DOI 10.1007/s10600-019-02666-y
Chemistry of Natural Compounds, Vol. 55, No. 2, March, 2019

TWO NEW SESQUITERPENES FROM THE ROOTS OF *Taraxacum coreanum*

**Jong Hoon Ahn, Eun Jin Mo, Yang Hee Jo,
Bang Yeon Hwang, and Mi Kyeong Lee***

Phytochemical investigation of the roots of Taraxacum coreanum *(Asteraceae) led to the isolation of two new sesquiterpenes, acetyldihydrotaraxinolide (**2**) and acetyltaraxinolide (**4**), together with two known sesquiterpene glycosides, 11*β*,13-dihydrotaraxinic acid (**1**) and taraxinic acid* β*-(6-*O*-acetyl)-glucopyranosyl ester (**3**). The structures of the isolated compounds were determined on the basis of spectroscopic analysis.*

Keywords: *Taraxacum coreanum*, sesquiterpene, germacranolide.

Dandelion, plants of *Taraxacum* species, is a perennial herb of the Asteraceae family. They are widely distributed throughout the world and have long been used as medicinal herbs and nutritious foods due to their health promoting effects. Previous studies have reported the antioxidant, anticancer, antibacterial, and anti-inflammatory effects of *Taraxacum* species [1–3]. Phenolic compounds, inositol derivatives, and sesquiterpenes have been isolated from *Taraxacum* species [4–7]. Recently, the roots of *Taraxacum* species have been suggested as a good source of sesquiterpene lactones and as active principles of this species [4–8]. Phytochemical investigation on the roots of *T. coreanum* Nakai afforded four sesquiterpene lactones **1–4**, including two newly reported ones.

Compound **2** was purified as a colorless oil, and its molecular formula was determined as $C_{23}H_{32}O_{10}$ from the HR-ESI-MS (*m/z* 491.18877 $[M + Na]^+$, calcd for $C_{23}H_{32}NaO_{10}$, 491.1893) and ^{13}C NMR data. The ^1H and ^{13}C NMR spectra (Table 1) suggested the presence of a glucose moiety at [δ_H 5.55 (1H, d, J = 8.0 Hz, H-1′), 3.35–3.45 (3H, m, H-2′, 3′, 4′), 3.59 (1H, m, H-5′), 4.20 (1H, dd, J = 12.4, 6.0 Hz, H-6′a) and 4.41 (1H, dd, J = 12.4, 2.0 Hz, H-6′b); δ_C 94.0 (C-1′), 72.6 (C-2′), 77.4 (C-3′), 69.8 (C-4′), 74.7 (C-5′), and 63.1 (C-6′)] and an acetyl moiety at [δ_H 2.06 (3H, s, $COC\underline{H_3}$); δ_C 19.3 ($CO\underline{C}H_3$), 171.2 ($\underline{C}OCH_3$)], which were supported by HMBC correlations. The configuration of the glucose moiety was determined to be *β* based on the coupling constant of J = 8.0 Hz. Moreover, the deshielded resonance of H-6′ [δ 4.20 and 4.41] and the HMBC correlation between H-6′ and acetyl group indicated the presence of a (6′-*O*-acetyl)-glucose moiety. The remaining 15 carbons in the ^{13}C NMR spectrum together with HMBC and COSY correlations, which were similar to those of 11,13-dihydrotaraxinic acid (**1**), suggested that **2** is a gemacranolide-type sesquiterpenoid with a 10-membered ring. Taken together, compound **2** was suggested to be 11,13-dihydrotaraxinic acid with a *β*-(6′-*O*-acetyl)-glucose moiety. Further HMBC correlation from H-1′ to C-14 confirmed the connection of the 6′-*O*-acetyl-glucose moiety to 11,13-dihydrotaraxinic acid. The relative stereochemistry was determined by NOESY correlations, in which cross-peaks from H-6 to H-11 and CH_3-15, and from H-5 to H-1 and H-7, confirm the *β*-orientation of H-6 and H-11. Thus, the structure of compound **2** was elucidated as 11*β*,13-dihydrotaraxinic acid *β*-(6-*O*-acetyl)-glucopyranosyl ester and named acetyldihydrotaraxinolide.

Compound **4** was purified as a colorless oil, and its molecular formula was determined as $C_{23}H_{30}O_{10}$ from the HR-ESI-MS *m/z* 489.173118 $[M + Na]^+$ (calcd for $C_{23}H_{30}NaO_{10}$, 489.1737) and ^{13}C NMR data. The ^1H and ^{13}C NMR spectra of **4** (Table 1) was similar to those of **2**, which suggested that **4** is also a germacranolide glycoside. In the ^1H NMR spectra of **4**, methyl signals at C-13 in **2** were replaced by exomethylene signals [δ 5.63 (1H, d, J = 3.2 Hz), 6.19 (1H, d, J = 3.2 Hz)]. In addition, the downfield shift of C-15 from δ 15.7 to δ 23.3 suggested the *Z*-geometry of C-4/C-5 [9].

