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CHEMOTAXONOMY OF FERNS, 3. TRITERPENOIDS FROM *POLYPODIUM POLYPODIOIDES*

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ABSTRACT.—From the fresh rhizomes of *Polypodium polypodioides* various triterpenoids belonging to the hopane, serratane, cycloartane, malabaricane, and polypodane groups were isolated. A new triterpenoid acetal, orton acetal [**14**], was also isolated, and its structure was characterized based on its physical data. *Polypodium polypodioides* (the type species of the genus *Marginaria*) was found to be chemically very similar to *Polypodium vulgare* (the type species of *Polypodium*). Thus, the genus name *Marginaria* should be discontinued.

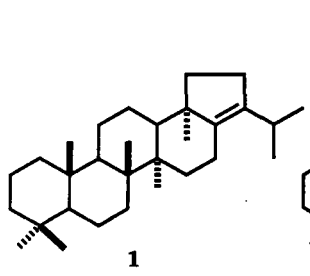
Polypodium polypodioides (L.) Watt. is distributed in North America and is usually found growing on large oak trees. It is called the "resurrection fern" because the fronds curl up when dry but revive after a rain. This fern was named *Marginaria ceteracina* by Bory in 1824 (1,2), and designated as the type species of the genus *Marginaria*, which included many Polypodiaceous species growing in Central and South America (3). As previously reported (4,5), some Japanese *Polypodium* species, such as *Polypodium niponicum* Mett. and *P. formosanum* Baker, contain very characteristic triterpenoid constituents; this information was used to separate these species from the genus *Polypodium*. Because these Japanese ferns were once described as *Marginaria niponica* (Mett.) Nakai and *Marginaria formosana* (Baker) Nakai (6), we decided to examine the chemical constituents of the type species of *Marginaria*. This paper therefore deals with the chemical studies on the *n*-hexane extract of the fresh rhizomes of *P. polypodioides*, the type species. Besides various kinds of known triterpenoids, including those characteristic of *Polypodium* species, a new hopane acetal, named orton acetal [**14**], and its derivative were isolated and their structures characterized.

RESULTS

The fresh rhizomes of *P. polypodioides*, collected in Wilmington, North Carolina, were extracted twice with *n*-hexane to give an oily extract. Inasmuch as the tlc pattern of this extract indicated triterpenoid hydrocarbons, esters, alcohols, and sterols, the extract was chromatographed on Si gel and yielded seven fractions: triterpenoid hydrocarbons (fraction I), sterol esters (fraction II), cycloartanoid esters (fraction III), cycloartanoid acetates (fraction IV), an acetal, a ketone, and alcohols (fraction V), sterols (fraction VI), and hemiacetal (fraction VII). The constituents of each fraction were identified as follows.

TRITERPENOID HYDROCARBONS.—Fraction I was separated by $AgNO_3$ Si gel cc to give three white crystal triterpenoid hydrocarbons, which were identified as hop-17(21)-ene [**1**] (4), serrat-14-ene [**2**] (7,8) and hop-22(29)-ene [**3**] (4). The occurrence of **1** among ferns is not common, while **3** was found in almost all kinds of ferns. Compound **2** is a very characteristic component of *Polypodium*, such as *Polypodium vulgare* L. (the type species of this genus), *Polypodium fauriei* Christ, and *Polypodium boreale* Haufler (=*Polypodium virginianum* L.) of Japan (9).

More polar oily triterpenoid hydrocarbons were also detected from the later eluted portion of fraction I and were identified as the bicyclic α-polypodatetraene [**4**] (10) and γ-polypodatetraene [**5**] (10), the tricyclic 13βH-malabaricatriene [**6**] (11) and the linear squalene [**7**] (10) by comparison of the gc and ms data with those of authentic samples.



