Diterpenoids from the Fruits of *Rhododendron molle*

Can-Jun Li, Li-Quan Wang, Shao-Nong Chen, and Guo-Wei Qin*

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 200031, People's Republic of China

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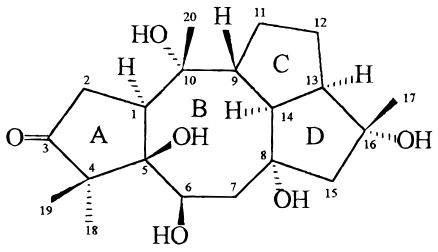
Four new diterpenoids, rhodomolleins XV (**1**), XVI (**2**), XVII (**3**), and XVIII (**4**), together with three known diterpenoids, kalmanol and rhodojaponins III and VI, were isolated from the dried ripe fruits of *Rhododendron molle*. Their structures were elucidated on the basis of spectroscopic data interpretation.

Rhododendron molle G. Don (Ericaceae), a well-known poisonous plant, is widely distributed in southern regions of the People's Republic of China.[1] Both the flowers and fruits of this plant have been recorded in ancient and modern monographs as analgesics and insecticides in traditional uses. Literature investigation has shown that seven diterpenoids, rhodojaponins II, III, and VI, rhodomolleins I and III, grayanotoxin III, and kalmanol, have been isolated from the plant.[2−5] Since 1972, rhodojaponin III, the major component of this plant, has proven to be an effective principle in medicinal practice.[6] In animal experiments and clinical trials, rhodojaponin III exhibited significant blood pressure lowering and heart rate slowing effects. In the treatment of 129 cases of hypertensive disease by intravenous drip or direct intravenous injection at doses of 1.0 and 2.0 mg, blood pressure was lowered by 28.2% and 34.4%, respectively.[6] The antihypertensive effect of rhodojaponin III involves central α_2-adrenoceptors.[7] Rhodojaponin III has shown strong antifeedant, growth inhibitory, and insecticidal activities against larvae of *Leptinotarsa decemlineata* and *Spodoptera frugiperda*, while grayanotoxin III and kalmanol were less active than rhodojaponin III as insect antifeedants.[2] The biological activity associated with these compounds encouraged us to reinvestigate the chemical constituents of the plants. In the course of our study on the fruits of the plant we have isolated three known diterpenoids, kalmanol, rhodojaponins III and VI, and four new diterpenoids, rhodomolleins XV (**1**), XVI (**2**), XVII (**3**), and XVIII (**4**), whose isolation and structural elucidation are the subject of this paper.



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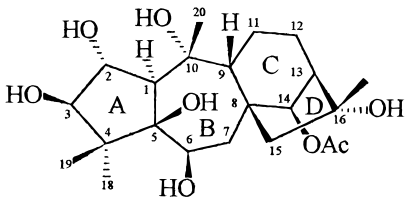

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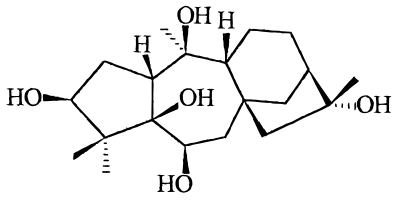

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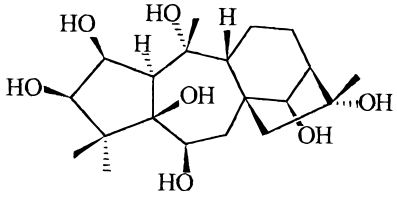

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Results and Discussion

An EtOAc-soluble fraction of the EtOH extract was subjected to repeated column chromatography on Si gel, Sephadex LH-20, and Lichroprep RP-18 to give four new diterpenoids, **1**−**4**, along with the known compounds, kalmanol,[2,8] rhodojaponin III,[3] and rhodojaponin VI,[3] which were identified by spectral data comparison with literature values. Rhodomollein XV (**1**) was assigned a molecular formula of $C_{20}H_{32}O_6$ on the basis of negative-ion HRFABMS and NMR data. The IR spectrum showed characteristic absorptions for hydroxyl (3429 cm^{-1}) and ketone (1718 cm^{-1}) groups. The ^1H NMR spectrum (Table 1) contained four methyls (δ 1.49, 1.52, 1.78, and 1.85) and one oxygenated methine proton (δ 5.11). The ^{13}C NMR and DEPT spectra (Table 1) showed the presence of four methyls, five methylenes, five methines (one oxygenated), and six quaternary carbons (four oxygenated and one carbonyl). The above data suggested that **1** was a diterpenoid compound.

