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Fern Constituents: Triterpenoids Isolated from the Leaves of *Adiantum pedatum*. 23-Hydroxyfernene, Glaucanol A and Filicenoic Acid

Kenji SHIOJIMA, Yūshō SASAKI and Hiroyuki AGETA*

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

Three new triterpenoids, 23-hydroxyfernene (1), glaucanol A (2) and filicenoic acid (3), were isolated from the leaves of *Adiantum pedatum* L., 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 (4—15) and the isolation and identification of six known compounds (16—21) from the same source are also described.

Keywords fern; *Adiantum pedatum*; triterpenoid; 23-hydroxyfernene; glaucanol A; filicenoic acid

Adiantum pedatum L. (maiden hair fern, "Kujaku-shida" in Japanese, Pteridaceae) is a rather common fern widely distributed over the temperate zone of Asia and North America. In China, the dried whole plants have been used as a diuretic.[1] In previous communications we have reported the structures of twelve kinds of triterpenoids belonging to the hopane and migrated hopane groups isolated from the extract of the dried leaves of this fern.[2] Further investigation of the same extract resulted the isolation of three new triterpenoids, 23-hydroxyfernene (**1**), glaucanol A (**2**) and filicenoic acid (**3**) (Chart 1), and seven known compounds. This paper deals with the structural elucidation and identification of these compounds, and also presents additional data for the previously reported compounds (**4**—**15**).

Results and Discussion

The *n*-hexane extract of the dried leaves was separated by various kinds of chromatography (see Experimental) to give compounds **1**—**21**, which are presented in Table I with the physical constants and yields. Isoglaucanone (17αH-trisnorhopan-21-one, **16**), hydroxyhopane (**17**), tetrahymanol (**18**), isoadiantol B (**19**), hydroxyadiantone (**20**) and ketohakonanol (**21**) were newly isolated from more polar fractions of the extract and identified by comparison with authentic specimens.

A new compound, 23-hydroxyfernene (**1**), was obtained as colorless plates. The infrared IR absorption 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* 426.3869 ($C_{30}H_{50}O$) and many significant fragments at *m/z* (rel. int.): 411 (90, M^+-CH_3), 395 (4, M^+-CH_2OH), 393 (9, $M^+-CH_3-H_2O$), 273 (14, a), 259 (100, b), 247 (13, c) (Chart 2). These fragment ions suggested that **1** is a fernene derivative with a hydroxyl group in the left-hand part of the molecule.[3]

The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** indicated the presence of five tertiary and two secondary methyl groups, a trisubstituted double bond and a primary hydroxyl group (Table II). The splitting pattern of the proton of the trisubstituted double bond and the chemical shifts of methyl groups were similar to those of fern-9(11)-ene (**5**) (Table II). Acetylation of **1** afforded the corresponding acetate (**1a**), the ^{13}C-NMR spectrum of which was assigned by the off-resonance decoupling technique or distortionless enhancement by polarization transfer (DEPT) method, as well as by comparison of the signals with those of compounds of the fernane group; **1a** appeared to be **23** (or **24**)-acetoxyfernene, because only the signals of C-3, 4, 5, 23 and 24

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

	mp (°C)	$[\alpha]_D^{23}$	Yield (%)	Lit.
23-Hydroxyfernene (**1**)	187—190	−22.4	0.038	—
Glaucanol A (**2**)	214.5—215.5	+36.9	0.0006	—
Filicenoic acid (**3**)	>300	—	0.0004	—
Fern-8-ene (**4**)	190—191	+31.5	0.020	2*a*
Fern-9(11)-ene (**5**)	170—171	−18.3	0.326	2*a*
Ferna-7,9(11)-diene (**6**)	202—203.5	−180.4	0.0016	2*b*
Fern-7-ene (**7**)	212—214	−29.0	0.020	2*a*
Neohop-13(18)-ene (**8**)	198.5—200	+2.1	0.0010	2*b*
Neohop-12-ene (**9**)	210—211	+41.6	0.0051	2*b*
Filic-3-ene (**10**)	232—234	+58.0	0.017	2*a*
Neohopa-11,13(18)-diene (**11**)	215—215.5	+20.7	0.017	2*b*
Filicenal (**12**)	272	+74.0	0.040	2*a*
Adiantone (**13**)	227—230	+79.9	0.500	2*a*
Isoadiantone (**14**)	236—237	+3.6	0.0015	2*a*
Adipedatol (**15**)	196—200	+84.6	0.711	2*a*
Isoglaucanone (**16**)	243—245	+140.1	0.0019	7
Hydroxyhopane (**17**)	253—255	+40.5	0.0050	7
Tetrahymanol (**18**)	>300	—	0.0034	9
Isoadiantol B (**19**)	213.5—215	+16.0	0.013	8
Hydroxyadiantone (**20**)	267—274	—	0.029	10
Ketohakonanol (**21**)	294.5—297	+8.3	0.0044	10

