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# Four geranyl-bearing polyisoprenylated benzoylphloroglucinol derivatives from *Hypericum sampsonii*

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ABSTRACT

Four new geranyl-bearing polyisoprenylated benzoylphloroglucinol derivatives, hypersampsone I (**1**), hypersampsone J (**2**), and hypersampsone K (**3**), together with hypersampsone L (**4**) which possessed a novel skeleton, were isolated from the fruit of *Hypericum sampsonii*. Their structures were determined on the basis of spectroscopic data, mainly 1D- and 2D-NMR spectroscopy and mass spectrometry. The structures of **1** and **2** were confirmed by X-ray crystallographic analysis.



## 1. Introduction

*Hypericum sampsonii* (Hypericaceae) is a Chinese herbal medicine used in the treatment of numerous disorders such as backache, burn, diarrhoea, snakebite and swelling (Jiang Su New Medical College, 1977). This plant has been found to have metabolites such as polyisoprenylated benzoylphloroglucinol derivatives (Hu and Sim, 1998, 1999a,b, 2000; Lin and Wu, 2003; Xiao et al., 2007), xanthones and other phenolic principles (Don et al., 2004; Hong et al., 2004). In our further search for biologically active compounds, we have isolated four new polyisoprenylated benzoylphloroglucinol derivatives from the petroleum ether extract of the fruits of *H. sampsonii*, namely hypersampsone I (**1**), hypersampsone J (**2**), hypersampsone K (**3**) and hypersampsone L (**4**) (Fig. 1), as well as two other polyisoprenylated benzoylphloroglucinol derivatives, hypersampsone G and H previously reported (Zeng et al., 2009). Their UV, IR, MS and NMR spectral data indicated that they were polyisoprenylated benzoylphloroglucinol derivatives. The structures of compounds **1** and **2** were confirmed by X-ray crystallographic analysis. One of the compounds, hypersampsone L (**4**), exhibited a highly unusual structure showing the value of acylphloroglucinols in general as a source of structural diversity and novelty.

## 2. Results and discussion

The powdered fruit of *H. sampsonii* was extracted with 95% ethanol. The resulting extract solution was evaporated to near dryness and the residue was extracted into petroleum ether, chloroform and water soluble fractions successively. The petroleum ether soluble fraction was chromatographed repeatedly on silica gel and RP-18 resin to afford four new geranyl-bearing polyisoprenylated benzoylphloroglucinol derivatives, hypersampsone I (**1**), hypersampsone J (**2**), hypersampsone K (**3**) and hypersampsone L (**4**).

Hypersampsone I (**1**) was obtained as colorless prism-like crystals, $[\alpha]_D^{22}$ +18.6 (c 0.262, $CHCl_3$). Its molecular formula was assigned as $C_{35}H_{44}O_4$ on the basis of HRESIMS with an ion observed at 551.31318 $[M+Na]^+$ (calcd. for $C_{35}H_{44}NaO_4$, 551.3140). In the infrared spectrum of **1**, carbonyl group bands were present with absorptions of 1683, 1695 and 1734 $cm^{-1}$. Furthermore, compound **1** exhibited similar $^1H$ NMR spectral features to those of hypersampsone G (Zeng et al., 2009), with a benzoyl group, two vinyl proton signals, together with several singlet methyl group signals, suggesting that compound **1** was also a polyisoprenylated benzoylated phloroglucinol derivative (Fig. 1). Extensive comparison of the 1D and 2D NMR spectral data ($^1H$–$^1H$ COSY, HSQC and

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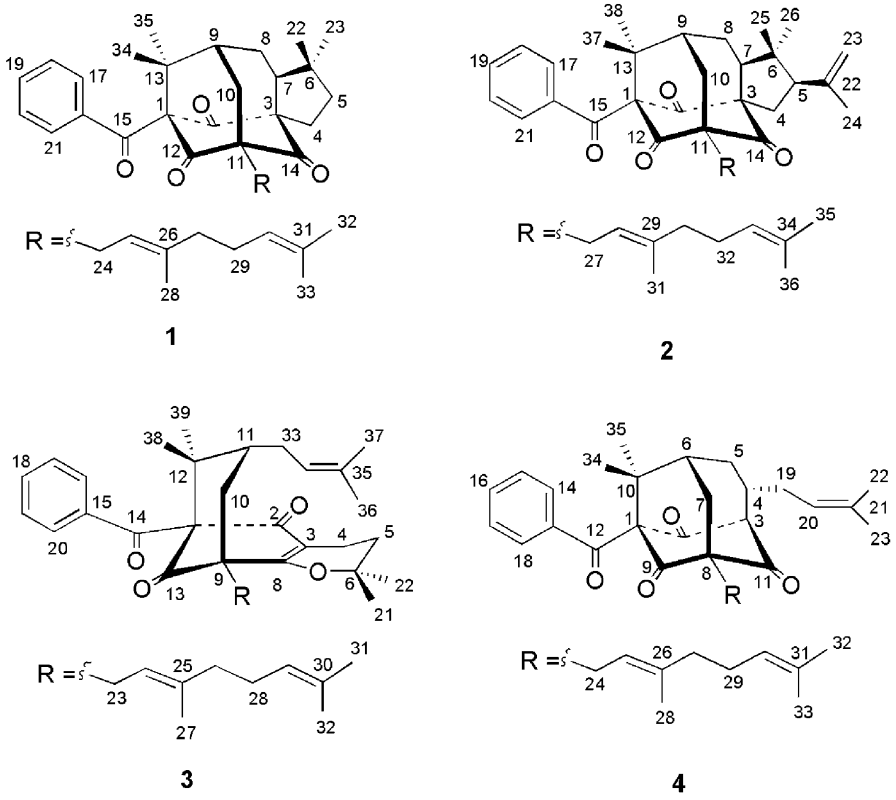


