Fern Constituents: Triterpenoids Isolated from the Leaves of *Adiantum monochlamys*. Filicenol A, Filicenol B, Isoadiantol B, Hakonanediol and Epihakonanediol

Kenji SHIOJIMA, Yōko ARAI, Toshio KASAMA and Hiroyuki AGETA*

Shōwa College of Pharmaceutical Sciences, Machida, Tokyo 194, Japan. Received June 24, 1992

Five new triterpenoids, filicenol A (1), filicenol B (2), isoadiantol B (3), hakonanediol (4) and epihakonanediol (5), were isolated from the leaves of *Adiantum monochlamys* EATON, and their structures were elucidated on the basis of spectral data and chemical correlations with known compounds. Additional data are presented for previously reported compounds (6—21) from the same source.

Keywords fern; *Adiantum monochlamys*; triterpenoid; filicenol; isoadiantol; hakonanediol

Adiantum monochlamys EATON (Hakone-shida in Japanese, Pteridaceae) is a rather common fern distributed in southern Honshū, Shikoku and Kyūshū, Japan, and has been used as a diuretic by suggestion of Kaempfer.[1] In the previous communications,[2] we have reported the structures of seventeen kinds of triterpenoids belonging to the hopane and migrated hopane groups isolated from the dried leaves. This paper deals with the isolation and structure elucidation of five new triterpenoids, filicenol A (**1**), filicenol B (**2**), isoadiantol B (**3**), hakonanediol (**4**) and epihakonanediol (**5**) (Chart 1) from the same source. Some additional data are also presented on previously reported compounds (**6**—**21**).

Results and Discussion

Air dried leaves were extracted with methanol. A suspension of the methanolic extract in water were extracted with ether. The ether extract was subjected to various kinds of chromatography (see Experimental) to obtain compounds **1**—**15** and **17**—**21**; Table I gives physical constants and yields. Adianene ozonide (**16**) was only obtained from *n*-hexane extract of fresh leaves of the same fern.[2d]

A new compound, filicenol A (**1**), was obtained as colorless needles. The infrared absorption (IR) spectrum indicated the presence of a hydroxyl group and a trisubstituted double bond. The mass spectrum (MS) of **1** showed a molecular ion, *m/z* 426.3850 ($C_{30}H_{50}O$) and many significant fragment ions at *m/z* (rel. int.) 408 (46; $M^+-CH_3-H_2O$), 383 (2; $M^+-C_3H_7$), 365 (7; $M^+-C_3H_7-H_2O$), 341 (22; a), 323 (12; a$-H_2O$), 273 (26; b), 255 (5; b$-H_2O$), 205 (19; c) and 191 (100; d) (Chart 2). These

TABLE I. Triterpenoids Isolated from the Leaves of *Adiantum monochlamys*

	mp (°C)	$[\alpha]_D$	Yield (%)	Lit.
Filicenol A (**1**)	222—225	+52.0	0.025	—
Filicenol B (**2**)	218—221	+57.0	0.055	—
Isoadiantol B (**3**)	213.5—215	+16.0	0.031	—
Hakonanediol (**4**)	270—272	+21.0	0.0059	—
Epihakonanediol (**5**)	299—301	+5.0	0.0066	—
Fern-8-ene (**6**)	190—192	+30.6	0.027	2*a*
Fern-9(11)-ene (**7**)	171—172	−19.6	0.0021	2*c*
Ferna-7,9(11)-diene (**8**)	202—203	−177.9	0.0051	2*c*
Fern-7-ene (**9**)	212.5—214	−28.8	0.028	2*a*
Adian-5-ene (**10**)	193.5—195	+51.9	0.042	2*a*
Neohop-13(18)-ene (**11**)	199—201	+2.1	0.001	2*c*
Neohop-12-ene (**12**)	210—211	+41.6	0.0081	2*c*
Filic-3-ene (**13**)	232—234	+50.0	0.028	2*a*
Hop-22(29)-ene (**14**)	210—212	—	0.0007	2*a*
Neohopa-11,13(18)-diene (**15**)	214.5—215.5	+25.7	0.002	2*c*
Adianene ozonide (**16**)	154—157	+19.4	0.121	2*d*
Adiantone (**17**)	227—230	+80.1	0.111	2*b*
Isoadiantone (**18**)	236—237	+3.6	0.0011	2*b*
Tetrahymanol (**19**)	>300	—	0.022	6
Ketohakonanol (**20**)	295—297	+8.0	0.0013	2*b*
Hydroxyadiantone (**21**)	270—275	+50.0	0.230	2*b*

