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# Saiyutones A–D: four new unusual biflavones from *Desmos chinensis*

Tharikarn Rittiwong [a], Thumnoon Mutarapat [a], Chanita Ponglimanont [a], Wilawan Mahabusarakam [a,b], Suda Chakthong [a,b,*]

[a] Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[b] Natural Products Research Center, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

Four new unusual biflavones, saiyutones A–D, were isolated from the leaves of *Desmos chinensis* together with 16 known compounds. Their structures were determined on the basis of UV, IR, NMR, and MS analysis, and by comparison of their spectroscopic data with those reported. Saiyutones A and B had a unique biflavone skeleton with a 3–6″ linkage through a methylene group. It was proposed that the formation of a cyclic hemiketal was the key step in the biosynthetic pathway of saiyutones C and D.



## 1. Introduction

*Desmos chinensis*, locally known in Thai as 'Sai-Yut', is a plant in the Annonaceae family, which is distributed widely in southern Asia and northern Australia.[1] This plant has been used as antimalarial, insecticidial, antirheumatic, antispasmodic, and analgesic agents in Chinese folk medicine.[2] In Thailand it has been used traditionally to treat pyretic and dysentery.[3] Previous chemical investigations of *D. chinensis* have revealed chalcones,[4,5] *C*-benzylated chalcones,[6] flavones,[4–9] oxoaporphine alkaloids,[10] steroids,[7,8] benzoic acid derivatives,[7,8] and benzoate ester derivatives[4] but the biflavonoids have not been reported. We report here the structural elucidation of four new biflavones (**1**–**4**) (Fig. 1), saiyutones A–D, and propose their biosynthetic pathways. In addition 16 known compounds were isolated; five flavones: isounonal,[8] unonal,[8] 6-formyl-2,5,7,-trihydroxy-8-methylflavanone, desmal,[11] and matteuorien,[12] nine benzoate esters: benzyl-2-hydroxybenzoate,[13] benzyl benzoate,[13] benzyl 2,6-dihydroxybenzoate,[13] cinnamyl benzoate,[14] benzyl 2-hydroxy-5-methoxybenzoate,[13] 2-methoxybenzyl benzoate,[13] benzyl 2-hydroxy-6-methoxybenzoate,[13] benzyl 2-methoxybenzoate,[13] and benzyl 3-hydroxybenzoate,[15] a diterpenoid: phytol,[16] and a benzoic acid derivative: 2-methoxybenzoic acid.

## 2. Results and discussion

### 2.1. Structural elucidation

Saiyutone A (**1**) was obtained as a pale yellow solid with a molecular formula $C_{34}H_{24}O_9$ assigned by HREIMS analysis (observed $[M]^+$ at *m*/*z* 576.1421, calcd $[M]^+$: 576.1420) suggesting 23 double bond-equivalents. The IR spectrum revealed hydroxyl (3494 $cm^{-1}$) and carbonyl (1655 $cm^{-1}$) groups. The $^{13}C$ NMR spectrum of **1** showed a total of 30 signals (Table 1) including three carbonyl carbons at $\delta$ 182.7, 182.9, and 189.8, eight quaternary oxygenated carbons at $\delta$ 154.0, 156.9, 158.0, 160.1, 163.4, 164.7, 165.1, and 168.0, two methyls at $\delta$ 6.4 and 8.3, and a methylene carbon at $\delta$ 19.6. The $^1H$ NMR spectrum indicated the presence of two sets of three-proton multiplets ($\delta$ 7.65–7.61 and 7.54–7.51) and two sets of two-proton doublet of doublets ($\delta$ 7.71, $J$=7.2, 1.8 Hz and $\delta$ 7.89, $J$=7.2, 1.7 Hz), respectively. These signals were typical of a flavonoid nucleus with an unsubstituted B ring, hence compound **1** should be a biflavonoid. Three singlets of chelated hydroxyl protons were evident at $\delta$ 12.34, 13.06, and 13.16 suggesting that two of them were due to 5-hydroxyflavone skeletons. A formyl proton was displayed at $\delta_H$ 10.28:$\delta_C$ 189.8 whose HMBC correlations to $\delta$ 102.3 (C-8), and $\delta$ 168.0 (C-7) of unit I placed a formyl group at C-8 and the third chelated hydroxyl proton at C-7. The fourth hydroxyl proton was shown at $\delta$ 10.04, which was placed at C-7″ of unit II by the HMBC correlations with $\delta$ 108.6 (C-6″), 160.1 (C-7″), and 104.6 (C-8″) (Fig. 2). Two methyl singlets were displayed at $\delta$ 2.12 (6-$CH_3$)

* Corresponding author. Tel.: +66 7421 2918; fax: +66 7455 8841; e-mail address: suda.ch@psu.ac.th (S. Chakthong).

