FERN CONSTITUENTS: TWO NEW SECOFILICANE TRITERPENOIDS FROM *ADIANTUM CUNEATUM*

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Two new secotriterpenoids 4,23-bisnor-3,4-secofilic-5(24)-en-3-al (**1**) and 4,23-bisnor-3,3-dimethoxy-3,4-secofilic-5(24)-ene (**2**) have been isolated from hexane extract of *Adiantum cuneatum*, and the structures were determined by extensive spectroscopic analyses

KEY WORDS *Adiantum cuneatum*; secotriterpenoid; 4,23-bisnor-3,4-secofilic-5(24)-en-3-al; 4,23-bisnor-3,3-dimethoxy-3,4-secofilic-5(24)-ene

Adiantum cuneatum LANGSD. & FISCH. (= *A. raddianum* PRESL, Adiantaceae) is widespread through tropical America, and has been used as an ornamental plant in Japan. On investigation of the fresh leaves of *A. cuneatum* (cultivated), we isolated two new secotriterpenoids, 4,23-bisnor-3,4-secofilic-5(24)-en-3-al (**1**, 0.0001 %), and 4,23-bisnor-3,3-dimethoxy-3,4-secofilic-5(24)-ene (**2**, 0.0015 %). In this paper, we report the isolation and structure elucidation of compounds **1** and **2** on the basis of spectral evidence.

A hexane extract of the fresh leaves (4.7 kg) was chromatographed on silica gel to give a benzene elute fraction (7.2 g, 0.74 % of the dried materials). This fraction was chromatographed repeatedly on silica gel and prep. HPLC [C-18 reverse phase, CH₃CN-CHCl₃ (9.5 : 0.5)] to give two new compounds. Compound **1** was obtained as colorless needles, mp 138–139° C, $[\alpha]_D^{23} + 0.9^\circ$ (CHCl₃, *c*=0.1), and IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 1700. The MS of **1** showed the molecular ion at *m/z* 398.3558 (C₂₈H₄₆O) and many significant fragment ions at *m/z* (rel. int.): 383 (20, M⁺–15), 355 (24, a), 287 (35, b), 274 (100, c), 259 (61, c–15), 205 (43, d), and 191 (67, e) (Chart 1). This fragmentation pattern was fundamentally identical with that of filic-3-ene (**3**)¹. The ¹H-NMR spectrum of **1** indicated the presence of four tertiary methyl groups, two secondary methyl groups, an exocyclic methylene group, and an aldehyde group in the molecule. The analyses of ¹H-¹H, ¹³C-¹H COSYs, HMBC, and HSQC spectra suggested that **1** was a secofilicane compound based on a comparison with **3** (Tables 1 and 2).² A partial structure of **1**, shown by heavy lines in Fig. 1, was revealed by the HMBC spectrum. Cross peaks in the NOESY spectrum of **1** were observed between methyl and methyl, methyl and methylene, or methine and methine groups situated on the α-side of the molecule [H-10 (δ, 1.701)—H-8 (δ 1.552)—H-27—H-28] and on the β-side [H-24 (δ 4.422, 4.813)—H-25—H-26]. Thus, the structure of **1** was established as 4,23-bisnor-3,4-secofilic-5(24)-en-3-al.

Compound **2** was obtained as colorless plates, mp 195–196° C, $[\alpha]_D^{23} - 5.4^\circ$ (CHCl₃, *c*=0.2). The MS of **2** showed the molecular ion at *m/z* 444.3979 (C₃₀H₅₂O₂) and the common fragments {*m/z* (rel. int.)} with those of **1** at 429 (3, M⁺–15), 354 (48, a–H), 287 (50, b), 274 (100, c), 259

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Table 1. ^1H -NMR Spectral Data (500 MHz, CDCl_3 , δ)

	1	2	3	6	7	8	10	11
1	1.66; 1.89	2.34; 2.59	9.773	1.97; 2.38	1.36; 1.60	1.55	1.70	1.42; 1.68
2	1.38; 1.78	1.38; 1.53	4.341	1.98; 2.37	1.34; 1.60	1.56	1.70	1.40; 1.62
3	1.47; 1.61	1.99; 2.04	5.16	1.24; 1.80	1.36; 1.48	1.32	1.24	1.38; 1.43
	12	15	16	18	19	20	21	22
1	1.08; 1.50	1.18;	1.62;	1.53	1.23; 1.37	; 1.82	0.98	1.45
2	1.08; 1.48	1.19; 1.43	1.60;	1.57	1.27; 1.39	1.17; 1.82	0.98	1.47
3	1.02; 1.48	1.37; 1.22	1.58; 1.67	1.57	1.20; 1.37	1.21; 1.82	1.00	1.45
	23	24	25	26	27	28	29	30
1	—	4.422; 4.813 (ddd, 1.52, 1.52, 1.22)	0.712	0.881	0.974	0.787	0.881 (d, 6.4)	0.825 (d, 6.4)
2	—	4.504; 4.795 (ddd, 1.53, 1.52, 1.52)	0.690	0.875	0.973	0.788	0.882 (d, 6.4)	0.824 (d, 6.4)
3	1.575 (dd, 2.0, 3.0)	0.975	0.892	0.912	0.921	0.775	0.886 (d, 6.7)	0.825 (d, 6.7)

Coupling constants are shown in parentheses; methoxyl proton signals were observed at δ 3.306 and δ 3.308 in **2**.

Table 2. ^{13}C -NMR Spectral Data (125 MHz, CDCl_3 , δ)

	1	2	3	4	5	6	7	8	9	10
1	15.79	43.22	203.05	—	147.95	38.04	23.72	48.78	39.19	57.20
2	31.55	18.45	105.10	—	148.44	38.14	23.74	48.80	39.06	57.74
3	17.50	27.22	120.30	144.33	38.44	38.73	18.27	49.36	37.62	57.16
	11	12	13	14	15	16	17	18	19	20
1	33.64	29.05	38.81	40.36	29.36	35.64	42.71	51.72	19.96	28.38
2	33.70	29.11	38.31	40.36	29.37	35.69	42.72	51.75	19.96	28.39
3	35.20	28.47	39.06	40.22	29.13	35.66	42.77	51.76	19.93	28.42
	21	22	23	24	25	26	27	28	29	30
1	60.07	30.77	—	106.40	18.09	16.06	15.41	16.23	21.95	22.90
2	60.08	30.78	—	106.32	18.19	16.05	15.34	16.22	21.95	22.91
3	60.09	30.77	17.94	20.65	20.61	16.08	15.65	16.34	21.95	22.91

Methoxyl signals in **2** were observed at δ 52.65 and 52.69.

(66, c-15), 205 (51, d), and 191 (48, e) (Chart 1). The ^1H -NMR spectrum of **2** indicated the presence of four tertiary methyl groups, two secondary methyl groups, and two methoxyl groups. The ^1H - and ^{13}C -NMR signals of rings B to E in **2** were similar to those of **1**. The partial structure of **2** was also revealed by the HMBC spectrum (Fig. 1). Thus, the structure of **2** was established as 4,23-bisnor-3,3-dimethoxy-3,4-secofilic-5(24)-ene.

It is the first time that the secotriterpenoids have been found from fern plants. Biogenetically, we suggest that the double bond at C-3—C-4 cleaves oxidatively; then the methyl ketone is eliminated from the intermediate seco-compound as shown in Chart 2.

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