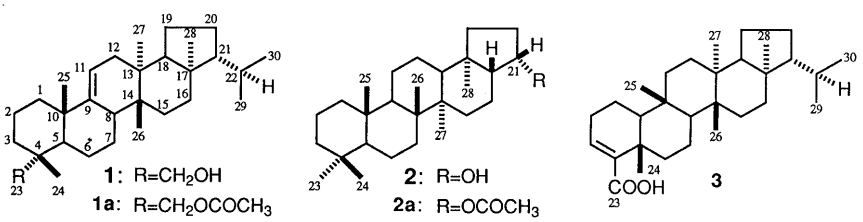
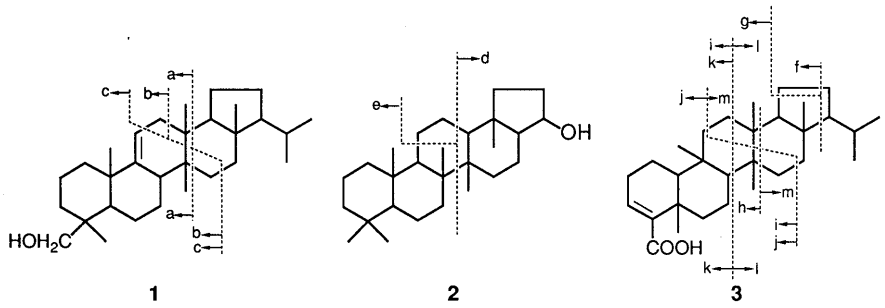


Chart 1



1 2 3

Chart 2

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

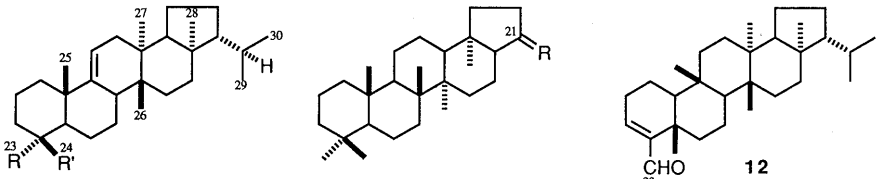
	1	1a	5	24a	2	2a	27	29	29a	3	12
H-23	3.130 (1H, d, 11.0) 3.388 (1H, d, 11.0)	3.718 (1H, d, 11.0) 3.788 (1H, d, 11.0)	0.847	0.946	0.850	0.848	0.845	0.850	0.848	—	9.294 (1H, s)
H-24	0.852	0.928	0.888	4.038 (1H, d, 11.0) 4.302 (1H, d, 11.0)	0.794	0.794	0.792	0.794	0.794	1.254	1.138
H-25	1.096	1.093	1.053	1.072	0.816	0.816	0.814	0.818	0.818	1.226	0.923
H-26	0.734	0.732	0.733	0.728	0.962	0.958	0.951	0.948	0.948	0.914	0.914
H-27	0.820	0.820	0.822	0.818	0.978	0.978	0.951	0.968	0.974	0.914	0.914
H-28	0.754	0.762	0.759	0.758	0.886 (d, 0.7)	0.830 (d, 2.3)	0.703	0.652 (d, 1.0)	0.696 (d, 1.0)	0.772	0.772
H-29[a]	0.890 (d, 6.6)	0.892 (d, 6.6)	0.890 (d, 6.4)	0.890 (d, 6.6)	—	—	0.927 (d, 6.0)	—	—	0.884 (d, 6.6)	0.884 (d, 6.6)
H-30[a]	0.828 (d, 6.6)	0.830 (d, 6.6)	0.830 (d, 6.4)	0.828 (d, 6.6)	—	—	0.812 (d, 6.0)	—	—	0.824 (d, 6.6)	0.824 (d, 6.6)
CH=C	5.308 (1H, ddd, 5.2, 2.4, 2.4)	5.310 (1H, ddd, 5.1, 2.4, 2.4)	5.286 (1H, ddd, 5.1, 2.4, 2.4)	5.312 (1H, ddd, 5.1, 2.4, 2.4)	—	—	—	—	—	6.772 (1H, dd, 3.7, 3.7)	6.544 (1H, dd, 3.5, 3.5)
CH–O	—	—	—	—	4.218 (1H, ddd, 7.6, 5.6, 1.8)	5.178 (1H, ddd, 6.9, 5.9, 2.0)	—	3.930 (1H, ddd, 9.3, 9.3, 4.7)	4.812 (1H, ddd, 9.5, 9.5, 4.6)	—	—
CH_3–CO	—	2.068	—	2.050	—	1.992	—	—	2.038	—	—