**Fig. 1.** Structures of compounds **1**–**4**.

HMBC) of **1** (Table 1) with those of hypersampsone G indicated that the skeleton of **1** was quite similar to that of hypersampsone G except for the difference at the C-5 position with a hydrogen at this position in **1** rather than an isopropyl substituent as observed in hypersampsone G.

The relative configuration of **1** was deduced from its ROESY spectrum (Fig. 2 in S18) and was the same as that of hypersampsone G (Zeng et al., 2009). In compound **1** the proton at C-7 was also oriented in an α-configuration. Therefore **1** was elucidated as (1*R**,3*S**,7*S**,9*R**,11*S**)-1-benzoyl-11-(3,7-dimethylocta-2(*E*),6-dienyl)-6,6,13,13-tetramethyltetracyclo[7.3.1.1$^{3,11}$.0$^{3,7}$]tetradecane-2,12,14-trione and was given the trivial name hypersampsone I.

Hypersampsone J (**2**) was obtained as colorless prism-like crystals, $[\alpha]_D^{22}$ +11.4 (c 0.573, $CHCl_3$). Its molecular formula was assigned as $C_{38}H_{48}O_4$ on the basis of an ion observable in the HRESIMS at 591.34448 $[M+Na]^+$ (calcd. for $C_{38}H_{48}NaO_4$, 591.3450). Inspection of the IR spectrum of **2** again revealed the presence of carbonyl group absorption bands at 1697 and 1735 cm$^{-1}$. Extensive comparison of the 1D- and 2D-NMR spectra ($^1$H–$^1$H COSY, HSQC and HMBC) of compound **2** (Table 2 in S20) with

**Table 1**
NMR spectral data for hypersampsone I (**1**) and hypersampsone L (**4**).

| No. | Hypersampsone I (**1**)[a] | | | No. | Hypersampsone L (**4**)[b] | | |
|---|---|---|---|---|---|---|---|
| | $\delta_H$ (*J* in Hz) | $\delta_C$, mult. | HMBC | | $\delta_H$ (*J* in Hz) | $\delta_C$, mult mult. | HMBC |
| 1 | | 81.9 | | 1 | | 84.5 | |
| 2 | | 205.8 | | 2 | | 205.3 | |
| 3 | | 76.6 | | 3 | 3.13, d (5.9) | 51.4 | 2, 4, 5, 6, 19 |
| 4α | 2.72, m | 29.0 | 3, 5, 6, 11, 14 | 4 | 2.94, m | 59.0 | 2, 3, 5, 19 |
| 4β | 2.56, ddd (14.1, 9.4, 3.9) | – | 3, 14 | 5α | 2.86, m | 37.8 | |
| 5α | 1.78, overlapped | 41.8 | 6, 22 | 5β | 2.03, m | – | 2, 3, 4, 6, 7, 10 |
| 5β | 2.00, m | – | 3, 6, 7, 14, 22 | 6 | 1.92, m | 41.9 | |
| 6 | | 44.3 | | 7a | 2.53, ddd (14.9, 6.1, 2.0) | 36.5 | 5, 6, 8, 9, 24 |
| 7 | 2.20, m | 58.0 | 2, 3, 8, 10, 22, 23 | 7b | 2.39, m | – | 5, 6, 8, 9, 10, 11 |
| 8α | 2.25, m | 28.9 | 3, 7 | 8 | | 70.2 | |
| 8β | 1.55, overlapped | – | 7 | 9 | | 205.1 | |
| 9 | 2.14, m | 43.5 | 1, 3, 6, 7, 8, 13, 14, 34 | 10 | | 53.0 | |
| 10a | 2.65, dd (13.9, 6.1) | 45.1 | 8, 9, 11, 14, 24 | 11 | | 200.8 | |
| 10b | 1.98, m | – | 7, 8, 9, 11, 12, 13 | 12 | | 194.0 | |
| 11 | | 69.1 | | 13 | | 137.6 | |
| 12 | | 206.1 | | 14 | 7.25, dt (7.8, 1.8) | 128.8 | 12, 16, 18 |
| 13 | | 51.9 | | 15 | 7.30, td (6.7, 1.7) | 127.7 | 13, 17 |
| 14 | | 205.9 | | 16 | 7.41, tt (7.0, 1.6) | 131.7 | 14, 18 |
| 15 | | 193.7 | | 17 | 7.30, td (6.7, 1.7) | 127.7 | 13, 15 |
| 16 | | 135.6 | | 18 | 7.25, dt (7.8, 1.8) | 128.8 | 12, 14, 16 |
| 17 | 7.54, br d (7.8) | 129.8 | 15, 18, 19, 21 | 19a | 2.67, br d (14.9) | 29.9 | |

