Limonoids and Tirucallane Derivatives from the Seeds of a Krishna Mangrove, *Xylocarpus moluccensis*

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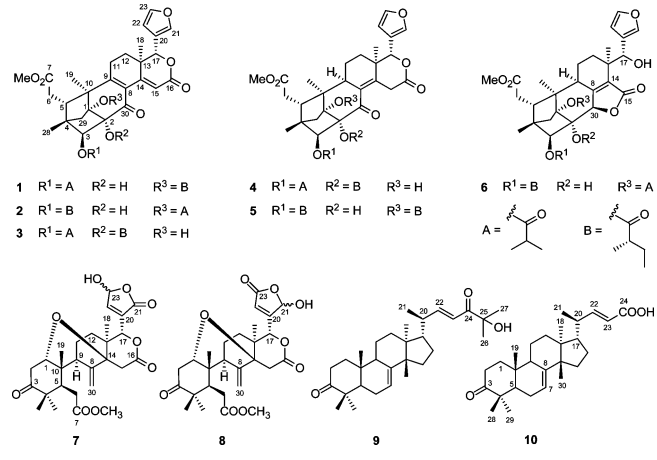
Six new phragmalins, moluccensins H−M (1−**6**), two new andirobin-type limonoids, moluccensins N and O (**7**, **8**), and two new tirucallane derivatives, moluccensins P and Q (**9**, **10**), were isolated from seeds of an Indian mangrove, *Xylocarpus moluccensis,* together with the known compound 3β,22*S*-dihydroxytirucalla-7,24-dien-23-one. The structures of these compounds were established on the basis of spectroscopic data. Moluccensins H−L were phragmalins with a C-30 carbonyl group, and moluccensin M was a unique ring-D-opened 16-norphragmalin. Moluccensins H−J possess conjugated $\Delta^{8,9}$ and $\Delta^{14,15}$ double bonds, moluccensins K and L contain a $\Delta^{8,14}$ double bond, and moluccensin M has a characteristic $C_{15}-C_{30}$ linked five-membered lactone ring. Moluccensins H and I showed moderate insecticidal activity against the fifth instar larvae of *Brontispa longissima* (Gestro) at a concentration of 100 mg/L.

Limonoids, triterpene derivatives from a precursor with a 4,4,8-trimethyl-17-furanylsteroid skeleton, have been found only in plants of the order Rutales. They are classified by the type of four—usually highly oxidized—rings (designated as A, B, C, and D) in the intact triterpene. Phragmalins, such as pseudrelones A_1 and A_2[1] isolated from *Pseudocedrela kotschyii* and khayanolides A−C[2] from *Khaya senegalensis*, have characteristic tricyclo[3.3.$1^{2,10}$.$1^{1,4}$]decane or tricyclo[4.2.$1^{10,30}$.$1^{1,4}$]decane ring systems.

The family Meliaceae has proved to produce a variety of antifeedant limonoids, such as azadirachtin[3] from the neem tree, *Azadiracha indica*, and harrisonin[4] from *Harrisonnia abyssinica*. Two meliaceous mangroves, *Xylocarpus granatum* and *X. moluccensis,* are known for producing antifeedant limonoids, especially phragmalins and mexicanolides. Previous investigations on seeds of these two species yielded an andirobin, two phragmalins, three gedunins, and 14 mexicanolides, including xyloccensins A−K.[5−9] Previously we have reported the isolation and identification of eight unique 8,9,30-phragmalin *ortho* esters and 13 limonoids with a new carbon skeleton from the bark and seeds of a Chinese mangrove, *X. granatum*.[10−12] To date, 42 mexicanolides and 23 phragmalins, including three 1,8,9-phragmalin *ortho* esters, eight 8,9,30-phragmalin *ortho* esters, and 12 polyhydroxylated phragmalins, have been isolated from the wood, seeds, and fruits of *X. granatum* and *X. moluccensis*.[13] We recently identified seven phragmalins, moluccensins A−G,[14] from seeds of an Indian mangrove, *X. moluccensis*, collected in the mangrove wetlands of Krishna estuary, Andhra Pradesh. In the current paper, we present the isolation and characterization of five additional phragmalins (**1**−**5**), each with a C-30 carbonyl group, and a unique ring-D-opened 16-norphragmalin (**6**), from seeds of the same Indian mangrove, *X. moluccensis* (Lam.) M Roem. (Meliaceae), together with two new andirobin-type limonoids (**7**, **8**), two new tirucallane derivatives (**9**, **10**), and the known compound 3β,22*S*-dihydroxytirucalla-7,24-dien-23-one.[15] The structures of these compounds were established on the basis of spectroscopic data or comparison with data in the literature. The new compounds were tested for insecticidal activity against the fifth instar larvae of *Brontispa longissima* (Gestro) at a concentration of 100 mg/L.



Results and Discussion

Compound **1** had the molecular formula $C_{36}H_{44}O_{11}$, as established by HR-TOFMS (*m*/*z* 675.2770, calcd for $[M + Na]^+$ 675.2776), indicating 15 degrees of unsaturation. The ^1H and ^{13}C NMR data of **1** (Tables 1 and 2) indicated that nine of the 15 elements of unsaturation came from a conjugated ketone group, four carbon−carbon double bonds, and four ester functionalities. Therefore, the molecule

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Table 1. ^{1}H NMR (500 MHz) Data (δ) for Moluccensins H−L (**1**−**5**) in $CDCl_3$ (J in Hz)