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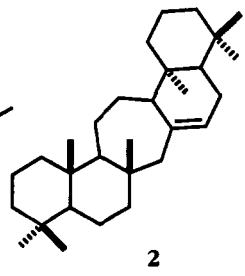

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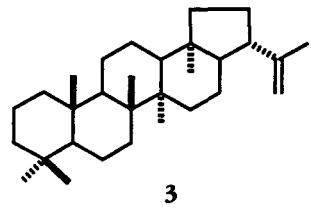

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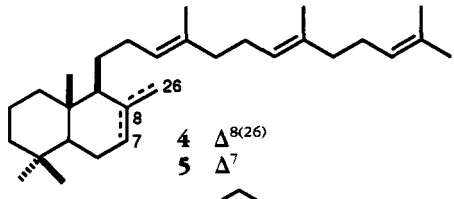
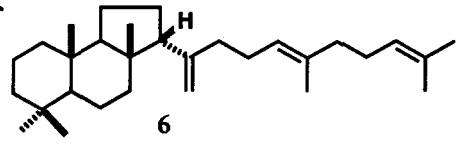


4 $\Delta^{8(26)}$
5 Δ^{7}



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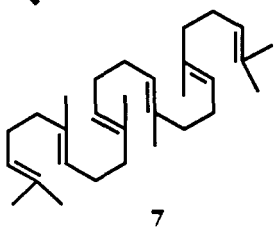

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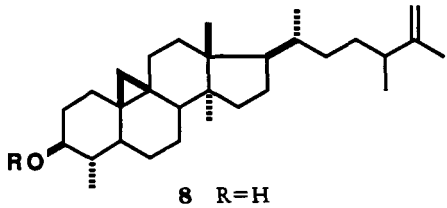

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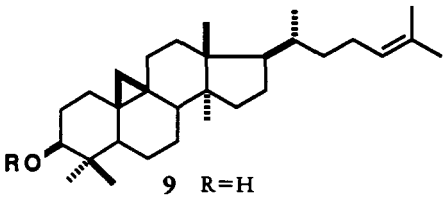

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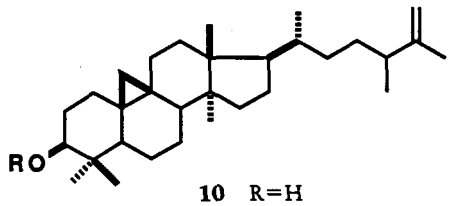

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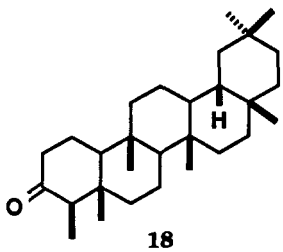

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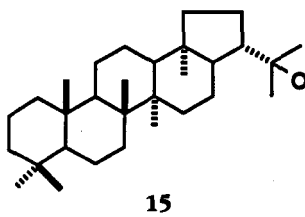

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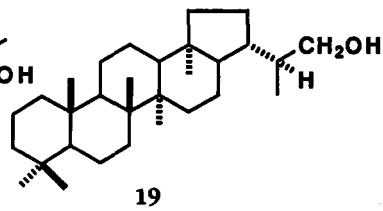

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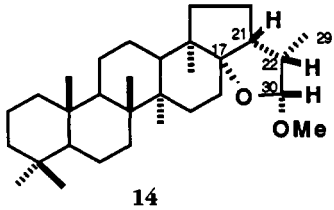
STEROL ESTERS.—The waxy ester, fraction II, was hydrolyzed with 5% KOH in EtOH followed by workup to give three alcohols, which were identified as sitosterol (80%), stigmasterol (13%), and campesterol (7%) by gc-ms. The acidic fraction was also identified as palmitic acid (>90%) by the gc-ms of its methyl ester. Thus, this fraction was confirmed to be a mixture of the three sterol palmitates.

CYCLOARTANOID ESTERS.—A mixture of oily esters was separated by chromatography from fraction III and suggested to be fatty acid esters of cycloartanoid triterpenes. The ^{1}H-nmr spectrum of the mixture exhibited the proton signals of the cyclopropane methylene of 31-norcycloartane and cycloartane [δ 0.149 and 0.401 (d, J = 4.1 Hz),



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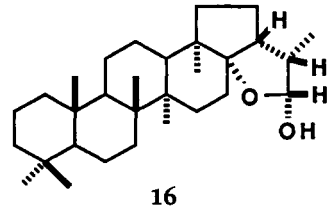

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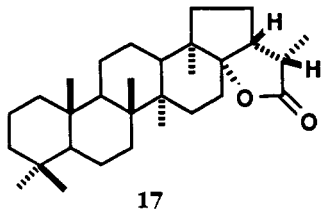

