New Cassane-Type Diterpenes of *Caesalpinia crista* from Myanmar

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Seven new cassane-type diterpenes, caesalpinin MF—ML (1—7), and a new norcassane-type diterpene, norcaesalpinin MD (8), have been isolated from the CH_2Cl_2 extract of seed kernels of *Caesalpinia crista* from Myanmar, together with sixteen known cassane-type diterpenes, 7-acetoxybonducellpin C, caesaldekarin e, caesalmin C, caesalmin G, 2-acetoxycaesaldekarin e, ζ-caesalpin, caesalpinin D, caesalpinin E, caesalpinin F, caesalpinin H, caesalpinin I, caesalpinin J, caesalpinin K, caesalpinin M, caesalpinin N, and caesalpinin O. The structures of the isolated compounds were elucidated by the use of spectroscopic techniques.

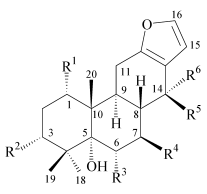
Key words cassane-type diterpene; norcassane-type diterpene; *Caesalpinia crista*; Myanmar

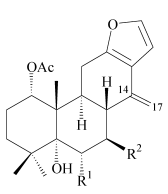
Caesalpinia crista L. (Fabaceae) is a famous medicinal plant widely distributed in tropical and subtropical regions of Southeast Asia. This plant is locally known as "Ka-Lain" in Myanmar and its seeds are used as anthelmintic, antipyretic, anti-inflammatory, and antimalarial agent.[1] In Indonesia, it is known as "Bagore" and the decoction of roots has been used as a tonic and for the treatment of rheumatism and back ache.[2] The plant belonging to the genus *Caesalpinia* is a rich source of cassane-type furanoditerpenes and is reported to have antimalarial,[3,4] antiviral,[5] and anticancer[6] activities. In continuation of our research on this plant species from different parts of Southeast Asia,[3,4,7,8] we have isolated seven new cassane-type diterpenes (**1**—**7**) and a new norcassane-type diterpene (**8**) together with sixteen known diterpenes from CH_2Cl_2 extract of seed kernels of this plant from Myanmar. In this paper, we report the structure elucidation of these new cassane- and norcassane-type diterpenes.

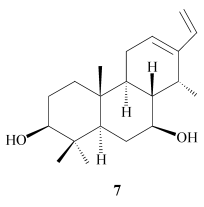
Results and Discussion

Air-dried seed kernels of *Caesalpinia 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 solvent system into seven fractions. The fractions 4 and 5 were further subjected to repeated silica gel column chromatography, followed by normal- and reversed-phase preparative TLC, to afford seven new cassane-type diterpenes, caesalpinins MF—ML (**1**—**7**), and a new norcassane-type diterpene, norcaesalpinin MD (**8**), together with sixteen known diterpenes, 7-acetoxybonducellpin C,[9] caesaldekarin e,[10] caesalmin C,[5] caesalmin G,[5] 2-acetoxycaesaldekarin e,[11] ζ-caesalpin,[12] caesalpinin D,[4] caesalpinin E,[4] caesalpinin F,[8] caesalpinin H,[8] caesalpinin I,[8] caesalpinin J,[8] caesalpinin K,[8] caesalpinin M,[8] caesalpinin N,[8] and caesalpinin O.[8]

Caesalpinin MF (**1**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +22.4° ($CHCl_3$) and its molecular formula was determined to be $C_{25}H_{34}O_8$ by high resolution fast atom bombardment mass spectrometry (HR-FAB-MS). The IR absorptions at 3500 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, two oxygen-substituted methines, and three aliphatic methines together with two protons of a 1,2-disubstituted furan ring (δ 7.24, 6.15), two acetyl methyls, and a sharp singlet due to a carbomethoxyl group. Moreover, the ^{13}C-NMR spectrum of **1** showed four olefinic carbons (δ 150.7, 141.1, 113.9, 108.8) and three oxygen-substituted carbons (δ 76.9, 76.8, 73.7) together with three ester carbonyl carbons (δ 169.3, 169.3, 174.5). These ^{1}H- and ^{13}C-NMR data were similar to those of 7-acetoxybonducellpin C (**9**),[9] except for the difference in the location of one of the acetyl groups. Analysis of the correlation spectroscopy (COSY) and heteronuclear multiple-quantum coherence (HMQC) spectra indicated downfield shift of H-3 (δ 4.95) and upfield shift of H-7 (δ 1.72) compared to those of **9** (H-3; δ 1.15, H-7; δ 5.22). Thus, the location of the acetyl group was assumed to be at C-3 in **1** instead of C-7 as in **9**, which were further confirmed on the basis of the long-range correlations observed