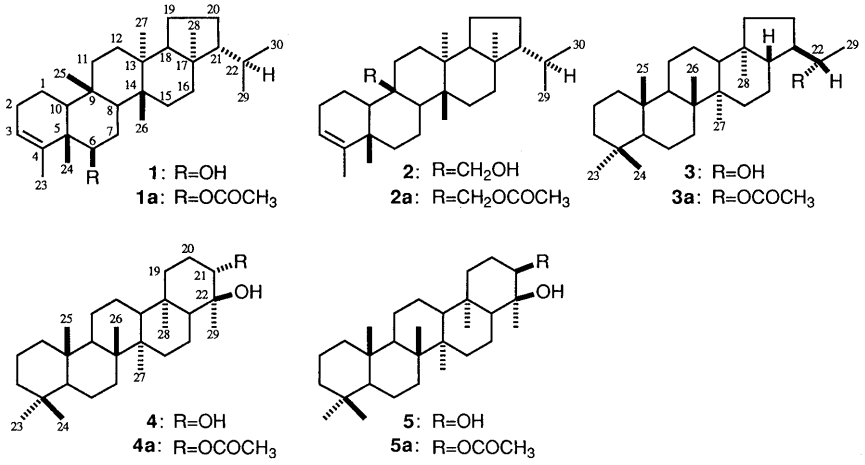

Chart 1

fragment ions suggested for **1** the filicane skeleton with a hydroxyl group in the left-hand part of the molecule.[3] The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum

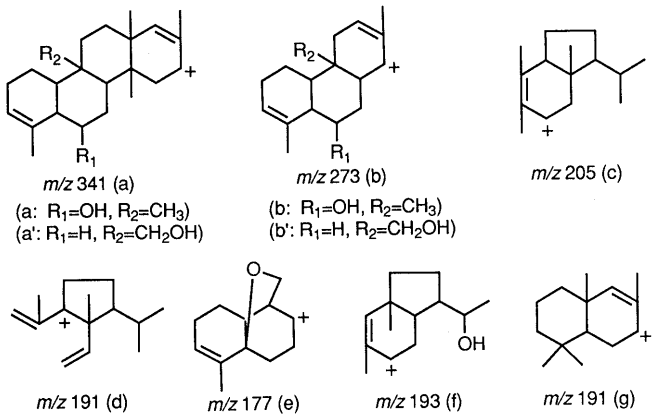

Chart 2

of **1** indicated the presence of five tertiary, two secondary and one olefinic methyl groups and one olefinic proton. The chemical shifts of methyl groups were similar to those of filic-3-ene (**13**) (Table II). The presence of a secondary hydroxyl group (equatorial) was suggested by a proton signal at δ 3.593 (1H, dd), and the signal of a trisubstituted double bond was observed at δ 5.199 (br s). In the ^{13}C-NMR spectrum (Table III), signals of **1** were coincident with those of **13** except for the hydroxy methine carbon and its neighbors. Assignments of the ^{1}H- and ^{13}C-NMR spectra of the compounds shown in Tables II and III were confirmed as necessary by proton–proton and ^{13}C–proton correlated spectroscopy (^{1}H–^{1}H and ^{13}C–^{1}H COSY), ^{1}H-detected heteronuclear multiple bond correlation (HMBC) spectrum and distortionless enhancement by polarization transfer (DEPT) spectrum methods. Acetylation of **1** in a usual manner afforded filicenol A acetate (**1a**), the ^{1}H-NMR data for which are given in Table II. Compound **1** was oxidized to give filicenone A (**22**), and

TABLE II. ^{1}H-NMR Spectral Data for Triterpenoids of Filicane, Adianane and Hopane Groups (270/400/500 MHz, $CDCl_3$, δ)

Protons	1	1a	2	2a	13	22	23	24	25
H-23	1.824 (dd, 3.2, 1.5)	1.574 (br s)	1.589 (dd, 2.5, 1.5)	1.584 (d, 1.5)	1.575 (dd, 3.0, 2.0)	1.856 (dd, 2.5, 1.5)	1.130	1.162	1.600 (dd, 3.0, 1.7)
H-24	0.999	1.092	1.063	0.994	0.975	1.350	1.066	0.936	0.892
H-25	0.886	0.924	3.839 (1H, d, 12.0) 3.915 (1H, d, 12.0)	4.202 (1H, d, 12.0) 4.388 (1H, d, 12.0)	0.892	1.116	1.036	0.886	10.210 (1H, s)
H-26	0.913	0.894	0.923	0.896	0.912	0.892	0.928	0.905	0.866
H-27	0.913	0.908	0.946	0.944	0.921	0.962	0.928	0.926	0.922
H-28	0.777	0.770	0.777	0.778	0.775	0.764	0.772	0.782	0.766
H-29[a]	0.886 (d, 6.4)	0.876 (d, 6.4)	0.884 (d, 6.4)	0.884 (d, 6.6)	0.886 (d, 6.7)	0.880 (d, 6.6)	0.876 (d, 6.6)	0.884 (d, 6.7)	0.880 (d, 6.6)
H-30[a]	0.826 (d, 6.4)	0.818 (d, 6.4)	0.824 (d, 6.4)	0.826 (d, 6.6)	0.825 (d, 6.7)	0.822 (d, 6.6)	0.824 (d, 6.6)	0.825 (d, 6.7)	0.820 (d, 6.6)
CH=C	5.202 (1H, br s)	5.172 (1H, br s)	5.188 (1H, br s)	5.202 (1H, br s)	5.161 (1H, br s)	5.340 (1H, br s)	—	—	5.164 (1H, br s)
CH–O–	3.595 (1H, dd, 10.2, 4.8)	4.744 (1H, dd, 9.8, 4.9)	—	—	—	—	—	3.577 (1H, ddd, 10.4, 10.4, 5.5)	—
CH_3–CO	—	2.032	—	2.052	—	—	—	—	—

