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Fern Constituents: Cheilanthenetriol and Cheilanthenediol. Sesterterpenoids Isolated from the Leaves of *Aleuritopteris khunii*

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Two sesterterpenoids, cheilanthenetriol (1) and cheilanthenediol (2), were isolated from the leaves of *Aleuritopteris khunii* together with hop-22(29)-ene, adiantone, hydroxyhopane, a mixture of sterols, 3,5-dihydroxy-7,4′-dimethoxyflavone, 5-hydroxy-3,7,4′-trimethoxyflavone and 4-methoxybenzoic acid. Cheilanthenetriol was found to be identical with authentic samples of cheilanthatriol and cheilarinosin isolated from Indian ferns. The new sesterterpenoid, cheilanthenediol, was established as (17*Z*)-13α,19-dihydroxycheilanth-17-ene.

Keywords fern; *Aleuritopteris khunii*; Pteridaceae; triterpenoid; sesterterpenoid; cheilanthenetriol; cheilanthenediol; flavonoid

The ferns belonging to the genus *Aleuritopteris*[1] of Pteridaceae are widely distributed in the world as typical ferns on limestone, though only three species of them have been reported in Japan. Some ferns in this group are very difficult to classify morphologically, and the occurrence of diterpenoids, sesterterpenoids, triterpenoids, flavonoids and other chemical components is, therefore, of chemotaxonomic interest. This paper concerns the isolation and characterization of two sesterterpenoids from the leaves of *Aleuritopteris khunii* (MILDE) CHING (*Cheilanthes khunii* MILDE, miyama-urajiro in Japanese), which is a beautiful summer-green species growing in the limestone areas of central Japan.

Results and Discussion

The dried leaves of the fern were extracted with *n*-hexane and the extract was separated into several fractions containing triterpenoids [hop-22(29)-ene (diploptene[2]), adiantone,[3] and hydroxyhopane[4]], sterols (a mixture of sitosterol, stigmasterol and campesterol, and a mixture of their fatty acid esters), flavonoids (3,5-dihydroxy-7,4′-dimethoxyflavone and 5-hydroxy-3,7,4′-trimethoxyflavone),[5] 4-methoxybenzoic acid[6] and two sesterterpenoids, namely cheilanthenetriol (**1**) and a new compounds, cheilanthenediol (**2**).

Cheilanthenetriol (**1**),[7] $C_{25}H_{44}O_3$, mp 179—180 °C, showed strong infrared (IR) absorption bands due to hydroxyl groups. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum (270 MHz) indicated the presence of five tertiary methyl groups, one olefinic methyl group (δ 1.780), one proton attached to the carbon bearing a hydroxyl group (δ 3.954), two protons of a hydroxymethyl group (δ 4.053 and