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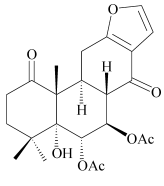
1 $R^1 = R^2 = OAc$, $R^3 = R^4 = R^6 = H$, $R^5 = COOCH_3$
2 $R^1 = R^3 = R^4 = OAc$, $R^2 = R^6 = H$, $R^5 = COOCH_3$
3 $R^1 = R^3 = OAc$, $R^2 = R^6 = H$, $R^4 = OH$, $R^5 = COOH$
4 $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = OH$, $R^6 = CH_3$
9 $R^1 = R^4 = OAc$, $R^2 = R^3 = R^6 = H$, $R^5 = COOCH_3$

5 $R^1 = H$, $R^2 = OAc$
6 $R^1 = OAc$, $R^2 = H$
10 $R^1 = R^2 = OAc$



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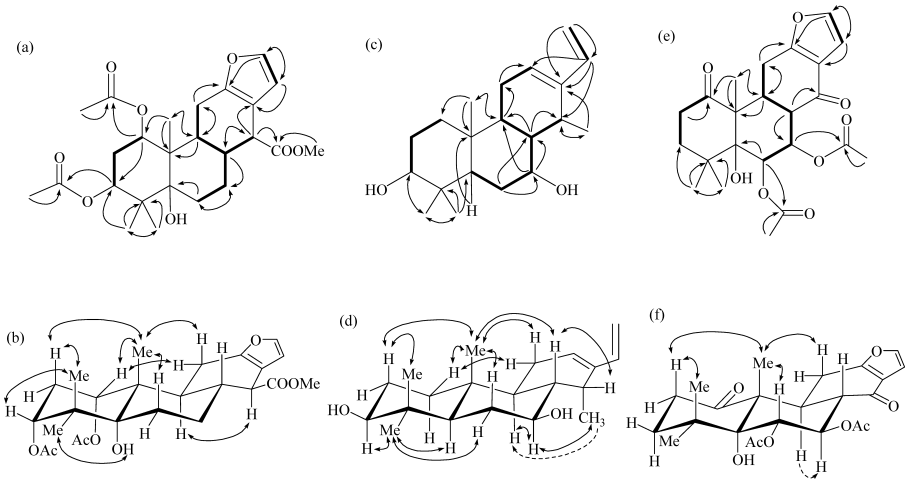

Fig. 1. Connectivities (Bold Lines) Deduced by the COSY Spectrum and Key HMBC Correlations (Arrow) (a), (c), (e) and Selected NOE (Dashed Arrow) and ROESY (Arrow) Correlations (b), (d), (f) for **1**, **7**, and **8**

in the heteronuclear multiple-bond connectivity (HMBC) spectrum. Significant long-range correlations were observed between the ester carbonyl carbon at δ 169.3 (1-OCO) and the protons at δ 2.05 (1-OCOCH_3) and 4.86 (H-1) and between the ester carbonyl carbon at δ 169.3 (3-OCO) and the protons at δ 2.05 (3-OCOCH_3) and 4.95 (H-3) (Fig. 1a).

