s	2.19 s		

[a] In ppm relative to internal TMS run at 400 MHz. Assignments are based on BB, DEPT, HSQC, ^{1}H−^{1}H COSY, HMBC, and NOESY experiments.

Table 2. ^{13}C NMR Data of Compounds **1**−**7**[a]

carbon	1	2	3	4	5	6	7
1	58.1 d	58.1 d	58.9 d	53.0 d	52.2 d	61.2 d	58.2 d
2	81.2 d	81.0 d	79.8 d	82.6 d	35.7 t	80.3 d	80.9 d
3	87.1 d	87.1 d	86.3 d	88.4 d	82.7 d	85.9 d	87.1 d
4	49.2 s	49.3 s	49.3 s	48.5 s	51.6 s	52.0 s	49.3 s
5	83.5 s	84.0 s	82.8 s	82.3 s	83.8 s	85.6 s	83.6 s
6	72.3 d	72.3 d	78.1 d	76.0 d	77.9 d	72.4 d	72.9 d
7	43.6 t	40.9 t	40.3 t	36.8 t	39.6 t	44.4 t	45.4 t
8	50.8 s	55.4 s	52.4 s	50.0 s	52.2 s	83.1 s	52.5 s
9	54.4 d	48.3 d	55.3 d	53.2 d	55.4 d	53.1 d	55.1 d
10	78.3 s	79.3 s	78.1 s	148.6 s	78.1 s	76.0 s	78.9 s
11	22.1 t	22.7 t	22.2 t	23.8 t	22.7 t	29.1 t	22.1 t
12	33.3 t	24.9 t	27.2 t	24.3 t	27.2 t	31.3 t	27.3 t
13	55.1 d	56.1 d	56.6 d	56.2 d	56.8 d	60.7 d	56.4 d
14	77.0 d	80.3 d	78.9 d	79.0 d	78.9 d	54.7 d	79.9 d
15	49.9 t	132.6	60.3 t	62.2 t	60.2 t	53.9 t	60.9 t
16	156.8 s	137.6 d	79.8 s	80.9 s	79.6 s	80.1 s	80.9 s
17	103.4 t	15.6 q	23.9 q	26.0 q	23.9 q	23.7 q	24.1 q
18	26.2 q	26.4 q	25.1 q	25.7 q	23.2 q	25.1 q	26.3 q
19	20.3 q	20.4 q	20.7 q	20.3 q	19.7 q	21.6 q	20.6 q
20	29.5 q	29.5 q	29.6 q	114.2 t	28.5 q	26.0 q	29.6 q
acetyl			21.7 q	21.5 q	21.6 q		
			169.8 s	171.8 s	170.0 s		

[a] In ppm relative to internal TMS run at 125 MHz. Assignments are based on BB, DEPT, HSQC, ^{1}H−^{1}H COSY, and HMBC experiments. The data of **7** are given because of their absence in the previous literature.

made. Therefore, **1** was deduced as 2α,3β,5β,6β,10α,14β-hexahydroxygrayan-16-ene and has been named rhodomollein IX.

Rhodomollein X (**2**), an amorphous powder, gave a molecular formula of $C_{20}H_{32}O_6$, the same as that of **1**, as found from its HRFABMS and NMR data. The IR spectrum showed the presence of hydroxyl (3420 cm^{-1}) and double-bond (1630 cm^{-1}) moieties. The ^{1}H spectrum (Table 1) contained signals for three singlet methyls (δ 1.64, 1.67, 1.74), one olefinic methyl (δ 2.01), four oxygenated methines (δ 4.16, 4.80, 5.21, 5.25), and one olefinic proton (δ 5.40). The ^{13}C NMR (DEPT) spectrum (Table 2) revealed 20 carbon signals for four methyls, three methylenes, eight methines (four oxygenated at δ 72.3, 80.3, 81.0, 87.1 and one olefinic at δ 132.6), and five quaternary carbons (one olefinic at δ 137.6 and two oxygenated at δ 79.3, 84.0). It was obvious that the ^{1}H and ^{13}C NMR data of **2** were very similar to those of **1** and **7**. The evident difference was that **2** has an intra-annular double bond (H-15, δ 5.40; C-15, C-16, δ 132.6 d, 137.6 s) instead of an exocyclic double bond in **1**, suggesting that **2** is also a dehydrated derivative of **7** and an isomer of **1**. The double bond at C-15/16 was deduced by HMBC correlations between H_3-17/C-13, C-15, C-16; H-13/C-15, C-16, C-17; H-14/C-15, C-16; and H-15/C-16, C-17. Further analysis of the NMR data of **2** and from the HMBC, HSQC, and NOESY experiments indicated **2** is a C-15(16) dehydrated derivative of **7**. Thus, **2** was determined to be 2α,3β,5β,6β,10α,14β-hexahydroxygrayan-15-ene and has been named rhodomollein X.

