Methyl Migrated Cassane-Type Furanoditerpenes of *Caesalpinia crista* from Myanmar

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From the CH_2Cl_2 extract of seed kernels of *Caesalpinia crista* from Myanmar, two rare and biogenetically interesting methyl migrated cassane-type furanoditerpenes [caesalpinins MM (1) and MN (2)] and two normal cassane-type furanoditerpenes [caesalpinins MO (3) and MP (4)] have been isolated, together with eight known cassane-type diterpenes, 1-deacetoxy-1-oxocaesalmin C (5), 1-deacetylcaesalmin C (6), caesalmin C (7), bonducellpin C (8), caesaldekarin e (9), 2-acetoxycaesaldekarin e (10), 2-acetoxy-3-deacetoxycaesaldekarin e (11), and norcaesalpinin E (12). Among the known compounds, compounds 5 and 6 were for the first time isolated from a natural source. The structures of these compounds were elucidated by the use of spectroscopic techniques.

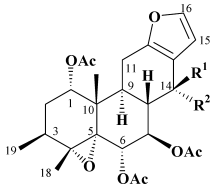
Key words cassane-type furanoditerpene; caesalpinin; *Caesalpinia crista*; Myanmar

Caesalpinia crista LINN. (Fabaceae) is a famous medicinal plant widely distributed in tropical and subtropical regions of Southeast Asia. This plant is locally known as "Ka-Lain" in Myanmar and its seeds are used as anthelmintic, antipyretic, anti-inflammatory, and antimalarial agent.[1] In Indonesia, it is known as "Bagore" and a decoction of the roots has been used as a tonic and for the treatment of rheumatism and backache.[2] The plants belonging to the genus *Caesalpinia* are rich sources of cassane-type furanoditerpenes, some of which have been reported to show antimalarial,[3,4] antiviral,[5] and anticancer[6] activities. In continuation of our research on this plant species from different parts of Southeast Asia,[3,4,7—9] we have isolated two new rearranged cassane-type diterpenes, caesalpinins MM (**1**) and MN (**2**) and two new normal cassane-type furanoditerpenes, caesalpinins MO (**3**) and MP (**4**), together with eight known cassane-type diterpenes, from a CH_2Cl_2 extract of the seed kernels of this plant from Myanmar. The isolation of compounds **5** and **6** from a natural source is for the first time; they were only reported as semisynthetic products of α-caesalpin.[10] In this paper, we report the structures of the new cassane-type diterpenes.

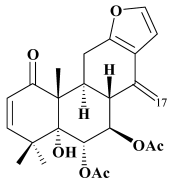
Results and Discussion

Air-dried seed kernels of *C. crista* were extracted with CH_2Cl_2 by overnight percolation at room temperature. The CH_2Cl_2 extract was first fractionated by silica gel column chromatography with a benzene/EtOAc gradient system into seven fractions. Fraction 6 was repeatedly subjected to silica gel column chromatography, followed by normal- and reversed-phase preparative TLC, to afford four new cassane-type furanoditerpenes, caesalpinins MM—MP (**1**—**4**), together with eight known diterpenes, 1-deacetoxy-1-oxocaesalmin C (**5**),[10] 1-deacetylcaesalmin C (**6**),[10] caesalmin C (**7**),[5] bonducellpin C (**8**),[11] caesaldekarin e (**9**),[12] 2-acetoxycaesaldekarin e (**10**),[13] 2-acetoxy-3-deacetoxycaesaldekarin e (**11**),[14] and norcaesalpinin E (**12**).[4]

Caesalpinin MM (**1**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +26.3° ($CHCl_3$) and its molecular formula was determined to be $C_{26}H_{34}O_9$ by high resolution (HR)-EI-MS. The IR absorptions at 3450 and 1730 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{1}H-NMR spectrum of **1** (Table 1) displayed signals corresponding to three tertiary methyls, a secondary methyl, three oxygen-substituted methines, three aliphatic



1 $R^1 = CH_3$, $R^2 = OH$
2 $R^1 = OH$, $R^2 = CH_3$



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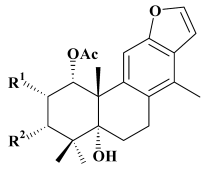
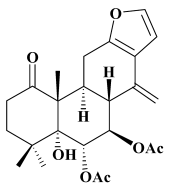
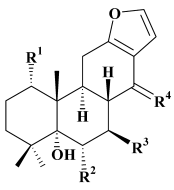