Previous investigation has reported a series of grayanane diterpenoids and kalmanol isolated in this plant. The ^1H−^1H COSY spectrum of **1** indicated the connectivities for a five-membered ring fragment, $-\overline{CH-CH_2-CH_2-CH-CH}-$, which differed from ring A or D in the grayanoids, but conformed to the ring C pattern of kalmanol. A close resemblance was apparent in the ^1H and ^{13}C NMR data of **1** (Table 1) and kalmanol.[2,8] However, there was an absence of the C-3 oxygenated methine signal in the ^1H NMR spectrum of **1**, while a ketone carbon (δ 221.8 s) for C-3 was observed in the ^{13}C NMR spectrum. Thus, **1** was

* To whom correspondence should be addressed. Tel.: +86-21-64311833. Fax: +86-21-64370269. E-mail: gwqin@mail.shcnc.ac.cn.

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Table 1. ^{1}H and ^{13}C NMR Data for Compounds **1**−**4** in C_5D_5N[a]

	1		**2**		**3**		**4**	
	proton	carbon	proton	carbon	proton	carbon	proton	carbon
1	3.29 (dd, 7.4, 10.3)	46.0 d	3.09 (d, 8.6)	56.9 d	3.30 (t, 9.9)	65.2 d	3.42 (d, 10.8)	52.4 d
2α	3.25 (d, 10.3)	39.2 t		80.9 d	2.60 (ddd, 4.7, 9.9, 14.3)	36.6 t	5.06 (dd, 10.8, 3.4)	75.0 d
2*β*	3.23 (d, 7.4)		5.23 (dd, 8.6, 4.5)		2.76 (dd, 9.9, 14.3)			
3		221.8 s	4.20 (d, 4.5)	86.7 d	4.06 (br s)	82.6 d	3.90 (br s)	84.2 d
4		58.4 s		49.0 s		50.7 s		47.8 s
5		83.9 s		82.8 s		86.2 s		84.1 s
6	5.11 (d, 9.3)	71.9 d	4.46 (m)	71.7 d	4.37 (d, 9.9)	70.7 d	4.55 (dd, 11.0, 4.1)	74.7 d
7α	2.54 (d, 14.5)	44.0 t	2.70 (dd, 3.5, 13.4)	44.3 t	2.06 (d, 13.8)	50.1 t	2.96 (dd, 4.4, 13.4)	44.5 t
7*β*	3.04 (dd, 14.5, 9.3)		2.56 (dd, 10.2, 13.4)		3.47 (dd, 13.8, 10.3)		2.52 (m)	
8		83.0 s		50.8 s		46.5 s		52.9 s
9	2.88 (m)	53.1 d	2.33 (d, 7.0)	54.9 d	2.02 (d, 6.6)	59.8 d	2.20 (m)	56.9 d
10		76.1 s		78.2 s		77.6 s		78.6 s
11α	2.12 (m)	29.5 t	2.18 (m)	21.8 t	2.87 (m)	20.4 t	2.23 (m)	21.7 t
11*β*	1.96 (m)		1.66 (m)		1.79 (m)		1.64 (m)	
12α	1.86 (m)	31.2 t	2.69 (m)	27.4 t	1.81 (m	27.5 t	2.68 (m)	27.4 t
12*β*	1.09 (m)		1.76 (m)		1.78 (m)		1.80 (m)	
13	3.01 (m)	60.8 d	2.60 (m)	54.6 d	2.33 (m)	49.5 d	2.61 (br s)	56.7 d
14α	3.46 (t, 8.8)	54.8 d	6.38 (s)	83.6 d	2.22 (d, 12.1)	37.9 t	5.12 (br s)	79.7 d
14*β*					2.49 (dd, 4.6, 12.1)			
15α	2.07 (s)	53.6 t	2.43 (d, 14.0)	61.7 t	2.16 (d, 14.1)	60.6 t	2.33 (d, 14.0)	60.4 t
15*β*	2.07 (s)		2.39 (d, 14.0)		1.96 (d, 14.1)		2.15 (d, 14.0)	
16		80.2 s		79.2 s		78.2 s		79.9 s
17	1.49 (s)	23.8 q	1.60 (s)	24.2 q	1.62 (s)	24.9 q	1.60 (s)	24.1 q
18	1.52 (s)	24.7 q	1.68 (s)	26.7 q	1.33 (s)	22.6 q	1.24 (s)	23.2 q
19	1.78 (s)	19.2 q	1.65 (s)	20.2 q	1.85 (s)	21.7 q	1.79 (s)	20.2 q
20	1.85 (s)	24.1 q	1.97 (s)	29.2 q	1.67 (s)	23.6 q	2.18 (s)	31.4 q
acetyl								
CH_3			2.06 (s)	21.3 q				
C═O				170.5 s				

[a] ^{1}H at 400 MHz; ^{13}C at 100 MHz; *J* in parentheses in Hz.

