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A NEW CARBAMIC ACID FROM *Dryopteris wallichiana*

Wen-Yi Kang,* Chang-Qin Li, and Zhi-Qiang Ji

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*A new carbamic acid, (1,7a-dihydro-1*H*-inden-2(7a*H*)-ylidene)methylcarbamic acid (**1**), along with three known ones, 12-ursen-28-oic acid-3*-O-β-*D-glucopyranoside (**2**), 12-ursen-3*-O-β-*D-glucopyranoside (**3**), and 3,7,11,15-tetramethyl-2-hexadecen-1-ol (**4**), was isolated and identified from* Dryopteris wallichiana.

Keywords: carbamic acid, *Dryopteris wallichiana.*

The genus *Dryopteris*, belonging to the Dryopteridaceae family, is a cosmopolitan genus comprising approximately 450 species, mostly occurring in temperate forests and mountainous areas of the tropics. China has more than 300 species distributed across the country, 21 of which can be used for medicine [1]. Many constituents, including sesquiterpenes, phloroglucins, phenolic glycosides, and sitosterols have been isolated from *D. crassirhizoma*, *D. parallelogramma, D. patula, D. hawaiiensis, D. fuscoatra, D. fragrans, D. abbreviate, D. polylepis*, *and D. dickinssi* [2–8]. Phloroglucins are characteristic constituents of *Dryopteris* plants and are of interest to many pharmaceutical scholars due to multiple physiological activities such as antivirus, antitumor, antibacterial, and anti-inflammatory effects [9–12]. To the best of our knowledge, there is no research on the chemical constituents of *D. wallichiana.*

In the present study, *D. wallichiana* growing in Xishuangbanna of Yunnan Province was examined. Samples of the aerial parts of *D. wallichiana* were collected in May 2006, and a voucher specimen was kept at the Herbarium of the Institute of Natural Products, Henan University. The dried aerial parts of *D. wallichiana* (3.5 kg) were extracted with ethanol (95%) at room temperature. After evaporation of the ethanol, the residue was suspended in water and extracted with petroleum ether, chloroform, and *n*-butanol. The *n*-butanol extract (120 g) was subjected to silica gel column chromatography (200–300 mesh, Qingdao Marine Chemical Inc, China) using chloroform–methanol mixtures (ϕ_r =10:1 to 8:2) and divided into three fractions by TLC detection. Fraction 1 was subjected repeatedly to column chromatography over silica gel (10–40 μ Qingdao Marine Chemical Inc, China), eluting with chloroform–methanol (ϕ_r = 10:1) to afford (1,7a-dihydro-1*H*-inden-2(7a*H*)-ylidene) methylcarbamic acid (**1**, 26.2 mg) and 3,7,11,15-tetramethyl-2-hexadecen-1-ol (**4**, 11.2 mg). Fraction 2 was chromatographed on Sephadex LH-20 using methanol as eluent and then subjected to C-18 eluting with methanol-water (ϕ_r = 7:3) to afford 12-ursen-28-oic acid-3-*O*-*β*-D-glucopyranoside (**2**, 19.4 mg) and 12-ursen-3-*O*-*β*-D-glucopyranoside (**3**, 28 mg). Compound **1** was a new compound, and **2** and **3** were isolated and identified from the genus for the first time.

Identification of the isolated compounds was performed by comparison of the physical constants and spectral data with those of known compounds [13–14]. Compound **1**, obtained as white needles, had the molecular formula $C_{11}H_{13}NO_2$, as deduced from the molecular-ion peak at *m/z* 192.1034 $[M + H]^+$ (calcd 192.1024) in the HR-EI-MS and from ^{13}C NMR and DEPT analyses. The ^{13}C NMR spectrum revealed 11 carbon signals that were sorted by DEPT experiments into a carbonyl group (δ 172.3), five olefinic methine groups (δ 134.3, 126.9 × 2 and 125.3 × 2), an olefinic quaternary carbon atom (δ 126.0), two methylene groups (δ 49.1 and 45.2), and two methine groups (δ 47.0 and 45.2). The signals of two methine protons [δ 1.16 (m, 1H, H-8a; 47.0, C-8a) and 1.51 (m, 1H, H-4a; 45.2, C-4a)], five olefinic methine protons [δ 5.11 (m, 1H, H-2; 126.0, C-2), 5.11 (m, 2H, H-5, 8; 125.3, C-5, 8), and 5.11 (m, 2H, H-6, 7; 126.9, C-6, 7)], and two methylene protons [δ 1.51, 1.16 (m, 2H, H-4; 49.1, C-4) and 1.40 (m, 2H, H-9; 45.2, C-9] were observed in the ^1H NMR and HMQC spectrum. HMBC analysis of **1** revealed the following long-range correlations between H-2 and C-3, H-4 and C-9, H-5 and C-4a, H-6 and C-4a, H-8a and C-9, and H-9 and C-8 (Fig. 1).