position	1	2	3	4	5
3	5.05 s	5.07 s	5.34 s	5.28 s	5.15 s
5	2.84 m	2.82 m	2.80 m	2.96 br d, 10.0	2.95 d, 9.5
6a	2.51[a]	2.51[a]	2.50[a]	2.37 br s	2.35 br s
6b	2.44[a]	2.44[a]	2.40[a]	2.37 d, 10.0	2.35 d, 9.5
9				2.64 br s	2.78 br s
11α	2.38[a]	2.39[a]	2.44 m	1.78 m	1.77 m
11β	2.38[a]	2.39[a]	2.40[a]	1.78 m	1.67 m
12α	1.69 br d, 12.4	1.66 br d, 12.4	1.64 m	1.50 m	1.71 m
12β	1.48 m	1.47 m	1.43 m	1.25 m	1.33 m
15	7.25, s	7.25, s	7.30, s	3.93 d, 16.5 3.85 dd, 16.5, 4.0	3.91 br s
17	5.02 s	5.02 s	5.05 s	5.43 s	5.48 s
18	1.03 s	1.03 s	1.03 s	1.20 s	1.20 s
19	1.11 s	1.11 s	1.25 s	1.14 s	1.10 s
21	7.51 br s	7.50 br s	7.51 br s	7.51 br s	7.51 br s
22	6.47 br s	6.46 br s	6.46 br s	6.44 br s	6.45 br s
23	7.44, br s	7.44, br s	7.44, br s	7.42, br s	7.43, br s
28	0.98 s	0.98 s	0.95 s	0.86 s	0.86 s
$29_{pro\text{-}S}$	2.39[a]	2.39[a]	2.02 d, 11.0	2.07 d, 11.0	2.24 d, 11.5
$29_{pro\text{-}R}$	2.39[a]	2.39[a]	1.81 d, 11.0	1.61 d, 11.0	2.02 d, 11.5
7-OMe	3.70 s	3.69 s	3.70 s	3.66 s	3.65 s
2-OH	4.69 br s	4.69 br s			4.51 br s
3-*Acyl*					
2′	2.46 m	2.28 m	2.51 m	2.32 m	2.07 m
3′	1.12 d, 7.0	1.40 m 1.60 m	1.14 d, 7.0	1.13 d, 7.0	1.38 m 1.60 m
4′	1.14 d, 7.0	0.86 t, 7.5	1.14 d, 7.0	1.16 d, 7.0	0.88 t, 7.5
5′		1.10 d, 7.0			1.14 d, 7.0
Acyl	1-*Acyl*	1-*Acyl*	2-*Acyl*	2-*Acyl*	1-*Acyl*
2″	2.29 m	2.48 m	2.53 m	2.53 m	2.33 m
3″	1.38 m 1.58 m	1.08 d, 7.0	1.55 m 1.80 m	1.53 m 1.80 m	1.41 m 1.62 m
4″	0.85 t, 7.5	1.08 d, 7.0	1.00 t, 7.5	1.01 t, 7.5	0.89 t, 7.5
5″	1.06 d, 6.5		1.24 d, 6.5	1.26 d, 6.0	1.11 d, 7.0

[a] Overlapped signals assigned by ^{1}H−^{1}H COSY, HSQC, and HMBC spectra without designating multiplicity.

Table 2. ^{13}C NMR (125 MHz) Data (δ) for Moluccensins H−L (**1**−**5**) in $CDCl_3$

position	1	2	3	4	5
1	90.9 qC	90.8 qC	86.7 qC	88.5 qC	90.4 qC
2	79.2 qC	79.1 qC	88.8 qC	91.1 qC	80.1 qC
3	87.3 CH	87.2 CH	82.2 CH	83.9 CH	89.1 CH
4	45.1 qC	45.1 qC	46.4 qC	45.3 qC	43.6 qC
5	44.2 CH	44.3 CH	43.4 CH	37.6 CH_2	39.2 CH
6	33.2 CH_2	33.2 CH_2	33.4 CH_2	34.0 CH_2	34.0 CH
7	173.0 qC	173.0 qC	173.1 qC	173.6 qC	173.3 qC
8	122.0 qC	122.0 qC	122.9 qC	130.7 qC	130.6 qC
9	152.3 qC	152.4 qC	152.3 qC	40.3 CH	44.7 CH
10	48.6 qC	48.6 qC	49.9 qC	48.6 qC	47.8 qC
11	25.1 CH_2	25.1 CH_2	25.4 CH_2	18.9 CH_2	19.9 CH_2
12	30.2 CH_2	30.1 CH_2	29.8 CH_2	29.4 CH_2	30.5 CH_2
13	36.5 qC	36.5 qC	36.7 qC	38.8 qC	39.1 qC
14	167.0 qC	167.3 qC	167.0 qC	145.6 qC	146.3 qC
15	115.9 qC	115.8 qC	116.2 qC	35.0 CH_2	36.3 CH_2
16	165.5 qC	165.5 qC	165.7 qC	168.6 qC	168.7 qC
17	80.3 CH	80.3 CH	80.3 CH	79.8 CH	79.9 CH
18	15.7 CH_3	15.7 CH_3	16.0 CH_3	17.8 CH_3	18.9 CH_3
19	16.2 CH_3	16.2 CH_3	16.6 CH_3	18.0 CH_3	18.0 CH_3
20	120.1 qC	120.1 qC	120.1 qC	120.3 qC	120.2 qC
21	141.3 CH	141.3 CH	141.3 CH	141.8 CH	141.7 CH
22	110.1 CH	110.1 CH	110.1 CH	109.8 CH	109.7 CH
23	143.1 CH	143.1 CH	143.1 CH	143.2 CH	143.3 CH
28	16.4 CH_3	16.4 CH_3	16.5 CH_3	14.7 CH_3	14.6 CH_3
29	41.5 CH_2	41.5 CH_2	41.6 CH_2	40.9 CH_2	41.7 CH_2
30	193.1 qC	193.1 qC	186.8 qC	193.1 qC	198.1 qC
7-OMe	52.1 CH_3	52.1 CH_3	52.1 CH_3	52.0 CH_3	52.0 CH_3
3-*Acyl*-1′	175.0 qC	174.0 qC	174.5 qC	175.7 qC	175.7 qC
2′	34.2 CH	41.3 CH	34.2 CH	34.2 CH	41.3 CH
3′	18.8 CH_3	26.4 CH_2	18.9 CH_3	18.2 CH_3	25.8 CH_2
4′	19.1 CH_3	11.6 CH_3	18.9 CH_3	19.9 CH_3	11.2 CH_3
5′		16.7 CH_3			17.6 CH_3
Acyl	1-*Acyl*	1-*Acyl*	2-*Acyl*	2-*Acyl*	1-*Acyl*
1″	175.3 qC	175.6 qC	178.0 qC	179.1 qC	176.2 qC
2″	41.3 CH	34.2 CH	41.4 CH	41.5 CH	41.0 CH
3″	26.5 CH_2	18.9 CH_3	26.7 CH_2	26.7 CH_2	26.6 CH_2
4″	11.6 CH_3	19.0 CH_3	11.6 CH_3	11.6 CH_3	11.6 CH_3
5″	16.7 CH_3		16.7 CH_3	16.7 CH_3	16.7 CH_3

was hexacyclic. DEPT experiments revealed that **1** had eight methyl (a methoxy, a primary methyl, three secondary methyls, and three tertiary methyls of the phragmalin nucleus), five methylene, nine methine (four olefinic), and 14 quaternary carbons (five carbonyls).

