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Two lanostane triterpenoids from *Abies koreana*

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Abstract

Two lanostane-type triterpenoids, namely, 24(*E*)-3,4-seco-9β*H*-lanosta-4(28),7,24-triene-3,26-dioic acid and 24(*E*)-3-oxo-9β*H*-lanosta-7,24-dien-26-ol were isolated from the root bark *of Abies koreana.* Their structures were established based on spectroscopic analyses. Compound **2** exhibited marginal cytotoxicity against human tumor cell lines.

Keywords: *Abies koreana*; Pinaceae; Lanostanes; 24(*E*)-3,4-seco-9β*H*-lanosta-4(28),7,24-triene-3,26-dioic acid; 24(*E*)-3-oxo-9β*H*-lanosta-7,24-dien-26-ol; Cytotoxicity

1. Introduction

The genus *Abies* (Pinaceae) consists of 51 species mainly ranged in temperate and boreal regions of the northern hemisphere, chiefly in mountainous regions (Li, 1975; Farjon and Rushforth, 1989). Considerable interest has continued in the 9β*H*-lanostane-type triterpenoids isolated from the needles, stem barks, seeds and resins of the genus *Abies*. The isolation and structure elucidation of 3,4-seco-9β*H*-lanost-7-enes and 3-oxo-9β*H*-lanost-7-enes were reported widely in some *Abies* species including *A. sibirica* (Raldugin et al., 1986, 1987, 1989, 1991; Roshchin et al., 1986; Shevtsov and Raldugin, 1988; Yaroshenko and Raldugin, 1989; Leibyuk et al., 1990; Kukina et al., 1988; Druganov et al., 2000), *A. sachalinensis* (Wada et al., 2002), *A. veitchii* (Tanaka and Matsunaga, 1991a), *A. firma* (Hasegawa et al., 1987a; Tanaka et al., 1990; Tanaka and Matsunaga, 1991b) and *A. mariesii* (Hasegawa et al., 1987b; Tanaka et al., 1999). These 9β*H*-lanost-7-enes have interesting stereochemical features that are different from euph-7-ene or tirucall-7-ene series of compounds. The configurations at C-9, C-13, C-14 and C-17 are *S*, *R*, *R* and *R* in a 9β*H*-lanost-7-ene skeleton, while *R*, *S*, *S* and *S* configurations in euph-7-ene or tirucall-7-ene systems, respectively (Baas, 1985; Niimi et al., 1989; Benosman et al., 1994).

Abies koreana Wilson (Pinaceae), Korean fir, is a shrub or broadly pyramidal evergreen tree endemic to southern Korea. Although several lignans (Kim et al., 1994) and triterpenoids (Kim et al., 2001) have been isolated from this plant in previous studies, extensive investigations for its chemical composition and biological evaluation have not yet been performed thoroughly. Moreover, no phytochemical work has been done on the root bark of *Abies* genus.

In this paper, we describe the isolation and characterization of two new 9β*H*-lanostane-type triterpenoids, namely, 24(*E*)-3,4-seco-9β*H*-lanosta-4(28),7,24-triene-3,26-dioic acid (**1**) and 24(*E*)-3-oxo-9β*H*-lanosta-7,24-dien-26-ol (**2**), together with two known compounds, β-sitosterol and its glucoside from the root bark of *A. koreana*, as well as evaluation of the cytotoxicity for **1** and **2** against a panel of human tumor cell lines.

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2. Results and discussion

The methanol extract of the air-dried root bark of *A. koreana* was partitioned with *n*-hexane, EtOAc and *n*-BuOH, successively. Fractionation and separation of the EtOAc soluble extract led to the isolation of two novel 9β*H*-lanostane triterpenoids, compounds **1** and **2** (Fig. 1). Their structures were elucidated based on spectroscopic methods.

