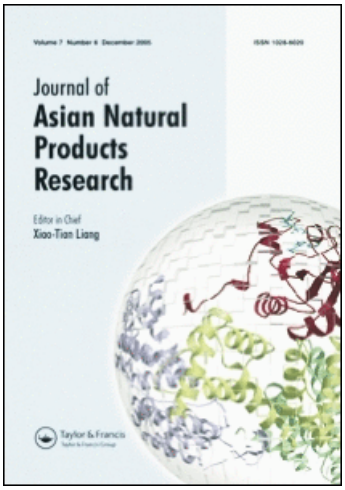


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# A new meroditerpenoid from *Mayodendron igeum*

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A new meroditerpenoid, igeumone (**1**), together with 18 known compounds (**2–19**), were isolated from ethanolic extract of the bark of *Mayodendron igeum*. Their structures were determined by analysis of spectral data or comparison with authentic samples. X-ray crystallographic analysis was employed to unambiguously determine the structure of **1**.

*Keywords*: *Mayodendron igeum*; Meroditerpenoid; Igeumone

## 1. Introduction

*Mayodendron igeum*, the unique species of *Mayodendron* Kurz (Bignoniaceae), is an evergreen big tree distributed over Burma and Yunnan Province of China [1], primarily known for its large edible flowers. Chemical study on *M. igeum* has not been reported.

Meroditerpenoids are well known in marine sponges and microorganisms, and several skeletons have been reported [2,3]. In the course of investigating the chemical constituents from the bark of *M. igeum*, a new meroditerpenoid, igeumone (**1**), was isolated along with other nineteen known compounds: β-sitosterol (**2**), β-daucosterol (**3**), vanillic acid, auranamide (**5**) [4], ethyl caffeate (**6**), lup-20 (29)-ene-3α,27β-diol (**7**) [5], eugenin (**8**), naringenin (**9**), syringalhyde, phlogacantholides B (**11**) [6], quercetin (**12**), paederoside (**13**), 2-hydroxy-3-hydroxymethyl-9,10-anthraquinone (**14**), 1-methoxy-3-hydroxy-2-carbon-methoxy-9,10-anthraquinone (**15**) [7], lucidin primeveroside (**16**) [8], nemoroside (**17**) [8], picroside (**18**) [9] and naringin (**19**). The known compounds were identified by comparing their spectral data with reported data or with those of authentic sample.

## 2. Results and discussion

Compound **1** (figure 1) was obtained as colourless needles (acetone). The molecular formula $C_{27}H_{40}O_4$ was determined from the ion peak at *m/z* 451.2822 $[M + Na]^+$ in the HRESI-MS spectrum. Seven methyl singlets at $\delta_H$ 1.97, 1.77, 1.74, 1.11, 1.07, 0.86, and 0.84 (each 3H, s)

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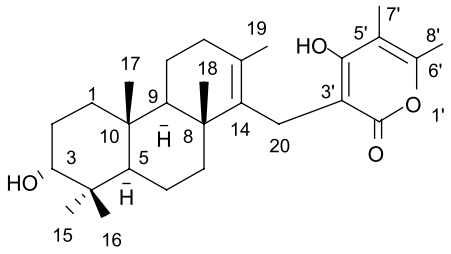


Figure 1. Structure of **1**.

were observed in the $^{1}$H NMR spectrum. The IR absorption bonds at 1681, 1651 and 1581 cm$^{-1}$ together with the $^{13}$C NMR signals at $\delta_C$ 165.2, 164.2, 155.0, 138.6, 131.1, 106.9 and 101.8 suggested the presence of an unsaturated lactone carbonyl and three tetrasubstituted double bonds. The $^{1}$H–$^{1}$H COSY and TOCSY experiments on **1** revealed three $^{1}$H–$^{1}$H spin-systems assignable to C1–C2–C3, C5–C6–C7, and C9–C11–C12. The presence of an ioscopalane-type diterpene moiety was deduced from the following HMBC cross-peaks: H-3/C-5 and C-16 ($\delta_C = 22.1$), H-5/C-9 and C-16, H-17/C-9 and C-1, H-18/C-9 and C-14 ($\delta_C = 138.6$), and H-19/C-12 and C-14. The HMBC correlations of H-8′/C-6′ and C-5′, H-7′/C-6′, C-5′, and C-4′, and H-20 ($\delta_H = 3.60$ and 3.50, each 1H, d, $J = 16.7$ Hz)/C-4′, C-3′ and C-2′ indicated the presence of a 4-hydroxypyran-2-one moiety, which was also supported by the UV absorption at $\lambda_{max}$ 291 (4.24) nm of **1** [10]. Based on the HMBC correlations of H-20/C-8, C-13, C-2′ and C-4′, the pyran-2-one moiety could be located at C-20 of the diterpene moiety.