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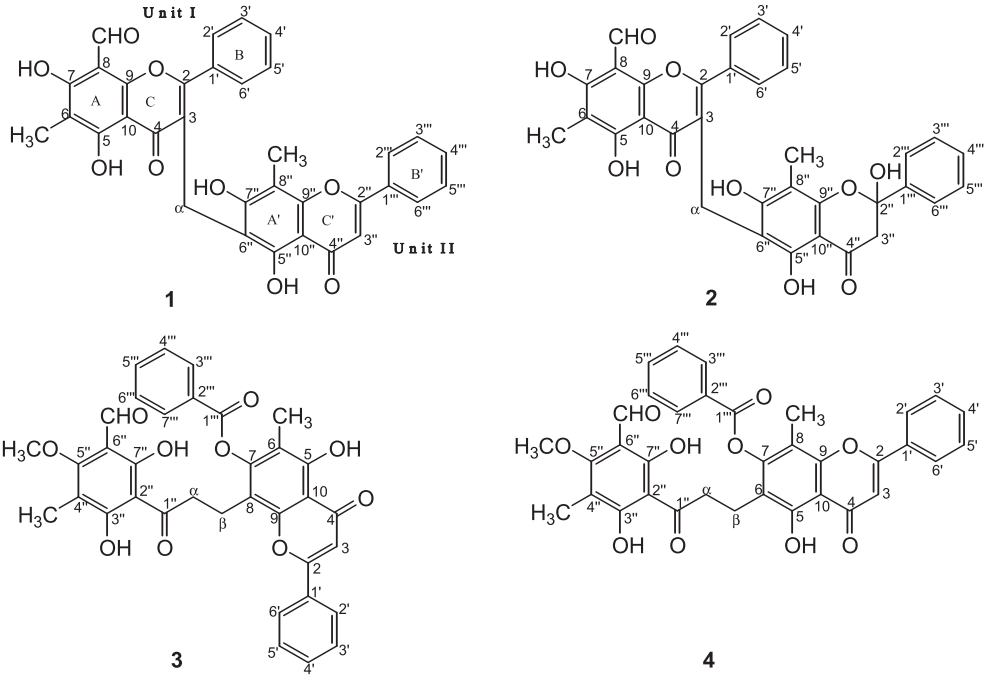



**Fig. 1.** Structures of compounds **1**–**4**.

**Table 1**
$^{1}H$ and $^{13}C$ NMR data of **1** and **2** (300 and 75 MHz, $CDCl_3$)

| No. | **1** | | **2** | |
|---|---|---|---|---|
| | $\delta_H$ ($J$ in Hz) | $\delta_C$ | $\delta_H$ ($J$ in Hz) | $\delta_C$ |
| 2 | | 165.1 | | 164.8 |
| 3 | | 119.3 | | 119.5 |
| 4 | | 182.9 | | 182.9 |
| 5 | | 164.7 | | 164.7 |
| 6 | | 108.9 | | 108.6 |
| 7 | | 168.0 | | 168.1 |
| 8 | | 102.3 | | 102.3 |
| 9 | | 156.9 | | 160.4 |
| 10 | | 103.0 | | 103.1 |
| α | 4.01 (s) | 19.6 | 3.93 (d, 3.3) | 19.2 |
| 1′ | | 132.5 | | 132.6 |
| 2′/6′ | 7.71 (dd, 7.2, 1.8) | 129.2 | 7.68–7.65 (m) | 129.2 |
| 3′/5′ | 7.65–7.61 (m) | 128.7 | 7.63–7.59 (m) | 128.7 |
| 4′ | 7.65–7.61 (m) | 131.1 | 7.63–7.59 (m) | 131.1 |
| 2″ | | 163.4 | | 100.9 |
| 3″ | 6.58 (s) | 105.1 | 2.96 (s) | 48.1 |
| 4″ | | 182.7 | | 194.3 |
| 5″ | | 158.0 | | 159.9 |
| 6″ | | 108.6 | | 105.8 |
| 7″ | | 160.1 | | 163.0 |
| 8″ | | 104.6 | | 106.3 |
| 9″ | | 154.0 | | 155.1 |
| 10″ | | 104.7 | | 101.8 |
| 1‴ | | 131.7 | | 142.2 |
| 2‴/6‴ | 7.89 (dd, 7.2, 1.7) | 126.2 | 7.68–7.65 (m) | 124.9 |
| 3‴/5‴ | 7.54–7.51 (m) | 129.1 | 7.45–7.42 (m) | 128.6 |
| 4‴ | 7.54–7.51 (m) | 131.7 | 7.45–7.42 (m) | 129.2 |
| 5-OH | 13.16 (s) | | 13.16 (s) | |
| 6-$CH_3$ | 2.12 (s) | 6.4 | 2.13 (s) | 6.4 |
| 7-OH | 13.06 (s) | | 13.06 (s) | |
| 8-CHO | 10.28 (s) | 189.8 | 10.27 (s) | 189.8 |
| 5″-OH | 12.34 (s) | | 11.56 (s) | |
| 7″-OH | 10.04 (s) | | 10.13 (s) | |
| 8″-$CH_3$ | 2.39 (s) | 8.3 | 2.15 (s) | 8.3 |