Compound **1** was isolated as white amorphous powder. The HR-EIMS of **1** gave a molecular ion at *m/z* 470.3384 (calc. for $C_{30}H_{46}O_4$, 470.3396), which is consistent with the molecular formula $C_{30}H_{46}O_4$. The signals in the ^{13}C NMR [δ_C 177.0 (C-3) and 170.7 (C-26)] and IR (ν_{max} 1701 cm^{-1}) spectra showed the presence of two carboxylic acids. The ^1H NMR spectrum (Table 1) displayed a total of six methyl signals, i.e., one secondary methyl at δ_H 0.94 (*d*, *J* = 6.5 Hz, H-21), three tertiary methyls at δ_H 0.78 (H-18), 0.93 (H-19), 1.07 (C-30), and two olefinic methyls at δ_H 1.86 (H-29), 2.11 (H-27). Two trisubstituted olefinic protons were revealed at δ_H 5.32 (*d*, *J* = 3 Hz, H-7) and 7.22 (H-24), as well as two proton signals of an sp^2 exomethylene at δ_H 5.01 (H-28a) and 5.00 (H-28b). These data suggested that compound **1** is a derivative of a 3,4-seco-triterpenoid.

In the HMBC spectrum of **1** (Table 1), the methylene H-l (δ_H 1.92 and 2.04), exomethylene H-28 and two methyls H-19 and H-29 were correlated with the C-5 methine carbon at δ_C 45.6. Also, two tertiary methyl protons, H-18 and H-30, showed long-range couplings with quaternary C-13 and C-14 carbons. Two carboxylic acids at C-3 and C-26 showed correlation with methylene protons H-l, H-2 (δ_H 2.58), and olefinic H-24, methyl H-27 protons, respectively. The partial structure from C-6 to C-12 was deduced from COSY correlations of H-6/H-7, H-7/H-9, H-9/H-11 and H-11/H-12. In addition, the connectivities of C-15, C-16 and C-17 were confirmed by the COSY correlations of H-15/H-16 and H-16/H-17.

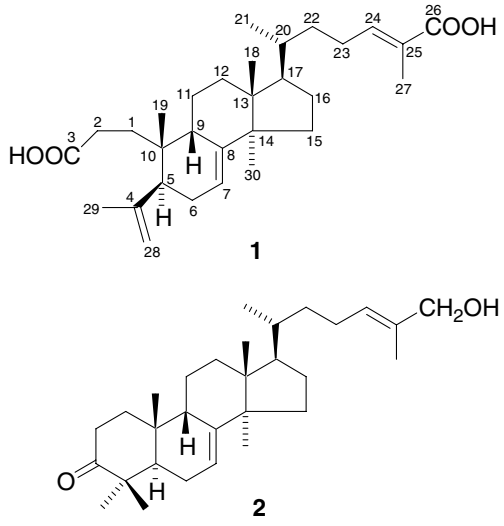

Fig. 1. Structures of the compounds **1** and **2**.

The stereochemistry of **1** was determined by selective NOE experiments. Irradiation of H-27 did not increase the intensity of H-24, which indicated that the double bond geometry is in the *E* configuration. H-9 showed NOE correlations with H-18, H-19 and H-29. Irradiation of H-30 caused NOE enhancement in the signals of H-11α, H-12α, H-15α, H-16α and H-17 protons. Also, H-21 secondary methyl exhibited NOE correlations with H-12α, H-12β and H-17 protons. On the basis of this spectroscopic evidence, the structure of **1** was assigned as 24(*E*)-3,4-seco-9β*H*-lanosta-4(28),7,24-triene-3,26-dioic acid.