The relative stereochemistry of **1** was determined on the basis of coupling constants and rotating-frame Overhauser enhancement spectroscopy (ROESY) correlations (Fig. 1b). The ROESY correlations of H_3-20 with H-2_{ax} (δ 2.29) and H-11_{ax} (δ 2.47), of H_3-19 with H-2_{ax} (δ 2.29), and of H_3-18 with 5-OH indicated that rings A and B have a chair conformation with a *trans*-fused ring junction. On the other hand, the small coupling constant between H-1 and H-2 (2.9 Hz) and between H-2 and H-3 (2.9 Hz) and ROESY correlations between H_3-20 and H-1 and between H_3-19 and H-3 indicated the acetoxyl substituents at C-1 and C-3 to be in α-axial orientation. Similarly, the configuration of carbomethoxyl group at C-14 was concluded to be β-orientation from the ROESY correlation between H-14 and H-9 (Fig. 1b) and large *J* value (9.5 Hz) between H-14 and H-8. From these spectral evidences, the structure of caesalpinin MF (**1**) was concluded as 7-*O*-deacetoxyl-3-*O*-acetoxylbonducellpin C.

Caesalpinin MG (**2**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +78.4° ($CHCl_3$) and its molecular formula was determined to be $C_{27}H_{36}O_{10}$ by HR-FAB-MS. The IR absorptions at 3550 and 1730 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{1}H-NMR spectrum of **2** displayed signals corresponding to three tertiary methyls, three oxygen-substituted methines, and three aliphatic methines together with two protons of a 1,2-disubstituted furan ring, three acetyl methyls, and a sharp singlet due to a carbomethoxyl group (Table 1). Moreover, the ^{13}C-NMR spectrum of **2** showed four olefinic carbons, four oxygen-substituted carbons, and four ester carbonyl carbons. These data were similar to those of bonducellpin A[9] except for the presence of one more acetyl group in **2**. The analysis of the COSY, HMQC, HMBC, and ROESY spectra indicated **2** to be 7-*O*-acetylbonducellpin A.

Caesalpinin MH (**3**) was also isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +11.3° ($CHCl_3$). The IR spectrum of **3** indicated the presence of hydroxyl and carbonyl groups, and HR-FAB-MS showed the molecular formula $C_{24}H_{32}O_9$. The ^{1}H-NMR spectrum of **3** displayed the signals due to three tertiary methyls, two acetyl methyls, three aliphatic methylenes, three oxygen-substituted methines, three methines, and two protons of a 1,2-disubstituted furan ring (Table 1). The ^{13}C-NMR spectrum of **3** had 24 signals including a carboxyl carbon, two ester carbonyl carbons, four olefinic carbons, four oxygen-substituted carbons, and three aliphatic methylene carbons (Table 1). These spectral data were similar to those of bonducellpin A,[9] except for the presence of a carboxylic acid functionality at C-17 instead of a carbomethoxyl group. Analysis of the COSY, HMQC, HMBC, and ROESY correlations assigned the structure **3** to caesalpinin MH.

Caesalpinin MI (**4**) was isolated as a colorless amorphous solid with $[\alpha]_D^{25}$ +214.3° ($CHCl_3$). The IR absorptions at 3550 cm^{-1} indicated the presence of hydroxyl group and its molecular formula was determined to be $C_{20}H_{30}O_3$ by HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data of **4** were similar to those of caesaldekarin b,[13] but the location of hydroxyl group was determined to be at C-7 by the analysis of the COSY, HMQC, and HMBC spectra. The relative stereochemistry of **4** was also determined by the analysis of coupling constants and the ROESY correlations. Thus, the structure of caesalpinin MI was assigned as **4**.

Caesalpinins MJ (**5**) and MK (**6**) both were isolated as colorless amorphous solid and their IR spectra indicated the presence of hydroxyl and ester carbonyl groups, respectively. Their molecular formula were determined to be the same $C_{24}H_{32}O_6$, by HR-FAB-MS. Their ^{1}H- and ^{13}C-NMR spectra were also similar to each other and resembled those of caesalmin C (**10**),[5] except for the absence of one acetyl group. The location of acetyl groups were determined to be at C-6 and C-7 in **5** and **6**, respectively, based on the analysis of the COSY, HMQC, and HMBC spectra. The relative stereochemistries of **5** and **6** were deduced by the analysis of the coupling constants and the ROESY correlations and found to be the same as **10**. Thus, the structure of caesalpinins MJ and MK were concluded as **5** and **6**, respectively.