and 2.39 (8″-$CH_3$) whose positions were due to the HMBC correlations with $\delta$ 164.7 (C-5), 108.9 (C-6), and 168.0 (C-7)/with $\delta$ 160.1 (C-7″), 104.6 (C-8″), and 154.0 (C-9″), respectively. A singlet of a methine proton ($\delta$ 6.58) was placed at C-3″ from the HMBC correlations with $\delta$ 163.4 (C-2″), 182.7 (C-4″), 104.7 (C-10″), and 131.7 (C-1‴). Furthermore a singlet of an isolated methylene was evident at $\delta_H$ 4.01:$\delta_C$ 19.6 implying a methylene bridge between two flavonoid units. The methylene linkage was formed between C-3 of unit I and C-6″ of unit II from the HMBC correlations to the carbons at $\delta$ 165.1 (C-2), 119.3 (C-3), 182.9 (C-4), 158.0 (C-5″), 108.6 (C-6″), and 160.1 (C-7″). The structure of **1** was therefore composed of 8-formyl-5,7-dihydroxy-6-methylflavone and 5″,7″-dihydroxy-8″-methylflavone with a methylene linkage between C-3 and C-6″. Thus saiyutone A was identified as (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6″-(5″,7″-dihydroxy-8″-methylflavone).

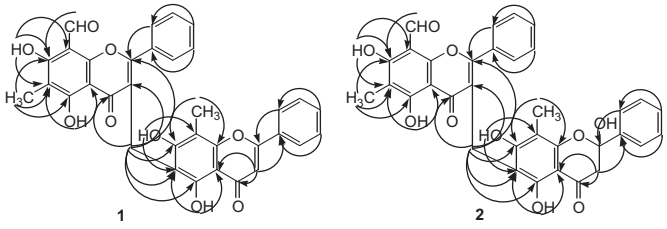



**Fig. 2.** Selected HMBC correlations (**H**→**C**) of **1** and **2**.

Saiyutone B (**2**) was obtained as a pale yellow solid. Its molecular formula of $C_{34}H_{26}O_{10}$ was established on the basis of a molecular ion peak at $m/z$ 594.1521 in HREIMS. Its IR spectrum revealed hydroxyl (3341 $cm^{-1}$) and carbonyl (1630 $cm^{-1}$) groups. The $^{1}H$ and $^{13}C$ NMR spectral data (Table 1) of **2** were similar to those of **1**. The differences were shown in unit II in which a methine proton H-3″ at $\delta$ 6.58 in **1** was replaced by a singlet methylene at $\delta_H$ 2.96:$\delta_C$ 48.1 in **2**. Furthermore a quaternary oxygenated carbon signal at $\delta$ 163.4 (C-2″) in **1** was replaced by a doubly oxygenated $sp^3$ carbon signal at $\delta$ 100.9 in **2**, hence suggesting an OH substitution at C-2″. A flavone–flavanone biflavonoid structure was proposed for **2** whose units were linked by a methylene bridge ($\delta_H$ 3.93:$\delta_C$ 19.2) between C-3 of a flavone and C-6″ of a flavanone units, as supported by the HMBC correlations (Fig. 2) with the carbons at $\delta$ 164.8 (C-2), 119.5 (C-3), 182.9 (C-4), 159.9 (C-5″), 105.8 (C-6″), and 163.0 (C-7″). Thus the structure of saiyutone B was identified as (8-formyl-5,7-dihydroxy-6-methylflavone)-3-methane-6″-(2″,5″,7″-trihydroxy-8″-methylflavanone).

As already known, the cyclic hemiketal[17–21] would ring open in the solution, this was implied from the close to zero optical rotation of **2** ($[\alpha]_D^{25}$+1.4, *c* 1.00, $CHCl_3$). Compound **2** could be regarded as a precursor of compound **1** because of the ease with which the former was dehydrated to the latter.