**Table 1** (*Continued*)

| No. | Hypersampsone I (**1**)[a] | | | No. | Hypersampsone L (**4**)[b] | | |
|---|---|---|---|---|---|---|---|
| | $\delta_H$ (*J* in Hz) | $\delta_C$, mult. | HMBC | | $\delta_H$ (*J* in Hz) | $\delta_C$, mult mult. | HMBC |
| 18 | 7.37, m | 128.5 | 16, 17, 19, 20 | 19b | 2.11, m | – | 3, 4, 20, 21 |
| 19 | 7.40, m | 132.5 | 17, 18, 20, 21 | 20 | 5.07, m | 120.2 | 22 |
| 20 | 7.37, m | 128.5 | 16, 18, 19, 21 | 21 | | 136.0 | |
| 21 | 7.54, br d (7.8) | 129.8 | 15, 17, 19, 20 | 22 | 1.60, s | 18.0 | 20, 21, 23 |
| 22 | 0.95, s | 21.8 | 5, 6, 7, 23 | 23 | 1.70, s | 26.0 | 20, 21, 22 |
| 23 | 0.92, s | 29.9 | 5, 6, 7, 22 | 24a | 2.89, m | 33.1 | 7, 8, 11, 25, 26 |
| 24a | 2.86, dd (14.5, 7.8) | 30.4 | 10, 11, 12, 25, 26 | 24b | 2.42, m | – | 7, 8, 9, 25, 26 |
| 24b | 2.74, m | – | 10, 25, 26 | 25 | 4.99, t (7.8) | 118.5 | 24, 27, 28 |
| 25 | 5.42, t (6.5) | 120.2 | 24, 27, 28 | 26 | | 139.4 | |
| 26 | | 138.1 | | 27 | 2.00, m | 40.0 | 25, 26, 29, 30 |
| 27 | 2.07, m | 40.3 | 11, 25, 26, 27, 30 | 28 | 1.62, s | 16.4 | 25, 26, 27 |
| 28 | 1.77, s | 16.6 | 11, 25, 26, 27 | 29 | 2.04, m | 26.5 | 26, 27, 30, 31 |
| 29 | 2.12, m | 26.9 | 26, 29, 30, 31 | 30 | 5.04, m | 124.1 | 32, 33 |
| 30 | 5.17, br t (7.4) | 124.6 | 27, 32, 33 | 31 | | 131.5 | |
| 31 | | 131.4 | | 32 | 1.67, s | 25.8 | 30, 31, 33 |
| 32 | 1.66, s | 25.8 | 30, 31, 33 | 33 | 1.59, s | 17.7 | 30, 31, 32 |
| 33 | 1.56, s | 17.7 | 30, 31, 32 | 34 | 1.30, s | 24.2 | 1, 6, 10, 35 |
| 34 | 1.58, s | 25.7 | 1, 9, 13, 35 | 35 | 1.39, s | 24.6 | 1, 6, 10, 34 |
| 35 | 1.62, s | 22.8 | 1, 9, 13, 34 | | | | |

[a] Recorded at 400 and 100 MHz for $^1$H and $^{13}$C in pyridine-$d_5$.
[b] Recorded at 400 and 100 MHz for $^1$H and $^{13}$C in $CDCl_3$.

hypersampsone G (Zeng et al., 2009) indicated that the skeleton of **2** was very similar to hypersampsone G except for the difference at the C-5 position where an isopropenyl substituent was present in **2** while an isopropyl substituent was present in hypersampsone G.