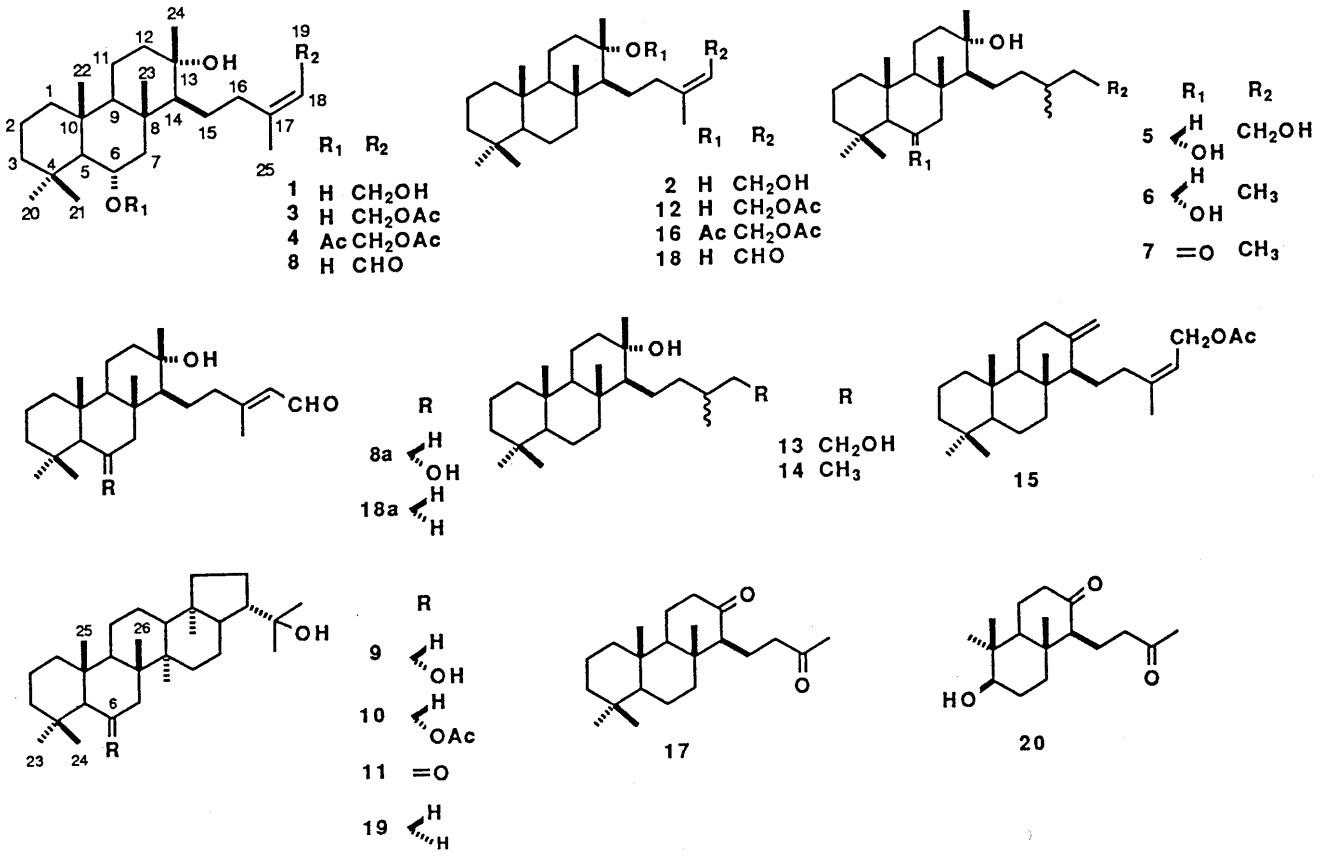

Chart 1

TABLE I. ^{1}H-Chemical Shifts of Compounds **1**, **2** and Their Derivatives (100 or 270 MHz, $CDCl_3$, δ Value)

Compound	H-20	H-21	H-22	H-23	H-24	H-25	H-19	H-18	H-6β	$OCOCH_3$
1[a]	1.168	1.010	0.856	0.844	1.124	1.780	4.053 (dd, 11.7, 7.3) 4.130 (dd, 11.7, 7.3)	5.451 (dd, 7.3, 7.3)	3.954 (ddd, 10.7, 10.7, 3.4)	
3	1.174	1.017	0.857	0.857	1.129	1.794	4.541 (dd, 11.7, 7.0) 4.686 (dd, 11.7, 7.0)	5.331 (dd, 7.0, 7.0)	3.958 (ddd, 10.5, 10.5, 3.1)	2.049
4	0.864	1.022	0.909	0.909	1.132	1.755	4.447 (dd, 12.0, 7.1) 4.683 (dd, 12.0, 7.1)	5.306 (dd, 7.1, 7.1)	5.246 (ddd, 11.0, 11.0, 3.5)	2.044 2.044
5[a]	1.159	1.015	0.851	0.878	1.132	0.921 (d, 6.6)	3.659 (dt, 10.5, 6.6) 3.716 (dt, 10.5, 6.6)		3.965 (ddd, 10.8, 10.8, 3.5)	
6[a]	1.159	1.015	0.853	0.882	1.131	0.860 (d, 6.5)	0.850 (t, 7.0)		3.965 (ddd, 10.7, 10.7, 3.7)	
7[a]	1.216	0.924	0.830	0.822	1.146	0.861 (d, 6.9)	0.843 (t, 6.5)			
8	1.171	1.028	0.879	0.862	1.145	2.000 (d, 1.5)	9.943 (d, 8.0)	5.847 (dd, 8.0, 1.5)	3.973 (ddd, 10.5, 10.5, 3.5)	
2[a]	0.861	0.797	0.808	0.783	1.130	1.775 (d, 1.5)	4.055 (dd, 12.0, 7.3) 4.133 (dd, 12.0, 7.3)	5.463 (ddd, 7.3, 7.3, 1.5)		
12	0.860	0.798	0.798	0.798	1.132	1.786	4.505 (dd, 12.0, 7.5) 4.685 (dd, 12.0, 7.5)	5.315 (dd, 7.5, 7.5)		2.044
13[a]	0.852	0.796	0.796	0.805	1.133	0.919 (d, 6.3)	3.664 (dt, 10.6, 6.6) 3.715 (dt, 10.6, 6.6)			
14[a]	0.853	0.797	0.797	0.805	1.133	0.868 (d, 6.8)	0.855 (t, 6.7)			
15	0.857	0.796	0.796	0.666	4.537 4.836	1.755	4.504 (d, 7.2)	5.348 (t, 7.2)		2.044
16	0.860	0.801	0.801	0.826	1.451	1.787	4.566 (d, 7.2)	5.336 (t, 7.2)		1.960 2.049
18	0.853	0.803	0.803	0.803	1.147	2.007 (d, 1.5)	9.944 (d, 8.0)	5.853 (dd, 8.0, 1.5)		
	(H-23)	(H-24)	(H-25)							
9	1.156	1.015	0.867							
10	0.853	1.031	0.924							
11	1.218	0.905	0.826							
19	0.846	0.796	0.818							

Multiplicity and coupling constants (J in Hz) are shown in parentheses. Hydrogen numbers given in parentheses are those of the hopane group. *a*) Measured at 270 MHz.

