***cis*-/*trans*-2-Methoxy-6-phenyl-5,6-dihydro-2*H*-pyran (14) Mixture.** The cis/trans mixture of compound **14** was prepared from benzaldehyde (5.3 g, 50 mmol) and 1-methoxybuta-1,3-diene (8.3 g, 100 mmol) under a pressure of 19.5 kbar at 50 °C in the same way as described for compound **12**: yield 6.8 g (80%); bp 119-120 °C (1.2 torr); IR (film) 1660 (C=C), 1160, 1050, 1035 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 7.7-7.0 (5 H, m, phenyl), 6.15-5.4 (2 H, m, olefin), 5.12, 4.85 (1 H, 2 br s, cis and trans H-2), 4.66 (1 H, 2 d, H-6), 3.40, 3.30 (3 H, 2 s, cis and trans OCH_3), 2.18 (2 H, m, H-5, H-5'). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.7; H, 7.4. Found: C, 75.3; H, 7.4.

6-Phenyl-5,6-dihydro-2-pyrone (4). Compound **4** was obtained from **14** according to the procedure described above for **3**: colorless crystals; mp 56-57 °C (hexane); IR (KBr) 1720 (C=O), 1635 (C=C), 1245 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 7.6-7.3 (5 H, m, phenyl), 6.99 (1 H, double pd, $J_{4,5} + J_{4,5'} = 8.2$ Hz, H-4), 6.12 (1 H, dt, $J_{3,4} = 8.9$, $J_{3,5} + J_{3,5'} = 3.5$ Hz, H-3), 5.45 (1 H, pd, $\sum J = 16.4$ Hz, H-6), 2.62 (2 H, m, H-5, H-5'). Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.8; H, 5.8. Found: C, 75.8; H, 5.8.

6-Phenyl-2-pyrone (15). A suspension of 360 mg of 10% palladium-on-charcoal in 50 mL of *p*-cymene was dried by azeotropic removal of approximately 5 mL of solvent until the temperature of the vapor was over 170 °C. To this mixture was added 174 mg (1 mmol) of **4**, and the resulting suspension was heated under reflux with stirring for 8 h under a blanket of nitrogen. The mixture was cooled and filtered, and the solvent was removed in vacuo. The residual oily material was purified on a silica gel column with petroleum ether-ethyl acetate (8:2 v/v) to give 79 mg (46%) of the pure α-pyrone **15**: mp 65-67 °C (hexane); IR (KBr) 1720 (C=O), 1625 (C=C), 1105, 1070 cm^{-1} (COC); ^1H NMR ($CDCl_3$) 8.2-7.1 (5 H, m, phenyl), 7.55 (1 H, invisible, chemical shift was assigned by double-resonance experiment, H-4), 6.71 (1 H, d, $J_{3,4} = 7.0$ Hz, H-3), 6.33 (1 H, d, $J_{4,5} = 9.0$ Hz, H-5).

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Registry No. 1a, 25556-21-2; **3**, 501-23-5; **4**, 2128-90-7; **5**, 74986-34-8; **6**, 75023-41-5; **7**, 74986-35-9; **8**, 74986-36-0; **9**, 74986-37-1; **10** (isomer 1), 74986-38-2; **10** (isomer 2), 75023-42-6; **11** (isomer 1), 74986-39-3; **11** (isomer 2), 75023-43-7; **12** (trans isomer), 74986-40-6; **12** (cis isomer), 74986-41-7; **13**, 74986-42-8; **14** (cis isomer), 74986-41-7; **14** (trans isomer), 74986-40-6; **15**, 4660-17-7; methyl undecanoate, 1731-86-8; 1-methoxybuta-1,3-diene, 3036-66-6; *n*-hexanal, 66-25-1; tosylhydrazine, 1709-52-0; benzaldehyde, 100-52-7; *n*-dodecanal, 112-54-9.

Spatane Diterpenoids from the Tropical Marine Alga *Stoechospermum marginatum* (Dictyotaceae)

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Ten new metabolites, **2**-**11**, are described as natural products of the tropical marine alga *Stoechospermum marginatum* from Sri Lanka. These new compounds all possess the novel "spatane" tricyclic diterpenoid ring system, and their structures were defined by spectral analyses and by interconversion with derivatives of spatol, a metabolite recently defined fully by X-ray crystallography.

Marine algae of the family Dictyotaceae (Phaeophyta) are prolific producers of interesting secondary metabolites, consisting of C_{11} acetate-derived compounds,[1] compounds of mixed biosynthesis,[2-9] sequiterpenoids,[10-14] and diterpenoids.[15-31] The diterpenoids from this group are particularly unique, as the novel ring systems produced represent unconventional diterpenoid cyclizations not yet

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observed from terrestrial sources. Algae of the family Dictyotaceae are also frequently encountered as the major vegetation in shallow-water tropical and subtropical habitats, even though herbivorous predators are plentiful. Hence, the correlation between secondary metabolite synthesis within this family and predator avoidance seems to be pronounced.

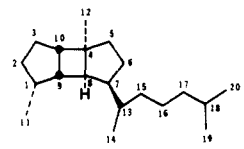
Stoechospermum marginatum (C. Agardh) Kuetzing, an Indian Ocean representative of the family Dictyotaceae, is found in abundance in the warm waters of Sri Lanka. Examination of the organic extracts of *S. marginatum* revealed the alga to contain a complex mixture of new diterpenoids related to the recently described diepoxide spatol (1).[31] We had earlier isolated spatol from the related alga *Spatoglossum schmittii* from the Galapagos Islands and found this metabolite to possess a tricyclic diterpenoid skeleton related, in part, to the sesquiterpene skeleton of bourbonene.[32] Herein, we report the structures of these new spatane diterpenoids as **2**–**11** (see Chart I). The new compounds have been defined by extensive spectral analysis and by interconversion to degradation products also obtained from spatol.

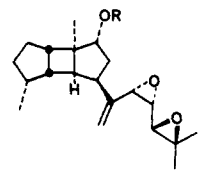
Conventional silica gel column chromatography of the $CHCl_3$/MeOH extract of air-dried *S. marginatum* provided fractions containing **2**–**11**, mostly as complex mixtures. The most polar fractions, however, contained **2** in nearly pure form, while **3**–**6** and **7**–**11** were obtained only after repeated silica gel HPLC.

The most polar and the major metabolite of *S. marginatum* was the tetraol **2**, which was isolated as an inseparable mixture of diastereomers ($[\alpha]_D$ (mixture) −10.7°). The tetraol showed strong infrared absorptions at 3500 cm^{-1}, reflecting multiple hydroxyl functionalities, and acetylation (Ac_2O/py/RT) yielded the ester **12** which was confirmed as a triacetate by mass spectrometry and ^1H NMR (Table I). The infrared spectrum of **12** (ν_{OH} = 3500 cm^{-1}) showed that a tertiary hydroxyl functionality remained unacetylated. High-resolution mass spectral analysis of **12** failed to illustrate the molecular ion; instead, an $M^+ - HOAc, H_2O$ fragment was observed. However, the molecular formula for **12**, and hence the formula for **2**, was readily derived from interpretation of ^{13}C NMR data (Table II). A formula of $C_{20}H_{32}O_4$ (5 unsaturation equivalents) for **2** and $C_{26}H_{38}O_7$ (8 unsaturation equivalents) for the triacetate **12** allowed the deduction that **2** was composed of two double bonds and three carbocyclic rings. Ozonolysis of **12**, followed by CH_2N_2 methylation, yielded the fragment **13**, which was recognized to possess, intact, the full tricyclic nucleus of compound **2**. Compound **13** (Chart II) analyzed for $C_{16}H_{24}O_4$ (5% unsaturation), and possessed secondary acetate and carbomethoxy functionalities. The ^1H and ^{13}C NMR spectra of this degradation product (Tables I and II) indicated that one quaternary and one secondary methyl group were present. Hence, ten carbon atoms remained to construct the tricyclic framework of **13**.

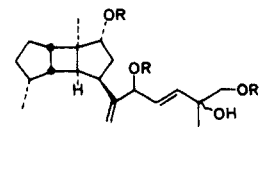
The acetate ester function at C-5 in **13** was next selectively saponified with Na_2CO_3 in MeOH to yield the free alcohol **14**, which was further utilized for ^1H NMR studies. With incremental additions of $Eu(fod)_3$ shift reagent (see Experimental Section for details), the protons at various centers in **14** became resolved and, subsequently, interrelated via spin decoupling. Couplings were established and measured between adjacent protons at C-5 through

Chart I

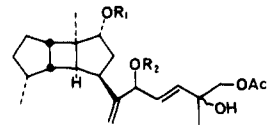




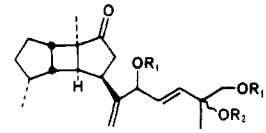
1 R = H
16 R = Ac



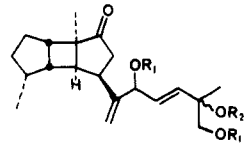
2 R = H
12 R = Ac



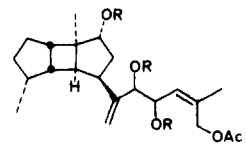
3 $R_1 = R_2 = H$
21 $R_1 = H$; $R_2 = Ac$
22 $R_1 = Ac$; $R_2 = H$



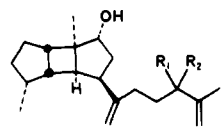
4 $R_1 = R_2 = H$
19 $R_1 = Ac$; $R_2 = H$
20 $R_1 = R_2 = Ac$



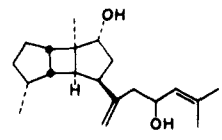
5 $R_1 = R_2 = H$
25 $R_1 = Ac$; $R_2 = H$
26 $R_1 = R_2 = Ac$



6 R = H
28 R = Ac



7 $R_1 = H$; $R_2 = OH$
8 $R_1 = OH$; $R_2 = H$



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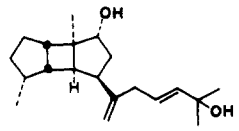

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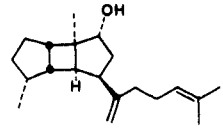

11

C-10, and protons at C-1 and C-3 were related to C-9 and C-10, respectively. While the methylene pair at C-2 was resolved in this shift study, coupling constants were not reliably measurable. The data thus obtained were highly analogous to the detailed ^1H NMR data obtained from bourbonene,[32] therefore indicating an identical cis-anti-cis arrangement of the cyclopentane and cyclobutane rings.

