### **CHAPTER 3**

#### RESULTS AND DISCUSSION

### 3.1 Structural Determination

The twigs and fruits of *Cratoxylum cochinchinense* were dried, ground and extracted with dichloromethane and acetone, whereas the minor low polarity fractions of the crude dichloromethane extract and the methanol extract of the roots were obtained from the previous work. The extracts from the twigs, fruits and roots were separated by means of chromatography over silica gel to give four new xanthones, fourteen known xanthones and a known anthraquinone. Separation of a dichloromethane and acetone extract of the twigs produced  $\beta$ -mangostin (PS1), 6,12dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2',3':7,8)xanthone (PS2) and cochinchinone A (PS3). The dichloromethane extract of the fruits produced 7-geranyloxy-1,3-dihydroxyxanthone (**PS4**), 1,8-dihydroxy-3-methoxy-6-methyl-2-(3-methyl-2-butenyl)anthraquinone (**PS6**) and 3-geranyloxy-1,7-dihydroxyxanthone (PS5) which is a new xanthone. Investigation of the minor fractions from the dichloromethane extract of the roots obtained from the previous study gave a new caged-prenylated xanthone: cochinchinone E (PS8) and five known xanthones: 5,10dihydroxy-9-methoxy-12-(1,1-dimethyl-2-propenyl)-2H,6H-pyrano[3,2-b]xanthen-6one (PS7), cratoxycochinchinone C (PS9), mangostin (PS10), isocudraniaxanthone B (PS11), celebixanthone (PS12). Whereas purification of methanolic extract from the roots gave three new xanthones: 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)-8-(3,7dimethyl-2,6-octadienyl)xanthone (PS13) which was isolated as acetoxyl derivative acetylation, 1,3,6-trihydroxy-8-methoxy-2,4-bis(3-methyl-2-butenyl)xanthone (PS14), which was mixed in PS15 and 1,3,6,7-tetrahydroxy-5-(3-methyl-2butenyl)xanthone (PS18) and nine known xanthones: (PS2), (PS3), (PS9), (PS11), (PS12), 1,2,8-trihydroxyxanthone (PS15), cudratricusxanthone E (PS16),

γ-mangostin (**PS17**) and norathyriol (**PS19**). Their structures were determined by spectroscopic data (1D and 2D NMR).

## The structures of compounds isolated from the twigs, fruits and roots of *C. cochinchinense*

 $\beta$ -mangostin (**PS1**)

6,12-dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2',3':7,8) xanthone (**PS2**)

cochinchinone A (PS3)

7-geranyloxy-1,3-dihydroxyxanthone (**PS4**)

OH O OH OCH3

1,8-dihydroxy-3-methoxy-6-methyl-2-(3-methyl-2-butenyl)anthraquinone (**PS6**)

5,10-dihydroxy-9-methoxy-12-(1,1-dimethyl-2-propenyl)-2*H*,6*H*-pyrano[3,2-b]xanthen-6-one (**PS7**)

cratoxycochinchinone C (PS9)

isocudraniaxanthone B (PS11)

1,3,7-trihydroxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (**PS13**)

cratoxycochinchinone A (PS8)

mangostin (PS10)

celebixanthone (PS12)

1,3,6-trihydroxy-8-methoxy-2,4 – bis(3-methyl-2-butenyl)xanthone (**PS14**)

1,2,8-trihydroxyxanthone (**PS15**)

γ-mangostin (**PS17**)

cudratricus xanthone E (PS16)

1,3,6,7-tetrahydroxy-5-(3-methyl-2-butenyl)xanthone (**PS18**)

norathyriol (PS19)

PS1: 1,6-Dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)xanthone  $(\beta\text{-Mangostin})$ 

**PS1** is a yellow solid, m.p. 176-180 °C. The <sup>1</sup>H NMR spectrum showed the singlet signal of a deshielded proton (1-OH) at  $\delta$  13.53. Singlet signals of *gem*-dimethyl protons H-4′ ( $\delta$  1.79, 3H), H-5′ ( $\delta$  1.66, 3H), H-4″ ( $\delta$  1.82, 3H) and H-5″ ( $\delta$  1.68, 3H), broad triplet signals of olefinic protons H-2′ ( $\delta$  5.23, 1H) and H-2″ ( $\delta$  5.26, 1H) and doublet of benzylic methylene protons H-1′ ( $\delta$  3.32, 2H) and H-1″ ( $\delta$  4.07, 2H) were assigned for two prenyl units. The presence of two methoxyl groups (3-OCH<sub>3</sub> and 7-OCH<sub>3</sub>) were displayed at  $\delta$  3.87 and 3.77, respectively. The <sup>1</sup>H NMR spectrum revealed two aromatic protons H-4 ( $\delta$  6.28) and H-5 ( $\delta$  6.77). The spectral data and melting point of **PS1** corresponded to those of 1,6-dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)xanthone (Nuangnaowarat, W, 2005).

Table 7 NMR spectral data of PS1

| Position           | PS1                         | eta-mangostin               |
|--------------------|-----------------------------|-----------------------------|
| 4                  | 6.28 (s, 1H)                | 6.28 (s, 1H)                |
| 5                  | 6.77 (s, 1H)                | 6.77 (s, 1H)                |
| 6-OH               | 6.44 ( <i>br s</i> , OH)    | 6.45 (br s, OH)             |
| 1'                 | 3.32 (d, 2H, J = 7.2 Hz)    | 3.33 (d, 2H, J = 7.2 Hz)    |
| 2'                 | 5.23 (br t, 1H, J = 7.2 Hz) | 5.23 (br t, 1H, J = 7.2 Hz) |
| 4′                 | 1.79 (s, 3H)                | 1.79 (s, 3H)                |
| 5′                 | 1.66 (s, 3H)                | 1.68 (s, 3H)                |
| 1"                 | 4.07 (d, 2H, J = 6.0 Hz)    | 4.07 (d, 2H, J = 6.0  Hz)   |
| 2"                 | 5.25 (br t, 1H, J = 6.0 Hz) | 5.26 (br t, 1H, J = 6.0 Hz) |
| 4''                | 1.82 (s, 3H)                | 1.83 (s, 3H)                |
| 5''                | 1.68 (s, 3H)                | 1.68 (s, 3H)                |
| 1-OH               | 13.53 (s, OH)               | 13.54 (s, OH)               |
| 3-OCH <sub>3</sub> | 3.87 (s, 3H)                | 3.88 (s, 3H)                |
| 7-OCH <sub>3</sub> | 3.77 (s, 3H)                | 3.79 (s, 3H)                |

PS2: 6,12-Dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano (2', 3': 7,8)xanthone (3-O-Methylgarcinone B)

**PS2** is a yellow solid, m.p. 246-247 °C. The  $^{1}$ H NMR spectrum exhibited a singlet signal of a chelated hydroxyl group at  $\delta$  13.48 (s, 6-OH) and a free hydroxyl proton at 9.18 (br t, 12-OH). A sharp singlet resonance with integration of three protons at  $\delta$  3.91 belonged to a methoxyl group. Two singlets in the aromatic region,  $\delta$  6.35 and 6.81 were assigned for the signals of isolated protons H-9 and

H-11. The presence of a prenyl side chain was shown in the spectrum at  $\delta$  3.32 (*d*, H-1'), 5.21 (*br t*, H-2'), 1.78 (*s*, H-4') and 1.67 (*s*, H-5'). The <sup>1</sup>H NMR spectrum revealed a characteristic signals of a dimethylchromene ring of which the signal of *gem*-dimethyl protons resonated as a singlet at  $\delta$  1.50 and two doublet signals of *cis*-olefinic protons H-3 and H-4 were at  $\delta$  5.82 and 8.00, respectively. The spectral data and melting point of **PS2** corresponded to those of 3-*O*-methylgarcinone B (Mahabusarakam, *et al.*, 2006).

Table 8 NMR spectral data of PS2

| Position           | PS2                         | 3- <i>O</i> -methylgarcinone B |
|--------------------|-----------------------------|--------------------------------|
| 3                  | 5.82 (d, 1H, J = 10.2 Hz)   | 5.81 (d, 1H, J = 10.2 Hz)      |
| 4                  | 8.00 (d, 1H, J = 10.2 Hz)   | 8.00 (d, 1H, J = 10.2 Hz)      |
| 9                  | 6.35 (s, 1H)                | 6.35 (s, 1H)                   |
| 11                 | 6.81 (s, 1H)                | 6.81 (s, 1H)                   |
| 13                 | 1.50 (s, 3H)                | 1.50 (s, 3H)                   |
| 14                 | 1.50 (s, 3H)                | 1.50 (s, 3H)                   |
| 1′                 | 3.32 (d, 2H, J = 7.2 Hz)    | 3.32 (d, 2H, J = 7.2 Hz)       |
| 2'                 | 5.21 (br t, 1H, J = 7.2 Hz) | 5.20 (br t, 1H, J = 7.2 Hz)    |
| 4′                 | 1.78 (s, 3H)                | 1.78 (s, 3H)                   |
| 5′                 | 1.67 (s, 3H)                | 1.67 (s, 3H)                   |
| 6-OH               | 13.48 (s, OH)               | 13.48 (s, OH)                  |
| 12-OH              | 9.18 ( <i>br s</i> , OH)    | 9.19 ( <i>br s</i> , OH)       |
| 8-OCH <sub>3</sub> | 3.91 (s, 3H)                | 3.90 (s, 3H)                   |
|                    |                             |                                |

PS3: 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)-4-(3,7-dimethyl-2,6-octadienyl)xanthone

**PS3** is a yellow solid, m.p. 119-120 °C. The UV spectrum showed maximum absorptions at 232, 268, 316 and 384 nm. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1641 cm<sup>-1</sup> and a hydroxyl group at 3413 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed a singlet signal of a deshielded proton 1-OH at  $\delta$  12.96. The ABX system in the aromatic region,  $\delta$  7.54 (d, J = 3.0 Hz), 7.36 (d, J = 9.0 Hz) and 7.24 (dd, J = 9.0, 3.0 Hz) were assigned for H-8, H-5 and H-6, respectively. The presence of characteristic signals of a prenyl unit, were shown at  $\delta$  3.37 (d, J = 7.0 Hz, H-1'), 5.20 (br t, J = 7.0 Hz, H-2'), 1.79 (s, H-4') and 1.69 (s, H-5'). The location of a prenyl group at C-2 was supported by HMBC correlation of H-1' to C-1, C-2 and C-3. The remaining signals revealed the presence of a geranyl group. A doublet signal at  $\delta$  3.48 and a broad triplet signal at  $\delta$  5.20 were assigned for the signals of methylene protons H-1" and an olefinic proton H-2", respectively. A broad triplet signal at  $\delta$  5.00 and multiplet at  $\delta$  1.93-2.10 were the signals of an olefinic proton H-6" and methylene protons H-4" and H-5", respectively. Three singlet signals at  $\delta$  1.50, 1.83 and 1.60 were those of three methyl groups. The geranyl side chain was located at C-4 which was confirmed by the cross peak of H-1" to C-3 and C-4a in HMBC correlation. The <sup>13</sup>C NMR spectral data deduced from DEPT and HMQC spectra showed 28 signals for 28 carbon atoms: a carbonyl carbon ( $\delta$  183.4), five methyl carbons ( $\delta$  25.8, 25.6, 17.9, 17.6 and 16.2), four methylene carbons  $(\delta 39.7, 26.4, 21.7 \text{ and } 21.6)$ , five methine carbons  $(\delta 124.0, 123.8, 121.5, 118.9 \text{ and } 18.9)$  109.0) and twelve quarternary carbons ( $\delta$  161.1, 158.3, 153.0, 152.2, 150.4, 137.8, 135.0, 131.0, 131.8, 120.6, 105.0 and 103.2). The assignment then suggested that **PS3** is cochinchinone A (Mahabusarakam, *et al.*, 2006).