4 $R^1 = R^2 = H$
9 $R^1 = H$, $R^2 = OAc$
10 $R^1 = R^2 = OAc$
11 $R^1 = OAc$, $R^2 = H$



5



6 $R^1 = OH$, $R^2 = R^3 = OAc$, $R^4 = CH_2$
7 $R^1 = R^2 = R^3 = OAc$, $R^4 = CH_2$
8 $R^1 = OAc$, $R^2 = H$, $R^3 = OH$, $R^4 = \alpha$-H, β-COOMe
12 $R^1 = OAc$, $R^2 = H$, $R^3 = OH$, $R^4 = O$

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methines, and two aliphatic methylenes, together with two protons of a 1,2-disubstituted furan ring (δ 7.24, 6.41) and three acetyl methyls. Moreover, the ^{13}C-NMR spectrum of **1** showed the signals of four olefinic carbons (δ 149.3, 141.6, 123.0, 107.7), three oxygen-substituted quaternary carbons (δ 68.5, 67.9, 64.5), three oxygen-substituted methines (δ 74.2, 73.4, 69.7), three aliphatic methines, and two aliphatic methylenes together with three ester carbonyl carbons (δ 170.9, 170.8, 170.4). The partial structures (O)–C(1)H–C(2)H_2–C(3)H–C(19)H_3 deduced by the ^{1}H–^{1}H shift correlation spectroscopy (COSY) and heteronuclear multiple-quantum coherence (HMQC) spectra, and the heteronuclear multiple-bond connectivity (HMBC) correlations of the secondary methyl protons at δ 1.15 (H_3-19) with C-2, C-3, and C-4 indicated that **1** should be a rearranged cassane-type diterpene having one of the two methyl groups at C-4 migrated to C-3, as caesalpinin.[15] The long-range correlations of H_3-19 with the carbon at δ 64.5 (C-4) and of H_3-18 with the carbons at δ 64.5 (C-4) and 67.9 (C-5) suggested that both C-4 and C-5 should be oxygen-substituted. The molecular formula and the ^{13}C-NMR chemical shifts of C-5 (δ 67.9), which appear at higher field than hydroxylated C-5 (δ 75.2—83.7) in normal cassane-type diterpenes of *Caesalpinia* species,[3—9] indicated that **1** might contain an epoxide ring between C-4 and C-5. The ^{1}H- and ^{13}C-NMR spectra indicated that **1** has one more acetyl group instead of a ketone carbonyl in caesalpinin.[15] The location of the acetoxy substituent was determined to be at C-1 based on the long-range correlations observed between the ester carbonyl carbon at δ 170.9 (OCO-1) and the protons at δ 2.02 ($OCOCH_3$-1) and 4.75 (H-1). Similarly, the locations of two other acetoxy substituents were determined to be at C-6 and C-7, based on the long-range correlations between the ester carbonyl carbon at δ 170.4 (OCO-6) and the protons at δ 2.03 ($OCOCH_3$-6) and 5.75 (H-6) and between the ester carbonyl carbon at δ 170.8 (OCO-7) and the protons at δ 2.05 ($OCOCH_3$-7) and 5.59 (H-7), respectively. On the other hand, a hydroxyl substituent was located at C-14 based on the long-range correlations of H_3-17 (δ 1.50) with C-8, C-13, and an oxygen-substituted quaternary carbon at δ 68.5 (C-14) in the HMBC spectrum.

The relative stereochemistry of **1** was determined on the basis of coupling constants, rotating-frame Overhauser enhancement spectroscopy (ROESY) correlations, and the results of difference NOE experiment. The small coupling constant between H-1 and H-2 (2.6 Hz) and the ROESY correlation between H_3-20 and H-1 suggested the acetoxy substituent at C-1 to be α-oriented. Similarly, the ROESY correlations between H_3-19 and H-2β (δ 1.83) and the large coupling constant between H-3 and H-2β (8.6 Hz) indicated H_3-19 to be β-oriented. Since the C-5 hydroxyl substituent is biogenetically α-oriented in cassane-type diterpenes of the *Caesalpinia* species, the epoxide ring between C-4 and C-5 should be α-oriented. This was supported by the ROESY correlations of H_3-20 with H-2β, H-6, H-8, and H-11β and of H_3-18/H-3 and H_3-18/H_3-19 (Fig. 1b). Furthermore, the ROESY correlations between H_3-20 and H-6 suggested the α-equatorial orientation of the C-6 acetoxy substituent, while the large coupling constant of H-7 with both H-6 and H-8 (10.0 Hz), together with NOE enhancement between H-7 and H-9, suggested the acetoxy substituent at C-7 to be β-equatorial. Similarly, the NOE enhancement between H_3-17 and H-8 indicated the C-17 methyl to be β-oriented *i.e.*, the hydroxyl group to be α-oriented. Thus, the structure of caesalpinin MM was concluded as **1**.

