630 Communications to the Editor *Chem. Pharm. Bull.* **44**(3) 630—632 (1996) Vol. 44, No. 3

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

Kenji SHIOJIMA,[a] Takahisa NAKANE,[a] Hiroyuki AGETA,*,[a] and Shao-Qing CAI[b]

Shôwa College of Pharmaceutical Sciences, [a] *Machida, Tokyo 194, Japan, and School of Pharmaceutical Sciences, Beijing Medical University,* [b] *Beijing, China*

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

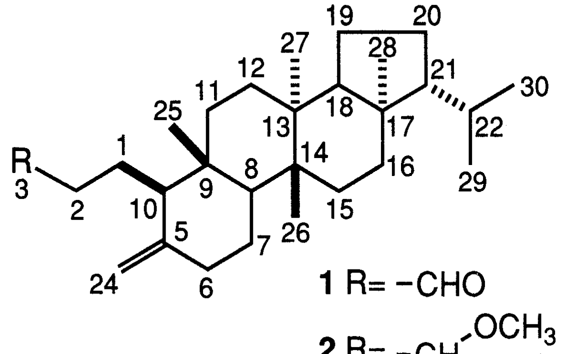
Adiantum cuneatum Langsd. & Fisch. (=*A. raddianum* Presl, Adiantaceae) is widespread through tropical America, and has been used as an ornamental plant in Japan. On investigation of the fresh leaves of *A. cuneatum* (cultivated), we isolated two new secotriterpenoids, 4,23-bisnor-3,4-secofilic-5(24)-en-3-al (**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, CH_3CN-$CHCl_3$ (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° ($CHCl_3$, c=0.1), and IR ν_{max}^{KBr} cm^{-1}:1700. The MS of **1** showed the molecular ion at m/z 398.3558 ($C_{28}H_{46}O$) 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, ^{13}C-^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° ($CHCl_3$, c=0.2). The MS of **2** showed the molecular ion at m/z 444.3979 ($C_{30}H_{52}O_2$) 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

---

* To whom correspondence should be addressed.