Table 2. NOESY NMR Data of **1**−**4** in C_5D_5N

proton	**1**	**2**	**3**	**4**
1	H-2, H-6, H-14	H-3, H-6, H-14, H-18	H-2, H-9	H-2, H-6, H-14
2α	H-1, H-18		H-1, H-2*β*, H-3, H-18, H-20	H-1, H-3, H-18
2*β*	H-1, H-20	H-3, H-20	H-1, H-2α, H-3	
3		H-1, H-2, H-18, H-19	H-2, H-18, H-19	H-2, H-18, H-19
6	H-1, H-7α, H-18,	H-1, H-18	H-7α, H-14α, H-18, H-20	H-1, H-18
7α	H-6, H-7*β*, H-15	H-7*β*	H-6, H-7*β*, H-14*β*, H-15α	H-7*β*, H-15α
7*β*	H-7α, H-9	H-7α, H-9	H-7α, H-9	H-7α, H-20
9	H-7*β*, H-11*β*, H-20	H-11*β*, H-15*β*, H-20	H-1, H-7b, H-11*β*, H-15*β*	H-11, H-20
11α	H-11*β*, H-12	H-11*β*, H-12*β*	H-11*β*, H-12	H-11*β*
11*β*	H-9, H-11α, H-12α	H-11α, H-17	H-9, H-11α, H-15*β*, H-17	H-11α
12α	H-11, H-12*β*, H-13	H-12*β*, H-13,H-14	H-11, H-13	H-12*β*
12*β*	H-11α, H-12α, H-17	H-12α, H-13, H-17	H-17	H-12α, H-13, H-17
13	H-12α, H-14	H-12, H-14, H-17	H-12, H-14, H-17	H-12*β*, H-17
14	H-1, H-13	H-1, H-12α, H-13	H-6, H-7α, H-13, H-20	H-1, H-13
15	H-7α, H-17	H-9, H-17	H-7α, H-9, H-17	H-7α, H-17
17	H-12*β*, H-15	H-11*β*, H-12*β*, H-13, H-15	H-11*β*, H-12*β*, H-15*β*	H-12*β*, H-15*β*, H-13
18	H-2α, H-6, H-19	H-1, H-3, H-6, H-19	H-2α, H-3, H-6, H-19, H-20	H-2, H-3, H-6, H-19
19	H-18	H-3, H-18	H-3, H-18	H-3, H-18
20	H-2*β*, H-9	H-2, H-9	H-2α, H-6, H-14α, H-18	H-7*β*, H-9

assigned as the 3-oxo derivative of kalmanol. Unambiguous assignments of the ^{1}H and ^{13}C NMR signals of **1** (Table 1) were made by comparison with the values for kalmanol and were verified using various 2D NMR techniques, and the NOESY and HMBC data obtained are presented in Tables 2 and 3, respectively. These data confirmed the proposed structure of **1** as an analogue of kalmanol. To the best of our knowledge, kalmanol is the only diterpenoid previously known to possess a 5/8/5/5 (trans, trans, cis) ring system.[2,8] Thus, rhodomollein XV (**1**) is the second example of compounds based on this rare diterpene skeleton.

Rhodomollein XVI (**2**) was obtained as an amorphous powder. The molecular formula was determined as $C_{22}H_{36}O_8$ by HRFABMS. Its IR spectrum indicated the presence of hydroxyl (3386 cm^{-1}) and ester carbonyl (1720 cm^{-1}) groups. The ^{1}H NMR spectrum (Table 1) showed four methyl singlets (*δ* 1.60, 1.65, 1.68, and 1.97), four oxygenated methines (*δ* 4.20, 4.46, 5.23, and 6.38), and one acetyl methyl (*δ* 2.06). Apart from the acetyl group (*δ* 21.3, 170.5), 20 carbon signals were observed in the ^{13}C NMR spectrum (Table 1), including four methyls, four methylenes, seven methines (four oxygenated), and five quaternary carbons (three oxygenated). The ^{1}H−^{1}H COSY spectrum revealed the following fragments: −CHCH(OH)CH(OH)−, −CH(OH)CH_2−, and −$CHCH_2CH_2$CH−. These structural features suggested that **2** was a grayanane diterpenoid with seven sites of oxygenation. Furthermore, comparison of the ^{1}H and ^{13}C NMR spectral data of **2** (Table 1) with those of rhodojaponin VI[3] showed that both compounds were quite similar except for the data for H-14 and C-14. Thus, the H-14 signal of **2** (*δ* 6.38, s) was at lower field than that of rhodojaponin VI (*δ* 5.05, s), while the C-14 signal of **2** (*δ* 83.6) was shifted downfield by 3.7 ppm in comparison with that of rhodojaponin VI (*δ* 79.9). Moreover,