For further confirmation that C-5 was a cyclopentane carbon, the alcohol **14** was oxidized with pyridinium

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Table I. Selected ^{1}H NMR Assignments for *Stoechospermum* Metabolites and Several Related Derivatives[a]

H's at C no.	compound												
	2	3	4	5	6	7	8	9	10	11	12	13	16[b]
C_5	3.68 (d, J = 4)	3.70 (d, J = 4)			3.73 (d, J = 4)	3.59 (d J = 4)	3.73 (d, J = 4)	3.59 (d, J = 4)	3.75 (d, J = 4)	3.73 (d, J = 4)	4.96 (d, J = 4)	3.91 (d, J = 4)	4.85 (d, J = 4)
C_6	2.21 (ddd, J = 13, 13, 4)	2.23 (ddd, J = 13, 13, 4)	2.95 (dd, J = 13, 13)	2.95 (dd, J = 13, 13)	2.23 (ddd, J = 13, 13, 4)	2.25 (ddd, J = 13, 13, 4)	2.26 (ddd, J = 13, 13, 4)	2.15 (ddd, J = 13, 13, 4)	2.26 (ddd, J = 13, 13, 4)	2.29 (ddd, J = 13, 13, 4)	2.32 (ddd, J = 13, 13, 4)	2.43 (ddd, J = 13, 13, 4)	2.32 (ddd, J = 13, 13, 4)
C_7	2.87 (m)	2.84 (m)	2.80 (m)	2.80 (m)	2.84 (m)	2.83 (m)	2.98 (m)	2.95 (m)	2.96 (m)	2.99 (m)	2.82 (m)	3.32 (m)	2.89 (m)
C_{11}	0.86 (d, J = 6)	0.91 (d, J = 6)	0.96 (d, J = 6)	0.96 (d, J = 6)	0.86 (d, J = 6)	0.86 (d, J = 6)	0.84 (d, J = 6)	0.87 (d, J = 6)	0.92 (d, J = 6)	0.86 (d, J = 6)	0.89 (d, J = 6)	0.88 (d, J = 6)	0.95 (d, J = 6)
C_{12}	0.93 (s)	0.99 (s)	0.96 (s)	0.96 (s)	0.98 (s)	0.98 (s)	0.98 (s)	0.91 (s)	1.00 (s)	0.98 (s)	0.88 (s)	0.95 (s)	0.90 (s)
C_{14}	5.28 (s)	5.30 (s)	5.42 (s)	5.43 (s)	5.32 (s)	4.92 (s)	4.85 (s)	4.82 (s)	4.83 (s)	4.83 (s)	5.23 (s)		5.11 (d, J = 1)
C_{14}	4.89 (s)	4.92 (s)	5.03 (s)	5.03 (s)	4.98 (s)	4.82 (s)	4.76 (s)	4.73 (s)	4.76 (s)	4.74 (s)	5.00 (s)		5.00 (s)
C_{15}	4.38 (d, J = 6)	4.41 (d, J = 6)	4.52 (d, J = 6)	4.52 (d, J = 6)	4.16 (d, J = 4)	4.05 (dd, J = 6, 6)	4.04 (dd, J = 6, 6)		2.73 (dd, J = 15, 5), 2.59 (dd, J = 15, 5)		5.52 (d, J = 6)		3.30 (d, J = 4)
C_{16}	5.68 (m)	5.70 (m)	5.75 (m)	5.75 (m)	4.55 (dd, J = 10, 4)			4.41 (ddd, J = 6, 6, 6)	5.70 (m)		5.80 (dd, J = 16, 6)		2.71 (dd, J = 8, 4)
C_{17}	5.68 (m)	5.70 (m)	5.75 (m)	5.75 (m)	5.42 (d, J = 10)			5.09 (d, J = 6)	5.70 (m)	5.10 (t, J = 7)	5.64 (d, J = 16)		2.32 (d, J = 8)
C_{19}	3.43 (s)	4.07 (d, J = 10), 3.93 (d, J = 10)	3.50 (m)	3.57 (m)	4.14 (d, J = 13), 4.02 (d, J = 13)	4.82 (s), 4.74 (s)	4.76 (s), 4.67 (s)	1.64 (s)	1.34 (s)	1.68 (s)	4.09 (d, J = 10), 3.98 (d, J = 10)		1.41 (s)
C_{20}	1.20 (s)	1.30 (s)	1.24 (s)	1.24 (s)	1.81 (s)	1.72 (s)	1.72 (s)	1.71 (s)	1.34 (s)	1.59 (s)	1.27 (s)		1.30 (s)
OAc		2.09 (s)			2.18 (s)						2.08 (s), 2.05 (s), 2.00 (s)	1.89 (s)	1.99 (s)

[a] Spectra were recorded in $CDCl_3$ at 220 MHz unless otherwise noted, and assignments were aided by spin-decoupling techniques. J values are given in hertz and the chemical shifts in δ units. [b] Recorded in CCl_4 solution.

Table II. Tabulated ^{13}C NMR Data for Spatol, *Stoechospermum* Metabolites, and Two Key Derivatives[a]

1[b]	2[d]	3[c]	4[c]	5[c]	6[c]	7[c]	8[c]	9[b]	10[c]	11[a]	12[b]	13[c]
148.6 s	150.1 s	171.7 s	*e*	222.4 s	169.0 s	148.4 s	148.5	146.2 s	147.5 s	148.6 s	170.3 s	173.7 s
110.8 t	136.4 d	149.6 s	147.5 s	148.1 s	147.1 s	147.5 s	147.3	133.7 s	139.8 d	131.4 s	169.9 s	170.4 s
	131.0 d	135.0 d	137.3 d	136.7 d	139.8 s	111.0 t	111.3	129.1 d	124.7 d	124.4 d	169.0 s	
	107.2 t	131.3 d	131.2 d	130.8 d	125.1 d	108.7 t	108.7	110.8 t	109.6 t	108.4 t	145.5 s	
		108.8 t	109.0 t	109.3 t	110.2 t						138.6 d	
											127.4 d	
											110.2 t	
79.9 d	78.9 d	79.8 d	73.4 s	73.1 s	79.9 d	80.4 d	80.4	80.3 d	80.3 d	80.5 d	81.7 d	82.1 d
58.4 s	73.7 d	73.8 d	73.1 d	73.1 d	75.5 d	75.7 d	75.7	68.3 d	70.6 s		75.4 d	
58.4 d	72.2 s	71.4 s	69.8 t	69.7 t	69.7 d						71.7 s	
57.1 d	69.5 t	70.2 t			61.7 t						70.8 t	
54.9 d												
47.5 s	46.5 s	46.7 s	48.8 s	48.9 s	46.9 s	46.7 s	46.8	47.0 s	46.7 s	46.7 s	46.6 s	51.3 q
44.0 d	43.0	43.0	42.2 d	42.3 d	43.3	45.5 d	45.6	46.6 d	45.4 d	45.6 d	43.5 d	46.6 s
43.6 d	42.8	42.2	39.7	39.8	43.2	43.2 d	43.3	44.9 t	43.2 t	43.2 d	43.5 d	46.4 d
43.5 d[f]	42.2	42.4	39.3	39.3	43.0	43.0 d	43.0	43.5 d	40.8 d	43.1 d	37.9 d	43.9 d
38.0 d	37.0	37.1	38.9	39.0	37.5	37.6 t	37.6	43.5 d	39.1 t	37.7 d	37.9 d	43.0 d
37.2 t[f]	36.8	36.5	37.0	37.0	36.3	37.0	36.7	37.9 d	37.5	36.7	36.7 t	39.8 d
36.8 d	36.2	36.0	33.8 t	33.8 t	36.3	36.7	36.5	37.1 t	36.5	36.5	35.3 d	36.4 d
35.4 t	35.0 t	34.9 t	27.3 t	27.3 t	35.1	36.5 t	35.1	36.8 d	36.5	36.4	35.3 t	34.6 t
28.1 t	27.6 t	28.8 t	24.2 q	24.3 q	29.7	35.1 t	33.2	35.3 t	35.1	35.1 t	28.0 t	34.1 t
24.1 q	23.9 q	24.2 q	21.2 q	21.1 q	27.9	33.2 t	32.2	28.2 t	29.7 q	27.9 t	24.7 q	27.8 t
19.2 q	14.0 q	20.9 q	14.1 q	14.0 q	22.0 q	32.2 t	29.7	25.7 q	29.7 q	26.6 t	20.8 q	21.1 q
14.6 q	12.9 q	14.1 q	12.5 q	12.6 q	14.3 q	27.9 t	27.9	18.3 q	27.9 t	25.7 q	20.8 q	13.5 q
13.4		13.0 q			13.2 q	17.6 q	17.5	14.6 q	14.5 q	17.7 q	20.5 q	12.8 q
						14.3 q	14.4	13.5 q	13.1 q	14.3 q	14.4 q	
						13.1 q	13.1			13.1 q	13.3 q	