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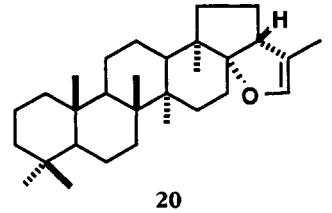

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0.341 and 0.576 (d, 4.1 Hz), respectively], terminal methylenes (δ 4.663, 4.667, 4.716), olefinic methyl (δ 1.603) and low field doublet methyls [δ 1.026, 1.031 (J = 6.8 Hz)] with several methyl singlets and aliphatic proton signals. The proton signals of the fatty acid parts were also observed at δ 1.303, 1.312, 2.035, 2.293, 2.770, and 5.341. The alcohols obtained by hydrolysis of the ester mixture gave three spots on tlc and separated into three components, 31-norcyclolaudenol [**8**] (12,13), a mixture of cycloartenol [**9**] (12,13) and cyclolaudenol [**10**] (5), and a sterol mixture. These were identified by comparison of the gc-ms data with those of authentic samples. Linoleic acid was also identified from the acidic part by comparison of the ^{1}H-nmr and ms data of its methyl ester with an commercial sample. Thus, this fraction was established to be a mixture of the three cycloartanoid alcohol linoleates accompanied by sterol linoleates.

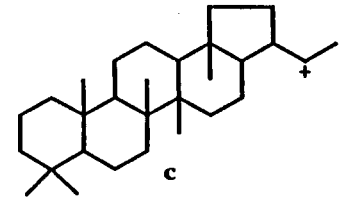
CYCLOARTANOID ACETATES.—Although fraction IV gave one spot on the tlc, it was found to be a mixture of cycloartanoid triterpene acetates. The ^{1}H-nmr spectrum showed very similar proton signals to those of linoleic acid esters: δ 0.151 and 0.400 (d, J = 4.1 Hz), 0.341 and 0.575 (d, 4.1), 4.665, 4.714, 1.605, 1.025 (d, 6.8), and 1.030 (d, 6.8). The gc of the mixture exhibited three main peaks at rel Rt 3.94, 4.05, and 4.52 with five additional small peaks. The three peaks were identified as 31-norcyclolaudenyl acetate [**11**] (5), cycloartenyl acetate [**12**] (12,13), and cyclolaudenyl acetate [**13**] (5) by comparison of the rel Rt and the typical fragment ion peaks of authentic cycloartanoid acetates.

ACETAL.—Compound **14**, named orton acetal, mp 197–201°, was isolated from fraction V by chromatography on Al_2O_3 (grade III). The molecular formula $C_{31}H_{52}O_2$ for this compound was suggested by its hrms peak, m/z 450.3979. The other fragment peaks indicated that this was a hopane type compound with a functional group containing two oxygen atoms (Table 1). The signals of six singlet methyls, one doublet methyl, and one methyl adjusted to oxygen were observed in the ^{1}H-nmr spectrum of **14** (Table 2). The six methyl signals were assigned by a solvent shift method and compared with the methyl signals of hopane. The C-28 methyl signal appeared at a very low field because of the influence of the oxygen function at C-17α. A doublet signal (δ 4.689, J = 5.0 Hz), due to the proton of the acetal carbon, and a multiplet proton signal (δ 2.384) were observed. Irradiation of the signal at δ 2.384 resulted in the doublet methyl signal (δ 1.049, J = 6.8 Hz) and the doublet proton signal at δ 4.689 becoming singlets. Because the nOe's were observed by the difference spectroscopy method (500 Mc) between the protons, H-28⟷C-30α OMe⟷H-30β⟷H-22β⟷H-21β and

TABLE 1. Ms Fragments of Orton Acetal [14] and Related Compounds.