Compound **2** was isolated as pale-yellow amorphous powder and was assigned the molecular formula $C_{30}H_{48}O_2$ based on the HR-EIMS experiment [HR-EIMS *m/z* 440.3670 (calc. for $C_{30}H_{48}O_2$, 440.3654)]. The IR and ^{13}C NMR spectra of **2** indicated the presence of a six-membered ring ketone (ν_{max} 1693 cm^{-1}, δ_C 219.0) and a hydroxymethyl [ν_{max} 3452 cm^{-1} (OH), δ_C 69.0]. The ^1H NMR spectrum showed six methyl signals in total, including a secondary methyl at δ_H 0.90 (*d*, *J* = 6.5 Hz, H-21), five tertiary methyl groups at δ_H 0.78 (H-18), 0.99 (H-19), 1.02 (H-30), 1.09 (H-28), 1.10 (H-29) and an olefinic methyl at δ_H 1.67 (H-27). Also, two trisubstituted olefinic protons at δ_H 5.40 (*dt*, *J* = 1.5, 7.5 Hz) and 5.64 (*dt*, *J* = 7.5, 3 Hz) were observed in the ^1H NMR spectrum, which were coupled with the carbon signals at δ_C 126.9 (CH), 134.4 (C) and 121.4 (CH), 148.8 (C), respectively.

Structure **2** was established based on analysis of the HSQC, COSY and HMBC spectral data (Table 2). In the HMBC spectrum, H-18 and H-19 methyls showed correlations with C-12, C-13, C-14, C-17 and C-l, C-5, C-9, C-10, respectively. All proton signals of H-l, H-2, H-28 and H-29 were correlated with a carbonyl carbon at δ_C 219.0 assigned to C-3. The hydroxymethyl protons at δ_H 4.00 (2H, s, H-26) showed HMBC correlations with the carbon signals of C-24, C-25 and C-27. In addition, the tertiary olefinic methyl functionality (H-27) showed allylic coupling with the olefinic proton at δ_H 5.40 (*dt*, *J* = 1.5, 7.5 Hz, H-24) in the COSY spectrum. Correlation peaks of H-5/H-6β, H-6/H-7, H-15/H-16, H-16/H-17, H-20/H-21 and H-20/H-22 indicated partial carbon sequences of C-5 to C-7, C-15 to C-17, and C-20 to C-22.

The stereochemistry at the C-24 position has been shown to be in the *E* configuration. It was established that irradiation of the olefinic proton at C-24 increased the intensity of hydroxymethyl protons at C-26, but not of the H-27 methyl protons in the selective NOE experiment. Irradiations of H-9 (δ_H 2.22) and H-30 showed NOE correlations with H-11β, H-12β, H-18, H-19 and H-11α, H-12α, H-15α, H-16α, H-17, respectively. Consequently, the structure of **2** was confirmed to be 24(*E*)-3-

Table 1
NMR spectral data for compound **1** (pyridine-d_5)

No.	δ_C		δ_H	HMBC (H → C)
1	29.7	a	2.04 (1H, *m*)	C-3, C-9
		b	1.92 (1H, *m*)	C-3, C-5, C-9
2	30.0		2.58 (2H, *dt*, *J* = 11, 5.5 Hz)	C-l, C-3
3	177.0			
4	150.4			
5	45.6		2.26 (1H, *d*, *J* = 7 Hz)	C-4, C-7, C-10, C-28, C-29
6	30.0	α	2.01 (1H, *m*)	
		β	2.39 (1H, *m*)	
7	118.3		5.32 (1H, *d*, *J* = 3 Hz)	
8	147.1			
9	39.2		2.65 (1H, *m*)	
10	36.7			
11	18.9	α	1.55 (1H, *m*)	C-8
		β	1.68 (1H, *m*)	
12	34.2	α	1.82 (1H, *m*)	
		β	1.65 (1H, *m*)	C-14
13	44.0			
14	51.8			
15	34.4	α	1.48 (1H, *m*)	C-14
		β	1.52 (1H, *m*)	C-14
16	28.5	α	1.94 (1H, *m*)	
		β	1.26 (1H, *m*)	
17	53.3		1.50 (1H, *m*)	C-20
18	21.9		0.78 (3H, *s*)	C-12, C-13, C-14, C-17
19	24.4		0.93 (3H, *s*)	C-1, C-5, C-9, C-10
20	36.3		1.44 (1H, *m*)	
21	18.4		0.94 (3H, *d*, *J* = 6.5 Hz)	C-17, C-22
22	35.2	a	1.60 (1H, *m*)	
		b	1.19 (lH, *m*)	
23	26.0	a	2.29 (1H, *m*)	C-24
		b	2.17 (1H, *m*)	C-22, C-24
24	142.5		7.22 (1H, *m*)	C-22, C-23, C-25, C-26, C-27
25	129.0			
26	170.7			
27	12.9		2.11 (3H, *s*)	C-24, C-25, C-26
28	112.1	a	5.01 (1H, *s*)	C-4, C-5, C-29
		b	5.00 (1H, *s*)	C-4, C-5
29	26.1		1.86 (3H, *s*)	C-4, C-5
30	27.6		1.07 (3H, *s*)	C-8, C-13, C-14, C-15