[a] Spectra were recorded at 20 MHz in the solvent indicated, and multiplicities were obtained by off-resonance decoupling techniques. [b] Recorded in C_6D_6 solution. [c] Recorded in $CDCl_3$ solution. [d] Recorded in $(CD_3)_2CO$ solution. [e] The carbonyl band was not observed under these instrumental conditions. [f] Assignments may be reversed.

chlorochromate to yield the ketone **15**. The ketone showed an infrared carbonyl absorption at 1735 cm^{-1} and a large negative rotation ($[\alpha]_D$ −226°) indicative of the five-membered ring with an adjacent asymmetric center at C-4.[33]

Unequivocal proof of the structure of the tricyclic nucleus in **2** was obtained by interconversion of both **2** and spatol acetate (**16**) to the aldehyde **17**. Treatment of **16** with H_5IO_6 in ether smoothly cleaved the epoxide, generating the aldehyde **17**. Similarly, **2**, when treated under analogous conditions, yielded a hydroxy aldehyde, which when acetylated also yielded **17**. This latter reaction was apparently facilitated by an allylic rearrangement of the C-18 hydroxyl to C-16. The aldehyde produced from **16** showed $[\alpha]_D$ +21.3°, and that from **2** showed $[\alpha]_D$ +30.1°, thus indicating that **1** and **2** possess the same absolute stereochemistry at comparable nuclear centers.

The structure of the side chain in **2** followed simply by analysis of ^1H and ^{13}C NMR data. The terminal olefin was positioned at C-13,C-14 on the basis of the results of ozonation and the measurable allylic coupling of the C-7 ring-juncture proton with one proton at C-14. The other disubstituted olefin was assigned as *E* (J = 15.5 Hz) and placed at C-16,C-17 on the basis of the lack of a UV absorption for the metabolite. The remaining spectral features, requiring one tertiary, one secondary, and one primary alcohol, could be assigned only as in **2**.

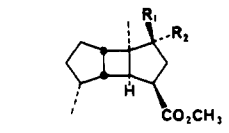
Repeated HPLC failed to separate the two diastereomers which must be epimeric at C-15, or C-18, or at both centers. Cleavage of the C-18,C-19 diol in **2** with $NaIO_4$ gave the expected methyl ketone **18**, which was a single compound ($[\alpha]_D$ +6.35°) by HPLC and ^1H NMR analysis. Hence, the epimeric center in **2** must be at C-18, and the structure of **2** is formulated as 5(*R*),15,18(*R* and *S*),19-tetrahydroxyspata-13,16(*E*)-diene.

A monoacetate mixture, **3**, recognized also to be composed of side-chain diastereomers, was isolated by repeated HPLC. High-resolution mass spectral analysis showed only an $M^+ - HOAc - H_2O$ fragment at m/z 300, corresponding to $C_{20}H_{28}O_2$. Consideration of ^1H and ^{13}C NMR data, however, allowed the formulation of **3** as $C_{22}H_{34}O_5$, which is isomeric (minus the acetate) with **2**. Acetylation of **3** yielded a triacetate, **12**, which was identical, including optical rotation, with that produced from **2**. The position of acetylation in **3** could readily be deduced to be at C-19 by ^1H NMR, since the primary acetate AB pattern was observed at δ 4.07 (d, J = 10 Hz) and 3.93 (d, J = 10 Hz) (Table I), as was the case for the triacetate **12**. Therefore, **3** is assigned in analogy with **2** as the identical diastereomeric mixture at C-18.

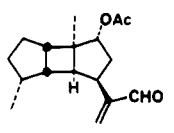
Two epimeric ketones, **4** and **5**, were isolated from the extract of *S. marginatum*, and in this case the mixture of diastereomers was successfully separated by silica gel HPLC. Ketone **4**, an oil, showed $[\alpha]_D$ −136.5° and analyzed for $C_{20}H_{30}O_4$ by combined ^{13}C NMR and high-resolution mass spectral methods. The ketone was readily recognized as being cyclopentanoid, and therefore placed at C-5, by its characteristic infrared absorption at 1730 cm^{-1}. This assignment was reinforced by ^{13}C NMR data, since the strained carbonyl carbon was observed at 222.4 ppm. Interpretation of additional ^1H and ^{13}C NMR data indicated the identical side-chain substitution in **4** as found in **2** and **3**. Acetylation of **4** yielded a 4:1 mixture of the diacetate **19** and the triacetate **20**. The diacetate thus obtained formed the basis of a precise comparison with **3**. Selective acetylation of **3** (Ac_2O/py/0 °C/3 h) gave a mixture of diacetates **21** and **22**, which were further oxidized with pyridinium chlorochromate to yield the keto diacetates **19** and **23**. The keto acetate **19** was separated by recycle-HPLC and found to be identical with the acetate produced from **4**. During the HPLC separation of **19** and **23**, the diastereomers at C-18 were rendered separable. We are not able, however, to assess which epimer was isolated, nor are we able to establish the absolute stereochemistry at C-18 in **4**. The ketone **4** was therefore assigned as 5-oxo-15,18(*R**),19-trihydroxyspata-13,16(*E*)-diene.[34]

(33) Crabbé, P. "Optical Rotary Dispersion and Circular Dichroism in Organic Chemistry"; Holden-Day: San Francisco, 1965; p 378.

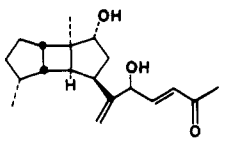
Chart II



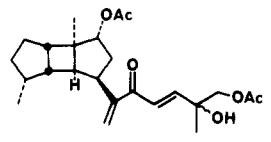
13 R_1 = H; R_2 = OAc
14 R_1 = H; R_2 = OH
15 R_1 = R_2 = O



17



18



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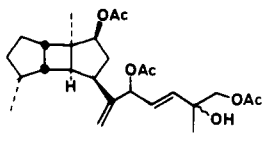
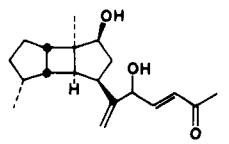
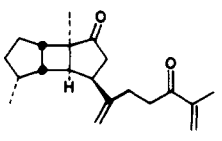


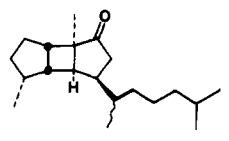
24



27



29



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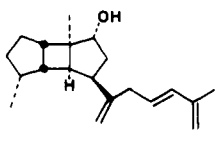
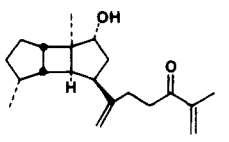


31



32

Reduction of the ketone **4** with Li(*t*-ButO)$_3$AlH in ethanol, followed by acetylation, yielded the triacetate **24**. This reduction selectively produced the nonnatural C-5 β-alcohol, as could be deduced from the C-5 methine proton NMR characteristics. In **24**, the C-5 proton is observed as a doublet of doublets with couplings of 8 and 10 Hz. In contrast, the epimeric C-5 proton in the natural products **1–3** and **6–11** is limited to a single 4-Hz coupling with the C-6 α-hydrogen. This observation provided considerable support in subsequent stereochemical assignments of derivatives at C-5.

The epimeric ketone **5** showed spectral characteristics (^{1}H and ^{13}C NMR, mass, IR) nearly superimposable with those of **4**, except for exhibiting an optical rotation of $[\alpha]_D$ −99.2°. As in the case of **2**, the question of epimerization at C-15 or C-18 remained. Acetylation of **5** produced the diacetate **25** and the triacetate **26** in a 4:1 ratio. The ^{1}H NMR features of **25** were nearly identical with those of **19**, reaffirming the epimeric relationship of **4** and **5**. To establish the site of epimerization, **5** was reduced with LiAlH$_4$, and the crude tetraol mixture was treated with NaIO$_4$ to yield the methyl ketones **18** and **27**. The methyl ketone **18** could be readily separated and was found to be identical ($[\alpha]_D$ +10.1°) with that produced from **2**. Ketones **4** and **5** are, therefore, shown to be epimeric at C-18, and via the favorable comparison with **2**, **5** may be described as 5-oxo-15,18(*S**),19-trihydroxyspata-13,16(*E*)-diene.[34]

A polar monoacetate, **6**, recognized to be isomeric with **3**, was isolated by repeated HPLC of the more polar fractions. As with **3**, high-resolution mass spectrometry showed only M$^+$ − HOAc − H$_2$O fragments, and the molecular composition was fully established as $C_{22}H_{34}O_5$ by ^{13}C NMR. As the tricyclic nucleus of **6** appeared to be identical with those of **1–5** by spectral analysis, the isomeric relationship was, here also, assigned within the side chain. Cleavage (NaIO$_4$) of the side-chain vicinal diol at C-15,C-16 yielded an aldehyde product, which when acetylated was identical with **17** ($[\alpha]_D$ +26.5°) as produced from both **1** and **2**. The composition of the tricyclic nucleus was, therefore, firmly established. ^{1}H NMR analysis (Table I) showed **6** to possess one olefinic methyl group (δ 1.81, 3 H, s) and one trisubstituted olefin (δ 5.42, 1 H, d). The coupling of the olefin proton with the alcohol methine proton at C-16 (J = 10 Hz) further established the diol at C-15,C-16 and allowed the formulation of the side-chain structure. The single acetate was clearly at C-19, since an isolated AB pattern at δ 4.14 and 4.02 (J = 13 Hz) was characteristic of the shift expected for a primary acetate. The stereochemistry of the C-17,C-18 olefin was tentatively assigned on the basis of a comparison of the ^{13}C NMR calculated values for *E* and *Z* geometrical isomers with that measured for **6**.[35] A calculated value of 21.9 ppm for the *Z* isomer is in rough agreement with our measured shift of >22 ppm, thus supporting the *Z* assignment.