		Fragment												
		$[M]^+$	$[M-Me]^+$	a	b	c	d	e	f	g	h	i	j	k
14	*m/z*	456	441	424[a]	409[c]	397	367	250	231	218	205	203	192	191
	%	51	10	50	12	33	14	32	27	37	23	17	67	100
16	*m/z*	442	427	424[b]	409[c]		367		231	218	205	203	192	191
	%	6	2	6	7		3		28	14	10	10	26	100
17	*m/z*	440	425				367			218	205	203	192	191
	%	13	7				3			11	16	9	23	100
20	*m/z*	429	409				367		231	218	205	203	192	191
	%	56	4				2		36	16	10	14	25	100

[a] $[M-MeOH]^+$.
[b] $[M-H_2O]^+$.
[c] $[a-Me]^+$.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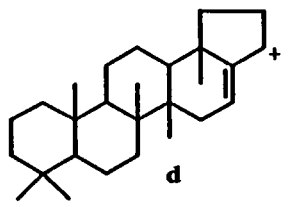
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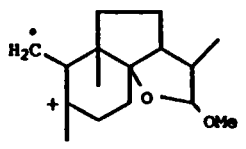

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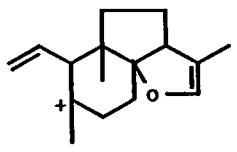

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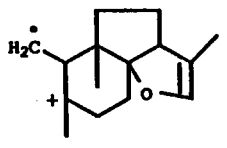

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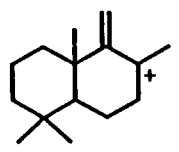
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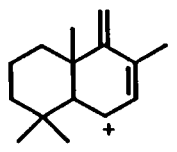
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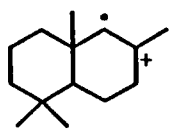
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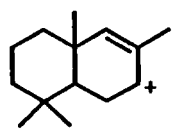
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TABLE 2. ^{1}H Chemical Shifts of Orton Acetal [**14**] and Related Compounds.[a]

Compound	H-23	H-24	H-25	H-26	H-27	H-28	H-29	H-30	H-22
14[b]	0.849	0.794	0.824	0.934	1.036	0.984	1.049 (d,6.8)	4.689 (d,5.0)	2.384 (m)
16	0.849	0.793	0.821	0.937	1.025	0.949	1.078 (d,6.8)	2.647 (d,6.6)	2.420 (m)
17	0.855	0.798	0.830	1.018	1.068	0.957	1.249 (d,6.8)		2.881 (m)
20	0.851	0.796	0.833	0.954	1.061	0.964	1.601 (dd,1.4,1.5)	5.938 (t,1.5)	

[a]Signals are singlet unless otherwise stated.
[b]Signal of H-21 was also observed at δ 1.455 (m), and that of methoxyl attached to C-30 at δ 3.304.

H-22β↔H-29, the structure of **14** was established as (30*R*)-methoxy-17α,30-epoxyhopane using the numbering according to neriifoliol (hopan-29-ol, 22*R*) and dryocrassol (hopan-30-ol, 22*S*) (14). The ^{13}C-nmr spectrum of **14** was assigned by comparison with those of hopane and hydroxyhopane **15** (Table 3), and supported the fact that **14** is a hopane derivative having an acetal linkage at C-30 to 17α. The correlation of **14** to hemiacetal **16** and lactone **17** described below also supported this conclusion.

KETONE AND ALCOHOLS.—Three white crystals were isolated from the chromatogram of fraction V subsequently to **14**. They were identified as friedelin [**18**] (15), hydroxyhopane [**15**] (4), and dryocrassol [**19**] (4) by mixed melting points and comparisons of the ir spectra with those of authentic samples.

STEROLS.—A sterol mixture was obtained as plates (MeOH) from fraction VI by chromatography and recrystallization. Its components were identified as sitosterol, stigmasterol, and campesterol by its gc-ms.

TABLE 3. ^{13}C Chemical Shifts of Orton Acetal [**14**], Hopane, and Hydroxyhopane [**15**].