Protons	26	27	3	4	4a	5	28	29	30
H-23	0.882	0.908	0.846	0.844	0.846	0.846	0.845	0.847	0.848
H-24	0.960	1.044	0.792	0.790	0.794	0.795	0.792	0.794	0.792
H-25	3.500 (1H, d, 8.3) 4.414 (1H, d, 8.3)	—	0.816	0.810	0.817	0.816	0.814	0.816	0.816
H-26	0.912	0.916	0.950	0.958	0.964	0.976	0.951	0.970	0.970
H-27	0.920	1.014	0.968	0.968	0.973	0.976	0.951	0.942	0.952
H-28	0.770	0.774	0.682 (d, 1.0)	0.790	0.812	0.795	0.703	0.648	0.662 (d, 1.0)
H-29[a]	0.882 (d, 6.6)	0.878 (d, 6.6)	1.160 (d, 6.1)	1.072	1.102	1.115	0.927 (d, 6.1)	0.889 (d, 6.7)	1.182 (d, 6.4)
H-30[a]	0.824 (d, 6.6)	0.826 (d, 6.6)	—	—	—	—	0.806 (d, 6.1)	0.788 (d, 6.7)	—
CH=C	—	—	—	—	—	—	—	—	—
CH–O–	—	—	3.732 (1H, dddd, 6.4, 6.4, 6.4, 6.4)	3.416 (1H, dd, 12.1, 4.4)	4.636 (1H, dd, 11.0, 5.0)	3.546 (1H, ddd, 4.8, 2.4, 2.4)	—	—	3.874 (1H, dddd, 6.4, 6.4, 6.4, 2.4)
CH_3–CO	—	—	—	—	2.086	—	—	—	—

Signals unless otherwise stated are 3H, singlet. Multiplicity and coupling constants are shown in parentheses. *a*) Assignments of signals might be reversed, although the signals of H-29 and H-30 correspond to those of C-29 and C-30 in Table III, respectively.

TABLE III. ^{13}C-NMR Spectral Data for Triterpenoids of the Filicane and Hopane Groups (68/100/125 MHz, $CDCl_3$, δ)

	1	2	13	24	3	4a	5	28	29	30
C-1	16.9	18.0	17.5[a]	25.5	40.4	40.4	40.3	40.4	40.3	40.4
C-2	26.9	28.3	27.2	22.1	18.7	18.8	18.7	18.7	18.7	18.7
C-3	122.1	120.7	120.3	44.1	42.1	42.2	42.1	42.2	42.1	42.1
C-4	143.4	144.0	144.3	33.8	33.3	33.3	33.3	33.3	33.3	33.3
C-5	44.4	38.7	38.4	51.8	56.2	56.3	56.2	56.2	56.1	56.2
C-6	77.6	39.2	38.7	73.8	18.7	18.8	18.7	18.7	18.7	18.7
C-7	29.2	20.4	18.3[a]	32.7	33.3	33.1	33.0	33.3	33.3	33.3
C-8	46.4	50.2	49.4	45.1	41.9	42.1	42.1	41.9[b]	41.9	42.0
C-9	37.3	42.5	37.6	36.5	50.5	50.4	50.3	50.5	50.5	50.5
C-10	55.8	58.3	57.2	50.4	37.4	37.5	37.5	37.4	37.4	37.4
C-11	35.1	29.6	35.2	34.3	20.9	21.1	21.0	21.0	20.9	20.9
C-12	28.4	29.6	28.4	28.8	22.8	21.6	21.4	24.1	23.9	21.2
C-13	39.1	39.2	39.1	38.9	48.5	50.1	49.9	49.3	48.6	48.4
C-14	40.0	39.7	40.2	39.8	42.0	41.9	41.9	41.8[b]	42.3	42.3
C-15	29.1	29.3	29.1	29.0	32.7	32.5	32.4	33.7	32.7	32.6
C-16	35.6	35.8	35.7	35.6	23.9	17.3	17.4	22.6	21.6	23.9
C-17	42.8	42.7	42.8	42.8	55.0	56.3	49.8	54.7	53.2	51.6
C-18	51.7	51.6	51.8	51.8	45.1	37.4	37.3	44.4	44.5	44.6
C-19	19.9	19.9	19.9	19.9	39.7	38.1	32.4	41.7	39.8	39.7
C-20	28.4	28.4	28.4	28.4	24.3	25.1	25.4	27.6	22.7	21.2
C-21	60.1	60.1	60.1	60.1	47.5	81.9	74.0	47.9	45.5	46.8
C-22	30.7	30.8	30.8	30.8	72.8	74.4	73.3	32.0	28.8	67.5
C-23	22.1	18.0	17.9	34.3	33.4	33.5	33.4	33.4	33.4	33.4
C-24	15.3	20.1	20.7	21.0	21.6	21.7	21.6	21.6	21.6	21.6
C-25	20.1	64.8	20.6	17.5	15.9	16.0	15.9	15.9	15.9	15.9
C-26	16.0	15.5	16.1	16.2	16.8	16.6	16.6[c]	16.7[c]	16.8	16.8
C-27	15.6	15.7	15.7	15.3	16.8	16.6	16.5[c]	16.8[c]	16.7	16.8
C-28	16.3	16.3	16.3	16.3	15.2	15.5	14.8	15.8	15.2	15.9
C-29	22.0[d]	22.0[d]	22.0[d]	22.0[d]	21.8	17.8	22.0	22.8[d]	22.1[d]	16.4
C-30	22.9[d]	22.9[d]	22.9[d]	22.9[d]	—	—	—	23.9[d]	17.5[d]	—
CO	—	—	—	—	—	171.7	—	—	—	—
CH_3	—	—	—	—	—	21.4	—	—	—	—