Table 3. HMBC NMR Data of **1**−**4** in C_5D_5N

proton	1	2	3	4
1	C-2, C-3, C-6, C-10, C-20	C-2, C-5, C-6, C-10, C-20	C-2, C-5, C-9, C-10, C-20	C-2, C-3, C-5, C-6, C-9, C-10, C-20
2α	C-1, C-3, C-5, C-10		C-1, C-10	C-1, C-3, C-5, C-10
2*β*	C-1, C-3, C-5, C-10	C-1, C-3, C-4, C-10	C-3, C-4, C-5	
3		C-1, C-2, C-5, C-18, C-19		C-1, C-5, C-18
6		C-1		C-1, C-7
7α	C-5, C-6, C-8, C-14, C-15	C-5, C-6, C-8, C-9, C-15	C-5, C-6, C-8, C-9, C-14, C-15	C-5, C-6, C-8, C-9, C-15
7*β*	C-5, C-6, C-8	C-5, C-6, C-8, C-9, C-15	C-5, C-6, C-8, C-14	C-5, C-6, C-8, C-9, C-14, C-15
9	C-8, C-11, C-14	C-7, C-8,C-10, C-11, C-12, C-14	C-8, C-10, C-12, C-15, C-20	C-7, C-8, C-11, C-14, C-15, C-20
11α	C-9, C-10, C-12	C-8, C-9, C-10, C-12, C-13	C-8,C-10, C-13	C-8, C-9, C-10, C-12, C-13
11*β*	C-9, C-10, C-12, C-13, C-14	C-10, C-12, C-13		C-9, C-10, C-12, C-13
12α	C-9, C-11, C-13, C-14	C-9, C-13	C-17	C-11, C-14, C-16
12*β*	C-11, C-13, C-16	C-13, C-16	C-17	C-11, C-14, C-16
13	C-8, C-12, C-16,	C-8, C-11, C-12, C-14		C-8, C-11, C-12, C-15
14α	C-8, C-9, C-10, C-12, C-13	C-9, C-12, C-15, C-16, C=O	C-13, C-15, C-16	C-15, C-16
14*β*			C-9, C-12, C-13	
15α	C-7, C-8, C-13, C-14, C-16, C-17	C-7, C-8, C-13, C-14, C-16, C-17	C-8, C-9, C-13, C-16	C-7, C-8, C-9, C-13, C-14, C-16
15*β*	C-7, C-8, C-13, C-14, C-16, C-17	C-7, C-8, C-13, C-14, C-16, C-17	C-8, C-9, C-14, C-17	C-7, C-8, C-13, C-14, C-16, C-17
17	C-13, C-15, C-16,	C-13, C-16	C-13, C-15, C-16	C-13, C-15, C-16
18	C-4, C-5, C-19	C-3, C-4, C-5, C-19	C-3, C-4, C-5, C-19	C-3, C-4, C-5, C-19
19	C-4, C-5, C-18	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18	C-3, C-4, C-5, C-18
20	C-1, C-10	C-1, C-9, C-10	C-1, C-9, C-10	C-1, C-9, C-10
CH_3		C=O		

in the HMBC spectrum of **2** (Table 3), the carbonyl carbon signal at *δ* 170.5 correlated with the signal of H-14 at 6.38 ppm. All of these data suggested that **2** is the C-14 acetate of rhodojaponin VI. The relative stereochemistry of **2** was confirmed from the NOESY spectrum (Table 2).