Saiyutone C (**3**) was obtained as a pale yellow solid. Its HRESIMS indicated a $[M+Na]^+$ ion peak at *m*/*z* 631.1585, suggesting a molecular formula of $C_{35}H_{28}NaO_{10}$ (calcd for $C_{35}H_{28}NaO_{10}$ *m*/*z* 631.1580) with 22° of unsaturations. The IR spectrum revealed hydroxyl (3447 $cm^{-1}$), carbonyl (1739, 1633 $cm^{-1}$), and aromatic (1542 $cm^{-1}$) groups. The $^1H$ NMR spectral data (Table 2) displayed two sets of signals in the aromatic region; the first set was a three-proton multiplet at $\delta$ 7.57–7.50 and a two-proton doublet at $\delta$ 7.92 (*J*=7.2 Hz), whereas the second set was a two-proton doublet at $\delta$ 8.25 (*J*=7.2 Hz), a one-proton triplet at $\delta$ 7.70 (*J*=7.2 Hz), and a two-proton multiplet at $\delta$ 7.57–7.50. The former set of signals was typical of a flavonoid nucleus with an unsubstituted B-ring whose singlet of a chelated hydroxyl at $\delta$ 12.98 indicated a 5-hydroxyflavone skeleton. The latter set of signals belonged to a benzoyloxy group, which was linked to C-7 ($\delta$ 153.7) of A-ring of a flavone nucleus from the HMBC correlation of H-3‴ at $\delta$ 8.25 with the ester carbonyl at $\delta$ 163.9. In turn a methyl singlet at $\delta$ 2.11 was placed at C-6 of a flavone nucleus from the HMBC correlations to the carbons at $\delta$ 114.7 (C-6), 153.7 (C-7), and 157.9 (C-5). A downfield singlet signal at $\delta$ 6.77 was assigned for H-3 of a flavone. Furthermore the following signals were displayed; two more singlets of chelated hydroxyl protons at $\delta$ 14.04 (7″-OH) and 14.87 (3″-OH), a methoxyl at $\delta$ 3.84 (5″-$OCH_3$), a methyl at $\delta$ 2.02 (4″-$CH_3$), a formyl proton at $\delta$ 9.87 (6″-CHO), and a methylene triplet of four protons at $\delta_H$ 3.51:$\delta_C$ 43.5 ($H_2$-α, $H_2$-β). These spectral data together with the fragment ions at *m*/*z* 223 and 385 in the EIMS suggested a 3-formyl-2,6-dihydroxy-4-methoxy-5-methylbenzoylethyl side chain whose connection to C-8 of a flavone nucleus was due to HMBC correlations of the methylene protons at $\delta$ 3.51 to the carbons at $\delta$ 112.0 (C-8) and 205.6 (C-1″). The NOESY cross peak of the methyl group at $\delta$ 2.02 (4″-$CH_3$) with $\delta$ 3.84 (5″-$OCH_3$) and of 5″-$OCH_3$ with $\delta$ 9.87 (6″-CHO) supported the assigned structure (Fig. 3). Therefore, the structure of **3** was proposed to be an unusual biflavone, named as saiyutone C.

**Table 2**
$^1H$ and $^{13}C$ NMR data of **3** and **4** (600 and 150 MHz, $CDCl_3$)

| No. | **3** | | **4** | |
|---|---|---|---|---|
| | $\delta_H$ (*J* in Hz) | $\delta_C$ | $\delta_H$ (*J* in Hz) | $\delta_C$ |
| 2 | | 163.4 | | 164.3 |
| 3 | 6.77 (s) | 105.9 | 6.77 (s) | 105.9 |
| 4 | | 183.3 | | 183.4 |
| 5 | | 157.9 | | 157.5 |
| 6 | | 114.7 | | 117.1 |
| 7 | | 153.7 | | 153.4 |
| 8 | | 112.0 | | 109.1 |
| 9 | | 159.0 | | 152.7 |
| 10 | | 108.9 | | 108.8 |
| α, β | 3.51 (t, 7.3) | 43.5 | 3.51 (t, 7.8) | 42.9 |
| 1′ | | 131.4 | | 131.9 |
| 2′/6′ | 7.92 (d, 7.2) | 126.3 | 7.93 (d, 6.8) | 126.3 |
| 3′/5′ | 7.57–7.50 (m) | 129.2 | 7.60–7.52 (m) | 129.1 |
| 4′ | 7.57–7.50 (m) | 131.9 | 7.60–7.52 (m) | 133.9 |
| 1″ | | 205.6 | | 206.0 |
| 2″ | | 106.2 | | 106.2 |
| 3″ | | 172.3 | | 172.4 |
| 4″ | | 110.9 | | 110.8 |
| 5″ | | 166.5 | | 166.3 |
| 6″ | | 107.1 | | 107.1 |
| 7″ | | 167.0 | | 167.1 |
| 1‴ | | 163.9 | | 164.0 |
| 2‴ | | 131.4 | | 131.9 |
| 3‴/7‴ | 8.25 (d, 7.2) | 130.3 | 8.23 (d, 7.5) | 130.3 |
| 4‴/6‴ | 7.57–7.50 (m) | 128.8 | 7.60–7.52 (m) | 128.7 |
| 5‴ | 7.70 (t, 7.2) | 134.0 | 7.60–7.52 (m) | 133.9 |
| 5-OH | 12.98 (s) | | 12.96 (s) | |
| 6-$CH_3$ | 2.11 (s) | 8.7 | | |
| 8-$CH_3$ | | | 2.31 (s) | 9.1 |
| 3″-OH | 14.87 (s) | | 14.97 (s) | |
| 4″-$CH_3$ | 2.02 (s) | 7.9 | 2.05 (s) | 7.9 |
| 5″-$OCH_3$ | 3.84 (s) | 62.8 | 3.86 (s) | 62.8 |
| 6″-CHO | 9.87 (s) | 192.4 | 9.91 (s) | 192.3 |
| 7″-OH | 14.04 (s) | | 14.02 (s) | |