a—d) Assignments of signals might be reversed. Spectra of **13**, **28** and **29** were run at 125 MHz, and assignments were confirmed by DEPT, ^{1}H–^{1}H and ^{13}C–^{1}H-COSY, and HMBC methods. Some of assignments reported[7] have been revised.

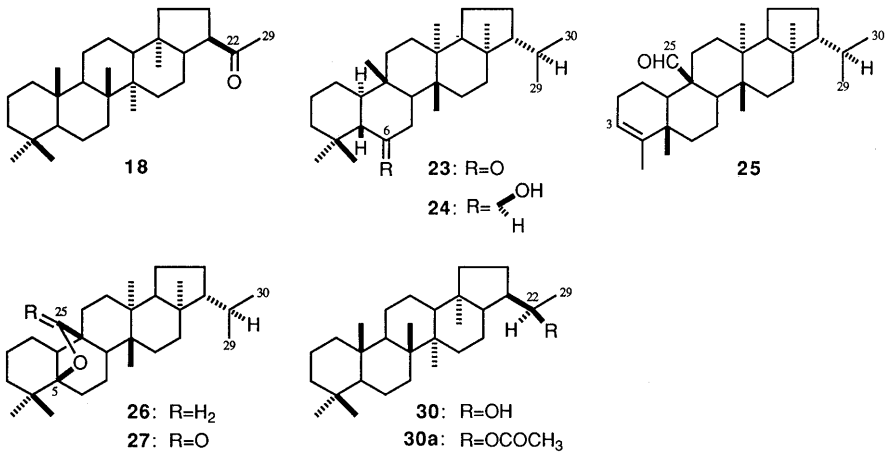

Chart 3

the chemical shifts of three methyl groups (H-23, H-24 and H-25) of **22** were shifted to lower fields compared with those of **13**. Compound **22** was reduced by the Wolff–Kishner–Barton method to give **13'**, which was identical with an authentic sample of **13**.[2a] On the other hand, **1** was treated with BF_3-etherate/ether to give a saturated ketone, adianan-6-one (**23**), reduction of which afforded adianan-6β-ol (**24**).[4] Compound **24** was dehydrated with $POCl_3$/pyridine to give adian-5-ene (**10**). Thus, the structure of filicenol A was established as filic-3-en-6β-ol (**1**), the absolute configuration of which was confirmed by the circular dichroism (CD) curve of **22**.

The second new compound, filicenol B (**2**) was obtained as colorless needles. The MS of **2** showed a molecular ion, *m/z* 426.3870 ($C_{30}H_{50}O$), and many significant fragment ions at *m/z* (rel. int.) 411 (10; M^+-CH_3), 395 (51; M^+-CH_2OH), 383 (4; $M^+-C_3H_7$), 341 (4, a'), 273 (7, b'), 255 (8, b'$-H_2O$), 205 (54; d), 191 (31; c) and 177 (100; e) (Chart 2). These fragment ions suggested that **2** has a filicane skeleton with a hydroxyl group on the left-hand

part of molecule.[3] The ^{1}H-NMR spectrum of **2** indicated the presence of four tertiary, two secondary, and one olefinic methyl groups, one hydroxymethyl group and one trisubstituted double bond. The chemical shifts of methyl groups were similar to those of **13**, as shown in Table II. Thirty carbon signals were observed in the ^{13}C-NMR spectrum of **2** and their chemical shift values were similar to those of **13** except for C-25, as shown in Table III. Compound **2** was acetylated in a usual manner to give filicenol B acetate (**2a**), the ^{1}H-NMR spctrum of which is shown in Table II. Oxidation of **2** with CrO_3–pyridine afforded an aldehyde (**25**), and **25** was reduced by the Wolff–Kishner–Barton method to give a hydrocarbon (**13'**), which was identified as filic-3-ene by comparison with an authentic sample.[2a] Furthermore, treatment of **2** with 1 N H_2SO_4/AcOH gave an epoxide (**26**), oxidation of which with $K_2Cr_2O_7$ afforded a five membered lactone (**27**). Compound **27** was assumed to be adianan-5β,25-olide and **26** to be adianan-5β,25-epoxide on the basis of their ^{1}H-NMR spectra (Table II). Thus, the structure of **2** was concluded to be 25-hydroxyfilic-3-ene.