Caesalpinin MN (**2**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +57.6° ($CHCl_3$) and its molecular formula was determined to be the same as that of **1** ($C_{26}H_{34}O_9$) by HR-EI-MS. The IR and ^{1}H- and ^{13}C-NMR spectral data of **2** were similar to those of **1** (Table 1) except for the difference in the ^{13}C chemical shifts for C-8, C-9, and C-14 (Table 1); these carbons in **2** appeared in lower field than those of **1**. Analysis of the COSY, HMQC, and HMBC data of **2** gave the same planar structure as **1**. However, **1** and **2** differed in the configuration at C-14 as analyzed by NOE difference experiment. The NOE enhancements from H_3-17 to H-7 and H-9 suggested the α-orientation of the methyl group (H_3-17) at C-14 in **2** (Fig. 1d). The differences in the ^{13}C-NMR chemical shifts between compounds **1** and **2** might be due to the anisotropic effect of β-orientation of the C-14 hydroxyl substituent in **2**. Thus, caesalpinin MN (**2**) was the stereoisomer of **1** at C-14.

Caesalpinin MO (**3**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +37.5° ($CHCl_3$) and its molecular formula was determined to be $C_{24}H_{28}O_7$ by HR-EI-MS. The IR absorptions at 3450 and 1730 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{1}H- and ^{13}C-NMR data for **3** (Table 1) closely resembled those of caesalmin C (**7**)[5] and displayed the signals due to three tertiary methyls, two oxygen-substituted methines, two aliphatic methines, two olefinic protons, and two protons of an exomethylene group, together with two protons of a 1,2-disubstituted furan ring and two acetyl methyls. However, they differed from each other due to the presence of a ketone carbonyl carbon and an olefinic double bond in **3**. The long-range correlations of H_3-20 and H-3 with the ketone carbonyl carbon indicated the ketone carbonyl carbon should be C-1, while the long-range correlations of the olefinic protons H-3 and H-2 with C-4 and of H-3 with C-1, C-18, and C-19 indicated the olefinic double bond should be C-2(3) (Fig. 1c). The relative stereochemistry of **3** was determined on the basis of coupling constants and ROESY correlations to be the same as that of **7**. Thus, the structure of caesalpinin MO was concluded as **3**.

Caesalpinin MP (**4**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +89.2° ($CHCl_3$) and its molecular formula was determined to be $C_{22}H_{28}O_4$ by HR-EI-MS. The IR absorptions at 3450 and 1730 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{1}H-NMR spectrum of **4** displayed signals corresponding to four tertiary methyls, an oxygen-substituted methine, and four aliphatic methylenes, together with an aromatic proton (δ 7.02), two protons of a 1,2-disubstituted furan ring (δ 7.51, 6.71), and an acetyl methyl (Table 1). Moreover, the ^{13}C-NMR spectrum of **4** showed 22 carbon signals including four tertiary methyls, an acetyl methyl, eight olefinic carbons (δ 153.5, 144.2, 140.2, 128.5, 128.4, 125.5, 104.9, 104.1), two oxygen-substituted carbons (δ 75.9, 75.6), an ester carbonyl carbon (δ 169.6), and four aliphatic methylenes (Table 1). These data were similar to those of caesaldekarin e (**9**),[12] except for the absence of signals due to one of two acetoxy substituents in **4**. The location of the deacetoxylation was determined to be at C-3 on the basis of high-field shift of H_2-3 (**4**,

Table 1. ^{1}H- and ^{13}C-NMR Data (δ) for Compounds **1**—**6** in $CDCl_3$ (*J* Values in Parentheses)

