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# Cassane diterpenoids from the stem of *Caesalpinia pulcherrima*

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ABSTRACT

Cassane diterpenoids: pulcherrin A, pulcherrin B, pulcherrin C, neocaesalpin P, neocaesalpin Q and neocaesalpin R, together with eight known compounds: isovouacapenol C, 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol, pulcherrimin E, pulcherrimin C, α-cadinol, 7-hydroxycadalene, teucladiol and bonducellin were isolated from the stem of *Caesalpinia pulcherrima*. The chemical structures were elucidated by analysis of their spectroscopic data.



## 1. Introduction

*Caesalpinia pulcherrima* Swartz. (Fabaceae), is known locally as "Hang Nok Yung Thai" (Smitinand and Larson, 2001) whose decoction of leaves, barks and roots is used to alleviate fungal infection and reduce fever. The genus *Caesalpinia* is a rich source of cassane-type diterpenoids. In the previous studies, we isolated several cassane-type diterpenes from *C. crista* (Cheenpracha et al., 2005, 2006). and *C. sappan* (Yodsaoue et al., 2008). As a continuation of our study on this genus, we now report the isolation and elucidation of six new cassane-type diterpenoids: pulcherrin A (**1**), pulcherrin B (**2**), pulcherrin C (**3**), neocaesalpin P (**4**), neocaesalpin Q (**5**), neocaesalpin R (**6**) and eight known compounds: isovouacapenol C (**7**) (Ragasa et al., 2002), 6β-cinnamoyl-7β-hydroxy-vouacapen-5α-ol (**8**) (McPherson et al., 1986), pulcherrimin E (**9**) (Roach et al., 2003), pulcherrimin C (**10**) (Patil et al., 1997), α-cadinol (**11**) (Kuo et al., 2003), 7-hydroxycadalene (**12**) (Lindgren and Svahn, 1968), teucladiol (**13**) (Bruno et al., 1993) and bonducellin (**14**) (McPherson et al., 1983) from the stem of *C. pulcherrima*. Their structures were identified on the basis of spectroscopic analysis.

## 2. Results and discussion

A portion of the $CH_2Cl_2$ extract (60.2 g) of the stem of *C. pulcherrima* was separated by chromatography on silica gel to give six new cassane-type diterpenes **1**–**6** and eight known compounds **7–14**. The basic skeleton of compounds **1–10** was identified to be that of a cassane diterpene on the basis of their IR and UV spectroscopic data and a positive Ehrlich test (Kuroda et al., 2004). The UV absorptions of **1–3** ($\lambda_{max}$ 211–225 nm) were characteristic of a furano cassane-type diterpene (Cheenpracha et al., 2005, 2006), whereas structures **4–6** showed absorption bands of an α,β-butenolide ring conjugated with an extra double bond ($\lambda_{max}$ 279–280 nm) (Kinoshita, 2000; Kinoshita et al., 2005). In addition, the IR spectrum of all new compounds indicated the presence of a carbonyl ester functionality (1700–1777 $cm^{-1}$).

Compound **1** was obtained as white powder with the molecular formula of $C_{29}H_{36}O_5$ on the basis of molecular ion peak $[M]^+$ at *m/z* 464.2573 in the HREIMS. The $^1H$ NMR spectroscopic data supported a cassane-type furanoditerpenoid framework (Cheenpracha et al., 2005, 2006; McPherson et al., 1986; Patil et al., 1997; Ragasa et al., 2002; Roach et al., 2003; Yodsaoue et al., 2008). Three tertiary methyl groups resonated at $\delta$ 1.04 (Me-19), 1.39 (Me-20), and 1.47 (Me-18) and one secondary methyl group resonated at $\delta$ 1.02 (d, $J$ = 6.9 Hz, Me-17). A 2,3-disubstituted furan ring was evident from the resonances at $\delta$ 6.19 (d, $J$ = 1.8 Hz, H-15) and $\delta$ 7.23 (d, $J$ = 1.8 Hz, H-16). Signals of a hydroxyl proton at $\delta$ 1.97 (d, $J$ = 2.1 Hz) and two oxymethine protons at $\delta$ 4.32 (dd, $J$ = 3.6, 2.1 Hz) and 5.58 (dd, $J$ = 11.1, 3.6 Hz) were also evident. These two oxymethine protons were assigned as H-6 and H-7, respectively, due to the HMBC correlation of the former proton to C5 ($\delta$ 77.8), C7 ($\delta$ 75.0), C8 ($\delta$ 35.2) and C10 ($\delta$ 40.7) and the COSY correlation to H-7. The remaining $^1H$ NMR signals were those of a *trans*-cinnamoyl side chain displayed as two doublets at $\delta$ 6.51 and 7.75