Rhodomollein XI (**3**), an amorphous power, had a molecular formula of $C_{22}H_{36}O_8$, as deduced from its HR-FABMS and NMR data. The IR spectrum showed the presence of hydroxyl (3450 cm^{-1}) and ester carbonyl (1720 cm^{-1}) moieties. The ^{1}H spectrum (Table 1) contained signals for four singlet methyls (δ 1.39, 1.60, 1.63, 1.98), one acetyl methyl (δ 2.10), and four oxygenated methines (δ 4.24, 5.17, 5.20, 5.86). The ^{13}C NMR (DEPT) spectrum (Table 2) revealed 22 carbon signals, including five methyls, four methylenes, seven methines (four oxygenated at δ 78.1, 78.9, 82.6, 86.3), and six quaternary carbons (one ester carbonyl at δ 169.8 and three oxygenated at δ 78.1, 79.8, 82.8). The ^{1}H−^{1}H COSY spectrum indicated the presence of the following fragments: CH−CH(OH)−CH(OH), CH(OAc)−CH_2, and CH−CH_2−CH_2−CH. These structural features suggested that **3** is a grayanane-type diter-

penoid with seven sites of oxygenation. The ^{1}H and ^{13}C NMR data of **3** were very similar to those of **7**. The only evident difference was that **3** has the resonances due to an additional acetyl group. The downfield shift of H-6 (δ 4.71 in **7** to δ 5.86 in **3**) and C-6 (δ 72.9 in **7** and δ 78.1 in **3**) indicated that the acetylation of **3** was at C-6. This deduction was confirmed by HMBC correlations between H-6/C-4 and the ester carbonyl carbon. Thus, **3** was established as 6β-acetoxyl-2α,3β,5β,14β,16α-pentahydroxygrayanane and has been named rhodomollein XI.

Rhodomollein XII (**4**), an amorphous power, gave a molecular formula of $C_{22}H_{34}O_7$, as deduced from its HR-FABMS and NMR data. The IR spectrum showed the presence of hydroxyl (3400 cm^{-1}), ester carbonyl (1710 cm^{-1}), and double-bond (1640 cm^{-1}) moieties. The ^{1}H spectrum (Table 1) contained signals for three singlet methyls (δ 1.44, 1.57, 1.67), one acetyl methyl (δ 2.12), four oxygenated methines (δ 4.24, 4.78, 4.86, 5.06), and two olefinic protons (δ 5.37, 5.56). The ^{13}C NMR (DEPT) spectrum (Table 2) revealed 22 carbon signals, including four methyls, five methylenes (one olefinic at δ 114.2), seven methines (four oxygenated at δ 76.0, 79.0, 82.6, 88.4), and six quaternary carbons (one ester carbonyl at δ 171.8, one olefinic at δ 148.6, and two oxygenated at δ 80.9, 82.3). The ^{1}H$-^1$H COSY spectrum indicated the presence of the following fragments: CH$-$CH(OH)$-$CH(OH), CH(OAc)$-$CH$_2$, and CH$-$CH$_2-$CH$_2-$CH, the same as those in **3**. These structural features suggested **4** is a grayanane-type diterpenoid with six sites of oxygenation. The ^{1}H and ^{13}C NMR data of **4** were very similar to those of **3**. By comparison of the NMR data of **4** and **3**, the only evident difference was that **4** had an exomethylene (H$_2$-20, δ 5.37, 5.56; C-10, C-20, δ 148.6 s, 114.2 t) instead of a methyl and an oxygenated quaternary carbon in **3**. This suggested **4** is a C-10/20 dehydrated derivative of **3**. The exomethylene at C-10/20 was confirmed by the HMBC correlations between C-20/H-1, H-9 and between C-1, C-9/H$_2$-20. Thus, **4** was determined to be 6β-acetoxyl-2α,3β,5β,14β,16α-pentahydroxygrayan-10 (20)-ene and has been named rhodomollein XII.