Caesalpinin ML (**7**) was isolated as colorless amorphous solid with $[\alpha]_D^{25}$ +114.4° ($CHCl_3$). IR spectum of **7** indicated the presence of hydroxyl and its molecular formula was de-

Table 1. ^{1}H- and ^{13}C-NMR Data (δ) for Compounds **1**—**8** in $CDCl_3$ (J Values in Parentheses)

Position	**1**		**2**		**3**		**4**		**5**		**6**		**7**		**8**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	4.86 t (2.9)	73.7	4.87 t (2.7)	75.5	4.82 br s	75.8	1.41 (2H) m	32.3	4.94 t (2.2)	75.5	4.86 t (1.9)	75.5	1.65 m 1.07 m	37.1		211.9
2	2.29 dt (16.6, 2.9) 2.13 dt (16.6, 2.9)	26.5	2.00 m 1.79 m	22.2	1.95 m 1.75 m	22.1	1.50 (2H) m	18.0	1.91 m 1.74 m	22.5	1.94 m 1.76 m	22.5	1.65 m 1.59 m	27.1	2.69 m 2.44 m	35.4
3	4.95 t (2.9)	76.9	1.79 m 1.06 m	32.3	1.75 m 1.12 m	32.2	1.60 m 1.25 m	35.8	1.74 m 1.16 m	29.9	1.76 m 1.15 m	32.5	3.25 dd (11.7, 4.1)	78.9	1.84 (2H) m	38.3
4		41.6		38.6		38.6		38.4		38.4		38.5		38.8		38.6
5		76.8		79.5		79.5		78.2		77.8		78.2	0.91 m	51.3		81.9
6	1.67 (2H) m	26.4	5.50 m	74.1	5.47 d (9.3)	77.0	2.01 dd (12.8, 5.6) 1.74 dd (12.8, 10.8)	35.3	2.37 m 1.60 m	31.4	5.52 dd (11.5, 4.2)	73.1	1.95 m 1.46 m	31.0	5.48 d (9.3)	35.3
7	1.72 (2H) m	26.1	5.50 m	74.1	3.84 t (9.3)	76.8	4.15 td (10.8, 5.6)	68.2	5.52 td (10.0, 6.6)	72.0	2.15 m 2.06 m	30.1	3.62 td (10.8, 5.1)	71.9	5.57 dd (10.0, 9.3)	70.9
8	2.05 m	34.5	2.65 m	38.4	2.51 m	41.2	1.67 m	42.9	2.51 dd (11.5, 10.0)	41.0	2.43 m	34.6	1.53 m	42.7	2.70 m	48.2
9	2.84 td (11.5, 5.9)	37.1	2.72 td (10.9, 4.6)	36.0	2.62 td (12.2, 5.1)	35.8	2.39 m	36.9	2.72 td (11.5, 5.1)	38.6	2.62 td (11.5, 5.6)	38.3	1.28 m	42.2	3.19 ddd (12.9, 11.5, 4.1)	39.9
10		43.8		45.1		45.2		41.0		43.1		45.3		36.6		54.8
11	2.47 m 2.18 m	21.6	2.47 m 2.31 dd (15.6, 4.6)	21.4	2.47 m 2.26 dd (15.6, 5.1)	21.4	2.49 m 2.40 m	22.3	2.62 dd (15.9, 11.5) 2.40 dd (15.9, 5.1)	23.0	2.49 dd (16.1, 11.5) 2.35 dd (16.1, 5.6)	22.3	2.12 m 1.93 m	25.1	3.68 dd (16.8, 4.1) 2.71 dd (16.8, 11.5)	26.4
12		150.7		149.6		150.0		149.4		150.8		151.1	5.62 t (3.9)	127.9		166.8
13		113.9		113.3		113.5		121.9		119.7		119.1		140.8		119.7
14	3.28 d (9.5)	49.2	3.46 d (9.7)	45.6	3.47 d (9.5)	45.7	3.07 quintet (6.8)	27.4		139.4		141.1	2.92 quintet (6.6)	27.2		191.8
15	6.15 d (1.7)	108.8	6.11 d (1.9)	108.3	6.31 d (1.9)	108.8	6.21 d 1.7)	109.7	6.42 s	106.6	6.44 d (1.9)	106.3	6.23 dd (17.8, 11.0)	138.4	6.58 d (1.7)	106.3
16	7.24 d (1.7)	141.1	7.23 d (1.9)	141.8	7.25 d (1.9)	141.5	7.23 d (1.7)	140.5	7.23 s	141.8	7.24 d (1.9)	141.8	5.15 d (17.8) 4.93 d (11.0)	110.1	7.30 d (1.7)	143.1
17		174.5		174.0		177.9	1.09 d (6.8)	17.1	5.11 s 4.77 s	105.6	5.11 d (2.2) 4.86 d (2.2)	104.6	0.99 d (6.6)	14.1		
18	1.09 s	25.4	1.10 s	29.7	1.13 s	30.6	0.98 s	27.9	1.07 s	28.2	1.14 s	31.0	1.02 s	28.2	1.16 s	28.7
19	1.14 s	23.1	1.15 s	24.5	1.13 s	24.7	1.10 s	24.7	1.11 s	25.5	1.19 s	24.9	0.85 s	15.8	1.25 s	26.1
20	1.15 s	17.9	1.29 s	17.0	1.22 s	16.9	1.10 s	17.4	1.23 s	17.7	1.20 s	16.9	0.86 s	14.1	1.55 s	15.9
1-OCO$\underline{C}H_3$	2.05 s	21.2	1.94 s	20.8	2.09 s	21.4			2.06 s	21.5	2.09 s	21.4				
1-O$\underline{C}OCH_3$		169.3		169.0		169.0				169.1		169.0				
3-OCO$\underline{C}H_3$	2.05 s	21.4														
3-O$\underline{C}OCH_3$		169.3														
6-OCO$\underline{C}H_3$			2.04 s	21.5	2.16 s	22.2					2.14 s	21.9			2.01 s	21.1
6-O$\underline{C}OCH_3$				170.3		172.7						170.4				170.4
7-OCO$\underline{C}H_3$			2.10 s	21.5					2.05 s	21.5					2.10 s	21.5
7-O$\underline{C}OCH_3$				170.2						170.4						169.8
5-OH	3.30 s		3.07 s		3.06 s				2.79 s							
17-O$\underline{C}H_3$	3.77 s	52.0	3.69 s	52.1												