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($J$ = 15.9 Hz, H-2' and H-3', respectively), together with multiplet signals of aromatic-protons between 7.41 and 7.55, whose location was placed at C7 due to HMBC correlation of H-7 ($\delta$ 5.58) to a carbonyl carbon of a cinnamate ester group ($\delta$ 166.0). NOESY cross-peaks of H-7 with H-6, H-9 and Me-17 indicated that these protons were on the same side of the molecule. The proton H-8 showed cross-peaks with H-14 and Me-20 but no cross-peak with H-7 and H-9, thus H-8, H-14 and Me-20 were on the same side as each other but opposite to that of H-6, H-7, H-9 and Me-17. The small vicinal coupling constant of H-6 and H-7 (3.6 Hz) supported their α-orientations. In addition, hydrolysis of compound **1** under methanolic $K_2CO_3$ afforded the parent alcohol, whose spectroscopic data were identical to those of 6β-hydroxyisovoucapenol C (Roach et al., 2003). Therefore, **1** was 6β-hydroxy-7β-cinnamoyloxyvoaucapen-5α-ol and was named pulcherrin A Fig. 1.

Compound **2**, $[M]^+$ $m/z$ 438.2407 ($C_{27}H_{34}O_5$) by HREIMS, showed related $^1$H (Table 1) and $^{13}$C NMR (Table 2) spectroscopic data to those of **1**. The signals of an oxymethine proton ($\delta$ 5.30, dd, $J$ = 11.5, 5.0 Hz, H-3) and methylene protons ($\delta$ 1.86, dd, $J$ = 13.0, 11.0 Hz and 2.05, dd, $J$ = 13.0, 5.5 Hz, 2H-6) in **2** replaced the methylene protons ($\delta$ 1.67 and 1.17, 2H-3) and an oxymethine proton ($\delta$ 4.32, H-6) in **1**. In addition, the resonances of a cinnamoyloxy moiety [$\delta$ 6.51 (d, $J$ = 15.9 Hz, H-2'), 7.75 (d, $J$ = 15.9 Hz, H-3') and 7.41–7.55] in **1** were replaced by a benzoate ester group resonating between $\delta$ 7.45 and 8.04, whose location was placed at C3 due to HMBC correlation of H-3 ($\delta$ 5.30) to the carbonyl carbon of benzoate ester group ($\delta$ 166.2). The proton H-3 was assigned to be axially oriented from the small and large vicinal coupling constants ($J_{3ax,2eq}$ = 5.0 Hz, $J_{3ax,2ax}$ = 11.5 Hz). The oxymethine H-7 at $\delta$ 4.12 (d$t$, $J$ = 11.0, 5.5 Hz) was deduced to be axially oriented from two large vicinal coupling constants ($J_{7ax,6ax}$ = 11.0 Hz and $J_{7ax,8ax}$ = 11.0 Hz) and a small vicinal coupling constant ($J_{7ax,6eq}$ = 5.5 Hz). It was further supported by NOESY correlations of H-7 with Me-17 and H-6α but no cross-peak with H-6β, H-8 and H-14. From these data, the protons H-3 and H-7 were located on the same side. Thus, **2** was assigned to be 3β-benzoyloxy-7β-hydroxyvoaucapen-5α-ol and was named pulcherrin B.