 Table 9
 NMR spectral data of PS3

| Position | PS3                            | cochinchinone A                |
|----------|--------------------------------|--------------------------------|
| 5        | 7.36 (d, 1H, J = 9.0 Hz)       | 7.36 (d, 1H, J = 9.0 Hz)       |
| 6        | 7.24 (dd, 1H, J = 9.0, 3.0 Hz) | 7.24 (dd, 1H, J = 9.0, 3.0 Hz) |
| 8        | 7.54 (d, 1H, J = 3.0 Hz)       | 7.59 (d, 1H, J = 3.0 Hz)       |
| 1'       | 3.37 (d, 2H, J = 7.0 Hz)       | 3.47 (d, 2H, J = 7.0 Hz)       |
| 2'       | 5.20 (br t, 1H, J = 7.0 Hz)    | 5.29 (br t, 1H, J = 7.0 Hz)    |
| 4′       | 1.79 (s, 3H)                   | 1.84 (s, 3H)                   |
| 5′       | 1.69 (s, 3H)                   | 1.76 (s, 3H)                   |
| 1''      | 3.48 (d, 2H, J = 7.0  Hz)      | 3.57 (d, 2H, J = 7.0 Hz)       |
| 2''      | 5.20 (br t, 1H, J = 7.0 Hz)    | 5.27 (br t, 1H, J = 7.0 Hz)    |
| 4''      | 1.93-2.10 ( <i>m</i> , 2H)     | 2.03-2.06 (m, 2H)              |
| 5"       | 2.11-1.93 (m, 2H)              | 2.11-2.08 (m, 2H)              |
| 6''      | 5.00 (br t, 1H, J = 7.0 Hz)    | 5.05 (br t, 1H, J = 7.0 Hz)    |
| 8''      | 1.50 (s, 3H)                   | 1.57 (s, 3H)                   |
| 9"       | 1.83 (s, 3H)                   | 1.88 (s, 3H)                   |
| 10''     | 1.60 (s, 3H)                   | 1.64 (s, 3H)                   |
| 1-OH     | 12.96 (s, OH)                  | 12.95 (s, OH)                  |

### PS4: 7-geranyloxy-1,3-dihydroxyxanthone

PS4 is a yellow solid, m.p. 137-138 °C. The UV spectrum showed maximum absorption bands at 204, 232, 259, 310 and 368 nm. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1650 cm<sup>-1</sup> and a hydroxyl group at 3137 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectral data revealed the presence of a chelated hydroxyl proton (1-OH) at  $\delta$  12.96 (s) and meta protons H-2 and H-4 at  $\delta$  6.29 (d, J = 3.0 Hz) and  $\delta$  6.38 (d, J = 3.0 Hz). The spectrum further showed the signals of ABX system of H-5, H-6 and H-8 at  $\delta$  7.35 (d, J = 9.0 Hz), 7.32 (dd, J = 9.0, 3.0 Hz) and 7.61 (d, J = 3.0 Hz), respectively. The geranyl unit was commemorated from distinctive signals of two olefinic protons at  $\delta 5.50$  (H-2', J = 6.6Hz) and 5.09 (H-6', J = 6.6 Hz), three methylene protons at  $\delta$  4.61 (d, J = 6.6 Hz, H-1') and 2.12 (m, H-4' and H-5') and three vinyl methyl protons at  $\delta$  1.60 (s, H-8'), 1.76 (s, H-9') and 1.67 (s, H-10'). It was assigned as an O-geranyl unit according to the chemical shift of H-1' ( $\delta$  4.61). The differential NOE technique by irradiation of the signal of H-1' affected the signal of H-8, accordingly O-geranyl unit was assigned at C-7. The <sup>13</sup>C NMR spectrum and DEPT experiments signified the presence of a carbonyl carbon ( $\delta$  180.6), three methylene carbons ( $\delta$  26.3, 39.5 and 65.6), seven methine carbons ( $\delta$  98.3, 94.1, 125.2, 106.2, 118.8, 118.8 and 123.7) and nine quarternary carbons ( $\delta$  163.5, 157.9, 142.0, 155.3, 120.6, 103.6, 150.7, 142.0 and 131.8). The signals at  $\delta$  163.5, 157.9, 142.0, 150.7 and 155.3 confirmed the presence of five oxygenated aromatic carbons. The correlation of H-1' to C-7 in HMBC experiment confirmed the position of a geranyl unit at C-7. PS4 was denoted as 7-geranyloxy-1,3-dihydroxyxanthone. (Nguyen, L. H. D. and Harrison, L. J., 1998).

Table 10 NMR spectral data of PS4

| Position | $\delta_{C}(C	ext{-Type})$ | δ <sub>H</sub> (multiplicity)   | НМВС                      |
|----------|----------------------------|---------------------------------|---------------------------|
| 1        | 163.5 (C)                  | -                               | -                         |
| 2        | 98.3 (CH)                  | 6.29 (d, J = 3.0  Hz, 1H)       | C-1, C-4                  |
| 3        | 157.9 (C)                  | -                               | -                         |
| 4        | 94.1 (CH)                  | 6.38 (d, J = 3.0  Hz, 1H)       | C-2, C-3, C-9a            |
| 4a       | 142.0 (C)                  | -                               | -                         |
| 4b       | 150.7 (C)                  | -                               | -                         |
| 5        | 118.8 (CH)                 | 7.35 (d, J = 9.0  Hz, 1H)       | C-6, C-7, C-8a            |
| 6        | 125.2 (CH)                 | 7.32 (dd, J = 9.0, 3.0  Hz, 1H) | C-10a                     |
| 7        | 155.3 (C)                  | -                               | -                         |
| 8        | 106.2 (CH)                 | 7.61 (d, J = 3.0  Hz, 1H)       | C-5, C-6, C-7, C-10a, C-9 |
| 8a       | 120.6 (C)                  | -                               | -                         |
| 9        | 180.6 (C)                  | -                               | -                         |
| 9a       | 103.6 (C)                  | -                               | -                         |
| 1′       | 65.6 (CH <sub>2</sub> )    | 4.61 (d, J = 6.6  Hz, 2H)       | C-2', C-3', C-7           |
| 2'       | 118.7 (CH)                 | 5.50 (t, J = 6.6  Hz, 1H)       | C-9a, C-4'                |
| 3'       | 142.0 (C)                  | -                               | -                         |
| 4′       | 39.5 (CH <sub>2</sub> )    | 2.12 (m, 2H)                    | C-2', C-3', C-5'          |
| 5′       | 26.3 (CH <sub>2</sub> )    | 2.12 (m, 2H)                    | C-3', C-4', C-6'          |
| 6′       | 123.7 (CH)                 | 5.09 (t, J = 6.6  Hz, 1H)       | C-5', C-10'               |
| 7′       | 131.8 (C)                  | -                               | -                         |

Table 10 (Continued)

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | HMBC              |
|----------|-------------------------------|-----------------------------|-------------------|
| 8′       | 17.6 (CH <sub>3</sub> )       | 1.60 (s, 3H)                | C-6', C-7', C-10' |
| 9′       | 16.7 (CH <sub>3</sub> )       | 1.76 (s, 3H)                | C-2', C-3', C-4'  |
| 10′      | 25.6 (CH <sub>3</sub> )       | 1.67 (s, 3H)                | C-6', C-7', C-8'  |
| 1-OH     | -                             | 12.96 (s, 1H)               | C-9, C-2          |

PS5: 3-Geranyloxy-1,7-dihydroxyxanthone

 H-1' ( $\delta$  4.62) indicated that the geranyl group formed bond to electron withdrawing atom which was assigned for an oxygen atom. Furthermore, the location of the O-geranyl side chain was assigned at C-3 from the HMBC correlations of H-1' to C-3 and C-2'; H-4 to C-3 and the differential NOE technique by irradiation of the signals of H-2 and H-4 which affected the signal of H-1'. The presence of five oxygenated aromatic carbons was deduced from the  $^{13}$ C NMR data at  $\delta$  166.2 (C-3), 163.2 (C-1), 157.5 (C-4a), 152.3 (C-7) and 150.7 (C-4b). Thus 3-geranyloxy-1,7-dihydroxy xanthone was assigned for **PS5**, which was isomer of **PS4**. It is a new xanthone derivative.

Table 11 NMR spectral data of PS5

| Position | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity)     | НМВС                 |
|----------|----------------------------|---------------------------------|----------------------|
| 1        | 163.2 (C)                  | -                               | -                    |
| 2        | 97.6(CH)                   | 6.33 (d, J = 3.0  Hz, 1H)       | C-1, C-4, C-9a       |
| 3        | 166.2 (C)                  | -                               | -                    |
| 4        | 93.2 (CH)                  | 6.39 (d, J = 3.0  Hz, 1H)       | C-2, C-3, C-4a, C-9a |
| 4a       | 157.5 (C)                  | -                               | -                    |
| 4b       | 150.8 (C)                  | -                               | -                    |
| 5        | 119.1 (CH)                 | 7.29 (d, J = 9.0  Hz, 1H)       | C-7, C-8, C-8a       |
| 6        | 124.2(CH)                  | 7.24 (dd, J = 9.0, 3.0  Hz, 1H) | C-5, C-7, C-8        |
| 7        | 152.3 (C)                  | -                               | -                    |
| 8        | 109.1 (CH)                 | 7.58 (d, J = 3.0  Hz, 1H)       | C-5, C-6, C-7, C-9   |
| 8a       | 120.7 (C)                  | -                               | -                    |
| 9        | 180.7 (C)                  | -                               | -                    |
| 9a       | 103.6 (C)                  | -                               | -                    |
| 1'       | 65.6 (CH <sub>2</sub> )    | 4.62 (d, J = 6.6  Hz, 2H)       | C-3, C-2', C-3'      |
| 2'       | 118.3 (CH)                 | 5.48 (t, J = 6.6  Hz, 1H)       | C-4', C-9'           |
| 3′       | 142.1 (C)                  | -                               | -                    |
| 4′       | 39.5 (CH <sub>2</sub> )    | 2.11 ( <i>m</i> , 2H)           | C-2', C-3', C-5'     |
| 5′       | 26.3 (CH <sub>2</sub> )    | 2.12 ( <i>m</i> , 2H)           | C-3', C-4', C-6'     |
| 6′       | 123.6 (CH)                 | 5.09 (t, J = 6.6  Hz, 1H)       | C-5', C-10'          |
| 7′       | 132.0 (C)                  | -                               | -                    |
| 8′       | 17.7 (CH <sub>3</sub> )    | 1.55 (s, 3H)                    | C-6', C-7', C-10'    |
| 9′       | 16.8 (CH <sub>3</sub> )    | 1.76 (s, 3H)                    | C-2', C-3', C-4'     |
| 10′      | 25.7 (CH <sub>3</sub> )    | 1.67 (s, 3H)                    | C-6', C-7', C-8'     |
| 1-OH     | -                          | 12.70 (s, 1H)                   | -                    |

