Fern Constituents: Triterpenoids Isolated from Leaflets of *Cyathea spinulosa*

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Four new triterpenoids, hopan-29,17α-olide (1), hopan-17α,29-epoxide (2), 3α-hydroxyfilic-4(23)-ene (3), and 2-oxofilic-3-ene (4), were isolated from the dried leaflets of *Cyathea spinulosa*, together with hop-22(29)-ene (5), fern-7-ene (6), fern-9(11)-ene (7), filic-3-ene (8), hydroxyhopane (9), dryocrassol (10), tetrahymanol (11) and cyclolaudenyl palmitate (12). The structures of the new compounds were elucidated on the bases of spectral data and chemical correlations.

Keywords *Cyathea spinulosa*; triterpenoid; hopan-29,17α-olide; hopan-17α,29-epoxide; 3α-hydroxyfilic-4(23)-ene; 2-oxofilic-3-ene

Cyathea spinulosa WALL. ex HOOK. (Cyatheaceae, "hego" in Japanese) is a tall tree fern (more than 4 m high) with large indeciduous leaves (2 m long) and is commonly distributed in the subtropical or tropical areas of Japan, Taiwan, the Philippines, China, Burma, India and Nepal. This paper deals with triterpenoid and steroid constituents isolated from the dried leaflets of the fern collected in Taiwan. The hexane extract of the plant materials was separated by chromatography on SiO_2 gel and Al_2O_3, as well as HPLC to give a new triterpenoid lactone (**1**), an epoxide (**2**), an alcohol (**3**) and a ketone (**4**), together with known triternoids, hop-22(29)-ene (**5**),[1] fern-7-ene (**6**),[1] fern-9(11)-ene (**7**),[1] filic-3-ene (**8**),[1] hydroxyhopane (**9**),[1] dryocrassol (**10**),[1] tetrahymanol (**11**),[2] cycloaudenyl palmitate (**12**),[3] sitosteryl palmitate (**13**), sitosterol (**14**), and sitostanol (**15**). The last four compounds, **12**, **13**, **14** and **15**, were isolated in a pure state, as described in Experimental.

Compound **1** is a triterpenoid lactone (IR (KBr): 1785 cm^{-1}) of molecular formula $C_{30}H_{48}O_2$, as determined from its high-resolution MS, *m/z* 440.3631. The EI-MS of **1** gave the characteristic fragment ion peaks of orton acetal ((30*R*)-methoxy-17α,30-epoxyhopane, **16**),[4] having a hemiacetal structure on the hopane skeleton, and its oxidation product, hopan-17α,30-olide (**17**)[4] (Table I). The ^{1}H-NMR spectrum of **1** showed proton signals due to six tertiary and one secondary methyl groups, which were assigned by comparison with those of **5**, **9** and **16** (Table II). Methyl proton signals assigned to H-23, H-24, H-25 and H-26 gave appropriate values for a hopane, while that of H-28 appeared at very low field (δ 1.007). The secondary methyl proton signal at lower field (δ 1.327, d) was also influenced by the tertiary oxygen function. Thus, the lactone ring of **1** was considered to be located at C-17α and C-29, not C-30, because **1** was not identical with **17** in TLC behavior. The ^{13}C-NMR spectrum of **1** showed thirty carbon signals, which were assigned by comparison with those of **5**, **16** and **17** (Table III). Cross peaks in the ^{1}H-detected heteronuclear multiple-bond coherence (HMBC) spectrum revealed the structure of

