

Dammarane triterpenes from the apical buds of *Gardenia collinsae*

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ABSTRACT

Two new dammarane triterpenes, named 20R,24R-epoxy-3-oxo-dammarane-25 ξ ,26-diol (**1**) and its C-24 epimer (**2**), were isolated from the apical buds of *Gardenia collinsae*, along with a known compounds (20R,24R)-ocotillone (**3**). The structures were elucidated on the basis of spectroscopic evidence. Their cytotoxic effect on five human tumor cell lines was examined.

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1. Introduction

The genus *Gardenia* (Rubiaceae) comprises more than 80 species distributed over the tropical forests in various parts of the world and 15 species of them were reported to be found in Thailand (Smitinand, 2001). Various species of *Gardenia* plants have been used ethnomedically for abortifacient and contraceptive purposes (Woo et al., 1981; Mbela et al., 1992; Jain, 1989), and for the treatment of headaches, asthma and malaria (Croft and Tu'Ipulotu, 1980; Chhabra et al., 1991; Gessler et al., 1995). Additionally, extracts of several species exhibiting anti-implantation and abortifacient effects (Lu et al., 1981), and antiulcer (Takase et al., 1989), antibacterial (Laurens et al., 1985), diuretic, analgesic, hypertensive and larvicidal activities (Hussian et al., 1991; Manson, 1939) have been reported. Previous investigations on the plants in this genus have led to the isolation of an array of structurally diverse flavonoids and cycloartane triterpenoids, with a wide range of biological activities, particularly cytotoxic and anti-HIV effects (Reutrakul et al., 2004; Tuchinda et al., 2002). Recently, we have also reported the isolation and identification of a number of cytotoxic 3,4-*seco*-cycloartane triterpenoids from two species found in Thailand, *Gardenia sootepensis* and *Gardenia tubifera* (Nuanyai et al., 2009, 2010). In the continuing search for potential anti-cancer drug leads from Thai *Gardenia* plants, a new dammarane triterpene (**1**) and its epimer (**2**) were isolated from the apical buds of *G. collinsae*, together with one known compound (20R,24R)-ocotillone (**3**), as well as their cytotoxicity was also evaluated.

2. Results and discussion

The MeOH-soluble fraction of the fresh apical buds of *G. collinsae* was partitioned between EtOAc and H₂O to afford an EtOAc extract, which was then subjected to silica gel column chromatography using EtOAc-hexane mixtures of increasing polarity as eluent. Further purification by repeated normal-phase column chromatography yielded a new dammarane-type triterpene (**1**) and its C-24 epimer (**2**), along with (20R,24R)-ocotillone (**3**) (Fig. 1).

Compound **1**, a white amorphous powder, had the molecular formula C₃₀H₅₀O₄ as established by the HRESIMS ion at *m/z* 497.3609 [M+Na]⁺ (calcd 497.3607). Its IR spectrum showed absorption bands at 1710 and 3466 (broad) cm⁻¹, which indicated the presence of carbonyl and hydroxyl groups. Inspection of the ¹³C NMR and HSQC spectra revealed the presence of 30 nonequivalent carbons consisting of one ketone carbonyl, seven tertiary methyls, 11 methylenes (one oxygenated), five methines (one oxygenated) and six quaternary carbons (two oxygenated). The ¹H NMR spectrum of **1** (Table 1) displayed seven singlet signals of tertiary methyls at δ_{H} 0.87, 0.93, 0.99, 1.01, 1.03, 1.08 and 1.16, associating with dammarane-type triterpenoid. The planar structure of **1** was elucidated on the basis of 2D NMR (¹H–¹H COSY, HSQC and HMBC) spectroscopic data (Fig. 2). The tetrahydrofuran ring was evident from a key HMBC correlation from an oxygenated methine proton at δ_{H} 3.82 (H-24) to C-20. An oxygenated methylene group (δ_{H} 3.37 and 3.67; δ_{C} 71.3) was located as C-26 which was addressed by HMBC correlations from H-26 to C-24 and C-25. Detailed analyses of the NMR spectroscopic data of **1** as described above led to the establishment of the same planar structure as 20S,24R-epoxy-3-oxo-dammarane-25 ξ ,26-diol (**4**) (Anjaneyulu et al., 1993). The NMR data of **1** were also similar to those of **4**, with the marked difference being the ¹³C resonances of Me-21 (δ_{C} 22.5 for **4**) and oxygenated carbons of the tetrahydrofuran unit [δ_{C} 86.4 qC