Position	**1**		**2**		**3**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	4.75 t (2.6)	74.2	4.72 t (2.7)	74.1		201.7
2	1.83 ddd (15.4, 8.6 2.6)	27.2	1.81 ddd (15.1, 8.3, 2.7)	27.1	5.80 d (10.2)	122.8
	1.61 br dd (15.4, 2.6)		1.66 br dd (15.1, 2.7)			
3	2.00 m	31.9	2.00 m	31.8	5.80 d (10.2)	152.4
4		64.5		64.9		41.7
5		67.9		68.1		80.4
6	5.75 d (10.0)	69.7	5.68 d (10.2)	69.6	5.56 m	75.9
7	5.59 t (10.0)	73.4	5.54 t (10.2)	72.5	5.56 m	74.1
8	2.23 dd (10.5, 10.0)	47.1	2.38 m	48.0	2.67 m	42.3
9	2.60 ddd (12.2, 10.5, 5.9)	33.8	2.49 m	35.5	2.86 ddd (12.4, 11.2, 4.4)	38.4
10		40.7		41.1		52.8
11	2.38 m	22.5	2.46 m	22.3	3.47 dd (16.0, 4.4)	26.7
	2.18 m		2.34 m		2.62 dd (16.0, 11.2)	
12		149.3		147.2		152.2
13		123.0		125.0		119.0
14		68.5		72.4		138.8
15	6.41 d (1.9)	107.7	6.38 d (2.0)	107.2	6.40 d (2.0)	106.4
16	7.24 d (1.9)	141.6	7.24 d (2.0)	141.9	7.23 d (2.0)	141.6
17	1.50 s	29.4	1.50 s	25.2	5.05 d (1.9), 4.76 d (1.9)	104.7
18	1.45 s	20.6	1.47 s	20.6	1.28 s	27.2
19	1.15 d (7.0)	17.1	1.14 d (7.1)	17.0	1.30 s	24.3
20	1.29 s	19.7	1.30 s	19.9	1.40 s	17.6
1-OCO$\underline{C}H_3$	2.02 s	21.5	2.02 s	21.4		
1-O$\underline{C}OCH_3$		170.9		170.6		
6-OCO$\underline{C}H_3$	2.03 s	21.3	2.02 s	21.3	1.99 s	21.3
6-O$\underline{C}OCH_3$		170.4		170.3		171.3
7-OCO$\underline{C}H_3$	2.05 s	21.5	2.02 s	21.2	2.13 s	21.7
7-O$\underline{C}OCH_3$		170.8		169.7		170.0

Position	**4**		**5**		**6**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	5.69 br s	75.6		211.7	3.70 br s	72.6
2	2.09 m, 1.94 m	23.0	2.74 m, 2.34 m	35.3	2.89 m, 1.68 m	25.4
3	2.01 m, 1.22 m	30.6	1.89 m, 1.75 m	39.2	2.00 m, 1.07 m	32.0
4		38.4		38.8		38.6
5		75.9	5.60 m	82.6		80.5
6	2.07 (2H) m	24.0	5.52 m	75.3	5.57 m	75.7
7	2.91 m, 2.80 m	23.7	2.63 t (11.6)	74.3	5.53 m	75.7
8		128.4	2.88 td (11.6, 4.6)	42.0	2.73 t (11.2)	41.3
9		140.2		39.0	3.04 td (11.2, 5.5)	37.7
10		46.8		54.9		44.4
11	7.02 s	104.1	3.31 dd (16.4, 4.6)	21.3	2.88 dd (16.1, 5.5)	23.2
			2.40 dd (16.4, 11.6)		2.59 dd (16.1, 11.2)	
12		153.5		152.1		151.3
13		125.5		119.0		119.6
14		128.5		138.6		139.0
15	6.71 d (2.2)	104.9	6.40 d (2.0)	106.3	6.41 d (2.0)	106.6
16	7.51 d (2.2)	144.2	7.23 d (2.0)	141.6	7.24 d (2.0)	141.8
17	2.37 s	15.9	5.04 d (2.0), 4.78 d (2.0)	104.6	5.07 d (2.0), 4.87 d (2.0)	105.2
18	1.13 s	27.9	1.16 s	29.0	1.00 s	30.5
19	1.15 s	25.0	1.30 s	21.6	1.15 s	24.8
20	1.37 s	30.7	1.53 s	16.2	1.21 s	16.9
1-OCO$\underline{C}H_3$	1.92 s	21.4				
1-O$\underline{C}OCH_3$		169.6				
6-OCO$\underline{C}H_3$			1.98 s	21.3	1.98 s	21.4
6-O$\underline{C}OCH_3$				170.2		171.0
7-OCO$\underline{C}H_3$			2.11 s	21.6	2.09 s	21.8
7-O$\underline{C}OCH_3$				170.1		170.5