The epimeric alcohols **7** and **8** were separable by HPLC and were isolated from the medium-polarity column chromatography fractions. Compound **7**, an optically active oil ($[\alpha]_D$ +35.2°), analyzed as a diol of molecular formula $C_{20}H_{32}O_2$ by combined spectral methods. The 5 unsaturation equivalents inherent in this formula could be accounted for by two olefinic bonds (both terminal) and the familiar tricyclic skeleton. An interconversion with degradation products from **1** could not be accomplished with **7**; however, complete analysis of ^{1}H and ^{13}C NMR data gave very convincing evidence in support of structure **7**. In the ^{1}H NMR spectrum, the characteristic methine protons of the spatane nucleus were clearly visible and possessed the same coupling constants. The superimposability of all comparable ^{13}C NMR bands further supported this assignment. What remained was to establish the structure of the side chain, and this was accomplished by ^{1}H NMR decoupling experiments and by chemical modification. Two terminal olefinic bonds were readily established by ^{13}C NMR, and the presence of an olefinic methyl group in the ^{1}H NMR spectrum secured the placement of olefins at C-13,C-14 and C-18,C-19. What

(34) The *R**,*S** notation is used here as an aid in nomenclature to indicate the site of epimerization for two diastereomeric molecules. In **4** and **5** the notation indicates a C-18 epimeric relationship, while in **7** and **8** the epimeric relationship lies at C-17. A more suitable method for naming compounds in this circumstance does not appear to exist.

(35) Calculated ^{13}C NMR shifts for the C-20 methyl group with the C-17, C-18 *E* and *Z* olefin involved the model compounds geraniol, the natural product **9**, and 2,6-dimethyl-1-hydroxyocta-2(*E*),7-diene. The *E* isomer yielded a value of 14.6 ppm while the *Z* isomer calculated for 21.9 ppm; see: Wehrli, F. W.; Nishida, T. in "Progress in the Chemistry of Organic Natural Products"; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Wien, Springer-Verlag: New York, 1979; p 24.

remained was to establish the position of the side-chain alcohol at one of three possible carbon sites. Pyridinium chlorochromate oxidation of **7** yielded the α,β-unsaturated ketone derivative **29**, which was readily assignable on the basis of the shifts observed in the terminal olefin protons at C-19. As expected for the deshielded β-carbon of the enone, the C-19 protons were shifted from δ 4.82 and 4.74 in **7** to δ 6.05 and 5.84 in **29**. Further, the C-20 methyl group was, expectedly, also shifted to δ 1.94. The diketone **29** also exhibited a large negative rotation ($[\alpha]_D$ −190°) in close accord with the rotation found for the chiral C-5 ketone in **15**. On the basis of these chemical and spectral analyses, the structure for **7** is formulated as 5(*R*),17-(*R**)-dihydroxyspata-13,18-diene.[34]

The epimeric diol **8** showed $[\alpha]_D$ +18.4° and was virtually superimposable spectrally with diol **7**. Since the ^1H NMR features of the C-5 alcohol methine proton were so clearly in support of the 5α-hydroxyl, the epimeric relationship of **8** was envisioned to be at C-17. Confirmation of the epimeric relationship at this center was obtained via oxidation of **8** to yield **29**. The diketone obtained was identical in all respects ($[\alpha]_D$ −185°) with that from **7**, thus establishing **8** as 5(*R*),17(*S**)-dihydroxyspata-13,18-diene.[34]

An isomeric diol, **9**, was also purified from the medium-polarity column fractions. Compound **9**, an oil, showed $[\alpha]_D$ +6.3° and analyzed for $C_{20}H_{32}O_2$ by combined ^{13}C NMR and high-resolution mass spectral methods. The ^1H and ^{13}C NMR features of **9** again clearly delineated the tricyclic nucleus, and spectral features to assign the elements of the side chain were also apparent. In addition to the consistent *exo*-methylene at C-13,C-14, the ^1H NMR spectrum showed two olefinic methyls at δ 1.71 and 1.64, a single olefin proton at δ 5.09, and an allylic alcohol methine proton at δ 4.41. This latter band was found to be coupled to the olefin proton at δ 5.09 (J = 6 Hz); hence, the allylic alcohol and olefin constellation were securely placed at the terminal position in the side chain.

Ozonolysis of **9**, followed by CH_2N_2 methylation and acetylation (Ac_2O/py), yielded **13** unexpectedly, in only modest yield. It would appear that dehydration occurred prior to ozonolysis or that more complex mechanisms afforded oxidative cleavage of the C-13,C-15 bond. The ester produced from **9** showed $[\alpha]_D$ +1.75°, thus indicating the nuclear stereochemistry of **9** to be identical with that of **1** and **2**. In addition, selective dehydration of the allylic alcohol in **9**, followed by hydrogenation and pyridinium chlorochromate oxidation, produced the saturated ketone **30**. The ketone showed a large negative rotation ($[\alpha]_D$ −101.2°), consistent with **15** and **29**. The diol **9** can therefore be assigned as 5(*R*),16-dihydroxyspata-13,17-diene.

HPLC separation of another medium-polarity column fraction yielded an additional isomeric diol assigned as **10**. The diol showed $[\alpha]_D$ +1.9°, and here also combined spectral methods indicated a molecular formula of $C_{20}H_{32}O_2$. Analysis of spectral data in a consistent fashion suggested the tricyclic nucleus to be present as well as indicated a side-chain composition isomeric with **9**. Infrared absorptions at 975 cm^{-1} and a two-proton olefin band at δ 5.70 suggested a trans-disubstituted double bond to be present. Also, two methyl groups were observed in the ^1H NMR spectrum at δ 1.34, suggesting the placement of these methyls at a carbon bearing the remaining hydroxyl group. Since the diol **10** lacked a UV chromophore, the olefin was securely placed at C-16,C-17, resulting in the final assignment of diol **10**. To confirm the relationship of **10** to **9**, and hence of diol **10** to both **1** and **2**, the compound was dehydrated with *p*-toluenesulfonic acid in aqueous acetone to yield the triene **31**. Hydrogenation of the triene followed by pyridinium chlorochromate oxidation gave the ketone **30** ($[\alpha]_D$ −99.5°) which was identical with the compound produced from **9**. Since **9** had been rigorously related to **1** and **2**, diol **10** may be formulated as 5(*R*),18-dihydroxyspata-13,16(*E*)-diene.

Evaluation of the relatively nonpolar column fractions from *S. marginatum* yielded only one monoalcohol, **11**. Alcohol **11** showed $[\alpha]_D$ +29.4° and analyzed for $C_{20}H_{32}O$ by ^{13}C NMR and high-resolution mass spectrometry. As with all the compounds from this source, the tricyclic portion of the molecule seemed intact by evaluation of ^1H and ^{13}C NMR data. In addition to these spectral features, several ^{13}C and ^1H NMR bands confirmed the presence of an additional trisubstituted double bond. Further, ^{13}C NMR bands at 124.2 (d) and 131.4 (s) ppm and ^1H NMR singlet resonances (3 H each) at δ 1.68 and δ 1.59 indicated the olefin was substituted with two methyl groups. In the ^1H NMR spectrum the single olefin proton appeared at δ 5.10 as a characteristic triplet (J = 7 Hz), indicating an adjacent methylene group. From these data the olefin was confidently placed at C-17,C-18 to complete the structure proposal for **11**.

Treatment of **11** with photochemically produced singlet oxygen (methylene blue sensitizer) produced the unsaturated ketone **32**, in modest yield, after the expected "ene" reaction and apparent autocatalytic decomposition of the intermediate hydroperoxide at C-17. Ketone **32** was further oxidized with pyridinium chlorochromate to yield the diketone **29**. The diketone showed $[\alpha]_D$ −150° and was identical with that produced from **7** and **8**.

The alcohol **11** was also converted to the ketone **30** as the final confirmation of structure. Hydrogenation (Pt/Et_2O), followed by pyridinium chlorochromate oxidation gave the ketone **30** ($[\alpha]_D$ −110°), identical in all respects with that produced from **9** and **10**. The structure of alcohol **11** is, therefore, securely assigned as 5(*R*)-hydroxyspata-13,17-diene.[36]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer, and optical rotations were measured on a Perkin-Elmer Model 141 polarimeter using a 10-cm microcell. ^1H NMR spectra were recorded on Varian HR-220 and T-60 spectrometers and on a home-built 360-MHz spectrometer, and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. All chemical shifts are reported relative to Me_4Si (δ 0), and coupling constants are in hertz. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5930-A mass spectrometer, and high-resolution mass spectra (HRMS) were obtained through the Department of Chemistry, University of California, Los Angeles. All solvents used were distilled from glass prior to use.

Collection, Extraction, and Chromatography. *Stoechospermum marginatum* was collected in shallow water along the coast of Sri Lanka in 1977 and air-dried prior to extraction (3.2 kg). A cold $CHCl_3$/MeOH (2/1) extraction yielded 120 g of extract after solvent evaporation, and a subsequent extraction with warm solvent (~50 °C) yielded an additional 82 g. No significant differences were observed between the two extracts.