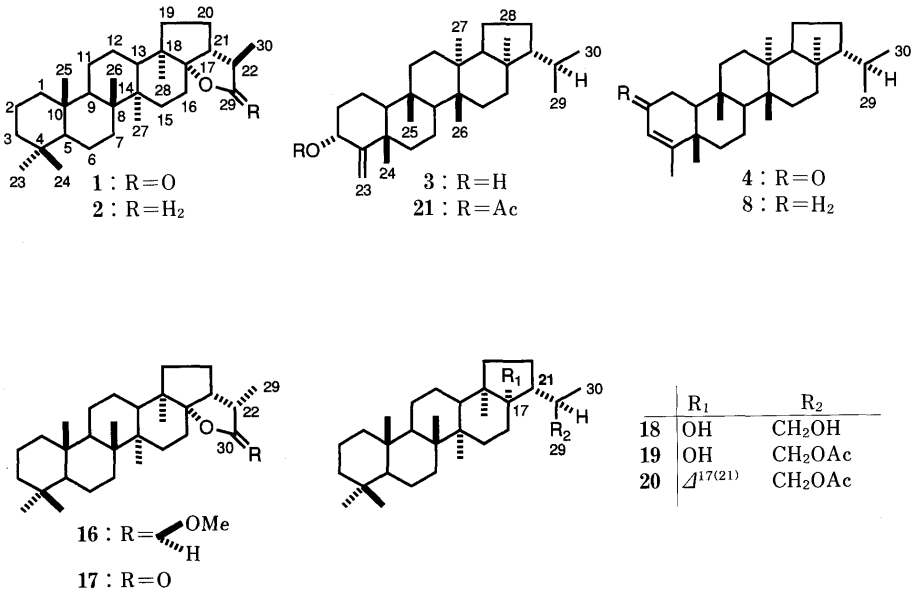

Chart 1

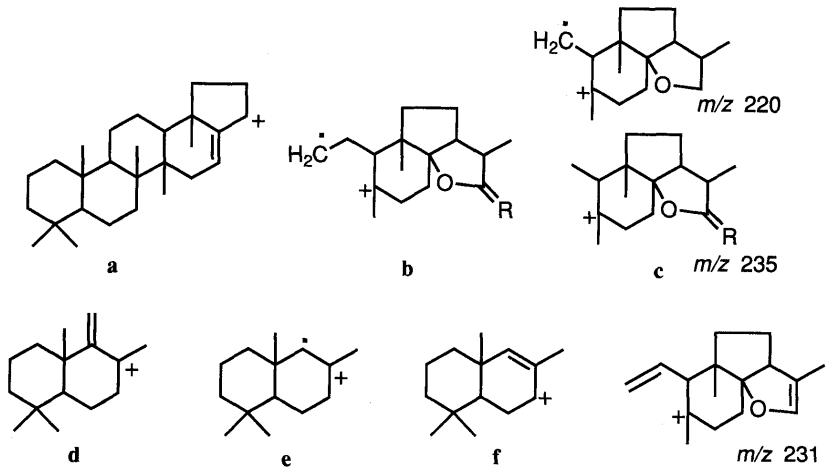

Chart 2

TABLE I. MS Fragments of **1**, **2**, **16**, **17** and **1'**

	M^+	M^+-CH_3	M^+-H_2O	a	b	c	d	e	f
1	440 (24)	425 (8)		367 (3)	248 (8)	235 (13)	205 (21)	192 (21)	191 (100)
2	426 (73)	411 (17)	393 (7)	367 (14)	234 (5)	220 (43)	205 (30)	192 (30)	191 (100)
16	456 (51)	441 (10)		367 (14)	—	250 (32)	205 (23)	192 (67)	191 (100)
					231 (27)	218 (27)[a]			
17	440 (13)	425 (7)		367 (3)	248 (6)	235 (7)	205 (16)	192 (23)	191 (100)
1'	440 (17)	425 (9)		367 (4)	248 (11)	235 (21)	205 (29)	192 (27)	191 (100)

a) $-CH_3OH$ fragment from c.

TABLE II. ^{1}H-NMR Spectral Data for Compounds **1**, **2**, **17**, **5**, **9**, **16** and **1'**

Proton No.	**1**	**2**	**17**	**5**	**9**	**16**	**1'**
H-23	0.853	0.847	0.855	0.845	0.848	0.849	0.853
H-24	0.798	0.794	0.798	0.794	0.796	0.794	0.796
H-25	0.830	0.828	0.830	0.818	0.818	0.824	0.829
H-26	0.960	0.940	0.957	0.963	0.960	0.934	0.959
H-27	1.063	1.029	1.068	0.948	0.960	1.036	1.062
H-28	1.007	0.951	1.018	0.728	0.767	0.984	1.008
H-29		3.391	1.249	4.777	1.181	1.049	
		(1H, dd, 8.4, 6.8)	(d, 6.8)	(br s)		(d, 6.8)	
		3.904					
		(1H, dd, 8.4, 6.8)					
H-30	1.327	1.075		1.750	1.208	4.689	1.375
	(d, 7.8)	(d, 6.8)				(d, 5.0)	(d, 7.9)
H-21						1.375	
						(1H, d, 7.9)	
$OC\underline{H}_3$						3.340	