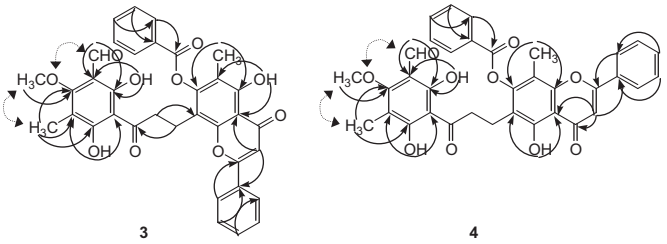



**Fig. 3.** Selected HMBC (**H**→**C**) and NOESY correlations (↷) of **3** and **4**.

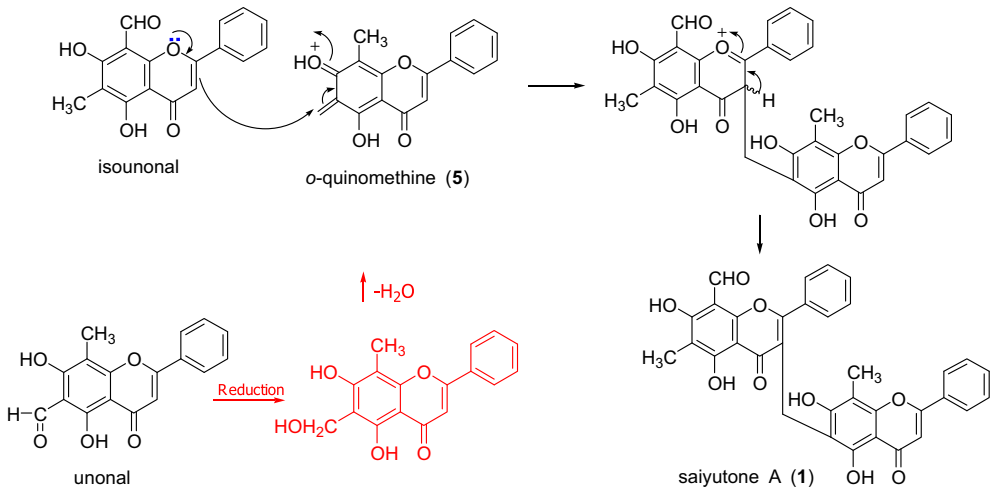
Saiyutone D (**4**) was obtained as a pale yellow solid, assigning a molecular formula of $C_{35}H_{28}NaO_{10}$ by HRESIMS (*m*/*z* 631.1585 $[M+Na]^+$, calcd for $C_{35}H_{28}NaO_{10}$ *m*/*z* 631.1580). The IR spectrum revealed hydroxyl (3439 $cm^{-1}$), carbonyl (1720, 1648 $cm^{-1}$), and aromatic (1542 $cm^{-1}$) groups. The $^1H$ NMR spectrum of **4** displayed similarity to those of **3** suggesting a 5-hydroxyflavone nucleus with linkages to a benzoyloxy and a 3-formyl-2,6-dihydroxy-4-methoxy-5-methylbenzoylethyl side chains as in **3** (Table 2). The differences were shown in the methyl singlet signal of a flavone nucleus of which **4** appeared at $\delta$ 2.31, more downfield than that of **3** at $\delta$ 2.11 (6-$CH_3$). In the HMBC spectrum (Fig. 3), the methyl protons at $\delta$ 2.31 correlated with the carbons at $\delta$ 109.1 (C-8), 152.7 (C-9), and 153.4 (C-7) resulting in its placement at C-8, hence the benzoylethyl side chain should be connected at C-6 ($\delta$ 117.1) of the flavone nucleus. The HMBC correlation of the chelated hydroxyl signal at $\delta$ 12.96 with the carbons at $\delta$ 108.8 (C-10), 117.1 (C-6), and 157.5 (C-5) supported a 5-hydroxyflavone structure. The NOESY correlations between 4″-$CH_3$ and 5″-$OCH_3$ and 5″-$OCH_3$ and 6″-CHO confirmed the assigned structure. Thus **4** was a structural isomer of **3** and named as saiyutone D.