The relative configuration of compound **2** deduced from its ROESY spectrum (Fig. 2 in S18) was the same as that of hypersampsone G (Zeng et al., 2009). The hydrogen at C-7 was oriented in an α-configuration and the isopropenyl group at C-5 was oriented in a β-configuration in **2**. Therefore compound **2** was elucidated as (1*R**,3*S**,5*R**,7*S**,9*R**,11*S**)-1-benzoyl-11-(3,7-dimethylocta-2(*E*),6-dienyl)-6,6,13,13-tetramethyl-5-(prop-1-en-2-yl)tetracyclo[7.3.1.1$^{3,11}$.0$^{3,7}$]tetradecane-2,12,14-trione, and was given the trivial name hypersampsone J.

Only very small and subtle differences in terms of structure are apparent for these isolates which were obtained in a small amount. We therefore decided to isolate larger quantities by repeated column chromatography using silica gel and RP-18 to yield pure hypersampsone I (**1**, 400 mg) and hypersampsone J (**2**, 82 mg). Fortunately, compounds **1** and **2** were readily crystallized as prisms and single crystal X-ray crystallographic analysis confirmed their structures (Fig. 2 and Fig. 4 in S9).

Hypersampsone K (**3**) was obtained as a colorless oil, with an $[\alpha]_D^{22}$ of +31.7 (c 0.376, $CHCl_3$). The same molecular formula, $C_{38}H_{50}O_4$, as that of hypersampsone H (Zeng et al., 2009) was assigned on the basis of the HRESIMS where an ion was observed at 593.36013 $[M+Na]^+$ (calcd. for $C_{38}H_{50}NaO_4$, 593.3614). As with compounds **1** and **2**, carbonyl group bands were present at absorptions of 1698 and 1723 cm$^{-1}$ in the IR spectrum of **3**. Extensive comparison of the 1D and 2D NMR spectral data ($^1$H–$^1$H COSY, HSQC and HMBC) of compound **3** (Table 2 in S20) with hypersampsone H (Zeng et al., 2009) indicated that the skeleton of **3** was very similar to that of hypersampsone H. The differences were that in hypersampsone H, C-2 ($\delta_C$ 167.7, s), C-4 ($\delta_C$ 80.3, s), C-5 ($\delta_C$ 31.2, t), C-6 ($\delta_C$ 16.3, t), C-7 ($\delta_C$ 113.6, s) and O-3 constituted an oxygen-bearing six-membered ring whereas by comparison with compound **3**, C-3 ($\delta_C$ 113.7, s), C-4 ($\delta_C$ 16.5, t), C-5 ($\delta_C$ 31.5, t), C-6 ($\delta_C$ 79.6, s), C-8 ($\delta_C$ 169.4, s) and O-7 constituted an oxygen-bearing six-membered ring. This was supported by the carbon signal at $\delta_C$ 79.6 (C-6) and fourteen degrees of unsaturated, along with the HMBC correlations between methyl-21 and C-5 and C-6, methyl-22 and C-5 and C-6, and extensive correlations between H-4α ($\delta_H$ 2.43, dt) and C-2, C-3, C-5, C-6 and C-8.

The relative configuration of **3** was deduced from its Δδ between the chemical shifts of the two hydrogens of the $CH_2$-10, $\delta_C$ for C-11, for the *gem*-dimethyl group at C-12 (Piccinelli et al., 2005). In compound **3**, the Δδ 0.06 of the two hydrogens of the $CH_2$-10, $\delta_C$ 48.4 ppm for C-11, and 26.7/22.3 ppm for the carbons of the *gem*-dimethyl group indicated that the substituent prenyl group at C-11 was axial as shown in Fig. 1. The ROESY spectrum of **3** supported this relative configuration arrangement (Fig. 2 in S18). Therefore compound **3** was elucidated as (1*R**,3*S**,5*R**,7*S**,9*R**,11*S**)-1-benzoyl-11-(3,7-dimethylocta-2(*E*),6-dienyl)-6,6,13,13-tetramethyl-5-(prop-1-en-2-yl)tetracyclo[7.3.1.1$^{3,11}$.0$^{3,7}$]tetradecane-2,12,14-trione and was given the trivial name hypersampsone K.

Hypersampsone H, which possesses a similar structure to hypersampsone K (**3**), had been isolated from the same plant and it was deduced to have an equatorial relative configuration for its prenyl group at the C-11 position via its ROESY specturm (Zeng et al., 2009). However, by consideration of the precedent