Signals, unless otherwise stated, are 3H, singlet. Multiplicity and coupling constants are shown in parentheses.

hopane-29,17α-olide as **1**. $LiAlH_4$ reduction of **1** gave a diol (**18**), and acetylation of **18** under various conditions gave a diol monoacetate (**19**) and a monool acetate (**20**) with a tetrasubstituted double bond. The configuration at C-22 of **1** was firmly established by the NOE difference spectrum (NOEDS). NOEs were observed at H-21 on irradiation of H-30, H-30 on irradiation of H-21, and H-22 and H-20 (β) on irradiation of H-19 (β). Assignments of the signals of H-22, H-21, H-20 and H-16 were confirmed by homonuclear single-quantum coherence (HSQC) and homo spin decoupling measurements. In the nuclear Overhauser enhancement spectroscopy (NOESY) of **1**, cross peaks were observed between methyl signals, H-24 and H-25, H-25 and H-26, and H-27 and H-28, and protons of H-22 and H-30, and H-20 and H-22. The above results showed that the methyl group at C-22 has β-configuration (22*R*) and is on the same side as H-21 (Fig. 1). Consequently, the structure of **1** is concluded to be hopan-29,17α-olide according to the numbering system of neriifoliol (hopan-29-ol 22*R*) and dryocrassol (hopan-30-ol 22*S*).[5] Thus, it was confirmed that **1** and **17** are diastereomeric at C-22, and the structures of **18**, **19** and **20** were determined to be 17α,29-dihydroxyhopane, 17α-hydroxy-29-acetoxyhopane and 29-acetoxyhop-17(21)-

TABLE III. ^{13}C-NMR Spectral Data for Compounds **1**, **2**, **5**, **16**, **17** and **19**

Carbon No.	1	2	5	16	17	19
C-1	40.7	40.4	40.3	40.4	40.3	40.3
C-2	18.6	18.7	18.7	18.8	18.6	18.7
C-3	42.0	42.1	42.1	42.2	42.0	42.1
C-4	33.2	33.3	33.3	33.3	33.3	33.3
C-5	56.3	56.4	56.1	56.3	56.2	56.3
C-6	18.6	18.7	18.7	18.8	18.6	18.7
C-7	33.2	33.8	33.3	33.3	33.1	33.2
C-8	42.2	42.2	41.9	42.2	42.1	42.0
C-9	50.7	51.0	50.4	50.8	50.5	50.7
C-10	37.4	37.5	37.4	37.5	37.4	37.4
C-11	21.5	21.7	20.9	21.6	21.4	21.6
C-12	24.0	24.3	24.0	24.0	24.0	23.7
C-13	38.5	39.1	49.4	39.3	38.4	41.2
C-14	40.3	40.6	42.1	41.1	41.1	41.6
C-15	31.7	31.4	33.6	29.7	25.2	27.7
C-16	27.7	27.6	21.7	28.1	29.7	23.0
C-17	95.4	95.9	54.9	98.4	97.5	83.7
C-18	48.6	48.9	44.8	49.4	49.1	49.7
C-19	38.1	39.0	41.9	38.2	37.9	37.1
C-20	28.8	28.5	27.4	29.1	28.2	28.5
C-21	48.0	53.1	46.5	46.5	37.8	42.5
C-22	45.9	45.3	148.8	40.4	44.4	32.1
C-23	33.2	33.4	33.4	33.4	33.3	33.4
C-24	21.5	21.6	21.6	21.6	21.5	21.6
C-25	16.2	16.3	15.8	15.6	15.7	16.1
C-26	16.2	16.2	16.7	16.3	16.1	16.4
C-27	15.7	15.7	16.8	17.5	17.1	16.1
C-28	17.6	17.5	16.1	16.2	16.2	16.9
C-29	180.4	33.3	110.1	10.1	11.1	69.2
C-30	19.2	19.2	25.0	105.6	179.1	15.6
Other				54.9		21.1
						171.2