termined to be $C_{20}H_{32}O_2$ by HR-FAB-MS. The ^{1}H-NMR spectrum of **7** displayed the signals for three tertiary methyls, a secondary methyl, two oxygen-substituted methines, four aliphatic methines, and four olefinic protons including characteristic signals for a vinyl group (Table 1). Moreover, the ^{13}C-NMR spectrum displayed the signals for four olefinic carbons (δ 140.8, 138.4, 127.9, 110.1), two oxygen-substituted methines (δ 78.9, 71.9), four methines, four aliphatic methylenes, two quaternary carbons, and four methyls (Table 1). These spectral data indicated the absence of the furan ring and the C-5 hydroxyl group in **7**. The location of the vinyl group was determined to be at C-13 based on the HMBC correlations of the vinylic proton at δ 6.23 (H-15) with C-12, C-13, and C-14 and of the vinylic protons at δ 5.15 and 4.93 (H_2-16) with C-13 and C-15. On the other hand, the locations of two hydroxyl substituents were determined to be at C-3 and C-7 by the COSY, HMQC and HMBC correlations (Fig. 1c). The COSY correlations and the significant long-range correlations of H-6 and H-8 with the hydroxyl-bearing carbon at δ 71.9 indicated that one of the hydroxyl groups should be located at C-7. Similarly, the HMBC correlations of H-18 and H-19 with the hydroxyl bearing carbon at δ 78.9 indicated the location of the other hydroxyl group to be at C-3. The relative stereochemistry of **7** was deduced by the analysis of the coupling constants and the ROESY correlations. A large coupling constant between H-3 and H-2$_{ax}$ (11.7 Hz) and the ROESY correlations of H-3 with H-18, H-5, and H-1$_{ax}$ (δ 1.07) indicated H-3 to be α-axial orientation, *i.e.*, the acetyl group to be β-equatorial. Similarly, a large coupling constant between H-7 and H-8 (10.8 Hz) and the ROESY correlations between H_3-20 and H-8, between H-14 and H-8, and between H-7 and CH_3-14 indicated H-7 and CH_3-14 both to be α-axial orientation (Fig. 1d). Thus, the structure of caesalpinin ML was assigned as **7**.