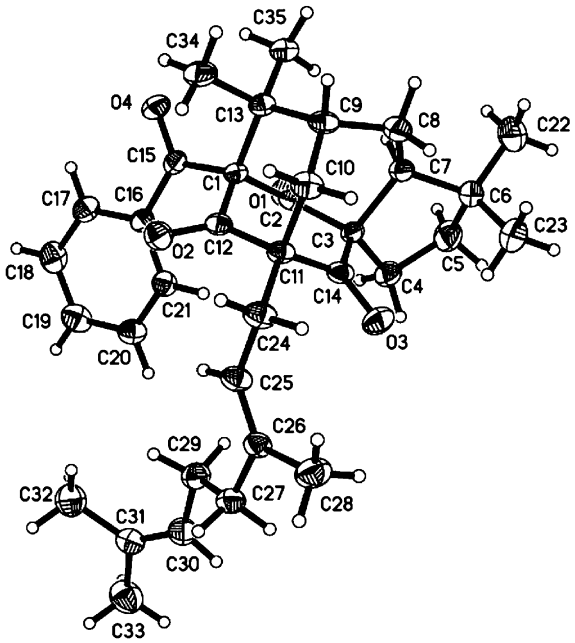


**Fig. 2.** ORTEP diagram for X-ray crystallography of **1**.

previously described for chemical shifts of $CH_2$-10, C-11 and *gem*-dimethyl group (Piccinelli et al., 2005), the relative configuration for its prenyl group at C-11 position should be corrected and rearranged in an axial orientation according to its the $\Delta\delta$ 0.08 for the two hydrogens of the $CH_2$-10, $\delta_C$ 48.7 ppm for C-11, and 27.2/23.3 ppm for carbons of the *gem*-dimethyl group.

Hypersampsone L (**4**) was obtained as a stramineous oil with an $[\alpha]_D^{22}$ of −67.4 (c 0.098, $CHCl_3$). Its molecular formula was assigned as $C_{35}H_{44}O_4$ on the basis of the HRESIMS with an ion at 551.31318 $[M+Na]^+$ (calcd. for $C_{38}H_{50}NaO_4$, 551.3138). The IR spectrum of **4** showed the presence of an absorption band for a carbonyl group at 1693 $cm^{-1}$. Comparison of the NMR data of compound **4** with that of **1** (Table 1) suggested that **4** had a benzoyl group, three specific carbonyl groups ($\delta_C$ 205.3, 205.1 and 200.8), vinyl moieties and seven methyl groups, and was also a geranyl-bearing polyisoprenylated benzoylated phloroglucinol derivative. The $^1H$–$^1H$ COSY and HMBC spectra of **4**, showed correlations of a cyclohexanone ring moiety (C-1, $\delta_C$ 84.5 s; C-9, $\delta_C$ 205.1 s; C-8, $\delta_C$ 70.2 s; C-7, $\delta_C$ 36.5 *t*; C-6, $\delta_C$ 41.9 d and C-10, $\delta_C$ 53.0 s). Further correlations between the high-field proton of H-5β at $\delta_H$ 2.03 with five carbons (C-2, $\delta_C$ 205.3 s; C-3, $\delta_C$ 51.4 d; C-4, $\delta_C$ 59.0 d; C-6, $\delta_C$ 41.9 d and C-10, $\delta_C$ 53.0 s) indicated connectivity to a cycloheptanone ring (C-1, C-2, C-3, C-4, C-5, C-6 and C-10). This indicated that compound **4** had a cage-moiety of a tricyclo[4.3.1.$1^{3,8}$] undecane-2,9,11-trione, which was partially similar to that of **1**.

In the structure of **4**, apart from a geranyl group, a further 3-methyl-2-butenyl side chain existed and was indicated by the presence of an overlapped vinyl proton ($\delta_H$ 5.07, m), two vinyl-bearing methyl groups, and two high-field protons ($\delta_H$ 2.11 m and $\delta_H$ 2.67 br d, 14.9 Hz). This moiety was attached at the cage structure at C-4 and formed a new skeleton for compound **4**.

The relative stereochemical configurations of C-4 in **4** were assigned by the ROESY spectrum (Fig. 2 in S18). Correlations of H-7b/H-5β and H-5β/H-4 indicated that H-4 was oriented in a β-configuration in **4**. Moreover, a weak NOE correlation between H-7b and H-4 in the NOESY spectrum of **4**, supported this conclusion. Therefore compound **4** was elucidated as (1*S**,3*S**,4*S**,6*R**,8*R**)-1-benzoyl-8-(3,7-dimethylocta-2(*E*),6-dienyl)-10,10-dimethyl-4-(3-methyl-2-butenyl)tricyclo[4.3.1.$1^{3,8}$]undecane-2,9,11-trione and given the trivial name hypersampsone L.

Compounds **1**, **2** and **3** are typical geranyl-bearing polyisoprenylated benzoylphloroglucinol derivatives, which are presumably biosynthesized from the biogenetically acceptable 2,4,6-trihydroxybenzophenone via a series of *C*-alkylations with dimethylallyl diphosphate (DMAPP) (Fig. 5 in S19) (Dewick, 2009; Hu and Sim, 2000; Ciochina and Grossman, 2006). A common intermediate **c** could form a polycyclic cage-like intermediate **e** by oxidation of a prenyl group followed by cyclization. Further oxidation and cleavage of the isopropenyl group for the intermediate **f** might give **g**, and reduction of the resulting carbonyl group could lead to hypersampsone I (**1**), whereas a loss of a molecule of $H_2O$ on the hydroxypropyl group might form compound **2**. Hypersampsone K (**3**) might possibly be biosynthesized via intermediate **c** by a nucleophilic addition reaction of the oxygen onto the prenyl group to form a dihydropyran moiety.