Compound **3**, with the molecular formula $C_{30}H_{36}O_9$ by HERIMS, had $^1$H (Table 1) and $^{13}$C NMR (Table 2) spectra related to **2** except at C6 and C17, where signals of the methylene protons at $\delta$ 1.86 and 2.05 on C6 and a secondary methyl at $\delta$ 1.10 (Me-17) in **2** were replaced by those of an oxymethine proton at $\delta$ 4.15 (d, $J$ = 3.3 Hz) and a methyl ester at $\delta$ 3.75, respectively in **3**. Besides **3** displayed an additional O-acetyl group as a $^1$H NMR singlet signal at $\delta_H$ 2.06: $\delta_C$ 21.0 and a carbonyl carbon at $\delta_C$ 170.2. In addition, H-14 ($\delta$ 3.38, $d$, $J$ = 8.7 Hz) showed HMBC correlations to the ester carbonyl carbon at $\delta$ 174.9, supporting the placement of a methyl ester at C14. The proton H-14 was in an axial position due to a large vicinal coupling constant ($J_{14ax,8ax}$ = 8.7 Hz) and NOESY cross-peaks of H-14 with H-7 and H-9 but not with H-8. Thus, **3** was deduced to be 3β-benzoyloxy-6β-hydroxy-7β-acetoxy-17β-methoxycarbonylvoaucapen-5α-ol and was named pulcherrin C.

For compound **4**, its molecular formula was deduced as $C_{29}H_{34}O_6$ from the HREIMS ($m/z$ 460.2225, $[M\text{-}H_2O]^+$). The UV absorption maximum at 279 nm and IR absorption at 1746 cm$^{-1}$ suggested an α,β-butenolide ring conjugated with an extra double bond similar to that found in neocaesalpin D (Kinoshita, 2000) and I (Kinoshita et al., 2005) previously isolated from the genus *Caesalpinia*. The $^1$H NMR spectrum of **4** displayed a singlet and a broad singlet at $\delta$ 5.68 (H-15) and 5.70 (H-11), respectively, instead of the doublet of signals associated with a 2,3-disubstituted furan as in **1**–**3**. There were resonances for three tertiary methyl groups at $\delta$ 0.99 (Me-18), 1.09 (Me-19) and 1.32 (Me-20), a secondary methyl group at $\delta$ 1.10 (d, $J$ = 7.5 Hz, Me-17) and two oxymethine protons at $\delta$ 4.33 (dd, $J$ = 11.5, 4.0 Hz, H-7) and 5.56 (d, $J$ = 4.0 Hz, H-6). The *trans*-cinnamoyloxy side chain was displayed as two doublets at $\delta$ 6.38 and 7.64 ($J$ = 16.0 Hz) and aromatic-proton signals between 7.31 and 7.45 whose location was placed at C6 due to HMBC correlation of H-6 ($\delta$ 5.56) with the cinnamate carbonyl carbon at $\delta$ 167.5. NOESY cross-peaks of H-7 with H-6 and Me-17 and between H-9 and H-7 suggested that these protons lay on the same side. In addition, the small coupling constant (4.0 Hz) supported the orientation at C6 and C7. From these data, **4** was deduced to be 6β-cinnamoyloxy-11,13(15)-diene-5α,7β-dihydroxycassan-12,16-olide and was named as neocaesalpin P.

Compound **5**, $C_{27}H_{32}O_5$, displayed related $^1$H (Table 1) and $^{13}$C NMR (Table 2) spectroscopic data to those of **4.** The differences were shown to result from the replacement of an oxymethine proton H-7 at $\delta$ 4.33 in **4** with methylene protons at $\delta$ 1.50 (m, H-7$_{eq}$) and 2.30 (td, $J$ = 13.8, 3.6 Hz, H-7$_{ax}$) in **5**. The cinnamoyloxy side chain in **4** was replaced with a benzoyloxy side chain in **5**, whose location at C6 was supported by HMBC correlation of H-6 ($\delta$ 5.44) with the benzoate carbonyl carbon at $\delta$ 165.6. The relative configuration was characterized by NOESY correlations, the protons H-6 and H-7$_{ax}$ were located on the same side due to