### PS6: 1,8-dihydroxy-3-methoxy-6-methyl-2-(3-methyl-2-butenyl)anthraquinone

**PS6** is an orange solid, m.p. 116-118 °C. The UV spectrum showed maximum absorption bands at 221, 273, 304 and 437. The IR spectrum showed the absorption bands of a chelated conjugated carbonyl group at 1623 cm<sup>-1</sup>, a non-chelated conjugated carbonyl group at 1668 cm<sup>-1</sup> and a hydroxyl group at 3406 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectral data of **PS6** in acetone- $d_6$  (**Table 12**) showed signals of two chelated hydroxyl protons at  $\delta$  12.44 (s, 1-OH) and 12.05 (s, 8-OH), methoxyl protons at  $\delta$  4.09 (s, 3-OCH<sub>3</sub>), methyl protons at  $\delta$  2.48 (s, 6-CH<sub>3</sub>), an isolated aromatic proton at  $\delta$  7.45 (s, H-4) and two *meta* aromatic protons at  $\delta$  7.60 (d, J = 0.5 Hz) and 7.16 (d, J = 0.5 Hz). The location of a methoxyl and methyl groups were assigned from the correlation between 3-OCH<sub>3</sub> to C-3 and 6-CH<sub>3</sub> to C-5, C-6 and C-7. The correlation of 1-OH to C-1, C-2 and C-9a; 8-OH to C-7, C-8, C-8a confirmed the position of hydroxyl groups at C-1 and C-8. Moreover, a prenyl unit was detected from the characteristic signals at  $\delta$  3.45 (d, H-1'), 5.20 (t, H-2'), 1.80 (s, H-4'), and 1.66 (s, H-5'). Therefore, **PS6** was assigned to be 1,8-dihydroxy-3-methoxy-6-methyl-2-butenyl)anthraquinone (Nagem, T. et al. 1990).

Major HMBC of **PS6** 

 $Table \ 12 \ {\hbox{NMR}} \ {\hbox{spectral data of}} \ PS6$ 

| Position           | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | НМВС                  |
|--------------------|-------------------------------|-----------------------------|-----------------------|
| 1                  | 162.9 (C)                     | -                           | -                     |
| 2                  | 124.0 (C)                     | -                           | -                     |
| 3                  | 165.2 (C)                     | -                           | -                     |
| 4                  | 113.0 (CH)                    | 7.45 (s, 1H)                | C-2, C-4a, C-9a, C-10 |
| 4a                 | 135.1 (C)                     | -                           | -                     |
| 5                  | 120.8 (CH)                    | 7.60 (d, J = 0.5  Hz, 1H)   | C-7, C-8a, C-10       |
| 6                  | 150.0 (C)                     | -                           | -                     |
| 7                  | 125.0 (CH)                    | 7.16 (d, J = 0.5  Hz, 1H)   | C-5, C-8a             |
| 8                  | 163.9 (C)                     | -                           | -                     |
| 8a                 | 114.8 (C)                     | -                           | -                     |
| 9                  | *                             | -                           | -                     |
| 9a                 | 111.3 (C)                     | -                           | -                     |
| 10                 | 182.3 (C=O)                   | -                           | -                     |
| 10a                | *                             | -                           | -                     |
| 1′                 | 21.8 (CH <sub>2</sub> )       | 3.45 (d, J = 8.0Hz, 2H)     | C-1, C-2, C-3         |
| 2'                 | 121.5 (CH)                    | 5.20 (t, J = 8.0  Hz, 1H)   | -                     |
| 3′                 | 133.1 (C)                     | -                           | -                     |
| 4′                 | 24.7 (CH <sub>3</sub> )       | 1.80 (s, 3H)                | C-2', C-3'            |
| 5′                 | 17.0 (CH <sub>3</sub> )       | 1.66 (s, 3H)                | C-2', C-3'            |
| 1-OH               | -                             | 12.44 (s, 1H)               | C-1, C-2, C-9a        |
| 8-OH               | -                             | 12.05 (s, 1H)               | C-7, C-8, C-8a        |
| 3-OCH <sub>3</sub> | 56.3 (CH <sub>3</sub> )       | 4.09 (s, 3H)                | C-3                   |
| 6-CH <sub>3</sub>  | 21.0 ( CH <sub>3</sub> )      | 2.48 (s, 3H)                | C-5, C-6, C-7         |
|                    |                               |                             |                       |

<sup>(\*)</sup> Not observed

PS7: 5,10-Dihydroxy-9-methoxy-12-(1,1-dimethyl-2-propenyl)-2H,6H-pyrano[3,2-b]xanthen-6-one

$$H_3CO$$

OH

OH

 $10a$ 
 $11a$ 
 $12$ 
 $12a$ 
 $13$ 
 $14$ 
 $14$ 

**PS7** is a yellow solid. The <sup>1</sup>H NMR spectrum exhibited the singlet signal of a chelated hydroxyl group (5-OH) at  $\delta$  13.57. The *ortho* coupling pattern in aromatic region,  $\delta$  7.78 (d) and 6.97 (d) were proposed for the characteristic signals of H-7 and H-8, respectively. The most deshielded aromatic proton signal was assigned for H-7 according to anisotropic effect of the carbonyl group. Two sharp singlet signals were due to the signal of 9-OCH<sub>3</sub> ( $\delta$  4.09) and 10-OH ( $\delta$  6.23). This was supported by the differential NOE technique; irradiation of a methoxyl group affected the signal of H-8. The typical signal of an isoprenyl unit was observed. The signals of two singlets of gem-dimethyl protons H-2' and H-3' ( $\delta$  1.67), two doublet of terminal olefinic protons H-5'E ( $\delta$ 5.19) and H-5'Z ( $\delta$ 5.03) and a methine proton resonating at  $\delta$  6.67 were assigned for the isoprenyl unit at C-12 according to the correlation of the proton H-4' to C-12 in the HMBC spectrum. The remaining signals were assigned for a chromene ring. Two vicinal protons H-3 and H-4 appeared as two doublet signals ( $\delta$  5.59 and 6.76). The correlations of H-4 to C-4a, C-5 and H-3 to C-4a, C-13, C-14 correctly determined that the dimethyl chromene ring was next to C-4a and C-12a. The <sup>13</sup>C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon ( $\delta$ 180.9), five methyl carbons ( $\delta$ 28.5, 28.5, 27.9, 27.2 and 56.6), a methylene carbon ( $\delta$  104.6), five methine carbons ( $\delta$  108.4, 116.6, 116.8, 127.1 and 154.9) and twelve quarternary carbons ( $\delta$  41.8, 79.2, 103.1, 105.4, 114.3, 114.4, 133.6, 144.4, 151.5, 154.1, 156.7 and 159.1. **PS7** was identified as 5,10-dihydroxy-9-methoxy-12-(1,1-dimethyl-2-propenyl)-2H,6H-pyrano[3,2-b]xanthen-6-one (Chen et al., 2005).

H<sub>3</sub>CO OH HI

NOE of **PS7** 

Major HMBC of **PS7** 

 Table 13
 NMR spectral data of PS7

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity)                      | НМВС                   |
|----------|-------------------------------|--|------------------------|
| 2        | 79.2 (C)                      | -  | -                      |
| 3        | 127.1 (CH)                    | 5.59 (d, J = 10.2  Hz, 1H)                       | C-4a, C-13, C-14       |
| 4        | 116.6 (CH)                    | 6.76 (d, J = 10.2Hz, 1H)                         | C-4a, C-5, C-12a       |
| 4a       | 105.4 (C)                     | -  | -                      |
| 5        | 156.7 (C)                     | -  | -                      |
| 5a       | 103.1 (C)                     | -  | -                      |
| 6        | 180.9 (C)                     | -  | -                      |
| 6a       | 114.4 (C)                     | -  | -                      |
| 7        | 116.8 (CH)                    | 7.78 (d, J = 9.0  Hz, 1H)                        | C-6                    |
| 8        | 108.4 (CH)                    | 6.97 (d, J = 9.0  Hz, 1H)                        | C-6a, C-10             |
| 9        | 151.5 (C)                     | -  | -                      |
| 10       | 133.6 (C)                     | -  | -                      |
| 10a      | 144.4 (C)                     | -  | -                      |
| 11a      | 154.1 (C)                     | -  | -                      |
| 12       | 114.3 (C)                     | -  | -                      |
| 12a      | 159.1 (C)                     | -  | -                      |
| 13       | 27.9 (CH <sub>3</sub> )       | 1.53 (s, 3H)                                     | C-3, C-14              |
| 14       | 27.2 (CH <sub>3</sub> )       | 1.53 (s, 3H)                                     | C-2, C-13              |
| 1′       | 41.8 (C)                      | -  | -                      |
| 2'       | 28.5 (CH <sub>3</sub> )       | 1.67 (s, 3H)                                     | C-1', C-12, C-3'       |
| 3'       | 28.5 (CH <sub>3</sub> )       | 1.67 (s, 3H)                                     | C-1', C-12, C-2'       |
| 4′       | 154.9 (CH)                    | 6.67 ( <i>dd</i> , <i>J</i> = 17.7, 10.8 Hz, 1H) | C-12, C-1', C-2', C-3' |

 Table 13 (Continued)

| Position           | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | HMBC             |
|--------------------|-------------------------------|-----------------------------|------------------|
| 5'E                | 104.6 (CH)                    | 5.19 (d, J = 17.7  Hz, 1H)  | C-1', C-4'       |
| 5′Z                | 104.6 (CH)                    | 5.03 (d, J = 10.8  Hz, 1H)  | C-1'             |
| 5-OH               | -                             | 13.57 (s, OH)               | -                |
| 10-OH              | -                             | 6.23 (s, OH)                | C-9, C-10, C-10a |
| 9-OCH <sub>3</sub> | 56.6 (CH <sub>3</sub> )       | 4.09 (s, 3H)                | C-9              |

### **PS8**: Cratoxycochinchinone A

**PS8** is a yellow solid, m.p. 208-209 °C. The UV spectrum showed maximum absorption bands at 205, 225, 281 and 350. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1633 cm<sup>-1</sup>, a non-conjugated carbonyl at 1734 cm<sup>-1</sup> and a hydroxyl group at 3411 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum exhibited the resonances of a chelated hydroxyl group 1-OH at  $\delta$  12.48 (s) and of olefinic proton H-8 at  $\delta$  7.44 (d) which was nearby the carbonyl group. The resonances of aromatic protons at  $\delta$  6.12 and 6.06 with J = 2.0 Hz corresponded to H-4 and H-2, respectively. The caged-prenylated xanthone structure was indicated from the resonances of two groups of methyl proton H-13 ( $\delta$  1.71, s) and H-14 ( $\delta$  1.32, s), a methine proton H-11 at  $\delta$  2.49 (d, d = 9.6 Hz) and non-equivalent methylene protons H<sub>a</sub>-10 and H<sub>b</sub>-10 at  $\delta$  2.37 (dd, d = 13.5 Hz, 4.0 Hz) and 1.33 (d m). The proton H-7, which was coupled to H<sub>a</sub>-10 and H-8 was resonated at  $\delta$  3.53 with the coupling constants of 4.0 and 7.0 Hz. The presence of a characteristic signal of a

prenyl unit was indicated from the signals at  $\delta$  4.43 (*br t*, J = 7.5 Hz, H-16), 2.64 (*d*, J = 7.5 Hz, H-15), 1.41 (*s*, H-18) and 1.12 (*s*, H-19). These spectral data and m.p. corresponded to those of cratoxycochinchinone A, which was previously isolated from this plant (Nuangnaowarat, W., 2005).