Norcaesalpinin MD (**8**) was also isolated as a colorless amorphous solid having $[\alpha]_D^{25}$ +163.3° ($CHCl_3$). Its molecular formula was determined to be $C_{23}H_{28}O_8$ by HR-FAB-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 **8** displayed signals of three tertiary methyls, two acetyl methyls, three methylenes, and two oxygen-substituted methines together with two protons of a 1,2-disubstituted furan ring (δ 7.30, 6.58). The ^{13}C-NMR spectrum of **8** showed the signals of two carbonyl carbons (δ 211.9, 191.8), four olefinic carbons, three oxygen-substituted carbons, and three methylene carbons together with two ester carbonyl carbons (δ 170.4, 169.8) (Table 1). The ^{1}H- and ^{13}C-NMR data of **8** were similar to those of caesalmin C (**10**),[5] except for the presence of the signals of two carbonyl carbons and lack of the signals of an exomethylene and an acetyl group in **10**. Therefore, excluding the signals due to two acetyl substituents, **8** contained only 19 carbons in the main carbon framework, suggesting it to be a norditerpene. The HMBC correalations of the methine proton H-8 with a carbonyl carbon (δ 191.8) indicated that one of the carbonyl carbons should be at C-14, *i.e.*, **8** is a 17-norcassane-type diterpene. The HMBC correlations of H_3-20 and H_2-2 with a carbonyl carbon at δ 211.9 indicated the location of the other carbonyl carbon to be C-1 (Fig. 1e). The relative stereochemistry of **8** was determined by coupling constants and the ROESY correlations to be the same as that of **10** (Fig. 1f). Thus, the structure of norcaesalpinin MD was concluded as **8**.

In this paper, we have reported eight new diterpenes, caesalpinins MF—ML (**1**—**7**) and norcaesalpinin MD (**8**). Among them, **1**—**7** are cassane-type furanoditerpenes, and **7** represents a cassane-type diterpene without the C-5 hydroxyl group and the furan ring, which are the characteristic structural features of diterpenes isolated from the plant of *Caesalpinia* genus. On the other hand, norcaesalpinin MD (**8**) is a 17-norcassane-type diterpene.

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-FAB-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 Materials Seed kernels of *Caesalpinia crista* L. were purchased from Theingyi market, Yangon City, Myanmar in April 2003. 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 have reported eight new and 12 known cassane-type diterpenes from fractions 2 and 3.[7]

Fraction 4 (1.5 g) was rechromatographed on a silica gel column (19×2.5 cm) with 5% acetone–hexane to afford three subfractions. Subfraction 4-1 (250 mg) was further subjected to reversed-phase preparative TLC with MeOH–CH_3CN–H_2O (2 : 1 : 1) to give caesalpinin MF (**1**, 9.0 mg), 2-acetoxycaesaldekarin e (18.2 mg),[11] caesaldekarin e (5.2 mg),[10] caesalmin C (15.7 mg),[5] and ζ-caesalpin (2.2 mg).[12] Subfraction 4-2 (400 mg) was separated by normal-phase preparative TLC with 2% acetone–$CHCl_3$ to give norcaesalpinin MD (**8**, 2.0 mg), 2-acetoxycaesaldekarin e (20.0 mg),[11] caesalpinin D (59.0 mg),[4] caesalpinin E (5.0 mg),[4] 7-acetoxybonducellpin C (3.0 mg),[9] and caesalmin G (3.0 mg).[5] Subfraction 4-3 (350 mg) was subjected to normal-phase preparative TLC with 2% acetone–$CHCl_3$ to give caesalpinin MG (**2**, 10.0 mg), caesalpinin MH (**3**, 7.0 mg), and caesalpinin F (9.0 mg).[8]