TABLE IV. ^{1}H-NMR Spectral Data for Compounds **18**, **19** and **20**

Proton No.	18	19	20
H-23	0.849	0.848	0.846
H-24	0.789	0.796	0.794
H-25	0.822	0.822	0.820
H-26	0.968	0.965	0.962
H-27	1.010	1.002	1.000
H-28	0.903	0.896	0.895
H-29	3.552	3.955	3.951
	(1H, dd, 11.0, 4.0)	(1H, dd, 11.0, 6.7)	(1H, dd, 11.0, 6.7)
	3.564	4.012	4.014
	(1H, dd, 11.0, 7.3)	(1H, dd, 11.0, 6.7)	(1H, dd, 11.0, 6.7)
H-30	0.970	0.997	0.998
	(d, 7.3)	(d, 5.0)	(d, 7.0)
CH_3CO		2.061	2.063

Signals, unless otherwise stated, are 3H, singlet. Multiplicity and coupling constants are shown in parentheses.

ene, respectively.

Compound **2** is a triterpenoid ether (IR (KBr): 1050 cm^{-1}) of molecular formula $C_{30}H_{50}O$ from its high resolution MS *m/z* 426.3853. The EI-MS of **2** gave similar fragment ion peaks to **1** and **16** (Table I). These results suggested that **2** has the hopane skeleton with an ether ring on the D and E rings, including a side chain like that of **1**. The ^{1}H-NMR spectrum of **2** exhibited the proton

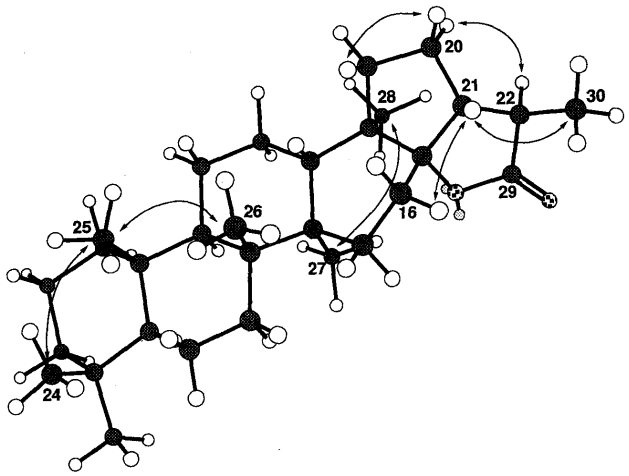

Fig. 1. Chem 3D Plus/MM2 Drawing of **1** with NOEs Observed in NOEDS and NOESY

signals of six tertiary and one secondary methyls, and one methylene (δ 3.391, dd; 3.904, dd) adjacent to the ether ring, which were assigned by comparison with those of **1**, **9** and **17** (Table II). Methyl proton signals resembled those of **1**, **9** and **17**, including H-28 signals at lower field (hopane skeleton). The ^{13}C-NMR spectrum obtained by the distortionless enhancement by polarization transfer (DEPT) method showed thirty carbon signals due to seven methyls, twelve methylenes, five methines, and six quaternary carbons, which were assigned by comparison with those of **5** and **16**, and were confirmed by ^{13}C–^{1}H correlated spectroscopy (C–H COSY) (Table III). These results suggested the location of the ether ring between C-17α and the side chain carbons. Compound **2** gave a lactone (**1'**) in good yield on oxidation with $K_2Cr_2O_7$, and **1'** was shown to be identical with **1** by comparison of the ^{1}H-NMR spectrum and MS (Tables I and II). Thus **2** was concluded to be hopan-17α,29-epoxide.

Compound **3** is a triterpenoid alcohol (IR (KBr): 1050, 1045, 1640, 895 cm^{-1}) of molecular formula $C_{30}H_{50}O$ from its high-resolution MS *m/z* 426.3766. The EI-MS of **3** showed fragment ion peaks corresponding to those of **8** (Table V),[6] and suggested **3** to be a filicene derivative with a hydroxyl group on the A or B ring. The ^{1}H-NMR signals (Table VI) of five primary methyl, two secondary methyl, one exomethylene (δ 4.884, 4.718) and one proton attached to the carbon bearings a hydroxyl group (δ 4.277) were observed. Comparison of the ^{1}H-NMR signals of **3** with those of filic-4(23)-ene (**21**)[7] and a lower-field shift of one exomethylene proton signal (H-23a δ 4.884) of **3** clearly indicated **3** to be 3-hydroxyfilic-4(23)-ene. Moreover, the splitting pattern of H-3 of **3** showed the proton to be axial (β), and this was confirmed by NOE between the acetoxyl methyl proton (δ 2.109) and H-23a (δ 4.698) in the NOEDS of the monoacetate (**22**) derived from **3**. Thus, **3** was established as 3α-hydroxyfilic-4(23)-ene.