Carbon	Compound			Carbon	Compound		
	14	Hopane	**15**		**14**	Hopane	**15**
C-1	40.4	40.4	40.4	C-16	22.0	22.7	22.0
C-2	18.8	18.8	18.7	C-17	98.4	54.7	54.0
C-3	42.2	42.2	42.2	C-18	49.4	44.4	44.2
C-4	33.3	33.3	33.3	C-19	40.4	41.9	41.3
C-5	56.3	56.2	56.2	C-20	28.1	27.6	26.6
C-6	18.8	18.8	18.7	C-21	40.4	48.0	51.2
C-7	33.3	33.4	33.3	C-22	56.3	32.0	74.0
C-8	42.7	41.8	42.0	C-23	33.4	33.4	33.5
C-9	50.8	50.6	50.4	C-24	21.6	21.6	21.7
C-10	37.5	37.5	37.4	C-25	15.6	15.9	15.9
C-11	21.6	21.1	21.0	C-26	16.3	16.6	16.8
C-12	24.0	24.1	24.2	C-27	17.5	16.6	17.1
C-13	46.5	49.4	49.9	C-28	16.2	15.9	16.2
C-14	41.2	41.7	41.9	C-29	10.1	22.8[a]	22.8[a]
C-15	38.2	33.8	34.4	C-30	105.6	23.9[a]	30.9[a]
				OMe	54.9		

[a]Values in the same column with the same superscript may be reversed.

HEMIACETAL.—Compound **16**, mp 244–246°, was isolated by chromatography from fraction VII. The hrms, *m/z* 442.3840, suggested it to have the molecular formula $C_{30}H_{50}O_2$, and its eims spectrum (Table 1) suggested it to be closely related to orton acetal [**14**]. This correlation was proved by treatment of **16** with boiling MeOH to give **14**. Compound **16** was also found to decompose during the process of recrystallization or gc into a dehydration product **20**, mp 262–263°. Oxidation of **16** with chromic acid/pyridine afforded a lactone **17**, mp 248–252°. The ir spectrum of **17** [ν max (KBr) 1780, 1263, 1142] indicated the presence of a five-membered lactone ring in the molecule. Chemical shifts of six singlet methyl groups in the ^{1}H-nmr spectra of **16**, **17**, and **20** were very similar to those of **14** (Table 2). Irradiation to a multiplet proton signal at δ 2.420 in the ^{1}H-nmr spectrum of **16** resulted a doublet proton signal attached to a carbon bearing a hydroxyl group [δ 2.647 ($J = 6.6$)] and a doublet methyl signal [δ 1.078 ($J = 6.8$)] becoming singlet. These findings confirmed the structure of **16** as (30*R*)-hydroxy-17α,30-epoxyhopane, **17** as hopan-17α,30-olide, and **20** as 17α,30-epoxyhop-22(30)-ene.

DISCUSSION

The previously mentioned results clearly indicate that *P. polypodioides* contains the same triterpenoid constituents, such as hop-22(29)-ene, serrat-14-ene, and various kinds of cycloartanoid esters, as does *P. vulgare*. Thus, *P. polypodioides* cannot be separated from other species of *Polypodium* on chemotaxonomic grounds. The generic name *Marginaria*, which was described by Bory based on the type specimen *P. polypodioides*, should be discontinued. On the other hand, the main constituents of *P. niponicum* and *P. formosanum* are quite different types of triterpenoids, namely oleanane and migrated oleanane hydrocarbons, alcohols, and esters. These have been isolated only from these two species and their allies among fern plants. Therefore, we recommend that the following *Polypodium* species, whose chemical constituents were hitherto studied, should belong to the genus *Polypodiodes*, Ching (16): *P. niponica* (Mett.) Ching (3,4,16), *P. formosana* (Baker) Ching (3,4,16), and *P. amamiana* (Tagawa) Saiki (17,18). The type species of this genus has been a Chinese fern, *Polypodium amoenum* Wall. [=*Polypodiodes amoena* (Wall.) Ching], whose rhizomes of Formosan origin were found in our laboratory to contain several kinds of the oleanane and migrated oleanane triterpenoids.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were measured using a Kofler block and are corrected. [α]D's were observed in $CDCl_3$ solution ($c = 0.2$–0.5) at 23°. ^{1}H- and ^{13}C-nmr spectra were obtained at 270 MHz and 68 MHz in $CDCl_3$ solution. TMS was used as an internal standard, and chemical shifts were given in δ values (ppm). Eims spectra were recorded for direct inlet at 70 eV unless otherwise stated, and relative intensities of peaks are reported with reference to the most intense peak higher than *m/z* 100. Tlc was carried out on Si gel (Merck 5721) with *n*-hexane–EtOAc solvent system, the spray reagent being H_2SO_4. Gc was performed on a 1-m glass column containing Chromosorb G HP with 1.4% SE-30 at 260°. Cholestane was used as an internal reference and its Rt was set at 3 min.