The NOESY cross-signals between H-3/$H_3$-15 and $H_3$-16, H-5/H-9 and $H_3$-15, $H_3$-17/$H_3$-18 and $H_3$-16 provided the relative configurations. Therefore, the structure of igeumone (**1**) was finally elucidated. The X-ray crystallographic analysis also confirmed the relative stereochemistry.

Igeumone (**1**) was the first meroditerpenoid isolated from the plants. It may be biosynthesised via combined biosynthetic pathway from acetate and mevalonate [11].

## 3. Experimental

### *3.1 General experimental procedures*

Melting points were determined using an XRC-1 melting point apparatus (Sichuan University Science Instruments Factory) and are uncorrected. Optical rotations were measured on a Perkin–Elmer 341 automatic polarimeter. UV and IR spectra were obtained on a Lambda 35 spectrometer and a Perkin–Elmer FT-IR spectrometer, respectively. NMR spectra were recorded on a Bruker Advance 600 spectrometer with TMS as internal standard. ESI-MS and HRESI-MS were carried out on Finnigan-LCQ$^{DECA}$ and Bio-TOF IIIQ mass spectrometers, respectively. X-ray crystallographic data were collected on a Bruker SMART 1000 CCD diffractometer. Silica gel (200–300 mesh, Qingdao Haiyang Chemical Co.) was used mostly for separation carried out by column chromatography. RP-18 silica gel (Prepex 40–63 μm) was purchased from Phenomenex Co. and macroporous resin $D_{101}$ (pore size 13–14 nm, 26–60 mesh) was acquired from Tianjin Haiguang Chemical Co. All solvents were distilled prior to use.

### *3.2 Plant material*

The stem bark of *M. igeum* was collected in November 1999 from Xishuangbanna, Yunnan Province of China. The plant material was identified by Professor Jing-Yun Cui at Xishangbanna Tropical Botanical Garden, the Chinese Academy of Sciences (CAS). A voucher specimen (GF-119) is deposited at the Herbarium of Chengdu Institute of Biology, CAS.