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

differed markedly from those of **5** (Table III). To confirm the carbon structure of **1**, **1** was oxidized to the aldehyde (23-oxofernene, **22**), and **22** was reduced by the Wolff–Kishner–Barton method to give the hydrocarbon (**5'**), which was identified by comparison with an authentic sample of fern-9(11)-ene.[2a] On the other hand, methyl davallate (**23**),[4] a fern constituent derivative, was reduced to give davallol (**24**),[4] which was not identical with **1** but showed similar MS fragments at m/z (rel. int.): 426 (M^+, 22), 411 (75, M^+-CH_3), 395 (6, M^+-CH_2OH), 393 (6, $M^+-CH_3-H_2O$), 273 (17, a), 259 (100, b) and 247 (15, c). As **24** afforded 24-oxofern-9(11)-ene (**25**) and 24-norferna-4(23),9(11)-diene (**26**) upon oxidation, the position of CH_2OH in **24** was chemically confirmed to be axial (4β).[5] These facts locate the hydroxyl group in **1** at C-23 (equatorial methyl) and **1** was established to be 23-hydroxy-fern-9(11)-ene.

The second new compound, glaucanol A (**2**), was obtained as colorless plates. The MS of **2** showed a molecular ion, m/z 386.3576 ($C_{27}H_{46}O$) and several significant fragments at m/z (rel. int.): 371 (10, M^+-CH_3), 353 (4, $M^+-CH_3-H_2O$), 191 (100, e), 165 (99, d') and 147 (46, d'$-H_2O$). These fragment ions suggested the trisnorhopane skeleton for **2** (Chart 2).[3] The ^{1}H-NMR spectra of **2** and its acetate (**2a**) indicated the presence of six tertiary methyl groups on the nucleus and the chemical shifts of the H-23, 24, 25, 26 and 27 methyl protons were similar to those of hopane (**27**),[6] while the H-28 methyl protons were observed at lower filed than those of **27** (Table II). Thus, the hydroxyl group of **2** was supposed to be located at 21α (the same side as the C-18 methyl). Furthermore, glaucanone (17βH-trisnorhopan-21-one, **28**)[7] was reduced with $LiAlH_4$ to give 17βH-trisnorhopan-21α-ol (**2'**; less polar) and 17βH-trisnorhopan-21β-ol (**29**; more polar), of which the former was proved to be identical (mp, IR and ^{1}H-NMR comparisons) with glaucanol A (**2**). The H-28 signals of **29** and its acetates (**29a**) were observed at higher field, indicating the hydroxyl or acetoxyl to be 21β. The ^{13}C-NMR spectrum of **2** and **29**, and their acetates (**2a** and **29a**) were assigned by the off-resonance decoupling technique or DEPT method, as well as by comparison of the signals with those of compounds of the hopane group (Table III).