The NMR data of **1** (Tables 1 and 2) and its 2D NMR studies (^{1}H−^{1}H COSY, HSQC, and HMBC) (Figure S1) indicated the presence of a methoxycarbonyl group (δ_H 3.70 s, δ_C 52.1 CH_3, 173.0 qC), an isobutyryl group [δ_H 2.46 m, 1.12 (d, J = 7.0 Hz), 1.14 (d, J = 7.0 Hz); δ_C 18.8 CH_3, 19.1 CH_3, 34.2 CH, 175.0 qC], a 2-methylbutyryl group [δ_H 0.85 (t, J = 7.5 Hz), 1.06 (d, J = 6.5 Hz), 1.38, m, 1.58, m, 2.29, m; δ_C 11.6 CH_3, 16.7 CH_3, 26.5 CH_2, 41.3 CH, 175.3 qC], and a β-furanyl ring (δ_H 6.47 br s, 7.44 br s, 7.51 br s; δ_C 110.1 CH, 120.1 qC, 141.3 CH, 143.1 CH). An α, β-unsaturated δ-lactone ring D, characterized by the following NMR data [δ_H 5.02 s, 7.25 s; δ_C 80.3 CH, 36.5 qC, 167.0 qC, 115.9 CH, 165.5 qC] (Tables 1 and 2), was confirmed by HMBC correlations between H-15/C-14, H-15/C-16, H-17/C-13, H-17/C-14, and H-17/C-16 (Figure S1). The above NMR data and the 2D NMR studies suggested that **1** was a phragmalin.

Protons of a tertiary methyl group (δ_H 1.03 s; δ_C 15.7), showing HMBC correlations to C-12, C-13, C-14, and C-17 (Figure S1), were assigned to H_3-18. Protons of the second tertiary methyl group (δ_H 1.11 s; δ_C 16.2), exhibiting HMBC correlations to C-1, C-5, C-9, and C-10, were identified as H_3-19, and those of the third tertiary methyl group (δ_H 0.98 s; δ_C 16.4), showing HMBC correlations to C-3, C-4, and C-5 (Figure S1), were assigned to H_3-28. Protons [δ_H 2.39[a] and 2.39[a]] of a methylene group (δ_C 41.5), exhibiting HMBC correlations to C-1, C-2, C-3, and C-4 (Figure S1), were identified as H_2-29. An OH group (δ_H 4.69 br s) located at C-2 was confirmed by its strong HMBC correlations to C-2, C-3, and C-30. Moreover, a $\Delta^{8,9}$ double bond was established by HMBC correlations between H-15/C-8, H_3-19/C-9, and H_2-11/C-9, and a C-30 ketone function was suggested by those between H-15/C-30, 2-OH/C-30, H-3/C-30, and H-29/C-30 (Figure S1). Connections of the five fragments CH_2-11−CH_2-12, CH-5−CH_2-6, CH-22−CH-23, CH_3-3′−CH-2′−CH_3-4′, and CH_3-4″−CH_2-3″−CH-2″−CH_3-5″ were confirmed by the corresponding five homonuclear proton−proton spin systems observed in the ^{1}H−^{1}H COSY spectrum of **1** (Figure S1). The strong HMBC correlation from H-3 (5.05, s) to C-1′ (175.0 qC) of an isobutyryl group disclosed its location at C-3. The 2-methylbutyryl group, however, was suggested to be attached to C-1 by its downshifted chemical shift (δ_C 90.9), being lower than 90 ppm.[14]

The relative configuration of **1** was established on the basis of the NOESY interactions. The significant NOE interaction (Figure S2) from H-3 to $H_{pro\text{-}R}$-29 helped to establish this 3α-H and the corresponding 3β-isobutyryl group. NOE interactions between H-5/H-11β and H-5/H-17 established the β-orientation of H-5 and H-17. Similarly, those between H_3-18/H-11α and H_3-18/H-15 indicated the α-orientation of H_3-18. Thus, the relative configuration of the phragmnalin nucleus of **1**, named moluccensin H, was established as shown in Figure S2. On the basis of the result that the literature specific rotation of (*R*)-2-methylbutyric acid is negative (−14.3)[16] and that of (*S*)-2-methylbutyric acid is positive (+19.3, 18.9),[17,18] the absolute configuration at C-2 in the 2-methylbutyryl group of **1** could be determined according to the specific rotation of its acid, which was obtained as a 1:1 mixture with isobutanoic acid from the alkaline hydrolysis of **1**. Since isobutanoic acid is optically inactive, the absolute configuration at C-2 in methylbutyric acid

was suggested to be *S* from the α_D value ($[\alpha]^{25}_D$ +10 (*c* 0.06, Me_2CO)) of this mixture.

Moluccensin I (**2**), a white, amorphous powder, had the same molecular formula as that of moluccensin H (**1**). The NMR data of **2**, indicating the presence of isobutyryl and 2-methylbutyryl groups, were similar to those of **1**. However, those of the isobutyryl and 2-methylbutyryl groups were slightly different. A strong HMBC correlation from H-3 (5.07, s) to C-1′ (174.0 qC) of the 2-methylbutyryl group placed it at C-3, whereas the isobutyryl group was attached to C-1, as suggested by its downshifted chemical shift (δ_C 90.8).[14] Thus, the structure of moluccensin I was established as shown in **2**.

The molecular formula of compound **3** was determined to be the same as that of **1**, and the NMR data of **3** were similar to those of **1**. Isobutyryl and 2-methylbutyryl groups were present, and the location of the isobutyryl group [δ_H 2.51 m, 1.14 (d, J = 7.0 Hz), 1.14 (d, J = 7.0 Hz); δ_C 18.9 CH_3, 18.9 CH_3, 34.2 CH, 174.5 qC] (Tables 1 and 2) at C-3 in β-orientation was again deduced by $^1H-^1H$ COSY, HMBC, and NOE correlations. The 2-methylbutyryl group, however, was present at C-2 by the downfield shift of C-2 (δ_C 88.8) and the upfield shift of C-1 (δ_C 86.7). The relative configuration of **3** was the same as that of **1** on the basis of NOE interactions. Therefore, the structure of moluccensin J (**3**) was identified as 2-*O*-2*S*-methylbutyryl-1-de-2-methylbutyrylmoluccensin H.