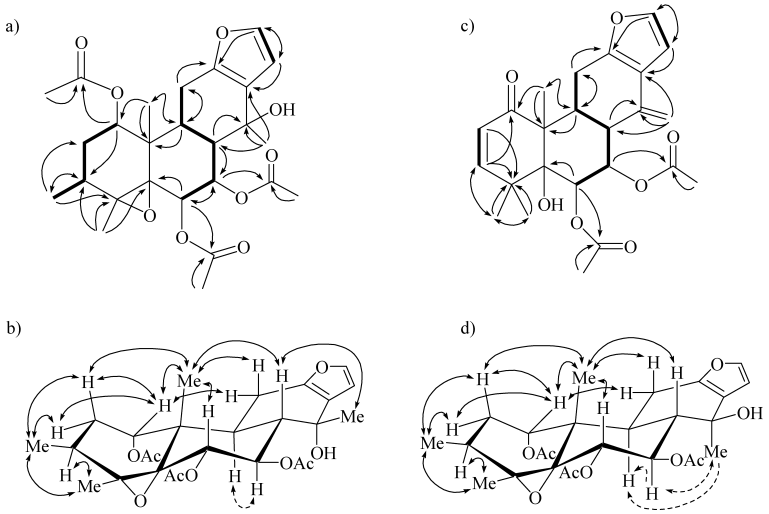

Fig. 1. Connectivities (Bold Lines) Deduced by the COSY Spectrum and Key HMBC Correlations (Arrows) (a) and (c) for Compounds **1** and **3** and Selected NOE (Dashed Arrows) and ROESY (Solid Arrows) Correlations (b) and (d) for **1** and **2**

δ 2.01, 1.22) as compared to H-3 (**9**, δ 5.05) deduced from the COSY and HMQC spectra. Thus, **4** should be 3-deacetoxylcaesaldekarin e which was supported by the analysis of the COSY, HMQC, HMBC, and ROESY spectra.

1-Deacetoxy-1-oxocaesalmin C (**5**) and 1-deacetylcaesalmin C (**6**) were both isolated as colorless amorphous solid and their molecular formulas were determined to be $C_{24}H_{30}O_7$ and $C_{24}H_{32}O_7$, respectively, by HR-EI-MS. Their ^{1}H- and ^{13}C-NMR spectral data (Table 1) closely resembled those of caesalmin C (**7**),[5] except for the presence of a carbonyl group in **5** and the hydroxyl group in **6** with the disappearance of the signals due to one of three acetoxyl groups in **7**. The location of the carbonyl group in **5** and the hydroxyl group in **6** was determined to be C-1, based on the analysis of the COSY, HMQC, and HMBC spectra. The relative stereochemistry of **5** and **6** was deduced by the analysis of the coupling constant data and ROESY correlations to be the same as that of **7**. The literature survey of these compounds suggested that **5** and **6** were 1-deacetoxy-1-oxocaesalmin C and 1-deacetylcaesalmin C, respectively, previously reported as semisynthetic reaction products of α-caesalpin.[10] In our present investigation, we isolated both **5** and **6** as natural products for the first time and assigned their ^{1}H- and ^{13}C-NMR data (Table 1).

In this paper, we reported the structures of four new diterpenes, caesalpinins MM—MP (**1**—**4**), together with 1-deacetoxy-1-oxocaesalmin C (**5**) and 1-deacetylcaesalmin C (**6**) and six other known cassane-type furanoditerpenes (**7**—**12**). Among the isolated compounds, **1** and **2** represent the biogenetically exclusive and rare cassane-type furanoditerpenes with a rearranged carbon skeleton, while diterpenes **5** and **6** have been isolated for the first time from natural sources.

Experimental

General Experimental Procedures Optical rotations were recorded on a JASCO DIP-140 digital polarimeter. IR spectra were measured with a Shimadzu IR-408 spectrophotometer in $CHCl_3$ solution. NMR spectra were taken on a JEOL JNM-LA400 spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard, and chemical shifts are expressed in δ values. HR-EI-MS measurements were carried out on a JEOL JMS-700T spectrometer and glycerol was used as matrix. Column chromatography was performed with BW-820MH silica gel (Fuji Silysia, Aichi, Japan). Analytical and preparative TLC were carried out on precoated silica gel $60F_{254}$ and RP-$18F_{254}$ plates (Merck, 0.25 or 0.50 mm thickness).