The third new compound, filicenoic acid (**3**), was ob-



22: R=CHO, R'=CH_3
23: R=CH_3, R'=$COOCH_3$
24: R=CH_3, R'=CH_2OH
24a: R=CH_3, R'=CH_2OCOCH_3
25: R=CH_3, R'=CHO
26: R, R'=CH_2

28: R=O
29: R=α-OH
29a: R=α-$OCOCH_3$

12

Chart 3

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

	1a	5	24a	2	2a	27	29	29a
C-1	40.0	41.5	41.3	40.4	40.4	40.4	40.4	40.3
C-2	19.7	19.6[a]	19.1[a]	18.7	18.7	18.7	18.7	18.7
C-3	36.7	42.4	36.7	42.1	42.1	42.2	42.1	42.1
C-4	37.0	33.6	37.1	33.3	33.3	33.3	33.3	33.3
C-5	41.0	44.9	45.8	56.1	56.1	56.2	56.1	56.1
C-6	18.7	19.5[a]	18.9[a]	18.7	18.7	18.7	18.7	18.7
C-7	17.8	17.9	17.8	33.3	33.3	33.3	33.3	33.3
C-8	39.9	40.0	39.6	42.0	42.0	41.9[b]	42.0	42.0
C-9	151.2	151.7	151.1	50.4	50.4	50.5	50.5	50.4
C-10	37.9	38.1	37.9	37.4	37.4	37.4	37.4	37.4
C-11	116.0	115.6	116.2	20.9	20.8	21.0	20.8	20.8
C-12	36.2	36.8	36.1	23.7	23.9	24.0	23.1	23.2
C-13	36.8	36.7	36.7	49.1	49.0	49.3	48.6	48.6
C-14	37.7	37.7	37.6	42.4	42.3	41.8[b]	42.2	42.2
C-15	29.3	29.3	29.2	33.7	33.4	33.7	32.3	32.2
C-16	36.2	36.2	36.1	32.9	32.7	22.6	31.6	28.9
C-17	43.0	43.0	42.9	56.6	55.3	54.7	56.1	55.3
C-18	52.0	52.0	51.9	43.5	43.9	44.4	43.0	42.5
C-19	20.2	20.2	20.1	41.4	41.0	41.7	38.9	39.0
C-20	28.2	28.2	28.2	18.8	19.0	27.6	20.4	20.3
C-21	59.7	59.7	59.6	75.0	76.5	47.9	75.5	78.0
C-22	30.8	30.8	30.8	—	—	32.0	—	—
C-23	73.2	32.8	26.6	33.4	33.4	33.4	33.4	33.4
C-24	17.4	21.7	66.7	21.6	21.6	21.6	21.6	21.6
C-25	25.5	25.1	25.9	15.9	15.8	15.9	15.9	15.9
C-26	15.8	15.8	15.8	16.8	16.7	16.7	16.6	16.7
C-27	15.4	15.4	15.4	16.8	16.8	16.8	16.6	16.3
C-28	14.0	14.0	14.0	16.4	15.7	15.8	15.3	15.1
C-29	22.1[c]	22.1[c]	22.1[c]	—	—	22.8[c]	—	—
C-30	23.0[c]	23.0[c]	23.0[c]	—	—	23.9[c]	—	—
CO	171.4	—	171.4	—	171.0	—	—	171.5
CH_3	21.1	—	21.0	—	21.3	—	—	21.3

a—*c*) Assignments of the signals might be reversed. Spectra of **5** and **27** were run at 125 MHz, and assignments were confirmed by DEPT, ^{1}H–^{1}H and ^{13}C–^{1}H-correlated spectroscopy (COSY), and heteronuclear multiple bond correlation (HMBC) methods. Some of the assignments reported[11] have been revised.

tained as a colorless powder. The MS of **3** showed a molecular ion, *m/z* 440.3660 ($C_{30}H_{48}O_2$), and many significant fragments at *m/z* (rel. int.): 425 (23, M^+-CH_3), 397 (3, $M^+-C_3H_7$), 370 (9, f), 355 (41, g), 287 (15, h), 273 (6, i), 261 (5, j), 233 (30, k), 205 (22, l) and 191 (100, m). These fragment ions suggested the filicane skeleton for **3** (Chart 2), and the IR and UV spectra indicated the presence of a conjugated carboxylic acid function. The ^{1}H-NMR spectrum of **3** showed the presence of five tertiary and two secondary methyl groups, which were similar to those of filicenal (**12**) (Table II). The structure of **3** was finally confirmed by direct comparison of **3** with a sample prepared from **12** by $Na_2Cr_2O_7$ oxidation.