oxo-9β*H*-lanosta-7,24-dien-26-ol. Compounds **1** and **2** were evaluated for in vitro cytotoxicity against cultured human tumor cell lines (Skehan et al., 1990; Kim et al., 2001). Compound **2** exhibited marginal cytotoxicity against A549 (non small cell lung carcinoma), SK-OV-3 (ovary malignant adenocarcinoma), SK-MEL-2 (malignant melanoma) and HCT-15 (colon adenocarcinoma) with ED_{50} (μg/ml) values of 4.1, 23.0, 9.2 and 7.9 μg/ml, while compound **1** showed weak activity with ED_{50} of 28.3, 20.9, 29.9 and 30.4 μg/ml, respectively.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured with a JASCO DIP 1000 digital polarimeter. Melting points were determined in capillary tubes with a Thomas Uni-Melt melting point apparatus. NMR experiments were recorded using a Varian Unity INOVA 500 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, and TMS was used as the internal standard. EIMS and HR-EIMS were determined on a Micromass Platform II GC/LC mass spectrometer and JEOL JMS-700 Mstation mass spectrometer, respectively. IR spectra were obtained on a Jasco FT/IR-410 spectrometer, and UV spectra were recorded on a Shimadzu UV-2401 spectrophotometer. TLC was carried out on Merck Silica gel F_{254}-precoated glass plates and RP-18 F_{254S} plates. MPLC was carried out with Silica gel 60 (230–400 mesh) and Merck Lobar RP-18 column. HPLC was performed on a Waters 600E multisolvent delivery system using Supelco Supelcosil LC-SI 10 × 250 mm semi-prep columns.

Table 2
NMR spectral data for compound **2** ($CDCl_3$)

No.	δ_C		δ_H	HMBC (H → C)
1	34.1	α	1.72 (1H, *m*)	C-3
		β	1.62 (1H, *m*)	C-l, C-3
2	34.4		2.49 (2H, *m*)	C-l, C-3, C-4, C-10
3	219.0			
4	47.0			
5	52.4		1.42 (1H, *m*)	C-1, C-4, C-10, C-19, C-28, C-29
6	23.0	α	1.88 (1H, *m*)	C-7, C-8
		β	1.82 (1H, *m*)	
7	121.4		5.64 (1H, *dt*, *J* = 7.5, 3 Hz)	C-4, C-6, C-9
8	148.8			
9	45.5		2.22 (1H, *m*)	C-8, C-11
10	35.8			
11	20.8		1.64 (2H, *m*)	C-9, C-12
12	34.3	α	1.84 (1H, *m*)	C-9, C-11, C-13, C-17, C-18
		β	1.63 (1H, *m*)	C-13
13	44.0			
14	51.9			
15	33.1	α	1.42 (1H, *m*)	C-13
		β	1.58 (1H, *m*)	C-30
16	28.3	α	1.97 (1H, *m*)	C-13
		β	1.29 (1H, *m*)	C-20
17	53.0		1.53 (1H, *m*)	C-13, C-18, C-20
18	22.4		0.78 (3H, *s*)	C-12, C-13, C-14, C-17
19	23.1		0.99 (3H, *s*)	C-l, C-5, C-9, C-10
20	36.0		1.40 (1H, *m*)	C-13
21	18.3		0.90 (3H, *d*, *J* = 6.5 Hz)	C-17, C-20
22	35.8	a	1.48 (1H, *m*)	
		b	0.95 (1H, *m*)	
23	24.6	a	2.10 (1H, *m*)	
		b	1.94 (1H, *m*)	C-24, C-25
24	126.9		5.40 (1H, *dt*, *J* = 1.5, 7.5 Hz)	C-22, C-23, C-26, C-27
25	134.4			
26	69.0		4.00 (2H, *s*)	C-24, C-25, C-27
27	13.6		1.67 (3H, *s*)	C-24, C-25, C-26
28	28.0		1.09 (3H, *s*)	C-3, C-4, C-5, C-29
29	21.3		1.10 (3H, *s*)	C-3, C-4, C-5, C-28
30	27.4		1.02 (3H, *s*)	C-8, C-13, C-14, C-15