Table 14 NMR spectral data of PS8

| Position | PS8   | Cratoxycochinchinone A                        |
|----------|---|---|
| 2        | 6.06 (d, J = 2.0  Hz, 1H)                     | 6.06 (d, J = 2.0  Hz, 1H)                     |
| 4        | 6.08 (d, J = 2.0  Hz, 1H)                     | 6.12 (d, J = 2.0  Hz, 1H)                     |
| 7        | 3.53 (dd, J = 7.0, 4.0  Hz, 1H)               | 3.53 (dd, J = 7.0, 4.0  Hz, 1H)               |
| 8        | 7.44 (d, J = 7.0  Hz, 1H)                     | 7.44 (d, J = 7.0  Hz, 1H)                     |
| 10       | $2.37 (dd, J = 13.5, 4.0 \text{ Hz}, H_a-10)$ | $2.36 (dd, J = 13.5, 4.0 \text{ Hz}, H_a-10)$ |
|          | 1.33 ( <i>m</i> , 1H, H <sub>b</sub> -10)     | 1.33 ( <i>m</i> , 1H, H <sub>b</sub> -10)     |
| 11       | 2.49 (d, J = 9.6  Hz, 1H)                     | 2.48 (d, J = 9.6  Hz, 1H)                     |
| 13       | 1.71 (s, 3H)                                  | 1.71 (s, 3H)                                  |
| 14       | 1.32 (s, 3H)                                  | 1.32 (s, 3H)                                  |
| 15       | 2.64 (d, J = 7.5  Hz, 2H)                     | 2.64 (d, J = 7.5  Hz, 2H)                     |
| 16       | 4.43 (br t, J = 7.5 Hz, 1H)                   | 4.44 (br t, J = 7.5 Hz, 1H)                   |
| 18       | 1.41 (s, 3H)                                  | 1.41 (s, 3H)                                  |
| 19       | 1.12 (s, 3H)                                  | 1.12 (s, 3H)                                  |
| 1-OH     | 12.48 (s, OH)                                 | 12.48 (s, OH)                                 |
|          |   |   |

### **PS9**: Cratoxycochinchinone C

**PS9** is a yellow solid, m.p. 147-148 °C,  $[\alpha]_D^{29} = +98^\circ$  (c  $1.0 \times 10^{-2}$  g/cm<sup>-3</sup> in CHCl<sub>3</sub>). In the <sup>1</sup>H NMR spectrum, the presence of a resonance at  $\delta$  12.00 suggested a hydroxyl proton which formed a hydrogen bond to a carbonyl group. The signal at  $\delta$  3.64 belonged to a methoxyl group which was assigned at C-7. The ABM pattern in aromatic proton region,  $\delta$  6.54 (dd, J = 8.4 and 1.0 Hz), 7.41 (t, J = 8.4 Hz) and 6.51 (dd, J = 8.4 Hz and 1.0 Hz) corresponded to H-2, H-3 and H-4, respectively. The singlet resonance of olefinic proton H-8 ( $\delta$  7.51) and two doublet of doublet signals ( $\delta$  1.59 and 2.38) of non-equivalent methylene protons H<sub>b</sub>-10 and H<sub>a</sub>-10 revealed the quarternary carbon at C-7. The presence of a prenyl unit was identified from two singlet signals of *gem*-dimethyl protons H-18 and H-19 at  $\delta$  1.37 and 1.01, a broad triplet of olefinic proton H-16 at  $\delta$  4.40 and a doublet of allylic methylene protons 2H-15 at  $\delta$  2.64. Its physical and spectral data were in agreement with those of cratoxycochinchinone C which was previously isolated from the roots of this plant (Mahausarakam, *et al.*, 2006).

Table 15 NMR spectral data of PS9

| Position           | PS9   | Cratoxycochinchinone C                                    |
|--------------------|---|---|
| 2                  | 6.54 (dd, J = 8.4, 1.0  Hz, 1H)                           | 6.55 ( <i>dd</i> , <i>J</i> = 8.4, 0.9 Hz, 1H)            |
| 3                  | 7.41 (t, J = 8.4  Hz, 1H)                                 | 7.41 (t, J = 8.4  Hz, 1H)                                 |
| 4                  | 6.51 (dd, J = 8.4, 1.0  Hz, 1H)                           | 6.52 (dd, J = 8.4, 0.9  Hz, 1H)                           |
| 8                  | 7.51 (s, 1H)  | 7.51 (s, 1H)  |
| 10a                | 2.38 ( $d$ , $J$ = 12.9 Hz, H <sub>a</sub> -10, 1H)       | $2.39 (d, J = 12.9 \text{ Hz}, H_a-10, 1\text{H})$        |
|                    | 1.59 ( $dd$ , $J = 12.9$ , 9.9 Hz, H <sub>b</sub> -10,1H) | 1.59 ( $dd$ , $J = 12.9$ , 9.9 Hz, H <sub>b</sub> -10,1H) |
| 13                 | 1.68 (s, 3H)  | 1.69 (s, 3H)  |
| 14                 | 1.32 (s, 3H)  | 1.33 (s, 3H)  |
| 15                 | 2.64 (d, J = 8.1  Hz, 2H)                                 | 2.64 (d, J = 8.1  Hz, 2H)                                 |
| 16                 | 4.40 (br t, J = 8.1  Hz, 1H)                              | 4.39 (br t, J = 8.1  Hz, 1H)                              |
| 18                 | 1.37 (s, 3H)  | 1.37 (s, 3H)  |
| 19                 | 1.01 (s, 3H)  | 1.01 (s, 3H)  |
| 1-OH               | 12.00 (s, OH)   | 12.00 (s, OH)   |
| 7-OCH <sub>3</sub> | 3.64 (s, 3H)  | 3.65 (s, 3H)  |

PS10: 1,3,6-Trihydroxy-7-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone (Mangostin)

**PS10** is a yellow solid, m.p. 180-182°C. The <sup>1</sup>H NMR spectrum exhibited a resonance of a chelated hydroxyl group 1-OH at  $\delta$  13.80 (s), a methoxyl group at  $\delta$  3.81 (s), aromatic H-4 at  $\delta$  6.27 (s) and H-5 at  $\delta$  6.82 (s). The methoxyl group was located at C-7. Two sets of characteristic signals of two prenyl groups were displayed at  $\delta$  5.27 (H-2' and H-2", br t), 3.44 (H-1', d), 4.10 (H-1", d), 1.85 (H-4', s),

1.82 (H-4", s), 1.78 (H-5', s) and 1.70 (H-5", s). Since the chemical shift of methylene protons of a prenyl side chain H-1" ( $\delta$  4.10) was at a lower field than that of methylene protons H-1' ( $\delta$  3.44), one prenyl group was then proposed at C-8 and another was located at C-2. The proposed structure of **PS10** was 1,3,6-trihydroxy-7-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone. The spectral data and melting point corresponded to those of mangostin (Mahabusarakam,  $et\ al.$ , 1987).

 Table 16
 NMR spectral data of PS10

| Position           | PS10                         | Mangostin                    |
|--------------------|------------------------------|------------------------------|
| 4                  | 6.27 (s, 1H)                 | 6.28 (s, 1H)                 |
| 5                  | 6.82 (s, 1H)                 | 6.82 (s, 1H)                 |
| 1'                 | 3.44 (d, J = 7.0  Hz, 2H)    | 3.45 (d, J = 7.0  Hz, 2H)    |
| 2'                 | 5.27 (br t, J = 7.0  Hz, 1H) | 5.28 (t, J = 7.0  Hz, 1H)    |
| 4′                 | 1.85 (s, 3H)                 | 1.85 (s, 3H)                 |
| 5′                 | 1.78 (s, 3H)                 | 1.78 (s, 3H)                 |
| 1''                | 4.10 (d, J = 7.0  Hz, 2H)    | 4.11 (d, J = 7.0  Hz, 2H)    |
| 2''                | 5.27 (br t, J = 7.0  Hz, 1H) | 5.28 (br t, J = 7.0  Hz, 1H) |
| 4''                | 1.82 (s, 3H)                 | 1.82 (s, 3H)                 |
| 5''                | 1.70 (s, 3H)                 | 1.70 (s, 3H)                 |
| 1-OH               | 13.80 (s, OH)                | 13.80 (s, OH)                |
| 3-ОН               | 6.15 (s, OH)                 | 6.16 (s, OH)                 |
| 6-OH               | 6.30 (s, OH)                 | 6.31 (s, OH)                 |
| 7-OCH <sub>3</sub> | 3.81 (s, 3H)                 | 3.81 (s, 3H)                 |

# PS11: 1,5,6-Trihydroxy-3-methoxy-4-(1,1-dimethyl-2-propenyl)xanthone (Isocudraniaxanthone B)

PS11 was a yellow solid, m.p. 226-228 °C. The UV spectrum showed maximum absorption bands at 204, 237, 253, 287 and 328. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1647 cm<sup>-1</sup> and a hydroxyl group at 3417 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed signals for a hydrogen-bonded hydroxyl group at  $\delta$  13.35 (s), an aromatic proton H-2 at  $\delta$  6.40 (s) and two ortho aromatic protons H-7 ( $\delta$ 6.95, d, J = 8.7 Hz) and H-8 ( $\delta$ 7.69, d, J = 8.7 Hz). H-8 was assigned to a low field chemical shift and from HMBC correlations of H-8 to C-6 and C-9; H-7 to C-5, C-6 and C-8a. The signals of two singlets of gem-dimethyl protons at  $\delta$  1.61 (H-2') and  $\delta$  1.61 (H-3'), an olefinic proton at  $\delta$  6.70 (H-4') and terminal olefinic methylene protons at  $\delta$  5.03 (H-5'Z) and 5.21 (H-5'E) were characteristic signals of an isoprenyl unit. The enhancement of H-2', H-3' and H-2 upon irradiation at 3-OCH<sub>3</sub> suggested that the isoprenyl was at C-4. The <sup>13</sup>C NMR spectrum and DEPT experiments signified the presence of a carbonyl carbon ( $\delta$  180.8), two methyl carbons ( $\delta$  27.8), a methylene carbon ( $\delta$  103.2), four methine carbons ( $\delta$  95.6, 112.6, 117.5 and 156.9). PS11 was indicated as isocudraniaxanthone B (Hay, A.-E. et al., 2004).