Conventional silica gel column chromatography using various proportions of CH_2Cl_2, EtOAc, and MeOH gave fractions rich in **2**–**11**. The least polar fractions (2% EtOAc/CH_2Cl_2) contained **11**, while moderate polarity fractions (20% EtOAc/CH_2Cl_2) contained **7**–**10**. Compound **3** was eluted with 100% EtOAc. The more polar compounds were eluted with 25% MeOH/EtOAc and

(36) We have recently determined, by direct comparison, that compound **11** is identical with the previously reported diterpenoid stoechospermol, also isolated from *S. marginatum*.[19] Since the structure of diterpenoid **11** has been confidently assigned, the structure of stoechospermol should be accordingly revised.

50% MeOH/EtOAc and consisted of 4–6 (25%) and 2 (50%). Each compound was subsequently purified by high-performance liquid chromatography (HPLC) on a 16 mm × 50 cm preparative silica gel column by using various proportions of EtOAc in isooctane.

Acetylations. Conversions of the natural products and several degradation products into their corresponding acetate esters were accomplished in the following general way. Excess acetic anhydride and dry pyridine were added to milligram quantities of natural products, and the resultant solution was stirred at room temperature overnight. The reaction was quenched with ice and water, and the reaction products were extracted with Et_2O (3×). The ether phase was washed with 5% HCl (3×), water (3×), and saturated $NaHCO_3$(3×), dried over anhydrous $MgSO_4$, and reduced in vacuo to yield the crude esters. Purification, when necessary, was provided by HPLC under the conditions mentioned above.

5(*R*),15,18(*R* and *S*),19-Tetrahydroxyspata-13,16(*E*)-diene (2). The tetraol mixture was isolated as 5.3% of the extract. The mixture was an oil with the following spectral features: $[\alpha]_D$ −10.7° (*c* 1.82, $CHCl_3$); IR ($CHCl_3$) 3450, 2950, 1710, 1450, 1370, 1250, 1025, 940, 908 cm^{-1}. **Acetate 12** was purified by using HPLC (50% EtOAc/isooctane), as an oil: $[\alpha]_D$ −36° (*c* 1.32, $CHCl_3$); IR ($CHCl_3$) 3550, 2950, 1730, 1650, 1460, 1375, 1250, 1040, 970, 910 cm^{-1}; LRMS (70 eV, 200 °C), *m/z* 402 (0.2), 384 (0.3), 342 (0.3), 269 (1.0), 260 (23), 225 (19), 200 (16), 187 (40), 135 (79), 81 (100); HRMS (70 eV, 180 °C), *m/z* (relative intensity) 384.2295 (M^+ − HOAc − H_2O, $C_{24}H_{32}O_4$, 5.0, −0.6 mamu dev), 342.2195 ($C_{22}H_{30}O_3$, 9.3), 269.1905 ($C_{19}H_{25}O$, 42), 260.1417 ($C_{16}H_{20}O_3$, 90), 225.1638 ($C_{17}H_{21}$, 36), 200.1206 ($C_{14}H_{16}O$, 38), 187.1112 ($C_{13}H_{15}O$, 56), 145.1024 ($C_{11}H_{13}$, 54), 143.0866 ($C_{11}H_{11}$, 56), 135.1171 ($C_{10}H_{15}$, 100).

19-Acetoxy-5(*R*),15,18(*R* and *S*)-trihydroxyspata-13,16(*E*)-diene (3). The monoacetate diastereomeric mixture was isolated as an oil as 1.4% of the extract and showed the following spectral features: $[\alpha]_D$ −16.1° (*c* 1.48, $CHCl_3$); IR ($CHCl_3$) 3500, 2975, 1735, 1650, 1450, 1375, 1240, 1110, 1040, 940, 908 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 300.2080 (M^+ − HOAc − H_2O, $C_{20}H_{28}O_2$, −1.0 mamu dev, 6), 287.1983 ($C_{19}H_{27}O_2$, 13), 269.1888 ($C_{19}H_{25}O$, 14), 211.1474 ($C_{16}H_{19}$, 14), 159.1182 ($C_{12}H_{15}$, 27), 145.1007 ($C_{11}H_{13}$, 35), 135.1175 ($C_{10}H_{15}$, 68), 105.0711 (C_8H_9, 54), 81.0319 (C_5H_5O, 100). **Acetate 12.** Standard acetylation conditions of 7.4 mg of **3** (0.0196 mmol) followed by preparative thin-layer chromatography yielded 5.4 mg (0.0117 mmol, 60%) of **12**, which showed $[\alpha]_D$ −41.3° (*c* 0.54, $CHCl_3$) and which was identical with **12** produced from **2** by 220-MHz ^1H NMR, IR, and LRMS.

5-Oxo-15,18(*R* or *S*),19-trihydroxyspata-13,16(*E*)-diene (4). The ketone was isolated as an oil by HPLC (100% EtOAc) as 0.23% of the extract. Ketone **4** showed the following spectral characteristics: $[\alpha]_D$ −136.5° (*c* 1.22, $CHCl_3$); IR ($CHCl_3$) 3450, 2950, 1730, 1450, 1380, 1240, 1110, 1040, 970, 910 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 303.1956 (M^+ − CH_3O, $C_{19}H_{27}O_3$, −0.4 mamu dev, 66), 298.1947 ($C_{20}H_{26}O_2$, 2), 285.1852 ($C_{19}H_{25}O_2$, 51), 227.1454 ($C_{16}H_{19}O$, 41), 199.1498 ($C_{15}H_{19}$, 22), 177.1269 ($C_{12}H_{17}O$, 24), 153.0928 ($C_9H_{13}O_2$, 73), 151.1132 ($C_{10}H_{15}O$, 100), 149.0962 ($C_{10}H_{13}O$, 43), 99.0448 ($C_5H_7O_2$, 52), 81.0691 (C_6H_9, 98). **Acetates 19 and 20.** Standard acetylation of 15.0 mg (0.045 mmol) of **4** followed by preparative thin-layer chromatography provided in a ratio of 4:1 the desired diacetate **19** (15.0 mg, 0.358 mmol, 80%) and unexpected triacetate **20** (1.96 mg, 0.009 mmol, 20%). Compound **19** produced from **4** showed the following: $[\alpha]_D$ −104.0° (*c* 1.50, $CHCl_3$); ^1H NMR (220 MHz, $CDCl_3$) δ 5.85 (1 H, d, *J* = 13), 5.66 (2 H, m) 5.37 (1 H, s), 5.08 (1 H, s), 4.11 (1 H, d, *J* = 10), 3.96 (1 H, d, *J* = 10), 2.87 (2 H, m), 2.76 (1 H, m), 1.4–2.5 (8 H, m), 2.08 (3 H, s), 2.07 (3 H, s), 1.33 (3 H, s), 0.99 (3 H, s), 0.92 (3 H, d, *J* = 7). The triacetate **20** displayed the following ^1H NMR bands (220 MHz, $CDCl_3$): 5.96 (1 H, d, *J* = 13), 5.60 (2 H, m), 5.37 (1 H, s), 5.08 (1 H, s), 4.26 (2 H, s), 2.91 (2 H, m), 2.80 (1 H, m), 1.2–2.5 (8 H, m), 2.11 (3 H, s), 2.07 (3 H, s), 2.01 (3 H, s), 1.57 (3 H, s), 0.96 (3 H, s), 0.93 (3 H, d, *J* = 7).

5-Oxo-15,18(*S* or *R*),19-trihydroxyspata-13,16(*E*)-diene (5). Ketone **5** was isolated along with **4** by HPLC. The ketone composed 0.4% of the extract and showed the following spectral features: $[\alpha]_D$ −99.2° (*c* 1.84, $CHCl_3$); IR ($CHCl_3$) 3450, 2975, 1730, 1460, 1375, 1240, 1030, 965, 910 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 303.1986 (obsd M^+ − CH_3O, $C_{19}H_{27}O_3$, 2.6 mamu dev, 1.4), 285.1845 ($C_{19}H_{25}O_2$, 1.5), 227.1415 ($C_{16}H_{19}O$, 7), 161.0965 ($C_{11}H_{13}O$, 15), 159.1163 ($C_{12}H_{15}$, 18), 153.0913 ($C_9H_{13}O_2$, 34), 151.1132 ($C_{10}H_{15}O$, 51), 149.0974 ($C_{10}H_{13}O$, 27), 99.0427 ($C_5H_7O_2$, 46), 93.0709 (C_7H_9, 43), 81.0702 (C_6H_9, 100). **Acetates 25 and 26.** Standard acetylation of 16.2 mg (0.0485 mmol) of **5**, followed by preparative thin-layer chromatography, provided two compounds, **25** (14.4 mg, 0.0344 mmol, 71%) and **26** (3.9 mg, 0.0086 mmol, 17.7%). The diacetate **25** showed the following: $[\alpha]_D$ −79.0° (*c* 1.44, $CHCl_3$); ^1H NMR (220 MHz, $CDCl_3$) δ 5.81 (1 H, d, *J* = 14), 5.65 (2 H, m), 5.36 (1 H, s), 5.05 (1 H, s), 4.09 (1 H, d, *J* = 10), 3.94 (1 H, d, *J* = 10), 2.88 (2 H, m), 2.77 (1 H, m), 1.4–2.5 (8 H, m), 2.09 (3 H, s), 2.06 (3 H, s), 1.30 (3 H, s), 0.95 (3 H, s), 0.89 (3 H, d, *J* = 7). The triacetate **26** displayed the following ^1H NMR bands (220 MHz, $CDCl_3$): δ 5.95 (1 H, d, *J* = 15), 5.61 (1 H, d, *J* = 8), 5.50 (1 H, dd, *J* = 15, 8), 5.36 (1 H, s), 5.05 (1 H, s), 4.23 (2 H, s), 2.88 (2 H, m), 2.77 (1 H, m), 1.5–2.4 (8 H, m), 2.10 (3 H, s), 2.08 (3 H, s), 2.00 (3 H, s), 1.55 (3 H, s), 0.95 (3 H, s), 0.89 (3 H, d, *J* = 7).