The third new compound, isoadiantol B (**3**) was obtained as colorless needles. The MS of **3** showed a molecular ion, *m/z* 414.3876 ($C_{29}H_{50}O$) and many significant fragments at *m/z* (rel. int.) 399 (9; M^+-CH_3), 381 (7; $M^+-CH_3-H_2O$), 367 (8; $M^+-C_2H_5O$), 193 (73; d), 191 (100; e) and 175 (63; d$-H_2O$) (Chart 2). These fragment ions suggested the 30-norhopane skeleton for **3**.[3] The ^{1}H-NMR spectrum of **3** indicated the presence of six tertiary and one secondary methyl groups (Table II). The secondary methyl proton of H-29 (δ 1.16, d, J=6.1 Hz) was observed at lower field than that of hopane (**28**) or isohopane (**29**). As shown in Table III, the ^{13}C-NMR spectrum of **3** revealed carbon signals that were very similar to those of **28** except for the C-22 hydroxymethine signal. Therefore, **3** was supposed to be 30-norisohopan-22-ol, and the structure was finally confirmed by direct comparison with the products prepared from isoadiantone (**18**)[2b] by $LiAlH_4$ reduction. The products were two diastereomeric 30-norisohopan-22-ols, isoadiantol A (**30**, less polar) and isoadiantol B (**3'**, more polar), of which the latter was proved to be identical with **3**. The establish the absolute configuration at C-22 of **30** and **3**, the differences between the molecular rotations $[M]_D$ of the alcohols (**30** and **3**) and their respective acetates were compared with those of paired adiantols[3] and pregnan-20-ol derivatives[5] (Table IV). As the $[M]_D$ increment for conversion of **3** to its acetate (**3a**) was negative, as found for the 20*S* compounds of adiantols and pregnan-20-ol derivatives, compound **3** was assumed to have 22*S* configuration. Thus, isoadiantol B (**3**) was established as (22*S*)-30-norisohopan-22-ol.

TABLE IV. Comparison of Molecular Rotation of Pregnane Derivatives and Isoadiantol A and B

		Alcohol (A) $[M]_D$	Acetate (B) $[M]_D$	B–A $\Delta[M]_D$
Isoadiantol A (**30**)	22R	+21	+73	+52
Isoadiantol B (**3**)	22S	+66	+46	−20
Adiantol A	22R	+161	+160	−1
Adiantol B[a]	22S	+306	+251	−55
Pregn-5-ene-3β,20-diol	20R	−204	−149	+55
	20S	−179	−197	−18
3-Oxopregn-4-en-20-ol	20R	+272	+483	+211
	20S	+319	+323	+4
3,11-Dioxopregn-20-ol	20R	+175	+280	+105
	20S	+230	+200	−30

a) The absolute configuration at C-22 of the bromoacetate was determined by X-ray analysis.[8]

The other two new compounds, hakonanediol (**4**) and epihakonanediol (**5**) were both obtained as colorless needles. The MS of **4** and **5** showed the molecular ions, *m/z* 430.3833 and 430.3815 ($C_{29}H_{50}O_2$), respectively, and significant fragment ions at *m/z* (rel. int.) 412 (7, 6; M^+-H_2O), 397 (5, 4; $M^+-CH_3-H_2O$) and 191 (100, 100; g) (Chart 2). These fragment ions suggested that both **4** and **5** have the hopane-like skeleton on the left-hand part, and a hydroxyl group on the right-hand part of the molecules.[3] The ^{1}H-NMR spectra of both **4** and **5** indicated the presence of seven tertiary methyl groups, and the chemical shifts of five methyl groups on rings A, B and C closely resembled to those of hopane (**28**) (Table II). Two hydroxyl groups of **4** and **5** were secondary and tertiary. The coupling pattern [δ 3.416 (dd, J=12.1, 4.4 Hz)] of a geminal proton of the secondary hydroxyl group in **4** suggests that the proton is axial, while the coupling pattern [δ 3.546 (ddd, J=4.8, 2.4, 2.4 Hz)] of that in **5** suggests that the proton is equatorial. Acetylation of **4** and **5** in a usual way afforded hakonanediol monoacetate (**4a**) and epihakonanediol monoacetate (**5a**). The ^{13}C-NMR data for **4a** and **5** are given in Table III, and support the above conclusion. The structures of **4** and **5** were finally established by the identity of the IR and ^{1}H-NMR spectra with those of two diols, **4'** and **5'**, respectively, obtained from ketohakonanol (**20**)[2b] by $LiAlH_4$ reduction.

It is noteworthy that all twenty-one triterpenoids obtained from the leaves of *Adiantum monochlamys* (Table I) are pentacyclic and belong to the hopane and migrated hopane or closely related groups. The isolation of the many nor-compounds, **3**, **4**, **5**, **17**, **18**, **20** and **21**, is also a characteristic feature of this *Adiantum* fern.