Compound **4** is a conjugated enone (IR (KBr): 1656, 1620, 845 cm^{-1}; UV λ_{max}^{EtOH} nm (ε): 237 (12900)) of molecular formula $C_{30}H_{48}O$ as revealed by its high-resolution MS, *m/z* 424.3699. The EI-MS of **4** showed some fragment ion peaks corresponding to those of **8**, and suggested **4** to be a filicene derivative (Table V). The

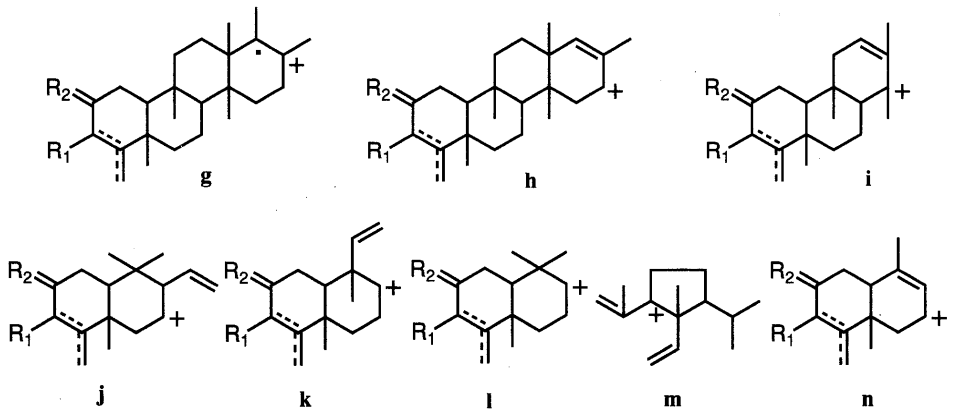

Chart 3

TABLE V. MS Fragments of **3**, **4** and **8**

		M^+	M^+-CH_3	M^+-H_2O	M^+-43	g	h	i	j	k	l	m	n
3	*m/z*	426	411	408		356	341	273	—	—	207	191	—
	(%)	(16)	(12)	(10)		(6)	(12)	(11)			(100)	(100)	
			393[a]				323[a]		229[a]	201[a]			173[a]
			(10)				(29)		(15)	(29)			(40)
4	*m/z*	424	409	381		354	339	271	245	217	205	191	189
	(%)	(45)	(99)	(5)		(7)	(99)	(17)	(14)	(24)	(17)	(100)	(19)
8	*m/z*	410	395		367	340	325	257	231	203	191	191	175
	(%)	(88)	(54)		(14)	(4)	(38)	(18)	(29)	(41)	(32)	(100)	(43)

a) $-H_2O$ fragment from fragments at *m/z* 411, 341, 247, 219, 191, respectively.

TABLE VI. ^{1}H-NMR Spectral Data for Compounds **3**, **4**, **8**, **21** and **22**

Proton No.	**3**	**4**	**8**	**21**	**22**
H-23	4.884 (1H)	1.871	1.575	4.491 (2H, m)	4.698 (1H)
	4.718 (1H)				4.669 (1H)
H-24	1.018	1.087	0.976	1.026	1.078
H-25	0.953	0.974	0.894	0.906	0.904
H-26	0.953	0.919	0.914	0.906	0.915
H-27	0.911	0.927	0.923	0.906	0.915
H-28	0.775	0.779	0.777	0.774	0.779
H-29	0.885 (d, 6.4)	0.886 (d, 6.1)	0.886 (d, 6.4)	0.871 (d, 6.6)	0.888 (d, 6.7)
H-30	0.828 (d, 6.4)	0.827 (d, 6.1)	0.825 (d, 6.4)	0.823 (d, 6.6)	0.825 (d, 6.7)
H-3	4.277 (dd, 5.4, 11.6)	5.688 (br s)			5.414 (dd, 5.2, 11.8)
CH_3CO					2.109

Signals, unless otherwise stated, are 3H, singlet. Multiplicity and coupling constants are shown in parentheses.