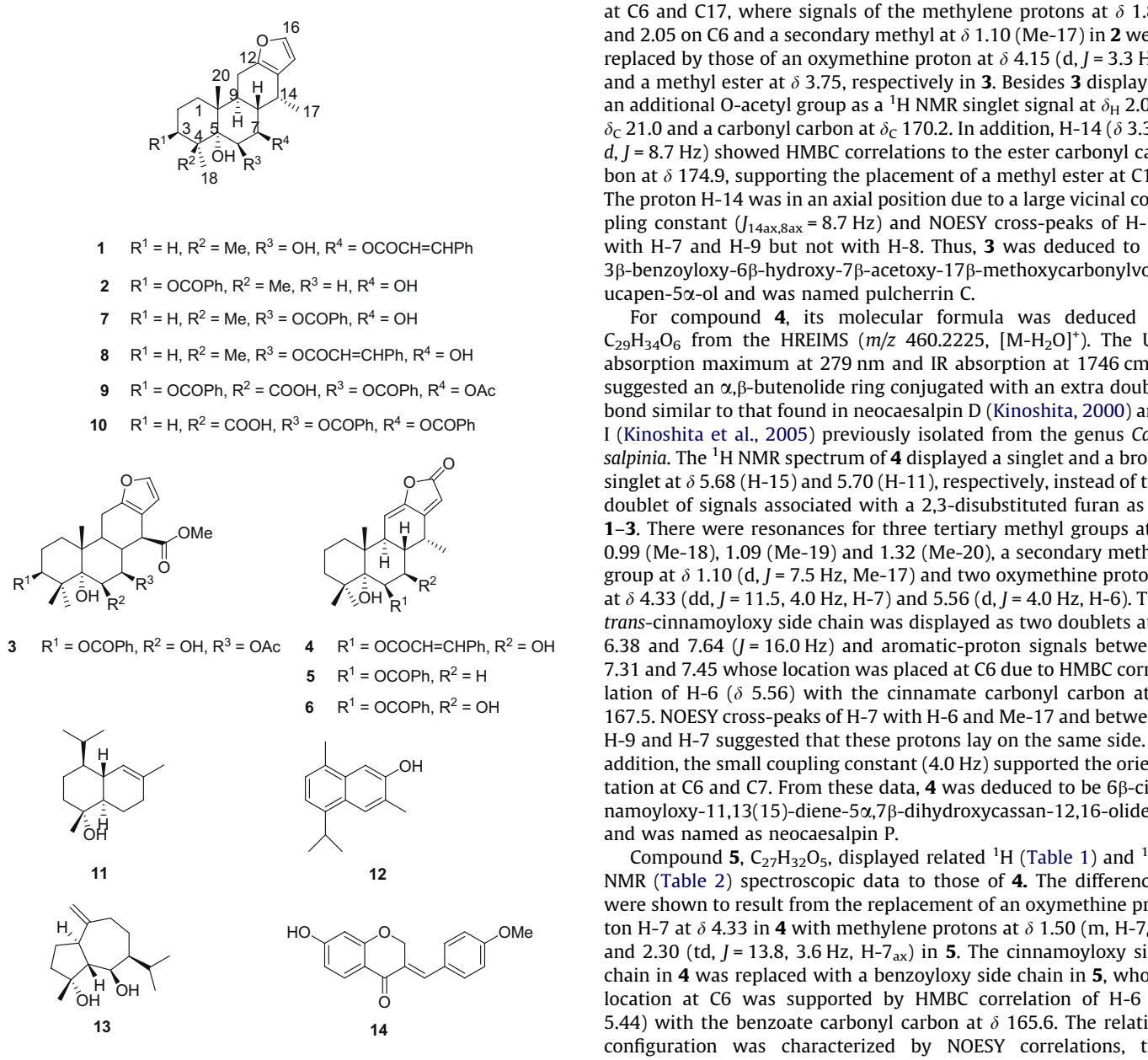


**Fig. 1.** Structures of compounds **1**-**14**.

**Table 1**
$^1$H NMR spectral data for compounds **1**,**2**,**3**, and **5** (300 MHz), **4** and **6** (500 MHz) in $CDCl_3$.