### *3.3 Extraction and isolation*

The air-dried and powdered stem bark of *M. igeum* (7.5 kg) was soaked with 95% ethanol (30 L × 3) at room temperature. The ethanol was evaporated under reduced pressure to give 1.1 kg residue, which was suspended in water (1.5 L), defatted with petroleum ether (3.0 L × 5), and extracted successively with $CHCl_3$ (3.0 L × 6), EtOAc (4.0 L × 4) and *n*-Butanol (3.5 L × 4) to give the corresponding fractions A (14.5 g), B (18.1 g), and C (112.5 g), respectively. Fraction A was divided into five subfractions A1–A5 by silica gel (500 g, 80 mm × 310 mm) column chromatography, eluted with petroleum ether/EtOAc (50:1, 20:1, 10:1, 5:1, each 500 ml). A2 (1.5 g) was separated by column chromatography on silica gel (45.2 g, 40 × 100 mm), eluted with petroleum ether-EtOAc (60:1, 30:1, each 500 ml) to afford **2** (23 mg) and **3** (45 mg). Compound **4** (2.1 g), **3** (56 mg), **1** (3 mg) and **5** (5 mg) were obtained from A3 (3.2 g) by silica gel (280 g, 50 × 230 mm) column chromatography with petroleum ether-EtOAc (20:1, 2.5 L) as solvents. A4 (1.3 g) was separated by silica gel (35 g, 38 × 90 mm) column chromatography, eluted with petroleum ether/EtOAc (10:1, 1.5 L) to give **4** (26 mg) and **6** (315 mg). Compounds **4** (90 mg), **7** (23 mg), **8** (8 mg), **9** (213 mg) and **10** (12 mg) were isolated from A5 (2.4 g) by silica gel (90 g, 50 × 150 mm) column chromatography using petroleum ether-acetone (15:1, 10:1, each 1.0 L) as solvents. Fraction B was divided into four subfractions B1–B4 by column chromatography on silica gel (1.0 kg, 80 × 340 mm), eluted with $CHCl_3$ (500 ml) and $CHCl_3$/acetone (30:1, 10:1, 5:1, each 500 ml). B2 (4.8 g) was separated by silica gel (300 g, 50 × 250 mm) column chromatography, eluted with $CHCl_3$/EtOAc (30:1, 10:1, 5:1, each 500 ml) to give **11** (323 mg). Compounds **12** (113 mg) and **13** (151 mg) were obtained from B3 (2.7 g) by silica gel (400 g, 60 × 260 mm) column chromatography using $CHCl_3$/EtOAc/acetic acid (10:1:0.5, 5:1:0.5, each 500 ml) as solvents. B4 (4.5 g) was separated by silica gel (300 g, 50 × 250 mm) column chromatography, eluted with $CHCl_3$/EtOAc/MeOH (30:1:0.5, 20:1:0.5, each 500 ml) to give **14** (75 mg) and **15** (105 mg). Fraction C was subjected to column chromatography (macroporous resin $D_{101}$, 1.2 kg, 80 mm × 1.2 m) to remove sugar by MeOH/$H_2O$ (0:1, 1:0, each 6.0 L), followed by column chromatography on RP-18 (180 g, 38 × 220 mm), using $H_2O$ (500 ml) and MeOH/$H_2O$ (50:1, 30:1, 10:1, 500 ml) as solvents, gave **16** (21 mg), **17** (95 mg), **18** (153 mg) and **19** (5.6 g).

### *3.4 X-ray crystal structure analysis of 1*

Crystal data for **1**: $C_{27}H_{40}O_4$; $M_r = 428.59$; dimensions 0.34 × 0.28 × 0.26 mm; orthorhombic, space group $P2_12_12_1$, $a = 11.4211(9)$Å, $b = 13.1397(10)$Å, $c = 15.5583(12)$Å, $\alpha = \beta = \gamma = 90°$, $V = 2334.8(3)$Å$^3$, $Z = 4$, $D_{calc} = 1.219$ g/cm$^3$, $\lambda = 0.71073$Å, $\mu$(Mo K$\alpha$) = 0.080 mm$^{-1}$, $F(000) = 936$, $T = 293(2)$ K. Data were collected up to 27.91° in $\theta$. Of the 15,838 reflections collected, 3142 were unique ($R_{int} = 0.0246$); the structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares on $F^2$. Final

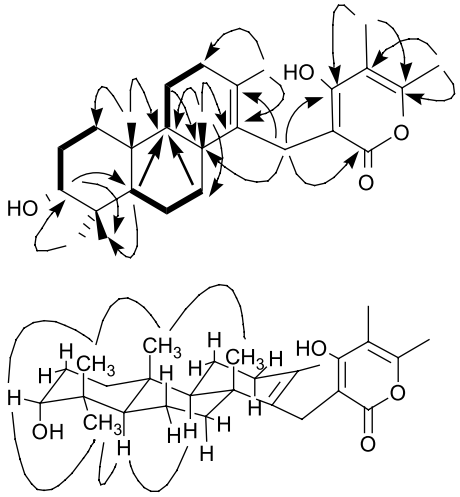


Figure 2. Major 2D NMR correlations of **1**. TOCSY (thick lines), HMBC (arrowed lines) and NOESY (thin lines).