^{1}H-NMR signals of **4** indicated the presence of eight methyl groups including two secondary and one olefinic methyls, and the chemical shifts of methyl groups at the D and F rings, including the side chain of the molecule, were in good accordance with those of **8** (Table VI). Compound **4** was shown to be identical with 2-oxofilic-3-ene, which was derived from **8** by CrO_3 oxidation, in TLC behavior and IR, MS, and UV comparison. This is the first report of the isolation of **4** from a natural source.

Triterpenoids of the leaves of *C. spinulosa* were pentacyclic, belonging to the hopane and migrated hopane groups. The isolation of two oxidized compounds, **1** and **2**, is very interesting because they are related to orton acetal (**16**),[4] isolated from the fresh rhizomes of *Polypodium polypodioides* (L.) WATT. (Polypodiaceae) collected in North America. Two other compounds, **3** and **4**, were also characteristic oxidation products at ring A of the filicane group. These new compounds may be characteristic components of the ferns belonging to Cyatheaceae. Further studies on the constituents of other Cyatheaceous ferns are in progress from the chemotaxonomical viewpoint.

Experimental

General Procedures Melting points were measured with a Yanagimoto microapparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were taken at 270 MHz (400 MHz for NOEDS and 500 MHz for HMBC and NOESY) and 68 MHz in $CDCl_3$ solution. Tetramethylsilane (TMS) was used as an internal standard and chemical shifts are given as δ-values (ppm). EI-MS were recorded using a direct inlet system at 70 eV unless otherwise stated, and the relative intensities of peaks are reported with reference to the most intense peak higher than *m/z* 100. TLC was carried out on SiO_2 gel (Merck 5721) with hexane–EtOAc solvent system, the spray reagent being H_2SO_4. GC was performed on a 1 m glass column containing Chromosolve G HP with 1.4% SE-30 with N_2 at 260 °C. Cholestane was used as an internal reference and its t_R was set at 3.0 min. HPLC was performed on a C_{18} reverse-phase column (8 mm × 250 mm) (detected by RI) with $CHCl_3$/MeOH/H_2O (76/14/10) as the eluent.

Plant Materials The leaves of *Cyathea spinulosa* were collected at Ta-Tung Shan, Peitou, Taipei, in October. A voucher specimen has been deposited in the Herbarium of Shōwa College of Pharmaceutical Sciences, Tokyo.

Extraction and Isolation The dried leaflets (9.6 kg) were extracted with hexane to give the extract (91.6 g), which was separated by SiO_2 gel column chromatography (CC) into fraction 1 (solvent: hexane, 12.6 g), fr. 2 (hexane (1): benzene (1), 6.4 g), fr 3 (benzene (9): ether (1), 14.8 g), fr. 4 (benzene (1): ether (1). 30.4 g) and fr. 5 (ether, 34.2 g).

Triterpenoid Hydrocarbons Fraction 1 was chromatographed repeatedly through 20% $AgNO_3$–silicic acid to give triterpenoid hydrocarbons by elution with hexane. Fern-9(11)-ene (**7**, 4.07 g), colorless plates (Me_2CO), mp 169—171 °C. IR ν_{max}^{KBr} cm^{-1}: 811, 796. Fern-7-ene (**6**, 100 mg), colorless plates (Me_2CO), mp 209—211 °C. IR ν_{max}^{KBr} cm^{-1}: 827, 818. Filic-3-ene (**8**, 430 mg), colorless plates (Me_2CO), mp 234—239 °C. IR ν_{max}^{KBr} cm^{-1}: 851, 821. Hop-22(29)-ene (**5**, 110 mg), colorless plates (Me_2CO), mp 214—216 °C. IR ν_{max}^{KBr} cm^{-1}: 1602, 883.

Hopan-29,17α-olide (1) Fraction 4 (30.4 g) was chromatographed repeatedly on SiO_2 gel (500 g), also on dry SiO_2 gel (200 g) (hexane (9.5): ethyl acetate (0.5)) and finally basic Al_2O_3 (200 g). The second eluate with benzene was recrystallized from Me_2CO–MeOH to give **1** (100 mg), mp 270—275 °C. $[\alpha]_D^{23}$ +67.1° (c=0.3, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1875, 1252, 1138.

Hopan-17α,29-epoxide (2) Fraction 3 was chromatographed on basic Al_2O_3, and the product from the hexane (9): benzene (1) eluate was recrystallized from Me_2CO to give **2** (30 mg), mp 286—287 °C, $[\alpha]_D^{23}$ +42.6° (c=0.3, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1050.