Unfortunately, the position of the benzoate groups of compounds **3** and **4** could not be precisely defined experimentally since there were neither HMBC nor NOESY correlations between the benzoyl ring and its attached ring. However, the position of attachment of the benzoate group was deduced from the following experimental data; there were seven oxy-quaternary carbons, six of them were clearly identified, three as those attached to three chelated hydroxyl groups (C-5, C-3″, and C-7″), one as a carbon attached to a methoxyl group (C-5″), two as carbons attached to an oxygen of the C-ring of a flavone nucleus (C-2 and C-9), thus leaving only C-7 of a flavone nucleus as possible position for attachment of the benzoate group. Furthermore the flavone nuclei of compounds **1** and **2** possessed two hydroxyl groups at positions C-5 and C-7 whose skeletons should be the same for compounds **3** and **4**.

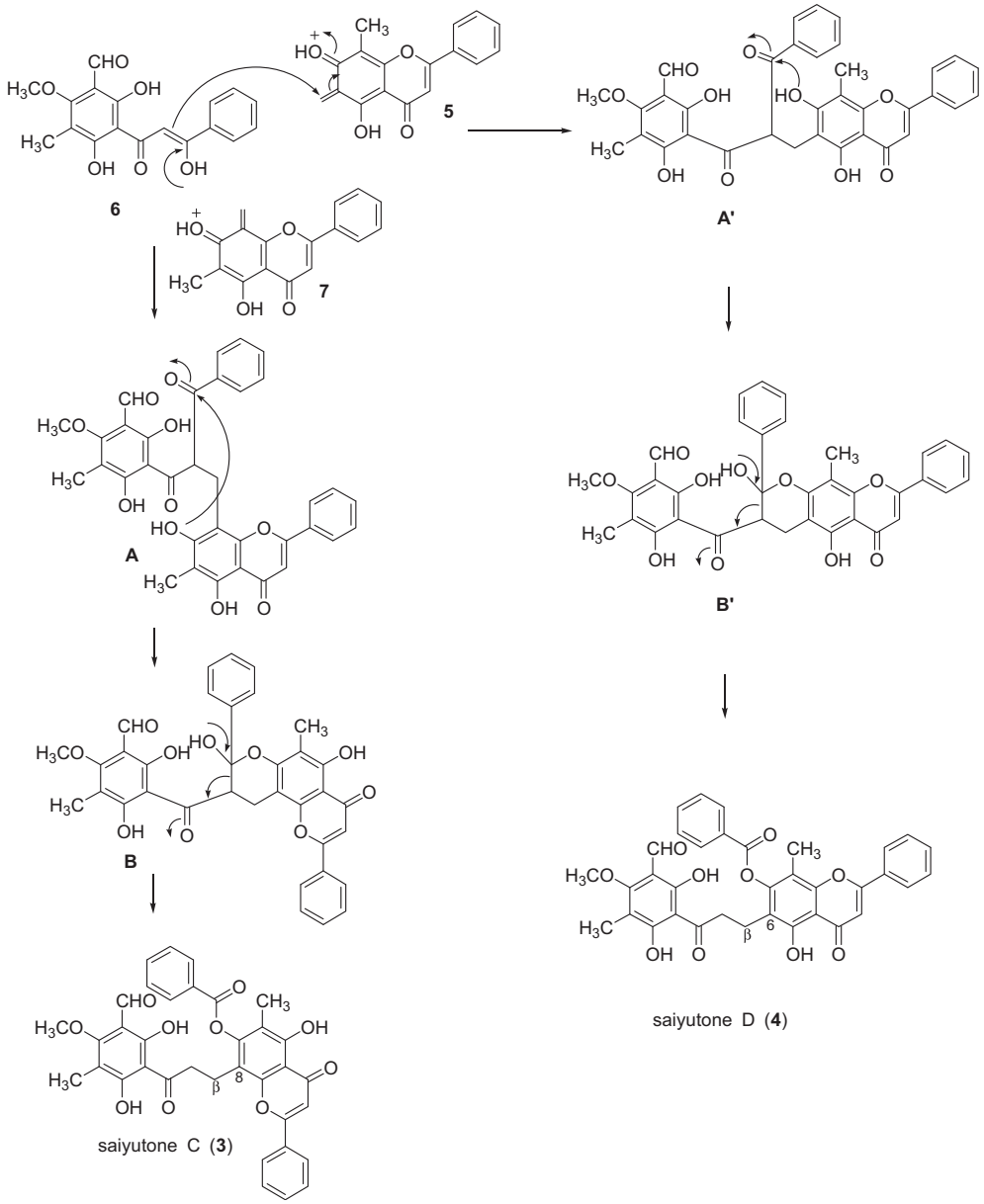
## 2.2. The proposed biosynthetic pathway of saiyutones A, C, and D