Experimental

Melting points were measured on a Yanagimoto micro apparatus and were corrected. Specific rotation was observed in $CHCl_3$ solutions (c=0.5—1.2) at 22—24 °C. CD was measured with a JASCO J-600 apparatus. ^{1}H- and ^{13}C-NMR spectra were taken at 270/400/500 and 68/100/125 MHz by the Fourier transform (FT) method with tetramethylsilane as an internal standard. MS were recorded (direct inlet) at 30 eV and relative intensities of peaks were reported with reference to the most intense peak higher than *m/z* 100. Gas liquid chromatography (GLC) was performed on a 1 m glass column containing Chromosorb G HP with 1.4% SE-30 at 260 °C under N_2 using cholestane as an internal standard (its retention time was set at 3.0 min). Silica gel 60, 230—400 mesh (Merck), Al_2O_3 (Woelm or Wako, neutral or basic, grade 1 or 3) and 20%-$AgNO_3$ impregnated silica gel were used for column chromatography (CC). Precoated Silica gel 60 plates (Merck) were used for thin layer chromatography (TLC), and spots were detected by spraying with concentrated H_2SO_4 followed by heating.

Plant Materials The leaves of *Adiantum monochlamys* were collected in August, 1965, and September 1976, at Mariko, Shizuoka, Shizuoka Prefecture. Voucher specimens have been deposited in the Herbarium of Showa College of Pharmaceutical Sciences, Tokyo.

Extraction of Dried Leaves and Separation The drid leaves (1.3 kg) were extracted three times with MeOH (40 l each). The extract was concentrated to 10 l in total, and was allowed to stand overnight. Waxy substances were filtered off, and the solution was evaporated to dryness. The resultant solid was extracted with Et_2O and water, and the Et_2O

solution was dried and evaporated to give a residue (48.5 g). The residue was refluxed with *n*-hexane (2 l). After cooling, the less soluble material (9.0 g) was filtered off (fraction A), and the solution was evaporated to dryness. The residue was chromatographed on silica gel with *n*-hexane (fr. B), *n*-hexane–benzene (8 : 2) (fr. C), *n*-hexane–benzene (1 : 1) (fr. D), benzene (fr. E), benzene–Et_2O (9 : 1) (fr. F), and Et_2O (fr. G) to give six fractions.

Fern-8-ene (6), Fern-9(11)-ene (7), Ferna-7,9(11)-diene (8), Fern-7-ene (9), Adian-5-ene (10), Neohop-13(18)-ene (11), Neohop-12-ene (12), Filic-3-ene (13), Hop-22(29)-ene (14) and Neohopa-11,13(18)-diene (15) Fraction B was repeatedly chromatographed on Al_2O_3 and 20% $AgNO_3$-impregnated silica gel to give the following crystalline solids (weight) in order of elution (recrystallized from acetone to obtain pure specimens): **6** (310 mg), **7** (23 mg), **8** (58 mg), **9** (318 mg), **10** (478 mg), **11** (12 mg), **12** (91 mg), **13** (313 mg), **14** (8 mg) and **15** (23 mg).[2a,c]

Adiantone (17) and Isoadiantone (18) Fraction C was chromatographed several times on silica gel. The crystalline product (3250 mg) from the *n*-hexane–benzene (8 : 2) eluate was recrystallized from MeOH to give **17**. IR ν_{max}^{KBr} cm^{-1}: 1705. The product (15 mg) from the second eluate with the same solvent was recrystallized from MeOH to give **18**. IR ν_{max}^{KBr} cm^{-1}: 1705.[2b]

Filicenol A Acetate (1a) and Filicenol B Acetate (2a) Fraction D was treated with pyridine–Ac_2O overnight at room temperature, and the reaction mixture was repeatedly chromatographed on Al_2O_3. The crystalline product (350 mg) from the first eluate with *n*-hexane was recrystallized from acetone to give **1a**, mp 249—252 °C, $[\alpha]_D$ +17.0°. IR ν_{max}^{KBr} cm^{-1}: 1720, 1246, 1023. The crystalline product (750 mg) from the second eluate with the same solvent was recrystallized from acetone to give **2a**, mp 214—216 °C, $[\alpha]_D$ +75.0°. IR ν_{max}^{KBr} cm^{-1}: 1737, 1245, 1035.

Filicenol A (1) 1a (250 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane–benzene (1 : 1) eluate was recrystallized from acetone to give **1**. IR ν_{max}^{KBr} cm^{-1}: 3550, 1013. *Anal.* Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found; C, 84.61; H, 12.06.

Filicenol B (2) 2a (700 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane–benzene (1 : 1) eluate was recrystallized from acetone to give **2**. IR ν_{max}^{KBr} cm^{-1}: 3525, 1032. *Anal.* Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found; C, 84.68; H, 11.82.