19-Acetoxy-5(*R*),15,16-trihydroxyspata-13,17(*Z*)-diene (6). The monoacetate **6** was isolated as an oil (0.26% extract) by HPLC (100% EtOAc) and showed the following spectral features: $[\alpha]_D$ −8.8° (*c* 1.22, $CHCl_3$); IR ($CHCl_3$) 3450, 2950, 1720, 1640, 1440, 1370, 1240, 1040, 1000, 940, 908 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 301.2158 (obsd M^+ − OAc − H_2O, $C_{20}H_{29}O_2$, −1.0 mamu dev, 1.3), 136.0362 ($C_9H_{12}O$, 100), 135.1157 ($C_{10}H_{15}$, 69), 107.0866 (C_8H_{11}, 55), 101.0596 ($C_5H_9O_2$, 69), 93.0703 (C_7H_9, 60), 81.0321 (C_5H_5O, 80). **Acetate 28.** Standard acetylation of 12 mg (0.032 mmol) of **6** followed by preparative thin-layer chromatography gave pure **28**, which displayed the following absorptions in the ^1H NMR (220 MHz, $CDCl_3$): δ 5.80 (1 H, dd, *J* = 10, 5), 5.51 (1 H, d, *J* = 5), 5.45 (1 H, d, *J* = 10), 5.23 (1 H, s), 5.02 (1 H, s), 4.93 (1 H, d, *J* = 4), 4.66 (1 H, d, *J* = 12), 4.54 (1 H, d, *J* = 12), 2.86 (1 H, m), 2.43 (1 H, ddd, *J* = 13, 13, 4), 1.1–2.2 (9 H, m), 2.25 (3 H, s), 2.20 (3 H, s), 2.19 (3 H, s), 2.17 (3 H, s), 1.93 (3 H, s), 0.95 (3 H, s), 0.83 (3 H, d, *J* = 6).

5(*R*),17(*S)-Dihydroxyspata-13,18-diene (7).** The diol **7**, an oil, was isolated by HPLC (50% EtOAc/isooctane) as 0.22% of the extract and showed the following spectral features: $[\alpha]_D$ +35.2° (*c* 0.83, $CHCl_3$); IR ($CHCl_3$) 3500, 2975, 1725, 1440, 1380, 1240, 1100, 910, 840 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 271.2053 (obsd M^+ − CH_5O (H_2O, CH_3), $C_{19}H_{27}O$, −0.9 mamu dev, 6.2), 204.1491 ($C_{14}H_{20}O$, 74), 187.1470 ($C_{14}H_{19}$, 33), 159.1189 ($C_{12}H_{15}$, 35), 151.1110 ($C_{10}H_{15}O$, 27), 133.1022 ($C_{10}H_{13}$, 39), 120.0940 (C_9H_{12}, 77), 93.0699 (C_7H_9, 80), 81.0702 (C_6H_9, 100), 79.0551 (C_6H_7, 60).

5(*R*),17(*R)-Dihydroxyspata-13,18-diene (8).** Diol **8**, an oil, was isolated by HPLC (50% EtOAc/isooctane) as 0.38% of the extract and showed the following spectral characteristics: $[\alpha]_D$ +18.4° (*c* 0.67, $CHCl_3$); IR ($CHCl_3$) 3500, 3590, 1725, 1640, 1440, 1370, 1230, 1110, 1030, 985, 940, 905 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 205.1563 (obsd M^+ − $C_6H_{11}O$ (CH_2C-$H_2CH(OH)C(CH_2)CH_3$), $C_{14}H_{21}O$, −2.9 mamu dev, 20), 204.1514 ($C_{14}H_{20}O$, 66), 161.1326 ($C_{12}H_{17}$, 30), 120.0942 (C_9H_{12}, 82), 107.0863 (C_8H_{11}, 73), 105.0706 (C_8H_9, 61), 93.0709 (C_7H_9, 75), 81.0692 (C_6H_9, 100), 79.0537 (C_6H_7, 75).

5(*R*),16-Dihydroxyspata-13,17-diene (9). The diol **9**, an oil, was isolated by HPLC (50% EtOAc/isooctane) as 0.05% of the extract and showed the following spectral features: $[\alpha]_D$ +6.3° (*c* 1.91, $CHCl_3$); IR (CCl_4) 3350, 3050, 1650, 1450, 1380, 1185, 1115, 1050, 945, 900 cm^{-1}; LRMS (75 °C, 35.5 eV), *m/z* (relative intensity) 304 (M^+, 0.8), 286 (1.5), 202 (5.3), 135 (37), 86 (100); HRMS (70 eV, 180 °C), *m/z* (relative intensity) 286.2300 (obsd M^+ − H_2O, $C_{20}H_{30}O$, 0.3 mamu dev, 2.6), 204.1519 ($C_{14}H_{20}O$, 27), 135.1174 ($C_{10}H_{15}$, 60), 107.0878 (C_8H_{11}, 41), 105.0707 (C_8H_9, 45), 93.0696 (C_7H_9, 47), 91.0537 (C_7H_7, 49), 85.0651 (C_5H_9O, 100), 81.0704 (C_6H_9, 69).

5(*R*)-18-Dihydroxyspata-13,16(*E*)-diene (10). The diol **10**, an oil, was isolated (0.3% extract) by HPLC (50% EtOAc/isooctane) and showed the following spectral features: $[\alpha]_D$ +1.9° (*c* 1.35, $CHCl_3$); IR ($CHCl_3$) 3500, 3000, 1650, 1460, 1370, 1140, 1110, 1035, 975, 940, 895 cm^{-1}; HRMS (70 eV, 180 °C), *m/z* (relative intensity) 286.2309 (obsd M^+ − H_2O, $C_{20}H_{30}O$, 1.2 mamu dev, 3.3), 268.2195 ($C_{20}H_{28}$, 20), 204.1515 ($C_{14}H_{20}O$, 93), 145.1005 ($C_{11}H_{13}$, 55), 119.0866 (C_9H_{11}, 76), 105.0699 (C_8H_9, 100), 91.0553 (C_7H_7, 88), 81.0711 (C_6H_9, 92).

5(*R*)-Hydroxyspata-13,17-diene (11). The alcohol **11**, an oil (1.3% of the extract), was isolated in pure form in the column chromatography process and showed the following spectral features: $[\alpha]_D$ +29.4° (*c* 1.07, $CHCl_3$); IR ($CHCl_3$) 3500, 2950, 1650, 1440, 1370, 1110, 1040, 985, 940, 895 cm^{-1}; LRMS (35.5 eV), *m/z* (relative intensity) 288 (obsd, M^+, 0.8), 270 (0.8), 259 (1.2), 227 (2.0), 206 (23), 145 (18), 137 (30), 121 (22), 107 (30), 81 (50), 69 (100), 42 (67); HRMS (70 eV, 180 °C), *m/z* (relative intensity) 270.2341 (obsd $M^+ - H_2O$, $C_{20}H_{30}$, −0.7 mamu dev, 61), 206.1679 ($C_{14}H_{22}O$, 65), 147.1168 ($C_{11}H_{15}$, 30), 137.0971 ($C_9H_{13}O$, 87), 135.1179 ($C_{10}H_{15}$, 70), 105.0710 (C_8H_9, 53), 93.0700 (C_7H_9, 56), 91.0541 C_7H_7, 58), 81.069 (C_6H_9, 100).

H_5IO_6 Degradation of 16 To Yield Aldehyde 17. A 5-mL sample of a saturated ether solution of H_5IO_6 was added dropwise to 54.9 mg (0.152 mmol) of **16** in 3 mL of ether over 0.5 h at 0 °C. The solution was allowed to warm to room temperature and further stirred for an additional 48 h. Filtration and removal of ether in vacuo yielded a complex oily mixture which was separated by HPLC (10% EtOAc/isooctane, μ-Porasil column). The major product produced was **17**: 4.8 mg (0.014 mmol, 11.5%); $[\alpha]_D$ +21.3° (*c* 0.48, $CHCl_3$); ^1H NMR (220 MHz, $CDCl_3$) δ 9.50 (1 H, s), 6.22 (1 H, s), 6.09 (1 H, s), 4.95 (1 H, d, *J* = 4.3), 3.36 (1 H, dddd, *J* = 5, 5, 13, <1), 2.39 (1 H, ddd, *J* = 13, 13, 4.3), 2.29 (1 H, m), 1.1–2.1 (8 H, m), 2.03 (3 H, s), 0.91 (3 H, s), 0.67 (3 H, d, *J* = 6.0).

Production of Aldehyde 17 from Diene 2. Compound **2** (330 mg, 0.96 mmol) was treated with 11 mL of saturated H_5IO_6 in ether solution for 2.5 h and the filtered. The ether was removed in vacuo to give, in high yield after HPLC purification (50% EtOAc/isooctane), the aldehyde (181 mg, 0.78 mmol, 81%). The aldehyde (29.2 mg, 0.125 mmol) was acetylated under standard conditions to yield, after μ-Porasil HPLC purification (10% EtOAc/isooctane), 17.8 mg (0.065 mmol, 52%) of pure **17**, which showed an $[\alpha]_D$ of +30.1° (*c* 1.75, $CHCl_3$). The ^1H NMR spectrum of **17** (220 MHz) was superimposable with that of the enone–acetate produced from spatol (**1**).