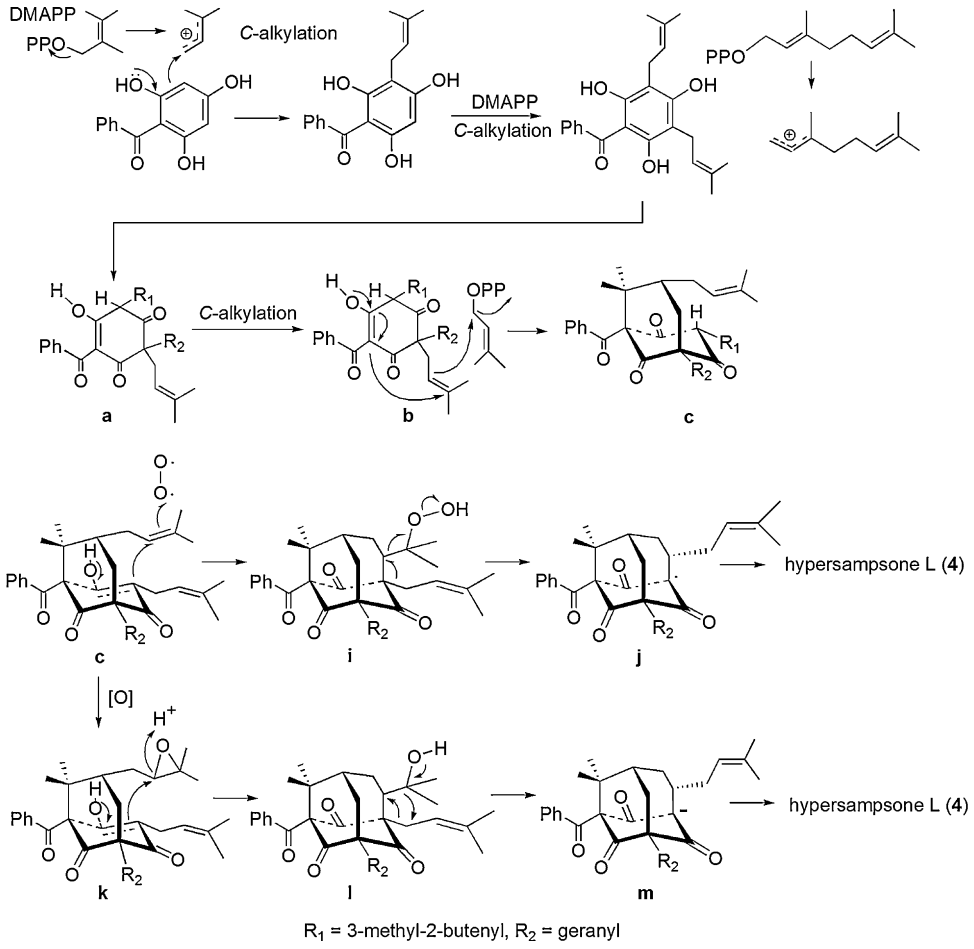


**Fig. 3.** Possible biosynthetic pathway of compound **4**.

The structurally related hypersampsone L (**4**), which also belongs to the same cage-like natural products from *H. sampsonii*, possesses a novel tricyclo[4.3.1.1$^{3,8}$]undecane-2,9,11-trione skeleton. In a biosynthetic speculation, a common intermediate **c** could be attacked by oxygen to form intermediate **i**, a cage-like skeleton with an hydroperoxy group at the *gem*-dimethyl carbon. The loss of acetone with migration of the prenyl group could lead to **4** via **j**. A biosynthetic pathway could also be speculated to occur by an alternative route via intermediate **c**. In this route an epoxide of a prenyl group could be produced as intermediate **k**. Similarly, the loss of acetone might result in the migration of the prenyl group and formation of intermediate **m**, then yielding hypersampsone L (**4**) (Fig. 3).

## 3. Experimental

### 3.1. General experimental procedures

Optical rotations were measured using a JASCO P-1020 polarimeter. IR spectra were recorded using an Avatar™ 360 E.S.P.™ FTIR spectrophotometer and UV spectra were recorded on a Shimadzu UV-1600PC spectropolarimeter. $^1$H and $^{13}$C NMR spectra were obtained on a Varian Mercury Plus 400 MHz. Column chromatography was carried out with silica gel (200–300 mesh, Qingdao Haiyang chemical Co., Ltd.), silica gel H (10–40 μm, Qingdao Haiyang chemical Co., Ltd.) and RP-18 (15–35 μm, Fluka). Fractions obtained from column chromatography were monitored by TLC (silica gel HGF254, 10–40 μm, Yantai, Huanghai, China). ESI mass spectra were obtained on an Agilent 1100 Series LC/MSD spectrometer and HRMALDIMS spectra on the IonSpec 4.7 Tesla FTMS. X-ray crystallographic analysis was carried out on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation λ = 0.71073 Å).