Isoadiantol B Acetate (3a) and Tetrahymanol Acetate (19a) Fraction E was treated with pyridine–Ac_2O overnight at room temperature, and the reaction product was recrystallized repeatedly from $CHCl_3$–MeOH to give less soluble crystals, **19a** (200 mg), mp >300 °C, $[\alpha]_D$ +32.1°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1250, and more soluble crystals, **3a** (250 mg), mp 217.5—220 °C, $[\alpha]_D$ +13.2°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1242. **19a** were identical (IR and TLC comparisons) with an authentic sample.[6]

Isoadiantol B (3) 3a (100 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane–henzene (1 : 1) eluate was recrystallized from Et_2O–MeOH to give **3**. IR ν_{max}^{KBr} cm^{-1}: 3470, 1111, 1072.

Tetrahymanol (19) 19a (150 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane–benzene (1 : 1) eluate was recrystallized from Et_2O–MeOH to give **19**. IR ν_{max}^{KBr} cm^{-1}: 3310, 1045, 1033.

Ketohakonanol (20) Fraction F was chromatographed on Al_2O_3, and the crystalline product (18 mg) from the benzene–Et_2O (9 : 1) eluate was recrystallized from $CHCl_3$–MeOH to give **20**. IR ν_{max}^{KBr} cm^{-1}: 3480, 1067, 1713.[2b]

Hakonanediol (4) and Epihakonanediol (5) Fraction G was chromatographed on Al_2O_3. The crystalline product (90 mg) from the Et_2O eluate was recrystallized from $CHCl_3$–MeOH to give **5**. IR ν_{max}^{KBr} cm^{-1}: 3300, 1080, 1070, 1040. *Anal.* Calcd for $C_{29}H_{50}O_2$: C, 80.87; H, 11.70. Found: C, 80.86; H, 11.68. The crystalline product (80 mg) from the methanol eluate was recrystallized from $CHCl_3$–MeOH to give **4**. IR ν_{max}^{KBr} cm^{-1}: 3400, 1069, 1044. *Anal.* Calcd for $C_{29}H_{50}O_2$: C, 80.87; H, 11.70; H, 11.70. Found: C, 80.88; H, 11.68.

Hakonanediol Monoacetate (4a) 4 (20 mg) are treated with pyridine–Ac_2O overnight at room temperature, and the product was recrystallized from acetone to give **4a**, mp 265—268 °C. IR ν_{max}^{KBr} cm^{-1}: 3550, 1075, 1039, 1713, 1256.

Epihakonanediol Monoacetate (5a) 5 (20 mg) was treated with pyridine–Ac_2O overnight at room temperature, and the product was chromatographed on Al_2O_3. The crystalline product from the benzene eluate was recrystallized from acetone to give **5a**, mp 255—258 °C. IR ν_{max}^{KBr} cm^{-1}: 3530, 1070, 1054, 1028, 1728, 1250.

Adiantone (17) and Hydroxyadiantone (21) Fraction A was refluxed with benzene (200 ml) for 1 h. After cooling, the less soluble material was filtered off (3.1 g, fr. H), and the solution was evaporated to dryness (4.5 g, fr. I). Fraction I was chromatographed on silica gel, and the crystalline product (1.5 g) from the *n*-hexane–benzene (8 : 2) eluate was recrystallized from $CHCl_3$–MeOH to give **17**.[2b] Fraction H was repeatedly recrystallized from tetrahydrofuran (THF)–MeOH to give **21**. IR ν_{max}^{KBr} cm^{-1}: 3430, 1082, 1695.[3]

Extraction of Fresh Leaves and Separation The fresh leaves (1.4 kg) were extracted twice with *n*-hexane (45 l each) to give extracts (20 g) and azeotropic H_2O (840 ml). The extracts were refluxed with *n*-hexane (2.0 l). After cooling, the less soluble material was filtered off (fr. J), and the solution was evaporated to dryness (fr. K). Fraction K was chromatographed on silica gel with *n*-hexane (fr. L), *n*-hexane–benzene (9 : 1) (fr. M), *n*-hexane–benzene (8 : 2) (fr. N), *n*-hexane–benzene (1 : 1) (fr. O), benzene (fr. P), benzene–Et_2O (9 : 1) (fr. Q) and Et_2O (fr. R) to give seven fractions.

Adianene Ozonide (16) Fraction M was rechromatographed on silica gel, and the product (700 mg) from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from *n*-hexane to give **16**.[2d]

Oxidation of Filicenol A (1) A solution of **1** (250 mg) in pyridine (20 ml) was combined with CrO_3 (200 mg) in pyridine (6 ml), and the mixture was stirred at room temperature for 2 h. The reaction mixture was chromatographed on Al_2O_3. The product (205 mg) from the *n*-hexane eluate was recrystallized from *n*-hexane to give filic-3-en-6-one (**22**), mp 280—281 °C. IR ν_{max}^{KBr} cm^{-1}: 1699. CD (c=0.11, dioxane) $[\theta]$ (nm): +9914 (298.5). Further elution with benzene gave the starting material.