Sodium Periodate Cleavage of 2 To Form the Methyl Ketone 18. $NaIO_4$ (171 mg, 0.8 mmol) was added over a 0.5-h period to a stirred solution containing 134.3 mg of **2** (0.4 mmol), 10 mL of dioxane, and 2.5 mL of H_2O at 0 °C. The reaction was warmed to room temperature and stirred for 3.75 h, at which time 100 mL of diethyl ether was added. The ether was collected, washed with H_2O (3 × 30 mL), dried over $MgSO_4$, filtered, and removed in vacuo to yield, after preparative silica gel HPLC (16 mm × 50 cm), 116.1 mg of the methyl ketone **18** (0.382 mmol, 96%) as an oil with the following spectral features: $[\alpha]_D$ +6.35 (*c* 3.01, $CHCl_3$); IR ($CHCl_3$) 3500, 2950, 1675, 1430, 1350, 1200, 1040, 910 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 6.67 (1 H, dd, *J* = 6, 16), 6.26 (1 H, d, *J* = 16), 5.39 (1 H, s), 5.03 (1 H, s), 4.62 (1 H, d, *J* = 6), 3.75 (1 H, d, *J* = 4), 2.94 (1 H, ddd, *J* = 6, 6, 13), 2.27 (3 H, s), 2.27 (1 H, ddd, *J* = 13, 13, 4), 1.0–2.1 (9 H, m), 0.97 (3 H, s), 0.87 (3 H, d, *J* = 6).

Ozonolysis of 12 To Form the Carbomethoxy Ester 13. The triacetate **12** (258 mg, 0.56 mmol) was treated with O_3 in EtOAc (30 mL) for 30 min, at which time the solution was light purple. Excess O_3 was removed by bubbling Ar through the solution, and 5% Pd/C and H_2 were added under pipet bulb pressure at 0 °C. After 3.5 h the solution was filtered and solvent removed in vacuo. The complex mixture was dissolved in 1 mL of MeOH, and excess ethereal CH_2N_2 was added and allowed to react for 1 h. Removal of excess reactants and solvents in vacuo was followed by chromatography over a short silica column. Fractions eluting with 50% CH_2Cl_2/isooctane contained **13**, which was further purified by using μ-Porasil HPLC (10% EtOAc/isooctane) to give 34.4 mg of **13** (0.123 mmol, 22%) with the following spectral features: $[\alpha]_D$ +2.7° (*c* 0.35, $CHCl_3$); IR (CCl_4) 3000, 1725, 1430, 1360, 1235, 1170, 1025, 965, 890 cm^{-1}; LRMS (70 eV), *m/z* (relative intensity) 280 (obsd M^+, 0.12), 249 (2), 238 (6), 220 (18), 205 (7), 188 (9), 161 (83), 119 (37), 105 (84), 81 (53), 43 (100).

Hydrolysis of Ester 13 To Yield Alcohol 14. The ester **13** (26.5 mg, 0.095 mmol) was stirred for 21.5 h at room temperature in 5 mL of MeOH and 2 mL of saturated Na_2CO_3, after which the reaction was diluted with 50 mL of H_2O and extracted (3 × 50 mL) with diethyl ether. The combined ether extracts were dried over $MgSO_4$, filtered, and reduced to yield a 1:1 mixture of starting material and desired alcohol by TLC. Preparative thin-layer chromatography gave a band of pure **14** (10.3 mg, 0.043 mmol, estimated yield 91%) with the following spectral features: IR ($CHCl_3$) 3500, 2950, 1715, 1430, 1350, 1205, 1100, 1040, 930 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 3.84 (1 H, d, *J* = 4), 3.68 (3 H, s), 3.28 (1 H, ddd, *J* = 6.5, 6.5, 13), 2.53 (1 H, ddd, *J* = 13, 13, 4), 2.26 (1 H, dd, *J* = 7, 7), 1.1–2.18 (9 H, m), 1.00 (3 H, s), 0.91 (3 H, d, *J* = 6); LRMS (70 eV), *m/z* (relative intensity) 238 (obsd M^+, 5), 220 (5), 206 (5), 191 (10), 178 (22), 161 (41), 160 (34), 105 (56), 91 (56), 81 (88), 55 (100).

^1H NMR Analysis of Alcohol 14 with Incremental Eu(fod)$_3$ Addition. The incremental addition of $Eu(fod)_3$ to **14** in $CDCl_3$ coupled with appropriate spin-decoupling experiments allowed for visualization of the couplings (in hertz) between all protons except those at C-2: $J_{1\beta-11}$ = 6.0, $J_{1\beta-9}$ = 7.0, $J_{3\beta-10}$ = 7.0, $J_{3\alpha-10}$ = 0, J_{9-10} = 7.0, J_{9-8} = 6.0, $J_{8-7\alpha}$ = 5.0, $J_{7\alpha-6\alpha}$ = 13.3, $J_{7\alpha-6\beta}$ = 5.0, $J_{6\alpha-6\beta}$ = 13.3, $J_{6\alpha-5\beta}$ = 0, $J_{6\beta-5\beta}$ = 4.4.

Oxidation of the Alcohol 14 to Ketone 15. A subsequent ozonolysis of **2** followed by treatment with CH_2N_2, following the procedure previously described, yielded an additional 18 mg of the alcohol–ester **14**. The alcohol **14** (12 mg, 0.051 mmol) was treated for 3.5 h with excess pyridinium chlorochromate (PCC) in CH_2Cl_2 (2 mL) with NaOAc buffer present, after which the reaction was quenched with the addition of 20 mL of diethyl ether and filtered through a thin-layer of silica gel. Purification of **15** using a μ-Porasil HPLC column (20% EtOAc/isooctane) yielded 10.6 mg (0.045 mmol, 89%) of product which showed: $[\alpha]_D$ −226° (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) 2950, 1735, 1460, 1440, 1370, 1230, 1175, 1025, 940 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$) δ 3.73 (3 H, s), 3.16 (2 H, m), 2.52 (2 H, m), 2.36 (1 H, dd, *J* = 7.5, 7.5), 1.0–2.0 (6 H, m), 0.93 (3 H, s), 0.90 (3 H, d, *J* = 6).

Synthesis of Ketone 19 from Alcohol 3. Eight drops of acetic anhydride were added to 46.5 mg of **3** (0.123 mmol) in 1 mL of CH_2Cl_2 and 0.5 mL of pyridine at 0 °C, and the mixture was stirred for 3 h. The solvents and excess reactants were next removed in vacuo. Preparative thin-layer chromatography of the resulting mixture gave a band (30.6 mg, 0.073 mmol, 59%) which contained a mixture of diacetates **21** and **22** and two other bands corresponding to starting material (13.8 mg, 0.037 mmol, 30%) and triacetate **12** (5.3 mg, 0.012 mmol, 9.3%). The band containing the mixture of diacetates was treated for 1 h at 0 °C in 2 mL of CH_2Cl_2 with excess PCC with powdered NaOAc buffer present. The reaction was quenched with 20 mL of diethyl ether and filtered through a thin layer of silica gel. Thin layer chromatography gave a band containing the two isomeric keto diacetates (19 mg, 0.0455 mmol, 62%) which were partially separated (>90% purity by ^1H NMR) by recycling through a μ-Porasil HPLC column (30% EtOAc/isooctane). The desired 5-ring ketone **19** (8.6 mg, 0.021 mmol, 44%) and the cross-conjugated keto diacetate **23** (9.2 mg, 0.022 mmol, 48%) were recovered. Compound **19** showed $[\alpha]_D$ −51.5° (*c* 0.67, $CHCl_3$) and was identical by 220-MHz ^1H NMR with the diacetate produced from **4**.

Li(*t*-BuO)$_3$AlH Reduction of Ketone 4 To Yield 24. Ketone **4** (10.8 mg, 0.0327 mmol) was treated with excess Li(*t*-BuO)$_3$AlH in 2 mL of absolute EtOH at 0 °C for 1.5 h. The reaction was quenched with H_2O, and then the ethanol and H_2O were removed in vacuo. The residue was partitioned between H_2O and Et_2O, and the latter was collected, dried over anhydrous $MgSO_4$, filtered, and reduced in vacuo. The resultant mixture was treated with acetic anhydride and pyridine (1 mL each) for 18 h at which time excess reactants were removed in vacuo. Preparative thin-layer chromatography yielded a band of pure **24** (8.9 mg, 0.0193 mmol, 59%) which showed the following: $[\alpha]_D$ −8.2° (*c* 0.89, $CHCl_3$); ^1H NMR (220 MHz, $CDCl_3$) δ 5.85 (1 H, d, *J* = 15), 5.69 (1 H, dd, *J* = 7, 15), 5.53 (1 H, d, *J* = 7), 5.28 (1 H, s), 5.01 (1 H, s), 4.80 (1 H, dd, *J* = 10, 8), 4.14 (1 H, d, *J* = 10), 4.01 (1 H, d, *J* = 10), 2.7–1.45 (11 H, m), 2.12 (3 H, s), 2.09 (6 H, s), 1.34 (3 H, s), 1.02 (3 H, s), 0.92 (3 H, d, *J* = 7).

Reduction and Periodate Cleavage of 5 To Yield the Methyl Ketone 18. Ketone **5** (117.8 mg, 0.312 mmol) was treated with excess $LiAlH_4$ in tetrahydrofuran (10 mL) for 2.0 h at room temperature and then quenched with ice and H_2O, extracted with ethyl acetate (150 mL), and dried over anhydrous $MgSO_4$ to give a high yield of tetraol **2** by TLC. This unpurified reaction product was treated with 154 mg of $NaIO_4$ (0.72 mmol, 2 equiv) in dioxane (10 mL) and H_2O (2.5 mL) for 2 h. The solution was extracted with diethyl ether (3 × 25 mL), which in turn was washed with

H_2O, dried over anhydrous $MgSO_4$, filtered, and reduced in vacuo to yield two UV-absorbing products by TLC. Preparative thin-layer chromatography followed by μ-Porasil HPLC (40% EtOAc/isooctane) yielded a 2:1 mixture of **27** and **18**. Repeated μ-Porasil chromatography (30% EtOAc/isooctane) eventually separated the two epimers, yielding **18** (7.3 mg, 0.24 mmol, 7.7%) which showed $[\alpha]_D$ +21.1° (*c* 0.44, $CHCl_3$) and **27** (14.6 mg, 0.048 mmol, 15.4%).