### 3.2. Plant material

*H. sampsonii* was collected from Chalin County in Hunan province, China in 2005 and identified by Dr. Zhang Wen-Ju, Associate Professor in the Center of Biodiversity of Biology School, Fudan University, China. A voucher specimen (No. HS-003) has been deposited at the Natural Medicine Chemistry Laboratory of the School of Pharmacy, Fudan University.

### 3.3. Extraction and isolation

The air-dried powdered fruits of *H. sampsonii* (8 kg) were extracted with 95% alcohol (10 L × 5) at room temperature (three days). These extracts were combined and evaporated under reduced pressure to give 1168 g of residue. The residue was re-extracted successively with petroleum ether (b.p. 60–90 °C, 2 L × 5), chloroform (2 L × 5) and water (2 L × 5). The petroleum ether soluble fraction (730.1 g) was subjected to column chromatography on silica gel (200–300 mesh) using a gradient elution of petroleum ether and ethyl acetate, with an increasing proportion of ethyl acetate and finally by washing with methanol. Fractions from the 2% ethyl acetate in petroleum ether eluent were further purified by repeated column chromatography on silica gel H (10–40 μm) with petroleum ether:ethyl acetate (98:2) and then on a RP-18 column with acetonitrile:water (95:5) to yield **1** (400 mg), **2** (82 mg), **3** (41 mg) and **4** (6 mg).

#### 3.3.1. Hypersampsone I (1)

(1*R**,3*S**,7*S**,9*R**,11*S**)-1-benzoyl-11-(3,7-dimethylocta-2(*E*),6-dienyl)-6,6,13,13-tetramethyltetracyclo[7.3.1.13,11.03,7]tetradecane-2,12,14-trione. Colorless crystals ($Me_2CO$); m.p. 92–93 °C; $[\alpha]_D^{22}$ +18.6 (c 0.262, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ nm (log ε): 249 (4.10); IR (film) $\nu_{max}$ (KBr): 2954, 2926, 2866, 1734, 1695, 1683, 1594, 1567, 1446, 1393, 1371 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR (pyridine-$d_5$) data see Table 1; HRMALDIMS *m*/*z*: 551.31318 [M+Na]$^+$ (calcd. for $C_{35}H_{44}NaO_4$, 551.3140).

X-ray Crystal Data for **1**: $C_{35}H_{44}O_4$, MW = 528.70; orthorhombic, space group $P2_12_12_1$; a = 7.805(3) Å, b = 11.276(4) Å, c = 33.981(12) Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$; $V = 2990.6(18)$Å$^3$; $T = 296(2)$ K; $Z = 4$; $D_{calc} = 1.174$ g/cm$^{-3}$; index ranges: $-10 \le h \le 6$, $-14 \le k \le 12$, $-40 \le l \le 42$; absorption coefficient = 0.074 mm$^{-1}$; completeness: 97.5%; $F(0\,0\,0) = 1144$; GOF (goodness of fit) = 0.673. A colorless prismatic crystal with approximate dimension of 0.15 mm × 0.10 mm × 0.05 mm was chosen and mounted on a Bruker SMART APEX CCD diffractometer; θ range for data collection: 1.90–27.21°; collected 14,451 reflections, of which 6435 were unique [*R*(int) = 0.0743] and 2872 considered observed [$I > 2((I)$]; absorption correction: semi-empirical from equivalents; max. and min. transmission: 0.9963 and 0.9889; refinement method: full-matrix least-squares on $F^2$; data/restraints/parameters: 6435/0/360. The structure was solved by direct methods using the program SHELXS-97. Non-hydrogen atoms were refined anisotropically with SHELXL-97. Hydrogen atoms were located by geometry and rode on the related atoms during refinements with a temperature factor 1.2 or 1.5 times that of the latter. The final *R* values were R1 = 0.0368, wR2 = 0.0572 for 2872 observed reflections and R1 = 0.1088, wR2 = 0.0658 for all. A full list of crystallographic data have been deposited at the Cambridge Crystallographic Data Center, CCDC 695039. It is available by mail at CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; by fax: +44 1223 336 033 or by Internet facilities.