It is very interesting to note that all the triterpenoids (**1**—**21**) except tetrahymanol (**18**) obtained from the dried leaves of *Adiantum pedatum* belong to the hopane and migrated hopane series, including five nor (**13**, **14**, **15**, **19**, **20**, **21**) and two trisnor (**2**, **16**) compounds. Among twenty-one compounds isolated, isoadiantone (**14**), ketohakonanol (**21**), and isoglaucanone (**16**) are supposed to be, at least in part, artefacts derived from adiantone (**13**), hydroxyadiantone (**20**), and glaucanone (**28**), respectively, during the course of chromatographic separation.[7,8]

Experimental

Melting points were measured on a Yanagimoto micro apparatus and were corrected. Specific rotations were observed in $CHCl_3$ solutions (c=0.5—1.1) at 22—24 °C. ^{1}H- and ^{13}C-NMR spectra were taken at 270/500 MHz and 68/125 MHz, respectively, by the Fourier transform (FT) method with tetramethylsilane as an internal standard. MS were recorded (direct inlet) at 70 eV and the 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 AW DMCS 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 concentrated H_2SO_4 followed by heating.

Plant Materials The leaves of *Adiantum pedatum* were collected in August, 1965, at Fujiyoshida city, Yamanashi Prefecture. A voucher specimen has been deposited in the Herbarium of Shōwa College of Pharmaceutical Sciences, Tokyo.

Extraction of Dried Leaves and Separation The dried leaves (1.36 kg) was extracted three times with *n*-hexane (45 l each). The extract was evaporated and the residue (58.4 g) was refluxed with *n*-hexane (1.5 l). After cooling, the less soluble material (5.1 g) was filtered off (fraction A), and the solution was evaporated to dryness. The residue (5.3 g) was chromatographed on silica gel with *n*-hexane (fr. B), *n*-hexane–benzene (9:1) (fr. C), *n*-hexane–benzene (8:2) (fr. D), *n*-hexane–benzene (7:3) (fr. E) and benzene (fr. F) to give five fractions.

Fern-8-ene (4), Fern-9(11)-ene (5), Ferna-7,9(11)-diene (6), Fern-7-ene (7), Neohop-13(18)-ene (8), Neohop-12-ene (9), Filic-3-ene (10) and Neohopa-11,13(18)-diene (11) Fraction B was chromatographed repeatedly 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): **4** (272 mg), **5** (4450 mg), **6** (21 mg), **7** (270 mg), **8** (14 mg), **9** (70 mg), **10** (234 mg) and **11** (230 mg).[2a,b]

Filicenal (12), Adiantone (13) and Isoadiantone (14) Fraction C was chromatographed several times on silica gel. The crystalline product (545 mg) from the *n*-hexane–benzene (8:2) elute was recrystallized from *n*-hexane to give **12**. UV λ_{max}^{EtOH} nm (ε): 234 (13,000). IR ν_{max}^{KBr} cm^{-1}: 2720, 1680, 1630. The product (4.0 g) subsequently eluted with the same solvent was recrystallized from MeOH to give **13**. IR ν_{max}^{KBr} cm^{-1}: 1705. The product (20 mg) from the third eluate with the same solvent was recrystallized from methanol to give **14**. IR ν_{max}^{KBr} cm^{-1}: 1705.[2a]

Isoglaucanone (16), Hydroxyhopane (17) and 23-Hydroxyfernene (1) Fraction D was chromatographed several times on Al_2O_3. The crystalline product (25 mg) from the *n*-hexane eluate was recrystallized from ether–MeOH to give **16**. IR ν_{max}^{KBr} cm^{-1}: 1732. The product (68 mg) from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from ether–acetone to give **17**. IR ν_{max}^{KBr} cm^{-1}: 3610, 3460, 1157. The product (520 mg) from the *n*-hexane–benzene (8 : 2) eluate was recrystallized from ether–MeOH to give **1**. IR ν_{max}^{KBr} cm^{-1}: 3360, 1038, 816, 795. Compounds **16** and **17** were identical (IR and TLC comparisons) with authentic samples.[7]