4.130) and one proton of a trisubstituted double bond (δ 5.451) as shown in Table I.

Compound **1** was acetylated with Ac_2O–pyridine to give a monoacetate (**3**) and a diacetate (**4**). Catalytic hydrogenation of **1** gave **5** and **6**, the latter being converted to a ketone (**7**). Oxidation of **1** with MnO_2 afforded an aldehyde (**8**) as a sole product, a part of which changed into its geometric isomer (**8a**) spontaneously in solution, until equilibrium was reached. In a comparison of the ^{1}H-NMR spectra of compounds **1**, **4** and **7** with those of zeorin (**9**) and its derivatives (**10** and **11**) (Table I), the three corresponding methyl groups on ring A have very similar chemical shifts. The coupling pattern [δ 3.954 (ddd, J= 10.7, 10.7, 3.4 Hz)] of a geminal proton of the secondary hydroxyl group in **1** suggests that the proton is an axial one, and it also resembles that in **9**[8]; therefore, one of the hydroxyl group of **1** can be located at C-6α. This compound was identical [mixture melting point, IR, mass spectrum (MS) and ^{1}H-NMR] with authentic samples of cheilarinosin[9] and cheilanthatriol[10] isolated from Indian so-called *Cheilanthes farinosa*.[11] Thus, the structure of cheilarinosin, which has been reported to have the ophiobolane skeleton, should be revised to formula **1**.

A new compound, cheilanthenediol (**2**),[7] mp 156—157 °C, $C_{25}H_{44}O_2$, which had a higher *Rf* value than **1** on thin-layer chromatography (TLC), showed IR absorption bands due to hydroxyl groups. The ^{1}H-NMR spectrum (270 MHz) indicated the presence of five tertiary methyl groups, one olefinic methyl group (δ 1.775), two protons of a hydroxymethyl group (δ 4.055 and 4.133) and one proton of a trisubstituted double bond (δ 5.463): the latter two are coupled to each other (Table I). The MS of **2** and **12** showed fragment peaks a, b, c and d corresponding to those of **1** and **3** (Table II), suggesting that **2** has no hydroxyl group on ring B. This was confirmed by the absence of a geminal proton of a secondary hydroxyl group in the ^{1}H-NMR spectrum.

Compound **2** was acetylated under a mild condition (Ac_2O–pyridine) to yield only a monoacetate (**12**) which has a free hydroxyl group considered to be tertiary, and catalytic hydrogenation gave two products, **13** and **14**. Dehydration of **2** with Ac_2O–NaOAc afforded a dehydrate (**15**), along with a diacetate (**16**), and furthermore ozonolysis of **15** gave a diketone (**17**). Oxidation of **2** with MnO_2 afforded an aldehyde (**18**) as a sole product, a part of which gradually changed into its geometric isomer (**18a**) until equilibrium was reached as observed in the case of **1**.

The ^{1}H-chemical shifts of three methyl groups of **2** and its derivatives (**12**—**16**, **18**) closely resembled those of hydroxyhopane (**19**) on ring A. By analogy of the chemical shifts and/or coupling patterns of the methyl group (C-24) and some protons of the side chain between each of the four pairs of **1** and **2**, **3** and **12**, **5** and **13**, **8** and **18** (Table I), compound **2** is expected to have the same side chain as **1**.

TABLE II. MS Data for Compounds **1**, **2** and Their Derivatives

Fragment		**1**	**3**	**2**	**12**
		m/z (rel. int.)			
Molecular ion	M^+			376 (<1)	418 (2)
	M^+-H_2O	374 (6)	416 (1)	358 (12)	400 (5)
	M^+-H_2O-Me	359 (9)		348 (13)	385 (3)
	M^+-2H_2O	356 (26)	398 (2)	340 (13)	
	M^+-2H_2O–Me	341 (14)		325 (7)	
	M^+-3H_2O	338 (10)			
	M^+-AcOH		374 (4)		358 (27)
	M^+-3H_2O-Me	327 (7)			
	$M^+-AcOH-Me$				343 (11)
	$M^+-AcOH-H_2O$		356 (20)		340 (35)
	$M^+-AcOH-H_2O-Me$		341 (11)		325 (13)
	$M^+-AcOH-2H_2O$		338 (11)		
	$M^+-AcOH-2H_2O-Me$		323 (9)		
Fragment a	M^+-116	276 (21)	276 (19)	260 (100)	260 (89)
	a–Me	261 (23)	261 (36)	245 (76)	245 (100)
	$a-H_2O$	258 (100)	258 (100)		
	$a-H_2O-Me$	243 (12)	243 (38)		
Fragment b	M^+-117	275 (16)	275 (28)	259 (54)	259 (59)
	$b-H_2O$	257 (27)	257 (22)		
Fragment c	M^+-171	221 (5)	221 (6)	205 (17)	205 (17)
	$c-H_2O$	203 (18)	203 (39)		
Fragment d	M^+-185	207 (13)	207 (21)	191 (68)	191 (42)
	$d-H_2O$	189 (28)	189 (55)		