NOE of PS11

Major HMBC of PS11

 Table 17
 NMR spectral data of PS11

| 1 162.4 (C)  | Position           | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity)                        | HMBC                  |
|--|--------------------|----------------------------|--|-----------------------|
| 3 165.2 (C) C-3 3-OCH <sub>3</sub> 55.7 (CH <sub>3</sub> ) 3.89 (s, 1H) C-3 4 113 (C)                  | 1                  | 162.4 (C)                  | -  | -                     |
| 3-OCH <sub>3</sub> 55.7 (CH <sub>3</sub> ) 3.89 (s, 1H) C-3 4 113 (C)                                  | 2                  | 95.6 (CH)                  | 6.40 (s, 1H)                                       | C-1, C-2, C-3         |
| 4 113 (C)  | 3                  | 165.2 (C)                  | -  | -                     |
| 4a 154.0 (C) -   | 3-OCH <sub>3</sub> | 55.7 (CH <sub>3</sub> )    | 3.89 (s, 1H)                                       | C-3                   |
|  | 4                  | 113 (C)                    | -  | -                     |
| 5 131.0 (C) -  | 4a                 | 154.0 (C)                  | -  | -                     |
|  | 5                  | 131.0 (C)                  | -  | -                     |
| 6 149.1 (C)  | 6                  | 149.1 (C)                  | -  | -                     |
| 7 112.6 (CH) 6.95 ( $d$ , $J$ = 8.7 Hz, 1H) C-5, C-6, C-8a   | 7                  | 112.6 (CH)                 | 6.95 (d, J = 8.7  Hz, 1H)                          | C-5, C-6, C-8a        |
| 8 117.5 (CH) 7.69 ( $d$ , $J$ = 8.7 Hz, 1H) C-6, C-9   | 8                  | 117.5 (CH)                 | 7.69 (d, J = 8.7  Hz, 1H)                          | C-6, C-9              |
| 8a 113 (C)   | 8a                 | 113 (C)                    | -  | -                     |
| 9 180.8 (C=O) -  | 9                  | 180.8 (C=O)                | -  | -                     |
| 9a 103.0 (C) -   | 9a                 | 103.0 (C)                  | -  | -                     |
| 1' 41.5 (C) -  | 1′                 | 41.5 (C)                   | -  | -                     |
| 2' 27.8 (CH <sub>3</sub> ) 1.61 (s, 3H) C-1', C-4, C-4'  | 2'                 | 27.8 (CH <sub>3</sub> )    | 1.61 (s, 3H)                                       | C-1', C-4, C-4'       |
| 3' 27.8 (CH <sub>3</sub> ) 1.61 (s, 3H) C-1', C-4, C-4'  | 3′                 | 27.8 (CH <sub>3</sub> )    | 1.61 (s, 3H)                                       | C-1', C-4, C-4'       |
| 4' 156.8 (CH) 6.70 (dd, J = 17.7 Hz, 10.5 Hz, 1H) C-1', C-2', C-3', C-                                 | 4′                 | 156.8 (CH)                 | 6.70 (dd, J = 17.7  Hz, 10.5  Hz, 1H)              | C-1', C-2', C-3', C-4 |
| 5'Z $103.2 \text{ (CH}_2)$ $5.03 \text{ (dd, } J = 10.5 \text{ Hz, } 1.5 \text{ Hz, } 1\text{H})$ C-1' | 5'Z                | 103.2 (CH <sub>2</sub> )   | 5.03 (dd, J = 10.5  Hz, 1.5  Hz, 1H)               | C-1'                  |
| 5'E 103.2 (CH <sub>2</sub> ) 5.21 ( <i>dd</i> , <i>J</i> = 17.7 Hz, 1.5 Hz, 1H) C-1', C-4'             | 5'E                | 103.2 (CH <sub>2</sub> )   | 5.21 ( <i>dd</i> , <i>J</i> = 17.7 Hz, 1.5 Hz, 1H) | C-1', C-4'            |
| 1-OH - 13.35 (s, OH) -   | 1-OH               | _                          | 13.35 (s, OH)                                      | -                     |
| 3-OCH <sub>3</sub> 55.7 (CH <sub>3</sub> ) 3.89 (s, 1H) C-3  | 3-OCH <sub>3</sub> | 55.7 (CH <sub>3</sub> )    | 3.89 (s, 1H)                                       | C-3                   |

PS12: 1,5,6-Trihydroxy-7-methoxy-8-(3-methyl-2-butenyl)xanthone (Celebixanthone)

**PS12** is a yellow solid, m.p. 219-220 °C. The <sup>1</sup>H NMR spectrum exhibited a signal of a hydrogen-bonded hydroxyl function at  $\delta$  13.25. The ABM pattern in aromatic region,  $\delta$  7.49 (t), 6.72 (dd) and 6.99 (dd), were proposed for H-3, H-2 and H-4, respectively. A sharp singlet signal with three protons at  $\delta$  3.83 was the signal of a methoxyl group at C-7. The signals of a prenyl side chain were assigned from the signals of an olefinic proton at  $\delta$  5.25 (br t, J = 6.3 Hz, H-2'), benzylic methylene protons at  $\delta$  4.05 (d, J = 6.3 Hz, H-1') and two methyl groups at  $\delta$  1.68 (s) and 1.84 (s). Due to the low field chemical shift of methylene protons H-1', the prenyl group then was placed nearby the carbonyl group. These assignment indicated that **PS12** was 1,5,6-trihydroxy-7-methoxy-8-(3-methyl-2-butenyl)xanthone. The spectral data and melting point was corresponded to those of celebixanthone (Nuangnaowarat, W., 2005).

Table 18 NMR spectral data of PS12

| Position           | PS12                                | Celebixanthone                                    |
|--------------------|-------------------------------------|---|
| 2                  | 6.72 (dd, J = 8.4  Hz, 1.5  Hz, 1H) | 6.91 ( <i>dd</i> , <i>J</i> = 8.4 Hz, 1.5 Hz, 1H) |
| 3                  | 7.49 (t, J = 8.4  Hz, 1H)           | 7.51 (t, J = 8.4  Hz, 1H)                         |
| 4                  | 6.99 (dd, J = 8.4, 1.5  Hz, 1H)     | 6.75 (dd, J = 8.4, 1.5  Hz, 1H)                   |
| 1′                 | 4.05 (d, J = 6.3  Hz, 2H)           | 4.04 (d, J = 6.3  Hz, 2H)                         |
| 2′                 | 5.25 (t, J = 6.3  Hz, 3H)           | 5.24 (t, J = 6.3  Hz, 3H)                         |
| 4′                 | 1.84 (s, 3H)                        | 1.84 (s, 3H)                                      |
| 5′                 | 1.68 (s, 3H)                        | 1.69 (s, 3H)                                      |
| 1-OH               | 13.25 (s, OH)                       | 13.19 (s, OH)                                     |
| 7-OCH <sub>3</sub> | 3.83 (s, 3H)                        | 3.84 (s, 3H)                                      |

PS13Ac: 1- Hydroxy-2- (3-methyl-2-butenyl)-8- (3,7-dimethyl-2,6-octadienyl)-3,7-diacetoxyx anthone

1-Hydroxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)-

3,7-diacetoxyxanthone was a yellow solid, mp. 128-129 °C. Its molecular formula of  $C_{32}H_{36}O_7$  was established on the basis of mass spectrum, EI-MS ([M]<sup>+</sup> m/z 532.2461). The UV spectrum showed maximum absorption bands at 204, 233, 257, 288, 309 and 369. The IR spectrum showed the absorption bands of carbonyl groups at 1779, and 1636 cm<sup>-1</sup> and a hydroxyl group at 3411 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum (**Table 19**) indicated the presence of a hydrogen-bonded hydroxyl group 1-OH at  $\delta$  13.39 (s) and an isolated aromatic proton H-4 at  $\delta$  6.67 (s). The signals of an AB system at  $\delta$  7.38

(*d*) and 7.30 (*d*) with an *ortho* coupling constant (9.3 Hz) belonged to H-6 and H-5. A prenyl unit was detected from the characteristic signals at  $\delta$  3.32 (*d*, H-1'), 5.15 (*br t*, H-2'), 1.78 (*s*, H-4'), and 1.69 (*s*, H-5'), whereas a geranyl group was observed from the proton resonances at  $\delta$  4.05 (*d*, H-1"), 5.15 (*br t*, H-2"), 1.97 (*m*, H-4"), 2.01 (*m*, H-5"), 5.05 (*br t*, H-6"), 1.55 (*s*, H-8"), 1.81 (*s*, H-9") and 1.61 (*s*, H-10"). The prenyl group was assigned at C-2 based on the HMBC correlation of H-1' to C-1, C-2 and C-3 and the differential NOE technique by irradiation of the signal of H-1' which affected a chelated hydroxyl group whereas the geranyl group was placed at C-8 due to the low field chemical shift of H-1" and which was confirmed by the correlation of H-1" to C-7, C-8 and C-8a. Two acetyl groups were established from the proton resonances at  $\delta$  2.39 (*s*, 6H) and carbon resonances at  $\delta$  20.9 (3-(C=O)CH<sub>3</sub>) and 21.0 (7-(C=O)CH<sub>3</sub>). In the <sup>13</sup>C NMR spectrum, three carbonyl groups appeared at  $\delta$  180.5 (C-9), 168.5 (3-(C=O)CH<sub>3</sub>) and 169.5 (7-(C=O)CH<sub>3</sub>). The structure of **PS13Ac** was therefore assigned as 1-hydroxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)-3,7-diacetoxyxanthone.