Rhodomollein XIII (**5**), an amorphous powder, was assigned a molecular formula of $C_{22}H_{36}O_7$, as deduced from its HRFABMS and NMR data. The IR showed characteristic absorptions for hydroxyl (3430 cm^{-1}) and ester carbonyl (1718 cm^{-1}) moieties. The ^{1}H and ^{13}C NMR spectra of **5** (Table 1 and Table 2) contained signals for five singlet methyls (δ_H 0.97, 1.60, 1.61, 1.94, 2.19; δ_C 19.7, 21.6, 23.2, 23.9, 28.5), three oxygenated methines (δ_H 3.95, 5.16, 5.78; δ_C 77.9, 78.9, 82.7), two oxygenated quaternary carbons (δ_C 78.1, 83.8), and one ester carbonyl (δ_C 170.0). The ^{1}H$-^1$H COSY spectrum revealed the presence of the following fragments: CH$-$CH$_2-$CH(OH), CH(OAc)$-$CH$_2$, and CH$-$CH$_2-$CH$_2-$CH. The above data were consistent with **5** being a grayanane-type diterpenoid. Further investigation showed that the ^{13}C NMR data of **5** were in good agreement with those of 6-acetylgrayanotoxin III,[15] a derivative of grayanotoxin III prepared by acetylation. However, **5** (6β-acetyloxy-3β,5β,10α,14β,16α-pentahydroxygrayanane) is reported here from natural origin for the first time. The ^{1}H and ^{13}C NMR data of **5** were assigned as shown in Tables 1 and 2, respectively.

Rhodomollein XIV (**6**), an amorphous powder, was assigned a molecular formula of $C_{20}H_{34}O_7$, as deduced from its HRFABMS and NMR data. The IR spectrum showed the presence of hydroxyl (3417 cm^{-1}) and carbon$-$carbon double-bond (1637 cm^{-1}) functionalities. The ^{1}H NMR spectrum (Table 1) contained signals for four singlet methyls (δ 1.47, 1.80, 1.92, 2.06) and three oxygenated methines (δ 4.19, 5.00, 5.27). In the ^{13}C NMR (DEPT) spectrum (Table 2), 20 carbon signals were observed, including four methyls, four methylenes, seven methines (three oxygenated at δ 72.4, 80.3, 85.9), and five quaternary carbons (four oxygenated at δ 76.0, 80.1, 83.1, 85.6). The ^{1}H$-^1$H COSY spectrum revealed a fragment with a five-membered ring system ($\overline{\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}}$) and the more common fragments CH$-$CH(OH)$-$CH(OH) and CH(OH)$-$CH$_2$, as found in grayanane-type diterpenoids. The five-membered ring moiety differed from ring A or ring D of any known grayanane-type diterpenoids, but conformed to ring C of kalmanol (3β,5β,6β,8α,10α,16α-pentahydroxykalmane) and its analogue rhodomollein XV (5β,6β,8α,10α,-16α-pentahydroxy-3-oxokalmane), which were both isolated from the same plant.[7] The ^{1}H and ^{13}C NMR data of **6** were very similar to those kalmanol. The major difference was that an oxygenated methine (H-2, δ 5.27; C-2, δ 80.3) in **6** replaced the signals of a methylene in kalmanol. Further study showed that the CH$-$CH(OH)$-$CH(OH) fragment of **6** replaced the CH$-$CH$_2-$CH(OH) fragment (ascribed to C-1, -2, -3) in ring A of kalmanol. Additionally, the NMR spectra showed that the other units (rings B, C, D moiety) were nearly identical to that of kalmanol. This suggested **6** is 2-hydroxykalmanol. The HMBC correlations between H$_3$-20/C-1, C-9, C-10; H-1/C-5, C-10, C-20; H-2/C-1, C-3, C-5, C-10; H-3/C-18; and H$_3$-18, H$_3$-19/C-3, C-4, C-5 confirmed the above deduction. The α-orientation of the 2-hydroxyl group was based on the additional observations. First, the ^{1}H and ^{13}C NMR data in the five-membered ring A of **6** were similar to those of **1**, **2**, **3**, **6**, and **7**, but quite different from those of rhodomollein XVIII[7] and rhodomoside B[9] (with a 2β-hydroxyl moiety in the five-membered ring A), which were isolated from the same plant. Second, NOESY correlations were observed between H$_3$-18/H-1, H-3, H-6, H-19; H-1/H-3, H-6; and H-2/H$_3$-20. Thus, **6** was determined to be 2α,3β,5β,6β,8α,10α,16α-heptahydroxykalmane and has been named rhodomollein XIV. Kalmane-type diterpenoids have a unique class of framework with a 5/8/5/5 (*trans*/*trans*/*cis*) tetracyclic system and occur only in poisonous species of the Ericaceae. Rhodomollein XIV (**6**) is the third example of a kalmane-type diterpenoid found so far.

It has been reported that treatment of grayanotoxin III with acetic acid in methanol or with anhydrous copper sulfate in dioxane produces a series of dehydrated derivatives, including grayanotoxins II [10(20)-dehydrate], VI [15-(16)-dehydrate], VII [10(20),15(16)-dehydrate], and VIII [10(20), 16(17)-dehydrate].[16] In general, dehydration occurs biosynthetically as enzyme-catalyzed reactions, similar to these chemical reactions, and leads to considerable structural diversity. The coexistence of grayanotoxins II, III, VI, VII, and VIII in the poisonous shrub *Leucothoe grayana* Max. has been observed.[17] Thus, the coexistence of the new diterpenoids **1**, **2**, and **4** and the known rhodomolleins I and XIX with **7** in the same plant is reasonable from a biogenetic point of view. Also, from the results of our ongoing study, it is clear that both the fruits and flowers of *Rhododendron molle* are rich in grayanane-type diterpenoids.[7]

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer MC-241 polarimeter. IR spectra were measured on a Nicolt-Magna 750 spectrophotometer. The NMR spectra were recorded on Bruker AM-400 or 500 NMR spectrometers. Mass spectra were recorded using a MAT-241 mass spectrometer.