TABLE III. ^{13}C-Chemical Shifts of Compounds **1**, **2** and Their Derivatives (68 MHz, $CDCl_3$, δ Value)

C	**1**	**4**	**7**	**2**	**12**	**13**	**14**	**15**	**16**
1	40.2	40.0	40.7	40.1	40.1	40.1	40.1	40.2	40.1
2	18.6	18.4	18.4	18.7	18.7	18.7	18.7	18.7	18.7
3	43.6	43.3	42.6	42.2	42.2	42.2	42.2	42.1	42.2
4	33.7	33.3	32.3	33.3	33.3	33.3	33.3	33.3	33.4
5	61.3	58.9	66.8	56.7	56.7	56.7	56.7	56.7	56.7
6	67.9	70.7	211.8	18.3	18.3	18.2	18.2	18.7	18.2
7	52.9	48.3	58.1	41.5	41.5	41.5	41.5	40.7	41.3
8	40.2	40.0	45.5	39.4	39.4	39.5	39.5	39.8	39.8
9	60.1	60.2	60.7	60.7	60.7	60.7	60.7	60.2	60.2
10	39.3	39.5	43.7	37.6	37.6	37.6	37.6	37.9	37.5
11	19.6	19.5	19.8	19.4	19.4	19.4	19.4	19.2	19.0
12	44.3	44.3	44.0	44.3	44.4	44.5	44.5	38.2	38.9
13	74.0	73.9	74.0	74.2	73.8	74.3	74.3	148.4	88.0
14	61.8	61.9	62.4	61.8	62.2	62.8	63.0	56.3	59.6
15	24.5	24.1	22.7	24.5	24.3	22.8	22.8	23.3	24.9
16	35.6	35.6	40.7	35.6	35.8	41.3	40.9	37.9	35.6
17	141.8	143.9	35.4	142.0	144.1	30.7	35.5	143.1	143.8
18	123.5	118.8	29.5	123.6	118.6	39.8	29.3	119.2	118.6
19	58.4	61.2	11.4	58.4	61.3	61.1	11.4	61.2	61.3
20	36.6	36.1	32.4	33.3	33.3	33.4	33.4	33.3	33.4
21	22.2	22.0	21.6	21.4	21.4	21.4	21.4	21.4	21.5
22	17.7	17.6	16.7	16.3	16.3	16.2	16.2	16.2	16.3
23	18.1	17.8	17.1	16.7	16.7	16.7	16.7	15.5	17.0
24	23.9	24.0	23.8	23.9	23.9	23.9	23.9	106.0	23.0
25	23.6	23.5	19.3	23.6	23.6	19.8	19.4	23.5	23.8
$OCOCH_3$		21.2			21.1			21.1	20.3
		22.1							21.1
$OCOCH_3$		170.3			170.8			170.8	170.1
		170.9							171.0

TABLE IV. Substituent Effects for the Cheilanthane and Hopane Groups

C	Cheilanthane group			Hopane group		
	6α OH	6α OAc	6 CO	6α OH	6α OAc	6 CO
1	+0.1	−0.1	+0.6	0	−0.3	+0.4
2	−0.1	−0.3	−0.3	−0.2	−0.4	−0.1
3	+1.4	+1.1	+0.4	+1.6	+1.2	+0.4
4	+0.4	0	−1.0	+0.3	−0.3	−0.8
5	+4.6	+2.2	+10.1	+4.9	+2.1	+10.2
6	+49.6	+52.4	+193.6	+50.6	+53.0	+195.2
7	+11.4	+6.8	+16.6	+12.2	+7.5	+18.1
8	+0.8	+0.6	+6.0	+0.9	+0.6	+6.6
9	−0.6	−0.5	0	−0.6	−0.7	+0.3
10	+1.7	+1.9	+6.1	+2.1	+2.0	+6.6
20 (23)	+3.3	+2.8	−1.0	+3.3	+2.7	−1.0
21 (24)	+0.8	+0.6	+0.2	+0.4	+0.3	+0.1
22 (25)	+1.4	+1.3	+0.4	+1.2	+1.1	+0.7
23 (26)	+1.4	+1.1	+0.4	+1.5	+1.1	+0.8

Carbon numbers given in parentheses are those of the hopane group.