Thus, the structure of **1** was established as (1,7a-dihydro-1*H*-inden-2(7a*H*)-ylidene)methylcarbamic acid.

Institute of Natural Products, Pharmaceutical College, Henan University, 475004, Kaifeng, China, e-mail: kangweny@hotmail.com. Published in Khimiya Prirodnykh Soedinenii, No. 1, pp. 82–83, January–February, 2011. Original article submitted November 11, 2009.

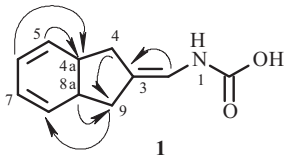

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Fig. 1. HMBC correlations of compound **1**.

EXPERIMENTAL

Melting points of these compounds were determined on an XRC-1 apparatus. The KBr IR spectra were obtained using a Bio-Rad-FTS-135 spectrometer. 1D and 2D NMR spectra were recorded on a Bruker-AM-400 spectrometer in DMSO-d_6 and $CDCl_3$ using TMS as internal standard. HR-MS were obtained using a VG AutoSpec-3000 spectrometeter.

Compound 1 [(1,7a-dihydro-1*H*-inden-2(7a*H*)-ylidene)methylcarbamic acid], $C_{11}H_{13}NO_2$, white needles, mp 193–195°C. IR (KBr, ν_{max}, cm^{-1}): 3445, 2982, 1729, 1583, 1405, 1188, 863, 702. HR-EI-MS *m/z*: 192.1034 $[M + H]^+$ (calcd 192.1024). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 5.11 (5H, m, H-2, 5, 6, 7, 8), 1.16, 1.51 (2H, m, H-4), 1.51 (1H, m, H-4a), 1.16 (1H, m, H-8a), 1.40 (2H, m, H-9). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 172.3 (COOH), 126.0 (C-2), 134.3 (C-3), 49.1 (C-4), 45.2 (C-4a), 125.3 (C-5, 8), 126.9 (C-6, 7), 47.0 (C-8a), 45.2 (C-9).

Compound 2 (12-ursen-28-oic acid-3-*O*-*β*-D-glucopyranoside), $C_{36}H_{58}O_8$, white powder, mp 262–264°C. FAB^- *m/z*: 617 (54) $[M - H]^+$. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.35 (1H, br.s, H-12), 4.21 (1H, d, J = 7.7, H-1′), 0.89 (3H, d, J = 6.4, H-29), 0.83 (3H, d, J = 6.4, H-30), 0.80 (3H, s, H-23), 0.80 (3H, s, H-24), 0.82 (3H, s, H-25), 0.99 (3H, s, H-26), 0.84 (3H, s, H-27), 0.67 (3H, s, H-28). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 38.9 (C-1), 28.2 (C-2), 76.1 (C-3), 37.3 (C-4), 56.2 (C-5), 19.0 (C-6), 31.9 (C-7), 39.8 (C-8), 45.9 (C-9), 36.1 (C-10), 24.3 (C-11), 121.1 (C-12), 140.3 (C-13), 42.4 (C-14), 28.2 (C-15), 26.2 (C-16), 34.0 (C-17), 56.8 (C-18), 39.0 (C-19), 39.8 (C-20), 31.9 (C-21), 42.4 (C-22), 28.2 (C-23), 12.0 (C-24), 11.8 (C-25), 19.0 (C-26), 19.8 (C-27), 174.5 (C-28), 19.3 (C-29), 20.1 (C-30), 101.2 (C-1′), 73.9 (C-2′), 76.1 (C-3′), 70.3 (C-4′), 79.6 (C-5′), 63.3 (C-6′).