Rhodomollein XVII (**3**), an amorphous powder, had the molecular formula $C_{20}H_{34}O_5$ on the basis of its negative-ion HRFABMS and NMR data. It showed an IR absorption for the presence of hydroxyl groups (3377 cm^{-1}). The ^1H NMR spectrum of **3** (Table 1) showed for four methyls (*δ* 1.33, 1.62, 1.67, and 1.85) and two oxygenated methines (*δ* 4.02 and 4.37). The ^{13}C NMR spectrum (Table 1) revealed the presence of four methyls, six methylenes, five methines (two oxygenated), and five quaternary carbons (three oxygenated). From the $^1H-^1H$ COSY spectrum the following fragments were observed: $-CHCH_2CH(OH)-$, $-CH(OH)CH_2-$, and $-CHCH_2CH_2CHCH_2-$, consistent with H-1 to H-3, H-6 to H-7, and H-9 to H-14 in a grayanane skeleton. The signal at *δ* 4.06 (br s) was assigned to H-3 because of the correlations of this signal to H-2, H-18, and H-19 in the NOESY spectrum (Table 2). The doublet signal at *δ* 4.37 (H-6α) with $J = 9.9$ Hz correlated with H-18 and H-20 in the NOESY spectrum. The relative stereochemistry of **3** was also determined from the NOESY spectrum (Table 2). It has been reported that grayanane diterpenoids in general possess trans/cis/cis junctions for the 5/7/6/5 ring system, but a few representatives such as grayanoside C and pierisformosin A[9,10] possess a cis/cis/cis configuration. In the latter case, H-1 has a *β*-orientation, resulting in a correlation with H-9*β* in the NOESY spectrum. The NOESY spectrum of **3** (Table 2) revealed a correlation between H-1 (*δ* 3.30) and H-9 (*δ* 2.02), suggesting that H-1 has a *β*-orientation and ring A/B a cis junction. In addition, the presence of correlations between H-20/H-18, H-20/H-6, and H-20/H-14α indicated that H-20, H-18, and H-6 all have an α-orientation. Further analysis of the NOESY spectrum led to the conclusion that H-9, H-17, and H-19 have a *β*-orientation and that H-3 has an α-orientation.

Rhodomollein XVIII (**4**) was assigned the molecular formula $C_{20}H_{34}O_7$ on the basis of negative-ion HRFABMS and NMR data. The IR spectrum showed a characteristic absorption for one or more hydroxyl groups (3373 cm^{-1}). The ^1H NMR spectrum (Table 1) included singlets for four methyls (*δ* 1.24, 1.60, 1.79, and 2.18) and four oxygenated methines (*δ* 3.90, 4.55, 5.06, and 5.12). From the ^{13}C NMR spectrum (Table 1), 20 carbon signals were observed, including four methyls, four methylenes, seven methines (four oxygenated), and five quaternary carbons (three oxygenated). The $^1H-^1H$ COSY spectrum revealed the following fragments: $-CHCH(OH)CH(OH)-$, $-CH(OH)-CH_2-$, and $-CHCH_2CH_2CH(OH)-$, establishing the proton sequence from H-1 to H-3, H-6 to H-7, and H-9 to H-14, respectively. All of the data obtained suggested that **4** is a grayanane diterpenoid with seven hydroxyls at C-2, C-3, C-5, C-6, C-10, C-14, and C-16. On comparing the ^1H and ^{13}C NMR data of **4** with those of rhodojaponin VI,[3] a known grayanoid with seven hydroxyl groups at the 2α, 3*β*, 5, 6*β*, 10α, 14, and 16α position (also obtained in the present investigation), a close resemblance was observed except for the NMR signals associated with the oxygenated C-2 and vicinal carbons, C-1 and C-3, as a result of the opposite configuration of C-2. The assignment of the C-2 hydroxyl in **4** as a *β*-substituent was evident because of the C-2 upfield shift in **4** (*δ* 75.0) relative to rhodojaponin VI (*δ* 80.9). In addition, H-2 of **4** correlated with H-1α and H-18 in a NOESY experiment (Table 2). The ^1H and ^{13}C NMR spectra of **4** (Table 1) were fully assigned by analysis of $^1H-^1H$ COSY, HMQC, HMBC, and NOESY experiments and by comparison of the NMR data with those of rhodojaponin VI. From the NOESY spectrum (Table 2), correlations between H-1/H-2, H-2/H-3, H-1/H-14, H-13/H-14, H-6/H-18, and H-3/H-18 were observed, suggesting that H-1, H-3, H-6, H-13, H-14, and H-18 are all α-orientated. Meanwhile, correlations between H-9/H-20, H-20/H-7*β*, and H-15*β*/H-17 revealed that H-9, H-17, and H-20 are all *β*-orientated. Rhodomollein XVIII (**4**) is the first grayanane diterpenoid that has been obtained with a *β*-hydroxyl group at C-2.