Plausible biosynthetic pathways for saiyutones A, C, and D (**1**, **3**, and **4**) are proposed as shown in Schemes 1 and 2.

The biosynthesis of saiyutone A (**1**) might be derived from a combination of isounonal and *o*-quinomethine of unonal (**5**) by nucleophilic addition and aromatization to yield **1** (Scheme 1). Saiyutones C and D (**3** and **4**) would involve an electrophilic addition between 3-formyl-2,6-dihydroxy-4-methoxy-5-methyldibenzoyl-methane[18] (**6**) and *o*-quinomethine of isounonal (**7**) or




**Scheme 1.** Plausible biosynthetic pathway for **1**.




**Scheme 2.** Plausible biosynthetic pathways for **3** and **4**.

(**5**) to form intermediates **A**/**A**′, followed by cyclization to give a cyclic hemiketal **B**/**B**′. Then a ring opening of **B**/**B**′ would lead to linkages of these units through C-β and C-8 or C-β and C-6 bonds of **3** and **4**, respectively.

In conclusion, although the biflavones with a methylene linkage have been reported earlier from *Pentagramma triangularis*,[22–24] and *Kunea ambigua*,[25] this is the first report of the dimerization of a flavone at C-3 and C-6″ through a methylene bridge from *D. chinensis* (**1** and **2**). The combination of a dibenzoylmethane and a flavone resulted in unusual structures of saiyutones C and D (**3** and **4**).

## 3. Experimental section

### 3.1. General experiment procedures

Melting point was recorded in °C on a digital Electrothermal 9100 Melting Point Apparatus. Ultraviolet spectra were measured in methanol solution on a UV-160A spectrophotometer (SHIMADZU). The IR spectra were recorded neat on a Perkin–Elmer FTS FT-IR spectrophotometer. Optical rotations $[\alpha]_D$ were measured in chloroform on a JASCO P-1020 digital polarimeter. The $^1H$ and $^{13}C$ NMR spectra were recorded on an FT-NMR Bruker Ultra Shield™ 300 and 600 MHz using tetramethylsilane (TMS) as internal standard. EI and HREI mass spectra were measured on ThermoFinnigan MAT 95 XL spectrometer. HRESIMS was recorded on a Bruker Daltonics microTOF spectrometer. Quick column chromatography (QCC) was carried out on silica gel 60 $GF_{254}$ (Merck). Column chromatography (CC) was performed by using silica gel 100 (70–230 mesh ASTM, Merck). Thin-layer chromatography (TLC) and preparative TLC were performed on silica gel 60 $F_{254}$ (Merck).

### 3.2. Plant material

The leaves of *D. chinensis* Lour. were collected from Krabi province in the southern part of Thailand, in April 2009. Identification was made by Assoc. Prof. Dr. Kitichate Sridith and a specimen (No. 0013593) deposited at PSU Herbarium, Department of Biology, Faculty of Science, Prince of Songkla University.