PLANT MATERIALS.—*P. polypodioides* was collected at Orton Plantation, Wilmington, North Carolina, in July 1988. The voucher specimen (#880801) was deposited in the Herbarium of Showa College of Pharmaceutical Sciences, Tokyo.

ISOLATION OF TRITERPENOIDS.—The fresh cut rhizomes (713 g) were extracted twice with *n*-hexane (3 liters each) to give 9.74 g of extracts and azeotropic H_2O (434 ml). The extracts were separated by cc on Si gel into fraction I (solvent *n*-hexane, yield 240 mg), fraction II [*n*-hexane–C_6H_6 (8.5:1.5), 340 mg], fraction III [*n*-hexane–C_6H_6 (7:3), 1840 mg], fraction IV [*n*-hexane–C_6H_6 (7:3), 250 mg], fraction V [*n*-hexane–C_6H_6 (1:1), 530 mg], fraction VI (C_6H_6, 1680 mg), and fraction VII (C_6H_6, 680 mg).

TRITERPENOID HYDROCARBONS.—Fraction I was repeatedly chromatographed on 20% $AgNO_3$-Si gel to give the following triterpenoid hydrocarbons in order of the *n*-hexane eluate. The compounds were identified with authentic samples by comparison of the described physical data.

Hop-17(21)-ene [**1**].—3.5 mg, mp 182–183°; ν max (KBr) 851; rel Rt 1.67; eims *m/z* $[M]^+$ 410 (45), 395 (31), 367 (100), 231 (76), 203 (13), 191 (76), 189 (51).

Serrat-14-ene [**2**].—7 mg, mp 240°; ν max (KBr) 3030, 1655, 790; rel Rt 2.35; eims *m/z* $[M]^+$ 410 (31), 395 (16), 218 (80), 204 (49), 203 (35), 191 (100).

Hop-22(29)-ene [**3**].—55 mg, mp 208–210°; ν max (KBr) 3055, 1647, 1629, 887; rel Rt 2.61; eims *m/z* $[M]^+$ 410 (19), 395 (10), 191 (100), 189 (94).

α-*Polypodatetraene* [**4**].—Trace, rel Rt 1.12; eims *m/z* $[M]^+$ 410 (32), 395 (38), 341 (15), 273 (15), 205 (17), 204 (10), 191 (32), 137 (100), 69 (100).

γ-*Polypodatetraene* [**5**].—Trace, rel Rt 1.24; eims *m/z* $[M]^+$ 410 (33), 395 (12), 341 (12), 273 (18), 205 (36), 204 (76), 191 (100), 137 (100), 69 (100).

13αH-Marabaricatriene [**6**].—Trace, rel Rt 1.46; eims *m/z* $[M]^+$ 410 (11), 395 (5), 231 (49), 218 (16), 204 (26), 191 (100), 137 (53), 69 (100).

Squalene [**7**].—Trace, rel Rt 0.91; eims *m/z* $[M]^+$ 410 (9), 395 (2), 341 (38), 205 (16), 203 (22), 137 (100), 123 (91), 69 (100).

ISOLATION AND HYDROLYSIS OF STEROL ESTERS.—Fraction II (100 mg) was chromatographed on Si gel to give a sterol ester (15 mg) from *n*-hexane–C_6H_6 (8.5:1.5). After hydrolyzing with 5% KOH/EtOH, an alcohol fraction was collected by Et_2O extraction, and an acid fraction in the H_2O layer was collected and esterified with CH_2N_2. Both fractions were purified by chromatography on Al_2O_3 (grade III) to give a mixture of sitosterol, rel Rt 2.85, eims *m/z* 414 $[M]^+$; stigmasterol, rel Rt 2.48, eims *m/z* 412 $[M]^+$; campesterol, rel Rt 2.31, eims *m/z* 400 $[M]^+$; and methyl palmitate, eims *m/z* 270 $[M]^+$.

HYDROLYSIS OF CYCLOARTANOID AND STEROL ESTERS.—Fraction III (420 mg) was hydrolyzed with 5% KOH/EtOH, resulting in an alcoholic and an acidic fraction. The alcoholic fraction was chromatographed on Al_2O_3 (grade III) with C_6H_6 to give **8**, **9**, and **10** (total 153 mg) and a sterol mixture (40 mg). The acidic fraction was treated with CH_2N_2 to give a fatty acid methylester (100 mg).