The *Z* configuration of the $\Delta^{17)}$ double bond of **1** has already been proposed from the carbon-13 nuclear magnetic resonance (^{13}C-NMR) data.[10b] This deduction was also supported by the following evidence: the ^{1}H-NMR signals of C-25 methyl groups in **8** and **18** appear at a higher field (−0.17 ppm in both) than those in their geometric isomers, **8a** and **18a**, which are affected more strongly by the anisotropy of the aldehyde group.

As shown in Table III, the ^{13}C-chemical shifts of **2** are in good agreement with those of **1**, except for C-3, C-4, C-5, C-6, C-7, C-8, C-9, C-10, C-20, C-21, C-22, and C-23. The ^{13}C-chemical shift deviations of **1**, **4** and **7** from **2**, **12** and **14** show substituent group effects of 6α-hydroxy, 6α-acetoxy and 6-oxo in the cheilanthane group. These values are compatible with those for the corresponding positions in the hopane group (**9**, **10** and **11**)[12] (Table IV).

The stereochemistry of the cheilanthane skeleton was unequivocally determined on the basis of the following spectral data of **1**, **2** and their derivatives: 1) The circular dichroism (CD) and optical rotatory dispersion (ORD) curves of compound **7** and zeorinone (**11**) showed the same negative Cotton effects. The differences of the respective

^{1}H-NMR solvent shift values [$\delta(C_6D_6)-\delta(CDCl_3)$] of four corresponding methyl groups between **7** and **14** are +0.19 (H-20), +0.12 (H-21), −0.04 (H-22) and −0.04 (H-23), which are characteristic of an isolated carbonyl group, excluding the solvent effect due to an additional hydroxy group (C-13α OH); in the case of zeorinone (**11**) and hydroxyhopane (**19**),[13] these differences are +0.21 (H-23), +0.10 (H-24), −0.04 (H-25) and −0.07 (H-26), showing a similar tendency to those mentioned above.[14] According to these indications, the cheilanthane group has the same absolute structure as the hopane group. 2) The ORD curve of **17** showed a positive Cotton effect similar to that of **20** derived from a diterpenoid, alepterolic acid.[15] This provided conclusive proof that the configuration of the side chain in **2** is β. This result is also reasonable from the biogenetic point of view.

All the above evidence leads to (17*Z*)-13α,19-dihydroxycheilanth-17-ene (**2**) for the structure of cheilanthenediol. Some new spectral data for **1**, **2** and their derivatives also support the conclusion that the structure of cheilanthenetriol is (17*Z*)-6α,13α,19-trihydroxycheilanth-17-ene (**1**).

Cheilanthenediol is one of the most primitive tricyclic sesterterpenoids derived from geranyl farnesyl precursor. Further chemotaxonomical studies on some ferns belonging to *Aleuritopteris* and *Cheilanthes* are in progress.

Experimental

Melting points were measured with a Yanagimoto microapparatus and are uncorrected. The ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM FX-100 and GX-270 spectrometers using tetramethylsilane as an internal stadard in $CDCl_3$ solution. Electron impact mass spectra (EI-MS) were measured at 70 eV (direct inlet) with a JEOL JMS D300 spectrometer and the relative intensities of peaks were reported with reference to the most intense peak higher than *m/z* 100. Gas chromatography (GC) was run on a Hitachi 163 using a glass column containing Chromosorb G HP coated with SE-30 (1.4%) at 260 °C in a flow of N_2. Cholestane was used as an internal reference; its retention time was set at 3.0 min. Gas chromatography mass spectra (GC-MS) were run on a JGC 20K-JMS D300 system using the same column as described above in a flow of He. TLC was carried on precoated Silica gel 60 plates (Merck) with *n*-hexane–EtOAc or $CHCl_3$–MeOH as the solvent system.

Plant Materials The leaves (6.7 kg) of *Aleuritopteris khunii* were collected in September at Shimonita, Gunma Prefecture, Japan. A voucher specimen has been deposited in the Herbarium of Showa College of Pharmaceutical Sciences, Tokyo.

Extraction and Separation The air-dried plant materials were extracted with *n*-hexane and the extract was treated with MeOH to remove aliphatic substances. The resulting extract was chromatographed on silica gel using *n*-hexane, C_6H_6 and Et_2O as eluents to be separated first into six fractions (frs. 1—6). By repeated chromatography and recrystallization, hop-22(29)-ene (0.094 g) was obtained from fr. 1, sterol esters (0.134 g) from fr. 2, adiantone (0.158 g) from fr. 3, hydroxyhopane (0.268 g), sterol mixture (1.474 g), 3,5-dihydroxy-7,4′-dimethoxyflavone (1.210 g) and 5-hydroxy-3,7,4′-trimethoxyflavone (0.020 g) from fr. 4, cheilanthenediol (**2**) (2.747 g) and 4-methoxybenzoic acid (0.007 g) from fr. 5, and cheilanthenetriol (**1**) (6.030 g) from fr. 6.