Compound **4** had the molecular formula $C_{36}H_{46}O_{11}$, as established by HR-TOFMS, two mass units more than **3**. The NMR data of **4** were similar to those of **3**, except for the lack of $\Delta^{8,9}$ and $\Delta^{14,15}$ double bonds. However, a $\Delta^{8,14}$ double bond was established by HMBC correlations between H_2-15/C-8, H_2-15/C-14, H-9/C-8, and H-9/C-14 (Figure S3). The existence of this double bond was corroborated by strong homoallylic coupling between H_2-15 and H-9 observed in the $^1H-^1H$ COSY spectrum. The significant NOE interaction observed in **4** (Figure S4) from H-3 to $H_{pro\text{-}R}$-29 helped to establish the 3α-H and the corresponding 3β-isobutyryl group. Moreover, NOE interactions between H-5/H-15β, H-5/H-17, and H-17/H-12β established the β-orientation of H-5 and H-17. Similarly, those between H-9/H_3-18, H-9/H_3-19, H-15α/H_3-18, and H-11α/H_3-18 indicated their mutual *cis* relationship and the α-orientation. On the basis of the above results, the relative configuration of **4**, named moluccensin K, was established as shown in Figure S4.

Compound **5** had the molecular formula $C_{37}H_{48}O_{11}$, as established by HR-TOFMS, larger than **4** by a CH_2 unit. The NMR data of **5** were similar to those of **4**, except for the presence of one more 2*S*-methylbutyryl group [δ_H 0.88 (t, J = 7.5 Hz), 1.14 (d, J = 7.0 Hz), 1.38, m, 1.60, m, 2.07, m; δ_C 11.2 CH_3, 17.6 CH_3, 25.8 CH_2, 41.3 CH, 175.7 qC] (Tables 1 and 2) and the absence of an isobutyryl group (3β-isobutyryl group in **4**). The second 2-methylbutyryl group in **5** was corroborated by $^1H-^1H$ COSY correlations between H_3-4′/H_2-3′, H_2-3′/H-2′, and H-2′/H_3-5′ and HMBC cross-peaks between H_3-4′/C-3′, H_3-4′/C-2′, H_3-5′/C-2′, H_3-5′/C-1′, and H-2′/C-1′. The HMBC cross-peak from H-3 (5.15, s) of **5** to the carbonyl carbon of the 2*S*-methylbutyryl group placed this group at C-3. Moreover, the significant NOE interaction observed in **5** from H-3 to $H_{pro\text{-}R}$-29 helped to establish the 3α-H and the corresponding 3β-2*S*-methylbutyryl group. Therefore, moluccensin L (**5**) was identified as 3-*O*-2*S*-methylbutyryl-3-deisobutyryloxymoluccensin K.

Moluccensin M (**6**) had the molecular formula $C_{35}H_{46}O_{11}$ (HR-TOFMS), with 13 degrees of unsaturation. From its ^1H and ^{13}C NMR data (Table 3), it was clear that seven of the 13 elements came from three carbon−carbon double bonds and four ester functions. Therefore, the molecule was hexacyclic. DEPT experiments revealed that **6** had eight methyl (a methoxy, a primary methyl, three secondary methyls, and three tertiary methyls of the phragmalin nucleus), five methylene, 10 methine (three olefinic), and 12 quaternary carbons (four carbonyls).

Table 3. ^1H (400 MHz) and ^{13}C (100 MHz) NMR Data for Moluccensin M (**6**)[a]

position	δ_H *J* (Hz) acetone-d_6	δ_C acetone-d_6	δ_H *J* (Hz) $CDCl_3$	δ_C $CDCl_3$
1		90.6 qC		90.3 qC
2		78.6 qC		78.7 qC
3	5.13 s	84.0 CH	5.06 s	84.9 CH
4		44.7 qC		44.7 qC
5	2.54[b]	36.0 CH	2.48[b]	36.1 CH
6	2.43 d, 12.0	33.4 CH_2	2.28 d, 10.0	34.0 CH_2
	2.55[b]		2.30 br s	
7		173.4 qC		172.8 qC
8		162.2 qC		160.8 qC
9	2.73 m	40.2 CH	2.57[b]	40.2 CH
10		51.2 qC		51.7 qC
11α	1.94 m	19.6 CH_2	1.85 m	19.8 CH_2
11β	1.76 m		1.65 m	
12α	1.68 m	34.7 CH_2	1.72 m	34.7 CH_2
12β	1.35 m		1.28 m	
13		39.3 qC		39.5 qC
14		133.0 qC		134.0 qC
15		175.6 qC		175.3 qC
17	5.09 s	72.3 CH	5.05 s	72.5 CH
18	1.25 s	17.1 CH_3	1.32 s	17.6 CH_3
19	1.16 s	17.4 CH_3	1.11 s	17.8 CH_3
20		125.8 qC		125.1 qC
21	7.53 br s	140.9 CH	7.48 br s	141.0 CH
22	6.53 br s	110.2 CH	6.48 br s	109.9 CH
23	7.52 br s	142.6 CH	7.41 br s	142.9 CH
28	0.80 s	14.6 CH_3	0.80 s	15.0 CH_3
$29_{pro\text{-}R}$	2.48 d, 11.6	38.4 CH_2	2.50 d, 11.6	38.7 CH_2
$29_{pro\text{-}S}$	2.66 d, 11.6		2.57 d, 12.4	
30	5.13 s	83.7 CH	5.04 s	84.1 CH
7-OMe	3.60 s	51.3 CH_3	3.64 s	52.0 CH_3
2-OH			3.49 br s	
17-OH			4.15 br s	
3-Acyl				
1′		176.1 qC		177.0 qC
2′	2.57 m	39.9 CH	2.48[b]	40.1 CH
3′	1.35 m	25.7 CH_2	1.32 m	25.5 CH_2
	1.61 m		1.74 m	
4′	0.89 t, 7.4	10.7 CH_3	0.94 t, 7.4	11.4 CH_3
5′	1.10 d, 6.8	17.4 CH_3	1.14 d, 7.2	18.0 CH_3
1-Acyl				
1″		175.4 qC		176.3 qC
2″	2.68 m	34.5 CH	2.55[b]	34.9 CH
3″	1.18 d, 6.8	18.9 CH_3	1.21 d, 7.2	19.1 CH_3
4″	1.14 d, 6.8	18.3 CH_3	1.21 d, 7.2	19.1 CH_3

[a] When detected in acetone-d_6, two singlet peaks of H-3 and H-30 are overlapped. But they are completely separated from that of H-17. When detected in $CDCl_3$, however, peaks of H-3, H-30, and H-17 are partially separated from each other. [b] Overlapped signals assigned by $^1H-^1H$ COSY and HSQC spectra without designating multiplicity.