| Position | 1<br>$\delta_H$ (m, *J* in Hz) | 2<br>$\delta_H$ (m, *J* in Hz) | 3<br>$\delta_H$ (m, *J* in Hz) | 4<br>$\delta_H$ (m, *J* in Hz) | 5<br>$\delta_H$ (m, *J* in Hz) | 6<br>$\delta_H$ (m, *J* in Hz) |
|---|---|---|---|---|---|---|
| 1 | 1.43 m, 1.54 m | 1.51 m, 1.77 m | 1.46 m, 1.89 m | 1.51 m | 1.62 m, 1.64 m | 1.52 m, 1.59 m |
| 2 | 1.50 m, 1.67 m | 1.80 m, 1.92 m | 1.84 m, 1.94 m | 1.50 m, 1.68 m | 1.52 m, 1.54 m | 1.34 m, 1.53 m |
| 3 | 1.67 m, 1.17 m | 5.30 dd (11.5,5.0) | 5.31 dd (9.0,6.0) | 1.67 m, 1.07 m | 1.69 m, 1.09 m | 1.15 m, 1.65 m |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | 4.32 dd (3.6,2.1) | 1.86 dd (13.0,11.0), 2.05 dd (13.0,5.5) | 4.15 d (3.3) | 5.56 d (4.0) | 5.44 t (3.6) | 5.70 d (4.0) |
| 7 | 5.58 dd (11.1,3.6) | 4.12 dt (11.0,5.5) | 5.33 dd (11.4,3.3) | 4.33, dd (11.5,4.0) | 1.50 m, 2.30 td (13.8,3.6) | 4.38 dd (11.5,4.0) |
| 8 | 2.31 td (11.1,4.8) | 1.74 td (11.0,7.0) | 2.76 td (11.4,8.7) | 2.10 td (11.5,4.5) | 2.15 tt (10.2,3.6) | 2.12 td (11.5,4.5) |
| 9 | 2.49 m | 2.46 m | 2.41 m | 2.90 brd (11.5) | 2.90 brd (10.2) | 2.92 brd (11.0) |
| 10 | | | | | | |
| 11 | 2.53 m | 2.43 m, 2.53 dd (13.5,5.0) | 2.56 brd (8.1) | 5.70 brs | 5.75 brs | 5.72 brs |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | 2.86 qd (6.9,4.8) | 3.09 quint (7.0) | 3.38 d (8.7) | 3.30 qd (7.5,4.5) | 2.73 qd (7.2,3.6) | 3.30 qd (7.5,4.5) |
| 15 | 6.19 d (1.8) | 6.22 d (2.0) | 6.13 d (1.5) | 5.68 s | 5.66 s | 5.70 s |
| 16 | 7.23 d (1.8) | 7.25 d (2.0) | 7.24 d (1.5) | | | |
| 17 | 1.02 d (6.9) | 1.10 d (7.0) | | 1.10 d (7.5) | 1.03 d (7.2) | 1.07 d (7.0) |
| 18 | 1.47 s | 1.08 s | 1.08 s | 0.99 s | 0.94 s | 1.00 s |
| 19 | 1.04 s | 1.26 s | 1.61 s | 1.09 s | 1.14 s | 1.07 s |
| 20 | 1.39 s | 1.18 s | 1.50 s | 1.32 s | 1.42 s | 1.41 s |
| 1' | | | | | | |
| 2' | 6.51 d (15.9) | | | 6.38 d (16.0) | | |
| 3'[a] | 7.75 d (15.9) | 8.04 dd (7.5,1.0) | 8.05 d (7.5) | 7.64 d (16.0) | 7.95 dd (7.5,1.5) | 7.96 d (7.5) |
| 4'[a] | | 7.45 t (7.5) | 7.24 t (7.5) | | 7.39 dt (7.2,1.5) | 7.40 t (7.2) |
| 5'[b] | 7.55 m | 7.57 tt (7.5,1.0) | 7.57 t (7.5) | 7.45 dd (7.5,2.5) | 7.52 tt (7.2,1.5) | 7.53 t (7.5) |
| 6'[b] | 7.41 m | | | 7.32 m | | |
| 7' | 7.41 m | | | 7.31 m | | |
| 1'' | | | | | | |
| 6-OH | 1.97 d (2.1) | | | | | |
| $OCOCH_3$ | | | 2.06 s | | | |
| $COOCH_3$ | | | 3.75 s | | | |

[a] Compounds **2**,**3**,**5**,**6**: **3** = **7** and **4** = **6**.
[b] Compounds **1**,**4**: **5** = **9** and **6** = **8**.

cross-peaks of H-$7_{ax}$ with H-6 and Me-17, of H-$7_{eq}$ with H-8 and of H-8 with H-14 and Me-20. In addition, the small vicinal coupling constant ($J_{6eq,7ax}$, $J_{6eq,7eq}$ = 3.6 Hz) supported the equatorial orientation of H-6. Therefore, **5** was assigned as 6β-benzoyloxy-11,13(15)-diene-5α-hydroxycassan-12,16-olide and was named as neocaesalpin Q.