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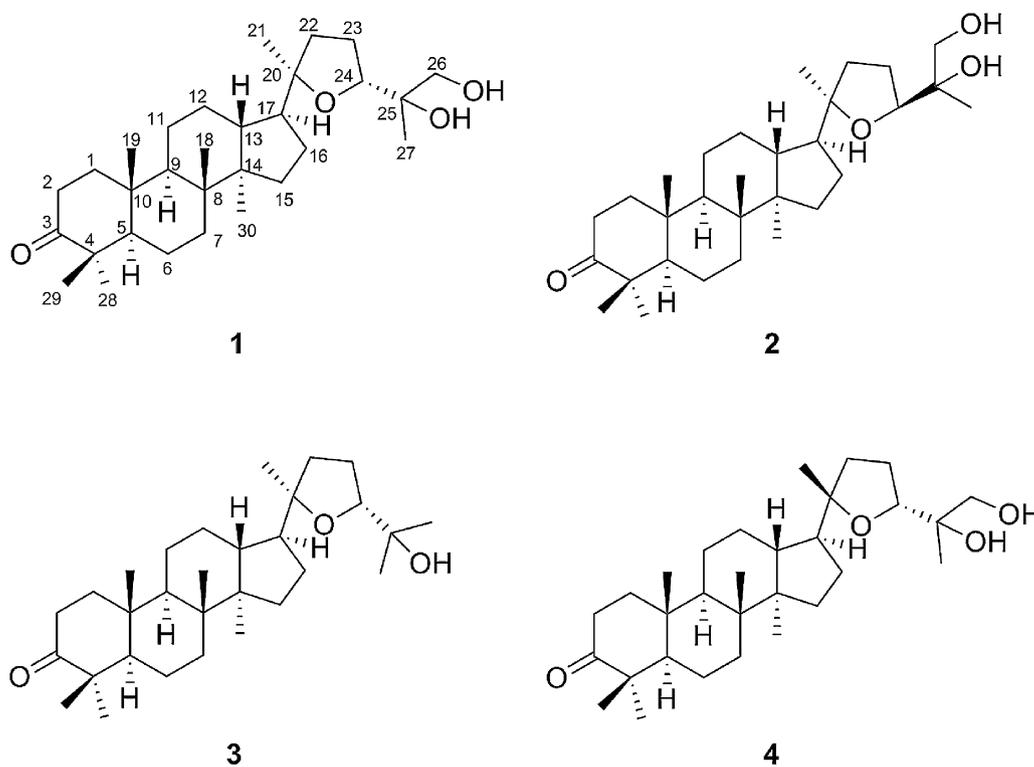


Fig. 1. Structures of the isolated dammarane triterpenes.

Table 1
NMR spectroscopic data (400 MHz, CDCl₃) for compounds 1–3.