23-Acetoxyfernene (1a) **1** (100 mg) was treated with pyridine–Ac_2O overnight at room temperature, and the product was chromatographed on silica gel. The crystalline product from the *n*-hexane–benzene (8 : 2) eluate was recrystallized from ether–MeOH to give **1a**, mp 181—183 °C, $[\alpha]_D$ −9.1°. IR ν_{max}^{KBr} cm^{-1}: 1148, 1228, 815, 795. *Anal.* Calcd $C_{32}H_{54}O_2$: C, 81.99; H, 11.18. Found: C, 81.73; H, 11.46.

Tetrahymanol Acetate (18a), Isoadiantol B Acetate (19a) and Glaucanol A Acetate (2a) Fraction E was treated with pyridine–Ac_2O overnight at room temperature, and the product was chromatographed on Al_2O_3 with *n*-hexane to give two crystalline materials (fr. G, H). Fraction G was repeatedly recrystallized from $CHCl_3$–MeOH to give less soluble crystals, **18a** (47 mg), mp > 300 °C, $[\alpha]_D$ +32.1°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1250, and more soluble crystals, **19a** (180 mg), mp 217.5—220 °C, $[\alpha]_D$ +13.2°. IR ν_{max}^{KBr} cm^{-1}: 1730, 1242. Fraction H was separated by preparative TLC followed by recrystallization from ether–MeOH to give **2a** (8 mg), mp 230—232 °C, $[\alpha]_D$ +21.1°. IR ν_{max}^{KBr} cm^{-1}: 1735, 1238. Compounds **18a** and **19a** were identical (mp, IR, and TLC comparisons) with authentic samples.[8,9]

Tetrahymanol (18) **18a** (20 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 ethyl ether–MeOH to give **18**. IR ν_{max}^{KBr} cm^{-1}: 3310, 1045, 1033, which was identical with an authentic sample.[9]

Isoadiantol B (19) **19a** (100 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 ether–MeOH to give **19**. IR ν_{max}^{KBr} cm^{-1}: 3470, 1111, 1072, which was identical with an authentic sample.[8]

Glaucanol A (2) **2a** (5 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 ether–MeOH to give **2**. IR ν_{max}^{KBr} cm^{-1}: 3550, 3400, 1060, 1035.

Adipedatol (15) Fraction F was chromatographed on Al_2O_3 with benzene to give white crystals (8.84 g), which were repeatedly recrystallized from *n*-hexane and acetone to give **15**. IR ν_{max}^{KBr} cm^{-1}: 3400, 1135, 1098, 1050.[2a]

Hydroxyadiantone (20), Ketohakonanol (21) and Filicenoic Acid (3) Fraction A was refluxed with benzene (150 ml). After cooling, the less soluble material was filtered off (1.68 g) (fr. I), and the solution was evaporated to dryness (3.40 g) (fr. J). Fraction I was repeatedly recrystallized from tetrahydrofuran (THF)–MeOH to give **20** (400 mg), $[\alpha]_D$ +50.0° (in pyridine). IR ν_{max}^{KBr} cm^{-1}: 3430, 1695, 1082. The filtrate was evaporated to dryness, and repeatedly chromatographed on Al_2O_3 with benzene–ether (9 : 1) to give white crystals (60 mg), which were recrystallized from ether–MeOH to give **21**. IR ν_{max}^{KBr} cm^{-1}: 3470, 1710, 1146, 1067. Compounds **20** and **21** were identical (mp, IR, and TLC comparisons) with authentic samples.[10] Fraction J was chromatographed on silica gel, and the benzene eluate gave a crystalline material (565 mg), which was a mixture of **12** and **13**. The product (30 mg) from the second eluate with the same solvent was refluxed with *n*-hexane. After cooling, the less soluble crystals were separated and recrystallized from $CHCl_3$–MeOH to give **3** (5 mg). UV λ_{max}^{EtOH} nm (ε): 216 (5600). IR ν_{max}^{KBr} cm^{-1}: 2650, 1677, 1627, 767.