The NMR data[19] of **6** (Table 3) and its 2D NMR studies ($^1H-^1H$ COSY, HSQC, and HMBC) (Figure S5) indicated the presence of a methoxycarbonyl group (δ_H 3.60 s; δ_C 51.3 CH_3, 173.4 qC), an isobutyryl group [δ_H 2.68 m, 1.18 (d, J = 6.8 Hz), 1.14 (d, J = 6.8 Hz); δ_C 18.9 CH_3, 18.3 CH_3, 34.5 CH, 175.4 qC], a 2-methylbutyryl group [δ_H 0.89 (t, J = 7.4 Hz), 1.10 (d, J = 6.8 Hz), 1.35, m, 1.61, m, 2.57, m; δ_C 10.7 CH_3, 17.4 CH_3, 25.7 CH_2, 39.9 CH, 176.1 qC], and a β-furanyl ring (δ_H 6.53 br s, 7.52 br s, 7.53 br s; δ_C 110.2 CH, 125.8 qC, 140.9 CH, 142.6 CH).

Two protons of a methylene group [δ_H 2.43 (d, J = 12.0 Hz), 2.55[a]; δ_C 33.4], showing HMBC correlations to C-5 (δ_C 36.0) and C-7 (δ_C 173.4), were assignable to H_2-6, corroborated by their $^1H-^1H$ COSY interactions with H-5 (Figure S5). A pair of geminally coupled protons [δ_H 2.48 (d, J = 11.6 Hz), 2.66 (d, J = 11.6 Hz)] of a methylene (δ_C 38.4), exhibiting HMBC correlations to C-1, C-2, C-3, and C-4 (Figure S5), were identified as H_2-29. The proton of an oxygenated methine group (δ_H 5.09 s; δ_C 72.3), showing HMBC correlations to C-13, C-18, C-20, C-21, and C-22

(Figure S5), was assigned as H-17, and protons of a tertiary methyl group (δ_H 1.25 s; δ_C 17.1), exhibiting HMBC cross-peaks to C-12, C-13, C-14, and C-17 (Figure S5), were identified as H_3-18. Moreover, a $\Delta^{8,14}$ double bond was suggested by HMBC interactions between H_3-18/C-14, H-9/C-8, and H-9/C-14. The proton of the second oxygenated methine group (δ_H 5.13 s; δ_C 84.0 in acetone-d_6 and δ_H 5.06 s; δ_C 84.9 in $CDCl_3$), showing HMBC correlations to C-2 and C-4 (Figure S5), was identified as H-3, and that of the third oxygenated one (δ_H 5.13 s; δ_C 83.7 in acetone-d_6 and δ_H 5.04 s; δ_C 84.1 in $CDCl_3$), exhibiting HMBC cross-peaks to C-1, C-2, C-8, and C-14, was identified as H-30.

HMBC correlations between H-3/C-30 and H-30/C-3 confirmed the linkage of the fragment $C_1-C_2-C_{30}$. Protons of the second tertiary methyl group (δ_H 1.16 s; δ_C 17.4), exhibiting HMBC cross-peaks to C-1, C-5, C-9, and C-10, were identified as H_3-19, and those of the third tertiary methyl group (δ_H 0.80 s; δ_C 14.6), showing HMBC correlations to C-3, C-4, and C-5 (Figure S5), were assigned to H_3-28. Furthermore, the strong HMBC cross-peak from H-3 (5.13 s in acetone-d_6 and 5.06 s in $CDCl_3$) to C-1′ (δ_C 176.1 in acetone-d_6 and 177.0 in $CDCl_3$) of the 2-methylbutyryl group disclosed its location at C-3. The isobutyryl group, however, was suggested to be attached to C-1 by its downshifted chemical shift (δ_C 90.6 in acetone-d_6 and 90.3 in $CDCl_3$) (Table 3), being almost the same as that of moluccensin A,[14] whose structure was confirmed by single-crystal X-ray diffraction. In addition, the $^1H-^1H$ COSY correlation between H-17/17-OH observed in $CDCl_3$ disclosed the opening of the ring-D.

Though the HMBC correlation from H-30 to the last carbonyl carbon (δ_C 175.6, C-15) was not observed due to the small quantity of **6**, a $C_{15}-C_{30}$ ester linkage, which was suggested by the downshifted chemical shift of C-30 (δ_C 83.7)[20] (Table 3), and being in accordance with 13 unsaturation degrees in **6**, was further corroborated by diagnostic fragments at *m/z* 569.2714 and 509.2554 in the positive HRTOF-MS^2 of **6** that originate from the subsequent loss of a molecule of furan-3-carbaldehyde and methyl formate (Scheme S1). Moreover, acylation of **6** with propionyl chloride in pyridine afforded the 2,17-*O*-dipropionyl derivative of **6**. This result supported the $C_{15}-C_{30}$ linkage.

The relative configuration of **6** was established on the basis of the NOESY interactions. The significant NOE interaction observed in **6** (Figure S6) from H-3 to $H_{pro\text{-}R}$-29 helped to establish the 3α-H and the corresponding 3β-2-methylbutyryl group. Moreover, NOE interactions between H-5/H-17, H-11β/H-17, and H-17/H_3-5′ established the β-orientation of H-5 and H-17. Similarly, those between H-9/H_3-18, H-9/H_3-19, H-9/H-30, and H_3-19/H-30 indicated their mutual *cis* relationship and the α-orientation. Thus, the relative configuration of the 16-norphragmanlin skeleton in **6** was established as shown in Figure S6. The absolute configuration at C-2′ in **6** was assumed to be *S*, the same as that in moluccensins H−L.