College of Pharmacy, Chungbuk National University, 28160, Cheongju, Korea, e-mail: mklee@chungbuk.ac.kr.
Published in *Khimiya Prirodnykh Soedinenii*, No. 2, March–April, 2019, pp. 240–242. Original article submitted December 13, 2017.

TABLE 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR Data of Compounds **2** and **4** (CD_3OD, δ, ppm, J/Hz)

C atom	**2**		**4**	
	δ_H	δ_C	δ_H	δ_C
1	5.84 (1H, d, J = 10.8)	148.4	6.08 (1H, br.s)	144.7
2	3.33 (1H, m) 2.31 (1H, m)	26.2	3.57 (1H, m) 2.22 (1H, m)	29.8
3	2.34 (2H, m)	38.7	2.20 (2H, m)	39.3
4	–	147.8	–	139.6
5	4.90 (1H, m)	126.0	5.06 (1H, d, J = 10.4)	121.3
6	4.73 (1H, t, J = 9.6)	81.9	5.37 (1H, dd, J = 10.4, 8.4)	79.8
7	1.78 (1H, m)	54.2	3.28 (1H, m)	44.4
8	2.05 (1H, m) 1.96 (1H, m)	29.9	2.58 (1H, m) 2.21 (1H, m)	30.2
9	2.83 (1H, m) 2.04 (1H, m)	36.0	2.84 (1H, m) 2.20 (1H, m)	29.5
10	–	130.5	–	129.9
11	2.37 (1H, m)	42.0	–	140.1
12	–	180.1	–	171.3
13	1.23 (3H, d, J = 7.2)	11.9	6.19 (1H, d, J = 3.2) 5.63 (1H, d, J = 3.2)	119.7
14	–	166.5	–	166.0
15	1.61 (3H, s)	15.7	1.74 (3H, s)	23.3
1′	5.55 (1H, d, J = 8.0)	94.0	5.54 (1H, d, J = 7.2)	94.1
2′	3.35–3.45 (1H, m)	72.6	3.35–3.45 (1H, m)	72.6
3′	3.35–3.45 (1H, m)	77.4	3.35–3.45 (1H, m)	76.7
4′	3.35–3.45 (1H, m)	69.8	3.35–3.45 (1H, m)	69.7
5′	3.59 (1H, m)	74.7	3.59 (1H, m)	74.7
6′	4.41 (1H, dd, J = 12.4, 2.0) 4.20 (1H, dd, J = 12.4, 6.0)	63.1	4.38 (1H, dd, J = 12.0, 2.0) 4.19 (1H, dd, J = 12.0, 6.0)	63.1
<u>CO</u>CH$_3$	–	171.2	–	171.1
CO<u>CH$_3$</u>	2.06 (3H, s)	19.3	2.05 (3H, s)	19.3

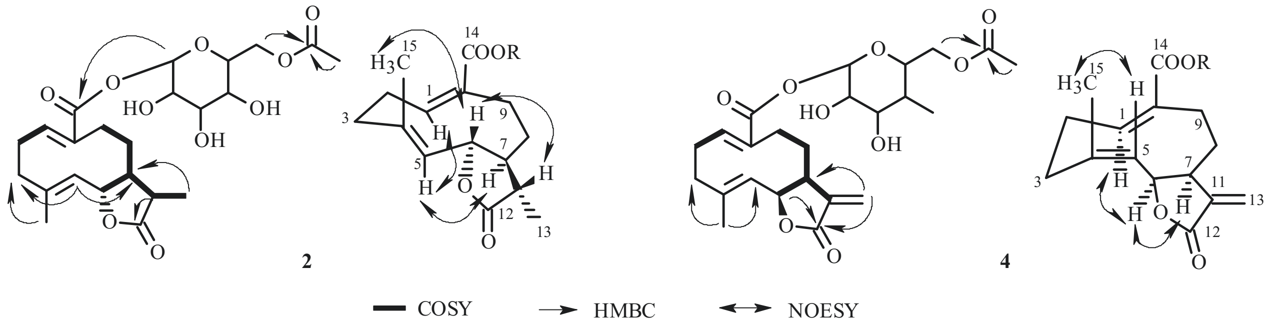

Fig. 1. Key COSY, HMBC, and NOESY correlations of compounds **2** and **4**.

The NOESY correlations between H-1, H-6, and H-7 confirmed their existence on same side, and further correlation between H-5 and CH$_3$-15 suggested the α-orientation of H-6 and H-7. Based on the above evidence, the structure of compound **4** was elucidated as shown and named acetyltaraxinolide.

Two known compounds were identified as 11β,13-dihydrotaraxinic acid (**1**) and taraxinic acid β-(6-*O*-acetyl)-glucopyranosyl ester (**3**) by comparison with literature values [7].