Oxidation of 23-Hydroxyfernene (1) A solution of **1** (110 mg) in pyridine (10 ml) was combined with CrO_3 (100 mg) in pyridine (3 ml), and the mixture was stirred at 12—13 °C for 2 h. The product was chromatographed on silica gel. The product (35 mg) from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from acetone to give 23-oxofern-9(11)-ene (**22**), mp 159—161.5 °C, $[\alpha]_D$ −3.5°. IR ν_{max}^{KBr} cm^{-1}: 2670, 1725, 812, 795. The eluate with benzene gave the starting material.

Reduction of 22 **22** (15 mg) was reduced by the Wolff–Kishner–Barton method. The product was chromatographed on Al_2O_3, and the product (12 mg) from the *n*-hexane eluate was recrystallized from ether–acetone to give a hydrocarbon, mp 170.0—171.0 °C, which was identical (mp, IR, and GLC comparisons) with an authentic sample of fern-9(11)-ene (**5**).[2a]

24-Hydroxyfern-9(11)-ene (Davallol,[4] 24) Methyl devallate (**23**)[4] (350 mg) was reduced with $LiAlH_4$, and the reaction product was chromatographed on Al_2O_3. The crystalline product from the *n*-hexane–benzene (1 : 1) eluate was recrystallized from *n*-hexane to give **24**, mp 177—179 °C, $[\alpha]_D$ −21.1°. IR ν_{max}^{KBr} cm^{-1}: 3290, 1031, 816, 797.

24-Acetoxyfern-9(11)-ene (24a) **24** (50 mg) was treated with pyridine–Ac_2O overnight at room temperature. The product was chromatographed on Al_2O_3, and the crystalline product from the *n*-hexane eluate was recrystallized from ether–MeOH to give **24a**, mp 193—195 °C, $[\alpha]_D$ −18.9°. IR ν_{max}^{KBr} cm^{-1}: 1743, 1247.

Oxidation of 24 **24** (120 mg) was treated with pyridine–CrO_3 in the same manner as mentioned above. The product was chromatographed on silica gel. The product from the *n*-hexane eluate was recrystallized from ether–acetone to give 24-norferna-4(23),9(11)-diene (**26**), mp 170—173 °C. IR ν_{max}^{KBr} cm^{-1}: 1639, 885, 814, 795. The product (33 mg) from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from acetone to give 24-oxofern-9(11)-ene (**25**), mp 171—174 °C, $[\alpha]_D$ −15.2°. IR ν_{max}^{KBr} cm^{-1}: 2720, 1723, 810, 794.

Reduction of Glaucanone (28)[8] **28** (500 mg) was treated with $LiAlH_4$, and the product was chromatographed on Al_2O_3. The product from the *n*-hexane–benzene (9 : 1) eluate was recrystallized from ether–MeOH to give 17β*H*-trisnorhopan-21α-ol (**2′**), mp 214.5—215.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3435, 1132, which was proved to be identical with **2**. Further elution with the same solvent gave a product which was recrystallized from ether–MeOH to give 17β*H*-trisnorhopan-21β-ol (glaucanol B, **29**), mp 215—216 °C. IR ν_{max}^{KBr} cm^{-1}: 3290, 1067.

Glaucanol B Acetate (29a) **29** (100 mg) was treated with pyridine–Ac_2O overnight at room temperature. The product was chromatographed on Al_2O_3, and the crystalline product from the *n*-hexane eluate was recrystallized from ether–MeOH to give **29a** (90 mg), mp 288—289 °C, $[\alpha]_D$ +9.9°. IR ν_{max}^{KBr} cm^{-1}: 1742, 1248.

Oxidation of Filicenal (12) **12** (25 mg) in benzene (5 ml) and AcOH (10 ml) was treated with $K_2Cr_2O_7$ (60 mg) in H_2O (0.1 ml) and AcOH (2 ml) at 30 °C for 5 h. The product insoluble in *n*-hexane was recrystallized from $CHCl_3$–MeOH to give **3** (6 mg), mp > 300 °C. IR ν_{max}^{KBr} cm^{-1}: 2650, 1680, 1628, 766.

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