NOE of PS13Ac

Major HMBC of PS13Ac

Table 19 NMR spectral data of PS13Ac

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity)  | HMBC                       |
|----------|-------------------------------|------------------------------|----------------------------|
| 1        | 161.0 (C)                     | -                            | -                          |
| 2        | 116.2 (C)                     | -                            | -                          |
| 3        | 155.3 (C)                     | -                            | -                          |
| 4        | 100.4 (CH)                    | 6.67 (s, 1H)                 | C-2, C-4a, C-9, C-9a       |
| 4a       | 153.7 (C)                     | -                            | -                          |
| 4b       | 155.1 (C)                     | -                            | -                          |
| 5        | 116.7 (CH)                    | 7.30 (d, J = 9.3  Hz, 1H)    | C-7, C-8a, C-9             |
| 6        | 129.9 (CH)                    | 7.38 (d, J = 9.3  Hz, 1H)    | C-4b, C-8                  |
| 7        | 145.0 (C)                     | -                            | -                          |
| 8        | 136.0 (C)                     | -                            | -                          |
| 8a       | 118.9 (C)                     | -                            | -                          |
| 9        | 183.4 (C=O)                   | -                            | -                          |
| 9a       | 107.2 (C)                     | -                            | -                          |
| 1′       | 22.3 (CH <sub>2</sub> )       | 3.32 (d, J = 7.0, 2H)        | C-1, C-2, C-2', C-3'       |
| 2'       | 121.3 (CH)                    | 5.15 (br t, J = 7.0, 1H)     | -                          |
| 3′       | 131.3 (C)                     | -                            | -                          |
| 4′       | 25.6 (CH <sub>3</sub> )       | 1.78 (s, 3H)                 | C-2', C-3', C-5'           |
| 5′       | 17.7 (CH <sub>3</sub> )       | 1.69 (s, 3H)                 | C-2', C-3', C-4'           |
| 1''      | 39.7 (CH <sub>2</sub> )       | 4.05 (d, J = 7.0, 2H)        | C-7, C-8, C-8a, C-2", C-3" |
| 2''      | 121.6 (CH)                    | 5.15 (br t, J = 7.0  Hz, 1H) | C-4", C-9"                 |
| 3''      | 136.0 (C)                     | -                            | -                          |
| 4''      | 26.4 (CH <sub>2</sub> )       | 1.97 (m, 2H)                 | C-2", C-3", C-5"           |
| 5''      | 26.6 (CH <sub>2</sub> )       | 2.01 (m, 2H)                 | C-3", C-4", C-6"           |
| 6''      | 124.2 (CH)                    | 5.05 (br t, J = 7.0, 1H)     | C-5", C-10"                |
| 7''      | 132.3 (C)                     | -                            | -                          |
| 8''      | 17.8 (CH <sub>3</sub> )       | 1.55 (s, 3H)                 | C-6", C-7", C-10"          |
| 9''      | 16.5 (CH <sub>3</sub> )       | 1.81 (s, 3H)                 | C-2", C-3", C-4"           |
| 10''     | 25.7 (CH <sub>3</sub> )       | 1.61 (s, 3H)                 | C-6", C-7", C-8"           |
| 1-OH     | -                             | 13.39 (s, 1H)                | C-1, C-3, C-9a             |
| 3-C=O    | 168.5 (C=O)                   | -                            | -                          |
|          | I                             | 1                            | 1                          |

 Table 19 (continued)

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | HMBC |
|----------|-------------------------------|-----------------------------|------|
| 3-OAc    | 20.9 (CH <sub>3</sub> )       | 2.39 (s, 3H)                | -    |
| 7-C=O    | 169.5 (C=O)                   | -                           | -    |
| 7-OAc    | 21.0 (CH <sub>3</sub> )       | 2.39 (s, 3H)                | -    |

PS14: 1,3,6-Trihydroxy-7-methoxy-2,4-bis(3-methyl-2-butenyl)xanthone

**PS14** is a yellow solid. The UV spectrum showed maximum absorption bands at 235, 255, 265, 314, 344 and 413. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1625 cm<sup>-1</sup> and a hydroxyl group at 3422 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed a singlet signal of a deshielded proton 1-OH at  $\delta$  13.27. Two singlet aromatic protons at  $\delta$  7.59 and 6.96 were assigned for H-8 and H-5, respectively. The assignment of H-8 was confirmed by HMBC correlation of H-8 to C-4b, C-6, C-7 and C-9 whereas H-5 was proved by the correlation of H-5 to C-4b, C-6, C-7 and C-8a. The presence of a characteristic signal of two prenyl units was shown at  $\delta$  3.47 (d, J = 7.2 Hz, H-1'), 3.53 (d, J = 7.2 Hz, H-1"), 5.28 (m, J = 7.2 Hz, H-2', H-2"), 1.73 (s, H-4'), 1.77 (s, H-4"), 1.85 (s, H-5') and 1.88 (s, H-5"). The location of prenyl groups at C-2 and C-4 were supported by HMBC correlations of H-1' to C-1, C-2, C-3 and H-1" to C-3, C-4, C-4a. The <sup>13</sup>C NMR spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms: a carbonyl carbon ( $\delta$  180.3), a methoxyl carbon ( $\delta$  56.5), four

methyl carbons ( $\delta$  25.8, 25.8, 17.9 and 17.9), two methylene carbons ( $\delta$  21.8 and 21.6), four methine carbons ( $\delta$  102.5, 104.6, 121.6 and 121.8) and ten quarternary carbons ( $\delta$  158.1, 110.2, 160.2, 108.8, 155.7, 152.4, 152.6, 144.2, 113.2 and 103.0). Therefore **PS14** was assigned to be 1,3,6-trihydroxy-7-methoxy-2,4-bis(3-methyl-2-butenyl)xanthone.

Major HMBC of PS14

Table 20 NMR spectral data of PS14

| Position | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity) | HMBC                      |
|----------|----------------------------|-----------------------------|---------------------------|
| 1        | 158.1 (C)                  | -                           | -                         |
| 2        | 110.2 (C)                  | -                           | -                         |
| 3        | 160.2 (C)                  | -                           | -                         |
| 4        | 108.8 (C)                  | -                           | -                         |
| 4a       | 155.7 (C)                  | -                           | -                         |
| 4b       | 152.6 (C)                  | -                           | -                         |
| 5        | 102.5 (CH)                 | 6.96 (s, 1H)                | C-4b, C-6, C-7, C-8a      |
| 6        | 152.7 (C)                  | -                           | -                         |
| 7        | 144.2 (C)                  | -                           | -                         |
| 8        | 104.6 (CH)                 | 7.59 (s, 1H)                | C-4b, C-6, C-7, C-9       |
| 8a       | 113.2 (C)                  | -                           | -                         |
| 9        | 180.3 (C=O)                | -                           | -                         |
| 9a       | 103.0 (C)                  | -                           | -                         |
| 1'       | 21.6 (CH <sub>2</sub> )    | 3.47 (d, J = 7.2  Hz, 2H)   | C-1, C-2, C-3, C-2', C-3' |
| 2'       | 121.6 (CH)                 | 5.28 (m, 1H)                | -                         |

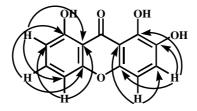
Table 20 (continued)

| Position           | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity) | НМВС                       |
|--------------------|----------------------------|-----------------------------|----------------------------|
| 3′                 | 135.2 (C)                  | -                           | -                          |
| 4′                 | 25.8 (CH <sub>3</sub> )    | 1.73 (s, 3H)                | C-2', C-3', C-5'           |
| 5′                 | 17.9 (CH <sub>3</sub> )    | 1.85 (s, 3H)                | C-2', C-3', C-4'           |
| 1''                | 21.8 (CH <sub>2</sub> )    | 3.53 (d, J = 7.2  Hz, 2H)   | C-3, C-4, C-4a, C-2", C-3" |
| 2''                | 121.8 (CH)                 | 5.28 (m, 1H)                | -                          |
| 3"                 | 133.6 (C)                  | -                           | -                          |
| 4''                | 25.8 (CH <sub>3</sub> )    | 1.77 (s, 3H)                | C-2", C-3", C-5"           |
| 5''                | 17.9 (CH <sub>3</sub> )    | 1.88 (s, 3H)                | C-2", C-3", C-4"           |
| 1-OH               | -                          | 13.27 (s, 1H)               | -                          |
| 7-OCH <sub>3</sub> | 56.5 (CH <sub>3</sub> )    | 4.01 (s, 3H)                | C-7                        |

### PS15: 1,2,8-Trihydroxyxanthone

**PS15** is a yellow solid, m.p. 248-250 °C. The UV spectrum showed maximum absorption bands at 203, 230, 255, 265, 312, 343 and 411. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1627 cm<sup>-1</sup> and a hydroxyl group at 3411 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed two sharp singlet signals of the chelated hydroxyl protons (1-OH and 8-OH) at  $\delta$  11.19 and 11.96, respectively. The ABM pattern in the aromatic region at  $\delta$ 7.04 (d, J = 8.0 Hz), 7.62 (t, J = 8.0 Hz), and 6.79 (d, J = 8.0 Hz) was proposed for the characteristic signals of H-5, H-6 and H-7, respectively. Protons H-5, H-6 and H-7 were confirmed by the cross peaks in the HMBC correlations of H-7 to C-8, C-8a, C-5; H-6 to C-8, C-4b and H-5 to C-7, C-4b, C-8a. Two doublet signals at  $\delta$  7.32 and 6.66 with an *ortho* coupling constant (J = 9.5 Hz) were observed and were assigned for aromatic protons

H-3 and H-4. The HMBC correlations of H-3 to C-4a, C-2, C-1 and of H-4 to C-3, C-1, C-9a supported the assignment of H-3 and H-4, respectively. The  $^{13}$ C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon ( $\delta$  186.3), five methine carbons ( $\delta$  110.6, 137.3, 107.3, 124.4 and 109.5) and seven quaternary carbons ( $\delta$  161.3, 156.2, 143.8, 137.1, 153.2, 107.8 and 108.0). **PS15** was identified as 1,2,8-trihydroxyxanthone (Wenkui, L., *et al.* 1999).



Major HMBC of PS15

 Table 21
 NMR spectral data of PS15

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | НМВС            |
|----------|-------------------------------|-----------------------------|-----------------|
| 1        | 153.2 (C)                     | -                           | -               |
| 2        | 137.1 (C)                     | -                           | -               |
| 3        | 124.4 (CH)                    | 7.32 (d, J = 9.5  Hz, 1H)   | C-1, C-2, C-4a  |
| 4        | 109.5 (CH)                    | 6.66 (d, J = 9.5  Hz, 1H)   | C-1, C-3, C-9a  |
| 4a       | 143.8 (C)                     | -                           | -               |
| 4b       | 156.2 (C)                     | -                           | -               |
| 5        | 107.3 (CH)                    | 7.04 (d, J = 8.0 Hz, 1H)    | C-4b, C-7, C-8a |
| 6        | 137.3 (CH)                    | 7.62 (t, J = 8.0  Hz, 1H)   | C-4b, C-8       |
| 7        | 110.6 (CH)                    | 6.79 (d, J = 8.0  Hz, 1H)   | C-5, C-8, C-8a  |
| 8        | 161.3 (C)                     | -                           | -               |
| 8a       | 108.0 (C)                     | -                           | -               |
| 9        | 186.3 (C=O)                   | -                           | -               |
| 9a       | 107.8 (C)                     | -                           | -               |
| 1-OH     | -                             | 11.19 (s, 1-OH)             | -               |
| 8-OH     | -                             | 11.96 (s, 1-OH)             | -               |

PS16: 1,3,6,7-Tetrahydroxy-2,4-bis (3-methyl-2-butenyl)xanthone (Cudratricusxanthone E)