refinement: data/restraints/parameters = 3142/2/293; $R_1 = 0.0456$ (all data), $wR_2 = 0.0994$ (all data), and GOF = 0.979. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.176 and $-0.130\ e^-/Å^3$, respectively. The final X-ray model is shown in figure 2. CCDC 259658 contains the supplementary, crystallographic data for this paper (for crystal structure diagram see figure 3). These data can be obtained free of charge via www.ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

### *3.5 Igeumone (1)*

Colourless needles from acetone; mp 222–224°C; $[\alpha]_D^{20} + 108$ (*c* 0.15, MeOH); UV (cyclohexane) $\lambda_{max}$(log $\varepsilon$) 264 (1.34), 291 (4.24) nm; IR (KBr) $\nu_{max}$ 3453, 3275, 2937, 2870, 1681, 1651, 1581, 1452, 1385, 1288, 1116, 1075, 1053, 758 $cm^{-1}$; $^1$H NMR and $^{13}$C NMR data, see table 1; ESI-MS (negative mode) *m/z* 427.1 $[M - H]^-$; ESI-MS (positive mode) *m/z* 429.0 $[M + H]^+$; HRESI-MS (positive mode) *m/z* 451.2822 $[M + Na]^+$ (calcd for $C_{27}H_{40}O_4Na$, 451.2819).

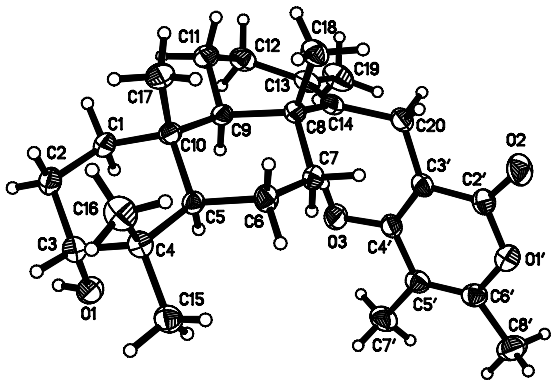


Figure 3. ORTEP drawing of **1**.

Table 1. NMR data of **1** in $C_5D_5N$ ($^1H$: 600 MHz; $^{13}C$: 150 MHz).

| *No.* | $\delta_H$ *(mult., J in Hz)* | $\delta_C$ | *No.* | $\delta_H$ *(mult., J in Hz)* | $\delta_C$ |
|---|---|---|---|---|---|
| 1β | 1.65 (dd, 12.6, 1.8) | 33.2 | 13 | | 131.1 |
| 1α | 1.46 (m) | | 14 | | 138.6 |
| 2α | 1.75 (m) | 26.2 | 15 | 1.07 (s) | 28.8 |
| 2β | 2.00 (dd, 12.8, 2.0) | | 16 | 0.84 (s) | 22.1 |
| 3 | 3.57 (t, 1.4) | 74.9 | 17 | 0.86 (s) | 16.5 |
| 4 | | 37.8 | 18 | 1.11 (s) | 20.9 |
| 5 | 1.68 (d, 12.1) | 49.0 | 19 | 1.74 (s) | 20.3 |
| 6α | 1.45 (m) | 18.5 | 20α | 3.60 (d, 16.7) | 24.8 |
| 6β | 1.39 (t, 12.5) | | 20β | 3.50 (d, 16.8) | |
| 7α | 2.11 (d, 12.6) | 38.2 | 2′ | | 164.2 |
| 7β | 1.46 (m) | | 3′ | | 101.8 |
| 8 | | 39.9 | 4′ | | 165.2 |
| 9 | 1.29 (d, 12.8) | 56.3 | 5′ | | 106.9 |
| 10 | | 37.5 | 6′ | | 155.0 |
| 11α | 1.62 (dd, 12.6, 4.8) | 17.8 | 7′ | 1.77 (s) | 9.9 |
| 11β | 1.46 (m) | | 8′ | 1.97 (s) | 16.7 |
| 12α | 2.02 (m) | 34.2 | | | |
| 12β | 2.02 (m) | | | | |



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