Hop-22(29)-ene Colorless needles (from EtOAc), mp 210—211 °C, $[\alpha]_D^{23}$ +60.5° (*c*=0.32, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3035, 1645, 1630, 886. MS *m/z* (rel. int.): 410 (M^+, 28), 395 (10), 376 (6), 299 (8), 218 (13), 205 (15), 204 (20), 203 (10), 191 (100), 189 (78). Identical (mixture melting point, IR and MS) with an authentic sample.[2]

Adiantone Colorless needles (from $CHCl_3$–MeOH), mp 227—230 °C, $[\alpha]_D^{23}$ +78.0° (*c*=0.44, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1700. MS *m/z* (rel. int.): 412 (M^+, 22), 397 (9), 369 (17), 191 (100). Identical (mixture melting point, IR and MS) with an authentic sample.[3]

Hydroxyhopane Colorless needles (from EtOAc), mp 253—255 °C, $[\alpha]_D^{23}$ +42.0° (*c*=0.38, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3600, 3040, 1152. MS *m/z* (rel. int.): 428 (M^+, 3), 410 (9), 395 (6), 369 (3), 207 (17), 205 (9), 191 (100), 189 (76), 177 (11), 163 (17). Identical (mixture melting point, IR and MS) with an authentic sample.[4]

Sterol Esters Colorless flakes (from EtOAc), mp 76—78 °C. Hydrolysis of sterol esters with 5% KOH–EtOH under reflux for 2 h gave the sterol and fatty acid fractions. The GC and GC-MS of the sterol mixture showed Rt_R 2.24 (6% of total peaks) (*m/z* 400, M^+), 2.41 (16%) (412, M^+) and 2.73 (78%) (414, M^+), which correspond to campesterol, stigmasterol and sitosterol respectively. The fatty acid fraction consisted of palmitic acid and a small amount of stearic acid, which were identified as their methyl esters by GC and GC-MS.

Sterol Mixture Colorless plates (from $CHCl_3$–MeOH), mp 137.5—139 °C. GC and GC-MS: Rt_R 2.24 (9% of total peaks) (*m/z* 400, M^+), 2.41 (4%) (412, M^+), 2.73 (87%) (414, M^+), which correspond to the three sterols mentioned above.

3,5-Dihydroxy-7,4′-dimethoxyflavone Yellow needles (from C_6H_6), mp 182—184 °C. IR ν_{max}^{KBr} cm^{-1}: 3295, 1650, 1600, 1510, 1325, 1260, 830. MS *m/z* (rel. int.): 314 (M^+, 100), 313 (9), 299 (10), 285 (5), 271 (10), 243 (5), 135 (5). ^{1}H-NMR (100 MHz) δ: 3.875 (3H, s), 3.885 (3H, s), 6.358 (1H, d, *J*=2.2 Hz), 7.020 (1H, d, *J*=9.2 Hz), 8.154 (1H, d, *J*=9.2 Hz). *Anal.* Calcd for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49. Found: C, 64.94; H, 4.49. (lit. mp 178—180 °C). Methylation of this compound (0.089 g) with diazomethane gave 5-hydroxy-3,7,4′-trimethoxyflavone, yellow needles (0.032 g) (from C_6H_6), mp 149—149.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3910, 1665, 1510, 1350, 1260, 1180, 830. MS *m/z* (rel. int.): 328 (M^+, 100), 327 (81), 313 (11), 299 (16), 285 (37), 135 (16). ^{1}H-NMR (100 MHz) δ: 3.858 (3H, s), 3.872 (3H, s), 3.897 (3H, s), 6.354 (1H, d, *J*=2.2 Hz), 6.441 (1H, d, *J*=2.2 Hz), 7.020 (1H, d, *J*=9.2 Hz), 8.074 (1H, d, *J*=9.2 Hz).

5-Hydroxy-3,7,4′-trimethoxyflavone Yellow needles (from C_6H_6), mp 149—149.5 °C. Identical (mixture melting point, IR, MS and ^{1}H-NMR) with the compound given above.

4-Methoxybenzoic Acid Colorless needles (from C_6H_6), mp 180—185 °C. IR ν_{max}^{KBr} cm^{-1}: 3000—2500, 2800, 1675, 1600, 1425, 1295, 1255, 1165, 1025, 840. MS *m/z* (rel. int.): 152 (M^+, 99), 135 (100), 107 (13), 92 (16), 77 (21). ^{1}H-NMR (100 MHz) δ: 3.870 (3H, s), 6.941 (2H, d, *J*=9.1 Hz). 8.062 (2H, d, *J*=9.1 Hz). Identical (mixture melting point, IR, MS and ^{1}H-NMR) with an authentic sample.