Fraction 5 (1.3 g) was rechromatographed on a silica gel column (24×3 cm) with 10% acetone–hexane to afford three subfractions. Subfraction 5-1 (180 mg) was subjected to normal-phase preparative TLC with 3% acetone–$CHCl_3$ to give caesalpinin MI (**4**, 6.1 mg) and caesalpinin K (96.3 mg).[8] Similarly, subfraction 5-2 (500 mg) was subjected to normal-phase preparative TLC with 3% acetone–$CHCl_3$ to give caesalpinin MJ (**5**, 7.0 mg), caesalpinin MK (**6**, 5.5 mg), caesalpinin J (15.0 mg),[8] caesalpinin H (25.0 mg),[8] caesalpinin M (8.0 mg),[8] and caesalpinin N (54.0 mg).[8] Subfraction 5-3 (150 mg) was subjected to reversed-phase preparative TLC with MeOH–CH_3CN–H_2O (2 : 1 : 1) to afford caesalpinin ML (**7**, 6.4 mg), caesalpinin I (86.1 mg),[8] and caesalpinin O (15.0 mg).[8]

Caesalpinin MF (**1**): Colorless amorphous solid. $[\alpha]_D^{25}$ +22.4° (c=0.15, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3500, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m/z*: 463.2287 $[M+H]^+$ (Calcd for $C_{25}H_{35}O_8$ 463.2332).

Caesalpinin MG (**2**): Colorless amorphous solid. $[\alpha]_D^{25}$ +78.4° (c=0.039, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3550, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m/z*: 521.2353 $[M+H]^+$ (Calcd for $C_{27}H_{37}O_{10}$ 521.2387).

Caesalpinin MH (**3**): Colorless amorphous solid. $[\alpha]_D^{25}$ +11.3° (c=0.3, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3550, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m/z*: 465.2112 $[M+H]^+$ (Calcd for $C_{24}H_{33}O_9$ 465.2125).

Caesalpinin MI (**4**): Colorless amorphous solid. $[\alpha]_D^{25}$ +214.3° (c=0.2, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3550. ^{1}H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m/z*: 319.2299 $[M+H]^+$ (Calcd for $C_{20}H_{31}O_3$ 319.2273).

Caesalpinin MJ (**5**): Colorless amorphous solid. $[\alpha]_D^{25}$ +164.9° (c=0.25, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3575, 1730. ^{1}H- and ^{13}C-NMR: see Table 1. HR-

FAB-MS *m*/*z*: 417.2276 $[M+H]^+$ (Calcd for $C_{24}H_{33}O_6$ 417.2277).

Caesalpinin MK (**6**): Colorless amorphous solid. $[\alpha]_D^{25}$ +99.1° (*c*=0.1, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3575, 1730. ^1H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m*/*z*: 417.2258 $[M+H]^+$ (Calcd for $C_{24}H_{33}O_6$ 417.2277).

Caesalpinin ML (**7**): Colorless amorphous solid. $[\alpha]_D^{25}$ +114.4° (*c*=0.1, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450. ^1H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m*/*z*: 305.2523 $[M+H]^+$ (Calcd for $C_{20}H_{33}O_2$ 305.2481).

Norcaesalpinin MD (**8**): Colorless amorphous solid. $[\alpha]_D^{25}$ +163.3° (*c*=0.1, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3450, 1730. ^1H- and ^{13}C-NMR: see Table 1. HR-FAB-MS *m*/*z*: 433.1886 $[M+H]^+$ (Calcd for $C_{23}H_{29}O_8$ 433.1862).

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