### 3.3. Extraction and isolation

The air-dried leaves of *D. chinensis* Lour. (550 g) were extracted with $CH_2Cl_2$ for 5 days (two times) at room temperature. The solvent was evaporated under reduced pressure to give concentrated solution of $CH_2Cl_2$ extract as brown residue (40.0 g). A portion of the extract (30.0 g) was subjected to QCC using silica gel as stationary phase and eluted with a gradient of hexane–$CH_2Cl_2$, $CH_2Cl_2$, $CH_2Cl_2$–MeOH, and MeOH as eluents. On the basis of their TLC characteristics, the fractions, which contained the same major components were combined to give fractions L1–L13. Fraction L9 (0.8138 g) was purified by CC over silica gel and eluted with $CH_2Cl_2$ to afford 8 fractions (9A–9H). Subfraction 9C (0.0314 g) was purified by CC over silica gel and eluted with $CH_2Cl_2$–hexane (3:2) to afford 5 fractions (9C1–9C5). Subfraction 9C4 (0.0059 g) was further purified on preparative TLC and eluted with $CH_2Cl_2$–hexane (7:3) to give **1** (0.0023 g). Subfraction 9F (0.0799 g) was purified by CC over silica gel and eluted with $CH_2Cl_2$ to afford 7 fractions (9F1–9F5). Subfraction 9F2 (0.0374 g) was purified by CC over silica gel and eluted with acetone–hexane (2.5:7.5) to afford 7 fractions (9F2A–9F2G). Subfraction 9F2E (0.0050 g) was further purified on preparative TLC and eluted with $CH_2Cl_2$ to give **3**: (0.0017 g) and **2** (0.0025 g). Subfraction 9G5 (0.0148 g) was further purified on preparative TLC and eluted with EtOAc–hexane (1:4) to afford 5 fractions (9G5A–9G5E). Subfraction 9G5A (0.0047 g) was further purified on preparative TLC and eluted with MeOH–$CH_2Cl_2$ (1:9) to give **4** (0.0016 g).

*3.3.1. Saiyutone A (**1**).* Pale yellow solid; mp 229–230 °C; UV $\nu_{max}$ (MeOH) (log $\varepsilon$): 203 (4.19), 248 (3.94), 281 (4.06), and 350 (3.33) nm; IR (KBr) $\nu$ ($cm^{-1}$): 3494 (O–H stretching), 1655 (C=O stretching). For $^1H$ NMR ($CDCl_3$, 300 MHz) and $^{13}C$ NMR ($CDCl_3$, 75 MHz) spectral data, see Table 1. EIMS *m*/*z* (% rel int.): 576 ($[M]^+$, 26), 575 (66), 382 (34), 309 (15), 307 (20), 280 (16), 269 (100), 267 (12), 194 (5), 115 (7); HREIMS $[M]^+$ *m*/*z* 576.1421 (calcd for $C_{34}H_{24}O_9$ 576.1420).

*3.3.2. Saiyutone B (**2**).* Pale yellow solid; mp 199–200 °C; $[\alpha]_D^{25}$ +1.4 (*c* 1.00, $CHCl_3$); UV $\nu_{max}$ (MeOH) (log $\varepsilon$): 203 (4.40), 294 (4.18), and 340 (3.64) nm; IR (KBr) $\nu$ ($cm^{-1}$): 3341 (O–H stretching), 1630 (C=O stretching). For $^1H$ NMR ($CDCl_3$, 300 MHz) and $^{13}C$ NMR ($CDCl_3$, 75 MHz) spectral data, see Table 1. EIMS *m*/*z* (% rel int.): 594 ($[M]^+$, 15), 576 (100), 382 (31), 307 (35), 280 (24), 269 (86), 267 (17), 194 (11), 115 (20), 77 (19); HREIMS $[M]^+$ *m*/*z* 594.1521 (calcd for $C_{34}H_{26}O_{10}$ 594.1526).

*3.3.3. Saiyutone C (**3**).* Pale yellow solid; mp 190–191 °C; UV $\nu_{max}$ (MeOH) (log $\varepsilon$): 203 (3.86), 274 (3.73), and 342 (3.55) nm; IR (KBr) $\nu$ ($cm^{-1}$): 3447 (O–H stretching), 1739, 1633 (C=O stretching), 1542 (aromatics). For $^1H$ NMR ($CDCl_3$, 600 MHz) and $^{13}C$ NMR ($CDCl_3$, 150 MHz) spectral data, see Table 2. EIMS *m*/*z* (% rel int.): 608 ($[M]^+$, 41), 607 (100), 503 (4), 385 (27), 223 (2), 105 (55); HRESIMS $[M+Na]^+$ *m*/*z* 631.1585 (calcd for $C_{35}H_{28}NaO_{10}$ 631.1580).

*3.3.4. Saiyutone D (**4**).* Pale yellow solid; mp 180–182 °C; UV $\nu_{max}$ (MeOH) (log $\varepsilon$): 203 (3.62), 278 (3.11), and 340 (3.64) nm; IR (KBr) $\nu$ ($cm^{-1}$): 3439 (O–H stretching), 1720, 1643 (C=O stretching), 1542 (aromatics). For $^1H$ NMR ($CDCl_3$, 600 MHz) and $^{13}C$ NMR ($CDCl_3$, 150 MHz) spectral data, see Table 2. ESIMS *m*/*z* (% rel int.): 609 ($[M+H]^+$, 75); HRESIMS $[M+Na]^+$ *m*/*z* 631.1585 (calcd for $C_{35}H_{28}NaO_{10}$ 631.1580).

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