1 R= $-$CHO

2 R= $-CH(OCH_3)_2$

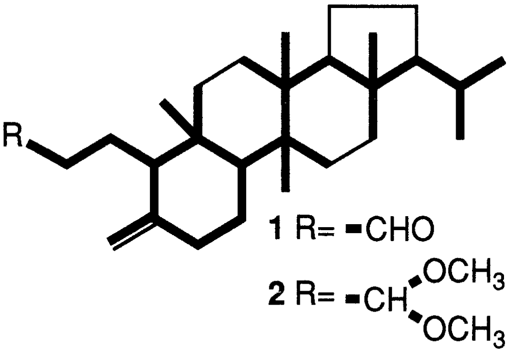


Fig. 1. Partial Structure of **1** and **2** by HMBC Spectrum

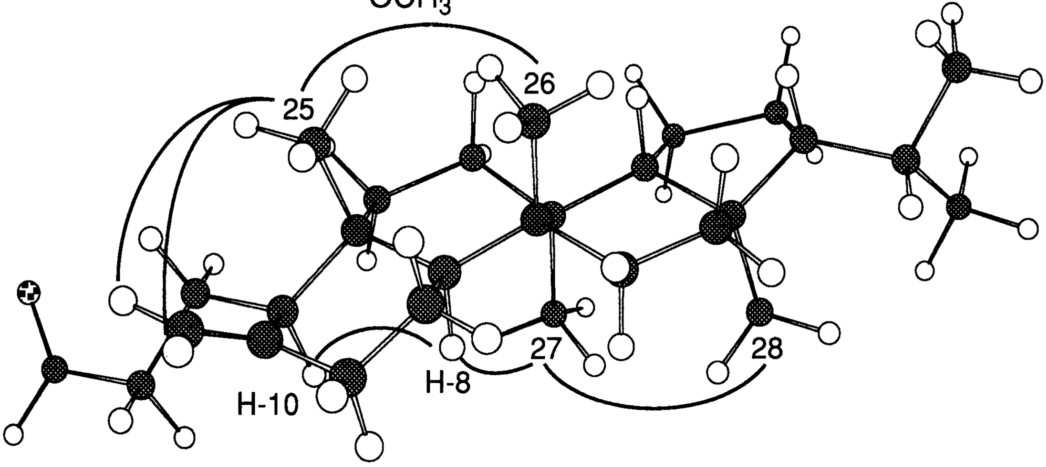


Fig. 2. Chem 3D Plus Drawing and NOEs of **1**

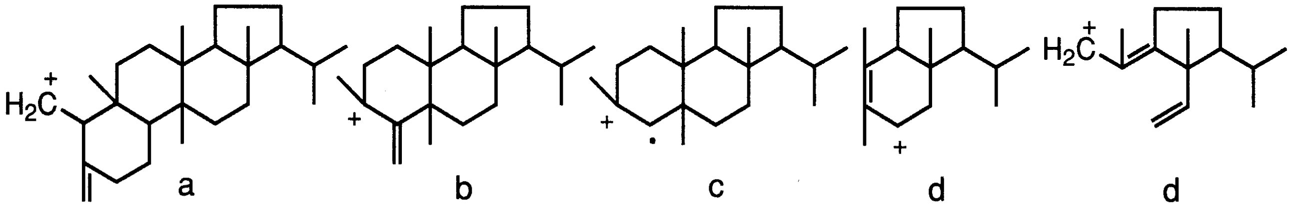


Chart 1

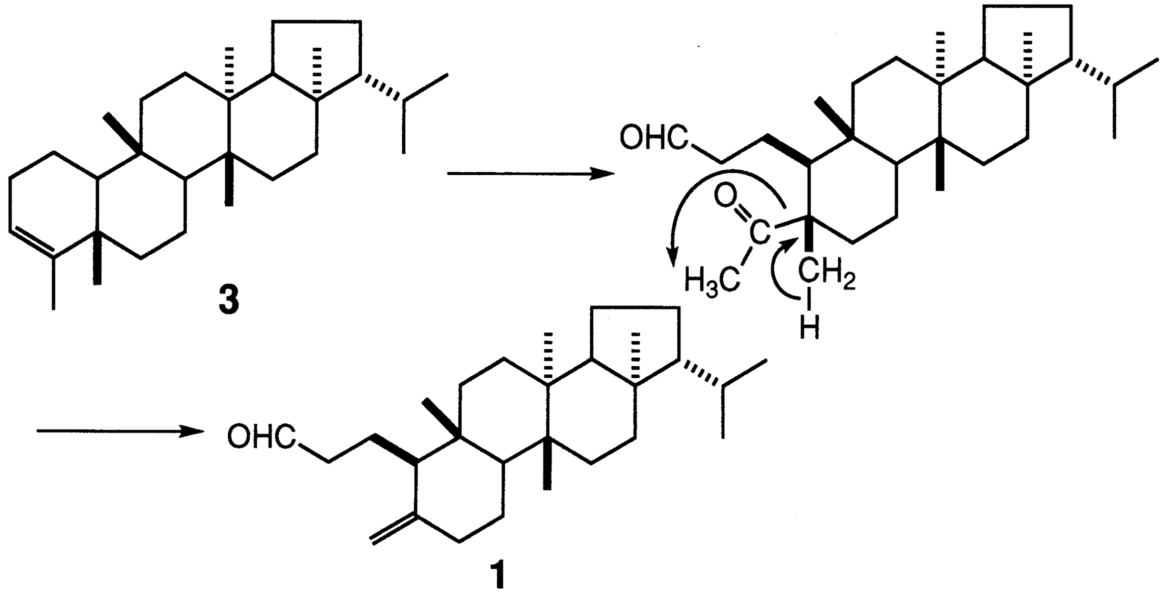


Chart 2

Table 1. ^{1}H-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 ^{1}H-NMR spectrum of **2** indicated the presence of four tertiary methyl groups, two secondary methyl groups, and two methoxyl groups. The ^{1}H- 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.

ACKNOWLEDGEMENT The authors are indebted to Mr. Yôichi Takase and Hideki Suzuki of this College for MS and NMR measurements.

REFERENCES

1) Shiojima K., Arai Y., Masuda K., Takase Y., Ageta T., Ageta H., *Chem. Pharm. Bull.*, **40**, 1683–1690 (1992).
2) Ageta H., Shiojima K., Arai Y., Suzuki H., Kiyotani T., *Chem. Pharm. Bull.*, **42**, 39–44 (1994).

(Received January 18, 1996; accepted February 7, 1996)