Compound **6**, $C_{27}H_{32}O_6$, displayed similar $^1$H and $^{13}$C NMR spectroscopic data to those of **5** except at C7 where methylene protons at $\delta$ 1.50 (m) and 2.30 (td, *J* = 13.8, 3.6 Hz) in **5** were replaced by an oxymethine proton at $\delta$ 4.38 (dd, *J* = 11.5, 4.0 Hz) in **6**. The NOESY cross-peaks of H-7 with H-6 and Me-17 supported the *cis*-configuration of H-6 and H-7. Therefore, **6** was assigned as 6β-benzoyloxy-11,13(15)-diene-5α,7β-dihydroxycassan-12,16-olide and was named as neocaesalpin R.

## 3. Concluding remarks

Six new cassane diterpenoids, pulcherrin A–C and neocaesalpin P–R were identified by analysis of their spectroscopic data. All new compounds except **2** and **5** and known compounds with a 6,7-dihydroxylation pattern isolated from *C. pulcherrima* possess the 6β,7β-orientation, while those isolated from the related *C. bonduc* possess the 6α,7β-orientation (Roach et al., 2003; Pudhom et al., 2007).

## 4. Experimental

### 4.1. General experimental procedures

Melting points were determined on the Fisher–John melting point apparatus. The optical rotation $[\alpha]_D$ values were determined with a JASCO P-1020 polarimeter. The IR spectra were measured with a Perkin–Elmer FTS FT-IR spectrophotometer. The $^1$H and $^{13}$C NMR spectra were recorded using 300 and 500 MHz Bruker FTNMR Ultra Shield™ spectrometers. Chemical shifts are recorded in parts per million ($\delta$) in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. Quick column chromatography (QCC) and column chromatography (CC) were carried out on silica gel 60 $F_{254}$ (Merck) and silica gel 100 (Merck), respectively. Precoated plates of silica gel 60 $F_{254}$ was used for analytical purposes.

### 4.2. Plant material

*Caesalpinia pulcherrima* (L.) Swartz. was collected from Songkhla Province, Thailand in October 2005. Identification was made by Assoc. Prof. Dr. Kitichate Sridith, Department of Biology, Faculty of Science, Prince of Songkla University and a specimen (No. SC51) was deposited at the Prince of Songkla University Herbarium.

### 4.3. Extraction and isolation

Air-dried stem tissue (15.0 kg) of *C. pulcherrima* was successively extracted with $CH_2Cl_2$ and acetone (each 2 × 2.5 l, for 5 days) at room temperature. The crude extracts were evaporated under reduced pressure to afford brownish $CH_2Cl_2$ (102.1 g) and acetone (10.6 g) extracts, respectively. A portion of the crude $CH_2Cl_2$ extract (60.2 g) was further purified by QCC using hexane as eluent and increasing polarity with EtOAc to give nine fractions (C1–C9). Fraction C2 (2.7 g) was further purified by QCC with EtOAc–hexane (1:19, v/v) to give seven subfractions (C2a–C2g). Subfraction C2b (80.5 mg) was separated by CC with EtOAc–hexane (1:19, v/v) to give **11** (10.2 mg). Subfraction C2c (50.8 mg) was purified by CC

**Table 2**
$^{13}$C NMR spectral data for compounds **1**,**2**,**3**, and **5** (75 MHz), **4** and **6** (125 MHz) in CDCl3.