Cheilanthenetriol (1) Colorless needles (from Me_2CO), mp 179—180 °C, $[\alpha]_D^{23}$ +30.2° (*c*=0.37, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3350, 2950, 1660, 1450, 1395, 1000, 980, 860. *Anal.* Calcd for $C_{25}H_{44}O_3$: C, 76.48; H, 11.30. Found: C, 76.11; H, 11.08. HRMS: *m/z* 374.3225 (M^+-H_2O, Calcd for $C_{25}H_{42}O_2$: 374.3185.)

Acetylation of 1 **1** (0.15 g) in pyridine (2.5 ml) and Ac_2O (1.3 ml) was allowed to stand at 5 °C for 0.5 h. Half of the solution was worked up, and the reaction mixture was chromatographed on silica gel to give **3** (0.03 g), colorless plates (from *n*-hexane–Me_2CO), mp 126—128.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3540, 3450, 1730, 1240, 1010. The rest of the solution was left at room temperature overnight. After the same work-up and separation as described above, the main product was **4** (0.04 g), colorless gum. MS *m/z* (rel. int.): 416 (M^+ −AcOH, 6), 401 (14), 398 (14), 389 (17), 356 (13), 341 (18), 338 (19), 329 (70), 316 (42), 301 (22), 261 (32), 259 (25), 258 (100), 257 (42), 243 (32), 203 (43), 191 (83), 189 (59), 187 (40).

Catalytic Hydrogenation of 1 **1** (0.2 g) was hydrogenated in the presence of PtO_2 (0.12 g) in AcOH (8 ml) and EtOAc (4 ml) at room temperature for 1.5 h. The reaction mixture was chromatographed on silica gel to yield **5** (0.054 g) and **6** (0.06 g). **5**: colorless needles (from EtOAc), mp 176—177.5 °C. IR ν_{max}^{KBr} cm^{-1}: 3450, 3330, 1130, 1010. MS *m/z* (rel. int.): 394 (M^+, 1), 376 (26), 361 (7), 358 (9), 343 (10), 306 (28), 305 (44), 261 (6), 243 (15), 223 (22), 205 (20), 203 (18), 191 (100), 189 (23), 163 (30). **6**: colorless needles (from *n*-hexane–Et_2O), mp 194—195 °C. IR ν_{max}^{KBr} cm^{-1}: 3520, 1110, 1040. MS *m/z* (rel. int.): 378 (M^+, 1), 360 (3), 345 (10), 342 (8), 327 (12), 307 (37), 289 (100), 275 (11), 261 (47), 258 (15), 243 (17), 207 (34), 203 (25), 191 (74), 190 (39), 189 (29), 163 (89).

Oxidation of 6 with CrO_3 A solution of **6** (0.045 g) in pyridine (2 ml) was combined with CrO_3 (0.1 g) in pyridine (3 ml) and the mixture was stirred at room temperature for 2.2 h. The product was subjected to silica gel chromatography to yield **7** (0.032 g), colorless plates (from *n*-hexane), mp 119—120 °C. IR ν_{max}^{KBr} cm^{-1}: 3450, 1710, 1070. MS *m/z* (rel. int.): 376 (M^+, 7), 361 (6), 358 (14), 343 (14), 305 (11), 291 (8), 277 (25), 206 (39). ORD and CD: [*M*] (nm): −550° (325) (trough), +700° (292) (peak); [θ] (nm): −1470 (310) (negative maximum) (*c*=0.084, MeOH) {zeorinone (**11**), [*M*] (nm): −1070° (324) (trough), +1790° (288) (peak); [θ] (nm): −2450 (360) (negative maximum) (*c*=0.037, MeOH)}. ^{1}H-NMR solvent shift values [$\delta(C_6D_6)-\delta(CDCl_3)$]: +0.24 (H-20), +0.17 (H-21), −0.08 (H-22), −0.10 (H-23).

Oxidation of 1 with MnO_2 **1** (0.15 g) in dry Me_2CO (15 ml) was treated

with activated MnO_2 (1.2 g) at room temperature for 4 h. The product (**8**), which showed one spot on TLC was recrystallized from *n*-hexane–EtOAc to give colorless plates, mp 159—160 °C, indicating an additional weak, lower *Rf* spot. **8**: IR ν_{max}^{KBr} cm^{-1}: 3480, 1670, 1175. MS *m/z* (rel. int.): 390 (M^+, 1), 375 (37), 372 (22), 357 (59), 339 (19), 329 (48), 289 (41), 275 (19), 271 (42), 261 (68), 258 (26), 257 (37), 243 (30), 203 (51), 191 (100), 189 (58). The density of the lower *Rf* spot gradually increased after standing in the $CHCl_3$ solution. The ^{1}H-NMR spectrum of this mixture exhibited signals at δ 2.174 (3H, d, J=1.0 Hz) and 10.012 (1H, d, J=8.0 Hz) due to **8a** in addition to the signals of **8** shown in Table I.