3α-Hydroxyfilic-4(23)-ene (3) and Hydroxyhopane (9) The first fraction in the final step of purification of **1** was recrystallized from ether–Me_2CO to remove hydroxyhopane (**9**, 700 mg), mp 253—258 °C. IR ν_{max}^{KBr} cm^{-1}: 3420, 1045, 1640, 895. ^{1}H-NMR δ: 0.844 (3H, H-23), 0.796 (3H, H-24), 0.811 (3H, H-25), 0.955 (3H, H-26), 0.955 (3H, H-27), 0.758d (3H, J=0.6, H-28), 1.208 (3H, H-29), 1.179 (3H, H-30). The soluble fraction was chromatographed on dry SiO_2 gel (hexane (9.5): ethyl acetate (0.5)) to give **3** (5 mg), mp 212—214 °C, $[\alpha]_D^{23}$ −22.2° (c=0.2, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3420, 1045, 1640, 895.

3-Oxofilic-3-ene (4), Dryocrassol (10) and Tetrahymanol (11) The third eluate with benzene (8): ether (2) of fraction 4 was subjected to HPLC to give **4** (8 mg), mp 222—224 °C, $[\alpha]_D^{23}$ +43.0° (c=0.5, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1656, 1620, 845. **11** (4 mg), mp >300 °C. IR ν_{max}^{KBr} cm^{-1}: 3310, 1045, 1035. ^{1}H-NMR δ: 0.884 (3H, H-23), 0.790 (3H, H-24), 0.811 (3H, H-25), 0.961 (3H, H-26), 0.952 (3H, H-27), 0.811 (3H, H-28), 0.960 (3H, H-29), 0.760 (3H, H-30), 3.195 (1H, dd, J=5.0, 10.0, H-21) and **10** (5 mg), mp 240—244 °C. IR ν_{max}^{KBr} cm^{-1}: 3330, 1026. ^{1}H-NMR: 0847 (3H, H-23), 0.791 (3H, H-24), 0.813 (3H, H-25), 0.954 (3H, H-26), 0.954 (3H, H-27), 0.721 (3H, d, J=6.4, H-28), 1.051 (3H, d, J=6.4, H-29), 3.391 (1H, dd, J=6.7, 10.5, H-30), 3.634 (1H, dd, J=3.2, 10.5, H-30) in order of retention.

Cyclolaudenyl Palmitate (12) and Sitosteryl Palmitate (13) Fraction 2 was recrystallized from Me_2CO, followed by repreated chromatography with Al_2O_3 to give two fractions that appeared closely related on TLC. The more polar fraction was purified by HPLC to give **12** (60 mg) as the main component, mp 67—69 °C. IR ν_{max}^{KBr} cm^{-1}: 1738, 1180, 880. MS m/z: 678 (M^+), 663 (M^+-CH_3), 422 ($M^+-C_{16}H_{32}O_2$), 300, 297, ^{1}H-NMR δ: 0.842 (3H, H-30), 0.889 (3H, H-31), 0.336, 0.572 (2H, d, J=4.1, H-19), 0.953 (3H, H-18), 0.890 (3H, H-32), 0.867 (3H, d, J=6.4, H-21), 0.998 (3H, d, J=6.7, H-24), 4.664, 4.668 (2H, H-26), 1.639 (3H, H-27), 1.253 ($\underline{CH_2}$). The presence of cyclomargenyl palmitate (MS m/z: 692 (M^+), 436, 314 and 297) as minor component was suggested. The less polar fraction was purified by HPLC to give **13** (20 mg), mp 83—84 °C. IR ν_{max}^{KBr} cm^{-1}: 1745, 1180. MS m/z: 652 (M^+), 396 ($M^+-C_{16}H_{32}O_2$). ^{1}H-NMR δ: 0.678 (3H, H-18), 1.019 (3H, H-19), 0.928 (3H, d, J=6.4, H-21), 0.812 (3H, d, J=6.9, H-26), 0.836 (3H, d, J=6.9, H-27), 0.846 (3H, t, J=7.0, H-29), 5.371 (1H, d, J=4.2, H-5), 1.253 ($\underline{CH_2}$).