| Position | 1 $\delta_C$ | 2 $\delta_C$ | 3 $\delta_C$ | 4 $\delta_C$ | 5 $\delta_C$ | 6 $\delta_C$ |
|---|---|---|---|---|---|---|
| 1 | 35.2 | 31.0 | 32.7 | 33.1 | 33.2 | 33.2 |
| 2 | 18.2 | 23.8 | 23.9 | 17.9[a] | 18.0 | 17.8 |
| 3 | 37.6 | 77.3 | 78.8 | 37.7 | 38.0 | 37.7 |
| 4 | 39.2 | 43.5 | 44.2 | 39.2 | 38.9 | 39.1 |
| 5 | 77.8 | 79.9 | 77.0 | 77.9 | 77.2 | 78.1 |
| 6 | 71.5 | 35.9 | 72.3 | 73.8 | 72.5 | 74.1 |
| 7 | 75.0 | 68.1 | 78.8 | 67.6 | 30.9 | 67.9 |
| 8 | 35.2 | 42.8 | 34.3 | 39.1 | 33.1 | 39.3 |
| 9 | 37.3 | 36.7 | 41.3 | 40.6 | 41.8 | 40.5 |
| 10 | 40.7 | 40.9 | 40.9 | 41.3 | 41.5 | 41.3 |
| 11 | 21.8 | 22.5 | 21.3 | 111.6 | 112.3 | 111.0 |
| 12 | 149.5 | 149.1 | 150.8 | 150.4 | 150.2 | 150.4 |
| 13 | 121.7 | 121.9 | 112.7 | 161.3 | 161.3 | 161.0 |
| 14 | 27.6 | 27.4 | 45.1 | 28.4 | 33.3 | 28.4 |
| 15 | 109.5 | 109.7 | 108.3 | 110.9 | 110.0 | 110.4 |
| 16 | 140.5 | 140.7 | 141.4 | 170.6 | 170.1 | 170.3 |
| 17 | 17.2 | 17.1 | 174.9 | 14.2 | 14.6 | 14.2 |
| 18 | 27.8 | 23.1 | 22.6 | 27.3 | 27.2 | 27.2 |
| 19 | 25.5 | 19.7 | 19.6 | 24.8 | 25.3 | 24.9 |
| 20 | 17.4 | 17.5 | 16.6 | 17.9[a] | 18.1 | 18.0 |
| 1' | 166.0 | 166.2 | 166.2 | 167.5 | 165.6 | 167.3 |
| 2' | 117.8 | 130.8 | 130.8 | 117.5 | 130.1 | 129.2 |
| 3'[b] | 145.6 | 129.5 | 129.6 | 146.5 | 129.7 | 129.9 |
| 4'[b] | 134.2 | 128.4 | 128.4 | 134.0 | 128.7 | 128.7 |
| 5'[c] | 128.2 | 140.7 | 132.9 | 128.3 | 133.3 | 133.5 |
| 6'[c] | 129.0 | | | 129.0 | | |
| 7' | 130.5 | | | 130.8 | | |
| 1'' | | | 170.2 | | | |
| $OCOCH_3$ | | | 21.0 | | | |
| $COOCH_3$ | | | 52.1 | | | |

[a] Interchangeable.
[b] Compounds **2**,**3**,**5**,**6**: **3** = **7** and **4** = **6**.
[c] Compounds **1**,**4**: **5** = **9** and **6** = **8**.

with EtOAc–hexane (1:13, v/v) to give **12** (1.5 mg). Fraction C3 (1.5 g) was separated by QCC using hexane as eluent and increasing polarity with acetone to afford four subfractions (C3a–C3d). Subfraction C3b (751.0 mg) was subjected to QCC using hexane as eluent and increasing polarity with EtOAc to afford four subfractions (C3b1–C3b4). Subfraction C3b2 (30.2 mg) was separated by CC with EtOAc–$CH_2Cl_2$–hexane (5:13:15, v/v) to give **13** (3.0 mg). Fraction C5 (3.5 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (C5a–C5f). Subfraction C5e (760.5 mg) was separated by CC with EtOAc–hexane (3:17, v/v) to afford **7** (48.3 mg) and **8** (6.4 mg). Fraction C6 (3.1 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to give eight subfractions (C6a–C6h). Subfraction C6f (1.3 g) was separated by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (C6f1–C6f6). Subfraction C6f2 (501.8 mg) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to give **1** (10.2 mg). Subfraction C6f4 (85.1 mg) was subjected to CC with EtOAc–$CH_2Cl_2$–hexane (1:2:17, v/v) to afford **2** (3.5 mg). Subfraction C6f5 (177.1 mg) was separated by CC with EtOAc–$CH_2Cl_2$–hexane (1:2:17, v/v) to afford **9** (4.5 mg). Subfraction C6f6 (85.9 mg) was purified by CC with EtOAc–hexane (1:3, v/v) to afford **10** (3.4 mg). Subfraction C6g (480.7 mg) was separated by QCC using hexane as eluent and increasing polarity with EtOAc to afford four subfractions (C6g1–C6g4). Subfraction C6g3 (79.1 mg) was separated using CC with EtOAc–$CH_2Cl_2$–hexane (1:2:17, v/v) to afford **3** (8.2 mg). Fraction C7 (1.2 g) was purified by QCC using hexane as eluent and increasing polarity with EtOAc to afford six subfractions (C7a–C7f). Subfraction C7a (50.8 mg) was separated by CC with EtOAc–hexane (1:4, v/v) to afford **5** (1.5 mg). Subfraction C7c (380.4 mg) was purified by CC with acetone–hexane (3:17, v/v) followed by prep TLC with acetone–hexane (1:4, v/v) to give **6** (1.5 mg), and **4** (2.3 mg). Subfraction C7e (111.6 mg) was separated by CC with EtOAc–hexane (1:4, v/v) to afford **14** (8.0 mg). Hydrolysis of **1** (10.0 mg) for 9 h using MeOH (10 ml) saturated with $K_2CO_3$ at room temperature afforded 6β-hydroxyisovoucapenol C (4.2 mg).