Cheilanthenediol (2) Colorless plates (from Me_2CO), mp 156—157 °C, $[\alpha]_D^{23}$ +5.1° (c=0.60, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3300, 1095, 1010, 800. HRMS *m/z*: 376.3331 (M^+, Calcd for $C_{25}H_{44}O_2$: 376.3339).

Acetylation of 2 **2** (0.062 g) in pyridine (1 ml) and Ac_2O (0.5 ml) was allowed to stand at room temperature for 1 h. The product was chromatographed on silica gel to give **12** (0.044 g) as a colorless gum.

Catalytic Hydrogenation of 2 **2** (0.102 g) was hydrogenated in the presence of PtO_2 (0.14 g) in AcOH (8 ml) and EtOAc (4 ml) at room temperature for 2 h. Chromatography on silica gel of the reaction mixture followed by recrystallization afforded **13** (0.016 g), **14** (0.025 g) and the starting material (0.010 g). **13**: colorless needles (from *n*-hexane–Me_2CO), mp 124—125 °C. IR ν_{max}^{KBr} cm^{-1}: 3350, 3330, 1135, 1090. HRMS *m/z*: 378.3491 (M^+, Calcd for $C_{25}H_{46}O_2$: 378.3496), MS *m/z* (rel. int.): 378 (M^+, 30), 363 (11), 360 (23), 345 (28), 307 (68), 289 (9), 260 (8), 259 (16), 245 (51), 205 (25), 204 (44), 193 (63), 192 (100), 191 (84), 177 (28). **14**: colorless needles (from *n*-hexane), mp 125—127.5 °C, IR ν_{max}^{KBr} cm^{-1}: 3500, 1140, 1105, 1010. MS *m/z* (rel. int.): 362 (M^+, 5), 344 (30), 329 (20), 291 (5), 260 (15), 259 (51), 245 (12), 205 (24), 204 (16), 192 (70), 191 (100), 177 (45). ^{1}H-NMR solvent shift values [$\delta(C_6D_6)-\delta(CDCl_3)$]: +0.05 (H-20), +0.05 (H-21), −0.04 (H-22), −0.06 (H-23).

Dehydration of 2 **2** (0.13 g) was refluxed with Ac_2O (5 ml) and AcONa (0.2 g) for 5 h. The product was chromatographed on silica gel to yield the following compounds; **15** (0.015 g), an amorphous powder; IR ν_{max}^{KBr} cm^{-1}: 1735, 1645, 1230, 1020, 885, and **16** (0.04 g), colorless needless (from *n*-hexane), mp 103.5—104 °C, IR ν_{max}^{KBr} cm^{-1}: 1730, 1250, 1020, MS *m/z* (rel. int.): 400 (M^+ −AcOH, 2), 385 (7), 340 (19), 325 (27), 272 (37), 260 (66), 259 (52), 245 (30), 205 (23), 204 (24), 191 (100), 177 (39), 163 (31).

Ozonolysis of 15 A gas mixture of 3% ozone/O_2 was passed into a solution of **15** (0.015 g) in $CHCl_3$ (6 ml) for 0.5 h. After evaporation of the solution, the resluting ozonide was treated with AcOH (6 ml) in the presence of Zn powder (0.15 g). The product was chromatographed on silica gel to give **17** (0.008 g), colorless gum, IR ν_{max}^{film} cm^{-1}: 1710, MS *m/z* (rel. int.): 332 (M^+, 20), 317 (100), 299 (18), 191 (44). ^{1}H-NMR (100 MHz) δ: 0.732, 0.816, 0.848, 0.877, 2.095 (3H,each), ORD: [*M*] (nm): +7330° (308) (peak), −8630° (270) (trough) (c=0.058, MeOH) {**20**; [*M*] (nm): +6750° (318) (peak), −7050° (280) (trough) (c=0.073, MeOH)}.

Oxidation of 2 with MnO_2 **2** (0.108 g) in dry Me_2CO (12 ml) was treated with activated MnO_2 (0.9 g) for 2.5 h at room temperature. The reaction product, **18**, IR ν_{max}^{KBr} cm^{-1}: 3400, 1660, 1100. MS *m/z* (rel. int.): 374 (M^+, 10), 359 (20), 356 (13), 341 (16), 291 (61), 273 (36), 259 (31), 245 (63), 191 (100), showed one spot on TLC, but the $CHCl_3$ solution of the above compound after standing for a while showed two spots on TLC, the lower *Rf* compound of which is the geometric isomer (**18a**). The ^{1}H-NMR spectrum of this mixture exhibited signals at δ 2.181 (3H, d, J=1.0 Hz) and 9.988 (1H, d, J=8.0 Hz) due to **18a** in addition to the signals of **18** shown in Table I.

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