| Position | 1 | | 2 | | 3 | |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | δ_C | δ_H (J in Hz) | δ_C | δ_H (J in Hz) | δ_C | δ_H (J in Hz) |
| 1a | 39.9 CH ₂ | 1.91 m | 39.9 CH ₂ | 1.91 m | 39.9 CH ₂ | 1.93 m |
| 1b | | 1.45 m | | 1.44 m | | 1.47 m |
| 2 | 34.1 CH ₂ | 2.46 m | 34.1 CH ₂ | 2.46 m | 34.1 CH ₂ | 2.47 m |
| 3 | 218.0 C | – | 218.1 C | – | 218.1 C | – |
| 4 | 47.4 C | – | 47.4 C | – | 47.4 C | – |
| 5 | 55.3 CH | 1.36 m | 55.3 CH | 1.37 m | 55.3 CH | 1.37 m |
| 6a | 19.6 CH ₂ | 1.55 m | 19.7 CH ₂ | 1.55 m | 19.7 CH ₂ | 1.56 m |
| 6b | | 1.45 m | | 1.46 m | | 1.46 m |
| 7a | 34.5 CH ₂ | 1.56 m | 34.6 CH ₂ | 1.56 m | 34.6 CH ₂ | 1.56 m |
| 7b | | 1.30 m | | 1.31 m | | 1.31 m |
| 8 | 40.2 C | – | 40.3 C | – | 40.3 C | – |
| 9 | 49.9 CH | 1.41 m | 49.7 CH | 1.42 m | 49.8 CH | 1.42 m |
| 10 | 36.8 C | – | 36.9 C | – | 36.9 C | – |
| 11a | 22.1 CH ₂ | 1.52 m | 22.3 CH ₂ | 1.51 m | 22.3 CH ₂ | 1.52 m |
| 11b | | 1.25 m | | 1.24 m | | 1.26 m |
| 12a | 25.7 CH ₂ | 1.75 m | 25.8 CH ₂ | 1.76 m | 25.8 CH ₂ | 1.77 m |
| 12b | | 1.33 m | | 1.29 m | | 1.32 m |
| 13 | 43.1 CH | 1.61 m | 43.0 CH | 1.64 m | 43.0 CH | 1.68 m |
| 14 | 50.0 C | – | 50.0 C | – | 50.0 C | – |
| 15a | 31.3 CH ₂ | 1.47 m | 31.4 CH ₂ | 1.46 m | 31.4 CH ₂ | 1.46 m |
| 15b | | 1.10 m | | 1.09 m | | 1.09 m |
| 16 | 26.1 CH ₂ | 1.80 m | 27.1 CH ₂ | 1.82 m | 27.0 CH ₂ | 1.84 m |
| 17 | 50.0 CH | 1.85 m | 50.1 CH | 1.86 m | 50.2 CH | 1.88 m |
| 18 | 16.0 CH ₃ | 0.99 s | 16.1 CH ₃ | 0.99 s | 16.1 CH ₃ | 1.01 s |
| 19 | 15.1 CH ₃ | 0.93 s | 15.2 CH ₃ | 0.93 s | 15.2 CH ₃ | 0.94 s |
| 20 | 87.8 C | – | 86.8 C | – | 86.5 C | – |
| 21 | 26.7 CH ₃ | 1.16 s | 26.7 CH ₃ | 1.16 s | 27.2 CH ₃ | 1.15 s |
| 22a | 34.4 CH ₂ | 1.78 m | 34.7 CH ₂ | 1.88 m | 34.8 CH ₂ | 1.88 m |
| 22b | | 1.68 m | | 1.70 m | | 1.68 m |
| 23a | | 2.08 m | 27.1 CH ₂ | 1.81 m | 26.4 CH ₂ | 1.79 m |
| 23b | | 1.81 m | | 1.23 m | | 1.32 m |
| 24 | 86.3 CH | 3.82 dd (4.9, 10.4) | 86.3 CH | 3.83 dd (4.7, 10.2) | 86.4 CH | 3.63 m |
| 25 | 70.6 C | – | 72.5 C | – | 70.2 C | – |
| 26a | 71.3 CH ₂ | 3.67 t (10.8) | 67.5 CH ₂ | 3.73 d (11.0) | 24.1 CH ₃ | 1.11 s |
| 26b | | 3.37 d (10.8) | | 3.39 t (11.0) | | |
| 27 | 20.0 CH ₃ | 1.01 s | 21.4 CH ₃ | 1.11 s | 27.8 CH ₃ | 1.19 s |
| 28 | 27.0 CH ₃ | 1.08 s | 26.9 CH ₃ | 1.07 s | 26.7 CH ₃ | 1.08 s |
| 29 | 21.0 CH ₃ | 1.03 s | 21.0 CH ₃ | 1.04 s | 21.0 CH ₃ | 1.04 s |

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