3.2. Plant material

The root bark of *A. koreana* was collected in October 2001, in Mt. Chiri, South Korea. Voucher specimens have been deposited in the herbarium of the College of Pharmacy, Chonnam National University (No. NPDD200103).

3.3. Extraction and isolation

The dried root bark of *A. koreana* (676 g) was extracted at room temperature with MeOH to give a MeOH extract (64 g). This was diluted with H_2O, and extracted with *n*-hexane, EtOAc, and *n*-BuOH, successively. The EtOAc extract (10 g) was subjected to silica gel column chromatography with a $CHCl_3$–MeOH–H_2O gradient solvent system (200:20:1 → 3:5:2 → MeOH 100%) to provide seven fractions. Fraction 3 was recrystallized using MeOH to afford compound **1** (16 mg). Fraction 1 was further subjected to MPLC with a *n*-hexane–Et_2O–MeOH gradient system (92:6:2 → 85:10:5) to give eleven subtractions.

Subfraction 9 was applied to a Lobar RP-18 column, and was purified on HPLC eluted with *n*-hexane–Et_2O–MeOH (80:19.5:0.5, 4 ml/min) to afford compound **2** (21 mg).

3.4. 24(*E*)-3,4-seco-9βH-lanosta-4(28),7,24-triene-3,26-dioic acid (*1*)

White amorphous powder, m.p. 232–236 °C; $[\alpha]_D^{20}$ − 13.4° (*c* = 0.2, EtOH); λ_{max}^{EtOH} nm (log ε): 231 (3.46); IR ν_{max}^{KBr} cm^{-1}: 2946, 2360, 1701 (–COOH), 1431, 1281; for ^1H and ^{13}C NMR spectra, see Table 1 HR-EIMS *m/z* 470.3384 (calc. for $C_{30}H_{46}O_4$, 470.3396); EIMS 70eV *m/z* (rel. int.): 470 $[M]^+$ (71), 397 $[M\text{-}C_3H_5O_2]^+$ (40), 175 (28), 161 (57), 147 (80), 95 (82), 55 (100).

3.5. 24(*E*)-3-oxo-9β*H*-lanosta-7,24-dien-26-ol (**2**)

Pale-yellow amorphous powder, m.p. 130–132 °C; $[\alpha]_D^{20} + 37.8°$ ($c = 0.2$, $CHC1_3$); λ_{max}^{EtOH} nm (log ε): 215 (3.26); IR ν_{max}^{KBr} cm^{-1}: 3452, 2951, 2924, 2360, 2337, 1693 (C=O), 1462, 1381; for ^1H and ^{13}C NMR spectra, see Table 2; HR-EIMS *m/z* 440.3670 (calc. for $C_{30}H_{48}O_2$, 440.3654); EIMS 70eV *m/z* (rel. int.): 440 $[M]^+$ (21), 425 (32), 407 (43), 257 (39), 245 (28), 159 (45), 147 (56), 95 (100).

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