Sitosterol (14) and Sitostanol (15) Fraction 5 was chromatographed on dry SiO_2 gel (hexane (18.5): ethyl acetate (1.5)) to give a sterol mixture (1.89 g), mp 138—141 °C. The HPLC pattern of which indicated it to be a mixture of sitosterol (55%, **14**), sitostanol (30%, **15**), campesterol (8%), campestanol (7%) and stigmasterol (trace). The mixture was separated by HPLC to give two pure components **14**, mp 136—137 °C. Relative t_R (Rt_R) 2.80 min. MS m/z (rel. int.): 414 (M^+, 100), 399 (M^+-CH_3, 35), 396 (M^+-H_2O, 52), 381 ($M^+-H_2O-CH_3$, 36), 255 (42), 231 (28), 213 (41). ^{1}H-NMR (δ): 0.678 (3H, H-18), 1.008 (3H, H-19), 0.928 (3H, d, J=6.7, H-21), 0.836 (3H, d, J=6.9, H-26), 0.813 (3H, d, J=6.9, H-27), 0.847 (3H, t, J=7.0, H-29), 3.525 (1H, dddd, J=10.8, 10.8, 4.3, 4.3, H-3), 5.353 (d, J=4.2, H-5) and **15**, mp 134—136 °C. Rt_R 2.79. MS m/z (rel. int.): 416 (M^+, 81), 401 (M^+-CH_3, 26), 398 (M^+-H_2O, 5), 383 ($M^+-H_2O-CH_3$, 11), 257 (10), 233 (100), 215 (90). ^{1}H-NMR (δ): 0.649 (3H, H-18), 0.802 (3H, H-19), 0.904 (3H, d, J=6.7, H-21), 0.830 (3H, d, J=5.8, H-26), 0.812 (3H, d, J=7.0, H-27), 0.844 (3H, t, J=7.0, H-29), 3.580 (1H, dddd, J=11.0, 11.0, 4.9, 4.6, H-3).

$K_2Cr_2O_7$–Oxidation of 2 An AcOH solution of (5 ml) of **1** (5 mg) was treated with $K_2Cr_2O_7$ (30 mg) at 100 °C for 6 h. The solution gave one spot on TLC and was treated in the usual manner to give hopane-29,17α-olide (**1'**, 3.5 mg).

$LiAlH_4$ Reduction of 1 A mixture of **1** (10 mg), anhydrous ether (30 ml) and a small quantity of $LiALH_4$ was stirred for 4 h, at room temperature. The reaction products were chromatographed on dry SiO_2 gel (hexane (8): EtOAc (2)) followed by recrystallization of the products from $CHCl_3$ to give **18**, mp 215—217 °C. IR ν_{max}^{KBr} cm^{-1}: 2350, 1042, 1058. MS m/z (rel. int.): 444 (M^+, 8), 426 (48), 411 (11), 393 (11), 367 (14), 344 (17), 231 (15), 220 (14), 218 (16), 191 (100), 189 (14), 187 (20).

Acetylation of 18 Compound **18** (5 mg) was treated with Ac_2O (5 ml) in pyridine (5 ml) and the product was chromatographed on dry SiO_2 gel (hexane (8): EtOAc (2)) to give **19** (3.4 mg), mp 173—174 °C. IR ν_{max}^{KBr} cm^{-1}: 3450, 1722, 1255, MS m/z (rel. int.): 486 (M^+, 18), 426 (40), 411 (8), 393 (15), 367 (12), 344 (24), 231 (18), 220 (14), 218 (14), 191 (100), 189 (14), 187 (21).

Acetylation and Dehydration of 19 A mixture of **19** (20 mg), Ac_2O (20 ml) and anhydrous sodium acetate (2 g) was refluxed for 6 h. The product was chromatographed on dry SiO_2 gel (hexane (8): EtOAc (2)) followed by HPLC to give **20** (5 mg), mp 180—185 °C. IR ν_{max}^{KBr} cm^{-1}: 1725, 1230. MS m/z (rel. int.): 468 (M^+, 19), 453 (10), 408 (72), 393 (44), 367 (42), 231 (94), 191 (100), 189 (50), 187 (68).

Acetylation of 3 Compound **3** (3 mg) was acetylated with pyridine (5 ml) and Ac_2O (2 ml) in the usual manner to give **22**, mp 172—173 °C. IR ν_{max}^{KBr} cm^{-1}: 1735, 1235; 1640, 890.

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