Compound 3 (12-ursen-3-*O*-*β*-D-glucopyranoside), $C_{36}H_{60}O_6$, white powder. FAB^- *m/z*: 587 (68) $[M - H]^+$. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.35 (1H, br.s, H-12), 4.21 (1H, d, J = 7.7, H-1′), 0.89 (3H, d, J = 6.4, H-29), 0.82 (3H, d, J = 6.4, H-30), 0.78 (3H, s, H-23), 0.80 (3H, s, H-24), 0.82 (3H, s, H-25), 0.95 (3H, s, H-26), 0.80 (3H, s, H-27), 0.65 (3H, s, H-28). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 38.8 (C-1), 28.3 (C-2), 77.5 (C-3), 37.3 (C-4), 55.9 (C-5), 19.1 (C-6), 31.9 (C-7), 40.0 (C-8), 45.6 (C-9), 35.9 (C-10), 24.3 (C-11), 121.7 (C-12), 140.9 (C-13), 42.3(C-14), 28.3 (C-15), 26.0 (C-16), 33.8 (C-17), 56.7 (C-18), 39.6 (C-19), 39.7 (C-20), 31.9 (C-21), 42.3 (C-22), 28.3 (C-23), 12.3 (C-24), 12.1 (C-25), 19.1 (C-26), 20.2 (C-27), 26.0 (C-28), 19.4 (C-29), 20.2 (C-30), 101.3 (C-1′), 74.8 (C-2′), 76.4 (C-3′), 70.3 (C-4′), 76.5 (C-5′), 61.5 (C-6′).

Compound 4 (3,7,11,15-tetramethyl-2-hexadecen-1-ol), $C_{20}H_{40}O$, yellow oil. EI-MS *m/z*: 296 (100) $[M]^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 5.03 (1H, dd, J = 10.7, 1.3, H-1), 5.18 (1H, dd, J = 17.3, 1.30, H-1), 5.92 (1H, dd, J = 17.3, 10.7, H-2). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 111.4 (C-1), 145.3 (C-2), 73.3 (C-3), 27.7 (C-3a), 42.7 (C-4), 21.3 (C-5), 32.7 (C-7), 19.7 (C-7a,11a), 37.4 (C-8), 32.8 (C-11), 37.3 (C-12), 24.8 (C-13), 39.4 (C-14), 28.01 (C-15), 22.6 (C-15a), 22.7 (C-16).

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REFERENCES

1. Delectis Florae Reipublicae Popularis Sinicae Agendae Academiae Sinicae Edita, *Flora Reipublicae Popularis Sinicae*, Beijing, Science Press, Vol. **5**, 2000, pp. 102–220.
2. X. L. Chang, W. Li, K. Koike, L. J. Wu, and T. Nijaido, *Chem. Pharm. Bull.*, **54**, 748 (2006).
3. T. T. Patama and C. J. Widen, *Phytochemistry*, **30**, 3305 (1991).
4. R. Tryon, C. J. Widen, A. Huhtikangas, and M. Lounasmaa, *Phytochemistry*, **12**, 683 (1973).
5. H. X. Kuang, C. Sun, T. L. Zhang, D. Chen, B. Y. Yang, and Y. G. Xia, *Fitoterapia*, **80**, 134 (2009).
6. S. Hisada, K. Shiraishi, and I. Inagaki, *Phytochemistry*, **10**, 2541 (1971).
7. S. Hisada, K. Shiraishi, and I. Inagaki, *Phytochemistry*, **11**, 2881 (1972).
8. S. Hisada, K. Shiraishi, and I. Inagaki, *Phytochemistry*, **11**, 1850 (1972).
9. G. J. Kapadia, H. Tokuda, T. Konoshima, M. Takasaki, J. Takayasu, and H. Nishino, *Cancer Letters*, **105**, 161 (1996).
10. D. Y. Kwon, O. H. Kang, J. G. Choi, Y. S. Lee, Y. C. Oh, H. S. Chae, G. H. Lee, P. S. Park, Y. C. Kim, D. H. Sohn, H. Park, and J. H. Lee, *Fitoterapia*, **78**, 430 (2007).
11. J. S. Lee, H. Miyashiro, N. Nakamura, and M. Hattori, *Chem. Pharm. Bull.*, **56**, 711 (2008).
12. B. S. Min, M. Tomiyama, C. M. Ma, N. Nakamura, and M. Hattori, *Chem. Pharm. Bull.*, **49**, 546 (2001).
13. F. S. Menezes, A. S. Borsatto, N. A. Pereira, F. J. A. Matos, and M. A. C. Kaplan, *Photochemistry*, **48**, 323 (1998).
14. V. U. Ahmad and M. S. Ali, *Photochemistry*, **30**, 4172 (1991).