**PS16** is a yellow solid, m.p. 228-229 °C. The UV spectrum showed maximum absorption bands at 204, 230, 261, 320 and 377. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1636 cm<sup>-1</sup> and a hydroxyl group at 3142 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed a singlet signal of a chelated hydroxyl proton (1-OH,  $\delta$  13.34). The appearance of two singlet signals at  $\delta$  6.83 and 7.52 were assigned for aromatic protons H-5 and H-8. The assignment of H-5 was confirmed by the HMBC correlation of H-5 to C-6, C-7, C-8a and C-9 whereas H-8 was proved by the correlation of H-8 to C-6, C-7 and C-9. The remaining signals were assigned for two prenyl units. The signals of two singlets of gem-dimethyl protons H-4' ( $\delta$  1.62) and H-5' ( $\delta$  1.78), a triplet of olefinic protons H-2' ( $\delta$  5.21) and a doublet of benzylic methylene protons H-1' ( $\delta$  3.35) were assigned for the prenyl unit at C-2. The HMBC correlation of H-1' to C-1, C-2, C-3, C-2', C-3' confirmed that the prenyl side chain was at C-2. Two singlet signals of gem-dimethyl protons H-4"  $(\delta 1.66)$  and H-5"  $(\delta 1.84)$ , a triplet of olefinic proton H-2"  $(\delta 5.21)$  and a doublet of benzylic methylene protons H-1" ( $\delta$  3.45) were assigned for the prenyl unit. The evidence from the HMBC correlation of H-1" to C-4, C-4a, C-2" and C-3" indicated that the prenyl side chain was at C-4. The <sup>13</sup>C NMR spectral data deduced from DEPT and HMQC spectra showed 23 signals for 23 carbon atoms: a carbonyl carbon ( $\delta$  180.2), four methyl carbons ( $\delta$  25.7 x 2, 17.9 and 17.8), two methylene carbons ( $\delta$ 21.8 and 21.5), four methine carbons ( $\delta$ 121.9, 122.1, 102.6 and 108.6) and twelve quarternary carbons ( $\delta$  159.7, 158.0, 152.9, 152.7, 151.7, 142.5, 133.8, 132.7, 112.9, 108.9, 105.2 and 102.8). 1,3,6,7-Tetrahydroxy-2,4-bis(3-methyl-2-butenyl)xanthone

then was assigned for **PS16**. The spectral data and the melting point corresponded to those of cudratricus anthone E (Zou *et al.*, 2004).

Major HMBC of PS16

Table 22 NMR spectral data of PS16

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity) | НМВС                      |
|----------|-------------------------------|-----------------------------|---------------------------|
| 1        | 159.7 (C)                     | -                           | -                         |
| 2        | 105.2 (C)                     | -                           | -                         |
| 3        | 142.5 (C)                     | -                           | -                         |
| 4        | 108.6 (C)                     | -                           | -                         |
| 4a       | 158.0 (C)                     | -                           | -                         |
| 4b       | 151.7 (C)                     | -                           | -                         |
| 5        | 102.6 (CH)                    | 6.83 (s, 1H)                | C-6, C-7, C-8a, C-9       |
| 6        | 152.7 (C)                     | -                           | -                         |
| 7        | 142.5 (C)                     | -                           | -                         |
| 8        | 108.6 (CH)                    | 7.52 (s, 1H)                | C-6, C-7, C-9             |
| 8a       | 112.9 (C)                     | -                           | -                         |
| 9        | 180.3 (C=O)                   | -                           | -                         |
| 9a       | 102.8 (C)                     | -                           | -                         |
| 1'       | 21.5(CH <sub>2</sub> )        | 3.35 (d, J = 9.9  Hz, 2H)   | C-1, C-2, C-3, C-2', C-3' |
| 2'       | 121.9 (CH)                    | 5.21 (t, J = 9.9  Hz, 1H)   | C-1', C-5'                |
| 3′       | 132.7 (C)                     | -                           | -                         |
| 4′       | 25.7 (CH <sub>3</sub> )       | 1.62 (s, 3H)                | C-1', C-2', C-3'          |
| 5′       | 17.8 (CH <sub>3</sub> )       | 1.78 (s, 3H)                | C-1', C-2', C-3'          |

 Table 22 (continued)

| Position | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity) | НМВС                  |
|----------|----------------------------|-----------------------------|-----------------------|
| 1''      | 21.8 (CH <sub>2</sub> )    | 3.45 (d, J = 9.9  Hz, 2H)   | C-4a, C-4, C-2", C-3" |
| 2''      | 122.1 (CH)                 | 5.21 (t, J = 9.9  Hz, 1H)   | C-1", C-4", C-5"      |
| 3''      | 133.8 (C)                  | -                           | -                     |
| 4''      | 25.7 (CH <sub>3</sub> )    | 1.66 (s, 3H)                | C-1", C-2", C-3"      |
| 5''      | 17.9 (CH <sub>3</sub> )    | 1.84 (s, 3H)                | C-1", C-2", C-3"      |
| 1-OH     | -                          | 13.34 (s, 1-OH)             | -                     |

PS17: 1,3,6,7-Tetrahydroxy-2,8-bis (3-methyl-2-butenyl)xanthone (7-Mangostin)

**PS17** was a yellow solid. The <sup>1</sup>H NMR spectrum showed signals for two aromatic protons H-4 and H-5 at  $\delta$  6.78 (s) and 6.30 (s). The assignment of H-4 and H-5 were supported by HMBC correlations of H-4 to C-2, C-3, C-4a, C-9a and H-5 to C-4b, C-6, C-7, C-8a. Two sets of characteristic signals of two prenyl groups were displayed at  $\delta$  5.28 (H-2' and H-2", br t),  $\delta$  3.40 (H-1', d), 4.18 (H-1", d), 1.87 (H-4', s), 1.82 (H-4", s), 1.72 x 2 (H-5' and H-5", s). Due to the low field chemical shift of methylene protons H-1" ( $\delta$  4.18), this prenyl group then was placed nearby the carbonyl group. Another one was located at C-2 according to the HMBC correlation of H-1' to C-1 and C-2. Thus **PS17** was assigned for 1,3,6,7-tetrahydroxy-2,8-bis(3-methyl-2-butenyl)xanthone, which was known γ-mangostin. as (Mahabusarakam, W., et al., 1987).

Major HMBC of **PS17** 

 Table 23
 NMR spectral data of PS17

| Position | δ <sub>H</sub> (multiplicity) | HMBC                  |
|----------|-------------------------------|-----------------------|
| 1        | -                             | -                     |
| 2        | -                             | -                     |
| 3        | -                             | -                     |
| 4        | 6.78 (s, 1H)                  | C-2, C-3, C-4a, C-9a  |
| 4a       | -                             | -                     |
| 4b       | -                             | -                     |
| 5        | 6.30 (s, 1H)                  | C-4b, C-6, C-7, C-8a  |
| 6        | -                             | -                     |
| 7        | -                             | -                     |
| 8        | -                             | -                     |
| 8a       | -                             | -                     |
| 9        | -                             | -                     |
| 9a       | -                             | -                     |
| 1′       | 3.40 (d, J = 7.8  Hz, 2H)     | C-1, C-2, C-2', C-3'  |
| 2'       | 5.28 ( <i>br t</i> , 1H)      | C-1', C-5'            |
| 3'       | -                             | -                     |
| 4'       | 1.87 (s, 3H)                  | C-1', C-2', C-3'      |
| 5′       | 1.72 (s, 3H)                  | C-1', C-2', C-3'      |
| 1''      | 4.18 (d, J = 7.8  Hz, 2H)     | C-7, C-8a, C-2", C-3" |
| 2''      | 5.28 (br t, 1H)               | C-1", C-4", C-5"      |

Table 23 (Continued)

| Position | $\delta_{H}$ (multiplicity) | НМВС             |
|----------|-----------------------------|------------------|
| 3"       | -                           | -                |
| 4''      | 1.82 (s, 3H)                | C-1", C-2", C-3" |
| 5''      | 1.72 (s, 3H)                | C-1", C-2", C-3" |
| 1-OH     | 13.89 (s, 1-OH)             | -                |

PS18: 1,3,6,7-Tetrahydroxy-5-(3-methyl-2-butenyl)xanthone

**PS18** was a yellow solid, m.p. 219 - 220 °C. The UV spectrum showed maximum absorption bands at 212, 237, 251, 284 and 329. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1650 cm<sup>-1</sup> and a hydroxyl group at 3400 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum showed two sets of doublets of *meta* aromatic protons at  $\delta$  6.47 (d, J = 2.0 Hz, H-2) and 6.29 (d, J = 2.0 Hz, H-4) and a singlet signal of an aromatic proton at  $\delta$  7.56 (s, H-8). The low field chemical shift of an isolated aromatic proton suggested that it was H-8. The HMBC correlation of H-8 to C-6, C-7 and C-9 was in agreement with the assignment of H-8. The presence of a characteristic signal of a prenyl unit was indicated by the signals at  $\delta$  3.40 (d, J = 7.0 Hz, H-1'), 5.37 (br t, J = 7.0 Hz, H-2'), 1.76 (s, H-4') and 1.73 (s, H-5'). The location of a prenyl group at C-5 was supported by HMBC correlation of H-1' to C-4b, C-5 and C-6. The DEPTQGPSP and HMBC spectra signified the presence of a carbonyl carbon ( $\delta$  180.4), two methyl carbons ( $\delta$  18.1 and 25.8), a methylene carbon ( $\delta$  28.4), four methine carbons ( $\delta$  94.2, 98.4, 116.5 and 121.3). **PS18** was then indicated as 1,3,6,7-tetrahydroxy-5-(3-methyl-2-butenyl)xanthone.

### Major HMBC of PS18

Table 24 NMR spectral data of PS18

| Position | $\delta_{\rm C}({ m C-Type})$ | $\delta_{H}$ (multiplicity)  | НМВС                |
|----------|-------------------------------|------------------------------|---------------------|
| 1        | 163.5 (C)                     | -                            | -                   |
| 2        | 97.5 (CH)                     | 6.47 (d, J = 2.0  Hz, 1H)    | C-1, C-3, C-4, C-9a |
| 3        | 163.5 (C)                     | -                            | -                   |
| 4        | 93.6 (CH)                     | 6.29 (d, J = 2.0  Hz, 1H)    | C-2, C-3, C-4a      |
| 4a       | 157.8 (C)                     | -                            | -                   |
| 4b       | 150.1 (C)                     | -                            | -                   |
| 5        | 115.2 (C)                     | -                            | -                   |
| 6        | 149.2 (C)                     | -                            | -                   |
| 7        | 145.0 (C)                     | -                            | -                   |
| 8        | 115.2 (CH)                    | 7.56 (s, 1H)                 | C-6, C-7, C-9       |
| 8a       | 112.5 (C)                     | -                            | -                   |
| 9        | 180.2 (C=O)                   | -                            | -                   |
| 9a       | 102.3 (C)                     | -                            | -                   |
| 1′       | 27.6 (CH <sub>2</sub> )       | 3.40 (d, J = 7.0  Hz, 2H)    | C-4b, C-5, C-6      |
| 2'       | 121.5 (CH)                    | 5.37 (br t, J = 7.0  Hz, 1H) |                     |
| 3'       | 133.1 (C)                     | -                            |                     |
| 4'       | 24.6 (CH <sub>3</sub> )       | 1.76 (s, 3H)                 | C-2', C-3'          |
| 5′       | 16.4 (CH <sub>3</sub> )       | 1.73 (s, 3H)                 | C-2', C-3'          |
| 1-OH     | -                             | 13.20 (s, 1H)                | -                   |