#### 3.3.2. Hypersampsone J (2)

(5*R**,7*S**,9*R**)-1-benzoyl-11-(3,7-dimethylocta-2,6-dienyl)-6,6,13,13-tetramethyl-5-(1-methyl-ethenyl)tetracyclo[7.3.1.1$^{3,11}$.0$^{3,7}$]tetradecane-2,12,14-trione. Colorless crystals ($Me_2CO$); m.p. 103–104 °C; $[\alpha]_D^{22}$ +11.4 (c 0.573, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ nm (log ε): 245 (4.14); IR (film) $\nu_{max}$ (KBr) 2933, 1735, 1697, 1447, 1394, 1374 cm$^{-1}$; for $^1$H NMR and $^{13}$C NMR ($CDCl_3$) data see Table 2; HRMALDIMS *m*/*z*: 591.34448 [M+Na]$^+$ (calcd. for $C_{38}H_{48}NaO_4$, 591.3450).

X-ray Crystal Data for **2**: $C_{38}H_{48}O_4$, MW = 568.76; monoclinic, space group $P2_1$; a = 7.789(3) Å, b = 11.713(4) Å, c = 17.834(7) Å; $\alpha = 90^\circ$, $\beta = 95.680(6)^\circ$, $\gamma = 90^\circ$; $V = 1619.0(11)$Å$^3$; $T = 293(2)$ K; $Z = 2$; $D_{calc} = 1.167$ g/cm$^{-3}$; index ranges: $-9 \le h \le 9$, $0 \le k \le 14$, $0 \le l \le 22$; absorption coefficient = 0.074 mm$^{-1}$; completeness: 99.4%; $F(0\,0\,0) = 616$; GOF (goodness of fit) = 1.039. A colorless prismatic crystal with approximate dimension of 0.20 mm × 0.15 mm × 0.12 mm was chosen and mounted on a Bruker SMART APEX CCD diffractometer; (range for data collection: 2.08–27.00°; collected 3676 reflections, of which 3676 were unique [*R*(int) = 0.000] and 2896 considered observed [$I > 2((I)$]; absorption correction: semi-empirical from equivalents; max. and min. transmission: 0.9912 and 0.9854; refinement method: full-matrix least-squares on $F^2$; data/restraints/parameters: 3676/1/387. The structure was solved by direct methods using the program SHELXS-97. Non-hydrogen atoms were refined anisotropically with SHELXL-97. Hydrogen atoms were located by geometry and rode on the related atoms during refinements with a temperature factor 1.2 or 1.5 times that of the latter. The final *R* values were R1 = 0.0488, wR2 = 0.1184 for 2896 observed reflections and R1 = 0.0655, wR2 = 0.1280 for all. A full list of crystallographic data has been deposited at the Cambridge Crystallographic Data Center, CCDC 747479. It is available by mail at CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; by fax: +44 1223 336 033 or by internet facilities.

*3.3.3. Hypersampsone K (**3**)*

(11*R**)-1-benzoyl-6,6,12,12-tetramethyl-9-(3,7-dimethylocta-2,6-dienyl)-11-(3-methyl-2-butenyl)-7-oxatricyclo[7.3.1.$0^{3,8}$]trideca-3(8)-ene-2,13-dione. Colorless oil; $[\alpha]_D^{22}$ +31.7 (c 0.376, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ nm (log $\varepsilon$): 248 (4.10), 277 (4.01); IR (film) $\nu_{max}$ (KBr): 2974, 2924, 1723, 1698, 1643, 1604, 1447, 1388 $cm^{-1}$; for $^1H$ NMR and $^{13}C$ NMR ($CDCl_3$) data see Table 2; HRMALDIMS *m*/*z*: 593.36013 $[M+Na]^+$ (calcd. for $C_{38}H_{50}NaO_4$, 593.3614).

*3.3.4. Hypersampsone L (**4**)*

(4*R**,6*R**)-1-benzoyl-8-(3,7-dimethylocta-2,6-dienyl)-10,10-dimethyl-4-(3-methyl-2-butenyl)tricyclo[4.3.1.$1^{3,8}$]undecane-2,9,11-trione. (1*S**,3*S**,4*S**,6*R**,8*R**)-1-benzoyl-8-(3,7-dimethylocta-2(*E*),6-dienyl)-10,10-dimethyl-4-(3-methyl-2-butenyl)tricyclo[4.3.1.$1^{3,8}$]undecane-2,9,11-trione. Stramineous oil; $[\alpha]_D^{22}$ −67.4 (c 0.098, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ nm (log $\varepsilon$): 245 (4.15). IR (film) $\nu_{max}$ (KBr): 2922, 2849, 1693, 1447, 1390 $cm^{-1}$; for $^1H$ NMR and $^{13}C$ NMR ($CDCl_3$) data see Table 1; HRMALDIMS *m*/*z*: 551.31318 $[M+Na]^+$ (calcd. for $C_{35}H_{44}NaO_4$, 551.3138).

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.phytol.2011.09.009.

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