Compound **7** had the molecular formula $C_{27}H_{34}O_9$ with 11 degrees of unsaturation. APT experiments and the HSQC spectrum revealed that it contained five tertiary methyl (one a methoxy), six methylene (one olefinic), six methine (one olefinic and three oxygenated), and 10 quaternary carbons (two olefinic and four carbonyls). A γ-hydroxybutenolide group at C-17 was characterized by two broad proton singlets at δ_H 7.35 (H-22) and 6.23/6.17 (H-23) and by resonances at δ_C 133.6/133.5 (C-20), 170.3/170.1 (C-21), 150.2/149.8 (C-22), and 97.5/97.0 (C-23), the same as that in febrifugin A.[21] The appearance of pairs of most proton and carbon resonances in the NMR spectra of **7** suggested the presence of C-23 epimers. The presence of a ketone carbonyl (δ_C 213.3/213.0), two ester carbonyls (δ_C 174.0/173.7 and 169.4/169.1), and a double bond (δ_C 145.3/145.2, 112.0) was also determined from its ^1H and ^{13}C NMR data. These groups accounted for seven degrees of unsaturation, and the remaining four degrees of unsaturation required **7** to be tetracyclic. A δ-lactone ring, characterized by the NMR data [δ_H 5.61/5.60 s, 2.95 (d, J = 19.0 Hz), 2.60 (d, J = 19.0 Hz); δ_C 78.04/77.97 CH, 41.9/41/8 qC, 79.65 qC, 33.79/33.75 CH_2, 169.4/169.1 qC] (Tables 4 and 5), was corroborated by HMBC correlations between H_2-15/C-14, H_2-15/C-16, H-17/C-13, H-17/C-14, and H-17/C-16 (Figure S7). This suggested that **7** was an andirobin-type limonoid closely related to methyl angolensate.[22] The oxygen bridge between C-1 and C-14 was confirmed by the HMBC correlation from H-1 to C-14. Moreover, the β-orientation of H-1, suggested to be the same as that of methyl angolensate by its two proton−proton coupling constants (6.0 and 4.0 Hz) with H_2-2,[22] was corroborated by the NOE interaction between H-1/H_3-19 (Figure S8). The relative configuration was supported by NOE interactions between H_3-19/H-9, H-11α/H-9, H-11α/H_3-18, H-15α/H_3-18, H-15β/H-1, and H-12β/H-17 (Figure S8). Therefore, the structure of moluccensin N was identified as **7**.

Table 4. ^1H NMR (500 MHz) Data (δ) for Moluccensins N−Q (**7**−**10**) in $CDCl_3$ (J in Hz)

position	7	8	9	10
1	3.52, dd (6.0, 4.0)	3.53, dd (6.0, 4.0)	2.01, dd (5.5, 3.0)	2.01, dd (5.5, 3.0)
			1.99, dd (5.5, 3.0)	1.99, dd (5.5, 3.0)
2a	2.88, dd (14.5, 6.0)	2.91, dd (14.5, 6.0)	2.26, m	2.24, m
2b	2.55, dd (14.5, 4.0)	2.50, dd (14.5, 4.0)	2.77, dt (14.5, 5.5)	2.76, dt (14.5, 5.5)
5	2.90, d (10.0)	2.82, d (10.0)	1.68, m	1.68, m
6a	2.30, m	2.26, m	2.10, m	2.10, m
6b	2.60, dd (15.5. 11.0)	2.63, dd (16.5. 10.0)	2.08, m	2.08, m
7			5.32, d (3.0)	5.31, d (3.0)
9	2.23, m[a]	2.22, m[a]	2.30, m[a]	2.29, m[a]
11α	1.60, m	1.67, m	1.60, m	1.60, m
11β	2.24, m[a]	2.22, m[a]	1.60, m	1.60, m
12α	1.08, m	1.31, m	1.86, m	1.85, m
12β	2.20, m	2.06, m	1.86, m	1.85, m
15α	2.95, d (19.0)	2.90, d (19.0)	1.58, m	1.60, m
15β	2.60, d (19.0)	2.62, d (19.0)	1.50, m	1.50, m
16			1.30, m	1.25, m
			1.30, m	1.28, m
17	5.61, s/5.60, s	5.62, s	1.73, t (8.5)	1.73, t (8.5)
18	0.95, s	0.93, s	0.86, s	0.86, s
19	0.92, s	0.95, s	1.02, s	1.02, s
20			2.33, m[a]	2.29, m[a]
21		6.14, br s	1.08, d (7.0)	1.07, d (7.0)
22	7.35, br s	6.24, br s	6.99, dd (15.0, 9.0)	6.96, dd (16.0, 9.0)
23	6.23, br s/6.17, br s		6.37, d (15.0)	5.79, d (16.0)
26			1.39, s	
27			1.39, s	
28	1.07, s	1.01, s	1.05, s	1.05, s
29	1.20, s	1.18, s	1.12, s	1.12, s
30a	5.20, s	5.20, s	1.01, s	1.01, s
30b	4.95, s/4.94, s	4.92, s		
7-OMe	3.74, s/3.73, s	3.73, s		

[a] Overlapped signals assigned by $^1H-^1H$ COSY, HSQC, and HMBC spectra without designating multiplicity.

Moluccensin O (**8**) had a molecular formula the same as that of **7**. The NMR data of **8** were similar to those of **7**, except for the presence of a different γ-hydroxybutenolide group substituted at C-17. The NMR data of the γ-hydroxybutenolide group in **8**, characterized by two broad proton singlets at δ_H 6.14 (H-21) and 6.24 (H-22) and by resonances at δ_C 163.7 (C-20), 98.1 (C-21), 121.8 (C-22), and 169.4 (C-23), were found to be the same as those of kihadanin A.[23] Thus, the structure of moluccensin O was elucidated as **8**.

The molecular formula of compound **9** was established to be $C_{30}H_{46}O_3$ by HR-ESIMS. APT experiments and the HSQC spectrum revealed signals for eight methyl (one secondary and seven tertiary), seven methylene, seven methine (three olefinic), and eight quater-

Table 5. ^{13}C (125 MHz) NMR Data (δ) for Moluccensins N−Q (**7**−**10**) in $CDCl_3$