Periodate Cleavage of Tetraol 6 To Yield the α,β-Unsaturated Aldehyde 17. Tetraol **6** (17.2 mg, 0.045 mmol) in 4 mL of dioxane and 1 mL of H_2O was treated with 25 mg of $NaIO_4$ for 3.25 h. The reaction mixture was extracted with diethyl ether (3 × 30 mL) which was washed with H_2O, dried over anhydrous $MgSO_4$, filtered, and reduced. The crude reaction product was treated with excess acetic anhydride (1 mL) in pyridine (1 mL) overnight, at which time the excess reagents and solvents were removed in vacuo. Preparative thin-layer chromatography gave a band of nearly pure **17**, which was further purified by using μ-Porasil HPLC (5% EtOAc/isooctane; 5.4 mg, 0.0195 mmol, 43%), showed $[\alpha]_D$ +26.5 (*c* 0.54, $CHCl_3$), and had an ^1H NMR (360 MHz, $CDCl_3$) identical with that of the enone produced from **1** and **2**.

Oxidation of Diol 7 to Diketone 29. Excess pyridinium chlorochromate and NaOAc buffer were added at 0 °C to 16.3 mg of **7** (0.0537 mmol) in 2 mL of CH_2Cl_2 and allowed to react for 2.75 h. Dilution with 20 mL of diethyl ether and filtration through silica gel, followed by removal of the solvent in vacuo, gave a low yield of **29** by TLC analysis. HPLC purification (μ-Porasil, 10% EtOAc/isooctane) yielded 2.7 mg of **29** (0.09 mmol, 17%) which showed the following: $[\alpha]_D$ −190° (*c* 0.27, $CHCl_3$); ^1H NMR ($CDCl_3$, 220 MHz) δ 6.05 (1 H, s), 5.84 (1 H, s), 5.00 (1 H, s), 4.93 (1 H, s), 2.93 (3 H, m), 2.39 (4 H, m), 1.94 (3 H, s), 1.2–1.9 (8 H, m), 1.00 (3 H, s), 0.94 (3 H, d, *J* = 7).

Oxidation of Diol 8 To Yield the Diketone 29. To 19.4 mg of **8** (0.0638 mmol) in 2 mL of CH_2Cl_2 were added excess PCC and powdered NaOAc at 0 °C, and the mixture was allowed to react for 2.75 h. The reaction was diluted with 20 mL of diethyl ether, filtered through a thin layer of silica gel, and reduced in vacuo to give a small yield of the diketone **29** by TLC. HPLC purification (μ-Porasil, 10% EtOAc/isooctane) gave 3.8 mg of **29** (0.0126 mmol, 20%) which showed $[\alpha]_D$ −185.0° (*c* 0.38, $CHCl_3$) and had a 220-MHz ^1H NMR spectrum identical with that of **29** produced from **7**.

Ozonolysis and Acetylation of 2 To Yield the Ester 13. The tetraol **2** (150 mg, 0.494 mmol) in 20 mL of EtOAc was treated with O_3 for 25 min at −78 °C, during which time the solution turned a light blue color. Excess O_3 was removed by flushing with Ar, and then 5% Pd/C was added at 0 °C under a slight pressure of hydrogen. The hydrogenation reaction was allowed to warm to room temperature and proceed for 6 h, at which time it was terminated and filtered. Chromatography of the crude mixture on a short silica column gave fractions (50% EtOAc/CH_2Cl_2) containing the alcohol–acid. Treatment of these combined fractions first with CH_2N_2 in Et_2O with 1 mL of MeOH present and then with acetic anhydride in pyridine at room temperature for 14 h provided a crude reaction mixture containing **13**. By use of μ-Porasil HPLC (10% EtOAc/isooctane), a low yield of pure **13** was obtained (5.7 mg, 0.020 mmol, 4.1% overall), which showed the following: $[\alpha]_D$ +1.75° (*c* 0.57, $CHCl_3$); IR ($CHCl_3$) 1727 cm^{-1}; LRMS (70 eV), *m/z* 280 (obsd M^+), 249, 238, 221, 220, 205, 188.

Dehydration, Hydrogenation, and Oxidation of 9 To Form Ketone 30. Diol **9** (35.3 mg, 0.116 mmol) was treated with excess *p*-toluenesulfonic acid in aqueous acetone for 1.5 h, at which time the solution was repeatedly extracted with diethyl ether (4 × 30 mL). The combined extracts were washed with saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, filtered, and reduced in vacuo to yield an oily residue. After thin-layer silica gel chromatographic purification, 21.6 mg of the desired dehydration product was recovered (0.076 mmol, 66%). The triene was treated with H_2 under pipet-bulb pressure in the presence of Pt catalyst for 42 h to yield 21.3 mg (0.075 mmol, 99%) of the saturated alcohol. The 60-MHz ^1H NMR spectrum of the crude reaction product showed no bands at lower field than 4.0 ppm and no methyl singlets in the region of 1.5–2.0 ppm. This crude reaction product was treated with excess pyridinium chlorochromate in CH_2Cl_2 (2 mL) at 0 °C in the presence of powdered NaOAc for 2 h. The reaction was quenched by the addition of 20 mL of diethyl ether and filtered through a thin layer of silica gel to give a modest yield of the saturated ketone **30** after μ-Porasil HPLC purification (10.5 mg, 0.376 mmol, 50.2%, 32% overall) which showed $[\alpha]_D$ −101.2° (*c* 0.37, $CHCl_3$).

Dehydration, Hydrogenation, and Oxidation of 10 To Form Ketone 30. Diol **10** (27 mg, 0.089 mmol) was treated with excess *p*-toluenesulfonic acid in aqueous acetone for 2.0 h, at which time the solution was repeatedly extracted with diethyl ether (4 × 30 mL). The combined extracts were washed with saturated $NaHCO_3$ (3 × 50 mL) and then H_2O (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and reduced in vacuo. The unpurified reaction product was treated with H_2 under pipet-bulb pressure in the presence of Pt catalyst for 70 h to yield, by 60-MHz ^1H NMR analysis, the saturated alcohol intermediate as the major product. Oxidation of this crude residue with excess pyridinium chlorochromate in CH_2Cl_2 (2 mL) at room temperature for 1.5 h in the presence of NaOAc buffer followed by dilution with diethyl ether (20 mL) and filtration through a thin layer of silica gel gave predominately the saturated ketone **30** by TLC. Purification of this ketone as produced from **10** by using μ-Porasil HPLC (10% EtOAc/isooctane) gave 10.8 mg (0.039 mmol, 44% overall) of product which showed $[\alpha]_D$ −99.5° (*c* 1.08, $CHCl_3$).

Hydrogenation and Oxidation of 11 to the Ketone 30. Alcohol **11** (23.1 mg, 0.08 mmol) in 5 mL of diethyl ether was treated with a catalytic amount of Adams catalyst (40 mesh, Alfa) and hydrogen (pipet-bulb pressure) at room temperature with stirring for 40 h, at which time the solvent was filtered and removed in vacuo. The 60-MHz NMR spectrum indicated complete hydrogenation had occurred at this time. This crude reaction product was dissolved in 2 mL of CH_2Cl_2 and treated for 1.25 h at room temperature with excess PCC with powdered NaOAc buffer present. The reaction was terminated with the addition of 20 mL of diethyl ether and filtration through a thin layer of silica gel followed by removal of solvents in vacuo. Purification of the major component by using μ-Porasil HPLC (15% EtOAc/isooctane) yielded 15.0 mg (0.050 mmol, 62.5%) of pure **30** which showed $[\alpha]_D$ −110.0° (*c* 1.50, $CHCl_3$) and the following ^1H NMR features (360 MHz, $CDCl_3$): δ 2.53 (2 H, m), 2.28 (3 H, m), 1.0–2.0 (14 H, m), 0.81–1.00 (15 H, m).

Oxidation of Alcohol 11 To Yield Diketone 29. Alcohol **11** (50.1 mg, 0.174 mmol) was dissolved in 10 mL of CH_2Cl_2 in a Pyrex glass tube containing ca. 1.0 mg of methylene blue sensitizer. This solution was irradiated with a 100-W tungsten bulb for 9.5 h, during which time a continuous stream of O_2 was bubbled through the solution. Analysis of the crude reaction product by TLC indicated several discrete UV-absorbing compounds had been produced. HPLC with a μ-Porasil column successfully purified 5(*R*)-hydroxy-17-oxospata-13,18-diene (**32**; 2.8 mg, 0.0093 mmol, 5.3%). Oxidation of this product in 1 mL of CH_2Cl_2 with pyridinium chlorochromate and powdered NaOAc buffer for 1.75 h led to the exclusive production, after workup by dilution with diethyl ether and filtration through a thin layer of silica gel, of the diketone **29**. Final purification involving μ-Porasil HPLC (10% EtOAc/isooctane) yielded 1.0 mg of **29** (0.0027 mmol, 1.6% overall) which showed $[\alpha]_D$ −150.0° (*c* 0.08, $CHCl_3$) and had a ^1H NMR (360 MHz) spectrum identical with that of the diketone formed from **7** or **8**.

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