#### 4.3.1. Pulcherrin A (*1*)

White powder; m.p. 125–127 °C; $[\alpha]_D^{26}$ + 10.4 ($CHCl_3$; *c* 0.51); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 216 (3.63) and 277 (3.64) nm; IR (neat) $\upsilon_{max}$: 3467, 2914, 2847, 2361, 2335, 1700, 1279, 1170, 1046, 997, 757, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 300 MHz), and $^{13}$C NMR ($CDCl_3$, 75 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M]^+$ 464.2573 (calcd for $C_{29}H_{36}O_5$, 464.2563).

#### 4.3.2. Pulcherrin B (2)

Amorphous solid; $[\alpha]_D^{26}$ + 10.9 ($CHCl_3$; *c* 0.18); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 226 (4.21) and 273 (3.63) nm; IR (neat) $\upsilon_{max}$: 3400, 2930, 2863, 2361, 2335, 1713, 1702, 1276, 1114, 1067, 1023, 770, 711, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 300 MHz), and $^{13}$C NMR ($CDCl_3$, 75 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M]^+$ 438.2407 (calcd for $C_{27}H_{34}O_5$, 438.2406).

#### 4.3.3. Pulcherrin C (*3*)

White powder; m.p. 180–182 °C; $[\alpha]_D^{26}$ + 13.9 ($CHCl_3$; *c* 0.41); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 226 (3.98) and 273 (3.17) nm; IR (neat) $\upsilon_{max}$: 3509, 2930, 2863, 1715, 1276, 1157, 1114, 1026, 760, 711, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 300 MHz) and $^{13}$C NMR ($CDCl_3$, 75 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M]^+$ 540.2383 (calcd for $C_{30}H_{36}O_9$, 540.2359).

#### 4.3.4. Neocaesalpin P (*4*)

Amorphous solid; $[\alpha]_D^{26}$ + 89.3 ($CHCl_3$; *c* 0.12); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 216 (4.39) and 279 (4.67) nm; IR (neat) $\upsilon_{max}$: 3338, 2919, 2852, 2356, 2341, 1746, 1702, 1449, 1274, 767, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 500 MHz) and $^{13}$C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M\text{-}H_2O]^+$ 460.2225 (calcd for $C_{29}H_{32}O_5$, 460.2250).

#### 4.3.5. Neocaesalpin Q (*5*)

White powder, m.p. 250–252 °C; $[\alpha]_D^{26}$ + 25.8 ($CHCl_3$; *c* 0.08); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 230 (3.96) and 280 (3.93) nm; IR (neat) $\upsilon_{max}$: 3524, 2935, 2356, 1749, 1713, 1452, 1271, 1108, 1067, 990, 757, 711, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 300 MHz) and $^{13}$C NMR ($CDCl_3$, 75 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M\text{-}H_2O]^+$ 428.2154 (calcd for $C_{27}H_{30}O_4$, 418.2144).

#### 4.3.6. Neocaesalpin R (*6*)

Amorphous solid; $[\alpha]_D^{26}$ + 33.3 ($CHCl_3$; *c* 0.08); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 227 (3.86) and 280 (3.79) nm; IR (neat) $\upsilon_{max}$: 3478, 2925, 2852, 2356, 2335, 1777, 1746, 1710, 1456, 1271, 767, 667 cm$^{-1}$; For $^1$H NMR ($CDCl_3$, 500 MHz) and $^{13}$C NMR ($CDCl_3$, 125 MHz) spectroscopic data, see Tables 1 and 2; HREIMS: *m/z* $[M]^+$ 452.2219 (calcd for $C_{27}H_{32}O_6$, 452.2199).

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