position	7	8	9	10
1	77.1, CH	77.0, CH	38.6, CH_2	38.5, CH_2
2	39.6/39.5, CH_2	39.3, CH_2	34.9, CH_2	34.9, CH_2
3	213.3/213.0, qC	213.0, qC	216.8, qC	216.8, qC
4	48.0/47.9, qC	48.0, qC	47.9, qC	47.9, qC
5	43.0/42.9, CH	43.0, CH	51.9, CH	51.9, CH
6	33.0/32.9, CH_2	32.6, CH_2	24.4, CH_2	24.4, CH_2
7	174.0/173.7, qC	174.0, qC	118.3, CH	118.2, CH
8	145.3/145.2, qC	144.9, qC	145.4, qC	145.5, qC
9	49.6/49.5, CH	49.6, CH	48.4, CH	48.4, CH
10	44.01/43.98, qC	44.0, qC	35.1, qC	35.1, qC
11	23.6/23.5, CH_2	23.8, CH_2	18.2, CH_2	18.2, CH_2
12	28.8, CH_2	29.4, CH_2	33.5, CH_2	33.5, CH_2
13	41.9/41.8, qC	41.9, qC	44.0, qC	44.0, qC
14	79.65, qC	79.9, qC	51.2, qC	51.1, qC
15	33.79/33.75, CH_2	33.5, CH_2	34.1, CH_2	34.1, CH_2
16	169.4/169.1, qC	169.0, qC	28.1, CH_2	28.1, CH_2
17	78.04/77.97, CH	80.0, CH	52.4, CH	52.4, CH
18	13.6/13.5, CH_3	14.2, CH_3	22.1, CH_3	22.1, CH_3
19	21.6, CH_3	21.7, CH_3	12.8, CH_3	12.8, CH_3
20	133.6/133.5, qC	163.7, qC	40.8, CH	40.3, CH
21	170.3/170.1, qC	98.1, CH	18.8, CH_3	18.7, CH_3
22	150.2/149.8, CH	121.8, CH	156.2, CH	157.5, CH
23	97.5/97.0, CH	169.4, qC	120.1, CH	118.3, CH
24			202.8, qC	171.3, qC
25			75.2, qC	
26			26.4, CH_3	
27			26.4, CH_3	
28	26.4/26.2, CH_3	25.8, CH_3	24.5, CH_3	24.6, CH_3
29	21.4/21.3, CH_3	21.4, CH_3	21.6, CH_3	21.6, CH_3
30	112.0, CH_2	112.3, CH_2	27.4, CH_3	27.4, CH_3
7-OMe	52.2/52.1, CH_3	52.3, CH_3		

nary carbons (one olefinic, one oxygenated, and two carbonyl). These data combined with two olefinic carbons (δ_C 118.3 CH, 145.4 qC) indicated that **9** was a tirucallane-type triterpene having a $\Delta^{7,8}$ double bond and a C-3 ketone group. Comparison of its NMR data with those of 23,26-dihydroxytirucalla-7,24-dien-3-one[15] revealed that they had the same tetracyclic core structure. The only difference between them was the different side chain at C-17. The presence of the $\Delta^{22,23}$ double bond in the side chain of **9** was corroborated by a homonuclear proton−proton spin system H_3-21−H-20−H-22−H-23 observed in its $^1H-^1H$ COSY spectrum, and that of the C-24 ketone group was confirmed by HMBC correlations between H-23/C-24, H_3-26/C-24, and H_3-27/C-24 (Figure S9). The *E*-geometry of the $\Delta^{22,23}$ double bond was established by the coupling constants of H-22 and H-23 (15 Hz). The 25-OH, suggested by the chemical shift of C-25 at δ_C 75.2 and the molecular formula of **9**, was confirmed by HMBC correlations between H_3-26/C-25 and H_3-27/C-25 (Figure S9). Therefore, the structure of moluccensin P was identified as **9**.

The molecular formula of compound **10** was established to be $C_{27}H_{40}O_3$. The NMR data of **10** were similar to those of **9**, except for the absence of three carbons in the side chain of **9**, viz., C-25, C-26, and C-27. The presence of a terminal C-24 carboxyl group was suggested by its chemical shift at δ_C 171.3 qC and was supported by the molecular formula of **10**. Connection of the *E*-double bond ($\Delta^{22,23}$) to the carboxyl group in the side chain of **10** was established by HMBC correlations between H-22/C-24 and H-23/C-24. Thus, the structure of moluccensin Q was elucidated as **10**.

The insecticidal activity of compounds **1**−**5** was tested using a conventional leaf disk method against the fifth instar larvae of *Brontispa longissima* (Gestro). Moluccensins H (**1**) and I (**2**) showed moderate insecticidal activity at a concentration of 100 mg/L, whereas other compounds showed no activity. The lethal rates of moluccensin H (**1**) at exposure times of 72 and 96 h were 20.7% and 27.6%, respectively, while those of moluccensin I (**2**) were 10.7% and 28.7%, respectively.

In summary, moluccensins H−L are rare phragmalins possessing a C-30 carbonyl group in conjugation with a $\Delta^{8,14}$ double bond or $\Delta^{8,9}$, $\Delta^{14,15}$ double bonds, and moluccensin M is a ring-D-opened 16-norphragmalin with an unprecedented carbon skeleton. Moluccensins N−O are andirobin-type limonoids, and moluccensins P-Q are tirucallane derivatives.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a Polaptronic HNQW5 automatic high-resolution polarimeter (Schmidt & Haensch Co. Ltd.). UV spectra were obtained on a Beckman DU-640 UV spectrophotometer, and MALDITOFMS spectra were measured on a Bruker APEX II spectrometer in positive ion mode. NMR spectra were recorded in $CDCl_3$ using a Bruker AV-400 or AV-500 spectrometer with TMS as the internal standard. Preparative HPLC was carried out on ODS columns (250 × 20 mm i.d. and 250 × 10 mm i.d., YMC) with a Waters 2998 photodiode array detector. For CC, silica gel (200−300 mesh) (Qingdao Mar. Chem. Ind. Co. Ltd.) and RP C_{18} gel (Cosmosil C18-PREP 140 μm, Nacalai Tesque, Kyoto, Japan) were used.

Plant Material. The seeds of *X. moluccensis* were collected in October 2007 in the mangrove wetlands of Krishna estuary, Andhra Pradesh, India. The identification of the plant was performed by one of the authors (T.S.). A voucher sample (No. IndianXM-01) is maintained in the Herbarium of the South China Sea Institute of Oceanology.

Extraction and Isolation. The dried seeds (7.0 kg) of *X. moluccensis* were extracted three times with 95% EtOH at room temperature. The extract was concentrated under reduced pressure, followed by suspension in H_2O and extraction with EtOAc. The resulting EtOAc extract (320 g) was chromatographed on silica gel and eluted using a $CHCl_3$−MeOH system (100:0−5:1) to yield 230 fractions. Fractions 70 to 80 (19.0 g) were combined and further separated using RP C_{18} CC (MeCN−H_2O, 50:50−100:0) to afford 60 subfractions. Then subfractions 27 to 37 were combined and further purified by preparative HPLC (YMC-Pack ODS-5-A, 250 × 20 mm i.d. and 250 × 10 mm i.d., MeOH−H_2O, 50:50 to 55:45) to yield **1** (8.0 mg), **2** (10.0 mg), **3** (4.0 mg), **4** (4.0 mg), **5** (5.2 mg), **6** (2.0 mg), **7** (4.0 mg), **8** (5.0 mg), **9** (4.0 mg), **10** (4.0 mg), and 3β,22*S*-dihydroxytirucalla-7,24-dien-23-one (3.0 mg).