### **PS19: 1,3,6,7-Tetrahydroxyxanthone (Norathyriol)**

**PS19** was a yellow solid, m.p. 330-331 °C. The UV spectrum showed maximum absorption bands at 204, 237, 254, 269, 313 and 365. The IR spectrum showed the absorption bands of a conjugated carbonyl group at 1653 cm<sup>-1</sup> and a hydroxyl group at 3417 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum exhibited a singlet signal of a hydrogen-bonded hydroxyl proton 1-OH at  $\delta$  13.18 and an AM system of H-2 and H-4 at  $\delta$  6.23 (d, J = 2.7 Hz) and 6.37 (d, J = 2.7 Hz). The assignment of H-2 and H-4 were supported by HMBC correlations of H-2 to C-3, C-4, C-9a and H-4 to C-2, C-3, C-4a, C-9a. Two singlets in the aromatic region at  $\delta$  6.88 and 7.55 were assigned for H-5 and H-8, respectively. The correlations of H-5 to C-4b, C-6, C-7, C-8a and H-8 to C-4b, C-6 in the HMBC experiment confirmed the position of H-5 and H-8. The <sup>13</sup>C NMR spectral data deduced from DEPT and HMQC spectra showed thirteen signals for 13 carbon atoms: a carbonyl carbon ( $\delta$  179.6), four methine carbons  $(\delta 97.9, 93.5, 102.6 \text{ and } 108.6)$  and eight quaternary carbons  $(\delta 164.5, 163.0, 157.7,$ 153.1, 142.9,151.5, 112.8 and 102.3). The signals at  $\delta$  164.5, 163.0, 157.7, 153.1, 142.9 and 151.5 were assigned for oxygenated aromatic carbons C-1, C-3, C-4a, C-4b, C-6 and C-7, respectively. **PS19** was proposed to be 1,3,6,7-tetrahydroxy xanthone which corresponded to norathyriol (Don et al., 2004).

Major HMBC of PS19

Table 25 NMR spectral data of PS19

| Position | $\delta_{C}(C	ext{-Type})$ | $\delta_{H}$ (multiplicity) | НМВС                 |
|----------|----------------------------|-----------------------------|----------------------|
| 1        | 164.5 (C)                  | -                           | -                    |
| 2        | 97.9 (CH)                  | 6.23 (d, J = 2.7  Hz, 1H)   | C-9a, C-3, C-4       |
| 3        | 163.0 (C)                  | -                           | -                    |
| 4        | 93.5 (CH)                  | 6.37 (d, J = 2.7  Hz, 1H)   | C-2, C-3, C-4a, C-9a |
| 4a       | 157.7(C)                   | -                           | -                    |
| 4b       | 153.1 (C)                  | -                           | -                    |
| 5        | 102.6 (CH)                 | 6.88 (s, 1H)                | C-4b, C-6, C-7, C-8a |
| 6        | 142.9 (C)                  | -                           | -                    |
| 7        | 151.5 (C)                  | -                           | -                    |
| 8        | 108.6 (CH)                 | 7.55 (s, 1H)                | C-4b, C-6            |
| 8a       | 112.8 (C)                  | -                           | -                    |
| 9        | 179.6 (C)                  | -                           | -                    |
| 9a       | 102.3 (C)                  | -                           | -                    |
| 1-OH     | -                          | 13.18 (s, 1-OH)             | -                    |

### 3.2 Evaluation of Biological activities

### 3.2.1 Antibacterial activity

Dried twigs and fruits of *C. cochinchinense* were extracted with dichloromethane and acetone to give dichloromethane extract (DT) and acetone extract (AT) of the twigs, dichloromethane extract (DF) and acetone extract (AF) of the fruits. The dichloromethane extract (DR) and methanolic extract (MR) of the roots were obtained from the previous work. Each extract was tested for antibacterial activity on *Staphylococus aureus* ATCC25923, and methicillin-resistant strain MRSA SK1. It was found that the extracts from the twigs showed activity with MIC 80-160  $\mu$ g/mL, the extracts from the roots inhibited the growth of bacteria with MIC 64  $\mu$ g/mL whereas the extracts from the fruits showed no activity (**Table 26**).

**Table 26** Antibacterial activity of crude extracts from *C. cochinchinense* 

| Part of the |  | Antibacterial activity (MIC, μg/mL) |          |  |
|-------------|--|-------------------------------------|----------|--|
| Plant       | Fractions                                    | S. aureus<br>ATCC25923              | MRSA SK1 |  |
| Twigs       | Acetone extract (AT)                         | 80                                  | 80       |  |
|             | CH <sub>2</sub> Cl <sub>2</sub> extract (DT) | 160                                 | 80       |  |
| Fruits      | Acetone extract (AF)                         | 640                                 | _        |  |
|             | CH <sub>2</sub> Cl <sub>2</sub> extract (DF) | -                                   | -        |  |
| Roots       | CH <sub>2</sub> Cl <sub>2</sub> extract (DR) | 64                                  | 64       |  |
|             | MeOH extract (MR)                            | 64                                  | 64       |  |
|             | Vancomycin                                   | 1                                   | 1        |  |

<sup>\*(-)</sup> Inactive at > 1,280  $\mu$ g/mL

Some of the pure compounds obtained from each extract were evaluated for their antibacterial activity against *S. aureus* ATCC25923, and MRSA SK1. Xanthones **PS2**, **PS3**, **PS4**, **PS5**, **PS13** and **PS16** were less active than the crude extract. **PS8**, **PS18** and **PS19** showed the same activity as the crude extract. Whereas **PS1**, **PS9**, **PS10**, **PS11** and **PS12** were more active than the crude extract. Among the active compounds **PS10** showed the strongest inhibitory activity with a MIC value of 4  $\mu$ g/mL, however it was less active than vancomycin, the standard antibiotic (MIC 1  $\mu$ g/mL). **PS6-PS7**, **PS14-PS15** and **PS17** were not tested due to insufficient quantities.

**Table 27** Antibacterial activity of compounds isolated from *C. cochinchinense* 

|             | Antibacterial activity (MIC, μg/mL) |          |  |
|-------------|-------------------------------------|----------|--|
| Compound    | S. aureus<br>ATCC25923              | MRSA SK1 |  |
| PS1         | 32                                  | 16       |  |
| PS2         | -                                   | -        |  |
| PS3         | >128                                | 128      |  |
| PS4         | -                                   | -        |  |
| PS5         | -                                   | -        |  |
| PS8         | 64                                  | 64       |  |
| PS9         | 8                                   | -        |  |
| PS10        | 4                                   | 4        |  |
| PS11        | 16                                  | 16       |  |
| PS12        | 8                                   | 8        |  |
| PS13        | -                                   | -        |  |
| <b>PS16</b> | 128                                 | >128     |  |
| PS18        | 64                                  | ≤200     |  |
| PS19        | 64                                  | 64       |  |
| Vancomycin  | 1                                   | 1        |  |

<sup>\*(-)</sup> Inactive at > 200  $\mu$ g/mL

### 3.2.2 Cytotoxic activity

The stable compounds of sufficient quantity were further evaluated for cytotoxicity against MCF-7 (breast adenocarcinoma), HeLa (Human cervical cancer), HT-29 (colon cancer) and KB (human oral cancer) cell lines. According to the MIC values shown in **Table 28**. Compounds **PS3**, **PS4**, **PS8**, **PS10**, **PS11**, **PS12**, **PS16** and **PS19** were found to inhibit most cancer cell lines with IC<sub>50</sub> in the range of 0.2-3.54  $\mu$ g/mL, whereas **PS2**, **PS5**, **PS14+PS15** and **PS15** were found to be inactive for cytotoxic activity. The result indicated that **PS4** and **PS12** strongly inhibited all cancer cell lines with IC<sub>50</sub> in the range of 0.32-0.45  $\mu$ g/mL and 0.2  $\mu$ g/mL except for KB cell. The results were comparable to that of camptothecin (0.2-2.0  $\mu$ g/mL), anticancer drug.

**Table 28** Cytotoxic activity of compounds isolated from *C. cochinchinense* 

|              | Cytotoxic activity (IC <sub>50</sub> µg/mL) |                   |                |                      |  |
|--------------|---|-------------------|----------------|----------------------|--|
| Compound     | MCF-7                                       | Hela              | HT-29          | KB                   |  |
|              | (Breast cancer)                             | (Cervical cancer) | (Colon cancer) | (Oral cavity cancer) |  |
| PS2          | -   | -                 | -              | -                    |  |
| PS3          | >5  | >5                | >5             | >5                   |  |
| PS4          | 0.32  | 0.4               | 0.4            | 0.45                 |  |
| PS5          | -   | -                 | -              | -                    |  |
| PS8          | >5  | >5                | >5             | >5                   |  |
| PS10         | >5  | >5                | 2.1            | >5                   |  |
| PS11         | 3.54  | 3.3               | 3.42           | >5                   |  |
| <b>PS12</b>  | 0.2   | 0.2               | 0.2            | >5                   |  |
| PS14+PS15    | -   | -                 | -              | -                    |  |
| PS15         | -   | -                 | -              | -                    |  |
| <b>PS16</b>  | 3.45  | 1.1               | 3.34           | >5                   |  |
| <b>PS19</b>  | 3.67  | >5                | >5             | >5                   |  |
| Camptothecin | 0.2-2.0                                     | 0.2-2.0           | 0.2-2.0        | 0.2-2.0              |  |

<sup>\*(-)</sup> Inactive at > 25  $\mu$ g/mL

In conclusion, the search on the chemical constituents of the twigs, fruits and roots of *C. cochinchinense* resulted in the isolation of nineteen compounds: β-mangostin (**PS1**), 6,12-dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethyl pyrano(2',3':7,8)xanthone (PS2) and cochinchinone A (PS3), 7-geranyloxy-1,3-(**PS4**), 3-geranyloxy-1,7-dihydroxyxanthone dihydroxyxanthone (PS5), 1.8dihydroxy-3-methoxy-6-methyl-2-(3-methyl-2-butenyl)anthraquinone (PS6), 5,10dihydroxy-9-methoxy-12-(1,1-dimethyl-2-propenyl)-2H,6H-pyrano[3,2-b]xanthen-6one (PS7), cratoxycochinchinone A (PS8), cratoxycochinchinone C (PS9), mangostin (PS10), isocudraniaxanthone B (PS11), celebixanthone (PS12), 1,3,7trihydroxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (**PS13**), 1,3,6-trihydroxyl-8-methoxy-2,4-bis(3-methyl-2-butenyl)xanthone (PS14), 1,2,8trihydroxyxanthone (PS15), cudratricusxanthone E (PS16), \( \gamma\)-mangostin (PS17), 1,3,6,7-tetrahydroxy-5-(3-methyl-2-butenyl)xanthone (**PS18**) and norathyriol (**PS19**). Compounds PS5, PS13, PS14 and PS18 are new substances.

**PS10** showed the best activity to inhibit the growth of *S. aureus* ATCC25923 and MRSA SK1 with a MIC value of 4  $\mu$ g/mL. **PS4** and **PS12** strongly inhibited MCF-7, HeLa, HT-29 and KB cell lines. Consequently, investigation of the antibacterial active compounds from the roots and study on cytoxicity of **PS4** and **PS12** should be continued.