EXPERIMENTAL

General. NMR spectra were recorded on a Bruker DRX 500 MHz NMR spectrometer. ESI-mass spectra were obtained on a VG Autospec Ultima mass spectrometer. Semipreparative HPLC was performed using a Waters HPLC system equipped with Waters 600 Q-pumps, a 996 photodiode array detector, and Waters Empower software using Gemini-NX ODS-column (5 μm, 10 × 150 mm). Silica gel (70–230 mesh, Merck, Germany) and Sephadex LH-20 (25–100 μm, Amersham Biosciences, Sweden) were used for open column chromatography. Thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 (0.25 mm, Merck, Germany). All other chemicals and reagents were of analytical grade.

Isolation of Compounds. The roots of *T. coreanum* were obtained from the local herbal market, Chungbuk, Korea in April 2015 and were identified by the Herbarium of the College of Pharmacy at Chungbuk National University, where a voucher specimen was deposited (CBNU201504-TC). The dried roots of *T. coreanum* (5.0 kg) were extracted twice with 80% MeOH, which yielded the total extract (1.2 kg). The total extract was then suspended in H_2O. Further successive partitioning with *n*-hexane, CH_2Cl_2, and EtOAc yielded the *n*-hexane, CH_2Cl_2, and EtOAc soluble fractions.

The CH_2Cl_2 fraction (TCM, 8.5 g) was subjected to silica gel column chromatography with a mixture of CH_2Cl_2–MeOH to give 12 fractions (TCM1–TCM12). Fraction TCM5 was subjected to silica gel column chromatography with the mixture of *n*-hexane–EtOAc to give 14 fractions (TCM5A–TCM5N). Fraction TCM5N was partitioned into 5 fractions (TCM5N1–TCM5N5) by Sephadex LH-20 eluting with 100% MeOH. Compound **1** (25.2 mg) was obtained from Fr. TCM5N3 by semipreparative HPLC eluting with CH_3CN–H_2O (30:70). The EtOAc fraction (TCE, 8.8 g) was subjected to MPLC with silica gel using a gradient mixture of *n*-hexane–EtOAc–MeOH to give 13 fractions (TCE1–TCE13). Fraction TCE9 was subjected to MPLC with RP-silica using a mixture of *n*-hexane–EtOAc to give five fractions (TCE9A–TCE9E). Compounds **2** (2.4 mg), **3** (1.7 mg), and **4** (0.9 mg) were purifed from Fr. TCE9E by semipreparative HPLC eluting with CH_3CN–H_2O (20:80).

Acetyldihydrotaraxinolide (2), brown syrup, $[\alpha]_D^{25}$ –14.0° (*c* 0.03, MeOH). IR (ν_{max}, cm^{-1}): 1735, 3332. ^1H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD), see Table 1. ESI-MS (positive mode) *m/z* 491 $[M + Na]^+$; HR-ESI-MS (positive mode) *m/z* 491.1888 $[M + Na]^+$ (calcd for $C_{23}H_{32}NaO_{10}$, 491.1893).

Acetyltaraxinolide (4), brown syrup, $[\alpha]_D^{25}$ –7.33° (*c* 0.03, MeOH). IR (ν_{max}, cm^{-1}): 1673, 3370. ^1H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD), see Table 1. ESI-MS (positive mode) *m/z* 489 $[M + Na]^+$; HR-ESI-MS (positive mode) *m/z* 489.1731 $[M + Na]^+$ (calcd for $C_{23}H_{30}NaO_{10}$, 489.1737).

ACKNOWLEDGMENT

This work was supported by the Basic Science Research Program (2015R1D1A1A09058498) through the National Research Foundation of Korea.

REFERENCES

1. C. Hu and D. D. Kitts, *J. Agric. Food Chem.*, **51**, 301 (2003).
2. K. H. Kim, H. J. Chun, and Y. S. Han, *Kor. J. Soc. Food Sci.,* **14**, 114 (1998).
3. M. Takasaki, T. Konoshima, H. Tokuda, K. Masuda, Y. Arai, K. Shiojima, and H. Ageta, *Biol. Pharm. Bull.*, **22**, 602 (1999).
4. C. Zidorn, E. P. Ellmerer-Muller, and H. Stuppner, *Phytochemistry*, **51**, 991 (1999).
5. J. H. Choi, K. M. Shin, N. Y. Kim, J. P. Hong, Y. S. Lee, H. J. Kim, H. J. Park, and K. T. Lee, *Biol. Pharm. Bull.*, **25**, 1446 (2002).
6. J. Liu, N. Zhang, and M. Liu, *Nat. Prod. Res.,* **28**, 420 (2014).
7. O. Kenny, T. J. Smyth, C. M. Hewage, N. P. Brunton, and P. Mcloughlin, *Phytochemistry,* **98**, 197 (2014).
8. K. Michalska, J. Marciniuk, and W. Kisiel, *Fitoterapia*, **81**, 434 (2010).
9. G. L. Lange and M. Lee, *Magn. Reson. Chem.*, **24**, 656 (1986).