Absolute Configuration of C-2 in the 2-Methylbutyryl Group of Moluccensins H−L (1−5). A portion of **1** (2 mg) was dissolved in EtOH (0.5 mL) and treated with 6% KOH in H_2O (1 mL), with stirring at room temperature for 24 h. The reaction mixture was concentrated and partitioned between EtOAc and H_2O (3:1). After extraction with EtOAc (×3), the aqueous layer was acidified with HCl to pH 3.0 and extracted again with CH_2Cl_2 (×3). The organic solubles were combined, subjected to Sephadex LH-20 CC (CH_2Cl_2−MeOH, 1:1), and dried over anhydrous Na_2SO_4 to provide a mixture of 1:1 isobutanoic acid and 2-methylbutyric acid (0.6 mg), which were identified on the basis of their mass spectra. Since isobutanoic acid is optically inactive, the absolute configuration at C-2 in 2-methylbutyric acid was suggested as *S* by the $[\alpha]^{25}_D$ +10 (*c* 0.06, Me_2CO) of the above mixture. In the same way, the absolute configuration of C-2 in the 2-methylbutyryl group of moluccensins I−L (**2**−**5**) was indicated to be *S*.

Moluccensin H (1): white, amorphous powder; $[\alpha]^{25}_D$ +137.8 (*c* 0.27, Me_2CO); UV (MeCN) λ_{max} 210.3, 284.4 nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; HR-TOFMS *m/z* 675.2770 [calcd for $C_{36}H_{44}O_{11}Na$ $[M + Na]^+$, 675.2776], *m/z* 691.2573 [calcd for $C_{36}H_{44}O_{11}K$ $[M + K]^+$, 691.2515].

Moluccensin I (2): white, amorphous powder; $[\alpha]^{25}_D$ +119.0 (*c* 0.42, Me_2CO); UV (MeCN) λ_{max} 206.2, 285.6 nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; HR-TOFMS *m/z* 675.2780 [calcd for $C_{36}H_{44}O_{11}Na$ $[M + Na]^+$, 675.2776], HR-TOFMS *m/z* 653.2969 [calcd for $C_{36}H_{45}O_{11}$ $[M + H]^+$, 653.2956].

Moluccensin J (3): white, amorphous powder; $[\alpha]^{25}_D$ +74.5 (*c* 0.11, Me_2CO); UV (MeCN) λ_{max} 206.1, 282.0 nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; HR-TOFMS *m/z* 675.2785 [calcd for $C_{36}H_{44}O_{11}Na$ $[M + Na]^+$, 675.2776], *m/z* 653.2979 [calcd for $C_{36}H_{45}O_{11}$ $[M + H]^+$, 653.2956].

Moluccensin K (4): white, amorphous powder; $[\alpha]^{25}_D$ +30.7 (*c* 0.14, Me_2CO); UV (MeCN) λ_{max} 206.5, 257.1 nm; ^1H and ^{13}C NMR data,

see Tables 1 and 2; HR-TOFMS *m/z* 677.2943 [calcd for $C_{36}H_{46}O_{11}Na$ $[M + Na]^+$, 677.2932], *m/z* 655.3126 [calcd for $C_{36}H_{47}O_{11}$ $[M + H]^+$, 655.3113].

Moluccensin L (5): white, amorphous powder; $[\alpha]^{25}_D$ +2.9 (*c* 1.13, Me_2CO); UV (MeCN) λ_{max} 210.9, 253.5 nm; ^1H and ^{13}C NMR data, see Tables 1 and 2; HR-TOFMS *m/z* 691.3101 [calcd for $C_{37}H_{48}O_{11}Na$ $[M + Na]^+$, 691.3089], *m/z* 707.2895 [calcd for $C_{37}H_{48}O_{11}K$ $[M + K]^+$, 707.2828].

Moluccensin M (6): white, amorphous powder; $[\alpha]^{25}_D$ +1.4 (*c* 0.2, acetone); UV (MeCN) λ_{max} 216.8 nm; ^1H and ^{13}C NMR data, see Table 3; HR-TOFMS *m/z* 665.2925 [calcd for $C_{35}H_{46}O_{11}Na$ $[M + Na]^+$, 665.2932], *m/z* 681.2679 [calcd for $C_{35}H_{46}O_{11}K$ $[M + K]^+$, 681.2672].

Moluccensin N (7): white, amorphous powder; $[\alpha]^{25}_D$ −16.2 (*c* 0.05, acetone); UV (MeCN) λ_{max} 214.0 nm; ^1H and ^{13}C NMR data, see Tables 4 and 5; HR-ESIMS *m/z* 525.2065 [calcd for $C_{27}H_{34}O_9Na$ $[M + Na]^+$, 525.2095]; HR-ESIMS *m/z* 541.1804 [calcd for $C_{27}H_{34}O_9K$ $[M + K]^+$, 541.1834].

Moluccensin O (8): white, amorphous powder; $[\alpha]^{25}_D$ −35.0 (*c* 0.04, acetone); UV (MeCN) λ_{max} 214.0 nm; ^1H and ^{13}C NMR data, see Tables 4 and 5; HR-ESIMS *m/z* 525.2076 [calcd for $C_{27}H_{34}O_9Na$ $[M + Na]^+$, 525.2095]; HR-ESIMS *m/z* 541.1817 [calcd for $C_{27}H_{34}O_9K$ $[M + K]^+$, 541.1834].

Moluccensin P (9): white, amorphous powder; $[\alpha]^{25}_D$ −56.2 (*c* 0.04, acetone); UV (MeCN) λ_{max} 190.0 nm; ^1H and ^{13}C NMR data, see Tables 4 and 5; HR-ESIMS *m/z* 489.3149 [calcd for $C_{30}H_{46}O_3Cl$ $[M + Cl]^-$, 489.3141].

Moluccensin Q (10): white, amorphous powder; $[\alpha]^{25}_D$ 69.0 (*c* 0.05, acetone); UV (MeCN) λ_{max} 192.0 nm; ^1H and ^{13}C NMR data, see Tables 4 and 5; HR-ESIMS *m/z* 447.2666 [calcd for $C_{27}H_{40}O_3Cl$ $[M + Cl]^-$, 447.2672].

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Supporting Information Available: Figures S1−S9 and Scheme S1; copies of HR-MS (HR-TOFMS or HR-ESIMS), ^1H and ^{13}C NMR spectra of compounds **1**−**5** and **7**−**10**; copies of RP-HPLC preparative chromatogram, ESI-MS, HRTOF-MS, HRTOF-MS-MS, 1D and 2D NMR spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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