Experimental Section

General Experimental Procedures. The optical rotations were obtained on a Perkin-Elmer MC-241 polarimeter. IR spectra were recorded with a Nicolet Magna FTIR-750 spectrometer. Mass spectra were measured with a MAT-241 mass spectrometer. ^1H, ^{13}C, and 2D NMR spectra were recorded using a Bruker AM-400 instrument. Chemical shifts are reported in ppm (*δ*) with solvent (C_5D_5N) signals used as internal standards.

Plant Material. The ripe fruits 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 in the Herbarium of Shanghai Institute of Materia Medica.

Extraction and Isolation. The air-dried and ground ripe fruits of *R. molle* (6 kg) were defatted with CH_2Cl_2 (3 × 25 L)

three times. The residue (5.5 kg) was extracted with 70% EtOH three times at room temperature. The EtOH extract was evaporated under a vaccum to yield a black residue (400 g). The residue was suspended in water (4000 mL) and then extracted with petroleum ether, ethyl acetate, and *n*-butanol, successively. The EtOAc fraction (100 g) was applied to a Si gel column (200−300 mesh, 2 kg) and eluted with EtOAc containing increasing amounts of EtOH to afford 50 fractions. Fractions 6−9 (obtained with EtOAc−EtOH, 30:1) were combined after monitoring by TLC and then chromatographed on a Si gel H column, using $CHCl_3$−Me_2CO (2:1) as eluent, to give five fractions (1−5). Fraction 1 was purified over a Lichroprep RP-18 column with H_2O−MeOH (5:2) to yield **4** (18 mg). Fraction 2 was separated over Si gel with $CHCl_3$−MeOH (20:1) and Lichroprep RP-18 with H_2O−MeOH (2:1) to yield **2** (15 mg). Fraction 3 was chromatographed over a Lichroprep RP-18 column with water−tetrahydrofuran (7:2) and further purified over Sephadex LH-20 with absolute ethyl alcohol as eluent to yield **1** (5 mg). Compound **3** (6 mg) was obtained by applying fraction 4 to a Lichroprep RP-18 column with H_2O−Me_2CO (3:1) as eluent.

Rhodomollein XV (1): amorphous powder, $[\alpha]^{23}_D$ 36.4° (*c* 0.22, EtOH); IR (KBr) ν_{max} 3430, 1718, 1379, 1109, 990 cm^{-1}; ^1H NMR (C_5D_5N), see Table 1; ^{13}C NMR (C_5D_5N), see Table 1; FABMS *m/z* 391 $[M + Na]^+$, 407 $[M + K]^+$; negative-ion HRFABMS *m/z* 367.2097 $[M - 1]^-$ (calcd for $C_{20}H_{31}O_6$, 367.2120).

Rhodomollein XVI (2): amorphous powder, $[\alpha]^{23}_D$ 8.7° (*c* 0.58, EtOH); IR (KBr) ν_{max} 3386, 1720, 1375, 1236, 1034, 756 cm^{-1}; ^1H NMR (C_5D_5N), see Table 1; ^{13}C NMR (C_5D_5N), see Table 1; HRFABMS *m/z* 427.2332 $[M - 1]^+$ (calcd for $C_{22}H_{35}O_8$, 427.2322).

Rhodomollein XVII (3): amorphous powder, $[\alpha]^{23}_D$ 53.3° (*c* 0.30, EtOH); IR (KBr) ν_{max} 3377, 2924, 1635, 1385, 1038 cm^{-1}; ^1H NMR (C_5D_5N), see Table 1; ^{13}C NMR (C_5D_5N), see Table 1; FABMS *m/z* 377 $[M + Na]^+$, 393 $[M + K]^+$; negative-ion HRFABMS *m/z* 353.2258 $[M - 1]^-$ (calcd for $C_{20}H_{33}O_5$, 353.2328).

Rhodomollein XVIII (4): amorphous powder, $[\alpha]^{23}_D$ −28.5° (*c* 0.35, EtOH); IR (KBr) ν_{max} 3373, 1632, 1446, 1041, 935 cm^{-1}; ^1H NMR (C_5D_5N), see Table 1; ^{13}C NMR (C_5D_5N), see Table 1; FABMS *m/z* 409 $[M + Na]^+$, 425 $[M + K]^+$; negative-ion HRFABMS *m/z* 385.2287 $[M - 1]^-$ (calcd for $C_{20}H_{33}O_7$, 385.2226).

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