Plant Material Seed kernels of *Caesalpinia crista* L. were purchased from Theingyi market, Yangon City, Myanmar in April 2003. The plant material was identified by Ms. Thida Swe, Botanist, Deputy Director (Research and Development), Department of Traditional Medicine, Ministry of Health, Yangon City, Myanmar. A voucher specimen (TMPW 22188) is preserved in the Museum of Matria Medica, Analytical Research Center for Ethnomedicines, Institute of Natural Medicine, Toyama Medical and Pharmaceutical University, Toyama, Japan.

Extraction and Isolation The powdered air-dried seed kernels of *C. crista* (780 g) were extracted with CH_2Cl_2 (3 l×3) at room temperature, overnight. The CH_2Cl_2 extract (130 g) was fractionated by silica gel column chromatography (7×45 cm) with a benzene–EtOAc gradient system to give seven fractions. Fraction 1 (115 g) was a mixture of fatty substances, as indicated by the NMR spectrum. Previously, we reported 16 new cassane- and norcassane-type diterpenes from fractions 2—5.[7,8]

Fraction 6 (2.5 g) was rechromatographed on a silica gel column (30×3 cm) with 5% acetone–hexane to afford four subfractions. Subfraction 6-1 (640 mg) was further subjected to reversed-phase preparative TLC with MeOH–CH_3CN–H_2O (2 : 1 : 1) to give caesalpinin MM (**1**, 2.1 mg), caesalpinin MN (**2**, 1.9 mg), bonducellpin C (4.6 mg),[11] 2-acetoxycaesaldekarin e (37.0 mg),[13] 2-acetoxy-3-deacetoxycaesaldekarin e (30.0 mg),[14] and caesaldekarin e (3.0 mg).[12] Subfraction 6-2 (400 mg) was separated by normal-phase preparative TLC with 3% acetone–$CHCl_3$ to give caesalpinin MO (**3**, 1.7 mg), caesalmin C (100 mg),[5] and caesaldekarin e (3.2 mg).[12] Subfraction 6-3 (650 mg) was further subjected to reversed-phase preparative TLC with MeOH–CH_3CN–H_2O (2 : 1 : 1) to give 1-deacetoxy-1-oxocaesalmin C (**5**, 40.9 mg),[10] 1-deacetylcaesalmin C (**6**, 6.2 mg),[10] and norcaesalpinin E (4.1 mg).[4] Subfraction 6-4 (75 mg) was also subjected to normal-phase preparative TLC with 4% acetone–$CHCl_3$ to give caesalpinin MP (**4**, 2.4 mg) and caesalmin C (5.3 mg).[5]

Caesalpinin MM (**1**): Colorless amorphous solid. $[\alpha]_D^{25}$ +26.3° (c=0.07, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: [M$^+$] 490.2181 (Calcd for $C_{26}H_{34}O_9$ 490.2203).

Caesalpinin MN (**2**): Colorless amorphous solid. $[\alpha]_D^{25}$ +57.6° (c=0.045, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: [M$^+$] 490.2219 (Calcd for $C_{26}H_{34}O_9$ 490.2203).

Caesalpinin MO (**3**): Colorless amorphous solid. $[\alpha]_D^{25}$ +37.5° (c=0.1, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: 428.1837 [M$^+$] (Calcd for $C_{24}H_{28}O_7$ 428.1835).

Caesalpinin MP (**4**): Colorless amorphous solid. $[\alpha]_D^{25}$ +89.2° (c=0.01, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: 356.2003 [M$^+$] (Calcd for $C_{22}H_{28}O_4$ 356.1988).

1-Deacetoxy-1-oxocaesalmin C (**5**): Colorless amorphous solid. $[\alpha]_D^{25}$ +226.3° (c=0.12, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: 430.2009 [M$^+$] (Calcd for $C_{24}H_{30}O_7$ 430.1992).

1-Deacetylcaesalmin C (**6**): Colorless amorphous solid. $[\alpha]_D^{25}$ +68.6°

(c=0.1, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^1H- and ^{13}C-NMR: see Table 1. HR-EI-MS m/z: 432.2142 [M^+] (Calcd for $C_{24}H_{32}O_7$ 432.2148).

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