31-Norcyclolaudenol [**8**].—Mp 137–139°; rel Rt 2.85; eims *m/z* $[M]^+$ 426 (17), 411 (50), 408 (69), 393 (100), 300 (25), 285 (31), 283 (22), 201 (39), 189 (53), 175 (72); ν max (KBr) 3320, 1040, 1640, 890.

Cycloartenol [**9**].—Rel Rt 3.08; eims *m/z* $[M]^+$ 426 (47), 411 (67), 408 (95), 393 (100), 297 (45), 286 (87), 203 (85), 201 (70).

Cyclolaudenol [**10**].—Rel Rt 3.52; eims *m/z* $[M]^+$ 440 (31), 425 (50), 422 (71), 407 (100), 300 (63), 297 (60), 203 (90), 201 (85).

Sterol mixture.—Sitosterol, rel Rt 2.88 (75%), eims 414 $[M]^+$; stigmasterol, rel Rt 2.50 (16%), eims 412 $[M]^+$; campesterol, rel Rt 2.40 (11%), eims 400 $[M]^+$.

Methyl linoleate.—Eims *m/z* $[M]^+$ 294 (100), 263 (31), 220 (9), 178 (9), 164 (25), 150 (35).

CYCLOARTANOID ACETATES.—Fraction IV was chromatographed on Si gel with *n*-hexane–C_6H_6 (7:3) to give the acetate mixture (200 mg).

31-Norcyclolaudenyl acetate [**11**].—Rel Rt 3.94; eims *m/z* $[M]^+$ 468 (3), 453 (18), 408 (100), 300 (10), 283 (36), 201 (28).

Cycloartenyl acetate [**12**].—Rel Rt 4.05; eims *m/z* $[M]^+$ 468 (12), 453 (13), 408 (84), 393 (100), 300 (5), 286 (26), 283 (21), 201 (42).

Cyclolaudenyl acetate [**13**].—Rel Rt 4.52; eims *m/z* $[M]^+$ 482 (31), 467 (13), 422 (100), 407 (39), 379 (24), 300 (50), 297 (27).

ACETAL, KETONE, AND ALCOHOLS.—Fraction V was chromatographed on Al_2O_3 (grade III) with *n*-C_6H_{14}–C_6H_6 (7:3) followed by recrystallization of the corresponding fraction from Me_2CO.

Orton acetal [**14**].—A white powder: 31 mg, mp 197–201°; $[\alpha]^{23}D$ +4.6° ($c = 0.2$, $CHCl_3$); ν max (KBr) 1097, 1040.

Friedelin [**18**].—60 mg, mp 271–272°; ν max (KBr) 1718.

Hydroxyhopane [**15**].—75 mg, mp 254–255°; ν max (KBr) 3600, 3450, 1030.

Dryocrassol [**19**].—26 mg, mp 245–246°; ν max (KBr) 3350, 1028.

STEROLS.—Fraction VI was chromatographed on Al_2O_3 (grade III) with *n*-hexane–C_6H_6 (2:3) to give a phytosterol mixture (140 mg), which was shown by gc-ms to consist of sitosterol, rel Rt 2.85 (70%),

eims 414 $[M]^+$; stigmasterol, rel Rt 2.48 (14%), eims 412 $[M]^+$; and campesterol, rel Rt 2.31 (16%), eims 400 $[M]^+$.

HEMIACETAL [**16**].—Repeated Si gel chromatography with C_6H_6-Et_2O (1:1) of fraction VII gave **16** (5 mg) as colorless needles from Me_2CO: mp 244–246°; ν max (KBr) 3320, 1035, 1115, 1090.

Conversion of **16** *into* **14**.—Compound **16** was refluxed with MeOH for 2 h, and the sole product **14** was confirmed by tlc.

Lactone **17**.—Compound **16** (2 mg) was oxidized with CrO_3/pyridine complex, and the product was chromatographed on Si gel with *n*-hexane–C_6H_6 (7:3) to afford compound **17**: mp 248–252°; rel Rt 5.82.

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