Reduction of 22 22 (20 mg) was reduced by the Wolff–Kishner–Barton method. The reaction product was chromatographed on Al_2O_3, and the crystalline product (16 mg) from the *n*-hexane eluate was recrystallized from acetone to give a hydrocarbon, mp 232—234 °C, which was identified by comparison (IR, GLC) with an authentic sample of filic-3-ene (**12**).[2a]

Acid Induced Rearrangement of Filicenol A (1) 1 (200 mg) was treated with BF_3-etherate (25 ml) in absolute Et_2O (120 ml) at room temperature for 2 d. The reaction mixture was chromatographed on Al_2O_3. The product (60 mg) from the *n*-hexane eluate was recrystallized from methanol to give adianan-6-one (**23**), mp 260—261 °C, $[\alpha]_D$ +16.5°. IR ν_{max}^{KBr} cm^{-1}: 1698.

Reduction of 23 23 (50 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane eluate was recrystallized from Et_2O–MeOH to give adianan-6β-ol (**24**), mp 213.5—216 °C; 227—229 °C, $[\alpha]_D$ +20.5°. IR ν_{max}^{KBr} cm^{-1}: 3495, 1065, 1044, 986.

Dehydration of 24 24 (15 mg) was treated with $POCl_3$ (1 ml) in pyridine (7 ml) at 100 °C for 1 h. The reaction mixture was chromatographed on Al_2O_3. The crystalline product (10 mg) from the *n*-hexane eluate was recrystallized from acetone to give a hydrocarbon, mp 187—189 °C, which was identical (IR and GLC comparisons) with an authentic sample to adian-5-ene (**10**).[2a]

Oxidation of Filicenol B (2) A solution of **2** (150 mg) in pyridine (15 ml) was combined with CrO_3 (200 mg) in pyridine (6 ml) and the mixture was stirred at −5 °C for 2 h. The product was chromatographed on Al_2O_3. The first product (100 mg) from the *n*-hexane–benzene (9.5 : 0.5) eluate was recrystallized from $CHCl_3$–MeOH to give filic-3-en-25-al (**25**), mp 248—252 °C, $[\alpha]_D$ +9.5°. IR ν_{max}^{KBr} cm^{-1}: 1690. *Anal.* Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.68; H, 11.43. Further elution with benzene gave the starting material.

Reduction of 25 25 (20 mg) was reduced by the Wolff–Kishner–Barton method. The product was chromatographed on Al_2O_3, and the crystalline product (15 mg) from the *n*-hexane eluate was recrystallized from acetone to give a hydrocarbon, mp 232—234 °C, which was identical (IR and GLC comparisons) with an authentic sample of filic-3-ene (**13'**).[2a]

Acid Treatment of Filicenol B (2) A solution of **2** (200 mg) in benzene (14 ml) was treated with concentrated H_2SO_4 (1.06 ml) in acetic acid (24 ml) at room temperature for 1 d in a nitrogen atmosphere. The reaction mixture was chromatographed on Al_2O_3. The crystalline product (90 mg) from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from acetone to give adian-5(25)-epoxide (**26**), mp 201—204 °C, $[\alpha]_D$ +16.5°. IR ν_{max}^{KBr} cm^{-1}: 1122, 1102. *Anal.* Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.50; H, 11.83.

Oxidation of 26 A solution of **26** (75 mg) in acetic acid (40 ml) was treated with $K_2Cr_2O_7$ (130 mg) at 100 °C for 8 h. The reaction mixture was chromatographed on Al_2O_3. Elution with *n*-hexane gave the starting material, and the product (40 mg) from the benzene eluate was recrystallized from MeOH to give adian-5β,25-olide (**27**), mp >300 °C, $[\alpha]_D$ +18.5°.

IR ν_{max}^{KBr} cm^{-1}: 1751.

Reduction of Isoadiantone (18) **18** (500 mg) was treated with $LiAlH_4$, and the mixture was repeatedly chromatographed on Al_2O_3. The product from the initial *n*-hexane–benzene (9 : 1) eluate was recrystallized from Et_2O–MeOH to give isoadiantol A (**30**), mp 194—196 °C. IR ν_{max}^{KBr} cm^{-1}: 3345, 1132, 1050. The product from the second eluate with the same solvent was recrystallized from Et_2O–MeOH to give isoadiantol B (**3′**), mp 211.5—212.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3470, 1111, 1072.

Isoadiantol A Acetate (30a) **30** was treated with pyridine–Ac_2O overnight at room temperature, and the product was chromatographed on Al_2O_3 with *n*-hexane to give a crystalline material, which was recrystallized from Et_2O–MeOH to afford **30a**, mp 197—199 °C, $[\alpha]_D$ +16.0°, IR ν_{max}^{KBr} cm^{-1}: 1726, 1250.

Reduction of Ketohakonanol (20) **20** (400 mg) in absolute THF (150 ml) was treated with $LiAlH_4$ at 40—45 °C for 5 h. The product was chromatographed on Al_2O_3. The product from the Et_2O eluate was recrystallized from $CHCl_3$–MeOH to give epihakonanediol (**5′**), mp 282.5—285 °C. IR ν_{max}^{KBr} cm^{-1}: 3300, 1080, 1070, 1040. The product from the methanol eluate was recrystallized from $CHCl_3$–MeOH to give hakonanediol (**4′**), mp 264—269 °C. IR ν_{max}^{KBr} cm^{-1}: 3400, 1069, 1044.

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