Plant Material. The flowers of *R. molle* were collected in Yingshan, Hubei Province, People's Republic of China, and identified by Prof. Zhi-Wei Wang of the Department of Pharmacognosy, Shanghai Medical University. A voucher specimen (No. SIMM97091203) has been deposited at the Herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried and powdered flowers of *R. molle* (5 kg) were extracted with 70% EtOH (3 × 25 L) three times at room temperature. The combined residue, after removal of solvent, was partitioned between $CHCl_3$ and H_2O. The water-soluble phase was applied to a resin 101 column (2 kg) and eluted with H_2O, 50% EtOH, and 95% EtOH, sequentially. The pooled 95% fractions (40 g) were subjected to passage over a silica gel column (200−300 mesh, 800 g) and eluted with $CHCl_3$, $CHCl_3$−MeOH (20:1) [part B], $CHCl_3$−MeOH (10:1) [part C], $CHCl_3$−MeOH (5:1) [part D], and MeOH [part E], respectively. Repeated column chromatography on silica gel H, Sephadex LH-20, and Lichroprep RP-18 afforded rhodojaponin II (300 mg) and grayanotoxin II (11 mg) from part B; rhodojaponin III (200 mg), kalmanol (20 mg), and rhodomolleins I (19 mg), XI (**3**, 200 mg), XIII (**5**, 12 mg), IX (**1**, 10 mg), X (**2**, 8 mg), XII (**4**, 6 mg), XIV (**6**, 10 mg), and XIX (20 mg) from part C; and rhodojaponin VI (**7**, 200 mg) from part D, respectively.

Rhodomollein IX (1): amorphous powder, mp 133−135 °C, $[\alpha]^{25}_D$ −32.8° (*c* 0.24, MeOH), IR (KBr) ν_{max} 3400, 2950, 1660, 1380, 1060 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 369 $[M + 1]^+$; HRFABMS *m/z* 369.2232 (calcd for $C_{20}H_{33}O_6$, 369.2280).

Rhodomollein X (2): amorphous powder, mp 223−224 °C, $[\alpha]^{25}_D$ −11.0° (*c* 0.45, MeOH); IR (KBr) ν_{max} 3420, 2950, 1630, 1410, 1380, 1124, 1030 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 369 $[M + 1]^+$; HRFABMS *m/z* 369.2244 (calcd for $C_{20}H_{33}O_6$, 369.2280).

Rhodomollein XI (3): amorphous powder, mp 170−172 °C, $[\alpha]^{25}_D$ −24.5° (*c* 0.89, MeOH); IR (KBr) ν_{max} 3450, 2940, 1720, 1370, 1250, 1030 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 429 $[M + 1]^+$; HRFABMS *m/z* 429.2449 (calcd for $C_{22}H_{37}O_8$, 429.2488).

Rhomollein XII (4): amorphous powder, mp 75−77 °C, $[\alpha]^{25}_D$ −14.5° (*c* 1.09, MeOH); IR (KBr) ν_{max} 3400, 2940, 1710, 1640, 1375, 1259, 1035 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 411 $[M + 1]^+$; HRFABMS *m/z* 411.2317 (calcd for $C_{22}H_{35}O_7$, 411.2382).

Rhodomollein XIII (5): amorphous powder, mp above 255 °C, $[\alpha]^{25}_D$ −14.7° (*c* 0.16, MeOH); IR (KBr) ν_{max} 3430, 2960, 1760, 1718, 1375, 1263, 1049 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 413 $[M + 1]^+$; HRFABMS *m/z* 413.2523 (calcd for $C_{22}H_{37}O_7$, 413.2539).

Rhodomollein XIV (6): amorphous powder, mp 133−135 °C, $[\alpha]^{25}_D$ −17.1° (*c* 0.08, MeOH); IR (KBr) ν_{max} 3417, 2940, 1637, 1450, 1383, 1108, 1080, 1032 cm^{-1}; ^1H and ^{13}C NMR data (in C_5D_5N), see Tables 1 and 2; FABMS *m/z* 387 $[M + 1]^+$; HRFABMS *m/z* 387.2348 (calcd for $C_{20}H_{35}O_7$, 387.2383).

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